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Synthesis and Characterisation of Potential Ceramic Sulphide Conductors

Abstract

This study investigates the synthesis methods, the thermal and electrochemical characterisation of potential ceramic sulphide ion conductors, namely $AB_2S_4 + xB_2S_3$, where A represents calcium or strontium and B represents neodymium or samarium, the excess, x, was varied from 10mol%, to 30mol%. This study also examines other potential sulphides such as $Ba_2In_2S_5$ and $Ba_3Zr_2S_7$ compounds.

In this work, synthesis was carried out using solid-state reactions. The product was analyzed using XRD to determine the compound formed. Temperature Programmed Oxidation (TPO) and Temperature Programmed Reduction (TPR) were employed to determine the thermal stability, the thermal activation energy and where possible, determination of the intermediate oxidation products that are formed during the oxidation reaction. The potential sulphide ion conductors were characterised using electrochemical impedance spectroscopy (EIS), 4-point DC resistivity and electrochemical pumping.

Based on TPO and TPR experiments, the sulphide electrolytes examined were stable up to at least 500°C in both a reducing and an oxidising atmospheres. Detailed mass balance on the oxidation of $CaNd_2S_4 + xNd_2S_3$ showed a complex oxidation mechanism, which resulted in the formation of a mixed oxy-sulphate product.

EIS confirmed $CaNd_2S_4 + 0.1Nd_2S_3$ as an ionic conductor; however all other compounds within this series as well all $SrNd_2S_4$ based compounds were at best mixed conductors. Similarly, EIS shows that $CaSm_2S_4 + 0.1Sm_2S_3$ is an ionic conductor, but all other compounds within this series were mixed ionic-electronic conducting. EIS of $SrSm_2S_4 + xSm_2S_3$ results in confirms ionic conduction. EIS of $Ba_2In_2S_5$, a novel compounds, is ionic conducting, while $Ba_3Zr_2S_7$ exhibits mixed-ionic electronic conduction.

Electrochemical pumping confirmed sulphide ion conduction in $CaNd_2S_4 + 0.1Nd_2S_3$, $CaSm_2S_4 + 0.2Sm_2S_3$, $SrSm_2S_4 + 0.1Sm_2S_3$, $SrSm_2S_4 + 0.3Sm_2S_3$ and $Ba_2In_2S_5$, $Ba_3Zr_2S_7$

Keywords:

SULPHIDE ELECTROLYTES, $CaSm_2S_4$, $CaNd_2S_4$, $SrSm_2S_4$, $SrNd_2S_4$ series, $Ba_2In_2S_5$, $Ba_2In_2S_5 + 0.2ZrS_2$, $Ba_3Zr_2S_7$, EIS, TPO, TPR, ELECTROCHEMICAL PUMPING

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It has been said before, but it is worth repeating, 'Klaus, you inspire'!

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Chapter 1

1. Introduction

Solid electrolytes have two traditional uses, namely as chemical sensors and as electrolytes for fuel cells and batteries. The technology of fuel cells involves creating electrical potential (energy) from a chemical reaction. With the application of an electrical potential on the solid electrolyte, a transfer of ions can be induced. Solid oxide fuel cells (SOFC's), similar to other fuel cells convert chemical energies to electrical energies utilising an appropriate anionic oxide ion conductor and can use cheap fuel such as air, CO₂ or CO. Anion conducting solid electrolytes have found use in high temperature (greater than 300°C) applications such as solid oxide fuel cells, sensor or membrane separators. The disadvantage of many oxide ion-conducting material is their high electrical resistance (this restricts use to high temperatures) which causes internal ohmic losses. While SOFC's are still being researched and optimised, high temperature sensors employing oxide ion conducting electrolytes are now commercial products, which are, for example installed, in most automobile engines.

New uses of ionic conducting electrolytes include promotion of reactions using 'pumped' ions or production of ultra-pure gases such as oxygen, Dyer, *et. al.* 2000. Potentially, sulphide ionic conductors could lead to new methods of scrubbing exhaust gases containing sulphur compounds such as SO_x or H₂S, i.e. an electrochemical reactor for sulphur removal could be created. It is also possible that, once there is a concentration gradient of sulphide ions across the electrolyte, this will induce the flow of ions across the electrolyte, thus causing a potential difference. The potential difference can then be correlated to the concentration or activity of sulphur or sulphide ions at the surface of the electrodes; therefore the creation of an in-situ sulphur sensor is possible.

Solid electrolytes which conduct O²⁻ such as Yttria Stabilized Zirconia (YSZ) have been studied extensively for SOFC's applications because of its high thermal stability (1000°C); but it is this high temperature requirement for significant oxide ion conduction which limits the use and application of YSZ in SOFC's. However YSZ has been investigated as a selective membrane material in pumping O²⁻ in order to facilitate the oxidation of propane and propene, Vernoux *et. al.*, 2002. Other compounds such as zirconium phosphate, sodium aluminates and lithium phosphate are examples of intercalation compounds, which are

proton, sodium or lithium ion conductors, respectively, have also been studied; De and De, 2005, Simkim, 1991, and Zhang *et. al.*, 2005, respectively.

Sulphur rich fuels limit the use of oxide ion conducting electrolytes in fuel cells, sensors or ion 'pumping' membrane due to the likely sulphidation of the oxide, Matsuzaki and Yasuda, *et. al.*, 2000. From an engineering point of view, *in situ* solid state sensors that directly measure sulphur potential are the preferred device. A galvanic sensor is advantageous since the output is an electrical potential, which can be used for accurate control. Such galvanic cells for measuring sulphur potentials could utilise a pure sulphide ion conductor as the electrolyte and mixed ionic-electronic conductor sulphide as the electrode.

Low temperature H₂S sensors with very promising characteristics such as a quick and reproducible response were achieved using three electrodes (Pt as working electrode, Teflon-bonded Pt black as counter and reference electrode) and a polymer based electrolyte, (acid treated Nafion®), Yourong *et. al.* 2001.

Measuring sulphur concentration at elevated temperatures (600°C), was address initially by Worrel *et. al.*, 1967 using calcium sulphide electrolyte, later modified by Nagata and Goto, 1974, with the characterisation of doped calcium based sulphide system (CaS+1wt%Y₂S₃ calcium ion conductor). Their proposed electrolyte could be used to measure sulphur pressures less than 10⁻⁶atm at temperatures greater than 700°C: lower temperatures and higher partial pressure caused positive hole conduction.

Jacob (1982) measured sulphur partial pressures in the presence of low concentrations of oxygen using an electrolyte composed of a mixture of calcia stabilised zirconia and calcium sulphide. This sensor was not useful at high concentrations of oxygen due to oxidation of calcium sulphide: at very low sulphur concentration (10⁻⁴ Pa), electronic conduction interfered. Therefore acid treated Nafion and calcium sulphide electrolytes have been made to measure *in situ* sulphur concentrations at different temperatures. However there have been no attempts at measuring sulphur potentials employing a sulphide ion conducting membrane.

Similarly the successful removal of sulphur from gaseous or liquid streams using a sulphide ion conductor has not been reported. The established method of sulphur removal uses a complicated process of aqueous scrubbing with regenerative scrubbing liquids yielding a concentrated H_2S liquid stream, which can then be converted to elemental sulphur using the Claus process. An electrochemical membrane method, proposed by Lim and Winnick, 1984, operated at high temperatures (700-1000°C). In this electrochemical concentration cell there is no overall reaction but rather a transfer of mass from a high concentration region to a low concentration. Using a molten mixture of Na_2S and Li_2S encased in inert magnesium oxide as the electrolyte a removal efficiency of H_2S of 98.8% was achieved. Even though this electrochemical concentration cell is simpler than the traditional scrubbing, regenerating and concentrating process, an even simpler process, in terms of a reduction of environmental, health and safety impact, could be achieved if a solid sulphide ion conducting membrane was available. This highlights the potential application of a solid sulphide ion conducting membrane.

The research to date supports the theory that ionic conduction is based on defects in the crystal lattice; therefore cationic conduction is easier than anionic conduction based only on the difference in size of the ions. For example Sodium, Lithium and Silver ions are more likely to occur because of their small size, in so much that materials, which conduct these cations, can do so at room temperature. However anionic conduction normally takes place at elevated temperatures, for example stabilised zirconia requires a minimum temperature of 600°C before it can be used as an oxide-ion conductor. Therefore to synthesise sulphide ion ceramic appears to be an insurmountable task since the sulphide is larger than the oxide ion. However recently, oxide ion conductor analogues (sulphides) have been synthesised, e.g. calcium-doped zirconium sulphide, where it is believed that most of the conduction occurs via the sulphide ion, and to a lesser extent the calcium ions, Kalinina, *et. al.*, 1995.

1.1. Scope of Thesis

The first objective of this research is to synthesis sulphide compounds identified by XRD and establish their thermal stability in different atmospheres (reducing or oxidising). Temperature programmed techniques such as temperature programmed reduction (TPR) and temperature programmed oxidation (TPO) will be employed for this purpose. This evaluation is necessary to establish the temperature stability range of the sulphide material for further studies such as impedance spectroscopy and four point-probe resistivity measurements.

The second objective of this research is to establish that electronic conductivity of the prepared sulphides is very low (avoid short-circuiting of the electrolyte). A four-point probe resistivity meter or a two-point resistivity meter will be initially used to measure the total ohmic resistance. The four point resistance meter was chosen because it gives both the surface resistivity as well as the bulk ohmic resistance. Both XRD and TPO/R will be carried out with synthesised materials. Four-point DC resistance and two-point DC resistance measurements, both requires a geometric factor (area and length), therefore pellets will be made.

The third objective is the confirmation of the mode of conduction, and the subsequent use as a sensor material. This task will employ impedance spectroscopy, which is a non-destructive technique that can accurately quantify both ionic and electronic conductivity. Impedance spectroscopy not only quantifies the total ionic conductivity (cation and anionic), it gives other information such as grain boundary conduction and intra-grain conduction, relaxation frequency and time constants of the materials. Recent research has shown that the phase angle (or phase shift) associated with ionic conduction is related to the ionic species conducted, therefore it possible that impedance can qualitatively identify a conducting species. Galvanic cells with a concentration gradient produced by varying the H_2S - H_2 gas composition will be constructed to confirm the ion conducting species, (i.e. to differentiate between cationic from anionic conduction).

This research is a joint venture between the departments of Chemical Engineering and Chemistry, to synthesis and characterise these prospective sulphide ion conducting species. Figure 1.1 shows the workflow diagram for the combined effort research effort.

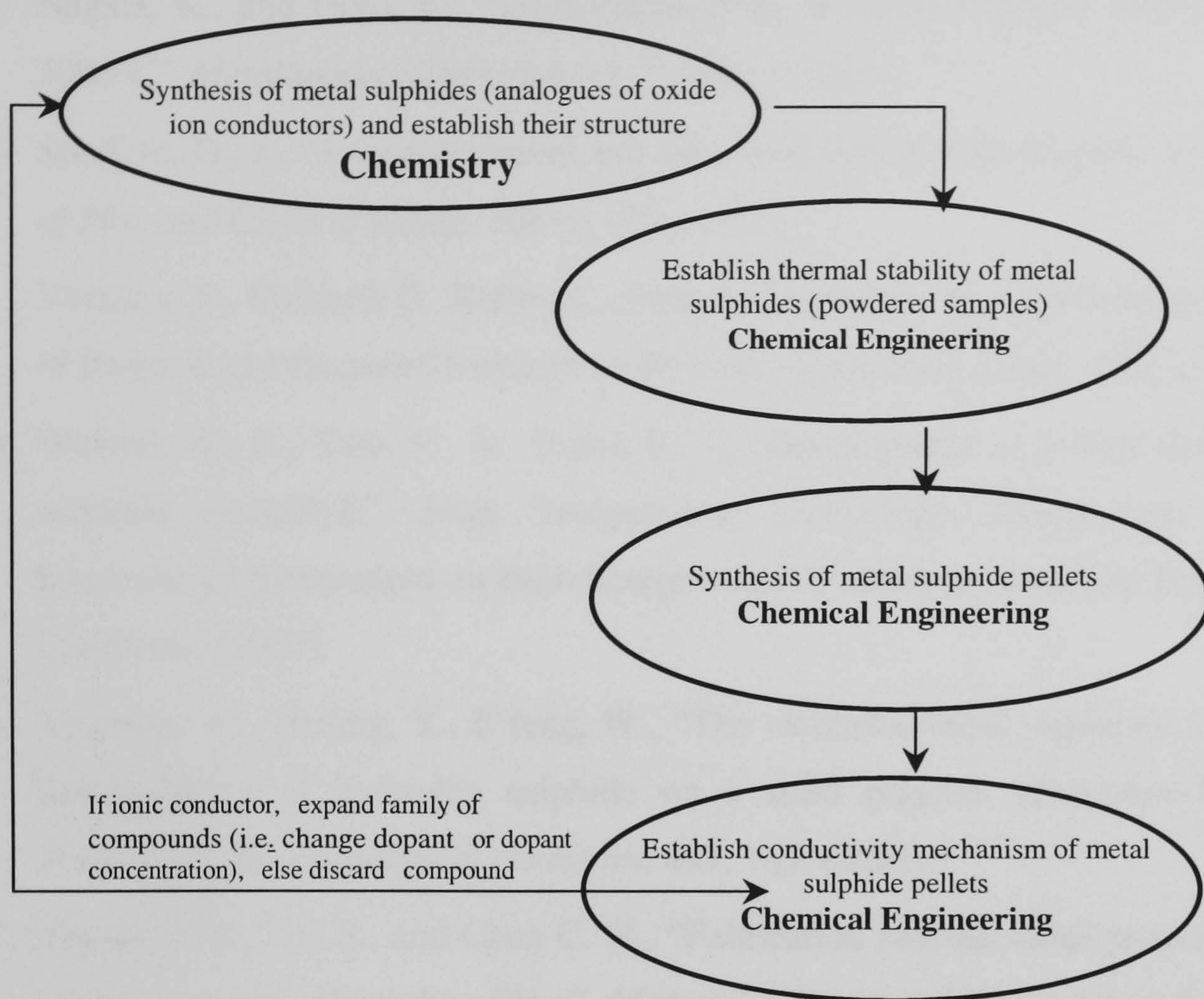


Figure 1-1. Research Work-Flow Plan

1.2 References

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Chapter 2

2. Literature Review

2.1 Introduction

This chapter is divided into three main sections. Initially the relevant theories are examined to facilitate a better understanding of solid-state reactions and ionic conduction. Secondly, justifications of materials that will be characterised for sulphide ion conduction (electrolytes) along with suitability electrode materials are considered. Finally the theories and experimental methods needed to identify ionic conduction and differentiating anion from cation and electronic conduction are discussed.

The first section of this chapter looks at the basic crystal structures and their defects, which are typical for ionic conducting materials (mainly oxides). The literature is proliferated with information on oxide ion conducting electrolytes (but not sulphides) hence will act as a reference point in understanding potential sulphide electrochemical properties.

The second section of this chapter looks at the main applications of ionic conducting solids such as fuel cells (creation of electrical energy from a chemical source) and direct measurement of gaseous concentration (partial pressures) using sensors. Electrochemical reactors used to generate on-site ultra pure gasses as well as electro-catalyst pumps ions, which in turn catalyses the desired reactions are examples of novel application of ionic conducting membranes.

The last section of this chapter addressed the theories, applications and limitations of selected thermal and electrochemical characterisation techniques. Assessment of thermal stability in oxidizing and reducing atmospheres will be carried out using temperature programmed (TP) techniques. Quantifying and identifying ionic conductivity will be assessed using impedance spectroscopy technique and electrochemical reactors respectively.

2.2. Crystal Structures

Introduction

A basic knowledge of crystal structures is necessary since ionic conduction is a function of crystal structure and their defects, which can be thermally or chemically created in these structures. Crystals generally consist of cation and anions arranged in such a manner that charge neutrality is maintained. Three major forces affect the crystal geometry, Greenwood, 1968:

- Electrostatic forces of oppositely charged adjacent ions, to preserve macroscopic electro-neutrality, which is self-explanatory, and calls for little comment.
- Steric factor, packing of different size ions to maximise binding energy.
- Polarisation forces, deviation from ideal crystal structures that arises from the assumption that ions are solid undistorted spheres.

2.2.1 Steric factors

Cations are typically smaller than anions; therefore the number of anions that can possibly be packed around the smaller cation usually determines the crystal structure. This can be expressed in terms of radius ratio, ρ , where

$$\rho = r_{\text{cation}} / r_{\text{anion}}$$

For very small cations only two anions can be placed around it, if anion-cation contact is to be retained (ρ is less than 0.155). Table 2.1 gives a guideline between coordination numbers and ρ .

Table 2.1 Influence of Radius Ratio, ρ , on Coordination Number, Greenwood, 1968, pg.45

$\rho = r_{\text{cation}} / r_{\text{anion}}$	Symmetry of Anions around Cations	Coordination Number of Cations
1.000-0.732	Corners of a cube	8
0.732-0.414	Corners of a regular octahedron / square	6 or 4
0.414-0.225	Corners of a regular tetrahedron	4
0.225-0.155	Corners of a regular triangle	3
0.155-0.000	Linear	2

2.2.2 Polarisation and Crystal Structure

Polarisation can be viewed as a distortion of electronic charge density around an ion and it can arise from a variety of interrelated causes. Extreme Polarisation results in the effective removal of an electron from an anion towards the cation and the formation of a covalent bond; polarisability is greatest for large ions. Therefore polarisation can thus be considered as the link between purely ionic interaction on the one hand and purely covalent bonding on the other, Greenwood, 1968. One effect of polarisation is that the ionic structure always decreases in interatomic distance and increases in lattice energy as the polarisability of the ion is increased.

Crystal structures are determined mainly by the value of the cation:anion ratio. However, if the anion is significantly more polarising than the cation, the crystal structure may be altered to balance this polarisation difference. Consider the schematic below, which shows a planar

view of a 4:2 coordination lattice which changes to a cadmium iodide lattice (layered lattice of 6:3 coordination) then to a molecular lattice, as the polarising power of the anion is increased, Greenwood, 1968.

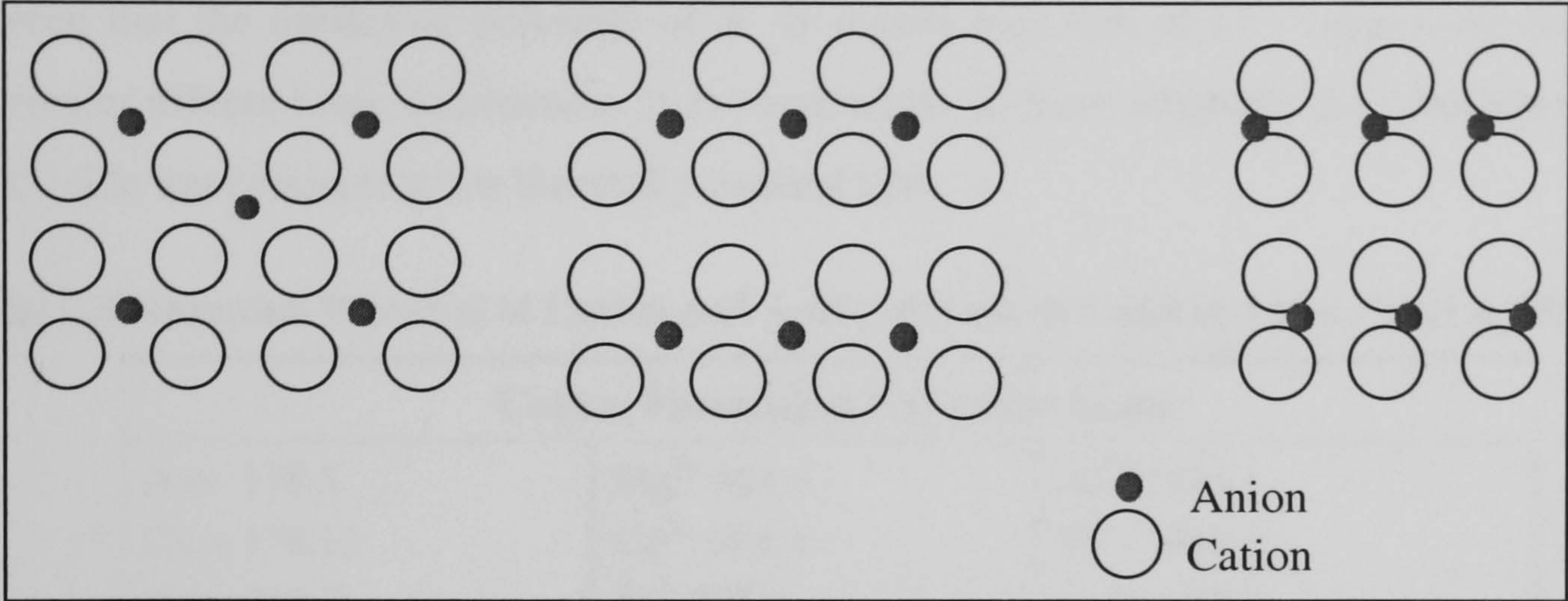


Figure 2-1 Effect of Polarisation on Crystal Lattice

Table 2.2 shows the polarisability of selected ions; of particular interest is S^{2-} versus O^{2-} , where the polarisability has more than doubled. This means that the structure of the metal sulphide analogue of the metal oxide is likely to have smaller interatomic distances, making ionic conductivity of sulphide ions even more difficult than for oxide ion conduction. If conduction still occurs, it is likely that it will be significantly smaller, based only on the high polarisability of S^{2-} . Iodide which has polarisability similar to S^{2-} , shows ionic conductivity in PbI for example, therefore a high polarisability does not eliminate ionic conduction. Lingras and Simkovich, 1983, have reported iodide conduction in PbI. Later, Kuiry *et. al.*, 1999 and Unagami, 1999 showed that at temperatures between 190 and 245°C the conduction is via iodide ions through iodide ion vacant points while at higher temperatures conduction is by the lead ions.

Table 2.2 Polarisability of Selected Ions in Various Atmospheres (Greenwood, 1968)

Electron con- Formation	Polarisability (in arbitrary units, F=1.0)					
Helium	Li ⁺	0.08	B ³⁺	0.01		
Neon	O ²⁻	3.1	F ⁻	1.0	Al ³⁺	0.07
Argon	S ²⁻	7.3	Cl ⁻	3.1	Ca ²⁺	0.6
Krypton	Se ²⁻	7.5	Br ⁻	4.2	Sr ²⁺	1.4
Xenon	Te ²⁻	9.6	I ⁻	6.3	Ba ²⁺	2.1

The energy required to remove an electron from an atom is called the ionisation potential, I_M . The production of a cation, expressed in terms of ionisation potentials is, ${}^0M \rightarrow M^{+} + e^{-}$; with $\Delta H = I_M$. Similarly, to produce an anion is expressed by

$X + e^- \rightarrow X^-$; where $\Delta H = -E_x$. This parameter may be useful in understanding ionic conduction, in cases where the ions are created thermally. With a high ionisation potential then it is likely that oxidation would occur at very high temperatures. From Table 2.3 it can be seen that the ionisation potential of S^{2-} is almost half that of O^{2-} , suggesting that if this parameter affects ionic conduction, it is more likely to have sulphide ion conduction rather than oxide ion conduction for thermally created ions.

Table 2.3 Ionisation Potential of Cation and Anion of interest Ladd and Lee , 1963 & 1965

Cation Formation Exkcal/g-Atom		
Na+ 118.5	Mg ²⁺ 523.0	Al ³⁺ 1228.1
Cu + 178.15	Ca ²⁺ 424.4	Y ³⁺ 902.3
Ag+ 212.7	Sr ²⁺ 385.6	La ³⁺ 835.2
	Ba ²⁺ 250.8	In ³⁺ 1214.9
Anion formation Exkcal/g-atom		
Cl- 85.5± 1.5	O- 33.8± 10	O ²⁻ -172± 5
Br- 80.5± 1	S- 49.6± 3	S ²⁻ -100± 2
I- 73.6± 1	Se- 50.7± 3	Se ²⁻ -117± 2

2.3. Ionic Conduction in Solids

The primary way in which solid materials conduct ions is via crystal defects. Crystal defects are generally classified into two groups - intrinsic, where charge neutrality is maintained throughout the crystal, and extrinsic defects where charge neutrality is not maintained. The intrinsic defects, both Frenkel defects and Schottky defects, do not affect the chemical stoichiometry of a compound nor the long-range crystal lattice electroneutrallity, Wold and Dwight, 1993. Wagner and Schottky, 1930, introduced the concept of extrinsic lattice defects and their interactions. An example is Iron oxide, FeO, where the actual stoichiometry varies from FeO_{0.94}, to FeO_{0.86} by leaving some Fe²⁺ sites vacant and raising the charge on twice this number of remaining cations from Fe²⁺ to Fe³⁺. A second type of composition defect or change may arise by substitution of one element by another. The maintenance of a particular structure is often dependent more on the relative size of an ion (in Å) than on its charge. For example Na⁺ (0.95Å) can substitute for Ca²⁺ (0.99Å); Li⁺ (0.60Å) can substitute for Mg²⁺ (0.65Å) but not for Na⁺ (0.95Å). Where there is a change in ionic charge, there must be a corresponding compensation elsewhere in the crystal. For example, (Fe³⁺ + Na⁺) can replace (Mg²⁺ + Ca²⁺).

2.3.1 Intrinsic Defects

A Frenkel defect is a point defect in a crystal, see Figure 2-2, where an ion occupies an interstitial site leaving a vacancy, hence it consists of both the vacancy created and the interstitial site. Vacancies can be seen as charge carriers in analogy to **holes** in semiconductors where the missing electron - a hole - is carrying the opposite charge of the electron. This type of defect normally occurs for large ions, e.g. Silver Iodide, AgI,

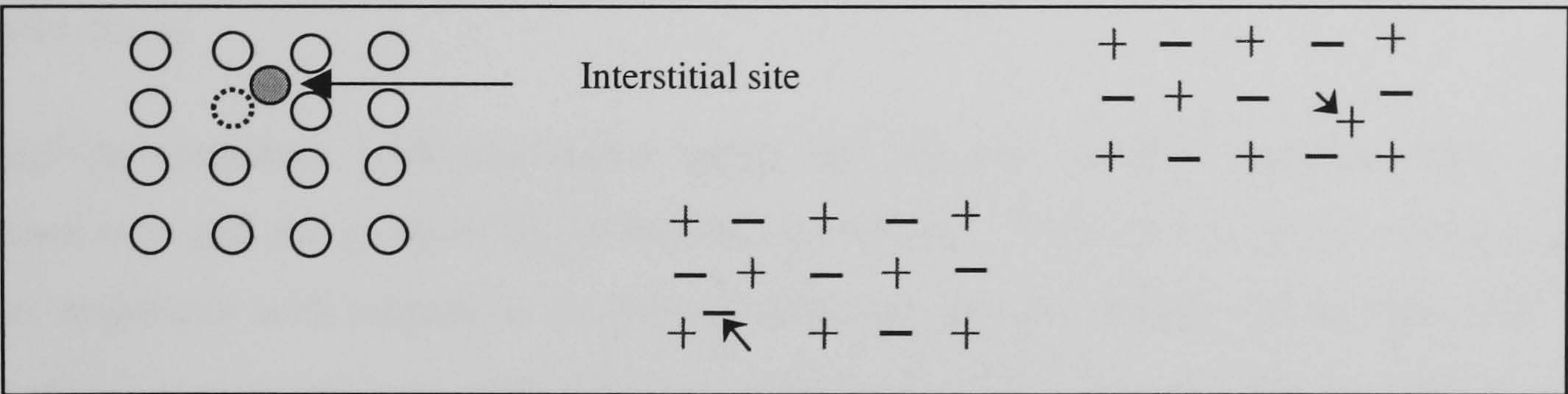


Figure 2-2. Frenkel Defect in Crystal, Negative and Positive Frenkel Defect in Crystal

A Schottky defect is a pair of nearby cation and anion vacancies, therefore it consists of at least two vacancies and electro-neutrality is maintained, Figure 2.3. This kind of defect is found in highly ordered crystals such as Sodium Chloride.

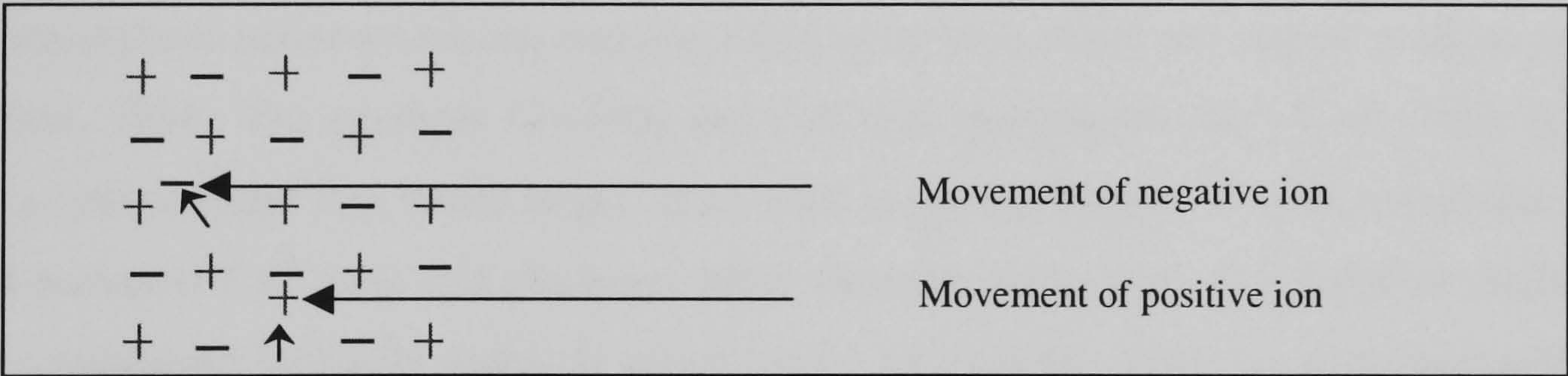


Figure 2-3 Schottky Defect

2.3.2 Extrinsic Defects

An extrinsic defect results in changes both in the stoichiometry and the chemical formula of the compound. Extrinsic defects can be created by adding dopants or impurities to the system, reducing or oxidizing the metal cation. For example, adding Fe^{3+} to a Fe^{2+} crystal lattice will create Fe^{2+} vacancies to maintain electroneutrality, Figure 2.4.

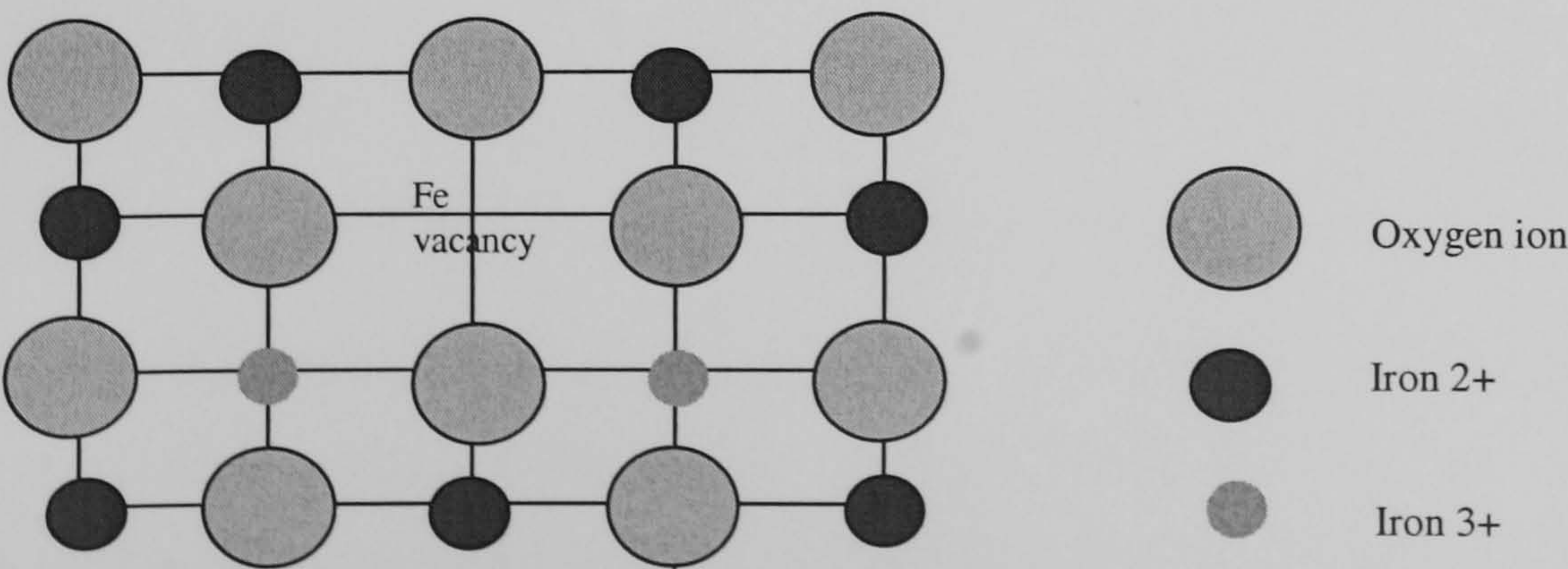


Figure 2-4 Extrinsic Defect in Iron Oxide System

2.4 Solid State Reactions

Most of the compounds investigated were synthesised in the Chemistry Department using solid-state reactions. Therefore it is necessary to consider the factors that affect this process. The reactivity between solids is complicated and the conditions are poorly defined so repeatability is challenging. To-date solid-state reactions are still considered to be empirical methods, which are developed specifically for each reaction. Solid-solid reaction processes are thermodynamic controlled, thus once a high enough temperature is reached, the reaction should occur.

Reactivity increases with decreasing grain size because smaller particles have a higher contact area and the product layers formed are thinner. Therefore surface reactions become more important with respect to the slower diffusion process. Wold, and Dwight, 1993, found that reaction rates increase with mechanical pressure, which was attributed to the increase in contact area. Increased reactivity is also seen near a transition point of one of the reactants called the Hedvall effect, Hedvall, 1952. This effect is generally related to a change in surface mobility.

The atmosphere under which the reaction takes place may affect the rate of reaction as noted by West, 1984. For example Co_2TiO_2 and CoCr_2O_4 synthesised from CoO , TiO_2 or Cr_2O_3 have a rate constant four times larger in air than in pure nitrogen. It is theorised that the air could transport Co^{2+} ions and electrons while nitrogen could not. The sulphide electrolytes were synthesised primarily under an argon (inert) atmosphere using the metal and sulphur as the starting materials. This was to ensure that a single stoichiometry was achieved. The use of an inert atmosphere for the solid state reactions lead to long reaction times, of the order of 30hrs.

2.5 Applications of Metal Sulphides and Ionic Conducting Solids

2.5.1 Introduction

Metal sulphides are used extensively in the elimination of sulphur from petroleum feedstock before refining, in the Hydrodesulphurization (HDS) reaction. Catalysts such as MoS_2 and WS_2 are catalytically active for HDS reactions Gates, 1992. This reaction involves the removal of organic sulphur compounds from petroleum by reaction with hydrogen to form H_2S , (HDS process), making the product suitable for catalytic reformers which employ sulphur sensitive catalysts such as $\text{Re-Pt/Al}_2\text{O}_3$, Browne *et. al.*, 1991. Even though metal sulphides are significantly less active than their pure metal equivalent, their advantage lies in the fact that they cannot be poisoned by sulphur containing feed stocks, Weisser and Landa, 1973. Supported metal sulphides have also found use in hydrogenation reactions where the residual sulphur concentration is very high. This represents the most significant use of metal sulphides as catalysts.

Metal sulphides have also been applied as semi-conductors and refractory materials because of their thermal stability, or thermoelectric devices. Examples are highlighted below:

- Cadmium sulphides are used in cathode ray tubes, Khiew, *et. al.*, 2005.
- Doped Strontium sulphide is used in the conversion of infrared light to visible light, Kravets, 2001.
- Many sulphides are being considered for use as battery materials because they form very stable sulphides in multiple oxidation states, examples include Lithium, Cobalt, Iron and Nickel, Ritchie *et. al.*, 2004.

2.5.2 Fuel Cells

The principle of fuel cells involves creating electrical potential (energy) from a chemical reaction. Many high temperature SOFC use zirconia (ZrO_2)₅ stabilized with the addition of Ytria (Y_2O_3) as the electrolyte, Larminie and Dicks, 1992. The anode of the SOFC is typically a mixture of zirconia and Nickel because it has high electronic conductivity and has good thermally stability in both oxidizing and reducing atmospheres. The cathode can be made from either electronically conducting oxides or mixed ionic-electronic conductors.

Zirconia electrolytes are very stable in both oxidizing and reducing atmospheres, both of which are present in SOFC. Their ability to conduct oxygen ions is attributed to the defect fluorite crystal structure of the material. When Zr^{4+} is doped with Y^{3+} , a number of oxide-ion sites become vacant because four O^{2-} ions are replaced by three O^{2-} . The oxide ion transport

occurs between vacancies. Zirconia-based electrolytes are very suitable for SOFC because they are known to be pure anionic conductors. Materials such as CeO_2 and Bi_2O_3 show even higher oxide ion conductivities compared with Zirconia stabilized with Ytria, YSZ, but are less stable at low oxygen partial pressures, Takahashi and Iwahara, 1978.

SOFC show an enhanced performance as the pressure is increased. This improvement is due mainly to the increased Nernst Potential, where the voltage change, ΔV , for an increase in pressure from P_1 to P_2 follows, approximately, the equation

$$\Delta V = 0.027 \ln \left(\frac{P_1}{P_2} \right) \quad (1)$$

The predominant effect of an increase in temperature is an increase in conductivities of the materials, and this leads to a reduction of ohmic losses within the cell.

Hydrogen Sulphide Concentration Cell

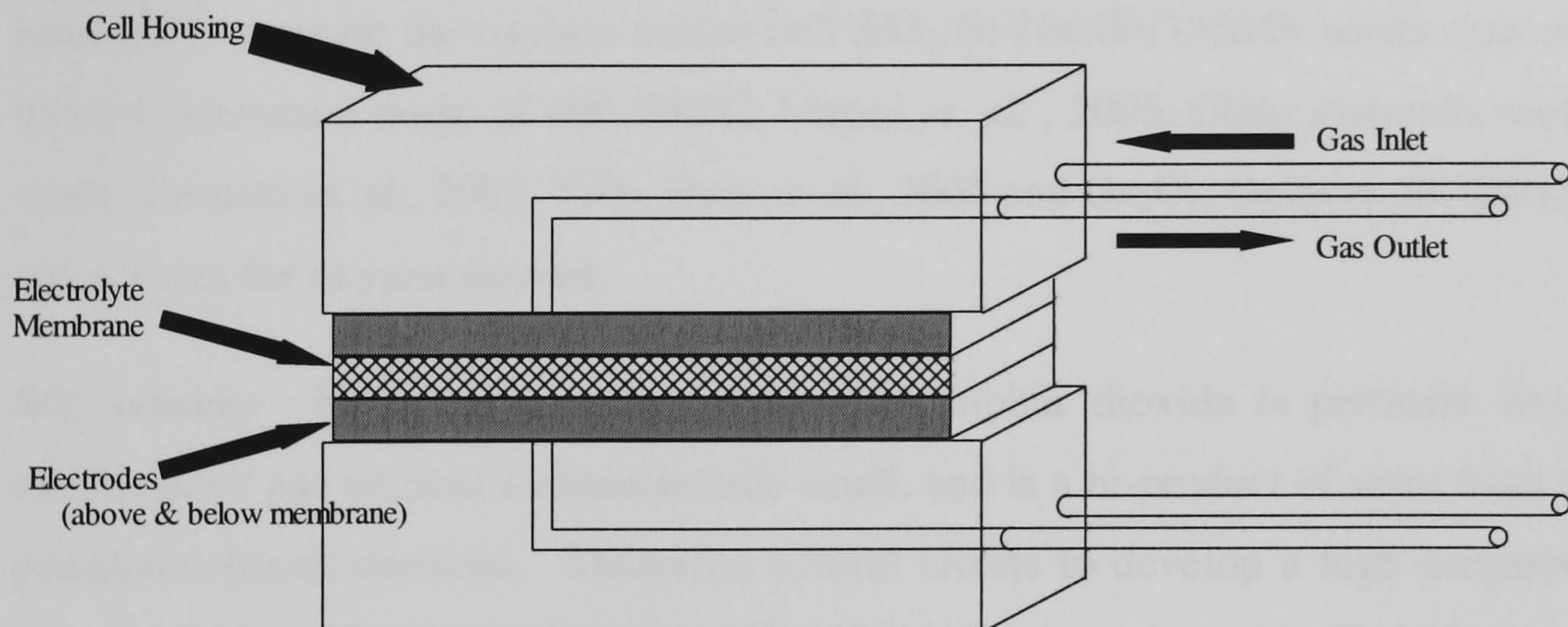


Figure 2-5 Schematics of H_2S Concentration Cell

Thomas and Winnick, 1993, 1984 proposed a hydrogen sulphide electrochemical cell of composition, $\text{H}_2\text{S}/\text{Pt}/\text{NaS}/\text{Li}_2\text{S}/\text{Pt}, \text{Ar}$ Figure 2.5. In principle, the gas with a high concentration of hydrogen sulphide is feed to the cathode, and elemental sulphur is emitted from the anodes, according to equations 2 and 3 below.



The cathodic reaction is



2.5.3 Solid Electrolyte Sensors

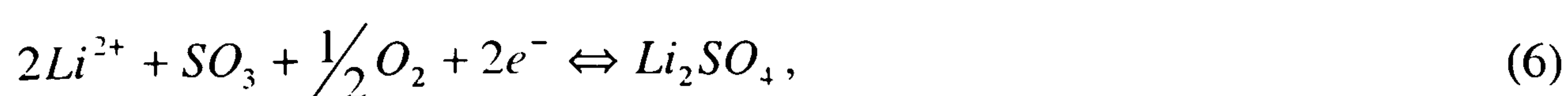
Great efforts have been made to develop sensors for the detection of environmentally unfriendly gases such as SO₂, NO_x and CO₂. However, the most common sensor is the O₂ sensor.

O₂ sensors: Oxygen sensors using yttria stabilised zirconia (YSZ) are now a common feature in many industrial processes where knowing the oxygen partial pressure is most important, examples include automobile engine (700°C) or glass making furnaces (operating temperature 1200-1600°C), Rodrigues *et. al.* 2000. High temperature oxygen sensors may take the form, Pt, air/YSZ/SiO₂, Pt, where the resistance of cell/sensor is a function of temperature and oxygen partial pressure. Sun *et. al.* 1998 established a response time of such a O₂ sensor to be less than 2.5s at temperatures greater than 1000°C. Combustion reactions typically occur at 500-700°C therefore YSZ oxygen sensors need to be conducting oxide ions at much lower temperature therefore thin film YSZ sensors are required. Magnetron sputtering of YSZ has been used to create the oxygen sensor cell SiO₂/Ni-NiO/Pt/YSZ/Pt which was useful in the lower temperature range of 400-500°C, Matsui *et. al.* , 2005. Other materials such as cerium oxide, Jasinski *et. al.*, 2003, TiO₂, Ruiz *et. al.*, 2005 and Ga₂O₃, Ogita *et. al.* 2001 are feasible electrolytes for oxygen sensors.

SO₂ sensors: Knowing the concentration of sulphur dioxide is pertinent since this is a carcinogenic gas without a characteristic smell, and is a bi-product of some high temperature petroleum based reactions. Therefore several efforts to develop a high temperature in-situ sensor resulted. One example is the SO₂ sensor represented as; Air, Pt (reference electrode) /MSZ (O²⁻ conductor) / Li₂SO₄ auxiliary phase (Li⁺ conductor) / Pt, SO₂ in air / (sensing electrode), Yamazoe and Miura, 1994,1996. This SO₂ sensor consists of a magnesium stabilised zirconia tube, MSZ, with a Li₂SO₄ auxiliary phase. The MSZ is an oxide ion conductor while the Li₂SO₄ is a Li⁺ ion conductor. This sensor operates on the reaction of SO₂ being oxidized in air to form SO₃ over the sensing electrode (Pt mesh). Equilibrium between SO₂ and SO₃ is assumed; hence the concentration of the gases can be calculated from the equilibrium constant for the reaction:



The sensing-electrode and the Li⁺ conductor forms a SO₃ sensitive half cell as expressed by the following reaction:



The reference electrode reaction is $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$ (7)

The cell was stable and unaffected by the presence of other gases such as CO₂, NO or NO₂, Yan *et. al*, 1996. When the $P_{SO_{2in\ Air}}$ is much less than the P_{O_2} the EMF of the cell is

$$E = E_o + \frac{RT}{2F} \ln P_{SO_{2in}} , \quad (8)$$

Where

E - electromotive force at temperature, T

R – Universal Gas constant

F - Faraday constant

T - Temperature (K)

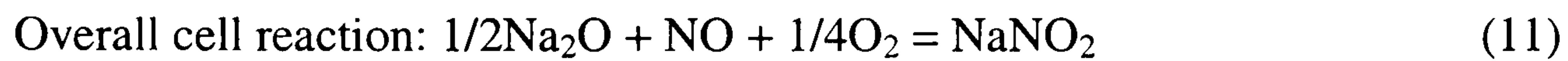
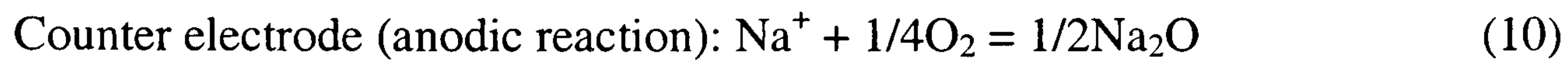
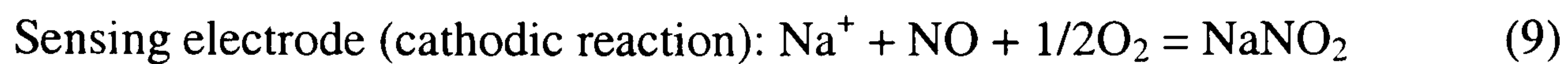
P – Partial pressure.

Therefore this SO₂ sensor consists of two gas/half cells (O₂ and SO₃). The EMF of the cell was sensitive to SO₃ and O₂, but to a lesser degree than that reported for metal sulphate based SO₂ sensors, Yan *et al.*, 1996

The semiconductor, WO₃, was tested as a SO₂ sensor for a concentration range of 0-800ppm and a temperature range of 200-800°C. Shimizu *et. al.*, 2001 observed that sensitivity increased with temperature until 500°C, where the sensitivity began to decline. WO₃ was doped with 1% Ag and this sensor showed a decrease in resistance as the SO₂ concentration increased. Both electrolytes were sensitive to the presence of NO and NO₂.

Another material, Na₂SO₄-Li₂SO₄-Y₂(SO₄)₃-SiO₂ was evaluated as a SO₂ sensor with a NiSO₄-NiO solid reference electrode. SO₂ concentration was varied from 200ppm to 1vol%, at a temperature of 700°C, and a linear relationship between the EMF and the SO₂ concentration was observed, Imanaka *et. al.*, 1987. In summary the SO₂ sensor utilises oxygen ion conductors as the conducting electrolyte, which is measuring the amount of oxygen needed to make sulphur trioxide from the sulphur dioxide (see equations 5 and 7).

NO_x sensor: The detection of NO₂ is important for environmental reasons since it is the dominant component of NO_x, even though the concentration may be in the ppb range. Miura *et. al* , 1993 proposed a NO_x sensor, that is sensitive to NO as well as NO₂. The electrolyte tested was Na₃Zr₂Si₂PO₁₂ known as NASCION with a NaNO₂ auxiliary electrode. The Pt counter/reference electrode was kept in static air.



Miura *et. al.*, 1993 noted that the response to NO and NO₂ at 150°C was in the order of 8s, and the EMF followed the Nernst equation with a slope of 1, when the gas concentration was above 10ppm. The limitation of the sensor lies in the stability of the auxiliary electrode; in that trace amount of NaNO₃ was formed when NaNO₂ was heated to above 270°C in air for 30mins, thus making the sensor unstable at 240°C and above. This type of NO_x detector utilises a Na⁺ ion conductor, NASION. The EMF resulting from Na⁺ ion conduction is proportional to NO partial pressure (see equations 9-11). This makes this sensor similar to SO₂ the type sensors.

CO₂ Sensor: Imanaka *et. al.* 2000 reported that the most effective CO₂ sensor consisted of a M³⁺ oxide ion conductor and platinum electrodes. The electrochemical cell was tested in the temperature range of 300-600°C with 1-5%CO₂ concentration. The sensor can be described as identical to that of the SO₂ sensor in equations 5-7 above, the only change is Li₂CO₃ was used rather than Li₂SO₄. Imanaka *et. al.*, 2000, found that the sensor gave reproducible EMF signals to CO₂ concentration. They also observed that the sensor was independent of changes in O₂, NO, NO₂ and H₂O. The sensor was stable up to a period of 150 days, when the trivalent cation, M³⁺ was Sc³⁺ but not Al³⁺.

2.5.4 Electrochemical Reactors

Recent research on the applications of solid ion conducting electrolytes is concerned with the separation of gases using an electrochemical reactor. The demand for high purity gases such as oxygen has lead to the development of this technology, employing ion-transporting membranes (ITM) because it has the potential to provide pure gases on site, Dyer, 2000. ITM use dense ceramic membranes such as an oxide ion conducting materials as shown in Figure 2.26. Another application of ITM is the conversion of methane to syngas where a dense oxygen ion or mixed ion conducting membrane is used to supply pure oxygen to convert methane to carbon monoxide and hydrogen. Mixed ion conductors imply that no external electrodes are needed, however an externally applied voltage is still required. Mixed conductors, Sr-Fe-Co-O system were reported to have CO selectivity of 98% up to 1000h and methane conversion efficiency of 99% Balachandran *et. al.*, 1995, 1997, 1998. The use of

ITM in the production of oxygen is the most developed of the technologies and is assumed to be very close to a commercial stage, Dyer, 2000.

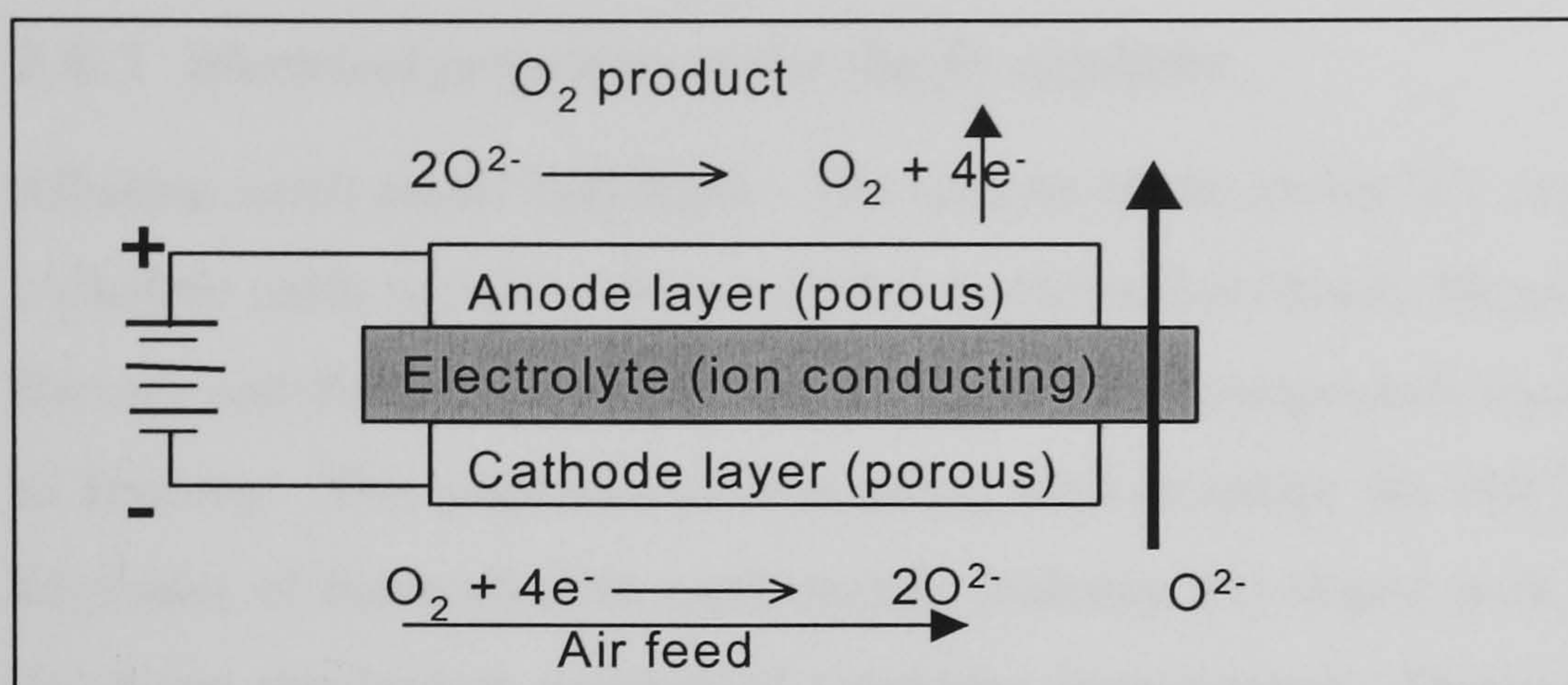


Figure 2-6 Schematic Operation of a Solid State Oxygen Generating Device

Another application of solid ion conducting electrolytes is the electrochemical activation of electrode-electrolyte-gas interface reactions. The rate of these surface reactions which are catalysed by the electrode can increase by several orders of magnitude, Bebelis *et. al.*, 2000. This effect is called nonfaradaic electrochemical promotion (NEMCA). NEMCA is also present in mixed conductors such as TiO_2 , or CeO_2 , Petrolekas *et. al.*, 1998. $\text{Pt/Ti}_2\text{O}$ was found to have electrochemical promotional behaviour at temperatures close to 500°C for ethylene oxidation even though Kofstad, 1972 determined TiO_2 to be only 3-15% ionic (O^{2-}) conductive with the remainder being electronic, Pliangos, 1995. There is an observed reduction in NEMCA effect for mixed ionic-electronic conductors when compared to pure ionic conductors.

Most of the work done recently involves the oxidation of light hydrocarbons on precious metals such as platinum, gold or silver that is deposited on an ion-conducting electrolyte. YSZ was investigated in the electrochemical oxidation of propane and propene oxidation, Vernoux *et. al.*, 1998. The reaction rates increased over 100 fold when current or voltage was applied compared to open circuit conditions, Vernoux *et. al.*, 1998. CaF_2 , a fluoride ion conductor, was used to electrochemically catalyse the oxidation of CO, Alcock, 1992.

2.6 Materials: Sulphide Electrolyte and Electrode

The electrical properties of starting sulphides, single cation compounds such as CaS , SrS , PbS , are discussed, since these inherent properties may influence the complex sulphides, defined as compounds with more than one cation, such as CaNd_2S_4 . Included also, is a discussion of complex sulphides as well as the oxide analogues.

This section also addresses the use of various electrode materials in terms of their suitability with sulphide electrolyte in an H₂S environment.

2.6.1 *Electrical properties of the simple sulphides*

Alkaline earth metal sulphides: The cations of the group IIA elements of the periodic table (Alkaline earth metals) consists of the elements Beryllium, Magnesium, Calcium Strontium, Barium and Radium; however this research used compounds consisting of Calcium through to Barium. The sulphides of this group tend to adopt the NaCl-type 6: 6 structure. The sulphides of these alkaline earth metals (valency 2+) doped with ternary sulphides (valency 3+) form the largest number of sulphides investigated. Doping group II metal sulphides creates ternary systems with extrinsic defects. Flauhaut *et. al.*, 1965. The resultant structure was a Th₃P₄ type structure exhibiting non-stoichiometric phases.

The atomic weight of the lanthanides increase across the series, where as the atomic radius decreases. This effect is called the ‘lanthanide contraction’, which occurs because the nuclear charge is balanced by an increase in electronic charge. Thus each unit increase in nuclear charge produces a net increase in attraction for the whole extra-nuclear electron cloud and each atom shrinks slightly relative to its predecessor. Therefore to expand the crystal structure to increase the cell volume, the larger lanthanides were selected, e.g. Neodymium sulphide or Samarium sulphide.

2.6.2 *MLn₂S₄ - xLn₂S₃ (where x = 10-30 mol % Ln₂S₃) systems*

Recently a group of complex sulphide materials have been investigated as potential sulphide-ion conductors, the materials being based on a high symmetry cubic sulphide lattice structure, which has been found to develop intrinsic sulphide vacancies on heating. Kalinina, *et. al.*, 1995,2000. A range of ion conducting chalcogenides have been prepared in the system MLn₂S₄-xLn₂S₃, where M = group II metals (Ca, Ba) and Ln = a range of lanthanides (Pr, Nd, Sm). The mode of conduction is believed to be mainly by sulphide ions with minor cationic (M) conduction present.

The disorder generated within the MLn_2S_4 systems, caused by the addition of the Ln_2S_3 dopant gives rise to both anion and cation disorder and associated vacancies in both the anion and cation sub-lattices. It was reported by Kalinina *et. al.*, 1995 that data collected at 500°C suggests that the systems have an intrinsic level of anion disorder created by the introduction of the Ln_2S_3 dopant, and also that the materials conduct ions via Schottky defects generated vacancies in the host lattice. Kalinina *et. al.*, 1995, found that there was no indication of a major organised structural transition within the system leading to the observed ionic conductivity. It was suggested that at elevated temperature, the already disordered system allows the motion of sulphide ions via Schottky defects in the lattice and the ion transport ratio for calcium and sulphide ions was determined by galvanic cell measurements Kalinina *et. al.*, 1995.

Kalinina and co-workers reported compounds in the system $CaNd_2S_4-xNd_2S_3$ showing sulphide ion conducting behaviour, using galvanic cells of varying concentration. The highest level of conductivity reported in the literature for the barium or calcium $MLn_2S_4-xLn_2S_3$ systems studied was $\sigma_{500^\circ C} = 1.51 \times 10^{-6} \text{ S cm}^{-1}$. Kalinina *et. al.*, 1995.

Investigation of the structure and properties of the MLn_2S_4 type sulphide materials have to date been very limited and is certainly worthy of further work. Research into the characterisation of solid solution based materials in the doped $MLn_2S_4-xLn_2S_3$ systems and in particular the strontium analogues is absent from the literature.

2.6.3 $Ba_2In_2S_5$ and $Ba_2In_{2-x}Zr_xS_5$

Zhen and Goodenough, 1990 showed that the compound $Ba_2In_2O_5$ displays fast oxide-ion conduction above 925°C. Since then barium oxide materials have been investigated as possible fast oxide-ion conductors for use in oxygen sensors, solid oxide fuel cells and other electrochemical devices, Ryu and Haile, 1999. These types of oxide compounds have been synthesised with the aim of developing fast oxygen ion conducting materials, superior to commercially available yttria-stabilised zirconia (YSZ).

There has been considerable research on the $Ba_2In_2O_5$ structure, properties, reaction with water at 300°C, Goodenough *et. al.* 1992, as well as applications as a proton and oxide-ion conductor Wang and Virkar, 2005. The work by Speakman *et. al.*, 2002, describes the results of *in-situ* neutron and X-ray diffraction experiments, used to determine the crystal structure of $Ba_2In_2O_5$ as a function of temperature. The ambient temperature structure of $Ba_2In_2O_5$ was found to adopt a orthorhombic symmetry, with lattice parameters $a = 6.086\text{\AA}$, $b = 16.790\text{\AA}$

and $c = 5.969\text{\AA}$. This structure was stable up to a temperature of 900°C , at which point oxygen vacancies began to disorder. The oxygen vacancy order–disorder transition is associated with a structural transition to a fast oxide-ion conducting state. At 1040°C , $\text{Ba}_2\text{In}_2\text{O}_5$ becomes a cubic oxygen-deficient perovskite, and lattice parameter 4.274\AA . Attempts to stabilise the high temperature cubic defect perovskite phase of $\text{Ba}_2\text{In}_2\text{O}_5$ at lower temperatures by doping the compound on the indium site with other trivalent cations, such as gallium, to give compounds of the form $\text{Ba}_2\text{In}_{2-x}\text{M}_x\text{O}_5$ where M is the added cation dopant have been done, Kendall *et. al.*, 1995. Doping the indium site in the $\text{Ba}_2\text{In}_2\text{O}_5$ compound with trivalent cations of various radii, altered the order-disorder transition temperature relative to the parent compound. For example doping with ions larger than the host In^{3+} ion, such as Y^{3+} and Yb^{3+} was found to cause an increase in the transition temperature, while doping with smaller ions like Sc^{3+} and Ga^{3+} was found to decrease the transition temperature of the material Yao, *et. al.*, 2000. Successful doping with zirconium on the indium sites increased the level of ionic conduction. The increase in zirconium content in the structure was also accompanied by a decrease in unit cell volume, attributed to the radius ratio for the In^{3+} and Zr^{4+} ions, also in agreement with previous work.

While extensive research has been done on the $\text{Ba}_2\text{In}_2\text{O}_5$, investigations into the sulphide analogue materials $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Zr}_x\text{S}_5$ is non-existent in the open literature. Therefore the structure and properties $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Zr}_x\text{S}_5$ novel compounds were investigated.

2.6.4 $\text{Ba}_3\text{Zr}_2\text{S}_7$

The perovskite structure tolerates a wide range of relative size and charge of the A and B cations. Incorporation of the dopant normally results in distortion of the ideal cubic structure. A variety of doped and un-doped Ruddlesden-Popper strontium, titanium oxide compounds have been previously prepared, Hungria, *et. al.* 2004, which have the ability to conduct oxide anions. There has also been considerable work on other oxide-ion conducting Ruddlesden-Popper phases together with the ionic conduction of layered perovskite oxides Norton, 2004. The conduction of M cations in Ruddlesden-Popper oxide phases has been strongly linked to the degree of covalency in the M-O bonding of the compound, Zvereva, *et. al.* 2003. Synthesis methods for the $\text{Ba}_3\text{Zr}_2\text{S}_7$ compound were described previously by Chen *et. al.*, 1994. The material was found to be a member of the Ruddlesden-Popper series of compounds, having an ($n = 2$) doubled perovskite layer. A BaCl_2 flux was used in the preparation and compounds were reacted from the appropriate metallic sulphides at 1323K (1050°C). The investigation of oxygen stoichiometry in the system $\text{Sr}_3\text{M}_2\text{O}_7$ and the

subsequent modification of the M cation site to create oxygen non-stoichiometry and disorder giving rise to high temperature anionic mobility have both been studied, Mogni, *et. al.*, 2005. Therefore doping modification of the B site in $A_3B_2S_7$ materials could potentially yield analogous sulphide-ion conductivity.

Table 2.4. Selected Sulphides Systems made with Extrinsic Defects

Sulphides	Examples
Zirconia based sulphides	$Ca_xZr_{1-x}S_{2-x}$ & $Ca_xZr_{2-x}S_{4-x}$ (x-0-4%mol) [Andrievskaya, <i>et. al.</i> ,1995] $ZrS_2 - xNd_2S_3$ (x- 2-10%mol) [Kalinina, <i>et. al.</i> , 1994] $ZrS_2 - xNd_2S_3 - xLn_2S_3$ (x- 2-10%mol) [Ono, <i>et. al.</i> 1981]
Calcia based sulphides	$CaS - ZrS_2 - Ln_2S_3, Ln - Y, Sm, Nd, Pr$, x=2%mol [Sammes, 1994]
Bismuth based sulphides	$Bi_2S_3 - xLn_2S_3$ (x = 22 – 57%mol) [Aurivillius, 1987]
Barium based sulphides	$BaBi_2S_4$ [Fisher, W, 1999], $Ba_2In_2S_4$ [Chen, 1997], $Ba_3Zr_2S_7$ [Kalinina, 2000]
Samarium based sulphide	$(Sm_{1-x}Gd_x)_3S_4$, [Sato, 1981]
Doped Lanthanide based sulphides [Kalinina, 1995, Hu, 1999, Pouzol-Julien, 1982,]	$CaLn_2S_4 - xLn_2S_3, x = 2 - 30\%mol, Ln = Pr, Nd, Sm$ $BaLn_2S_4 - xLn_2S_3, x = 2 - 30\%mol, Ln = Pr, Nd, Sm$ $CaNd_2S_4 - xNd_2S_3, x = 10 - 30\%mol$ $SrNd_2S_4 - xNd_2S_3, x = 10 - 30\%mol$

2.7. Electrode Materials

Electrodes are needed on the pellet for current collection when making impedance spectroscopy and electrochemical pumping measurements. However electrochemical pumping of sulphur across the electrolyte requires the electrodes to perform a secondary function, which is to catalyse the conversion of H_2S to sulphide ions. For both types of experiments the prerequisites for electrodes are low resistance, i.e. a good electronic conductor, as well as being un-reactive towards electrolytes. The open literature has used platinum, gold, silver, TiS, and carbon, as electrode materials; therefore each material will be discussed.

2.7.1 Platinum

Platinum was used by He *et. al.*, 2002, as the anode material in a $\text{H}_2\text{S}-\text{O}_2$ solid fuel cell which operated at 5% H_2S and 700-900°C, however corrosion of the anode was recorded due to the reversible formation and decomposition of PtS on the Pt-YSZ interface. This led to instability at the electrochemical interface between Pt and YSZ. The stability of Pt electrode in an H_2S environment was improved by adding a layer of TiO_2 . Electrochemical pumping experiments of sulphide electrolyte with Pt electrodes may also result in the conversion of Pt to PtS. The life of the electrode may be extended by coating with TiS_2 or by using TiS on the side of the pellet surface that is exposed to $\text{H}_2\text{S}-\text{H}_2$ atmosphere. Similarly, the degradation of Pt in H_2S at the anode was also observed by Liu *et. al.*, 2001 where PtS was formed when their solid oxide fuel cell was operated at 5% H_2S at 750-800°C.

Furthermore detailed studies, by Loucka 1972 showed that Pt not only reacts with H_2S , but it can adsorb more than one layer of sulphur on its surface. This property is useful, since a three phase boundary between sulphur from H_2S , electrode and electrolyte is needed to make a good sensor and electrochemical reactor. Platinum stability in the presence of hydrogen sulphide was significantly improved with the addition of tin, which essentially blocks the sites that S^{2-} , HS and S would attack, Rodriguez, 1998.

2.7.2 Carbon and graphite

Both carbon and graphite are used extensively in commercial electrochemical applications including battery electrodes, industrial electrolytic processes and as a counter electrode for corrosion studies or in cyclic voltammetry, Stafford *et. al.*, 1991. The microstructure of carbon varies widely in so much that there are hundreds of grades of carbon or graphite. The properties of each grade of carbon/graphite may differ significantly, for example Tasaka *et. al.*, 1987 showed that the activation energies of graphite, carbon, amorphous carbon are 6.5, 8.4, and 5.5 kcal.mol^{-1} respectively.

Carbon has been used in applications where noble metals could not be considered. For example carbon has been used as the anode material for applications involving molten fluoride (HF, KF), even though at high current densities, the carbon may degenerate.

The limitation of carbon is that it is difficult to improve the characteristic of the carbon electrode, Tasaka *et. al.*, 1987. Interestingly though Hart & Bass, 1997 made a carbon electrode modified with cobalt phthalocyanine which catalyses hydrogen sulphide by the following mechanism:



Therefore it seems possible that carbon could be modified to catalyse the formation of a sulphide ion (S^{2-}). Carbon has also been modified with platinum to oxidise sulphite (SO_3^{2-}), which is used as a preservative in the food industry, Casella and Marchese, 1995. Pulsing with a positive voltage of 1.35V removed the adsorbed species thereby cleaning the fouled electrode. Highly porous (80%) carbon can become fouled with elemental sulphur Zhang & Cha, 1992.

2.7.3 Gold

Ding and Seyfried, 1996 used gold as the electrode in the cell, Au|YSZ|Hg-HgO at temperature 375-400°C, in a reducing atmosphere of hydrogen. The results, in terms of electrode stability, were similar to that expected with platinum. The experiments were done in liquid conditions, however the information would also be applicable in a gaseous atmosphere. Elnakat *et. al.*, 1993 noted that, both platinum and gold formed MH_2S and $M(H_2S)_2$ complexes where M = Au or Pt.

2.7.4 Titanium Sulphide

Titanium sulphide is one of the chalcogenides, which are sometimes referred to as two-dimensional solids, because of the strong covalent/ionic bonds holding the layered structure together, Martinez *et. al.*, 1998. Resistivity measurements of the layered TiS_2 made by Logothetis *et. al.*, 1980 observed only metallic behaviour. Saidi, 1992 prepared cubic titanium sulphide by synthesising a copper titanium thiospinel followed by room temperature extraction of copper, to be used as a cathode material. However graphite was added to improve electronic conductivity. Scrosati, 1995 and Armstrong and Bruce, 1996 exploited TiS_2 as a positive electrode in rechargeable lithium batteries. However titanium sulphide has a strong tendency to form non-stoichiometric compound with excess of titanium, which can then behave either as a semi-metal or as a semiconductor as reported by Chen *et. al.*, 1980.

2.8 Thermal and Electrochemical Characterisation Techniques

Several techniques will be used to characterise the sulphides prepared by the Chemistry department; namely X-ray diffraction for compound identification; Temperature Programmed

Oxidation of sulphides (TPO-S) and Temperature Programmed Reduction of sulphides (TPR-S) to determine the thermal stability in oxidising and reducing atmospheres, four-point-DC-resistivity measurement and two point DC-resistance measurements to determine the ohmic resistance of the material. Impedance spectroscopy and electro-chemical pumping will allow the deduction of the mode and degree of ionic conduction.

XRD, TPO-S and TPR-S characterisation techniques will be done on the material in a powdered form while DC, impedance spectroscopy and electrochemical pumping cell measurements will be done on materials in the form of a pellet. Therefore pellet making which involves determining sintering conditions such as reaction time and atmosphere will be addressed. To determine the effectiveness of the sintering process, SEM images will be used to observe the size of pores in pellets.

2.8.1 *X-ray diffraction*

The basic components of an X-Ray diffractometer are an X-ray source, a specimen holder and an X-ray detector. X-rays are generated by bombarding a metal anode with a high power electron beam inside a vacuum X-ray tube copper being the most frequent material used as the target. This experimental method measures the diffraction angle of incident Xrays, because of the sample.

A thin layer of homogeneous crystalline powder (the specimen) is spread onto a planar non-diffracting material such as glass (the specimen holder); quantities as small as 1mg can be sufficient. Suryanarayana 1998, Musi, 2004 amongst others noted that an XRD sample should be made up of many small randomly oriented grains of size less than 1 μ m, because larger particle sizes broaden the peaks.

The XRD trace generated from the metal sulphides made by White, 2003 is compared to a library of patterns, and if a complete overlap of all reflections (peaks) occurs, then this indicates the desired compound is produced. This method is therefore a qualitative means of compound identification. If the compound is novel, that is no pattern exist in the library, then the compound is identified by comparing the novel compound to its analogue, if all the reflections are present, all shifted by the same degree, then this is used as a positive means of identification.

2.8.2 Temperature Programmed Techniques

Temperature programmed (TP) techniques involves the heating, linear heating rate, of a sample, under a controller atmosphere and measuring the composition of the exhaust. The method allows for determining the thermal stability of compounds under various atmosphere. Also the thermal activation energy, and reaction kinetics can be determined from this technique. TP techniques are useful techniques for the characterisation of metal oxides (traditionally, but can be applied to other metal compounds) Zupanc, *et. al.*, 2002. The technique is quantitative and can be related to the reaction kinetics of the material. Decomposition temperatures; extent of reaction (stoichiometry) and thermal activation energy can also be deduced from temperature programmed techniques Cortés, 1976, Park 2004. TP techniques do not give much information on the compound structure, which is typically given by most spectroscopic methods; therefore these techniques (X-ray diffraction and TP techniques) complement each other in terms of the information gathered. The suite of temperature programmed techniques include

- Temperature programmed reduction (TPR),
- Temperature programmed oxidation (TPO),
- Temperature programmed sulphidation (TPS),
- Temperature programmed desorption (TPD) (not discussed).

The typical experimental set-up for TPR\O\S includes a reactor, mass spectrometer (MS) or a thermal conductivity detector (TCD) to measure hydrogen, oxygen, and sulphur content liberated or consumed during a TPR, TPO or TPS experiments.

Typical reactions analysed by TPR techniques include:



Temperature programmed techniques use a reactor, which is heated at a constant rate as, determined by a temperature programmable controller. The effluent from the reactor is analysed by a Mass Spectrometer. The gas mixture used in TP techniques should be considered carefully, for example when performing a TPR experiment, using a gas mixture of H_2/Ar rather than H_2/N_2 is better, because at elevated temperatures the hydrogen and nitrogen could react. TPO studies are analogous to TPR experiments with the gas mixture of Air/Ar .

2.8.3 Mass Spectrometer

A mass spectrometer, MS, is an instrument where atoms or molecules are ionised and separated based on their mass to charge ratio (m/z). MS is therefore a destructive method of analysis. A mass spectrometer has two major components, the ionisation chamber and the mass analyser.

Ionisation Chamber: The gas to be measured enters the ionisation chamber where it is bombarded, at a right angle with a beam of electrons, generated from a rhenium filament held at -60V, Barker, 1999. The stray electrons are collected in a source cage held at 5V. The ionisation chamber converts atoms and molecules from the source gas into ions and accelerates/injects the positively charged ions into the mass analyser.

Mass Analyser: The mass analyser is a quadrupole type. Quadrupole mass analyzers and quadrupole ion traps [QIT] use electrical fields to selectively stabilize or destabilize ions falling within a narrow window of m/z values. The analyzer changes the direction ions are flying through the mass analyzer.

The entire measurement system is kept at a low pressure (1×10^{-5} bar) in order to:

1. Prolong the life of the ion-source filament, (reduce the oxidation of the filament).
2. Prevents ions from colliding with atmospheric gas molecules and hence lose the charge, and by extension not reach the detector.
3. Low vacuum reduces the memory effect, that is, the mass spectrometer atmosphere returns quickly to the background conditions when operated under a good vacuum.

2.8.4 Kinetic Model for TP Techniques

The thermal activation energy of a compound can be calculated from a series of TP experiments in which the heating rate is varied. It is assumed that the solid-gas reaction can be described mathematically by considering two factors, the temperature and concentrations, Barker, 1999.

$$\frac{dX}{dt} = K(T) \cdot f(X) \cdot f'(p_{c1} p_{c2}) \quad (18)$$

Where

X - Degree of conversion of solid reactant

K – Equilibrium constant

P_{c1}, P_{c2} – partial pressure of gases c_1 and c_2

Assume that the gas concentration is constant and is incorporated into $K(T)$ (equilibrium constant), thus equation 18 reduces to

$$\frac{d(X)}{dt} = K(T) \cdot f(X) \quad (19)$$

For a heating program with a constant heating rate, β , the temperature is given by:

$$T = \beta t + T_o \quad (20)$$

Where

T_o - Starting temperature, K

t - Time, min

β - Heating rate, K/min

T - Temperature, K

The temperature dependence of the rate equation is assumed to follow the Arrhenius equation:

$$K(T) = A_o \cdot \exp\left(\frac{-E}{RT}\right) \quad (21)$$

Where

E - Activation energy

R – Universal gas constant

T - Temperature

Combining equations (19), (21) and the differential of (20)

$$\frac{d(X)}{dT} = \frac{A_o}{\beta} \exp\left(\frac{-E}{RT}\right) \cdot f(X) \quad (22)$$

Equation (22) can be solved by separating the variables

$$g(X) = \int_0^X \frac{dX}{f(X)} = \int_{T_0}^T \frac{A_0}{\beta} \exp\left(\frac{-E}{RT}\right) dT \quad (23)$$

The functions $g(x)$ and $f(x)$ are given Table 2.5.

Table 2.5. Examples of Reduction Kinetics Models

Model	$f(X)$ - differential form	$g(X)$ - integral form
nth order	X^n	$X^{n+1}/(n+1)$
Random nucleation	$(1-X)$	$-\ln(1-X)$
Phase boundary area controlled	$(1-X)^{1/2}$	$2(1-(1-X)^{1/2})$
Phase boundary volume controlled	$(1-X)^{2/3}$	$3(1-(1-X)^{1/3})$

2.8.5 Activation energy from TP Techniques

The maximum of any polynomial is defined as, that point on the curve where the gradient is zero. Therefore the maximum of TPR peak, the following equation holds

$$\frac{d}{dT} \left(\frac{dX}{dT} \right)_{T=T_{\max}} = 0 \quad (24)$$

Combining equation (22) and (24)

$$\frac{d}{dT} \left(\frac{A_0}{\beta} \exp\left(\frac{-E}{RT}\right) f(X) \right)_{T=T_{\max}} = 0 \quad (25)$$

This equation reduces to

$$\frac{dX}{dT} \left[\frac{E}{RT^2} + \left(\frac{A_0}{\beta} \exp\left(-\frac{E}{RT_{\max}}\right) \right) \left(\frac{df(X)}{dX} \right)_{T=T_{\max}} \right] = 0 \quad (26)$$

Assuming that $f(x)$ and x are independent of heating rate and that $d(X)/dT$ is not equal to zero, equation 26 can be written as:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) + \ln\left(\frac{E}{RA_0}\right) = -\frac{E}{RT_{\max}} + \ln\left(-\frac{df(X)}{dX}\right)_{T=T_{\max}} \quad (27)$$

Therefore plotting $\ln\left(\frac{\beta}{T_{\max}^2}\right)$ vs $\frac{1}{T_{\max}}$ should give straight lines with a slope $-E/R$. These plots are sometimes called ‘Arrhenius plots’, Barker, 1999.

2.8.6 Application of TP techniques

TPO: TPO has found application in determining the thermal stability of catalysts with varying compositions. For example, automotive exhaust catalyst used for both the oxidation of CO, C_nH_m and the reduction of NO_x , such as 14.5%CeO₂/Al₂O₃ reacts with H₂ at 500°C, while 0.52%-13.3%Ce/O₂Al₂O₃ reacts at 350°C, Serre *et. al.* 1991. This TPO can be used, study, to establish varying compositions of catalysts. This also implies that if the TPO onset temperature remains independent of the batch of sample used, then material consistency can be assumed.

TPR: This is normally carried out using hydrogen as the reducing gas; however CO can be used when surface reactions are being studied. The peaks associated with TPR typically span a temperature range of over 300°C with heating rate of 10°C/min, Lööf *et. al.*, 1989, 1991. The total amount of hydrogen consumed, (moles of H₂/moles of compound) in a TPR of an oxide can be determined by integrating the area under the H₂O trace logged by a Mass Spectrometer. This can be roughly correlated to the number of electrons transferred in the reduction reaction. For example, CeO₂ uses 0.20-0.27 μmol H₂/μmol CeO₂, which correlates to one-electron transfer per CeO₂, Yao, 1987, Yao, 1984. From their TPR data, they determined that the reduction reaction was from Ce⁴⁺ to Ce³⁺, and complete reduction to Ce was not achievable even at 900°C.

TPS and TPR-S: These techniques became useful when metal sulphides were found to have catalytic activity towards removing organic and inorganic sulphides from petrochemical feedstock. TPS has been used to formulate the best sulphiding conditions needed to produce the most effective catalyst, while TPR-S may give an insight into the reaction mechanism of the catalyst in the sulphide reactions. The use of both TPS and TPR-S can also yield the extent of sulphiding of a catalyst. For example, Bonne *et. al.*, 1995, used a mixture of 3Vol%H₂S and 28Vol%H₂/Ar, as the feed gas for TPS while TPR-S feed gas was 15Vol%H₂S/67Vol%H₂/Ar, to understand the sulphiding mechanism of V₂O₅. They observed that up to four types of sulphur were present on sulphided catalyst; namely adsorbed H₂S, non-stoichiometric sulphur (S_x), stoichiometric sulphur and S-H groups. The presence of adsorbed H₂S on the catalyst can be identified by the liberation of H₂S without any consumption of H₂; non-stoichiometric sulphur is typically removed at low temperature with the consumption of hydrogen. They observe that H₂S was the reactive gas in the TPS

experiments and the mechanism of vanadium substitution starting from V_2O_5 to V_2O_3 ; $V_2O_5 \rightarrow V_2O_3 \rightarrow V_2S_3$, Janssens, 1999. A three stage reduction process of V_2O_5 based TPR data was also proposed by Wang *et. al.*, 2003, the reduction mechanism (assuming that V is constant) of $3V_2O_5 \rightarrow V_6O_{13} \rightarrow 3V_2O_4 \rightarrow 3V_2O_3$ was proposed. TPR-S of MoS_2/Al_2O_3 has two peaks; the low temperature peak was attributed to the presence of over-stoichiometric S_x , and the second to S^{2-} ions at the surface or edge, Loos *et. al.*, 1990.

2.9 Electrochemical Characterisation Techniques

2.9.1 Four Point DC Resistivity

Measurement of the bulk resistivity using a 4-point resistance meter was not successful. However a brief mention of the theory is included to understand the technique. The bulk resistivity, Ohms-cm (Ω) of a semi-infinite wafer with equal probe spacing (s) is given by the equation 28, (Figure 2.7).

$$\Omega = 2 \times \pi \times s \times \frac{V}{I}, \text{ Valdes, 1954} \quad (28)$$

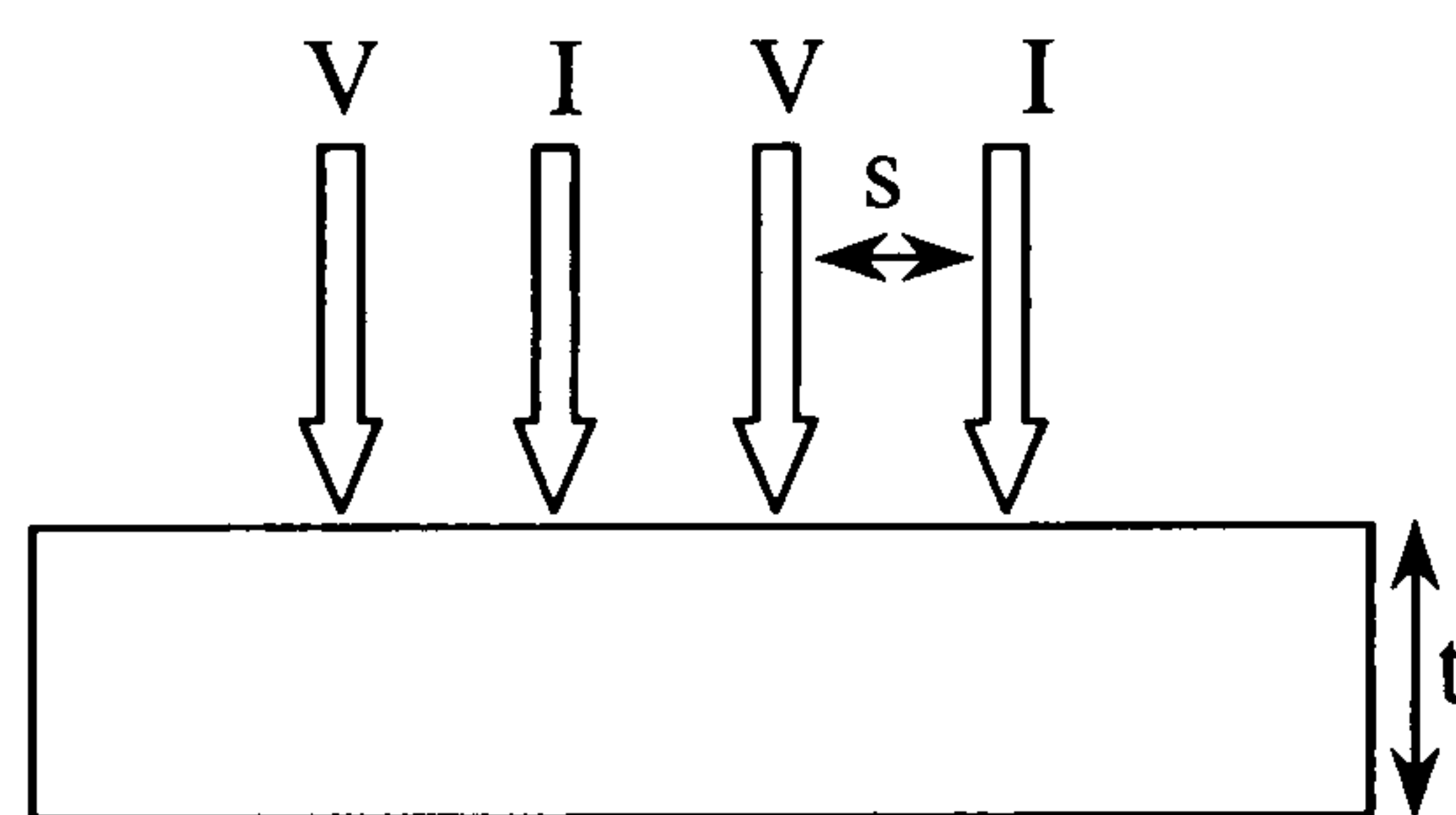


Figure 2-7. Schematic of a Four-Electrode DC Measurement Cell

Where,

- t - sample thickness, mm,
- V - applied voltage, V,
- I - current measured, amps,
- s - is the probe spacing,
- Ω - Bulk resistivity

The sheet resistance, R_s , is given by:

$$R_s = \frac{\Omega}{t} \quad (29)$$

L. Valdes reported that once the edge of the nearest boundary is at least 5 times the probe spacing, equation 28 is valid without any correction (thin film resistance). Equation 29

requires a correction factor. Once the samples thickness is less than at least 5 times the probe spacing, equation (28) becomes (30), Smits, 1958.

$$\Omega = a \times 2 \times \pi \times s \times V/I \quad (30)$$

Where $a = 0.72 \text{ t/s}$, for $(t/s) \geq 0.5$, Figure 2.7

2.9.2 Impedance Spectroscopy

Electrical Impedance spectroscopy, EIS, is a non-destructive tool that can be used for analysing the electrochemical properties of ceramic materials. EIS has been utilized to provide information on practical issues such as corrosion rates, efficiency of protective coatings, testing of batteries, surface treatments, conduction mechanism for ceramics etc. The advantages of EIS include short measuring time, high accuracy and capability of continuous measurement. While the disadvantage of EIS is that the process being investigated is perturbed from its normal state by an external signal, which can change or alter the properties of the system. The perturbation is typically an alternating current (a.c) because smaller perturbations are used when compared to direct current (d.c.); this allows materials with lower conductivity to be investigated as well as introducing less interface problems.

Impedance Spectroscopy Theory

The electronic properties of a system can generally be defined in terms of its ability to store and transfer an electric charge (i.e. its capacitance and conductance). EIS records the response of a system to an applied sinusoidal perturbation, over a selected frequency range. The applied ac voltage (V) and the resultant ac current (I) are measured and the impedance (Z) is calculated ($Z = V/I$). The material being measured is perturbed with a sinusoidal voltage through electrodes using a frequency response analyser (FRA). The result is a current having the same frequency but a different phase and amplitude. The system response can be separated into real and imaginary terms (i.e. conductance- real and capacitance -imaginary).

Complex impedance is expressed as,

$$Z^* = V/I = V \sin(\omega t) / I \sin(\omega t + \theta) \quad (30)$$

Where $\omega = 2\pi f$, and

$$Z^* = a \cos \theta + b \sin \theta = Z' + Z''; \quad (31)$$

$$\text{Impedance Magnitude} = |Z| = \sqrt{a^2 + b^2} \quad (32)$$

$$\text{Impedance Phase Angle} = \theta = \arctan |Z''| / |Z'| = \arctan(b/a) \quad (33)$$

Armstrong *et. al.*, 1977, 1968 and Gabrielle, 1981 amongst other showed that frequency response analysers, FRA, can determine the impedance by correlating the cell response $S(t)$ with two synchronous reference signals, one of which is in phase with the sine wave perturbation, $P(t)$ and the other shifted 90° in phase. Macdonald, 1987. The sine wave perturbation function $P(t)$ is applied to the cell;

$$P(t) = P^o \sin(\omega t) \quad (34)$$

Where

P^o is the amplitude; ω is the frequency

The cell response maybe written as

$$S(t) = P^o |Z(\omega)| \sin[\omega t + \phi] + \sum_m A_m \sin[m\omega t - \phi_m] + N(t) \quad (35)$$

The first term in equation 35 is the transfer function, the second and third terms represent the harmonics and noise respectively, and both harmonics and noise are rejected due to high integration periods.

1.5 Experimental Requirements

1. Measuring the electrochemical behaviour of an electrolyte requires two identical electrodes to be applied on either side of the sample; the electrode maybe sputtered, painted, thermally evaporated or mechanically contacted.
2. The atmosphere under which the electrochemical measurement is made should remain constant, for example a homogenous oxidizing environment.
3. Constant temperature is required during the measurement of the system impedance, remembering impedance is a type of resistance, and that impedance for ceramic materials decreases as temperature increases.

Capabilities and Limitations

Impedance spectroscopy can be used to study intrinsic properties of materials that affect conductivity of the electrode-material interface, Ramzan and Brydson, 2005. These parameters can be divided into two groups: (1) Those that are material dependent such as dielectric constant, conductivity, equilibrium of charged species; and (2) Those that are related to the electrode-material interface, for example capacitance of the interface, diffusion coefficient at the interface and adsorption/reaction rates. E.I.S has also found use in predicting the performance of sensors, Ménil *et. al.*, 2005, and fuel cells Andreaus *et. al.*, 2002; determining ionic conductivity, Tiwari and Shahi, 2005, grain boundary effects, Song, *et. al.*, 2005; determining diffusion coefficients for systems such as membranes or thin oxide films etc, Santiago *et. al.*, 2005; determining the kinetics of the ionic/electronic conduction interfaces, Makhoulouf and Khalil, 2003.

Apparatus Effect on Impedance Spectroscopy Data

A given material phenomenon e.g. bulk response, grain boundary conduction, interfacial barrier transport of the considered to have resistive and capacitive components, operating in parallel. The time constant for this system is the corresponding resistance-capacitance or RC product, and this is related to frequency at maximum impedance, f , using equation 36, (Figure 2-8).

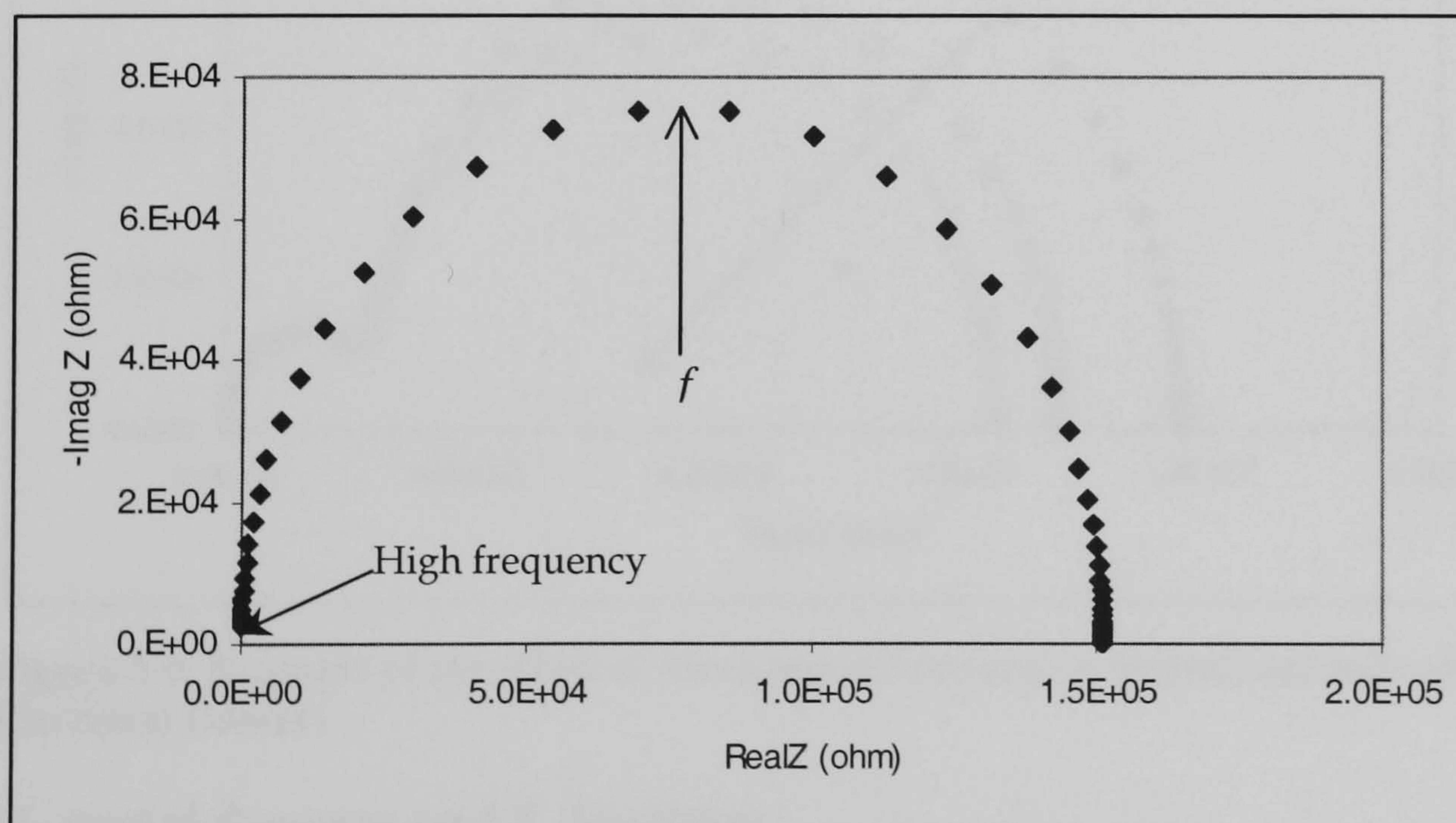


Figure 2-8 Nyquist Plot for a Resistor and Capacitor in parallel

$$RC = \frac{1}{2\pi f} \quad (36)$$

Where,

R- resistance, Ω ; C- capacitance F; f -frequency, Hz.

In an a ideal Nyquist plot, imaginary vs real impedance, the frequency corresponding to the top of the arc gives the numerical value of 'f' in the equation above as shown in Figure 2-8. However apparatus inductance can distort the E.I.S. data particularly at high frequency. Distortion can occur at high frequencies when the impedance of the apparatus is comparable to or larger than the sample impedance, Campestrini *et. al.*, 2002. Ultimately, equivalent circuit simulations are the best test of whether or not a reliable sample response is being obtained. The appropriate equivalent circuit consisting of resistors, inductors and capacitors, which replicate as closely as possible the impedance behaviour of the actual specimen, should be selected.

Effect of Mechanical Force on Impedance Spectroscopy Data

Increasing the mechanical loading on the electrode-electrolyte system may result in a decline in the overall resistance as the pressure increases, Figure 2-9.

This significant reduction of the low frequency arc is due to the 'air-gap' between the mechanically contacted electrode and the electrolyte. In this case the true sample resistance was not obtained at the highest mechanical pressure. Hsieh, *et. al.* 1996.

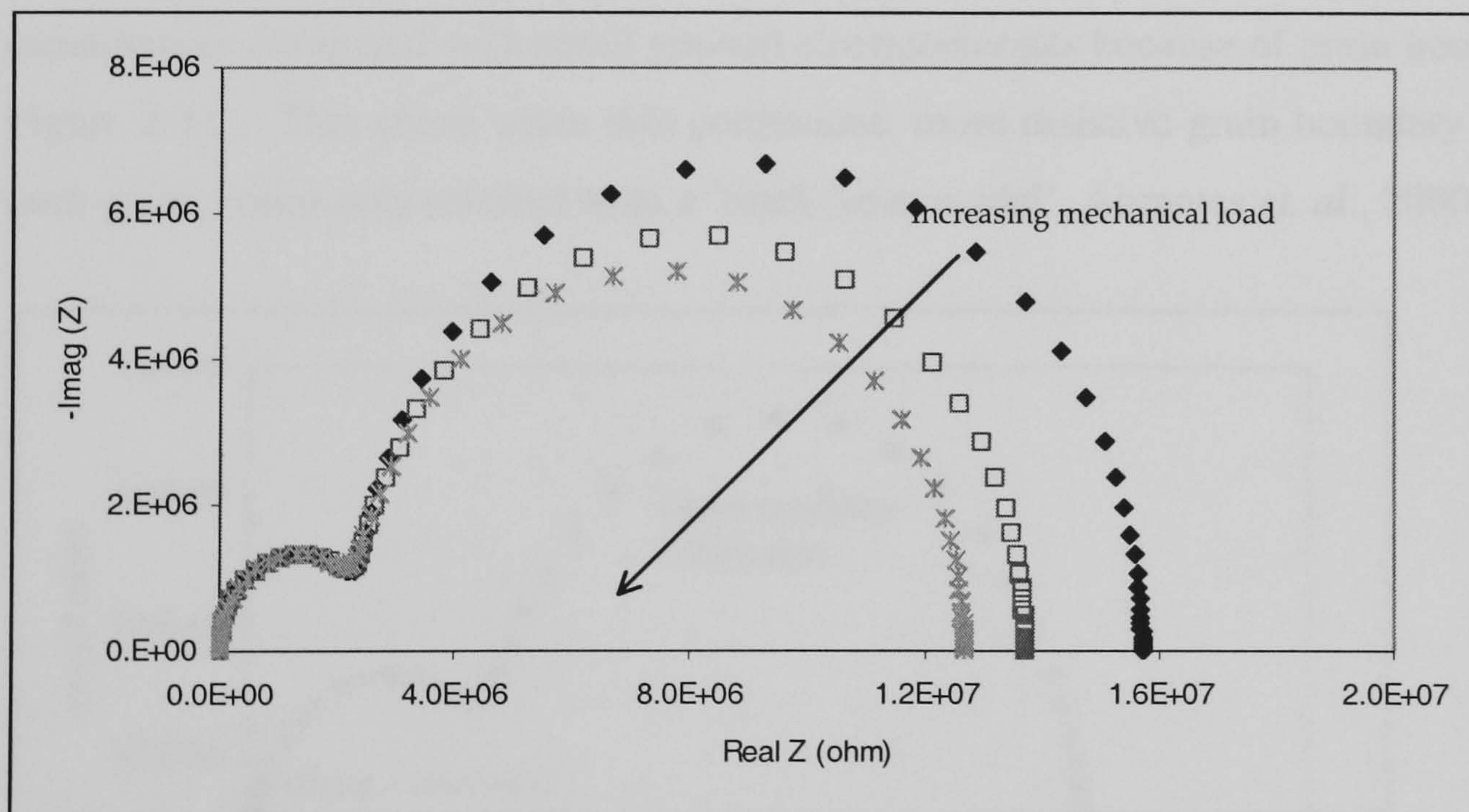


Figure 2-9. Example of the effect of Mechanical Pressure on Impedance indicating Poor Electrical Contact

O₂ partial Pressure on I.S. Spectrum

The geometry of the sample is constant and the geometry of the contacts, a , does not vary, if the distance between the contacts is larger than the radii of the contacts. Assuming perfect electrode-electrolyte contact, then only the bulk arc is observed (assuming also not grain boundary effect). If two arcs are observed; both vary with the O₂ partial pressure, see Figure

2-10. Jiang *et. al.* , 2002 plotted the slope of the inverse resistance of the high frequency arc vs partial pressure, which gave an indication to the point defect mechanism.

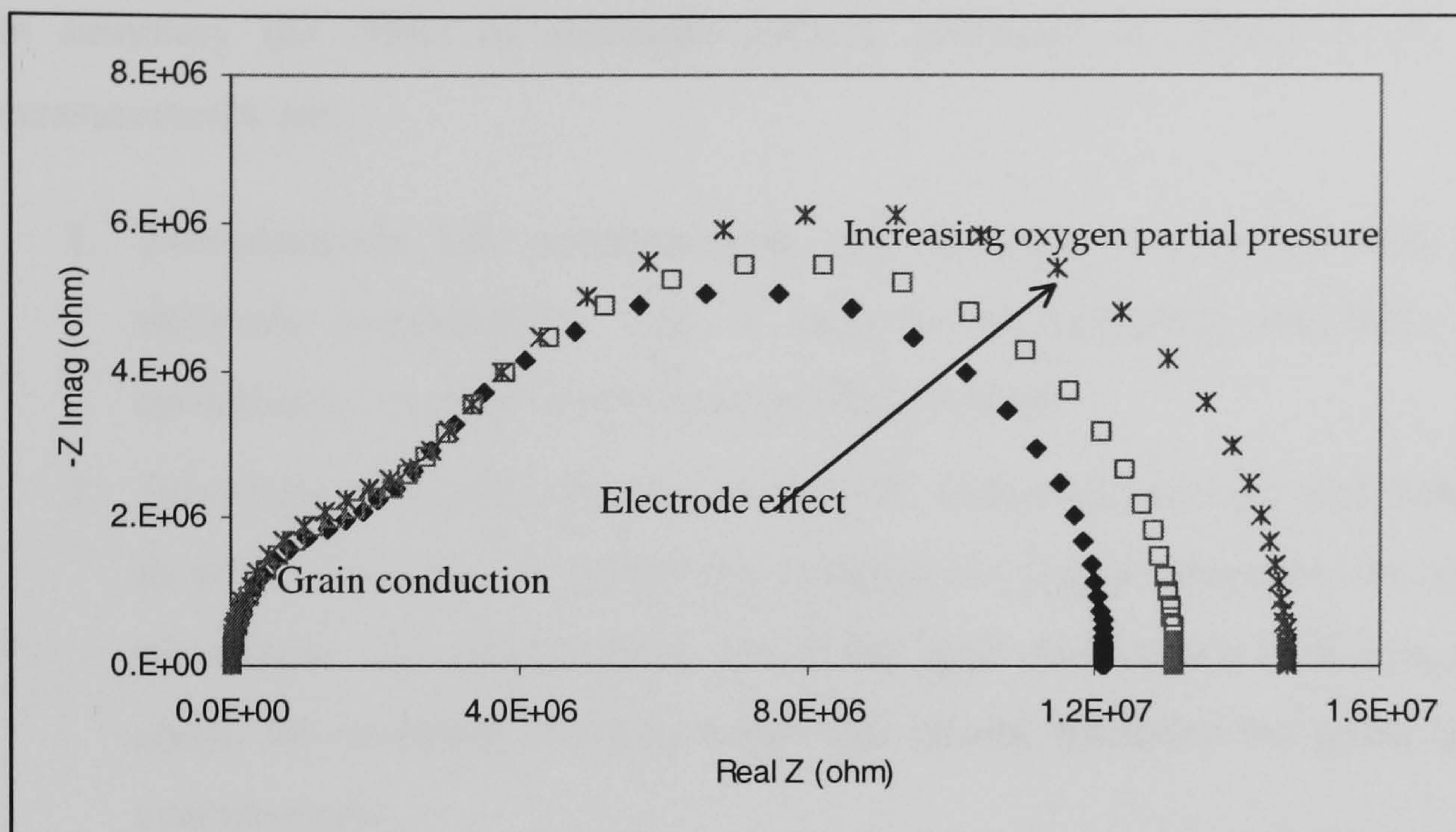


Figure 2-10. Effect of O₂ Partial Pressure on Impedance Nyquist Plot

Grain Boundary Effect on I.S. Spectra

In large grained electroceramics, it is possible to achieve substantially larger sample capacitances compared with small grained electroceramics because of grain boundary effects, Figure 2-11 . This arises when thin continuous, more resistive grain boundary layers isolate each grain, commonly referred to as a ‘brick layer model’, Abrantes *et. al.*, 2000.

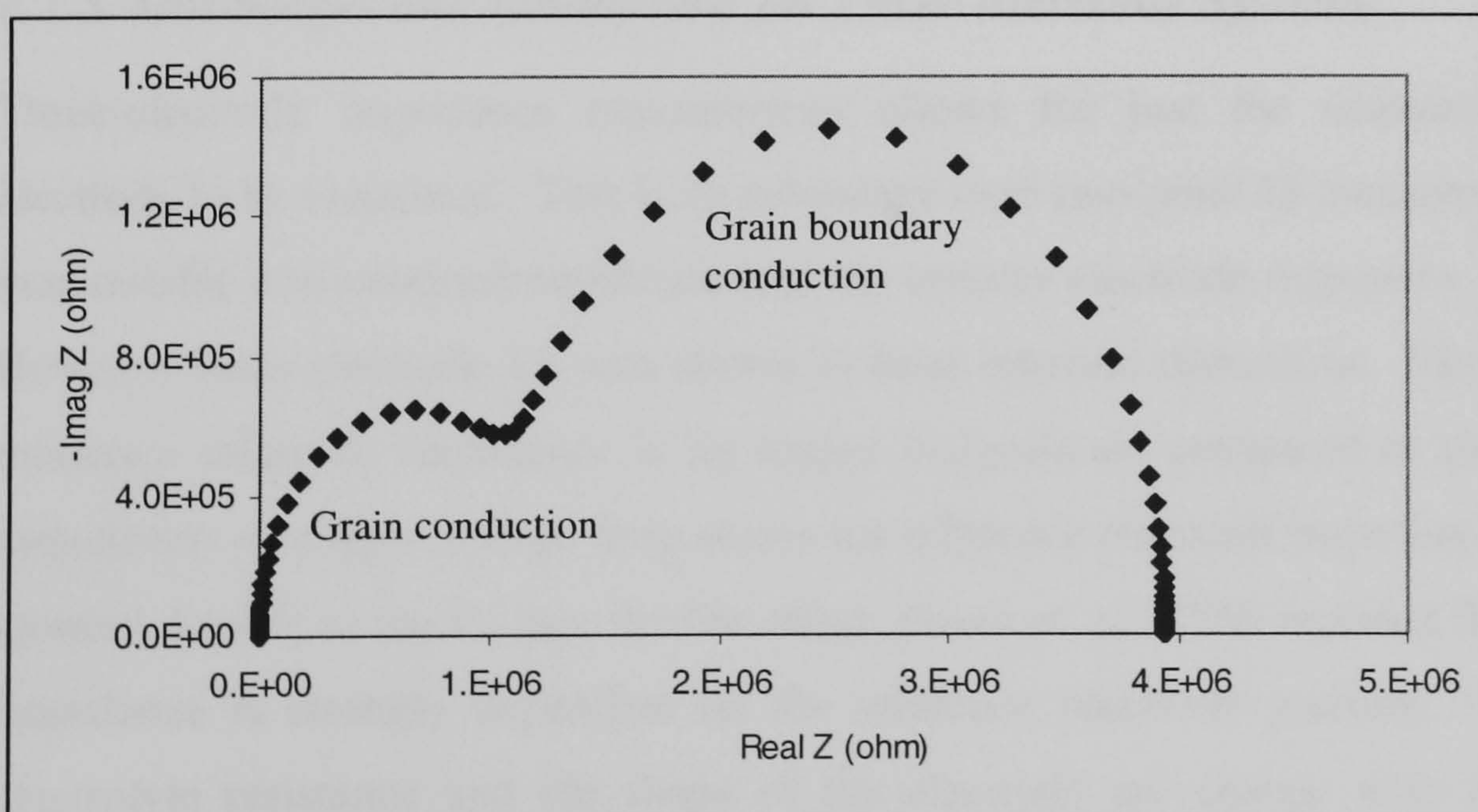


Figure 2-11. Effect of Grain Boundaries on Impedance Nyquist Plot

The large low frequency arc has the resistance and capacitance of the grain boundaries, (R_{gb} , C_{gb}), the smaller high frequency arc indicated the resistance and capacitance of the grain interiors (R_{gi} , C_{gi}). These would look like those seen in Figure 2-11, that a small high

frequency arc and a large low frequency arc. However these arcs should not vary upon changing oxygen partial pressure, only with a change in temperature.

In summary the effect of electrode contact, proposed by Hsieh *et. al.*, 1996, on EIS measurements are:

1. Two-electrode I.S. measurements can be used to separate bulk response from electrode contributions, only if there is no spreading resistance effect (contact resistance), i.e. good electrode-electrolyte contact.
2. Spreading resistance effect can affect the bulk resistance arc and bulk time constants as well. Also the low frequency intercept no longer represents the true resistance of the sample. An additional arc due to the 'gap' capacitance is also possible. In certain cases, the resulting two arcs behaviour can be mistaken for grain interior and bulk contributions.
3. Making simultaneous 4-point DC resistivity measurement on every specimen best eliminates spreading resistance effect. If the low frequency intercept of the bulk features agrees with the true DC resistance, spreading resistance can be neglected.
4. Careful attention to polishing and electroding is the best means to avoid spreading resistance contributions. Good contact was achieved only when samples were finely polished and adequately plated.

E.I.S Advantages and Limitations for Three Electrode Systems

Three-electrode impedance measurement allows for just the response of the working electrode to be examined. This is an advantage over two-point IS measurement which has an unavoidable convolution/complication of the counter electrode responses, Hsieh *et. al.* 1996. However three-electrode I.S was shown to have inherent distortions. These occur when the reference electrode impedance is no longer insignificant compared to the instrument input impedance, causing a voltage drop across the reference electrode impedance, which cannot be ignored, known as the voltage divider effect. Fiaud *et. al.*, 1986 reported that electrochemical impedance is strongly dependent on the reference electrode position. Both the apparent electrolyte resistance and the shape of the electrode arc change with reference electrode placement. Despite this fact many cell geometries are used, see Figure 2-12 where arrangement (1) and (2) are typical.

Electrode configurations with high aspect ratios (the separation between the reference and working electrode is at least 30 times the thickness of the electrolyte) were suggested to

eliminate the geometry effect on measurements, Hsieh *et. al.*, 1996. The best means to establish the presence of spreading resistance effects for a two-point I.S measurement is to perform simultaneous four point DC resistivity measurements. The DC measurement should agree with R_s (specimen resistance) while the apparent bulk resistance in two point E.I.S. is the sum of the R_s and R_c (contact resistance).

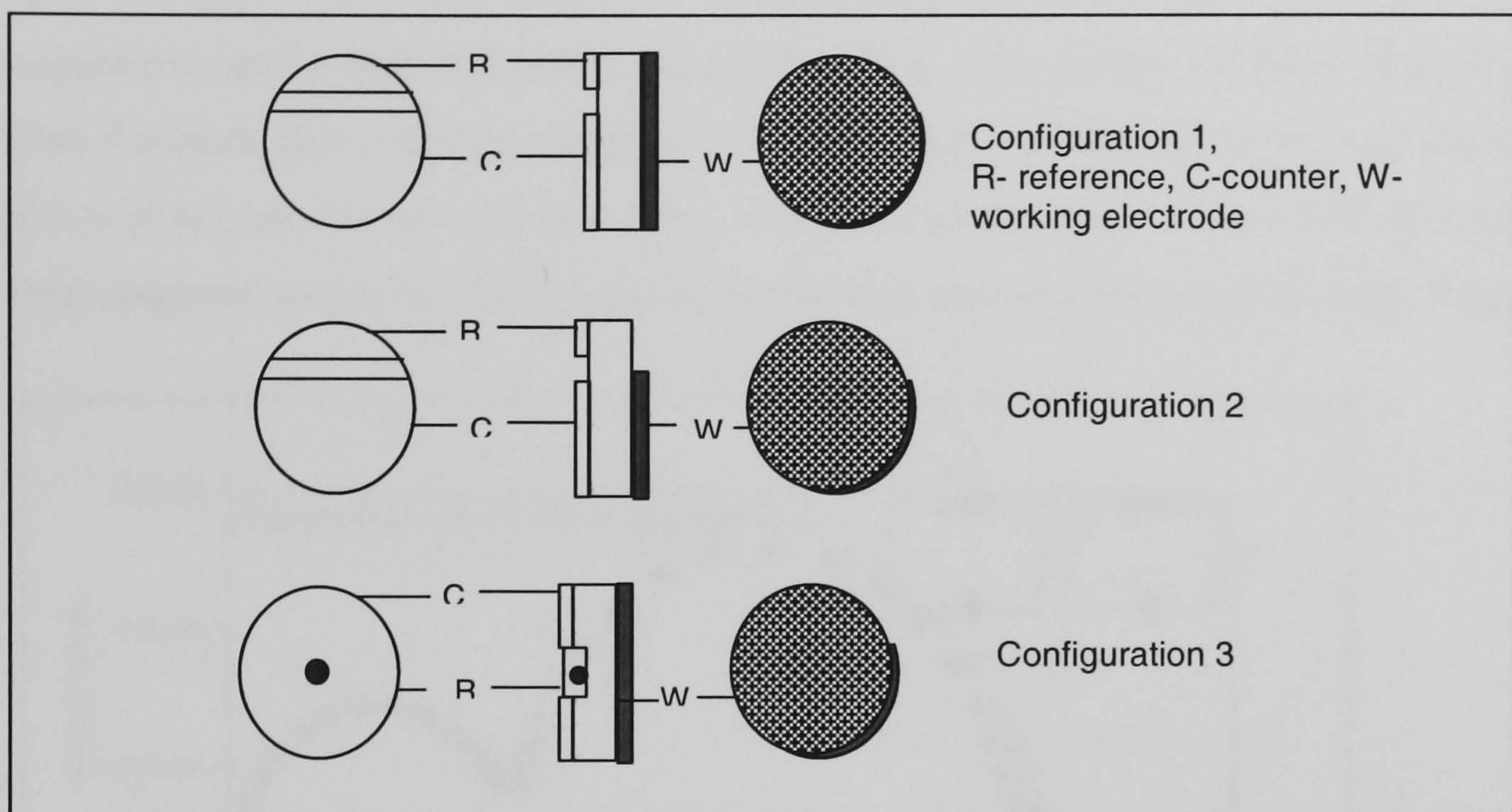


Figure 2-12. Various Configurations of Electrode Placement for 3-Point Impedance

* Configuration 3 is the solid electrolyte analogue of the Luggin capillary reference used in aqueous systems.

A distorted spectrum is possible for asymmetric electrode arrangements such as phase shifts, inaccurate electrode resistances, and artificial features. No simple relationship between electrolyte resistance and the geometry of the cell was observed for surface mounted reference electrode, Hsieh *et. al.* 1996.

In summary experimental I.S data rarely produce arcs of full semicircles with the centre on the real axis of the complex plane. There are three explanations that could yield only a fraction of the semicircle, which are:

1. The presence of other arcs at high frequencies could cause the experimental arc not to pass through the origin.
2. The presence of distributed elements at the electrode-material interface can shift the centre of the experimental arc below the real axis.

3. The experimental arc can be distorted significantly by the presence of other relaxations with time constants smaller by two orders of magnitude relative to the experimental relaxation time.

2.10 Equivalent Circuit and Physical Models

Any electrode–electrolyte system in a measuring cell is assumed to have a geometrical capacitance and a bulk resistance in parallel with it. The product of these elements gives the time constant, also called the dielectric relaxation time of the electrolyte. It is often so small, that it is not seen in an impedance plot. However lowering the temperature will increase the time constant, so that this arc representing the bulk measurements will be seen, Figure 2-13.

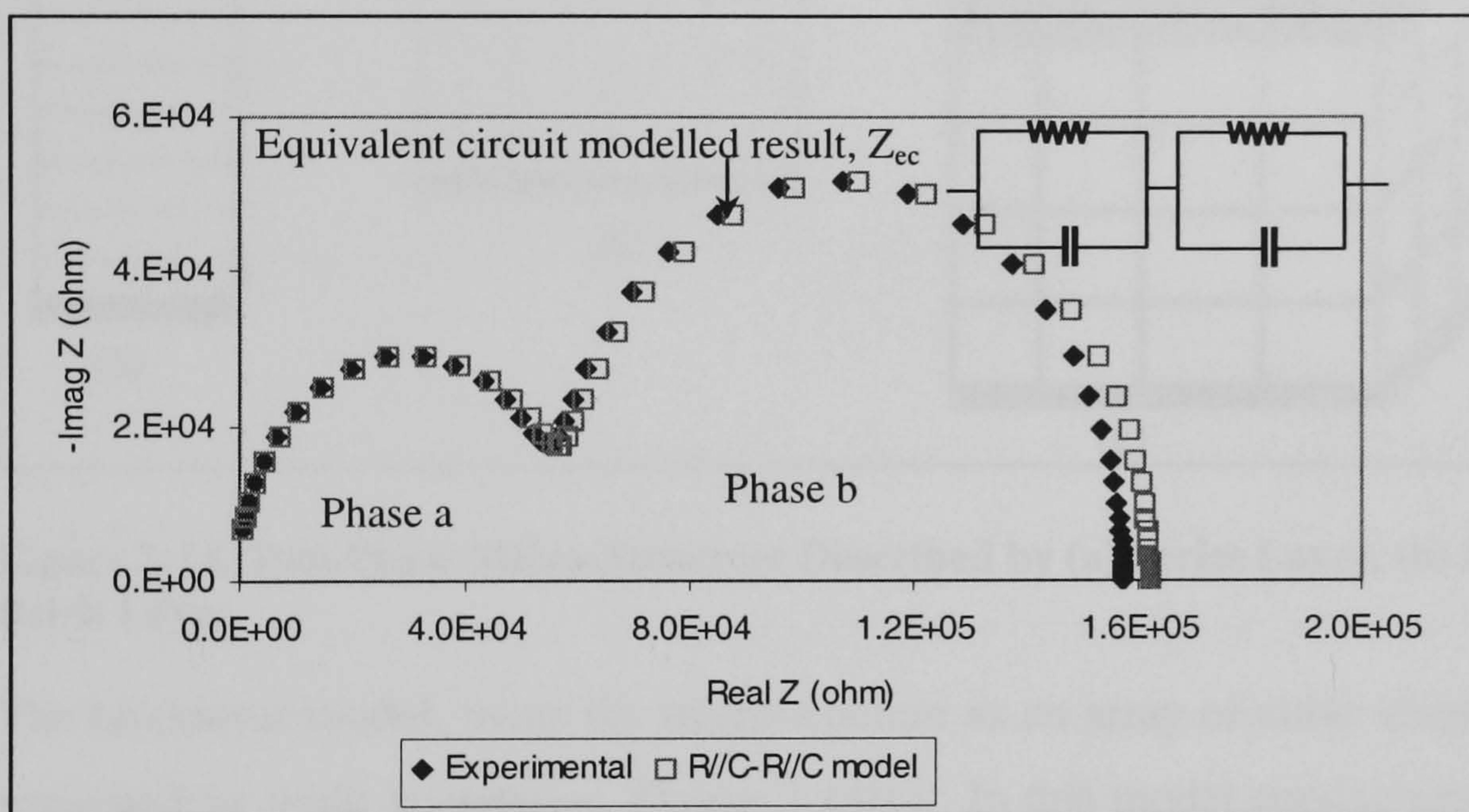


Figure 2-13. Typical Nyquist Plot and Equivalent Circuit

A typical Impedance Plot for a Two-Phase Microstructure and (b) a Possible Equivalent Circuit (b) is shown in Figure 2-13. Equivalent circuit uses ideal lumped parameters such as resistors and capacitors, even though most electrochemical cells are distributed in space. Thus equivalent impedance $Z_{ec}(\omega)$ may need more than the ideal capacitance and resistances to approach the experimental impedance, $Z_e(\omega)$. This misalignment can be accounted for by using distributed impedance elements, for example constant-phase elements (CPE's). $Z_{ec}(\omega)$ has a further possible ambiguity because any circuit that has three or more elements can be arranged differently all of which gives the same $Z_e(\omega)$. This problem can only be solved by applying chemical and physical principles (an educated guess) or by varying parameters in $Z_e(\omega)$ to validate which of the $Z_{ec}(\omega)$ is correct.

The layer models (parallel, series or brick model) relate the impedance of material to the microstructure. The series layer model assumes that the grain are stacked parallel to the

electrode, Figure 2-14(a); McDonald, 1987 described the model of the impedance by a linear mixing rule the complex resistivity of $\rho_t = x_1\rho_1 + x_2\rho_2$, where ρ_i -complex resistivity and x_i -volume fraction of a phase i . However the parallel model shown in Figure 2-14(b), assumes the grains are stacked perpendicular to the electrode; showed that in this case the complex conductivities followed a linear mixing rule of $\psi_t = x_1\psi_1 + x_2\psi_2$, where ψ_i is the complex conductivity and x is the volume fraction of phase i . If the phases differ significantly in their complex resistivity, two well-defined arcs would be in the complex plot as shown in Figure 2-13 above.

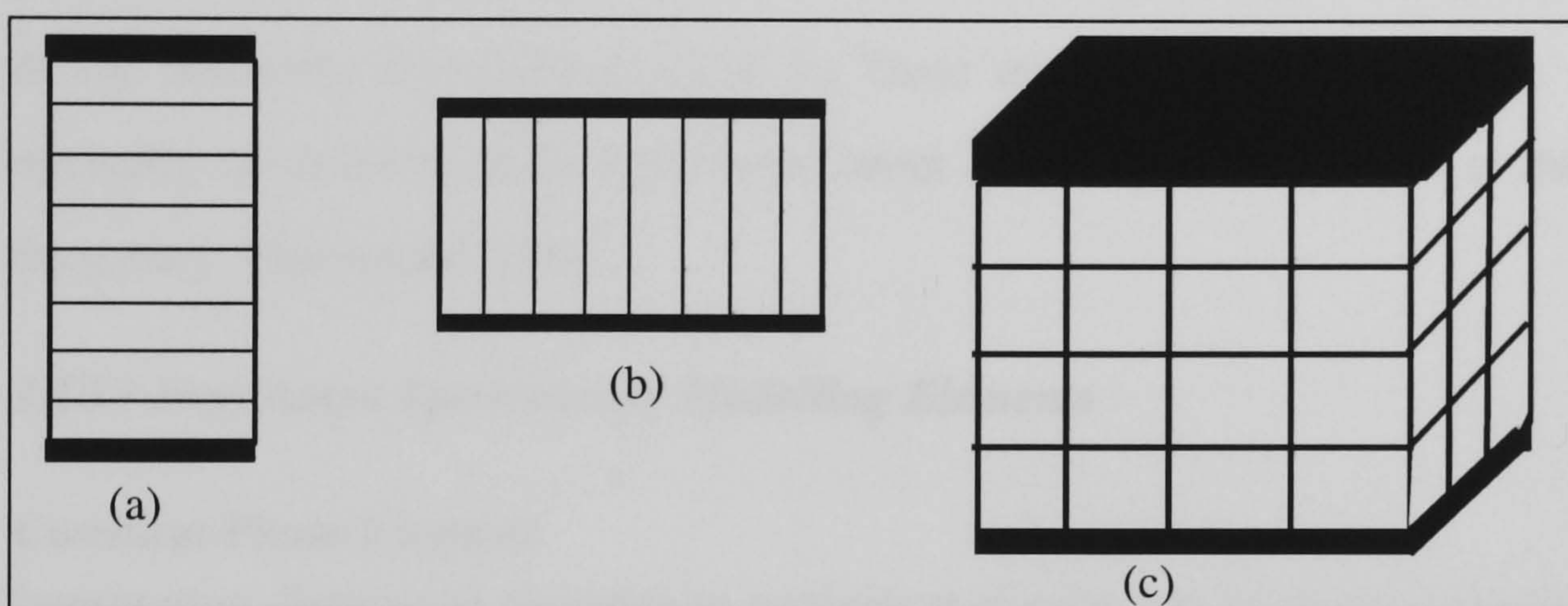


Figure 2-14. Two Phase Micro-Structure Described by (a) Series Layer, (b) Parallel Layer, (c) Brick Layer

The bricklayer model, treats the microstructure as an array of cubic shaped grains which are separated by grain boundaries, Figure 2-14(c). In this model conduction may occur through the grains and across the grain boundaries or along the grain boundaries therefore the extreme cases are when the grain boundaries are blocking (little conduction) or dominant (major conduction).

Generally the experimental impedance $Z_e(\omega)$ is approximated to a, $Z_{ec}(\omega)$, equivalent circuit made up of real resistors, capacitors inductances and distributed elements, Figure 2-15. In such a circuit, the resistance represents a conductive pathway thus it can be used to indicate for example bulk conductivity or a chemical reaction occurring at the electrode interface. Capacitances and inductances normally indicate some sort of space charge polarisation of an absorption process or electro-crystallization process.

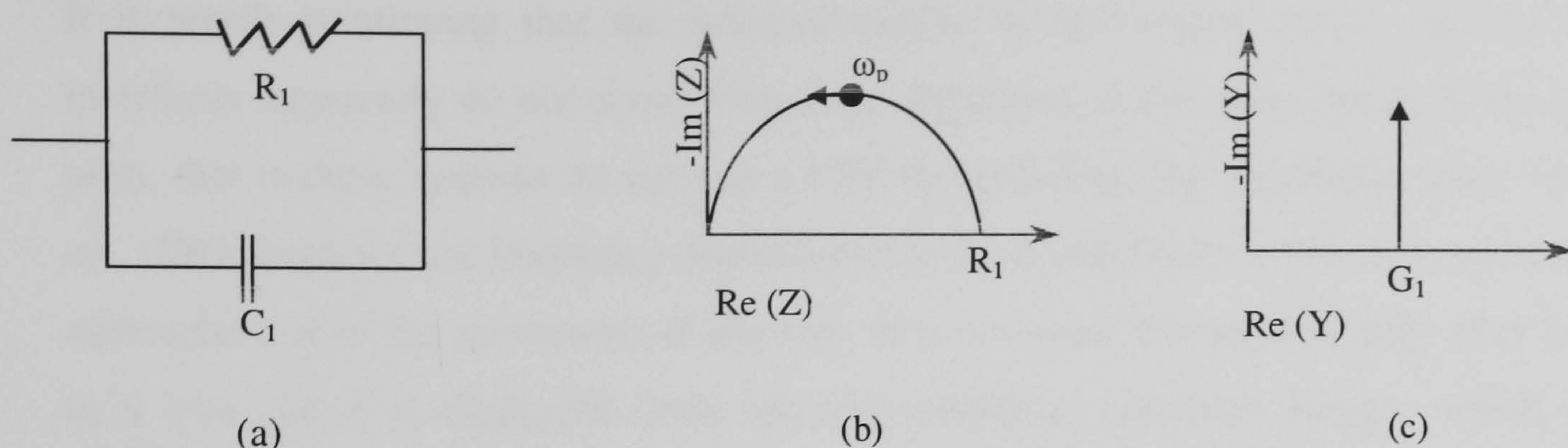


Figure 2-15. (a) Typical RC Circuit, (b) Equivalent Impedance Plot and (c) The Admittance Plot
 The electrode–material system in a measuring cell has a geometrical capacitance C_1 and a bulk resistance R_1 in parallel with it. These two elements lead to a time constant $\tau_D = R_1 C_1$, or the dielectric relaxation time of the basic material, Figure 2-15. This time constant is normally the smallest in the E.I.S experiment ($< 10^{-7} \text{ s}$), which occurs at the highest angular frequency, Macdonald, 1987.

2.10.1 Impedance Spectroscopy Modelling Elements

Constant Phase Element

Interpreting distributed elements in equivalent circuits can be divided into two types that are related to the spatial arrangement of the real system. The first type relates to non-local processes such as diffusion. The other type of constant-phase element (CPE) is associated with the microscopic properties of the material that is a distributed parameter. For example, the solid electrolyte interface on a microscopic level is not smooth nor uniform, which is the normal assumption, used in modelling solid electrolyte and solid-solid interfaces as shown by Almond *et. al*, 1982, 1983, 1984 and Jonscher, 1977 and 1980. Constant phase elements (CPE) are used to model impedance in the Nyquist plane when arcs centres do not lie on the real axis, Figure 2-16.

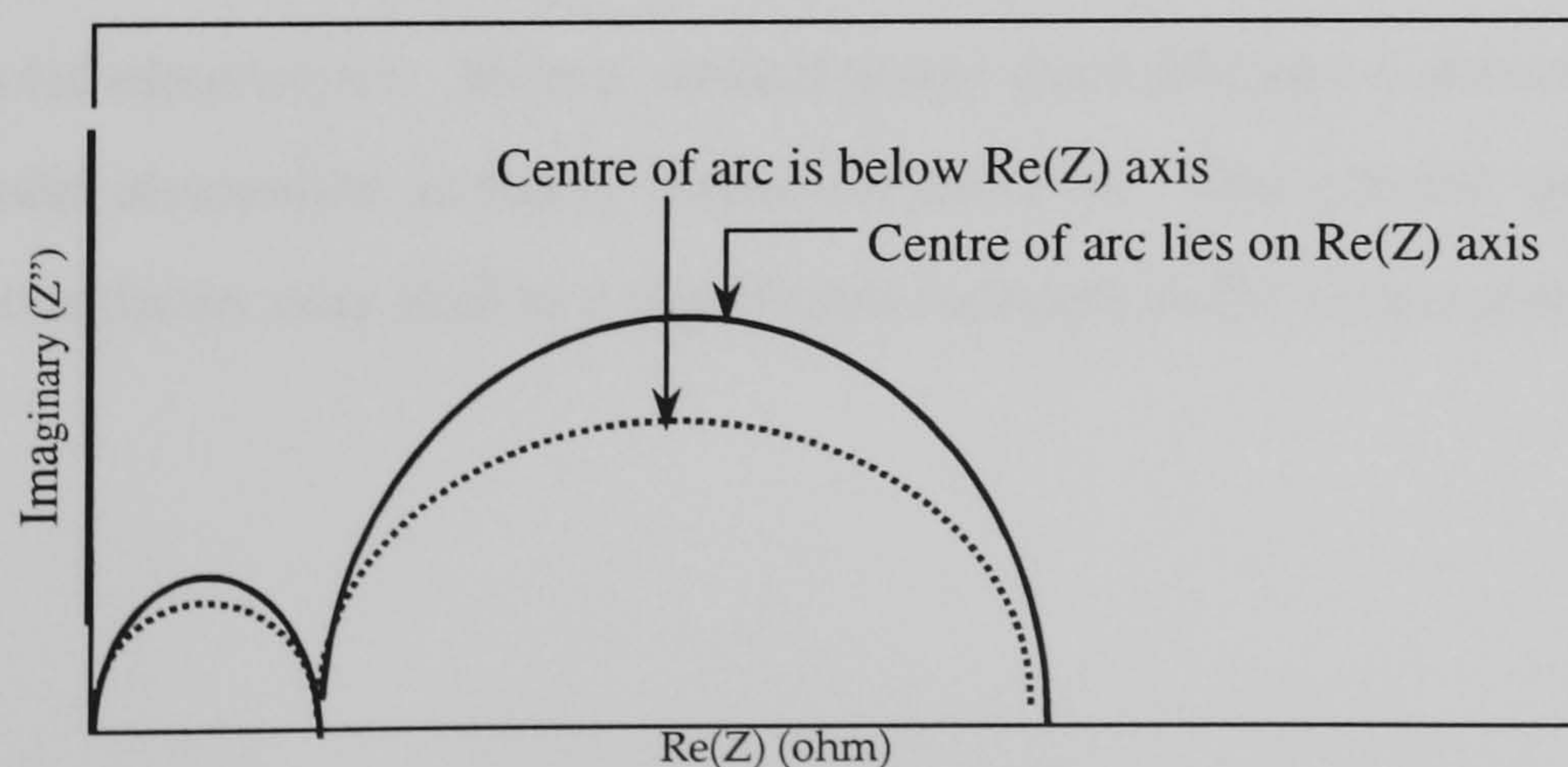


Figure 2-16. Nyquist Plot of Circuit with CPE

It is worth mentioning that the microscopically smooth liquid metal aqueous electrolyte interfaces apparently do not show frequency dispersion of the capacitance if the systems are pure, that is these systems do not use a CPE in modelling the impedance data. Jonscher *et. al.*, 1980 attributed the frequency dependence of the conductivity to the relaxation of the ionic atmosphere after the movement of the ion. It is assumed that immediately after an ion hops to a new site it is displaced from the true minimum potential energy, which includes a contribution from other mobile defects. After long time, the defect cloud relaxes; a true minimum coincides with lattice site. Whenever reaction resistance and capacitive components differ with electrode location it is best modelled by CPE element. Macdonald, 1987 noted that conduction processes, either interface or bulk, which are thermally activated with a distribution of activation energies, is also best modelled by a CPE rather than the just a capacitor-resistor combination. Franceschetti and Shipe, 1984 proposed a model describing the motion of the defect species as several distinguishable jump processes, each governed by a different activation energy. The interpretation of the relaxation branches in the circuit is that they describe a polarisation arising from the inequalities in jump probabilities

Raistrick *et. al.*, 1976 studied dense polycrystalline alumino silicates, and noted that except for the densest of materials, the polycrystalline samples always showed some frequency dependence. Here, again, the experimental data was fitted best by the use of a CPE. Adham and Hammou, 1985 studied single crystal of CaO-doped CeO_2 , and found two arcs present, depending on the presence or absence of CaO enrichment at the grain boundary. It is also possible that close to the grain boundary, the transport properties of the crystal are controlled by imperfections, expected to be present there in higher concentration than in the centre of a grain, leading to an additional contribution to the inter-grain impedance. This idea is very close to the observation of conductivity enhancement due to the heterogeneous doping of solid electrolytes. Here a second phase insoluble non-conducting phase is introduced into the solid electrolyte as finely dispersed particles. The internal space charge created at the phase boundaries may lead to a significant increase in the concentration of mobile defects.

Charge Transfer Resistance and Capacitance

A single semi-circle displaced from the origin is characteristic of kinetic control by an electrochemical charge transfer step at the electrode-electrolyte interface, as represented in the Z plot, Figure 2-17.

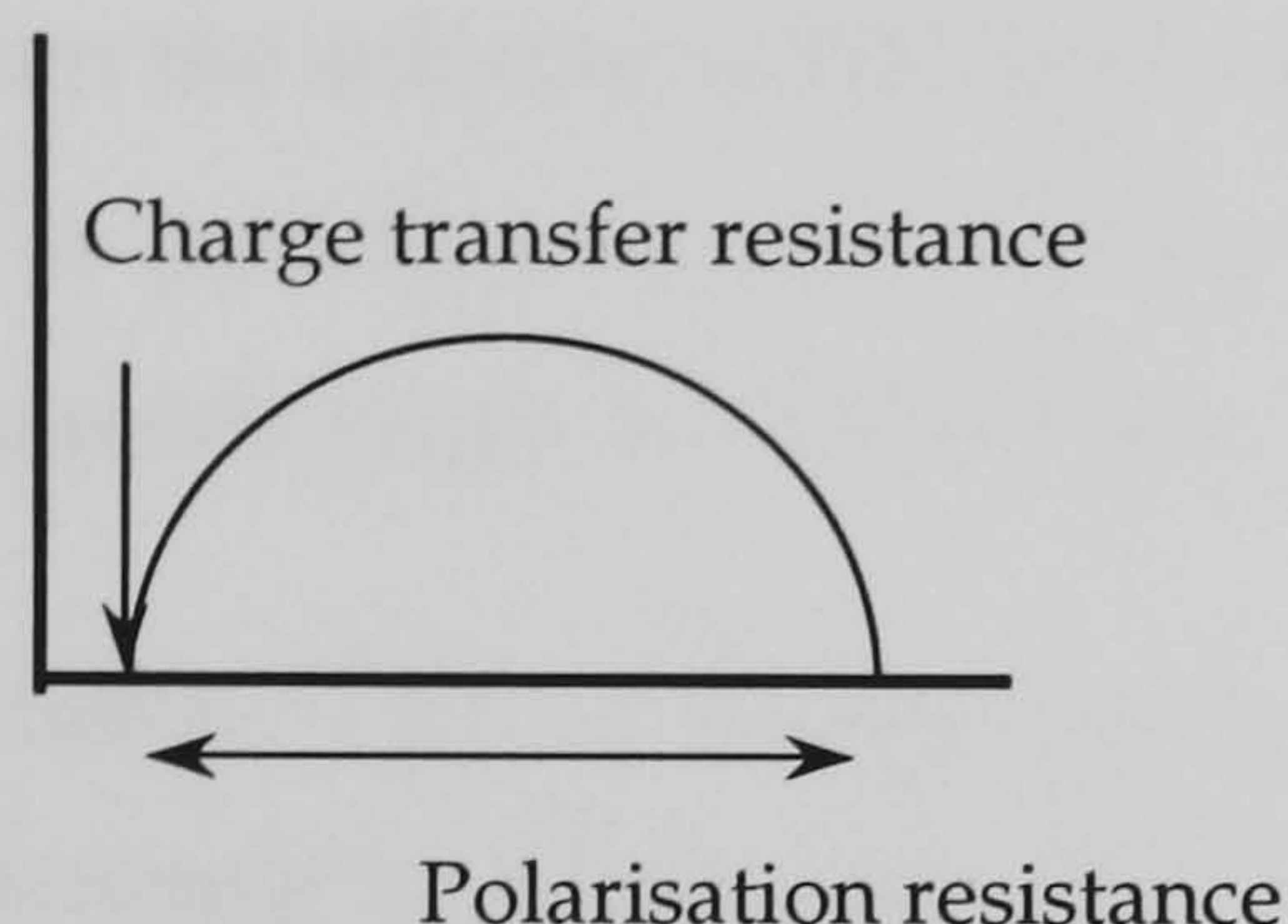


Figure 2-17. Nyquist Plot Showing Charge Transfer Resistance, Polarisation Resistance

Polarisation Resistance

In the case of reactive surfaces, the polarisation resistance is taken as the difference between the impedance measured at low and high frequencies respectively, see Figure 2-17. To measure impedance at low frequencies 3-10 Hz range, a low sinusoidal perturbation, low voltage scan rate is needed. This resistance is normally associated with reactive surfaces such as corrosion.

Capacitance- Diffuse double layer

This refers to the use of a capacitive component to model space charge double layer near the electrode surface. Contacting of the electrolyte and electrode results in a small charge flow and a field is created on the electrolyte side of contact. The mobile charge carriers in the electrolyte distribute themselves over this field; charge density of the metal is confined to its surface leading to the concept of diffuse double layer capacitance. Under these conditions, the diffuse double layer behaves like an ideal capacitor.

Warburg Impedance

Warburg impedance is used to model diffusion related systems. When the Warburg impedance is plotted in the complex plane, a semicircle combined with a straight line at an angle of 45° to the real axis is seen, McDonald, 1987. The Warburg impedance is obtained from the solution of Fick's second law, the diffusion equation, for one-dimensional diffusion of a particle in a semi-infinite space. Diffusion of atomic oxygen in an infinitely thick electrode might be described by this type of impedance., McDonald, 1987

General Warburg impedance for charge motion in a finite-length region of an electrolyte was discussed by McDonald, 1987. The Warburg impedance effect is seen primarily at the low frequency regions where the more mobile or more abundant charged species have time in a half-cycle to rearrange positions so as to screen the less mobile or less abundant charges from the electric field, thus leaving diffusion as the primary conduction method for such low frequencies. Since this diffusion process occurs in the bulk electrolyte, the Warburg impedance is normally placed in series with the bulk resistance, Figure 2-18.

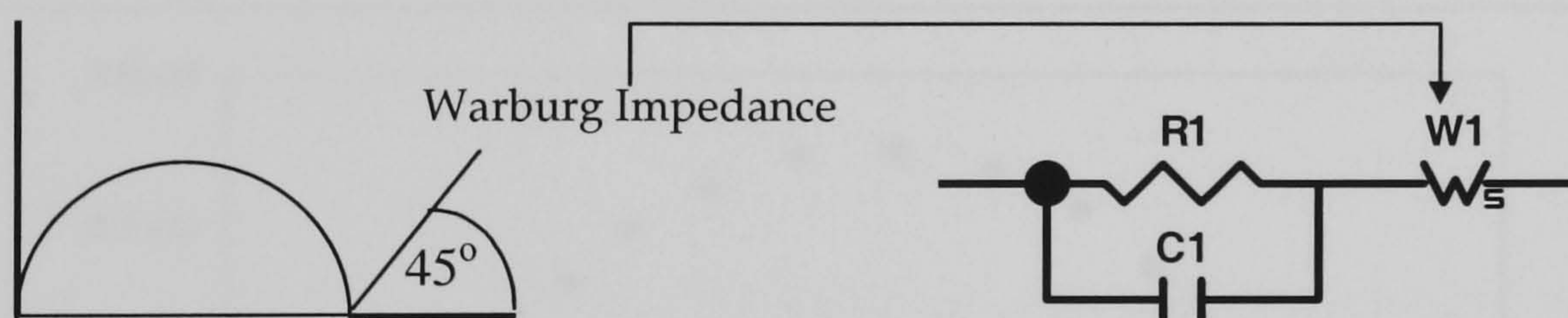


Figure 2-18 . Nyquist Plot and Equivalent Circuit Showing Warburg Impedance

2.10.2 Empirical Models for Mixed Conductors

Mixed conductors have at least two mobile charge carriers, usually ionic and electronic defect. Impedance of mixed conductors was modelled by. Jamnik *et. al.*, 1999, 2003. Comparing the results to the exact solutions of Nernst-Planck-Poisson set of equations validated the models.

At high frequencies (short times), the measured impedance is the parallel sum of ionic and electronic species. At low frequencies, only the resistance of the unblocked species (electronic) is detected.

Two equivalent circuits were developed to address situations where ionic transport exceeds electronic and vice-versa. The models assumed perfectly contacted samples and any space

charge layer adjacent to the electrodes were ignored (that is the models do not address electrode effects). The equivalent circuits are shown in Figure 2-19.

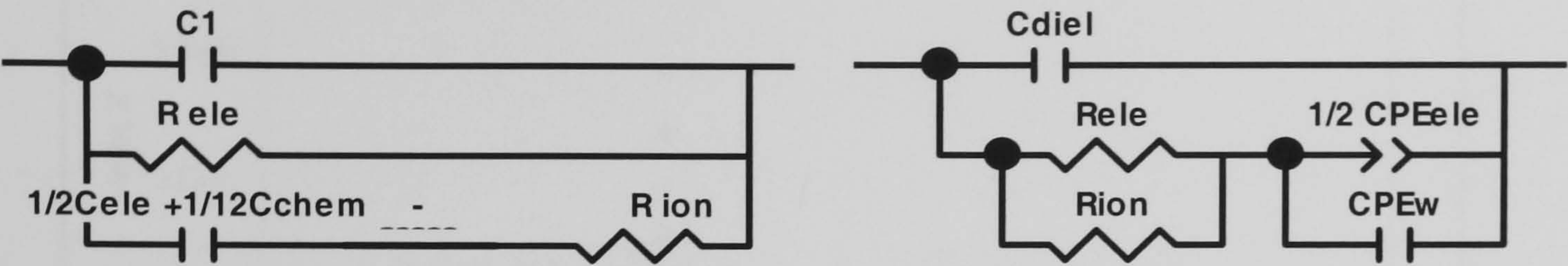


Figure 2-19. Jamnik Equivalent Circuits for Significant Electronic(a) Contribution and Predominant ionic Conductors (b)

The typical response of the low frequency part of the Nyquist plot for an electrolyte with equal amount of conducting species, ionic and electronic, is shown in Figure 2-20. The characteristic shape of a predominantly mixed ionic-electronic conductor is the -asymmetric arc at the high frequencies. As the ionic component increases, the low frequency arc approaches a perfect semi-circle and vertical line at lowest frequencies in the Nyquist plot, Figure 2-21.

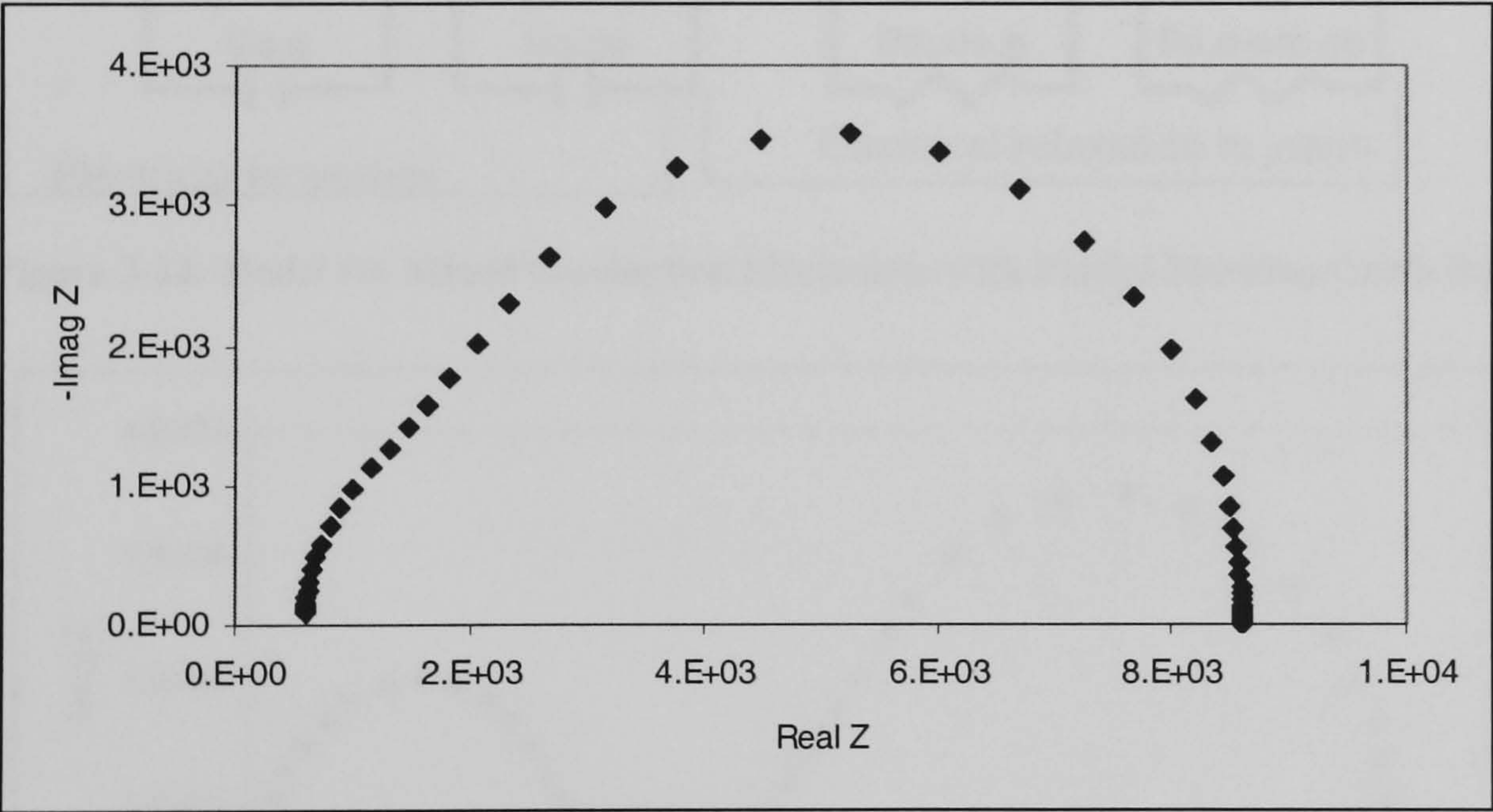


Figure 2-20. Jamnik Equivalent Circuit for Equal ionic and Electronic Conductivity at Low Frequencies using Equivalent Circuit in Figure 2.21(a).

Jamnik, 2003 also proposed models for poly-crystals with blocking grain boundaries for both ions and electrons, Figure 2-22. All modelling element are as defined as R-resistance, C-capacitance, with 'ion' referring to ionic conduction and 'ele' referring to electronic conduction, C'diel' relates to the discharging of electrode capacitance. The results of his models, an example in Figure 2-23 shows that Warburg-type impedance can occur because of blocking grain boundaries, not just blocking electrodes.

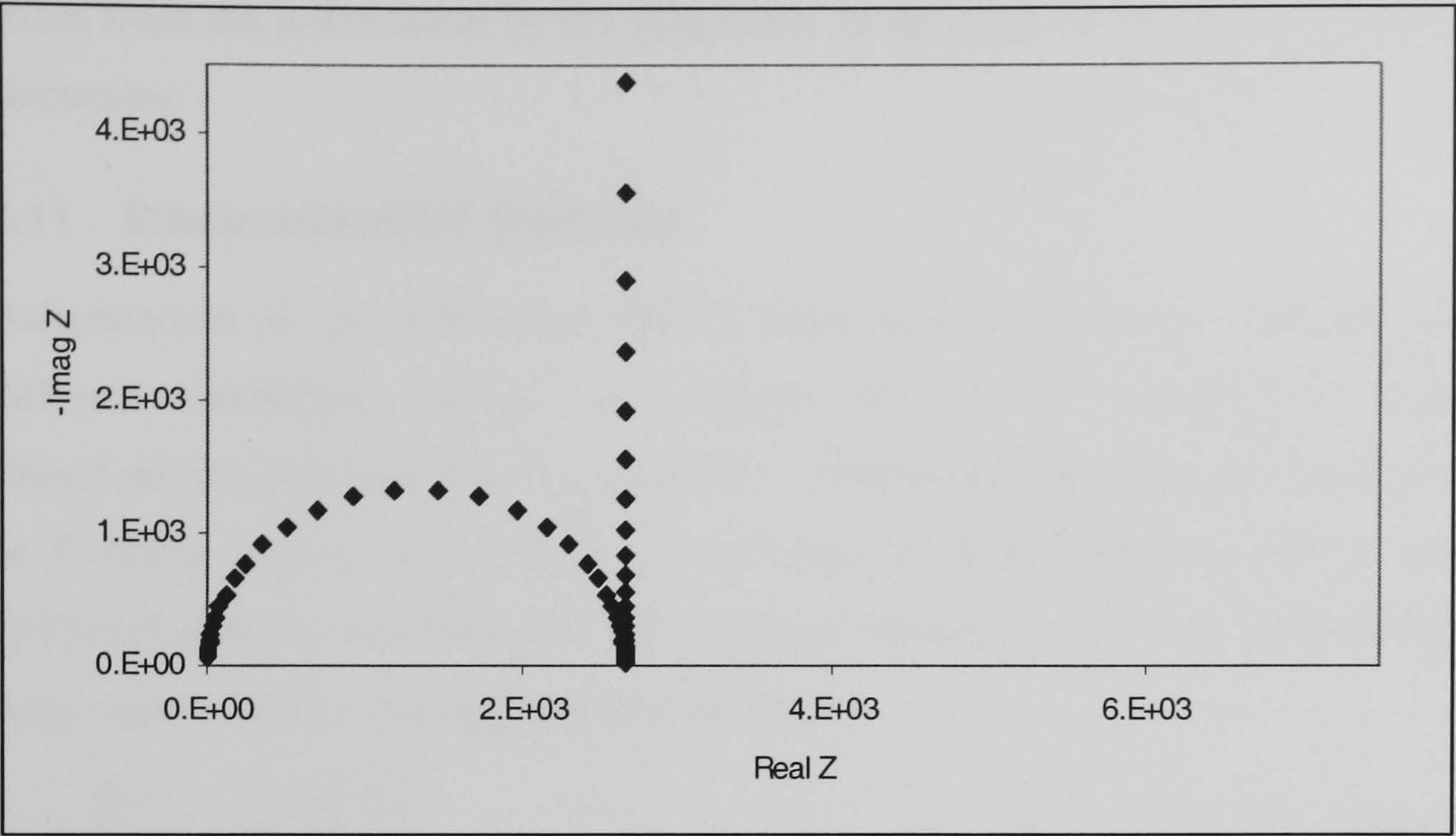


Figure 2-21. Jamnik Equivalent Circuit Low Equal Ionic Electronic Conductivity at High Frequencies using Equivalent Circuit in Figure 2.21(b).

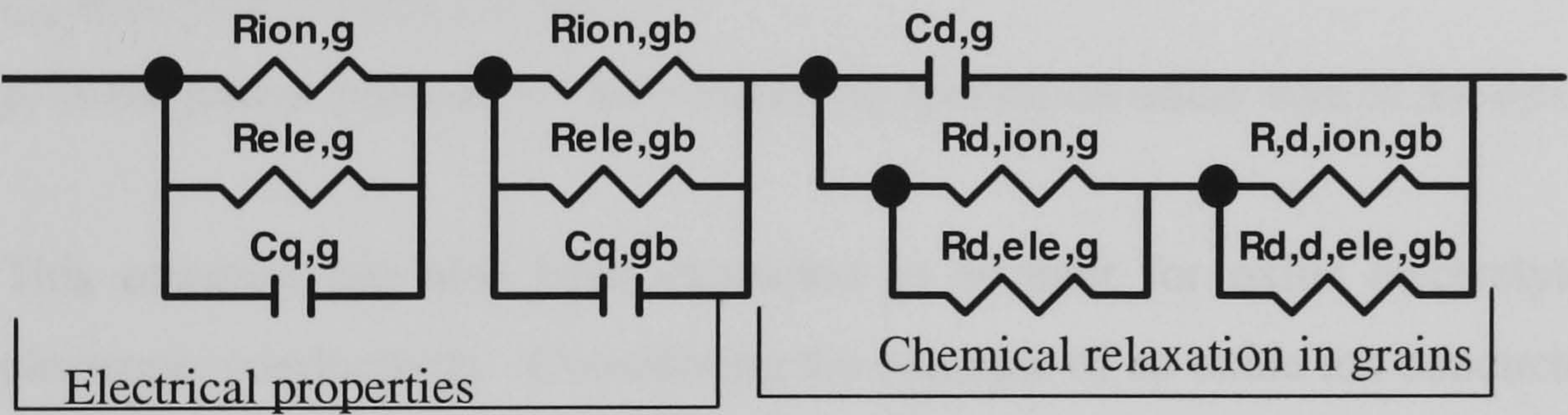


Figure 2-22. Model for Mixed Conduction Electrolyte with Partial Blocking Grain Boundaries

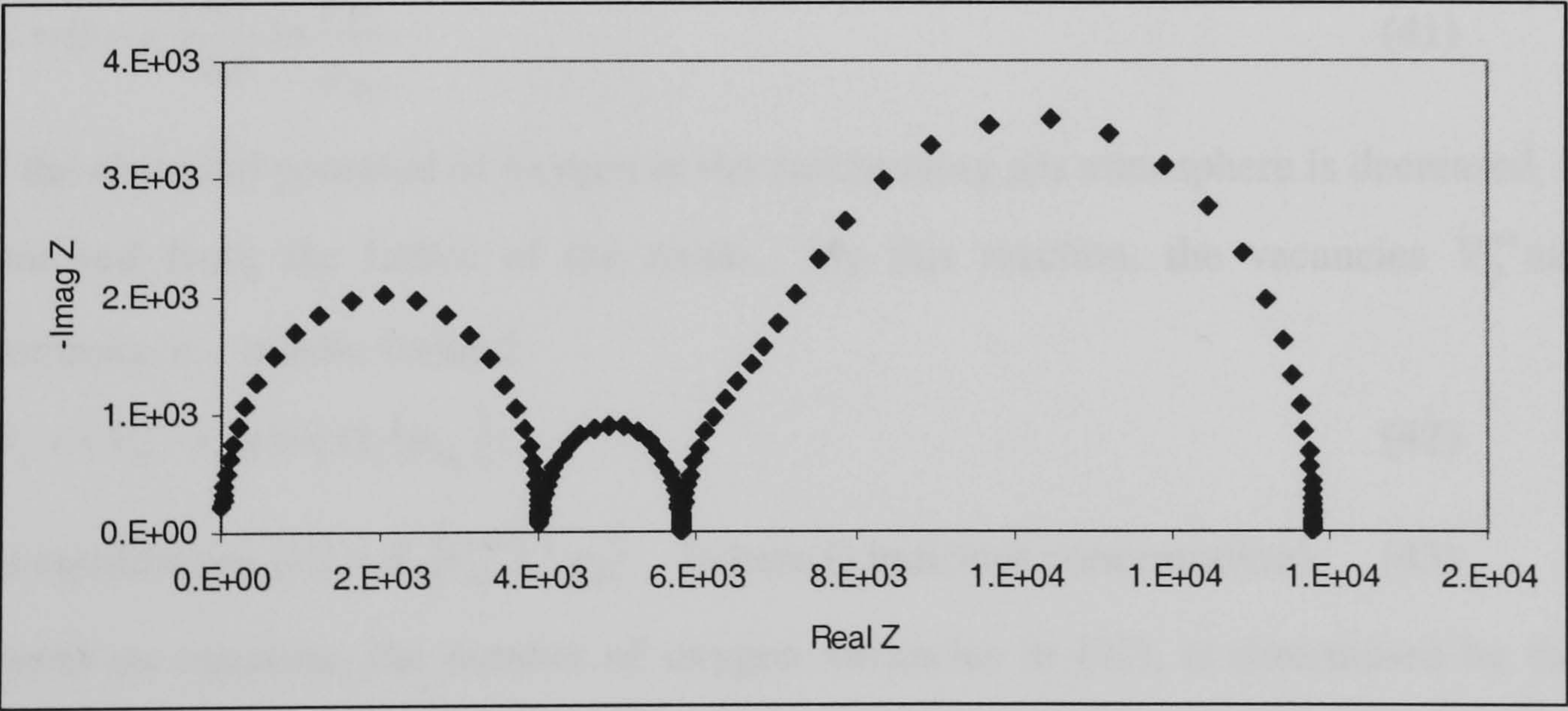


Figure 2-23. Nyquist Plot for Mixed Conduction Electrolyte with Partial Blocking Grain Boundaries

The first two semi-circles in the Nyquist plot relate to bulk and grain boundary conduction (relaxation), which are similar to Nyquist plot of pure ionic conductors, Figure 2-23. The third ‘distorted’ arc is characteristic for mixed conductors and for this type of electrolyte; it

arises from the polarisation by the selectively blocking grain boundaries rather than blocking electrodes

2.11 Electrochemical Reactors

Balachandran *et. al.*, 1998 used (OCV) methods to measure the transport number for the different conducting species, for example H^+ and O^{2-} transport in $BaCe_{0.95}Y_{0.05}O_{3-x}$. Therefore this technique has the potential to identify anionic conductivity of electrolytes such as $CaNd_2S_3$ doped with Nd_2S_3 by forming an electrochemical cell of the form $H_2S, Ar//AB_2S_4//H_2, Ar$; measuring the open circuit voltage (OCV). The relationship between the open circuit voltage and the transport number is

$$V_{oc} = \frac{RT}{4F} \left[t_{ion} \ln \left(\frac{p_x''}{p_x'} \right) \right] \quad (40)$$

Where, V_{oc} - open circuit voltage,

t_{ion} -transport number for ion 'i'

p -is the partial pressure of the conducting species on either side of the electrolyte.

This equation has also been expanded to account for oxide electrolytes with significant electronic conductivity. Considering the example of an oxide ion conductor where the partial pressure p_{O_2}'' does not differ very much from p_{O_2}' , the following equation is obtained

$$E = (1 - \bar{t}_e) \frac{RT}{4F} \ln \frac{p_{O_2}''}{p_{O_2}'} \quad (41)$$

If the chemical potential of oxygen in the surrounding gas atmosphere is decreased, oxygen is removed from the lattice of the oxide. By this reaction, the vacancies $V_O^{\bullet\bullet}$ and excess electrons, e' , maybe formed:



$$\text{At equilibrium } (e') = K_1 (V_O^{\bullet\bullet})^{-\frac{1}{2}} p_{O_2}^{-\frac{1}{4}} \quad (\text{where } () \text{ indicates concentration}) \quad (43)$$

Based on equation, the number of oxygen vacancies in (42), is determined by the oxygen partial pressure, only. Therefore the concentration of electrons in equation 43 reduces to equation (44)

$$(e') = K_1' p_{O_2}^{-\frac{1}{6}}. \quad (44)$$

If the oxygen vacancy is fixed, for example by making a solid solution, the conduction is then predominantly ionic. Only at very small oxygen pressures do electrons also contribute to the electrical conduction, the equation therefore reduces to

$$(e') = K_1'' p_{O_2}^{-\frac{1}{4}}. \quad (45)$$

The other limiting case occurs when there is large oxygen potential in the gas phase, which then leads to accommodation of oxygen into the crystal lattice. The defects produced are interstitial oxygen ions or cationic vacancies. To maintain electrical neutrality, holes are produced.

The transport number can be determined experimentally by measuring the molar flow of conduction gas (using a Mass Spectrometer) as a function of applied voltage to a concentration cell, Figure 2-24. If the measured molar flow is equal to the theoretical molar flow of the conduction species, equation 46, caused by the applied voltage, the transport number is 1, Hladik, 1972. In addition, the transport number can be determined by this method, equation 47.

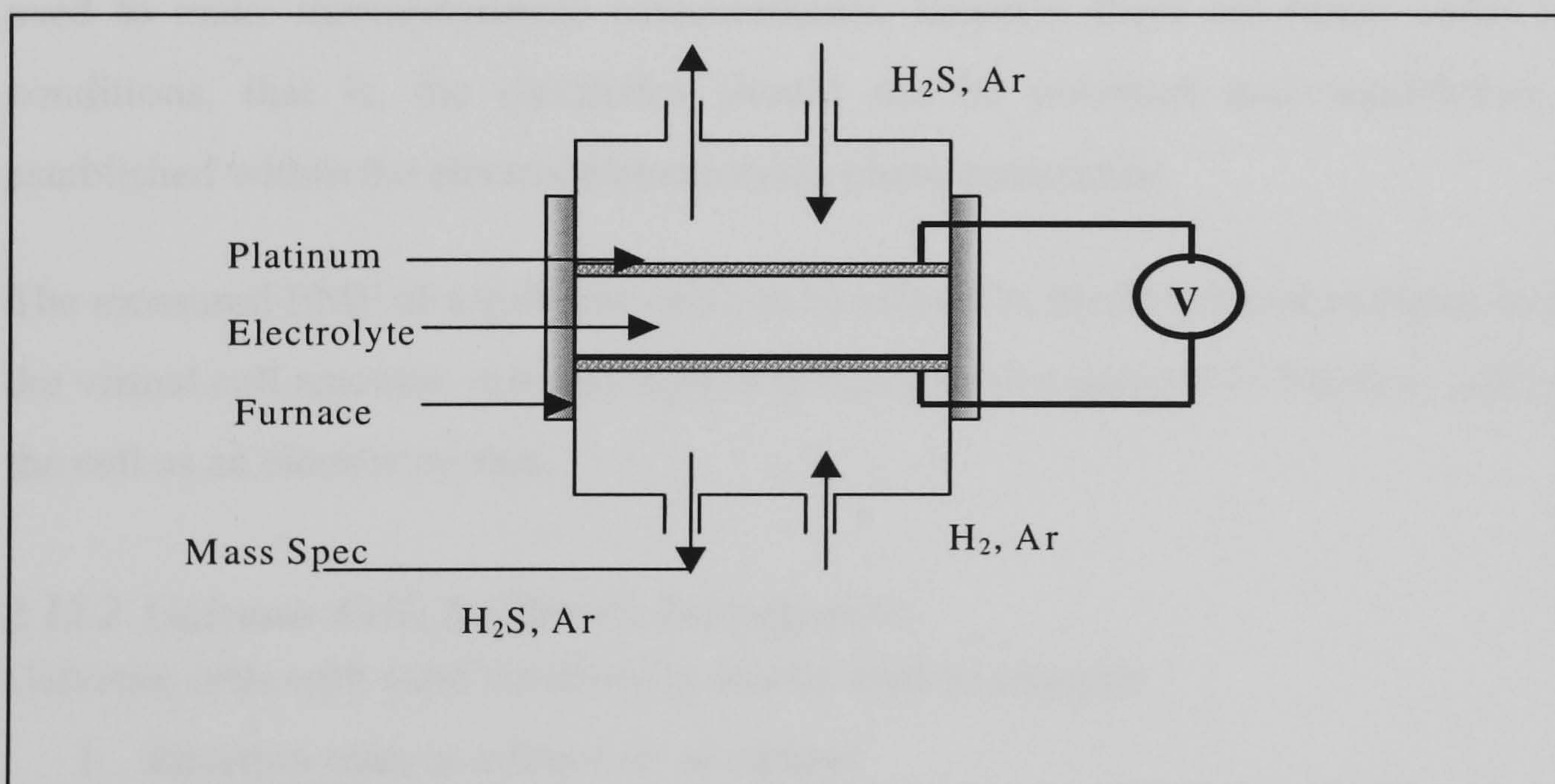


Figure 2-24 Concentration Cell used for Transport Number Measurement

Alternatively a sulphide concentration cell, $AB_2S_4 \cdot AS / AB_2S_4 / B_2S_3 - AB_2S_4$ may be set up with a homogeneous electrolyte AB_2S_4 to establish the conduction of sulphide ions. If the application of a voltage results in a certain amount of electrical charge being passed through the cell, the double sulphide, AB_2S_4 , will partially decompose into its constituent AS and B_2S_3 . To evaluate the e.m.f, the following cell is given in Hladik, 1972, as;

$$Pt - p_{S_2} \left| \begin{array}{c} AB_2S_4 \\ AS \end{array} \right| \left| \begin{array}{c} AB_2S_4 \\ B_2S_3 \end{array} \right| \left| \begin{array}{c} AB_2S_4 \\ p_{S_2} \end{array} \right| - Pt$$

It is assumed that the left hand side of the electrolyte contains isolated particles of pure sulphide AS and the right hand side has particles B₂S₃ and that consequently there are oppositely directed activity gradients of AS and B₂S₃ across with the intermediate layer of homogeneous oxide AB₂S₄, Alcock, 1968. The transport of four faradays of current in a pure sulphide ion conductor as given in Hladik, 1972 as;

$$E = \frac{RT}{4F} \ln \frac{p_{S_2}''}{p_{S_2}'} + \frac{1}{4} \left(\frac{2}{3} \bar{t}_{B^{3+}} - 2\bar{t}_{A^{2+}} \right) \Delta F_{AB_2S_4}^o \quad (46)$$

Deviation of the measured EMF to that calculated from equation (46) infers electronic contribution.

2.12 Other Electrochemical Characterisation Techniques

2.12.1 Galvanic Cells

The typical galvanic cell consists of a solid electrolyte located between two electrodes. The electrodes are connected and hence the EMF can be measured. The galvanic cell can also be used to make thermodynamic measurements, however these are made under open circuit conditions, that is, the electrodes should not be polarised and equilibrium should be established within the electrode/electrolytes phase boundaries.

The measured EMF of a galvanic cell can be related to the Gibbs free energies by considering the virtual cell reaction, one assumption is that a known amount of faradays will pass through the cell as an electric current.

2.12.2 Galvanic Cells for Kinetic Investigation

Galvanic cells with solid electrolytes can be used to measure

1. Reaction rates as a function of current
2. Electromotive forces give thermodynamic information for chemical potentials or activities

The galvanic cells can be operated in four mains ways, Hladik, 19 72

- Potentiometric measurements: These are carried out at zero potential therefore the cells are used as potential probes for measuring chemical potentials, thermodynamic properties, activities or partial pressures
- Steady state measurements: currents and corresponding potentials are measured under steady state conditions. These measurements are independent of whether the

potentials or the currents are controlled. It is preferable to separate potential probes so that the reference electrode is not polarised by a current.

- Measurements with controlled potentials: These measurements are normally potentiostatic, i.e. constant potential is applied to the galvanic cell and the current is measured as a function of time
- Measurements with a controlled current: These are normally galvanostatic. A current is applied to the cell and the potential is measured as a function of time. This technique has been applied to mixed ionic-electronic conductor, $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\alpha}$, Bucher *et al.*, 2003

2.13 Literature Review Summary

Based on the available literature, solid state reactions is a viable method to produce solid state solutions. Using the correct conditions, solid solutions with defect structures can be successfully synthesised.

Characterising these solid solutions for thermal properties using temperature programmed technique is a easy and reliable method of determining the thermal stability and activation energies. and electrochemical properties.

Using impedance spectroscopy, as the main electrochemical characterisation methods allows for the application of other characterisation methods, since this method is none destructive. The bulk conductivity, activation energy for bulk conduction and time constants are outputs from EIS. This method is susceptible to errors introduced in the selection of the appropriate equivalent circuit. To reduce errors in modelling, several statistical parameters should be minimised. Another limitation of EIS is that, explicit identification of the conducting species is not possible. Therefore identification of the conducting species is best done by concentration or galvanic cell.

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Chapter 3

3 Experimental

This chapter describes the procedures and techniques used to synthesis and characterise metal sulphides investigated during this research project. It is divided into three sections: The first section deals with the preparation of the possible sulphide ion conductors. The second section describes the set-up of experiments used to evaluate the material thermal stability in different atmospheres. The third section describes the electro-chemical techniques to assess the materials ionic conductivity and electronic conductivity.

3.1 Material Synthesis

3.1.1 Sulphide Ion Synthesis

The most commonly used method of preparing ceramics is by high temperature, solid-state reaction. The sulphides were prepared by combining the metal sulphide starting materials, in the correct molar proportions, grinding, in a glove box (under an argon atmosphere avoiding oxidation of the compounds) to a particle size $<50\mu\text{m}$ in a agate mortar and pestle. The mixture was reacted in sealed silica tubes, and heated to a maximum temperature of 1300°C for up to 24hours. Once cooled the compound was transferred to XRD mounting discs for X-ray analysis where the new compound and its structure was identified.

Some metals do not react with elemental sulphur to form the corresponding metal sulphide. Typically, the sulphide can be made from the oxide, carbonate or chloride by heating under sulphur containing atmospheres (CS_2 or H_2S) where the starting material was placed in an inert high temperature boat made from typically alumina or carbon, Figure 3-1. The reactor is initially purged to remove trace oxygen and then heated under the sulphur, containing atmosphere up to the required temperature. Exit gas is scrubbed with sodium hydroxide to remove sulphur before releasing to the atmosphere in a fume cupboard. For example, Yan *et. al.*, 1995 showed that combining stoichiometric amounts of BaS, Zr and S at 1350°C was not successful in producing a pure phase of Ba_2ZrS_4 . However when a mixture of BaS, BaCl, Zr and S was used, the required phase was the major product, however the use of chloride as the starting material led to the requirement of a washing stage after reaction.

Similarly, Tsay *et. al.*, 1999 synthesised CaLa_2S_4 from calcium methoxide and lanthanum methoxide at 1000°C in pure H_2S after 20mins. The methoxide was used to lower the sintering temperature, thereby producing smaller particles, which tend to give denser pellets that were made at 1350°C (350°C above reaction temperature). An alternative synthesis route,

for this material was made by Tsai *et. al.*, 1994 using $\text{La}(\text{OH})_3$ and CaCO_3 with nitric acid after washing with alcohol and sintering at a maximum temperature of 1150°C for 30mins in pure CS_2 .

In this project metal sulphide synthesis was carried out using reactions from the starting sulphides using the stoichiometric amounts. For example calcium neodymium sulphide was prepared from equal molar amounts of calcium sulphide and neodymium sulphide according to the following reaction;



Generally, the sulphides for the group two metals are readily available, for e.g. calcium sulphide and barium sulphide. However if the starting sulphide is not available directly from suppliers, as is the case for neodymium sulphide, the starting sulphide (Nd_2S_3) can be created from the metal and sulphur or by reacting the metal with hydrogen sulphide.

Neodymium and Samarium Sulphide Synthesis

The following procedure was used to make starting sulphides from metals, which react directly with elemental sulphur

1st Step: Drying of Sulphur

- A known amount of sulphur was placed in an evacuated schlenk flask
- The schlenk tube was placed in an oil bath ($70\text{-}80^\circ\text{C}$) and connected to vacuum pump
- Water was removed from the sulphur for 36hrs
- The schlenk tube was closed under vacuum and disconnected from the vacuum pump

2nd Step: Solid State Reaction Sulphide Synthesis

- Dried sulphur was combined with the appropriate pure metal under argon (glove box apparatus)
- Metal and sulphur were mixed until homogeneous and placed in a silica tube
- The silica tubes were sealed and heated to 900°C at a heating rate of $2.5^\circ\text{C}/\text{min}$, and held at this temperature for 36hrs.

The product from this process was pure neodymium sulphide provided that the small particle sizes of neodymium were used. If neodymium chips, approximately $1\text{mm} \times 1\text{mm} \times 1\text{mm}$, was used, a mixture of neodymium sulphide, neodymium and sulphur was formed, see X-ray patterns in Appendix A. This process yielded approximately 50% output, based on mass, which is a low yield. The main reason for this low yield was due to explosion of the sealed silica tubes caused by water contamination or possibly faulty silica tubes. .

The process was modified to react neodymium with hydrogen sulphide at 100°C below its melting point of 950°C in an open silica boat for 8hrs, Figure 3-1. The XRD result was the neodymium oxi-sulphide Nd_2S_3 with Nd_2O_3 , Appendix A. The reaction conditions were changed to 1200°C in graphite capped cylinder and monoclinic Nd_2S_3 was formed, see X-ray pattern in Appendix A. The source of oxygen to form the oxi-sulphide was not known since the inlet gas flow rate was equal to the outlet but it is possible that oxygen could have entered the reaction chamber by decomposition of the silica boats or diffusion of oxygen through the reactor walls, which was made from 99.97% dense alumina.

Cerium Sulphide Synthesis

Cerium sulphide is not readily available, unlike cerium oxide. Cerium is one of those metals which react only very slowly with hydrogen sulphide, in so much so that improving the corrosion resistance of steel by adding cerium was investigated by Niu *et al.*, 1997. The results were not promising due to the low solubility of cerium in steel.

Cerium sulphide was made from cerium oxide, CeO_2 and carbon using hydrogen sulphide at 1200-1400°C for 2 to 3 hours in a graphite reactor, (Figure 3-1) Eastman, *et al.*, 1950. The reaction temperature can be lowered to 600°C by using CS_2 rather than H_2S , Hirai, 1998.

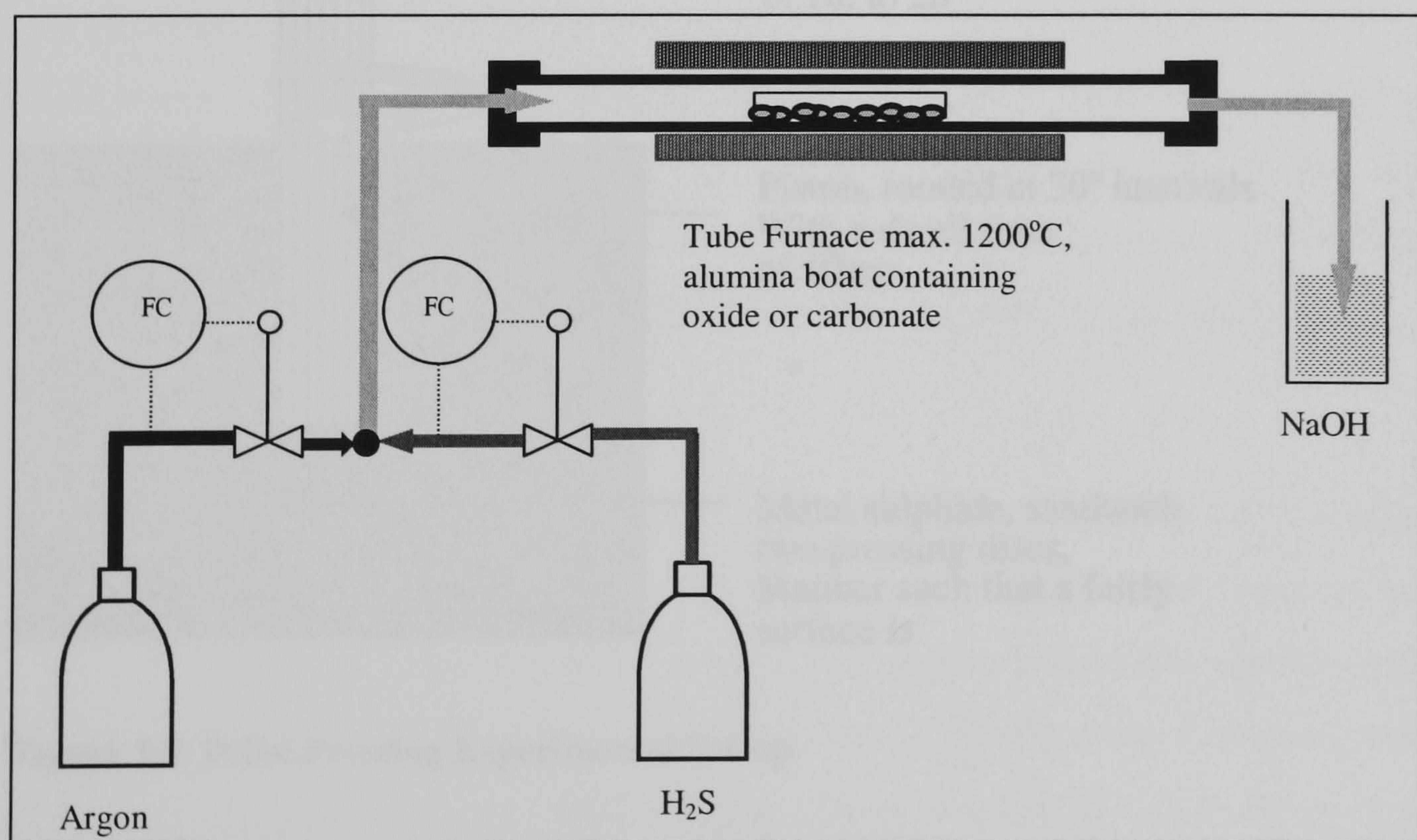


Figure 3-1 Sulphide Synthesis Experimental Set-up

3.2 Sulphide Pellet Synthesis

Powders of metal sulphides synthesised in the Chemistry Department according to the methods described previously were compressed into pellets (20cm diameter) using a maximum pressure of 12t at temperatures from room temperature up to 100°C. It was observed that lower pressures (4t) would yield good pellets, i.e. pellets free from visible cracks. Perfect pellets could be achieved at room temperature provided only a small volume of binder was used. Therefore the maximum pressure and elevated temperature were not the main parameters, which determined the quality of the pellets.

The important stages of pressing pellets are, (i) Rotation by 30° at the lower pressures, 0.5, (ii) Dwell time of 10sec at each pressure was used, Figure 3-2. In the absence of the 30° rotations at the low pressures the pellets being formed exhibited either uncompressed forms or significant fractures along the diameter. These cracks cannot be removed by sintering; once cracks were observed after pressing, the process had to be restarted from the grinding stage.

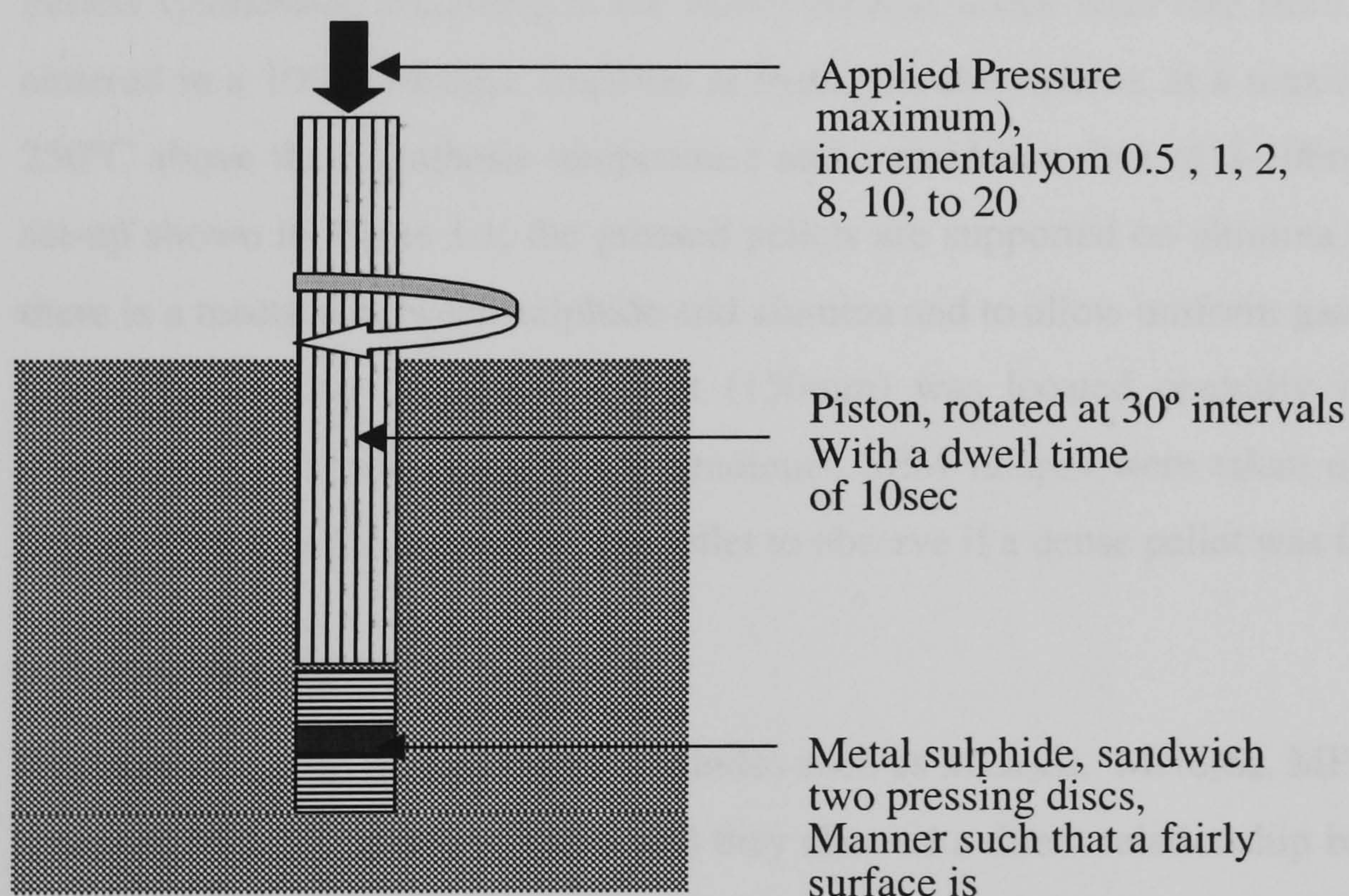


Figure 3-2. Pellet Pressing Experimental Set-up

The use of binder helps in creating pellets that are mechanically stable. In the absence of a the pellets are very fragile and they tend to break when they are moved from the dye to the sintering boat. Binders used included hexane, 2%poly vinyl alcohol, PVA, MW range of 30,000-120,000, which needs to be dissolved at 60°C while stirring for 24hrs to form a solution), as well as liquid paraffin. Mechanically stable pellets were formed using either a PVA solution or liquid paraffin. However PVA produced black spots when used with the

oxide ion conductor, Yttria Stabilised Zirconia, YSZ. Further investigation showed, that the black spots were corrosion products formed from the dye polished surfaces. PVA was subsequently discontinued. Hexane did not yield mechanically stable pellets

In summary the following recipe for pellet preparation was used;

- 1.4g of sulphide was used in order to yield a 1.5mm thickness pellet (diameter 20mm) with a particle size range of 0.2-10 μ m (the sulphides made by solid state reaction has a mean particle size of 100 μ m, hence a particle size reduction stage will be discussed in the following section)
- 2 –4 drops of liquid paraffin
- Mixing binder and powder until homogeneous agglomerates (free from large initial agglomerates)
- Flattening of the powder with the piston without the upper disc,
- Pressing at low pressures 0.5-5t, then press at maximum pressure 8 or 25t

Pellets synthesised according to the above method which were free from visible cracks were sintered in a 10% hydrogen sulphide in hydrogen atmosphere, at a maximum temperature of 250°C above their synthesis temperature and a residence time of 8-10hrs. The experimental set-up shown in Figure 3-1; the pressed pellets are supported on alumina balls to minimise if there is a reaction between sulphide and alumina and to allow uniform gas atmosphere around the pellets. Also the alumina boat (150mm) was located centrally in the tube furnace (600mm) to minimise temperature gradients. SEM images were taken of the surface of the pellet, as well as the internal of the pellet to observe if a dense pellet was formed.

3.2.1 Grinding metal sulphides

Chess *et. al.*, 1983 studied many sulphides such as MLa_2S_4 , MNd_2S_4 , MPr_2S_4 , M_2S_4 , MSm_2S_4 where M=Ca, Sr, amongst others and they showed a direct relationship between particle size and densification of metal sulphides where a maximum achievable density occurred with particles of 5 μ m. Later Tsay *et. al.*, 1999 made $CaLa_2S_4$ from calcium methoxide and lanthanum methoxide as the methoxide produces smaller particles which lowered their sintering temperature while producing denser pellets. Chess *et. al.*, 1983 observed that a sintering time (of up to 300mins) as well as high temperature (max 1600°C) were essential for the formation of dense sulphide pellets. They also showed that using the maximum temperature and sintering time with the smallest particle size, only 90% of the theoretical density was achieved. To increase the density of the pellet beyond this, hot pressing at

1400°C and 20Mpa for at least 15mins was needed. The metal sulphides of the type MNd_2S_4 and MSm_2S_4 , $\text{M}=\text{Ca}, \text{Sr}$ produced by solid state reaction have a mean particle size of 150 μm , measured using standard mesh sieves, therefore particle size reduction is necessary in order to produce dense pellets. To observe the relationship between particle size and pellet densification, scanning electron microscopy, SEM, was used.

Scanning Electron Microscope: The Scanning Electron Microscope (SEM) has developed into one of the most widely utilized instruments for material imaging. The SEM is a microscope that uses electrons rather than light to form an image. SEM's have high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEM only require the sample to be conductive. Particles of submicron size can be easily imaged using SEM.

The resulting sintered pellet, 150 μm mean particle size, without grinding is shown in Figure 3-3, where the SEM showed that no sintering took place, since no grain boundaries could be seen. Also, the diameter and thickness of the 'sintered' pellet, measured by digital vernier calliper remained constant (at 20mm diameter) before and after sintering, confirms that densification did not occur. Therefore the pellets made from this material, pressed to 20t and heated at 1200°C for 48hrs did not increase in density.

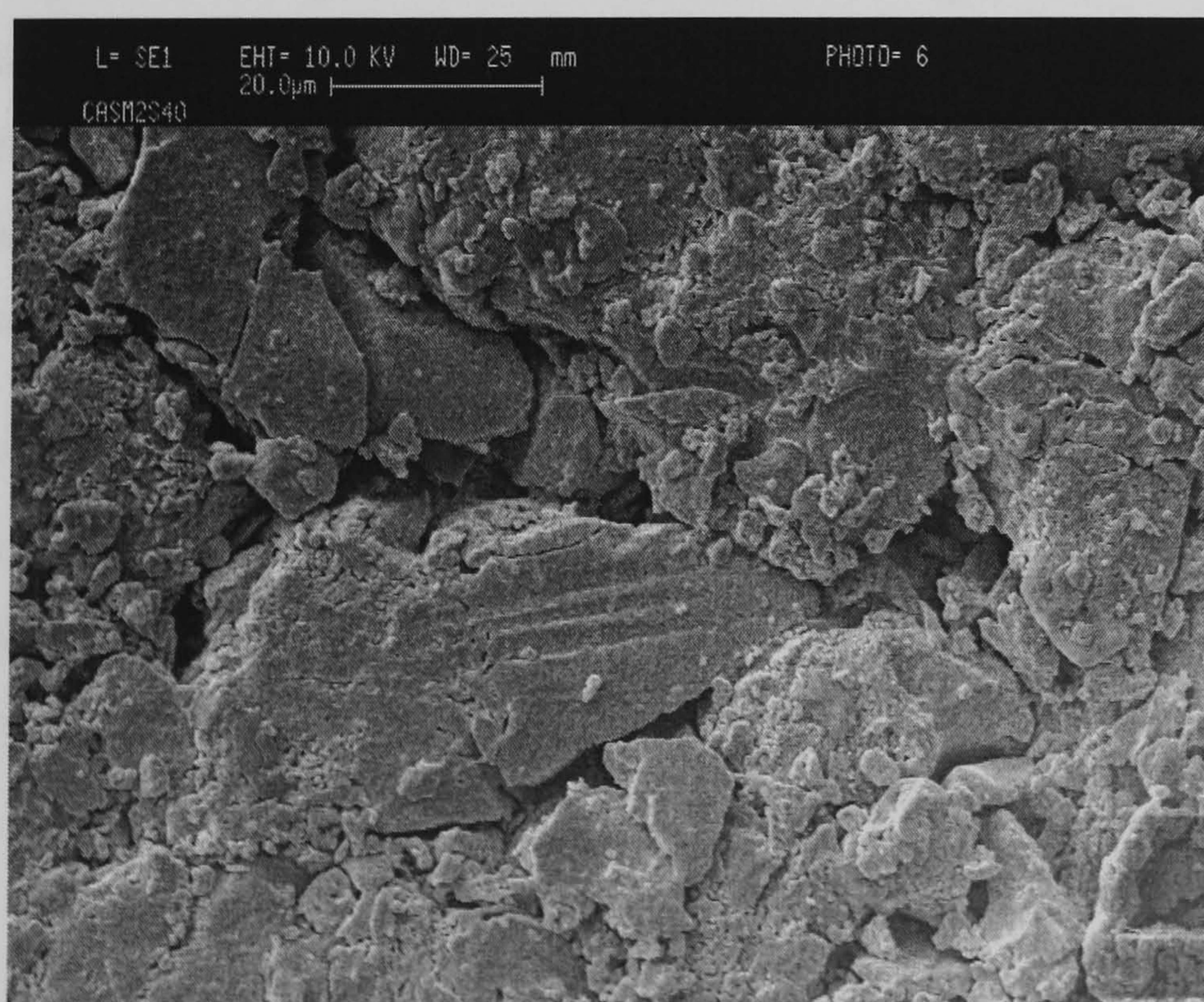


Figure 3-3. SEM of pellet made from ungrounded CaNd_2S_4 sulphide@ 1200°C for 48hrs in H_2S

Pellets were then made after sulphide powder had been ground by hand in an agate mortar and pestle to a maximum diameter of $90\mu\text{m}$. SEM images of these pellets show the formation of grain boundaries, however many pores, with a maximum diameter of $20\mu\text{m}$ are visible, Figure 3-4. The pellet diameter showed a slight reduction in the diameter of the pellet (0.02mm) suggesting some densification.

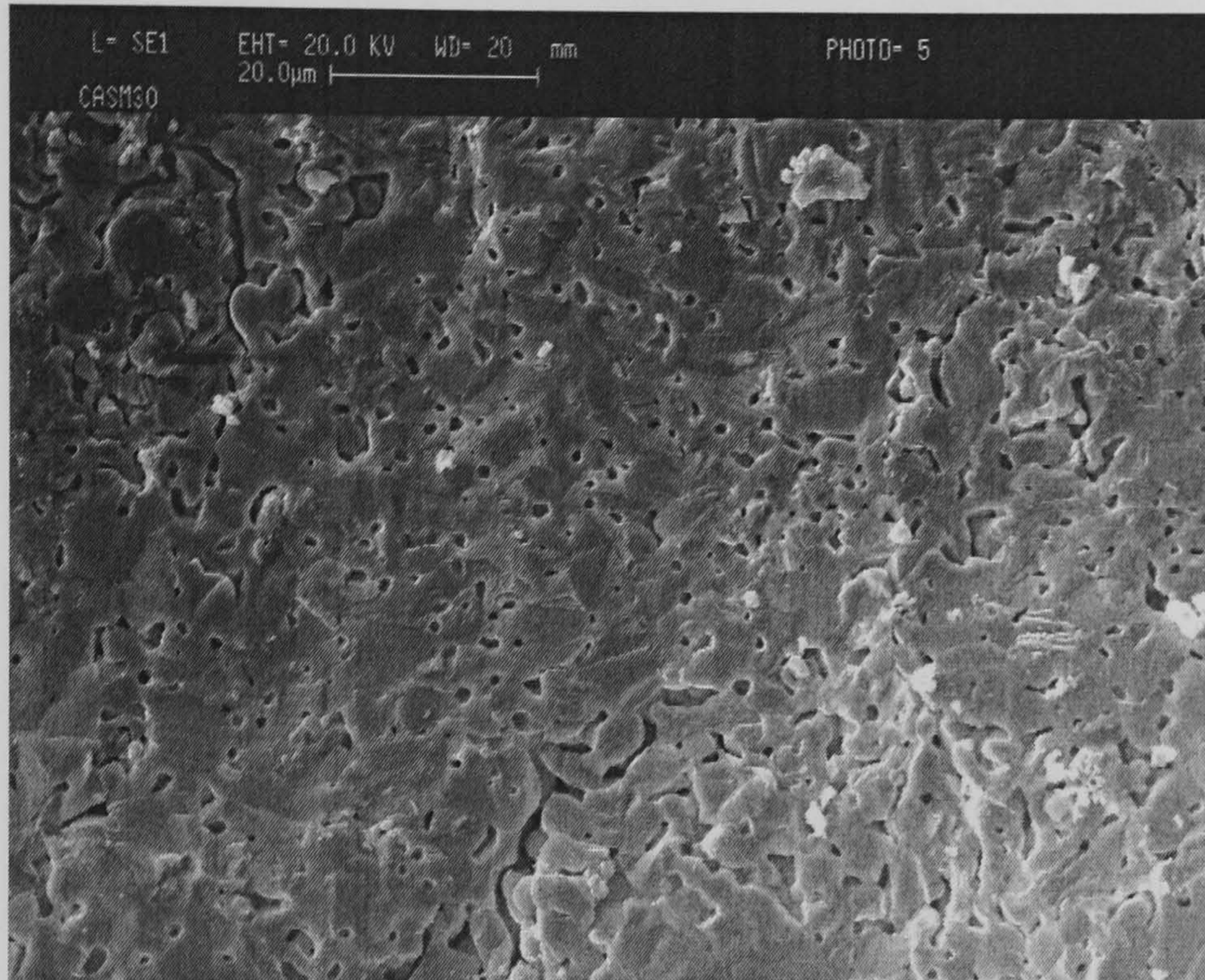


Figure 3-4. SEM of pellet made from grounded CaNd_2S_4 sulphide@ 1200°C for 48hrs in H_2S

The SEM images in Figure 3-3 and Figure 3-4 shows that grinding of material from $150\mu\text{m}$ down to $90\mu\text{m}$ improves the densification of pellet and sintering process. Therefore the sulphides were ground further by hand in an agate mortar and pestle to a maximum particle size of $35\mu\text{m}$. This material was heated to 1200°C for 10hrs under H_2S , with the pellet diameter decreasing by 0.05mm suggesting a slight increase in densification was achieved when the average particle size was reduced from $90\mu\text{m}$ to $35\mu\text{m}$. SEM images of pellets made with the latter particle size are shown in Figure 3-5.

Figure 3-5 shows the SEM of a pellet made from grounded CaNd_2S_4 doped with Nd_2S_3 ($<35\mu\text{m}$) powder, has less pores compared to un-doped CaNd_2S_4 , Figure 3-6. The significant difference in SEM images is clearly seen even though similar particle size and sintering conditions were used.

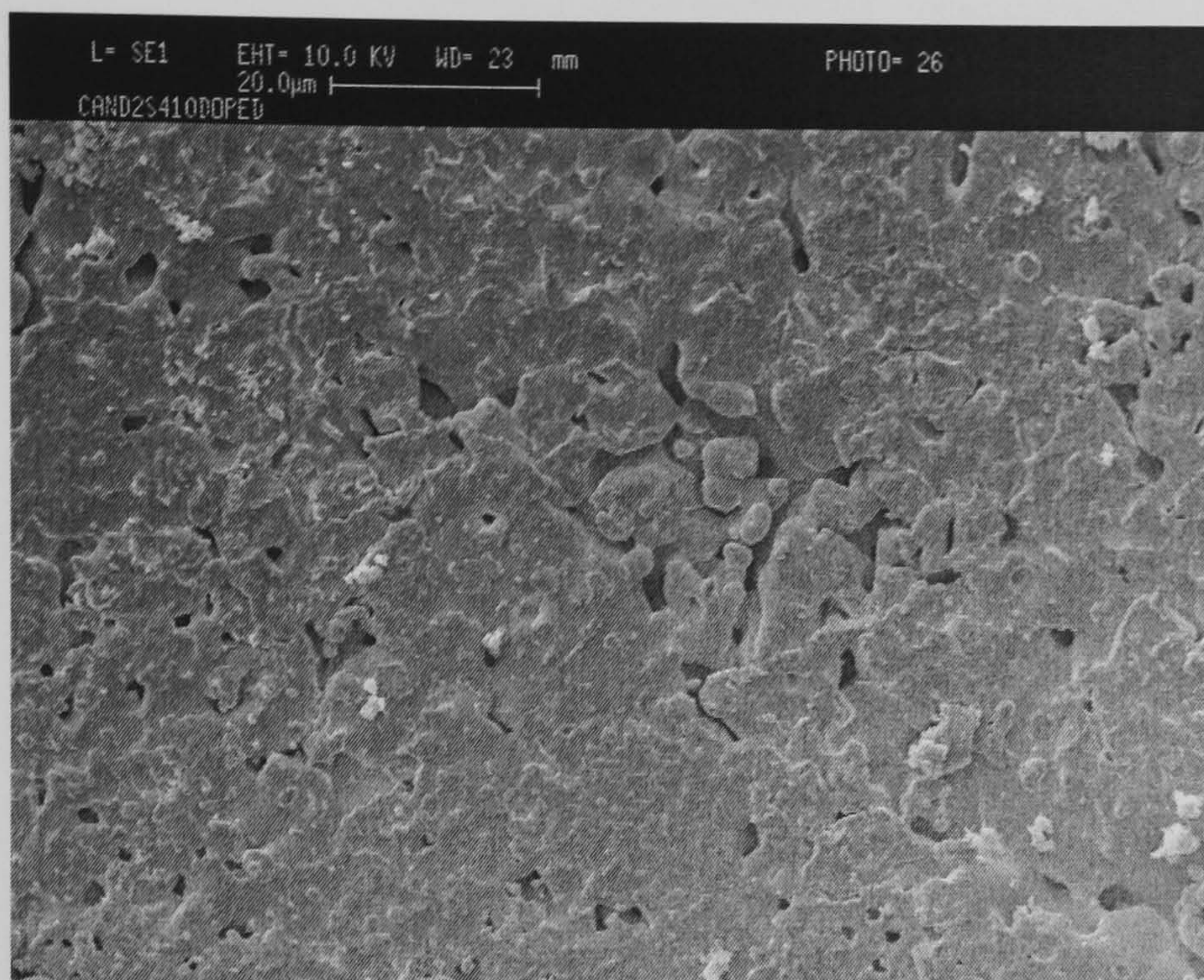


Figure 3-5. SEM of un-doped CaNd_2S_4 made with $35\mu\text{m}$ powder

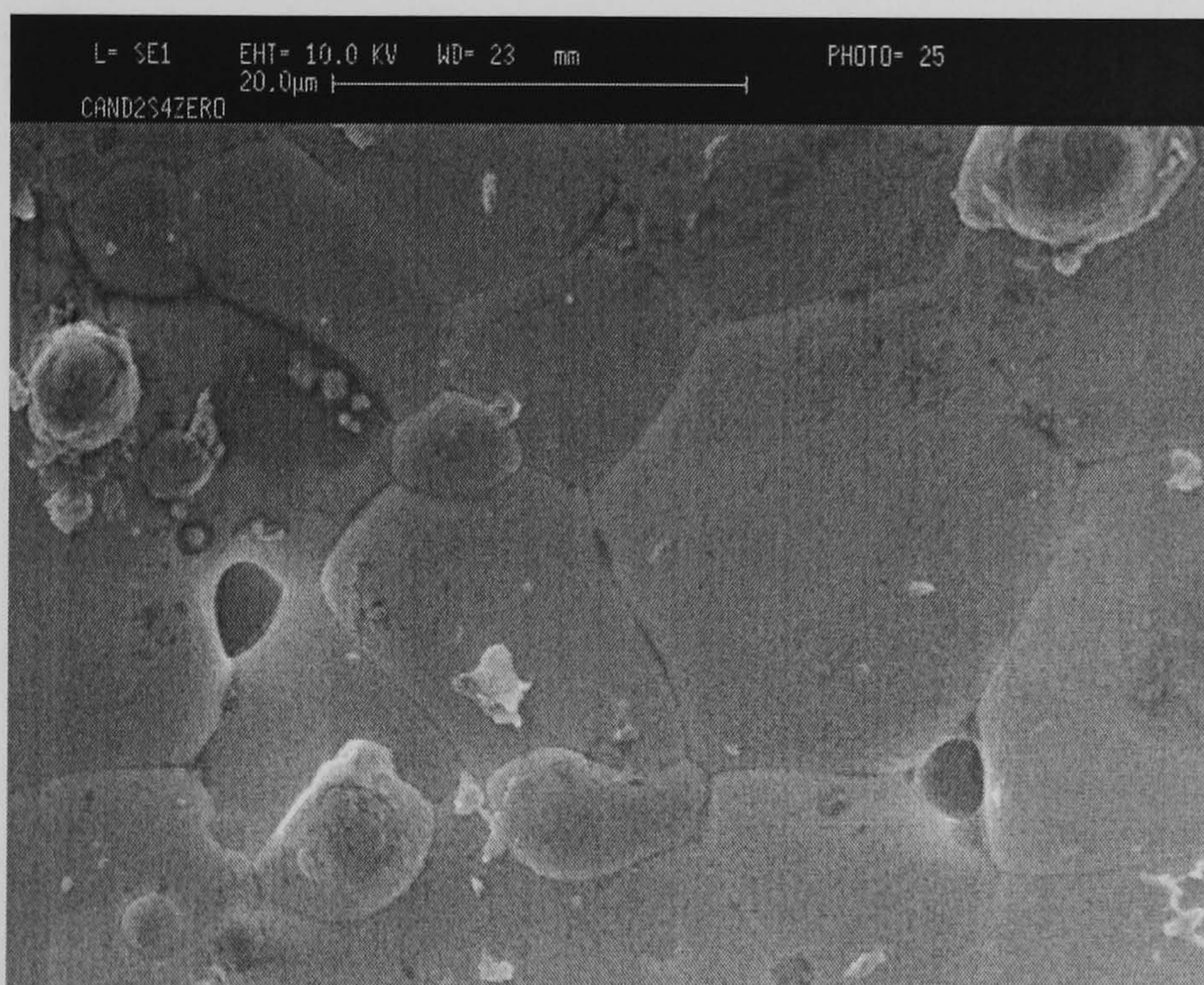


Figure 3-6. SEM of $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ made with $35\mu\text{m}$ powder .

In order to improve the grinding operation, metal sulphides were ground in an agate ball mill operating using five 10mm diameter agate balls to reduce the particle size to less than $35\mu\text{m}$. The particle size distribution of the resulting powder product was analysed using a Coulter counter. The principle of the laser coulter counter is based on laser diffraction techniques, which requires that the particles be dispersed in a liquid (dispersant). Therefore various liquids were experimented with; water, hexane and acetone were used. The use of hexane caused agglomeration. Agglomeration was identified when repetition of the particle size distribution analyses resulted in a reduced fraction of larger particles, Figure 3-7.

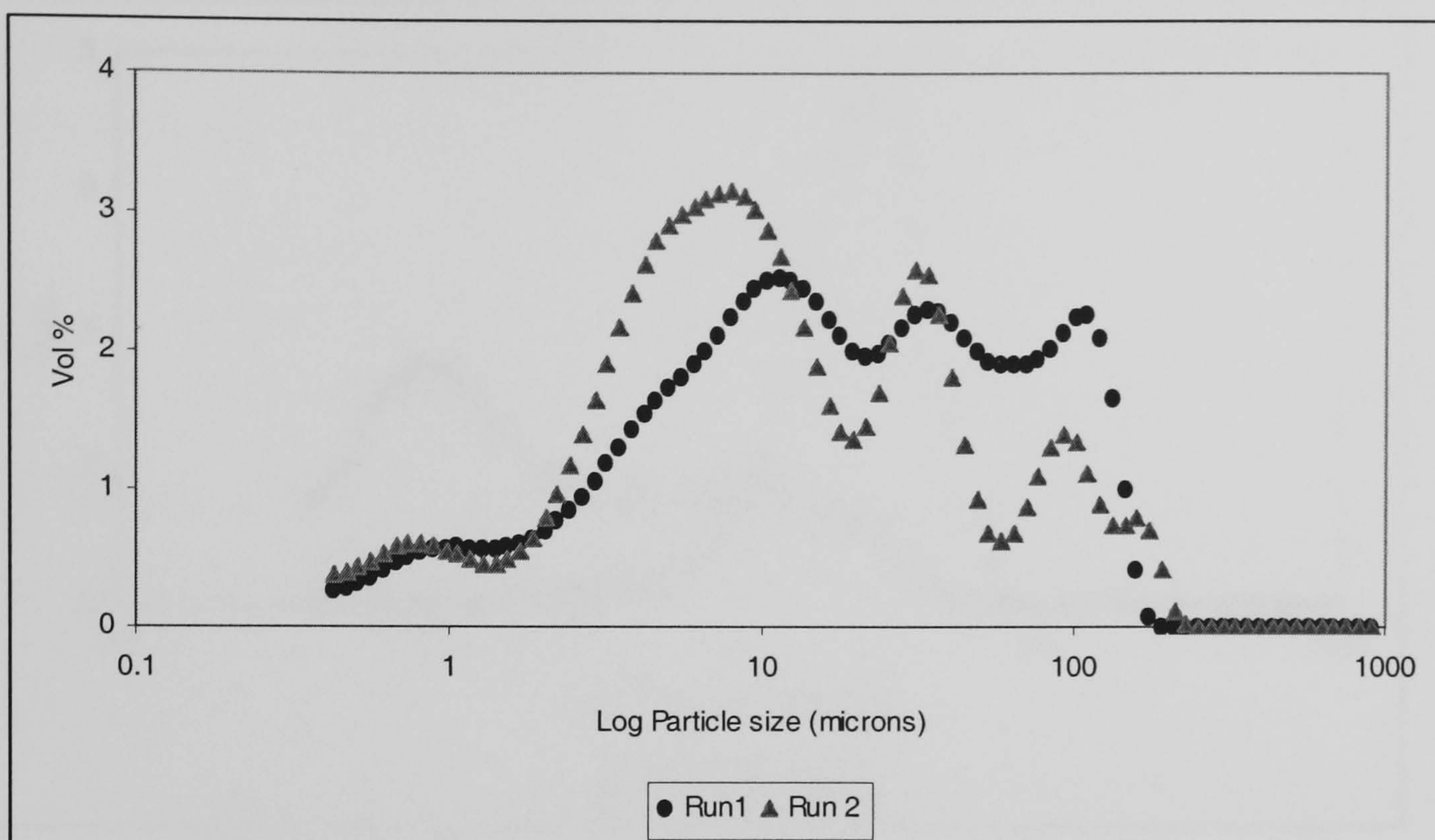


Figure 3-7. Particle size distribution using Hexane solvent versus number of repetition which shows the agglomeration effect

Using water as the dispersant, particle size of above 100 μ m after 3hrs of grinding in ball mill and 17 μ m after 11hrs, see Figure 3-8. However acetone indicated that most particles were less than 10 μ m, Figure 3-8. This discrepancy was solved using SEM images of the same material (powdered) suggested a maximum particle size of 5 μ m, Figure 3-9, suggesting that water causes agglomeration of the particles therefore water was also discontinued for the AB₂S₄ type compounds. Therefore the ball mill can be used to produce a particle size distribution with a significant mass fraction of mean diameter of 10 μ m, which meets the requirements to form a dense pellet. However the grinding was changed from the ball mill, which used centrifugal forces for grinding due to significant loss of material (10%), to shaker apparatus with 350-500rev/min where material loss was reduced to less than 1%, with similar particle reduction in either method.

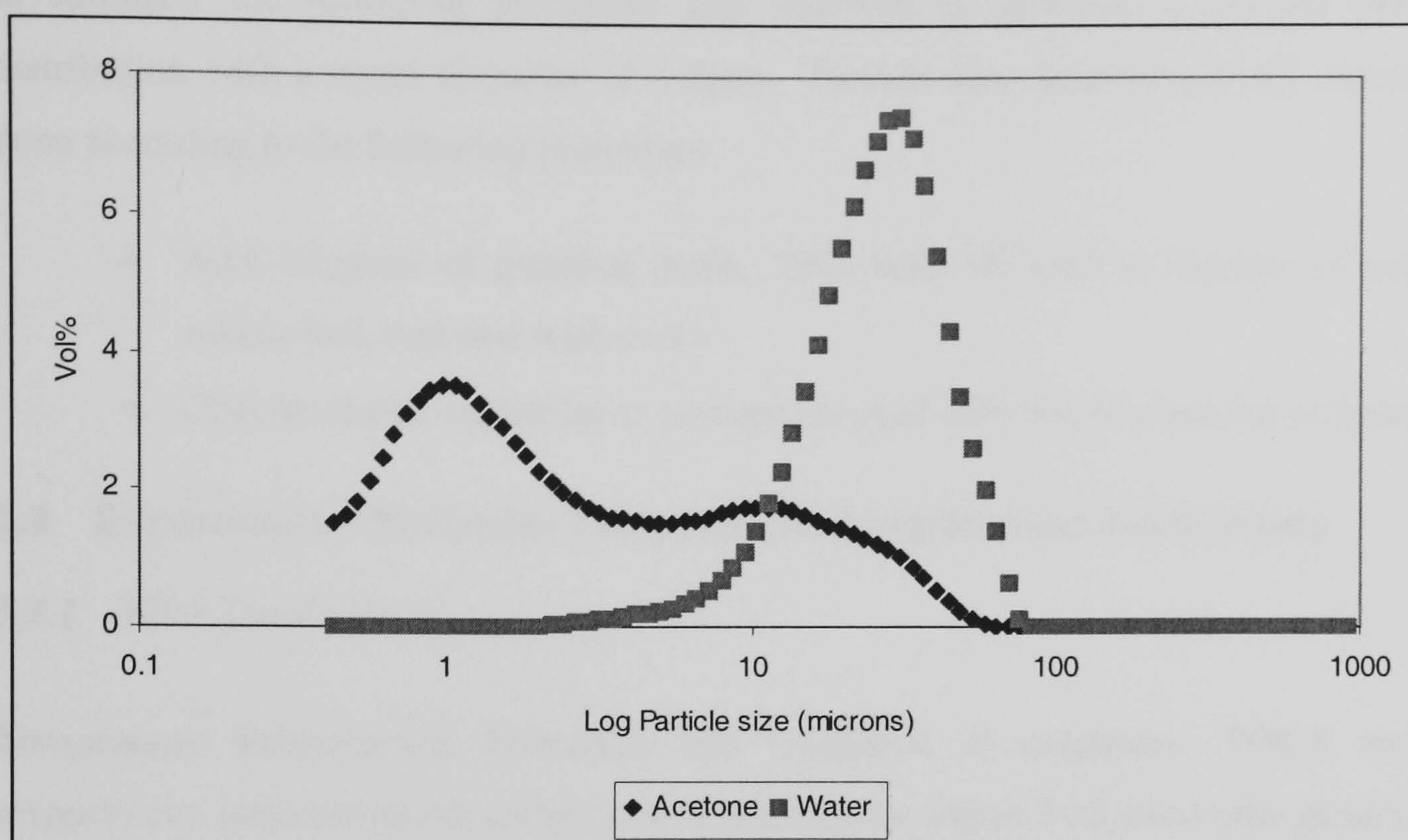


Figure 3-8. Effect of dispersant on particle size distribution

Sintered pellets made from material ground to an average particle size $17\mu\text{m}$, measured by the Laser (acetone dispersant) or $5\mu\text{m}$ by SEM showed a decrease in pellet diameter from 20.0mm to 18.6mm, thus indicating an increase in density, , shows the SEM image of the sintered pellet surface, confirming reduced porosity, Figure 3-9.

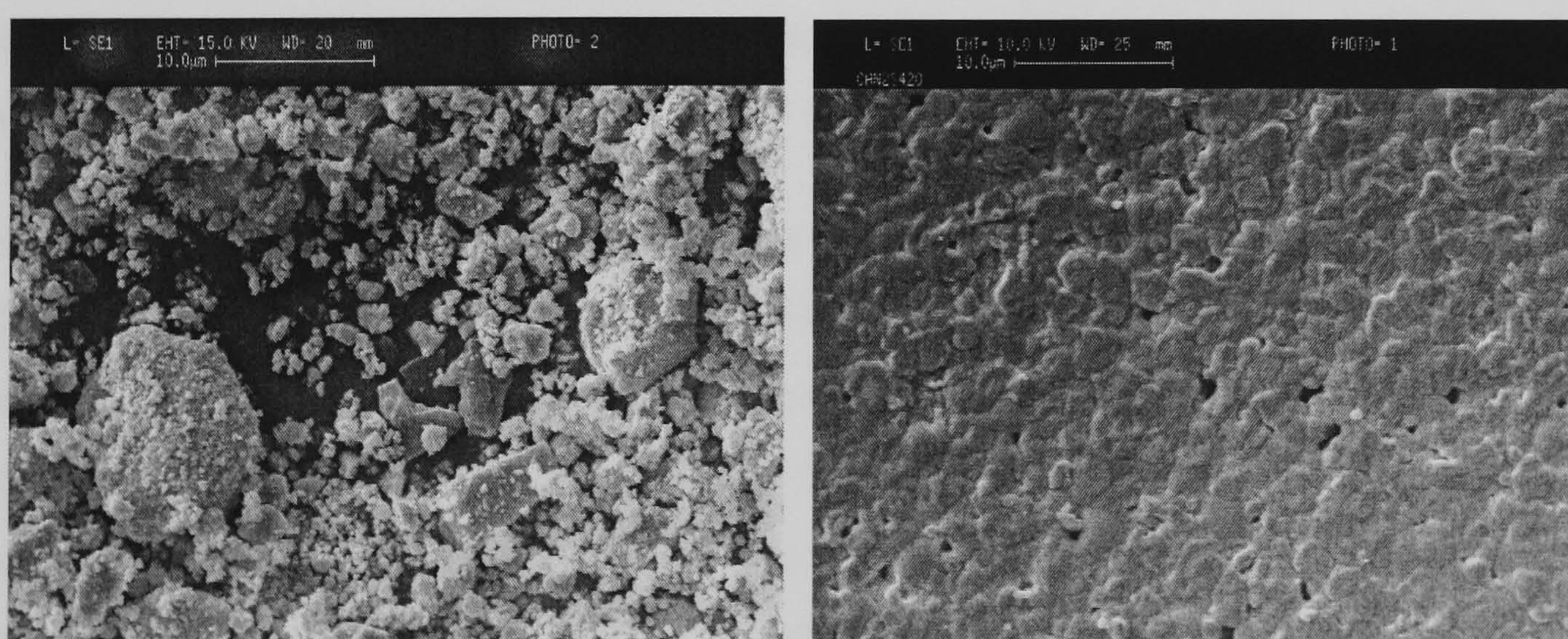


Figure 3-9. SEM of particles ground and resulting CaNd_2S_4 sintered pellet

Grinding performed in a rubber ball attached to a shaker initially using Al_2O_3 cylinders as grinding material. The grinding media was changed to ZrO_2 balls because Al_2O_3 cylinders may led to contamination of the product due to loss of mass of the Al_2O_3 cylinders in the grinding process. The shaker apparatus, with operating speed of 400-500rev/min, achieved similar mean particle size compared to the centrifugal ball mill grinder.

In summary the following procedure was followed to generate a powder particle size distribution with a mean diameter of 1-5 μ m. Particle size reduction of all materials were done according to the following procedure:

- Add, 25grams of grinding media, ZrO₂ balls (8) with 8-10grams of sulphide, to rubber ball, and seal with corks.
- Operate shaker operating at average speed of 350-500 rev/min for at least 2days

2.3 Experimental Methods- Temperature Programmed Techniques

3.3.1 TPO-S and TPR-S

Temperature Programmed Reduction and Oxidation of sulphides, TPR-S and TPO-S respectively, was carried out using an in-house system. Figure 3-10 shows the general setup of the system which is similar to existing experimental set-up, Loof, 1989. The systems' significant components are:

- Gas supply, usually from a cylinder or from a hydrogen generator;
- Programmable high temperature furnace and a Mass spectrometer as a detector-;

The reaction gas (20vol% hydrogen in Argon for TPR-S, 10vol%O₂ in argon or air for TPO-S) is controlled with mass flow controllers. The gas flows through a 1/4" quartz reactor, fitted with or without a frit. Quartz wool is used to support 5-20mg of metal sulphide for reactors without a frit, but it is also used, in a smaller amount, on the reactors with frit as a liner (to prevent clogging of the frit).

The first reactor was without a frit, with a large bore (4mm diameter) and a large bulb (12mm³ volume), this led to very broad TPO-S peaks, Figure 3-11(a-b). The second reactor was also without frit and the bore was reduced to 2mm diameter, however the bulb size was retained, Figure 3-11(c). This led to narrowing of the TPO traces, but it was difficult to remove the quartz wool used to support the sample. The large bulb reactor may cause a significant difference in thermocouple temperature and material temperature, an error that will severely affect experimental results. The temperature bias was minimised by placing the thermocouple inside of the reactor, however corrosion of thermocouple by SO₂ liberated in the oxidation reduced the life of the thermocouple, Figure 3-11(d).

The reactor bulb was reduced to 8mm diameter by 8mm height and the (2mm diameter) narrow bore maintained. This led to even sharper TPO-S traces, (Figure 3.12). A frit was added to remove the need of quartz wool, however in a relatively short time period the frit became blocked with residual material which could not be dislodged with compressed air.

Finally, the bulb was removed to allow easily cleaning of the reactor and the narrow bore of 2mm diameter maintained. The frit was removed to prevent permanent blocking of reactor and replaced with quartz wool to support the sample. The absence of the bulb allowed for accurate positioning of the thermocouple outside the reactor whilst narrow TPO-S traces were maintained, Figure 3-12.

The reactor was heated in the oven at a predetermined rate, typically from 10 to 40K/min, up to a maximum of 1273K, followed by an isothermal period at maximum temperature (using a WEST temperature controller). The exit gas from both TPR-S and TPO-S experiments were monitored using a Mass Spectrometer (ESS, VG). A schematic description of the procedure used in TPR-S and TPO-S is given below:

TPR-S and TPO-S procedure

1. Steady flow of hydrogen or air in argon mixture to remove air from reactor
2. Heating of reactor at heating rate range of 5-50K/min to 1273K
3. Isothermal period, at 1273K, of 10-30mins, to allow complete reaction
4. Cooling to room temperature

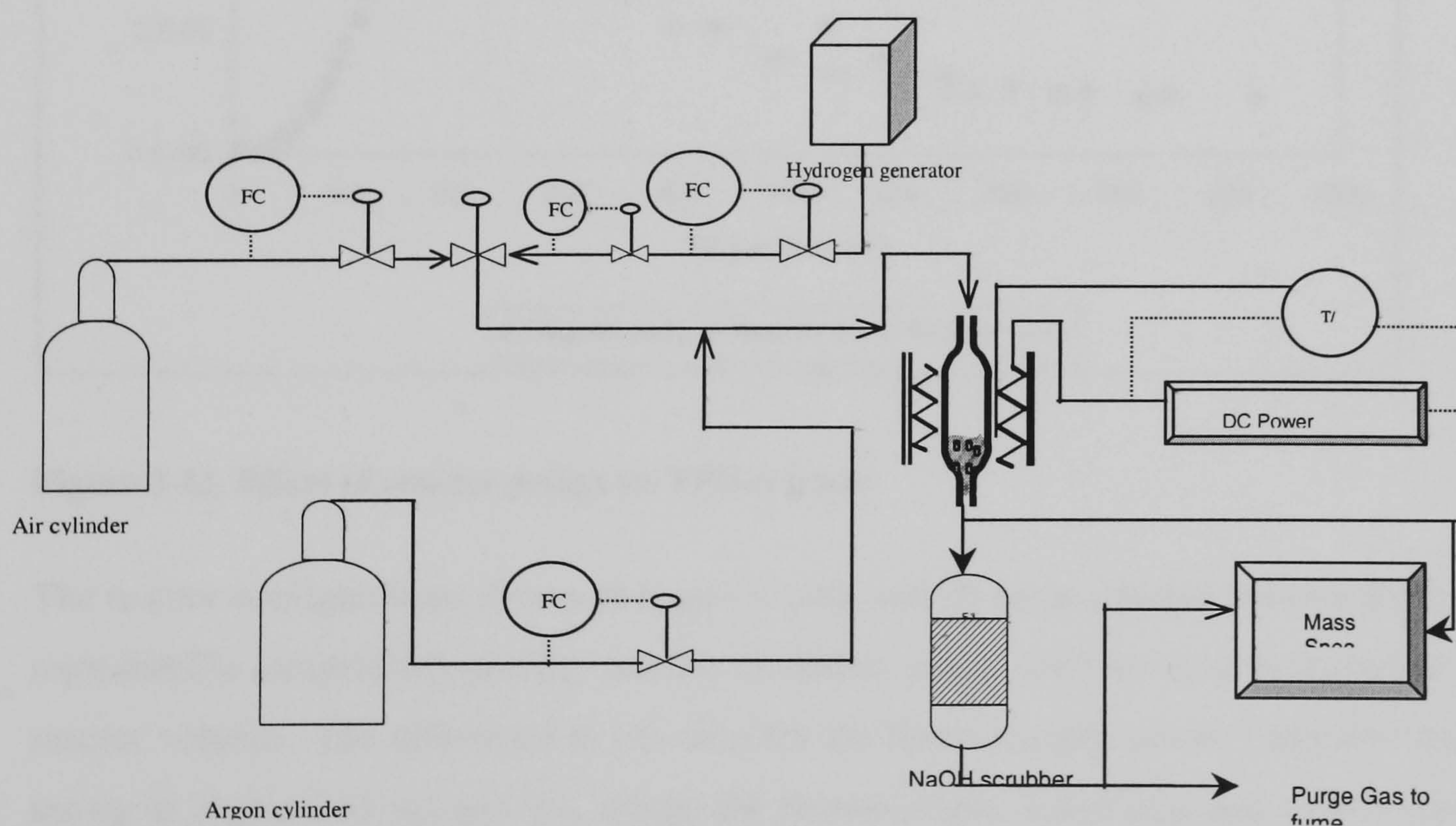


Figure 3-10. TPR/O Experimental Set-up for Complete SO₂ or H₂S scrubbing

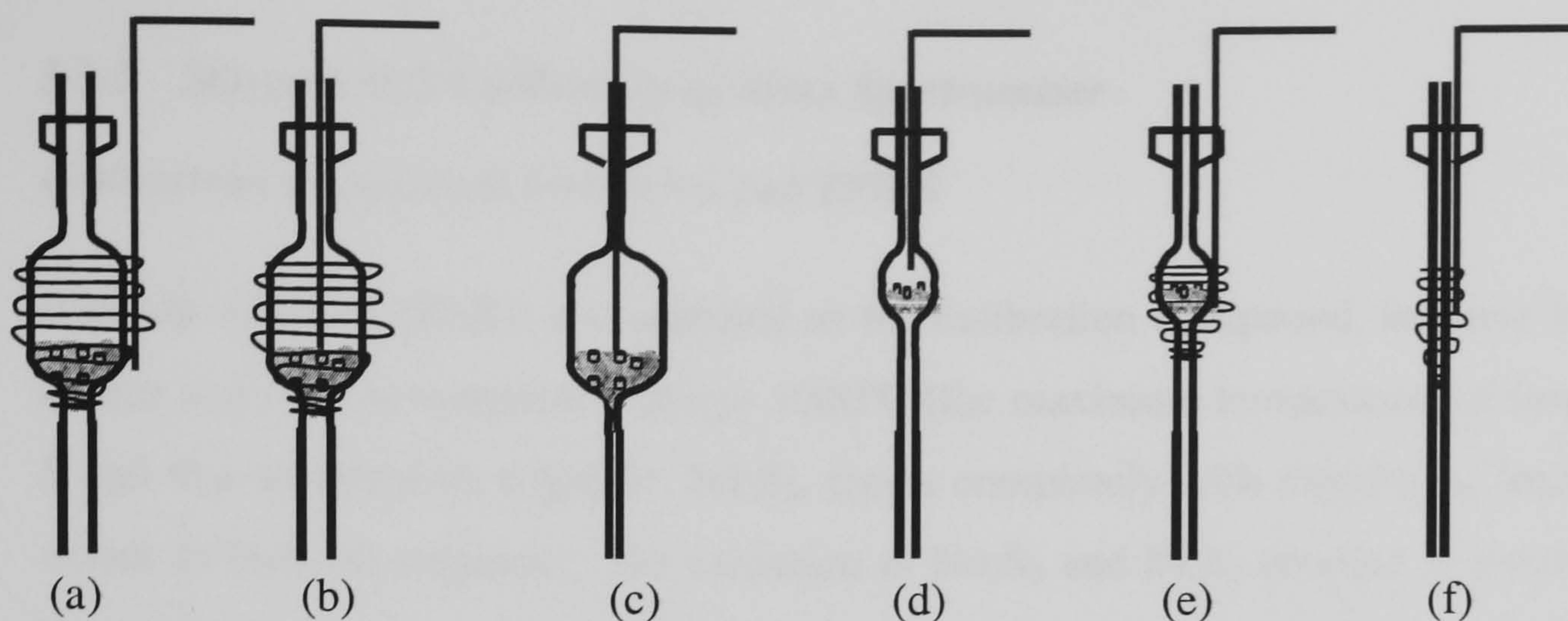


Figure 3-11. Alternative reactor designs and thermocouple location

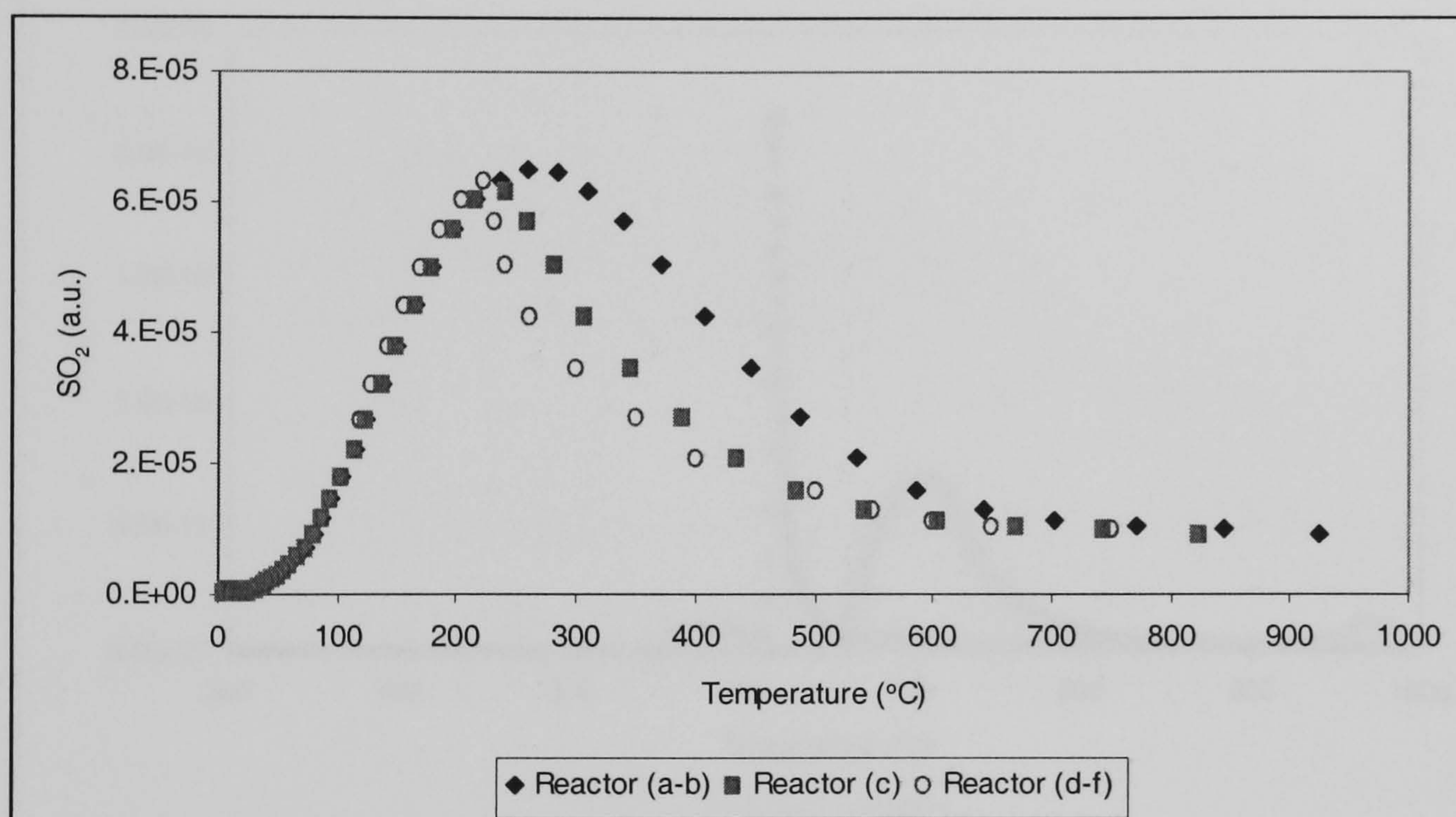


Figure 3-12. Effect of reactor design on TPO-S trace

The reactor configurations shown in Figure 3-11(d) and (f) were selected because these gave a reproducible temperature profile, narrow oxidation peaks, with an area independent of the reactor volume. The difference in life time for the thermocouple can be compared using the set-up in Figure 3-11 (a) and (c), where the thermocouple lasted less than 80hrs (operating time) due to corrosion from H_2S and SO_2 gases, while in set-up (b) and (d) over 2months operating time was achieved. The only disadvantage with set-up in Figure 3-11 (e) and (f), is that the actual temperature of the reacting material may be slightly lower than the temperature measured, because of the possible temperature gradient. This effect was minimised by the use of thin tubes of <2mm wall thickness, a small reactor volume (<5ml) and a small diameter (15mm o.d.) furnace.

3.3.2 SO_2 and H_2S Calibration of Mass Spectrometer

Calibration Compounds for TPO-S and TPR-S

Bismuth sulphide (Bi_2S_3) was selected as the calibration compound, because it is known to reduce and oxidise completely below 1000°C (the maximum temperature of furnace). It was found that neodymium sulphide, Nd_2S_3 , reacts completely with oxygen (at least to the same extent as bismuth sulphide). The oxidation of Nd_2S_3 and Bi_2S_3 resulted in similar peak areas (based on the same molar sulphide content), even though the shape of the oxidation curves was completely different. The TPO trace of Nd_2S_3 showed one peak while the oxidation trace of Bi_2S_3 showed three peaks, Figure 3-13

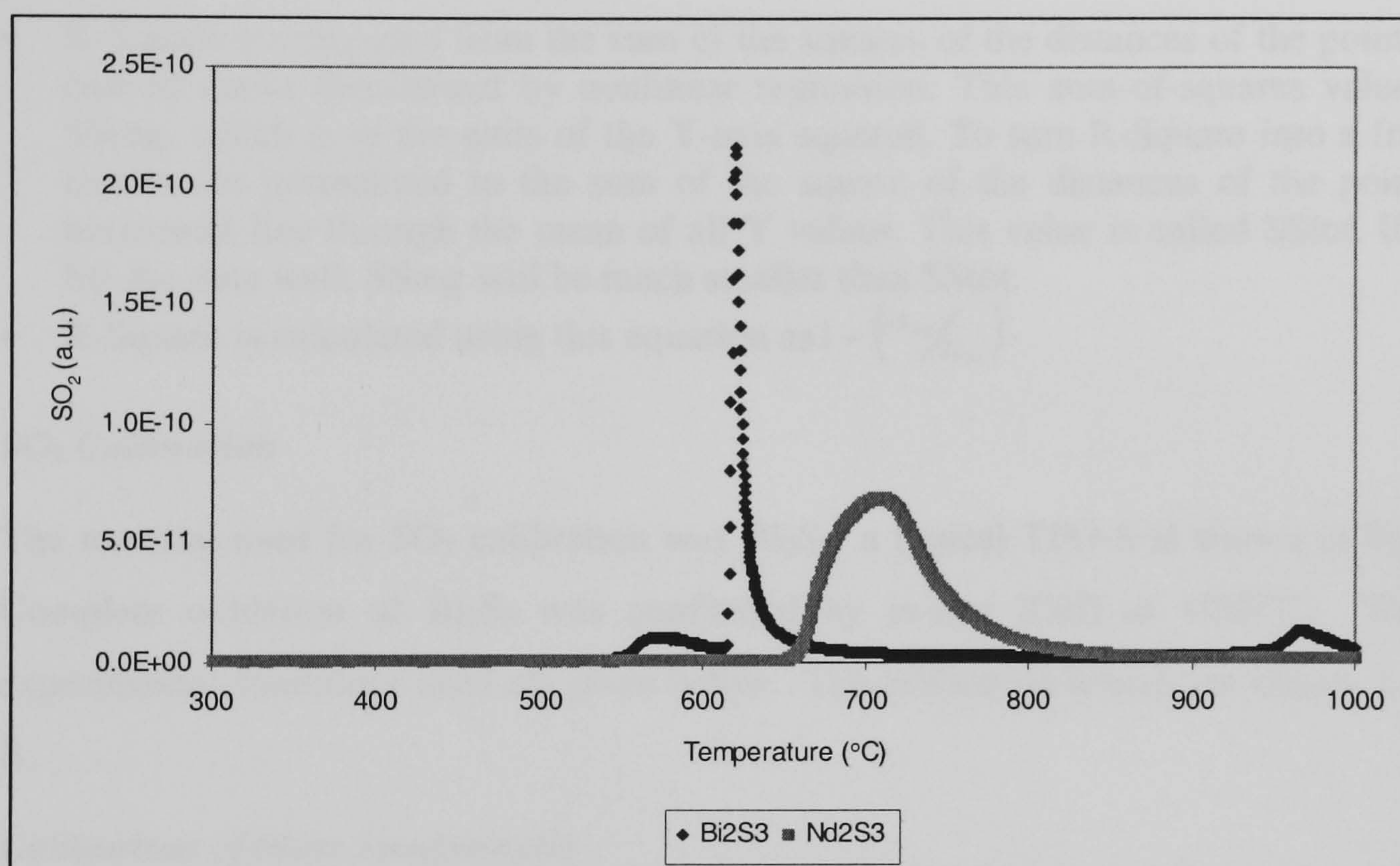


Figure 3-13. TPO traces for Nd_2S_3 and Bi_2S_3

The calibration process requires the following sequence of activities to be performed:

1. Charging sufficient amount of the sample, Bi_2S_3 for example, measured using a scale with at least four decimal place accuracy. Using a large amount of sample ($>25\text{mg}$) may have led to oxygen/hydrogen diffusion limitations in the reaction, which may broaden the TPO-S, TPR-S peaks, hence generating larger areas.
2. Variation in the mass of calibration material should be small, 4-20mg for linearity of calibration curve
3. Using the same experimental conditions such as, heating rate, hydrogen concentration and flow-rate, vacuum in Mass Spectrometer using and the same electron multiplier (EM) voltage

4. Integrating the area under the H₂S/SO₂ signal
5. Plotting area vs molar amount of sulphur in sample to get a linear calibration

H₂S Calibration

The mass spectrometer was calibrated with 20% hydrogen/Argon. samples of Bi₂S₃ between 4-30mg were used. The TPR-S results of Bi₂S₃ are shown in Appendix B where the derived calibration line with R-Square value is above 0.96; hence the calibrations are valid. R-square is the square of the correlation between the response values and the predicted response values.

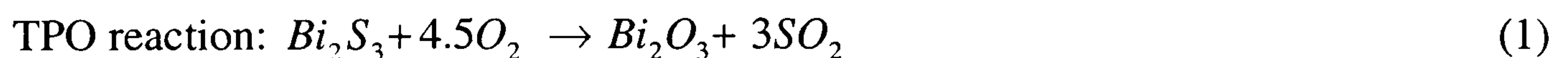
- R-Square is computed from the sum of the squares of the distances of the points from the best-fit curve determined by nonlinear regression. This sum-of-squares value is called SSreg, which is in the units of the Y-axis squared. To turn R-Square into a fraction, the results are normalized to the sum of the square of the distances of the points from a horizontal line through the mean of all Y values. This value is called SStot. If the curve fits the data well, SSreg will be much smaller than SStot.
- R-Square is calculated using this equation as $1 - \left(\frac{SS_{reg}}{SS_{tot}} \right)$

SO₂ Calibration

The material used for SO₂ calibration was Bi₂S₃; a typical TPO-S is shown in Figure 3-13. Complete oxidation of Bi₂S₃ was confirmed by *in-situ* XRD at 1000°C. The varying experimental conditions used are given below. The calibration results are shown in Appendix B.

Calibration of Mass Spectrometer

The number of moles of sulphur was calculated using:



$$\text{Theoretical number of moles of SO}_2 = 3 \times \frac{\text{Mass}_{\text{Bi}_2\text{S}_3}}{\text{RMM}_{\text{Bi}_2\text{S}_3}} \quad (2)$$

Where RMM – Relative Molecular Weight of compound; Bi₂S₃=144 and H₂S =64

Therefore from the mass of calibration sample, the total number of moles of SO₂ liberated is known. This assumes that all the sulphide oxides to form the oxide. This gives the Y-axis of the calibration curve., *In-situ* Xrd of the oxidation of Bi₂S₃ confirms complete oxidation at 1000°C, Johnson *et. al.*, 2003

The X axis is calculated based on the area below the SO₂ trace in TPO-S. This area was calculated using different software packages such as PEAKFIT® and CUREEXPERT®.

Provided that a small variation in mass was used, this relationship between Area and Moles of SO₂ was shown to be linear. The linear relationship between moles of SO₂ and Area of SO₂ for Bi₂S₃ was;

$$Y (\text{SO}_2 \text{ in moles}) = C \times (\text{Area of SO}_2 \text{ in au.min}) \quad (3)$$

Where C, is the calibration constant, Appendix B

3.3.3 Determination of degree of oxidation

The metal sulphides were oxidised using the experimental set-up described in Figure 3-10. The procedure was identical to that of oxidising the calibration compounds, i.e. the mass of the metal sulphide was recorded and all other experimental conditions such as heating rate and gas composition were kept constant. Using the mass of the sample and assuming complete oxidation reaction, the theoretical maximum oxidation is determined.

Example:

Consider the oxidation of CaNd₂S₄



1mole CaNd₂S₄ gives 4moles SO₂

Therefore using the mass of metal sulphide the maximum number of moles of SO₂ that can be released is determine as

$$\text{SO}_{2(\text{theoretical max.})} = \frac{\text{CaNd}_2\text{S}_{4(\text{mass})}}{\text{CaNd}_2\text{S}_{4(\text{Molecular weight})}} \times 4 \quad (5)$$

The SO₂ signal collected with a mass spectrometer during the oxidation of the sample is integrated using CUREEXPERT© or PEAKFIT4.1©. Using the calibration equation (3) the actual SO₂ liberated during the oxidation process

$$\text{SO}_{2(\text{actual})} = \text{Area} \times C \quad (6)$$

Where the units are

C - Calibration constant , e.g. 14635 moles/a.u-min

Area - a.u.min (arbitrary unit)

The degree of oxidation is defined in equation (7) below as;

$$\% \text{ Oxidation} = \frac{\text{SO}_{2(\text{actual})}}{\text{SO}_{2(\text{theoretical-max})}} \times 100 \quad (7)$$

3.3.4 Determination of O_2 Consumed

- The oxygen concentration is kept constant at 5vol% corresponding to an O_2 molar flow rate, e.g. 1.247×10^{-4} moles/min, resulting in an O_2 signal (measured in arbitrary units, a.u., by the mass spectrometer) and is denoted as $O_{2(signal)}$, (in the absence of any reactions)
- The O_2 peak was integrated using CURVEEXPERT© or PEAKFIT 4.1©, denoted as $O_{2(area)}$ with units (a.u.min)
- Therefore the relationship between area and moles of oxygen consumed is defined as

$$O_{2(moles)} = \frac{M.F}{O_{2(signal)}} \times O_{2(area)} \quad (8)$$

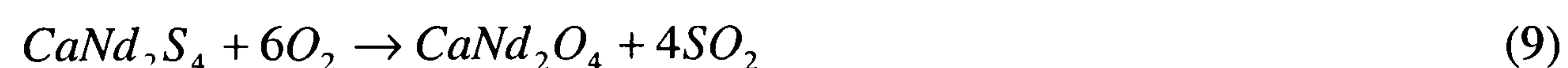
Where the units are

M.F- Molar flow rate constant (moles/min); $O_{2(area)}$ (a.u.·min); $O_{2(signal)}$ (-a.u);
 $O_{2(moles)}$ (moles)

Determining the amount of oxygen consumed allows a complete mass balance to be constructed for the oxidation of the sulphide investigated. Therefore considering the molar amount of sulphur dioxide liberated and oxygen consumed can identify the formation of sulphates, oxy-sulphates or oxides. The mass balance for the formation of sulphates, oxy-sulphates or oxides is considered below with the material $CaNd_2S_4$ as the case study material.

Oxide formation

The formation of oxide follows equation (9), where 6 moles of oxygen are needed for each mole of sulphide that is converted to the oxide. The equation shows that oxygen is consumed and sulphur dioxide is produced during this process.



Sulphate formation

The formation of sulphate from the sulphide requires 8 moles of oxygen for each mole sulphide converted. This process would not liberate any sulphur dioxide, equation (10)



Therefore, if the number of moles of oxygen consumed lies between 6-8 it indicates that a mixture of oxide and a sulphate has formed. The extent of oxide formation is determined by the amount of sulphur dioxide liberated.

Oxy-Sulphide formation

Consider the situation where the number of moles of O_2 consumed is less than 6. This indicates that at the end of the experiment, neither the sulphate nor the oxide was formed, for example, see equation (11). In this theoretical example, 3 moles of oxygen are consumed and two moles of sulphur dioxide released. Such a mass balance would infer, the formation of a compound that is typically called an oxy- sulphide. The formation of oxy-sulphides from oxides occurs during the sulphidation of lanthanides such as cerium where the transformation from the oxide CeO_2 to Ce_2S_3 was observed by Hirai, 1998 with CS_2 as the sulphiding gas. Ce_2O_2S was also formed when CeO_2 is sulphided with H_2S in the absence of carbon, Eastman, 1950, and the formation of oxy-sulphides was eliminated only when carbon was used. Ma, 1996, observed the formation of the oxy-sulphide, La_2O_2S , which has found application as a catalyst in the reduction of SO_2 by CO by Lau, 2003 and 1996. Neodymium oxide Nd_2O_3 also formed the oxi-sulphide Nd_2O_2S when Nd_2O_3 is heated to $500^\circ C$ in the presence of elemental sulphur, Wu, 2003 and Yttria also forms an oxi-sulphide state of Y_2O_2S , Dwivedi, and Ray, 1984. This shows that the formations of oxi-sulphides are likely and they take the form of M_2O_2S , therefore Equation (13) will possible be the most likely out come for the sulphides studied.



Other possible oxi-sulphides includes



3.4 Impedance Spectroscopy

Electrochemical Impedance spectroscopy, EIS, combined with appropriate modelling was used to characterise materials for bulk conductivity, time constants for the conduction process and activation energies. These parameters when compared to oxide ion conduction may infer what ion is conducting. For example, if sulphide ion is the main ion being conducted in the sulphide electrolytes, then the expectation is higher activation energy with a smaller conductivity, also a longer time constant. This expectation is attributed to the larger sulphide ion which intuitively would need more energy to hop from one vacant site to another, and the sulphide ion may move slower giving longer time constant, and less of the sulphide ion may move hence lower conductivity.

To make accurate and repeatable EIS measurements the three most important considerations in the design of the impedance measurement cell are:

- Accurate control of the temperature
- Consistent control of the gaseous environment inside the cell
- The provision of good and repeatable electrical contact with the sample.

The temperature control has achieved by the use of a Eurotherm 2216e controller, which is programmable through the impedance software, provided by Solartron. This ensures that the impedance measurement does not begin until the set point and the actual temperatures are the same, which was achieved after holding for one hour at each temperature. The gaseous atmosphere was $\text{H}_2\text{S}/\text{H}_2$, Argon or an $\text{H}_2\text{S}/\text{Ar}$ mixture; selection of gas will be discussed in detail later. The atmosphere was maintained by the use of an O-ring seal between two stainless steel plates. Gases enter and exit the reactor via heat-treated stainless steel tubing, Figure 3-14. Engineering drawings of EIS systems are presented in Appendix E.

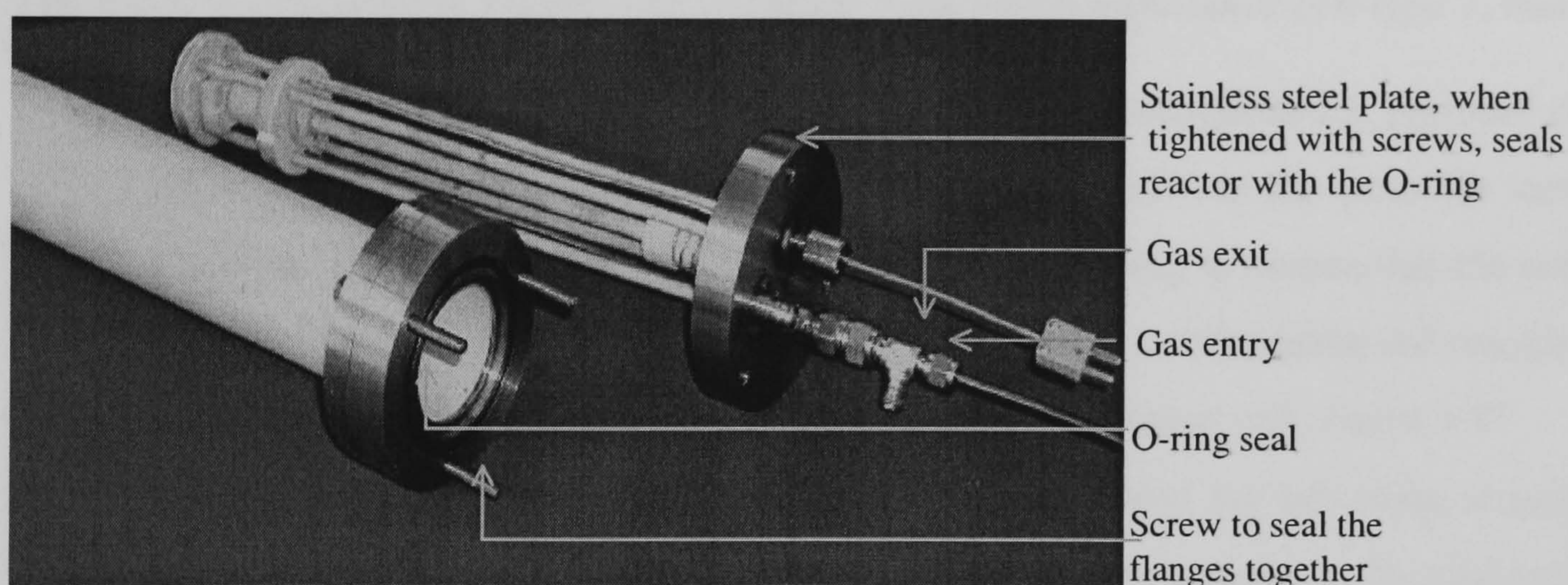


Figure 3-14 Impedance measurement cell-type 1 showing sample holder (upper object) and reactor casing (lower object)

The electrical contact between sample holder and EIS instrument was made through the BNC connectors and cables. The BNC connector was located in the stainless steel plate, Figure 3-15. Connection between the BNC connector and electrode on pellet is made using current collectors made of platinum wire and mesh, the schematics shown in Figure 3-16. The pellet and current collectors were held in a fixed position though the central pin held in place by a stainless steel spring, Figure 3-16.

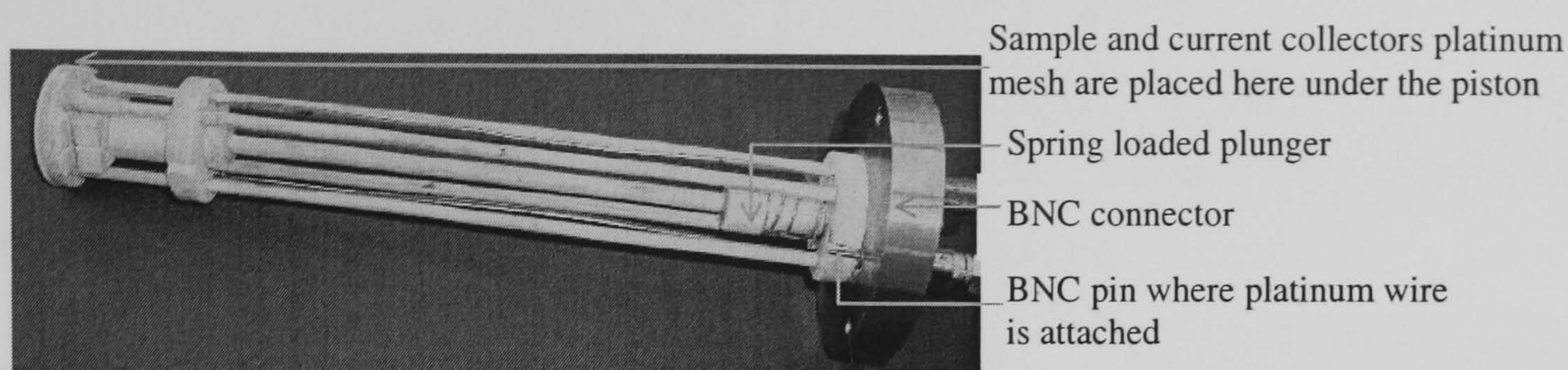


Figure 3-15. Sample holder

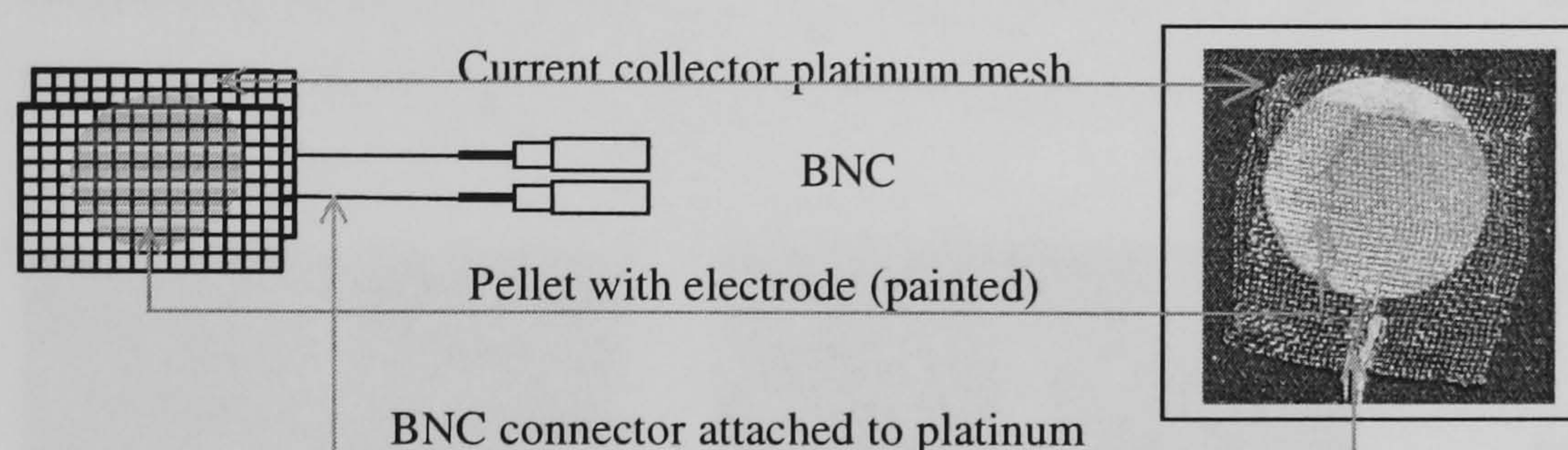


Figure 3-16. Schematics of electrical contact to sample

The EIS cell described in Figure 3.18 to Figure 3.20, called *impedance cell-type 1*, had operational limitations of:

- The BNC was welded to the stainless steel head, so separation for periodic cleaning was impossible. Blowing compressed air onto the pin was the possible method of cleaning. The BNC connectors required periodic cleaning to ensure that the centre pin remains insulated from the other conducting materials used to make the reactor, hence removable BNC connectors were used in type-II impedance cell, Figure 3-17.
- The main limitation of type-I impedance cell design was the laborious inserting and removing of the pellet and the two current collectors, which are located below the spring-loaded piston. In order to compress the spring while inserting the pellet and two current collectors, two pairs of hands were needed. With these limitations in mind, type-II impedance cell was built, from Figure 3-17 to Figure 3-20

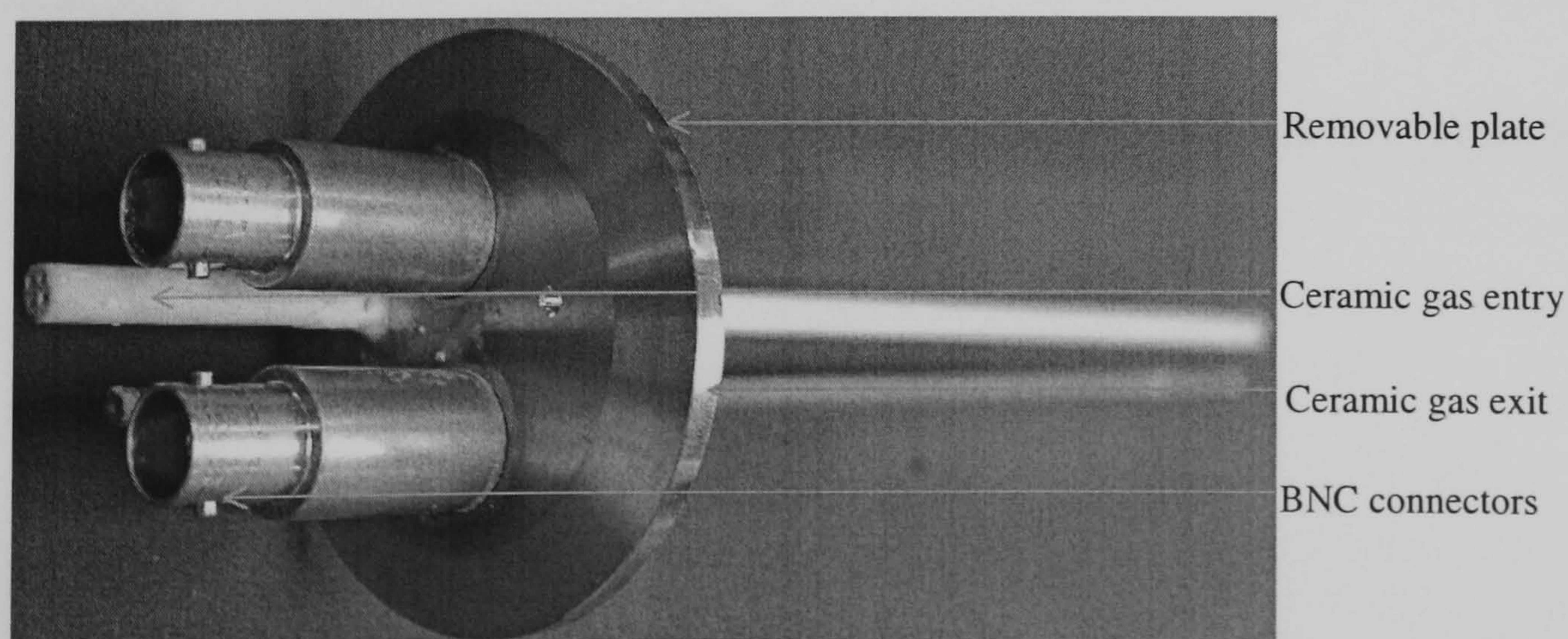


Figure 3-17. BNC on removable plate with a ceramic tubes for gas entry and exit

Figure 3-17 shows the removable stainless plate with BNC connectors, which gave easy access so that they can be cleaned easily. Two separate ceramic tubes were used gas entry and exit to the EIS cell.

Figure 3-18 shows the modified sample holder. The design is much simpler than the original design because rather than having four ceramic tubes joined to a base plate using high temperature ceramic cement . A single half ceramic tube was cemented to the base plate. Engineering drawings of EIS systems are presented in Appendix E.

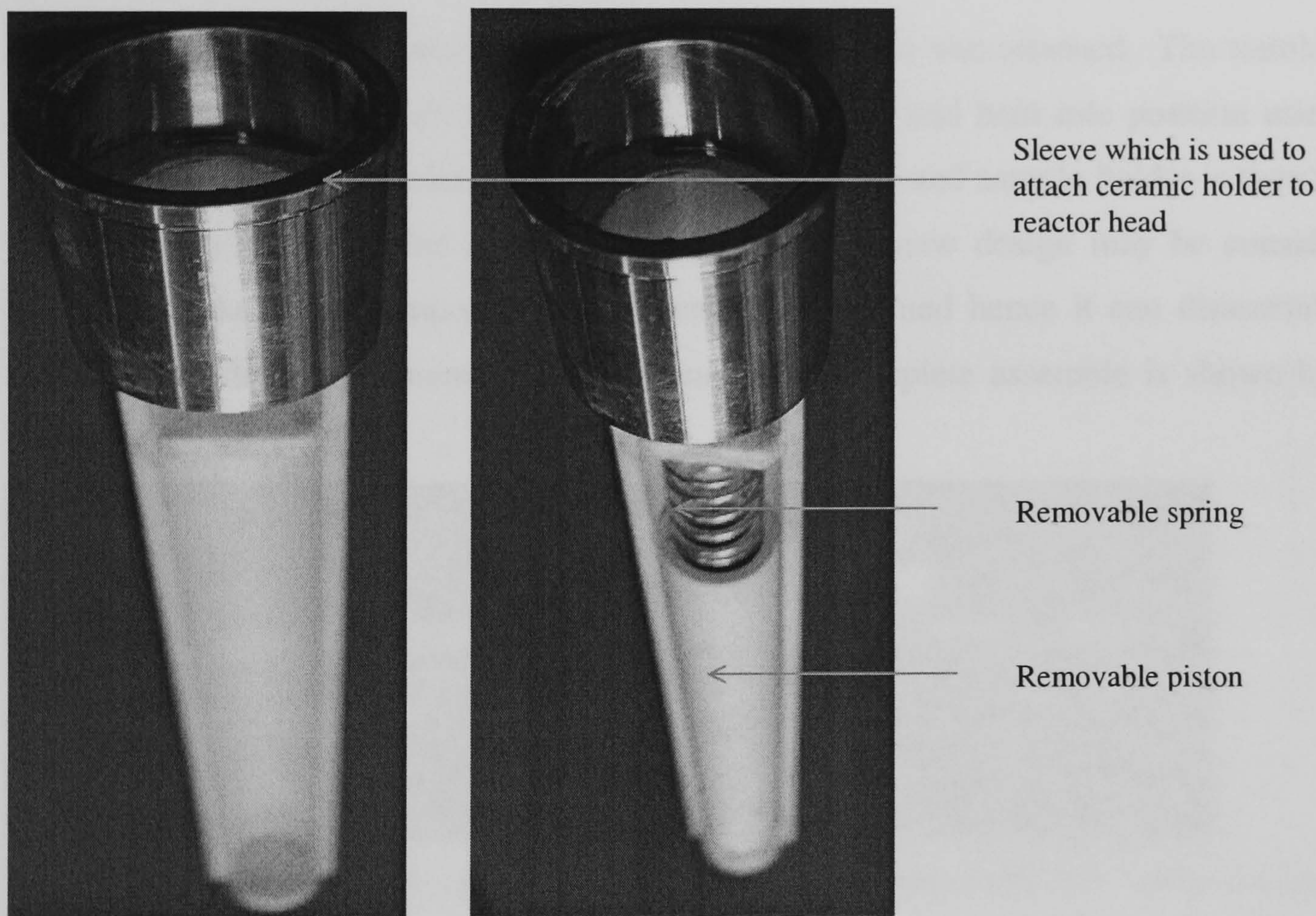


Figure 3-18. (a)Sample holder (empty) and (b) sample holder with removable spring loaded internals

This design is user friendly in that the sample along with the current collectors was first inserted before spring-loading the piston.

A gas-tight seal was achieved by using O-rings seals, Figure 3-19.

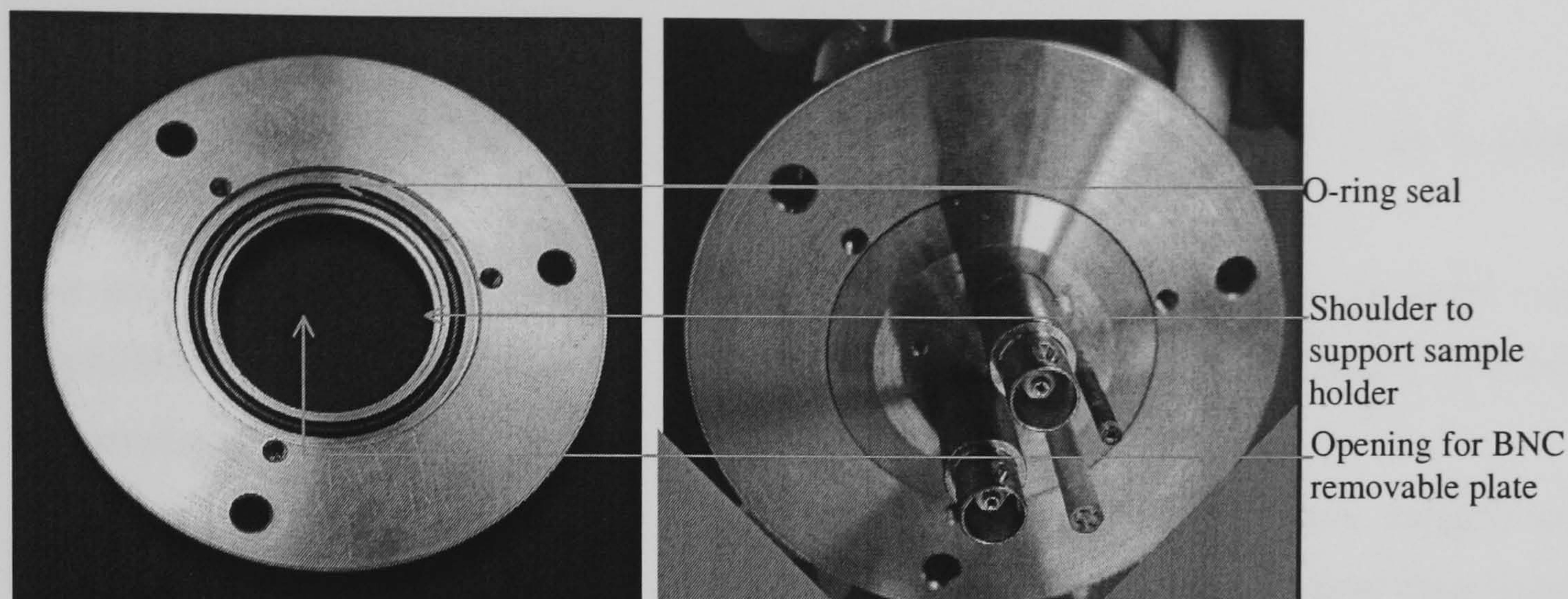


Figure 3-19. Stainless steel reactor head showing the O-ring seal for BNC plate and shoulder to attach sample holder

Figure 3-20 shows the shoulder to which the sample holder was attached. The stainless steel plate with the 2BNC connectors is slotted in the middle and held into position using three screws. The complete stainless steel plate with BNC plate and sample holder is then inserted into the same ceramic tube in Figure 3-14, hence this new design may be considered as modular, in that each component is not permanently joined hence it can disassemble into these independent component for maintenance. The complete assemble is shown below in Figure 3-20.

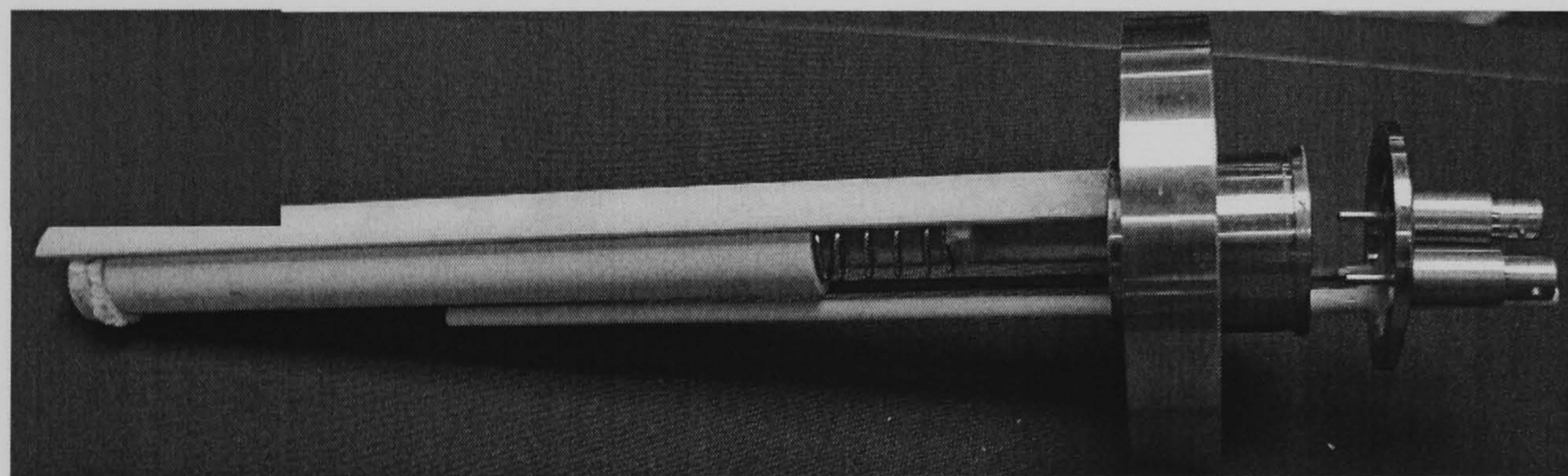


Figure 3-20. Impedance cell- - type 2 -: sample holder with removable BNC plate and spring loaded piston

Figure 3-17 to Figure 3-20, shows the modified impedance reactor. The assembling procedure for this impedance reactor is as follows:

- Inserting BNC plate with ceramic gas tubes, into the sample holder, Figure 3-17
- Insert pellet, then the spring loaded piston, Figure 3-18, this is now the complete sample holder
- Insert the complete sample holder into stainless steel plate, Figure 3-20 and Figure 3-20. Screw to tighten and seal with O-rings.
- This assembly was then attached to a 50mm id, closed one end ceramic tube, and tighten crews for gas tight O-ring seals, inserted into a vertical furnace with no magnetic field, after which impedance measurements were made.

3.5 Impedance spectroscopy experimental conditions

Experimental conditions for impedance spectroscopy, were established in order to produce repeatable and reliable data.

Gas atmosphere: the gas should not react with either the electrolyte or electrode. Some sulphides, (e.g. cerium sulphide) needs sulphur partial pressure, 1×10^{-10} atm, at elevated temperatures to maintain stability.

Maximum temperature: At elevated temperatures, the electrolyte may lose sulphur to the atmosphere that may cause an increase in conductivity due to hole-conduction. This situation can be prevented either by using low temperatures or by having a sulphur partial pressure.

Applied voltage: The signal should be as small as possible, so that linearity can be assumed between applied signal and cell response. However at too small a voltage, no polarisation may occur. Typical values of applied voltage were between 0.01 and 1 Vrms.

Electrode material: the material should be stable, not reacting with the electrolyte or the atmosphere

Each of these aspects is discussed in detail below.

3.4.1 Impedance Atmosphere

Electrochemical impedance spectroscopy of sulphide pellets was initially carried out in 10ppmH₂S/H₂ mixture, using platinum electrodes. The results were inconsistent and erratic; no modelling could be done on the results because a scatter of data points rather than impedance arc(s) were observed, e.g. Figure 3-21. This scatter was possibly due to a reaction between H₂S and Pt or H₂ and Pt; thus this problem can be solved by either replacing the reactive gas with an inert one, or by changing the electrode material to one which exhibits electrical conductivity, but is un-reactive in hydrogen-hydrogen sulphide gas at elevated temperature. Changing the atmosphere from H₂S/H₂ to argon gave typical impedance plots as shown in Figure 3-22.

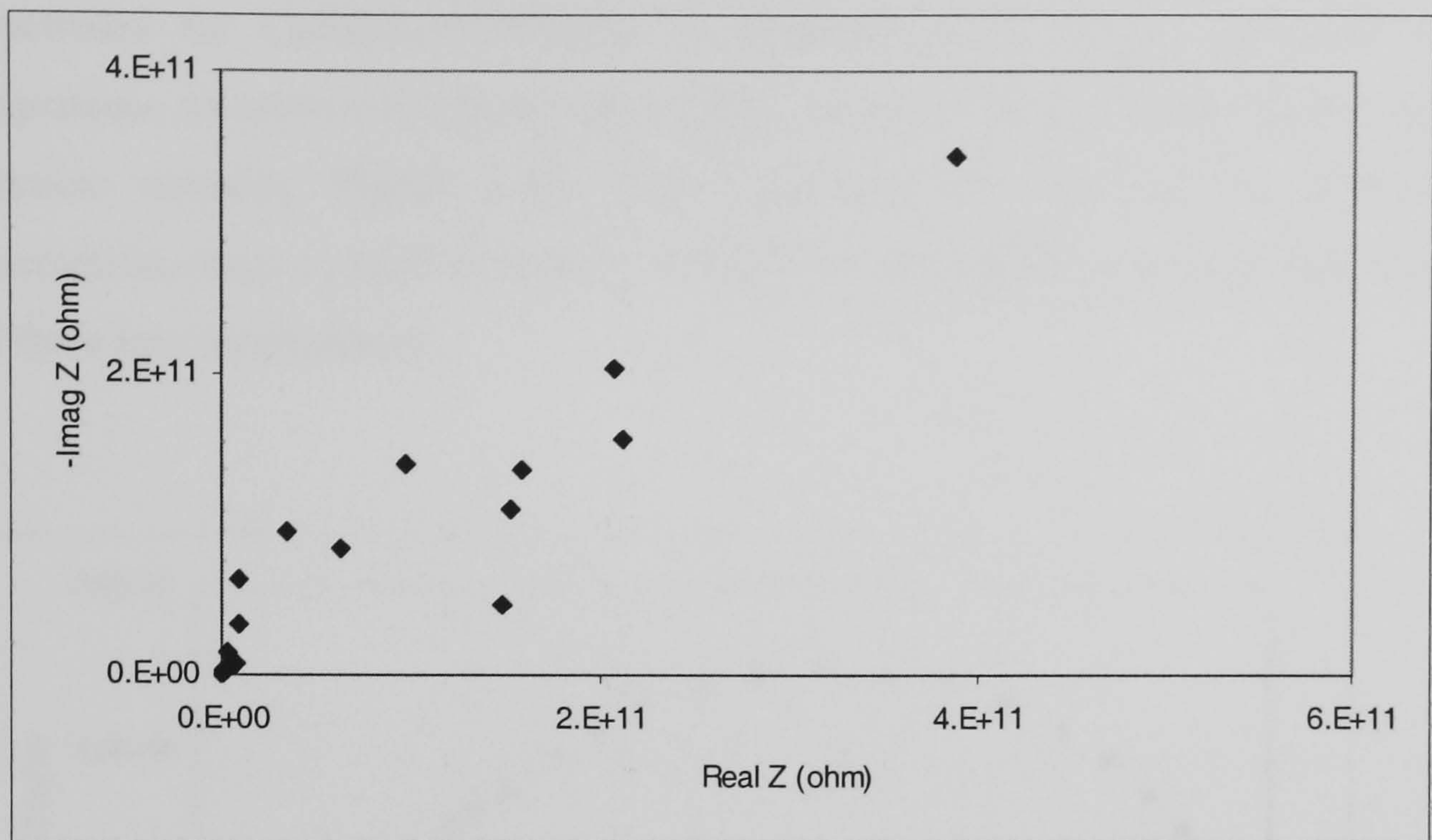


Figure 3-21. Electrochemical Impedance Spectroscopy of $\text{CaNd}_2\text{S}_4\text{-0.0Nd}_2\text{S}_3$ in $10\text{ppmH}_2/\text{H}_2\text{S}$ @ 600°C with platinum electrodes and an applied volts of 0.01Vrms

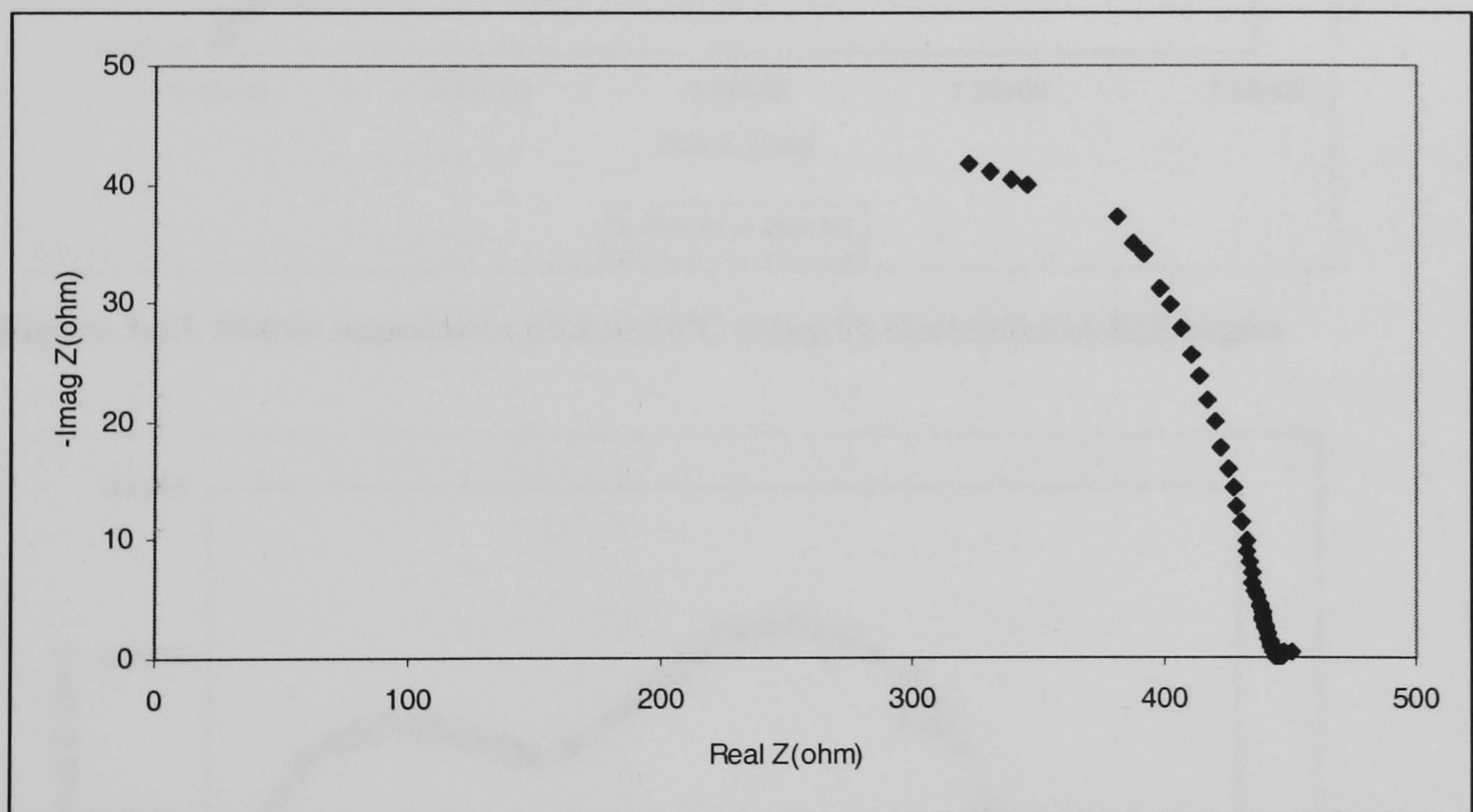


Figure 3-22 Electrochemical Impedance Spectroscopy of $\text{CaNd}_2\text{S}_4\text{-0.0Nd}_2\text{S}_3$ in argon @ 600°C with platinum electrodes and an applied volts of 0.01Vrms

Therefore using platinum electrodes in an argon or $\text{H}_2\text{S}/\text{Ar}$ atmosphere is suitable, however $\text{H}_2\text{S}/\text{H}_2$ was not suitable. Low voltages of 0.01Vrms was sufficient to produce reproducible impedance arcs, hence higher voltages were not used.

3.4.2 Maximum Temperature

Stable arcs were observed in $\text{H}_2\text{S}/\text{argon}$ at temperatures which are 250°C less than the oxidation onset temperature. An impedance arc is stable if upon repetition, the plots overlap.

Figure 3-23 and Figure 3-24 shows stable impedance arc at 50°C and 200°C with platinum electrodes for $\text{CaNd}_2\text{S}_4+30\%\text{Nd}_2\text{S}_3$ in $\text{H}_2\text{S}/\text{argon}$ with 1hour isothermal period before impedance measurement. However at 300°C under the same conditions, the impedance arcs become unstable, Figure 3-25. This could only be attributed to electrode-electrolyte interaction, since a positive pressure of H_2S was used, hence the electrolyte should be stable at these low temperatures.

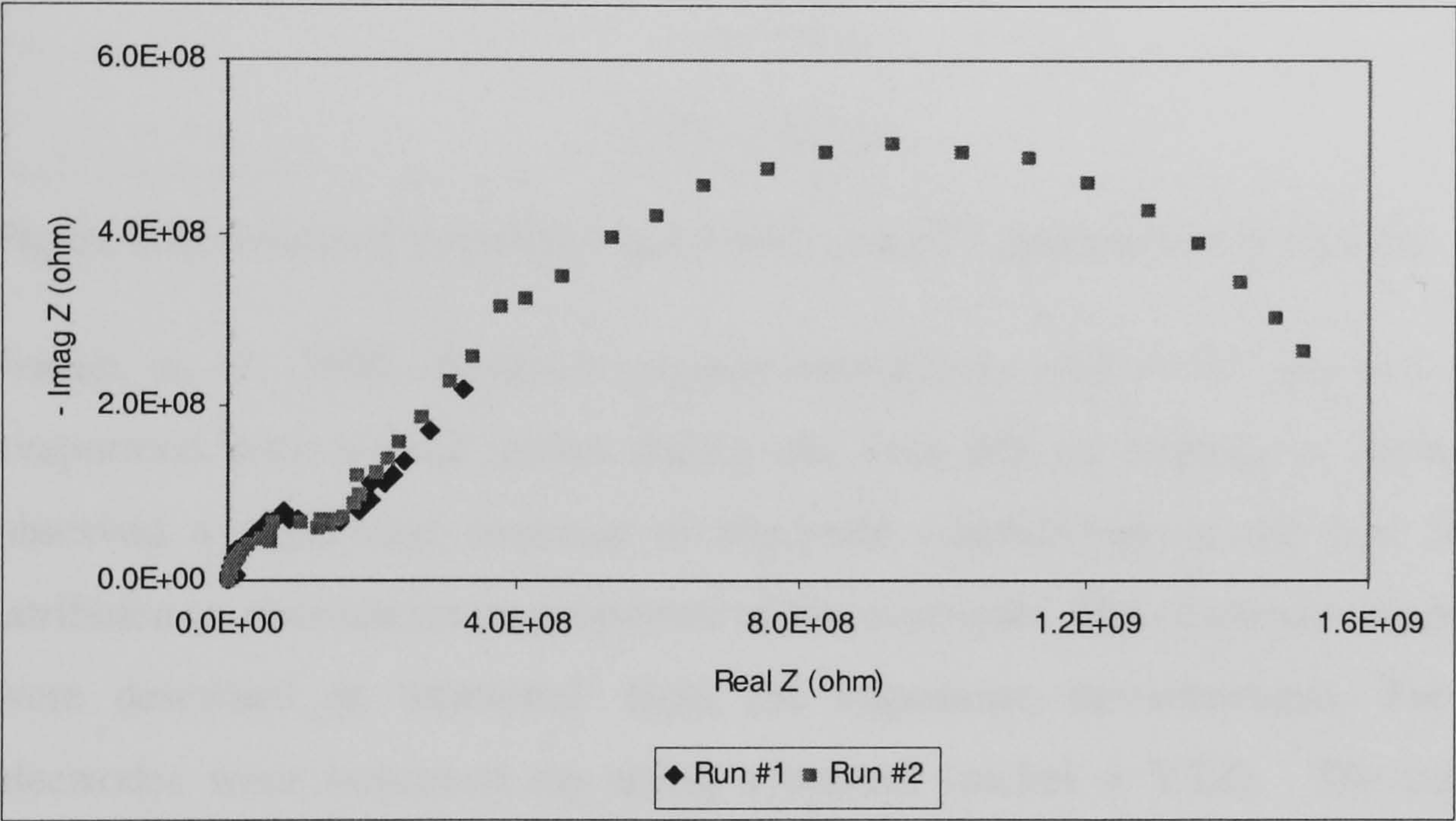


Figure 3-23. Stable impedance plot at 50°C using Pt electrodes in $\text{H}_2\text{S}/\text{argon}$

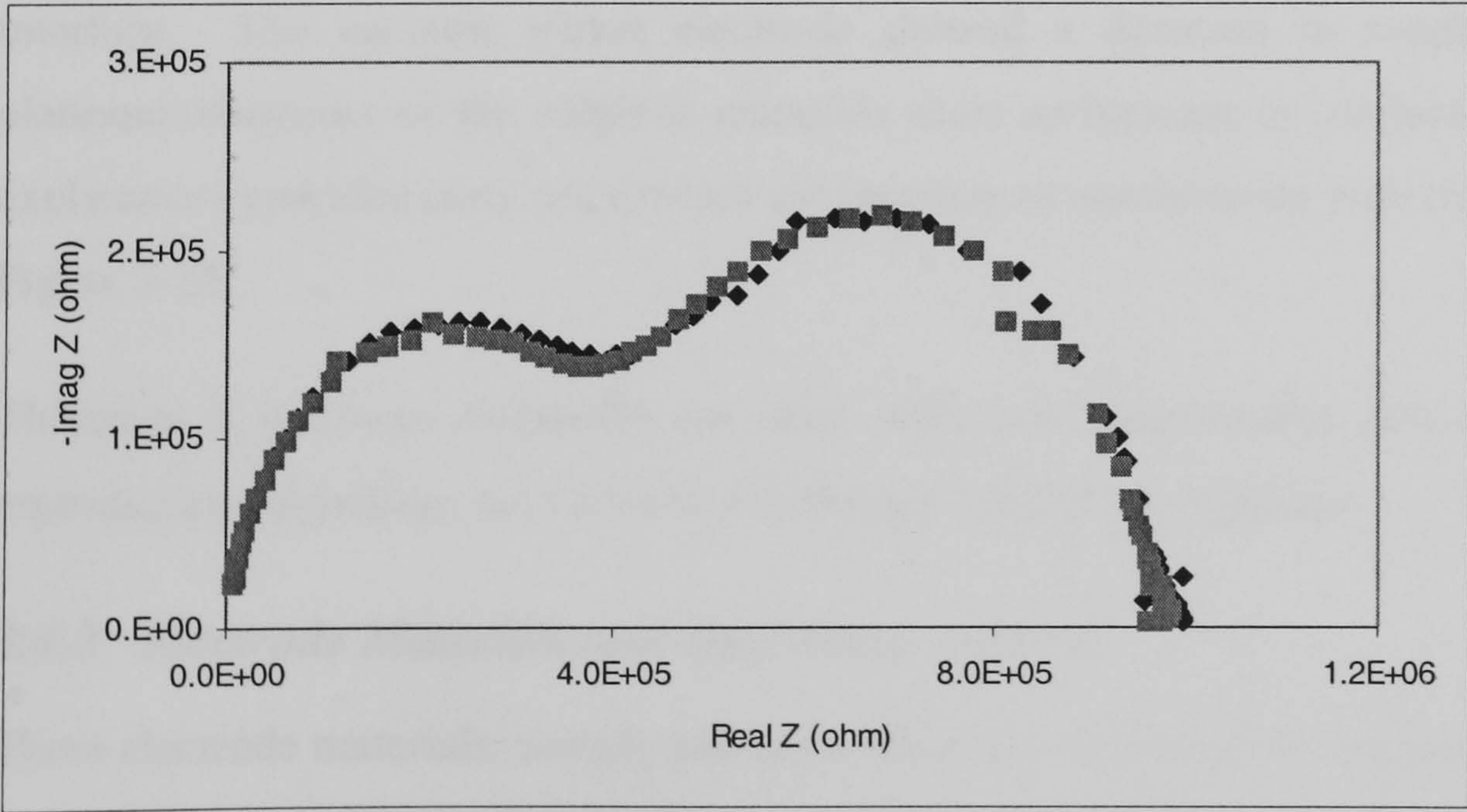


Figure 3-24. Stable impedance plots at 250°C using Pt electrodes in $\text{H}_2\text{S}/\text{argon}$

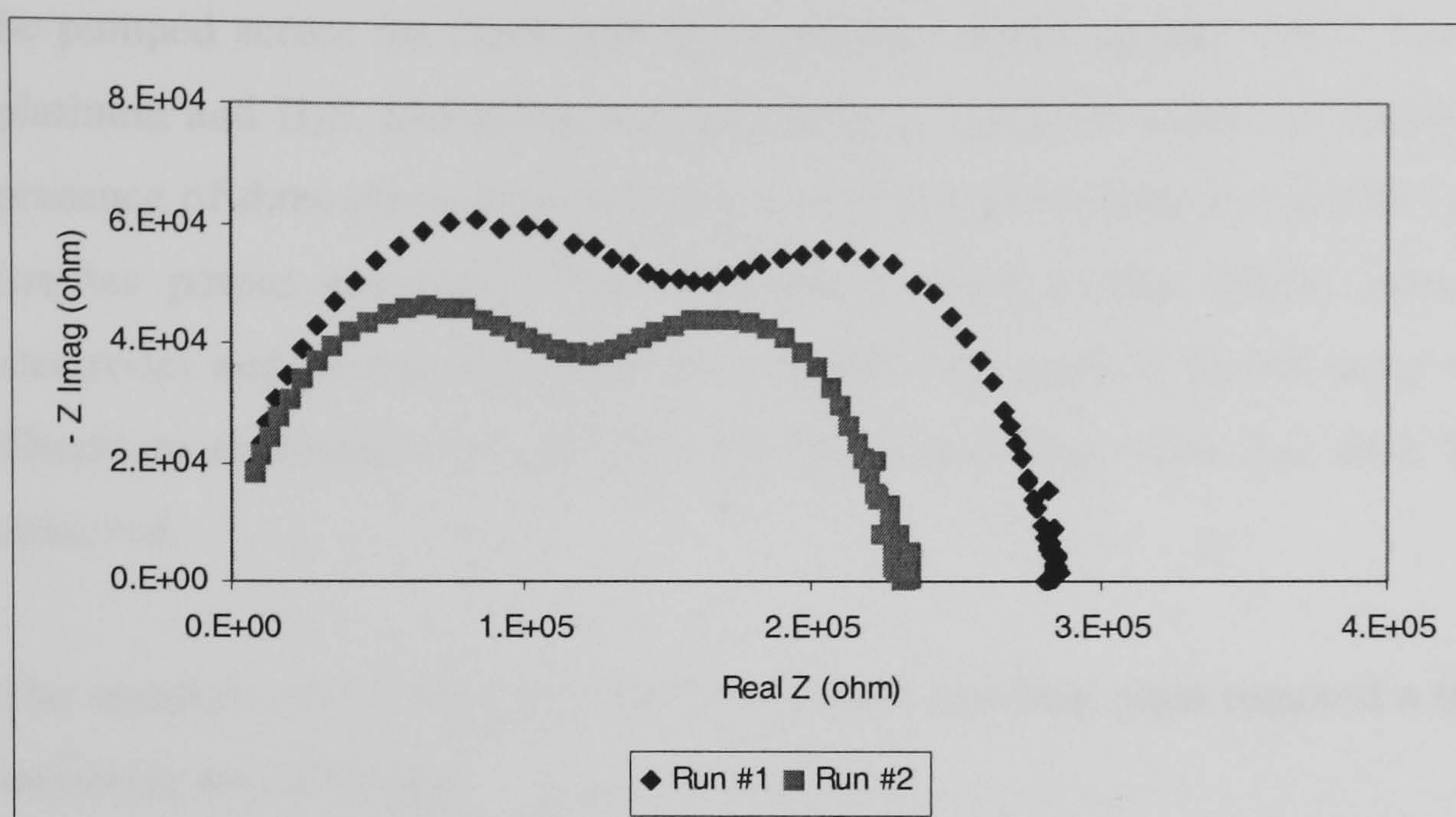


Figure 3-25. Unstable impedance plot 300°C using Pt electrodes in H₂S/argon

Jensen, *et. al.*, 2003, observed unstable impedances with nickel electrode that was thermal evaporated onto a YSZ pellet during the first 50h of impedance measurements. They observed a significant decrease in electrode conductivity in the first 30hrs, which was attributed to microstructure properties of the electrode. The electrodes made from pure metal were described as ‘shattered’ from the impedance measurements. The stability of the electrodes were improved by using a cement (nickel + YSZ). The conductivity of the electrode made from the cement was higher than the pure metal. This unusual observation was attributed to the expansion of the three-phase boundary due to roughing of the YSZ interface. The unstable nickel electrode showed a decrease in conductivity while the platinum electrodes on the sulphide materials show an increase in conductivity, therefore the explanation provided does not explain the increase in conductivity with time, as observed in Figure 3-25.

Therefore if platinum electrodes are used, only low temperatures, less than 300°C, yield reproducible impedance arcs even in a hydrogen sulphide atmosphere.

3.4.3 Electrode Materials and application method

Three electrode materials, namely platinum, gold and carbon, were employed, combined with a number of methods of application: namely spray painting, brush painting, sputtering, thermal evaporation, or simple physical contact.

Platinum

Platinum catalyses many reactions; for example, the shifting of the equilibrium of H₂S, H₂, and S₂ molecules. This reaction may become important when sulphide ions are attempted to

be pumped across the electrolyte by applying a direct current, (DC). The reaction between platinum and H_2S , and subsequent pumping of sulphide across the membrane, requires the presence of three-phase boundary between electrode, hydrogen sulphide and electrolyte, this implies porous electrodes. The literature-surveyed to-date speaks loosely of conducting electrodes and porous electrodes even though the value of conductivity was not specified. Therefore electrodes were initially deemed conducting when less than 5Ω resistance was achieved.

The creation of low resistance electrodes from platinum paint required a three-stage process involving the following:

- Painting each side of the pellet with Gwent Chemicals platinum paste made with 99.99% purity platinum mixed with low and high temperature organic binder (binders helps in the formation of porous electrodes)
- The low temperature binder is removed from the platinum paste by drying in air at 200°C . The high temperature binder was removed by thermal treatment using a reducing atmosphere of 5% H_2S and 95% H_2 at a temperature of 950°C with a dwell time of 4hrs. This stage produces a black coating, with a resistance of 20Ω , due to the formation of platinum sulphide
- Platinum sulphide is converted to platinum by treating the coatings in 100% H_2 at 450°C with a dwell time of four hours; this reduces the electrode resistance to 0-2 Ω . However the cross-sectional resistance of the pellet, which was greater than $200\text{M}\Omega$ prior to application of the platinum paste, fell to approximately $0.5\text{k}\Omega$. The reduction in resistance of the pellet could only be attributed to the entrainment of conducting particles within the cross section of the pellet. The conducting particles could either be due small Pt particles since the paint was thinned for easy painting, hence the smallest particles would settle first or high temperature organic binder (carbon) and based on the SEM images pore size of $2\text{-}5\mu\text{m}$ on the pellet surface was typical. If this was the case, no heat treatment could restore the conductivity. If this drop in cross sectional resistance is related to carbon from the binder then heat-treating in trace amount oxygen could restore the resistivity. Therefore a carbon removal stage was added.
- The coated pellet was heated to 490°C for four hours in a very dilute oxygen stream (0.01% oxygen). Pellet resistance increased to $20\text{M}\Omega$
- This process produced 0Ω electrode on the exposed surface of the pellet and 50Ω electrode on the under-side of the pellet.

The electroding process was subsequently altered to heating of the Platinum paint in 1100°C for 1hr in pure argon, converting the organics to carbon which was subsequently removed by heating to 600°C at 40K/min in pure hydrogen. This process gave perfect electrodes on both sides however the pellet may crack. The cracking of the pellet was attributed to thermal shock of the high heating rate used, hence heating rate was lowered to 10K/min. SEM images of this electrode showed that the resulting electrode was porous, Figure 3-26. Bauerle, 1969 produced porous platinum electrodes by painting platinum paste, sintering to 1400°C for 1hr, which gave non-porous Pt electrodes; porosity was increased by passing a current of 1A/cm³ at 800°C. The porosity of the electrode was estimated by applying a small drop of liquid to the electrode surface; observing of the liquid its disappearance (or lack of it) by capillary action.



Figure 3-26. Pt electrode painted on CaNd_2S_4 , which has a porous structure similar to base material.

Initial impedance experiments were carried out in 10ppm $\text{H}_2\text{S}/\text{H}_2$ using Platinum electrodes. This resulted in data with so much scatter that no arcs could be discerned. To obtain reproducible experimental data, the experimental parameters available to change were the electrode material or the atmosphere under which the experiments were performed. Initially the electrode material was changed; painting platinum on to the sintered pellet was changed to sputtering of gold unto the pellet surface.

Gold

Gold was used as an alternative electrode material due to its high electronic conductivity. Gold was sputtered for 120s onto the sample pellet. The surface resistance of the pellet fell from greater than $200\text{M}\Omega$ to $2\text{k}\Omega$. A repetition of the sputtering reduced the surface resistance to 600Ω . Sputtered electrodes were found to be reasonably porous without any additional treatment as stated by Bauerle, 1969. The limitation of sputtered electrodes was continuity; that is achieving little resistance across the surface of the pellet (less than 20Ω).

Pellets were also coated with gold using thermal evaporation using gold wire $2\text{mm} \times 5\text{mm}$ for multiple pellets. The evaporation process vessel was initially purged with Argon followed by evacuation. The resulting surface resistance varied from 0 – 20Ω . Boer *et al.*, 2000 have coated YSZ with nickel applied by evaporation followed by annealing at 1000°C for 2hr under reducing conditions ($10\text{vol}\%\text{H}_2$ in N_2). They have shown SEM images of porous electrodes.

Pellets of samarium based electrolytes with initial gold electrode resistance of 0 – 20Ω increased to greater than $200\text{M}\Omega$ after impedance in argon with a maximum temperature of 400°C , therefore SEM images were taken to understand the change in electrode resistance. Figure 3-27. Gold electrode on samarium based electrolyte after impedance in argon shows gold as the white and electrolyte as black, and it is clear that the gold is not continuous, and this explains the high electrode resistance.

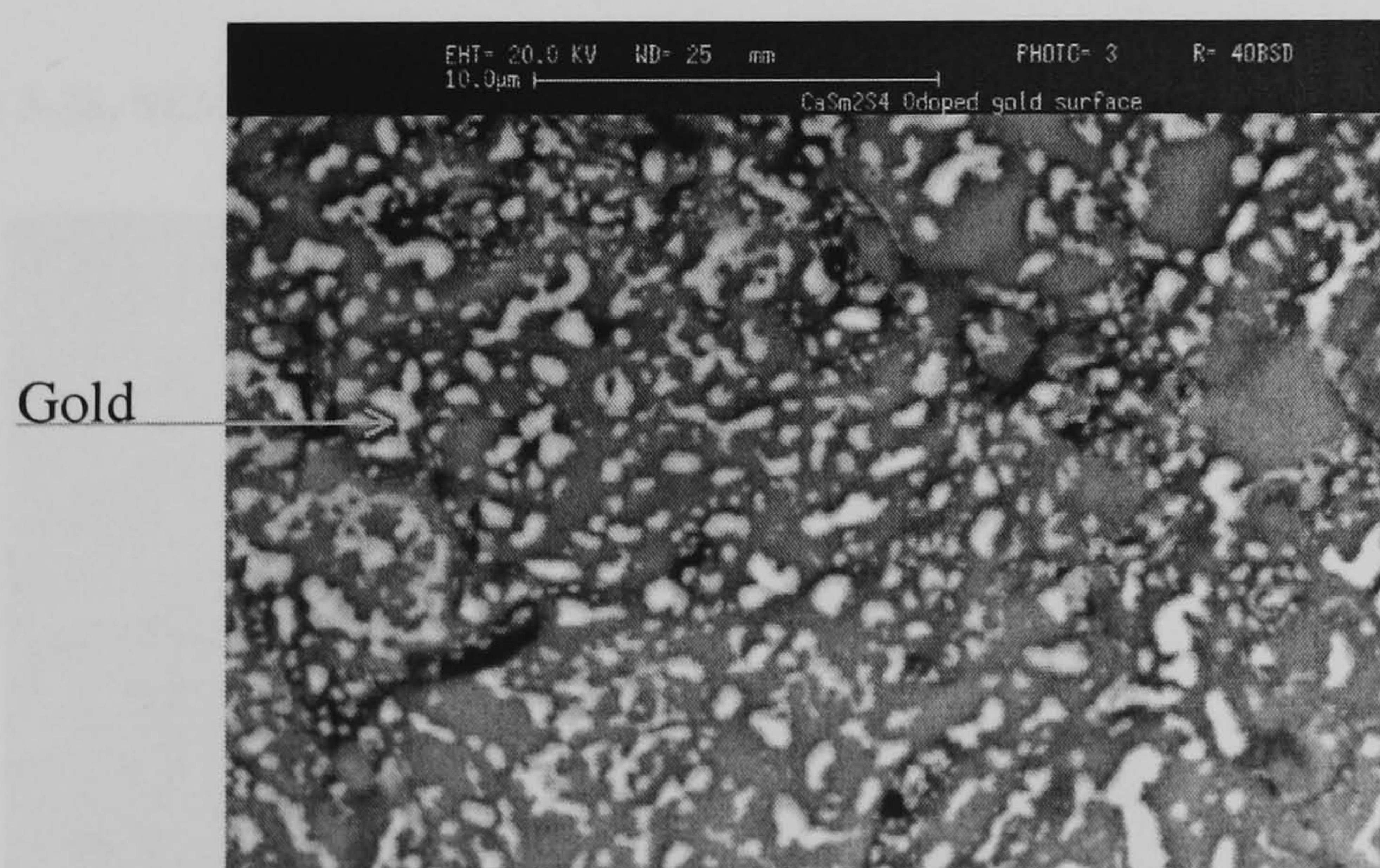


Figure 3-27. Gold electrode on samarium based electrolyte after impedance in argon

The colour of the electrode changed from a gold colour to an orange-red and the exposed cross-section of the pellet changed from yellow to brick red. This observation led to the investigation this increase in surface resistance using SEM analysis of the electrode surface.

SEM showed the electrode was not uniform but rather globules of gold could be seen on the surface, i.e. the electrode had become discontinuous Figure 3-27. SEM of the exposed cross section of the pellet before and after EIS measurements is shown in Figure 3-28 and Figure 3-29.

Morris *et al.* 2001 reports that gold can react with sulphur to form Au-S or Au-S₂ both of which are more covalent than ionic bonding therefore if sulphide ions are conducted to the electrode during the impedance measurements then the sulphide ions could subsequently react with the electrode to form Au-S or Au-S₂. The impedance was done in argon, and no other source of sulphur is present in the system to allow for such a reaction. Gold sulphide has a golden brown colour that matches the colour the electrode colour after E.I.S measurements.

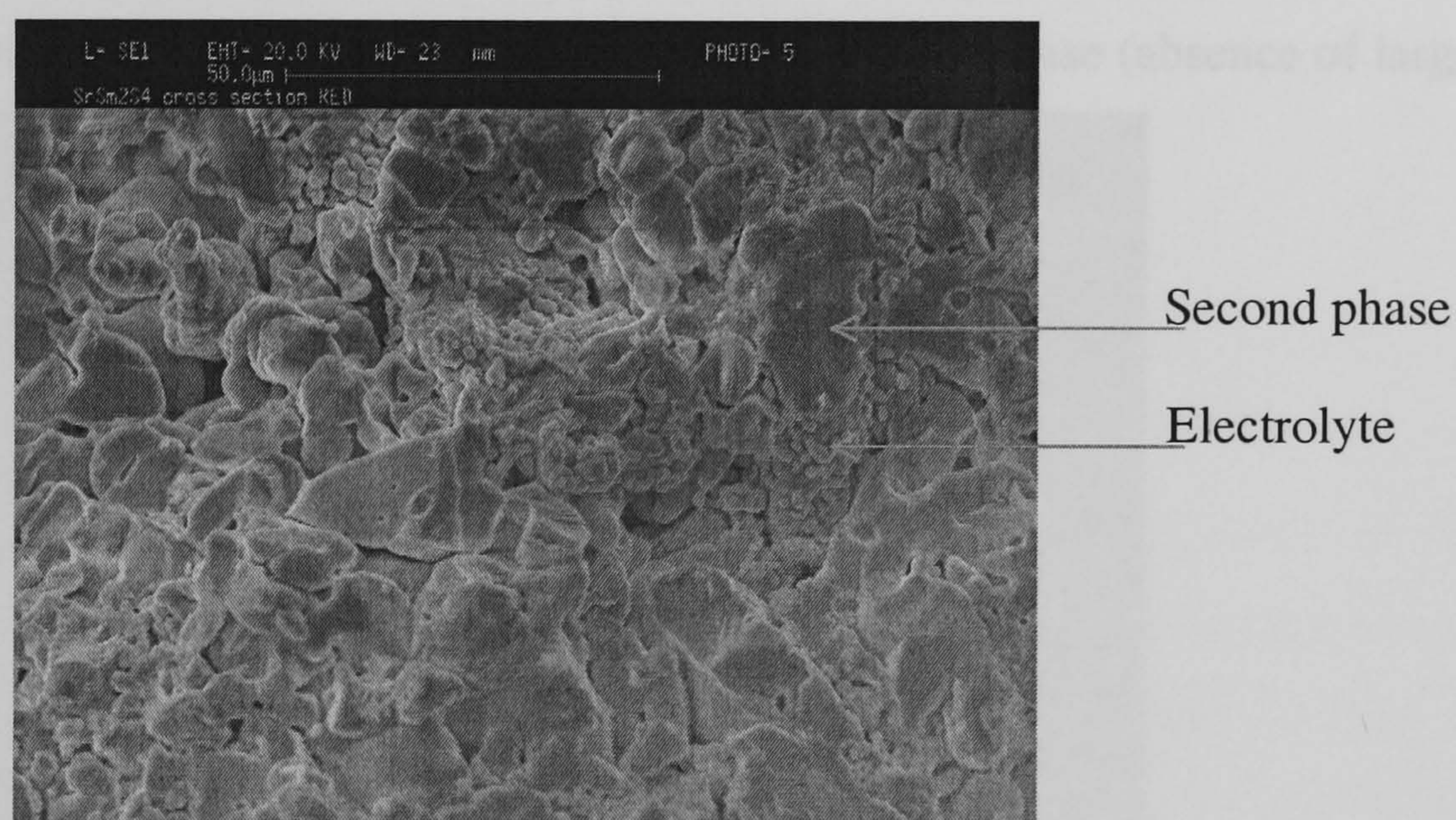


Figure 3-28. SEM image of cross section of samarium sulphide based pellet after EIS measurements



Figure 3-29. SEM image of cross section of samarium sulphide based pellet before EIS measurement

SEM analysis of the reddish cross section of the pellet showed that a second phase had formed on the primary metal sulphide phase, Figure 3-29 when compared to SEM images taken before EIS measurements, Figure 3-29. Furthermore no gold was observed in the cross section of the pellet. This result led to the conclusion that the use of sputtered or thermal evaporated gold electrode on samarium based pellets was not successful due to a surface reaction between the gold and the electrolyte. The increase in surface resistance of the electrode was not due to loss of gold or due to gold entering the electrolyte, but rather attributed to the formation of discontinuous gold globules.

Neodymium sulphide doped materials formed stable gold electrodes since no significant change in electrode resistance was observed before and after EIS experiments. Also no colour change of electrode or electrolyte was observed after EIS measurements. SEM image of the electrode after EIS in Figure 3-30 shows a continuous phase (absence of large globules).



Figure 3-30. SEM image of gold electrode on undoped CaNd_2S_4 after EIS at 400°C in argon

In summary, gold is not suitable electrode material due to the apparent reaction with the electrolyte; hence this electrode was discontinued.

Graphite

The failure of gold in forming a stable electrolyte and the complexity of creating a stable platinum electrode led to the investigation of carbon electrodes. The initial investigation of sulphide ion conduction of CaNd_2S_4 was done using graphite electrodes, with no report of electrode-electrolyte interaction, Kalinina *et. al.* 1994. Figure 3-31 shows stable Nyquist plot of a sulphide electrolyte at 400°C in argon using graphite electrodes. The applied voltage was

increased from 0.01Vrms (used with gold and platinum electrodes) to 0.1Vrms on graphite electrodes to reduce the scattering observed at low frequencies. The need for higher applied voltage is possible due to the lower contact area between the mechanically pressed graphite plates and electrolyte.

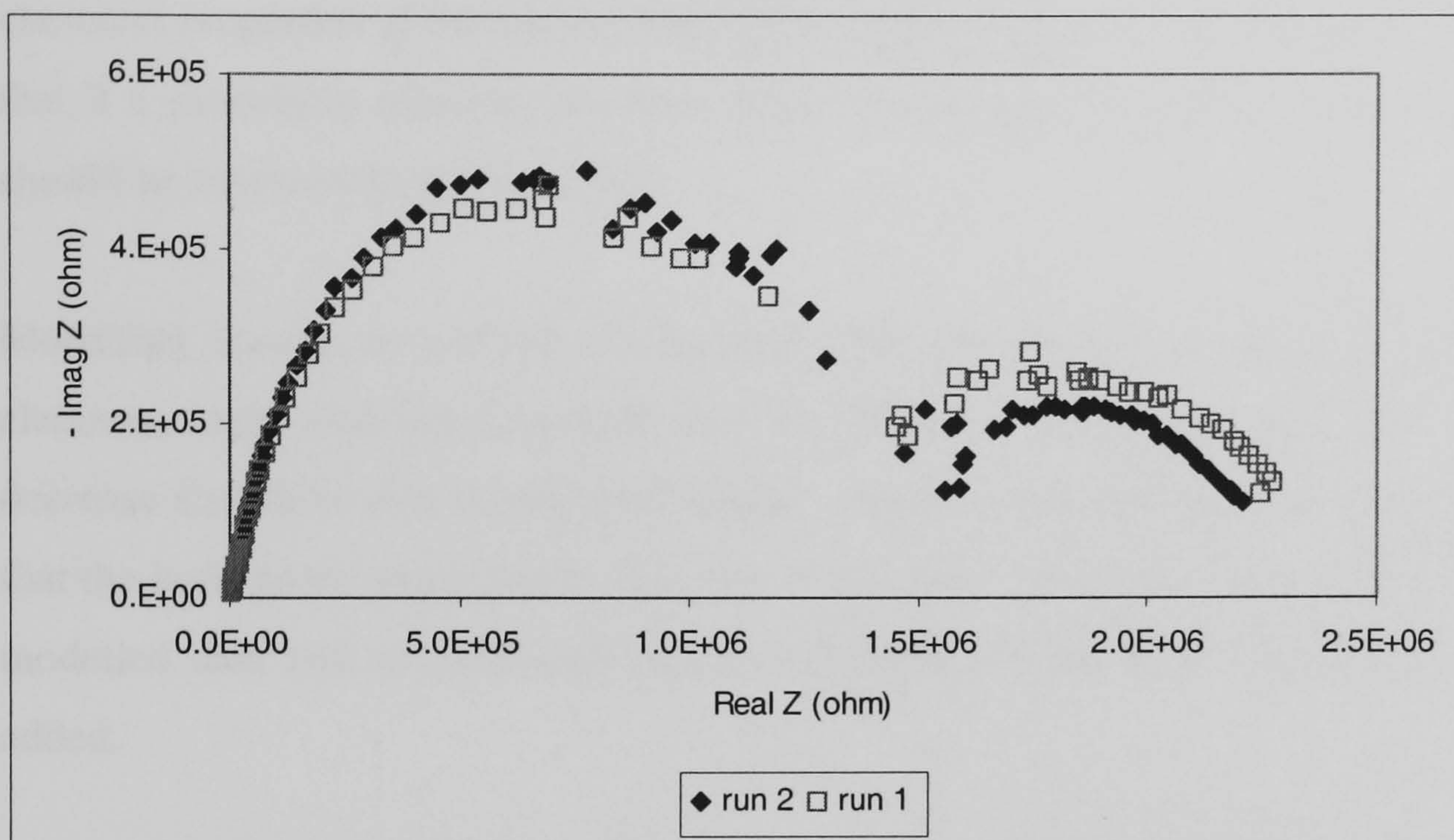


Figure 3-31. Nyquist plot at 400°C in argon using graphite electrodes

Therefore the use of graphite electrodes allows higher temperatures to be examined, 400°C in argon, this suggests that the instability at lower temperatures with platinum electrodes was due to the electrode-electrolyte interaction and not loss of sulphide from electrolyte to the atmosphere. However higher applied voltages were needed, 0.1Vrms for graphite electrode, compared to 0.01Vrms for platinum electrode.

3.4.4 Modelling E.I.S Experimental data

The aim of modelling of EIS data is to understand the conduction process and to derive characteristic parameters that describe this process. To understand the electro-chemical process, information of the physical conditions such as thickness, porosity, roughness etc, should be established. EIS data is best understood by the use of an appropriate model, hence modelling, which can be rather difficult, is the most important part of EIS technique.

Once reliable, repeatable experimental data are obtained, usually an equivalent circuit is chosen to fit the experimental data using complex non-linear least-squares (CNLS) which is a part of the Z-view© software. The CNLS procedure may deduce a complex equivalent circuit even though only one arc is seen; in such cases the number of arc should be estimated before modelling. The other main problem of modelling is that the same experimental data

maybe represented using different equivalent circuits. The choice of the equivalent circuit is based on which circuit can be explained in terms of the likely experimental conditions. Other errors in impedance modelling are associated with experimental errors in the data. This represents the greatest challenge in model identification and hence the utmost test of analysing impedance data. The challenge is tackled by using knowledge of the physical and chemical properties of the system and CNLS approximations. Macdonald, 1987, recommends that if a modelling element has more than 30% relative error, then this modelling element should be removed from the model.

Modelling should be carried out starting with the smallest number of equivalent circuit elements, then additional element can be added to decrease in the sum of squares; the decrease should be statistically significant. Apart from statistical test, it has been suggested that the bode phase angle plot is sensitive to the time constants. If the difference between the modelled data and experimental data is not random, then more circuit elements should be added.

General Chemistry of the system

The electrolyte material is not a single crystal but a rather a pellet made by compression followed by sintering, which gave a maximum of 94% of the theoretical density. This means that if conduction by ions occurs, one expects three arcs provided that their time constants are in the measurable range (greater than 10^{-7} s). These arcs would be attributed to conduction in the bulk of the material, conduction/blocking by the grain boundary and if the electrodes are insert, blocking of the ions by electrodes which should be an ionic insulation material.

The electrode materials used were gold, platinum and graphite plates; gold showed a reaction with the electrolyte which led to an easily observable colour change. Platinum showed unstable arcs in that experimental data was not repeatable. Carbon plates gave repeatable experimental data. The use of carbon plates which are mechanically pressed to the pellet leads to phenomena which has been coined as spreading resistance effect, Hwang, 1997. This effect is identified if the related impedance arc changes with the mechanical pressure, or if the activation energy of the resistance of the bulk and electrode arcs similar; activation energy is determined by plotting $\log(1/R)$ vs $1/T$.

Practical Guidelines for E.I.S modelling

- Use the simplest equivalent circuit, however this circuit should model impedance at all frequencies, temperatures and partial pressure

- Use Bode plot of phase angle vs frequency for time constant evaluation. Also there should not be a uniform difference between the modelled and experimental results, if this occurs it is an indication that more circuit elements should be added, see Appendix C, where a single R-CPE gives a poor fit in both Nyquist plot and the Bode plot, *Sum-of squares of 32.67*. Since a good fit between the modelled and experimental data was not obtained with one R-CPE element, another R-C or R-CPE can be added, *Sum-of squares of 1.869*. Modelling using the Z-view© software gives two statistical parameters to judge the goodness of fit, namely Chi-square and Weighted sum of squares, where both numbers reduce in value as the goodness of fit is increased. However each modelling parameter needs a physical justification, and this limits the number of circuit elements that can be used.

The ratio of the weight sum of squares, the variance ratio, of the old to new model gives an indication if the new model is justified by using the Fisher table. A shortened table is given below.

Table 3.1 Variance ratio $\frac{\sum_{new model} weighted squares}{\sum_{old model} weighted squares}$ and the degrees of freedom v1 and v2 for old and new model respectively (Fisher table)

	V1	1	4	8	24	∞
V2						
6		5.99	4.53	4.15	3.84	3.67
8		5.32	3.84	3.44	3.12	2.93
10		5.99	3.48	3.07	2.74	2.54
20		4.96	2.87	2.45	2.08	1.84
30		4.35	2.69	2.27	1.89	1.62
40		4.17	2.61	2.18	1.79	1.51
60		4.08	2.53	2.10	1.70	1.39
∞		3.84	2.37	1.94	1.52	1.00

The degree of freedom for a model is the difference between the number of data-points used in the model and the number of circuit elements for the respective model. The degree of freedom used is approximately 60, therefore a change in models that gives a variance ratio greater than 1.39 is statistically correct. Considering the examples of Appendix C, the variance ratio changed from 17.48 when going from a 1-R//CPE model to a 1-R//CPE &

1R//C-1R//CPE; 4.019 when going from 1R//C-1R//CPE to 2R//CPE model, therefore both modelling changes are justified statistically.

- It is not recommended to use CPE for modelling impedance arc in the lower frequency range, because it is most used to model materials with distributed parameters. The high frequency arc is equivalent to that of a single crystal (that is the true bulk impedance) and is hence not a distributed physical property. Therefore even though the variance ratio is greater than 1.39, the physical explanation is not clear.

3.5 Four-Point DC resistivity measurement

Nyquist plot of real versus imaginary component of impedance may yield multiple arcs, and hence modelling using equivalent circuit is done to obtain the intercept of value of the real components. This intercept, determined by equivalent circuit modelling, at lowest frequency corresponds to the DC conductivity of the material. Different equivalent circuit models may give different values, hence four point DC resistivity measurements allows for an independent measurement of this value which will also aid in selecting the most appropriate equivalent circuit.

Two cells were designed, one for room temperature resistivity measurement and a second for elevated temperature resistivity measurement ($<673\text{K}$) to be used with Danbridge 501 four point DC resistivity meter, Figure 3-32. The probe has four BNC connectors located in the first insulating plate. Four pins in the second plate are located in an insulating plate made of machine-able ceramic while the third plate moves the sample towards and away from the pins in the second plate through a screw mechanism. All three plates are bolted to the aluminium supporting plate. The schematics of the pins contacting pellet is given in Figure 3-33.

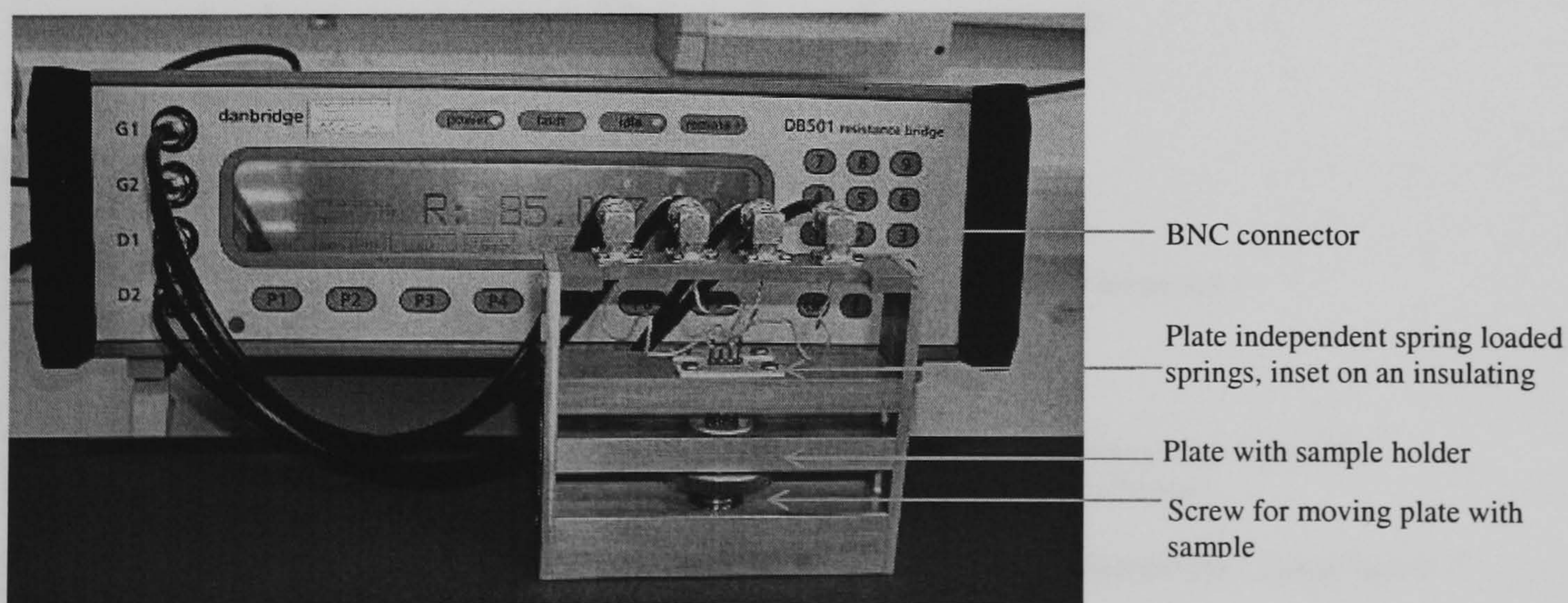


Figure 3-32 Actual equipment set up for 4-point DC resistivity measurement at low temperatures

Figure 3-34. High temperature 4-point DC resistivity measurement setup

The measurement follows the procedure below:

- a. Inserting reference sample into the measurement cell
- b. Contacting reference pellet to four pins,
- c. Performing zero check using a reference sample
- d. Removing reference sample then inserting sulphide sample
- e. Elevating sample until all four pins have made contact with sample
- f. Recording resistance
- g. Measuring thickness and diameter of sample

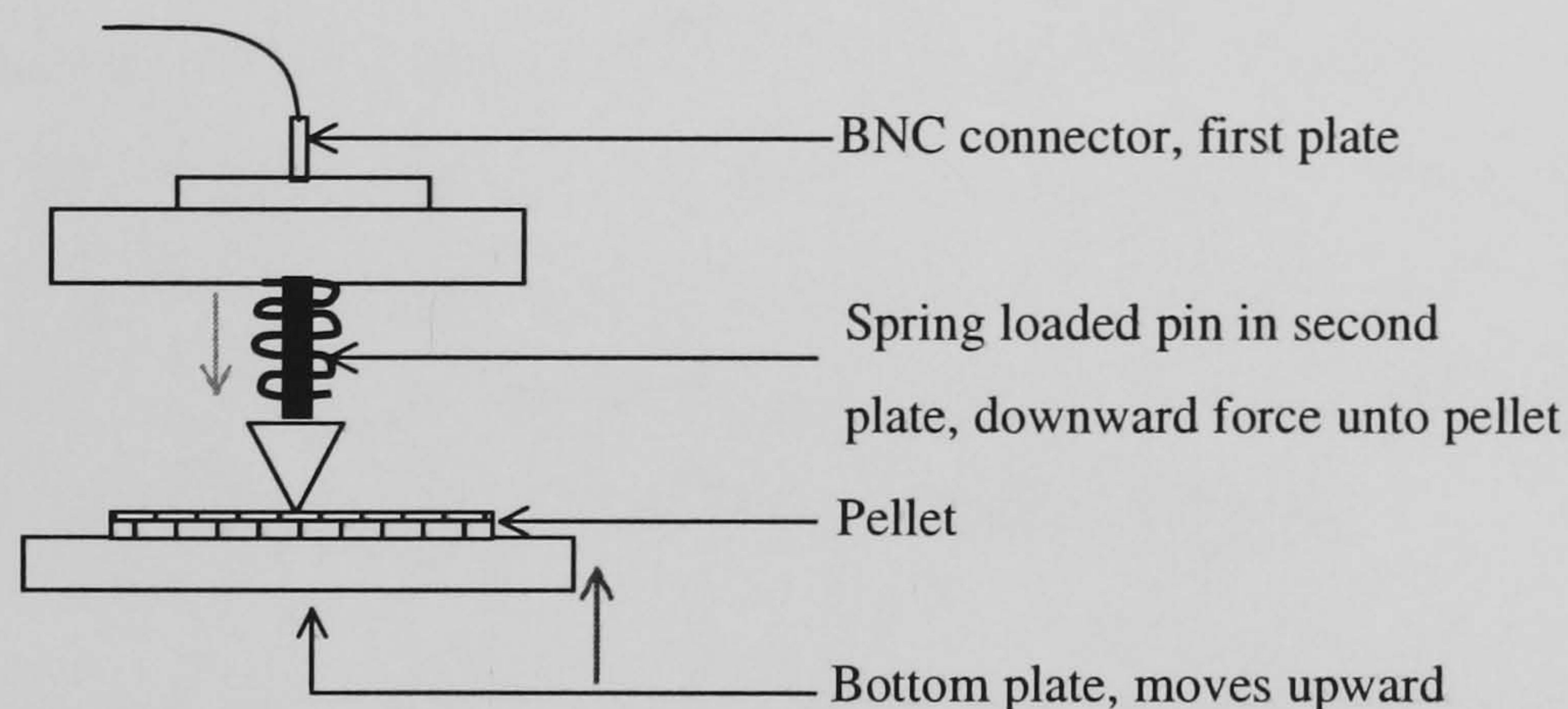


Figure 3-33 Schematics of spring loaded pin

2. The measurement for high temperature resistivity follows the procedure below:
 - a. Inserting reference sample into the measurement cell, Figure 3-34
 - b. Contacting sample to pins
 - c. Inserting measurement cell in to oven,
 - d. Isothermal period until target temperature (less than 200°C) is achieved
 - e. Performing zero check using a reference sample
 - f. Inserting sulphide sample
 - g. Elevating sample until all four pins have made contact with pellet
 - h. Isothermal period, 20mins, Recording resistance
 - i. Measuring thickness and diameter of sample

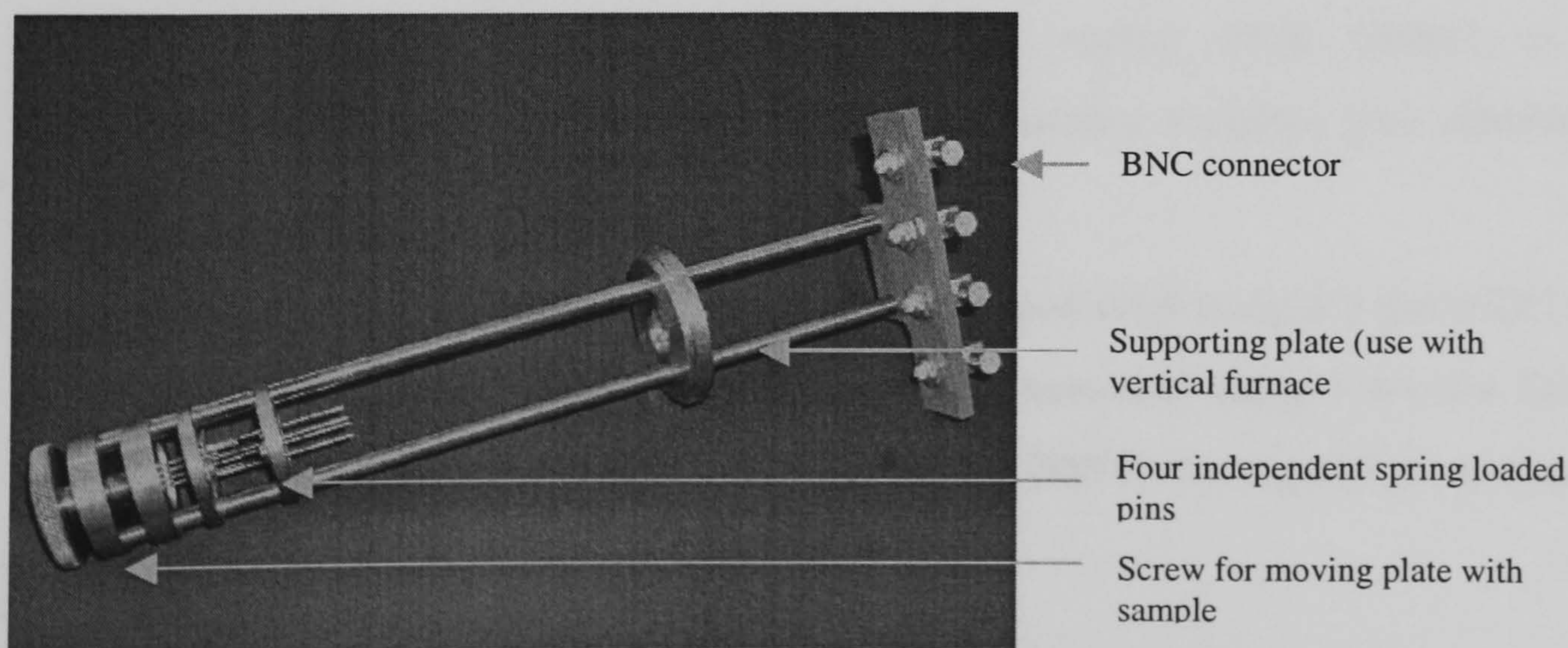


Figure 3-34. High temperature 4-point DC resistivity measuring cell

- The surface resistivity was measured at room temperature using apparatus in Figure 3-32 as well as elevated temperatures, using apparatus in Figure 3-34, not exceeding 150°C. The instrument, Danbridge DB 501 High Speed DC Resistance Bridge, was operated in two modes, namely trig and continuous mode.

The resistance bridge gave consistent, within 2 decimal places, and quick reading for copper sulphide pellet, with a resistivity not greater than 3.545mΩ. For Yttria stabilised Zirconia, which is a known oxide ion conductor, the measurements fluctuated by several orders of magnitude. This suggests that the resistance bridge for measuring ohmic resistance may have significant deviations in the absolute value. The variation of the 4-point dc measurements is shown in Figure 3-35. However, it might become a qualitative indicator of differentiating pure electronic conductors versus ionic conductors; because electronic conductors give consistent results, while a known oxide ion conductor gave unstable results.

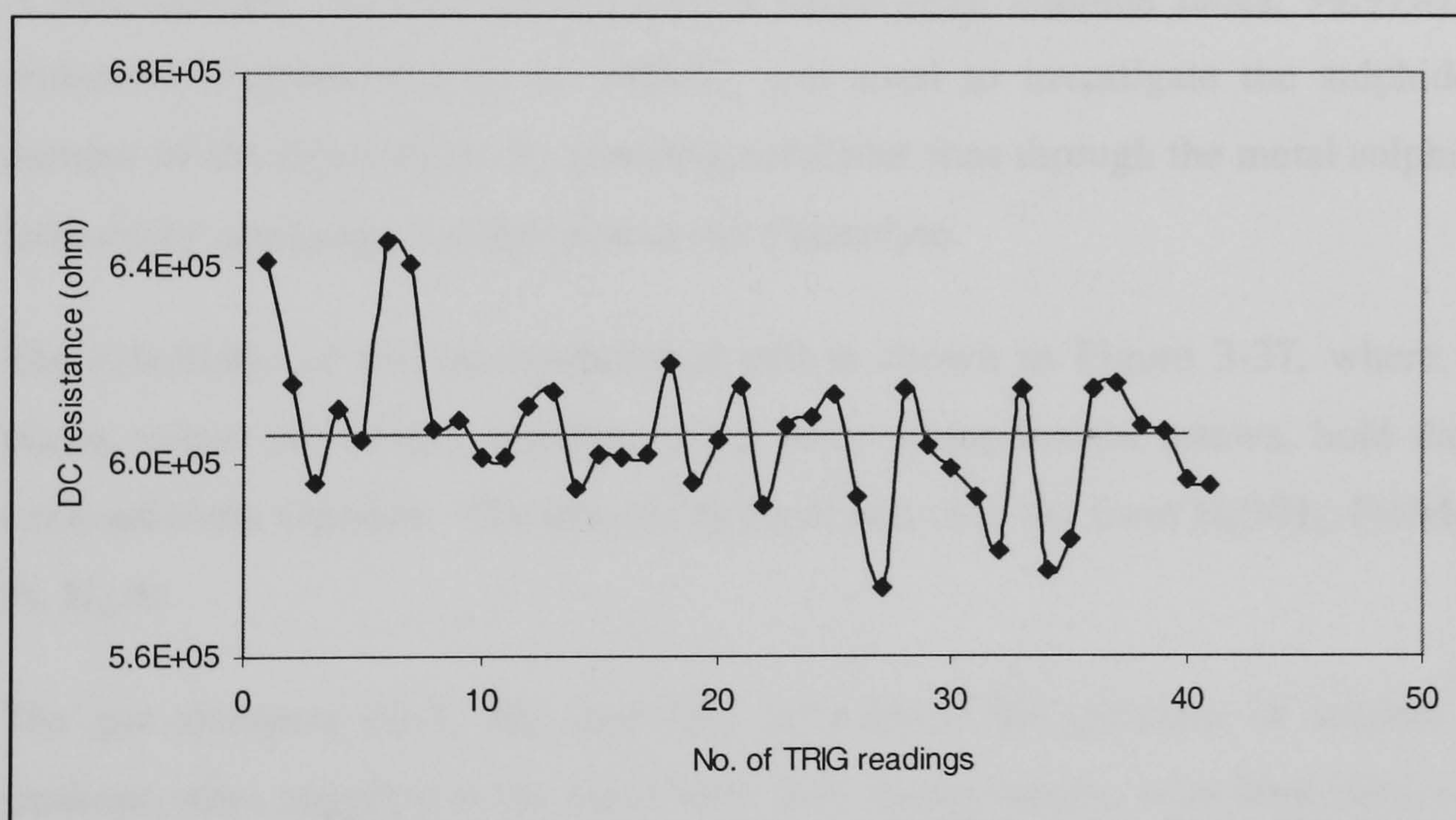


Figure 3-35. Variation in 4-point DC using manual mode for $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$

Figure 3-35. shows the DC resistivity values varied from 580kΩ to 640kΩ. for $\text{CaNd}_2\text{S}_4+30\text{mol}\%\text{Nd}_2\text{S}_3$ at room temperature. A similar variance was observed with the oxide ion conductor YSZ.

The resistance remained greater than 200MΩ when measured using a 2-point DC multi-metre at elevated temperatures. However the resistance measured using a 4-point DC resistivity bridge gave very high resistivity, until 150°C but at 200°C, the 4-point dc method showed a significant reduction in resistivity, Figure 3-36.

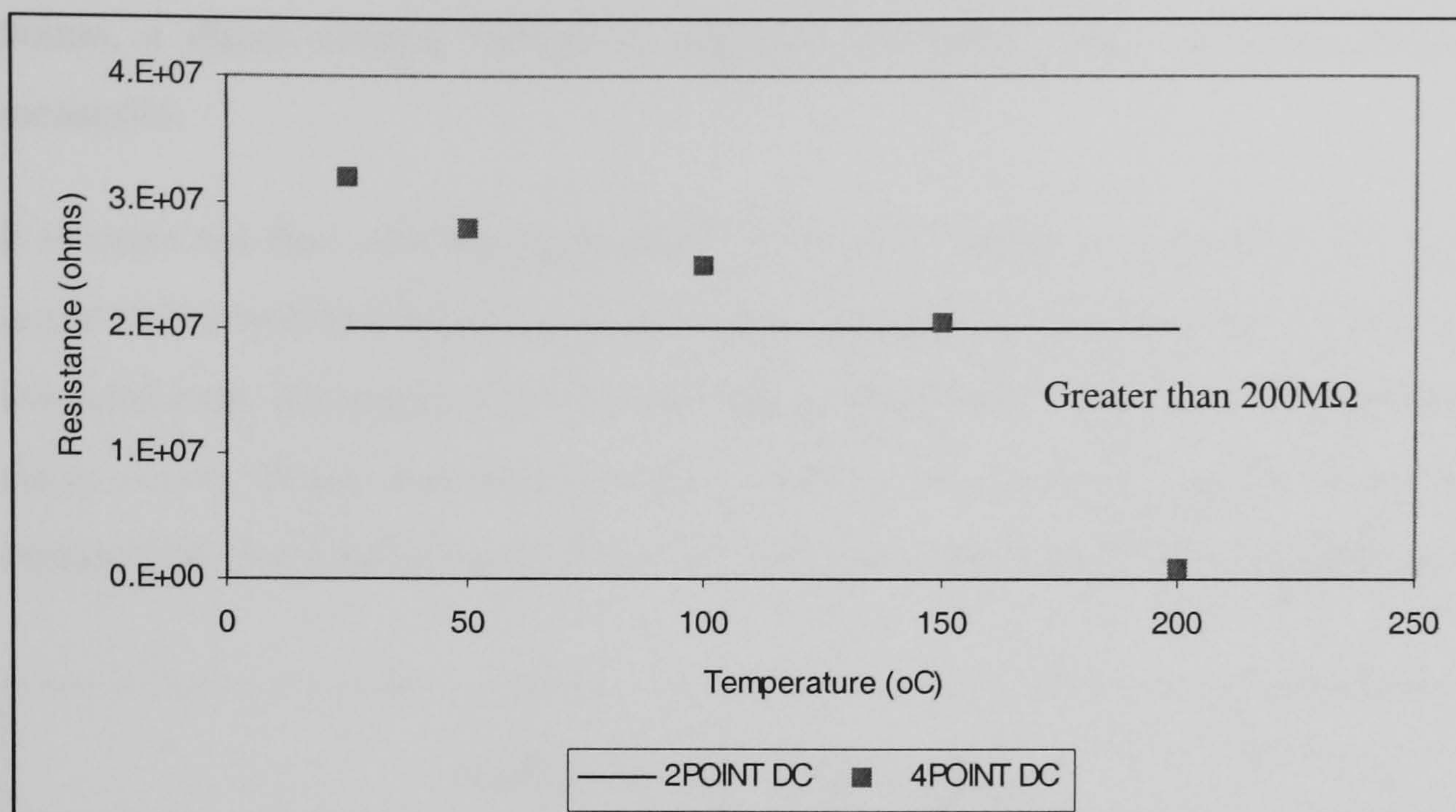


Figure 3-36. DC Resistivity, 4 & 2 point, for $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$

3.6 Reactor for Galvanic cell or Electrochemical Measurements

A two-chamber electrochemical reactor made from alumina tubes, 99.97wt%, which can withstand temperatures up to 1800°C, was used to investigate the sulphide transference number of the electrolytes, by pumping sulphides ions through the metal sulphide electrolyte, induced by applying a voltage across the electrolyte.

The schematic of the electrochemical cell is shown in Figure 3-37, where stainless steel plates, which are bolted, together using three spring-loaded screws, hold the two ceramic compartments together. The electrochemical cell is of the form $\text{H}_2\text{S}/\text{H}_2$, Pt//Metal Sulphide//Pt, H_2 , Ar

The gas mixtures (H_2S , H_2) and (H_2 , Ar), hence the presence of sulphur concentration gradient, were supplied at the same flow rate. Temperatures were kept isothermal for 30min before application of the DC voltages.

The solid electrolyte was prepared by methods discussed in the pellet sintering section and the platinum electrode was prepared as documented in the section presented in the impedance spectroscopy section. Platinum electrodes were used rather than gold since platinum catalyses the reaction (1).



The electrochemical cell consists of hydrogen sulphide concentration on half of the cell and hydrogen (zero partial pressure of H_2S) on the adjacent side thus creating a concentration gradient, Figure 3-39 and Figure 3-39. At elevated temperatures, 450-800°C – three data

points, a direct current voltage is applied (maximum 10V), and the response current is measured.

It is expected that with the application of the DC voltage, a corresponding current flow will occur on the half-cell with H_2S according to equation (1). If the electrolyte is a pure sulphide ion conductor, no current flow is expected on the H_2 half-cell, i.e. is the current should have a decay curve. If the electrolyte conducts positive ions as well, suggesting mixed conductor, a current flow would also occur when DC voltage is applied to the H_2 containing half-cell.

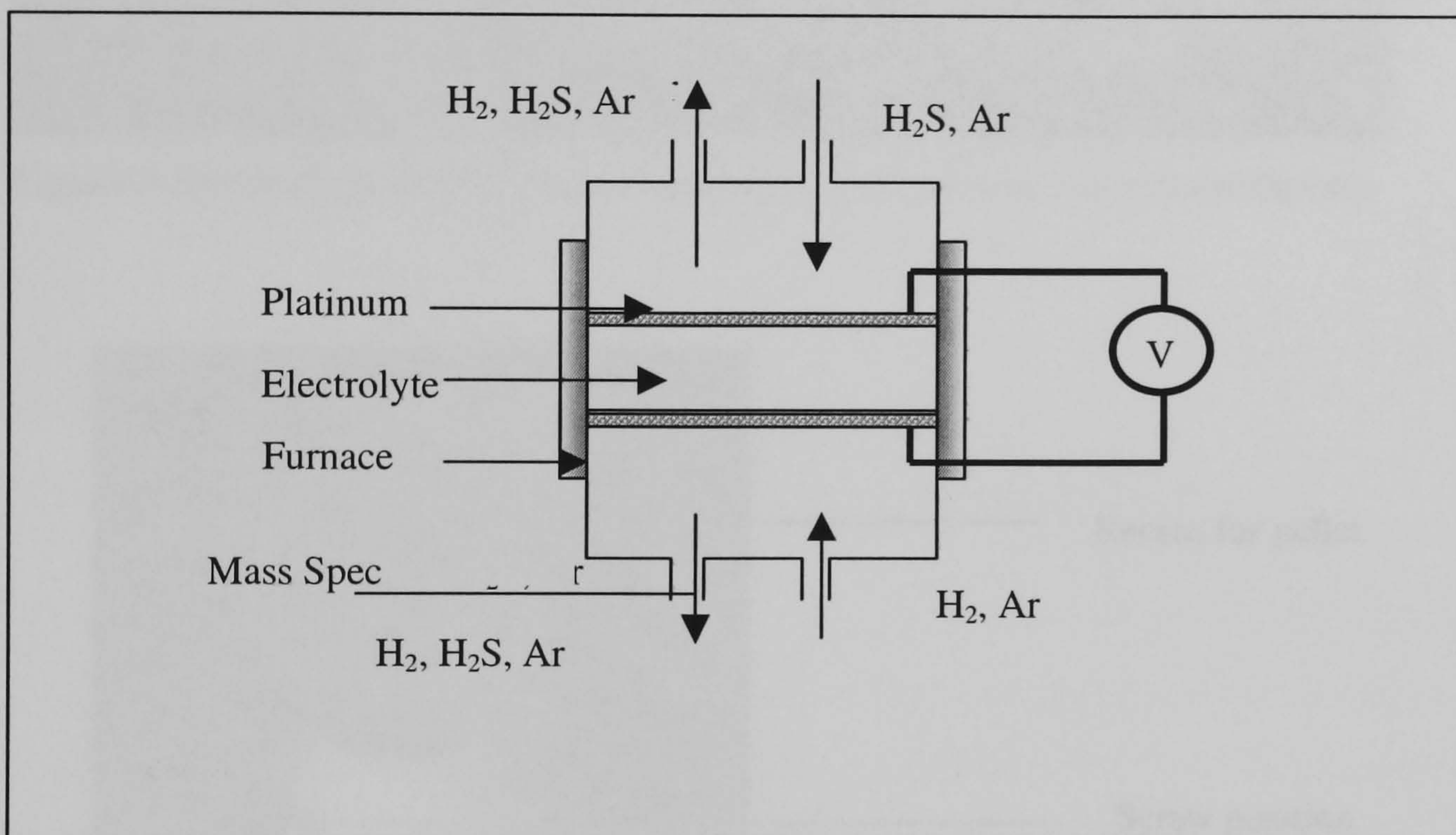


Figure 3-37. Sketch of reactor cell used for pumping sulphide ions

The measurement follows the procedure below:

- Insert pellet in the recess, Figure 3-39; this will be membrane that separates the two gaseous atmospheres, one hydrogen and the other hydrogen sulphide in hydrogen, and seal using high temperature cement.
- Insert ceramic tubes into the high temperature stainless steel which when tightened using spring loaded screw will aid the sealing of the compartments, , Figure 3-38
- Using same total flow rate of gases on either side of the reactor, measure the response current at 450, 550, 650, or 750°C, controlled with a Eurotherm 2416 temperature controller, to 1°C accuracy, when applied 0.1-5V (DC)
- At maximum temperature and highest DC applied volts, (maximum pumping rate), the exhaust gas, monitored for H_2S using a quadruple mass spectrometer. If sulphide ions are pumped through the membrane with application of a DC voltage, then an

increase in H_2S is expected (provided the change is significant and within the measurement range of the Mass spectrometer).

- Under no applied voltage, measure the open circuit voltage, OCV.

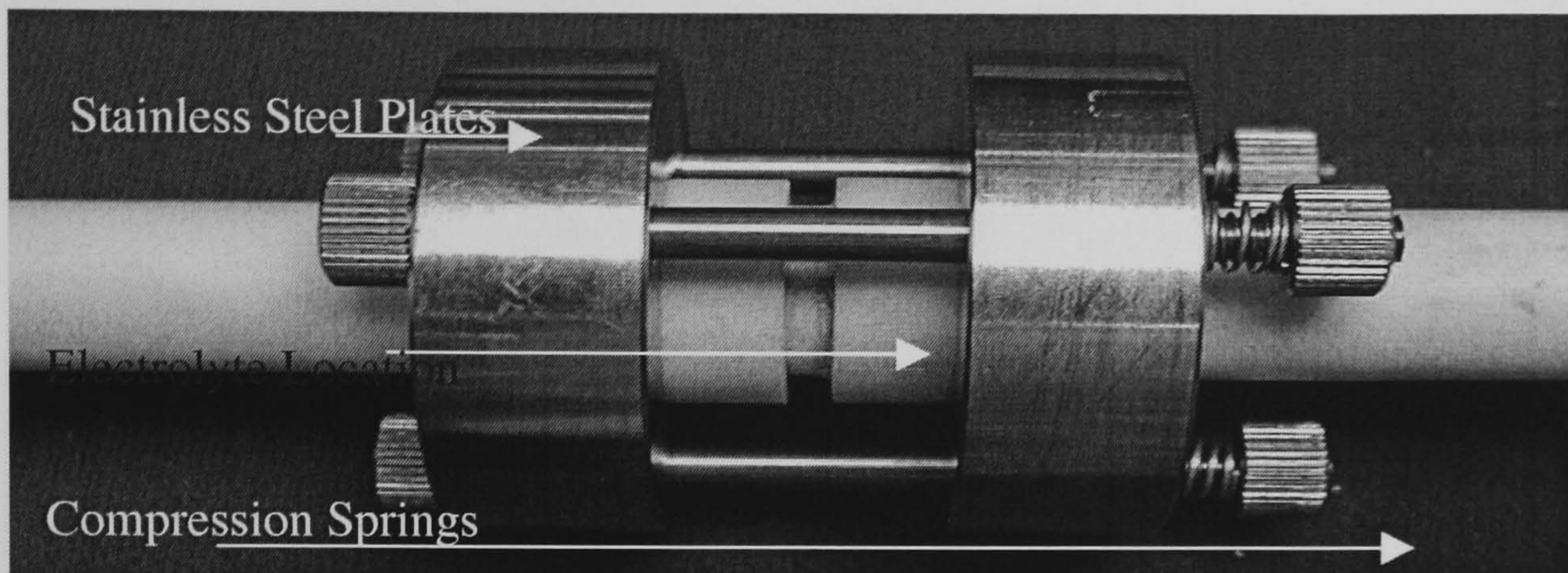


Figure 3-38. Reactor for two phase impedance and Galvanic cell measurements

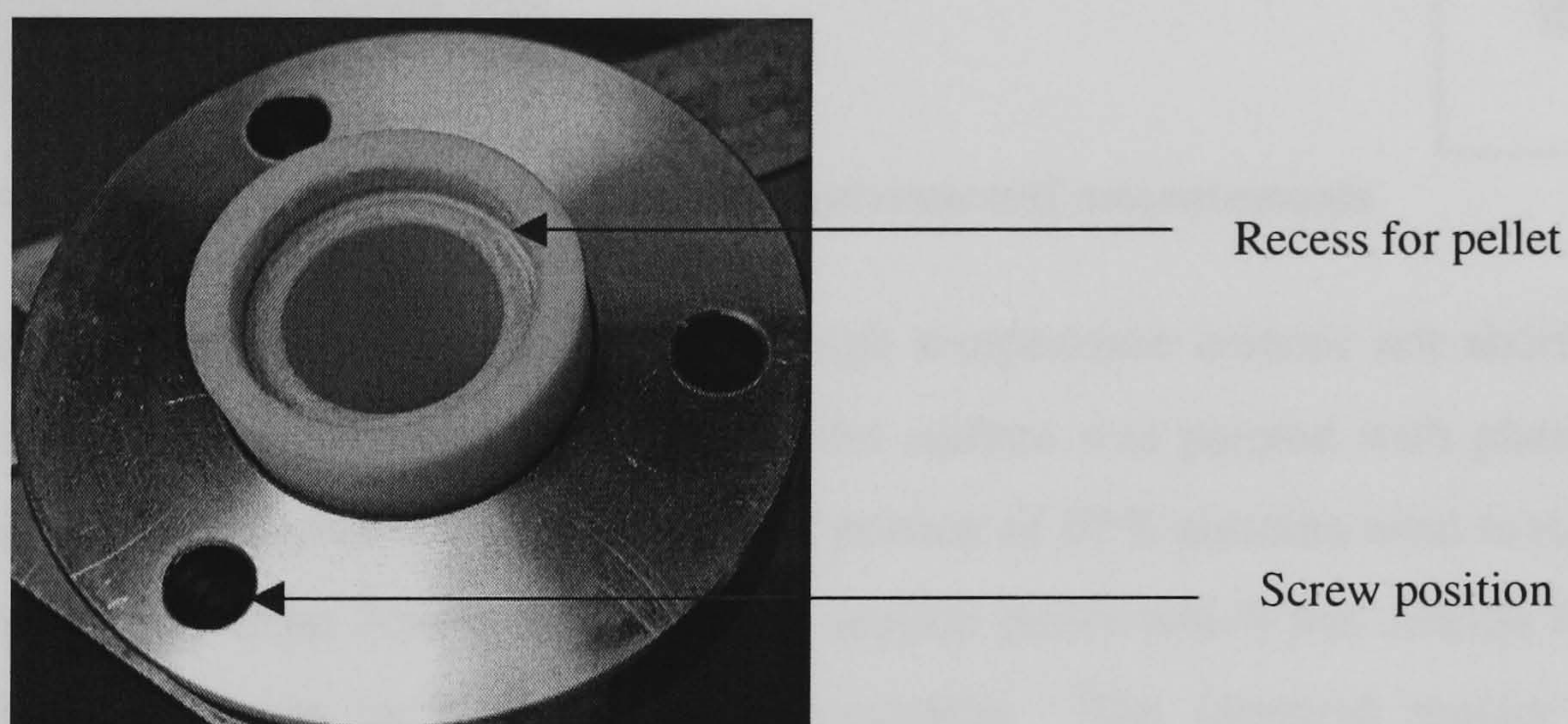


Figure 3-39. Internals of two electrochemical phase reactor

The reactor is clamped together using three screws. Gas will enter using 1/16'' swage-lock fittings to be added to the open end of both tubes. Over tightening one of the screws caused the pellet to crack. This limitation lead to the design of an electrochemical cell that has limited weight exerted onto the pellet.

The modified cell used only high temperature cement as sealant, while the compartment were made either of 67% alumina, 99.7% alumina or quartz. Gas tight compartments was not formed when high purity alumina, 99.7%, Al_2O_3 , was used, hence this material was discontinued. Figure 3-40 and Figure 3-41 shows slight variations in design of the electrochemical cell used.

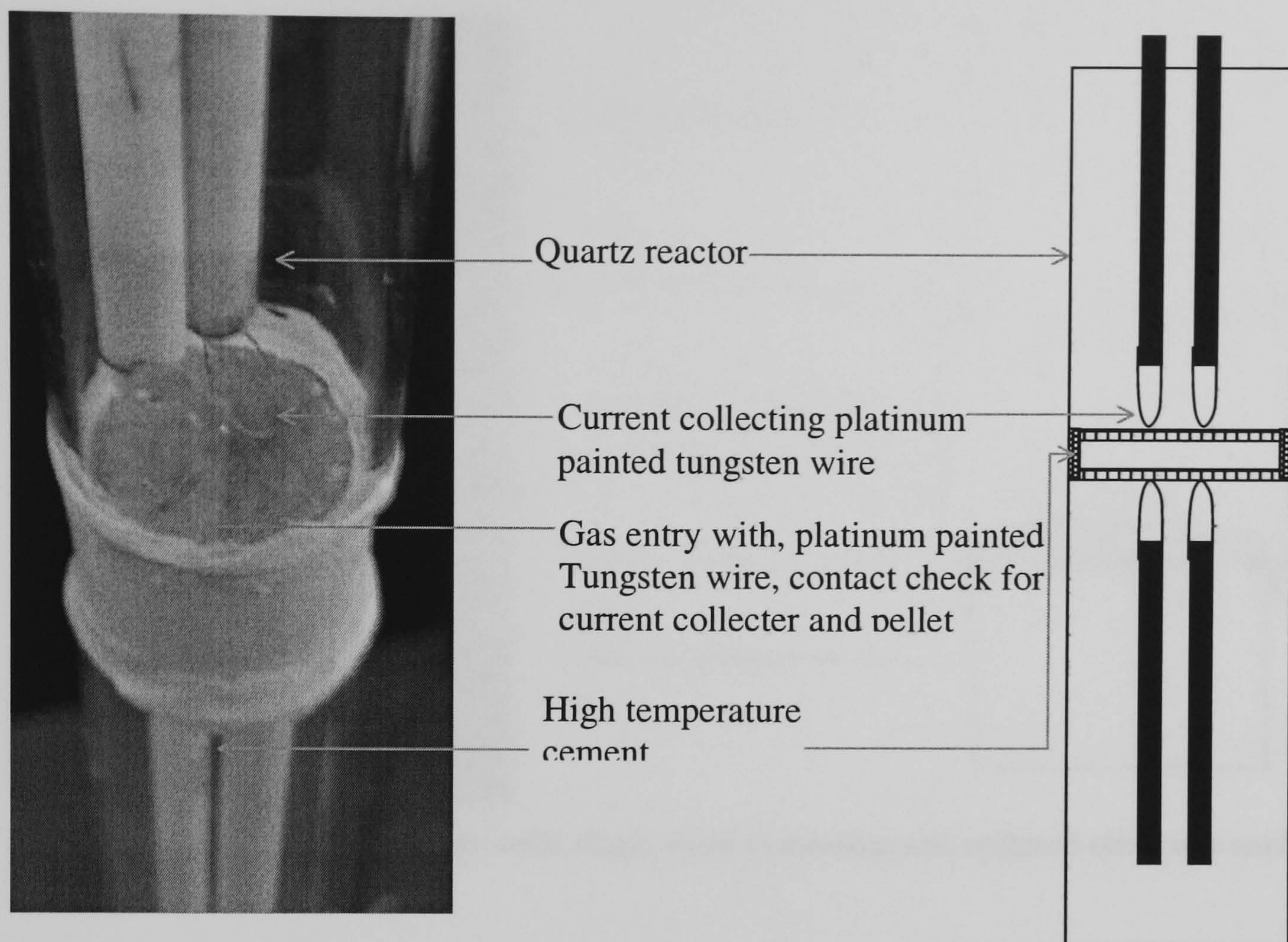


Figure 3-40. Quartz two phase reactor for galvanic cell measurements

This set-up, Figure 3-40, relies on the high temperature cement not shorting circuiting at elevated temperatures since the entire pellet surface was painted with platinum, which was contacting high temperature cement. The portion of 67% alumina used to reduced the inside diameter, i.d., from 20mm to 18.5mm to support pellet which has outside diameter, o.d., of 18.7mm to 19mm, is assumed to be insulation. The identical reactor was also made completely of 66% alumina, as shown in Figure 3-40, and the only change in operation was the contact between platinum electrode and tungsten (Pt painted) was established my continuity measurement using a 2point DC multi-meter.

The second version of the two phase reactor was made either from 66% alumina or quartz tubes with reduced electrode area so that the high temperature sealant does not short circuit the system at high temperatures, Figure 3-40. Also the pellet is sealed on one side only, this was achieved by using a cap or recess design similar to Figure 3-40. The reactor and schematic is represented in Figure 3-40.

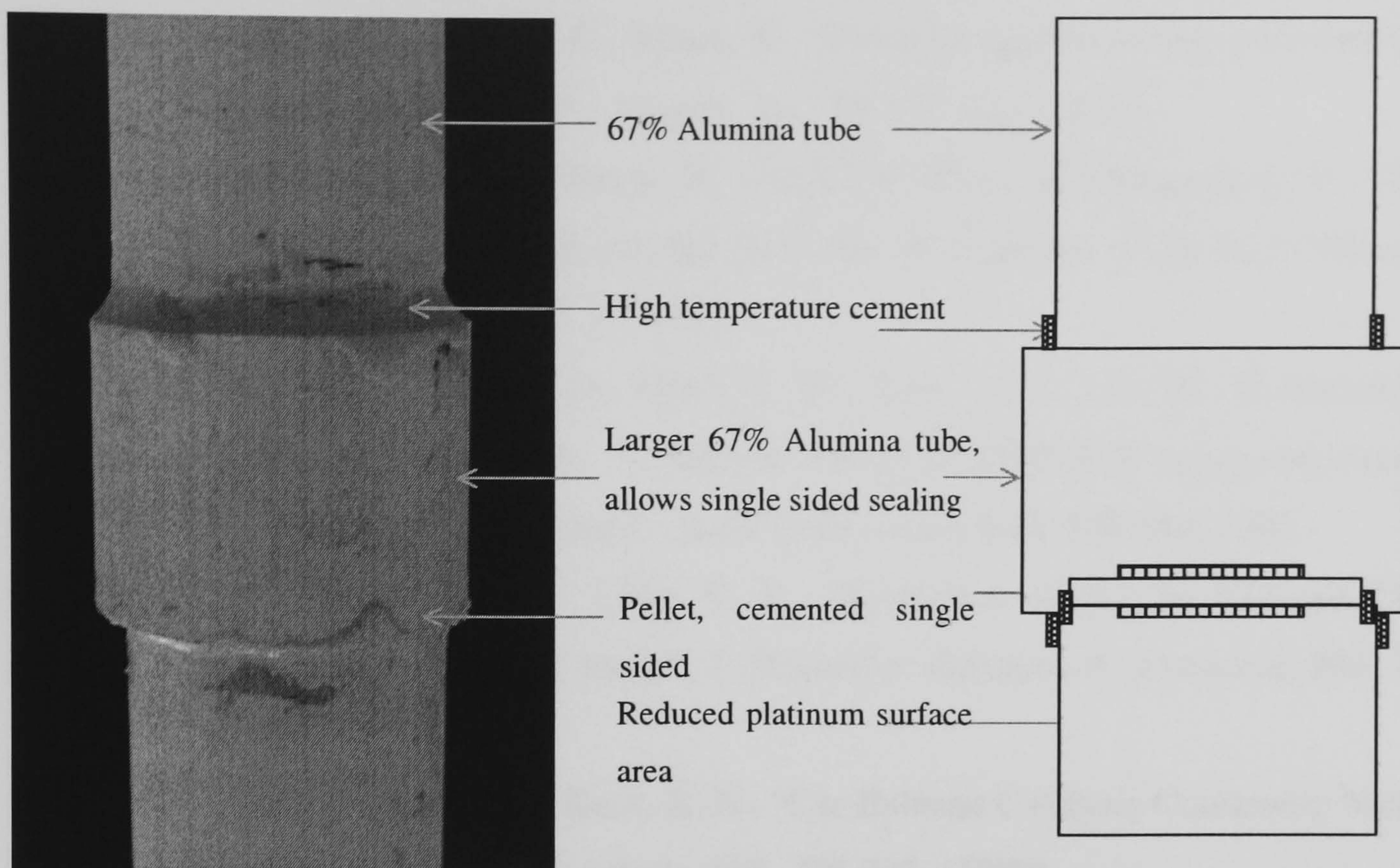


Figure 3-41. Electrochemical cell with single sided cementing and reduced electrode surface area

3.7 Experimental References

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Chapter 4

4 Characterisation and electrochemical application of CaNd_2S_4 and SrNd_2S_4 doped with Nd_2S_3

The ionic conductor calcium neodymium sulphide doped with excess neodymium sulphide has previously been synthesised and characterised by Kalinina *et. al.*, 1995. Two galvanic cells operating by using an instant touch method described by equations (1) and (2) were used to differentiate cation conduction from anion conduction; equation (1) describes the galvanic cell, which is reversible to the calcium ion conduction, and equation (2) describes the galvanic cell, which is reversible to sulphide ion conduction.



Based on the measured electromotive force, e.m.f, in the temperature range of 400-500°C the anionic transport number, defined, as the ratio of anion conduction to total conduction, was determined. These galvanic cells identified the electrolytes to be predominantly sulphide ion conductors at these temperatures with the remainder of the conduction attributed to calcium ions, with no mention of electronic conduction. With increasing temperature the anionic transport number (sulphide ion conduction) increased while the reverse is true for the cationic transport number (calcium ion conduction), see Table 4.1.

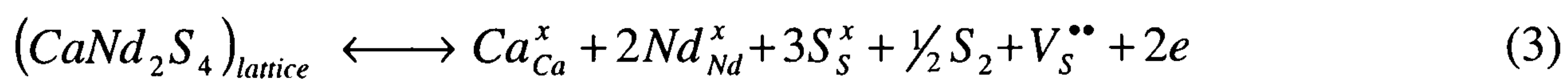
The instant touch method does not measure the steady state response of a system, and as such the technique has an inherent vulnerability. Considering equation (1), the cell that is reversible to calcium ions, mobile calcium ions needs to be activated from calcium, enter the $\text{AB}_2\text{S}_4\text{-xB}_2\text{S}_3$ unit cell, conduct through and then enter AB_2S_4 . This progression path includes many steps beyond calcium ion conduction through the electrolyte being tested. It requires formation of Ca^{2+} from Ca as well as mobility of this species across several interfaces. Therefore if any of these steps were inherently slow, they could significantly influence the instantaneous measurement of S^{2-} and Ca^{2+} conduction.

Table 4.1. Transport numbers for calcium and sulphide ions in $\text{CaNd}_2\text{S}_4\text{+10mol\%Nd}_2\text{S}_3$, Kalinina *et. al.* 1995

Temperature (°C)	Transport numbers	
	Sulphide ion (± 0.02)	Calcium ion (± 0.02)
450	0.92	0.10
470	0.95	0.05
500	0.97	0.03

The high transport number for sulphide ion conduction was attributed to the presence of channels in the crystal structure. The channel size radius, which is required for sulphide ion conduction, is 0.911Å for a Th₃P₄ cubic lattice and apparently is satisfied in this crystal structure. However, the channel size, which is required for calcium ion in this cubic structure, is 0.493Å and this crystal structure does not meet this requirement. Does this mean that once the channel has the correct size the ion can therefore move in it? Probably not, because other parameters such as local electro-neutrality must be met and a sufficient number of vacancies must also be present.

Kalinina *et. al.* 1995 further describe these sulphides as having intrinsic defects, where charge neutrality is maintained. These defects are known to increase with temperature, which provides a possible explanation of the increase in S²⁻ transport number as the temperature is increased. The defect formation in these sulphides is described by equation 3 using Kröger-Vink notation:



Where Ca_{Ca}^x - calcium ion on a calcium lattice site

Nd_{Nd}^x - neodymium ion on a neodymium lattice site

S_S^x - sulphur ion on a sulphur lattice site

$V_S^{\bullet\bullet}$ - vacant sulphur lattice site

e - electron

The equilibrium equation (3) shifts to the right with an increase in temperature, hence sulphur loss to the atmosphere increases and the formation of sulphur vacancies, $V_S^{\bullet\bullet}$, which is responsible for sulphide ion transport, also increases. It should be noted that maintenance of electro-neutrality requires that for every sulphur vacancy formed an associated calcium vacancy, $V_{Ca}^{\bullet\bullet}$, must also be present, thereby increasing the calcium ion conduction with increasing temperature. Based on the work of Kalinina *et. al.*, 1995 this series appears to be a promising start in order to find sulphide ion conductors.

Varying the dopant concentration as well as the host cation has been done to optimise ionic conductivity for high temperature oxide ion conducting electrolytes such as cerium-based system. For example ceria doped with lanthana, gadolinia or ytterbia established that gadolinia was the best dopant cation and that maximum conductivity, Faber *et. al.*, 1989.

Earlier work by Worrel *et. al.* 1967 attempted to develop high temperature sulphide ion conducting electrolytes by using a calcium sulphide based compound, however the secondary sulphide used was Y_2S_3 rather than Nd_2S_3 . The resulting compound was not characterised for its crystal structure but electrochemical measurements made at sulphur partial pressures greater than 10^{-6} atmosphere showed that the resistance was a function of partial pressure which is an indication of electron-hole conduction. At lower sulphur partial pressures doping with Y_2S_3 leads to an increase in cation conduction. It should be noted that Kalinina *et. al.*, 1995 mentioned $\text{CaS-Y}_2\text{S}_3$ as a sulphide ion conductor.

A family of compounds was prepared, White 2005, by combining stoichiometric amounts of calcium sulphide (CaS) and neodymium sulphide (Nd_2S_3) with 10-30mol% excess Nd_2S_3 , by heating in an argon atmosphere up to 1200°C for 24hrs to form the compound $\text{CaNd}_2\text{S}_4+x\text{Nd}_2\text{S}_3$ according to a procedure established by Kalinina *et. al.* 1995. X-ray analysis for these compounds lead to the identification and crystal structure calculation using Rietveld analysis. $\text{CaNd}_2\text{S}_3+(0, 0.1, 0.2, 0.3)\text{Nd}_2\text{S}_3$ has a cubic unit cell, see Figure 4.1, White, 2004. Where black spheres represent Nd, smallest grey spheres represent Ca and larger grey spheres represent sulphur. The X-ray pattern shows that an increase in dopant level does not lead to great changes in the general XRD pattern; however slight shifts in the peak locations were noted, Figure 4.1, White, 2005

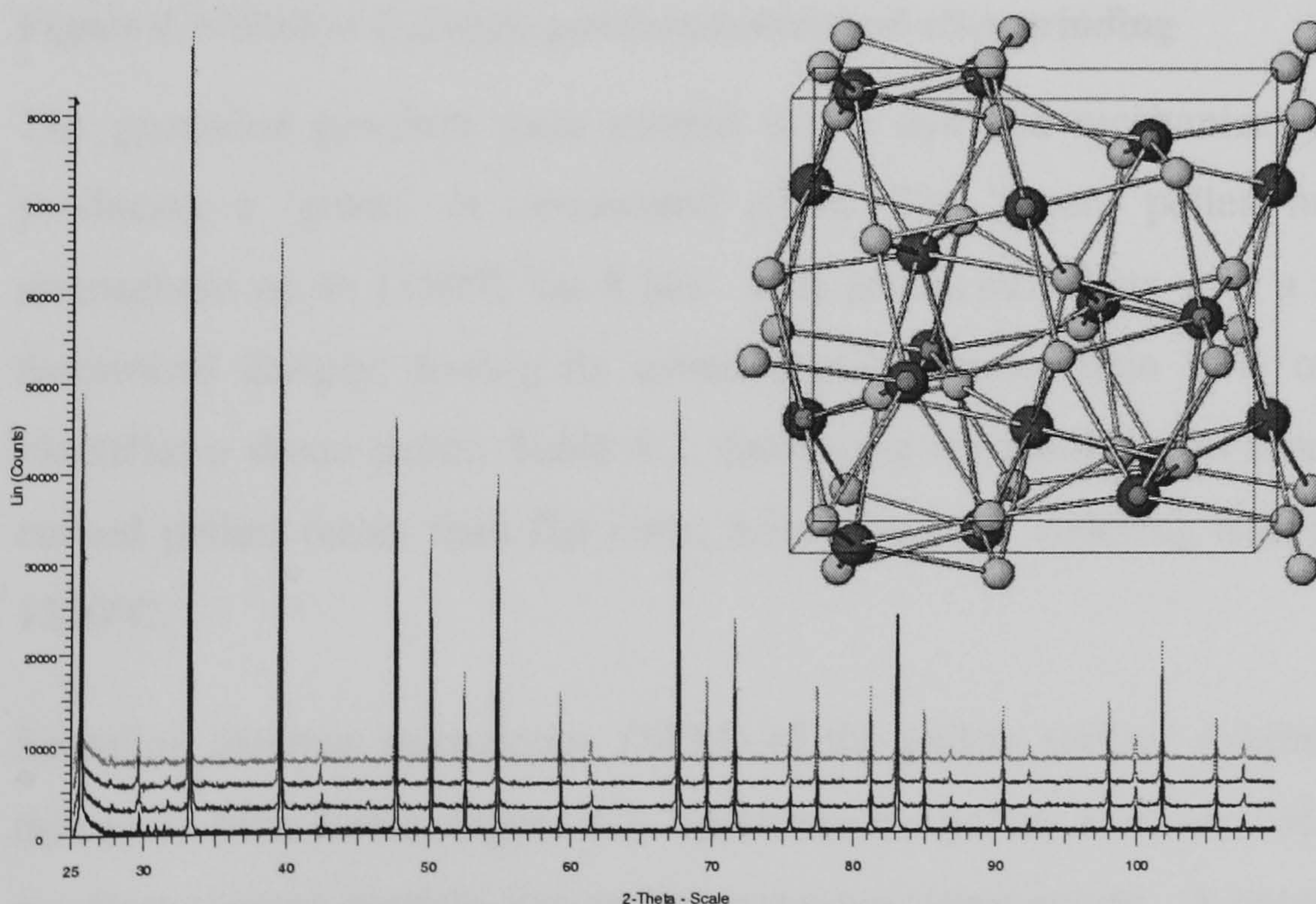


Figure 4-1. Unit Cell Structure and X-ray pattern of $\text{CaNd}_2\text{S}_3+0.0-0.3\text{Nd}_2\text{S}_3$, White, 2005

Pelletizing CaNd_2S_4 series

Successful synthesis of dense, crack free pellets is needed for impedance spectroscopy and electrochemical pumping experiments. Densification processing of sulphides requires that the starting materials should have a very small average diameter ($<10\mu\text{m}$) to achieve sintered pellet density greater than 80% of the theoretical density, Chess, 1983. The particle size distributions for CaNd_2S_4 series measured using a coulter counter (with acetone as dispersant) or scanning electron microscopy, SEM. The initial mean particle size of $90\mu\text{m}$ was reduced to less than $5\mu\text{m}$, Figure 4.2, after 3 days ball milling with zirconia balls.

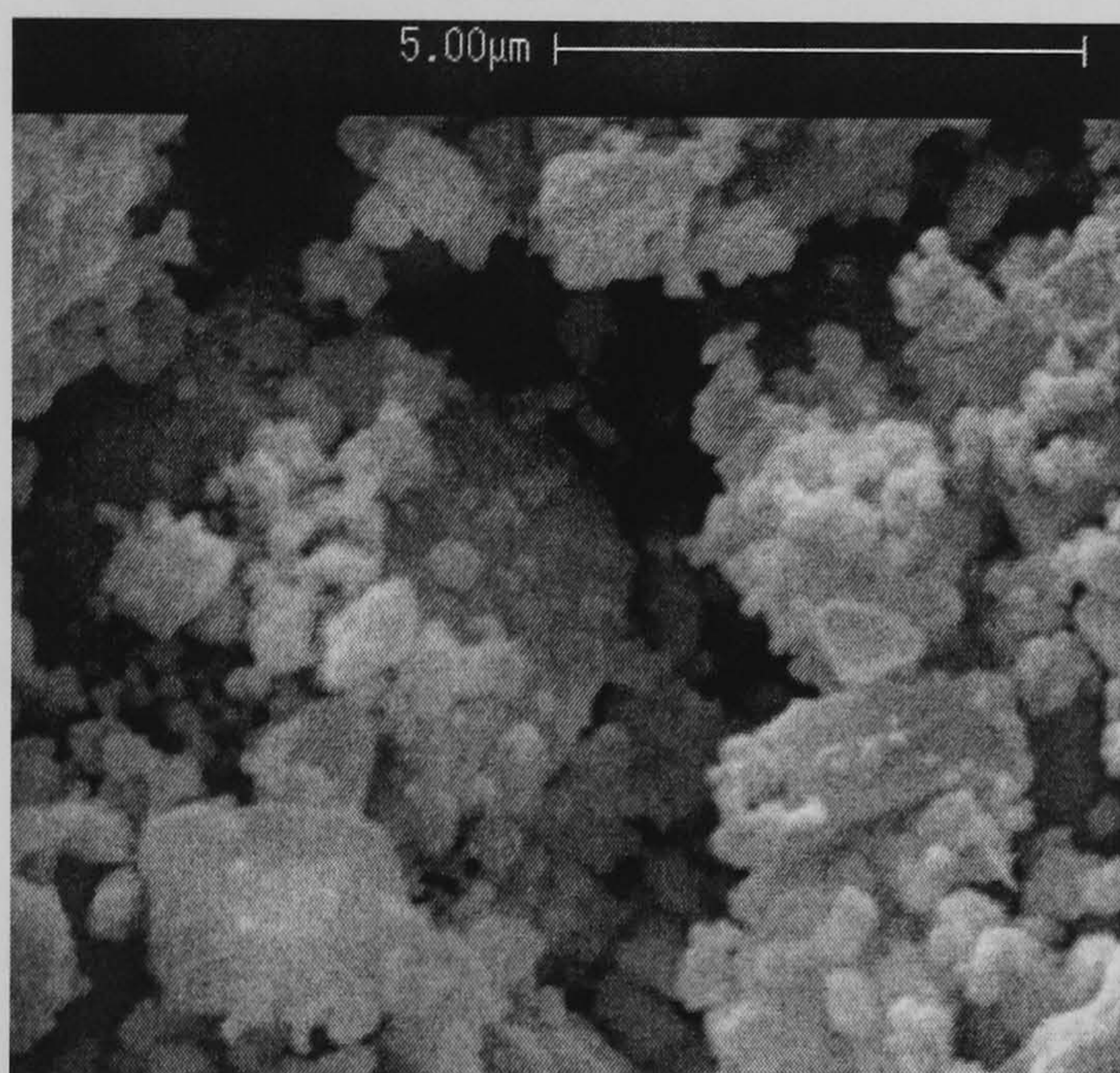


Figure 4-2 SEM of CaNd_2S_4 powders before and after grinding

The grounded powders were poured into a die and mechanically pressed up to 10 tons, producing a 'green' or un-sintered pellet. The 'green' pellet, heated in a 10 vol% H_2S atmosphere up to 1350°C for 8 hrs. This produced pellets with a maximum of 95% of the theoretical density; having its actual density greater than 95% of the theoretical density identifies a dense pellet, Table 4.2. Increasing temperatures to more than 1350°C produced curved pellets rather than flat ones; hence the final sintering temperature was chosen to be 1350°C .

Scanning electron microscopy (SEM) of the pellets surface exhibits $2\mu\text{m}$ pores with fairly thin grain boundaries, Figure 4-3. Therefore the pellets were not fully dense when made with smallest average particle size and at maximum temperature. A consequence of using a pellet that is not dense for impedance spectroscopy is the observation of Nyquist plots with the depressed arcs, that is, the centres of the arcs are likely to be below the real axis. The presence of depressed arcs is successfully modelled by constant phase elements (CPE).

An even more pronounced consequence of using a pellet which is not dense in characterising by electrochemical pumping, is the possibility of mixing of the gases in the separate chambers due to diffusion through the pores. Thus a symmetric current response could result with the application of anodic or cathodic potential. This could be misinterpreted as electronic conduction in the electrolyte rather than the bypassing of H_2S through the electrolyte.

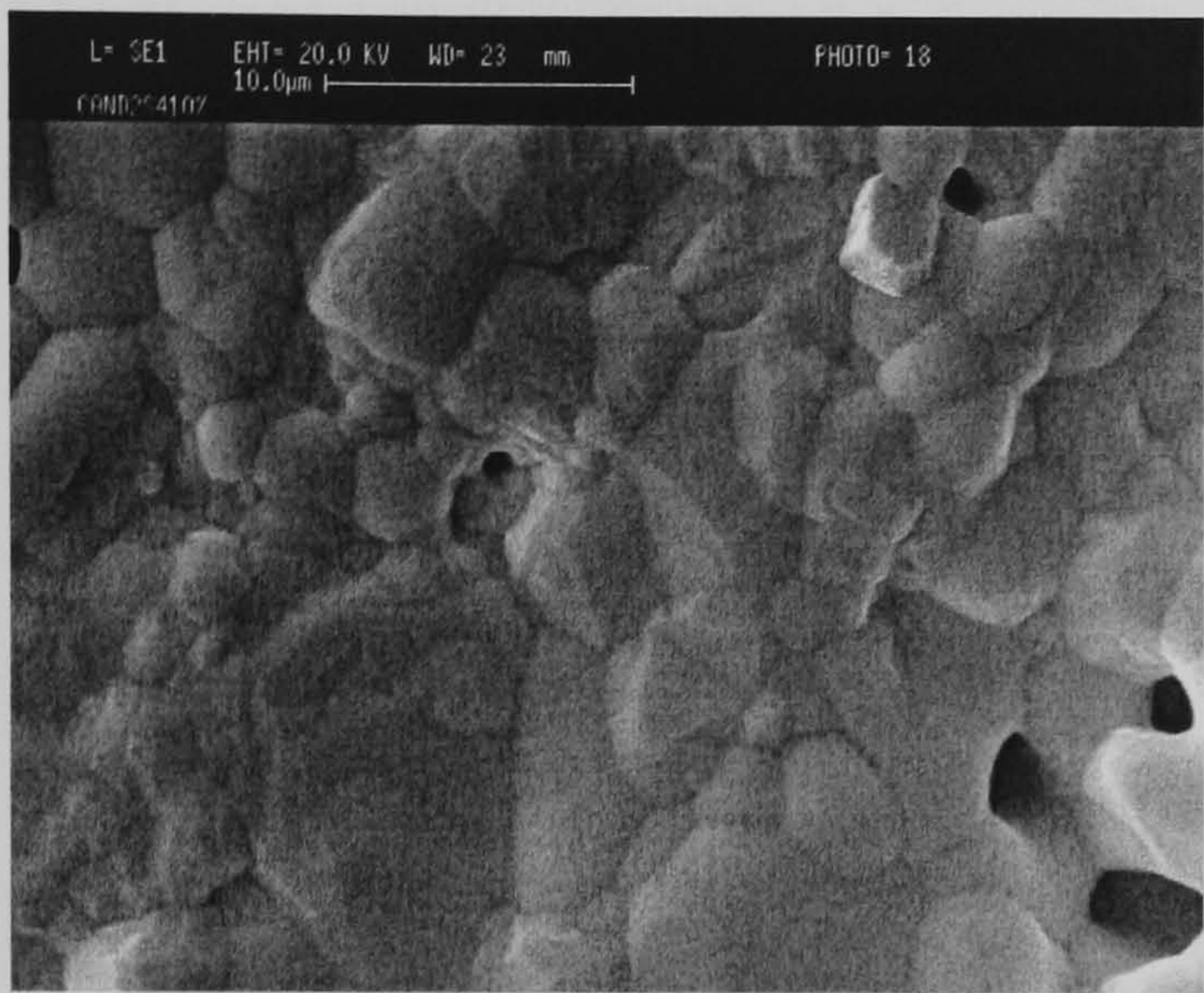


Figure 4-3. SEM CaNd_2S_4 sintered pellet made with pre-grounded powder

Table 4.2 Actual and theoretical densities for CaNd_2S_4 series

	Theoretical density (g/cm^3)	Actual density (g/cm^3)
Un-doped	4.888	4.646
10mol% doped	4.819	4.356
20mol% doped	4.76	4.524
30mol% doped	4.715	4.425

4.1 Temperature Programmed Oxidation and Reduction of CaNd_2S_4 series

The thermal stability of the prepared series $\text{CaNd}_2\text{S}_4+\text{xNd}_2\text{S}_3$ was established using temperature programmed oxidation (TPO) and temperature programmed reduction (TPR). The TPO trace of this series consists of one major peak with a shoulder to the higher temperature side, Figure 4-4, with the undoped compound showing a minor peak at 825°C . Because of its insignificant small area (less than 3% of the major peak) the small peak was ignored. The presence of one major peak indicates that only one type of sulphur reacts to form sulphur dioxide. Since neodymium sulphide was formed by direct combination of the metal with sulphur it is conceivable that non-stoichiometric sulphur could be present. Also the absence of post treatments such as regrinding and heating to remove any trace amounts of excess (non-stoichiometric) sulphur causes the solid state synthesis method to be vulnerable

to produce compounds with non-stoichiometric sulphur. However the presence of excess sulphur would be identified in TPO by the presence of a sulphur dioxide peak at low temperature (less than 300°C), but this was not observed. Hence the presence of a single phase was also supported in this series of compounds.

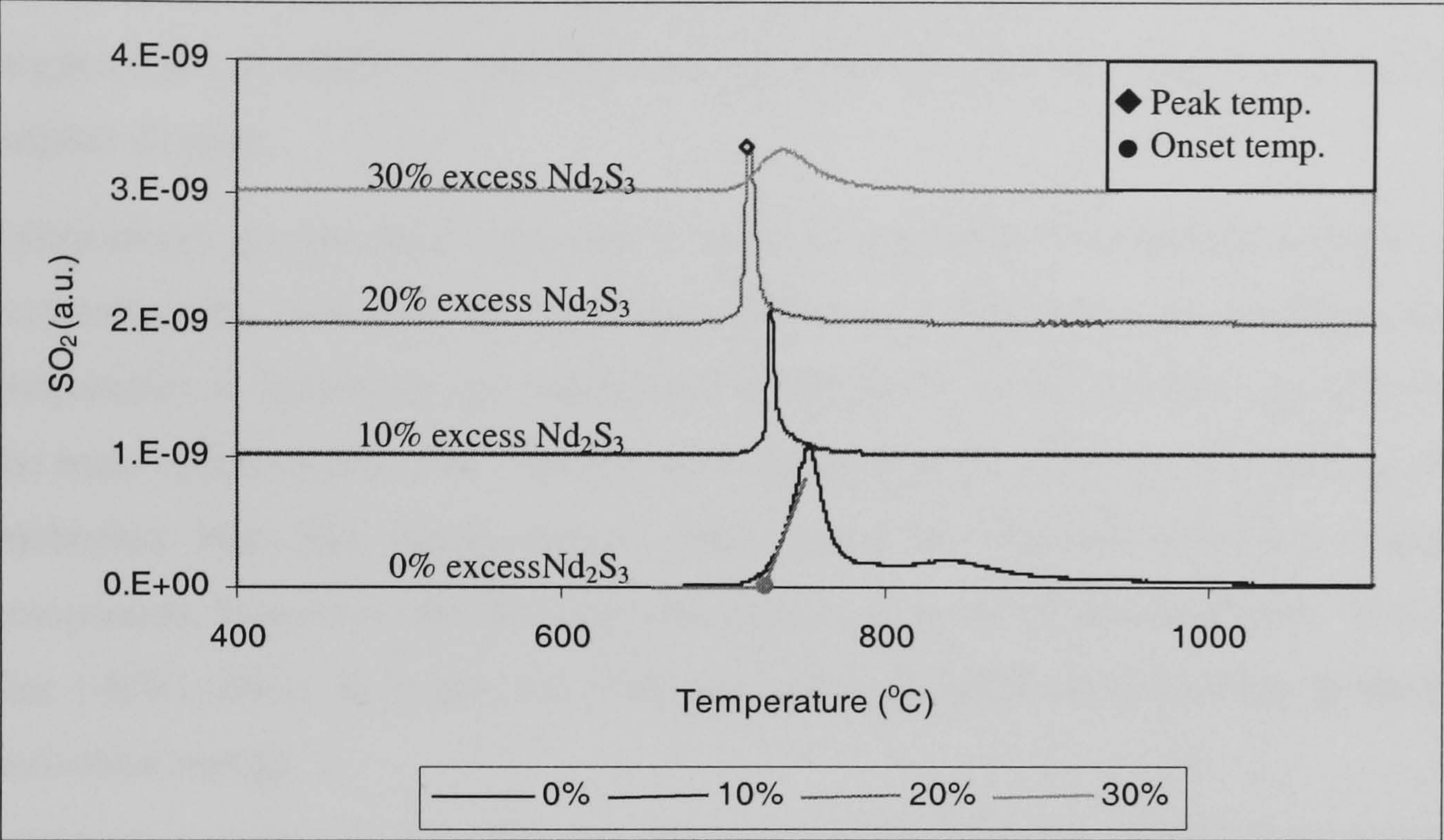


Figure 4-4 TPO of CaNd₂S₄-0.0-0.3Nd₂S₃ using a heating rate of 10°C/min

The sulphur dioxide peak for this family of compounds is located in the range of 671-723°C when a heating rate of 10°C/min is used, Figure 4.4. The onset temperatures, Table 4.3, for the oxidation of these compounds are fairly similar with approximately 60°C increase in temperature at 10mol% excess Nd₂S₃. Further increase in excess Nd₂S₃ caused the onset temperature to decrease. The absence of a second peak up to the maximum dopant concentration of 30mol% Nd₂S₃, indicates that a single phase compound was formed (in agreement with the X-ray pattern in Figure 4.1). This high solubility is unusual for sulphides since 1-16mol% is the typical range, Lowe-Ma *et. al.*, 1992.

Table 4.3. Oxidation onset and peak temperatures for CaNd₂S₄ series and lattice parameter

	Onset temp. (°C)	Peak temp. (°C)	Lattice parameter Å (a-site)
CaNd ₂ S ₄ +0.0Nd ₂ S ₃	671	754	8.5301(1)
CaNd ₂ S ₄ +0.1Nd ₂ S ₃	723	726	8.5399(1)
CaNd ₂ S ₄ +0.2Nd ₂ S ₃	708	715	8.5280(1)
CaNd ₂ S ₄ +0.3Nd ₂ S ₃	703	730	8.5273(1)

The volume of the unit crystal decreases as the dopant level is increased. Contraction of the unit cell, Table 4.2 (due to creation of cation and anion vacancies) is accompanied by an increase in onset temperatures, Table 4.3. The increased TPO onset temperature for all doped- CaNd_2S_4 relative to CaNd_2S_4 may be due to the general decrease in ionic distances of the crystal lattice. Reduced lattice distance may create stronger ionic bonds and hence the higher temperatures at which the sulphide ions leave the structure and reacts with oxygen forming sulphur dioxide.

Temperature programmed oxidation is used to determine the thermal activation energy of compounds by measuring the peak temperature as a function of the heating rate. The peak temperature is defined as the temperature at which the maximum SO_2 signal is measured by the mass spectrometer. The relationship between peak temperature and heating rate gives an Arrhenius plot, the corresponding slope gives the thermal activation energy for the compounds, Figure 4-5. The heating rates used were 5, 10, 20 and $40^\circ\text{C}/\text{min}$. The slope of the line ($-E/R$) where R is the universal gas constant (8314.4J/kg-mol-K), gives the thermal activation energy.

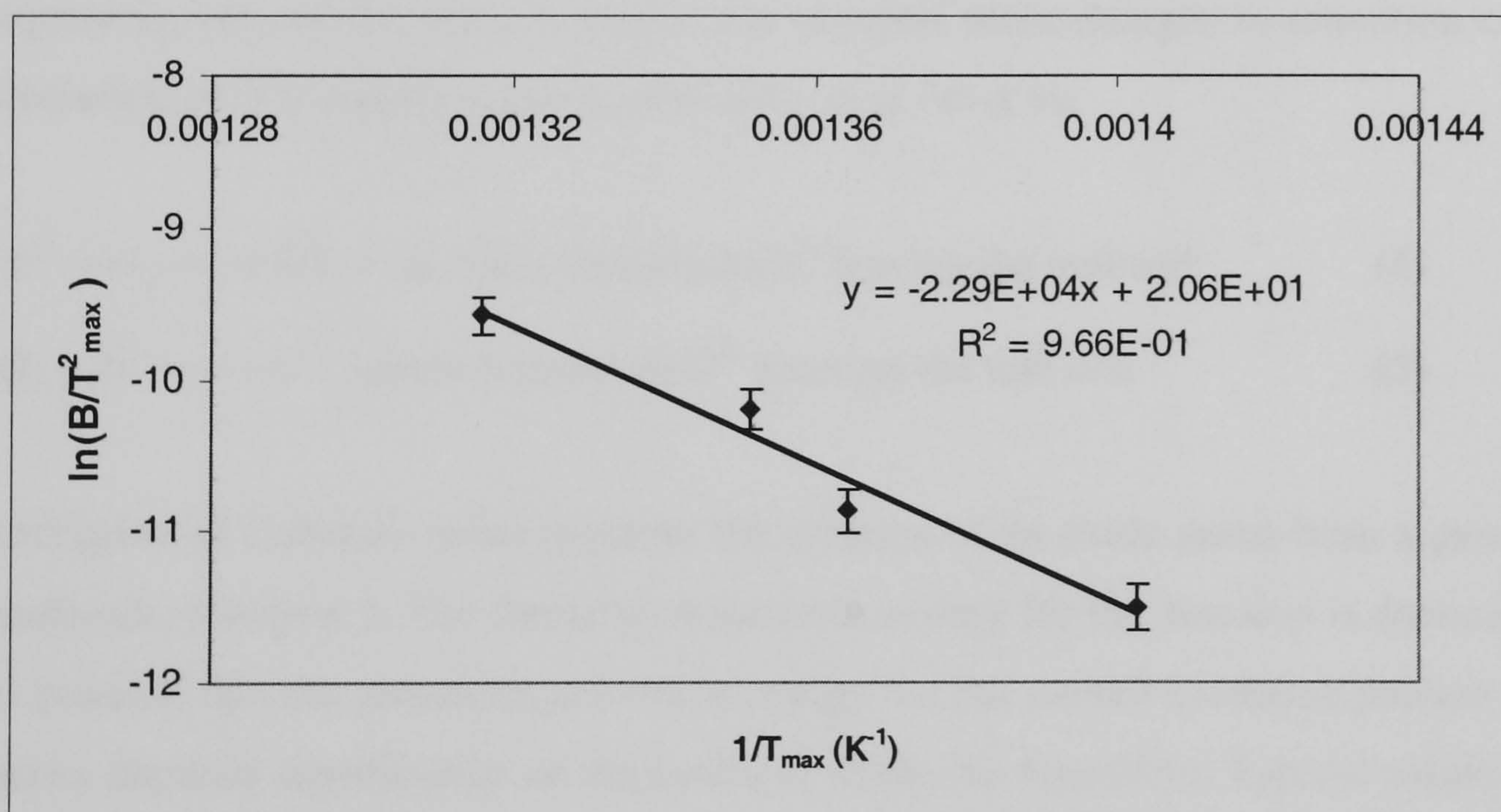


Figure 4-5. Arrhenius plot of thermal activation energy for undoped CaNd_2S_4

The thermal activation energy increases as the dopant level is increased to 10mol% Nd_2S_3 , which is consistent with the knowledge of an unexpanded unit cell being more stable, Figure 4-6. However the increase of thermal activation energy approximately by a factor of two with the initial addition of excess Nd_2S_3 , appears to be anomalous. Further increase of dopant causes a reduction in the activation energy, possibly due to the larger number of lattice vacancies at 20 and 30mol% doping.

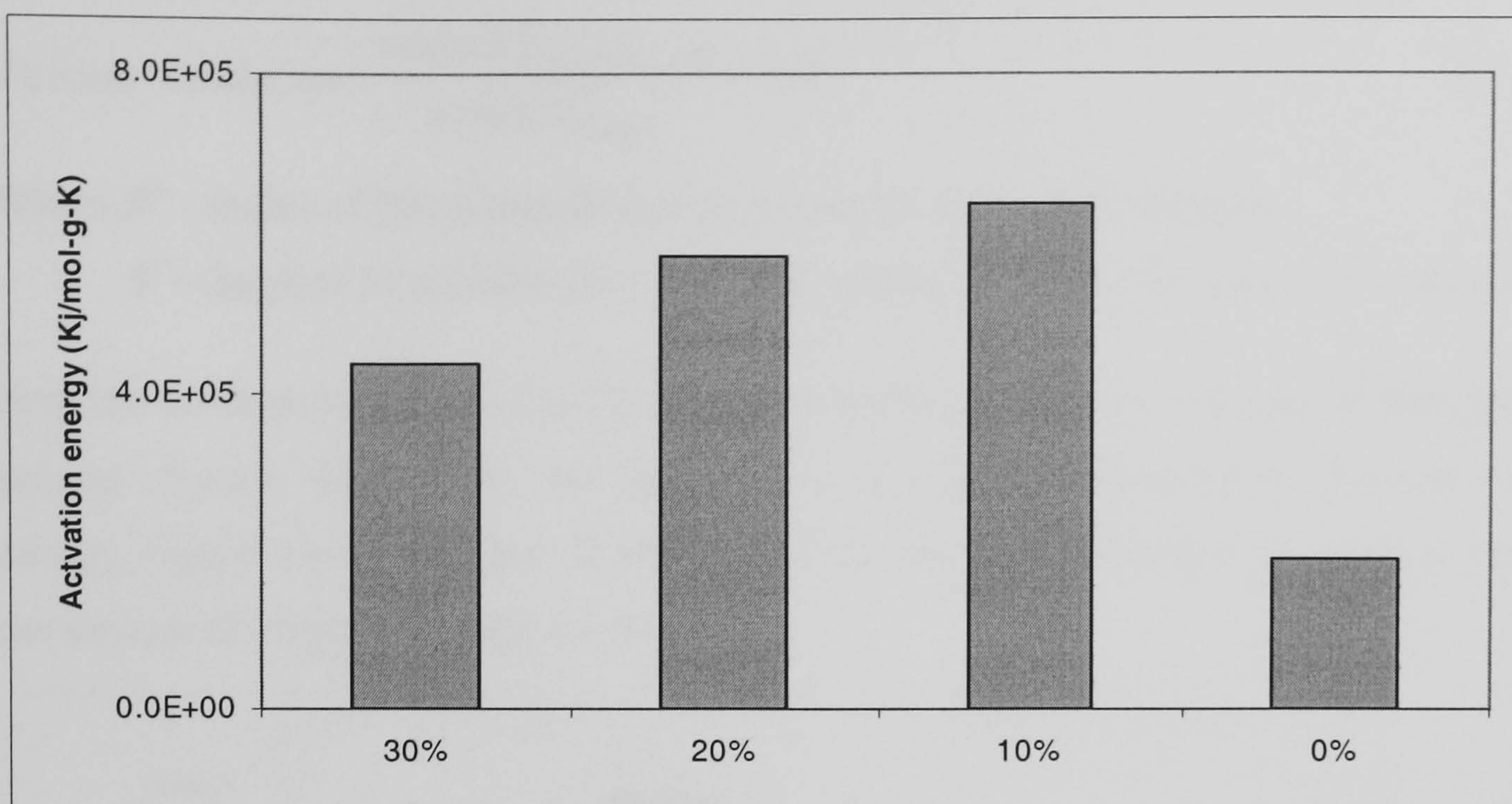
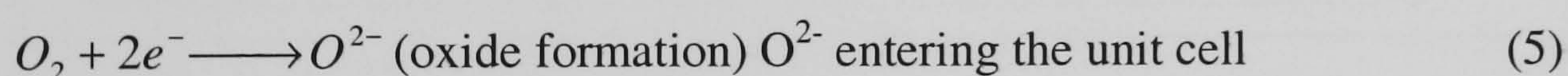
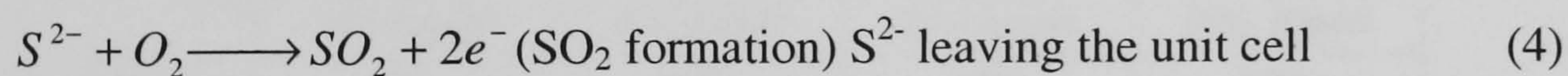


Figure 4-6. Activation energy trend for the $\text{CaNd}_2\text{S}_4+0.0-0.3\text{Nd}_2\text{S}_3$ series

The lowering of the activation energy with the addition of greater than 10mol% Nd_2S_3 , coinciding with an increase in the number of vacancies is consistent. The following equations, (4) and (5), were considered to interpret these changes in activation energies. The liberation of SO_2 and the consumption of O_2 may occur as:



Oxidation of CaNd_2S_4 series involves the creation of an oxide anion from a gaseous oxygen molecule, equation 5. The formation/ionization energy for this reaction is documented, and it is possible that the measured activation energy for the overall oxidation process of CaNd_2S_4 series depends significantly on the extent of oxide ion formation. Typical values reported by Greenwood, 1968 for the formation of an oxide ion is 732 ± 8.4 kJ/mol, which is similar in order of magnitude to the activation energy for the oxidation of CaNd_2S_4 series.

The extent of oxidation is calculated by integrating the SO_2 peak in the TPO trace, (with units a.u.·min), Figure 4.4, and using the SO_2 calibration curves in Appendix B to convert the area in arbitrary unit to moles·min. The percent sulphur liberated from the structure was calculated using the mass of reacted sulphur (based on SO_2 measured) relative to the total sulphur in the compound (based on sample mass oxidised), expressed by equation 6.

$$\text{Percent Oxidation} = \frac{\text{moles } S^{2-}_{\text{measured as } SO_2}}{\text{moles } S^x_{\text{in sample}}} \times 100, \tag{6}$$

Where S^{2-} - moles of SO_2 liberated and measured by Mass Spectrometer

S^x – Sulphur in crystal lattice, moles of sulphur based on the mass of the sample

Both the un-doped $CaNd_2S_4$ and the $CaNd_2S_4+0.1Nd_2S_3$ liberate over half of their sulphur as sulphur dioxide, Figure 4-7, yet there was a significant difference in thermal activation energy, Figure 4-6. Hence the thermal activation energy is related to parameters other than the amount of sulphur released (as SO_2).

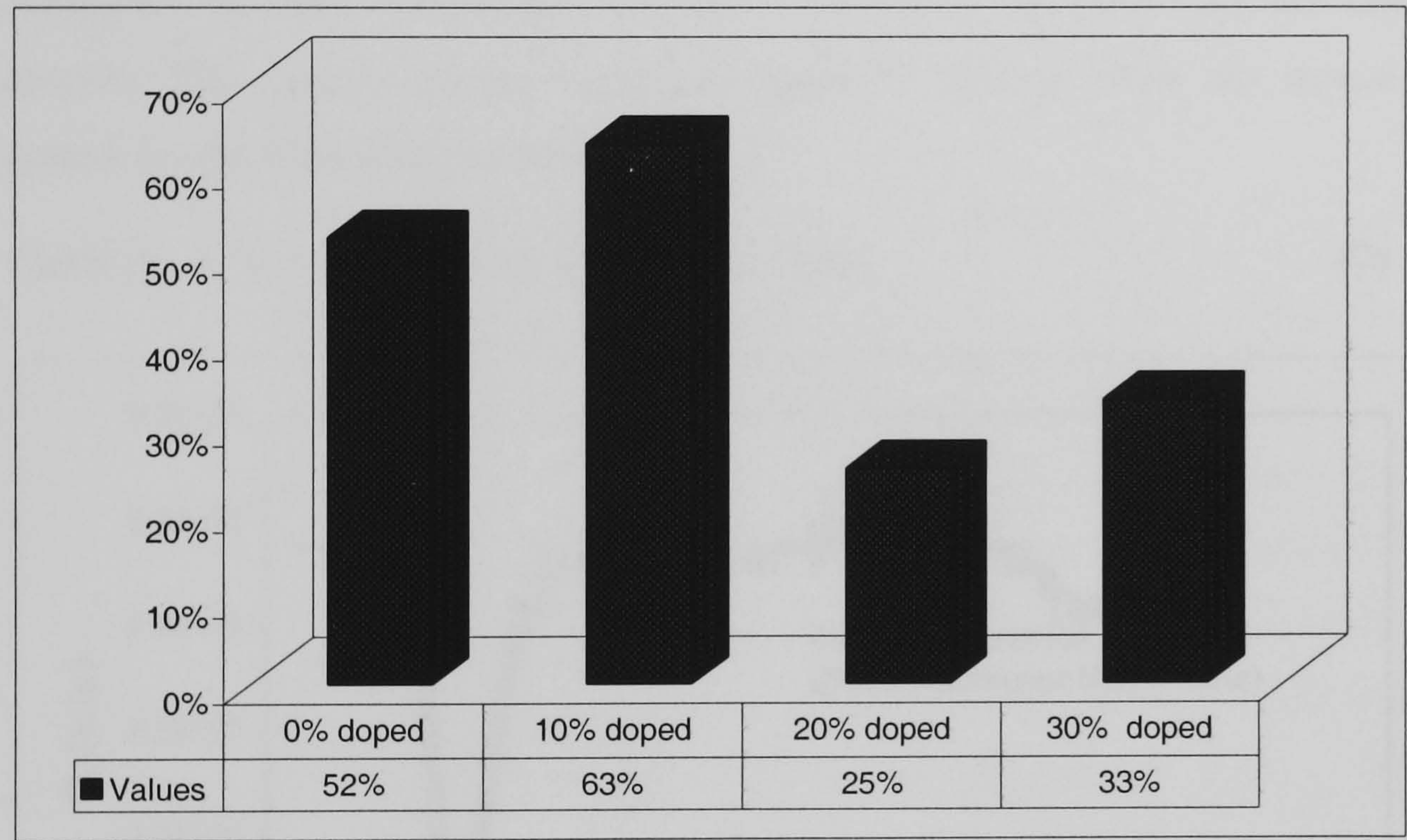


Figure 4-7. Percent Oxidation of sulphide to form sulphur dioxide

$CaNd_2S_4+0.2Nd_2S_3$ and $CaNd_2S_4+0.3Nd_2S_3$ releases less than 50% of the total sulphide ions available, this was accompanied by a reduction in the thermal activation energy relative to $CaNd_2S_4+0.1Nd_2S_3$, Figure 4-7. Therefore a loose relationship between the thermal activation energies and the extent of SO_2 released appears to exist for the doped compounds. However undoped $CaNd_2S_4$ has a low activation energy even though the amount of sulphur released from the unit cell was comparable to $CaNd_2S_4+0.1Nd_2S_3$, this result does not fit into the general assumption that the thermal activation energy is directly proportional to the amount of sulphur removed from the crystal lattice.

A typical mass spectrometer trace for oxygen consumed during the oxidation $CaNd_2S_4+0.1Nd_2S_3$ is shown in Figure 4-8. The presence of significant noise when compared with the SO_2 trace in Figure 4-4 is due to the high background value of oxygen in the mass spectrometer (mass spectrometer O_2 background signal is 2×10^{-8} while that of SO_2 is 1×10^{-12}). The oxygen trace can be described as having two peaks, the first peak with an onset

temperature of 700°C and the higher temperature second peak with an onset temperature of 911°C. The low temperature peak is narrow and well defined while the high temperature peak is much wider with an ill-defined shape. Analysing the oxygen consumption traces for this series showed that the second peak became smaller as the dopant increased except for $\text{CaNd}_2\text{S}_4 + 0.2\text{Nd}_2\text{S}_3$ where no high temperature peak was observed. Because the second oxygen consumption peak has no corresponding sulphur dioxide peak, it is attributed to the formation of the sulphate.

When considering the oxygen balance for undoped CaNd_2S_4 , excess oxygen was consumed compared, to what was needed for the formation of the oxide and the release of sulphur dioxide. The excess oxygen consumed could be used to form the mixed sulphate-oxide system by the following reaction

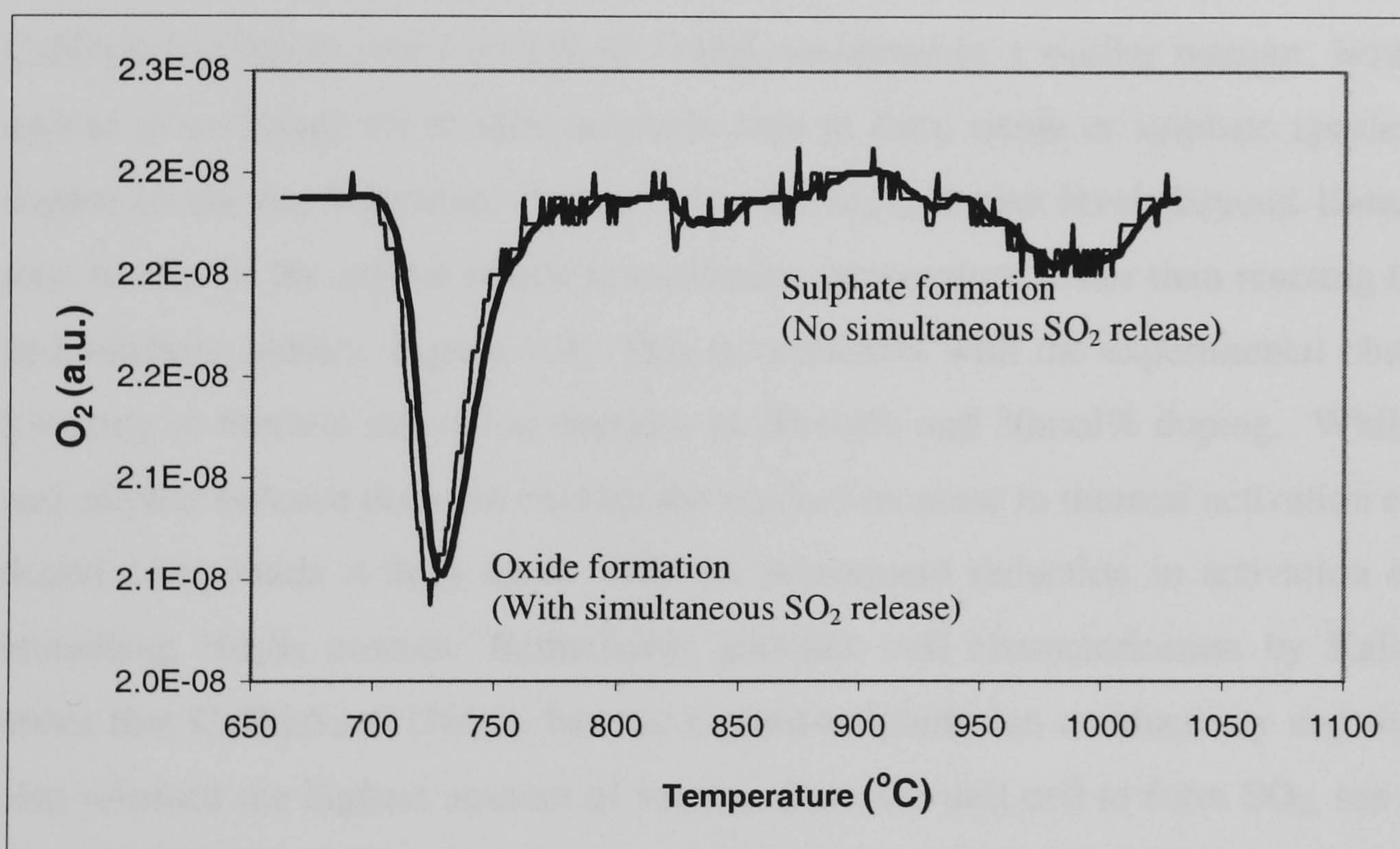
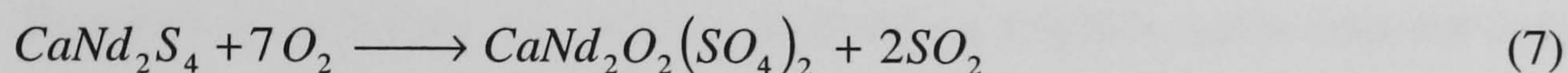
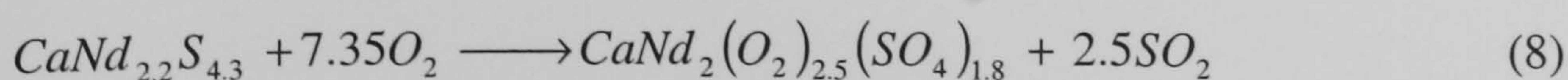
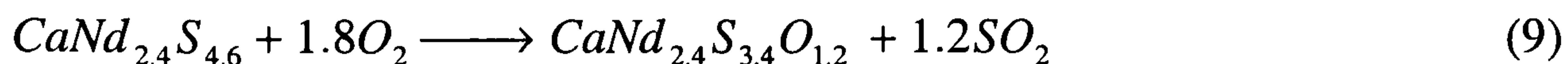


Figure 4-8. TPO showing O_2 trace for un-doped CaNd_2S_4

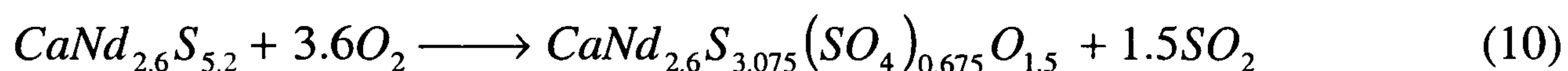
Therefore, based on the high oxygen uptake and the low sulphur release, a mixed oxide-sulphate system was produced under the current oxidising conditions. Similar analysis was done for the doped $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$ which shows that even more oxygen was consumed, equation (8), to a mixed oxide-sulphate, which also agrees with the increased activation energies. The summary of the sulphur and oxygen balance gives the following



Sulphur and oxygen balance for the $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ showed a significant decrease in the oxygen consumption such that a compound free of a sulphate group appeared to have been formed. The proposed reaction as a result of the sulphur and oxygen balance is given in equation (9)



Repeating the oxygen and sulphur balances for the $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ showed an increase in the amount of sulphur dioxide liberated relative to the $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$, as well as increase in the amount of sulphate formation. The proposed reaction as a result of the sulphur and oxygen balance is given in equation (10)



Therefore, in summary, the calcium neodymium sulphide series does not form a pure oxide at 1000°C but all compound seem to form a mixed oxide-sulphate system, Figure 4-9. The $\text{CaNd}_2\text{S}_4+0.0\text{Nd}_2\text{S}_3$ and $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ oxidised in a similar manner. Both compounds appear to exchange all of their sulphide ions to form oxide or sulphate species. At higher dopant levels this behaviour changes since at Nd_2S_3 dopant levels beyond 10mol%, sulphide ions remain in the crystal lattice at maximum temperature rather than reacting to form oxide and sulphate species, Figure 4-9. This is consistent with the experimental observation of a lowering in thermal activation energies at 20mol% and 30mol% doping. While the oxygen and sulphur balance does not explain the marked increase in thermal activation energy for the doped compounds it does agree with the subsequent reduction in activation energies with increasing Nd_2S_3 content. Remarkably galvanic cell characterisation by Kalinina , 1994, states that $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ has the highest sulphide ion conductivity and this compound also released the highest amount of sulphur from the unit cell to form SO_2 , see equation (8). This could imply that conductivity is related to the mobile sulphide ions via electrochemical activation is related to thermally activated mobile sulphide ions, but further investigation is needed to confirm this observation.

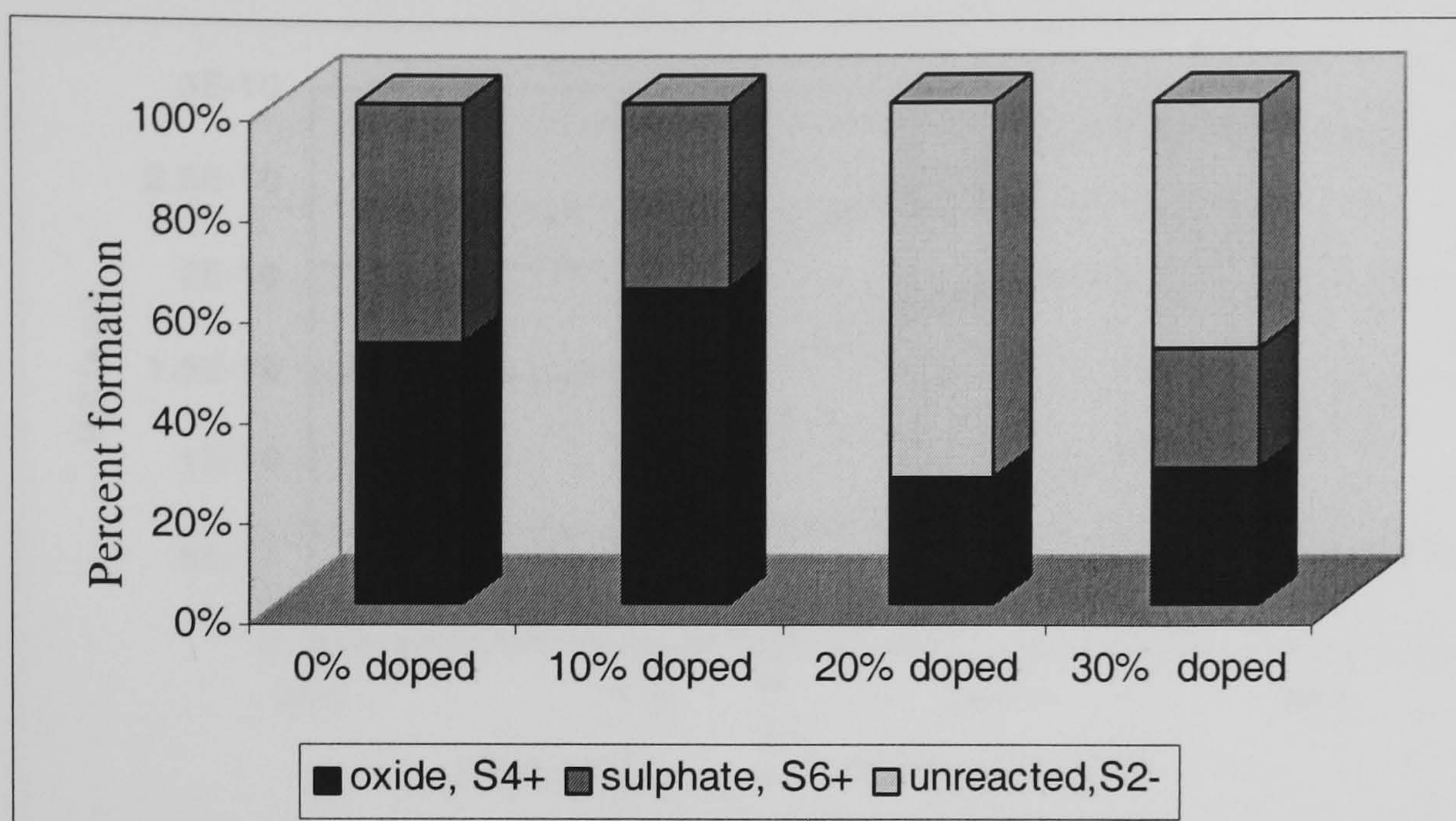


Figure 4-9. Oxide and sulphate formation for CaNd_2S_4 series

4.2 Temperature Programmed Reduction

TPR experiments were conducted up to 1000°C in an H_2/Ar atmosphere (10vol% H_2). The resulting H_2S signal for the CaNd_2S_4 series remained at the maximum detection level at 1000°C suggesting that the reduction reaction was incomplete at this temperature, Figure 4-10. The onset temperature was determined by a graphical procedure where a line was drawn parallel to the steepest slope of the H_2S trace, and the intercept of this line with the base line H_2S signal gives the onset temperature.

The onset temperature of 766°C , the highest for $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ is comparable with the TPO experiments, where a maximum oxidation onset temperature of 723°C was measured. The CaNd_2S_4 based compounds were all marginally more stable under reducing conditions, Table 4.4

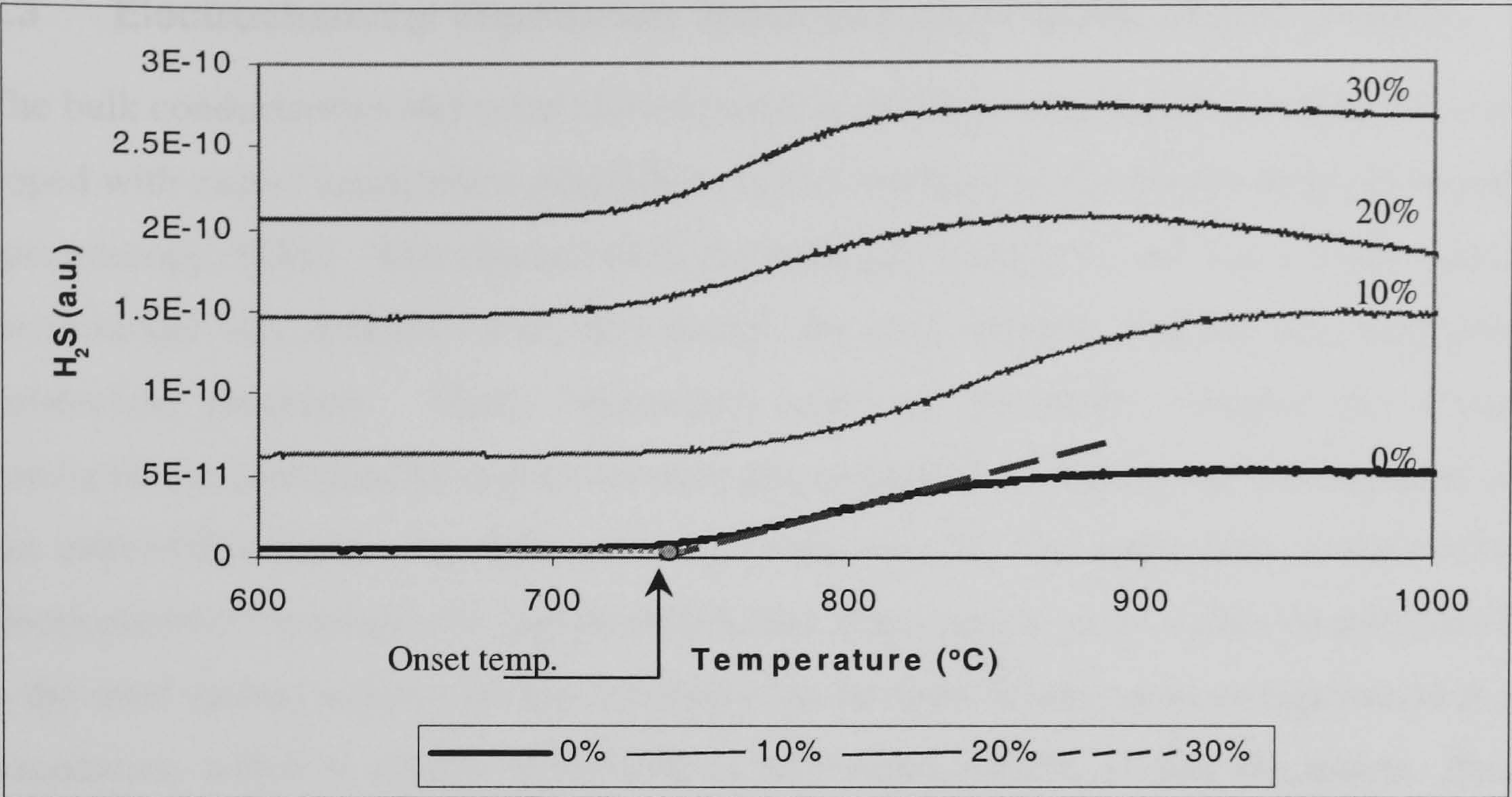


Figure 4-10. TPR of $\text{CaNd}_2\text{S}_4+0.0-0.3\text{Nd}_2\text{S}_3$

Table 4.4 TPR onset temperatures for the Calcium Neodymium Sulphide series

	TPR Onset temp (°C)	TPO onset temp (°C)
$\text{CaNd}_2\text{S}_4+0.0\text{Nd}_2\text{S}_3$	737	671
$\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$	766	723
$\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$	711	708
$\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$	724	703

4.3 Electrochemical Impedance Spectroscopy of Nd_2S_3 doped CaNd_2S_4

The bulk conductivities and other electrochemical properties of calcium neodymium sulphide doped with excess neodymium sulphide were characterised using electrochemical impedance spectroscopy, (EIS). This characterisation technique combined with the correct equivalent circuit model also measures activation energy for ionic hopping and the time constants for conduction processes. Other information such as identifying whether the material's conduction is controlled by highly resistive grain boundaries causing significant ohmic losses (an undesirable feature for these materials if they are to find application in fuel cells and electrochemical reactors) can also be established. For example yttria stabilised zirconia (YSZ) is the most studied solid oxide ion conductor has its main limitation in its high resistive grain boundaries, which is clearly observable in EIS measurements of this electrolyte, Bauerle, 1969. EIS is also used to distinguish between bulk properties from bulk/electrode interface properties, which can lead to the selection of the most appropriate electrode material.

The bulk conductivities of Nd_2S_3 doped CaNd_2S_4 was investigated in the temperature range between 50°C and 400°C using gold or carbon electrodes. An ac voltage of 0.1Vrms was applied at frequencies between 1×10^6 and 0.1Hz in an argon atmosphere. A delay of 1 hour was employed for temperature stabilization.

Generic interpretation of a Nyquist plot is that the high frequency arc for ionic conductors gives the bulk conductivity of the material. The low frequency arc may indicate grain boundary conduction or electrode effects depending on the capacitive values, for example, 0.3pF is a typical value for the capacitance for grain boundary conduction while 3.5pF (10 times greater) is associated with electrode effects.

4.3.1 Impedance Spectroscopy of CaNd_2S_4 series using gold electrodes

The Nyquist plot of all doped compounds of the CaNd_2S_4 series using gold electrodes shows a single arc, except for the 10mol% doped, which has two arcs, Figure 4-11 to Figure 4-11. The second arc for $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_4$ suggests either very resistive grain boundaries or ionic blocking electrodes. At low frequencies (less than 10Hz) the arc appears to intercept the real axis however, at even lower frequencies the real part of the impedance decreases significantly, hence the horizontal set of points along the real axis. This behaviour was observed at 200°C and upwards at low frequencies (less than 100Hz), which is generally associated with electrode effects. The arc observed at high frequencies (greater than 100Hz) can be ascribed to the bulk resistivity of the material. While the number of arcs in the Nyquist plot of CaNd_2S_4 remains independent of temperature, Figure 4-11, the direction of the lowest

frequency (less than 10Hz) horizontal line reverses at higher temperature. Therefore a switching behaviour occurs when going from 350°C to 400°C at low frequencies. The formation of the horizontal line was observed in the same frequency range as before, namely, between 10 and 0.01Hz (again range corresponding to electrode reactions), Figure 4-11.

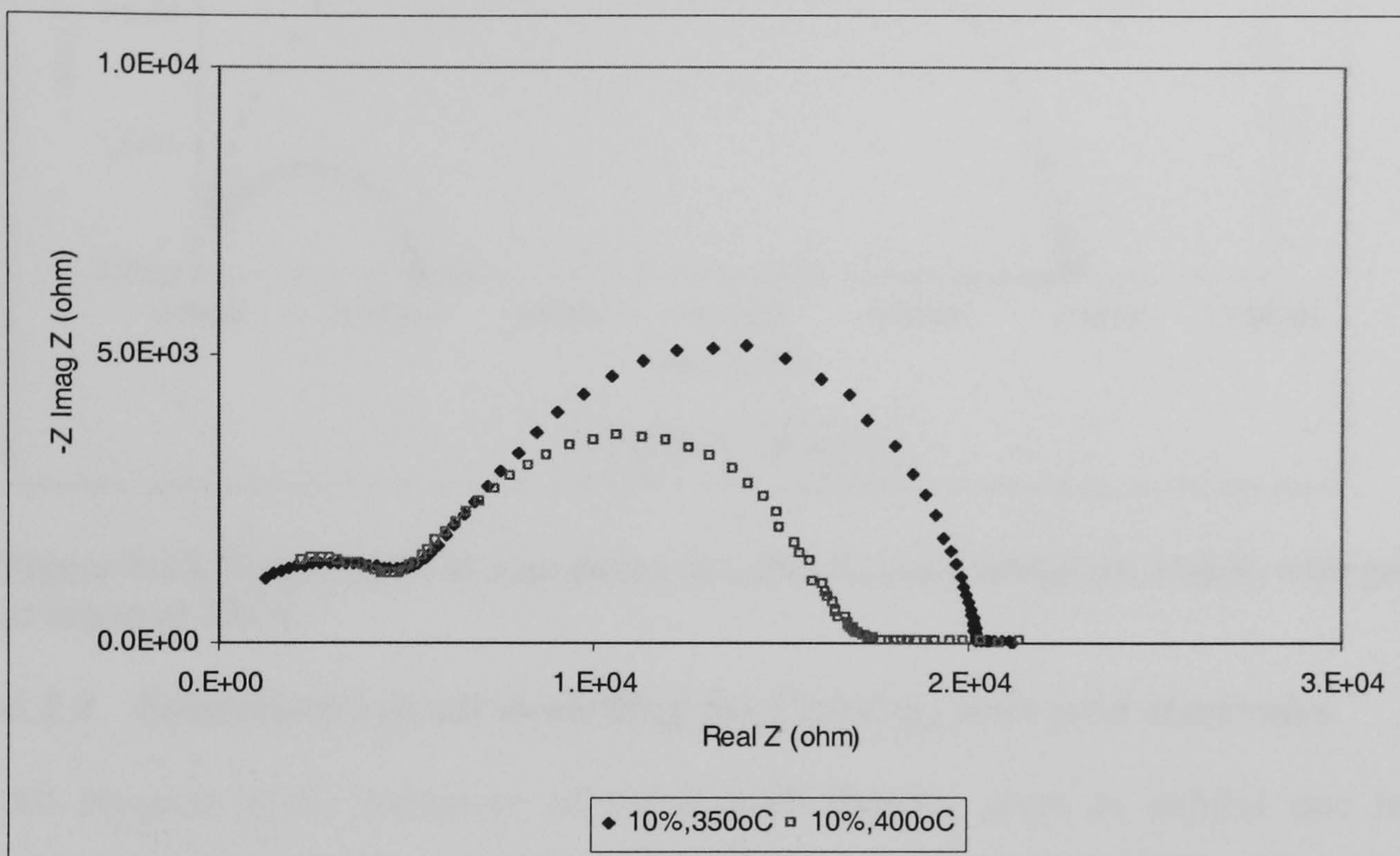


Figure 4-11. Nyquist plot of $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$ using gold electrodes at elevated temperatures

The low frequency switching effect was also observed at similar temperatures for all CaNd_2S_4 compounds. The Nyquist plot has an exceptional feature for $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$ which is a second arc that could represent either blocking grain boundaries or ionic blocking electrode, Figure 4-11 and 4.13.

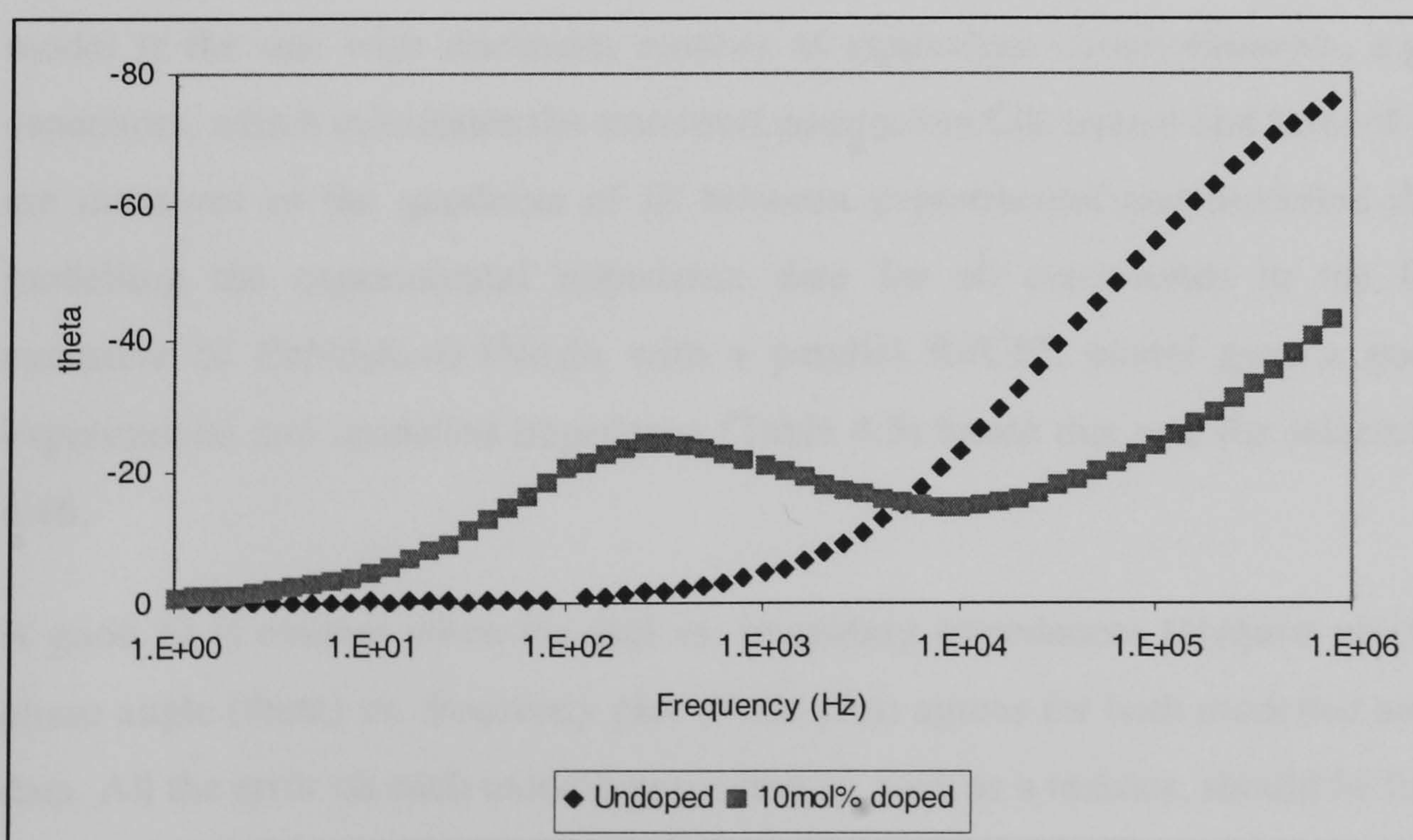


Figure 4-12 Bode plot of $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$ using gold electrodes at elevated temperatures

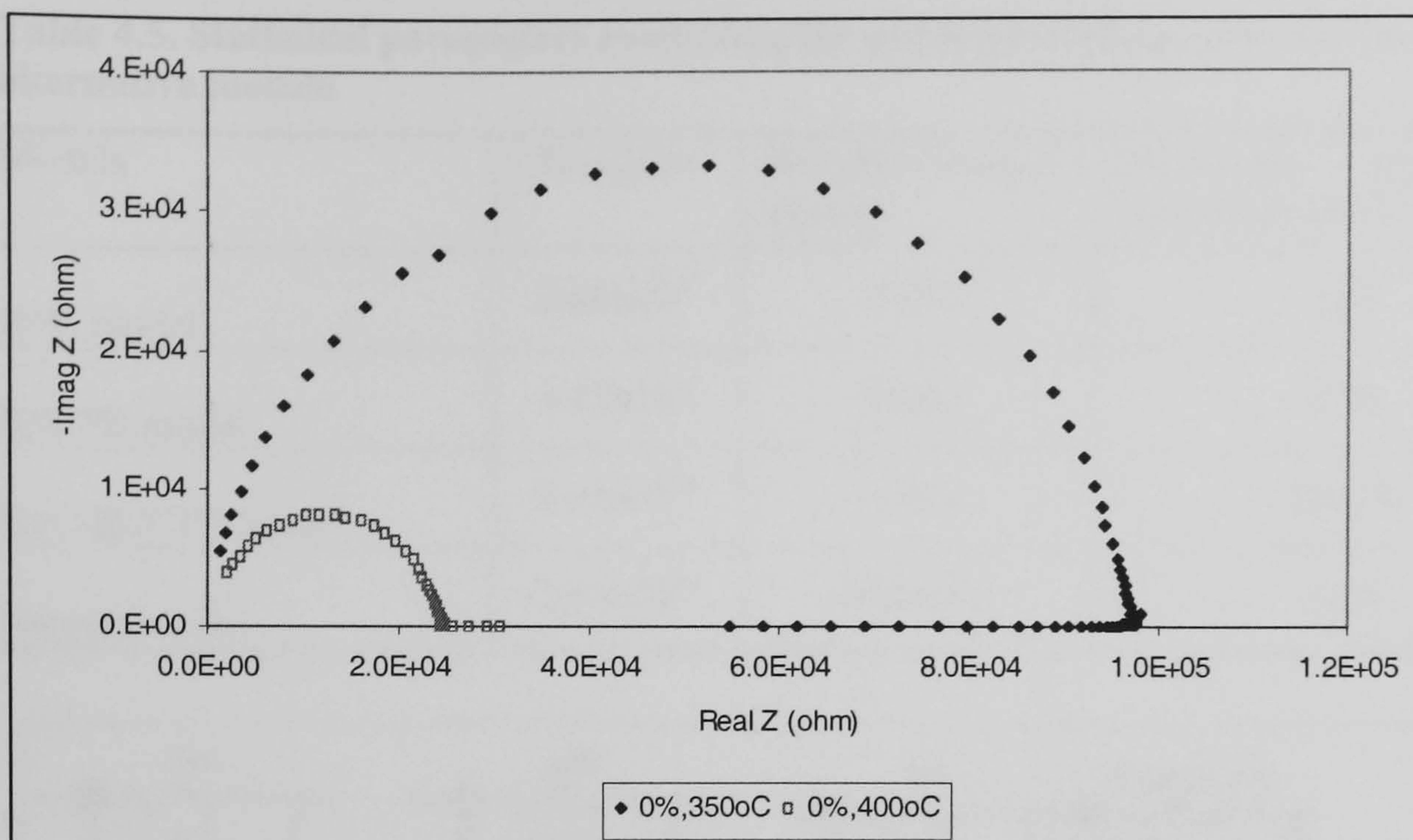


Figure 4-13. Nyquist plot of impedance of CaNd_2S_4 and $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ with gold electrodes in argon at 350°C

4.3.2 Equivalent circuit modelling for CaNd_2S_4 with gold electrodes

All Nyquist plots, exclusive of $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$, seem to exhibit one major arc; the experimental impedance data were modelled initially with a single R//C element. The fit between the R//C equivalent circuit and experimental data was not excellent, Figure 4-14. A significant improvement in the goodness of fit between the modelled and experimental data was achieved by replacing the ideal capacitive component with a distributed capacitor, Constant Phase Element (CPE), Table 4.5, Figure 4-15. The depression of the arc in the Nyquist plot could be associated with the low-density of the pellet, Table 4.5. The optimum model is the one with minimum number of equivalent circuit elements, e.g. resistors and capacitors, which minimizes the statistical parameters Chi-square and Sum-of-squares (which are measures of the goodness of fit between experimental and modelled data). Therefore modelling the experimental impedance data for all compounds in the CaNd_2S_4 series exclusive of $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ with a parallel R//CPE model gave a good fit between experimental and modelled impedance (Table 4.5) hence this was the selected model, Figure 4-16.

A good fit is evident when the real vs. imaginary impedances (Nyquist plot) as well as the phase angle (theta) vs. frequency plot (Bode plot) agrees for both modelled and experimental data. All the error on each modelling parameter, such as a resistor, should be less than 30%.

Table 4.5. Statistical parameters evaluating the goodness of fit for gold coated CaNd_2S_4 series alternative models

Models	Chi-square	Weighted-sum-of-squares	Maximum error on equivalent circuit element
R//C model	3.66×10^{-4}	0.071	24%
R//CPE model	3.87×10^{-4}	0.061	42%
R//C-R//CPE Model	8.13×10^{-4}	1.651	5042%
Bauerle model	2.64×10^{-4}	0.04151	12%

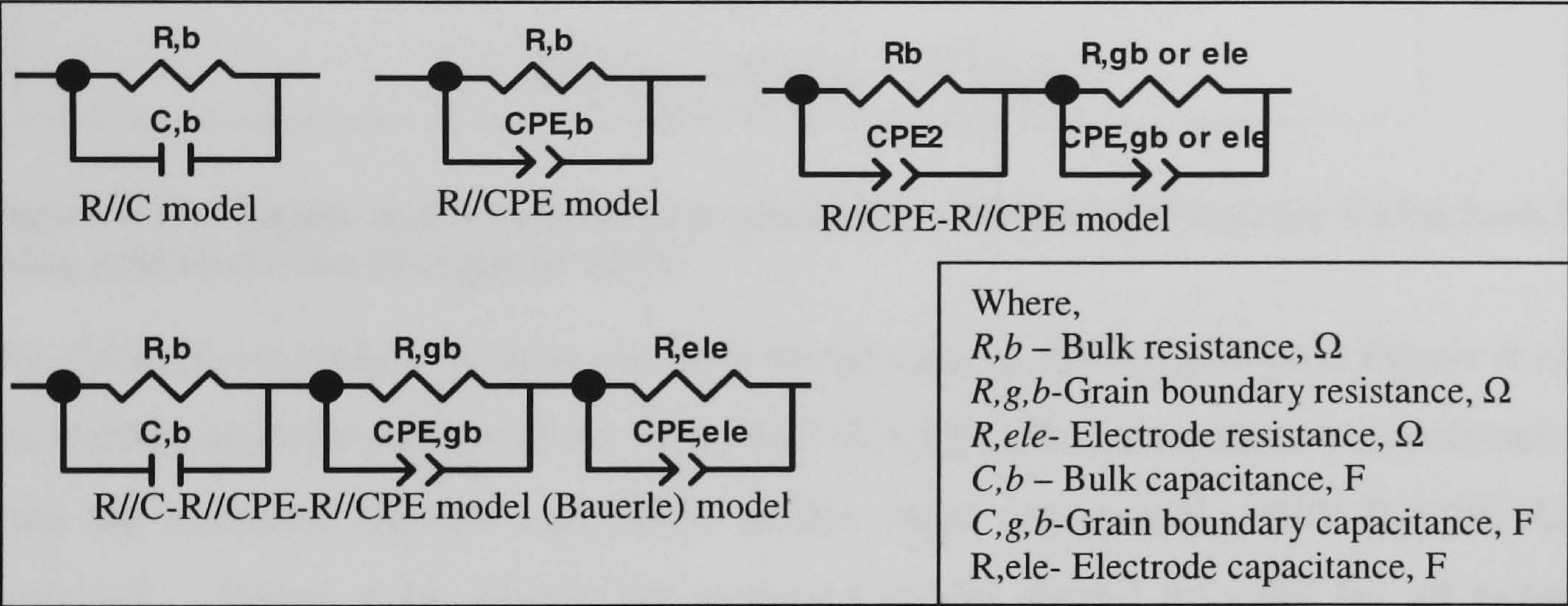


Figure 4-14. Alternative equivalent circuits for CaNd_2S_4 series with gold electrode

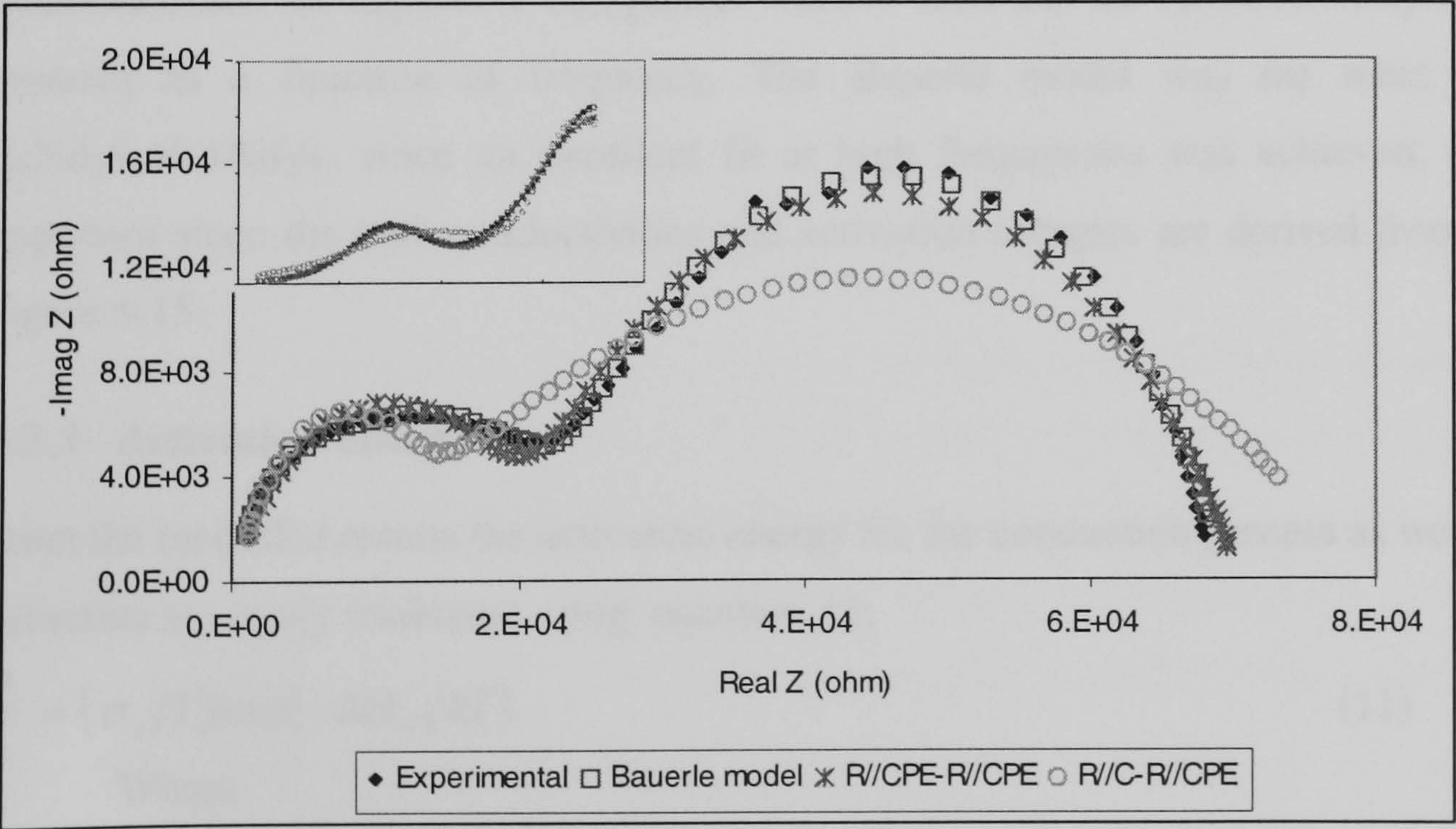


Figure 4-15. Nyquist and Bode plots experimental and modelled result for undoped gold-coated CaNd_2S_4 at 350°C using R//C and R//CPE models

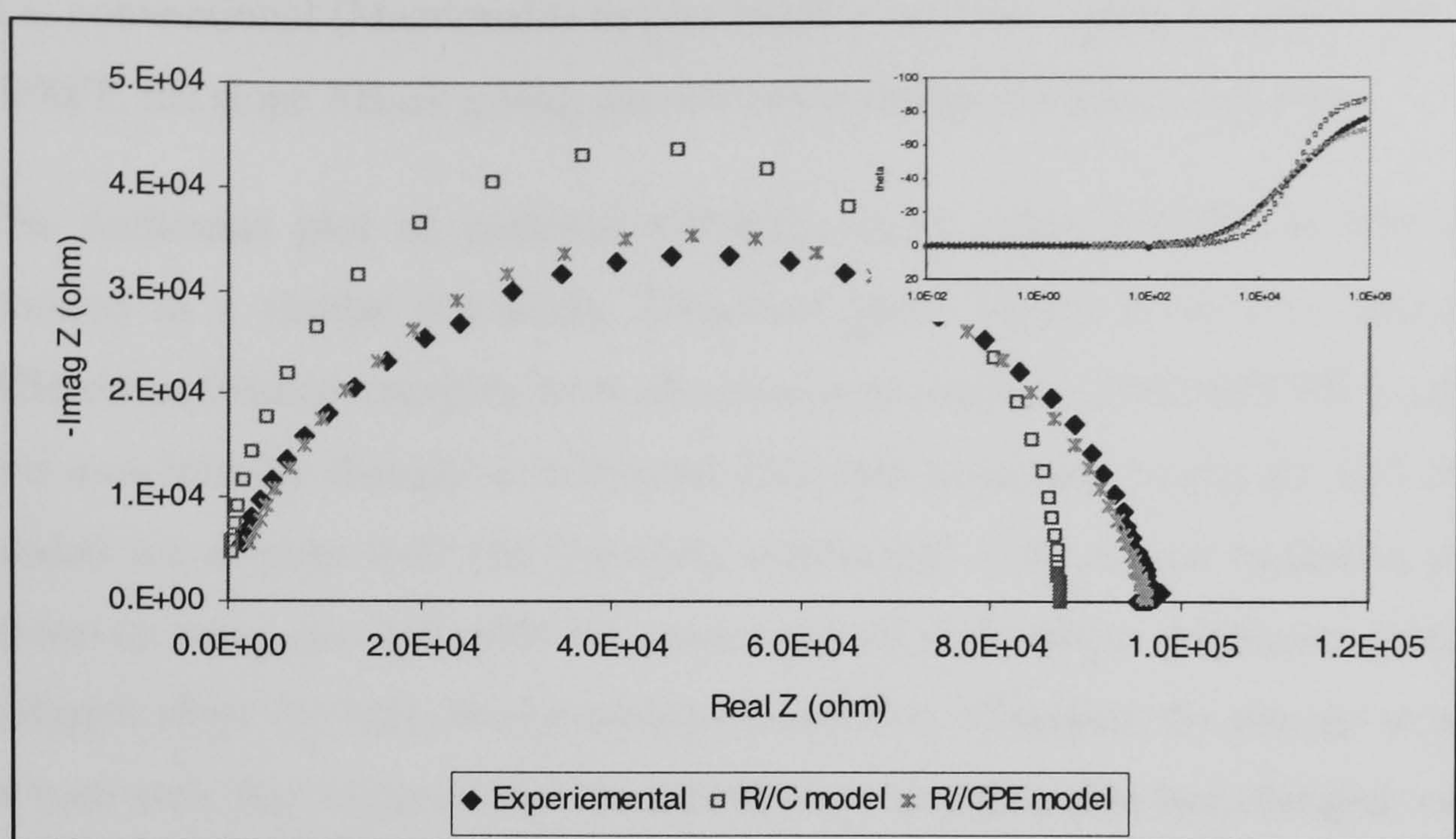


Figure 4-16. Nyquist and Bode plots of experimental and modelled data for $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ using gold electrodes in argon at 250°C

For $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$, at least two arcs are present in the Nyquist plot, Figure 4-14, hence the starting model would be of the form $R//C-R//CPE$. If however there is significant overlap, then the modified Bauerle equivalent model, three arc system, $R//C-R//CPE-R//CPE$ is proposed, , Figure 4-14. Ideally the proposed model should be valid for all experimental conditions inclusive of frequencies and temperatures, however based on , Figure 4-14, the experimental data in the frequency range of 1-10Hz (known to be electrode effect) was not modelled since the capacitive component went to zero and the resistive component was not constant as a function of frequency. The Bauerle model was the most suitable for $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ since an excellent fit at high frequencies was achieved, (this is very important since the bulk conductivities and activation energies are derived from this value), Figure 4-15.

4.3.3 Activation energy

From the modelled results the activation energy for the conduction process as well as the time constants are easily evaluated using equation 11;

$$\sigma = (\sigma_o/T) \exp(-\Delta H_m/kT) \quad (11)$$

Where

σ – conductivity S.cm^{-1}

σ_o – conductivity at standard temperature and pressure S.cm^{-1} (pre-exponential factor)

T – temperature (K)

ΔH_m – activation energy for ionic migration

k - Boltzman constant, $8.6175 \times 10^{-5} \text{ eV/K}$

It is conventional (Macdonald) to plot $\ln(\rho/T)$, i.e., the resistivity rather than conductivity vs $1000/T$, the slope $\Delta H_m/k$ giving the activation energy for ionic migration.

The Arrhenius plot of undoped CaNd_2S_4 using either R//CPE or R//C-1R//CPE model resulted in a similar non-linear Arrhenius plots, Figure 4-17. Two distinct regions with different activation energies were observed even with the R//C-R//CPE model which models two arcs initially thought to represent bulk and boundary. Using the R//CPE model, which models the average bulk and boundary conduction, a non-linear Arrhenius plot is reasonable. However using the R//C-R//CPE model should yield linear Arrhenius plots with a slightly different slope for bulk and boundary conduction. Therefore the change in activation energy of both arcs, this suggests that the mechanism of conduction has changed; either a change in the conducting specie or a change in crystal, Figure 4-17.

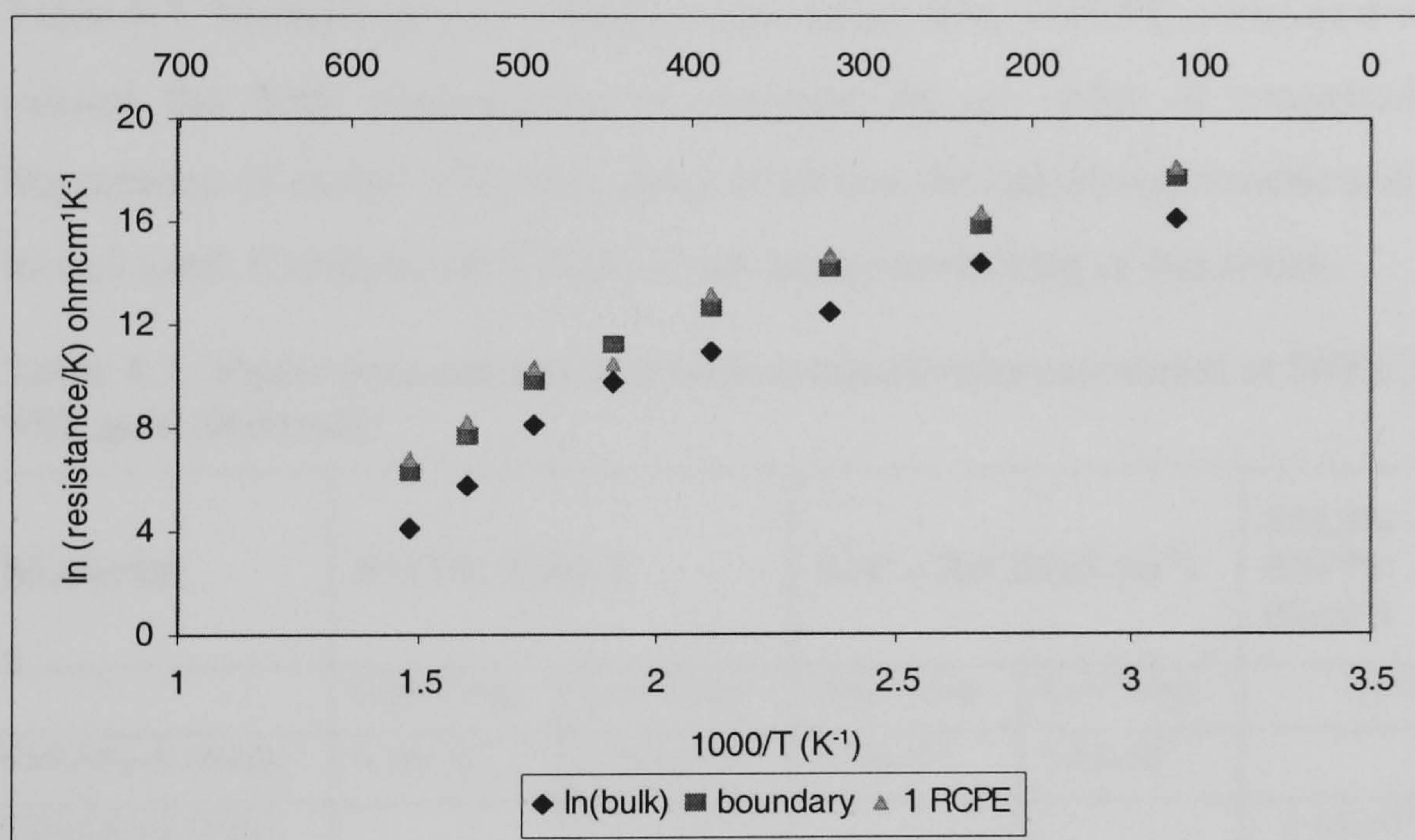


Figure 4-17 Arrhenius plot for ionic mobility for undoped CaNd_2S_4 with gold electrodes

Table 4.6 gives the activation energies for the CaNd_2S_4 series using both models for both temperature ranges. It can be seen that at high temperatures the activation energy is much higher for the un-doped CaNd_2S_4 compared to the doped- CaNd_2S_4 compounds. Also the low temperature range (50-250°C) has an activation energy of 0.44-0.52eV which is 50% lower than the activation energy in the high temperature range, suggesting that at low temperature the conduction process is different from the high temperature range, possibly involving calcium ions. The doped $\text{CaNd}_2\text{S}_4+0.1-0.2\text{Nd}_2\text{S}_3$ gave very low activation energies, which is atypical for anionic conduction, and no activation energy could be calculated for $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ due to extremely unstable impedance data.

Table 4.6. Activation energies for CaNd₂S₄ series using gold electrodes

Electrolytes with gold Electrodes, 1 st run	R//CPE		R//C-R//CPE (250-400°C)		R//C-R//CPE (50 -200°C)	
	High temp.	Low temp.	High temp (eV)		Low temp. (eV)	
	(eV)	(eV)	Bulk	Boundary	Bulk	Boundary
CaNd ₂ S ₄ +0.2Nd ₂ S ₃	0.35	0.19	0.12	0.48	0.19	0.28
CaNd ₂ S ₄ +0.1Nd ₂ S ₃	N/A	N/A	0.44	0.59	N/A	N/A
Undoped CaNd ₂ S ₄	1.19	0.52	1.02	0.44	1.15	0.45

N/A- not available

4.3.4 Bulk conductivities for gold coated CaNd₂S₄ series

The derived parameter, bulk conductivity, based on the equivalent circuit model is given in Table 4.7. Modelling the CaNd₂S₄ series using R//C-R//CPE compared with an R//CPE model caused the bulk conductivity to increase by an order of magnitude. This shows the importance of model selection, since it affects the calculated conductivity. Irrespective of the model used, CaNd₂S₄ +0.1Nd₂S₃ is the least conducting of the series.

Table 4.7. Equivalent circuits and bulk conductivities calculated at 500°C for CaNd₂S₄ series with gold electrodes

Material	R//CPE (S.cm ⁻¹)		R//C – R//CPE(S.cm ⁻¹)		R//CPE – R//CPE (S.cm ⁻¹)	R//C- R//CPE R//CPE (S.cm ⁻¹)
	High Temp.	Low Temp.	High Temp.	Low Temp.	No temp effect	
CaNd ₂ S ₄ +0.2Nd ₂ S ₃	6.18x10 ⁻³	2.74x10 ⁻⁶	5.75x10 ⁻²	1.83x10 ⁻⁵		
CaNd ₂ S ₄ +0.1Nd ₂ S ₃					2.10x10 ⁻⁶	1.55x10 ⁻⁵
Undoped CaNd ₂ S ₄	1.67x10 ⁻²	9.00x10 ⁻⁵				

The total conductivity for CaNd₂S₄ series of 1-1.5x10⁻⁶S.cm⁻¹ at 500°C, Kalinina *et. al.*, 1995, was previously established using a galvanic cell with graphite electrodes. With the exception of 10mol% doped, the bulk conductivities for all other compounds are several orders of smaller greater. However when the bulk conductivity was measured using impedance spectroscopy of CaNd₂S₄ series with gold electrode gave larger conductivities than what was previously stated. Using galvanic cell measurements.

4.3.5 Time constant analysis for gold coated CaNd_2S_4 series

The time constant is given by the following expressions where the choice of equation is based on the modelling elements used. For a simple resistor-capacitor (R//C) circuit, the time constant for that process is

$$\tau = RC \quad (12)$$

For the case of a resistor-constant phase element (R//CPE) circuit, the time constant for that process is given as

$$\tau = (RA_o)^\psi \quad (13)$$

Where τ – time constant, s

R - resistor, Ω

C -capacitor, F $A_o = C$, when $\psi = 0$,

ψ - fractional exponent, to model depressed arc, varies from 0 to 1

Time constant analysis, Table 4.8 and Table 4.9, for the conducting species in the un-doped CaNd_2S_4 is much faster than the oxide anion in YSZ at comparable temperatures. The $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$ has similar time constant to YSZ, making this compound more likely to be conducting sulphide ions. $\text{CaNd}_2\text{S}_4 + 0.2\text{Nd}_2\text{S}_3$ has time constants three orders of magnitude smaller than YSZ, which is unexpected for ionic conduction; such small time constant is rationally attributed to electron-hole conduction. Assuming that sulphide ions were hopping, then their time constants would arguable be larger than those of oxide, assuming similar hopping distance. These data suggest that the low activation energies and very fast time constants are not a measure of bulk anionic conduction of ions within these electrolytes.

Table 4.8. Circuit parameters for $\text{Zr}_2\text{O} + 6\text{mo}\% \text{Y}_2\text{O}_3$, Bauerle 1969 at 240°C

Grain interior (bulk)	Grain Boundary	Electrode blocking
$R_{gi} = 2.1\text{M}\Omega$	$R_{gb} = 1.5\text{M}\Omega$	$R_e = 5.0\text{M}\Omega$
$C_{gi} = 4.8\text{pF}$	$C_{gb} = 1.7\text{nF}$	$C_e = 2.0\mu\text{F}$
$\tau = 1.01 \times 10^{-5}\text{s}$	$\tau = 2.55 \times 10^{-3}\text{s}$	$\tau = 1.0\text{s}$

Where:

gi - grain interior; bg - rain boundary; e - electrode

Table 4.9. Time constant analysis for CaNd_2S_4 series at 250°C using gold electrodes, application of alternative models of R//CPE or R//C-R//CPE

Undoped CaNd ₂ S ₄				
R//C-R//CPE		R//CPE		
Bulk	Grain boundary	Bulk		
R _{gi} = 0.54MΩ	R _{gb} = 2.4MΩ	R _{bg} =2.86 MΩ		
C _{gi} = 60.7pF	C _{gb} = 0.2455nF	C _{gb} = 0.122nF		
τ _{gi} = 3.38x10 ⁻⁵ s	τ _{gb} = 2.45x10 ⁻⁵ s	τ _{gb} = 1.52x10 ⁻⁴ s		
CaNd ₂ S ₄ +0.1Nd ₂ S ₃				
R//CPE-R//CPE		R//C-R//CPE-R//CPE		
Bulk	Grain boundary	Bulk	Grain boundary	Electrode
R _{gi} = 2.9x10 ⁺⁴ Ω	R _{gb} = 1.5x10 ⁵	R _{gi} = 1.7x10 ⁺² Ω	R _{gb} = 3.5x10 ⁴	R _e = 1.6x10 ⁺⁵
C _{gi} = 2.1x10 ⁻⁸	C _{gb} = 2.7x10 ⁻⁷ F	C _{gi} = 3.01x ⁻¹⁰	C _{gb} = 3.9x10 ⁻⁸	C _e = 1.9x10 ⁻⁷
ψ _{gi} =0.67	ψ _{gi} =0.66		ψ _{gi} =0.64	ψ _e =0.74
τ _{gi} = 1.5x10 ⁻⁵ s	τ = 9.42x10 ⁻³ s	τ _{gi} = 5.0x10 ⁻⁷ s	τ _{bg} = 3.3x10 ⁻⁵ s	τ _e = 8.7x10 ⁻³ s
CaNd ₂ S ₄ +0.2Nd ₂ S ₃				
R//C-R//CPE		R//CPE		
Bulk	Grain boundary	Bulk		
R _{gi} = 9.1x10 ²	R _{gb} = 4.6e3Ω	R _{gb} =5.5x10 ³ Ω		
C _{gi} = 1.01x10 ⁻¹⁰	C _{gb} = 1.47x10 ⁻⁹	C _{gb} = 3.3x10 ⁻⁹ F		
	ψ _{gb} =0.85	ψ _{gb} =0.77		
τ _{gi} = 9.98x10 ⁻⁸ s	τ _{gb} = 8.8x10 ⁻⁷ s	τ _{bg} = 6.5x10 ⁻⁷		

4.3.6 Interface phenomena of Gold electrode and CaNd_2S_4 Electrolyte

Using Figure 4-18 it may be possible to explain the different behaviour between the electrolyte and gold electrodes at different temperatures. Mobile sulphide ions (predominantly from the bulk) may be conducted to the surface of the electrolyte due to the application of the small electrical potential (0.1Vrms). At low temperatures activated mobile sulphur could then react with the gold electrode to form Au_2S or AuS . These covalent compounds dissociate as the temperature is further increased. This possible phenomena occur between the bulk and the electrolyte, leaving the grain boundaries unaffected. The extent of the proposed reaction would be affected by the likelihood of the sulphide ions to reach the electrode, and since the number of sulphur vacancies increases with doping, the activation energy for this reaction to take place should decrease as the dopant is increased, as observed, Table 4.10

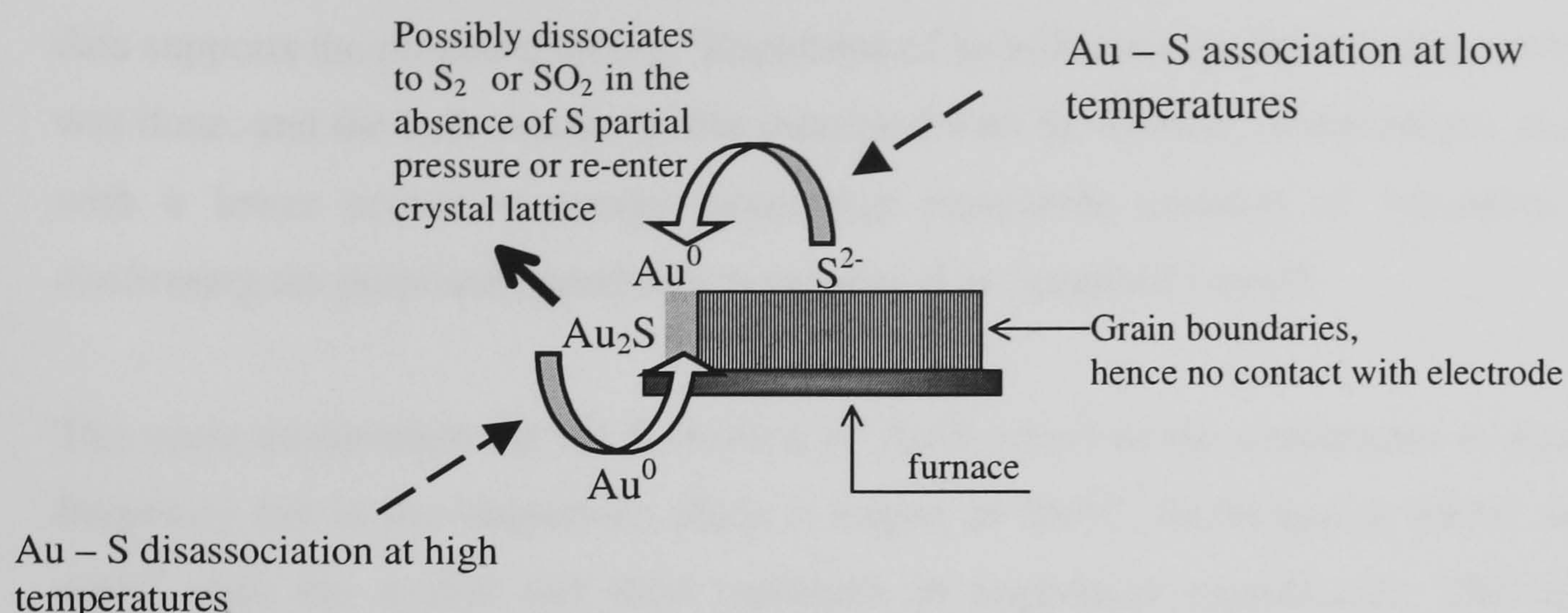
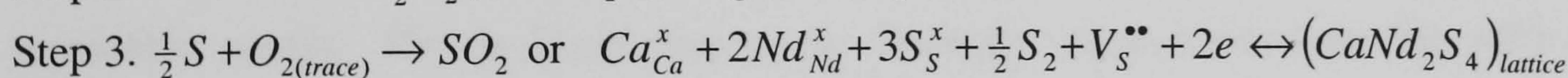
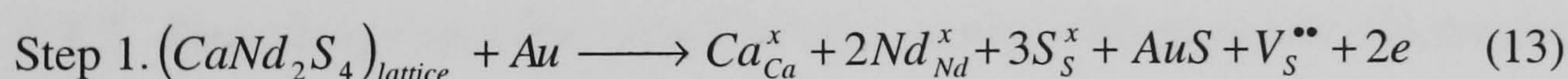


Figure 4-18. Proposed mechanism for low activation with gold electrode

If this reaction occurs, then the resistance of the electrolyte should decrease as the reaction of a gold-sulphide compound proceeds due to the creation of vacant sulphide ion lattice sites. Decomposition of interfacial gold-sulphide compound at higher temperatures could lead to re-substitution of sulphide, thus restoring the initial resistance of the electrolyte is expected. However due to the absence of a positive sulphur partial pressure (argon atmosphere), sulphur liberated from the decomposition of AuS or Au₂S could form SO₂ with oxygen traces in the argon (laboratory grade Ar has ppm O₂) making complete re-substitution not likely. If this theory describes the reaction between gold electrode and the CaNd₂S₄ series, repeating the impedance experiment should result in an increase in conductivity and further lowering of the activation energy. The increase in conductivity would be due to the formation of vacancies as sulphur leaves the crystal structure.



Where Ca_{Ca}^x -calcium ion on a calcium lattice site

Nd_{Nd}^x -neodymium ion on a neodymium lattice site

S_{S}^x - sulphur ion on a sulphur lattice site

$\text{V}_{\text{S}}^{\bullet\bullet}$ - vacant sulphur lattice site

The Nyquist plot, Figure 4-11. Nyquist plot of CaNd₂S₄ +0.1Nd₂S₃ using gold electrodes at elevated temperatures shows that at 350°C the impedance is reducing with time at low frequencies, possibly due to the reaction with the electrode according to equation 13-step1 (because of the AuS decomposition). At higher temperature, 400°C, the reverse occurs, this is possibly due to

re-substitution of sulphur into the crystal lattice, equation 13-step3. Therefore impedance data supports the proposed theory. Repetition of impedance experiments using gold electrode was done, and the bulk conductivities increased with the number of repetitions, accompanied with a lower activation energy suggesting permanent creation of vacancies, therefore confirming the proposed hypothesis as expressed in equation 13-step2.

The onset temperature for the formation of Au-S varies as the experiment is repeated (low frequency tail in the impedance plot); it begins at 250°C, increasing to 350°C and then to 400°C with the second and third repetition of impedance experiments. The initial onset temperature agrees with decomposition the temperature of 230°C of colloidal gold sulphide (Au₂S), Morris *et. al.*, 2002. A. Scott, 2000 mentioned that gold sulphide amongst other sulphides such as silver and copper have voltage dependent switching characteristics as was observed simply by changing the temperature by 50°C. This theory, (equation 13) assumes that gold can absorb S²⁻ ions, provided that the electrolyte conducts this ion to the electrode-electrolyte interface. Wierse *et. al.* 1978, showed that gold electrodes can adsorb a monolayer of sulphide in liquid phase system, which can be desorbed by application of a cathodic current. They observed a decrease in capacitance, attributed to the formation of the insulating layer, with a dielectric constant of 2., thereby showing the charging and discharging of the capacitance with gold electrodes with CaNd₂S₄ as electrolyte. The absence of ionic blocking electrode mechanism with gold could be attributed to the uptake mechanism represented in step 1 and 3 (equation 13) or due to the partial electronic conduction property of Au₂S, Ishikawa, *et. al.* 1995.

4.3.7 Impedance spectroscopy CaNd₂S₄ series with graphite electrodes

Impedance spectroscopy of the CaNd₂S₄ series using gold electrode resulted in non-repeatable results. This is likely due to an electrode reaction between the gold and the electrolyte. Therefore graphite plates were used as the electrode material for further. Graphite is suitable for galvanic cells in terms of chemical inertness. When used as a thin pellet it poses a significant disadvantage when it is used in impedance spectroscopy, in that it is mechanically pressed into pellets. This means spreading resistance may result causing an overlap between electrode arc and grain boundary arc. If spreading resistance is significant, improvement in electrolyte-electrode contact can be achieved by painting. The electrode arc for mechanically contacted electrodes is a function of the number of contact points between the electrode and the electrolyte which will affect the assembly of the cell, causing the electrode arc not to be reproducible. However Fleig, 2000, 1996 showed that the high

frequency arc is free from electrode effects associated with contact resistance or spreading effects, therefore the high frequency arc should be equal to the true bulk resistance of the electrolyte, a value which should be similar to that of the single crystal.

Impedance spectroscopy of undoped, 20mol% and 30mol%, using graphite electrodes gave two arcs without significant overlap so that they were easily distinguished in the Bode plot, while only one arc could be seen on the Nyquist plot, Figure 4-19. Also $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ has three distinguishable arcs in the Bode plot, Figure 4-20.

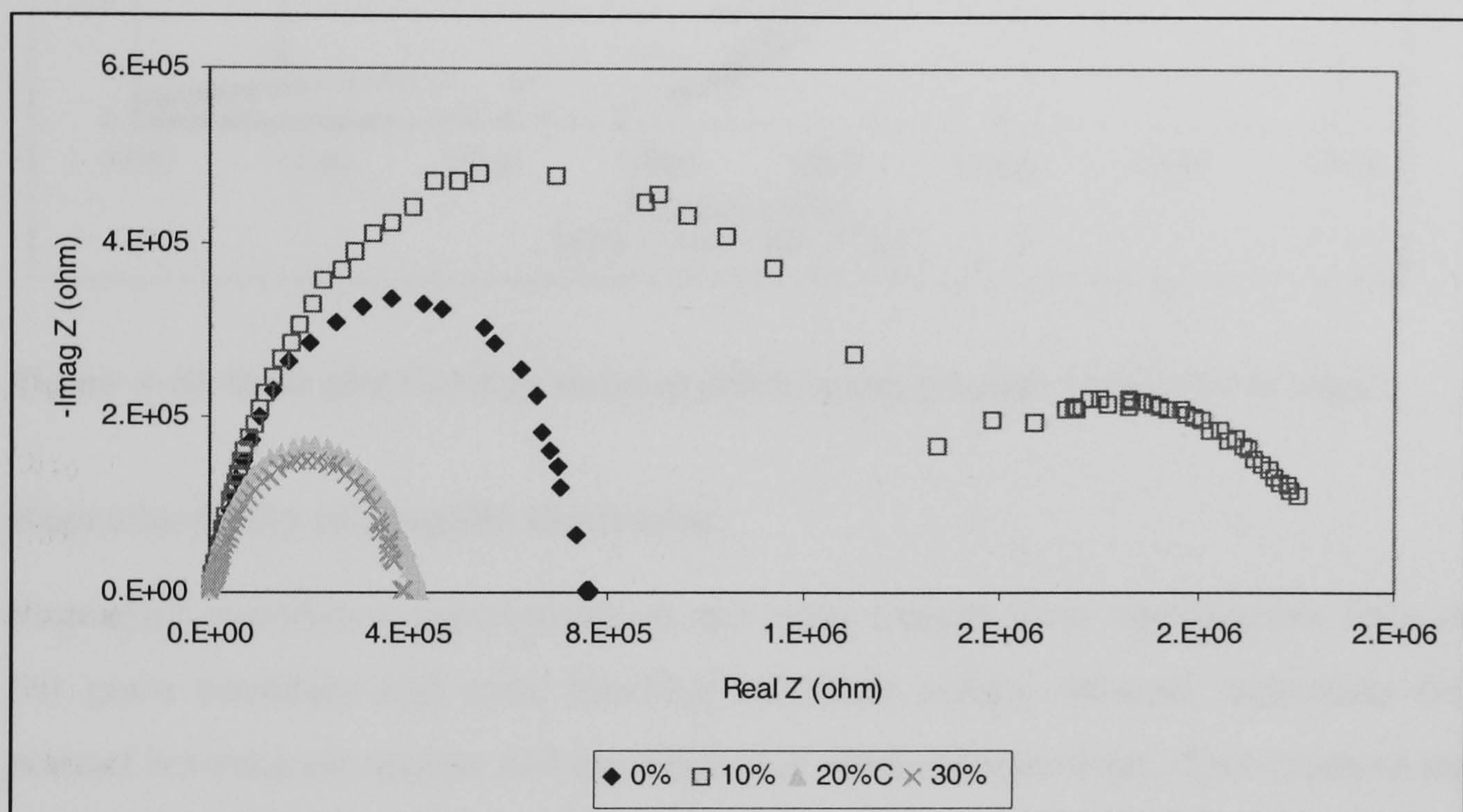


Figure 4-19. Nyquist plot CaNd_2S_4 series at 400°C using graphite electrodes in Argon

The multiple arcs were observed at all temperatures between 200°C and 400°C for all CaNd_2S_4 compounds. Graphite electrodes at low temperatures (less than 200°C) result in significantly scattered impedance data, such that no arcs could be resolved. Higher temperatures yielded reproducible high frequency arcs but signal scattering at lower frequencies was apparent which was not observed with gold electrodes.

The use of graphite electrodes with $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ at higher temperatures produced three arcs including a frequency ion blocking arc as shown in Figure 4-19 and Figure 4-20. The low frequency effect is attributed to blocking electrodes, limiting ions to traverse the electrolyte-electrode interface.

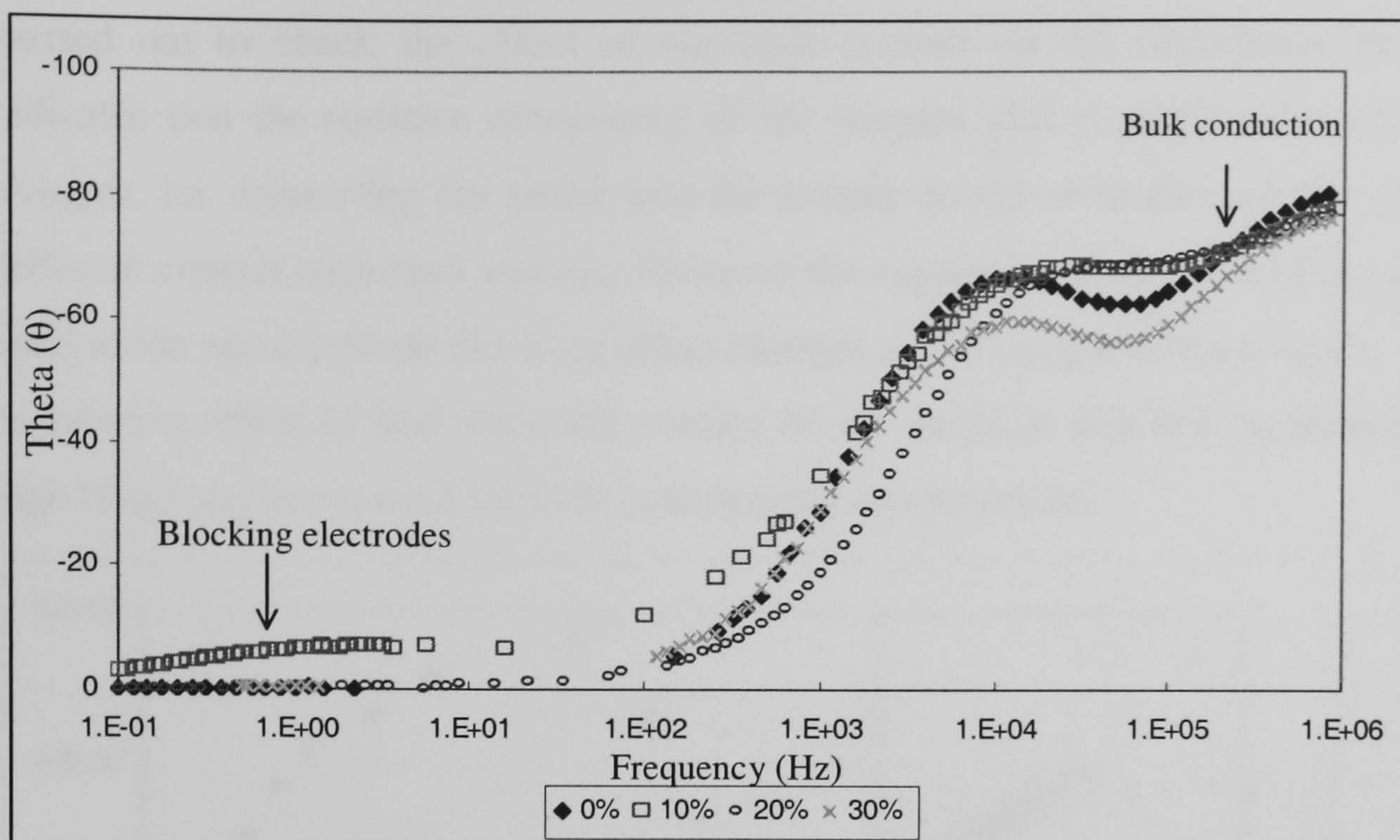


Figure 4-20. Bode plot CaNd_2S_4 series at 400°C using graphite electrodes in argon

Reproducibility of graphite electrodes

Repeating impedance experiments on the same sample gave reproducible bulk conduction, but grain boundary and ionic blocking electrode effects reduced, indicating that a better contact between electrolyte and electrode was obtained over time. Two types of repeatability tests were performed: the first test was to maintain identical cell geometry including electrode contact with the sample; this tested the material stability which resulted in identical Nyquist plots at 400°C , indicating that the electrolyte is stable up to this temperature when graphite electrodes and argon atmosphere are used, Figure 4-21.

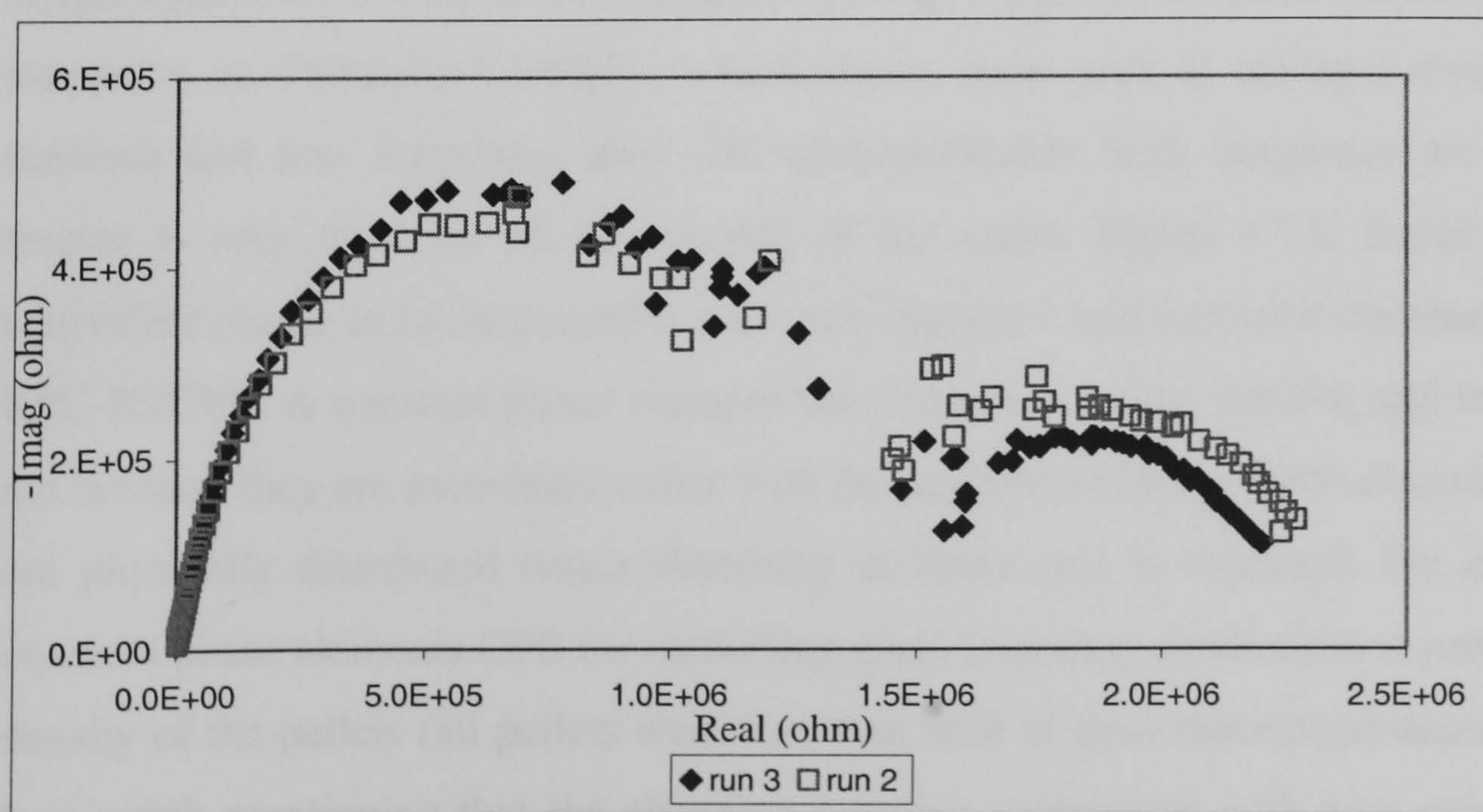


Figure 4-21. Reproducibility test using graphite electrode with identical cell geometry

The second test used involves reassembling the electrolyte-electrode interface; this was carried out to check the effect of electrode contact on the impedance plot. Figure 4-22 indicates that the resistive component of the Nyquist plot is stable even when the contact changes, i.e. reinserting the pellet into the sample holder with the graphite plates will give different contact with each attempt. However the capacitive component of the grain boundary conduction and electrode blocking effect changes as the sample contact varies. Therefore due to inherent effect of bad electrode contact on the medium and low frequency arc, only the high frequency arc is used for bulk conductivity measurement.

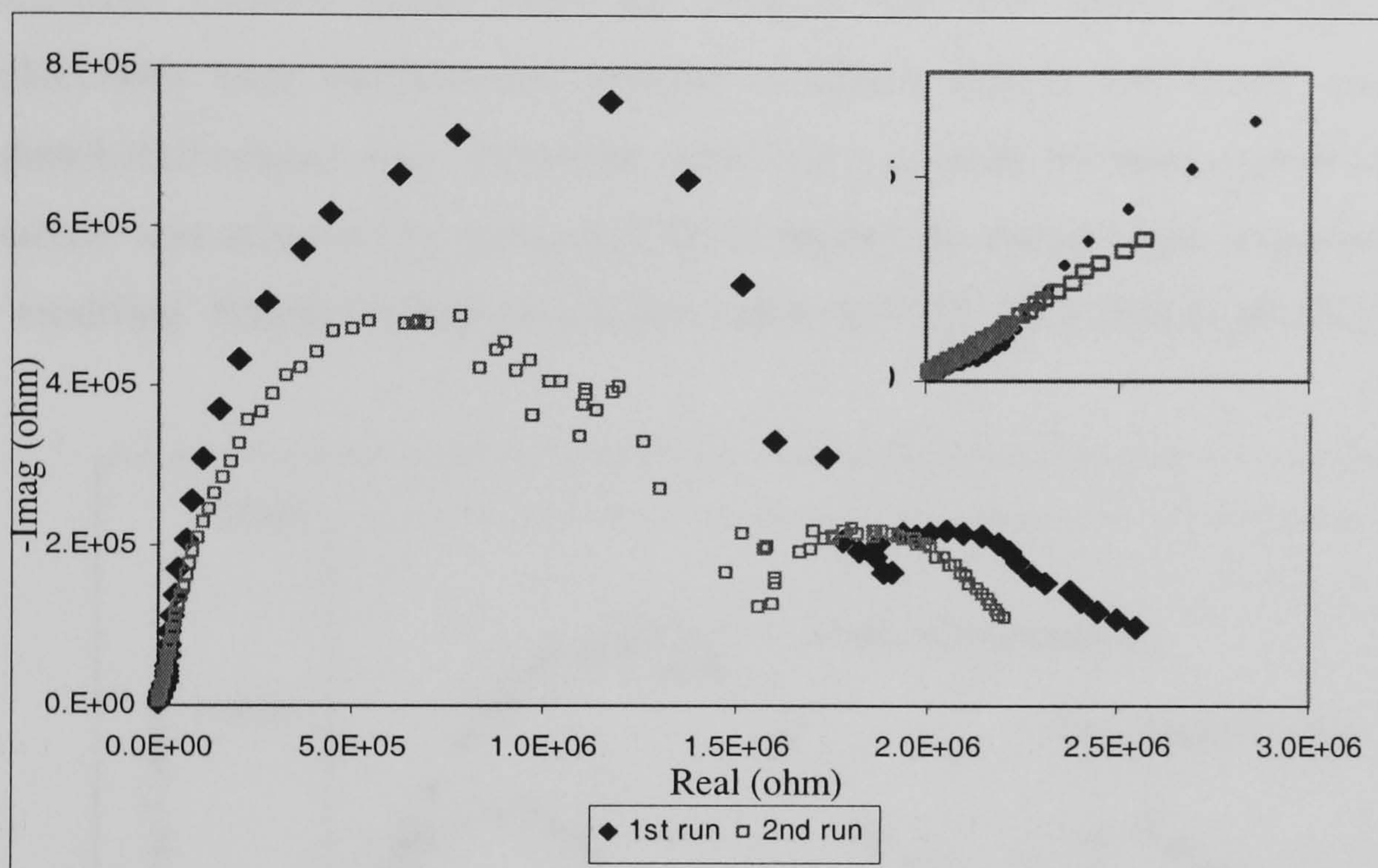


Figure 4-22. Reproducibility test using graphite electrode with different cell geometry

4.3.8 Equivalent circuit modelling for CaNd_2S_4 series with graphite electrodes

Nyquist plots for CaNd_2S_4 series exhibit two arcs (high and medium frequency arcs) with the exception of $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$, which shows three arcs at elevated temperatures (high, medium and low frequency arc). The distinguishable high frequency arc (closest to the origin) is very clear for all compounds of the series, Figure 4-23, therefore the simplest equivalent circuit to be employed is a resistor-capacitor and a resistor-constant phase element, $R//C-R//CPE$. A constant phase element was chosen to model the low and middle frequency arc because they are associated either with the grain boundaries or the electrode contact, both are physically distributed hence flattening of these arcs is expected. For example using a constant phase elements CPE for modelling grain boundary conduction is justified by the low density of the pellets (all pellets were less than 95% of their theoretical densities, Table 4.2). It is worth mentioning that the changing resistive component with zero capacitance change effect, seen with gold electrodes at low frequencies was not observed with the graphite

electrodes, which confirms that the low frequency phenomena is attributed to the gold-electrolyte interface.

The fit between the experimental and Bauerle model for $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ is shown in Figure 4-23 and Figure 4-24. Since $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ is the only compound in the CaNd_2S_4 series which has a distinct low frequency arc using either gold or graphite electrode, Figure 4-12 and Figure 4-23. This electrode effect is characteristics feature for pure ionic conductors, hence this compound, based on experimental evidence, and is an ionic conductor. Classical Bauerle model takes the form of $R//C-R//C-R///C$, however since the graphite electrodes were mechanically pressed to obtain pellets, this would also cause a physical distributed contact area. Therefore achieving a good fit between experimental and equivalent circuit was achieved by using $R//CPE$ to model the distinct low frequency arc, therefore the ‘modified’ Bauerle model used is $R//C-R//C-R//CPE$, for $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$.

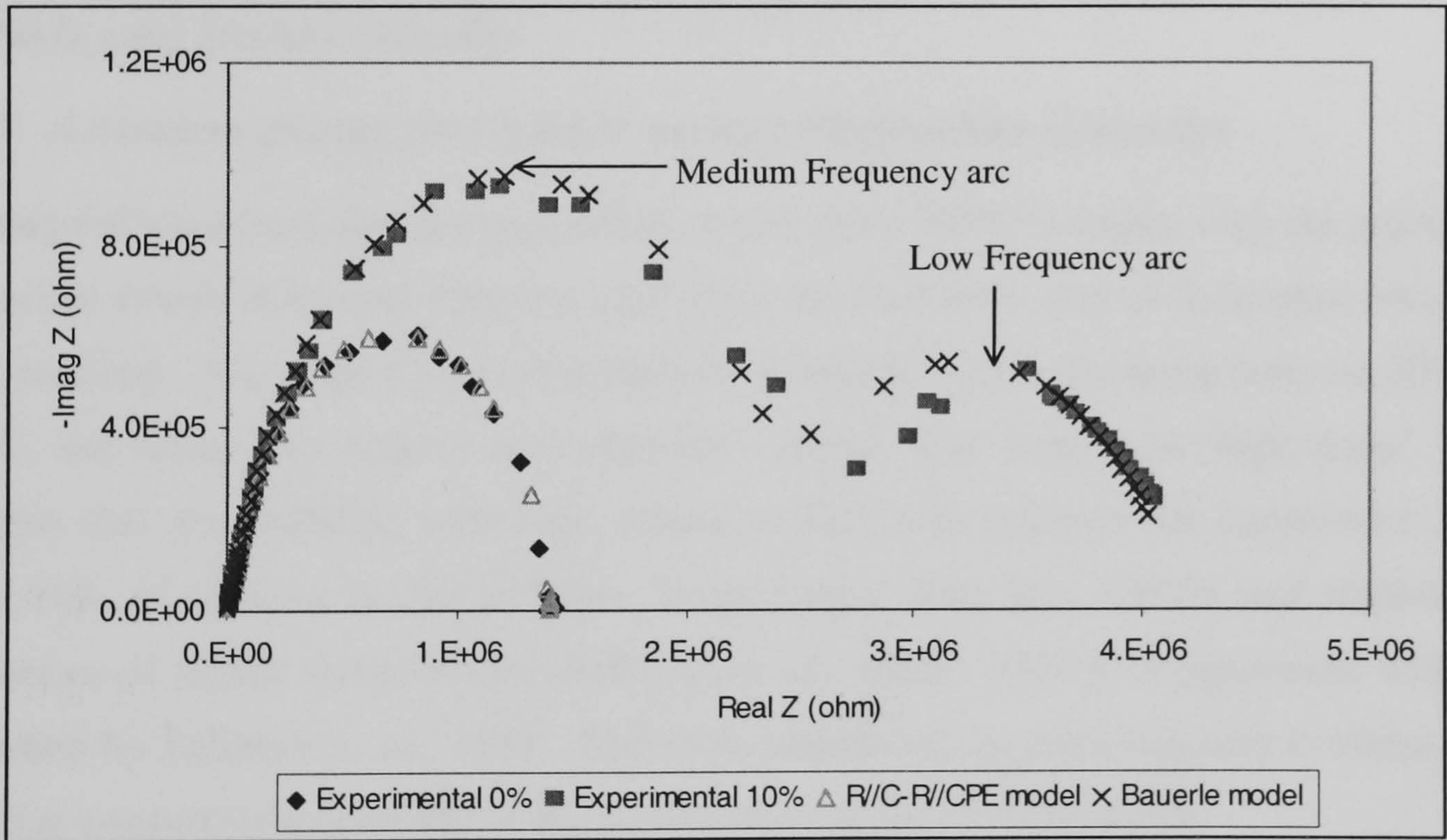


Figure 4-23. Nyquist Modelled and experimental results for CaNd_2S_4 and $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ using graphite electrodes

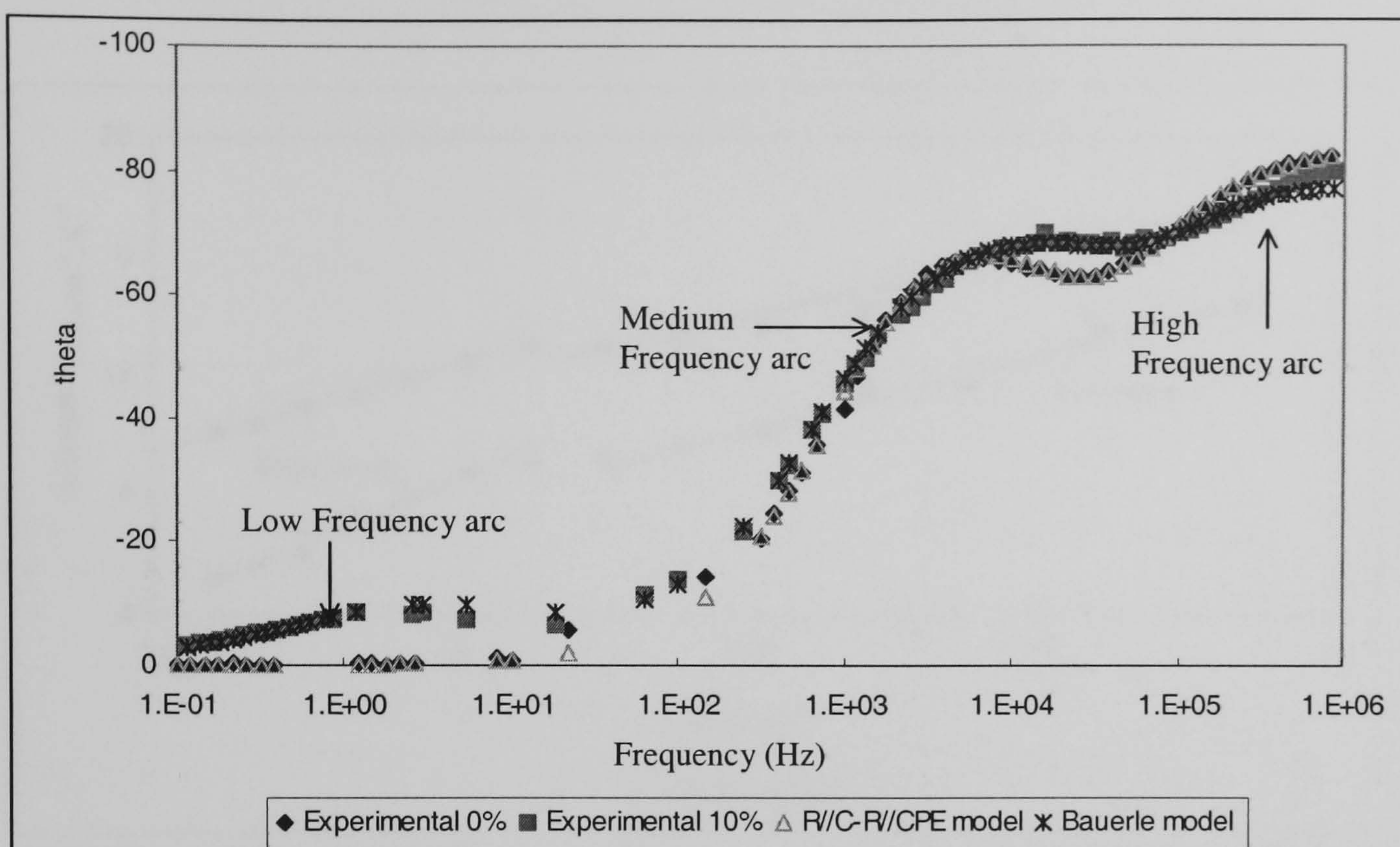


Figure 4-24. Bode plot of modelled and experimental results for CaNd_2S_4 and $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$ using graphite electrodes

4.3.9 Activation energy for CaNd_2S_4 series with graphite electrodes

Varying the impedance spectroscopy temperatures up to 500°C in argon, with the appropriate equivalent circuit and using equation (11) gives the Arrhenius plot of activation energy for ionic hopping. The slope of the Arrhenius plot in Figure 4-25 is not linear between 50°C and 450°C , but rather two regions are observed, coined, 'low temp' and 'high temp'. This suggests that the CaNd_2S_4 series are mixed calcium and sulphide ion conductors, where conduction of calcium occurs at lower temperatures (less than 450°C) and sulphide ion conduction at higher temperatures, Kalinina *et. al.*, 1995. This is in agreement with data published by Kalinina *et. al.*, 1995. Therefore impedance spectroscopy also confirms more than one conducting species due to the non-linearity of the Arrhenius plot.

The graph shows slight scattering of data points in the low temperature region; this is attributed to the difficulty in collecting reliable data at these very low conductivities. Activation energies listed in Table 4.9 are collected from the higher temperatures.. Since the non-linear Arrhenius plot using either graphite or gold electrode indicates more than one conducting species.

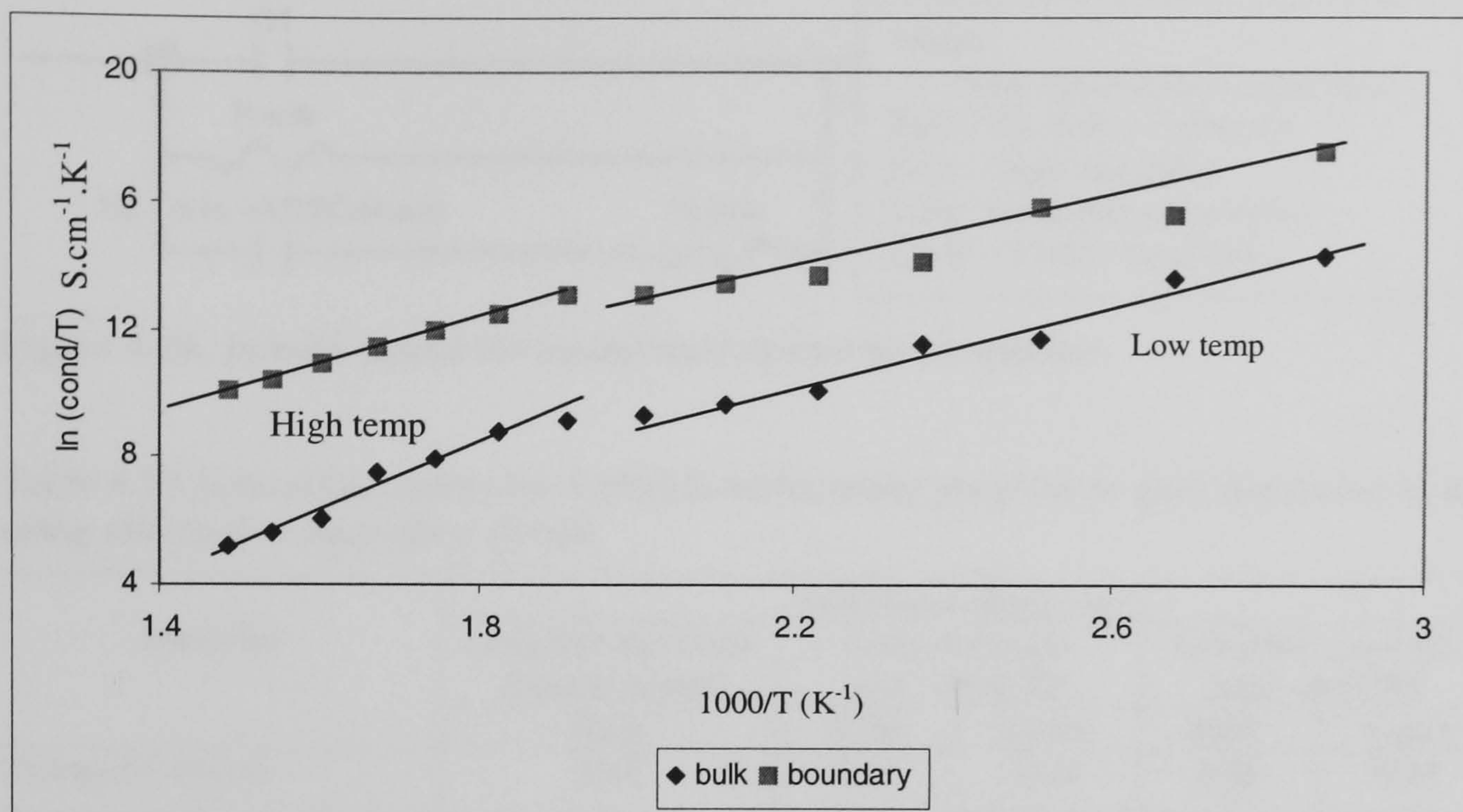


Figure 4-25. Typical Arrhenius plot doped for CaNd_2S_4 with graphite electrodes using RC/RCPE equivalent circuit

Using graphite electrodes resulted in a maximum activation energy of 0.97eV for $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ while gold electrodes resulted in a maximum activation energy of 1.02eV for undoped- CaNd_2S_4 . The activation energy is clearly dependent on the electrode material used, Table 4.10. Also while the activation energies and bulk conductivities obtained with gold electrodes decreases as the dopant concentration was increased from 0% to 20mol%, graphite electrodes shows increased activation energy (to a maximum) with increasing dopant concentration. Therefore the mismatch between activation energy between gold and graphite electrodes with CaNd_2S_4 series could be related to the reaction between gold and the electrolyte. No activation energy could be collected for the 30% doped compound with gold electrodes, due to significant scattering of the impedance data. The thermally evaporated gold electrode on $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ was discoloured to reddish-brown when stored at room temperature indicating a reaction between the electrolyte and gold. See Appendix D.

The activation energy for the CaNd_2S_4 series was also sensitive to the equivalent circuit. For example, using Jamnik equivalent circuit, Figure 4-26, for mixed ionic-electronic conductors, identifies the minimum activation energy at 10mol%, while the R//C-R//CPE model results in a maximum activation energy at 20mol%, Table 4.10. A minimum activation energy as a function of doping is observed for many high temperature solid oxide ion-conducting electrolytes, typically between 5mol% and 10mol%, H. Inaba and H. Tagawa, 1996, but with higher absolute values for activation energy.

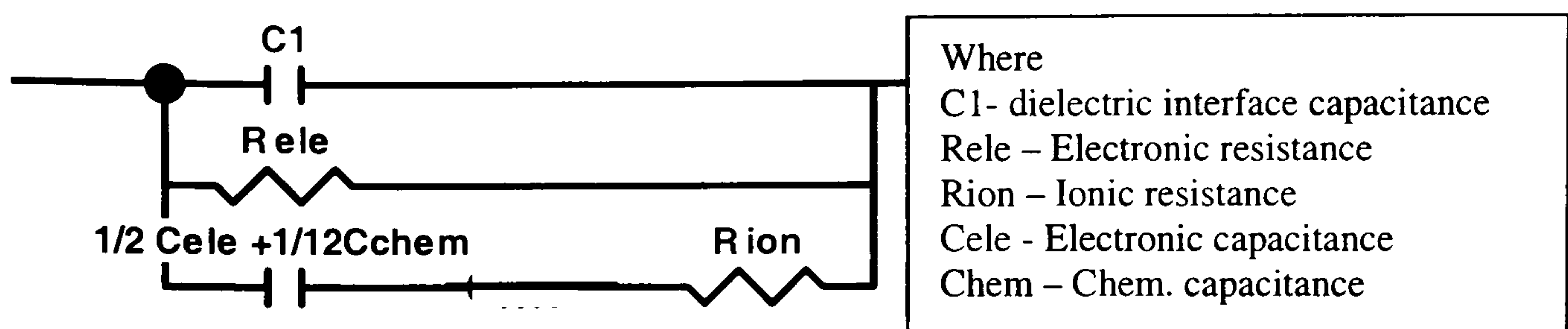


Figure 4-26. Jamnik model for mixed ionic-electronic conductor

Table 4.10 Activation energy for CaNd_2S_4 series using graphite or gold electrodes in argon, using alternative equivalent circuit

Material	Activation energy (eV)				
	Graphite electrode Jamnik model	Gold electrode R//C –R//CPE		Graphite electrode R//C –R//CPE	
	Bulk	Bulk	Grain	Bulk	Grain
Undoped CaNd_2S_4	0.43	1.02	0.44	0.48	0.45
$\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$	0.23	0.44	0.59	0.62	0.54
$\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$	0.46	0.12	0.48	0.97	0.49
$\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$	0.65	NA	NA	0.64	0.70

N/A - not available

Considering the high temperature region only, the largest activation energies values for bulk conduction for the CaNd_2S_4 series occurs when using graphite electrodes and R//C-R//CPE equivalent circuit, Table 4.10, shows a range of 0.97eV to 0.48eV with a maximum of 0.97eV for 20% doped. Since the sulphide ion is larger than the oxide one, it approximately would be expected that the activation energy for ionic hopping would be larger. However, the activation energy for ionic conduction varies not only with size of ion, but also with dopant, crystal structure, as well as synthesis method. For example Bi_2O_3 is known to have one of the largest oxide ion conductivities, and its activation energy varies from 0.7 to 1.4eV depending on whether the dopant used is Pb^{2+} or Ca^{2+} (Pb^{2+} was the better dopant), Drache *et. al.*, 1992.

Another well-researched pure oxide ion conductor is YSZ, and its activation energy lies at (or near to, depending on choice of reference) 1.25eV. Cerium oxide is a mixed ionic-electronic conductor, with oxide ion conductivity dominating at high oxygen partial pressure, and its activation energy when doped with Ytria varies from 0.75eV to 1.1eV (depending on the quantity of dopant); for gadolinia doped ceria the activation energy is 0.71eV, Tschöpe *et. al.* 2001. Since the range of activation energies for anionic conduction for these oxides lies between 0.71-1.25eV, then the low activation energies for CaNd_2S_4 series indicates the possibility of mixed ionic-electronic conduction.

Activation energy for sulphide ion conduction has not been researched much in the literature, even though some attempts were made to synthesize sulphide ion conductor. Most recently . Kalinina *et. al.* 1995 reported predominant sulphide ion conduction in doped CaNd_2S_4 based compounds, with no mention on the activation energy. Calcium sulphide has a defect structure and theoretical calculations of its activation energy show that sulphide ion conductors are likely through conduction of interstitial S^{2-} with an activation energy of 1.96eV which is higher than the experimental value of 1.21eV, Otowa *et. al.*, 1980. CaS vacancies are introduced thermally and a significant proportion of the activation energy could be attributed to the association enthalpy, which for oxides lies in the range of 0.3-0.5eV. In CaNd_2S_4 sulphide systems the vacancies are created by doping rather than thermally and the activation energy for sulphide ion conduction is likely to be within 0.61-1.66eV, using available literature and equation (14);

$$E_{\sigma} = E_m + E_a \quad (14)$$

Where E_{σ} = measured activation energy (apparent), eV [1.96-1.21, Pandey, 1984, Otowa *et. al.*, 1979]

E_m – ionic migration activation energy, eV

E_a – association enthalpy, eV, [0.3eV, 0.5eV; Tschöpe *et. al.*, 2001, Nowick and Liang 2000]

All activation energies for the doped CaNd_2S_4 compound are within this range, and hence it is possible that conduction is via sulphide ions, however the undoped system has a somewhat lower activation energy outside the expected range. It is possible that the undoped electrolyte is a calcium ion conductor since the presence of neodymium ions creates equal amounts of calcium and sulphide ion defects. The absence of an ion-blocking arc in the Nyquist plot indicates the presence of electron or hole conduction.

4.3.10 Effect of equivalent circuit modelling on derived parameters

The derived parameters, time constant and bulk conductivity, depend on the absolute values of resistance and capacitance that are the outputs of equivalent circuit modelling. Initial modelling using R//C-R//CPE or R//C-R//C for two arcs type Nyquist plots and Bauerle for three arcs type Nyquist plots gave good fit between experimental and modelled data, Figure 4-23 and Figure 4-24.

However a slight improvement was achieved using Jamnik predominant ionic (mixed with electronic conduction) equivalent circuit with the derived bulk parameters or conductivity and time constant changing significantly compared to the previous Randles or Bauerle equivalent circuit.

Kalinina *et. al.*, 1995, reported that all the doped CaNd_2S_4 compounds had conductivities at 500°C between 10^{-7} and 10^{-6}S.cm^{-1} with $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ having the maximum conductivity of $1.15 \times 10^{-6}\text{S.cm}^{-1}$ as having the highest conductivity. However the equivalent circuits used to model impedance spectroscopy yield much higher conductivities, Table 4.11.

Table 4.11. Time constant and bulk conductivity derived from R//C-R//CPE, Bauerle and Jamnik equivalent circuits

	R//C-R//CPE equivalent circuit		Jamnik equivalent circuit	
Material	<i>Bulk conductivity @ 500 °C</i>	<i>Time constant @ 250 °C</i>	<i>Bulk conductivity @ 500 °C</i>	<i>Time constant @ 250 °C</i>
Undoped CaNd_2S_4	7.05×10^{-7}	1.27×10^{-5}	2.19×10^{-8}	5.59×10^{-5}
$\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$	$4.26 \times 10^{-4*}$	$7.56 \times 10^{-6*}$	1.09×10^{-6}	1.03×10^{-3}
$\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$	2.51×10^{-3}	4.40×10^{-5}	3.09×10^{-5}	1.78×10^{-3}
$\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$	3.19×10^{-4}	3.07×10^{-5}	1.85×10^{-5}	1.22×10^{-3}

*Based on Bauerle equivalent circuit; Conductivity is quoted at 500°C because of reference data is quoted at this temperature, Kalinina *et. al.*, 1995; Time constant is quoted for YSZ at 250°C , M^cDonald, 1981.

The Jamnik mixed ionic-electronic equivalent circuit identifies $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ with a bulk conductivity of $1.09 \times 10^{-6}\text{S.cm}^{-1}$ agreeing with Kalinina bulk conductivity determined through galvanic cells. However all other bulk conductivities were several orders of magnitude larger than the ones obtained by Kalinina galvanic cell method. The Kalinina galvanic cell used Ca, CaNd_2S_4 and Fe, FeS, CaNd_2S_4 discs adjacent to the electrolyte and the carbon electrode, as ionic sources and sinks for Ca, Nd and S. These disks are not electronic conductors therefore there experimental method would not allow the conduction of electrons, and as such the possibly low bulk conductivities.

The time constant for bulk conduction also varies by several orders of magnitude depending on the model used, Table 4.11. The constant using the traditional equivalent circuits, R//C-R//CPE or Bauerle, gave similar time constant to YSZ of approximately 10^{-6}s at comparable temperature for $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$. However the other doped compounds have larger time

constants, by an order of magnitude. Using Jamnik equivalent circuit, time constant for bulk conduction was several orders of magnitude larger than YSZ at similar temperature, Table 4.11 and Table 4.7.

If the basic assumption that a larger ion moves slower than a smaller, then both models identify the conducting species to be at least similar in size to the oxide ion if not larger due to the significantly larger time constants for doped CaNd_2S_4 compounds.

4.3.11 Effect of electrode material on time constant and bulk conductivity for CaNd_2S_4 series

Time constant

Impedance measurement up to 400°C with graphite electrodes in argon gave repeatable results unlike gold electrodes, therefore the impedance data using graphite electrodes should give conductivity and time constants for the bulk properties of the electrolyte. The similar time constants of all doped compounds in the CaNd_2S_4 series using graphite electrode suggest similar conducting species, while the small time constant for the undoped compound may indicate electronic or hole conduction, Table 4.12.

The time constants for bulk conduction in doped CaNd_2S_4 compounds using gold electrodes were significantly smaller than those for oxide ion conduction in YSZ, Table 4.7. The small time constants for gold-coated CaNd_2S_4 support the proposed reaction mechanism, in equation (13), of a gold-electrolyte interaction rather than the bulk properties of the electrolyte.

The time constant, using graphite electrodes, for the second lower frequency, 6.08×10^{-4} s to greatly exceeds the time constant for electrode response for YSZ of 1 s @250°C. Since the time constants the second arc for all CaNd_2S_4 compounds are too small to be related to ionic blocking electrode therefore it must relate to a material property, namely grain boundary conduction. The presence of the third arc, which unambiguously identifies a pure ionic conductor, occurs only with $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$. Therefore the other members of this series are at best predominant ionic conducting conductors.

Table 4.12. Time constant analysis for CaNd₂S₄ series with gold and graphite electrode with R//C-R//CPE equivalent circuit at 250°C

Undoped CaNd ₂ S ₄					
GOLD - R//C-R//CPE			GRAHITE - R//C-R//CPE		
Bulk	Grain boundary		Bulk	Grain boundary	
R _{gi} = 5.4x10 ⁵ Ω	R _{gb} = 2.4x10 ⁶		6.0x10 ⁶	2.5x10 ⁵	
C _{gi} = 6.1x10 ⁻¹¹	C _{gb} = 2.5x10 ⁻¹⁰ F		1.4x10 ⁻¹⁰	1.8x10 ⁻¹⁰	
	ψ _e =0.91		ψ _e =1	0.93	
τ = 3.3x10 ⁻⁵ s	τ = 2. 8x10 ⁻⁴ s		τ = 2.1x10 ⁻⁵ s	τ = 8.4x10 ⁻⁴ s	
CaNd ₂ S ₄ +0.1Nd ₂ S ₃					
GOLD - R//C-R//CPE-R//CPE			GRAPHITE - R//C-R//CPE-R//CPE		
Bulk	Grain boundary	Electrode	<i>Bulk</i>	Grain boundary	Electrode
R _{gi} = 1.7x10 ⁴ Ω	R _{gb} = 3.5x10 ⁴	R _e = 1.6x10 ⁵	R _{gi} = 3.4x10 ⁴	R _{gb} = 5.7x10 ⁶	R _e = 2.58x10 ⁶
C _{gi} = 3.0x10 ⁻¹¹	C _{gb} = 3.9x10 ⁻⁸	C _e = 1.9x10 ⁻⁷	C _{gi} = 1.2x10 ⁻¹⁰	C _{gb} = 3.2x10 ⁻¹⁰	C _e = 1.42x10 ⁻⁷
	ψ _{gb} = 0.64	ψ _e = 0.74		ψ _{gb} = 0.87	ψ _e = 0.71
τ _{gi} = 5.0x10 ⁻⁷ s	τ _{bg} = 3.3x10 ⁻⁵ s	τ _e = 8.7x10 ⁻³ s	τ _{gi} = 3.3x10 ⁻⁶ s	τ _{gb} = 6.08x10 ⁻⁴ s	τ _e = 2.4x10 ⁻¹ s
CaNd ₂ S ₄ +0.2Nd ₂ S ₃ (300°)					
GOLD – R//C-R//CPE			GRAPHITE - R//C-R//CPE		
Bulk		Grain boundary	Bulk		Grain boundary
R _{gi} = 9.1x10 ²		R _{gb} = 4.6x10 ³ Ω	R _{gi} = 1.3x10 ⁵		R _{gb} = 6.3x10 ⁶
C _{gi} = 1.01x10 ⁻¹⁰		C _{gb} = 1.47x10 ⁻⁹ F	C _{gi} = 3.4x10 ⁻¹⁰		C _{gb} = 7.3x10 ⁻¹⁰
ψ _{gi} = 1.0		ψ _{gb} = 0.85	ψ _{gi} = 1.0		ψ _{gb} = 0.83
τ _{gi} = 9.98x10 ⁻⁸ s		τ _{bg} = 8.8x10 ⁻⁷ s	τ _{gi} = 4.4x10 ⁻⁵ s		τ _{bg} = 1.6x10 ⁻³ s
CaNd ₂ S ₄ +0.3Nd ₂ S ₃					
		GRAPHITE - R//C-R//CPE			
		Bulk		Grain boundary	
		R _{gi} = 2.1x10 ⁵		R _{gb} = 9.9x10 ⁶	
		C _{gi} = 1.7x10 ⁻¹⁰		C _{gb} = 5.5x10 ⁻¹⁰	
		ψ _{gi} = 1.0		ψ _{gb} = 0.86	
		τ _{gi} = 3.1x10 ⁻⁵ s		τ _{bg} = 2.43x10 ⁻³ s	

Bulk Conductivity

The bulk conductivity reaches a maximum at $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ irrespective of the choice of electrode or equivalent circuit, Table 4.11. The conductivity of $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ and $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ using impedance is significantly greater than that the previously reported conductivities (10^{-7} to $10^{-5} \text{ S.cm}^{-1}$), Kalinina *et. al.*, 1995.

Impedance with graphite electrodes proves that the significant increase in conductivity with increasing dopant levels, and using gold electrode was in fact related to the electrolyte interface rather than bulk properties of the material, Table 4.13.

Table 4.13 Relationship between equivalent circuit and bulk conductivity calculated at 500°C for the CaNd_2S_4 series with gold and graphite electrodes using Bauerle Equivalent circuit

Material	Model	Bulk conductivity @500°C (Scm^{-1})	
		Gold electrode	Graphite electrode
$\text{CaNd}_2\text{S}_4-0.0\text{mole}\%\text{Nd}_2\text{S}_3$	R//C –R//CPE	1.67×10^{-2}	1.78×10^{-6}
$\text{CaNd}_2\text{S}_4-10.0\text{mole}\%\text{Nd}_2\text{S}_3$	R//C –R//CPE – R//CPE	1.55×10^{-5}	1.56×10^{-6}
$\text{CaNd}_2\text{S}_4-20.0\text{mole}\%\text{Nd}_2\text{S}_3$	R//C –R//CPE	5.75×10^{-2}	2.54×10^{-5}
$\text{CaNd}_2\text{S}_4-30.0\text{mole}\%\text{Nd}_2\text{S}_3$	R//C –R//CPE	NA	1.30×10^{-6}

Doping Ca^{2+} of 0.99Å diameter with Nd^{3+} of similar diameter, 0.995Å, seems appropriate since research has shown that doping with similar ionic radius is an important prerequisite to improve ionic conductivity. For example improving the ionic conductivity of CeO_2 was achieved by using Ca^{2+} , Yahiro *et. al.*, 1989, or Sm^{3+} , Eguchi *et. at.*, 1992, since both dopants have similar radius as the host cation (0.99Å). Using similar diameter of host relative to dopant ion, results in minimizing the association enthalpy between dopant ion and vacant site, Inaba and Tagawa, 1996. Apparently this association enthalpy is more pronounced for smaller dopant cation relative to the host cation, Kilner, 1983.

Using graphite electrodes, maximum conductivity for CaNd_2S_4 series was achieved at 20mol% even though the minimum activation energy at 0mol% was achieved, agreeing with literature of the mismatch between minimum activation energy and maximum conductivity. Similar observation was made for cerium oxide based electrolytes doped with alkaline earth metals: it has a maximum conductivity between 10 and 20mol%, Yahiro *et. al.*, 1988, 1989 and Wang, *et. al.*, 1981. They noted that maximum conductivity and minimum activation energy did not always coincide at the same dopant concentration, apparently due to the pre-exponential, σ_0 in equation 11. Using data from Cohen *et. al.*, 1981, it seems that pre-exponential factor remains constant a low levels of doping, then a significant increase occurs after the minimum activation energy, and maximum conductivity is achieved at higher

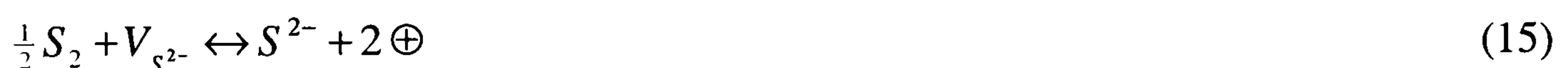
dopant after passing the minimum activation energy. Therefore the mismatch between maximum conductivity and minimum activation energy could be attributed to the concentration dependency of the pre-exponential factor, Inaba and Tagawa, 1996.

4.4 H₂S Concentration dependence of bulk conductivity for CaNd₂S₄ series

Impedance spectroscopy of CaNd₂S₄ series using either gold or graphite in argon did not produce an ionic blocking electrode arc, except 10mol% doped, which is apparently compulsory for pure ionic conductors. Therefore it stands to reason that these compounds are not pure ionic conductors, but possibly mixed ionic-electronic conductors.

The conductivity for a pure ionic conductor is independent of concentration changes in the atmosphere therefore impedance spectroscopy was carried out from 350°C to 550°C with concentration of H₂S/Ar varying from 18vol% to 0.1vol% for each temperature. Using one-hour isothermal period-allowed temperature and concentration stabilization of the sample prior to impedance measurements. Song and Yoo, 2003, have studied BaTiO₃, a mixed-ionic-electronic conductor; they established BaTiO₃ to be an ionic conductor if the ratio $(\partial(\log \sigma_{total})/\partial(\log P_{H_2S})) \leq 0.01$, i.e. the (conductivity change/ concentration change) is considered independent of oxygen partial pressure if the ratio is less than 0.01.

Results for CaNd₂S₄ show that the conductivity is not independent of H₂S concentration, Figure 4-27, but increases with increasing sulphur concentration. The onset of hole conduction may occur at high H₂S concentrations, according to equation (15).



Where

$V_{S^{2-}}$ - sulphide anion vacancy

S^{2-} - sulphur anion in unit cell

\oplus - electron hole

Thus increasing the sulphur partial pressure increases the number of electron holes and therefore increases the conductivity of the electrolyte.

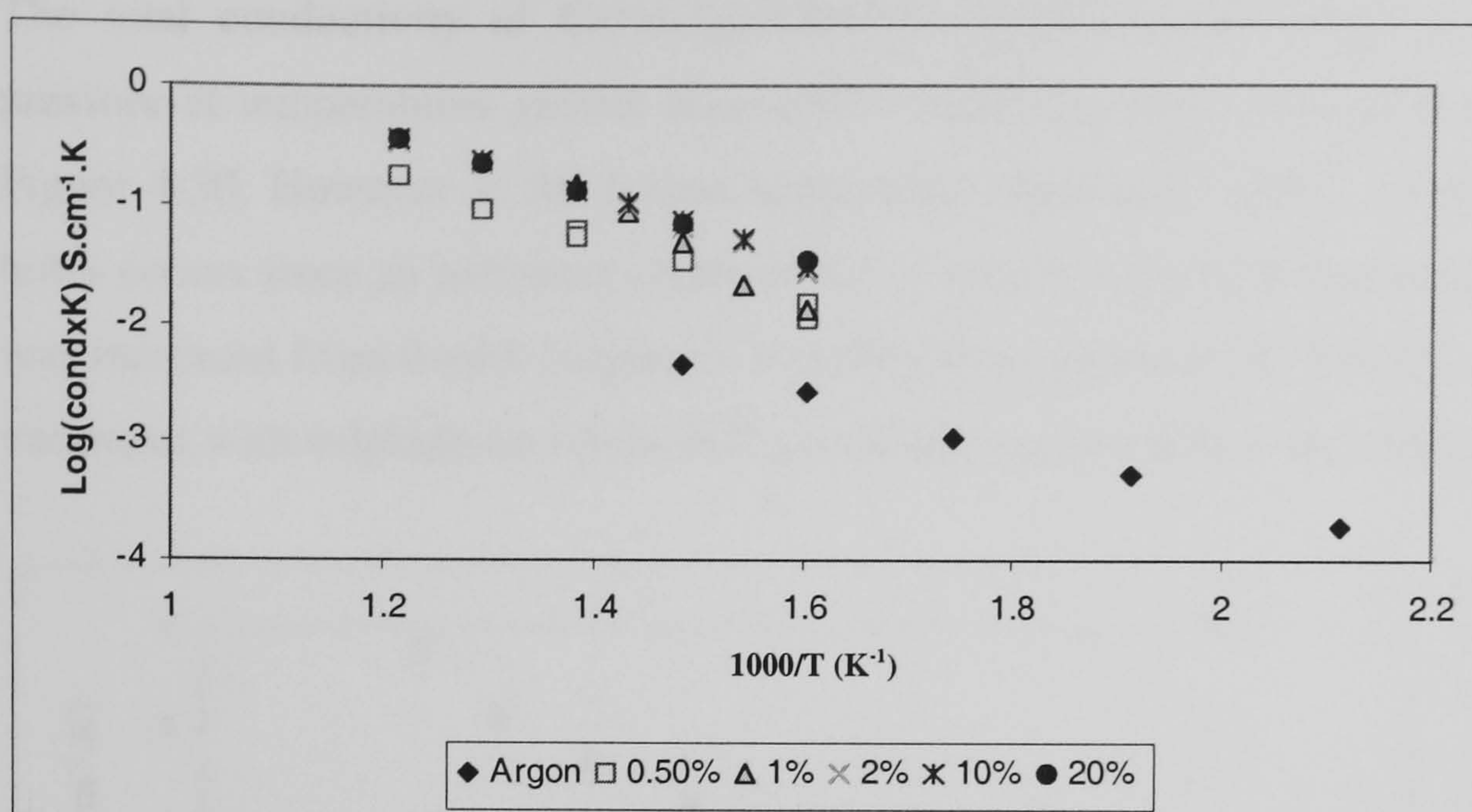


Figure 4-27 Concentration dependence (vol% H₂S) of bulk conductivity vs. temperature for undoped CaNd₂S₄

A plot of total conductivity vs. inverted temperature, $(\log \sigma_{total})$ vs $(\log P_{H_2S})$ for CaNd₂S₄ shows that at temperatures greater than 450°C and H₂S concentration greater than $P_{H_2S} = -2$ or 0.5v/v%, the total conductivity is independent of H₂S, Figure 4-28.

At lower temperatures, the conductivity increases with increasing H₂S concentration, which is indicative of positive hole conduction. Interestingly, hole conduction has been reported to dominate conduction in calcium sulphide at H₂S partial pressures greater than 10⁻⁶kPa,. Worrell, 1976.

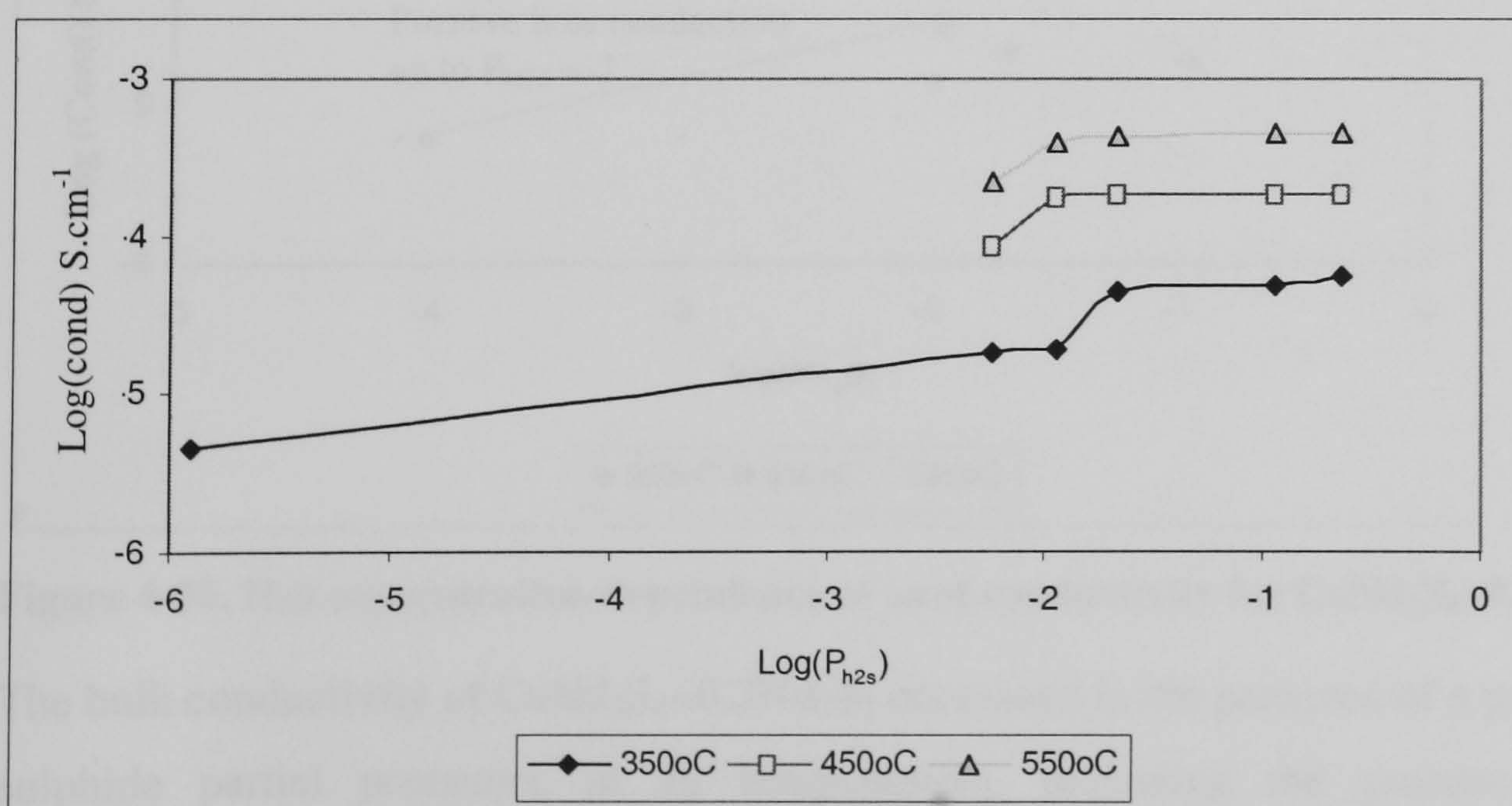


Figure 4-28. H₂S concentration dependence of total conductivity for undoped CaNd₂S₄

The total conductivity of $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ appears to be independent of H_2S partial pressure at temperatures greater than 450°C indicating ionic conductivity, Figure 4-29 and Figure 4-30. However at the lowest temperature measured, 350°C , conduction via positive holes occurs since an increased conductivity occurred as the hydrogen sulphide concentration was increased from 0vol% (argon) to 1vol% $\text{H}_2\text{S}/\text{Ar}$, Figure 4-30. The filling of sulphide ions vacancies with sulphide ions from H_2S producing positive hole is described by equation (15).

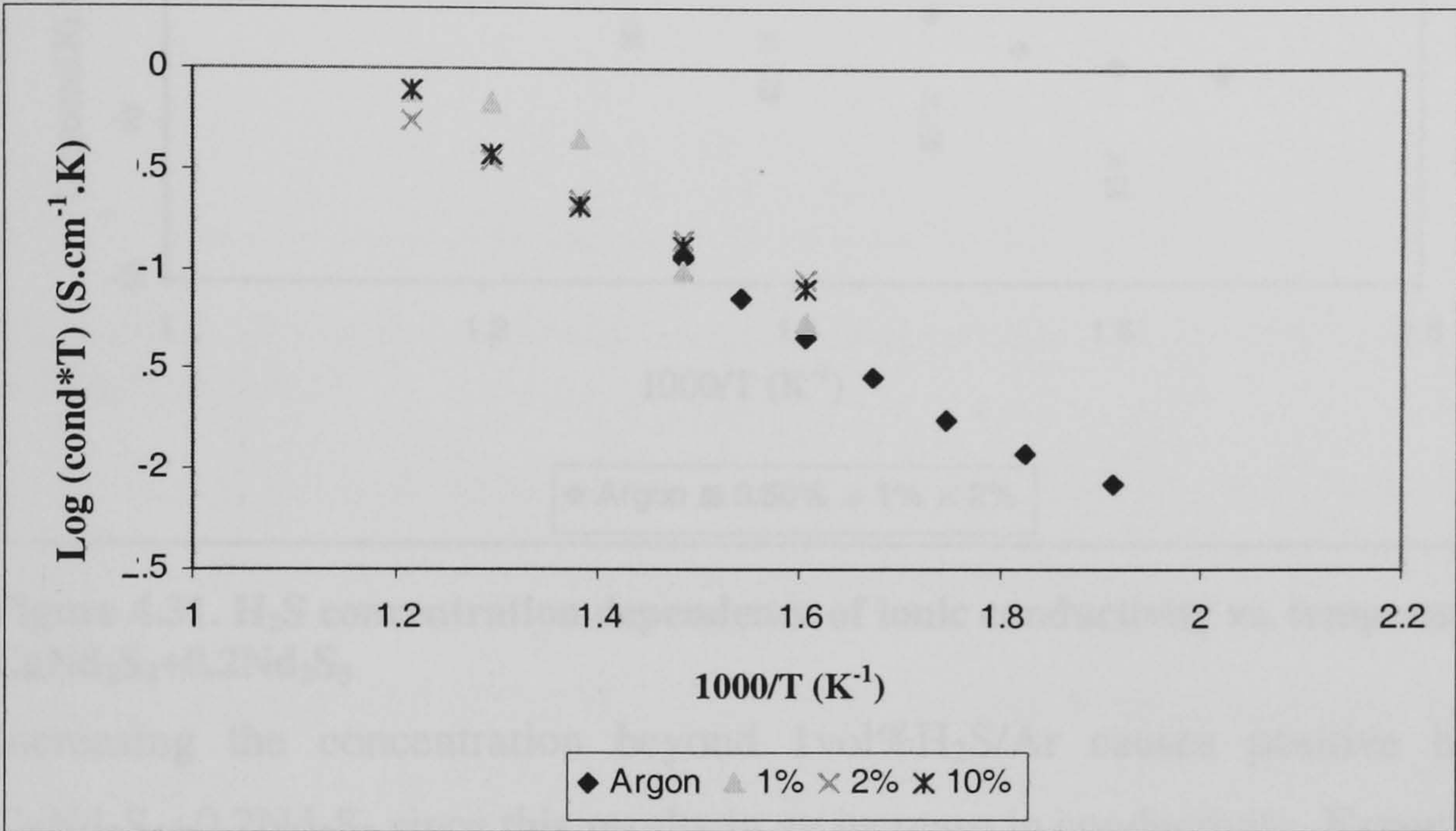


Figure 4-29. H_2S concentration dependence of ionic conductivity vs. temperature for $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$

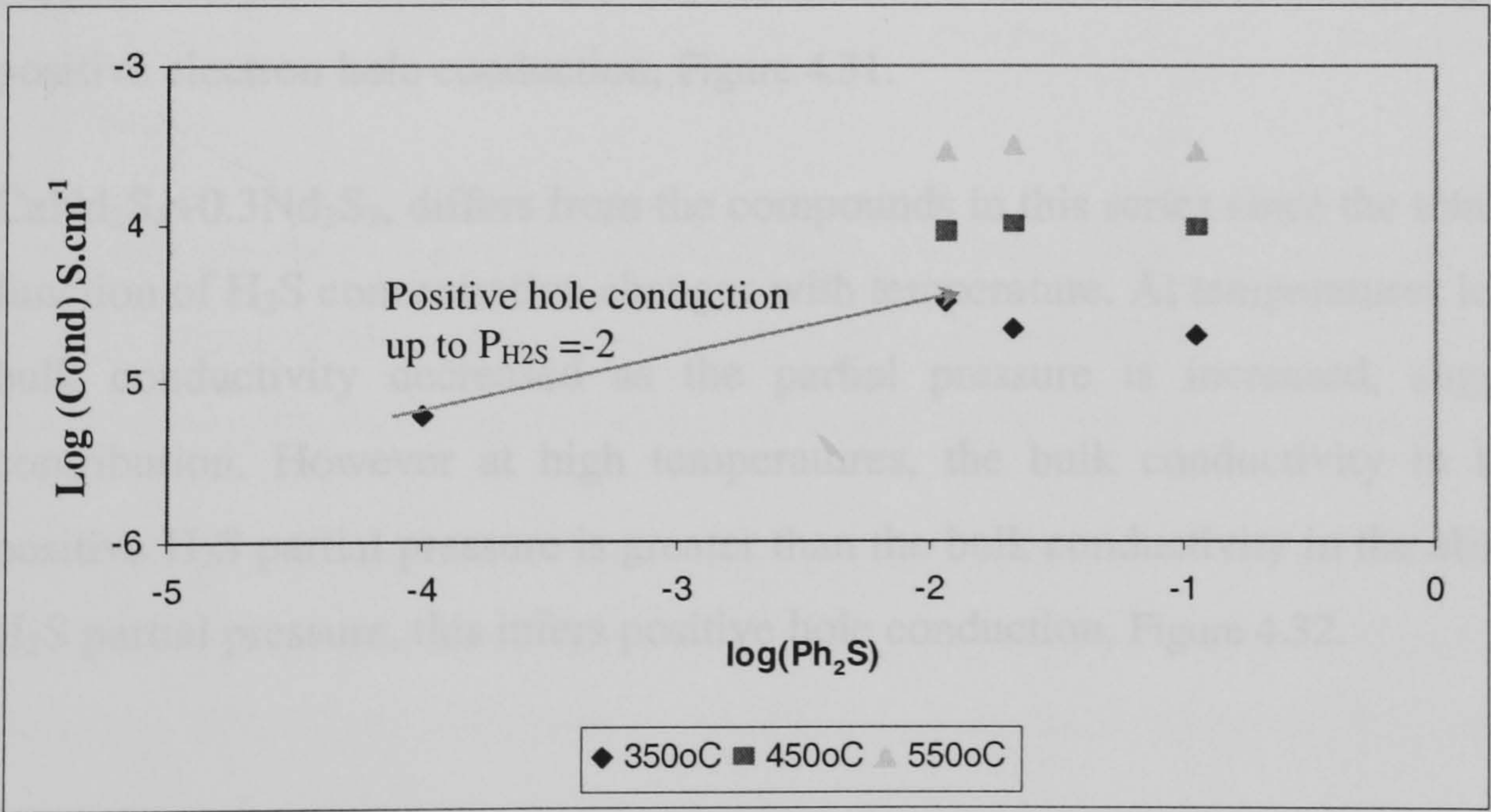


Figure 4-30. H_2S concentration dependence of total conductivity for $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$

The bulk conductivity of $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ decreased in the presence of a positive hydrogen sulphide partial pressures, at all temperatures, indicating the presence of electronic conduction, Figure 4.31. The formation of quasi-free electrons at low partial pressures may be expressed by equation (16).



Where

$V_{S^{2-}}$ - sulphide anion vacancy

S^{2-} - sulphur anion in unit cell

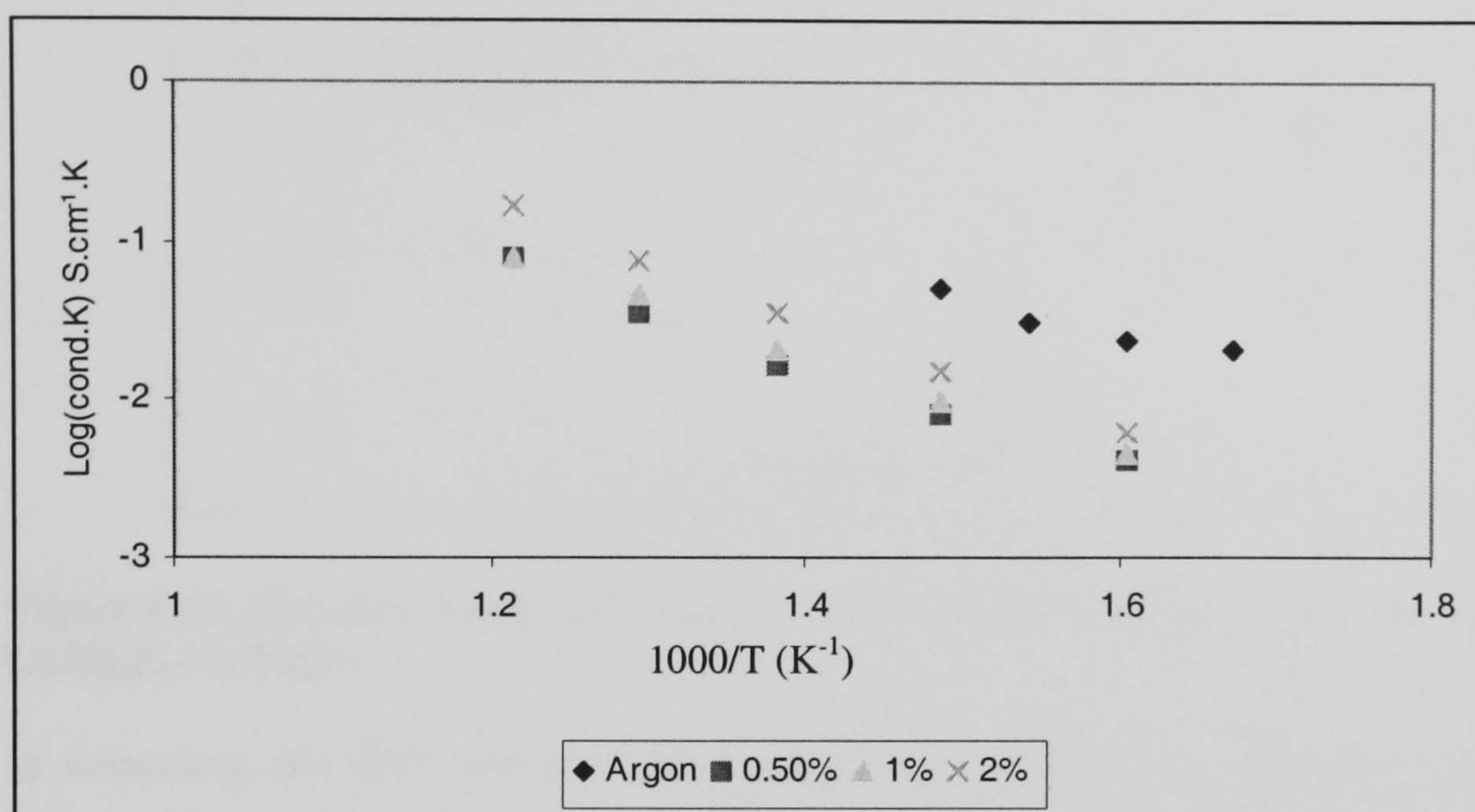


Figure 4.31. H₂S concentration dependence of ionic conductivity vs. temperature for CaNd₂S₄+0.2Nd₂S₃

Increasing the concentration beyond 1vol%H₂S/Ar causes positive hole conduction in CaNd₂S₄+0.2Nd₂S₃ since this results in an increase in conductivity, **Error! Reference source not found.** The formation of positive electron holes at high H₂S is governed by equation (15). Therefore CaNd₂S₄+0.2Nd₂S₃ has inherent electronic conduction, Figure 4.31, as well as positive electron hole conduction, Figure 4.31.

CaNd₂S₄+0.3Nd₂S₃, differs from the compounds in this series since the total conductivity as a function of H₂S concentration changes with temperature. At temperatures less than 450°C, the bulk conductivity decreased as the partial pressure is increased, suggesting electronic contribution. However at high temperatures, the bulk conductivity in the presence of a positive H₂S partial pressure is greater than the bulk conductivity in the absence of a positive H₂S partial pressure, this infers positive hole conduction, Figure 4.32.

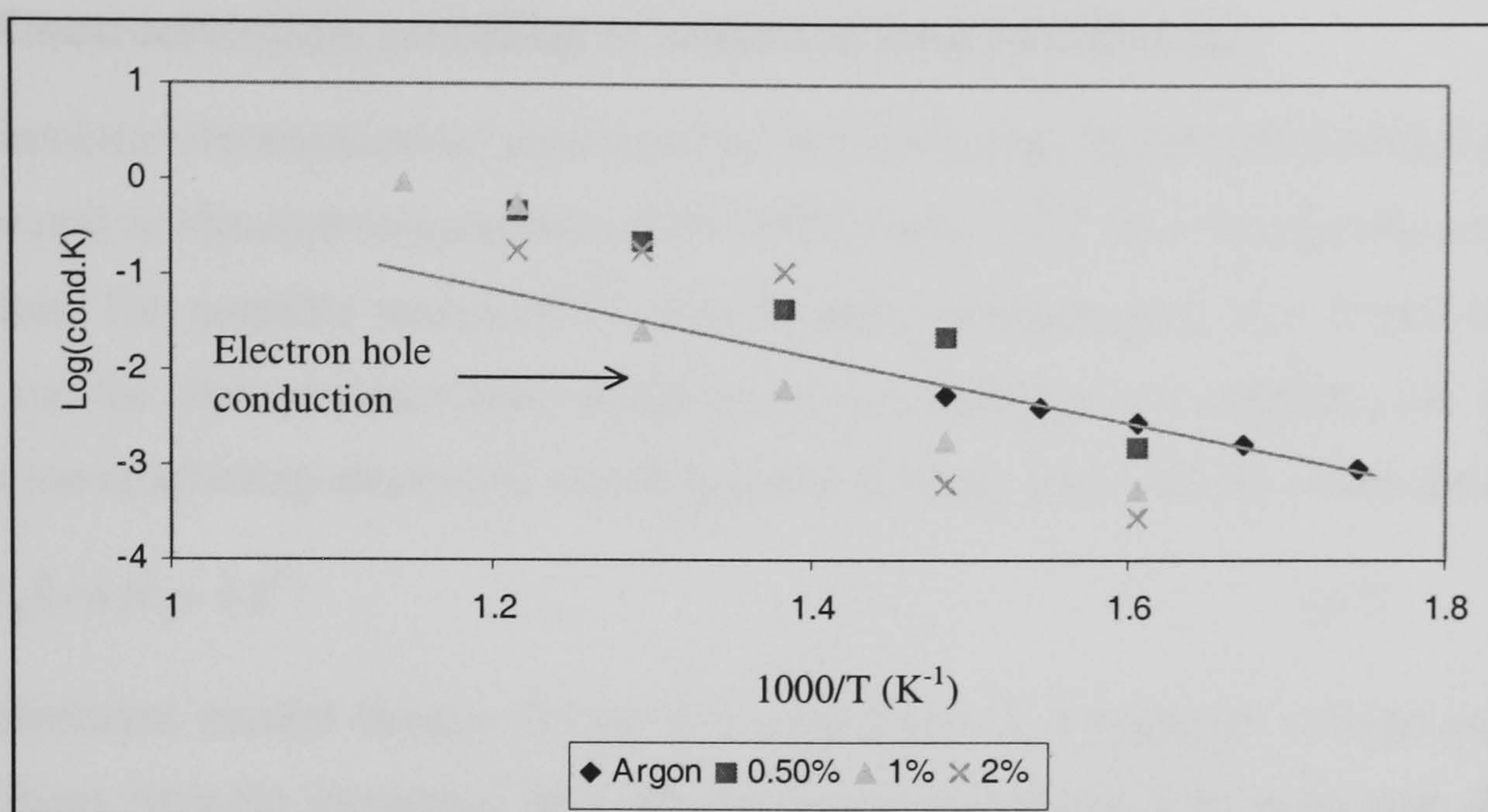


Figure 4.32. H₂S concentration dependence of ionic conductivity vs. temperature for CaNd₂S₄+0.3Nd₂S₃

In summary, the bulk conductivity for undoped CaNd₂S₄ is dependent on H₂S concentration from 0.5vol% to 2vol%H₂S, therefore may be used as a sensor at high H₂S concentration.

The bulk conductivity of CaNd₂S₄+0.1Nd₂S₃, appears to be independent of H₂S concentration from 0vol% to 2vol%H₂S and in the temperature range from 400°C to 500°C. Therefore this electrolyte may find use in application as sensors, electrochemical membranes or even high temperature fuel cells since the conductivity is independent of hydrogen sulphide concentration. At low temperature, the bulk conductivity was controlled by positive hole conduction.

The bulk conductivities CaNd₂S₄+0.2Nd₂S₃, switches between electronic and hole conductor as H₂S concentration changes from 0vol% to 2vol% between 350 to 500°C, therefore this material might prove useful as electrode materials in hydrogen sulphide rich atmospheres.

The bulk conductivity for CaNd₂S₄+0.3Nd₂S₃ appears to be controlled by positive hole conduction at greater than 500°C for all H₂S concentration studied, However at temperatures less than 400°C, the electronic conduction was deduced based on the reduction in the bulk conductivity with increasing temperature.

4.5 Electrochemical pumping of sulphide ions in CaNd_2S_4

The asymmetric electrochemical concentration cell of the type $\text{H}_2\text{S}/\text{H}_2//\text{Pt}/\text{CaNd}_2\text{S}_4/\text{Pt}//\text{Ar}/\text{H}_2$ was operated at elevated temperatures (550-750°C) with 1-2V (d.c) to identify sulphide ion conduction. The constant source of S^{2-} ions formed by application of a negative potential applied on the H_2S compartment, equation (17), conduction of sulphide ion through a sulphide ion conducting electrolyte would generate a steady state current within the cell.



If the generated current decays during the application of a negative voltage on the H_2S compartment, then the movement of a positive ion is interpreted. This is because there is no continuous source of positive ions, only from the electrolyte and as such the peak current could be expressed by equation (18).



Alternatively, a decaying current could also indicate a mixed conductor, the peak current related to the total ionic and electronic, while a reversible steady state current related to the electronic current.

A current flow, which occurs without an applied voltage, would confirm the presence of electronic conduction. Simple EMF measurements of the asymmetric electrochemical concentration cell of the type $\text{H}_2\text{S}/\text{H}_2//\text{Pt}/\text{CaNd}_2\text{S}_4/\text{Pt}//\text{Ar}/\text{H}_2$ should approach zero in if the cell is electronic conducting.

Electrochemical pumping with CaNd_2S_4 gave decaying current generation, Figure 4.33, may indicate that the pumping cell had mixed ionic/electronic conduction. The identical negative and positive peak current suggest that the peak current was independent of H_2S concentration therefore the conducting ionic species could be cationic. The steady state current was relatively comparable with either the application of a cathodic or an anodic voltage and this infers electronic conduction. The cross-sectional resistance, of 257Ω (measured with a FLUKE, 5 decimal place multimeter, at room temperature) prior to the pumping experiment shows that short-circuiting of electrolyte occurred as a result of either the electroding process or cementing of the electrochemical cell rather than a inherent property of the material.

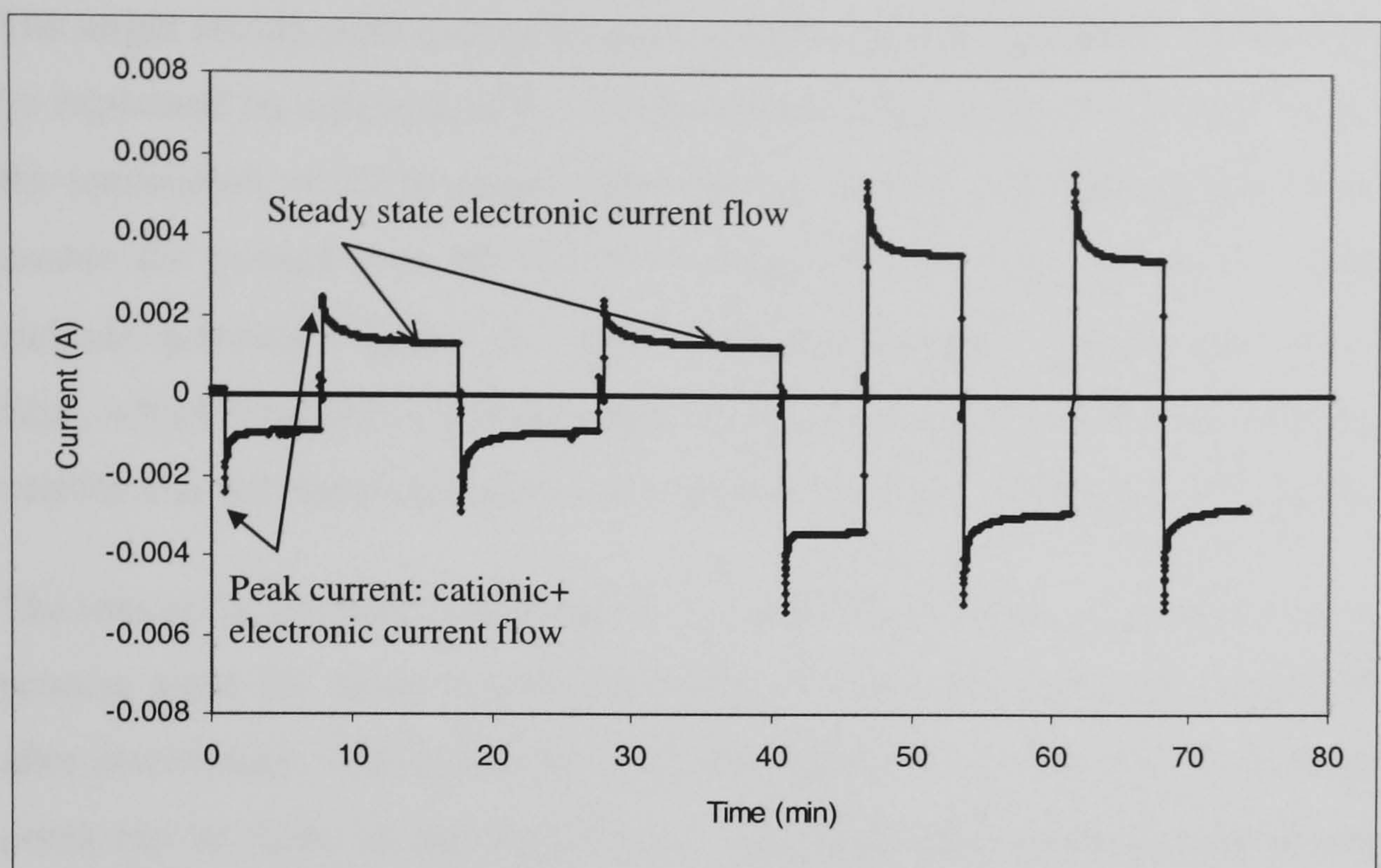


Figure 4.33 Electrochemical pumping of CaNd_2S_4 at 600°C with 1V and 2Vdc

Electrochemical pumping with $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$ also gave decaying current generation, Figure 4-34, which may indicate that the pumping cell had mixed ionic electronic conduction. The height of the negative and positive peak current is identical, suggesting that the peak current could be attributed to the conduction of cations. However a snap shot in time, for example at 15 minutes, after the application of the cell voltage on the H_2S rich reactor compartment, the resulting current was at least 30% greater suggesting conduction of sulphide ions.

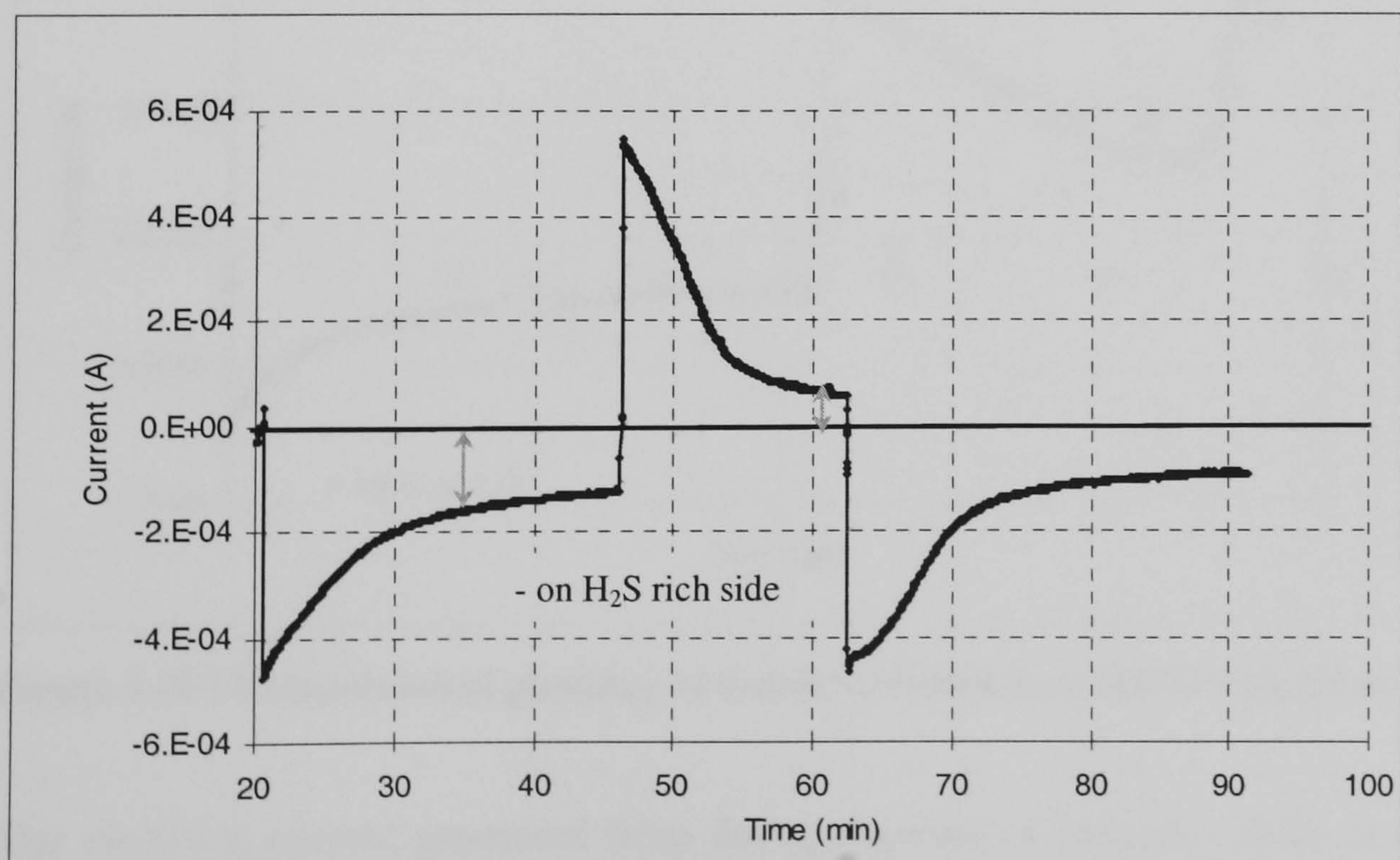


Figure 4-34 Electrochemical pumping of $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$ at 600°C with 5V dc

The larger steady state current generated with a negative potential on the H_2S atmosphere can be explained by equation (17). A current flow after 15mins of $1.6 \times 10^{-4} \text{ A}$ was achieved with the application of 5Vdc anodic potential on the H_2S rich atmosphere which was more than double the current flow of $6.4 \times 10^{-5} \text{ A}$, achieved after 15mins with the application of 5Vdc cathodic potential, Figure 4-34. Also increasing the H_2S partial pressure increased the current flow, which conclusively shows that flow has a anionic component, Figure 4-35. The peak current was not sustainable due to the short-circuiting by electronic conduction.

The reason for the short circuiting of $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$ is most likely due to the electroding process since the cross sectional resistance of the electrolyte decreased $200\text{M}\Omega$ to $0.5\text{M}\Omega$ after electroding. The reason for this contamination was due to flow of binder (organic) into pores (up to $5\mu\text{m}$) in the electrolyte. This high temperature binder would carbonize in a reducing atmosphere hence the resulting carbon could conduct electrical current in the electrochemical experiments. A reduction in the contamination of the pellets of the binder/solvent was achieved by painting with a thick platinum paste (rather than thinned paste) and drying immediately. For example using the thinned paste without hot air drying, the cross sectional resistance was 200Ω compared with $0.5\text{M}\Omega$ achieved using platinum paste and hot air drying.

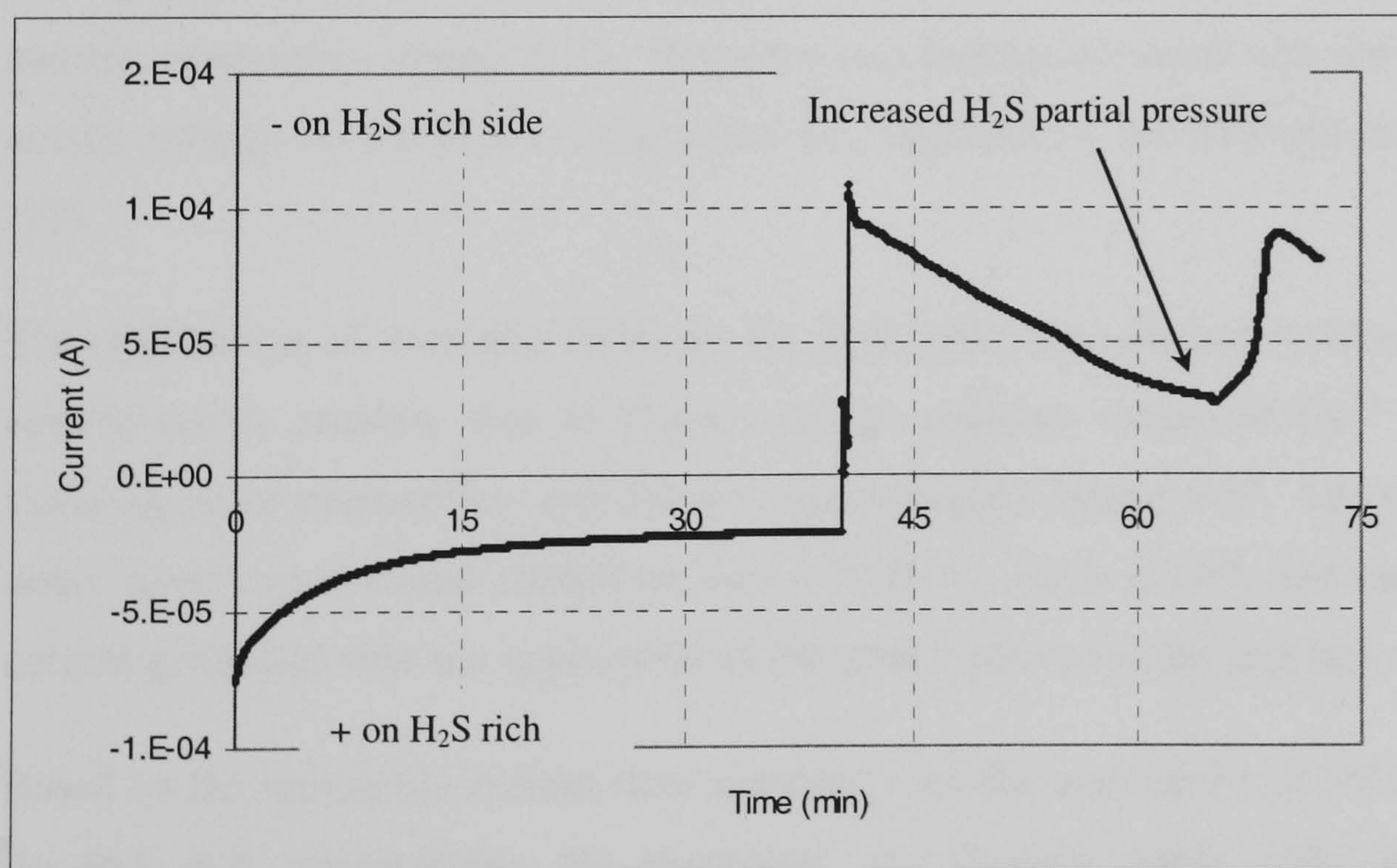


Figure 4-35 Electrochemical pumping of $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$ at 600°C with 5V dc

The electrical current generated from the application of cathodic 2Vdc or anodic 2Vdc to $\text{CaNd}_2\text{S}_4 + 0.2\text{Nd}_2\text{S}_3$ produced a symmetric current response, which indicates electronic conduction, Figure 4-36. The dc current generated was independent of the H_2S partial

pressure, suggesting the absence of sulphide ion conduction, Figure 4-36. This suggests that 20mol% Nd_2S_3 resulted in onset of electronic conduction.

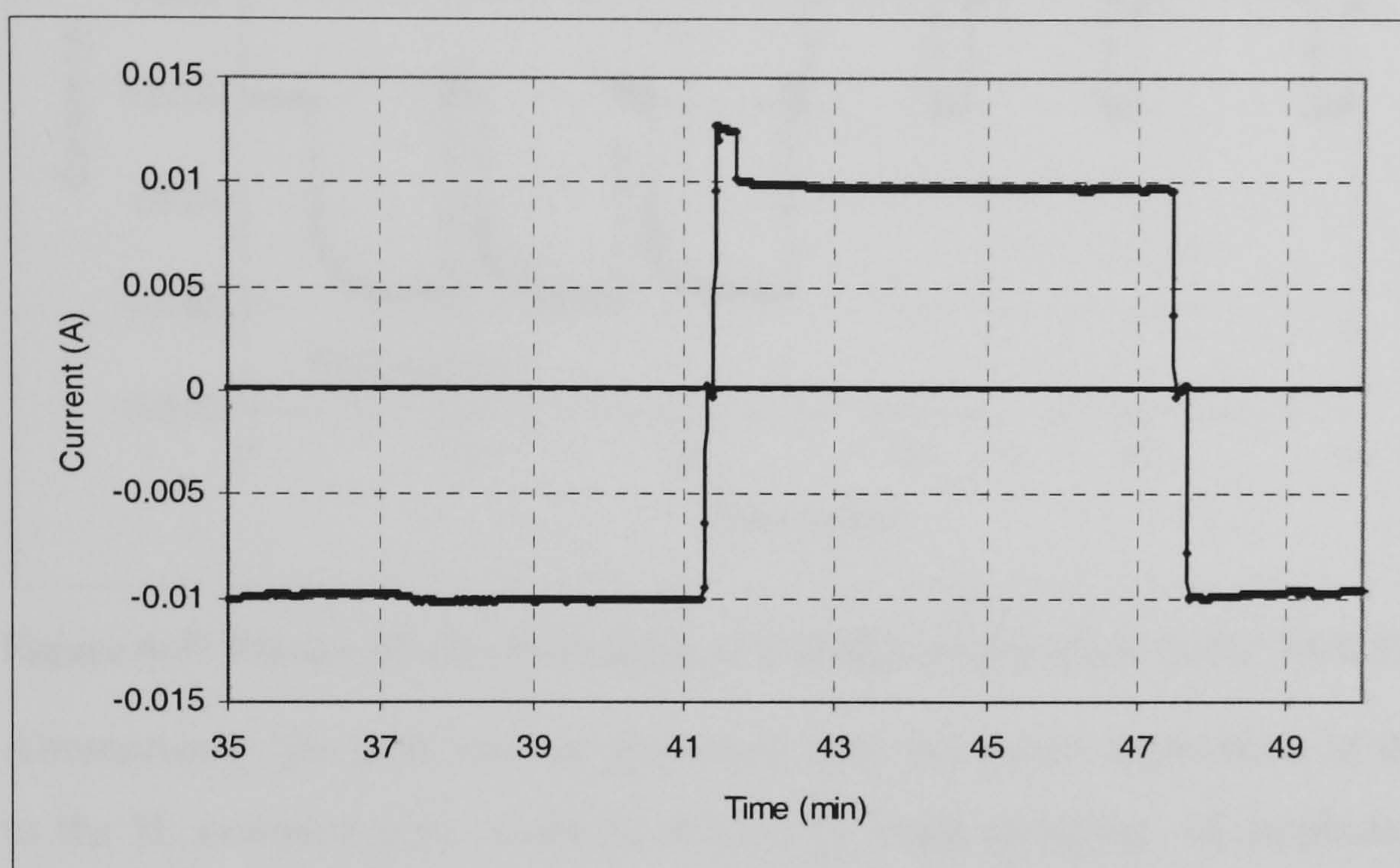


Figure 4-36 Electrochemical pumping of $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ at 550°C with 2V dc

The electrical current generated from the application of cathodic 5Vdc or anodic 5Vdc to $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ produced asymmetric current at 650°C and 750°C , which indicates anionic conduction, Figure 4-37. The increased current occurred with the application of the anodic voltage on the H_2S compartment, as expressed by the half-cell reaction in equation (17).

The application of cathodic 2Vdc to the H_2S rich compartment resulted in a decreasing current curve, possibly due to absence of the constant source of Ca^{2+} ion, therefore the lowering of the current flow according to equation (18), Figure 4-37. The steady state current under these experimental conditions was $1.1 \times 10^{-3}\text{A}$, which is 50% less than the steady state current generated with the application of the anodic current to the H_2S rich compartment.

Based on the repeatable current flow achieved with the application of 2V anodic potential to the H_2S rich compartment, the electrolyte was deemed stable under these experimental conditions. Application of the 2V cathodic potential did not lead to repeatable current, this could be due to electrochemical decomposition of the electrolyte or due 'back pumping' of sulphur previously pumped.

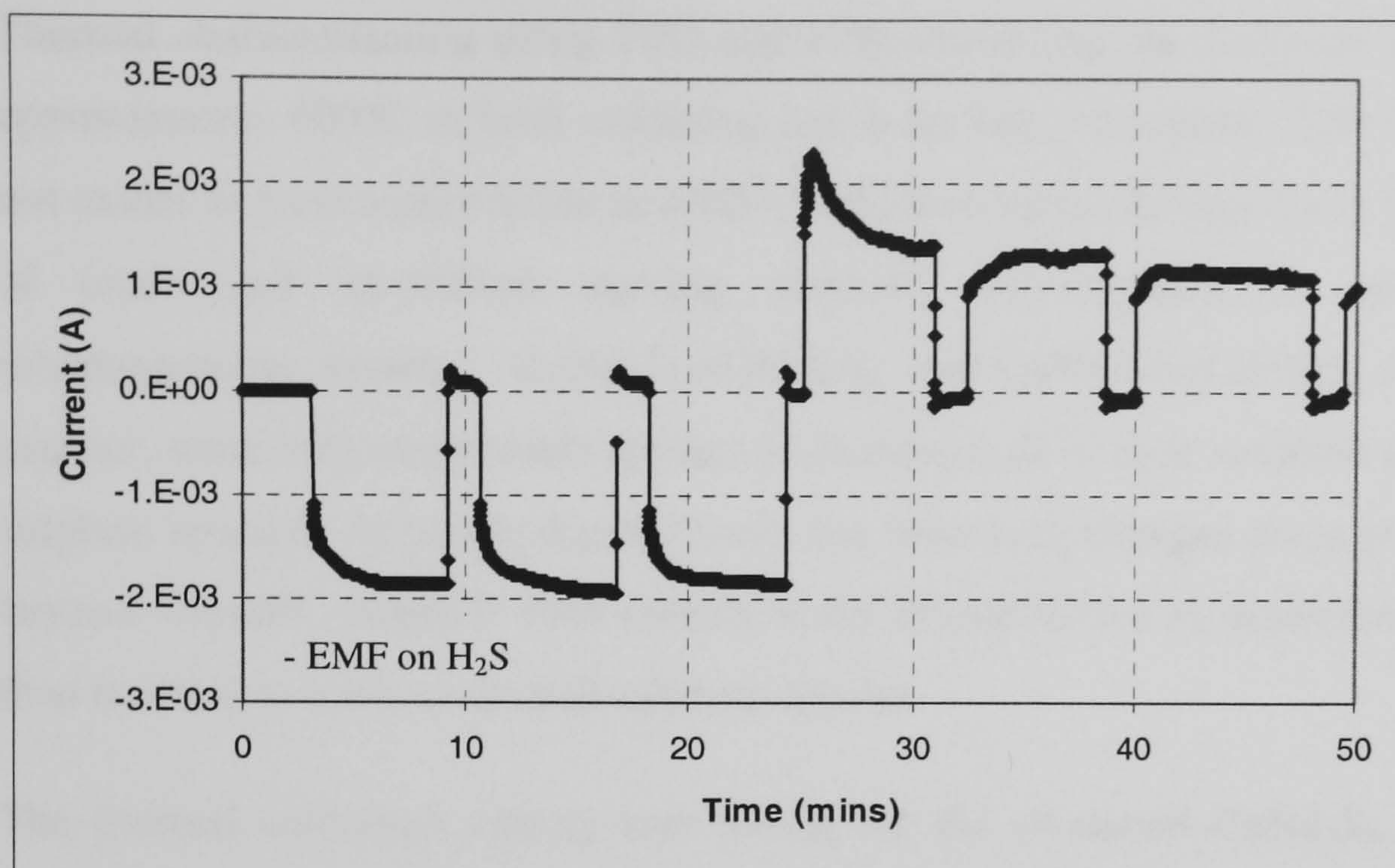


Figure 4-37 Electrochemical pumping of $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ at 750°C with 2V dc

Alternatively, the peak current generated with the initial application of the positive potential to the H_2 compartment, could be related to 'back pumping' of sulphide ion, equation (19), through the membrane as explained in Figure 4-37. Since the current was not sustainable, conduction could not be attributed to H^+ ions, therefore current flow

Reverse pumping of sulphide is conceivable since the applied potential is switched almost instantaneously, therefore pumped sulphide ions may still remain at the electrolyte interface, i.e. the 'pumped sulphur' remains does not react to form hydrogen sulphide via the reaction with hydrogen in the presence of the platinum electrodes and purged from the reactor.

4.6 Conclusion for the CaNd_2S_4 series

The search for a high temperature conducting electrolyte began with the CaNd_2S_4 doped compounds; they apparently exhibit predominant sulphide ion conduction at temperatures higher than 450°C . Therefore CaNd_2S_4 compounds were synthesised using solid state reaction method developed by Kalinina *et. al.* The XRD refinements of these compounds showed that the desired cubic Th_3P_4 type structure was formed. Therefore the thermal properties (including thermal stability, thermal activation, extent of oxidation) and electrochemical properties (bulk conductivity, time constant, activation energy for ionic-hopping, amongst others) were determined using the appropriate characterisation technique.

Thermal characterisation using TPO and TPR shows that the CaNd_2S_4 series is stable up to approximately 600°C in both oxidising and reducing atmosphere. The CaNd_2S_4 series does not oxides to form a pure oxide at 1000°C but all compounds appears to form either a mixture of oxide and un-reacted starting material, oxy-sulphide or mixed oxide-sulphate inhomogeneous system. $\text{CaNd}_2\text{S}_4+0.0\text{Nd}_2\text{S}_3$ and $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ oxidise in a similar manner, since both compounds appears to exchange all of their sulphide ions to form oxide or sulphate species. At higher dopant levels this behaviour changes since at Nd_2S_3 dopant levels beyond 10mol%, sulphide ions remain in the crystal lattice at maximum temperature rather than reacting to form oxide and sulphate species.

The thermal activation energy was lowest for the un-doped CaNd_2S_4 . A step increase in activation energy at 10mol%doping was observed, followed by a subsequent lowering on the thermal activation energy at higher doping. While the oxygen and sulphur balance does not explain the marked increase in thermal activation energy for the doped compounds it does agree with the subsequent reduction in activation energies with increasing Nd_2S_3 content. Since the extent of oxidation reduces for 20mol% and 30mol% doped CaNd_2S_4 compounds.

The identifying feature of a pure ionic conductor is the presence of an ion blocking low frequency arc in the Nyquist plot; this was observed only for $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$. Therefore all the other investigated compounds in this series are at best mixed ionic-electronic conductors. The absence of an ion blocking arc at low frequency occurs with materials with ionic transport numbers as high as 0.9999, Jamnik 2003, even though a material is considered to be an ionic conductor once the transport number for ionic conduction exceeds 0.95, Vayenas, 2003. Therefore the absence of the conclusive low frequency ionic blocking arc in the Nyquist diagram does not mean that the electrolyte is not predominantly ionic conducting. Ionic conduction is identified if the bulk conductivity is independent of H_2S partial pressure. Varying the H_2S concentration (and therefore the S_2 partial pressure) from 0vol% (pure Argon) to 18vol% H_2S , confirmed that $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ is an ionic conductor over this range of H_2S concentration and at temperatures as low as 300°C. Further doping to 20mol% Nd_2S_3 resulted in electronic conduction, since a decrease in conduction occurred with the increase in H_2S concentration, as well as hole conduction at high H_2S concentration.

Similarly the bulk conductivity for $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ appears to be controlled by positive hole conduction at greater than 500°C for all H_2S concentration studied, while at temperatures less than 400°C , the electronic conduction was deduced based on the reduction in the bulk conductivity with increasing temperature. Un-doped CaNd_2S_4 exhibits positive hole conduction since the bulk conductivity increased with the increasing H_2S partial pressure from pure argon to 2vol% $\text{H}_2\text{S}/\text{Ar}$ mixture.

While performing impedance spectroscopy in various hydrogen sulphide concentrations differentiates ionic conduction from electronic, it does not differentiate cationic from anionic conduction. However, derived information from EIS such as the activation energy for the hopping process associated with ionic motion within a crystal lattice (from Arrhenius plot of bulk conductivity) could give an insight to the conducting species. For example, low activation energy for hopping occurs when there is little resistance, such small cations compared to larger anions, assuming that the jump distance for cations and anions are comparable in the unit cells. Therefore a relatively low activation energy would be indicative of cation conduction. Since there are no published results for experimentally determined activation energy for sulphide conduction, the theoretical value for sulphide ion conduction in CaS , modified for the association energy of vacancies, lead to the development of a reasonable activation energy for sulphide ion conduction of 0.61-1.66eV. This was used as reference point, to infer anionic conduction. The activation energy for bulk conduction in CaNd_2S_4 series lies within the probable range for sulphide ion conduction.

Time constants are another derived data from impedance spectroscopy; they quantify the time taken for an ion to hop from a vacant site to another. The conduction of larger sulphide ions is expected to move slower than oxide ions at a given temperature. Therefore larger time constants for CaNd_2S_4 compounds (with respect to oxide ion conduction in YSZ) would more likely indicate anionic conduction. The complication for determining the time constants is that they depend on the absolute values of resistive and capacitive components of the impedance, which are derived from equivalent circuit modelling. Using the most appropriate model, Jamnik mixed-ionic electronic conductor, time constants for doped CaNd_2S_4 compounds are slower than reported values for YSZ at similar temperature; this thus favours anionic conduction. This is of course a basic analogy because factors other than temperature will affect the time constant such as lattice parameter (distance between lattice sites), polarizability of other ions within the unit cell etc.

The bulk conductivity of $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ using graphite electrodes and Jamnik equivalent circuit is $1.09 \times 10^{-6} \text{S.cm}^{-1}$, which compares well with that of Kalinina's galvanic cell bulk conductivity of $1.15 \times 10^{-6} \text{S.cm}^{-1}$. The bulk conductivity measured using impedance spectroscopy remained independent of H_2S partial at all temperatures; it indicates ionic conduction. Electrochemical pumping experiments showed a larger current flow in a higher H_2S partial pressure, indicating the conduction of sulphide ions. The generated current in the electrochemical pumping experiments was not steady indicating short-circuiting by electronic conduction. However the onset of electronic conduction may relate to experimental errors set-up of the experiment.

While the bulk conductivity depends on the equivalent circuit, all applicable models identified $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ with the maximum bulk conductivity. $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ bulk conductivity decreased with an increase in H_2S partial pressure, thus confirming the presence of electronic conduction. The symmetrical current response with application of 5Vdc in the electrochemical pumping experiments also indicates predominant electronic conduction. However time constant analysis of $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ in argon suggested ionic conduction since the values were comparable to $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$. This could simply mean that $\text{CaNd}_2\text{S}_4+20\text{mol\%Nd}_2\text{S}_3$ becomes a predominant electronic conductor at high H_2S partial pressures. However considering all data available for this compounds, it appears to have significant electronic conduction.

The bulk conductivity of $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ is comparable to $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$, in that this electrolyte exhibits electronic conduction at low temperature, followed by hole conduction at higher temperatures up to 500°C . However at 550°C , the absence of a H_2S partial pressure dependence of the bulk conductivity shows that this compound is predominantly ionic conduction at high temperatures. The asymmetric cell response of the electrochemical pumping of $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ favours sulphide ion conduction at 700°C .

4.7 Thermal and Electrochemical Characterisation of Strontium Neodymium Sulphide doped with excess Nd₂S₃ Series

SrNd₂S₄ doped with excess Nd₂S₃ was previously mentioned to be a sulphide ion conductor, Kalinina *et. al.*, 1995. Therefore the analogue, SrNd₂S₄ series, of the CaNd₂S₄ series was synthesised using the identical reactions procedure according to Kalinina *et. al.*, 1995. The expectation of changing the host cation is that the conductivity would improve without significant change in the activation energy provided the unit structure is maintained. For example, Drache *et. al.*, 1992, showed that changing the dopant cation in a bismuth oxide based system favourably alters the oxide ionic conductivity depending on the cation substituted.

The X-ray diffraction pattern shows that the SrNd₂S₄ series has a cubic unit cell similar to CaNd₂S₄ shown in Figure 4.1 where the smallest spheres now represents Sr rather than Ca atoms, White, 2004. The X-ray diffraction pattern shows that an increase in dopant level does lead to similar changes as observed with the CaNd₂S₄ system, Figure 4.1. The volume of the unit cell increased as the cation is changed from calcium to strontium, Table 4.14, expressed by an increase in the lattice parameter while increasing the dopant level in each group of compounds causes a contraction of the unit cell, White, 2004. The increase in lattice parameter with the cation change from calcium to strontium is expected since the strontium ion is larger than the calcium ion, and as such an increase is inevitable. Doping with excess Nd₂S₃ lead to a decrease in lattice parameter which is the norm when Schottky defects are formed

Table 4.14 Lattice parameter for CaNd₂S₄ series and SrNd₂S₄ series, White, 2004

	Lattice parameter Å (a-site) SrNd ₂ S ₄	Lattice parameter Å (a-site) CaNd ₂ S ₄
Undoped	8.6204(1)	8.5301(1)
10mol%Nd ₂ S ₃	8.6200(4)	8.5299(1)
20mol%Nd ₂ S ₃	8.6181(3)	8.5280(1)
30mol%Nd ₂ S ₃	8.5919(2)	8.5273(1)

Large grain particles of SrNd₂S₄ do not sinter well, similarly to CaNd₂S₄, therefore the average particle size was reduced to increase the density of the sintered pellet using dry ball milling for up to four days. Pellets were made with ground material by uniaxial pressing to 10 tonnes and sintering at 1350°C; pellets were produced with a maximum of 93% of the

theoretical density, Table 4.15. Increasing temperatures to more than 1350°C produced curved pellets rather than flat ones.

Table 4.15. Theoretical and actual densities for SrNd₂S₄ series

	Theoretical density SrNd ₂ S ₄ (g/cm ³)	Actual density SrNd ₂ S ₄ (g/cm ³)	% of theoretical density
Undoped	5.229	4.35	83
10mol%Nd ₂ S ₃	5.118	4.25	83
20mol%Nd ₂ S ₃	5.028	4.35	87
30mol%Nd ₂ S ₃	4.993	4.06	81

SEM's of the sintered pellets shows large pores of diameter up to 15µm with fairly thin grain boundaries, Figure 4-38. Therefore the pellets were not dense when made with smallest particle size distribution and maximum temperature, Table 4.15. SrNd₂S₄+0.2Nd₂S₃ achieved the highest percentage of theoretical density similarly to what was observed in the CaNd₂S₄ series.

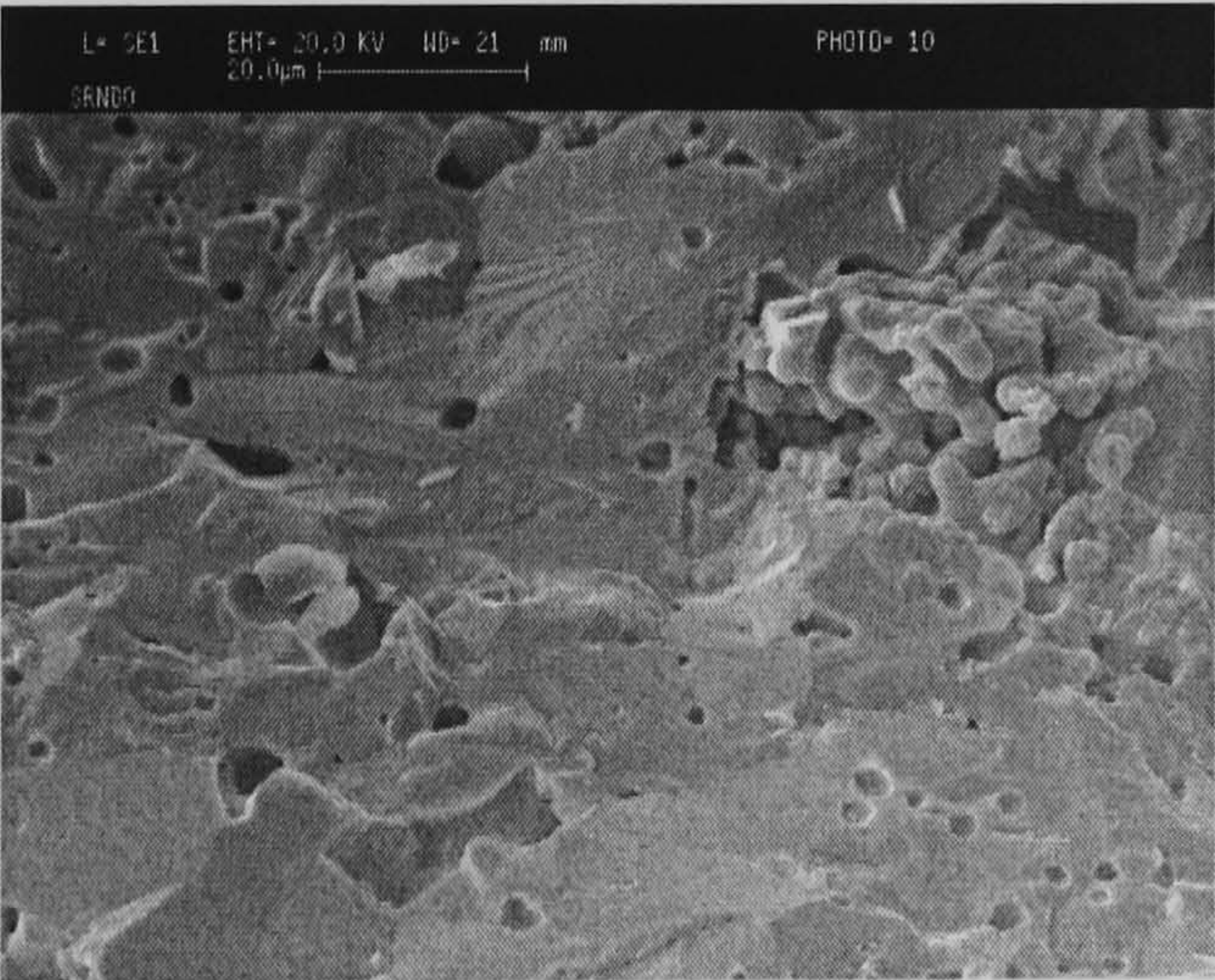


Figure 4-38. SEM of SrNd₂S₄ sintered pellet at 1350°C in H₂S/Ar mixture with 93% of theoretical density

4.7.1 TPO and TPR for SrNd₂S₄ series

The thermal stability of the proposed SrNd₂S₄ series was established using TPO and TPR. The TPO traces of this series consist of one major peak with a shoulder at the high temperature side, which mimics the CaNd₂S₄ series TPO traces, Figure 4-39. The presence of only one major peak at elevated temperatures indicates that only one type of sulphur peak is being reacted to form sulphur dioxide. The onset temperature is higher for doped SrNd₂S₄ compounds relative to un-doped SrNd₂S₄; while all CaNd₂S₄ compounds are more stable relative to the undoped-CaNd₂S₄, Table 4.16.

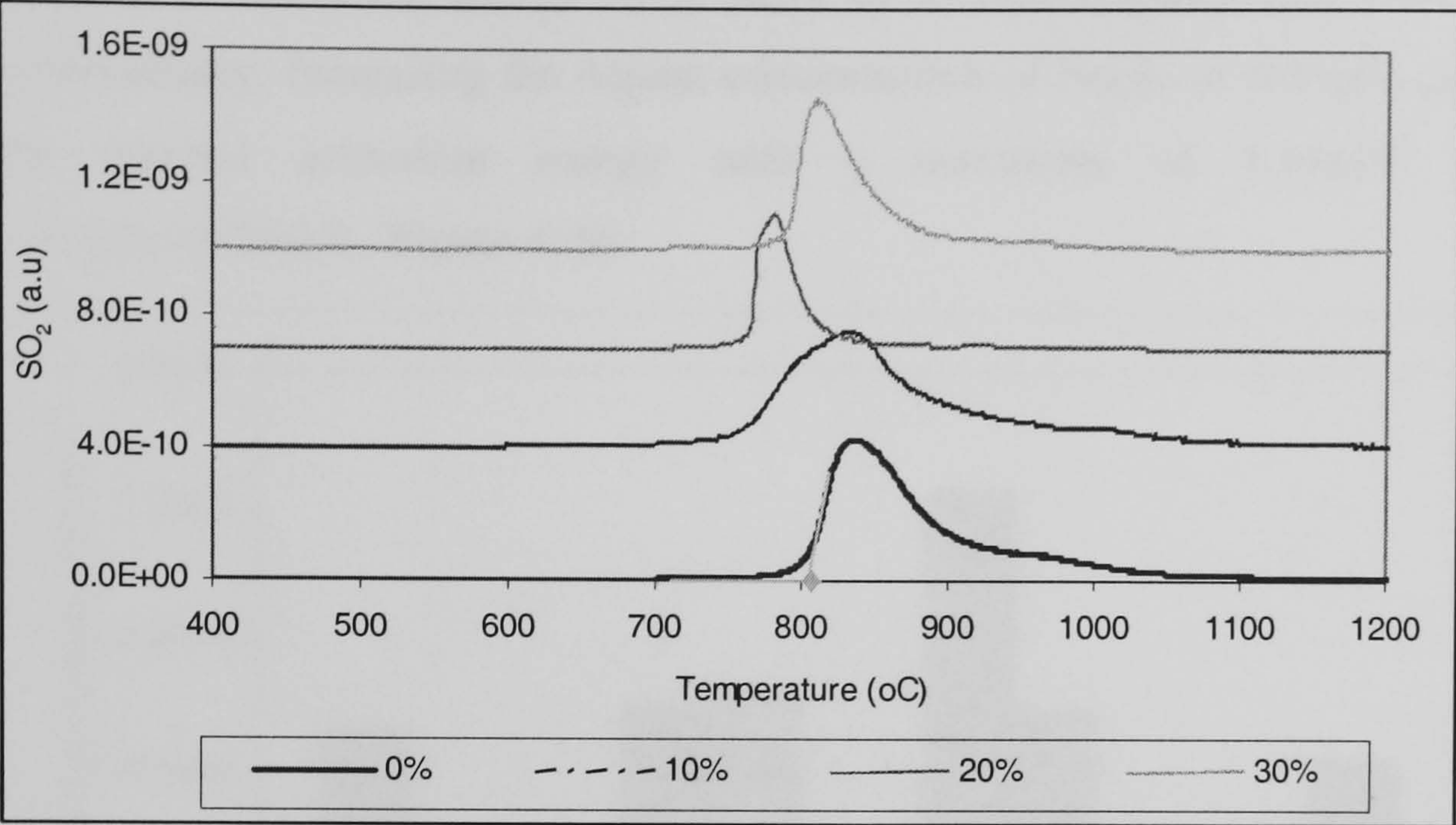


Figure 4-39. Temperature programmed oxidation of SrNd₂S₄ series

Table 4.16 Effect of doping on onset temperatures for SrNd₂S₄ and CaNd₂S₄ series

Dopant level	SrNd ₂ S ₄ onset temperatures	CaNd ₂ S ₄ onset temperatures
0%	808	671
10%	755	723
20%	761	708
30%	789	704

Therefore changing the calcium ion to the strontium ion (a larger cation) led to an increase in the onset temperatures for the undoped electrolyte of approximately 130°C, Table 4.16. This increase in oxidation onset temperature may be explained by using the basic theory of polarisation effect, which states that, the more polarising an ion, the stronger the bond between oppositely charged ions. Since strontium ion has a polarisability number of 1.4 which is approximately three times greater than calcium with polarisability number of 0.4, higher oxidizing onset temperatures are expected.

The effect of doping with excess Nd₂S₃ caused a increase in onset temperatures for SrNd₂S₄ series, while for the CaNd₂S₄ series increasing the dopant caused a decrease in onset temperatures, however no simple explanation is possible for this contrasting observation.

The thermal activation energies of these compounds were evaluated by the method descried in Chapter 4.1. On changing the cation from calcium to strontium (without doping) lead to an

increase in activation energy by a factor of 2, which agrees well with the increasing in polarisability. Increasing the dopant concentration of Nd_2S_3 in SrNd_2S_4 caused variations in the thermal activation energy with a maximum of 1.24×10^6 kJ/kg-mol-K for $\text{SrNd}_2\text{S}_4 + 0.2\text{Nd}_2\text{S}_3$, Figure 4-40.

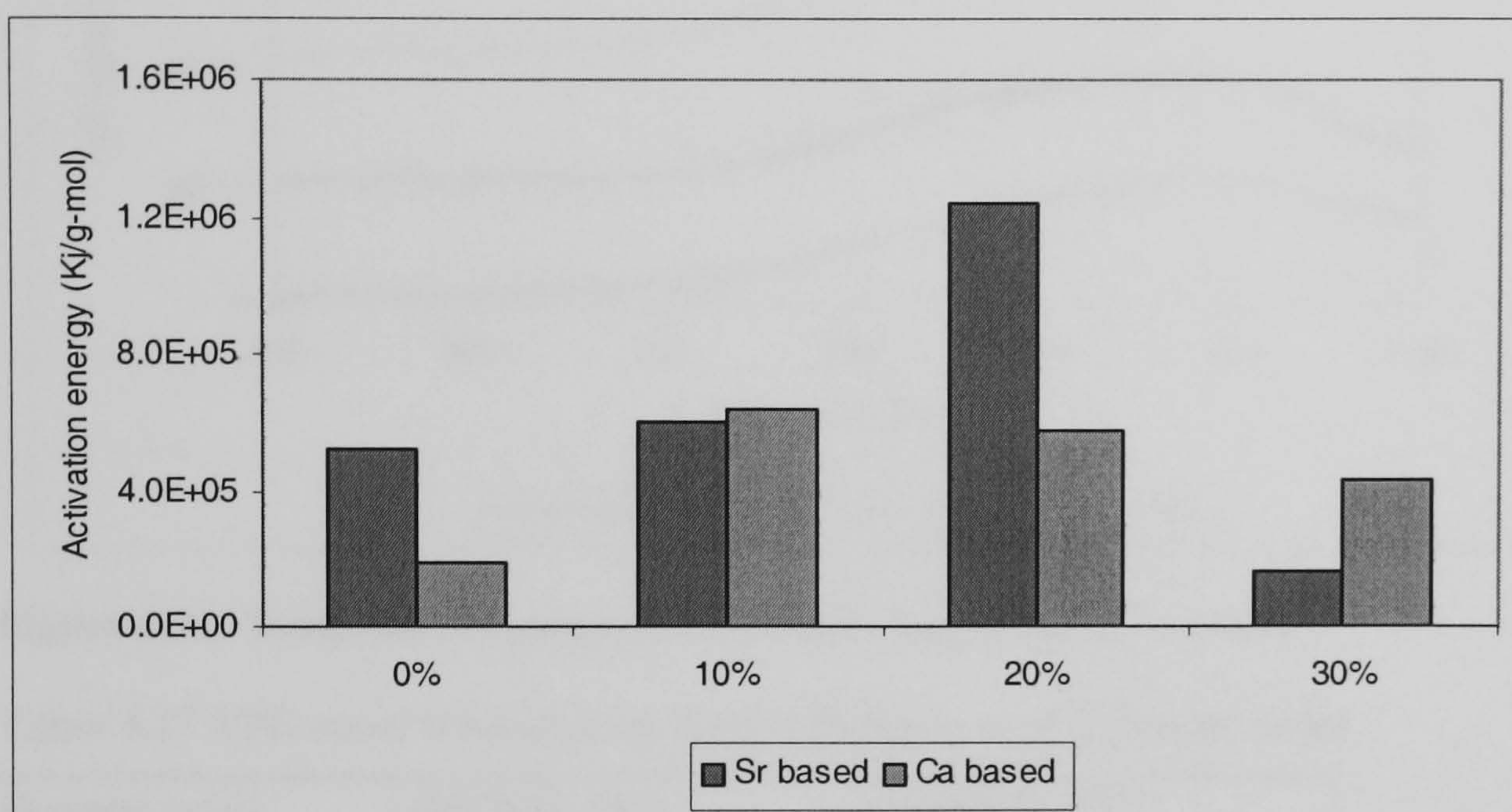


Figure 4-40 Thermal Activation energy for SrNd_2S_4 and CaNd_2S_4 series

No clear relationship is apparent between thermal activation energies and the two types of neodymium sulphide based compounds. What is known is that the unit cell contracts once the excess Nd_2S_3 content increases beyond 10mol%, this should cause an increase in thermal activation energy, as observed for $\text{SrNd}_2\text{S}_4 + 0.2\text{Nd}_2\text{S}_3$, Figure 4-40. Increasing the excess Nd_2S_3 also increases the number of cation and ion vacancies, which should cause a lowering in activation energy, due to increased number of free pathways for sulphide ions to leave the unit cell as well as for inserting of oxide ions into to the vacant sites. This lowering of activation energy was only observed at $\text{SrNd}_2\text{S}_4 + 0.3\text{Nd}_2\text{S}_3$, Figure 4-40.

No significant trend was observed between the reduction onset temperatures and dopant level or unit cell lattice parameter for the SrNd_2S_4 series, Figure 4-41, Table 4.17. $\text{SrNd}_2\text{S}_4 + 0.2\text{Nd}_2\text{S}_3$, which is most stable under reducing conditions, also had the highest thermal activation energy, Figure 4-40 even though $\text{SrNd}_2\text{S}_4 + 0.2\text{Nd}_2\text{S}_3$ was not the most stable, within the SrNd_2S_4 series, in an oxidising atmosphere, Table 4.16. The thermal stabilities of both the SrNd_2S_4 and CaNd_2S_4 series in a reducing atmosphere are comparable, Table 4.17.

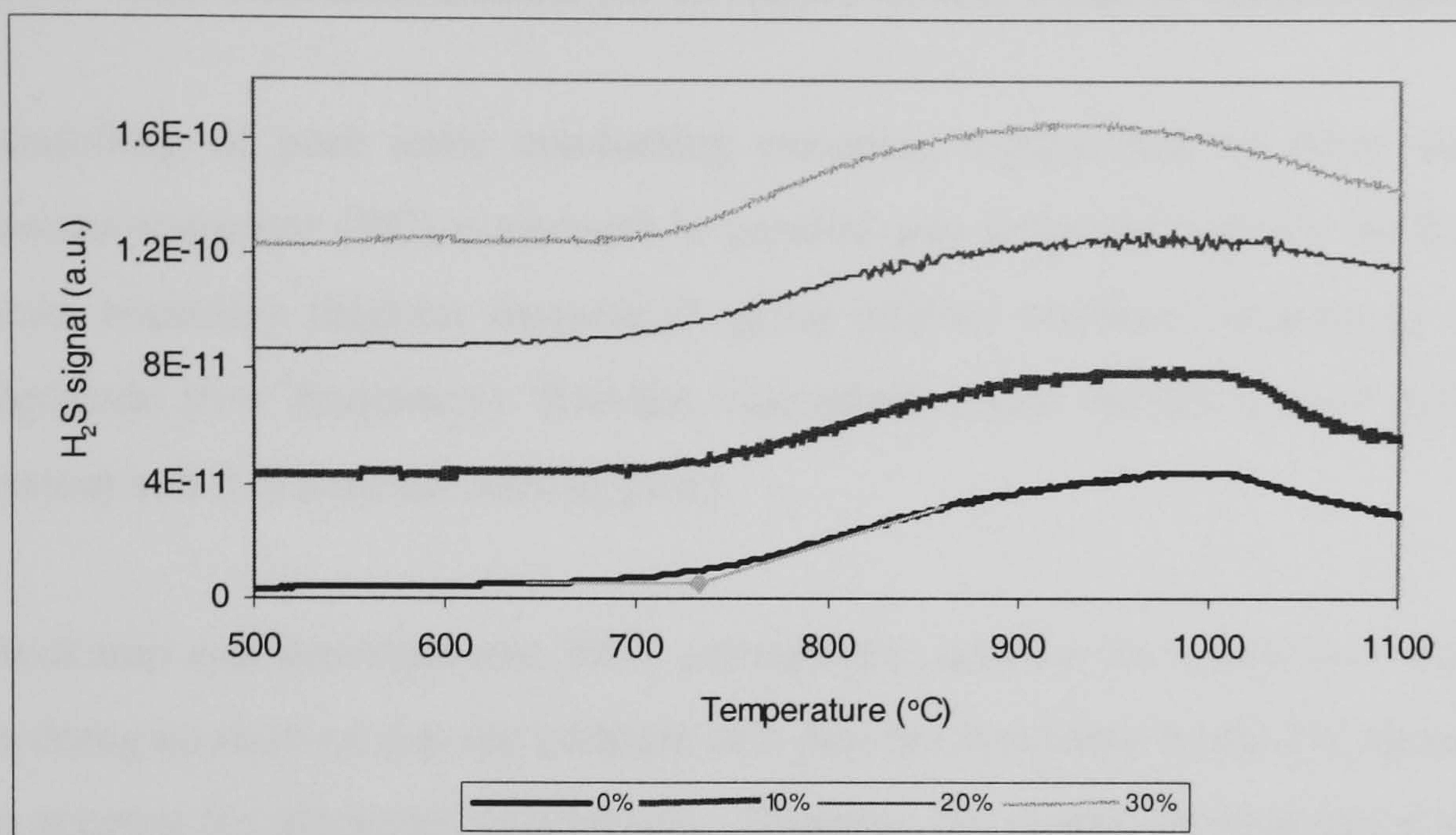


Figure 4-41. Temperature programmed reduction of SrNd₂S₄ series

Table 4.17 TPR onset temperature for the SrNd₂S₄ and CaNd₂S₄ series

Dopant level	SrNd ₂ S ₄ (°C)	CaNd ₂ S ₄ (°C)
0%	712	737
10%	723	766
20%	793	711
30%	713	724

4.8 EIS of Nd₂S₃ doped SrNd₂S₄ series

The electrochemical behaviour of strontium neodymium sulphide doped with neodymium sulphide was characterised by using EIS. The bulk conductivities were measured in the temperature range from 150 to 400°C with 25°C increments with a one-hour temperature isothermal period before measuring in the frequency range from 0.1Hz to 1GHz (10 points per decade) in an atmosphere. Graphite electrodes, with an applied ac voltage of 0.1V_{rms} were used. Other electrode materials such as gold and platinum were not used due to the previously discussed apparent reaction with the electrolyte at low temperatures.

4.8.1 EIS characterisation for SrNd_2S_4 series: ionic or mixed conductors

Modelling of pure ionic conducting ceramics represented by three series connection of resistor-capacitor (RC) connected in parallel was proposed initially by Bauerle, 1969 where grain boundary (highest frequency), grain interior (medium frequency) and ionic blocking electrode (low frequency). Randles equivalent circuit model is used extensively for liquid system and it is a useful starting point.

Boukamp and Bouwmeester 2003, attempted to address the situation of mixed conductor and in doing so showed that the addition of a parallel resistance to the RC elements of the Bauerle to account for electronic conduction. However the results showed that it was inaccurate, and that the situation was accurately modelled by using a Gerisher impedance element, a modelling tool available in Z-view©. Jamnik *et. al.*, 1999, proposed two models for the two extreme cases of mixed conductor; firstly a system where conduction takes place predominantly by ionic conduction, Figure 4-42, and secondly where conduction takes place predominantly by electronic movement, Figure 4-43. Two complex situations were modelled, one of partial blocking grain boundaries to one of the conduction species and secondly the conduction mechanism is observed in lithium insertion reaction into a mixed electronic ionic lithium based electrolyte, Figure 4-44 and Figure 4-45, Jamnik *et. al.*, 2003.

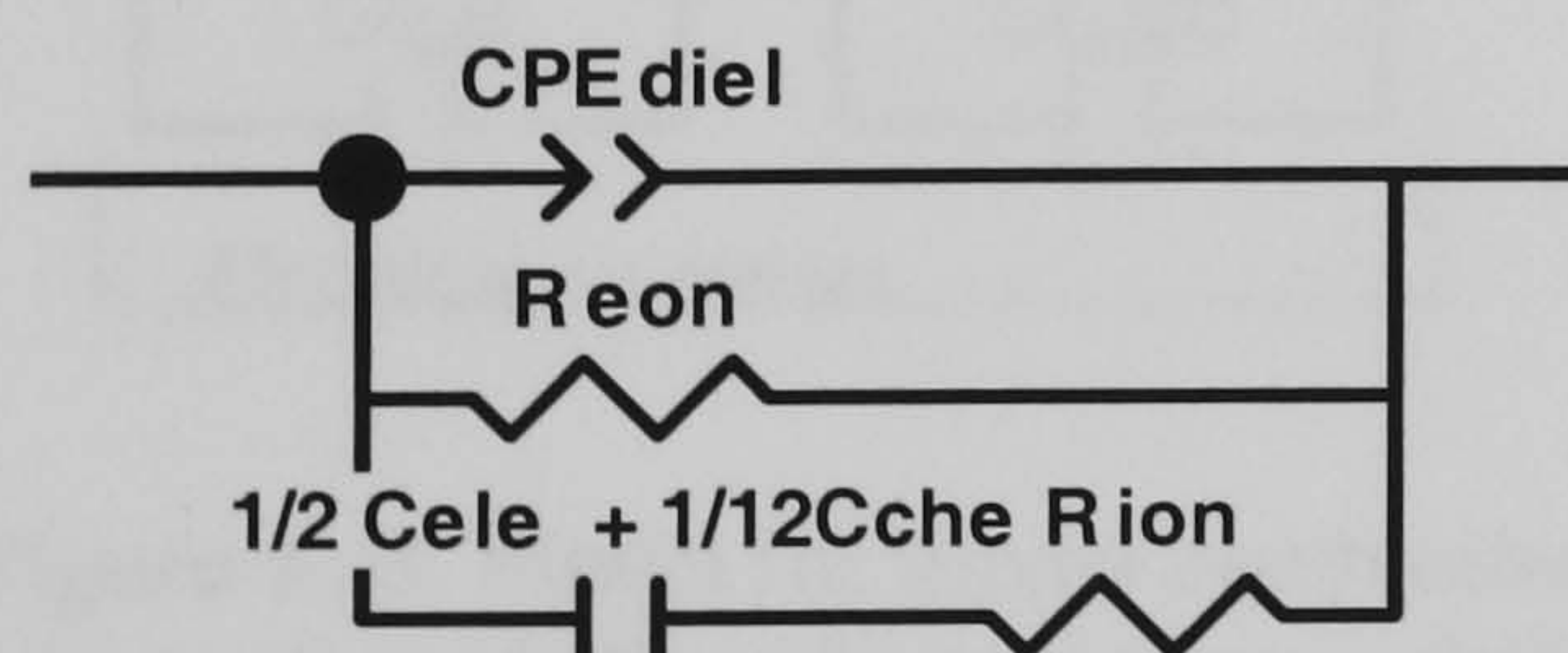


Figure 4-42 Equivalent circuit for a mixed conductor with ideal selectively blocking electrodes with predominant electronic conductivity

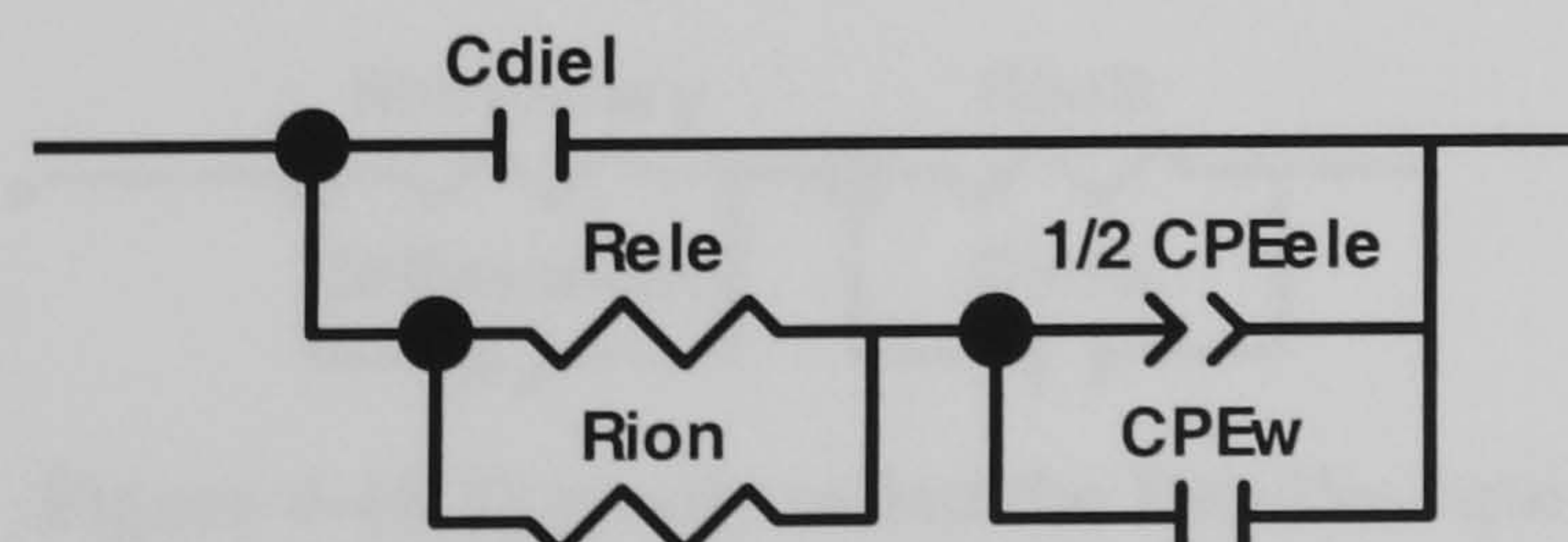


Figure 4-43 Equivalent circuit for a mixed conductor with ideal selectively blocking electrodes with predominant ionic conductivity

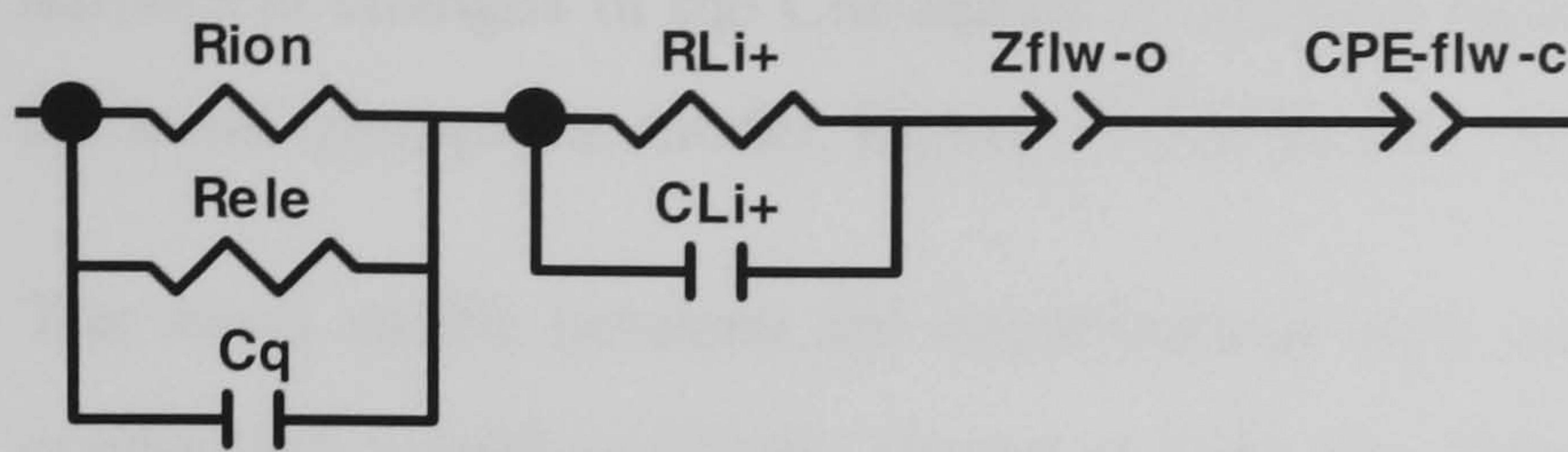


Figure 4-44 Equivalent circuit for Lithium ion insertion into a Lithium based mixed conducting electrolyte

Where

R_{ion} – Resistance to ionic movement

R_{ele} – Resistance to electronic movement

C_{diel} – Electrode capacitance

C_{ele} – Chemical capacitance

C_q – Electrostatic (bulk) capacitance

R_{li+} – Interfacial resistance,

C_{li+} - interfacial capacitance,

Z_{flw-o} and Z_{flw-c} are the open and closed finite Warburg diffusion elements related to the chemical diffusion of lithium ion into the electrolyte.

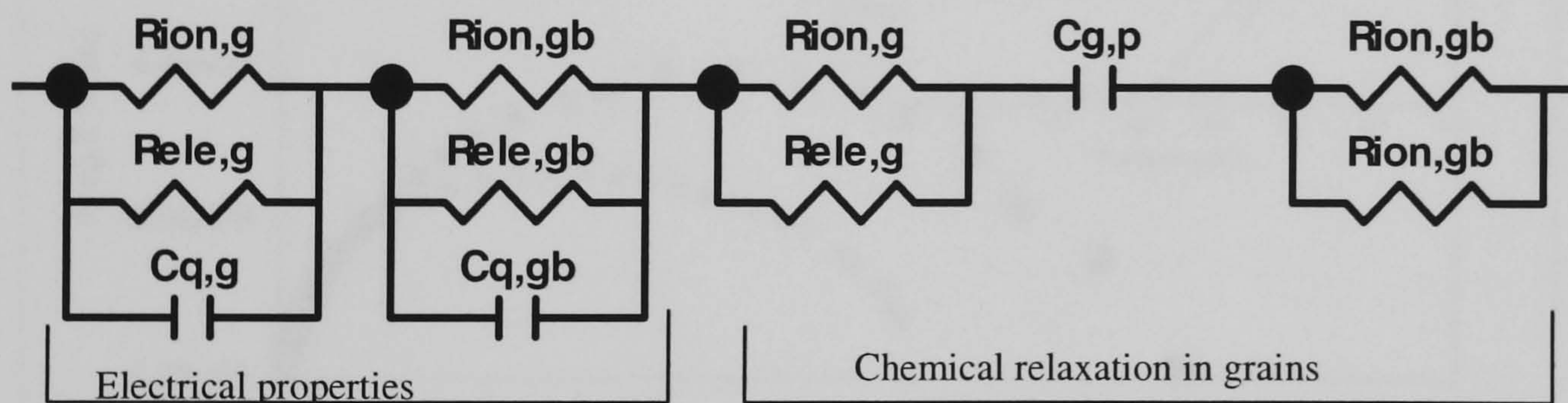


Figure 4-45. Model for mixed conduction electrolyte with partial blocking grain boundaries where all modelling elements are as defined in previous figure with 'g' referring to grain conduction and 'gb' referring to grain boundary conduction, $C_{g,p}$ relates to the parallel discharging of grain chemical capacitance

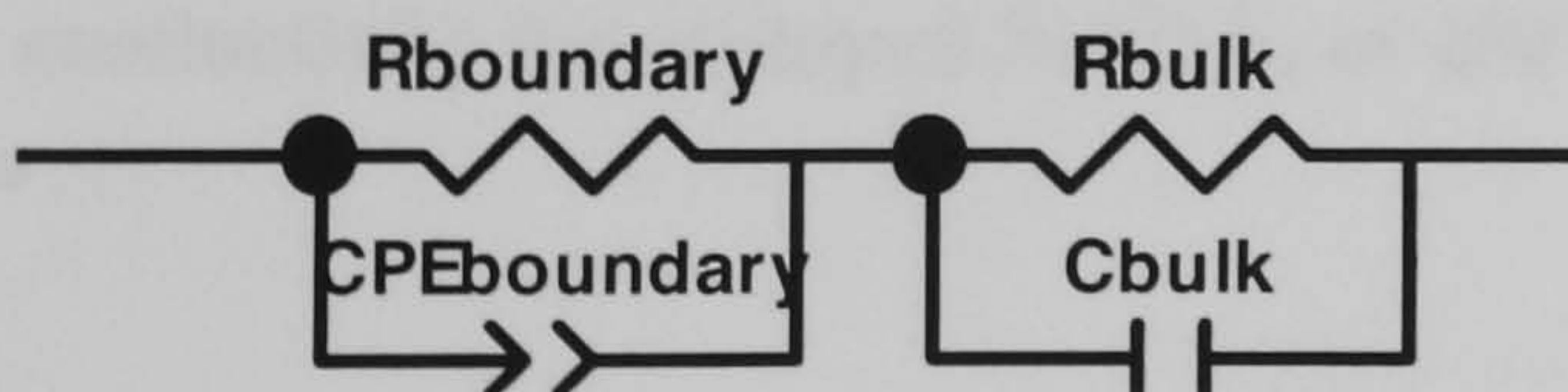


Figure 4-46. Typically called the Randles equivalent circuit used to model ionic conduction

The correct model was selected based on goodness of fit between modelled and experimental data determined by the Chi-square and Sum-of-squares statistical parameters. For mixed ionic-electronic conducting electrolyte, the Bode plot is very sensitive to apparently small

numerical changes in the Chi-square or Sum-of squares and therefore qualitatively identifies the most appropriate model, Figure 4-47 to Figure 4-50.

The vivid misfit between the experimental data and the Jamnik predominantly electronic conducting model is clearly shown in both the Nyquist and Bode plot in Figure 4-47. This infers that SrNd_2S_4 is not predominately electronic conducting.

The Nyquist plots for either Jamnik predominantly ionic conductor or Randles equivalent circuit give comparable results, but based the fitted results as shown in the Bode plot shows, the Jamnik predominant ionic conducting model yields a better fit at low frequencies (electrode response), Figure 4-48 and Figure 4-50

The insertion type reaction model produced a better fit at high frequencies (see Bode plot inserted in Figure 4-49), but the misfit was clearly shown at lower frequencies mainly in the Nyquist plot, Figure 4-49. This infers that no reaction (insertion) occurred during the impedance measurement.

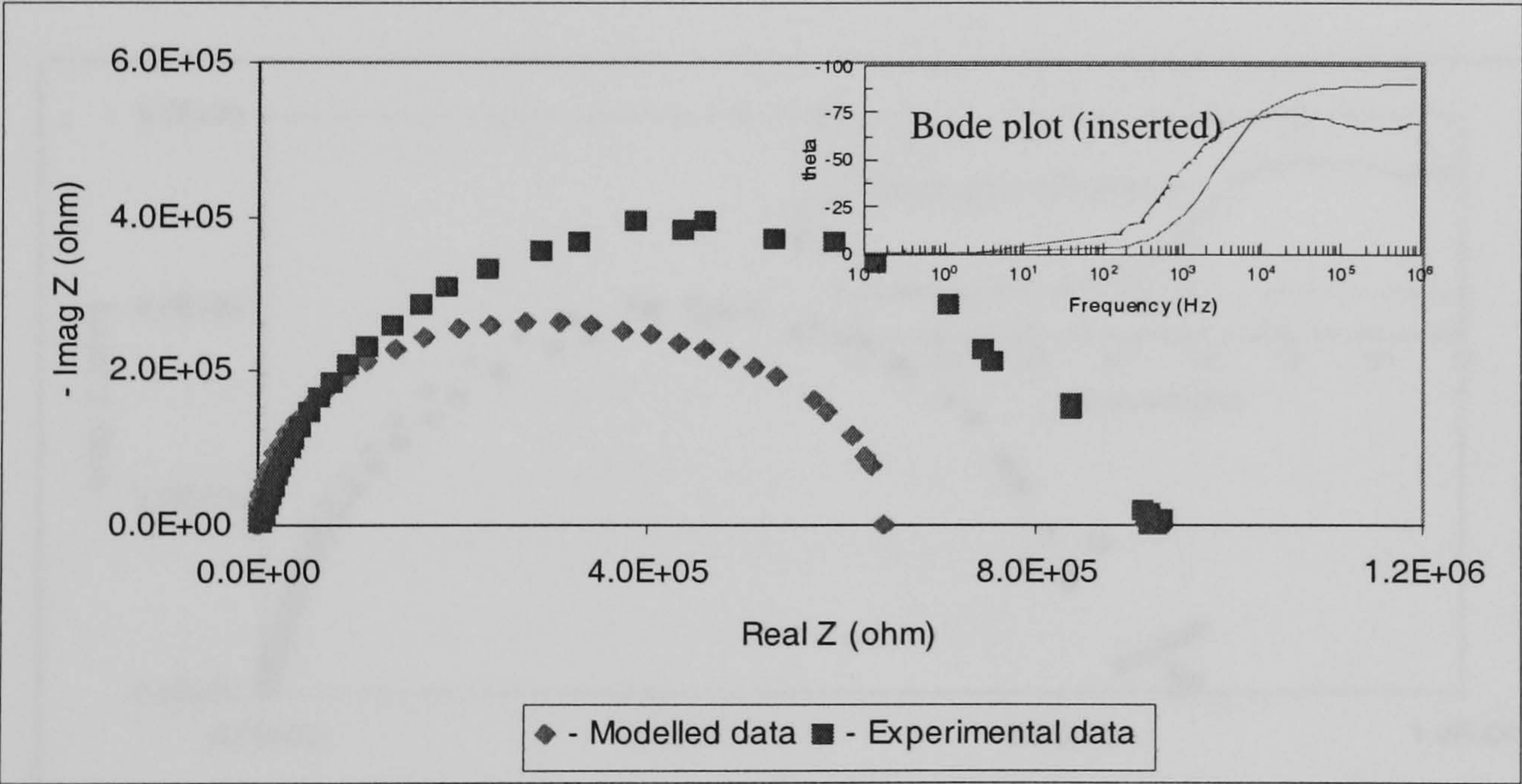


Figure 4-47. Model result using perfectly blocking boundaries for predominant electronic conductivity for undoped SrNd_2S_4 at 400°C

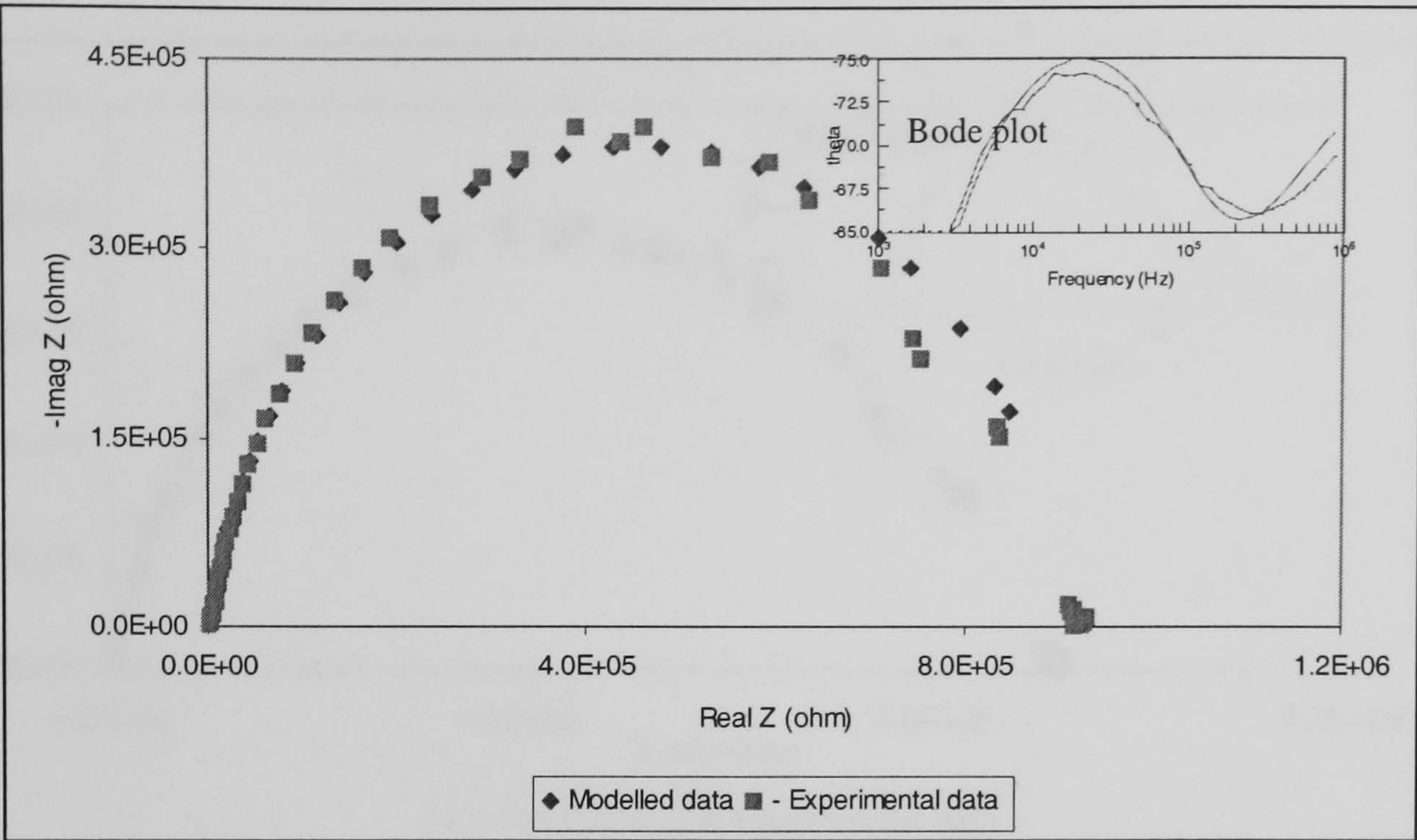


Figure 4-48. Model result using perfectly blocking boundaries for Jamnik predominant ionic conductivity for undoped SrNd_2S_4 at 400°

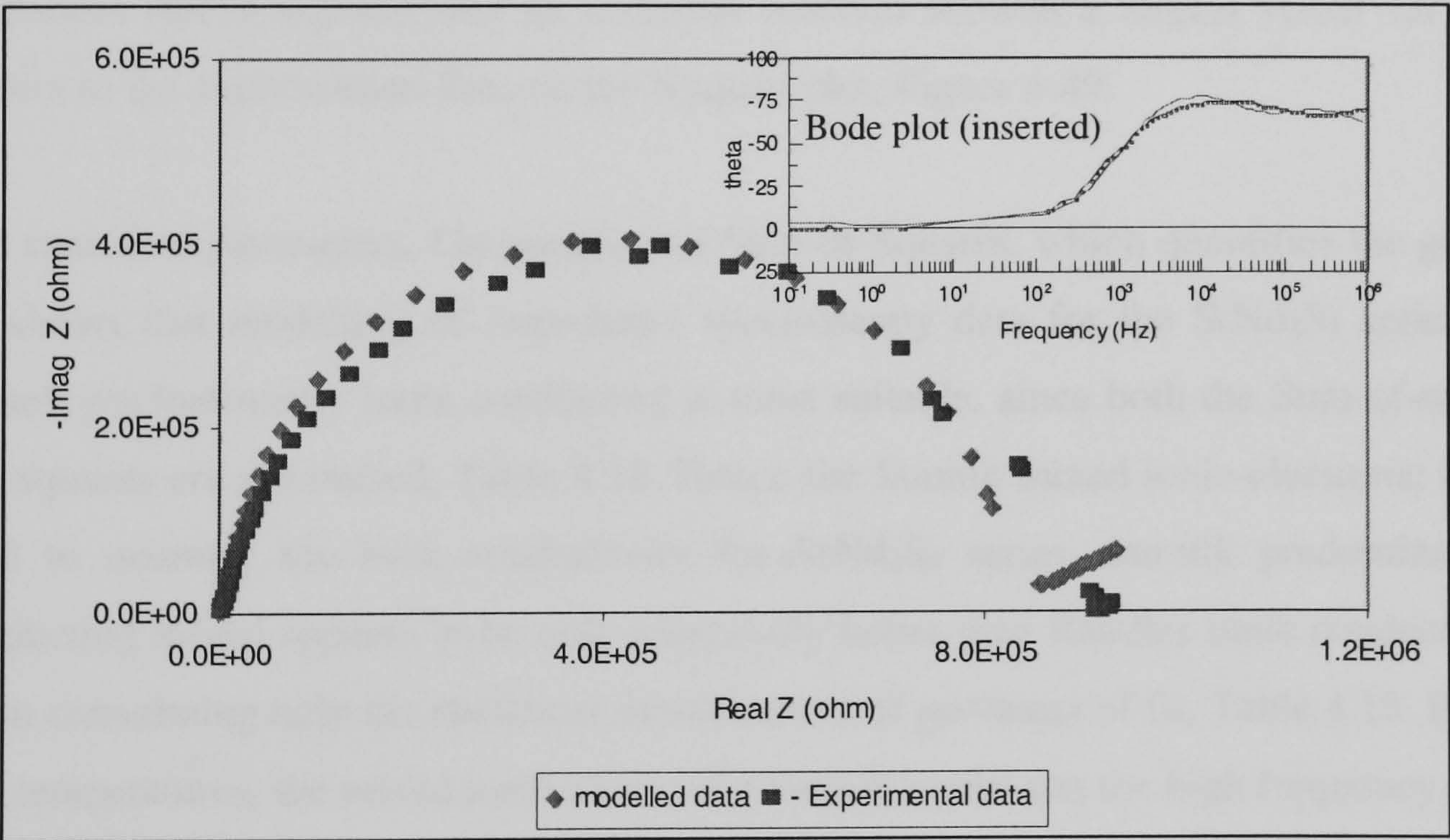


Figure 4-49. Model result using partially blocking boundaries with an insertion reaction for undoped SrNd_2S_4 at 400°C

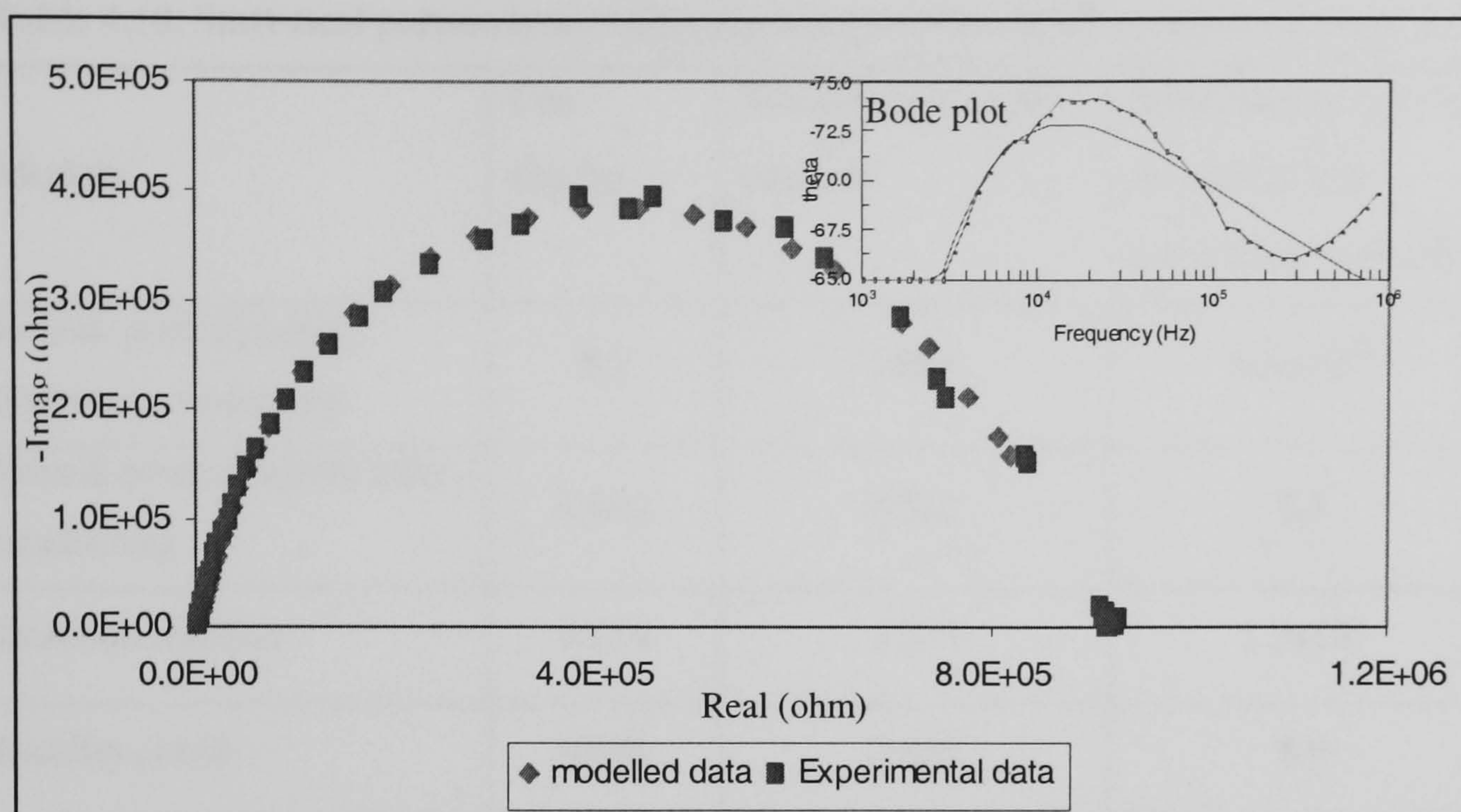


Figure 4-50 Model result using Randles circuit for ionic conducting membrane blocking boundaries without an insertion reaction for undoped SrNd_2S_4 at 400°C

The Nyquist and Bode plot gives a visual impression of the goodness of fit which varied significantly for different models as shown in Figure 4-47 through to Figure 4-50. The equivalent circuit representing an insertion reaction showed a largest visual variance with respect to the experimental data on the Nyquist plot, Figure 4-49.

The statistical parameters, Chi-square and Sum-of-Squares, which quantifies the goodness of fit, shows that modelling of impedance spectroscopy data for the SrNd_2S_4 series with the Jamnik predominantly ionic conducting is most suitable, since both the Sum-of-squares and Chi-squares are minimised, Table 4.18. Hence the Jamnik mixed ionic-electronic model was used to quantify the bulk conductivity for SrNd_2S_4 series. Jamnik predominantly ionic conducting model appears to be only marginally better than Randles ionic conducting model when considering only the statistical measurement of goodness of fit, Table 4.18. However at low temperatures, the mixed ionic-electronic Jamnik model fits the high frequency data much better than the pure ionic conductor represented by Randles models. Macdonald, 1981 suggest that the best model is one which fits data at all experimental conditions, hence the Jamnik mixed model most appropriate since fit is good at all temperatures measured.

Table 4.18. Statistical parameters evaluating the goodness of fit for alternative models

Models	Chi-square	Weighted-sum-of-squares	Maximum error on an equivalent circuit element (%)
Jamnik predominantly electronic conducting	8.1	1082	6.0×10^{11}
Jamnik predominantly ionic conducting	0.002	0.322	2.8
Insertion reaction	0.014	1.917	1.3×10^8
Randles circuit	0.003	0.452	8.0

However, for $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ only the Bauerle equivalent circuit fitted the experimental data under all experimental conditions, indicating that the electronic component is less than 0.0001% which is the lower limit of electronic component for Jamnik model. The addition of a third RC element to Randles model that is the Bauerle model, in an attempt to model the observed low frequency phenomena did not result in any improvement in goodness of fit for all other compounds exclusive of $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$.

4.7.2 Effect of changing from CaNd_2S_4 series to SrNd_2S_4 series

The host cation was changed from calcium ion to the larger strontium ion in order to increase the lattice parameter of the unit cell thereby increasing the ionic conductivity. Since mechanically contacted graphite electrodes on the electrolytes introduces spreading resistance, only the high frequency arc was used to measure bulk conductivity. The Nyquist plots for both un-doped CaNd_2S_4 and SrNd_2S_4 have similar shape and if an improvement in bulk conductivity was made it cannot be seen clearly, Figure 4-51. However equivalent circuit modelling can quantify the bulk conductivity; the results are discussed in section 4.8.3.

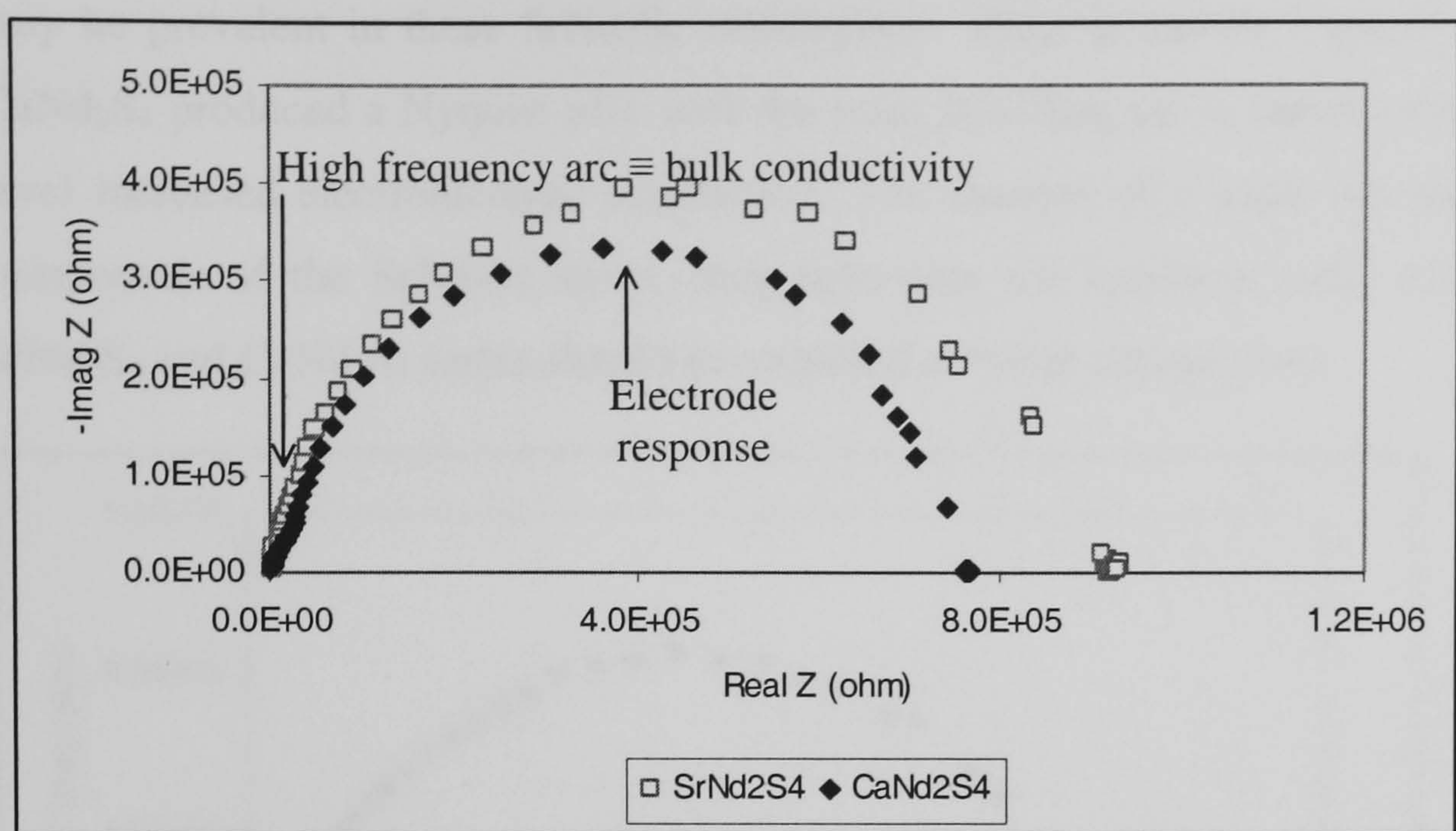


Figure 4-51. Experimental impedance of SrNd_2S_4 and CaNd_2S_4 at 400°C in Argon with graphite electrodes

The $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ Nyquist plot has a distinct low frequency arc (ionic blocking electrode effect), however the Nyquist plot for $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ appears to lack this feature, Figure 4-52. Also the very large imaginary component of medium frequency arc of $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ reduced significantly with host cation change, Figure 4-52. Therefore the increase in conductivity for $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ apparently without the low frequency ionic blocking arc in the Nyquist plot suggests that the increase in conductivity could be attributed to an increase in electronic conductivity rather than ionic conductivity.

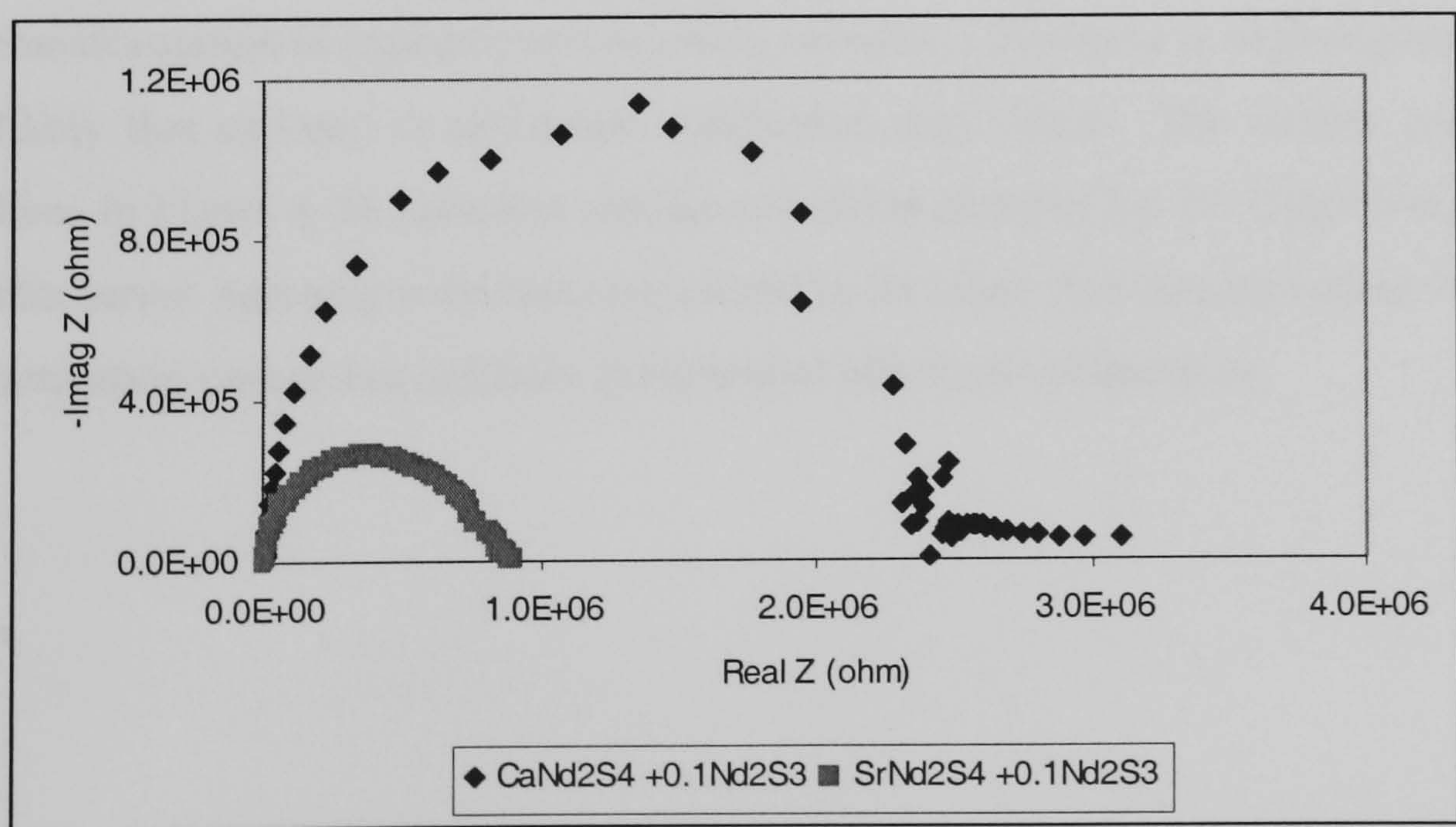


Figure 4-52. Impedance of $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ and $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ at 300°C

The Nyquist plots of both $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ and $\text{SrNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ electrolytes have total impedance which is much less than their respective equivalent calcium sulphide based electrolyte, Figure 4-53. The absence of ionic blocking suggests that electronic conduction

may be prevalent in these SrNd_2S_4 electrolytes. Only at excess 10mol% Nd_2S_3 doping of CaNd_2S_4 produced a Nyquist plot with the ionic blocking arc; a future increasing the dopant level increased electronic-type conduction. The absence of a clear ion blocking arc for all compounds of the SrNd_2S_4 series, may infer that the optimum ionic conduction for both SrNd_2S_4 and CaNd_2S_4 series should be explored at lower dopant level.

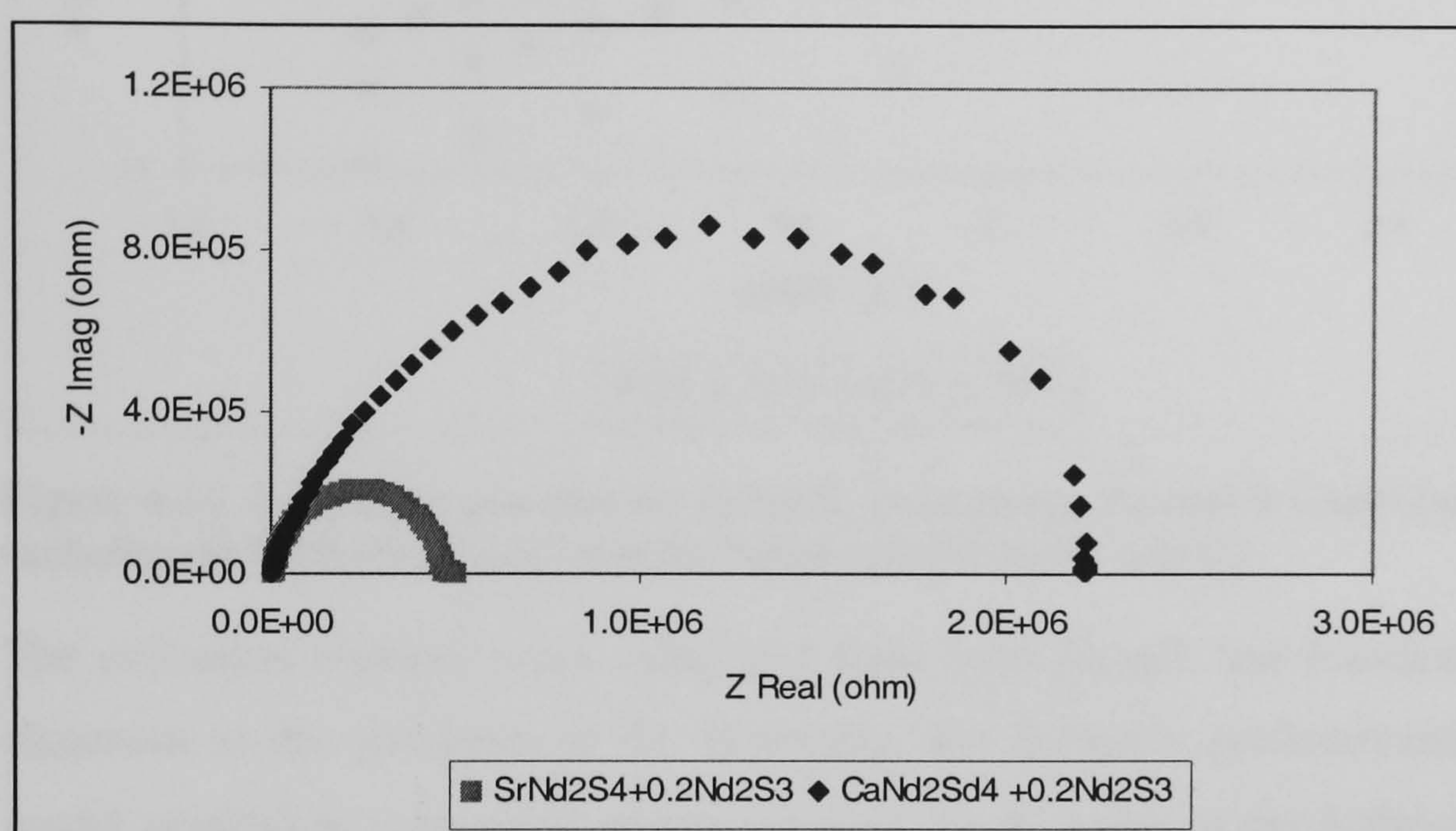


Figure 4-53 Impedance of the $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ and $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ with graphite electrodes at 300°C

4.8.2 Activation energy for SrNd_2S_4 series

The Arrhenius plot for all compounds of the SrNd_2S_4 series was linear excluding $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$. Since the unit cell is cubic, a highly order symmetric structure, no phase transformation is expected or can easily explained. However at high dopant concentration it is likely that cationic or electronic conduction may occur. The similar gradient of the other lines in Figure 4-54 indicates similar activation energies for the respective compounds within this series, agreeing with ideas expressed in literature that doping causes very little change in activation energy but can have pronounced effect on conductivity.

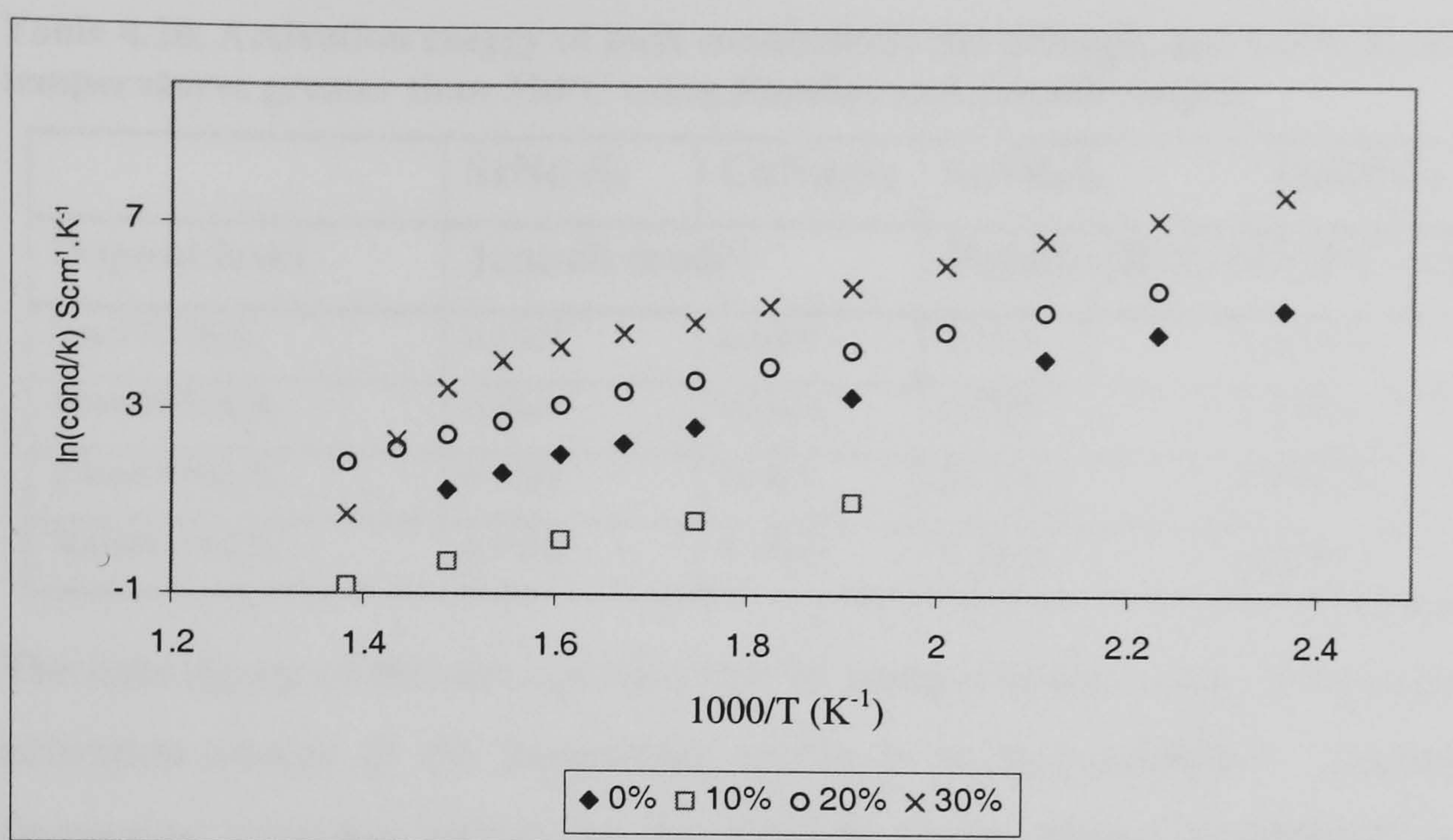


Figure 4-54. Activation energies for SrNd_2S_4 series using Jamnik's model for all compounds excluding $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ (was modelled using Bauerle model)

The activation energies were calculated from both Jamnik and Randles models due to the closeness in the goodness of fit. Generally, the Jamnik's predominantly ionic conducting model resulted in a marginal improvement in the R^2 value of the Arrhenius plot, Table 4.19. Also the activation energies derived from the Jamnik model resulted in lower values, of 0.05-0.1eV, relative to Randles model; excluding $\text{SrNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$. However, both models identify that $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ has the minimum activation energy.

Table 4.19. Activation energy for SrNd_2S_4 series using Jamnik or R//C- R//CPE model

	Jamnik model		R//C – R//CPE	
	High temp	Low temp	High temp	Low temp
Undoped SrNd_2S_4	0.35eV, $R^2=0.997$		0.46eV, $R^2=0.982$	
* $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$	0.32eV, $R^2=0.999$		0.37eV, $R^2=0.978$	
$\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$	0.37eV, $R^2=0.997$		0.51eV, $R^2=0.999$	
$\text{SrNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$	1.77eV, $R^2=.96$	0.38eV, $R^2=.999$	0.72eV, $R^2=0.999$	0.47eV, $R^2=0.985$

*Bauerle model used due to the lack of fit for the Jamnik model

Based on available literature for sulphide ion conduction in symmetric unit cells an expected range of activation energy for bulk conduction was previously established to be 0.61-1.61eV in Chapter 4.45. While the activation energy, determined using R//C-RCPE (Randles) model, for sulphide ion conduction lies in the expected range for the doped CaNd_2S_4 compounds, only $\text{SrNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ has an activation energy greater than 0.61eV, Table 4.20.

Table 4.20. Activation energy of bulk conductivity for SrNd_2S_4 and CaNd_2S_4 series at temperatures greater than 350°C using Randles and Jamnik models

	SrNd_2S_4	CaNd_2S_4	SrNd_2S_4	CaNd_2S_4
Dopant level	Jamnik model		Randles(R//C-R//CPE) model	
0mol% Nd_2S_3	0.35eV	0.42eV	0.46eV	0.48eV
10mol% Nd_2S_3	0.32eV	0.23eV	0.37eV	0.62eV
20mol% Nd_2S_3	0.37eV	0.46eV	0.51eV	0.97eV
30mol% Nd_2S_3	1.77eV	0. 65eV	0. 72eV	0.64eV

The opening up of the unit cell structure by using a larger cation, should cause a lowering in activation energy if the conducting specie is in fact sulphide. Therefore the trend of decreasing activation energy for the SrNd_2S_4 series relative to CaNd_2S_4 is consistent with conduction of sulphide ions; based on activation energies derived from either Jamnik or Randles models, Table 4.20. This theory assumes no impact (if present) of electronic conduction for both CaNd_2S_4 and SrNd_2S_4 based compounds.

Both the undoped SrNd_2S_4 and CaNd_2S_4 have comparable activation energies for ionic hopping, Table 4.19. Using Jamnik model for predominat ionic conduction for electrolytes doped with excess Nd_2S_3 for both CaNd_2S_4 and SrNd_2S_4 series lead to the minimum activation energy occurring at 10mol% Nd_2S_3 . Faber *et. al.*, 1989, also found a minimum activation energy in every series of doped cerium oxide based compounds. Faber ascribes this minimum to changes in the energy of oxygen sites in the vicinity of dopant cation. Other theories are proposed to explain this minimum such as the theory related to the electrostatic effect of dopant ion, Wang *et. al.*, 1981. Butler *et. al.*, 1983 proposed that this phenomena was the effect of the elastic strain energy on the association enthalpy of a simple pair of vacant site and dopant site. Irrespective of the founding reason the presence of the minimum activation energy, for the Nd_2S_3 based series apparently exhibit similar behaviour to cerium oxide compounds

4.8.3 Conductivity energy for SrNd_2S_4 series

Using either Randles or Jamnik equivalent circuits to model EIS experimental data gave conductivity values with a difference of over 2 orders of magnitude, Table 4.21. This highlights the importance of model selection and hence need to use complimentary techniques to characterise materials.

The change from undoped- CaNd_2S_4 to undoped- SrNd_2S_4 caused a significant increase in conductivity from $1.69 \times 10^{-5} \text{ S.cm}^{-1}$ to $6.73 \times 10^{-4} \text{ S.cm}^{-1}$ without a major alteration of the activation energy for ionic hopping, Table 4.20 and Table 4.21.

Table 4.21. Bulk conductivities at 500°C, energies for CaNd_2S_4 and SrNd_2S_4 series using Jamnik or Randles equivalent circuit

	$\text{SrNd}_2\text{S}_4 \text{ (S.cm}^{-1}\text{)}$		$\text{CaNd}_2\text{S}_4 \text{ (S.cm}^{-1}\text{)}$
0mol% Nd_2S_3	6.73×10^{-4}	$*3.81 \times 10^{-6}$	2.19×10^{-8}
10mol% Nd_2S_3	3.39×10^{-3}	$*9.16 \times 10^{-4}$	1.09×10^{-6}
20mol% Nd_2S_3	2.61×10^{-4}	$*3.49 \times 10^{-5}$	3.09×10^{-5}
30mol% Nd_2S_3	2.95×10^{-3}	$*2.87 \times 10^{-5}$	1.85×10^{-5}

*Conductivities calculated from Randles equivalent circuit

Both the Randles and Jamnik models identifies the $\text{SrNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$ as having the maximum conductivity in this series of compounds, Table 4.21.

4.8.4 Concentration dependence of SrNd_2S_4 series bulk conductivity

The conductivity for a pure ionic conductor is independent of atmospheric concentration changes. Therefore the conductivity for the SrNd_2S_4 series was measured in a varying concentration of H_2S . Impedance spectroscopy was carried out from 350°C to 550°C, one hour isothermal period, with the concentration ranging from pure argon to 2vol% $\text{H}_2\text{S}/\text{Ar}$ for each temperature. Oxide based electrolytes were considered to be ionic conducting rather than mixed ionic-electronic if the gradient of $(\log \sigma_{total})$ vs $(\log P_{O_2}) \leq 0.01$, that is the total conductivity was considered to be independent of the oxygen partial pressure if the ratio is less than 0.01, C. Song and H. Yoo 2000. This establishes a realistic definition for a pure ionic conductor, and as such was used as the benchmark for the characterisation sulphide ion conductors

The bulk conductivity of undoped- SrNd_2S_4 appears to be independent of H_2S concentration at elevated temperatures, Figure 4-55. However, at lower temperatures and H_2S concentration greater than 1vol%, a decrease in conductivity was observed, suggesting the onset of electronic conduction, Figure 4-55. Plotting conductivity isotherms of total conductivity vs. H_2S partial pressure, the gradient, $(\log \sigma_{total})$ vs $(\log P_{H_2S})$, was 0.05 indicating predominant ionic conduction at 550°C and a H_2S concentration range 0vol% to 1vol% $\text{H}_2\text{S}/\text{Ar}$, Figure 4-56.

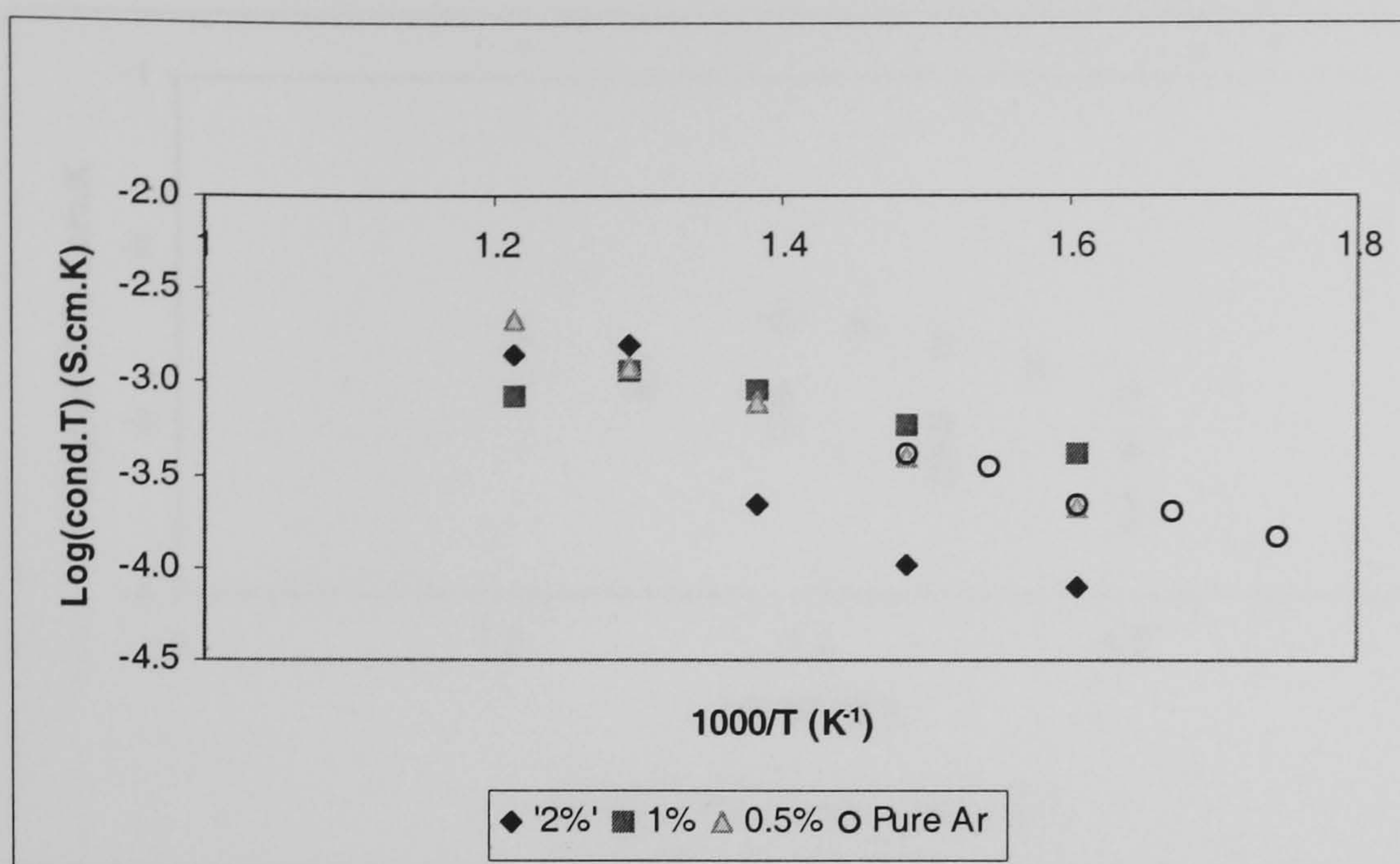


Figure 4-55. Concentration dependence of bulk conductivity vs. temperature for undoped SrNd_2S_4

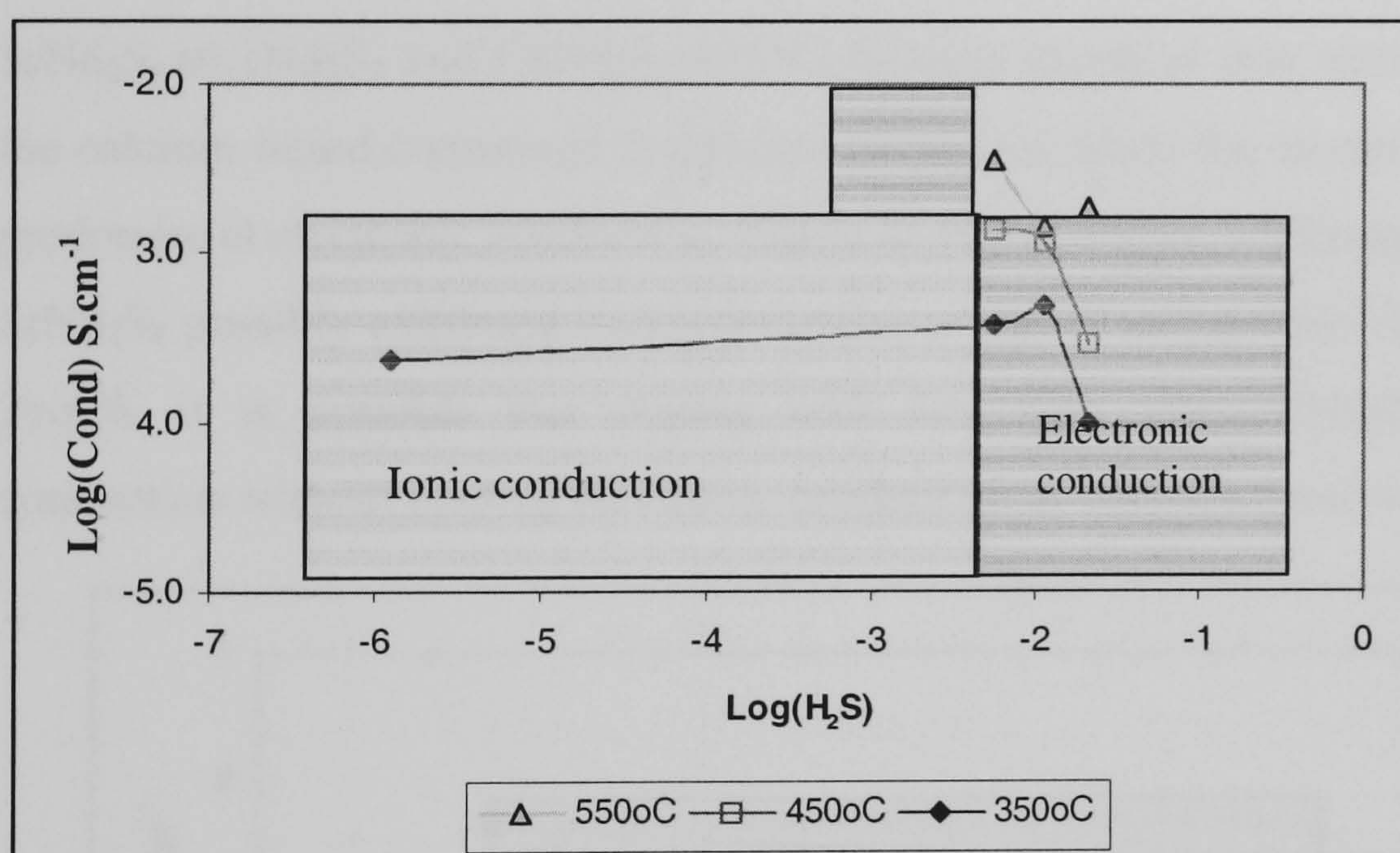


Figure 4-56. H_2S concentration dependence of total conductivity for undoped SrNd_2S_4

The bulk conductivity for $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ decreased with the presence of a positive H_2S partial pressure, Figure 4-57. This indicates the presence of electronic conductivity. Therefore the significantly increased bulk conductivity for $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ with respect to $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$, Table 4.21, could be attributed to the onset of electronic conduction. On increasing the H_2S concentration from 1vol% to 2vol% the conductivity also increased, therefore implying the onset of hole conduction at high H_2S concentration, Figure 4-57.

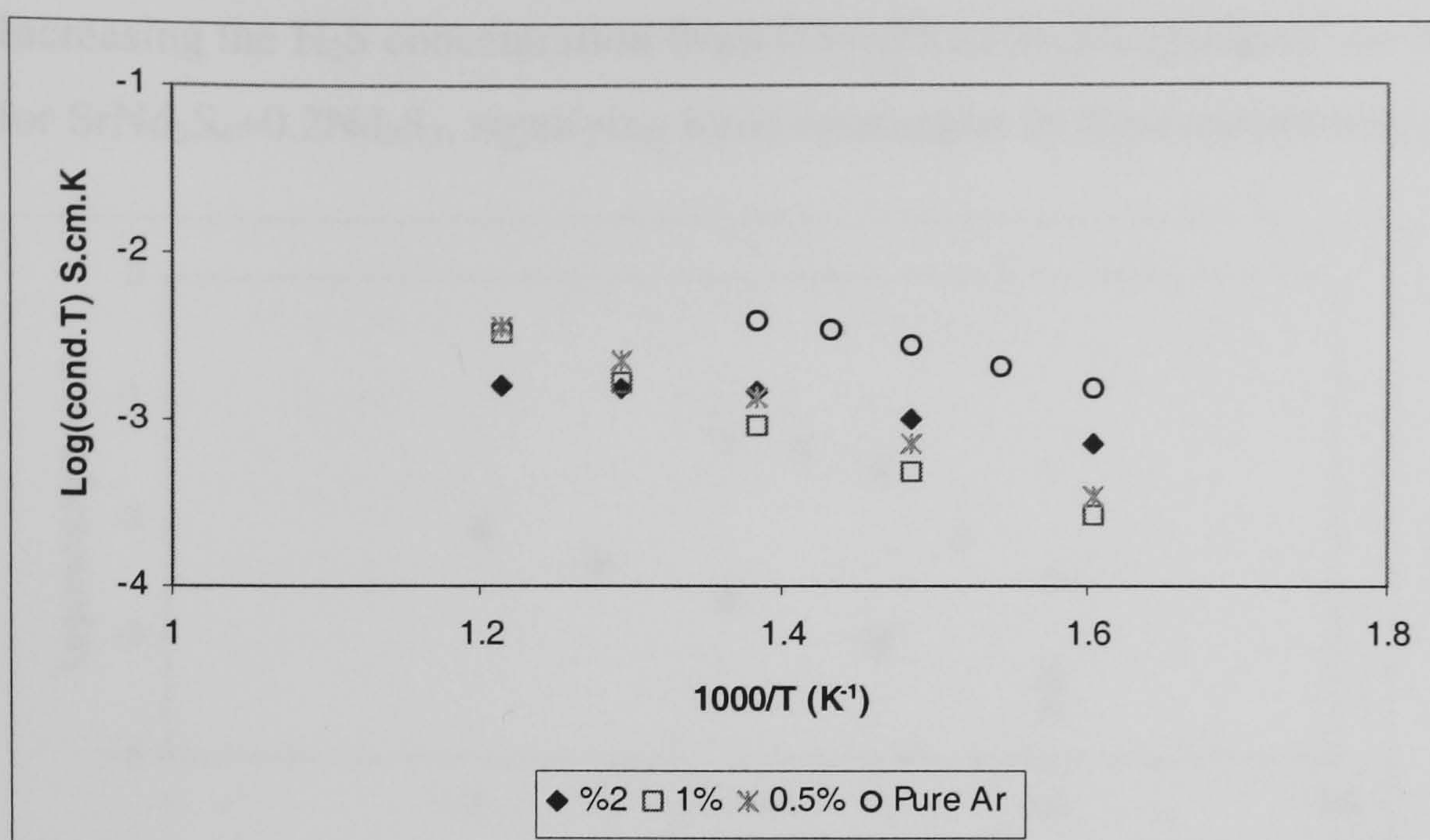


Figure 4-57. Concentration dependence of bulk conductivity vs. temperature for $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$

$\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ and $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ have identical unit cells and symmetry, and yet the calcium based compound is an ionic conductor while the strontium based compound has predominant electronic conduction, Figure 4-58 and Figure 4-29 respectively. Since undoped SrNd_2S_4 possibly exhibited ionic conduction at 500°C and at $\text{H}_2\text{S}/\text{Ar}$ concentrations less than 2vol%, it is possible that doping with less than 10mol% Nd_2S_3 could improve ionic conduction without causing electronic conduction as was observed with $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$.

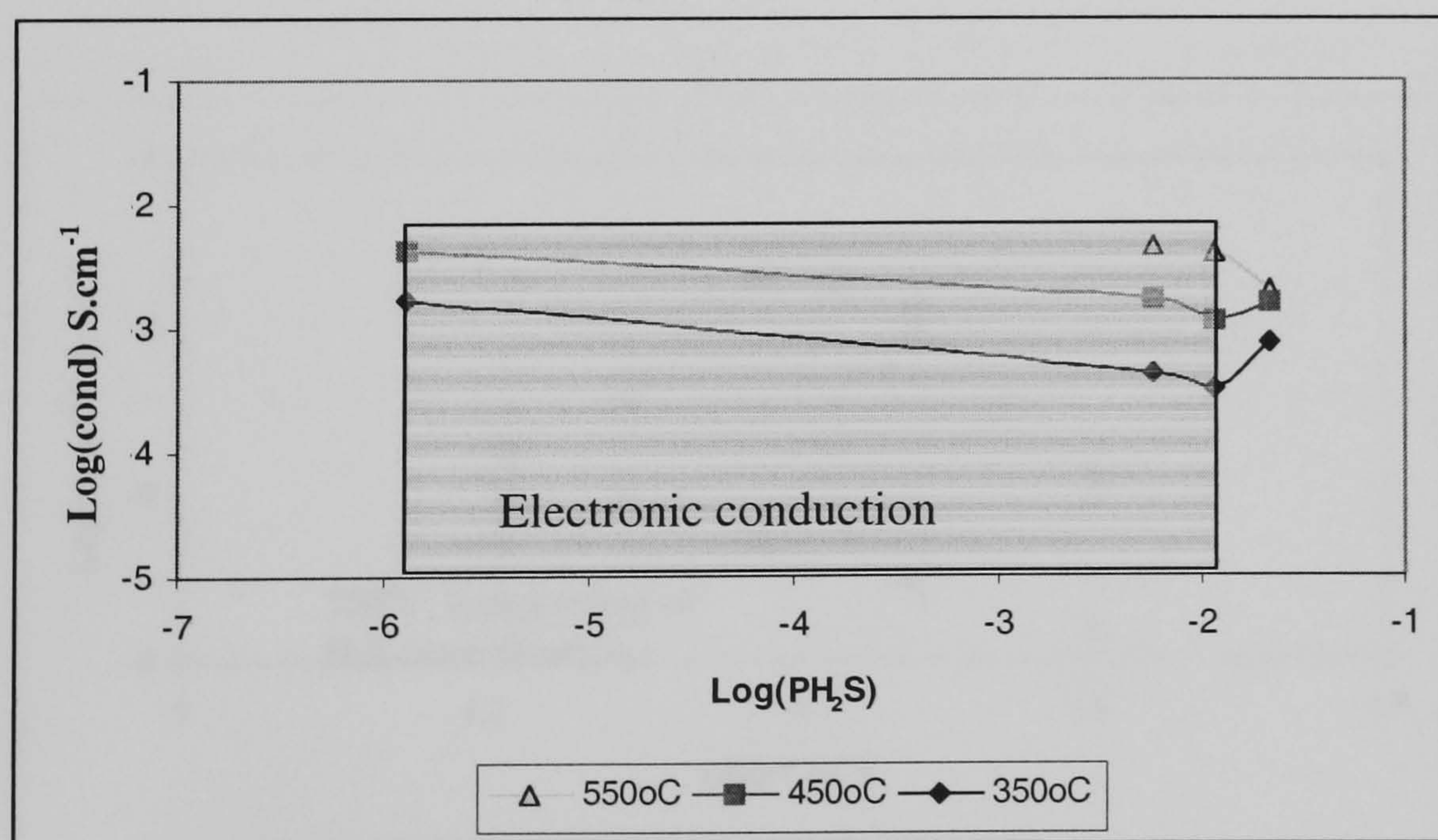


Figure 4-58. H_2S concentration dependence of total conductivity for $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$

The conductivity of $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ decreased in presence of a positive H_2S partial pressure thus implying electronic conduction that is similar behaviour to $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$, Figure 4-59. It would appear that the high level of doping, 20mol%, causes the onset of electronic conduction since electronic conduction also occurred for $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$.

Increasing the H₂S concentration from 0.5vol% to 2vol% produced no change in conductivity for SrNd₂S₄+0.2Nd₂S₃, signifying ionic conduction in this concentration range, Figure 4-59.

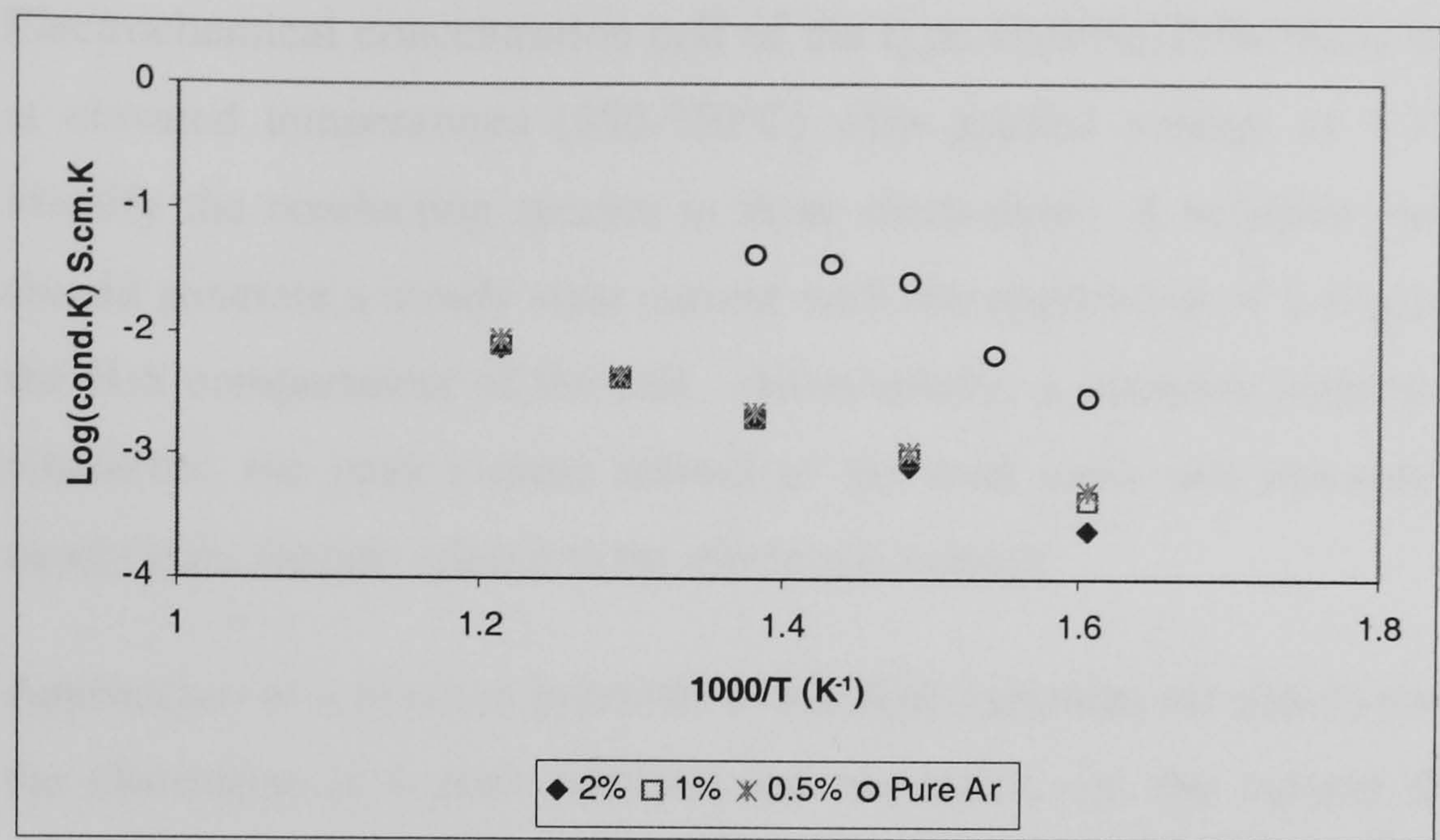


Figure 4-59. Concentration dependence of bulk conductivity vs. temperature for SrNd₂S₄+0.2Nd₂S₃

SrNd₂S₄+0.3Nd₂S₃ decreased in conductivity, as the partial pressure is increased, symptomatic of electronic contribution, Figure 4-60. However at 550°C the conduction becomes independent of all partial pressures studied, signifying ionic conductivity, Figure 4-60.

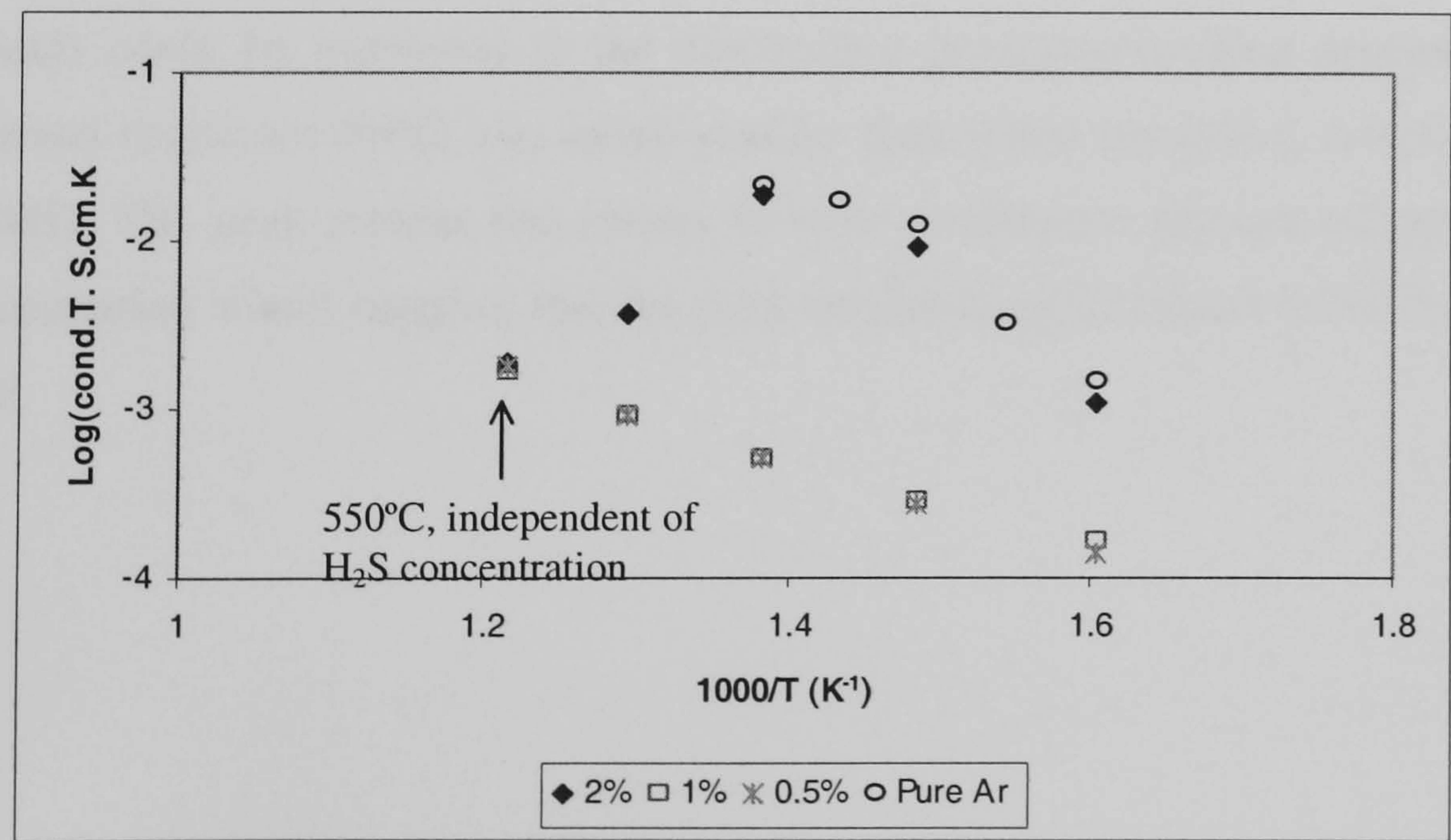


Figure 4-60. Concentration dependence of bulk conductivity vs. temperature for SrNd₂S₄+0.3Nd₂S₃

4.8.5 *Electrochemical pumping of sulphide ions in SrNd₂S₄*

Electrochemical concentration cell of the type H₂S/H₂//Pt/SrNd₂S₄ series/Pt//Ar/H₂ operated at elevated temperatures (550-750°C) with applied voltage of 1-2V (d.c) was set up to identify the conducting species in these electrolytes. A sulphide ion conducting electrolyte should generate a steady state current with the application of a negative potential applied on the H₂S compartment of the cell. Alternatively, a decaying current could indicate a mixed conductor, the peak current related to the total ionic and electronic, while the reversible steady state current related to the electronic current.

Application of a positive potential to the H₂S compartment should not produce any current if the electrolyte is a pure sulphide ion conductor, i.e. the current should decay rapidly to baseline. If the current decays slowly, then the movement of a positive ion is interpreted, (decay because there is no continuous source of ions, only from the electrolyte).

An electronic conducting electrolyte would produce a steady state current irrespective of the polarity of the applied voltage. An offset from the origin with no applied voltage is indicative of electronic current.

The asymmetric result of pumping SrNd₂S₄ at 550°C with 5V dc indicates mixed conduction. The source of large electronic contribution (difference between peak current and steady state current) could be attributed to the electroding process/cementing process since the cross sectional resistance 890Ω was much smaller than initial resistance, which was greater than 200MΩ. The peak current that relates to ionic conduction appears independent of the H₂S concentration which suggests that the peak current is cation based rather than anionic, Figure 4-61.

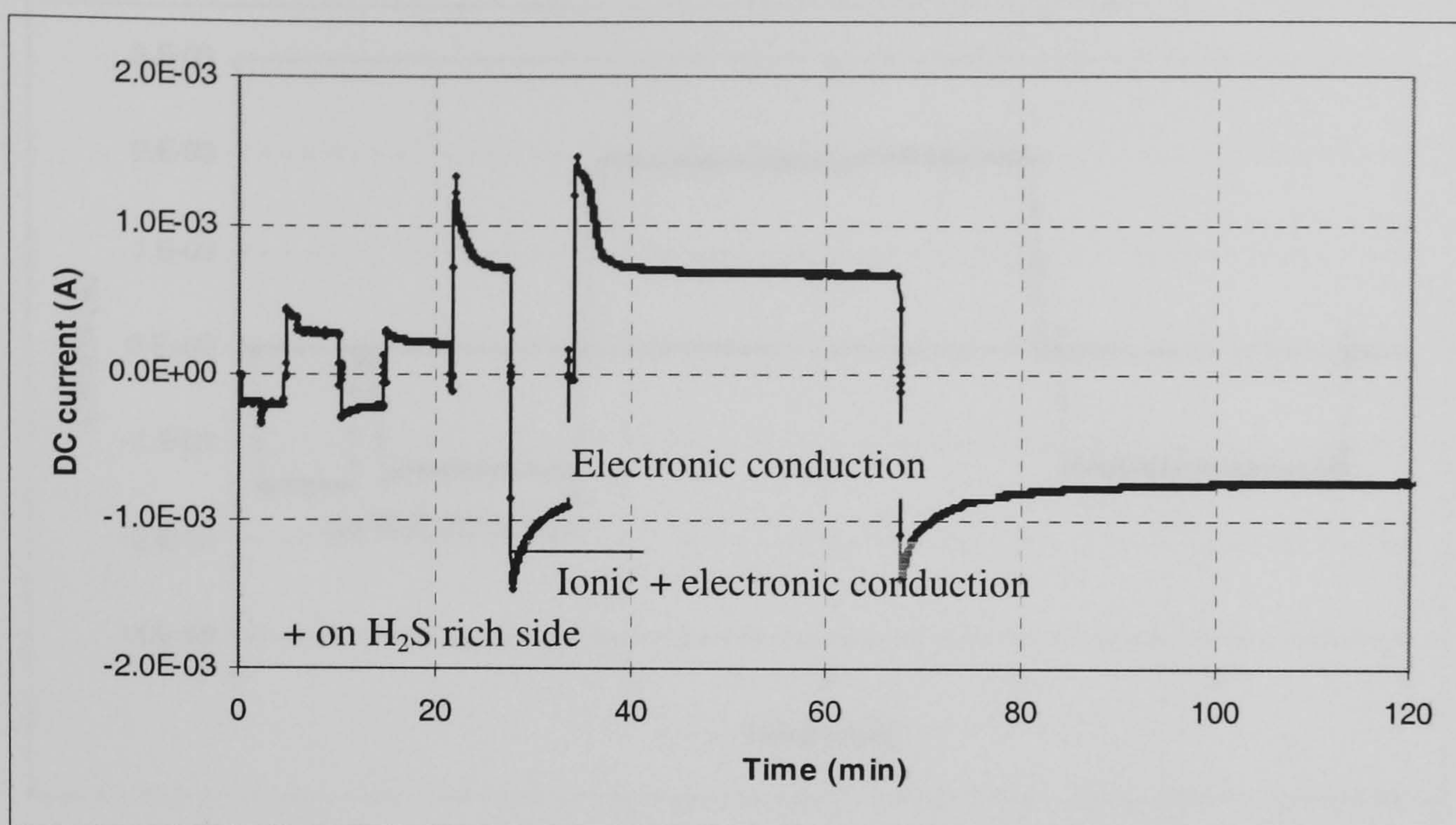


Figure 4-61. Electrochemical pumping of SrNd_2S_4 at 550°C with 1V & 5V dc

Electrochemical pumping of $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ also resulted in a symmetric current generation plot as the direction of the applied voltage was reversed, Figure 4-62. The absence of a significant peak suggests that the current flow is electronic, Figure 4-62.

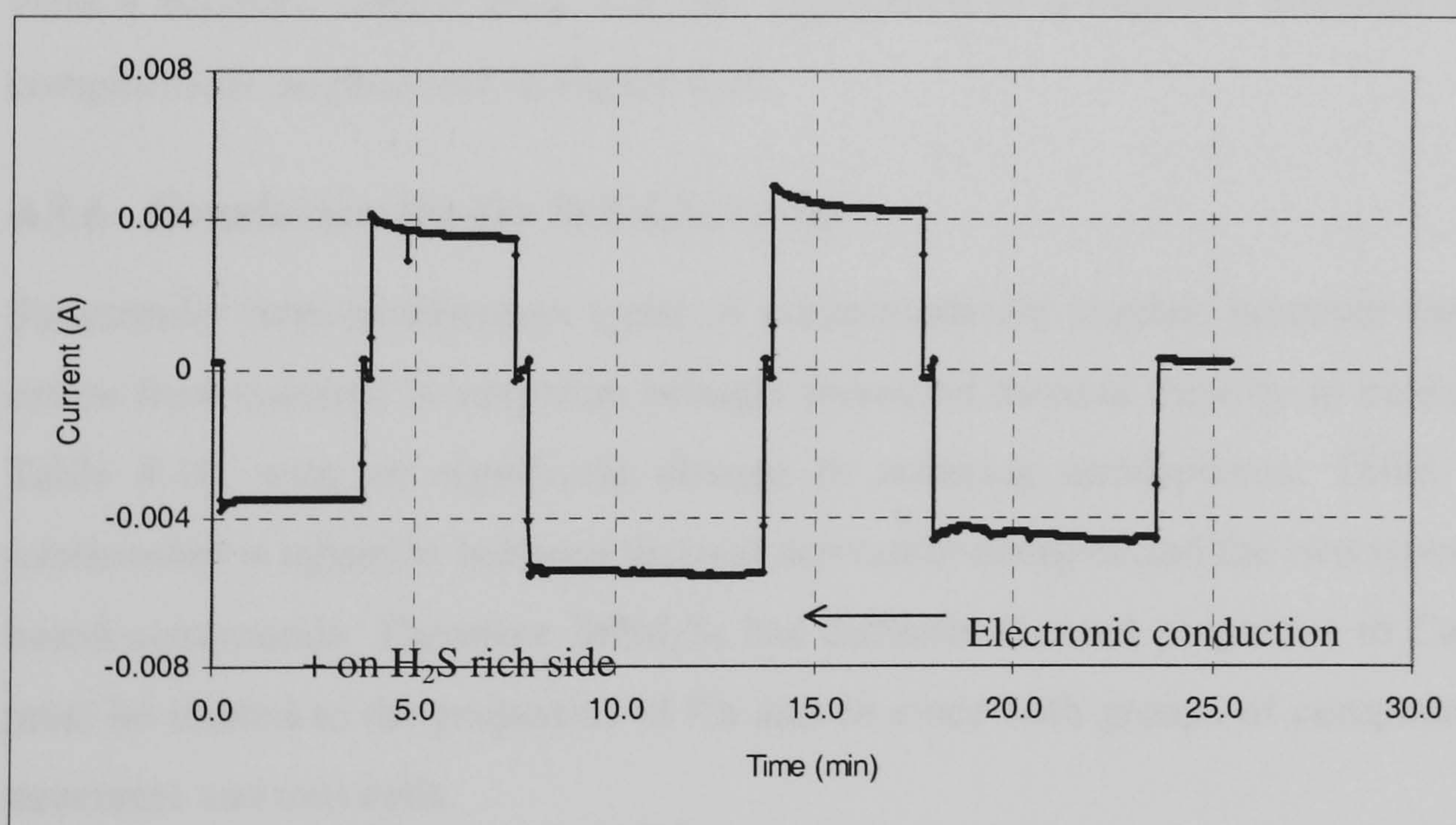


Figure 4-62. Electrochemical pumping of $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ at 500°C with 5V dc

Electrochemical pumping at 650°C resulted in asymmetric current response, Figure 4-63. Currents generated from a positive as well as negative applied voltage did not decay, and the higher current corresponds to the higher H_2S concentration side of the reactor.

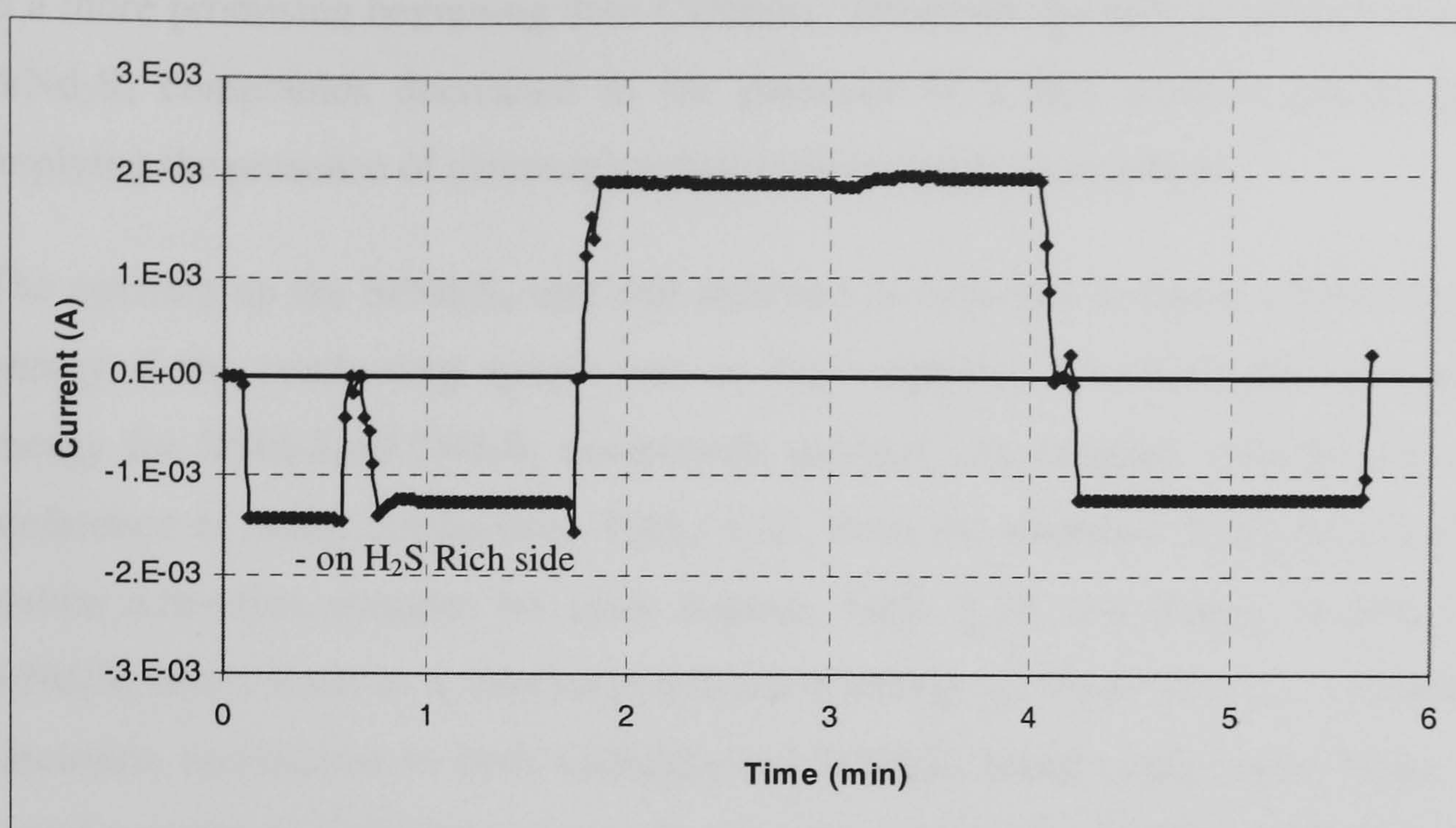


Figure 4-63. Electrochemical pumping of $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ at 650°C with 1V dc

Figure 4-63 shows the only asymmetric result obtained for $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ when pulsed at 650°C with 1V dc. A higher current was generated when 1V dc was applied to the H_2S rich side indicating the movement of negatively charged S^{2-} ions. Movement of S^{2-} ions would yield a constant current flow with the application of a negative potential on the H_2S rich compartment, as observed in Figure 4-63.

4.8.6 Conclusion for the SrNd_2S_4 series

Structurally both neodymium types of compounds are similar; however replacing the host cation from calcium to strontium brought increased thermal stability in oxidizing conditions, Table 4.16, with no significant change in reducing atmospheres, Table 4.17. No clear relationship is apparent between thermal activation energies and the two types of neodymium based compounds. Therefore SrNd_2S_4 has different thermal properties to CaNd_2S_4 , and this must be related to the properties of Ca and Sr since both groups of compounds have similar structures and unit cells.

Electrochemical characterisation by using impedance spectroscopy on SrNd_2S_4 series in an argon atmosphere indicates at best mixed ionic-electronic conduction since no ionic blocking electrode response was present in the Nyquist plots. Therefore increased bulk conductivities of SrNd_2S_4 and $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ are most likely electronic rather than ionic.

The H_2S concentration dependency of bulk conductivity of undoped SrNd_2S_4 showed electronic conduction at lower temperatures; on increasing the temperature it seems to be ionic conductivity because no change occurred with the increase in H_2S concentration, which

is a more promising beginning than CaNd_2S_4 . However the bulk conductivities for all doped SrNd_2S_4 compounds decreased in the presence of a H_2S positive partial pressure, thus implying the presence of electronic conduction in argon atmosphere.

The opening up the SrNd_2S_4 unit cell structure is expected to cause a lowering in activation energy if the conducting specie was in fact sulphide. Therefore the increased activation energy for $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ compounds qualitatively suggests cationic ion conduction in preference to anion conduction, Table 4.20. Both the undoped SrNd_2S_4 and CaNd_2S_4 have similar activation energies for ionic hopping, Table 4.20, and doping in both CaNd_2S_4 and SrNd_2S_4 series leads to a minimum activation energy at 10mol% Nd_2S_3 , assuming negligible electronic conduction in both CaNd_2S_4 and SrNd_2S_4 based compounds. Faber *et. al.*, 1989 found a minimum activation energy in any case of cerium oxide based compounds. Therefore these neodymium sulphide based compounds have similar behaviour to cerium oxide compounds. Interestingly CeO based electrolytes exhibit electronic conduction in low concentrations of oxygen as was observed for doped SrNd_2S_4 electrolytes.

Finally the asymmetric result of pumping SrNd_2S_4 at 550°C with 5V dc indicates mixed conduction and the peak current that relates to ionic conduction appears independent of the H_2S concentration, which suggests that the peak current is cation based rather than anionic. Electrochemical pumping of $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ gives symmetric response at 550°C , indicating electronic conduction, but at 750°C an asymmetric current response indicates sulphide ion conduction. The frequent short-circuiting of the electrolytes in the pumping cells could have skewed the data enormously and such data cannot be used to differentiate ionic from electronic conduction.

4.9 References For Chapter 4

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Chapter 5

5 Characterisation and electrochemical application Samarium Sulphide doped CaSm_2S_4 and SrSm_2S_4 series

Finding a suitable high temperature sulphide ion-conducting electrolyte began with verification of the previously reported sulphide ion conducting calcium neodymium sulphide series. While, Kalinina *et al.*, 1995, identified all doped CaNd_2S_4 compounds as purely ionic (a mix of anions and cations). However only $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ was found to exhibit this property when characterised by impedance spectroscopy. The bulk conductivity of $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ (at 500°C) was low, $1.09 \times 10^{-6} \text{S.cm}^{-1}$. Therefore modification of the material was sought, which entailed changing the host cation from calcium to strontium. This led to an increase in bulk conductivity but was later established to have significant electronic or positive hole conduction. Therefore the next logical change in modifying the electrolyte was to change the dopant compound. Therefore calcium samarium sulphide doped with excess samarium sulphide was characterised in order to identify if these materials are indeed sulphide ion conductors.

Calcium samarium sulphide doped with excess samarium sulphide has previously been synthesised and characterised by Kalinina *et al.* 2000 where they reported that these materials exhibited sulphide ion conductivity. Therefore the analogue CaSm_2S_4 of CaNd_2S_4 was synthesised using an identical solid-state reaction procedure as established by Kalinina *et al.*, 1995.

The XRD pattern shows the defining reflections of CaNd_2S_4 ; this compound has a cubic unit cell similar to CaNd_2S_4 shown in Figure 4.1, Chapter 4, where the larger black spheres now represent Sm rather than Nd atoms, White, 2005. The X-ray diffraction pattern shows that an increase in dopant level does lead to similar changes as observed with the CaNd_2S_4 system, Figure 4.1, Chapter 4, White, 2005. The volume of the unit cells decreased as the cation was changed from neodymium to samarium expressed by the reduction in the lattice parameter while increasing the dopant level in each group of compounds caused a contraction of the unit cell, Table 5.1. The decrease in lattice parameter with the cation change from neodymium to samarium was expected since the samarium ion is smaller than the neodymium ion, and as such a decrease is inevitable.

Table 5.1. Lattice parameter for CaNd₂S₄ series and CaSm₂S₄ series

Dopant level (Sm ₂ S ₃ or Nd ₂ S ₃)	Lattice parameter Å (a-site) CaSm ₂ S ₄	Lattice parameter Å (a-site) CaNd ₂ S ₄
Undoped	8.4708(1)	8.5301(1)
10%	8.4701(8)	8.5299(1)
20%	8.4684(8)	8.5280(1)
30%	8.4653(1)	8.5273(1)

Large grain particles of CaSm₂S₄ do not sinter well, similar to CaNd₂S₄, therefore the average particle size was reduced by dry ball milling for up to four days to increase the density of the sintered pellet. Pellets were made with ground material by uniaxial pressing to 10 tonnes followed by sintering at 1350°C; pellets were produced with a maximum of 97% of the theoretical density, Table 5.2. Increasing temperatures to 1550°C produced severely cracked pellets and the high quality alumina (99% Al₂O₃) support changed colour from white to yellow indicating a reaction between pellet and support. The final sintering temperature of 1350°C was selected.

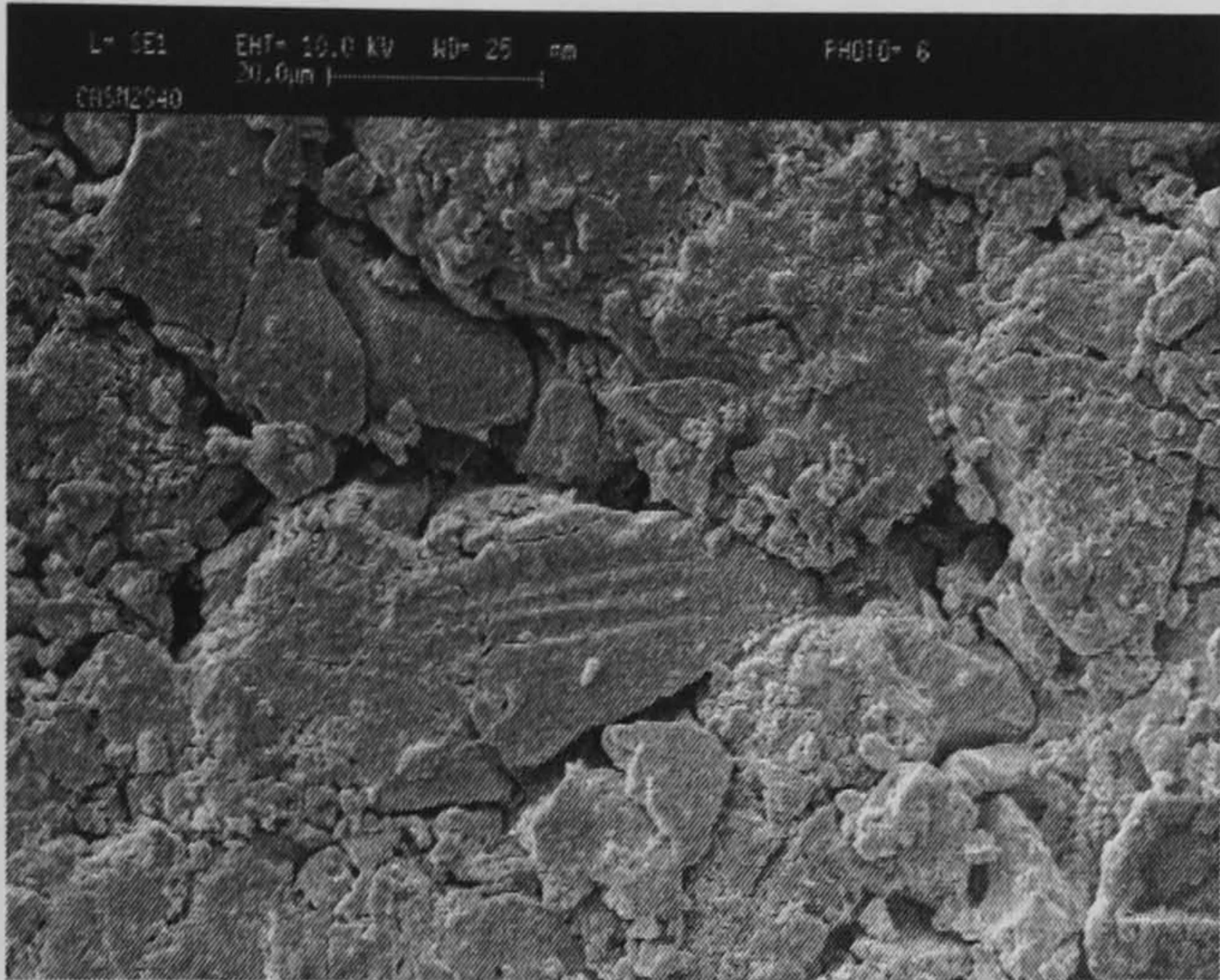
Table 5.2. Theoretical and actual densities for CaSm₂S₄ series

	Theoretical density CaSm ₂ S ₄ (g/cm ³)	Actual density CaSm ₂ S ₄ (g/cm ³)		% Of theoretical density	
		Before grinding	After grinding	Before grinding	After grinding
Undoped	5.125	4.09	4.69	80	91
10mol%Nd ₂ S ₃	5.055	4.00	4.34	79	90
20mol%Nd ₂ S ₃	4.995	3.91	4.84	78	93
30mol%Nd ₂ S ₃	4.953	n/a	n/a	n/a	n/a

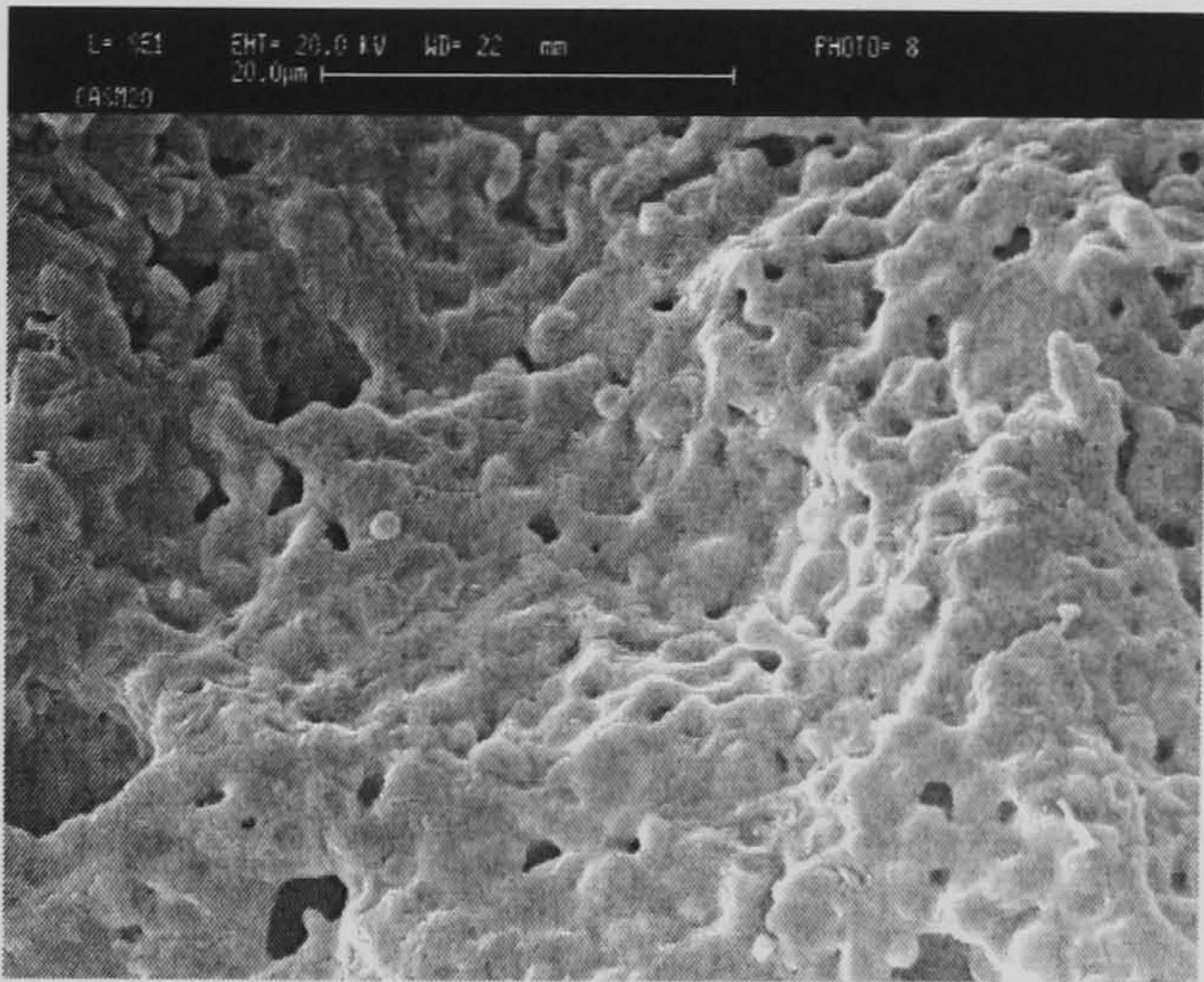
n/a – not available

SEM's of the sintered pellets made with un-ground powders shows many large pores of diameter up to 20µm with fairly thin grain boundaries, Figure 5-1. These pores are the cause of the low density of the sintered pellet. The pellet is so porous that its SEM resembles that of compressed powder. Reducing the mean particle size by grinding resulted in a significant improvement in the final density of the sintered pellet, Figure 5-2. The density increased by 10% when the pellets were made with ground powder, Table 5.2. While the density of pellets of SrNd₂S₄+0.2Nd₂S₃ and CaNd₂S₄+0.2Nd₂S₃ were higher when compared to other

compounds in either family, the CaSm_2S_4 series all appear to have similar ‘sinterability’ since the percentage of theoretical density was comparable.



(Before grinding)



(After grinding)

Figure 5-1. $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ sintered pellets at 1350°C in $\text{H}_2\text{S}/\text{Ar}$ mixture with 78% and 92% of theoretical density

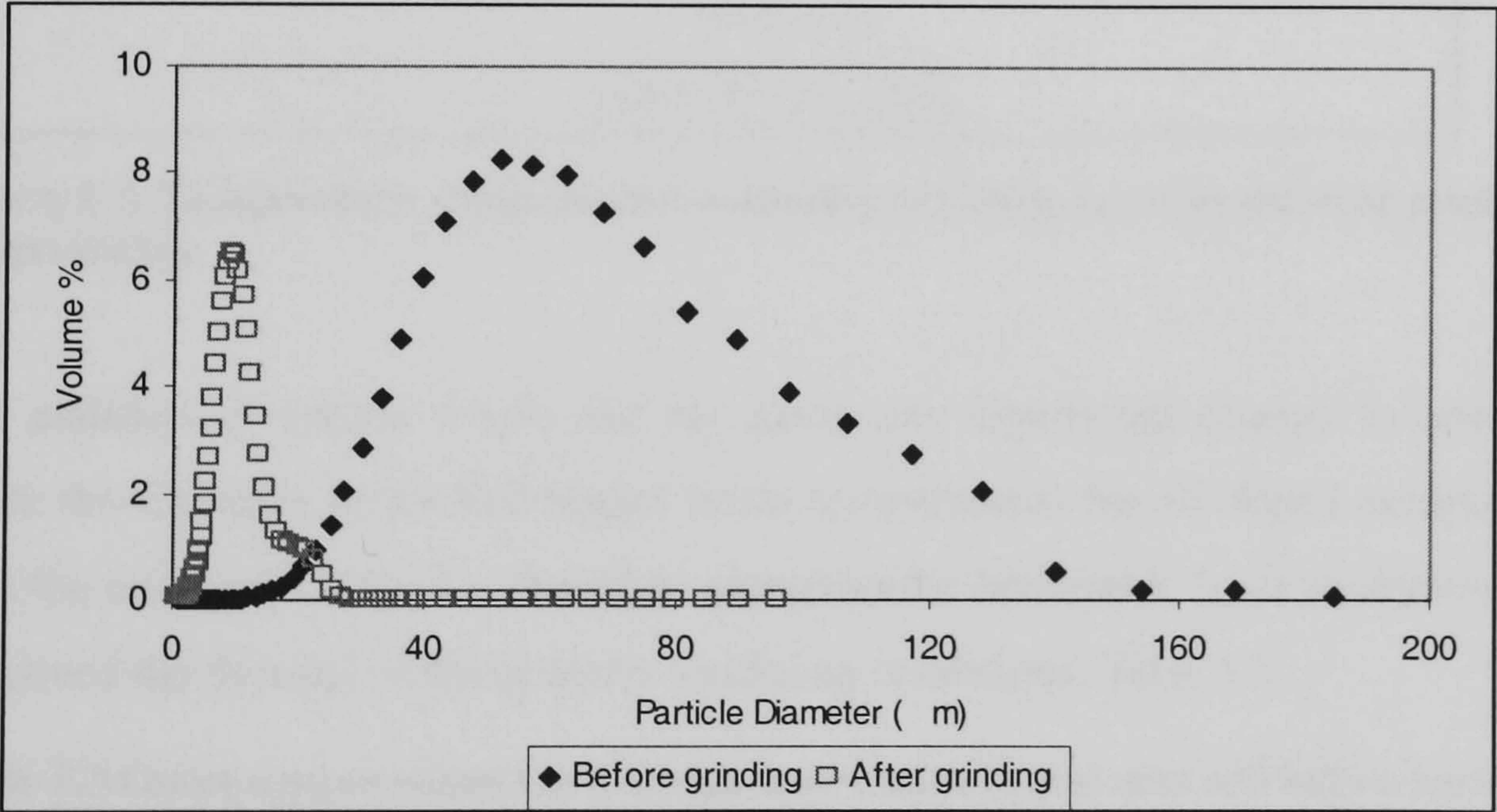


Figure 5-2 Particle size distribution of before and after grinding of $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$

5.1 TPO and TPR for CaSm₂S₄ series

The thermal stability of CaSm₂S₄ series was established using TPO and TPR techniques. The TPO traces of this series consist of one major peak with a shoulder at the higher temperature, which mimics the CaNd₂S₄ series TPO traces, Figure 5-3. The presence of a single major SO₂ peak at elevated temperatures indicates that only one type of sulphur is being reacted to form sulphur dioxide, implying a single-phase compound

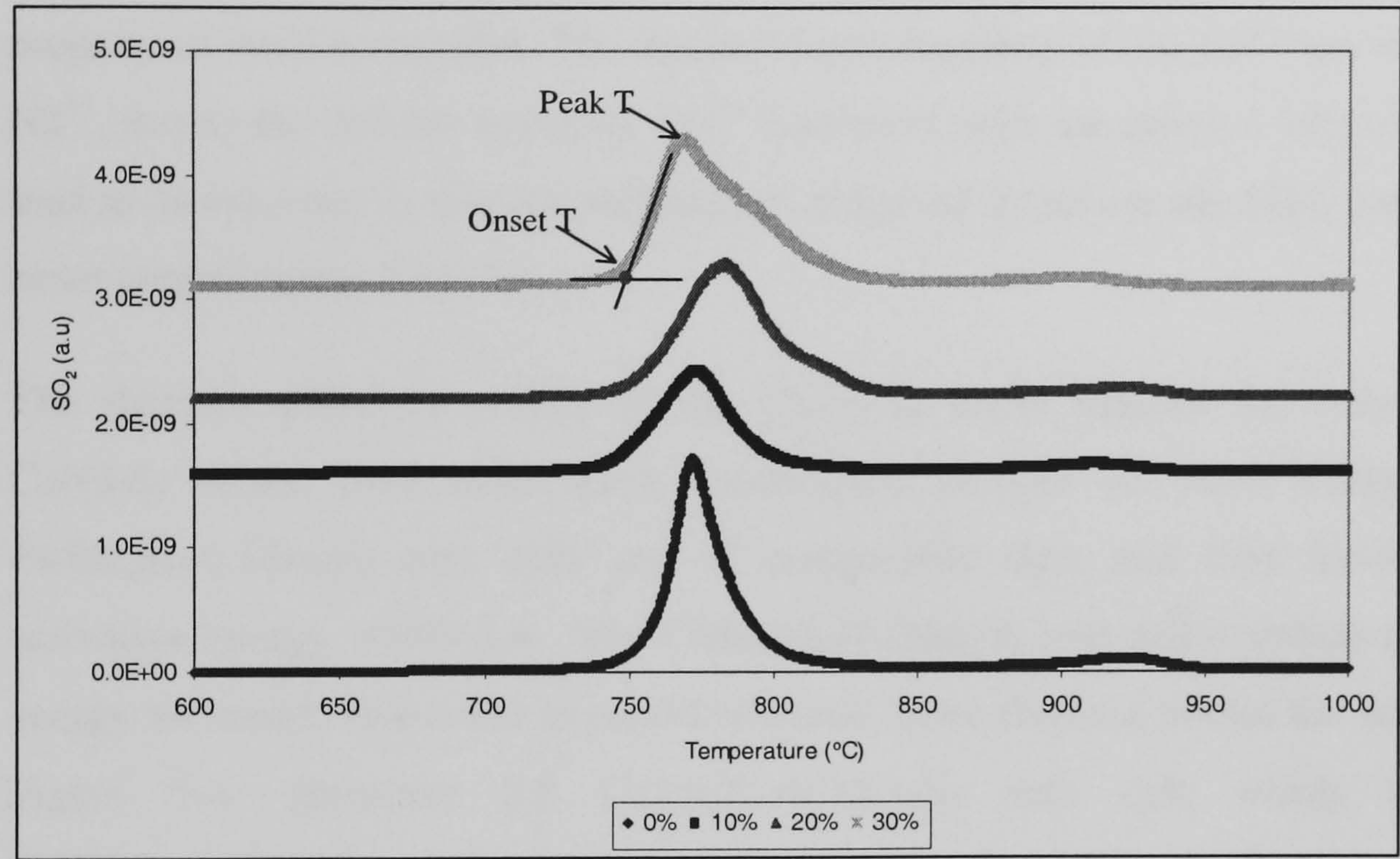


Figure 5-3. Temperature programmed oxidation of CaSm₂S₄ series showing peak and onset temperatures

The addition of excess Sm₂S₃ did not cause any significant change in onset temperatures while the CaNd₂S₄ series had higher onset temperatures for all doped compounds compared with the undoped CaNd₂S₄. Therefore changing the lanthanide from neodymium to samarium improved the thermal stability under oxidizing conditions, Table 5.3.

Table 5.3 Onset temperatures for CaNd₂S₄ and CaSm₂S₄ and unit cell lattice parameter

	Onset Temperatures		Lattice parameter for ‘a’ site Å	
	CaNd ₂ S ₄	CaSm ₂ S ₄	CaNd ₂ S ₄	CaSm ₂ S ₄
0%	671	755	8.5301(1)	8.4708(1)
10%	723	745	8.5299(1)	8.4701(8)
20%	708	750	8.5280(1)	8.4684(8)
30%	703	750	8.5273(1)	8.4653(1)

*Bracketed () number indicates the standard deviation on the fourth decimal place

The increase in oxidation onset temperature with increasing dopant content for CaNd_2S_4 series could be related to the reduction in the lattice parameter, Table 5.3 that indicates a reducing unit cell volume. However the CaSm_2S_4 unit cell decreased with increasing dopant content, yet the oxidation onset temperature remains unchanged implying that unit cell size is not the only parameter, which governs oxidation onset temperature. None of the groups of sulphides studied so far, CaNd_2S_4 , SrNd_2S_4 and CaSm_2S_4 , have a similar trend in oxidation onset temperatures as a function of dopant content. It implies that this temperature is a unique property of each compound. The increased polarisability of the Sm^{3+} ion with respect to the Nd^{3+} , due to the smaller radius of Sm^{3+} combined with the reduced lattice parameter should lead to an increase in thermal stability, as observed based on the slight improvement in the onset temperatures, Table 5.3.

The thermal activation energy of the CaSm_2S_4 series follows the same trend as in the CaNd_2S_4 series: both series have a maximum thermal activation energy. CaSm_2S_4 and $\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ unit cells are of comparable size, and they have similar thermal activation energy, Table 5.4. The $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ unit cell contracts and the activation energy increases; this is the expected response since the ions within the unit cell are closer, Figure 5-4. However for $\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ unit cell which is smaller than $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ yet the activation energy reduced; this is not the expected response since this ions within the unit cell are closer, Figure 5-4. Greenwood, 1968, explained that when ions are in close proximity, an effective repulsive force operates which resists closer contact. Though it is a short-range interaction it increases exponentially with a decrease in inter-nuclear distance. Therefore this repulsive force at short lattice parameter could explain the decreased thermal activation energy for 30mol% doped CaNd_2S_4 and CaSm_2S_4 , Table 5.4.

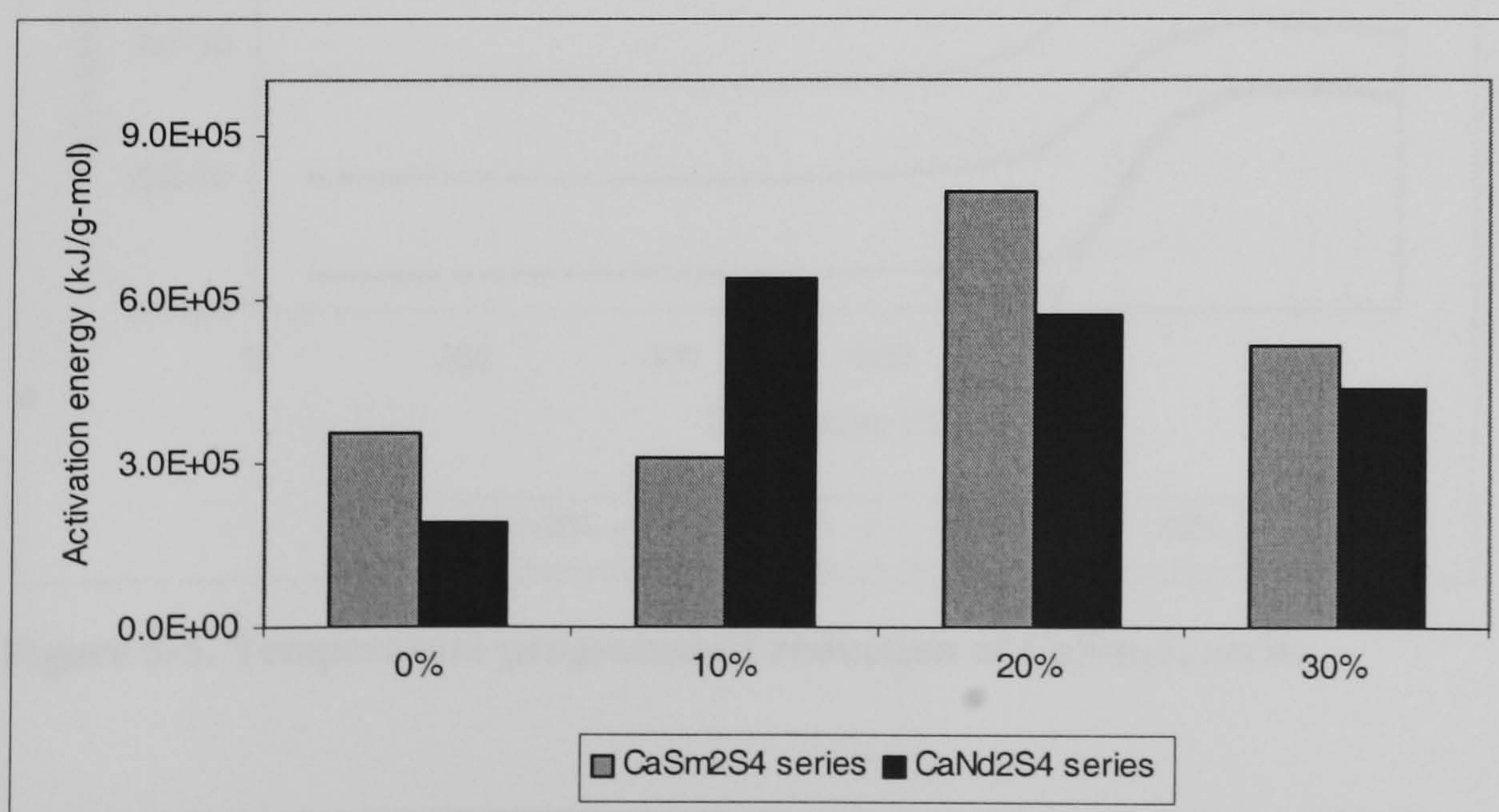


Figure 5-4 Thermal Activation energy for CaSm_2S_4 and CaNd_2S_4 series

Small concentrations of Schottky defects in stoichiometric compounds lower the density because these defects expand the crystal lattice . Frenkel defects are created within the crystal volume by an equivalent number of interstitial ions therefore small concentrations of Frenkel defects in a stoichiometric crystal cause no change in X-ray based densities. However, for doped or non-stoichiometric crystals, Frenkel defects may increase the density if the supernumerary ions are incorporated in interstitial sites without the corresponding number of vacant sites, Greenwood, 1968. Therefore the decrease in theoretical density for these non-stoichiometric sulphides infers Schottky defects.

Table 5.4 Thermal activation energies and XRD-based densities for CaNd₂S₄ and CaSm₂S₄ series

	Activation energy (kJ/g-mol)		Lattice parameter for ‘a’ site Å	
	CaNd ₂ S ₄	CaSm ₂ S ₄	CaNd ₂ S ₄	CaSm ₂ S ₄
0%	1.90x10 ⁵	2.78x10 ⁵	8.5301(1)	8.4708(1)
10%	6.37x10 ⁵	2.79x10 ⁵	8.5299(1)	8.4701(8)
20%	5.71x10 ⁵	8.42x10 ⁵	8.5280(1)	8.4684(8)
30%	4.36x10 ⁵	5.69x10 ⁵	8.5273(1)	8.4653(1)

The doped compounds of the CaSm₂S₄ series are less stable in hydrogen than the undoped- CaSm₂S₄, Figure 5-5. However CaSm₂S₄ series is more stable than CaNd₂S₄ in a reducing atmosphere, Table 5.5. Both series have CaSm₂S₄+0.2Sm₂S₃ and CaNd₂S₄+0.2Nd₂S₃ with the lowest onset temperature.

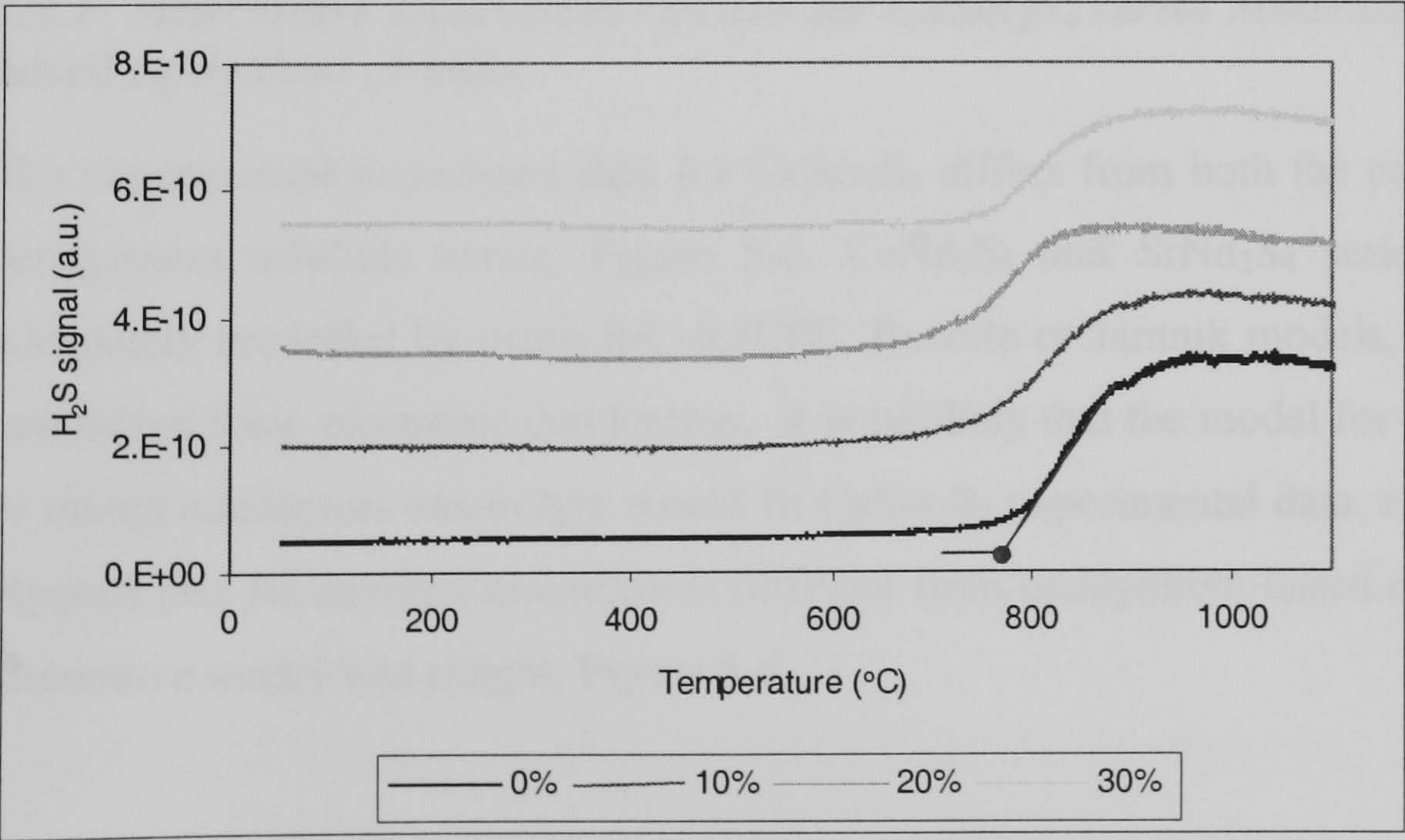


Figure 5-5. Temperature programmed reduction of CaSm₂S₄ series

Table 5.5 TPR onset temperature for the SrNd₂S₄ and CaNd₂S₄ series

Dopant level	CaSm ₂ S ₄ (°C)	CaNd ₂ S ₄ (°C)
0%	775	737
10%	745	766
20%	720	711
30%	750	724

5.2 Electrochemical characterisation of CaSm₂S₄ series

Impedance spectroscopy of the calcium samarium series was carried out in the temperature range from 250 to 400°C using graphite electrodes, with an ac voltage of 0.1 V_{rms}, frequency range from 0.1 Hz to 1x10⁶ Hz under argon atmosphere with 1 hour delay for temperature stability. Other electrode materials such as gold and platinum were not used based on the apparent reaction, previously discussed, with the electrolytes at low temperatures.

The Nyquist plots show a significantly increase in the real and imaginary components compared with either CaNd₂S₄ or SrNd₂S₄ indicating that changing the dopant from neodymium sulphide to samarium sulphide caused a loss in bulk conductivity, an undesired effect, Figure 5-6. The lowest temperature at which reliable impedance spectroscopy could be measured for CaSm₂S₄ series was 275°C. At 250°C, significant scattering of the data occurred due to high impedance values.

5.2.1 Alternative Equivalent circuits for CaSm₂S₄ series Modelling: Diffusion based equivalent circuits

The experimental impedance data for CaSm₂S₄ differs from both the calcium and strontium neodymium sulphide series, Figure 5-6. CaNd₂S₄ and SrNd₂S₄ series Nyquist data are adequately modelled by using R/C-R//CPE, Bauerle or Jamnik models, which address ionic and mixed ionic-electronic conduction. It is unlikely that the model for pure ionic conductor or mixed conductors electrolyte would fit CaSm₂S₄ experimental data, since the shape of the Nyquist plot for calcium samarium is different from neodymium based electrolytes, hence an alternative model was sought, Figure 5-6.

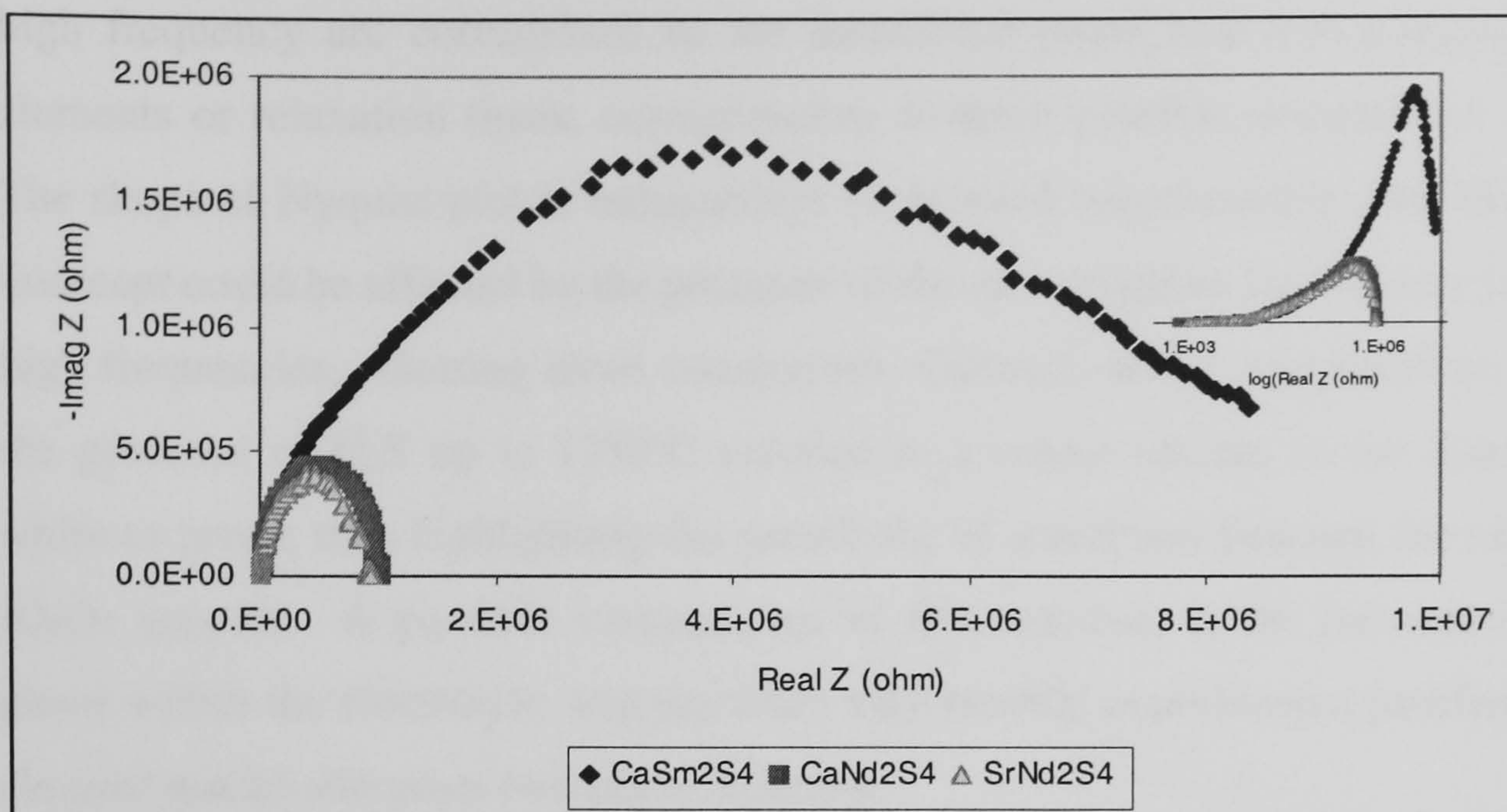


Figure 5-6. Impedance of undoped CaSm_2S_4 , CaNd_2S_4 and SrNd_2S_4 at 400°C

The Nyquist plot of CaSm_2S_4 series can be described as flattened semicircles related normally to predominant diffusion process, Fleischmann *et. al.* 1988, 1991. A complete mathematical treatment was done on different geometric shapes, however only a generic equivalent circuit model was produced for diffusion disc electrode, Figure 5-7. The governing equations for this model correspond to the two-dimensional diffusion of an electrode proposed equivalent circuit by Fleischmann *et. al.*, 1988, 1991. As the initial impedance spectroscopy was done in the absence of a positive sulphur partial pressure, it is conceivable that diffusion of sulphur from the electrolyte may occur at elevated temperature. However this is not likely since comparable thermal activation energy and oxidation onset temperature for CaSm_2S_4 series was achieved relative to the CaNd_2S_4 series. Caution should be exercised in this theory since these parameters do not justify the mobility of sulphur within the unit cell nor does it address the electrochemical activation of mobile sulphur.

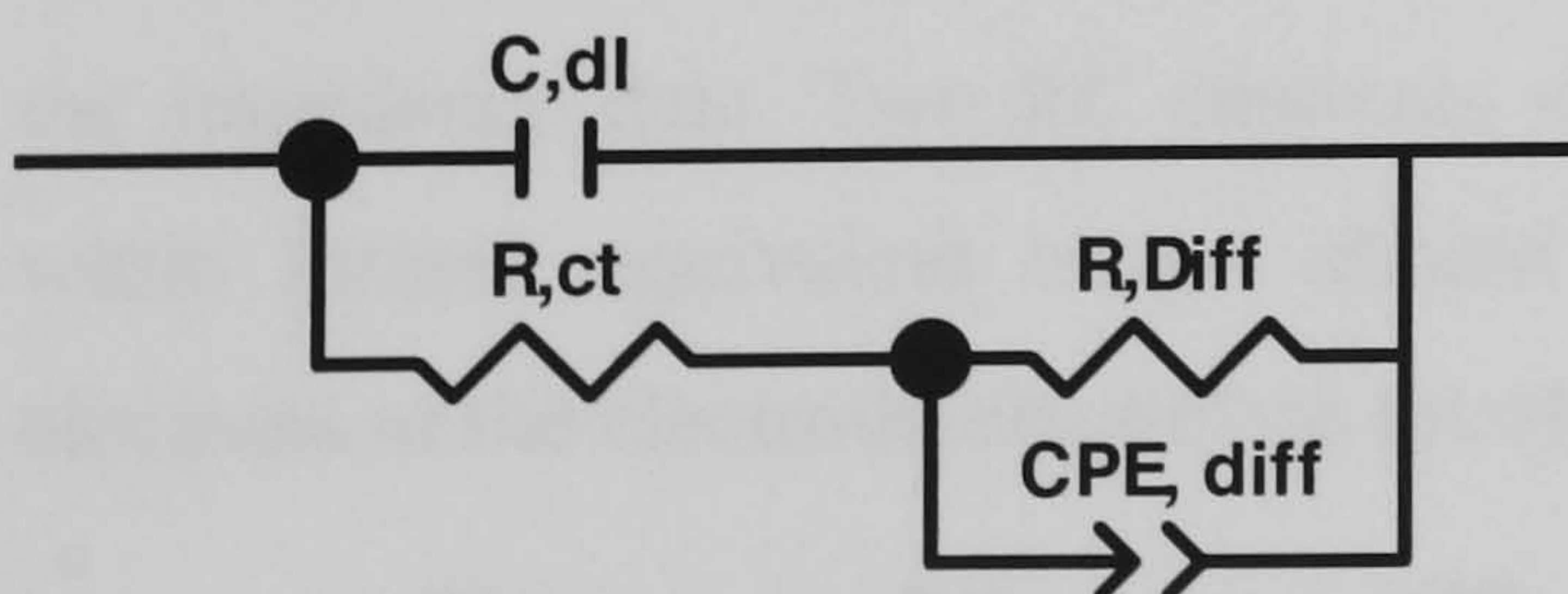


Figure 5-7. Fleischmann model for diffusion onto a disc micro electrode

Modelling of impedance data with more than three R/C combinations is done for two-phase systems, McDonald, 1987. If the phases are randomly distributed, with irregular shaped grains such as ellipsoids rather than spheres, the number of RC elements may increase beyond four. The low frequency arc corresponds to the low conductivity continuous phase, which would appear in the Nyquist plot by an apparent perfect semi-circle, Fricke, 1953. The

high frequency arc corresponds to the suspended phase and it is composed of three RC elements or relaxation times, corresponding to three possible orientations of the ellipsoids. The shape of Nyquist plot is independent of detailed microstructure, but the high frequency intercept could be affected by the presence of the second phase leading to a small distortion at high frequencies. Heating these compounds, CaSm_2S_4 series, supported on Al_2O_3 plates, in the presence of H_2S up to 1350°C resulted in a colour change in the alumina plates from white to green; thus highlighting the possibility of a reaction between the electrolyte and the Al_2O_3 support. A possible consequence of this reaction, is the formation of a secondary phase within the electrolyte, and therefore may provide experimental justification of the 4RC element model addresses two-phase systems.

McDonald and others, McDonald, 1976, Bauerle, 1969, Bruin and Badwal, 1976, also proposed an equivalent circuit that addresses the diffusion process. The equivalent circuit has five RC circuit elements, which are related to bulk conduction, a reaction mechanism, an adsorption mechanism, a recombination process and a diffusion process, respectively, Figure 5-8. Generally not all semicircles are observed, and even then a very wide frequency range, 10^{-3} to 10^8 Hz is used, Armstrong and Taylor, 1975.

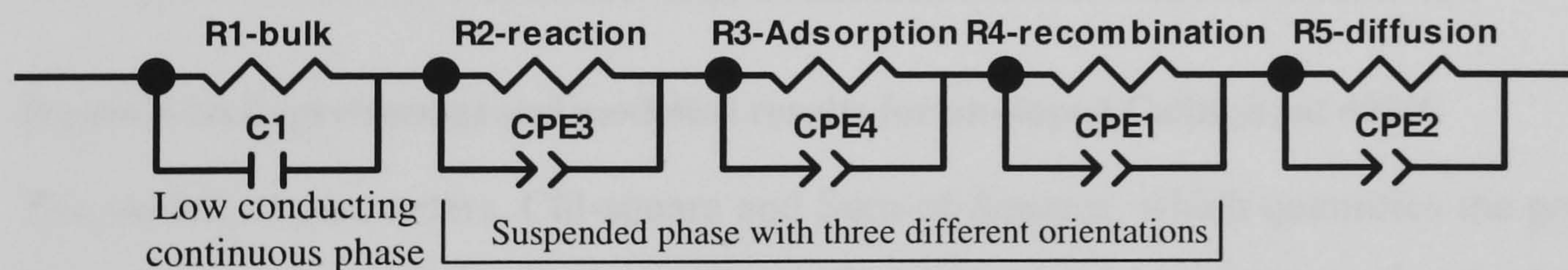


Figure 5-8. McDonald 5RC model (upper labels) or Fricke two non-spherical composite (lower labels)

If the material is a mixed ionic electronic conductor with distinguishable grain boundary and interior condition, then a combined model of Bauerle and Jamnik may adequately describe the impedance data. Two RC elements should model bulk and grain boundary conduction, while Jamnik equivalent circuit should address the relaxation process of the ions and electrons at the electrode-electrolyte interface, Figure 5-9.

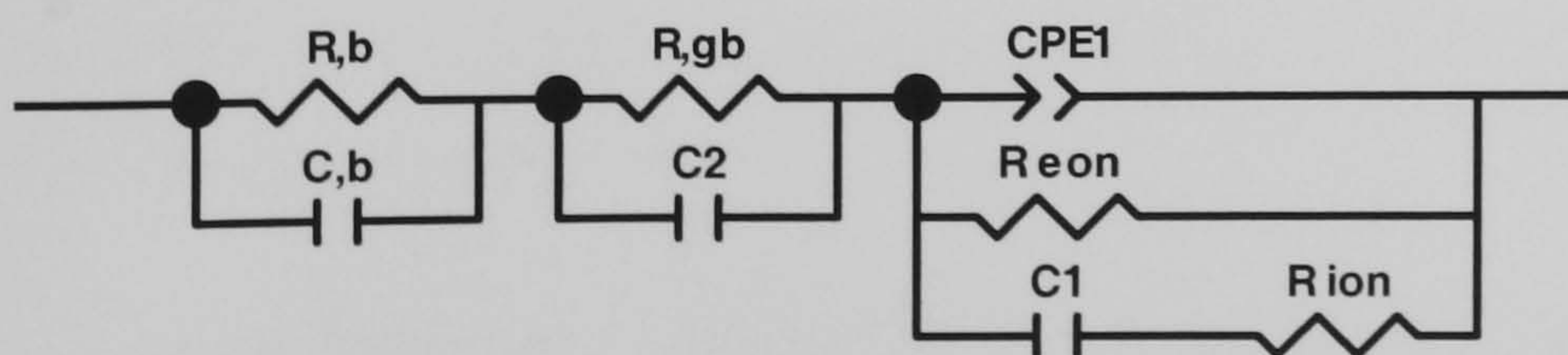


Figure 5-9. Combined Bauerle and Jamnik model for electrolyte with predominant ionic conduction

Figure 5-10 shows a visual impression of the goodness of fit between the various proposed equivalent circuits and a typical experimental EIS result at high temperature. Generally, all the proposed equivalent circuits matched closely the experimental data at high frequencies but at low frequencies only the combined Bauerle & Jamnik or McDonald model fitted the experimental data.

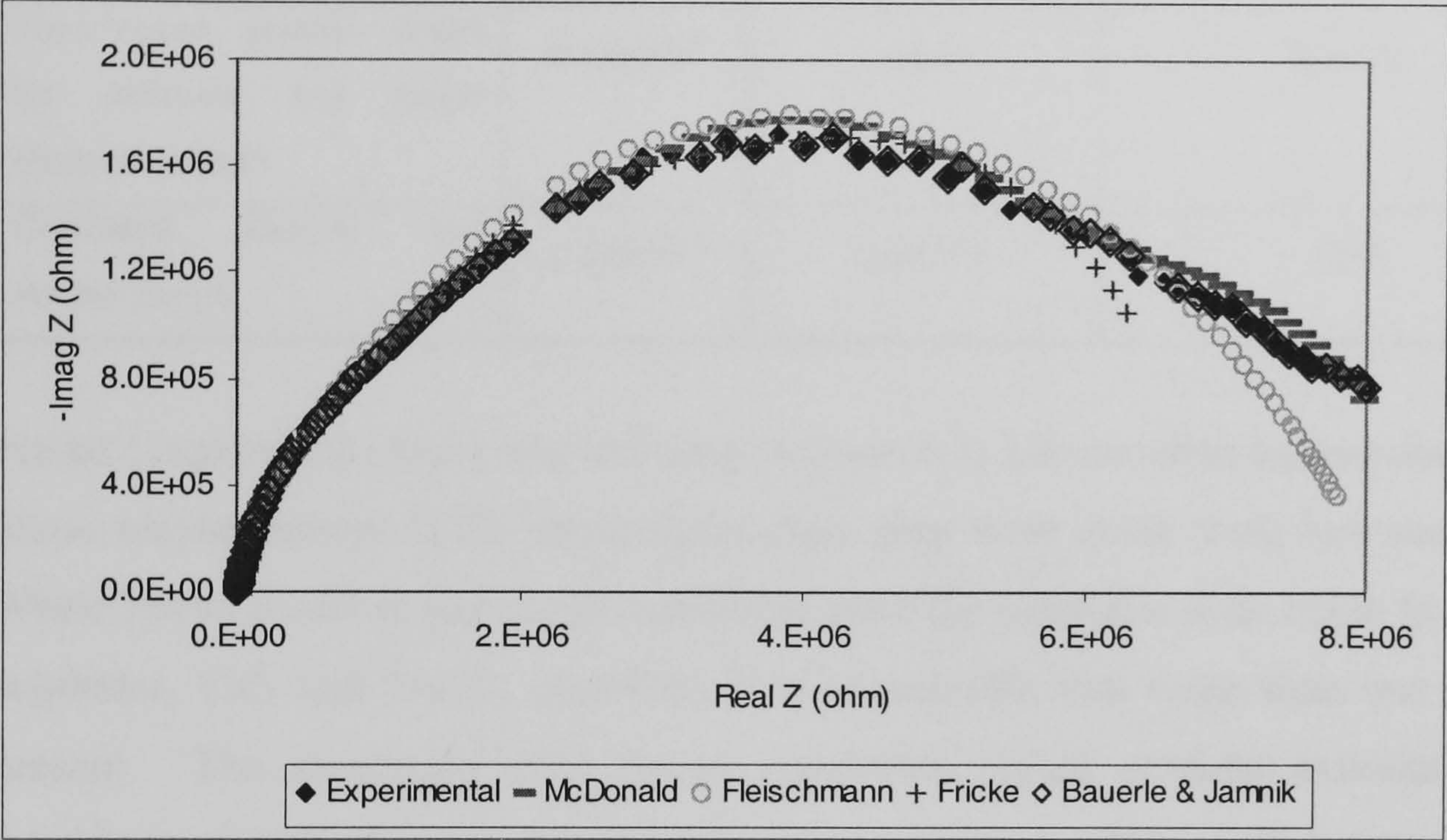


Figure 5-10 Experimental and modelled results for un-doped CaSm₂S₄ at 400°C

The statistical parameters, Chi-square and Sum-of-Squares, which quantifies the goodness of fit and are outputs of the Z-view software©; both should be minimum for the best model, Table 5.6. The combined Bauerle and Jamnik equivalent circuit was most suitable since the Chi-square, Sum-of-Squares and maximum error on an equivalent circuit element were minimised. However the sum-of-squares and Chi-square for McDonald, are comparable with the combined Bauerle &Jamnik model, hence either is justified statistically, Table 5.6.

Table 5.6. Statistical parameters evaluating the goodness of fit for alternative models

Models	Chi-square	Weighted-sum-of-squares	Maximum error on equivalent circuit element
McDonald diffusion from a cylinder	3.66×10^{-4}	0.071	24%
Fricke model (two phase mixture)	3.87×10^{-4}	0.061	42%
Fleischmann generic model for diffusion and micro electrode effects	8.13×10^{-4}	1.651	5042%
Combined Bauerle and Jamnik model	2.64×10^{-4}	0.04151	12%

Fricke’s equivalent circuit was included because it is a reasonable assumption that a second phase maybe present in the electrolytes since they were made from two starting materials. While Fricke model is physically justifiable since the sulphides were made from two starting sulphides, CaS and Sm_2S_3 , therefore it is conceivable that more than one phase may be present. The maximum error on an equivalent circuit element exceeded the allowed maximum of 30%, therefore this model is not appropriate. This misfit between Fricke model and experimental impedance spectroscopy, infers that CaSm_2S_4 compounds are indeed homogeneous, thus confirming the XRD results, White, 2005. However powered XRD measures the bulk properties and a minor impurity between grains may not be detectable. The single TPO peak also suggests a single phase for CaSm_2S_4 series confirming the XRD data.

The McDonald’s model should be used over a wide frequency range, of 10^8Hz to $1 \times 10^{-3}\text{Hz}$, to observe the presence of five RC equivalent circuit elements. However the frequency range from 10^{-1}Hz to 10^6Hz was used for the experimental impedance spectroscopy measurements. Therefore, the narrow frequency range used does not satisfy the criteria for this model. Nevertheless Armstrong and Taylor, 1975 used McDonald’s model in a smaller frequency range of 10^6Hz to 10^{-1}Hz , without mention of significant errors, which compares with these experimental conditions.

Therefore McDonald’s equivalent circuit model was used to model the impedance data of CaSm_2S_4 series since this model has been previously established. It should be noted that the combined Bauerle and Jamnik equivalent circuit has a better fit than the McDonald, however

this model has not been verified mathematically, and therefore McDonald's model was used to model this series of compounds

5.2.2 Effect of doping CaSm_2S_4 Series with excess Sm_2S_3 on Impedance Spectroscopy

The Nyquist plot for $\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ and $\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ appears to be a single arc or two arcs with significant overlap so that they cannot be seen clearly in the plot. However CaSm_2S_4 and $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ shows an asymptotic shape, which is typical for diffusion related process, Figure 5-11. This asymptotic shape at occurred at medium frequency and therefore is material property rather than electrode (including contact error). Since the arc for bulk conductivity is not easily seen in the Nyquist plot due to significant overlap with other arcs, the effect of doping on the bulk conductivity could not be determined from the Nyquist plot.

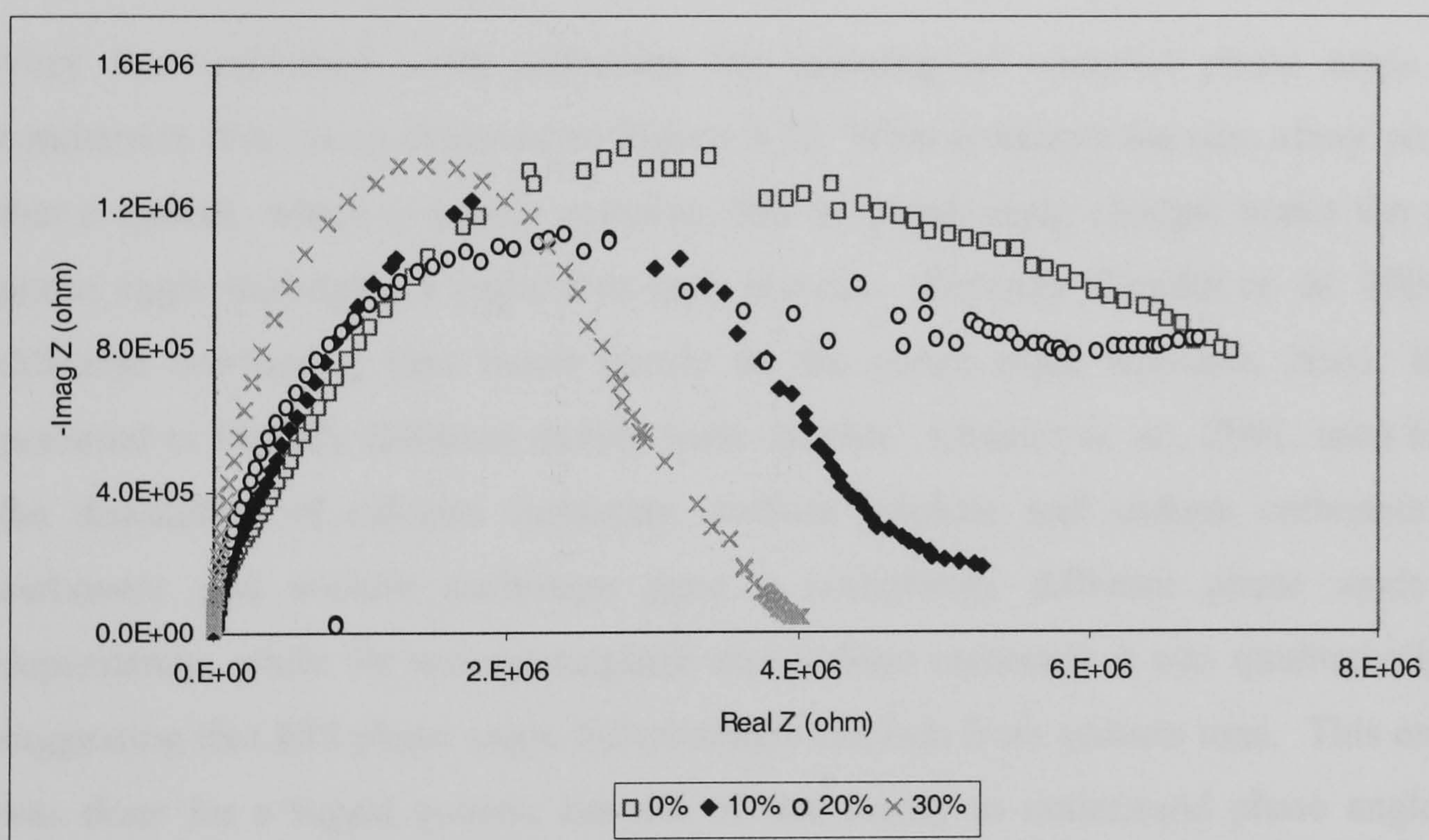


Figure 5-11. Effect of doping CaSm_2S_4 with Sm_2S_3 at 400°C in argon on nyquist plot

The Bode plot for CaSm_2S_4 series shows that each compound in this series of compounds has a unique phase angle frequency dependency in the range measured, Figure 5-12. At low frequency both 10mol% and 30mol% have no phase shift, but at high frequencies the phase angles differ significantly. Impedance of undoped CaSm_2S_4 and $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ have similar frequency dependency of phase angle at low frequencies, but different phase change at medium frequencies, Figure 5-12.

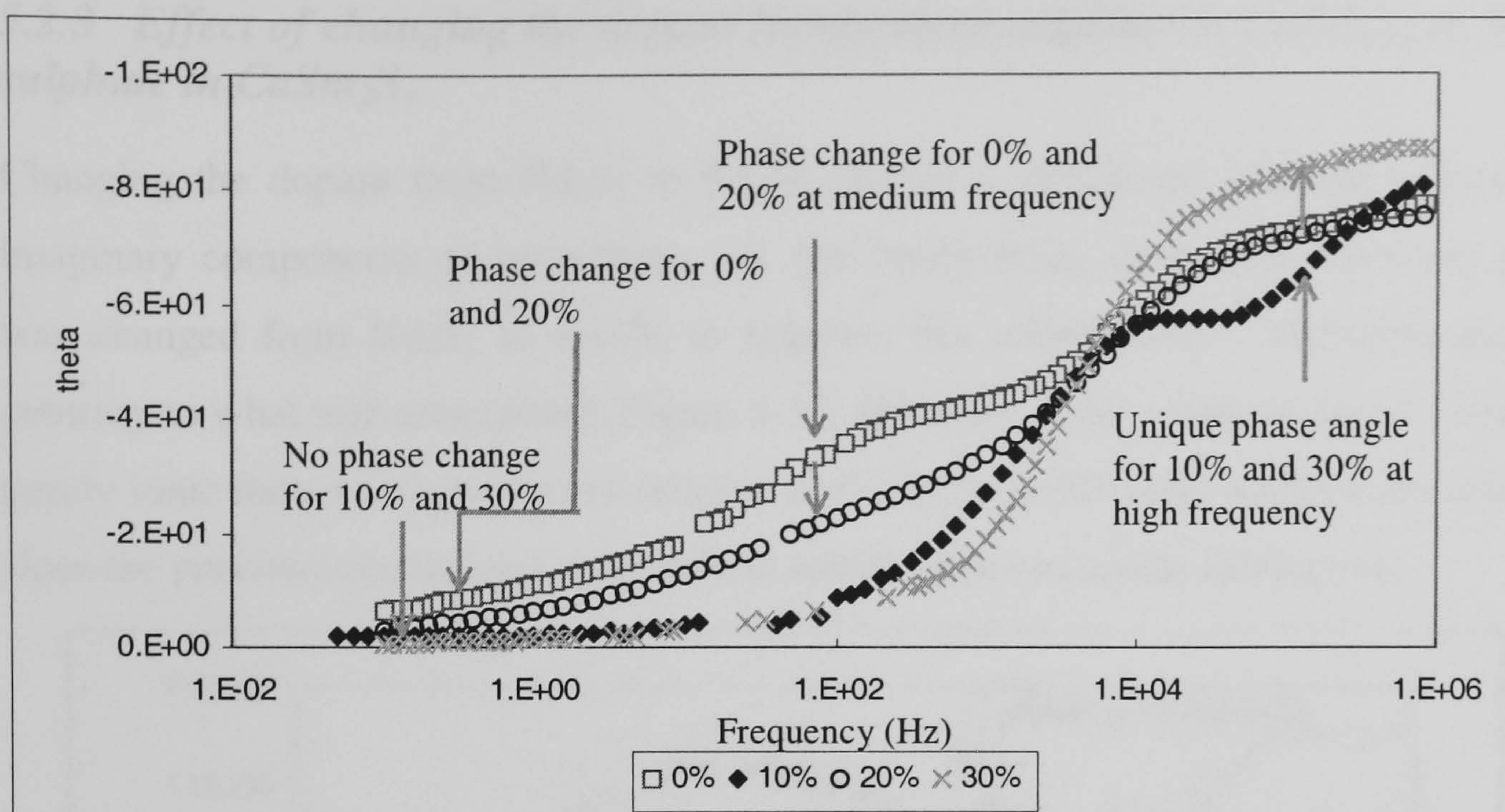


Figure 5-12. Effect of doping CaSm_2S_4 with Sm_2S_3 at 400°C in argon on nyquist plot

Very few published work addresses the meaning of complex phase angle change to conduction process as observed in Figure 5-12. What is known for sure about phase angle is that a system, which is purely resistive, has no phase angle change; hence the presence of phase angle highlights a capacitive type process. Recently Chaulet *et. al.* 2001 identified different conducting ions based purely on the phase angle response, hence EIS has the potential to identify different mobile ionic species. Chaulet *et. at.*, 2001, used EIS to study the dissolution of calcium carbonate, sodium sulphate and sodium carbonate. Calcium carbonate and sodium carbonate gave a completely different phase angle frequency dependency, while for sodium sulphate and sodium carbonate it was qualitatively the same, suggesting that EIS phase angle differentiates calcium from sodium ions. This empirical test was done for a liquid system; the use of this theory to understand phase angle frequency dependency in solid-state systems is not established. However, if the solids being compared have identical unit cell and crystal structure, a similar frequency dependency of phase angle would be expected. Considering the CaSm_2S_4 compounds, which have similar unit cell and identical crystal structure, yet they have different phase angle change as a function of frequency, Figure 5-12. Does this imply that the conducting species changed? These non-stoichiometric compounds have equal cation and anion vacancies, so it is possible to have a change in the mobile conducting species from anion to cation or indeed to electronic.

5.2.3 Effect of changing the dopant Neodymium sulphide in CaNd_2S_4 to Samarium sulphide in CaSm_2S_4

Changing the dopant from Nd_2S_3 to Sm_2S_3 caused a significant increase in both real and imaginary components of impedance, i.e. the conductivity decreased. However the dopant was changed from Nd_2S_3 to Sm_2S_3 to improve the conductivity. Therefore this result is contrary to what was anticipated, Figure 5-13. However if the conductivity of CaSm_2S_4 were purely ionic then an improvement relative to CaNd_2S_4 or SrNd_2S_4 would have still occurred, since the previous electrolytes were at best mixed ionic-electronic conductors.

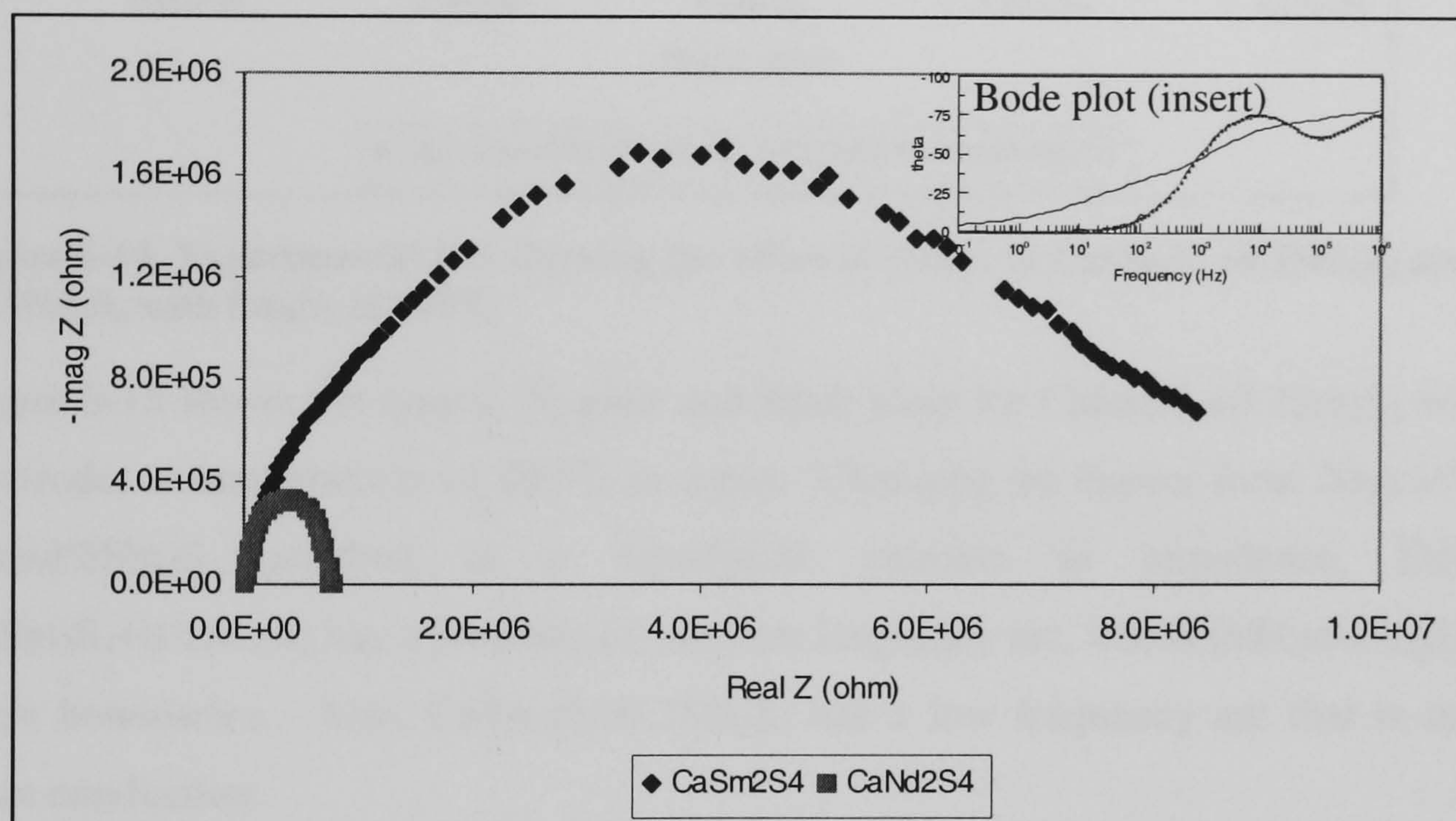


Figure 5-13. Experimental EIS showing the effect of cation in CaSm_2S_4 and CaNd_2S_4 at 400°C

The frequency dependency of the phase angle of CaSm_2S_4 differs to that CaNd_2S_4 , Figure 5-14. Qualitatively, a change in phase angle frequency dependency may indicate a change in conducting species since the change in phase angle at high frequencies refers to a change in bulk properties. The unit cell for either compound does not contain any known Sm or Nd defects, hence these ions cannot conduct through the unit cell. Cationic (Ca^{2+}) and anionic (S^{2-}) vacancies are present, so either ion may conduct via these vacant sites. Since many of the CaNd_2S_4 compounds may have mixed cationic-electronic conduction, therefore by deduction, CaSm_2S_4 compounds may exhibit anionic conduction. The presence of anionic conduction should lead to a significant increase in activation energy for CaSm_2S_4 in comparison to CaNd_2S_4 .

The impedance for $\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ is much larger than $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$. Also, the frequency dependency of the phase angle differed for each compound, Figure 5-14.

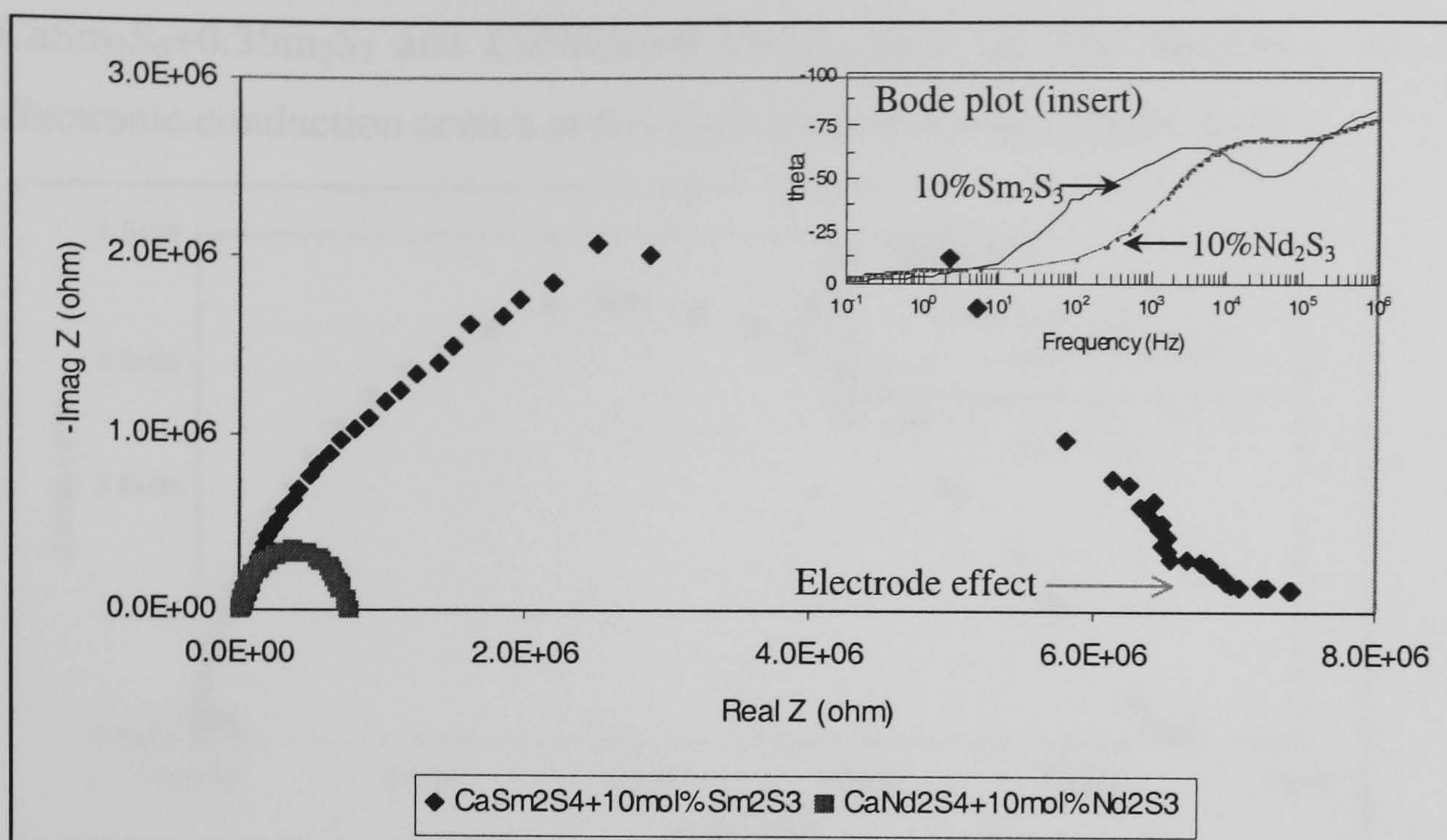


Figure 5-14. Experimental EIS showing the effect of cation in $\text{CaSm}_2\text{S}_4 + 0.1\text{Sm}_2\text{S}_3$ and $\text{CaNd}_2\text{S}_4 + 0.1\text{Nd}_2\text{S}_3$ with Sm_2S_3 at 400°C

Figure 5-15 shows the typical Nyquist and Bode plots for $\text{CaSm}_2\text{S}_4 + 0.2\text{Sm}_2\text{S}_3$ with graphite electrodes at temperatures of 400°C in argon. Changing the dopant from 20mole% Nd_2S_3 to 20mol% Sm_2S_3 resulted in a significant increase in impedance, Figure 5-15. $\text{CaSm}_2\text{S}_4 + 0.2\text{Sm}_2\text{S}_3$ has a pronounced medium frequency arc, which indicates highly resistive grain boundaries. Also, $\text{CaSm}_2\text{S}_4 + 0.2\text{Sm}_2\text{S}_3$ has a low frequency arc that is indicative of ionic conduction.

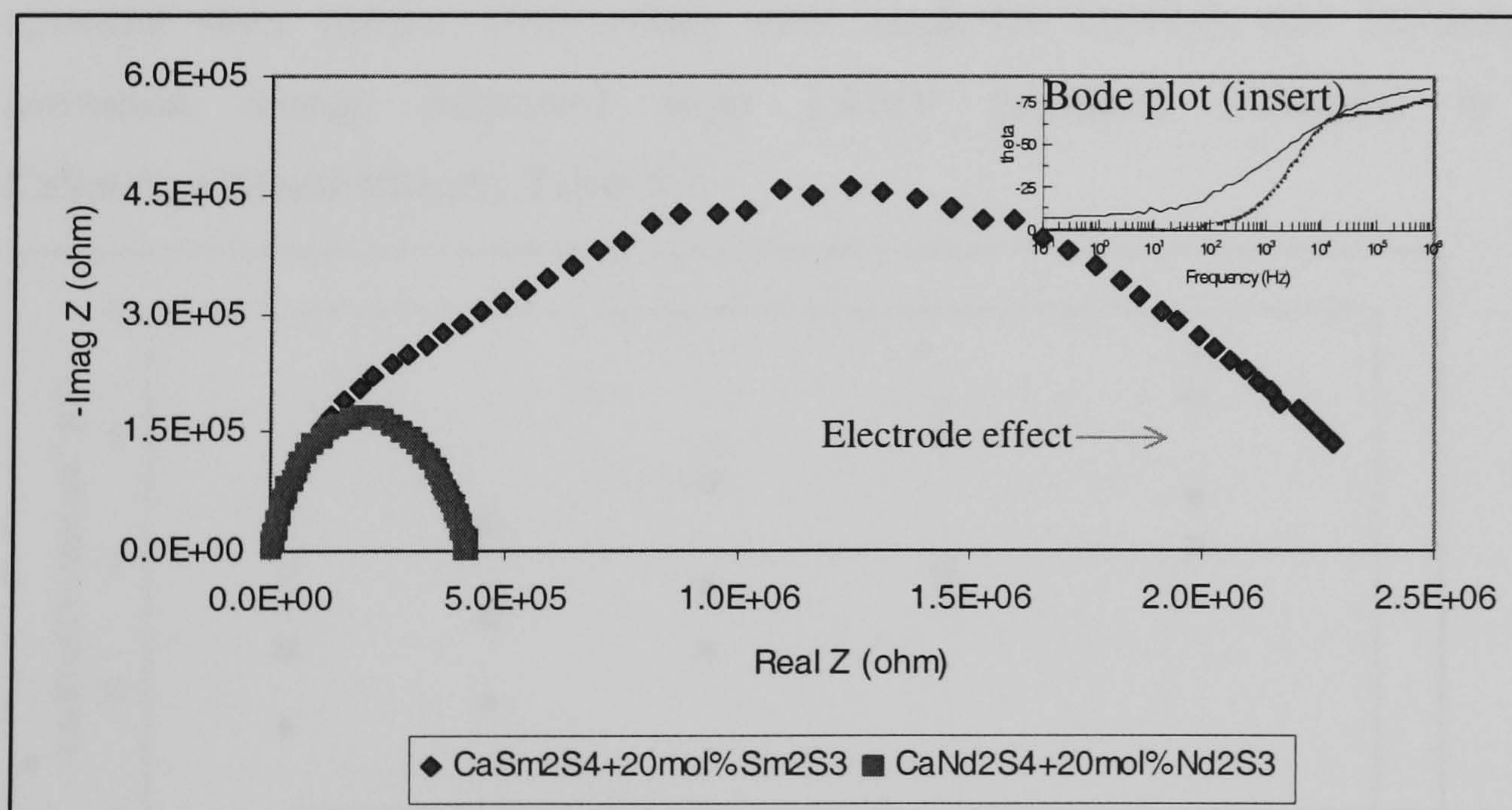


Figure 5-15. Nyquist plot for CaSm_2S_4 , $\text{CaSm}_2\text{S}_4 + 0.2\text{Sm}_2\text{S}_4$ and $\text{CaNd}_2\text{S}_4 + 0.2\text{Nd}_2\text{S}_4$ at 400°C in argon

The typical Nyquist and Bode plots for $\text{CaSm}_2\text{S}_4 + 0.3\text{Sm}_2\text{S}_3$ with graphite electrodes at temperatures of 400°C in argon is shown in Figure 5-16. Changing the dopant from 30mole% Nd_2S_3 to 30mol% Sm_2S_3 , resulted in a significant increase in impedance. Both

$\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ and $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ have no low frequency arc, suggesting that electronic conduction occurs at this high level of doping, Figure 5-16.

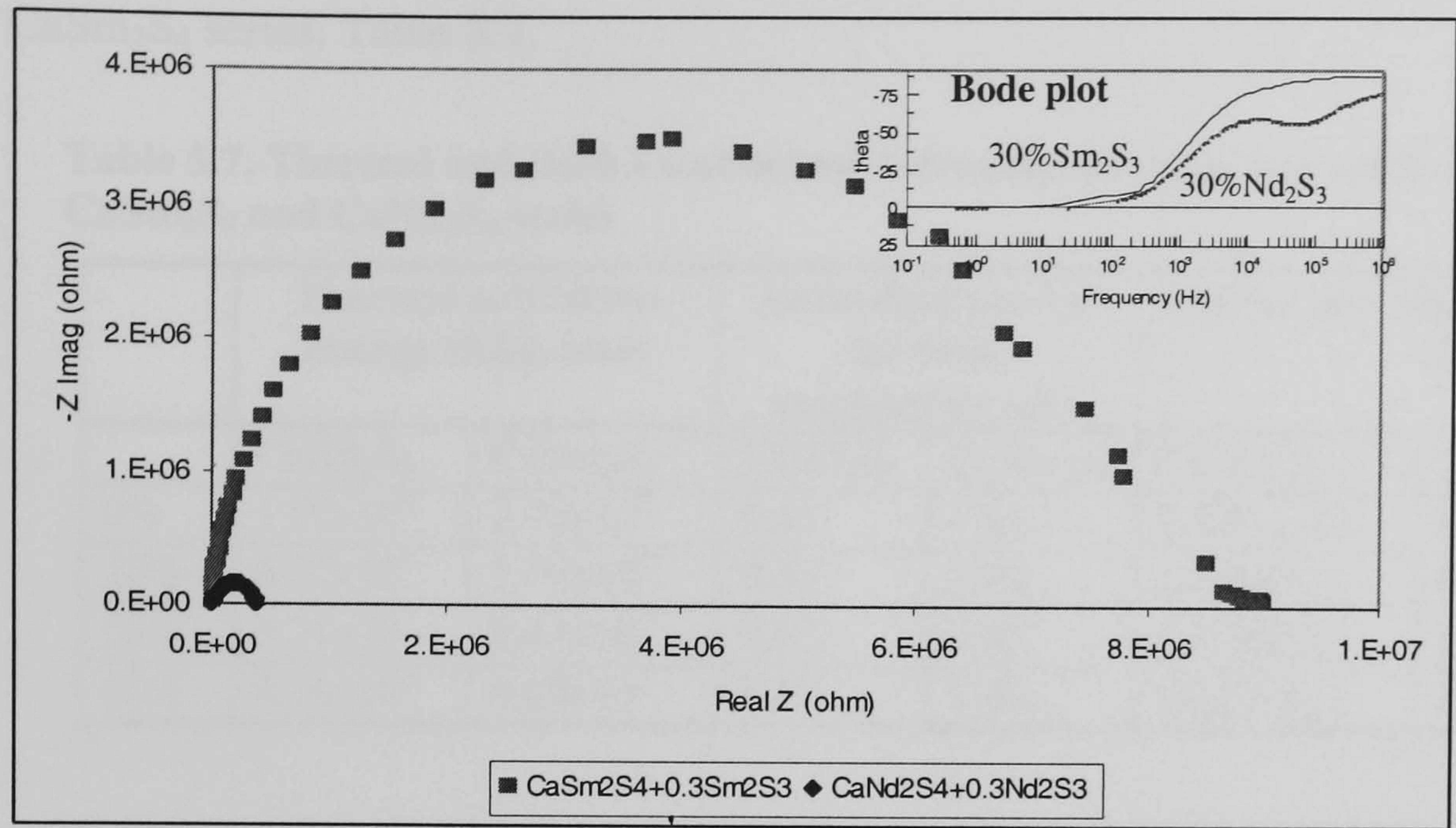


Figure 5-16. Nyquist plot of experimental EIS showing the effect of cation in $\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ and $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ at 400°C

5.2.4 Activation energy for CaSm_2S_4 and CaNd_2S_4 series with Lattice parameter

The Arrhenius plot for ionic hopping for the CaSm_2S_4 series is linear within 350-450°C, Figure 5-17. The activation energy for ionic hopping passes through a minimum at $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$, Table 5.7, which now seems to be a typical feature for this crystal structure since similar observations were made for CaNd_2S_4 and SrNd_2S_4 series. The activation energy decreased from 1.41eV (undoped CaSm_2S_4) to 0.60eV for $\text{CaSm}_2\text{S}_4+20\text{mol}\%\text{Sm}_2\text{S}_3$, Table 5.7.

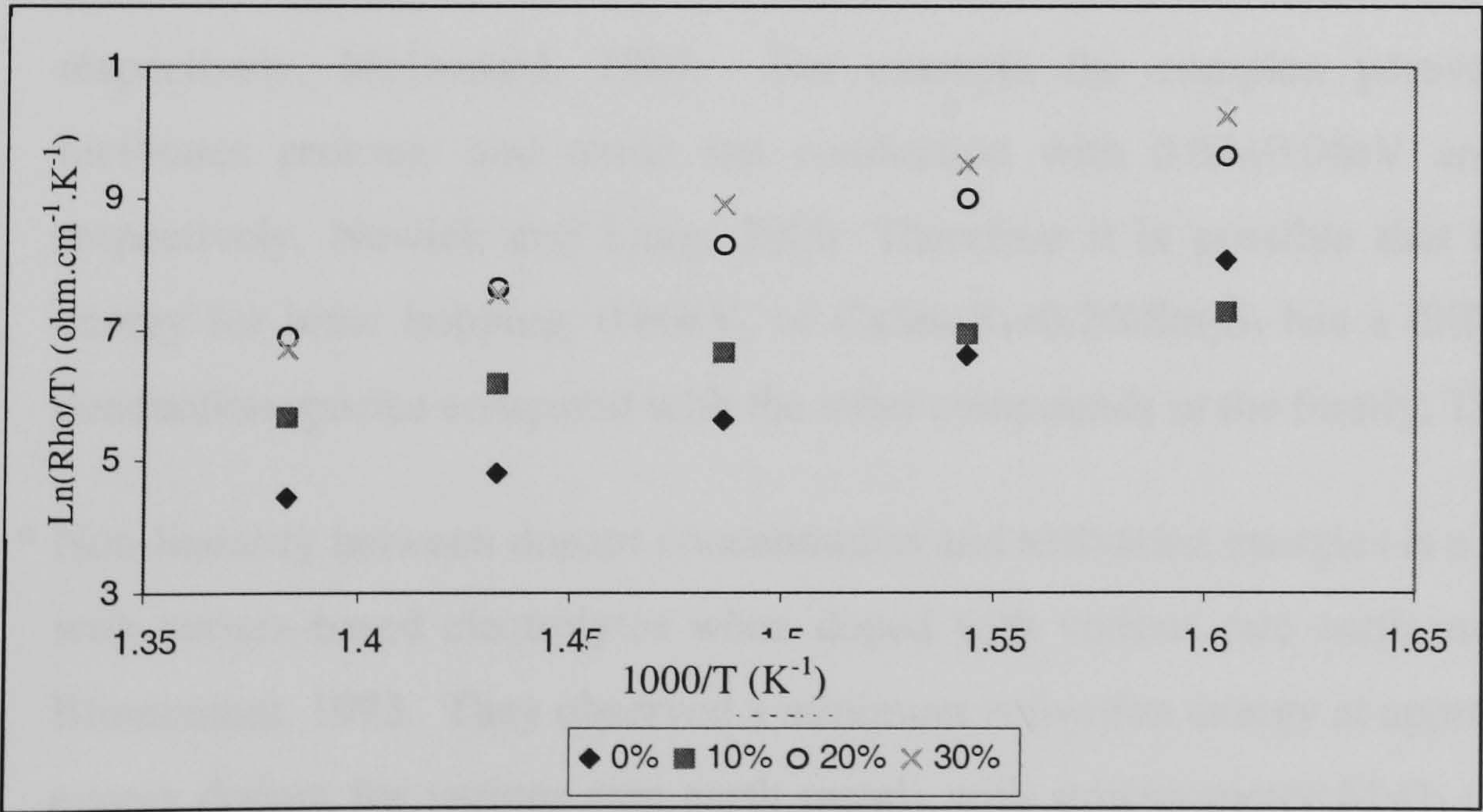


Figure 5-17. Activation energy for CaSm_2S_4 series at elevated temperatures

The minimum activation energy for CaNd_2S_4 series is at 10mole% Nd_2S_3 dopant level while it occurs at 20mol% dopant for CaSm_2S_4 , Table 5.7. Doping at 30mol% excess in both

groups of compounds, leads to a decrease in the activation energy. No relationship between thermal activation energy and ionic mobility activation energy was observed for CaNd_2S_4 and CaSm_2S_4 series, Table 5.7.

Table 5.7. Thermal and Bulk Conduction Activation energies and lattice parameter for CaSm_2S_4 and CaNd_2S_4 series

	Thermal activation energy (kJ/g-mol)		Activation energy for bulk conduction (eV)		Lattice parameter for ‘a’ site Å	
	CaNd_2S_4	CaSm_2S_4	CaNd_2S_4	CaSm_2S_4	CaNd_2S_4	CaSm_2S_4
0%	1.90×10^5	2.78×10^5	0.44	1.41	8.5301(1)	8.4708(1)
10%	6.37×10^5	2.79×10^5	0.33	1.03	8.5299(1)	8.4701(8)
20%	5.71×10^5	8.42×10^5	0.52	0.60	8.5280(1)	8.4684(8)
30%	4.36×10^5	9.69×10^5	0.62	1.40	8.5273(1)	8.4653(1)

Arrhenius plots for YSZ, pure oxide ion conducting, does not exhibit a phase change, and as a result the Arrhenius plot is linear in the temperature range from 200°C to 500°C,. McDonald, 1987. Since the Arrhenius plot for CaSm_2S_4 appears to be linear in the temperature range from 200°C to 500°C, then the CaSm_2S_4 series is assumed to have no phase in the temperature range examined. Therefore the conductivity is expected to vary linearly with temperature (plotted on a log scale).

Mixed conductors of anion and cation are known to have two significantly different activation energies. This variation supersedes the typical variation in activation energy for bulk and grain boundary conduction in pure ionic conductors such as YSZ, which has activation energy of 1.07eV and 1.12eV for bulk and grain boundary conduction respectively, McDonald, 1987. For example the complex perovskite $\text{Sr}_2(\text{ScNb})\text{O}_6$ facilitates protonic and oxide ion conduction with $0.64 \pm 0.04\text{eV}$ and $1.38\text{eV} \pm 0.15\text{eV}$ respectively, Nowick and Lang, 2000. Therefore it is possible that the low activation energy for ionic hopping, 0.60eV, of $\text{CaSm}_2\text{S}_4 + 0.2\% \text{Sm}_2\text{S}_3$ has a different predominant conduction species compared with the other compounds in the family, Table 5.8.

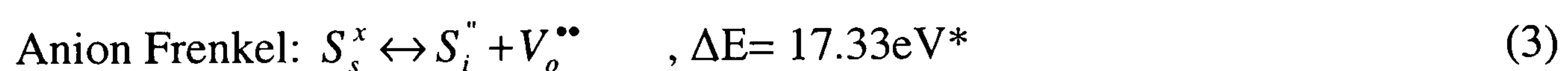
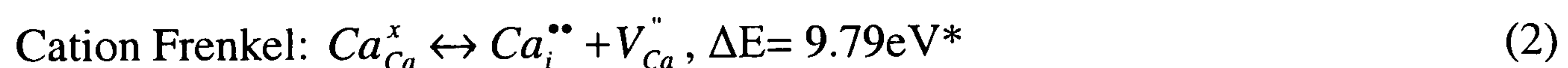
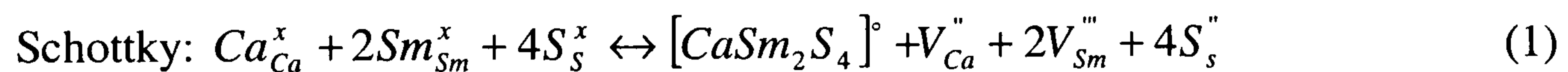
Non-linearity between dopant concentration and activation energies is a typical occurrence with cerium-based electrolytes when doped with various rare earth metals, Panhans and Blumenthal, 1993. They observed a minimum activation energy at approximately 10mol% excess dopant for various rare earth metals with stoichiometry M_2O_3 (M indicates metal cation). For CeO_2 based compounds, the difference between the maximum and minimum activation energies for a series of CeO_2 compounds, as a function of doping, was 20%, Panhans and Blumenthal, 1993. However the variation between the maximum and

minimum activation energies, 1.41eV and 0.60eV, for CaSm_2S_4 series based compounds is 60%, Table 5.8.

Minervini *et al.*, 1999 developed a system of equations describing the possible defect mechanism, which may occur when CeO_2 is doped with M_2O_3 . Their results show that conduction can switch from anionic to cationic even though the systems have similar unit cell and crystal structure. Also they showed that conduction via the dopant cation is unlikely, that is conduction via samarium ion is unfavourable. Also the earlier work by Banks and Ward, 1949, which characterised a cerium dilute solution of cerium sulphide (maximum 10mol%) in strontium sulphide exhibited cationic conduction. Doping caused a decrease in lattice constant, which indicates that the cerium enters substitutional positions and remains trivalent. Vacant cation positions were postulated because of this decrease in lattice parameter. For every two-cerium ions (dopant), one vacant Sr lattice point (hole) should be introduced. The presence of Sr (host) vacancies was confirmed by the direct relationship between low temperature conductivity and cerium concentration.

By using Minervini *et al.*, 1999 defect equations, the following equations are proposed to describe CaSm_2S_4 electrolytes.

Undoped CaSm_2S_4 could conduct ions by intrinsic disorder based on:

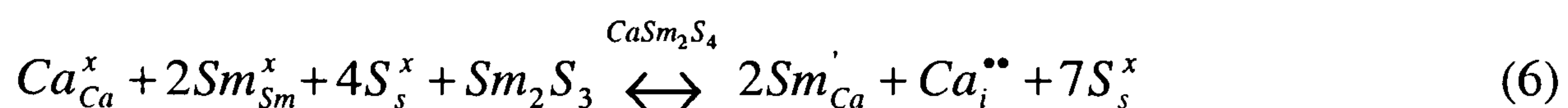
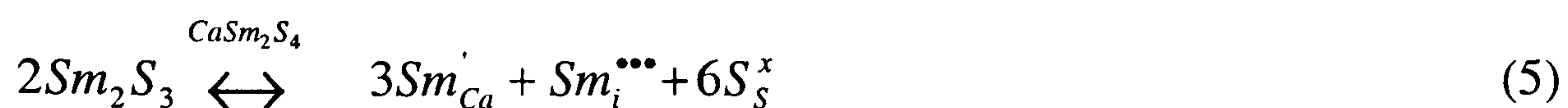


* Taken from CaS unit cell, R. Pandey and H Harding, 1984

The disorder mechanism with the lowest reaction enthalpy will dominate. If the measured activation energy, from Arrhenius plot, is the enthalpy for Schottky defects, then enthalpy for Schottky defects of CaSm_2S_4 is much lower than the enthalpy for conduction via Frenkel defects, assuming that the enthalpy for Frenkel defects (Ca and S) remains unchanged when going from CaS to CaSm_2S_4 electrolytes. However the enthalpy for Frenkel defects should be determined for the compound of interest since the value is likely to be dependent on the unit cell size and type. Therefore the reaction enthalpy for each defect mechanism in each compound must be determined individually.

When a secondary solid (aliovalent solute) is dissolved in a crystal lattice, the unit cell must compensate the resulting charge imbalance. Sm_2S_3 can be incorporated into CaSm_2S_3

via a three intrinsic disorder mechanism: sulphide vacancy compensation (equation 4), dopant interstitial compensation (5) and calcium vacancy compensation (6).



Solving equations (1) to (6) requires detailed simulation, which considers Coulombic forces, which lie outside the scope of this project. However Minervini *et. al.*, 1999, solved this system of equations for CeO₂-M₂O₃ systems. They found that the intrinsic defects had very high activation energies and would therefore not contribute significantly to the overall conduction process. Also the activation energy for equation (3) was enormous and this compensation method would be trivial, since conduction via Sm ions would not occur. Solving the equations governing the defects, Minervini *et. al.*, 1999, they found that a variation of the dopant could cause the conduction to change from anionic to cationic.

In summary, XRD of previous sulphide system of 90mol%SrS+10mol%Ce₂S₃ showed that the lattice parameter for unit cell decreased, which meant Schottky defects, and this compound showed cationic conduction, Banks and Ward, 1949. CaSm₂S₄ also experienced a decrease in lattice parameter, an indication of Schottky defect, and yet this was reported as sulphide ion conducting, Kalinina, *et. al.* 1995. Therefore Kalinina *et al.* and Banks and Ward have shown that ceramic sulphides exhibit cationic conduction or anionic conduction. Minervini, *et. al.*, 1999 developed a system of equations which describes the possible defect mechanisms which was solved for cerium oxide systems. Their results show that conduction can switch from anionic to cationic, even though the systems have similar unit cell and crystal structure. Therefore, theoretically, changing from CaNd₂S₄ system to CaSm₂S₄ system can cause a change from cationic to anionic or vice versa.

5.2.5 Conductivity and Activation energy for CaSm₂S₄ and CaNd₂S₄ series

A summary of the bulk conductivities for both CaSm₂S₄ series and CaNd₂S₄ series is given in Table 5.8 where both series reach a maximum conductivity prior to reaching the highest level of 30mol% doping. The maximum conductivity occurs at different concentrations depending on the dopant composition; 20 mol% for Nd₂S₃ and 10mol% for Sm₂S₃. Figure 5-18. Wang *et. al.*, 1981, studied strontium oxide based electrolytes and found maximum

conductivity before reaching the minimum activation energy, therefore it the true maximum conductivity should occur at less than 20mol%Sm₂S₃.

Table 5.8. Bulk Conductivity for CaSm₂S₄ and CaNd₂S₄ series at 500°C in argon

	Bulk conductivity @500°C in argon (S.cm)		Activation energy for bulk conduction (eV)	
	CaNd ₂ S ₄	CaSm ₂ S ₄	CaNd ₂ S ₄	CaSm ₂ S ₄
0%	2.55x10 ⁻⁴	3.11x10 ⁻⁴	0.44	1.41
10%	1.43x10 ⁻⁴	3.51x10 ⁻⁴	0.33	1.03
20%	6.94x10 ⁻⁴	2.32x10 ⁻⁵	0.52	0.60
30%	4.21x10 ⁻⁴	5.06x10 ⁻⁷	0.62	1.40

The occurrence of these maximum conductivities has been ascribed to the formation of defect clusters, Figure 5-18, beginning with simple defect pairs at low concentrations, which are also called, associated pairs. Defect pairs occur between dopant cation and the charge compensating anion vacancy and once the pair has formed, the anion vacant site does not participate in the conduction process and hence the overall conductivity is lowered, Kilner, 2003.

At high doping the associated pairs may become more complex and form ‘trimers’ which are stable to higher temperatures, Minervini. *et. al.*, 1999. This is the main reason why maximum conductivity does not occur at maximum doping. These simple defect pairs dominate bulk conductivity at low concentrations for dopant with an effective charge of –1 or –2., Kilner and Steele, 1981.

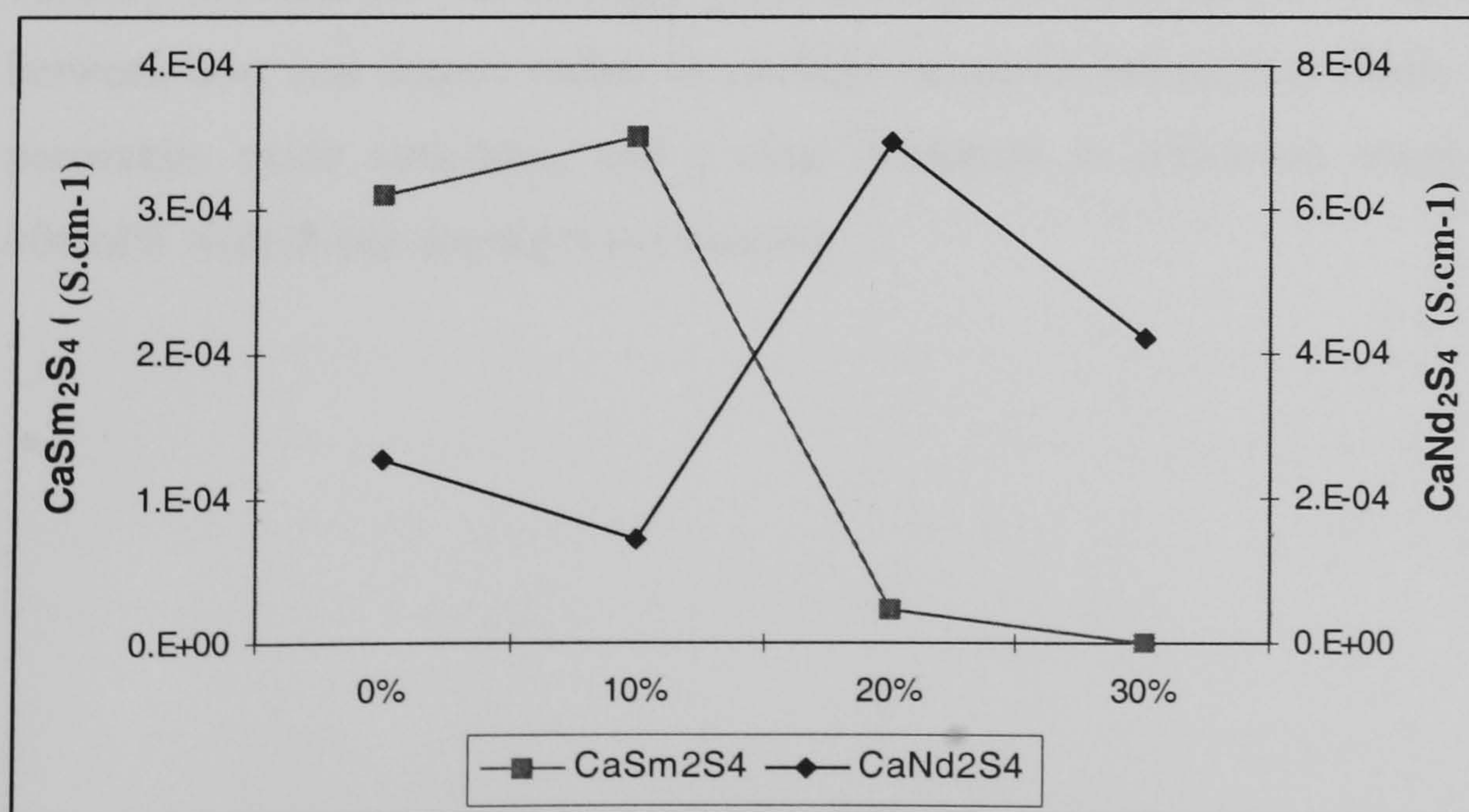


Figure 5-18. Bulk Conductivity for CaSm₂S₄ and CaNd₂S₄ series at 500°C in argon

Cerium oxide doped with alkaline earth oxides, CaO, MgO, BaO, with fluorite structures showed maximum conductivities between 10mol% and 20mol%, similar to the observed maximum conductivities for CaSm₂S₄ and CaNd₂S₄ series, Figure 5-18, Yahiro *et. al.*, 1988. The maximum and minimum activation energy are not associated with the same dopant concentration, Table 5.8, because the pre-exponential factor is also a function of dopant concentration, see equation 7.

$$\sigma T = A \exp(-E_a/kT) \quad (7)$$

σ = conductivity

A- pre-exponential factor

E_a – activation energy of electrical energy

At low dopant concentrations, the pre-exponential factor remains constant, and a decrease in activation energy is observed with increasing dopant concentration for cerium oxide electrolytes. At high dopant concentration, typically 20mol% above, the pre-exponential factor increases after the minimum activation energy is reached, Hideaki and Tagwawa, 1996. Similarly a minimum activation energy followed by a sharp increase occurs for CaSm₂S₄ and CaNd₂S₄ series, Figure 5-19.

Other structures such as A₂B₂O₇ pyrochlore, which can be considered as a severely doped fluorite structure, also have a minimum activation energy. For example Gd₂Ti₂O₇, when doped on either cation sites, has a minimum activation energy, Kramer and Tuller, 1994 & 1995. This indicates the presence of associated vacancy interactions. The extent of associated vacancy interactions was strongly dependent on the ionic radius of the dopant; a mismatch between host and dopant radius exacerbate vacancies interaction. Petric and Huang studied perovskite oxide structures, and a clear minimum in activation energy at approximately 10mol% with B-site doping was observed.

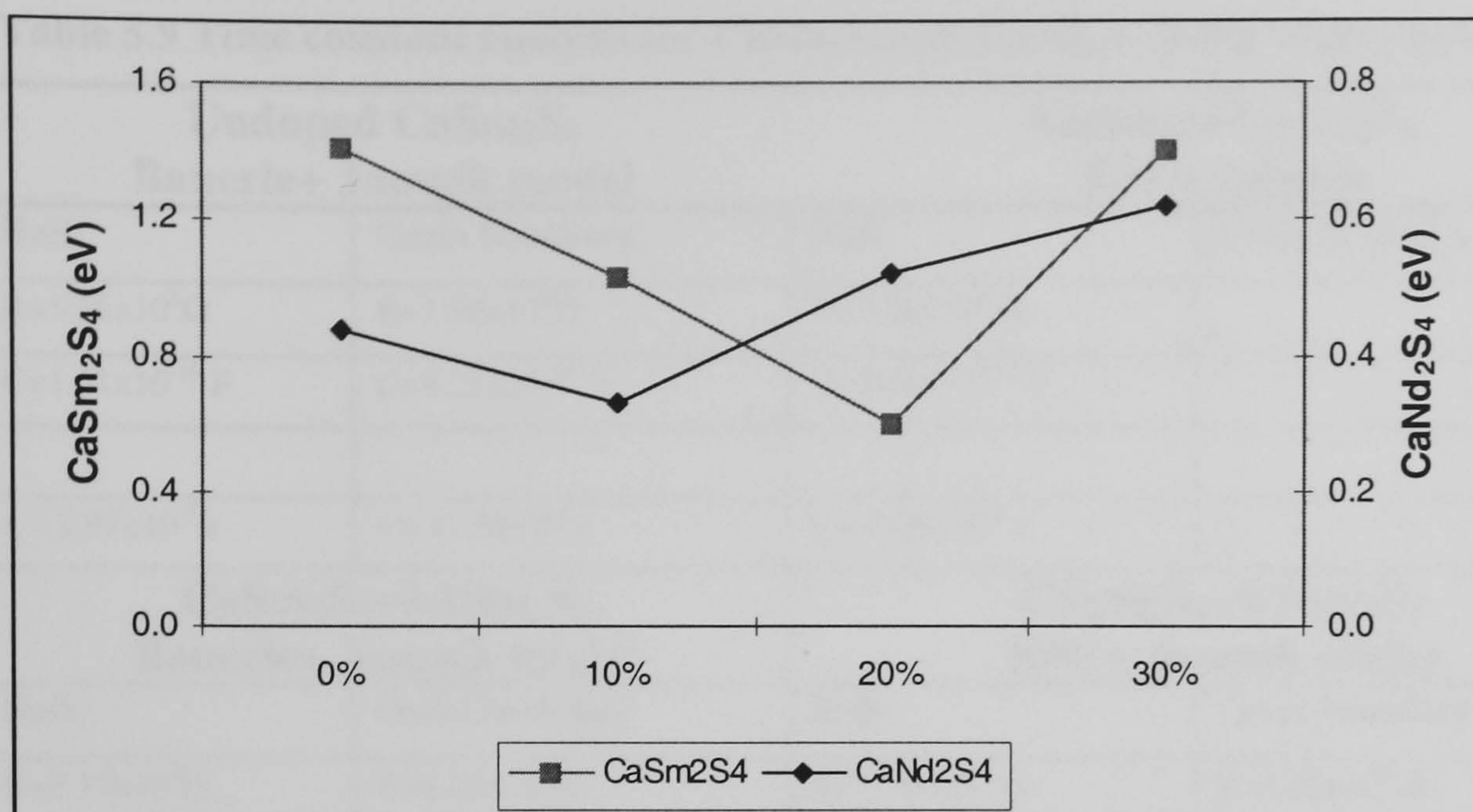


Figure 5-19. Activation energies for CaNd₂S₄ and CaSm₂S₄ series

In summary, defect association has significant effects on conductivities and activation energies. The literature agrees that using a dopant with an effective charge of -1 causes a concentration dependency in conductivity by which has an associated minimum in activation energy however the explanations vary for this observation, Kilner, 2003. The difference in relative size of the dopant to the host exacerbates the vacancy association. Since a clear minimum in activation energy was observed for both CaNd₂S₄ and CaSm₂S₄ series, Figure 5-19, association of defects occurs, therefore lower concentration of dopant should be used since, at these high concentrations, the associated defect pairs do not contribute to bulk conductivities.

5.2.6 Time Constant Analysis for CaSm₂S₄ series

Time constants for bulk conduction in the CaSm₂S₄ series has a minimum for the undoped CaSm₂S₄ series of 1.74×10^{-5} s at 20mol% doping; followed by an increase at 30mol% doping, Table 5.9. On the contrary the time constants for doped CaNd₂S₄ compounds remained almost constant, from 1×10^{-6} to 3×10^{-6} s, with a slight reduction at 30mol% doped.

The time constants for doped CaSm₂S₄ are larger than those for oxide ion conducting YSZ at similar temperature, Table 5.9 and Table 4.9. If CaSm₂S₄ is sulphide ion conducting, then the larger time constants are consistent with anionic conduction. However concentration cell experiments were necessary to confirm the conducting ion.

Table 5.9 Time constant analysis for CaSm₂S₄ and CaNd₂S₄ series with graphite electrode

Undoped CaSm₂S₄ Bauerle+ Jamnik model		Undoped CaNd₂S₄ R//C+ Jamnik	
Bulk	Grain boundary	Bulk	Grain boundary
R=5.86x10 ³ Ω	R=1.96x10 ⁶ Ω	R=7.06x10 ⁶ Ω	
C=1.51x10 ⁻¹⁰ F	C=4.21x10 ⁻¹⁰ F	C=2.96x 10 ⁻¹¹ F	
τ = 8.87x10 ⁻⁷ s	τ = 8.33x10 ⁻⁴ s	τ = 2.09x10 ⁻⁴ s	
CaSm₂S₄+0.1Sm₂S₃ Bauerle+ Jamnik model		CaSm₂S₄+0.1Sm₂S₃ R//C+ Jamnik model	
Bulk	Grain boundary	Bulk	Grain boundary
R=2.15x10 ⁵ Ω	R=8.69x10 ⁵ Ω	R=1.70x10 ⁴ Ω	R=1.32x10 ⁶ Ω
C=3.93x10 ⁻¹¹ F	C=5.31x10 ⁻¹⁰ F	C=7.02x10 ⁻¹¹ F	C=1.63x10 ⁻¹⁰ F
τ = 8.24x10 ⁻⁶ s	τ =4.61x10 ⁻⁴ s	τ = 1.196x10 ⁻⁶ s	T = 2.14x10 ⁻⁴ s
CaSm₂S₄+0.2Sm₂S₃ Bauerle+ Jamnik model		CaNd₂S₄+0.2Nd₂S₃ R//C+ Jamnik	
Bulk	Grain boundary	Bulk	Grain boundary
R=1.69x10 ⁵ Ω	R=9.58x10 ⁶ Ω	R=7.50x10 ³ Ω	
C=1.03x10 ⁻¹⁰ F	C=6.95x10 ⁻¹⁰ F	C=2.58x10 ⁻¹⁰ F	
	Ψ =0.85	Ψ =1.0	
τ = 1.74x10 ⁻⁵ s	τ = 2.79x10 ⁻³ s	τ = 1.94x10 ⁻⁶ s	
CaSm₂S₄+0.3Sm₂S₃ Bauerle+ Jamnik model		CaNd₂S₄+0.3Nd₂S₃ R//C+ Jamnik	
Bulk	Grain boundary	Bulk R//C-R//CPE	Grain boundary
R=1.09x10 ⁶ Ω	R=1.74x10 ⁷ Ω	R=1.999x10 ⁴ Ω	
C=6.98x10 ⁻¹¹	C=1.82x10 ⁻¹¹	C=1.61x10 ⁻¹⁰	
τ =7.41x10 ⁻⁵ s	τ =3.18x10 ⁻⁴ s	τ =3.20x10 ⁻⁶ s	

5.3 The effect of Hydrogen sulphide concentration on bulk conductivities and activation energies

The total conductivities of the CaSm₂S₄ series with varying H₂S concentration were determined by impedance spectroscopy. If the bulk conductivity is independent of hydrogen sulphide at low concentration, then ionic conduction predominates. At higher H₂S concentrations the sulphide vacancies may interact with hydrogen sulphide to produce excess holes:

$$S_2 + 2V_s^{\bullet\bullet} = 2S^{\times} + 4\oplus$$
 (8)

Where

$V_s^{\bullet\bullet}$ - vacant sulphide ion site; S^{\times} - occupied sulphide site; \oplus - electron hole

Perovskites have the tendency to exhibit hole conduction at high oxygen partial pressures, Huang and Petric, 1995. If there were an increase in conductivity at low hydrogen sulphide concentrations, then this would suggest electronic conduction, Kofstad, 1972.

Figure 5-20 shows the Arrhenius plot for bulk conductivity for CaSm_2S_4 in different atmospheres. Bulk conductivity of undoped CaSm_2S_4 remained independent of hydrogen sulphide partial pressure from pure argon up to 1vol% H_2S . At 2%vol of H_2S , an increase in conductivity was achieved at all temperatures measured, 350-550°C, which suggests hole conduction according to equation (2), Huang and Petric, 1995.

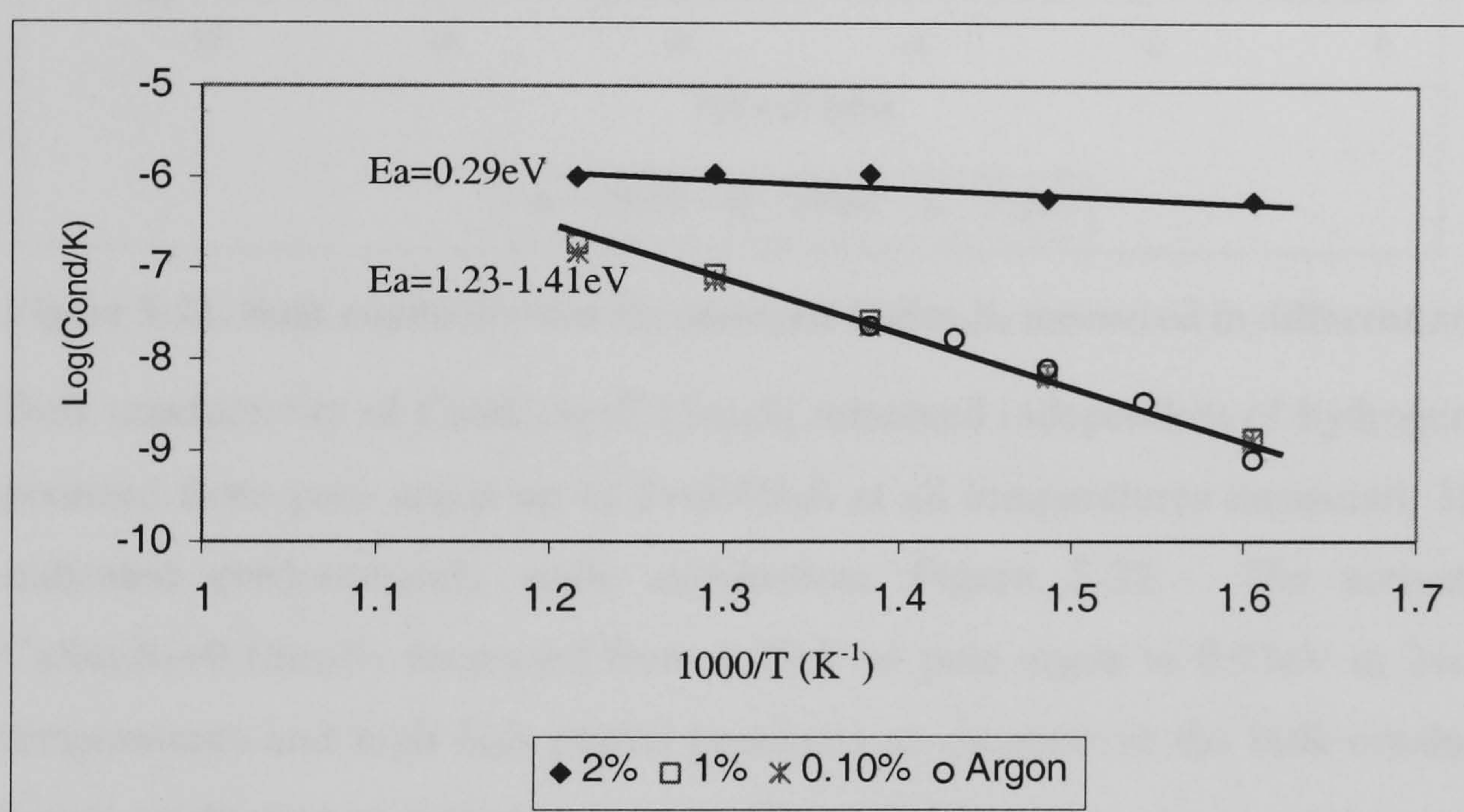


Figure 5-20. Bulk conductivities for undoped CaSm_2S_4 measured in different atmospheres

The activation energy, 1.23-1.41eV, remained constant for CaSm_2S_4 , up to 1vol% H_2S . However at 2vol%, the activation energy decreased to 0.29eV, suggesting that the predominant conducting species had changed. This low activation energy is consistent with the expectation that sulphide ion vacancies react with H_2S producing electrons holes as in equation (8).

Song and H. Yoo, 2003 studied BaTiO_3 , which is a mixed ionic-electronic conductor, in which the conducting species changed from anionic to electronic then to electronic hole by simply changing the oxygen partial pressure. CaSm_2S_4 appears to have similar behaviour, since the conduction changed from electronic to electron hole as the H_2S concentration increased from 0vol% to 0.1vol% $\text{H}_2\text{S}/\text{Ar}$. Song and H. Yoo proposed that if the ratio r determined from the gradient of a plot of $(\log \sigma_{\text{total}} \text{ vs } \log P_s)$ is less than or equal to 0.1, then

ionic conductivity was assumed. CaSm_2S_4 has a ratio r of 0.07 between 1vol% H_2S and 2vol% H_2S at 550°C, which suggests ionic conductivity in this narrow range, Figure 5-21.

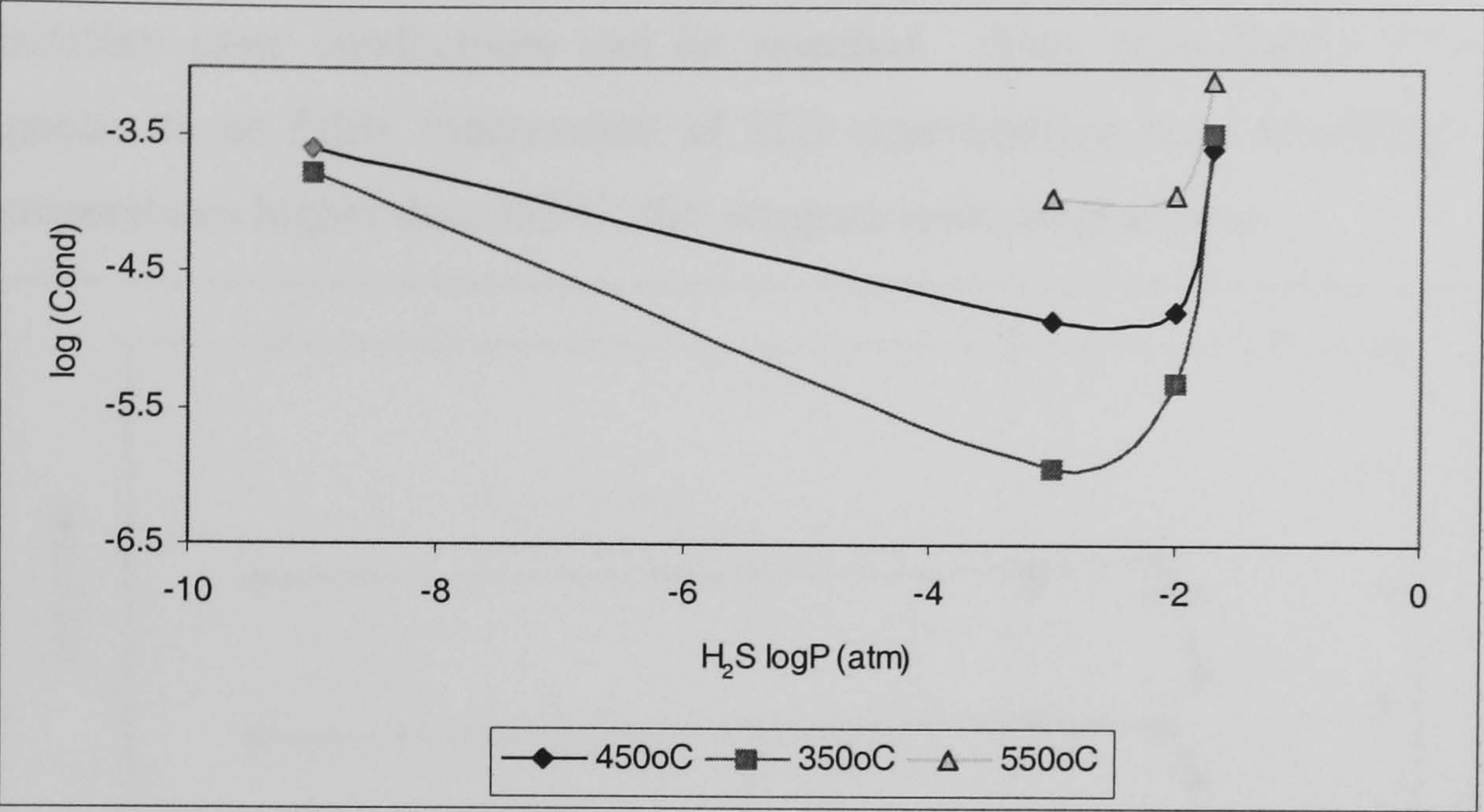


Figure 5-21. Bulk conductivities for undoped CaSm_2S_4 measured in different atmospheres

Bulk conductivity of $\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ remained independent of hydrogen sulphide partial pressure from pure argon up to 2vol% H_2S at all temperatures measured, 350-550°C, which indicated predominantly ionic conduction, Figure 5-22. The activation energy for $\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ decreased from 1.25eV in pure argon to 0.93eV in 2vol% H_2S . At low temperatures and high H_2S partial pressures an increase in the bulk conductivity occurred, hence a reduction in activation energy, Figure 5-23.

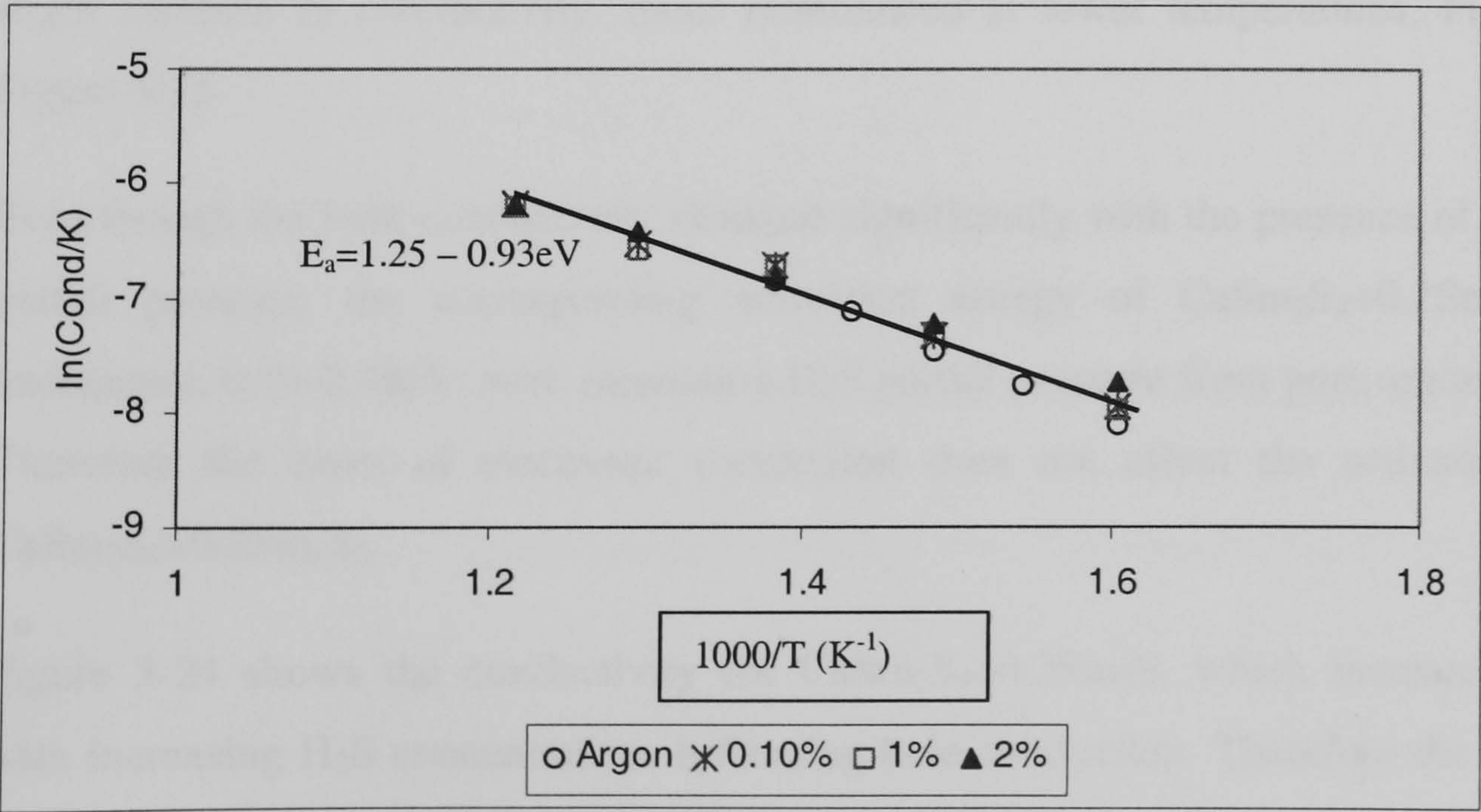


Figure 5-22 Bulk conductivities for $\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ measured in different atmospheres

Figure 5-23 shows that the conductivity for $\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ is independent of H_2S partial pressure up to 1vol% H_2S . The reduction in conductivity at 2vol% H_2S at 350°C and 400°C indicates electronic conductivity. The gradient of a plot of $(\log \sigma_{\text{total}} \text{ vs } \log P_s)$ is 0.03, therefore ionic conductivity can be assumed. Also, from Figure 5-23, the conductivity appears to be fairly independent of H_2S concentration from 0vol% H_2S to 1vol% H_2S at temperatures higher than 350°C; this suggests ionic conductivity.

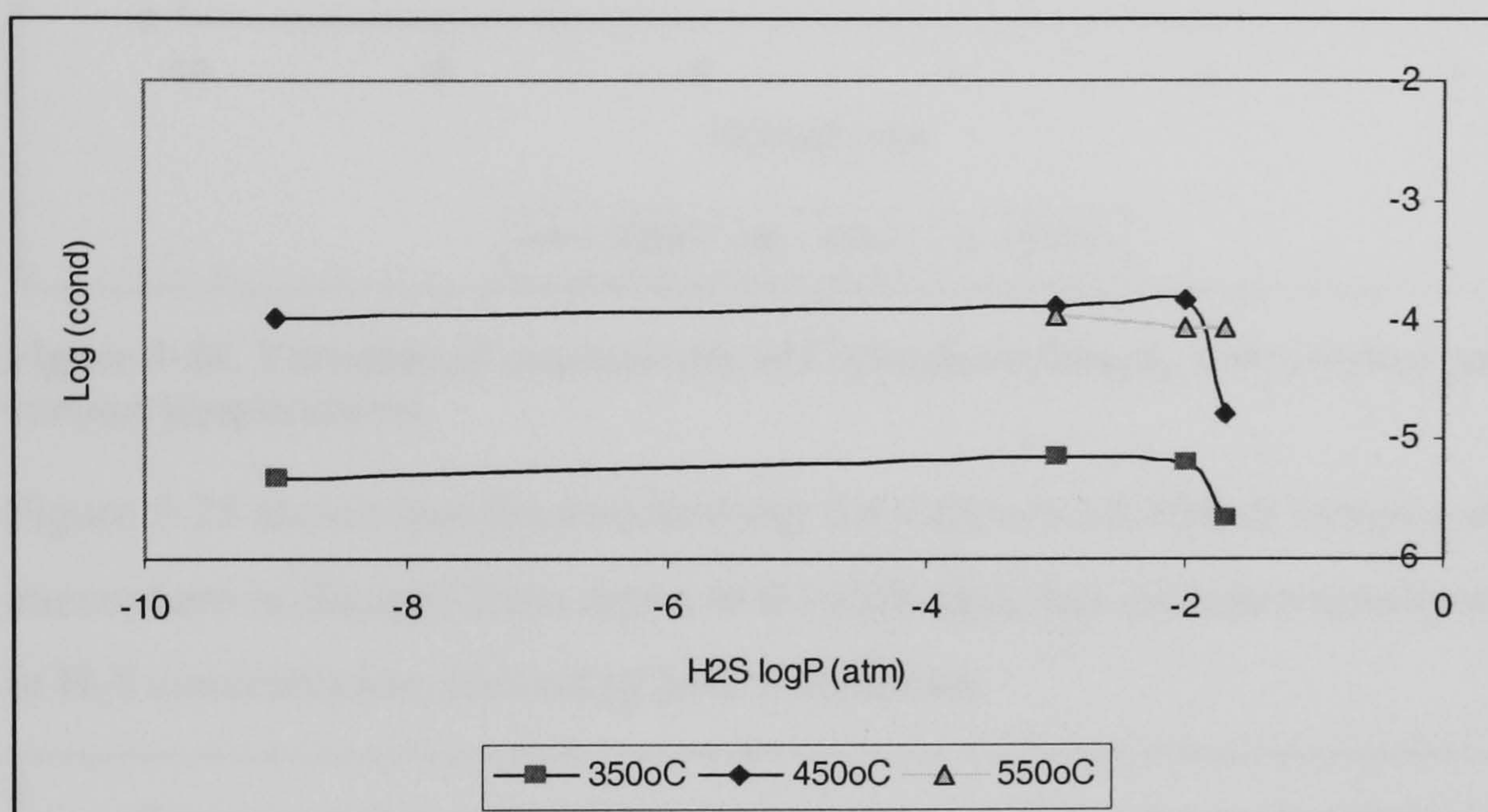


Figure 5-23. Variation of conductivity of $\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ with sulphur partial pressure at various temperatures

Bulk conductivity of $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ increased significantly upon changing the gas from argon to 0.1vol% $\text{H}_2\text{S}/\text{Ar}$. A further increase in the H_2S concentration to 2vol% caused a slight increase in conductivity, more pronounced at lower temperatures, Figure 5-24 and Figure 5-25.

Even though the bulk conductivity changed significantly with the presence of a positive H_2S partial pressure, the corresponding activation energy of $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ remained unchanged, 0.44-0.48eV, with increasing H_2S partial pressure from pure argon to 1vol% H_2S . Therefore the onset of electronic conduction does not affect the activation energy for $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$.

Figure 5-24 shows the conductivity for $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$, which increases significantly with increasing H_2S concentration, indicating hole conduction. Therefore the low activation energy for this compounds shows that it is hole conduction under these experimental conditions (350-500°C and 0-2vol% H_2S).

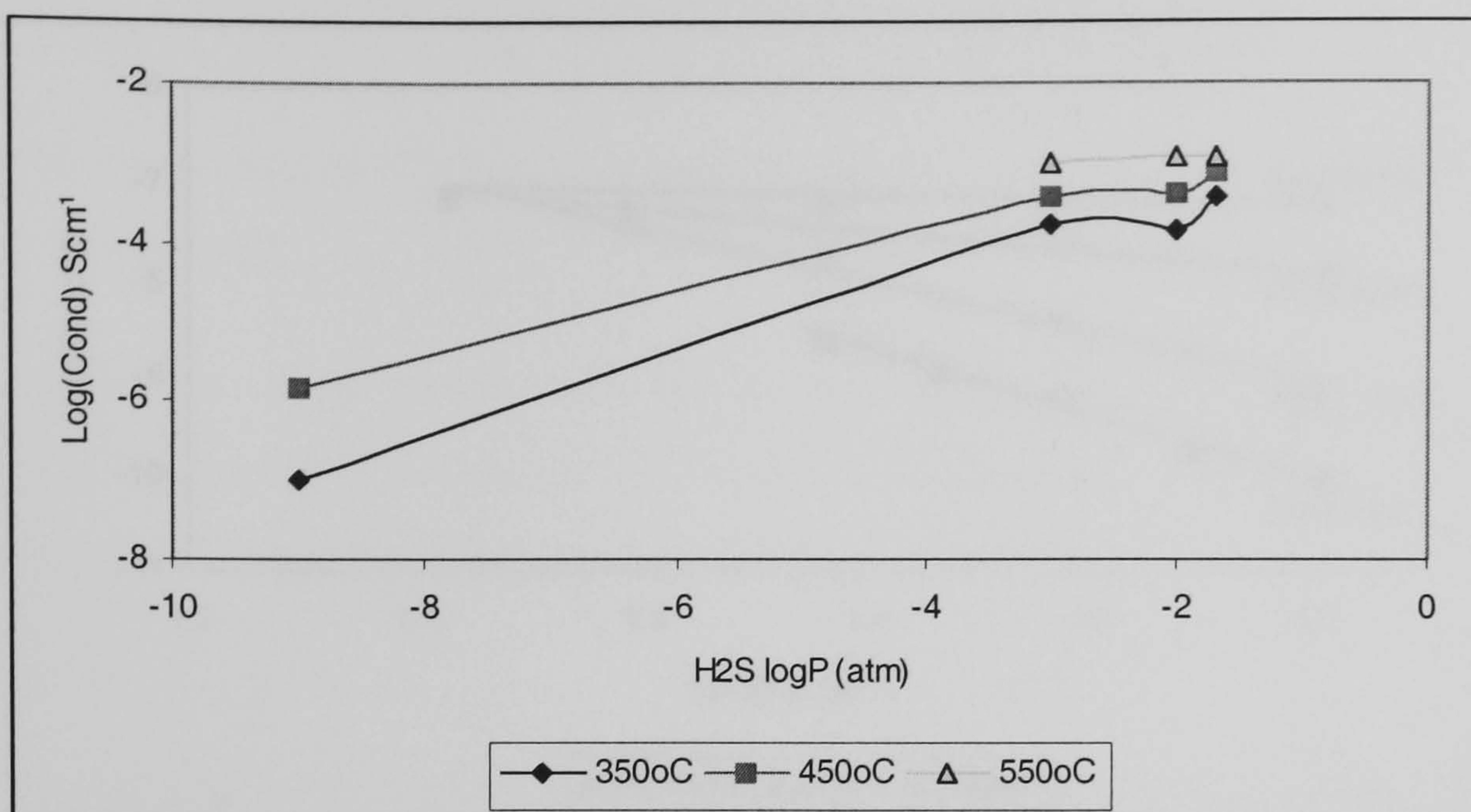


Figure 5-24. Variation of conductivity of $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ with sulphur partial pressure at various temperatures

Figure 5-25 shows that the conductivity for $\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}$ remains unchanged when the atmosphere is changed from argon to 0.1 vol% H_2S , but increases rapidly with further increase in H_2S concentration, indicating hole conduction.

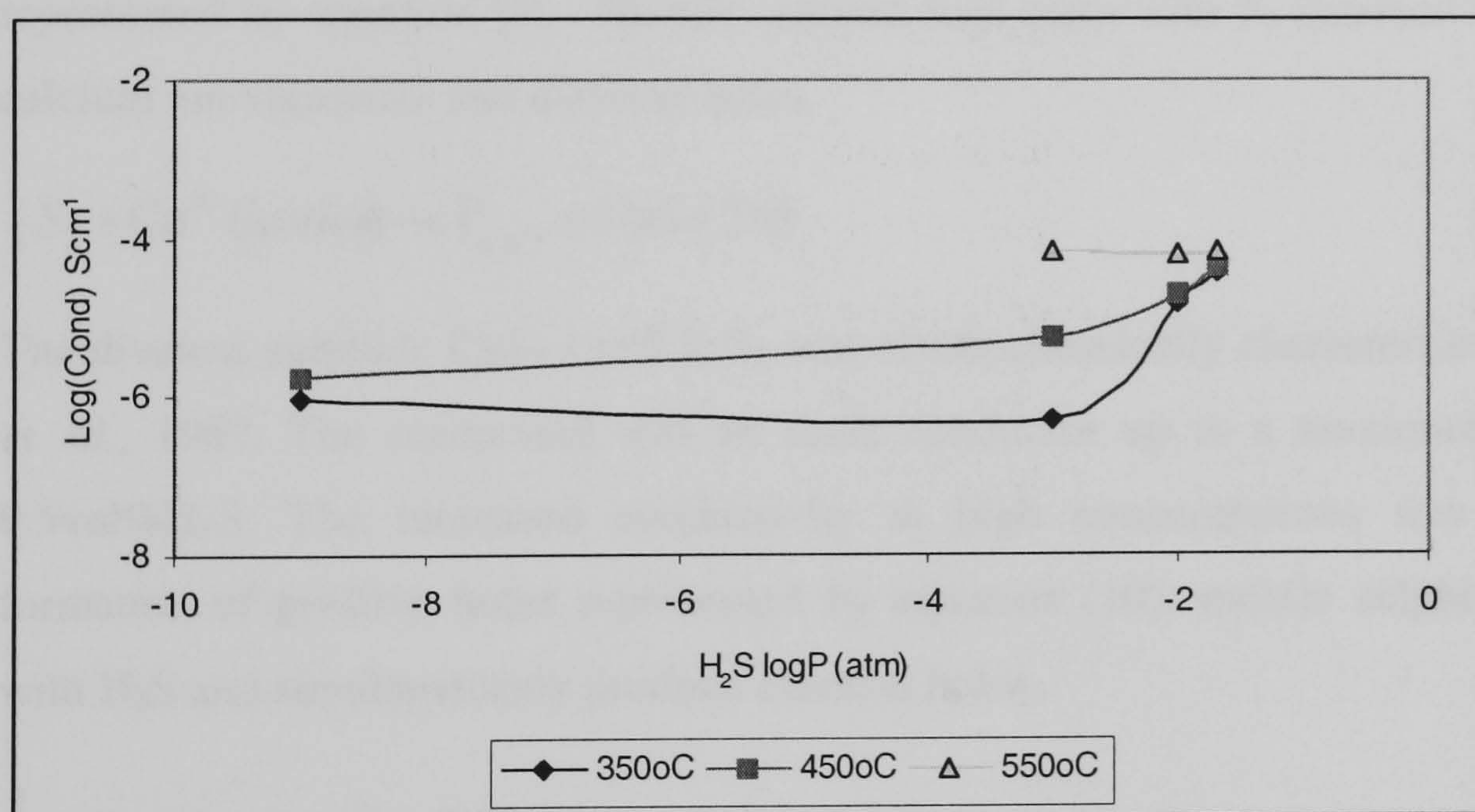


Figure 5-25. Variation of conductivity of $\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ with sulphur partial pressure at various temperatures

The activation energy for bulk conductivity of $\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ decreased from 1.41 eV in pure argon to 0.09 eV in 2 vol% H_2S , Figure 5-26. The major reduction in activation energy occurs between 1 vol% H_2S and 2 vol% H_2S , which is also the point when the bulk conductivity increased, Figure 5-26. Therefore the onset of hole conduction is shown by the increased conductivity and the reduced activation energy.

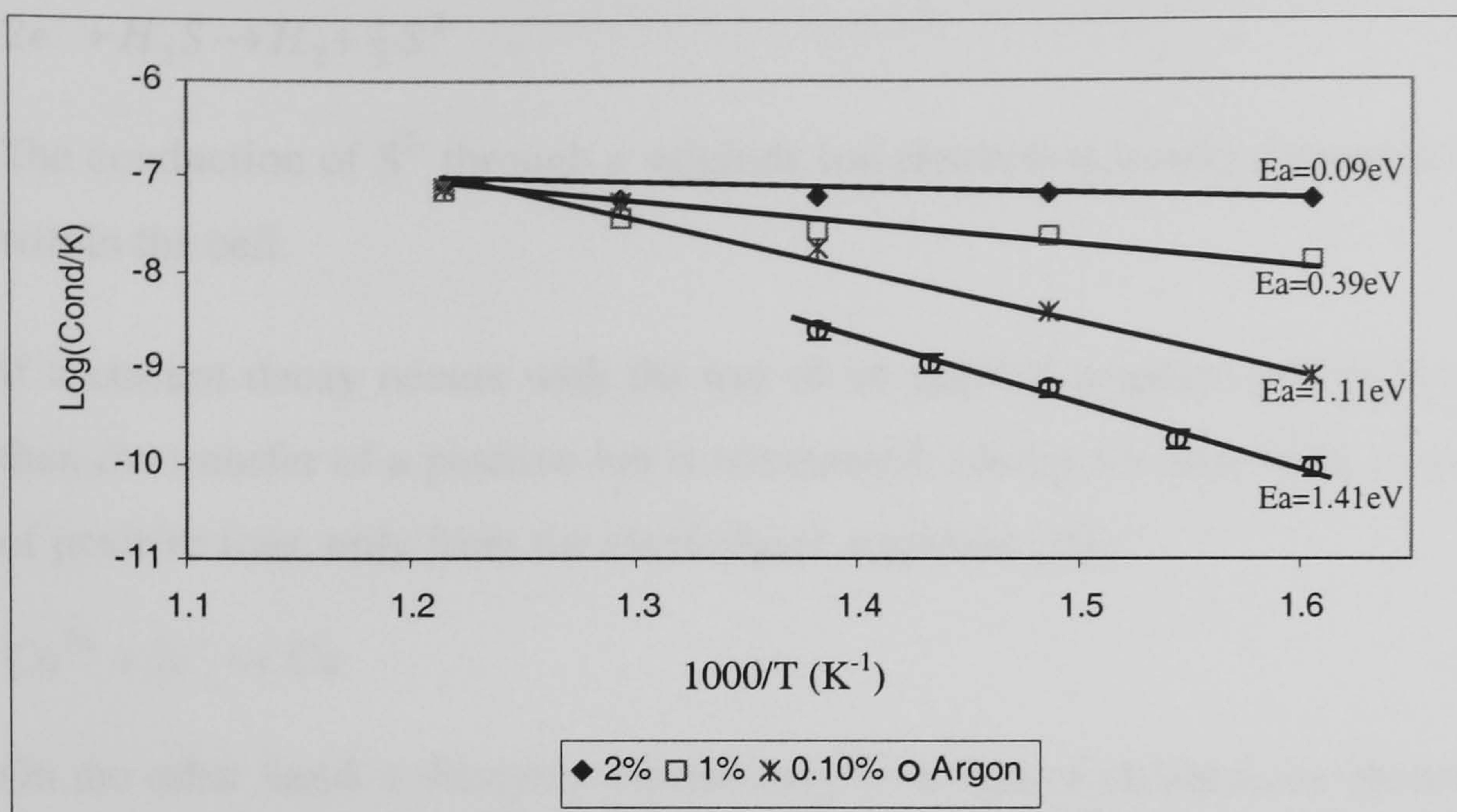


Figure 5-26. Bulk conductivities for $\text{CaSm}_2\text{S}_4+30\text{mol}\%\text{Sm}_2\text{S}_3$ measured in different atmospheres

The early work of Nagata and Goto, 1974 showed that the bulk conductivity for CaS increased as H_2S partial pressure increased beyond 10^{-6} atm. The increased conductivity was represented by equation (9). Mobile calcium ions react with S_2 (derived from H_2S) to form calcium ion vacancies and electron holes.



The divalent sulphide $\text{CaS}+1\text{wt}\%\text{Y}_2\text{S}_3$ was electrochemically characterised by W. L. Worrel *et. al.*, 1967. The compound was an ionic conductor up to a maximum concentration of 0.5vol% H_2S . The increased conductivity at high concentrations was attributed to the formation of positive holes represented by equation (10); mobile sulphide vacancies react with H_2S and simultaneously produce electron holes.



The conductivity of $\text{CaS}+1\text{wt}\%\text{Y}_2\text{S}_3$ is higher than CaS; it was accredited to the creation of cationic rather than anionic vacancies. Cationic vacancies were postulated due the reduction in lattice parameters.

5.4 Electrochemical Pumping of Selected SrSm_2S_4 compounds

The asymmetric electrochemical concentration cell of the type $\text{H}_2\text{S}/\text{H}_2//\text{Pt}/\text{SrSm}_2\text{S}_4/\text{Pt}//\text{Ar}/\text{H}_2$ was operated at elevated temperatures (550-750°C) with 1-10V (d.c) to identify sulphide ion conduction. The constant source of S^{2-} ions was formed by the application of a negative potential applied on the H_2S compartment, equation (9);



The conduction of S^{2-} through a sulphide ion electrolyte would produce a steady state current within the cell.

If a current decay occurs with the use of an applied negative potential on the H_2S section, then the transfer of a positive ion is interpreted, (decay because there is no continuous source of positive ions, only from the electrolyte), equation (10).



On the other hand, a decaying current may be a sign of mixed ionic-electronic conductor, the peak current related to the total ionic and electronic, while the steady state current related to the electronic current. A current flow with no applied voltage is indicative of electronic; it will confirm the presence of electronic conduction.

At room temperature, the cross-sectional resistance for the $H_2S/H_2//Pt/CaSm_2S_4/Pt//Ar/H_2$ cell was $20k\Omega$, suggesting short-circuiting of this cell. The symmetric response of both the peaks and steady state current suggests that the conduction is mixed electronic-cationic, Figure 5-27. The rate of current decay was also the same in both compartments, indicating that the dc current flow was H_2S independent.

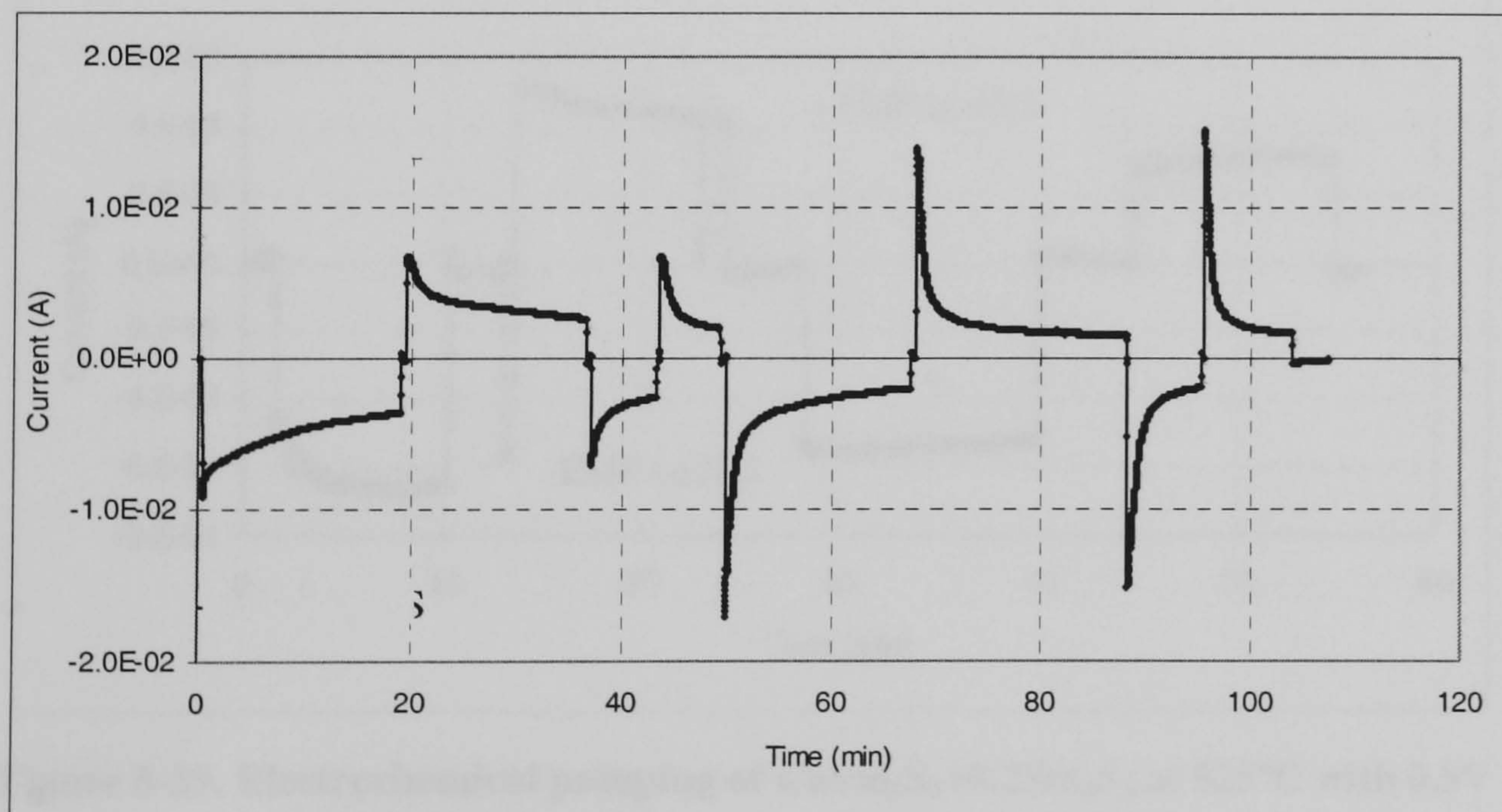


Figure 5-27. Electrochemical pumping of $CaSm_2S_4$ at $750^\circ C$ with 1V and 2V

The electrochemical concentration cell of the type, $H_2S/2//Pt/CaSm_2S_4+0.2Sm_2S_3/Mo//Ar/H_2$ operating at $700^\circ C$ with 10V (d.c), produced asymmetric results shown in Figure 5-28. The steady state current with the application of a negative 10V dc on the H_2S section of the reactor indicates sulphide. The absence of a current flow on the reverse section of the reactor is ambiguous. The negligible reversible current flow with no applied potential infers that the

electronic current flow is an order of magnitude less than the peak current, indicating very little electronic contribution.

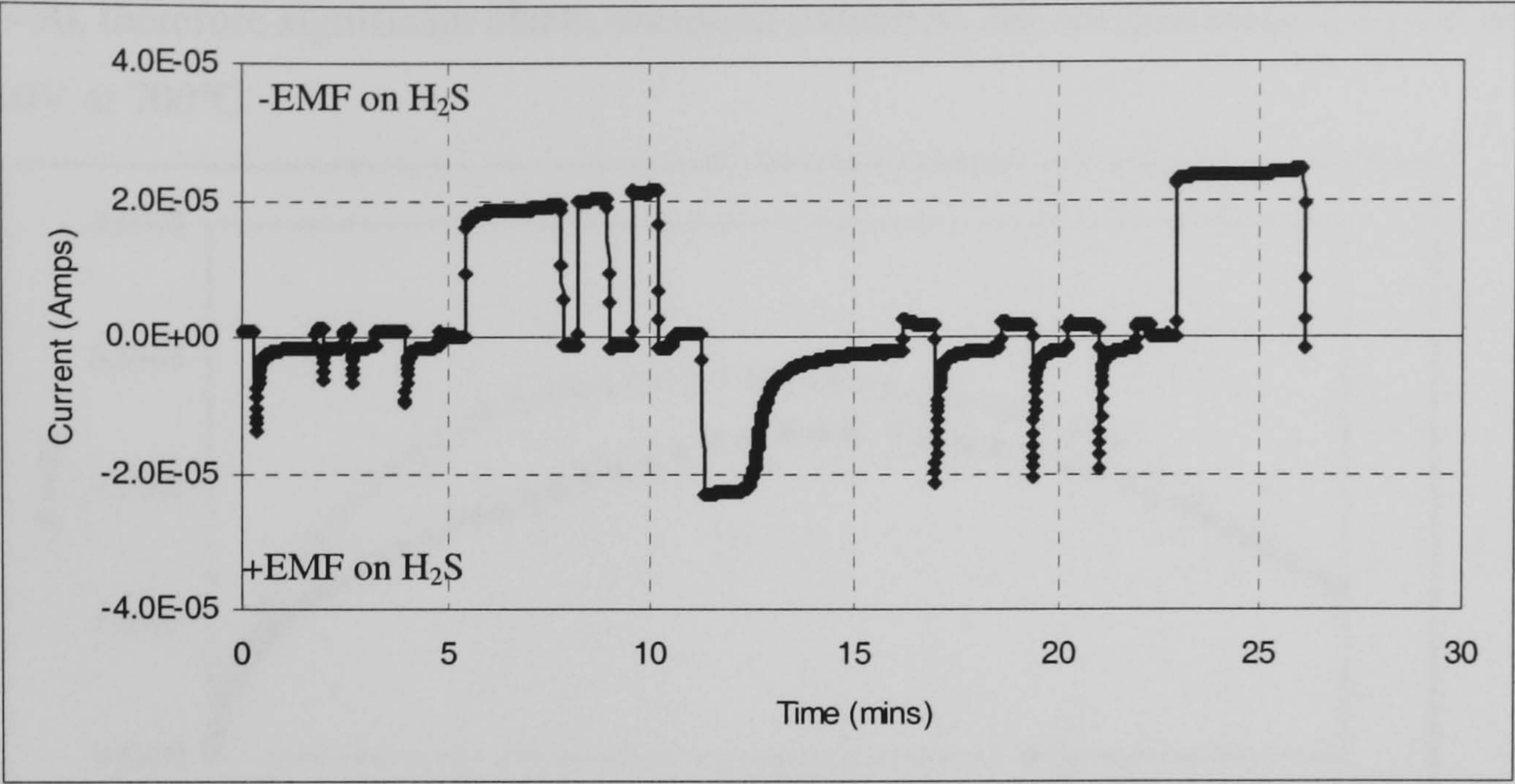


Figure 5-28. Electrochemical pumping of $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ at 700°C with 10V

Repetition of the experiment produced a generative current when -0.5V was applied to H_2S compartment, confirming sulphide ion conduction, Figure 5-29. Reversing the current also produced a smaller steady state current, which was interpreted as a leakage of H_2S through the membrane, since the OCV of the cell was 0.04mV, showing that the pellet broke.

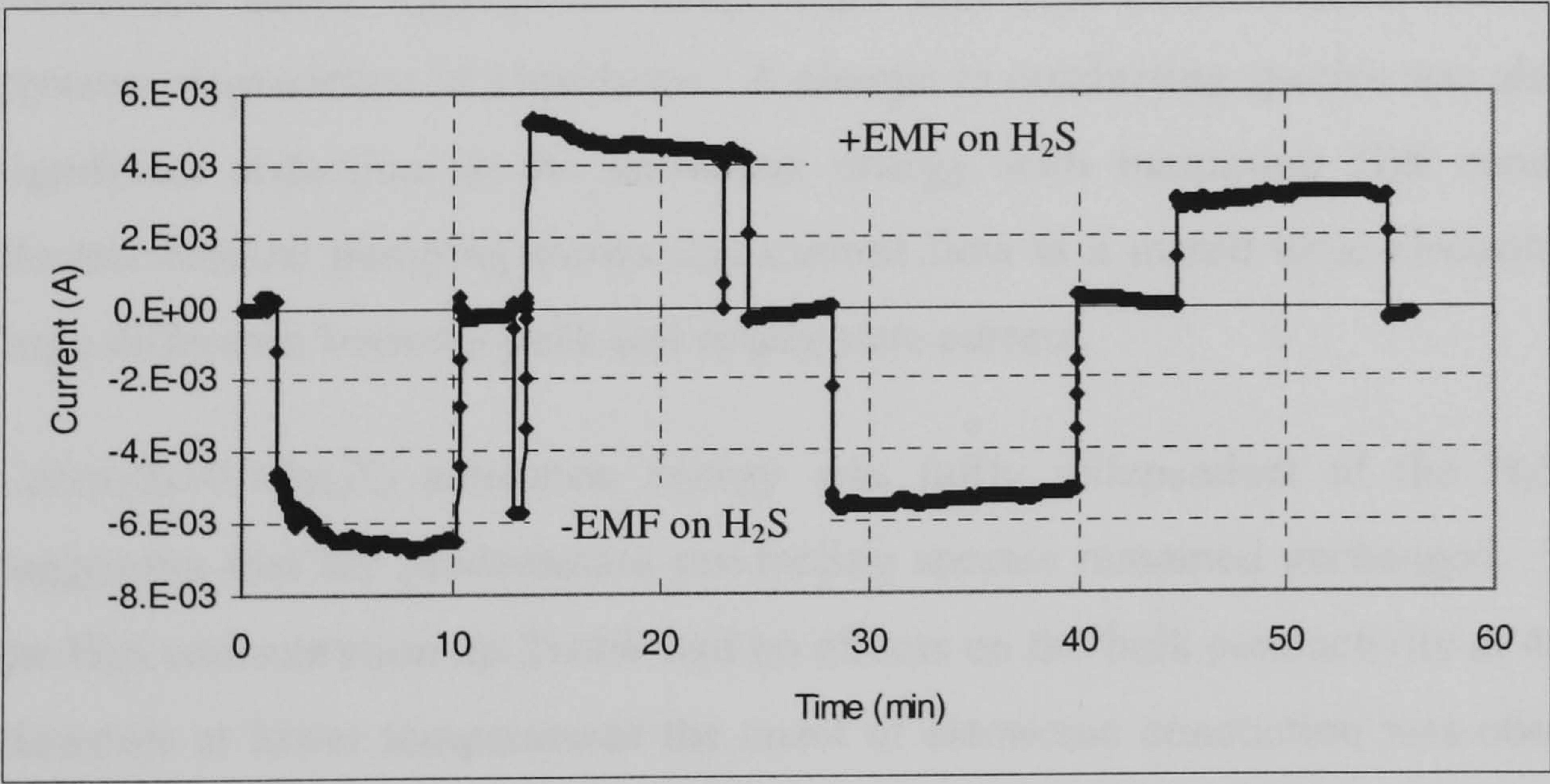


Figure 5-29. Electrochemical pumping of $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ at 825°C with 0.5V

Impedance spectroscopy of $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ after pumping experiments resulted in comparable Nyquist plot what was obtained prior to pumping with 10V dc as shown in Figure 5-30, therefore significant electrochemical reduction did not take place with the application of 10V at 700°C.

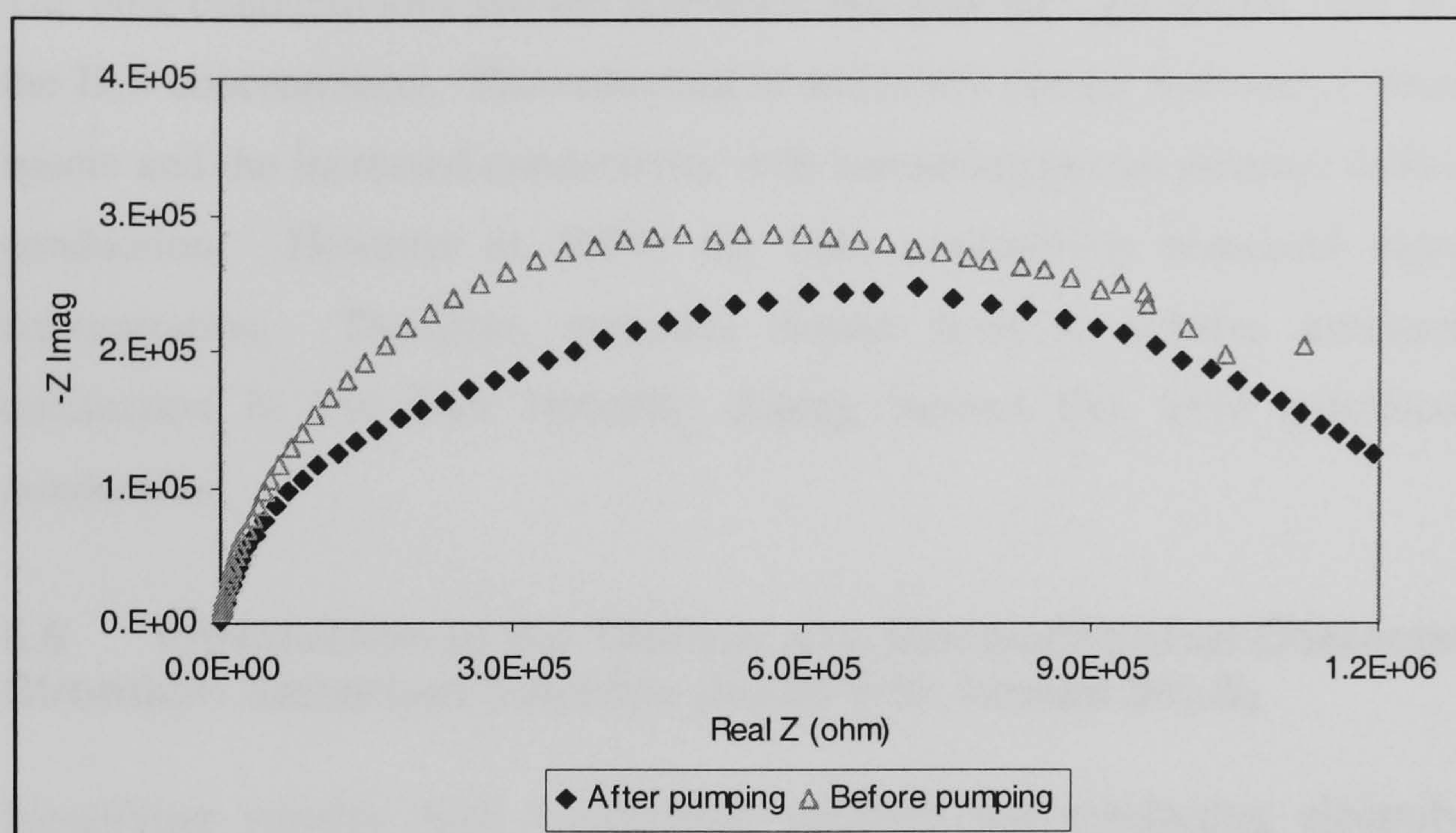


Figure 5-30. Nyquist plot of $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$, for before and after pumping experiments, at 450°C

In summary, undoped CaSm_2S_4 is a mixed conductor, exhibiting electronic and electron-hole conduction under appropriate temperature and H_2S concentration, based on the partial pressure dependence of impedance. A change in conducting species was also evident with a significant reduction in the activation energy with increasing H_2S concentration. The electrochemical pumping shows that current flow is a mixed ionic-electronic, based on the large difference between peak and steady state current.

$\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ activation energy was fairly independent of the H_2S concentration, suggesting that the predominant conducting species remained unchanged. The variation of the H_2S concentration up 2vol% had no effects on the bulk conductivity at 450°C and above. However at lower temperatures the onset of electronic conduction was observed at H_2S up 2vol%.

A further increase in dopant level to $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ caused hole conduction up to 450°C, since the increase in conductivity with increasing H_2S concentration. The marginal change in activation energy suggests unchanging conducting species. However the low activation energy, 0.44eV, is atypical for S^{2-} . Both the pumping experiments carried out at 700°C and 825°C show that dc conductivity increases in the presence of H_2S , which is a typical response for a sulphide ion conduction electrolyte. Electrochemical pumping at lower temperatures

yielded symmetric results; it is an indication of electronic type conduction, thus agreeing with the low activation energy observed for impedance spectroscopy as well as the H₂S dependent conductivity.

The bulk conductivities and the activation energies for CaSm₂S₄+0.3Sm₂S₃ were sensitive to the H₂S concentration. The reduction in activation energy indicates a change in conducting specie and the increased conductivity with increasing partial pressure indicates positive hole conduction. However at 500°C the bulk conductivity remained independent of H₂S concentration. Therefore, optimum dopant level to achieve maximum sulphide ion conduction is less than 10mol%; doping beyond this level introduced electron hole conduction.

5.6 Introduction to the Thermal and Electrochemical Characterisation of Strontium Samarium Sulphide doped with excess Sm₂S₃

Identifying suitable high temperature sulphide ion conducting electrolytes began with verification of the previously identified sulphide ion conductors, Nd₂S₃ doped-CaNd₂S₄, as stated by Kalinina *et al.*, 1995. However, only CaNd₂S₄+0.1Nd₂S₃ was found to exhibit sulphide ion conduction when characterised by impedance spectroscopy and electrochemical pumping. The bulk conductivity, $1 \times 10^{-6} \text{ S.cm}^{-1}$, of CaNd₂S₄+0.1Nd₂S₃ (at 500°C) is marginal, hence optimisation of conductivity was sought; by changing the host cation from calcium to strontium. This led to an increase in bulk conductivity but was later established to cause significant electronic or positive hole conduction. Therefore the next logical change in optimising the electrolyte is to change the dopant; the dopant Nd₂S₃ was changed to Sm₂S₃ as well as the host cation, from Ca to Sr, therefore forming the SrSm₂S₄ series.

Calcium samarium sulphide doped with excess samarium sulphide has previously been synthesised and characterised by Kalinina *et. al.* 2000 where they reported that these materials exhibited sulphide ionic conduction. Therefore the analogue SrSm₂S₄ of CaSm₂S₄ was synthesised using the identical solid-state reactions procedure according to Kalinina *et. al.*, 1995.

The XRD pattern of the SrSm₂S₄ series shows that these compounds have a cubic unit cell similar to the CaNd₂S₄ series shown in Chapter-Figure 4.1, White, 2005. The larger black spheres now represent Sm rather than Nd atoms and the smallest spheres represents Sr rather than Ca atoms. The X-ray diffraction pattern shows that an increase in dopant level does lead

to similar changes as observed with the CaNd_2S_4 system, Chapter-Figure 4.2, (White 2005) see Appendix A for XRD's.

The volume of the unit crystal increases as the host cation is changed from calcium to samarium, expressed by an increase in the lattice parameter. The increase in lattice parameter with the host cation changing from calcium to strontium is excepted since the latter cation is larger. However increasing the dopant level in each group of compound causes a contraction of the unit cell, Table 5.10.

Table 5.10. Lattice parameter for SrSm_2S_4 series and CaSm_2S_4 series

Dopant level (Sm_2S_3 or Nd_2S_3)	Lattice parameter Å (a-site) CaSm_2S_4	Lattice parameter Å (a-site) SrSm_2S_4
Undoped	8.4708(1)	8.5361(1)
10%	8.4701(8)	8.5595(3)
20%	8.4684(8)	8.5523(1)
30%	8.4653(1)	8.5467(1)

The pellet making process began with grinding the materials; particle size distribution of the ground product is shown in Figure 5-31, followed by pressing to 10 tonnes and then sintering at 1350°C in a H_2S atmosphere. The sintered pellets achieved a maximum of 91% of the theoretical density. Both the theoretical and actual density decreased with increasing dopant concentration, Table 5.11.

Table 5.11. Theoretical and actual densities for SrSm_2S_4 series

	Theoretical density SrSm_2S_4 (g/cm ³)	Actual density SrSm_2S_4 (g/cm ³)	% of theoretical density
Undoped	5.464	4.98	91
10mol% Nd_2S_3	5.375	4.71	88
20mol% Nd_2S_3	5.268	4.57	87
30mol% Nd_2S_3	5.202	4.40	86

SEM's of the sintered pellets show large pores of diameter up to 25µm with fairly thin grain boundaries, Figure 5-31. Therefore the pellets were not dense even when made with grounded material and maximum temperature, Table 5.11. Undoped SrSm_2S_4 achieved the highest percentage of theoretical density.

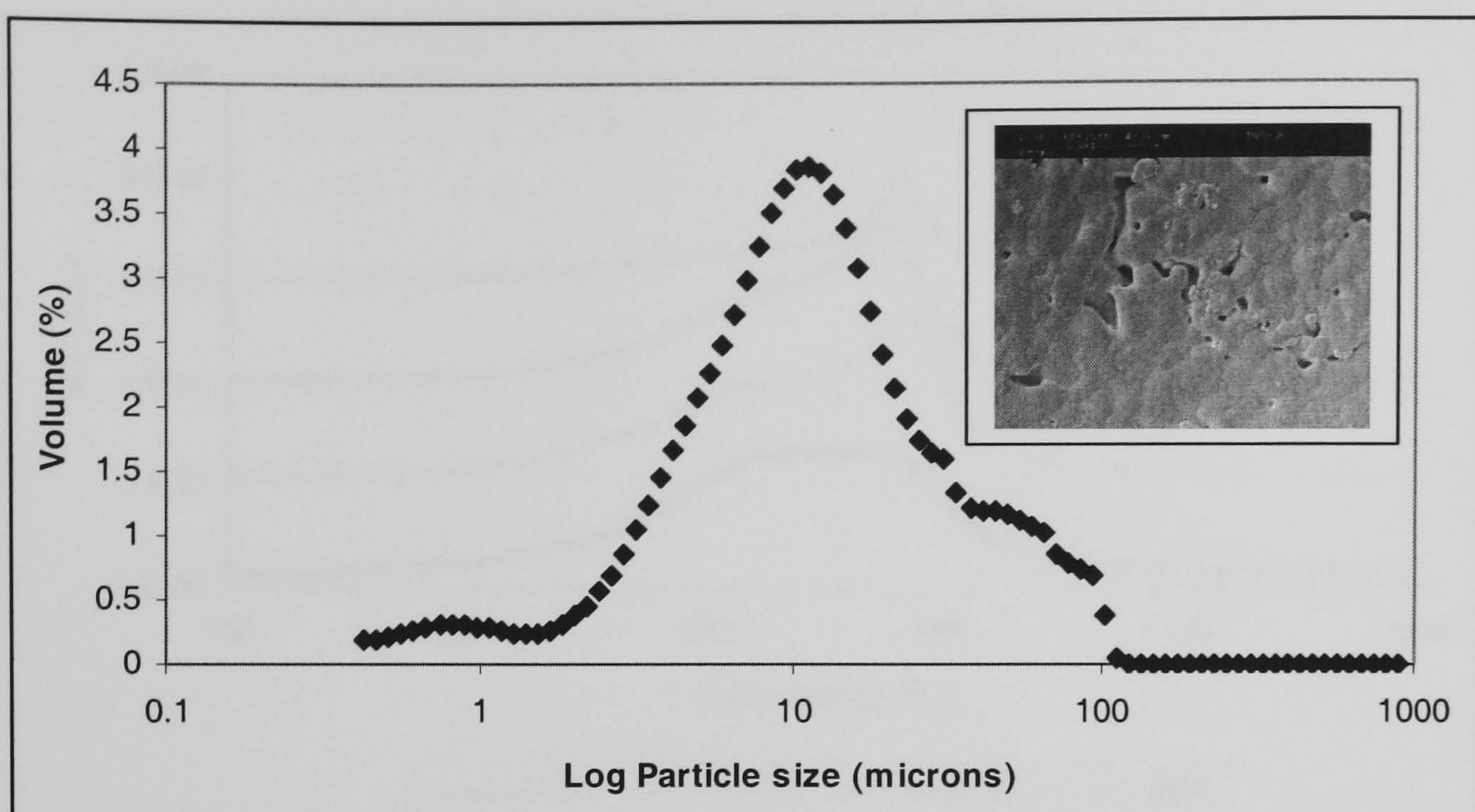


Figure 5-31. $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ sintered pellet at 1350°C in $\text{H}_2\text{S}/\text{Ar}$ mixture exhibiting 86% of theoretical density

5.7 TPO and TPR for SrSm_2S_4 series

The thermal stability for the prepared series $\text{SrSm}_2\text{S}_4+x\text{Sm}_2\text{S}_3$ was established using TPO and TPR techniques. The TPO traces of this series consist of possibly two peaks with a shoulder at the lower temperatures, which differs from all other sulphide series previously investigated, Figure 5-32. The presence of multiple SO_2 peaks at elevated temperatures may indicate a complex reaction mechanism for the oxygen-sulphur exchange of the oxidation SrSm_2S_4 series. The low temperature peak reduced to a shoulder, as the dopant was increased beyond 10mol% Sr_2S_3 .

Further detailed analysis involving oxygen and sulphur balances was not done for the SrSm_2S_4 series since no relationship was found between percentage of oxidation and ionic conductivity in the CaNd_2S_4 series. Therefore TPO was done solely to determine the thermal stability of these materials in an oxidising atmosphere.

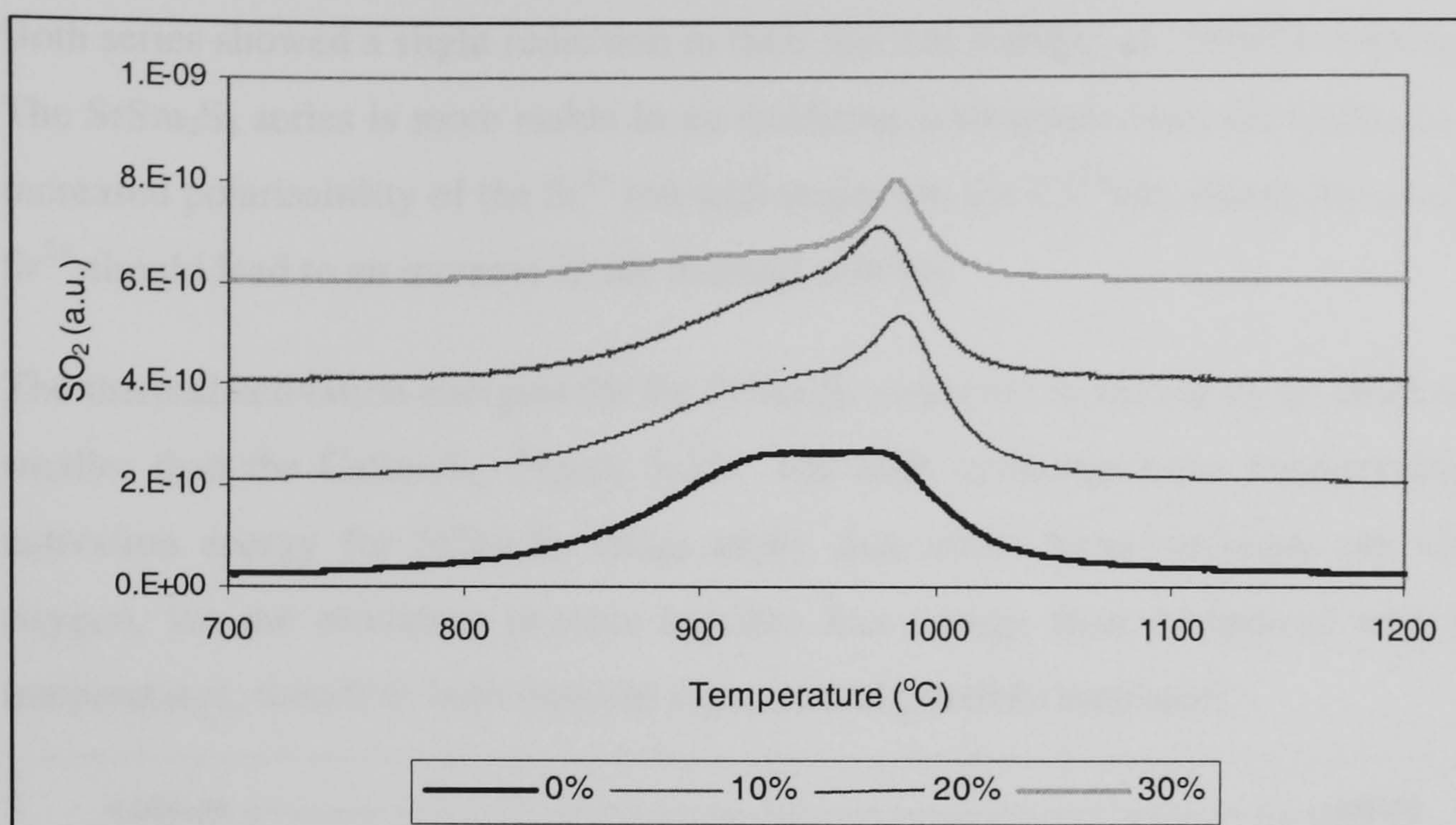


Figure 5-32. Temperature programmed oxidation of SrSm₂S₄ series

The sulphur dioxide peak for this family of compounds is located in the temperature range from 818°C to 844°C when a heating rate of 10°C/min is used, Table 5.12. The addition of excess Sm₂S₃ did not cause any significant change in onset temperatures of both SrSm₂S₄ and CaSm₂S₄ series while doping with Nd₂S₃ in the CaNd₂S₄ series caused increased onset temperatures for all doped compounds. Changing the host cation from calcium to samarium improved the thermal stability in oxidizing conditions, Table 5.12.

Table 5.12 Onset temperatures for SrSm₂S₄ and CaSm₂S₄ and unit cell lattice parameter

	Onset Temperatures		Lattice parameter for 'a' site Å	
	SrSm ₂ S ₄	CaSm ₂ S ₄	SrSm ₂ S ₄	CaSm ₂ S ₄
0%	832	755	8.5361(1)	8.4708(1)
10%	818	745	8.5595(3)	8.4701(8)
20%	844	750	8.5523(1)	8.4684(8)
30%	832	750	8.5467(1)	8.4653(1)

*Bracketed () number indicates the standard deviation on the fourth decimal place

The unit cells for both SrSm₂S₄ and CaSm₂S₄ series decreased with increasing dopant content yet the oxidation onset temperature remains unaffected; suggesting that the unit cell size is not the only factor which controls oxidation onset temperature, Table 5.12. While the CaNd₂S₄ series showed increased oxidation onset temperatures with increasing dopant content, which correlates with the reduction in the lattice parameter, Table 5.3, the Sm₂S₃ doped material did not show such a correlation.

Both series showed a slight reduction in their thermal stability at 20mol% doping, Table 5.12. The SrSm_2S_4 series is more stable in an oxidising atmosphere than the CaSm_2S_4 series. The increased polarisability of the Sr^{2+} ion with respect to the Ca^{2+} ion, due to the smaller radius of Sr^{2+} should lead to an increase in the thermal stability.

The thermal activation energies for the SrSm_2S_4 series are in excess by an order of magnitude smaller than the CaSm_2S_4 , Figure 5-33. The high oxidation onset temperatures and small activation energy for SrSm_2S_4 series imply that while these materials are very stable in oxygen, yet the oxidation process requires less energy than compound with lower onset temperatures, therefore both data are separate and possibly unrelated.

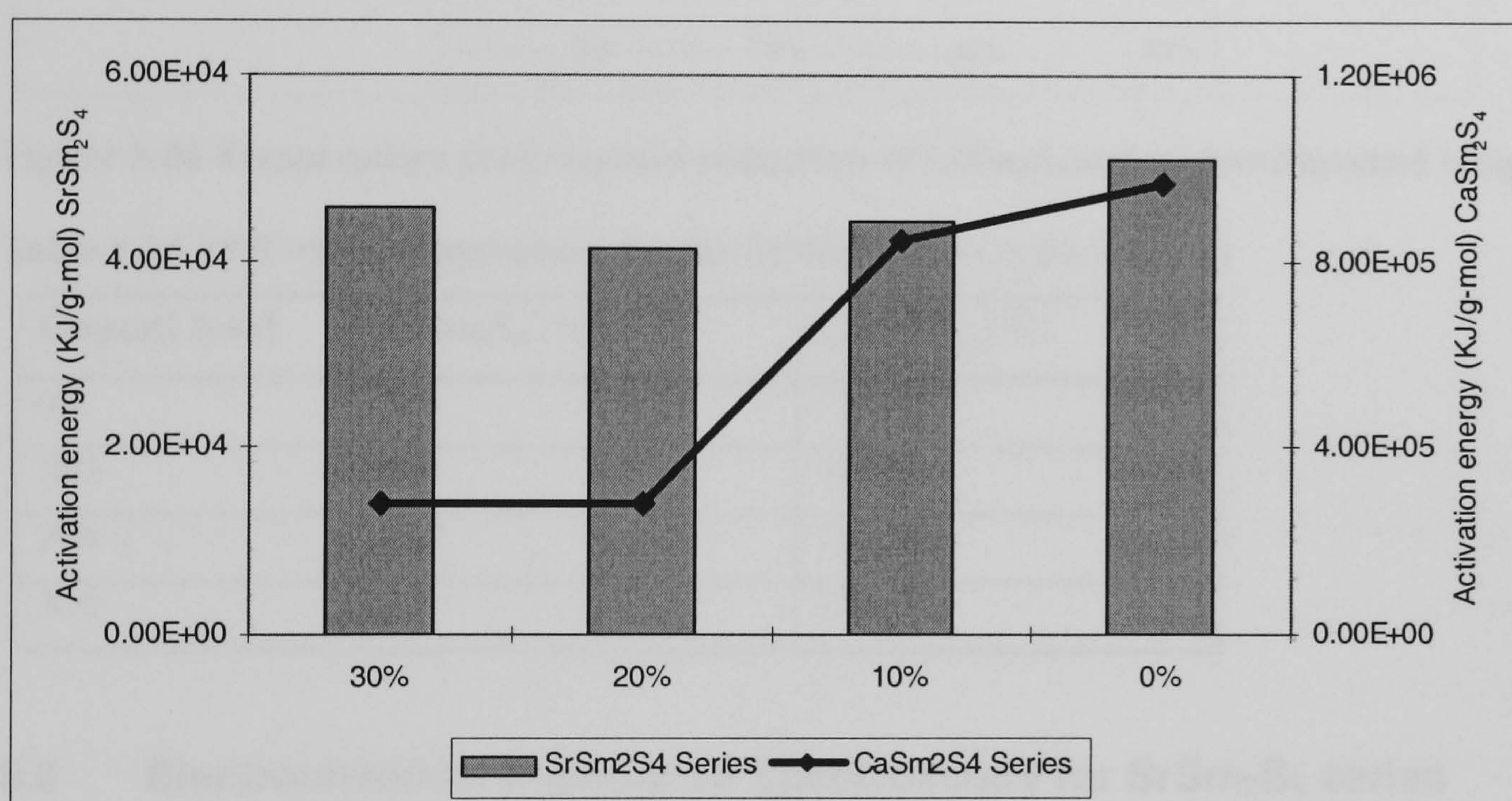


Figure 5-33. Thermal Activation energy for SrSm_2S_4 and CaSm_2S_4 series

The thermal activation energies of the CaSm_2S_4 series showed that, by increasing the doping the unit cell contracts and the activation energy decreases. The phenomenon may be explained by considering that when ions are in close proximity, an effective repulsive force operates which resists closer contact. Though it is a short-range interaction it increases exponentially with a decrease in inter-nuclear distance. Therefore this repulsive force could explain the decreased thermal activation energy for the 20mol% and 30mol% doped CaSm_2S_4 , Figure 5-33. However the thermal activation energies for the SrSm_2S_4 series remains unchanged with increasing dopant levels.

The compounds of the SrSm_2S_4 series all showed similar TPR traces, Figure 5-34. The doped compounds of the SrSm_2S_4 series are less stable in hydrogen than in air, Table 5.12 and Table 5.13. Also the CaSm_2S_4 series is more stable than the SrSm_2S_4 series in a reducing atmosphere while the reverse is true under oxidizing conditions, Table 5.12 and Table 5.13.

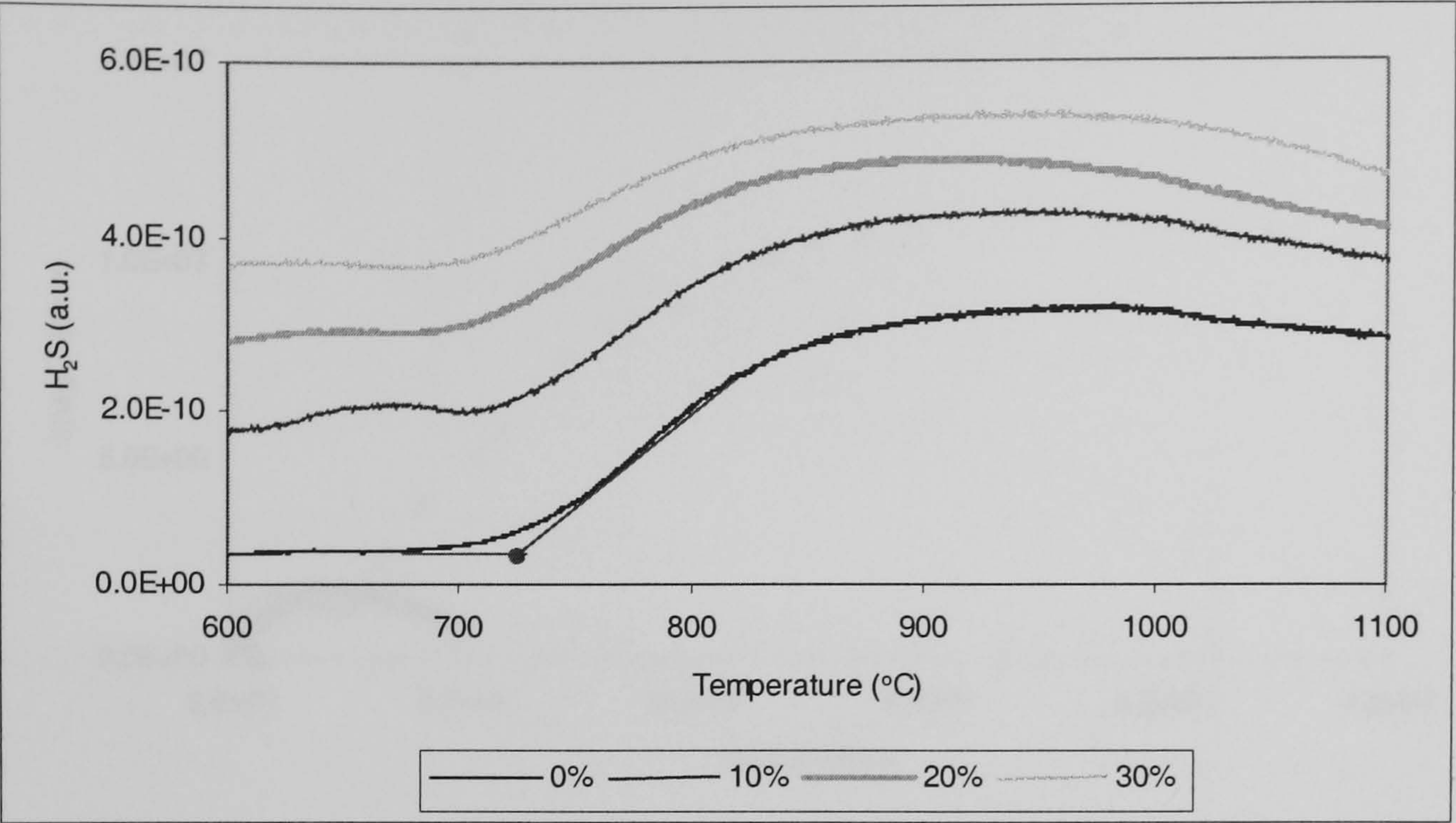


Figure 5-34 Temperature programmed reduction of SrSm₂S₄ series showing onset temperatures

Table 5.13 TPR onset temperature for the SrNd₂S₄ and CaNd₂S₄ series

Dopant level	SrSm ₂ S ₄ (°C)	CaSm ₂ S ₄ (°C)
0%	722	775
10%	700	745
20%	694	720
30%	701	750

5.8 Electrochemical Impedance Spectroscopy for SrSm₂S₄ series

The electrochemical properties of the SrSm₂S₄ series was characterised using impedance spectroscopy. Impedance spectroscopy of the SrSm₂S₄ series was carried out in argon atmosphere and the temperature range from 150 to 450°C with a one-hour temperature isothermal period. The spectra were collected using graphite electrodes and the frequency range from 0.1Hz to 1x10⁶Hz to (10 points per decade).

The Nyquist plot for undoped SrSm₂S₄ has the most pronounced low frequency effect of all sulphides characterised by impedance spectroscopy, thus strongly inferring the possibility of pure ionic conduction, Figure 5-35.

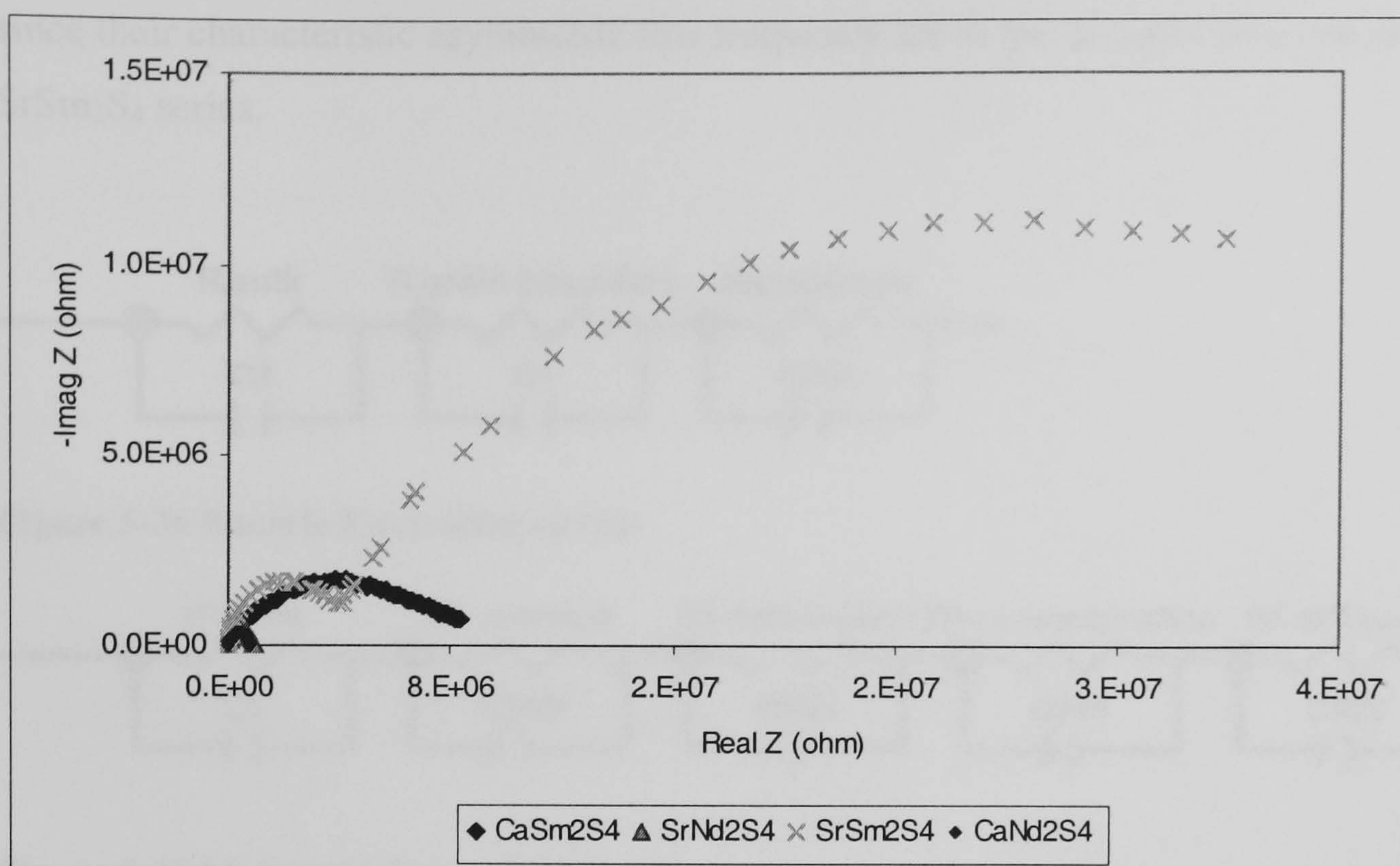


Figure 5-35 Impedance of undoped SrSm_2S_4 , CaSm_2S_4 , and SrNd_2S_4 at 400°C in argon

Jamnik's predominantly ionic conducting model provided an adequate fit between modelled and experimental data for CaNd_2S_4 series (excluding $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$) and SrNd_2S_4 series, since neither had a noticeable ionic locking electrode arc. CaSm_2S_4 had a unusual Nyquist plot which was asymptotic rather than composed of multiple arcs therefore the impedance data were modelled using either, Bauerle, Figure 5-36, McDonald five RC components or combination of R//C –R//CPE elements (this models the high frequency curve), Figure 5-37. However an excellent fit between modelled and experimental data for SrSm_2S_4 series was achieved, using the model developed by Bauerle, 196, Figure 5-38.

5.8.1 Equivalent circuits for modelling SrSm_2S_4 series

The Nyquist plot for the SrSm_2S_4 series can be described as one with three arcs, which agrees with Bauerle model, suggesting pure ionic conduction. Figure 5-38 shows the goodness of fit for both the Bauerle and McDonald modelled results versus a typical experimental data at 400°C.

Both models fit the high frequency arc, but the McDonald model appears to have a better fit at lower frequencies, Figure 5.38. The statistical parameters for quantifying the goodness of fit, Chi-square and the Sum-of-Squares, should be minimized for the best model. Therefore, based on the smaller values for the Sum-of-squares and the Chi-squares for the McDonald model, this should be the best model. However the maximum error of 81% on an equivalent circuit parameter exceeds in the McDonald model, exceeds the upper allowable limit of 30%, hence the rejection of this model, Table 5.14. Models for mixed conduction were not used

since their characteristic asymmetric low frequency arc in the Nyquist plot was absent for the SrSm_2S_4 series.

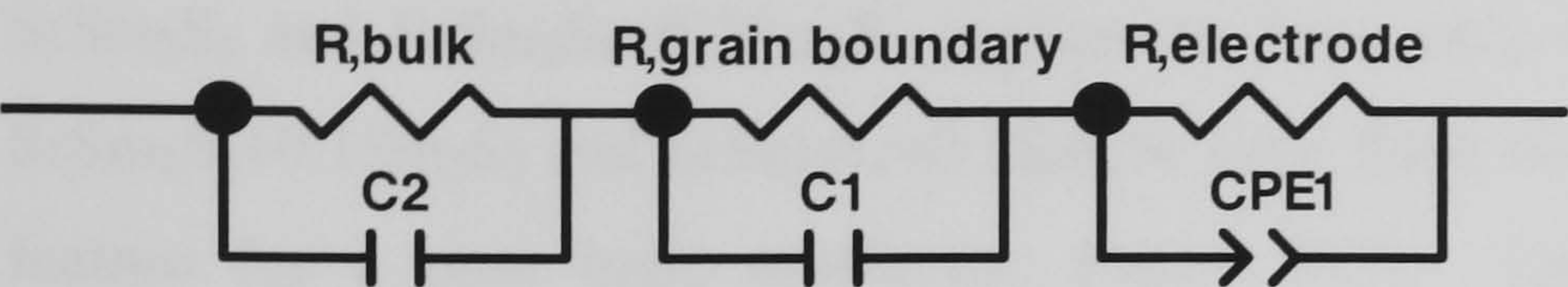


Figure 5-36 Bauerle Equivalent circuit

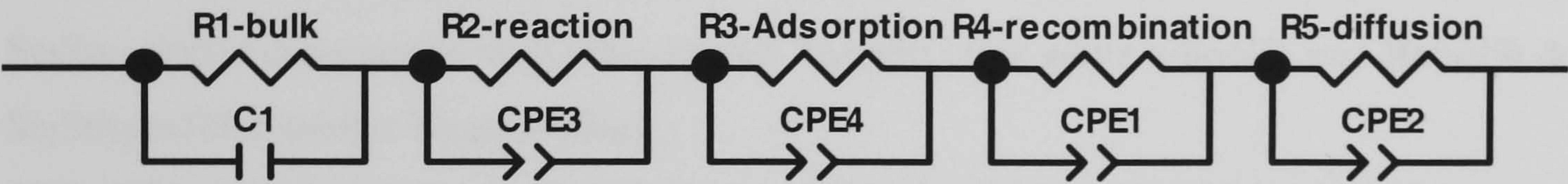


Figure 5-37 McDonald Equivalent circuit

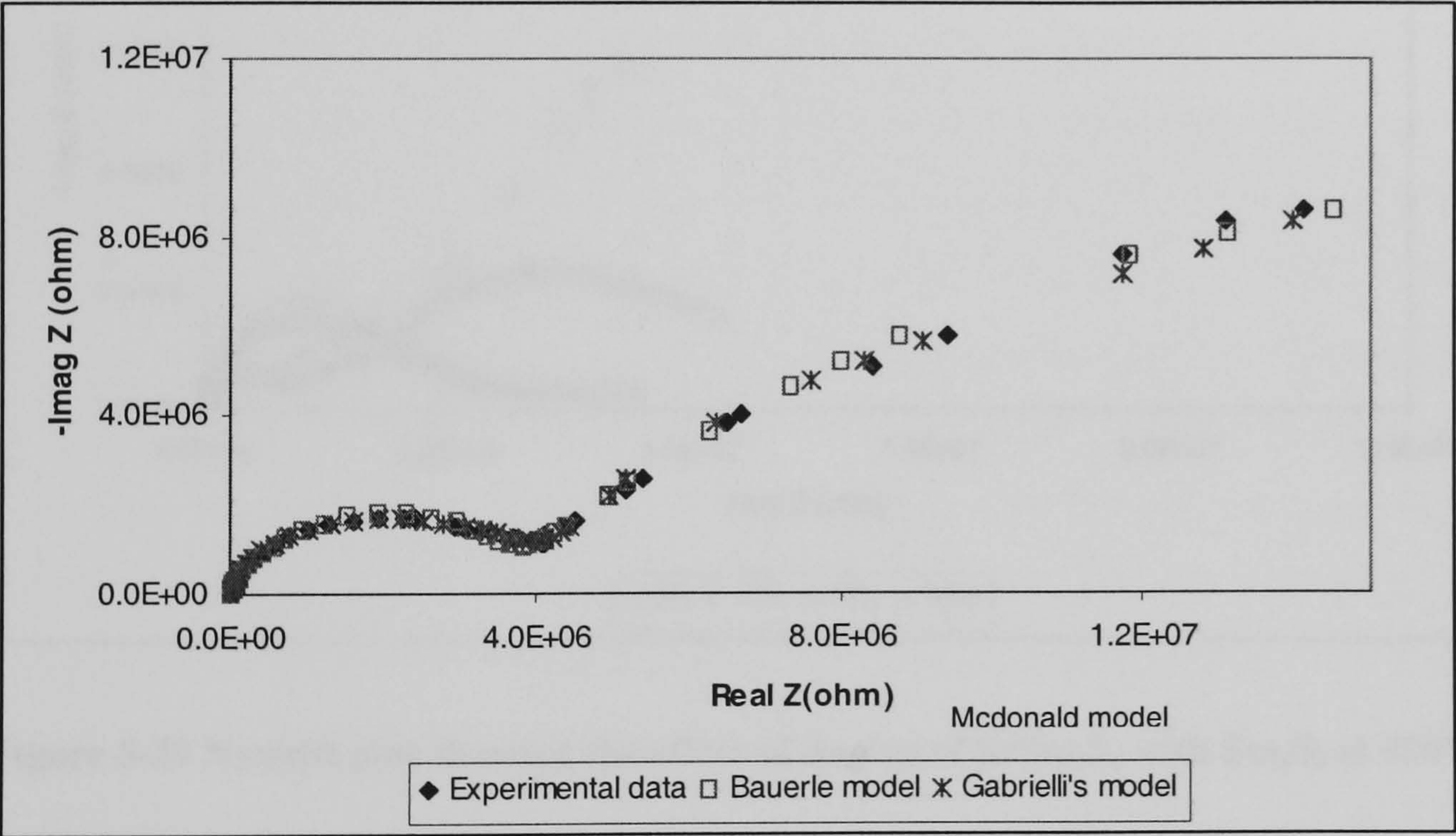


Figure 5-38 Experimental and modelled results for undoped CaSm_2S_4 400°C

Table 5.14. Chi-square and Sum-of-Squares results for alternative models used to model SrSm_2S_4 at 400°C

Models	Chi-square	Weighted-sum-of-squares	Maximum error on equivalent circuit element
Bauerle model with ionic blocking electrode	0.00402	0.479	17%
McDonald model with diffusion effect	0.00168	0.190	81%

5.8.2 Impedance Spectroscopy: Effect of doping SrSm_2S_4 with excess Sm_2S_3

The Nyquist plot for the SrSm_2S_4 series appears to have the low frequency arc which is identifying feature for pure ionic conductors, Figure 5-39. However both the undoped SrSm_2S_4 and $\text{SrSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ appears to have only two arcs in the Bode plot, while $\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ and $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ have three distinguishable arcs which is typical feature for a pure ionic conductor, Figure 5-39. Interestingly the Nyquist plots for $\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ and $\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ also show similar forms while the Nyquist plots for CaSm_2S_4 and $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ are comparable. Therefore the undoped and 20mol% Sr_2Sm_3 doped compounds with have similar Nyquist plots while 10mol% and 30mol% doped Sr_2Sm_3 exhibit similar Nyquist plots.

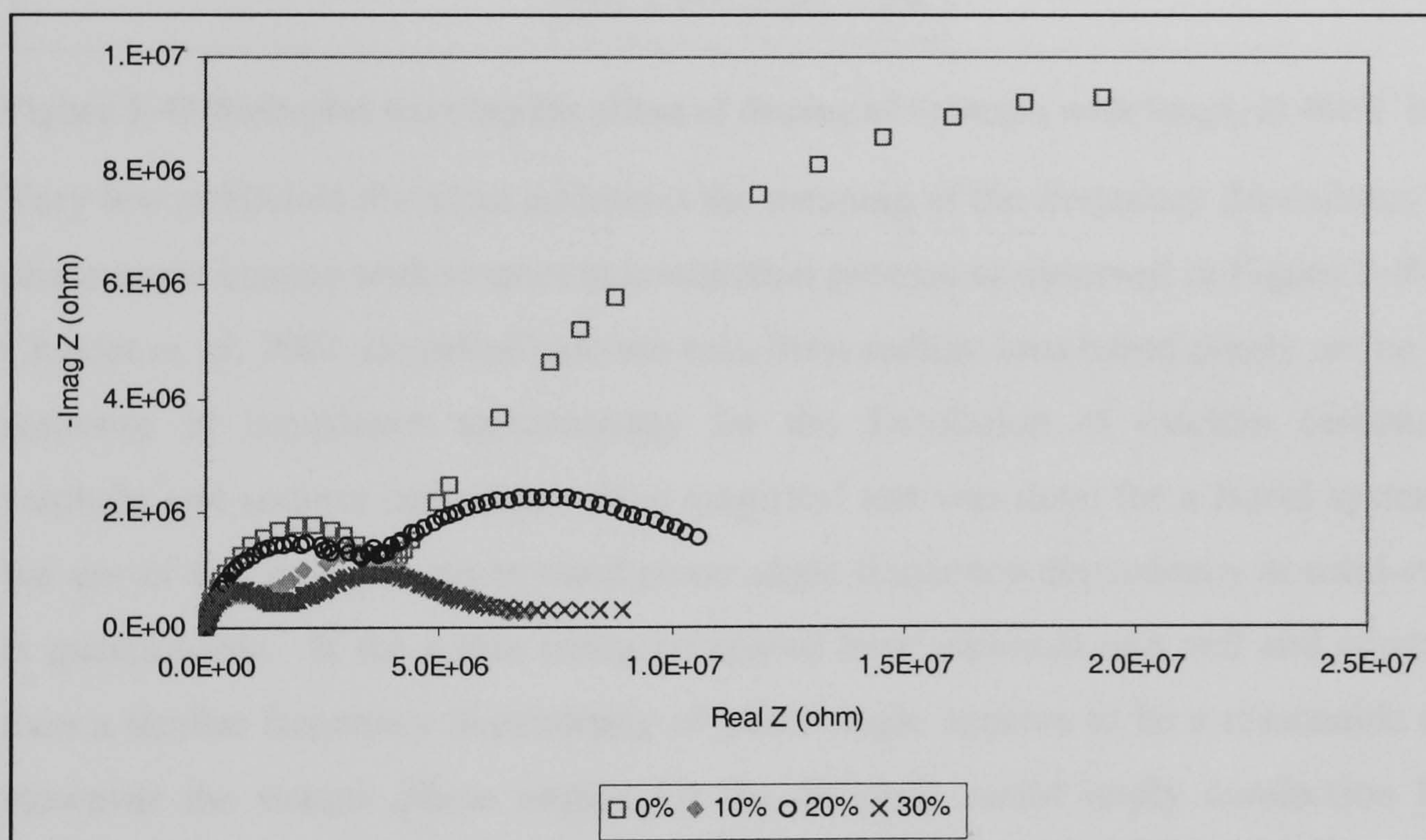


Figure 5-39 Nyquist plot showing the effect of doping of SrSm_2S_4 with Sm_2S_3 at 400°C

The Bode plot for the SrSm_2S_4 series shows a phase angle change at low frequencies for all compounds within the series, inferring that all compounds of this series are ionic conductors, Figure 5-40. The phase angle change for the SrSm_2S_4 based compounds are similar except for $\text{SrSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$, which has a distinctive change in phase angle at medium frequencies, Figure 5-40.

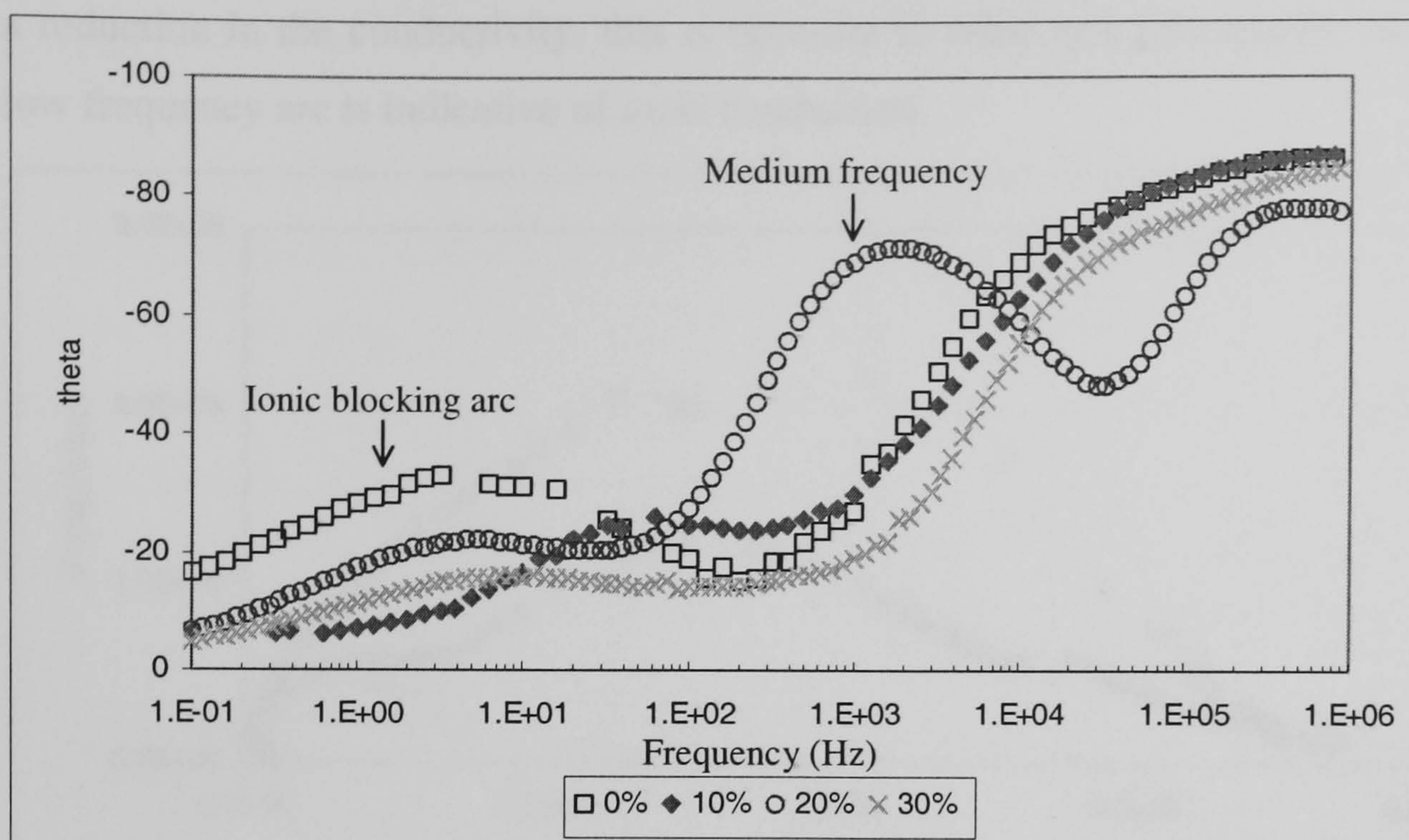


Figure 5-40 Bode plot showing the effect of doping of SrSm_2S_4 with Sm_2S_3 at 400°C in argon

Very few published literature addresses the meaning of the frequency dependency of complex phase angle change with respect to conduction process as observed in Figure 5-40. Recently, Chaulet *et. al.* 2001 identified calcium ions from sodium ions based purely on the phase angle response of impedance spectroscopy for the dissolution of calcium carbonate, sodium sulphate and sodium carbonate. This empirical test was done for a liquid system; therefore the use of this theory to understand phase angle frequency dependency in solid-state systems is questionable. If the solids being compared have identical unit cell and crystal structure, then a similar frequency dependency of phase angle appears to be a reasonable expectation. However the unique phase angles for the SrSm_2S_4 could imply conduction by different species, Figure 5-40. The varying phase angle frequency dependency was also apparent in the CaSm_2S_4 series. Could this imply that the conducting species changes? These non-stoichiometric compounds have equal cation and anion vacancies, so it is possible to have a change in the mobile conducting species from anion to cation or electronic, or this could simply be an inherent property of Sm_2S_3 .

5.8.3 Effect of changing host and dopant cation: CaNd_2S_4 , SrNd_2S_4 , CaSm_2S_4 and SrSm_2S_4 series

Doping at 10mol%

The matrix of electrolytes, $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$, $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$, $\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ and $\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$, show that the electrochemical property is determined predominantly by dopant, therefore the Nd_2S_3 based electrolytes are similar and likewise the Sm_2S_3 based electrolytes, Figure 5-41. Even though changing the dopant from Nd_2S_3 to Sm_2S_3 caused a significant increase in both real and imaginary components of impedance, which may lead to

a reduction in the conductivity; this is opposite to what was anticipated. However the clear low frequency arc is indicative of ionic conduction

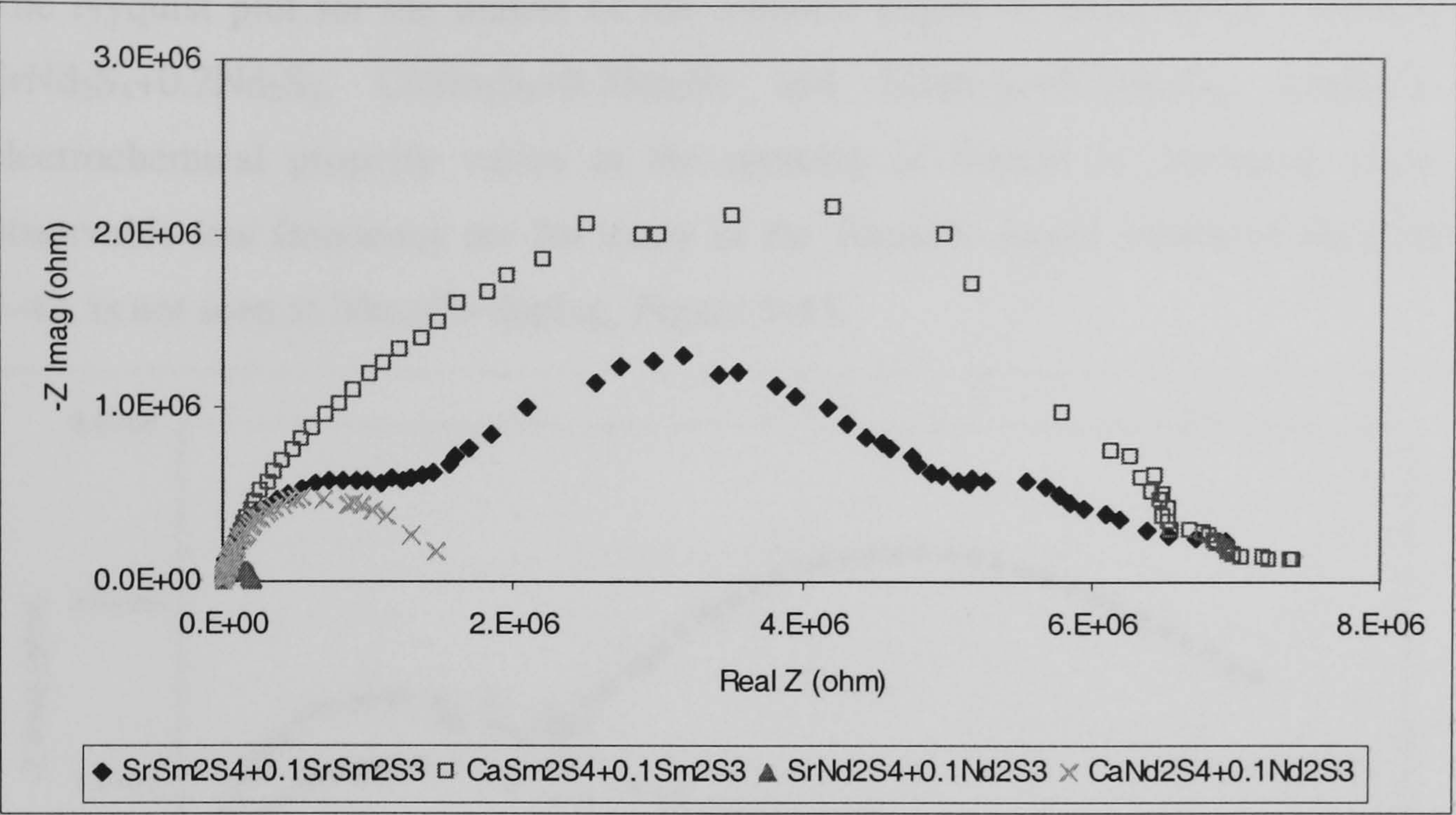


Figure 5-41 Nyquist for 10mol% doped CaNd₂S₄, SrNd₂S₄, CaSm₂S₄ and SrSm₂S₄ 400°C

The Bode plot for matrix of 10mol% doped electrolytes is shown in Figure 5-42, where a low frequency phase angle dependency is present for both the SrSm₂S₄+0.1Sm₂S₃ and CaNd₂S₄+0.1Nd₂S₃. The Bode plot for CaSm₂S₄+0.1Sm₂S₃ shows that the phase angle at low frequencies is reduced while SrNd₂S₄+0.1Nd₂S₃ has no phase angle change at low frequencies, Figure 5-42.

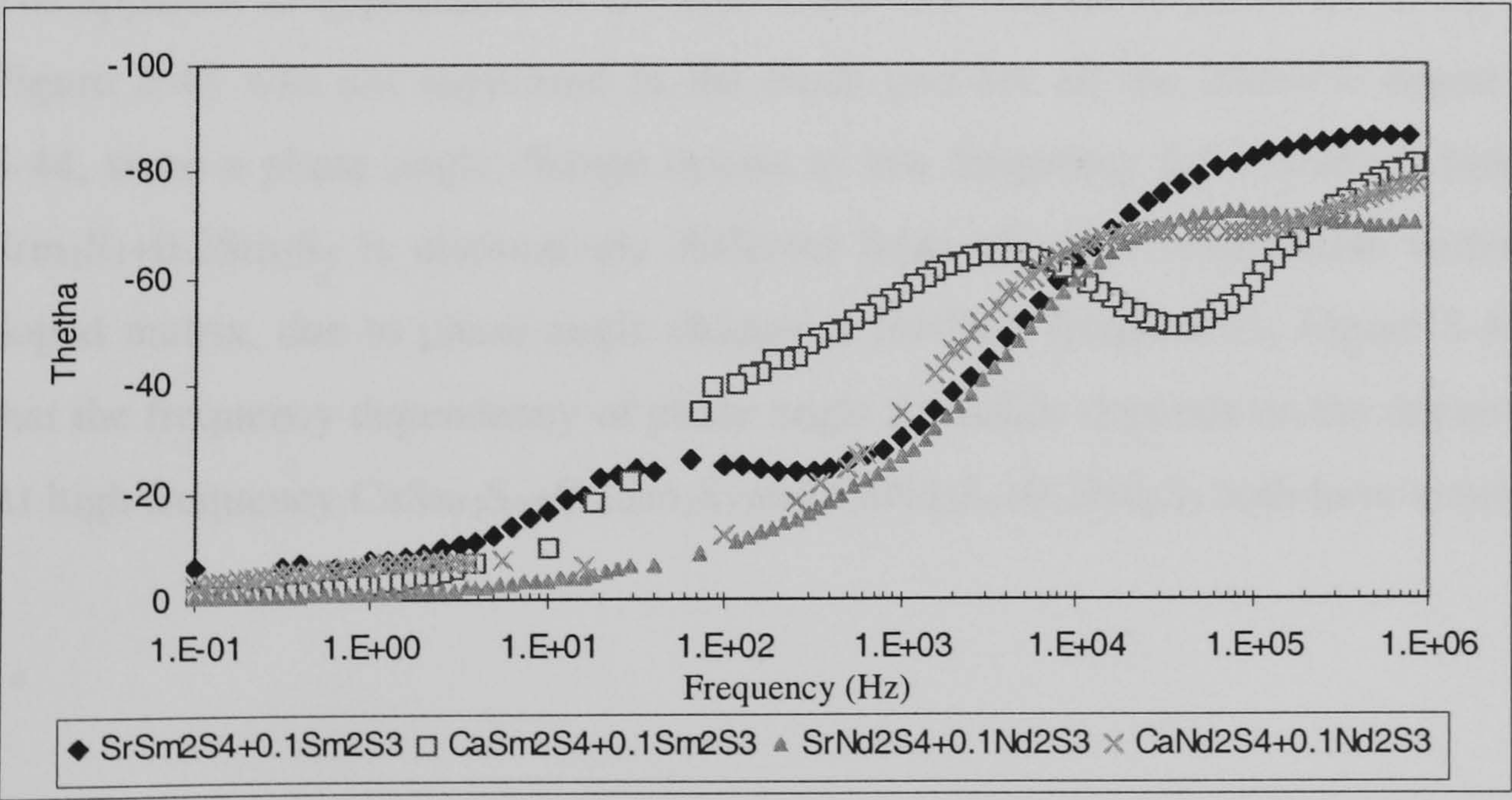


Figure 5-42. Bode plot for 10mol% doped CaNd₂S₄, SrNd₂S₄, CaSm₂S₄ and SrSm₂S₄ 400°C

Doping at 20mol%

The Nyquist plot for the matrix of the 20mol% doped of electrolytes, $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$, $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$, $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ and $\text{SrSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$, confirms that the electrochemical property varies as the quantity of dopant is increased, since the easily observable low frequency arc for many of the 10mol% doped matrix of electrolytes, Figure 5-42, is not seen at 20mol% doping, Figure 5-43.

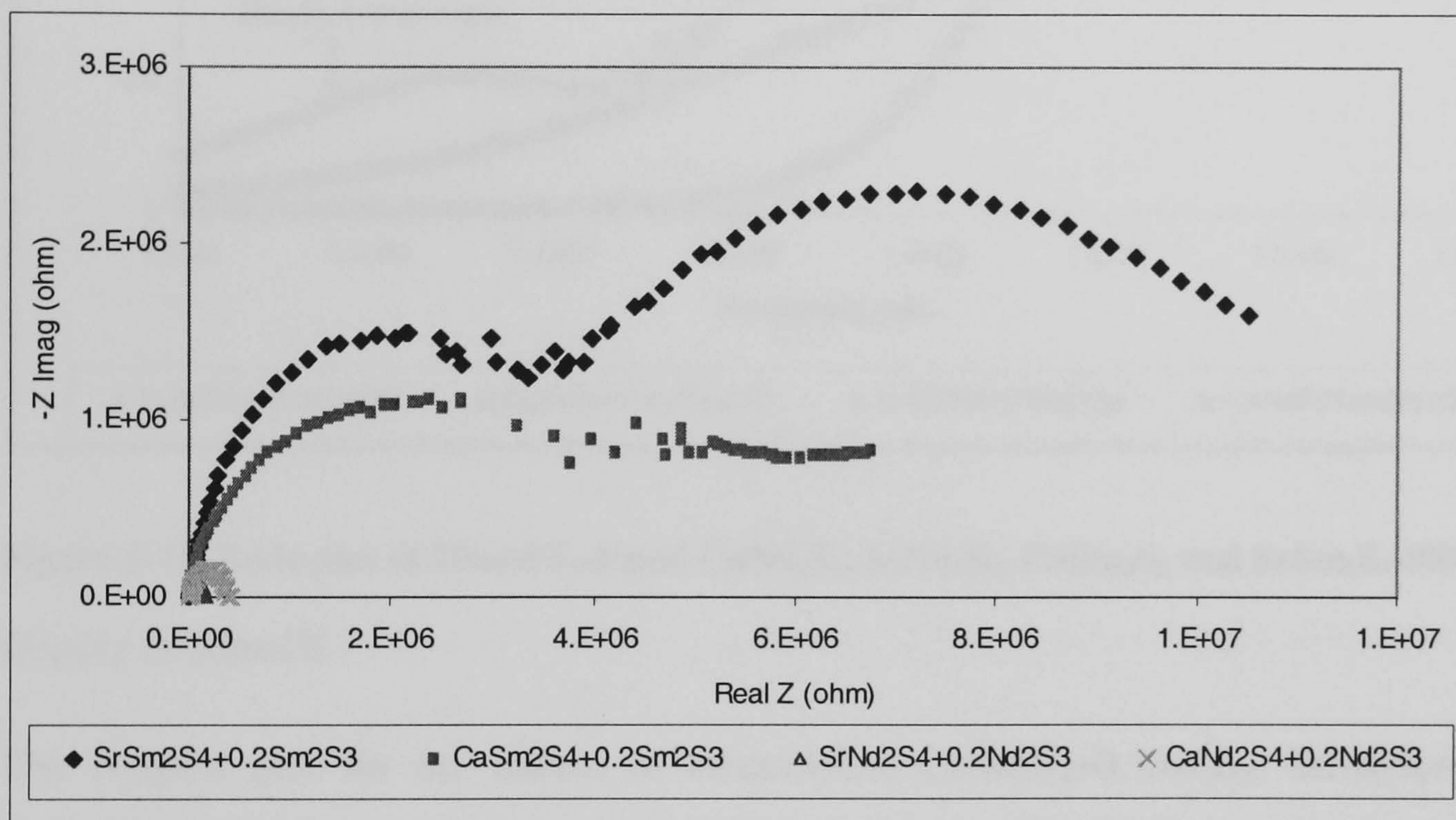


Figure 5-43. Nyquist plot of 20mol% doped CaNd_2S_4 , SrNd_2S_4 , CaSm_2S_4 and SrSm_2S_4 400°C

The apparent disappearance of the distinctive low frequency phase arc in the Nyquist plot in Figure 5-43 was not supported in the Bode plot for all the 20mol% doped matrix, Figure 5-44, since a phase angle change occurs at low frequency for samarium based electrolytes. $\text{Srsm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ is distinctively different from all other compounds within this 20mol% doped matrix, due to phase angle change at medium frequencies, Figure 5-44. This implies that the frequency dependency of phase angle for solids depends on the dopant concentration. At high frequency $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ and $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ both have similar phase angle.

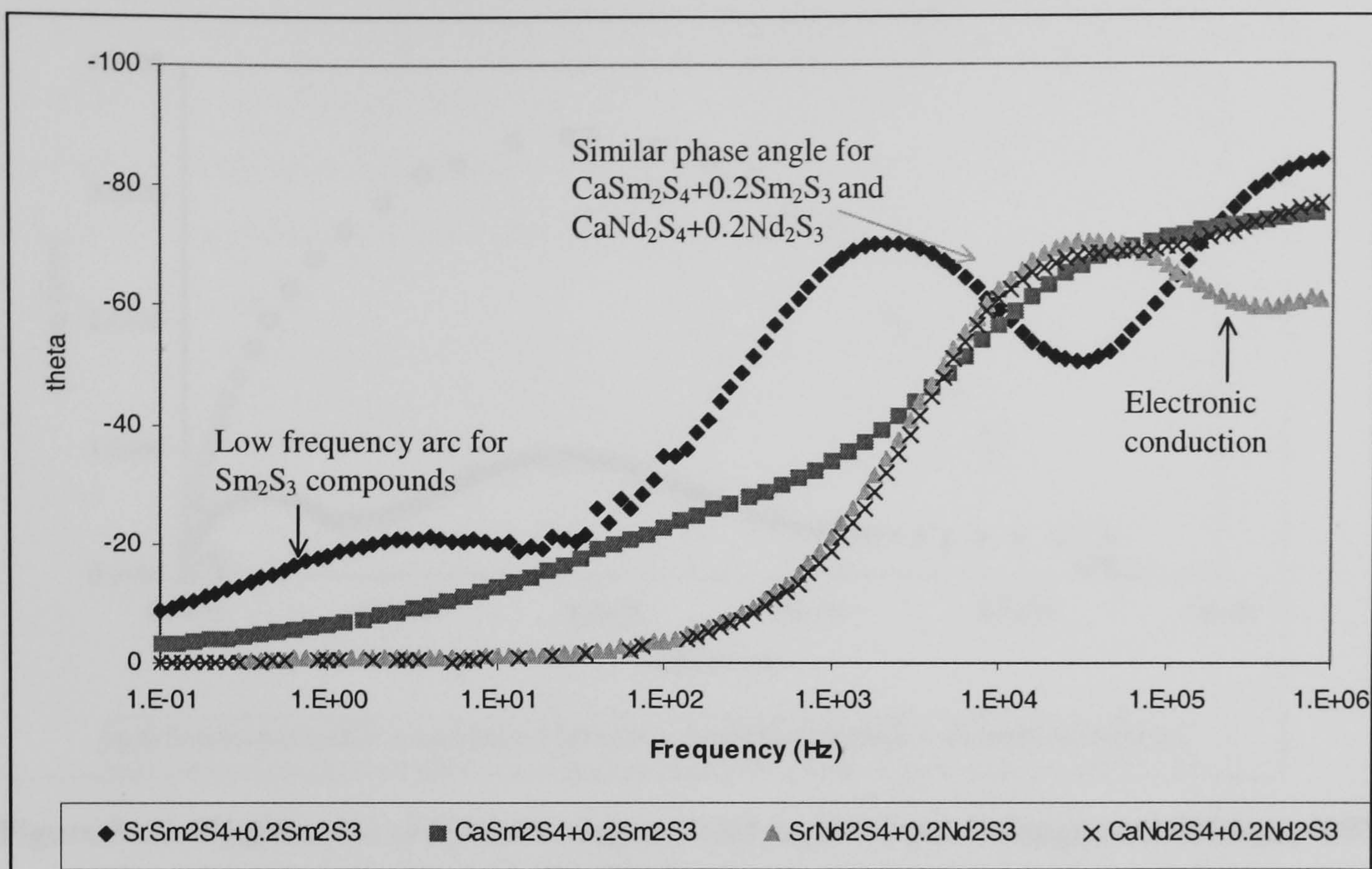


Figure 5-44. Bode plot of 20mol% doped CaNd_2S_4 , SrNd_2S_4 , CaSm_2S_4 and SrSm_2S_4 400°C

Doping at 30mol%

The Nyquist plot for the matrix of electrolytes, $\text{CaNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$, $\text{SrNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$, $\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ and $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$, shows that the Sm_2S_3 based electrolytes each has a unique Nyquist plot, while the Nyquist plots for the Nd_2S_3 based electrolytes are similar, Figure 5-45. Changing from $\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ to $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ caused a reduction in very large medium frequency (blocking grain boundaries), Figure 5-45. Therefore at 30mol% doping $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ differs from $\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$.

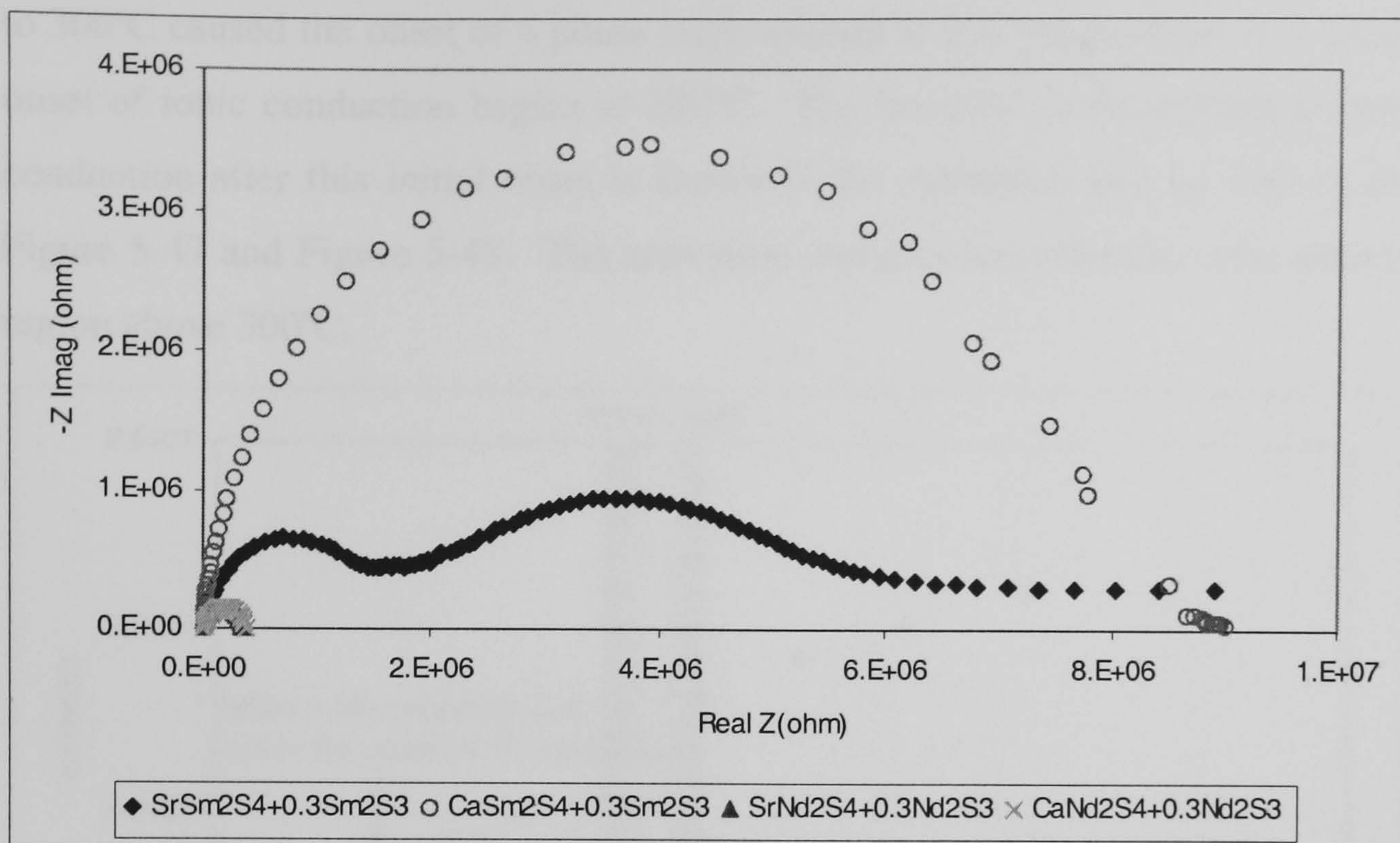


Figure 5-45. Nyquist plot of 30mol% doped CaNd_2S_4 , SrNd_2S_4 , CaSm_2S_4 and SrSm_2S_4 400°C

The Bode plot for matrix of 30mol% doped electrolytes shows that the frequency dependency of their phase angle for each electrolyte differs from one to the other, Figure 5-46. $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ is the only electrolyte that has a phase angle change at low frequencies, therefore this electrolyte may exhibit ionic conduction under argon.

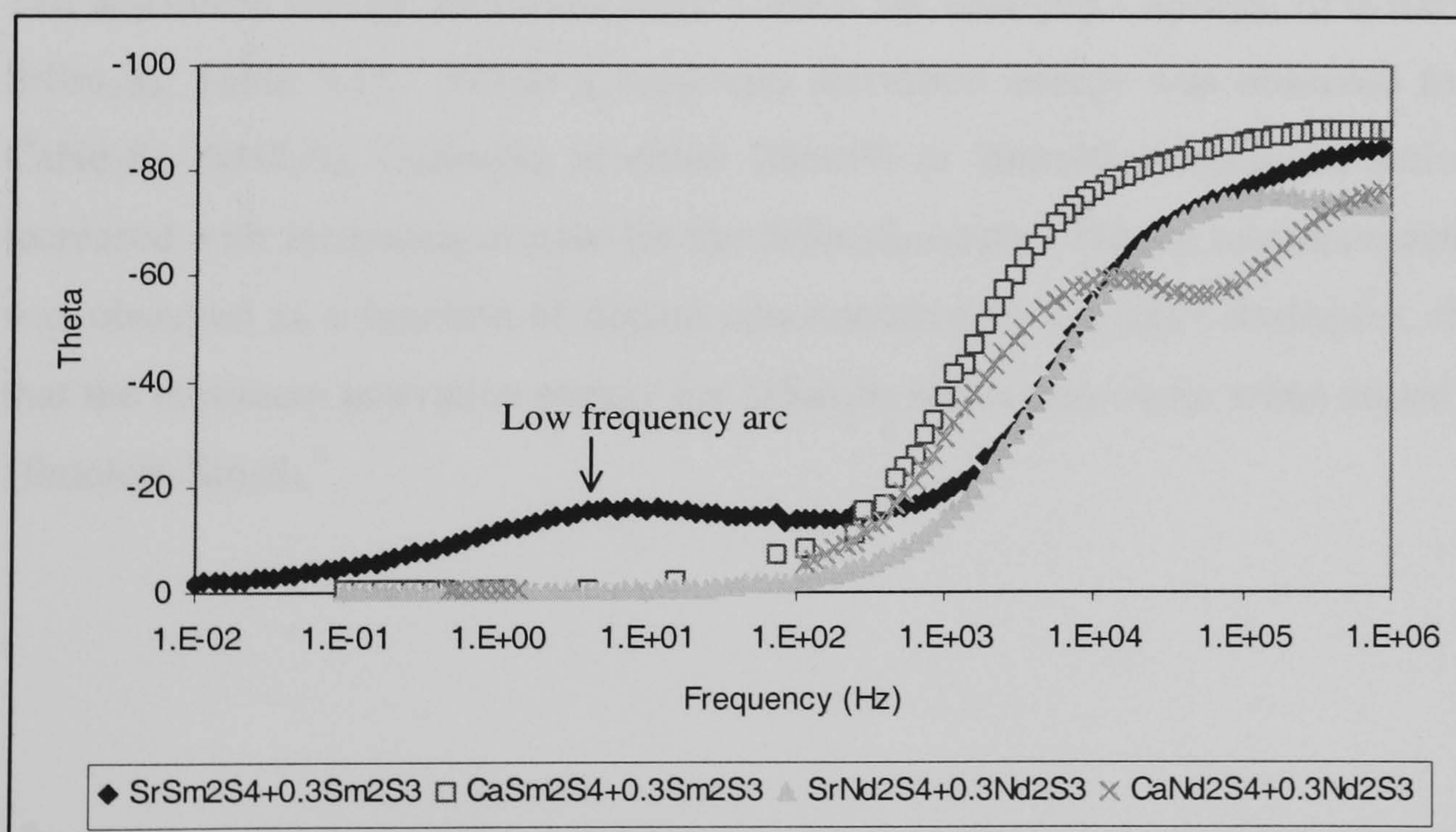


Figure 5-46. Bode plot of 30mol% doped CaNd_2S_4 , SrNd_2S_4 , CaSm_2S_4 and SrSm_2S_4 400°C

5.8.4 Activation energy for SrSm_2S_4 considering temperature effect on Bode plot

The Arrhenius plots for the SrSm_2S_4 series shows nonlinearity in the temperature range from 175°C to 450°C, Figure 5-47, however from temperatures greater than 300°C, the plot becomes linear. This nonlinearity was also evident in the Bode plot at 300°C, since the trend in the phase angle changed at this temperature. The 25°C increase in temperature from 275°C

to 300°C caused the onset of a phase angle change at low frequencies. It is plausible that the onset of ionic conduction begins at 300°C. The linearity of the activation energy for ionic conduction after this initial onset is shown in the Arrhenius plot as well as the Bode plot, Figure 5-47 and Figure 5-48. The activation energies for SrSm_2S_4 series refers to the linear region above 300°C.

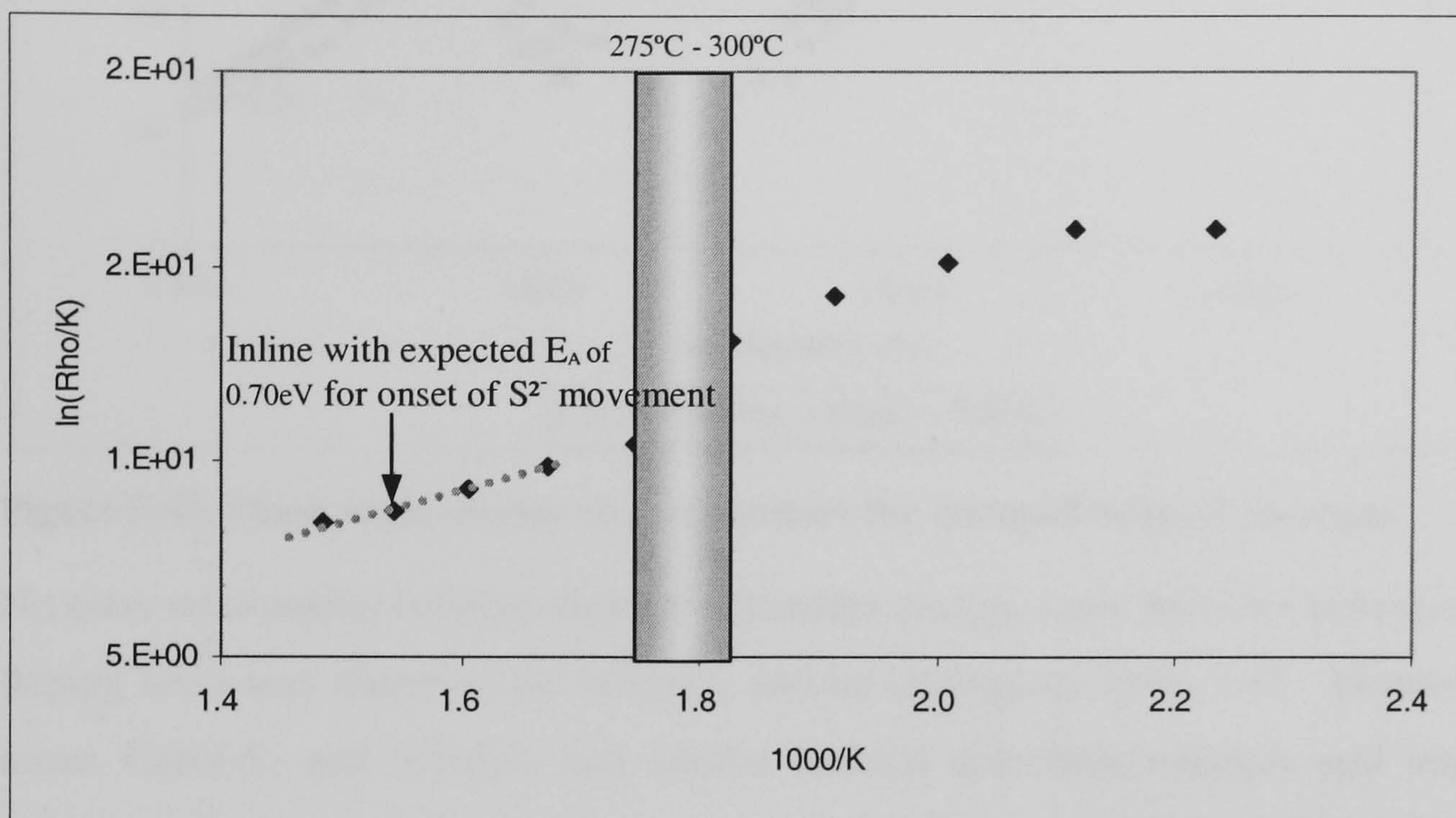


Figure 5-47 Arrhenius plot of SrSm_2S_4 from 175°C to 450°C in argon

The activation energy decreased from 1.49eV for undoped CaSm_2S_4 to 0.70eV for undoped SrSm_2S_4 , Table 5.15. While a minimum activation energy was observed for these series, CaNd_2S_4 , SrNd_2S_4 , CaSm_2S_4 , at either 10mol% or 20mol% doping, the activation energies increased with increasing dopant for the SrSm_2S_4 series. Since a minimum activation energy was observed as a function of dopant concentration for all other analogues, this could infer that the minimum activation energy for SrSm_2S_4 series may occur when doped with less than 10mole% Sm_2S_3 .

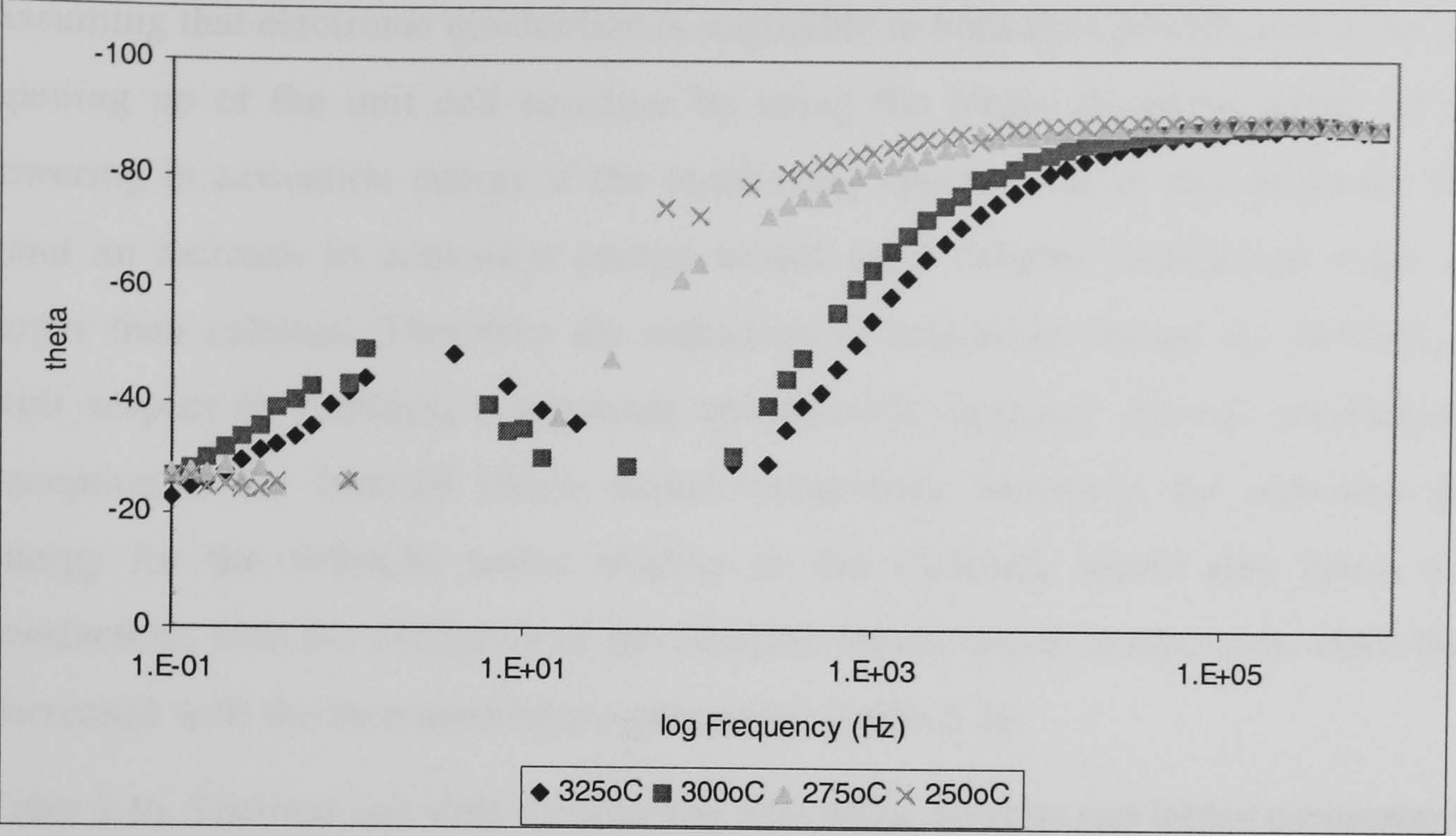


Figure 5-48. Phase angle change vs. temperature for undoped SrSm₂S₄ in argon

No clear relationship between thermal activation energy, ionic mobility activation energy and doping level was observed for SrSm₂S₄ and its analogues, Table 5.15. However in general terms CaNd₂S₄ and SrNd₂S₄ had similar thermal activation energies and ionic activation energies. The thermal activation energy for SrSm₂S₄ decreased by an order of magnitude and the activation energy for ionic conduction decreased by approximately 50% relative to the CaSm₂S₄ series.

Table 5.15. Thermal and Bulk Conduction Activation energies for CaSm₂S₄, CaNd₂S₄, CaSm₂S₄ and CaNd₂S₄ series

	Thermal activation energy (kJ/g-mol)				Activation energy for bulk conduction (eV)			
	CaNd ₂ S ₄	SrNd ₂ S ₄	CaSm ₂ S ₄	SrSm ₂ S ₄	CaNd ₂ S ₄	SrNd ₂ S ₄	CaSm ₂ S ₄	SrSm ₂ S ₄
0%	1.90x10 ⁵	1.85x10 ⁵	2.78x10 ⁵	4.85x10 ⁴	0.46	0.42	1.41	0.70
10%	6.37x10 ⁵	1.24x10 ⁶	2.79x10 ⁵	4.13x10 ⁴	0.37	0.23	1.03	0.80
20%	5.71x10 ⁵	5.98x10 ⁵	8.42x10 ⁵	4.43x10 ⁴	0.51	0.46	0.60	1.24
30%	4.36x10 ⁵	5.19x10 ⁵	9.69x10 ⁵	5.51x10 ⁴	0.72	0.65	1.40	0.89

The likely range of activation energies for bulk conduction was previously established to be 0.61-1.61eV in Chapter 4-Section 4.45. All the Sm₂S₃ based compounds have activation energy within the range expected for sulphide ion conduction, Table 5.15. The activation energies for the Nd₂S₃ based electrolytes are based on modelling results using the Jamnik model which is always 0.2-0.5eV smaller than the typical RC element based model, e.g. the Bauerle. Since the activation energy of Sm₂S₃ sulphide base electrolytes was obtained from the Bauerle model, a direct comparison between the two models is not recommended.

Assuming that electronic conduction is negligible in both the CaNd_2S_4 and SrNd_2S_4 series, the opening up of the unit cell structure by using the larger strontium cation should cause a lowering in activation energy if the conducting species was in fact sulphide. On the other hand an increase in activation energy would infer cationic conduction since strontium is larger than calcium. Therefore the reduction in activation energy for SrNd_2S_4 compounds with respect to CaNd_2S_4 compounds qualitatively suggests anionic conduction, with the exception of the 10mol% Nd_2S_3 doped compounds. Similarly, the reduction in activation energy for the SrSm_2S_4 series relative to the CaSm_2S_4 series also infers sulphide ion conduction; with the exception of the 20mol% Sm_2S_3 doped compounds, since the activation decreased with the increased lattice parameter, Table 5.16.

Table 5.16. Thermal and Bulk Conduction Activation energies and lattice parameter for CaSm_2S_4 and CaNd_2S_4 series

	Activation energy for bulk conduction (eV)				Lattice parameter for ‘a’ site Å			
	CaNd_2S_4	SrNd_2S_4	CaSm_2S_4	SrSm_2S_4	CaNd_2S_4	SrNd_2S_4	CaSm_2S_4	SrSm_2S_4
0%	0.42	0.35	1.41	0.70	8.5301(1)	8.6204(1)	8.4708(1)	8.5361(1)
10%	0.23	0.32	1.03	0.80	8.5299(1)	8.6200(4)	8.4701(8)	8.5595(3)
20%	0.46	0.37	0.60	1.24	8.5280(1)	8.6181(3)	8.4684(8)	8.5523(1)
30%	0.65	0.38	1.40	0.89	8.5273(1)	8.5919(2)	8.4653(1)	8.5467(1)

5.8.5 Conductivity and Activation energy for SrSm_2S_4 series and all analogues

A summary of the bulk conductivities for the SrSm_2S_4 series and all analogue series is given in Table 5.17 where all series reach a maximum conductivity prior to reaching the highest level of doping (30mol%). The maximum conductivity for SrSm_2S_3 is at 20mol% while the analogues reach their maximum conductivity at 10mol%.

Table 5.17. Bulk Conductivity and activation energy for SrSm_2S_4 series and all analogue series at 500°C in argon

	Bulk conductivity @500°C in argon ($\text{S}^{-1}.\text{cm}$)				Activation energy for bulk conduction (eV)			
	CaNd_2S_4	SrNd_2S_4	CaSm_2S_4	SrSm_2S_4	CaNd_2S_4	SrNd_2S_4	CaSm_2S_4	SrSm_2S_4
0%	2.19×10^{-8}	6.73×10^{-4}	3.11×10^{-4}	1.46×10^{-6}	0.44	0.46	1.41	0.70
10%	1.09×10^{-6}	3.39×10^{-3}	3.51×10^{-4}	6.12×10^{-6}	0.33	0.37	1.03	0.80
20%	3.09×10^{-5}	2.61×10^{-4}	2.32×10^{-5}	1.93×10^{-4}	0.52	0.51	0.60	1.24
30%	1.85×10^{-5}	2.95×10^{-3}	5.06×10^{-7}	3.83×10^{-6}	0.62	0.72	1.40	0.89

The presence of a maximum conductivity with respect to dopant level has been attributed to the formation of defect clusters, beginning with simple defect pairs (associated pairs) at low concentrations. Defect pairs occur between dopant cation and the charge compensating anion vacancy and once formed the anion vacant site does not participate in the conduction process and therefore the decrease in the overall conductivity, Kilner, 2003. At high doping, the associated pairs may become more complex and form ‘trimers’ which are stable to higher temperatures, Minervini. *et. al.*, 1999. This is the main reason why maximum conductivity does not occur at maximum doping. These simple defect pairs dominate bulk conductivity at low concentrations for dopant with an effective charge of -1 or -2 , Kilner and Steele, 1981.

A direct comparison for bulk conductivities between the Nd_2S_3 doped electrolytes and the Sm_2S_3 doped electrolytes is not possible since Jamnik equivalent circuit was used to model many of the EIS experimental data for most of the Nd_2S_3 compounds. Therefore the resulting conductivity values are greater than 2 orders of magnitude than conductivity calculated based on models made up of multiple R//C elements (Bauerle or Randles equivalent circuits). However, comparison within Nd_2S_3 based compounds, similarly Sm_2S_3 based compounds, is plausible since comparable equivalent circuit was used. While the cation change from calcium to strontium in Nd_2S_3 electrolytes caused an increase in conductivity, an opposite trend was observed for the Sm_2S_3 doped sulphides. The bulk conductivities for Nd_2S_3 doped compounds (except for $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$) occurred with no phase angle change at low frequencies which infers the presence of electronic conduction. Therefore the high conductivities for Nd_2S_3 doped compounds are not purely ionic. The lower conductivities for the Sm_2S_3 doped electrolytes occurred with the presence of a phase change in low frequencies indicating ionic conductivity.

The Jamnik equivalent circuit for predominately ionic conduction for $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ calculates a bulk conductivity of $1.09 \times 10^{-6} \text{S}^{-1} \cdot \text{cm}$ agreeing with Kalinina *et. al.* 1994, bulk conductivity established through galvanic cells. The Kalinina *et. al.* 1994, galvanic cell used CaS and Nd_2S_3 discs as ionic sources and sinks for Ca, Nd and S ions between the electrolyte (and the carbon electrode) which are not electronic conductors, therefore the experimental method would not allow for the measurement of electronic flow and therefore may account for significantly lower low bulk conductivities for the highly doped CaNd_2S_4 .

5.8.6 Time Constant Analysis for SrSm_2S_4 series

The time constants for the bulk conduction in the SrSm_2S_4 series approached a minimum for the $\text{SrSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$, Table 5.18, which also has the maximum conductivity as well as the

highest activation energy for the doped SrSm_2S_4 compounds, Table 5.17. The time constants for both CaSm_2S_4 and SrSm_2S_4 series decreased as the dopant is increased from no excess dopant to 30mol% dopant, Table 5.18. The similar time constants of all compounds in the SrSm_2S_4 series suggests similar conducting species, Table 5.18.

The time constants for doped SrSm_2S_4 compounds are greater than those for the oxide ion conducting YSZ at similar temperature, Tables 5.18 and 4.7. Assuming that a larger ion moves slower than a smaller one, then the larger time constant is consistent with anionic conduction for doped SrSm_2S_4 compounds. The observation of asymmetric concentration cell experiments is necessary to identify the conducting ion.

Table 5.18. Time constant, at 350°C, analysis for SrSm_2S_4 and CaSm_2S_4 series with graphite electrode

Undoped CaSm_2S_4 Bauerle+ Jamnik model		Undoped SrSm_2S_4 Bauerle model	
Bulk	Grain boundary	Bulk	Grain boundary
$R=5.86\times10^3\Omega$	$R=1.96\times10^6\Omega$	$R=7.06\times10^6\Omega$	$R=1.30\times10^6\Omega$
$C=1.51\times10^{-10}\text{ F}$	$C=4.21\times10^{-10}\text{ F}$	$C=2.96\times10^{-11}\text{ F}$	$C=3.38\times10^{-11}\text{ F}$
$\tau = 8.87\times10^{-7}\text{ s}$	$\tau = 8.33\times10^{-4}\text{ s}$	$\tau = 2.09\times10^{-4}\text{ s}$	$\tau = 4.41\times10^{-5}\text{ s}$
$\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ Bauerle+ Jamnik model		$\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ Bauerle model	
Bulk	Grain boundary	Bulk	Grain boundary
$R=2.15\times10^5\Omega$	$R=8.69\times10^5\Omega$	$R=3.38\times10^6\Omega$	$R=3.092\times10^6\Omega$
$C=3.93\times10^{-11}\text{ F}$	$C=5.31\times10^{-10}\text{ F}$	$C=8.90\times10^{-11}\text{ F}$	$C=1.11\times10^{-7}\text{ F}$
$\tau = 8.24\times10^{-6}\text{ s}$	$\tau = 4.61\times10^{-4}\text{ s}$	$\tau = 3.01\times10^{-4}\text{ s}$	$\tau = 3.42\times10^{-1}\text{ s}$
$\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ Bauerle+ Jamnik model		$\text{SrSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ Bauerle model	
Bulk	Grain boundary	Bulk	Grain boundary
$R=1.69\times10^5\Omega$	$R=9.58\times10^6\Omega$	$R=2.36\times10^5\Omega$	$R=7.29\times10^6\Omega$
$C=1.03\times10^{-10}\text{ F}$	$C=6.95\times10^{-10}\text{ F}$	$C=4.26\times10^{-11}\text{ F}$	$C=2.27\times10^{-10}\text{ F}$
$\tau = 1.74\times10^{-5}\text{ s}$	$T = 2.79\times10^{-3}\text{ s}$	$\tau = 1.00\times10^{-5}\text{ s}$	$\tau = 1.66\times10^{-3}\text{ s}$
$\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ Bauerle+ Jamnik model		$\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ Bauerle model	
Bulk	Grain boundary	Bulk	<i>Grain boundary</i>
$R=1.09\times10^6\Omega$	$R=1.74\times10^7\Omega$	$R=3.76\times10^5\Omega$	$R=3.70\times10^6\Omega$
$C=6.98\times10^{-11}$	$C=1.82\times10^{-11}$	$C=3.54\times10^{-11}$	$C=2.25\times10^{-11}\text{ F}$
$\tau = 7.41\times10^{-5}\text{ s}$	$\tau = 3.18\times10^{-4}\text{ s}$	$\tau = 1.33\times10^{-5}\text{ s}$	$\tau = 9.52\times10^{-5}\text{ s}$

5.8.7 H_2S Concentration dependence of bulk conductivity for $SrSm_2S_4$ series

Impedance spectroscopy of the $SrSm_2S_4$ series using graphite electrodes in argon produced an ionic blocking electrode arc which indicates pure ionic conductors. The conductivity for a pure ionic conductor is also independent of concentration changes in the atmosphere; therefore impedance spectroscopy was carried out from 350°C to 550°C with the concentration of H_2S/Ar varying from 0vol% to 18vol% for each temperature. Using one-hour isothermal period allows for the stabilization of temperature and concentration prior to impedance measurements.

The conductivity which increases with increasing sulphur concentration at high H_2S concentration indicates the presence of hole conduction: it may occur via equation 15.



Where

$V_{S^{2-}}$ - sulphide anion vacancy

S^{2-} - sulphur anion in unit cell

\oplus - electron hole

Thus increasing the sulphur partial pressure increases the number of electron holes and increases the conductivity of the electrolyte.

The increasing conductivity with increasing H_2S concentration from 0vol% (pure argon) to 0.1vol% H_2S/Ar for $SrSm_2S_4$ indicates electron hole conduction, Figure 5-49. This may result from the interaction between vacant sulphide ion sites and gaseous sulphur, as expressed in equation 15.

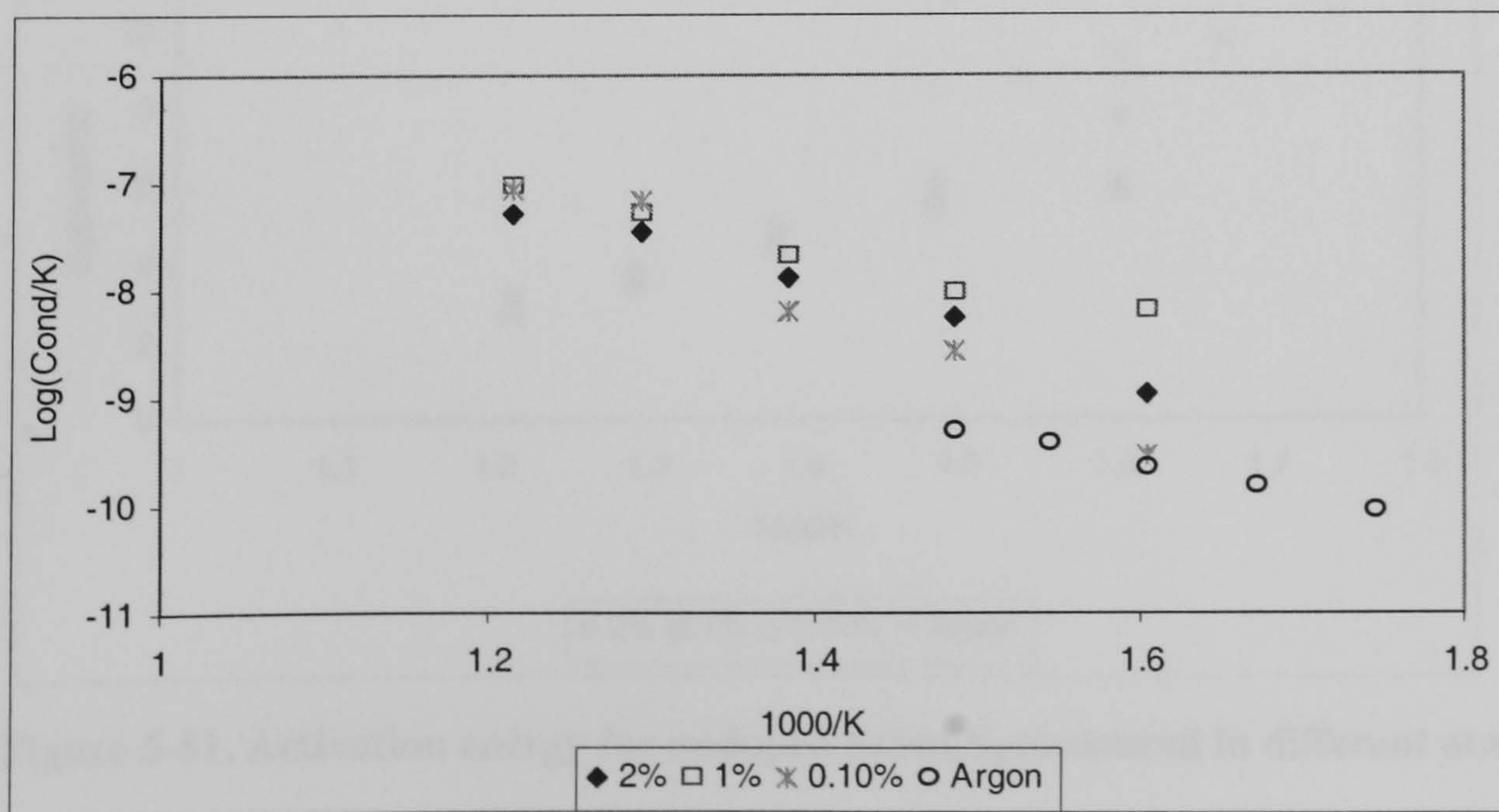


Figure 5-49. Bulk conductivities for undoped $SrSm_2S_4$ measured in different atmospheres

However at temperatures greater than or equal to 500°C, a further increase in H₂S concentration resulted in no change in the conductivity for undoped SrSm₂S₄, Figure 5-49. This is shown clearly in Figure 5-50, that at high temperatures, the bulk conductivity appears to be independent of H₂S concentration.

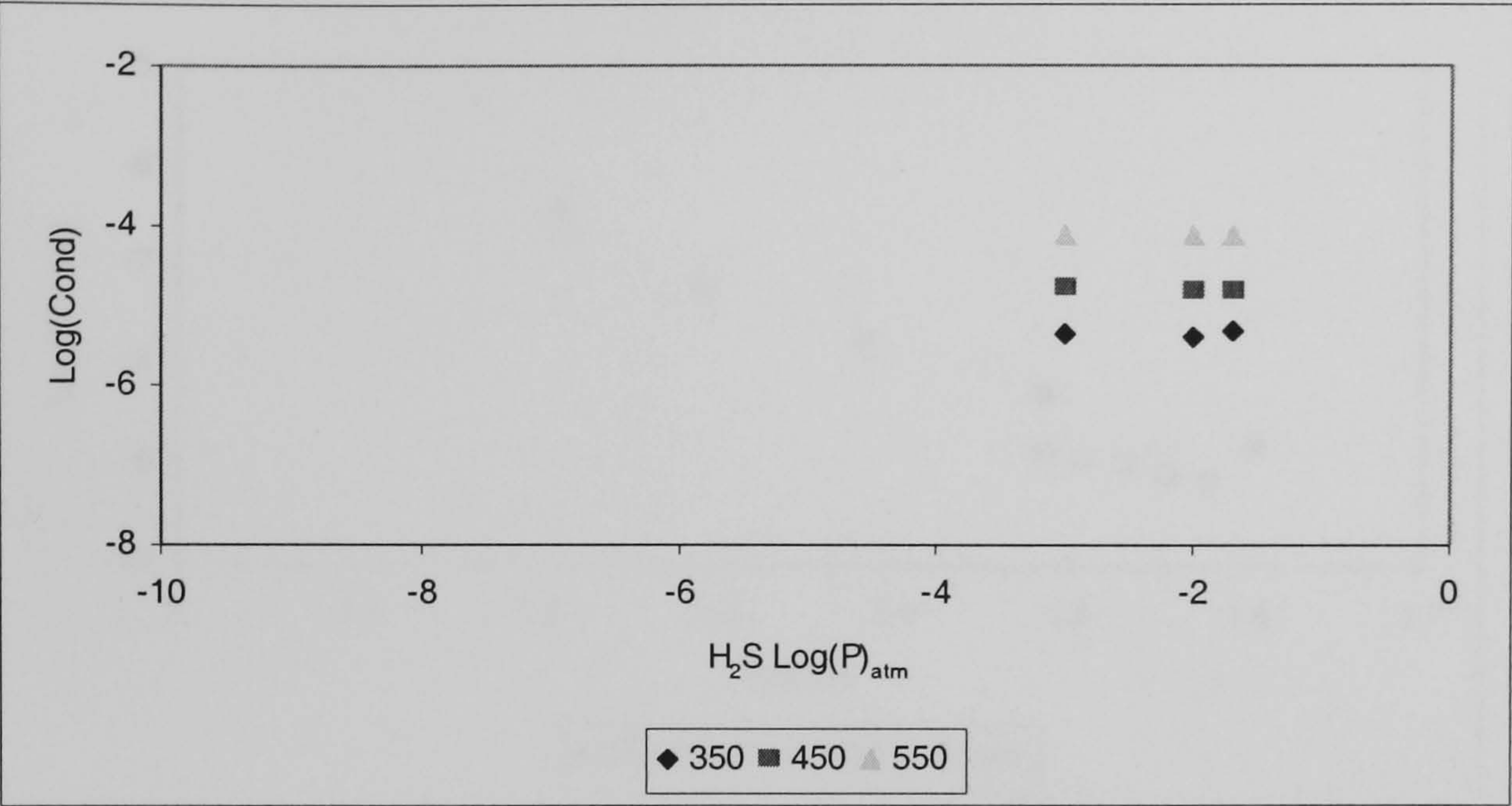


Figure 5-50. Bulk conductivities for undoped SrSm₂S₄ measured in different atmospheres

The activation energy for SrSm₂S₄, 0.69-0.74eV, remained constant up to 1vol%H₂S. However at 2vol%, the activation energy increased to 0.99eV, suggesting a change in the mechanism of conduction. If equation 15 accurately describes the conduction process, then as the vacant sulphide ion sites become occupied, the inevitable decrease in sulphur vacant sites may cause an increase in activation energy for the conduction of sulphide ions, Figure 5-51.

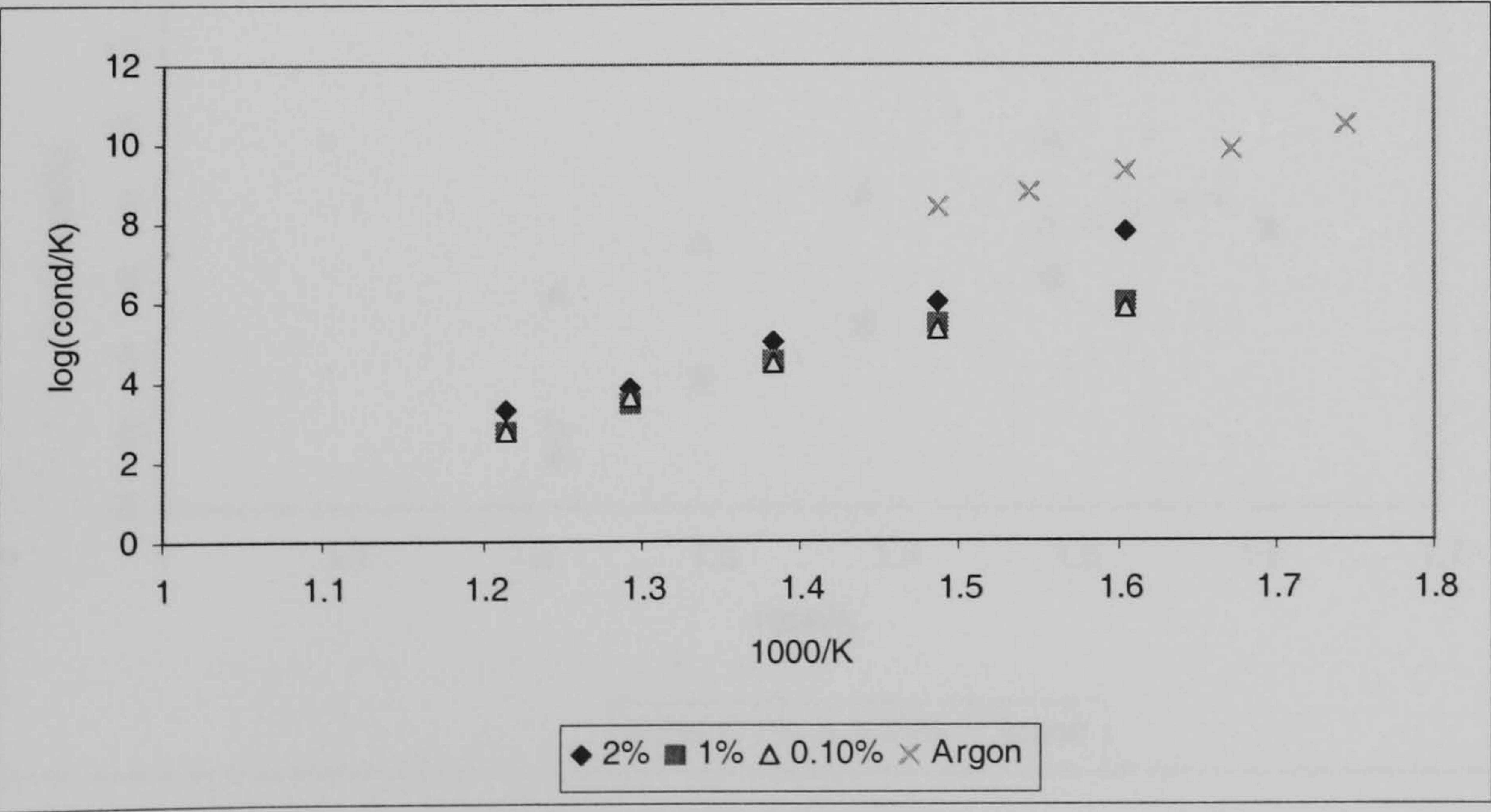


Figure 5-51. Activation energy for undoped SrSm₂S₄ measured in different atmospheres

The bulk conductivity of $\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ appears to be somewhat independent of hydrogen sulphide partial concentration, ranging from 0vol% $\text{H}_2\text{S}/\text{Ar}$ up to 2vol% $\text{H}_2\text{S}/\text{Ar}$ at all temperatures measured, 350-550°C, which indicates predominant ionic conduction, Figure 5-52.

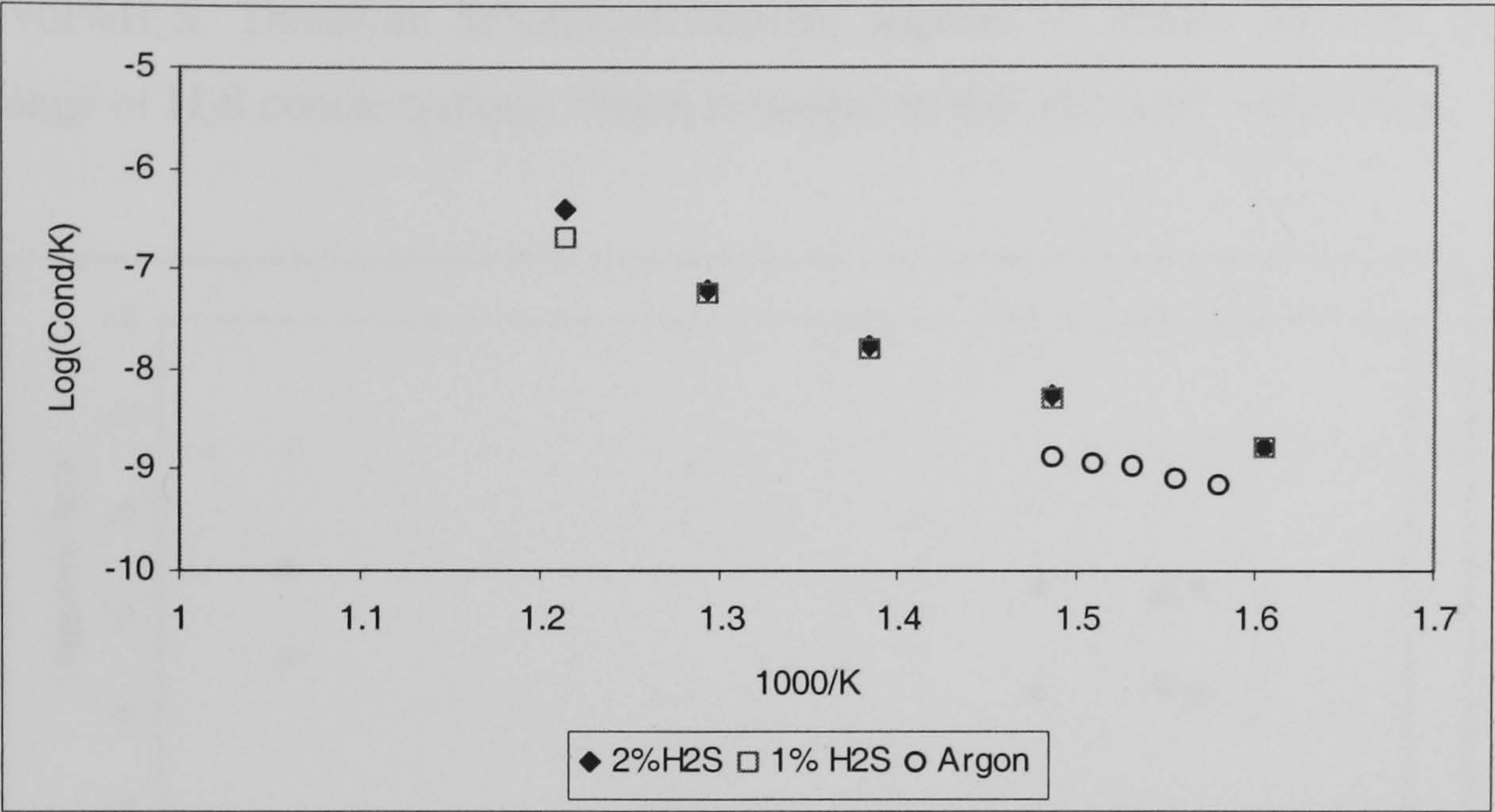


Figure 5-52. Bulk conductivities for $\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ measured in different atmospheres

The activation energy for $\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ increased from 0.70eV in pure argon to 1.25eV in 2vol% H_2S , Figure 5-53. Therefore undoped SrSm_2S_4 and $\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ compounds exhibit an in increased in activation energy for bulk conductivity with increasing H_2S concentration. A corresponding increase in conductivity with increasing H_2S concentration is attributed to hole conduction, equation 15.

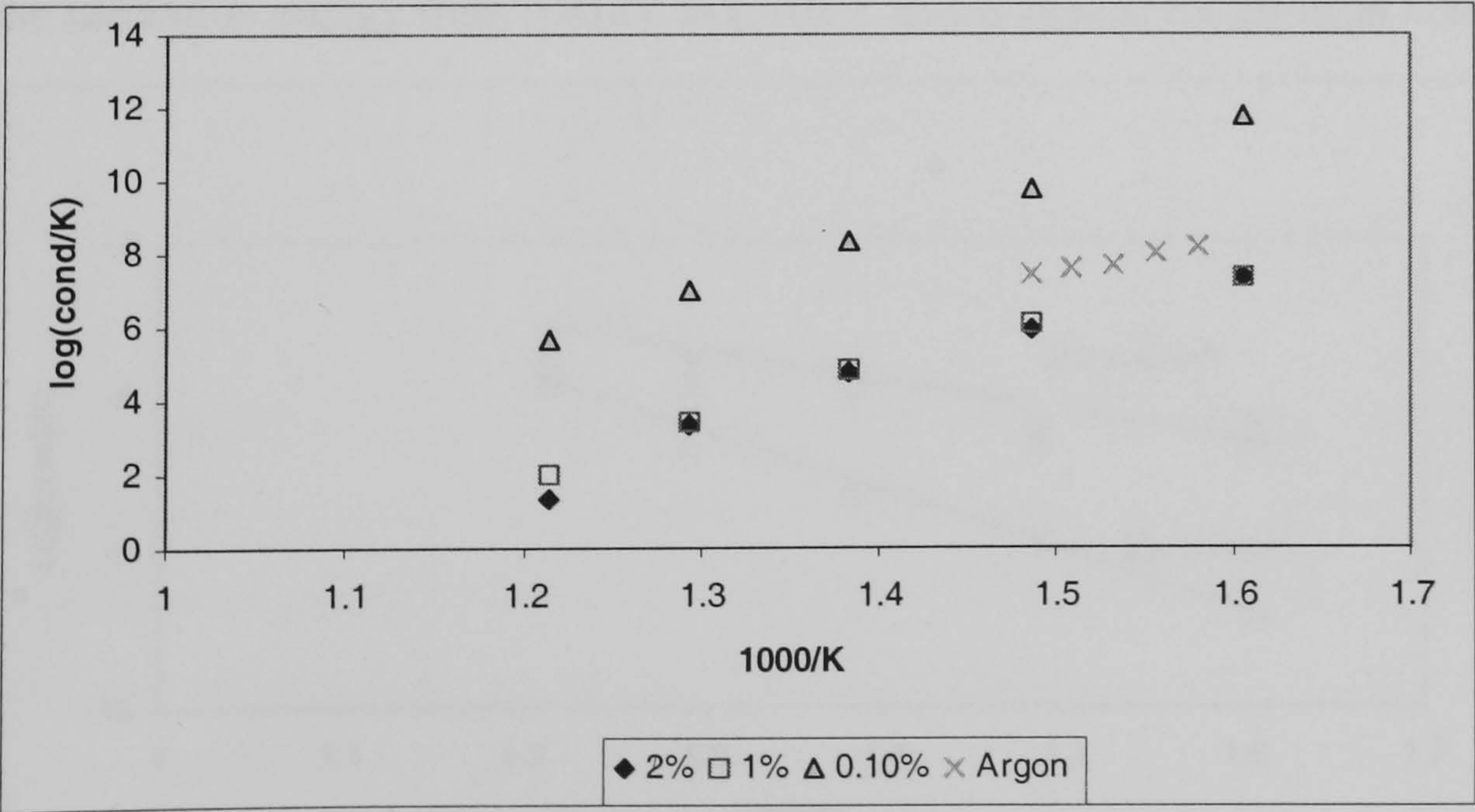


Figure 5-53. Activation energy for $\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ measured in different atmospheres

Bulk conductivity of $\text{SrSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ remains independent of H_2S concentration from pure argon to 0.1vol% $\text{H}_2\text{S}/\text{Ar}$, indicating ionic conduction over this wide concentration range, Figure 5-54. Similarly the corresponding activation energy of $\text{SrSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ remained unchanged, 1.3-1.2eV, with increasing H_2S partial pressure from pure argon to 1vol% H_2S . Therefore $\text{SrSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ appears to remain an ionic conductor over this range of H_2S concentrations, which is unique to this series of compounds.

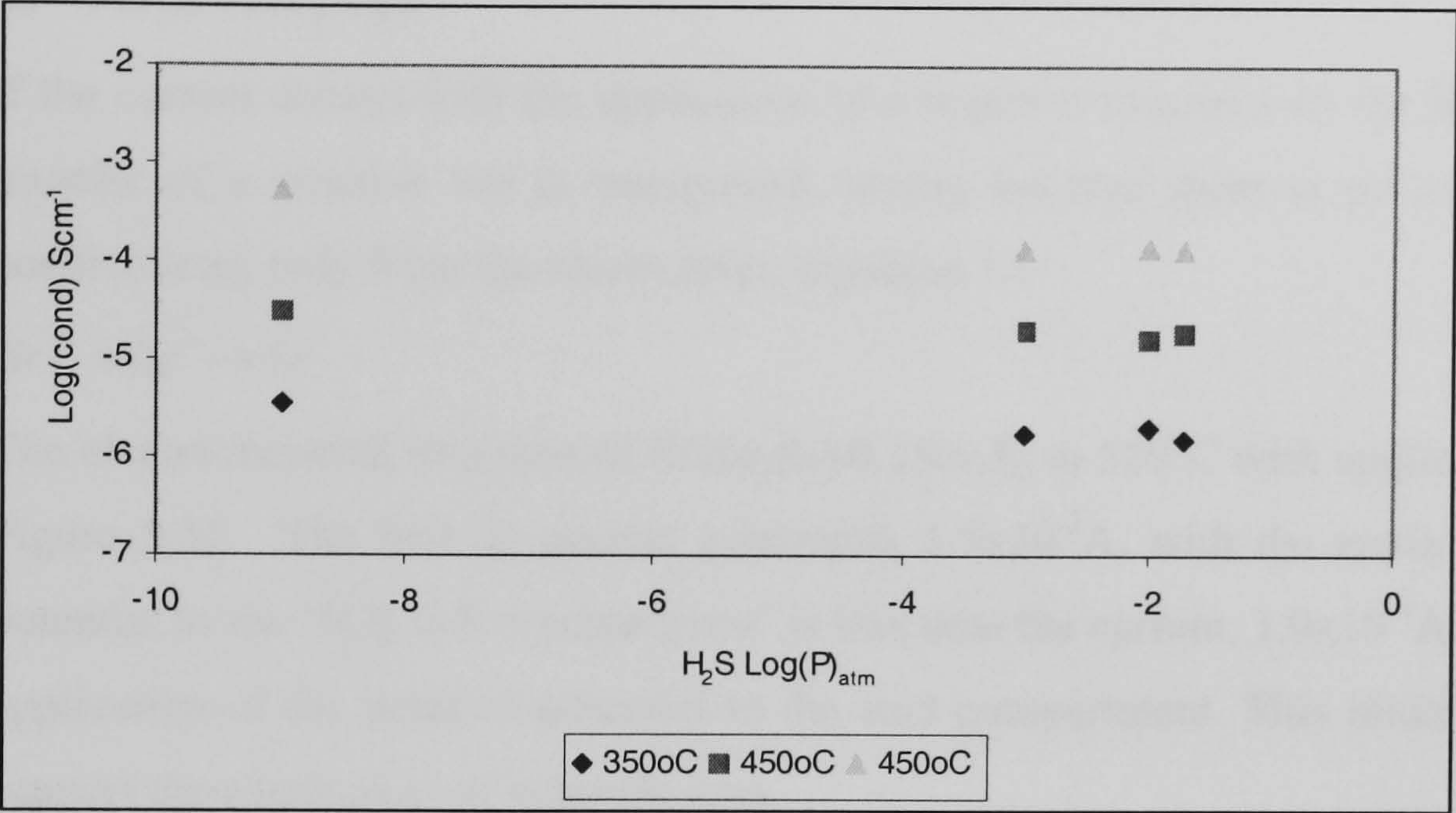


Figure 5-54. Bulk conductivities for $\text{SrSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ measured in different atmospheres

Figure 5-55 shows that the conductivity for $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}$ increases as the gas is changed from argon to a H_2S rich atmosphere. This increased conductivity occurs with a lowering of the activation energy from 0.81eV to 0.40eV, this is typical for electron hole conduction.

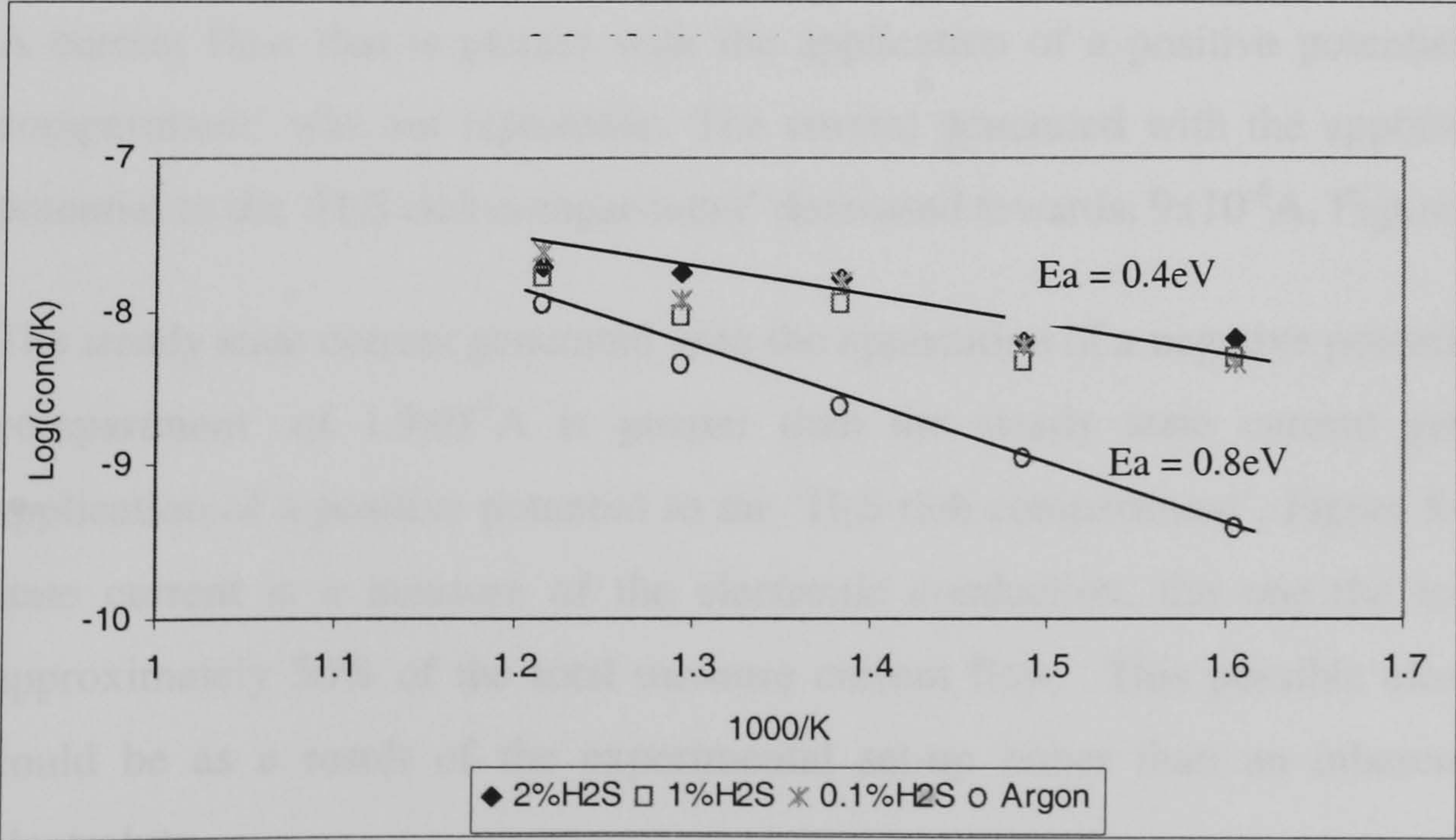
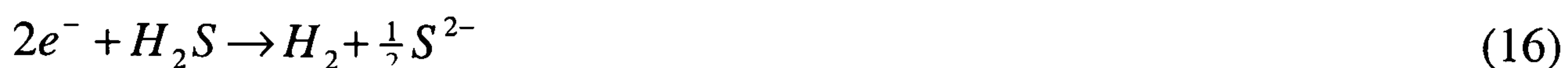


Figure 5-55. Variation of conductivity of $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ with sulphur partial pressure

5.9 Electrochemical Pumping of Selected SrSm₂S₄ compounds

The electrochemical concentration cell of the type H₂S/H₂//Pt/SrSm₂S₄/Pt//Ar/H₂ was operated at temperatures (550-650°C) with 1-2V (d.c.) to identify sulphide ion conduction. The constant source of S²⁻ ions was formed by the application of a negative potential applied on the 'H₂S rich' compartment, equation 16; conduction of the sulphide ion through a sulphide ion conducting electrolyte would produce a steady state current.



If the current decays with the application of a negative potential on the H₂S section, then the transfer of a positive ion is interpreted, (decay because there is no continuous source of positive ions, only from the electrolyte), equation 17.



The electrochemical response of SrSm₂S₄+0.1Sm₂S₃ at 550°C with applied 1Vdc is shown in Figure 5-56. The first dc current generated, 1.5x10⁻³A, with the application of a negative potential to the 'H₂S rich compartment' is less than the current, 1.9x10⁻³A, generated with the application of the positive potential to the said compartment. This initial response does not support the conduction of sulphide ions.

However the initial response was not repeatable since the subsequent repetition led to a larger current being generated with the application of a negative potential to the 'H₂S rich compartment', Figure 5-56. The trend of second and subsequent response supports the conduction of sulphide ions.

A current flow that is greater with the application of a positive potential to the 'H₂S rich compartment' was not repeatable. The current generated with the application of a positive potential to the 'H₂S rich compartment' decreased towards, 9x10⁻⁴A, Figure 5-56.

The steady state current generated with the application of a negative potential to the 'H₂S rich compartment' of 1.9x10⁻⁴A is greater than the steady state current generation with the application of a positive potential to the 'H₂S rich compartment', Figure 5-56. If this steady state current is a measure of the electronic conduction, the one the ionic conduction is approximately 50% of the total measure current flow. This possible electronic conduction could be as a result of the experimental set-up rather than an inherent property of the electrolyte.

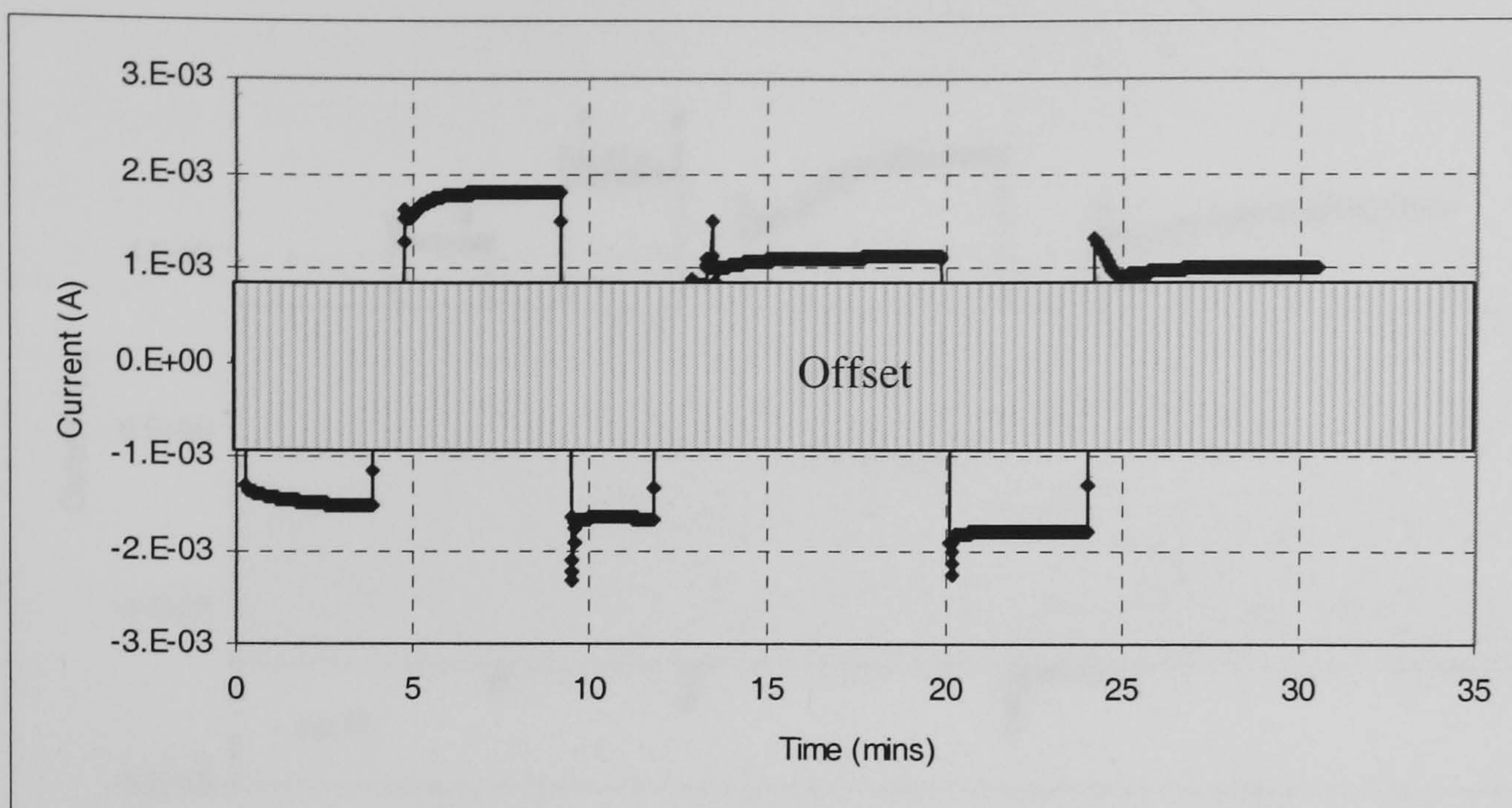


Figure 5-56 Electrochemical pumping $\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ at 550°C with applied 1Vdc

The result of $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ electrochemical pumping at 650°C with applied 1Vdc is shown in Figure 5-57. The peak dc current generated, $6.3 \times 10^{-3} \text{ A}$ occurred with the application of a negative potential on the H_2S rich 'compartment' is greater than the peak current generated with the application of the positive potential to the H_2S rich 'compartment' of $-5.4 \times 10^{-4} \text{ A}$; this response supports the conduction of sulphide ions according to equation 16.

If an offset of $\pm 4 \times 10^{-3} \text{ A}$ is used (because this is the lowest steady state current), then the current generated with the application of a negative potential to the H_2S rich 'compartment' is greater, when compared to the application of a positive potential to the said compartment, Figure 5-57. This response indicates sulphide ion conduction. However each successive application of a negative potential to the H_2S rich 'compartment', the bulk resistance of the electrolyte decreased during the experiment (based on the increasing dc current with the application of a positive potential to the H_2S rich 'compartment'), Figure 5-57. Therefore while sulphide ion conduction was qualitatively identified for $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$, it appears that the electrolyte is not stable at 650°C with the application of 1V(d.c.).

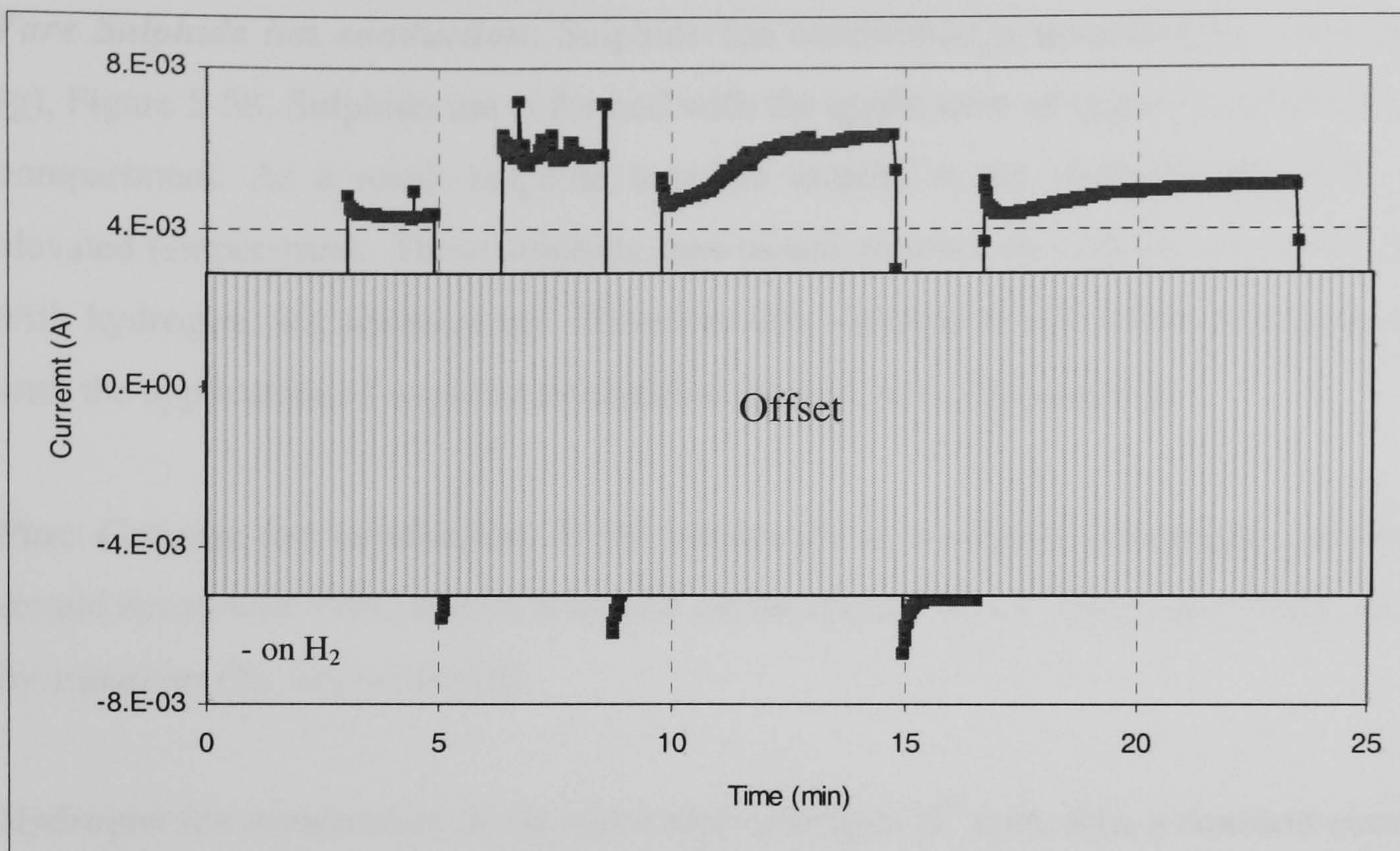


Figure 5-57. Electrochemical pumping $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ at 650°C with applied 1Vdc

Based on the complex asymmetric response during the electrochemical pumping of doped SrSm_2S_4 compounds, a complete list of possible half reactions that may occur with the application of a positive or negative potential to the electrochemical cell is presented in order to propose an explanation of the results. For example, consider the application of a negative potential to the 'H₂S rich' compartment and hence a positive potential to the H₂ compartment, Figure 5-58 highlights the possible reactions, assuming that all ions are mobile

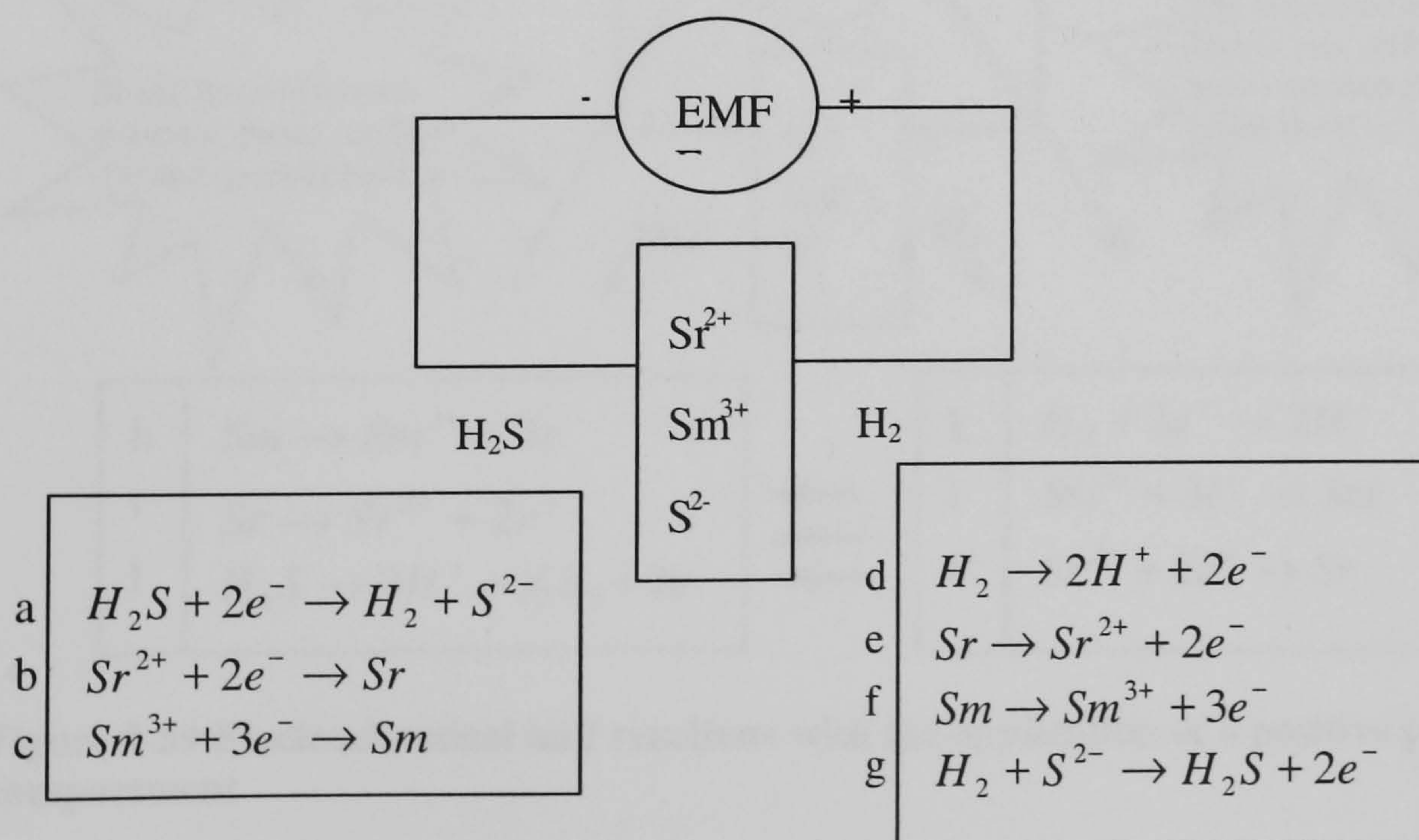


Figure 5-58. Electrochemical half reactions with the application of a negative potential to H₂S compartment

Based on Figure 5-58, the following scenarios may be deduced with the application of a negative potential to the 'H₂S rich compartment':

Pure Sulphide ion conduction: Sulphide ion conduction is described by equations (a) and (g), Figure 5-58. Sulphide ion is formed with the application of negative potential to H₂S rich compartment. As a result sulphide ions are created at the platinum electrode surface at elevated temperatures. These sulphide ions would conduct through the electrolyte and reacts with hydrogen, via equation (g). Therefore this scenario would result in a constant current with the application of negative potential to the H₂S rich compartment.

Pure Cationic ion conduction: If the electrolyte is a cationic conductor, then the current should decay with time, since the mobile cation species is not being replenished, as expressed by equations (b), (c), (e) and (f).

Hydrogen ion conduction: If the electrolyte conducts H⁺ ions, then a constant current would as expressed by equation (d). Therefore differentiation between sulphide ion conduction and H⁺ ions would not be possible using the current electrochemical cell.

Considering the opposite scenario, that is the application of positive potential to the H₂S rich compartment and hence a negative potential to the H₂ compartment, the following half reactions, Figure 5-59, are possible if all ions conduct.

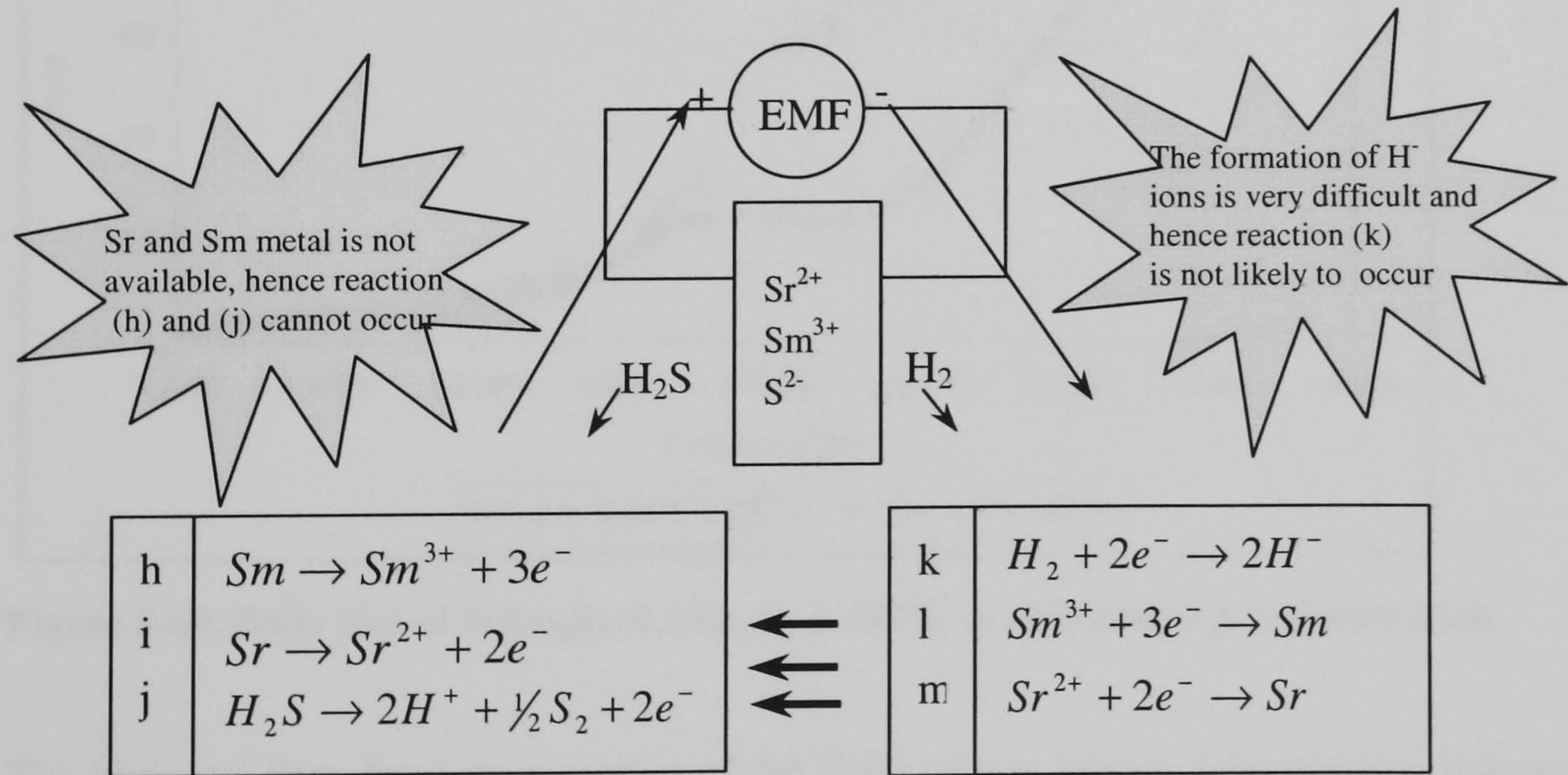


Figure 5-59 Electrochemical half reactions with the application of a positive potential to H₂S compartment

The current flow with the application of a positive potential to the H₂S rich compartment could generate H⁺ ions via equation (j) in Figure 5-59. Therefore the application of a negative voltage current to the H₂ compartment could also lead to steady state current if the electrolyte is a H⁺ conductor.

A current generated under from equations (l) and (m) could be associated with the direct electrochemical reduction of the electrolyte. The corresponding experimental observation could include either a decaying current with time, as well as the inability to obtain repeatable current measurements (because the electrochemical reduction of the electrolyte changes the bulk resistivity) to confirm this scenario.

Producing H^- is rather difficult and as such equation (k) should not occur.

The complicated behaviour of these compounds was also observed in the EIS experiments, since the conductivity as well as the frequency dependency of phase angle changed when the atmosphere was changed from argon to H_2S/Ar mixtures, Figure 5-60 and Figure 5-61. Varying the concentration of H_2S from 0.1vol% to 2vol% resulted in no further increase in conductivity or a different phase angle dependency. The distinct change in the frequency dependency of phase angle with the introduction of Ar/H_2S is shown in Figure 5.60 and 5.61 below.

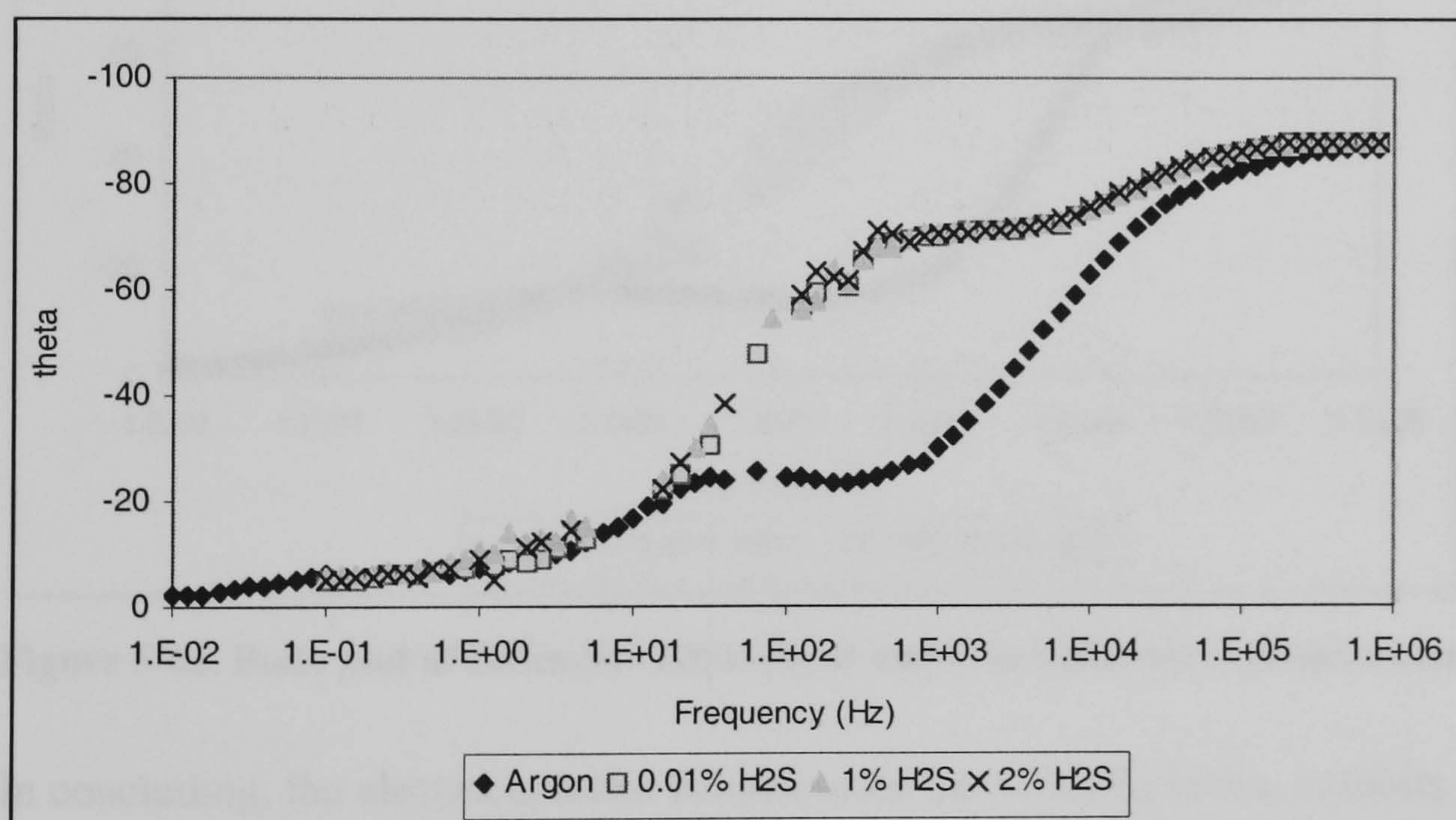


Figure 5-60. Bode plot of $SrSm_2S_4+0.1Sm_2S_3$ at 400°C in different H_2S concentration

The high and low frequency section of the Bode plot in Figure 5-60 remains independent of the H_2S concentration. However the middle frequency range has a distinct shift with changing the atmosphere from pure argon to mixed Ar/H_2S . The middle frequency is normally attributed to the grain boundary conduction of the electrolyte, hence the change does not appear to be related to the electrolyte-electrode interface since the low frequency arc remains unchanged, but rather a change in the bulk property of the material.

Only the flow frequency section of the Bode plot for $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ in Figure 5-61 remains independent of the H_2S concentration. The middle and high frequency range has a distinct shift with changing the atmosphere from pure argon to mixed Ar/ H_2S . High frequency refers to bulk properties and the middle frequency is normally attributed to the grain boundary conductivity of the electrolyte, hence the change does appear to be related to the material property.

The SrSm_2S_4 compounds have very low thermal activation energy therefore the loss of sulphur to the atmosphere during the EIS under argon may have altered the bulk properties, Table 5.15. Also, sulphur vacancies within the unit cell may interact with sulphur in the atmosphere creating hole, thus increasing the bulk conductivity which was observed for this series of compounds, Figure 5-60 and Figure 5-61.

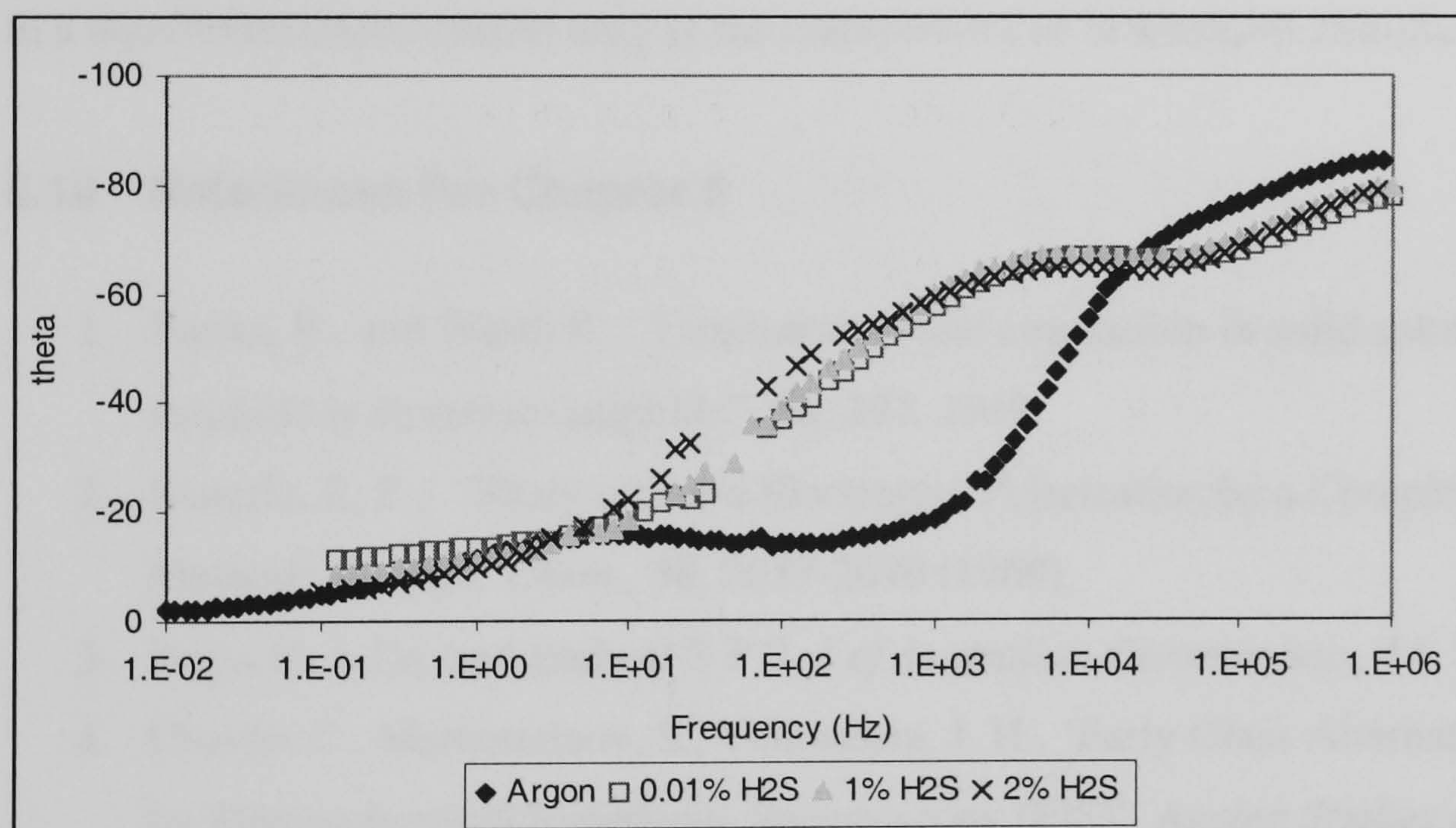


Figure 5-61. Bode plot of $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ at 400°C in different H_2S concentration

In concluding, the electrochemical behaviour of the SrSm_2S_4 series, exhibits the ion blocking electrode arcs in their Nyquist plots, which indicates ionic conduction under an argon atmosphere. Further EIS characterisation shows that the at high H_2S concentrations, greater than 0.01vol%, the bulk conductivities changes suggesting the onset of electron hole conduction.

The results of the electrochemical pumping experiments confirms sulphide ion conduction in $\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ and $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ because of the increasing current observed with the application of a negative potential to the H_2S rich atmosphere. A constant current was also observed with the application of a negative potential to the H_2 rich compartment, also inferring that positive ions or holes are also conducting.

In comparison, the Bode plot of the CaSm_2S_4 series showed phase angle change at low frequency (ionic blocking electrode arc) in argon atmosphere, also suggesting ionic conduction. The bulk conductivity of doped- CaSm_2S_4 based compounds changed marginally with varying the partial pressure of H_2S (at 550°C) and this confirms ionic conductivity. Therefore both CaSm_2S_4 and SrSm_2S_4 series exhibits ionic conduction.

Electrochemical pumping experiments of a doped CaSm_2S_4 compound shows a current flow only in the presence of H_2S , thus identifying sulphide ion conductivity. While the characterisation of the CaSm_2S_4 series shows sulphide ion conduction, the bulk conductivity remains low (10^{-4} to $10^{-7} \text{ S}^{-1}.\text{cm}$ at 500°C in Ar). Therefore the host cation was changed from calcium to the larger strontium ion to form the SrSm_2S_4 series. However this change resulted in a significant improvement only in the conductivity of $\text{SrSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$.

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Chapter 6

6. Thermal and Electrochemical Characterisation of Barium Based sulphides

$\text{Ba}_2\text{In}_2\text{O}_5$, displays oxide ion conduction above 925°C , Goodenough *et. al.*, 1990. Since then oxide materials of the form $\text{A}_2\text{B}_2\text{O}_5$ have been investigated as possible fast oxide-ion conductors for use in oxygen sensors, solid oxide fuel cells and other electrochemical devices, Goodenough *et. al.*, 1992. These types of oxide compounds have been synthesised with the aim of developing fast oxide ion conducting materials, superior to the commercially available yttria-stabilised zirconia (YSZ). $\text{Ba}_2\text{In}_2\text{O}_5$ is both a proton and oxide-ion conductor, Yao, *et. al.* 2002, Schober and J. Friedrich, 1998.

The structure of $\text{Ba}_2\text{In}_2\text{O}_5$ at ambient temperature is the Brownmillerite type orthorhombic Icmm symmetry, Figure 6.1, with lattice parameters $a = 6.086\text{\AA}$, $b = 16.790\text{\AA}$ and $c = 5.969\text{\AA}$. $\text{Ba}_2\text{In}_2\text{O}_5$ is stable up to 900°C , above this temperature the point oxygen vacancies begin to disorder, Speakman *et. al.*, 2002. The oxygen vacancy order–disorder transition is associated with a structural transition to a fast oxide-ion conducting state. At 1040°C $\text{Ba}_2\text{In}_2\text{O}_5$ becomes a cubic oxygen-deficient perovskite, with lattice parameter of 4.274\AA . Doping the indium site in the $\text{Ba}_2\text{In}_2\text{O}_5$ compound with trivalent cations of various radii alters the order-disorder transition temperature. For example, doping with ions larger than the host In^{3+} ion, such as Y^{3+} and Yb^{3+} caused an increase in the transition temperature, while doping with smaller ions like Sc^{3+} and Ga^{3+} lead to a decrease in the transition temperature of the material, Yamamura, 1998. It was reported that $\text{Ba}_2\text{In}_2\text{O}_5$ undergoes an approximate six-fold increase in its ionic conductivity over the temperature range from about $900\text{--}950^\circ\text{C}$, in broad agreement with previous studies, Berastegui, *et. al.*, 2002.

Based on impedance spectroscopy experiments, $\text{Ba}_2\text{In}_2\text{O}_5$, exhibits cationic, (In^{3+}) ions, conduction, Berastegui *et. al.* 2002. Introducing a higher valency cation such as Zr^{4+} into the $\text{Ba}_2\text{In}_2\text{O}_5$ structure induces anionic disorder which causes a transformation from the Brownmillerite type orthorhombic to the cubic defect perovskite structure as adopted by the high-temperature phase of $\text{Ba}_2\text{In}_2\text{O}_5$, Berastegui *et. al.*, 2002. An increase conductivity of $\text{Ba}_2\text{In}_2\text{O}_5$ was also observed with La doping. A discontinuous jump of ion conductivity in the Arrhenius plot was observed with the increasing La content, which was related to the disordering of the oxygen vacancies. The activation energy remained constant with respect to the La content. Moreover, the conductivity for $\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x=0.6$) was $0.042\text{ (S.cm}^{-1}\text{)}$ at 1073K , which exceeded that of 8 mol% yttria-stabilized zirconia. The higher oxide-ion

conductivity of this system could be dominated by the amount of mobile oxygen ions, Kakinuma, *et. al.* 2001.

The primary consideration for selecting the dopant cation was similarity to the host cationic radius ($\text{In}^{3+} = 0.81\text{\AA}$), to assist the inclusion of the dopant ion onto the indium site, the ions considered were $\text{Sn}^{4+}(0.71\text{\AA})$, $\text{Zr}^{4+}(0.79\text{\AA})$ and $\text{Pb}^{4+}(0.84\text{\AA})$, White, 2005. Due to the combination of the closest ratio of ionic radii to the In^{3+} ion and the previous successful inclusion of zirconium onto the indium site in the oxide system, Zr^{4+} was chosen as the selected dopant in this case, White, 2005. Therefore the sulphide analogue materials $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Zr}_x\text{S}_5$, where $x = 0.2$, were prepared, White, 2005, with the aim of creating a sulphide ion conducting compound, and the structure and properties of the compounds were investigated.

The XRD data for both compounds show that the materials crystallised with an orthorhombic unit cell, White 2005. Rietveld refinements for the compounds $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Zr}_x\text{S}_5$ are shown in Figure 6-1 with refined structural data summarised in Table 6.1, White 2005. Atomistic simulation techniques used by Fisher *et. al.*, 2002, to investigate the crystal structure and defect energetics of $\text{Ba}_2\text{In}_2\text{O}_5$ shows that the orthorhombic brownmillerite structure has alternating layers of oxygen octahedral and tetrahedral, with intrinsic defects of the Frenkel type. Calculated formation energies of electronic defects suggest that $\text{Ba}_2\text{In}_2\text{O}_5$ will oxidize with the formation of positive holes, Fisher *et. al.*, 2002

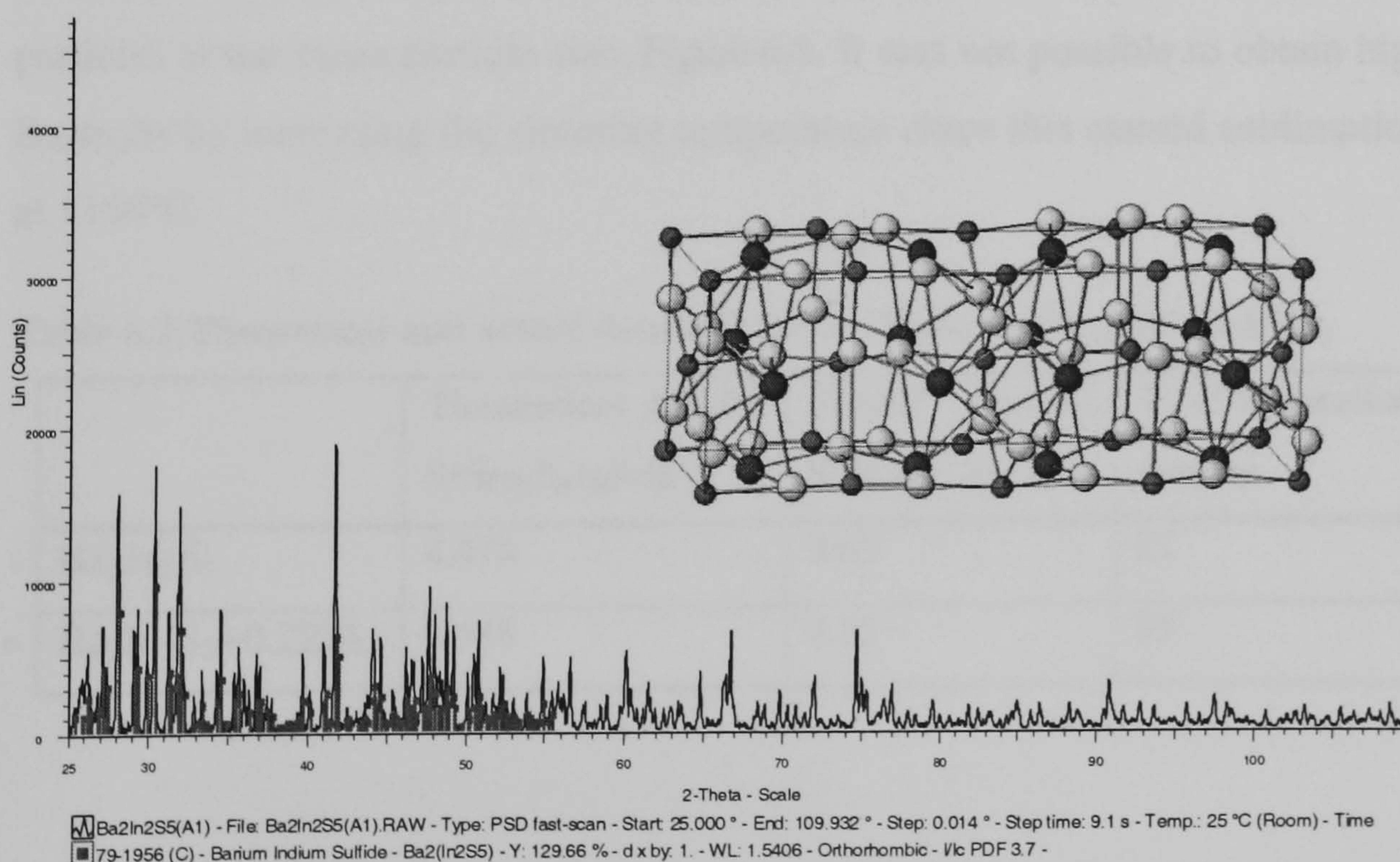


Figure 6-1. Powder X-RD pattern and unit cell structure for $\text{Ba}_2\text{In}_2\text{S}_5$, White, 2005

Table 6.1. Refined unit cell parameter and theoretical density for orthorhombic Ba₂In₂S₅ and Ba₂In_{2-x}Zr_xS₅

Parameter	Ba ₂ In ₂ S ₅	Ba ₂ In _{2-x} Zr _x S ₅
Space group	Pbca	Pbca
Refined cell parameter <i>a</i> (Å)	13.1643(3)	13.1508(3)
Refined cell parameter <i>b</i> (Å)	12.7251(3)	12.7165(3)
Refined cell parameter <i>c</i> (Å)	11.7805(3)	11.7732(2)
Density g/cm ³ (<i>theoretical</i>)	4.474	4.448

Based on the XRD pattern of Ba₂In_{2-x}Zr_xS₅, this compound has an orthorhombic unit cell similar to Ba₂In₂S₅ shown in Figure 6-1. The volume of the unit crystal decreases with the introduction of Zr⁴⁺ expressed by the decrease in the lattice parameter, i.e. is the Zr⁴⁺ dopant causes a contraction of the unit cell, Table 6.1. Doping with Zr⁴⁺ also causes a decrease in density even though the unit cell contracts, thus inferring the formation of vacant sites within the unit cell.

Pellets were made by pressing ground material, to 10 tonnes and sintering to 1050°C. The resulting pellets have a maximum of 95% of the theoretical density, Table 6.2. The significant difference between Ba₂In₂S₅+0.2ZrS₂ and the un-doped BaIn₂S₅ was also evident in the particle size distribution, where Ba₂In₂S₅+0.2ZrS₂ has a larger volume percent of particles at the mean particle size, Figure 6-2. It was not possible to obtain higher densities for Ba₂In₂S₅ by increasing the sintering temperature since this caused sublimation of the material at 1150°C.

Table 6.2.Theoretical and actual densities for Ba₂In₂S₅ and Ba₂In₂S₅+0.2ZrS₂

	Theoretical density SrSm ₂ S ₄ (g/cm ³)	Actual density SrSm ₂ S ₄ (g/cm ³)	% of theoretical density
Ba ₂ In ₂ S ₅	4.474	3.65	85
Ba ₂ In ₂ S ₅ +0.2ZrS ₂	4.448	4.25	95

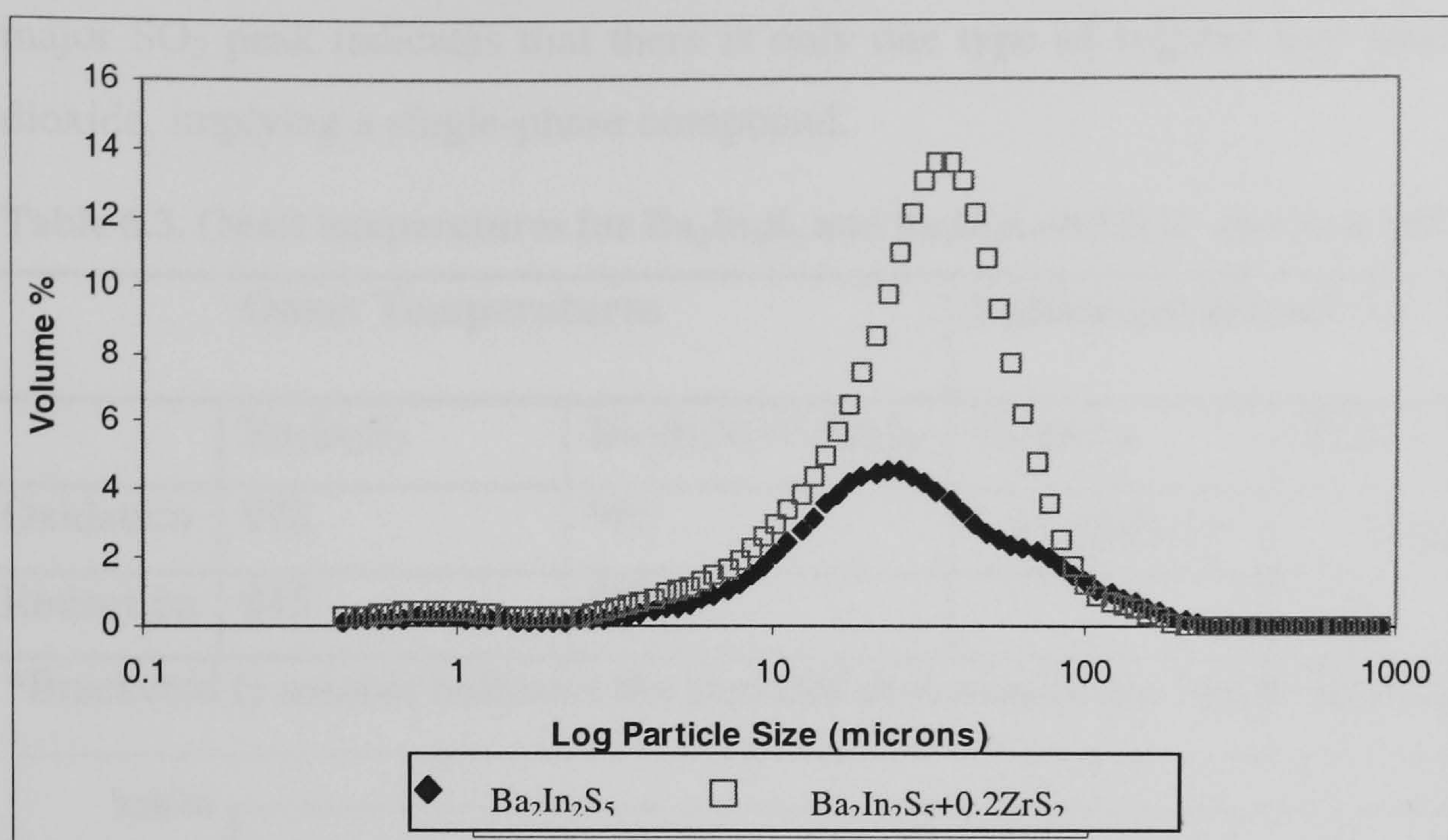


Figure 6-2. Particle size distribution of $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$ and un-doped $\text{Ba}_2\text{In}_2\text{S}_5$

Figure 6-3 shows an SEM of the sintered pellets with pores of $2\mu\text{m}$ diameter up with fairly thin grain boundaries. The thin lines in Figure 6-3 suggest that thermal stresses occurred in the sintering process therefore decreasing the heating and cooling rate should improve the actual density.

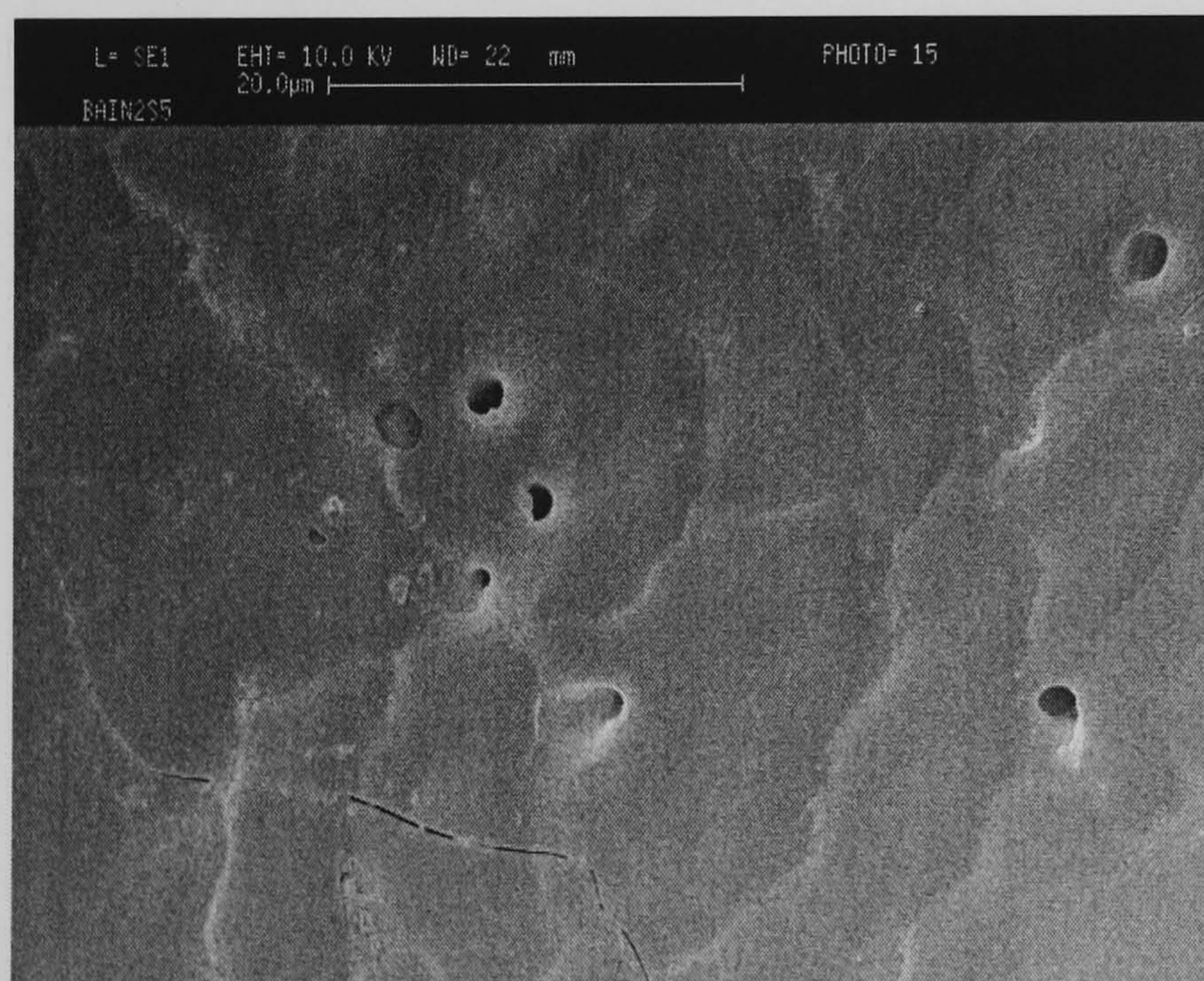


Figure 6-3 SEM of $\text{Ba}_2\text{In}_2\text{S}_5$ sintered at 1050°C in H_2S

6.1.2 TPO and TPR for $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Zr}_x\text{S}_5$

The thermal stability of $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$ was established using TPO and TPR techniques. The TPO traces of this series consist of one major peak with onset temperatures higher than any of the previous AB_2S_4 compounds, Figure 6-4. The addition of ZrS_2 to $\text{Ba}_2\text{In}_2\text{S}_5$ increased the onset temperature for oxidation, Table 6.3. The presence of a single

major SO₂ peak indicates that there is only one type of sulphur that reacts to form sulphur dioxide, implying a single-phase compound.

Table 6.3. Onset temperatures for Ba₂In₂S₅ and Ba₂In₂S₅+0.2ZrS₂ and unit cell lattice parameter

Onset Temperatures			Lattice parameter for ‘a’ site Å	
	Ba ₂ In ₂ S ₅	Ba ₂ In ₂ S ₅ +0.2ZrS ₂	Ba ₂ In ₂ S ₅	Ba ₂ In _{2-x} Zr _x S ₅
Oxidation	978	995	13.1643(3)	13.1508(3)
Reduction	845	865		

*Bracketed () number indicates the standard deviation on the fourth decimal place

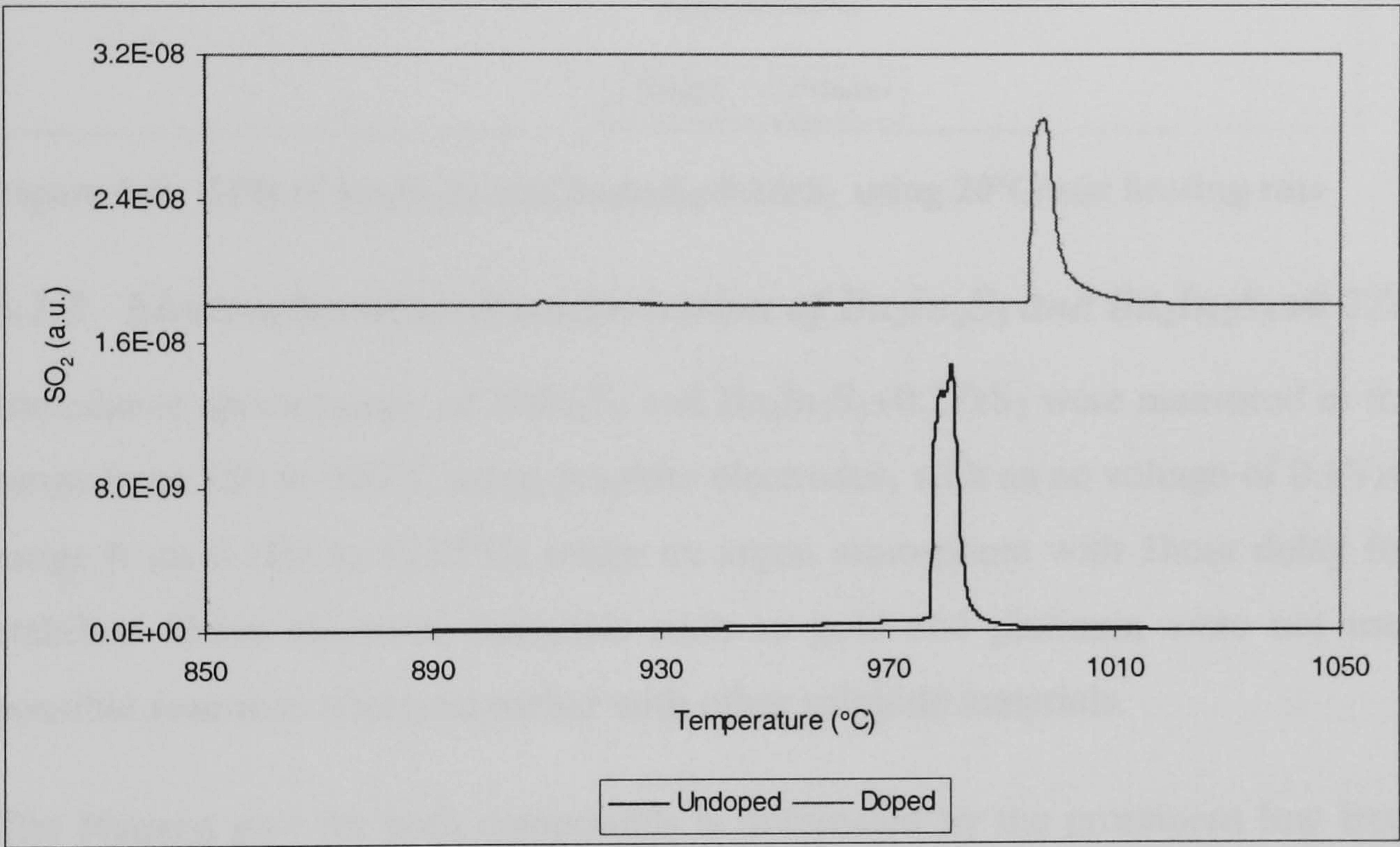


Figure 6-4. TPO of Ba₂In₂S₅ and Ba₂In₂S₅+0.2ZrS₂ using 10°C/min heating rate

The doped compound, Ba₂In₂S₅+0.2ZrS₂, with an onset temperature of 880°C in a reducing atmosphere is also more stable than the undoped-compound which has an onset temperature of 820°C, Figure 6-5. Therefore Ba₂In₂S₅+0.2ZrS₂ is more stable than Ba₂In₂S₅ in both oxidizing and reducing atmospheres. This infers that the reduced ionic distance results in an increased stability.

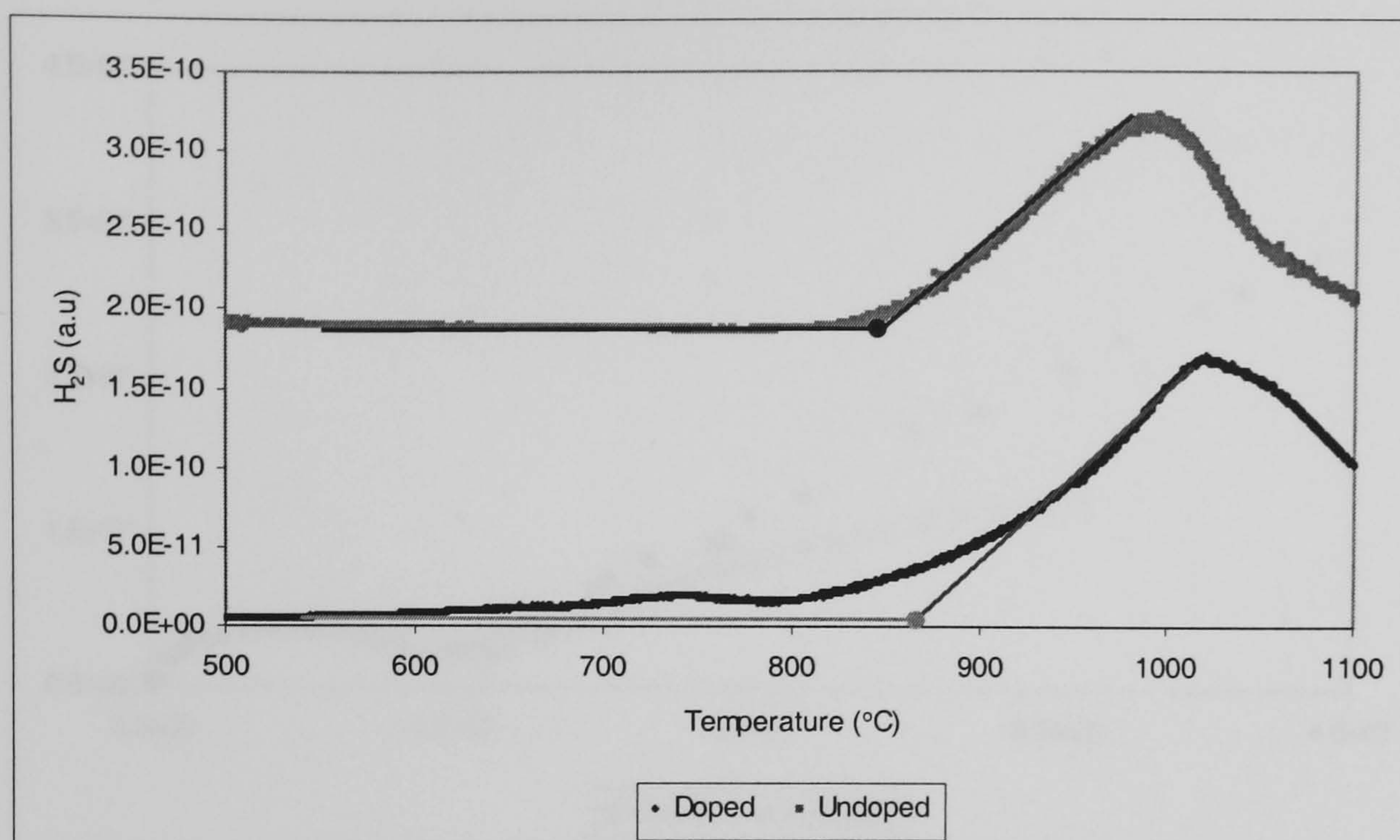


Figure 6-5. TPR of $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$ using $20^\circ\text{C}/\text{min}$ heating rate

6.1.3 Electrochemical characterisation of $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$

Impedance spectroscopy of BaIn_2S_5 and $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$ were measured in the temperature range from 250 to 400°C using graphite electrodes, with an ac voltage of 0.1V_{rms} , frequency range from 0.1Hz to $1 \times 10^6\text{Hz}$ under an argon atmosphere with 1 hour delay for temperature stability. Other electrode materials such as gold and platinum were not used due to the possible reactions observed earlier with other sulphide materials.

The Nyquist plot for both compounds is dominated by the prominent low frequency effect, known as Warburg impedance, Figure 6-6. Pure ionic conductors exhibit Warburg impedances, 45° line changes, at unique temperatures before the 45° line changes to a typical arc. Even though Warburg impedance is defined by the characteristic 45° line, the angle may reduce from 45° to approximately 21° , due to mechanical contact of the electrodes, Doi, 1990. Therefore the large low frequency line, in Figure 6-6, can be called Warburg impedance. This property is unique to ionic conducting materials; therefore both $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$ are ionic conductors. The experimental impedance data for $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$ differ from all AB_2S_4 type compounds, none of which exhibited Warburg impedance, at the temperatures examined.

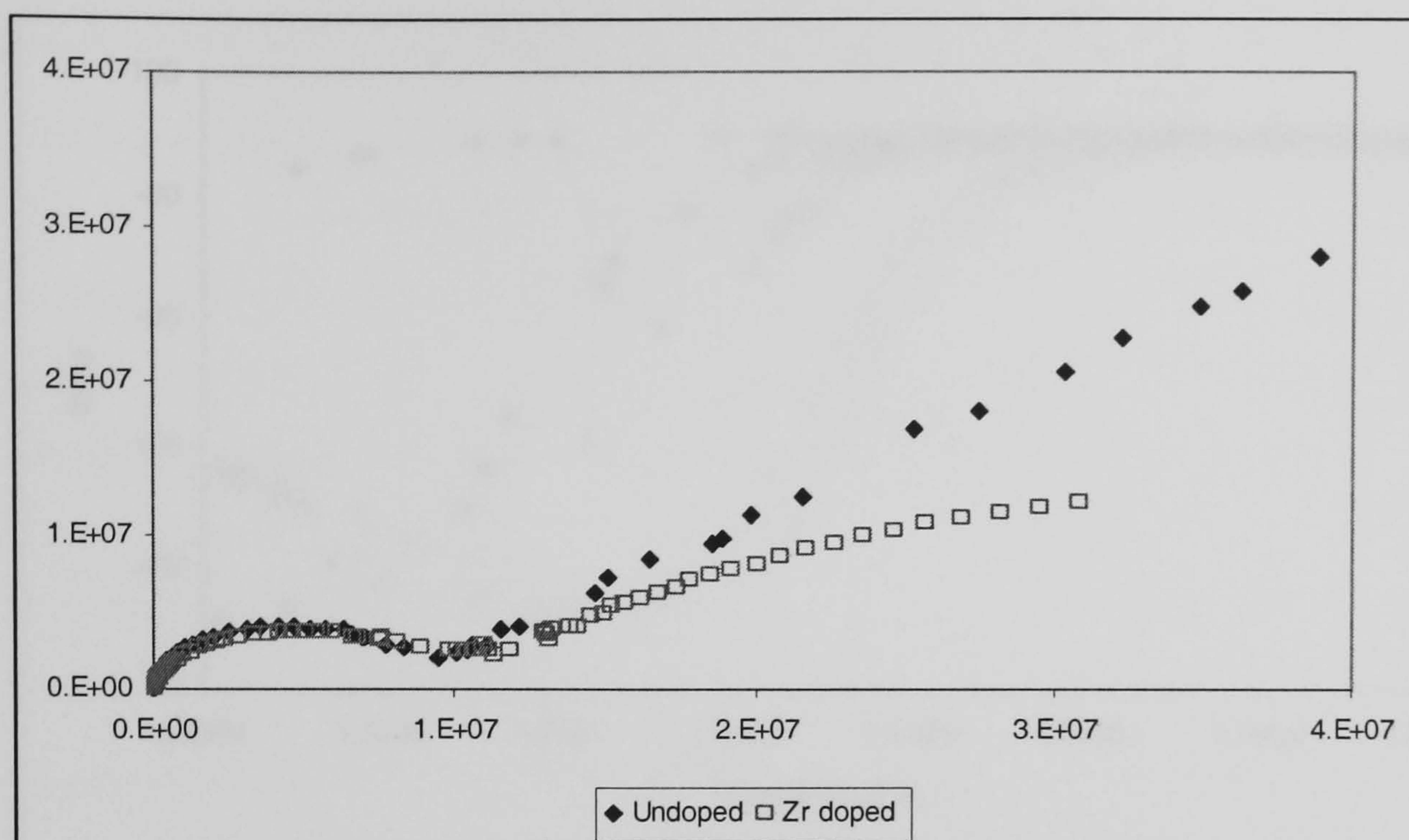


Figure 6-6. Nyquist plot of $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Zr}_x\text{S}_5$ at 350°C in argon

The oxide analogue $\text{Ba}_2\text{In}_2\text{O}_5$ has a Brownmillerite type orthorhombic, here oxygen vacancies begin to disorder at temperatures in excess of 900°C , Speakman *et. al*, 2002. The oxygen vacancy order–disorder transition is directly related to the structural transition to a fast oxide-ion conducting deficient perovskite unit cell. At 1040°C , $\text{Ba}_2\text{In}_2\text{O}_5$ becomes a cubic oxygen-deficient perovskite with lattice parameter of 4.274\AA .

The Bode plot of $\text{Ba}_2\text{In}_2\text{S}_5$ possibly shows the transformation from a Brownmillerite type orthorhombic Icmm symmetry to a deficient perovskite unit cell since the low frequency arc begins at 300°C , i.e. no ionic conduction takes place at lower temperatures, Figure 6-7. While the temperature at which ionic conduction occurs in the $\text{Ba}_2\text{In}_2\text{S}_5$ is much lower than its equivalent oxide, it appears that the principle governing the change, explained by the change in the unit cell, is also valid for $\text{Ba}_2\text{In}_2\text{S}_5$. The identification of this phase could be determined by XRD isotherm measurements at these temperatures in future works.

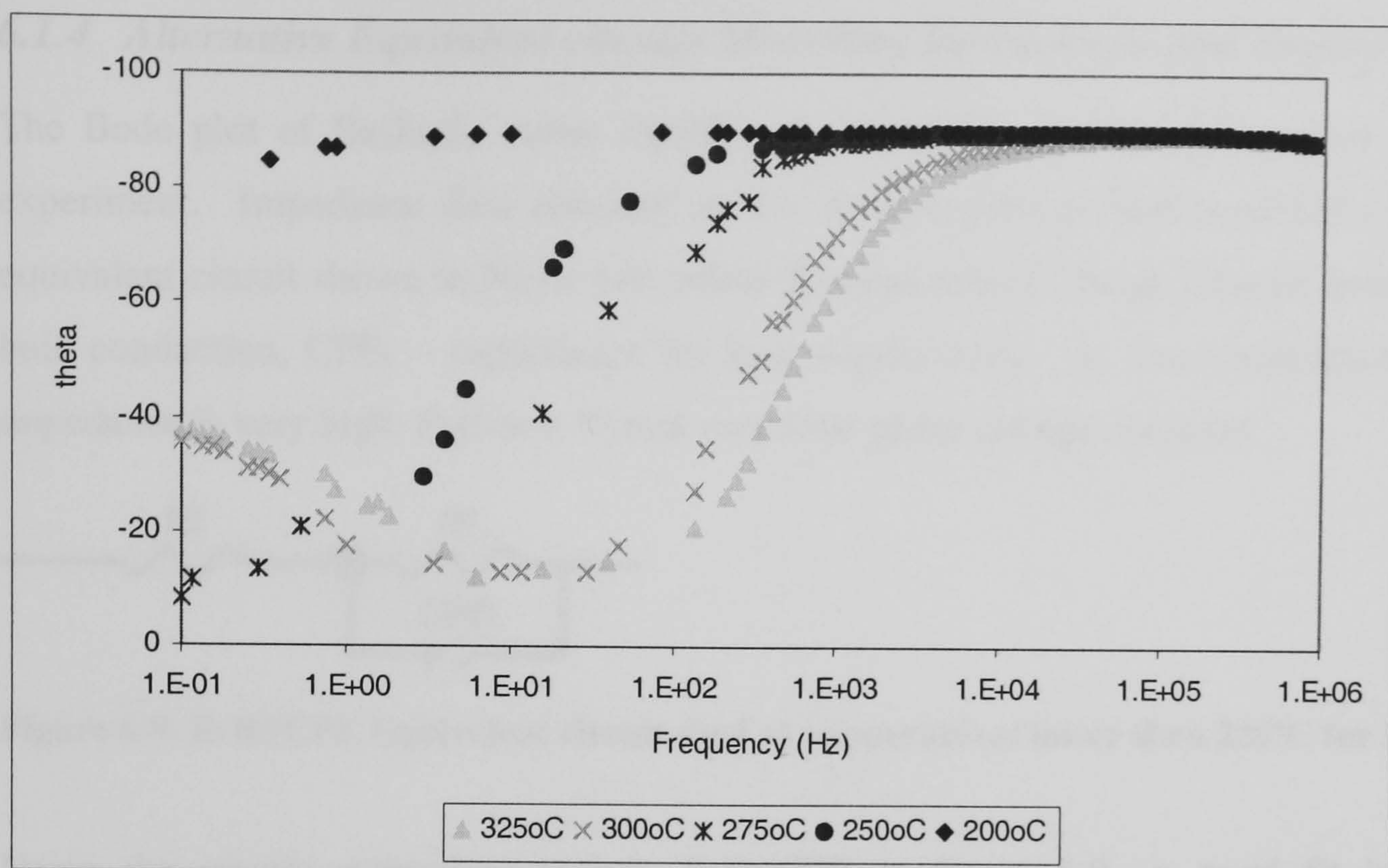


Figure 6-7. Bode plot of temperature effect on phase angle of $\text{Ba}_2\text{In}_2\text{S}_5$ in argon

The Nyquist plot for $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$ shows that the phase change at low frequencies was present at temperatures as low as 200°C , hence the stabilisation of conduction was lowered by doping with Zr^{2+} , Figure 6-8. Therefore the sulphide analogues of $\text{Ba}_2\text{In}_2\text{O}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Zr}_x\text{O}_5$ compound have similar electrochemical behaviour in terms of the transformation to an ionic conducting electrolyte at elevated temperatures, as well as the stabilisation of ionic conduction to lower temperatures by doping with the smaller Zr^{4+} cation.

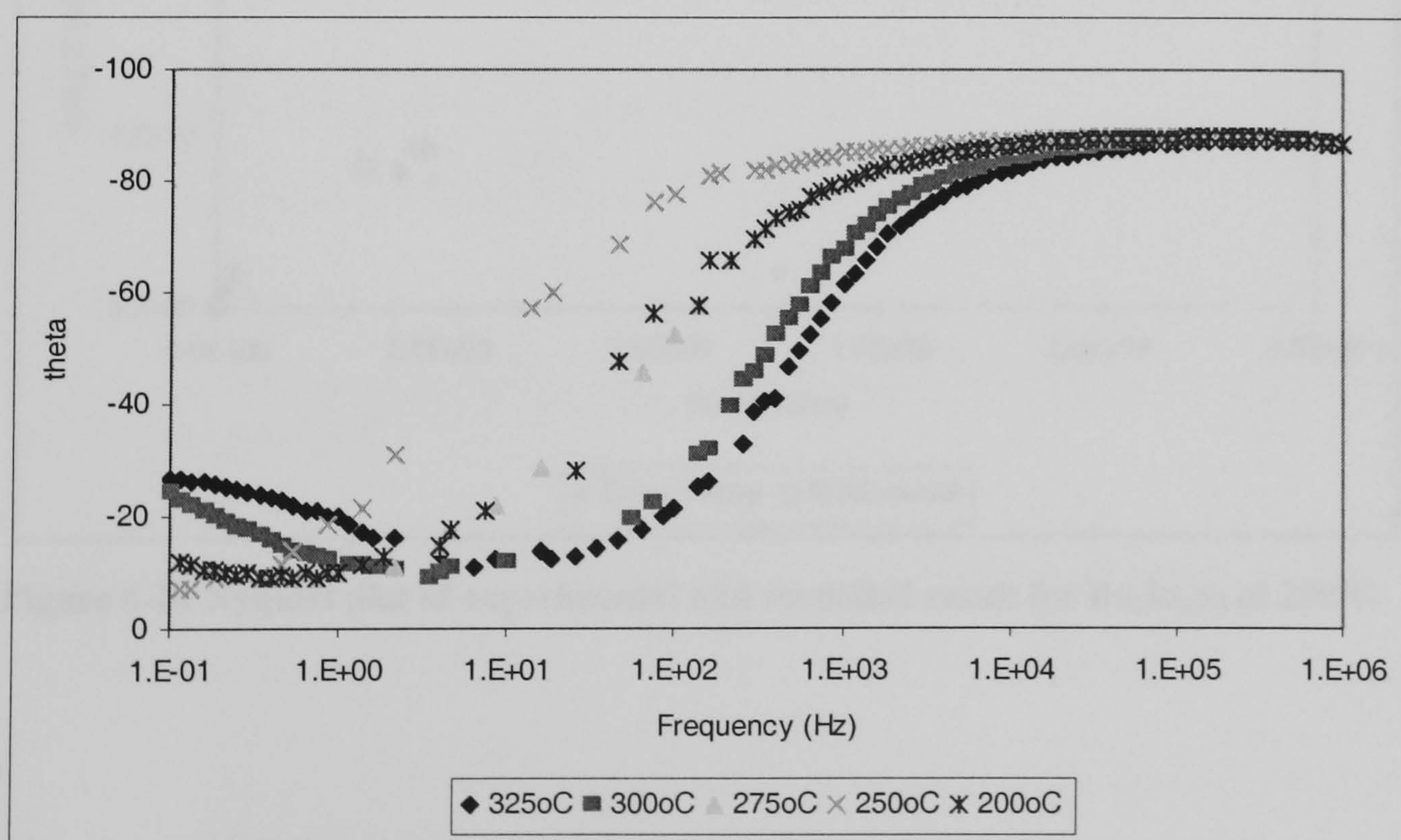


Figure 6-8. Bode plot of temperature effect on phase angle of $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$ in argon

6.1.4 Alternative Equivalent circuits Modelling for $Ba_2In_2S_5$ and $Ba_2In_2S_5+0.2ZrS_2$

The Bode plot of $Ba_2In_2S_5$ varies significantly depending on the temperature used in the experiment. Impedance data obtained at low temperatures is best modelled by using the equivalent circuit shown in Figure 6-9, where R_2 represents a charge transfer resistance, R_1 – bulk conduction, CPE_1 – capacitance for bulk conductivity. At low temperatures, the total impedance is very high, Figure 6-10 and very little phase change occurred.

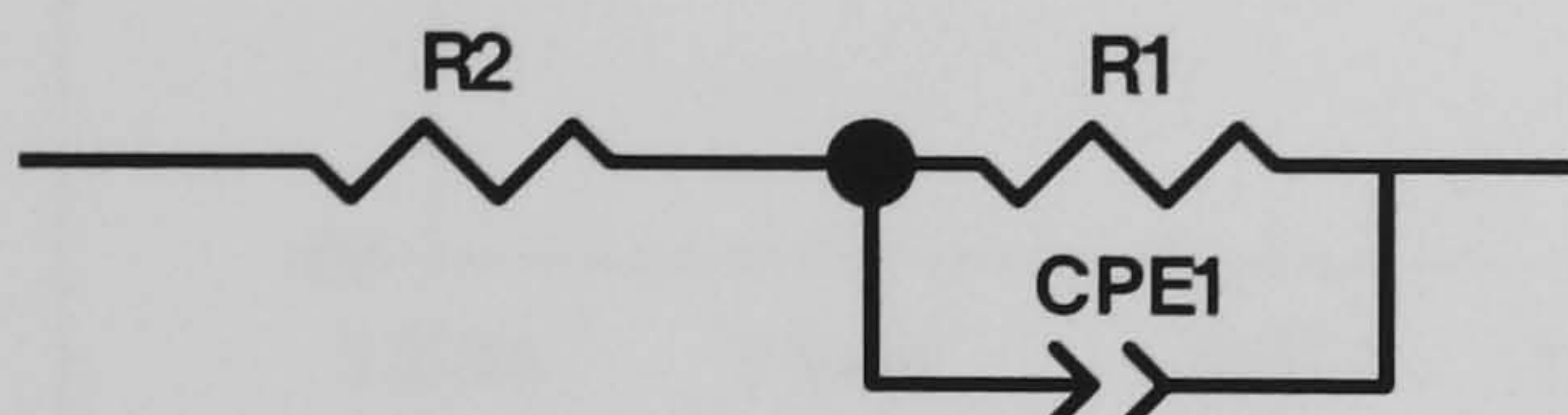


Figure 6-9. R-R//CPE Equivalent circuit used at temperatures lower than 225°C for $Ba_2In_2S_5$

Using the simple equivalent circuit, R-R//CPE in Figure 6-9,, a good fit between the experimental and the modelled data was achieved, as shown by Nyquist and Bode plots in Figure 6-10 and Figure 6-11 respectively.

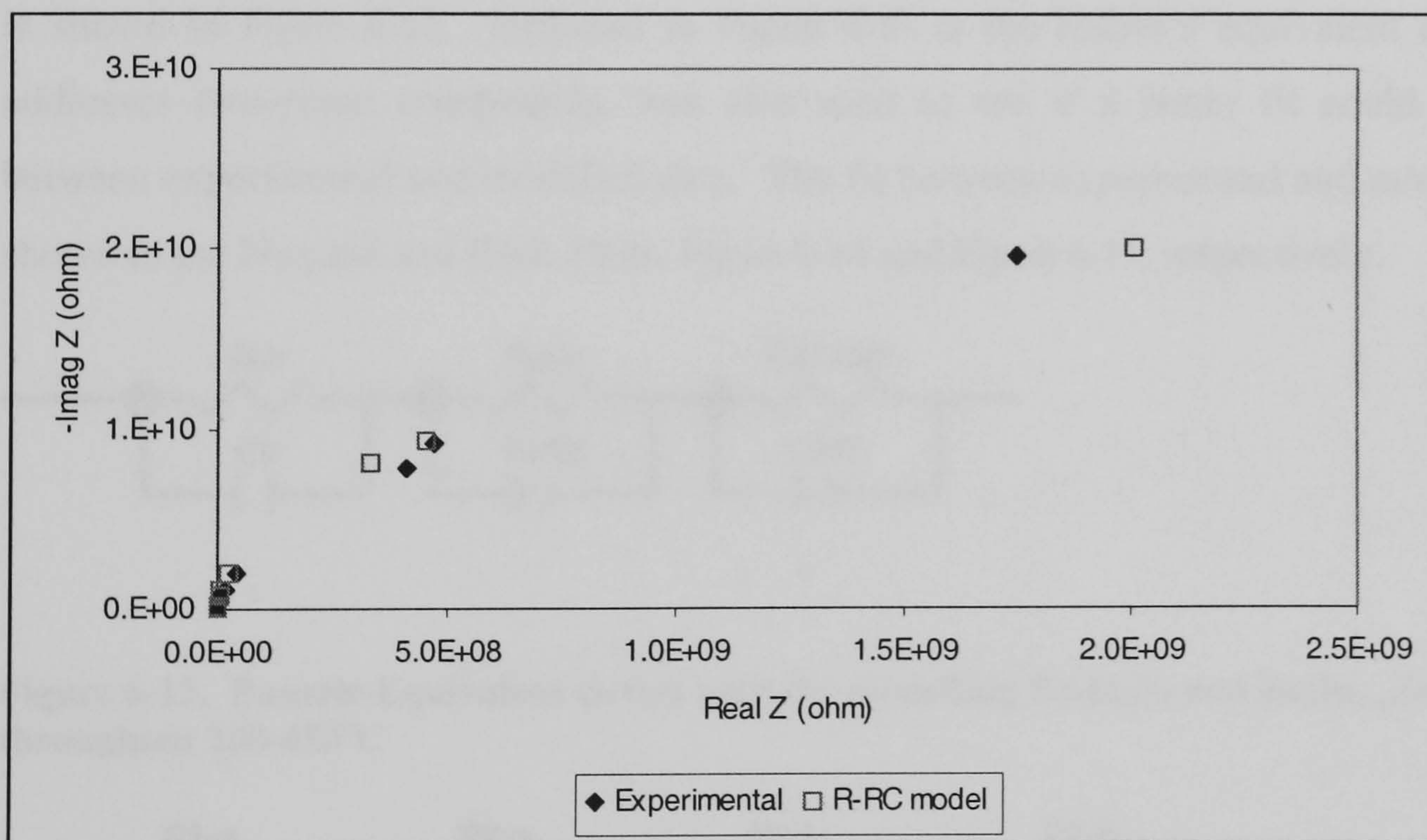


Figure 6-10 Nyquist plot of experimental and modelled result for $Ba_2In_2S_5$ at 200°C

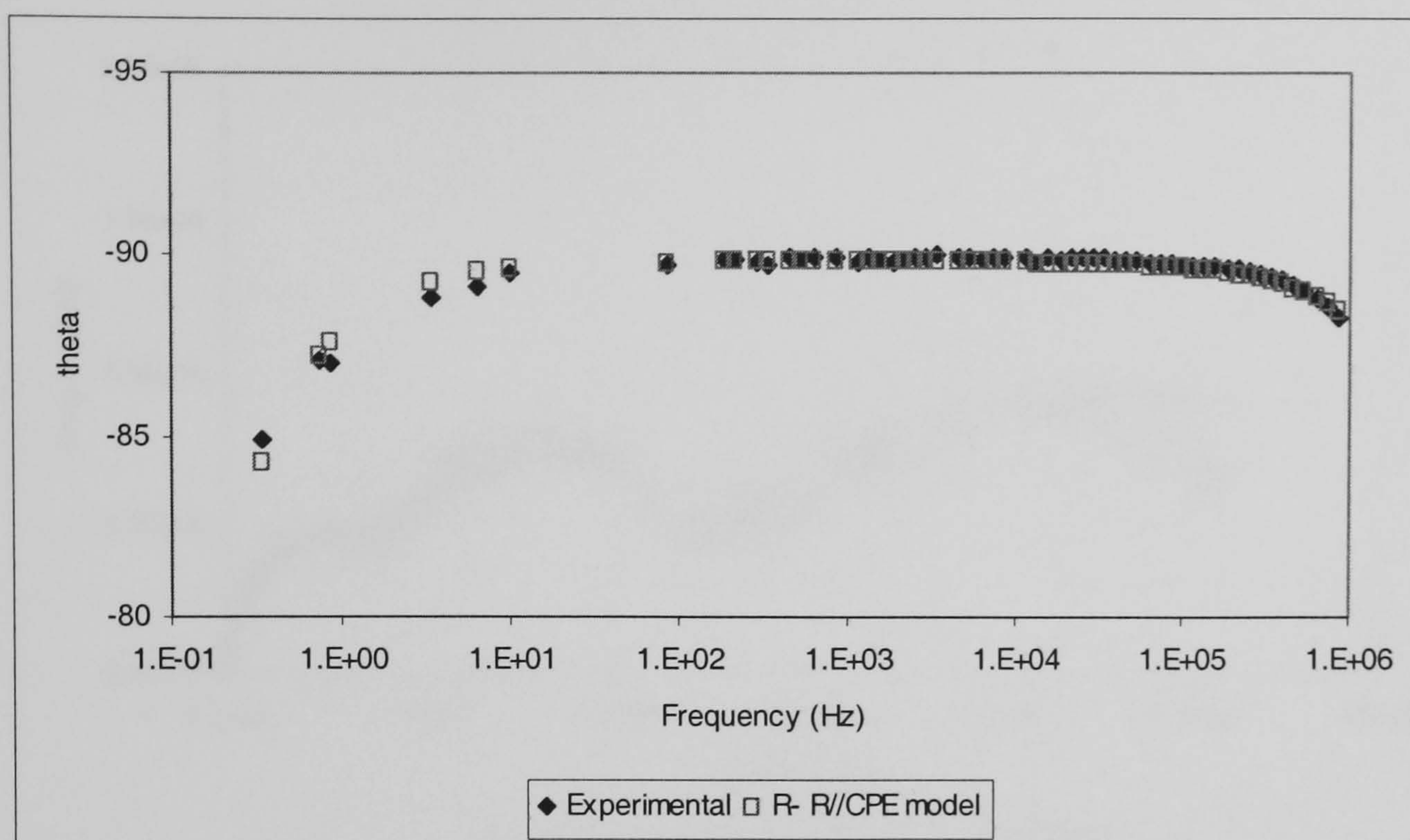


Figure 6-11. Bode plot of experimental and modelled result for $\text{Ba}_2\text{In}_2\text{S}_5$ at 200°C

The Nyquist plot for $\text{Ba}_2\text{In}_2\text{S}_5$ has three arcs at temperatures higher than 250°C , therefore the Bauerle equivalent circuit was used to model impedance data. The Bauerle equivalent circuit is shown in Figure 6-12. Included in Figure 6-13 is the Fricke's equivalent circuit which addresses two-phase compounds, was also used to see if a better fit could be achieved between experimental and modelled data. The fit between experimental and modelled data is shown in the Nyquist and Bode Plots, Figure 6-14 and Figure 6-15, respectively.

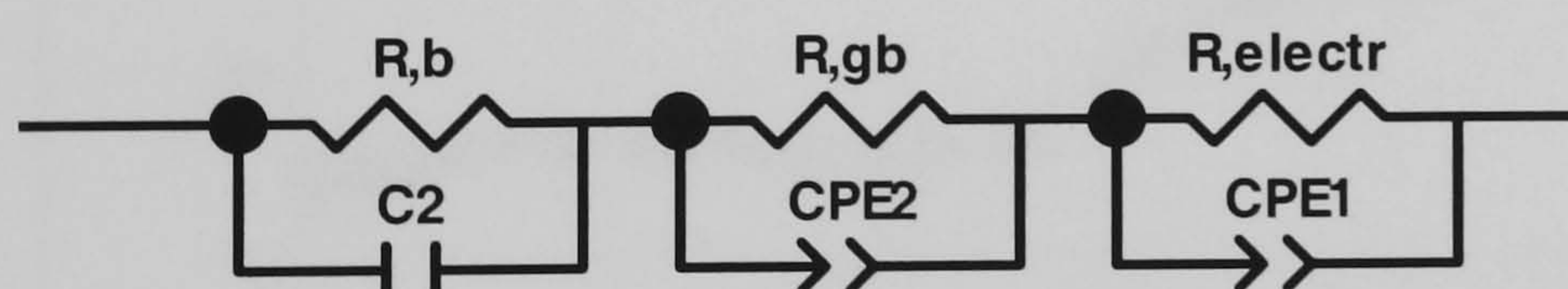


Figure 6-12. Bauerle Equivalent circuit used for modelling $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Zr}_x\text{S}_5$ throughout $200\text{--}450^\circ\text{C}$

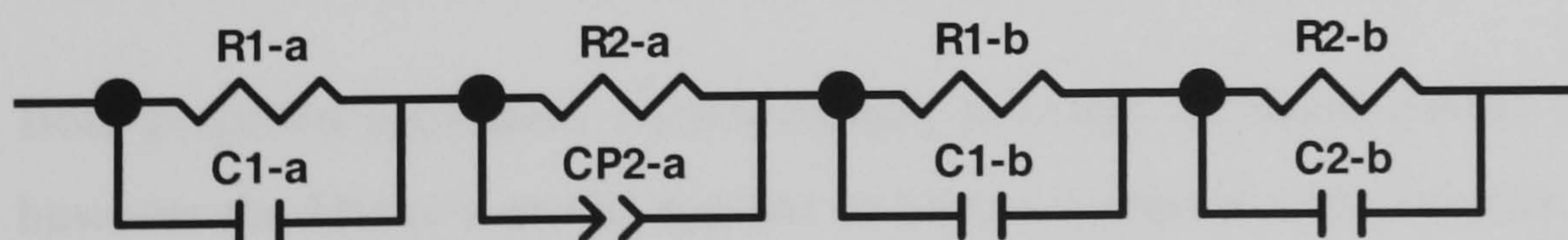


Figure 6-13. Fricke equivalent circuit for a matrix of two phases used for modelling $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Zr}_x\text{S}_5$ throughout $200\text{--}450^\circ\text{C}$

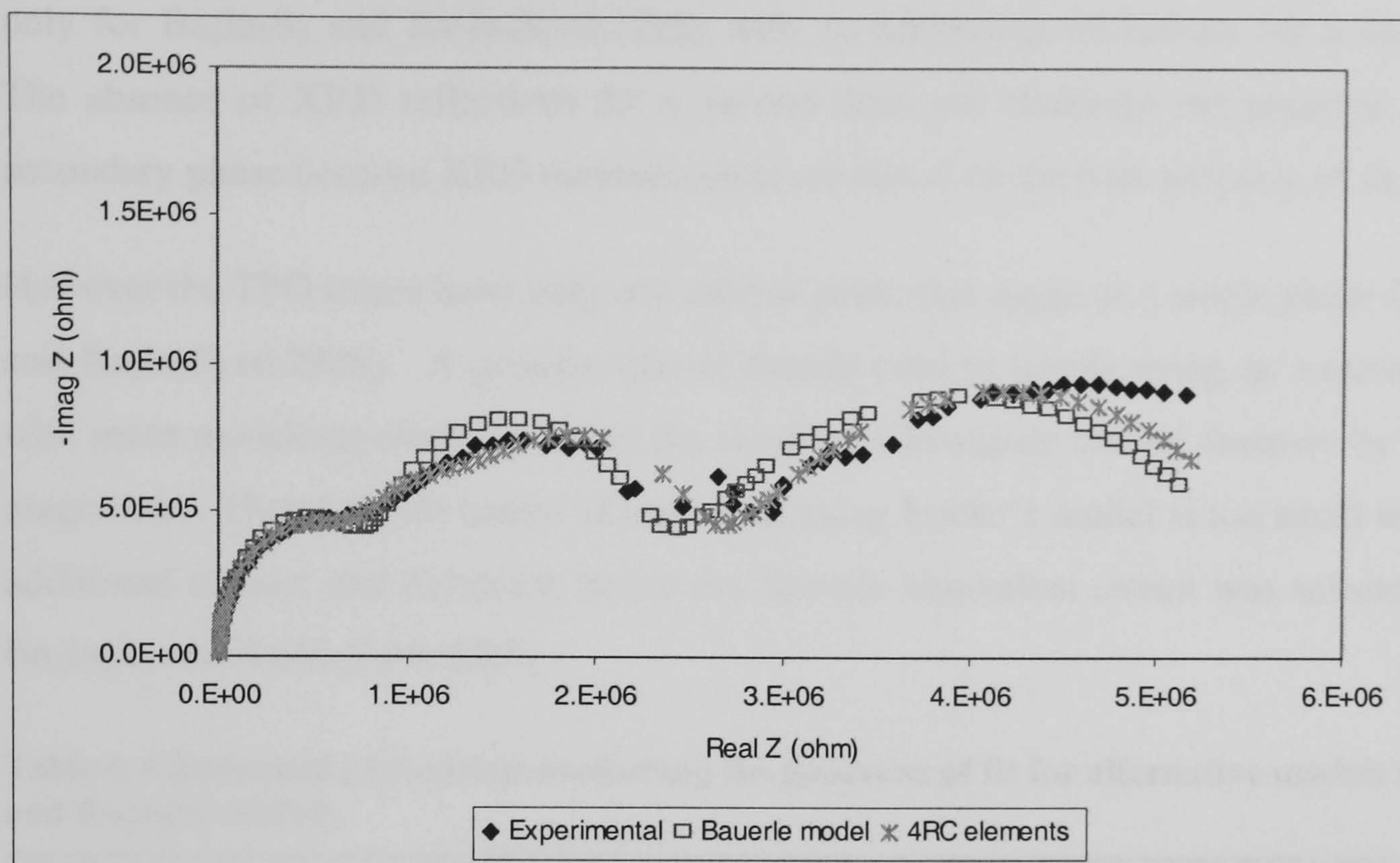


Figure 6-14 Nyquist plot of experimental and modelled results for $\text{Ba}_2\text{In}_2\text{S}_5$ at 450°C in argon

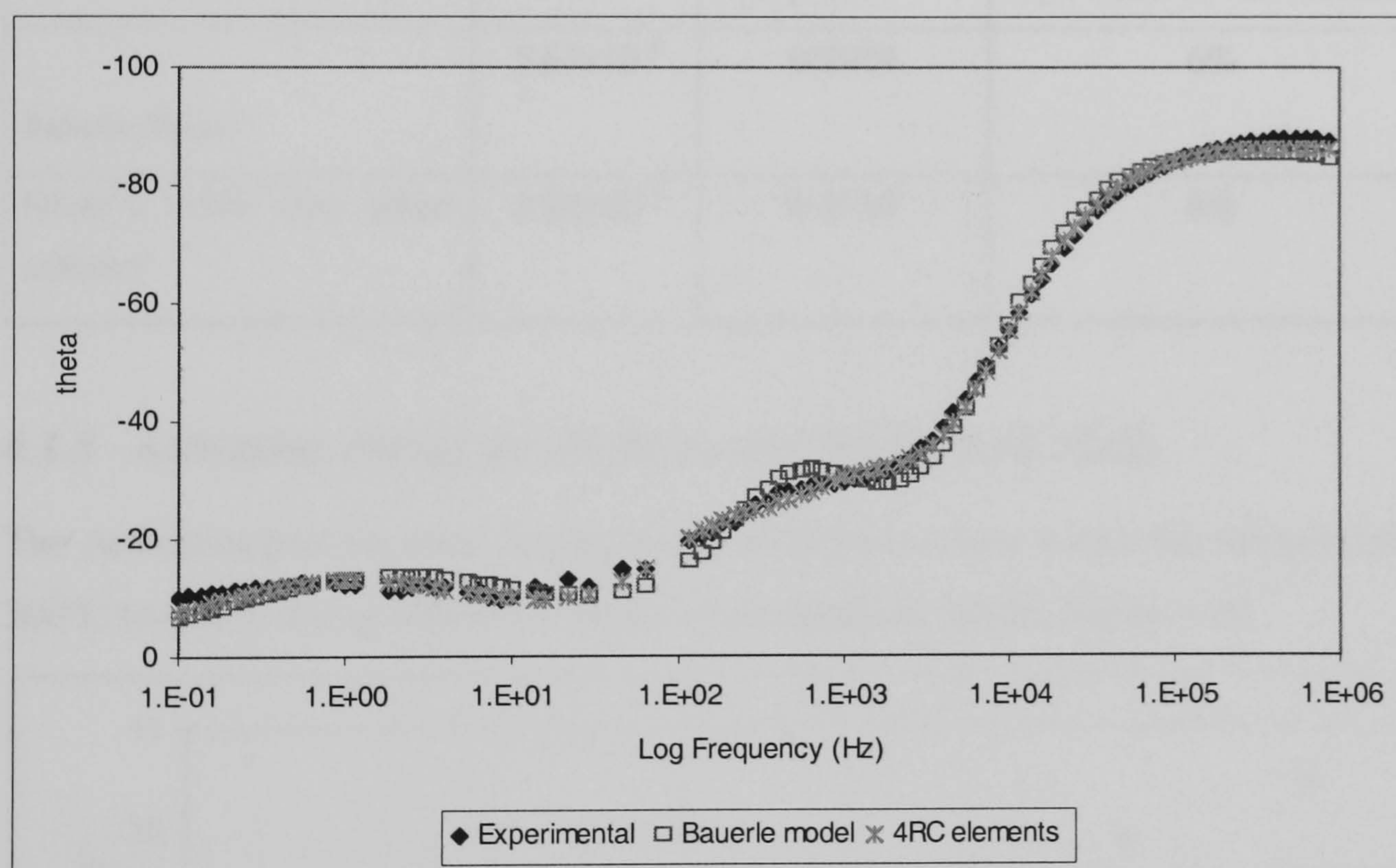


Figure 6-15 Bode plot of experimental and modelled results for $\text{Ba}_2\text{In}_2\text{S}_5$ at 450°C in argon

Both proposed equivalent circuits closely matched the experimental data at all frequencies, however the Fricke's model appears to have a marginal improvement in the goodness of fit, Figure 6-15. The statistical parameters Chi-square and Sum-of-Squares, should be minimised for the best model, Table 6.4. The Fricke equivalent circuit was most suitable since the Chi-square and Sum-of-Squares and maximum error on an equivalent circuit element were minimum. The Fricke model is physically justifiable since the sulphides were made from two starting sulphides, $\text{Ba}_2\text{In}_2\text{S}_5$ and ZrS_2 or BaS and In_2S_3 , therefore it is conceivable that more than one phase may be present. However, the XRD's of these compounds have reflections

only for $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$ with no additional reflections for a second phase. The absence of XRD reflections for a second does not eliminate the presence of a minor secondary phase because XRD measurements are based on the bulk property of the sample.

However the TPO traces have only one narrow peak, this suggests a single phase for $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$. A generic rule of thumb used to justify using an equivalent circuit with more modelling elements is that the resulting Chi-square should decrease by an order of magnitude. Therefore the extent of reduction using Fricke’s model is too small to justify the additional resistor and capacitor, hence the Bauerle equivalent circuit was selected to model $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$.

Table 6.4 Statistical parameters evaluating the goodness of fit for alternative models for BaIn_2S_5 and $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$

Models	Chi-square	Weighted-sum-of-squares	Maximum error on equivalent circuit element
Bauerle Model	5.65×10^{-3}	0.9904	6%
Fricke’s model (two phase mixture)	2.02×10^{-3}	0.3539	6%

6.1.5 Activation energy for $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$

The Arrhenius plot for ionic hopping in the BaIn_2S_5 is linear within the temperature range from 300°C to 450°C using either the Fricke or the Bauerle model, Figure 6-16.

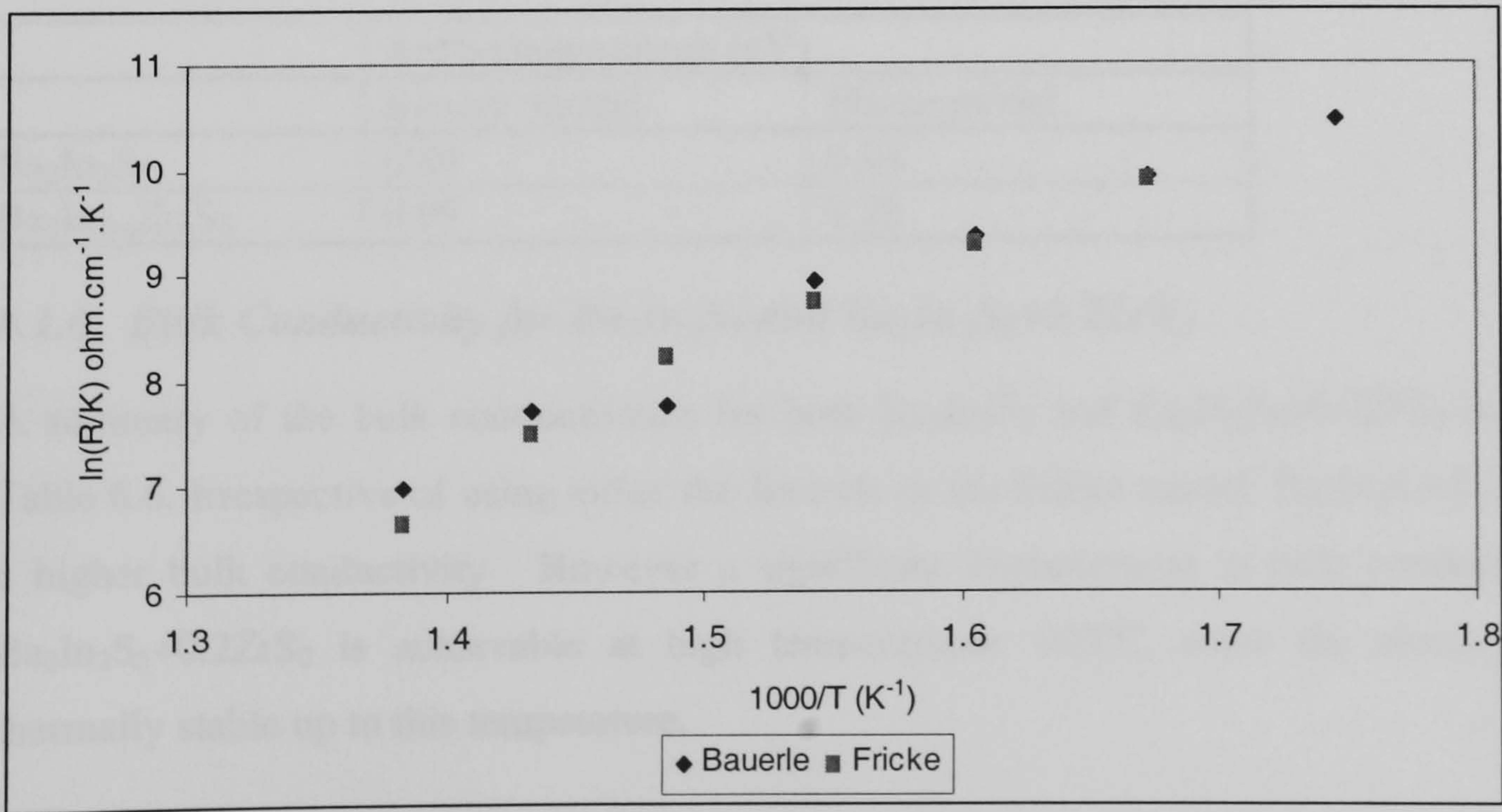


Figure 6-16 Activation energy for ionic hopping of $\text{Ba}_2\text{In}_2\text{S}_5$ in argon from 300-450°C

The activation energy is slightly smaller when calculated using the Bauerle model compared with the Fricke model, Table 6.5 Therefore the selection of the appropriate equivalent circuit affects the activation energy that is a derived parameter

The Arrhenius plot for ionic hopping in the $Ba_2In_{2-x}Zr_xS_5$ is also linear between 300-450°C using either the Fricke or the Bauerle model, Figure 6.16. The activation energy reduces slightly when calculated using the Bauerle model compared to the Fricke model, Table 6.5.

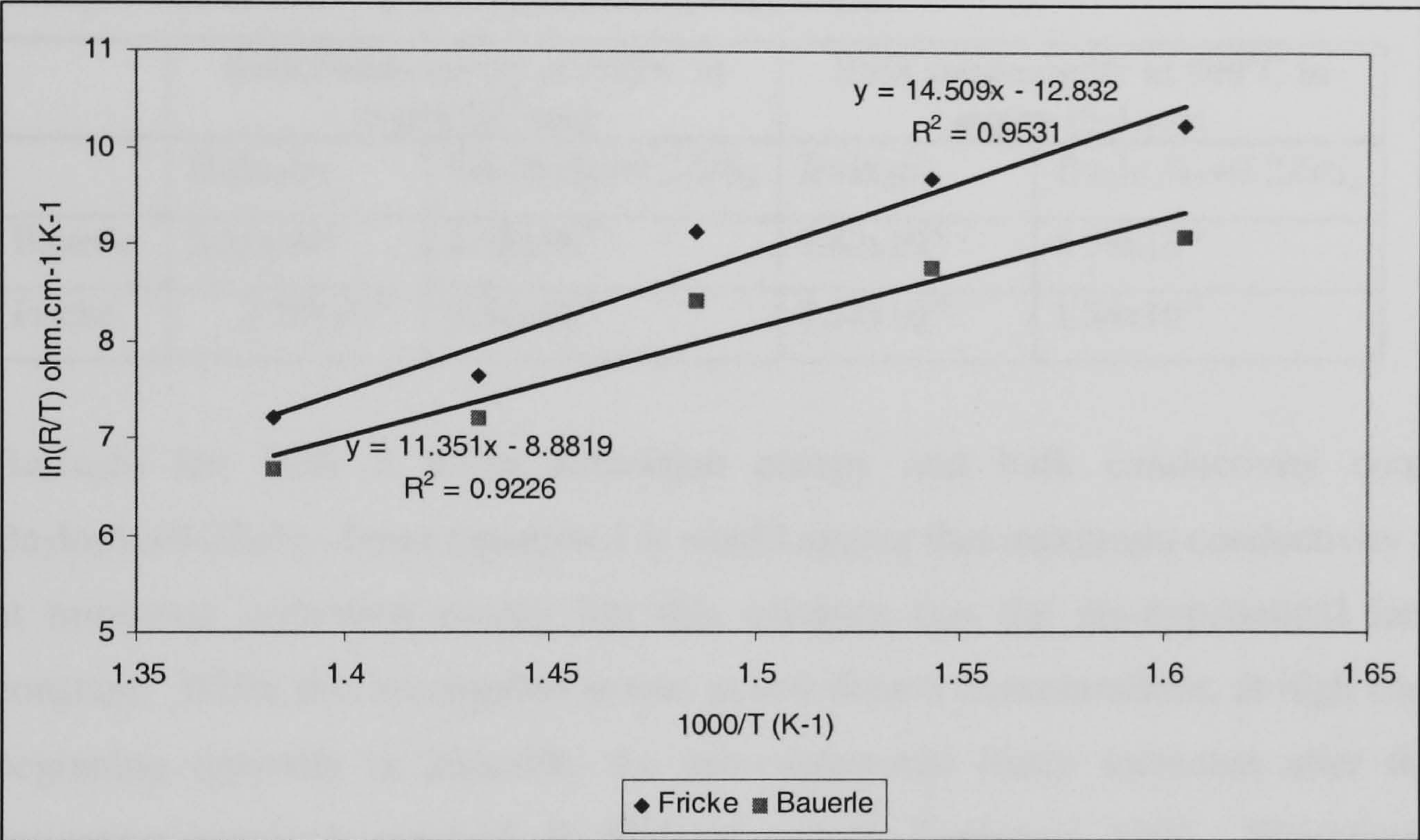


Figure 6-17. Activation energy for $Ba_2In_2S_5+0.2ZrS_2$ in argon from 300-450°C

Table 6.5. Activation energy for $Ba_2In_2S_5$ and $Ba_2In_2S_5+0.2ZrS_2$ based on the Fricke and the Bauerle models

	Activation energy (eV)	
	Bauerle model	Fricke model
$Ba_2In_2S_5$	0.84	0.94
$Ba_2In_{2-x}Zr_xS_5$	0.99	1.25

6.1.6 Bulk Conductivity for $Ba_2In_2S_5$ and $Ba_2In_2S_5+0.2ZrS_2$

A summary of the bulk conductivities for both $Ba_2In_2S_5$ and $Ba_2In_2S_5+0.2ZrS_2$ is given in Table 6.6. Irrespective of using either the Bauerle or the Fricke model, $Ba_2In_2S_5+0.2ZrS_2$ has a higher bulk conductivity. However a significant improvement in bulk conductivity for $Ba_2In_2S_5+0.2ZrS_2$ is achievable at high temperatures, 900°C, since the electrolytes are thermally stable up to this temperature.

The bulk conductivity was calculated using equation 1:

$$\sigma T = A \exp(- E_a / kT) \tag{1}$$

- σ - conductivity
- A- pre-exponential factor
- E_a - activation energy of electrical energy

Table 6.6. Bulk Conductivity for Ba₂In₂S₅ and Ba₂In₂S₅+0.2ZrS₂ measure at 500°C and extrapolated to 900°C in an argon atmosphere argon

	Bulk conductivity at 500°C in argon (S ⁻¹ .cm)		Bulk conductivity at 900°C in argon (S-1.cm)	
	BaIn ₂ S ₅	Ba ₂ In ₂ S ₅ +0.2ZrS ₂	BaIn ₂ S ₅	Ba ₂ In ₂ S ₅ +0.2ZrS ₂
Bauerle	2.61x10 ⁻⁶	4.28x10 ⁻⁶	1.42x10 ⁻⁴	5.38x10 ⁻⁴
Fricke	3.20x10 ⁻⁶	3.44x10 ⁻⁶	2.54x10 ⁻⁴	1.54x10 ⁻³

Ba₂In₂S₅ has both a lower activation energy and bulk conductivity compared with Ba₂In₂S₅+0.2ZrS₂. From equation 1 it would appear that maximum conductivity would occur at minimum activation energy but this assumes that the pre-exponential factor remains constant. While this assumption is true at low dopant concentrations, at high concentrations, beginning typically at 20mol%, the pre-exponential factor increases after the minimum activation energy is reached, H. Hideaki and H. Tagwawa, 1996. Therefore doping the BaIn₂S₅ with a large excess of 20mol% ZrS₂ led to an increase in bulk conductivity and activation energy. Therefore the pre-exponential factor could not have remained constant since the minimum activation does not coincide with maximum conductivity.

6.1.7 Time Constant Analysis for Ba₂In₂S₅ and Ba₂In₂S₅+0.2ZrS₂

Conduction of the larger sulphide ion is expected to have a larger time constant compared with oxide ion conduction at comparable temperature. The time constants for doped BaIn₂S₅ and Ba₂In₂S₅+0.2ZrS₂ are several orders of magnitude greater than the oxide ion conducting YSZ, even though the measurement was done at a higher temperature, 350°C verses 240°C, Tables 6.7 and 6.8. Therefore the large time constant for the bulk conduction in BaIn₂S₅ and Ba₂In₂S₅+0.2ZrS₂ favours the larger sulphide ion conduction.

Table 6.7. Time constant analysis for Ba₂In₂S₅ and Ba₂In₂S₅+0.2ZrS₂ with graphite electrode

Ba₂In₂S₅ at 350°C Bauerle		Ba₂In₂S₅+0.2ZrS₂ at 350°C Bauerle	
Bulk	Grain boundary	Bulk	Grain boundary
R = 4.91x10 ⁶ Ω	R = 3.64x10 ⁶ Ω	R = 5.48x10 ⁶ Ω	R = 1.74x10 ⁶⁷ Ω
C = 2.50x10 ⁻¹¹ F	C = 5.79x10 ⁻¹⁰ F	C = 6.05x 10 ⁻¹¹ F	C = 6.46x10 ⁻¹¹ F
τ = 1.33x10 ⁻⁴ s	τ = 1.82x10 ⁻³ s	τ = 2.22x10 ⁻⁴ s	τ = 1.12x10 ⁻³ s
Ba₂In₂S₅ at 350°C Fricke		Ba₂In₂S₅+0.2ZrS₂ at 350°C Fricke	
Bulk	Grain boundary	Bulk	Grain boundary
R = 6.80x10 ⁶ Ω	R = 3.17x10 ⁶ Ω	R = 1.75x10 ⁶ Ω	R = 6.27x10 ⁶ Ω
C = 2.60x10 ⁻¹¹ F	C = 3.40x10 ⁻¹⁰ F	C = 2.88x10 ⁻¹¹ F	C = 3.10x10 ⁻⁹ F
τ = 1.77x10 ⁻⁴ s	τ = 1.08x10 ⁻³ s	τ = 6.44x10 ⁻⁴ s	τ = 1.95x10 ⁻² s

Table 6.8. Circuit parameters for Zr₂O+6mo% Y₂O₃ at 240°C, Bauerle 1969

Grain interior (bulk)	Grain Boundary	Electrode blocking
R _{gi} = 2.1MΩ	R _{gb} = 1.5MΩ	R _e = 5.0MΩ
C _{gi} = 4.8pF	C _{gb} = 1.7nF	C _e = 2.0μF
τ = 1.01x10 ⁻⁵ s	τ = 2.55x10 ⁻³ s	τ = 1.0s

6.1.8 H₂S Concentration dependence of bulk conductivity for Ba₂In₂S₅ and Ba₂In₂S₅+0.2ZrS₂

Impedance spectroscopy of Ba₂In₂S₅ and Ba₂In_{2-x}Zr_xS₅ using graphite electrodes in an argon atmosphere produced an ionic blocking electrode arc, thus inferring pure ionic conduction. A secondary condition for ionic conduction. However if the bulk conductivity remains unchanged when the H₂S partial pressure is varied. Therefore impedance spectroscopy was carried out from 350°C to 550°C with the concentration of H₂S/Ar varying from 18vol% to 0.0vol% for each temperature measured. Using one-hour isothermal period allows for both the temperature and concentration stabilization prior to impedance measurements.

A conductivity that increases with increasing sulphur concentration at high H₂S concentration indicates the presence of hole conduction: it may occur via equation 2.



Where

$V_{S^{2-}}$ - sulphide anion vacancy

S^{2-} - sulphur anion in unit cell

\oplus - electron hole

Thus increasing the sulphur partial pressure increases the number of electron holes and increases the conductivity of the electrolyte.

The bulk conductivity of $Ba_2In_2S_5$ remains independent of H_2S concentration from 0vol% H_2S /Ar to 1.0vol% H_2S /Ar confirming ionic conduction under these conditions, Figure 6-18. However increasing the H_2S concentration from 1.0vol% H_2S /Ar to 2.0vol% H_2S /Ar caused a corresponding increase in bulk conductivity at higher temperatures, Figure 6-18. This infers that the interaction between vacant sulphide ion sites and sulphur expressed in equation 2 begins at concentrations higher than 1vol% H_2S /Ar, Figure 6-18.

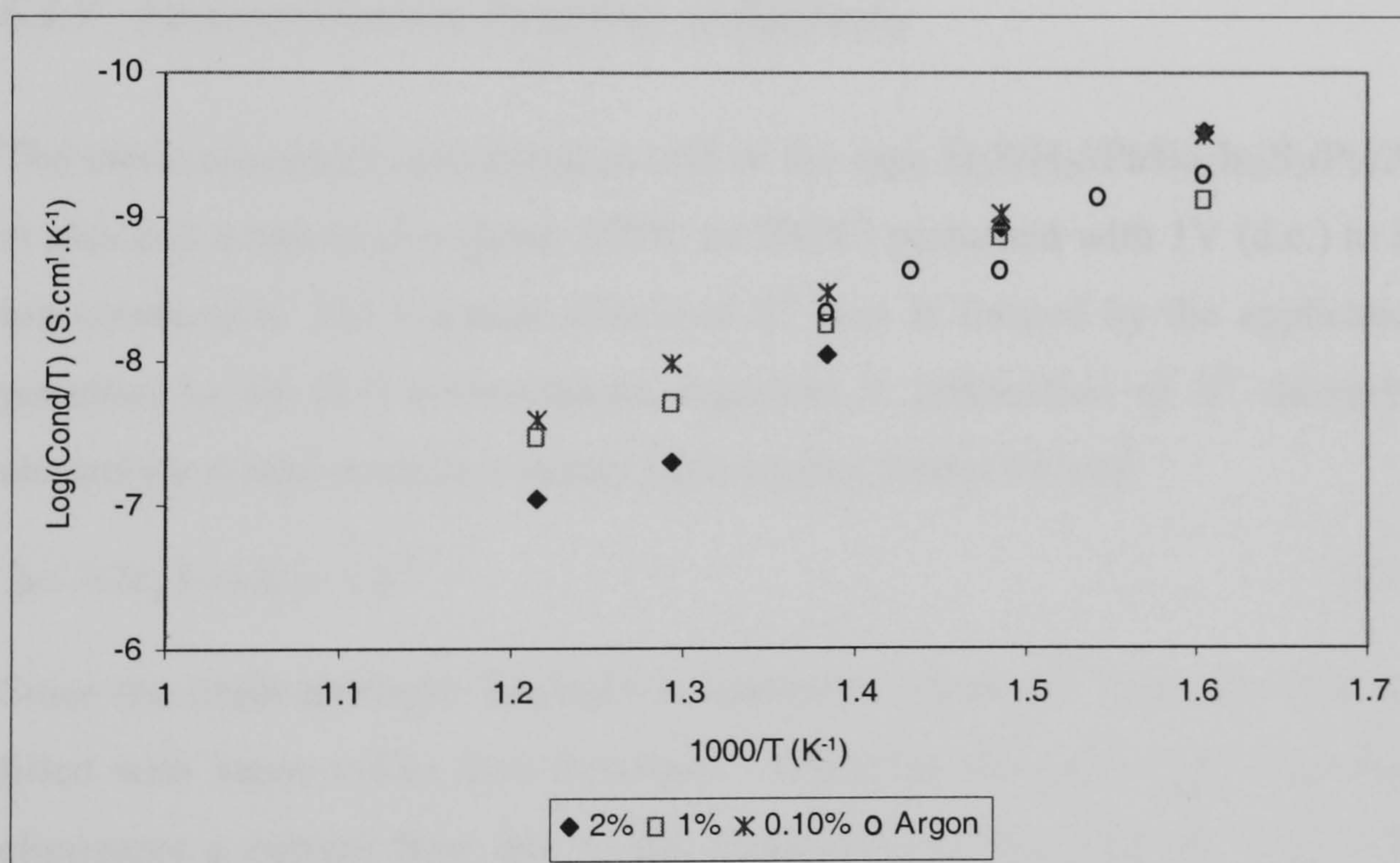


Figure 6-18 Bulk conductivity of $Ba_2In_2S_5$ measured in different atmospheres

Similarly, the bulk conductivity of $Ba_2In_2S_5+0.2ZrS_2$ remained independent of the concentration of hydrogen sulphide from 0vol% H_2S /Ar to 1vol% H_2S at all temperatures measured, from 350 to 550°C, which indicates ionic conduction, Figure 6-19. However increasing the H_2S concentration from 1.0vol% H_2S /Ar to 2.0vol% H_2S /Ar causes a corresponding decrease in bulk conductivity confirming the onset of electronic conduction at 2vol% H_2S /Ar, Figure 6-19.

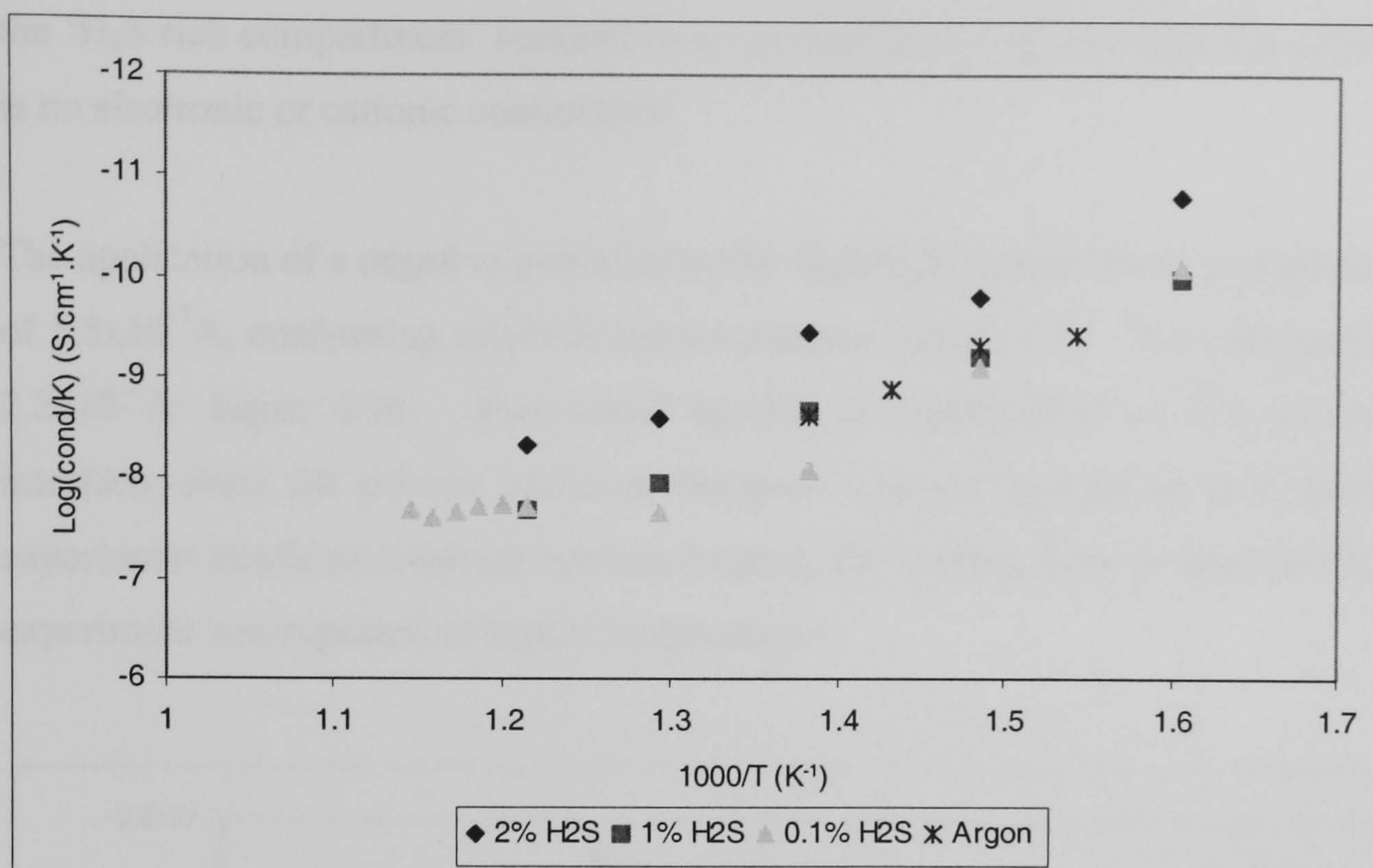


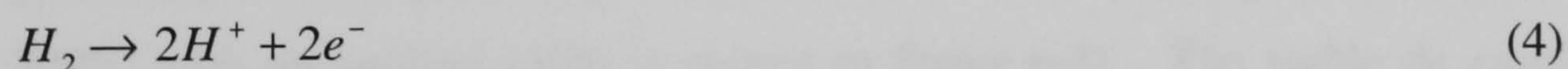
Figure 6-19. Bulk conductivity of $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$ measured in different atmospheres

6.1.9 Electrochemical Pumping of $\text{Ba}_2\text{In}_2\text{S}_5$

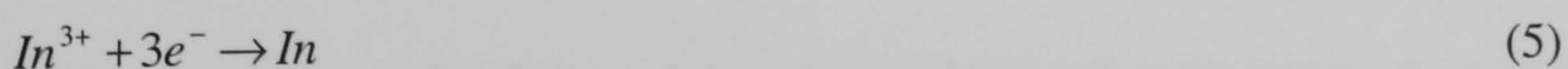
The electrochemical concentration cell of the type $\text{H}_2\text{S}/\text{H}_2//\text{Pt}/\text{Ba}_2\text{In}_2\text{S}_5/\text{Pt}/\text{Ar}/$ was operated at elevated temperatures (from 550°C to 700°C) perturbed with 1V (d.c.) to identify sulphide ion conduction. The constant source of S^{2-} ions is formed by the application of a negative potential to the H_2S compartment, equation 3; conduction of S^{2-} through a sulphide ion electrolyte would produce a steady state current within the cell.



Since the oxide analogue $\text{Ba}_2\text{In}_2\text{O}_5$ is known to conduct H^+ ions, the H_2S free chamber was filled with argon rather than hydrogen. Changing the carrier gas from hydrogen to argon eliminates a current flow due to the conduction of H^+ ; with the application of a positive potential, see equation 4.



If the current generated with the application of a negative potential to the 'H₂S rich compartment' decays, then the transfer of a positive ion is interpreted; a decaying current because there is no continuous source of positive ions, only from the electrolyte). For example the conduction of indium ions, via the electrolytic reduction to metal, equation 5.



The electrochemical response of BaIn_2S_5 at 600°C with an applied 1Vdc is shown in Figure 6-20. The first dc current generated, $4.5 \times 10^{-8}\text{A}$, with the application of a positive potential to

the 'H₂S rich compartment' resulted in no current flow, and therefore this confirms that there is no electronic or cationic conduction.

The application of a negative potential to the 'H₂S rich compartment' produced a peak current of 5.5×10^{-7} A, confirming sulphide ion conduction, Figure 6-20. The peak current decayed to 2.2×10^{-7} A; Figure 6-20. This could be due to stabilization of the electrode-electrolyte interface, since the painted platinum electrode was not previously heat-treated. While this experiment confirms sulphide ion conduction, the current flow is very small; therefore the experiment was repeated at higher temperatures.

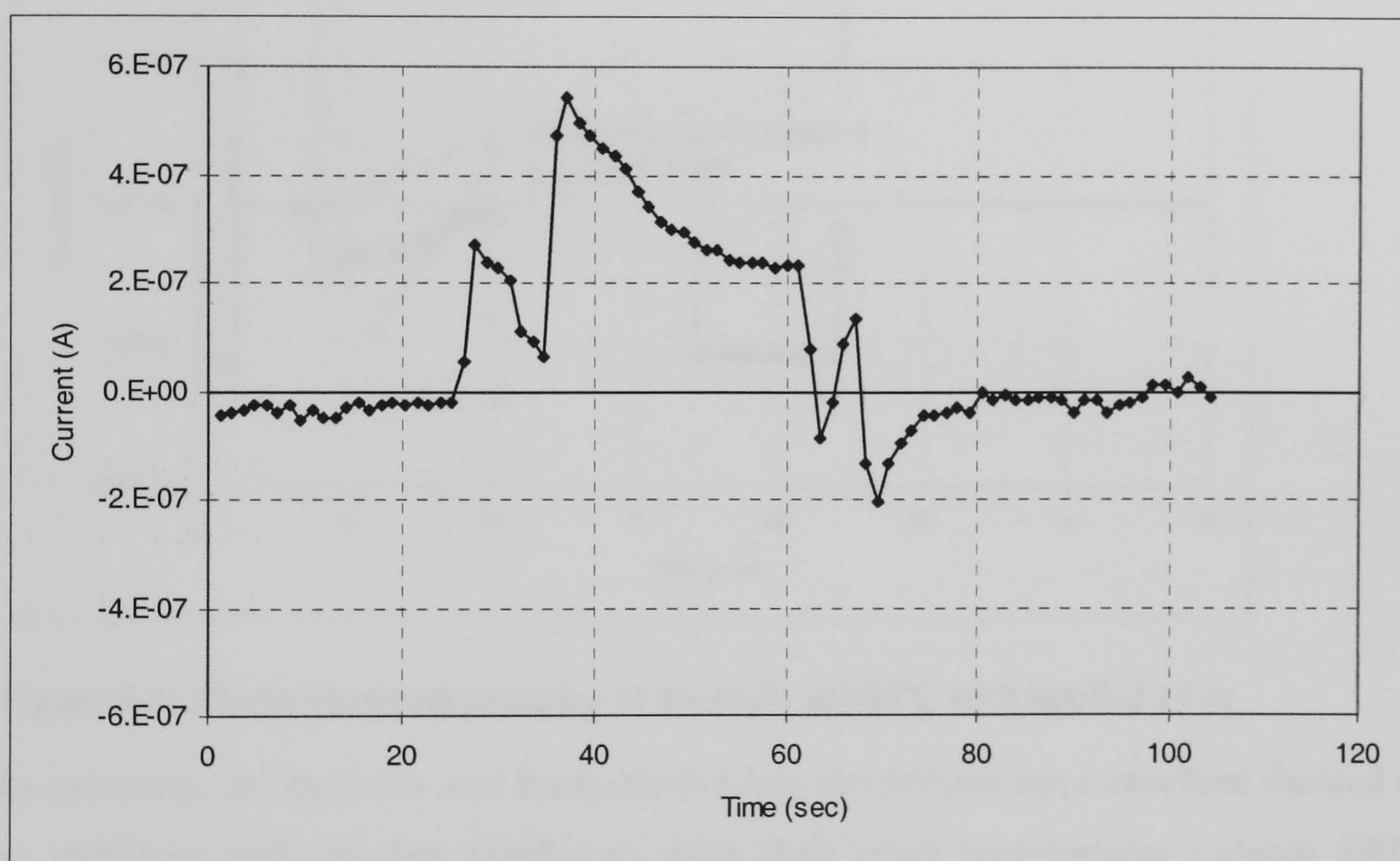


Figure 6-20. Electrochemical pumping of Ba₂In₂S₅ at 600°C with applied 1Vdc

Electrochemical pumping of Ba₂In₂S₅ was repeated at higher temperatures to observe the possibility of an improvement in current flow. The electrochemical response of Ba₂In₂S₅ at 700°C with an applied 1Vdc is shown in Figure 6-21. The stable dc current generated of 1.1×10^{-4} A, with the application of a negative potential to the 'Ar rich compartment' indicates either that there is electronic conduction or that H₂S is bypassing into this chamber. The presence of electronic conduction was deduced by the significant current flow that occurred without the application of a potential, Figure 6-21.

The repeatability and stability of the current flow with application of a negative potential to the 'Ar rich compartment' infers no cationic conduction or electrolytic reduction of the

electrolyte under these experimental conditions, since this would have lead to decaying current according to equation 5.

The application of a negative potential to the 'H₂S rich compartment' produced a much larger peak current of 1.75×10^{-4} A, confirming sulphide ion conduction, Figure 6-21. While this experiment also confirms sulphide ion conduction, the reason for the significant current with the application of a negative potential to the 'Ar rich compartment', exclusive of the leakage of H₂S into the 'Ar rich compartment' needs to be determined and possibly eliminated.

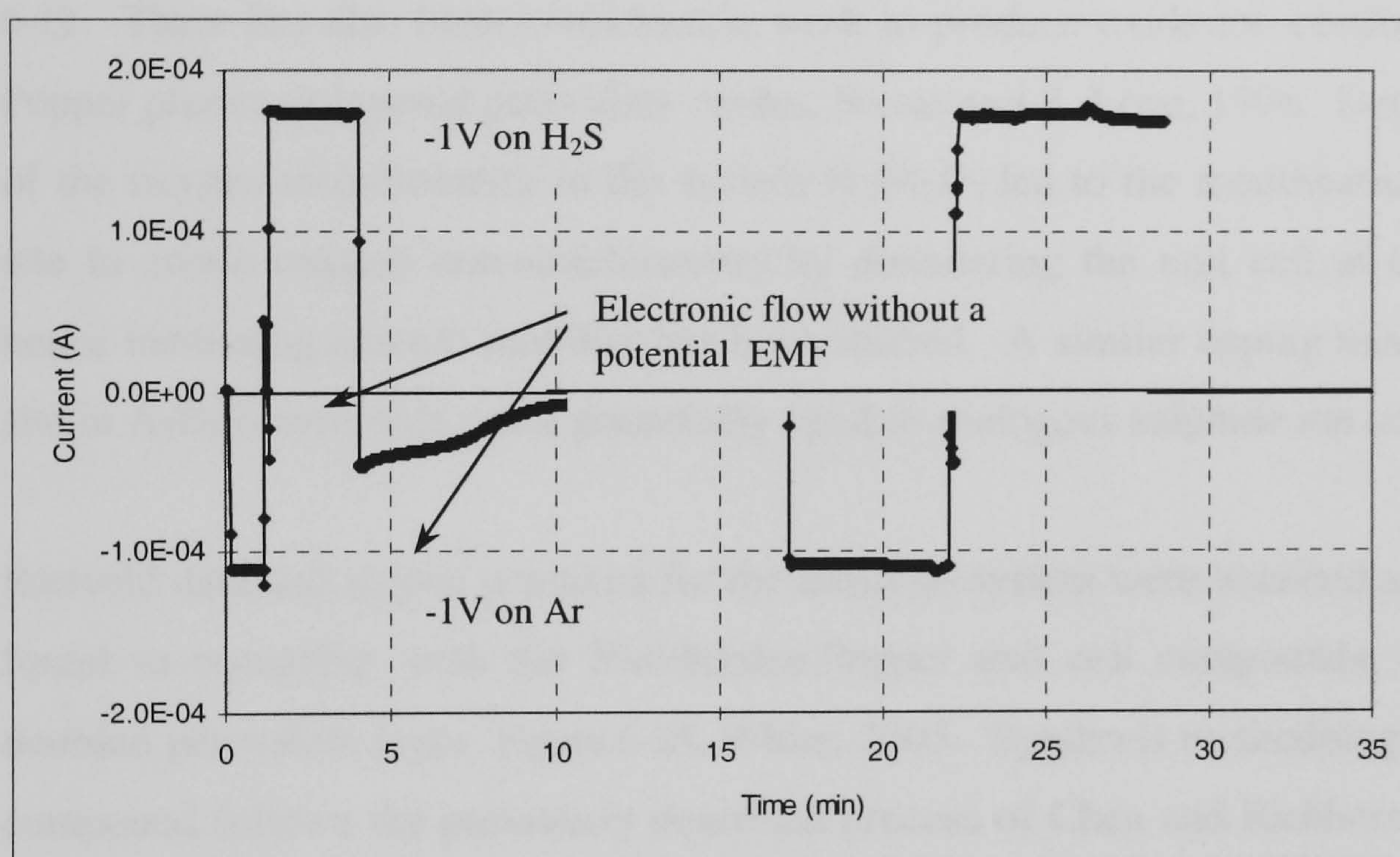


Figure 6-21 Electrochemical pumping of Ba₂In₂S₅ at 700°C with applied 1Vdc

In summary, the Ba₂In₂S₅ and Ba₂In₂S₅+0.2ZrS₂ electrolytes have excellent thermal stability in oxidizing and reducing conditions since their onset temperatures exceeds 840°C. The electrochemical characterisation of both compounds shows the distinct Warburg impedance that confirms that these electrolytes are pure ionic conductors. Further investigation of the variation of the bulk conductivity with respect to various H₂S concentrations was measured using impedance spectroscopy. The results of these experiments shows that the bulk conductivity for both electrolytes remains independent of the atmosphere as it varied from 0vol%H₂S/Ar to 1vol%H₂S/Ar confirming ionic conduction. However a further increase in H₂S concentration causes the onset of electronic conduction that is more pronounced for Ba₂In₂S₅+0.2ZrS₂. Therefore using a dopant concentration less than 20mol%ZrS₂ could improve the bulk conductivity without introducing electronic conduction.

6.2 The Ruddlesden-Popper BaZr_3S_7 Electrolyte

Various doped and un-doped strontium, titanium oxide compounds with Ruddlesden-Popper crystal structure have been previously synthesised that have the ability to conduct oxide anions, Shimura, *et. al.* 1998. The Ruddlesden-Popper, or layered perovskite, unit cell is considered as a distortion of the ideal cubic structure. Ruddlesden-Popper phases consist of intergrowths of perovskite blocks (ABO_3) with rock salt layers (AO); these blocks arrange themselves in the form $(\text{ABO}_3)_n (\text{AO})$ according to the “n” number of the compound, Figure 6-22. There has also been considerable work to produce oxide-ion conducting Ruddlesden-Popper phases or layered perovskite oxides, Navas and Z. Loe, 1996. Detailed investigation of the oxygen stoichiometry in the system $\text{Sr}_3\text{M}_2\text{O}_7$ led to the modification of the M cation site to create oxygen non-stoichiometry by disordering the unit cell at high temperatures; hence increasing anionic mobility has been studied. A similar doping modification of the B site in $\text{A}_3\text{B}_2\text{S}_7$ materials could potentially yield to analogous sulphide ion conductivity.

Rietveld data and atomic positions for the $\text{Ba}_3\text{Zr}_2\text{S}_7$ system were obtained and the system was found to crystallise with the Ruddlesden-Popper unit cell compounds, having a ($n = 2$) doubled perovskite layer, Figure 6-23, White, 2005. Synthesis methodology for the $\text{Ba}_3\text{Zr}_2\text{S}_7$ compound follows the previously described process of Chen and Eichhorn, 1997 that uses a BaCl_2 common ion flux in the preparation from appropriate metallic sulphides, and reacted from the at 1323K (1050°C).

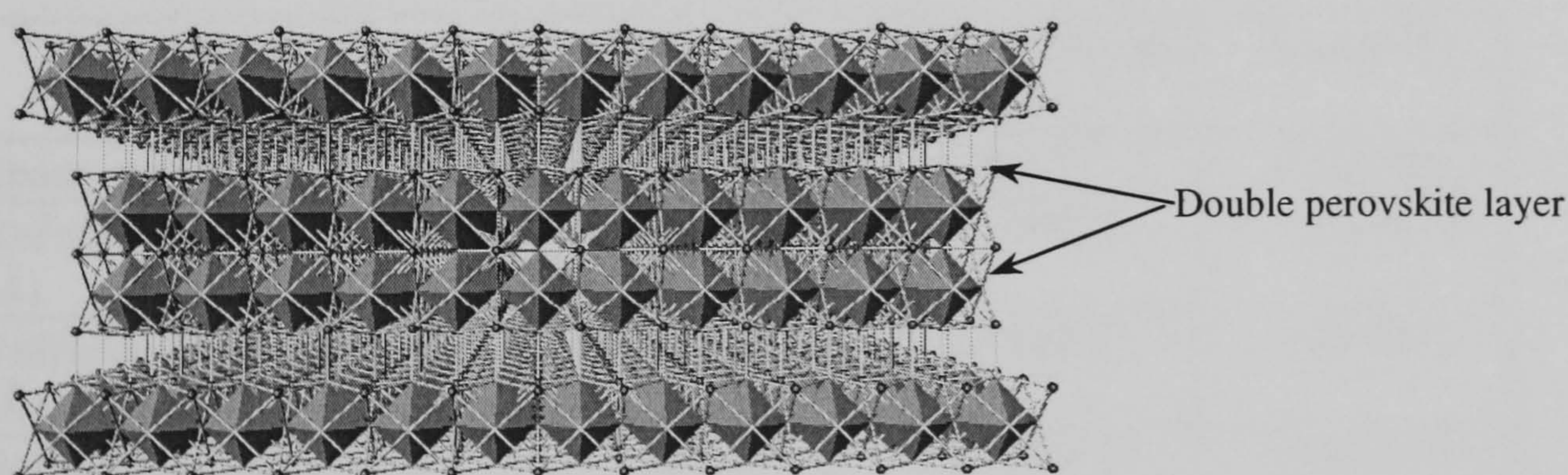


Figure 6-22. Ruddlesden-Popper structure of $\text{Ba}_3\text{Zr}_2\text{S}_7$ ($n = 2$), White, 2005.

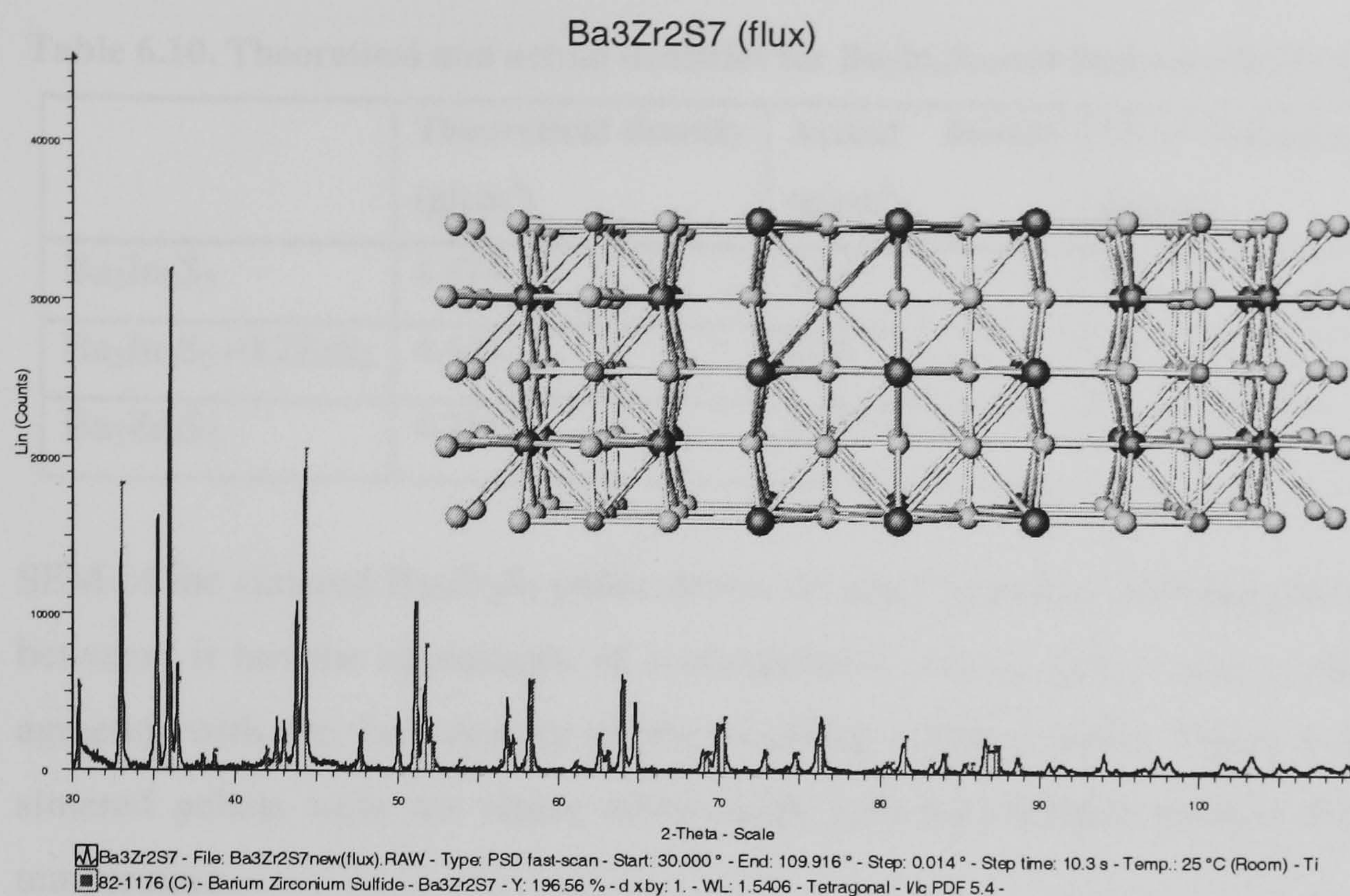


Figure 6-23. Powder X-ray diffraction pattern obtained for the Ba₃Zr₂S₇ material, White 2005

The large cell parameter for the 'c' lattice site shows that this large channel would favour ionic conduction, Table 6.9. Because of the 'open' cell, caused by the large lattice parameter, 'c' for Ba₃Zr₂S₇, the onset temperature for oxidation and reduction maybe small in comparison with the previous AB₂S₄ compounds.

Table 6.9 Refined Atomic Parameters for Ba₂In₂S₅, Ba₂In₂S₅+0.2ZrS₂ and Ba₃Zr₂S₇

Parameter	Ba ₂ In ₂ S ₅	Ba ₂ In ₂ S ₅ +0.2ZrS ₂	Ba ₃ Zr ₂ S ₇
Space group	Pbca	Pbca	I4/mmm
Refined cell parameter <i>a</i> (Å)	13.1643(3)	13.1508(3)	5.0040(3)
Refined cell parameter <i>b</i> (Å)	12.7251(3)	12.7165(3)	5.0040(3)
Refined cell parameter <i>c</i> (Å)	11.7805(3)	11.7732(2)	25.5301(2)
Density g/cm ³ (theoretical)	4.474	4.448	4.254

BaZr₃S₇, ground using a dry ball mill to reduce the average particle size and hence increase the density of the sintered pellet. Ground material was pressed to 10t and sintered to 1080°C. The resulting sintered pellets had a maximum of 75% of the theoretical density, Table 6.10. Increasing the sintering temperature leads to severe curving of pellet.

Table 6.10. Theoretical and actual densities for Ba₂In₂S₅ and Ba₂In₂S₅+0.2ZrS₂ and Ba₃Zr₂S₇

	Theoretical density (g/cm ³)	Actual density (g/cm ³)	% of theoretical density
Ba ₂ In ₂ S ₅	4.474	3.65	85
Ba ₂ In ₂ S ₅ +0.2ZrS ₂	4.448	4.25	95
Ba ₃ Zr ₂ S ₇	4.254	3.17	75

SEM of the sintered Ba₃Zr₂S₇ pellet shows no grain boundary between particles or any pores between; it has the appearance of a compressed powder rather than a sintered pellet, thus agreeing with the low density of the resulting sintered pellet, Figure 6-24. Therefore the sintered pellets were not dense when made with the smallest particle size and maximum temperature.

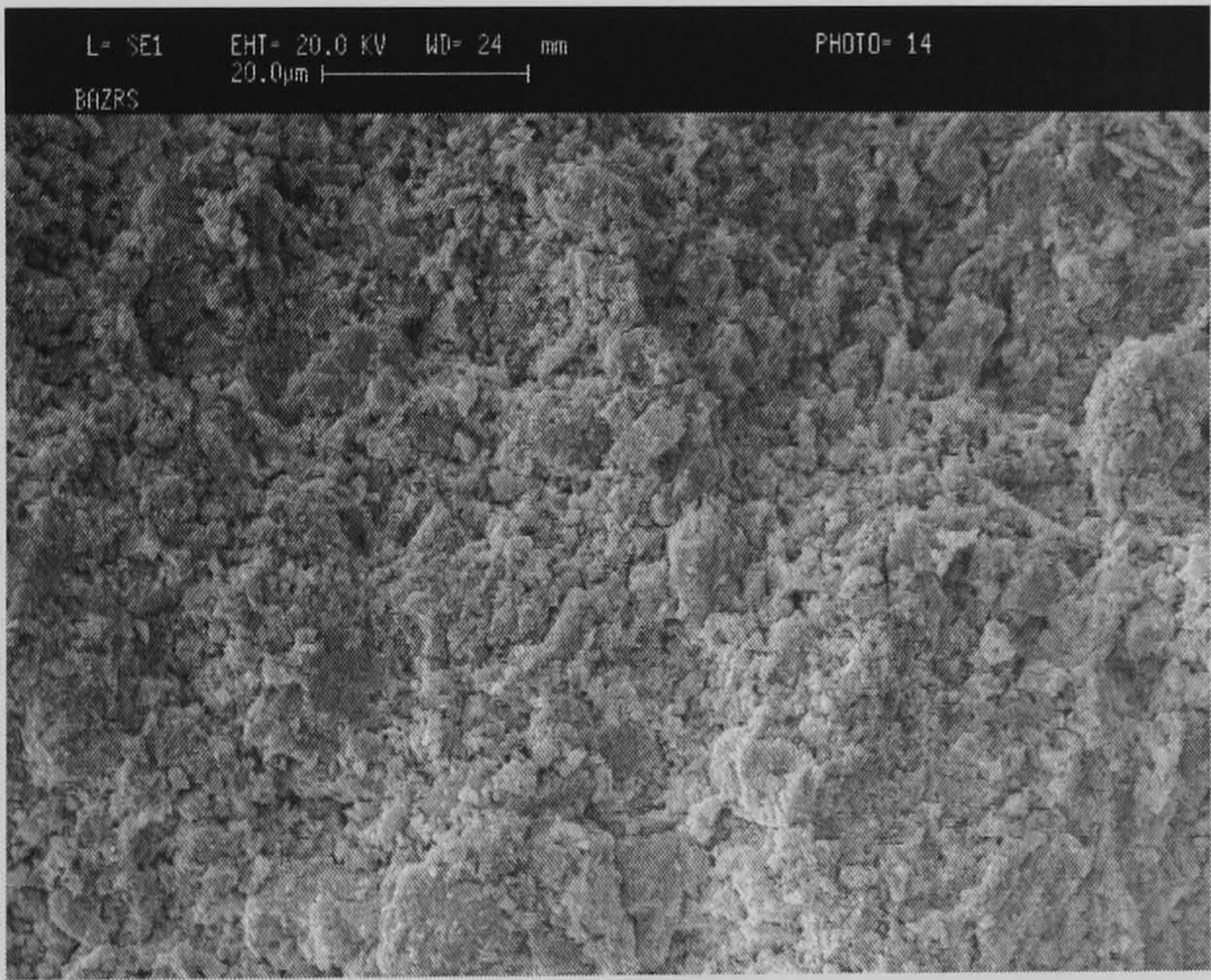


Figure 6-24. Ba₃Zr₂S₇ sintered pellet at 1080°C in H₂S/Ar mixture achieving 75% of theoretical density

6.2.1 TPO and TPR for Ba₃Zr₂S₇

The thermal stability of Ba₃Zr₂S₇ was established using both TPO and TPR techniques. The TPO trace appears to consist of two peaks close to each other with an oxidation onset temperature of 690°C, Figure 6-25. Since the sulphide ion is not equidistant to all cations, the multiple peak of the TPO is a likely characteristic for this type of unit cell. TPO of Ba₃Zr₂S₇ showed that it is the least stable compound in an oxidising atmosphere of the barium-based compounds, Table 6.11. Further detailed analysis involving oxygen and sulphur balances was not done since no relationship was found between percentage of oxidation and ionic conductivity in the CaNd₂S₄ series.

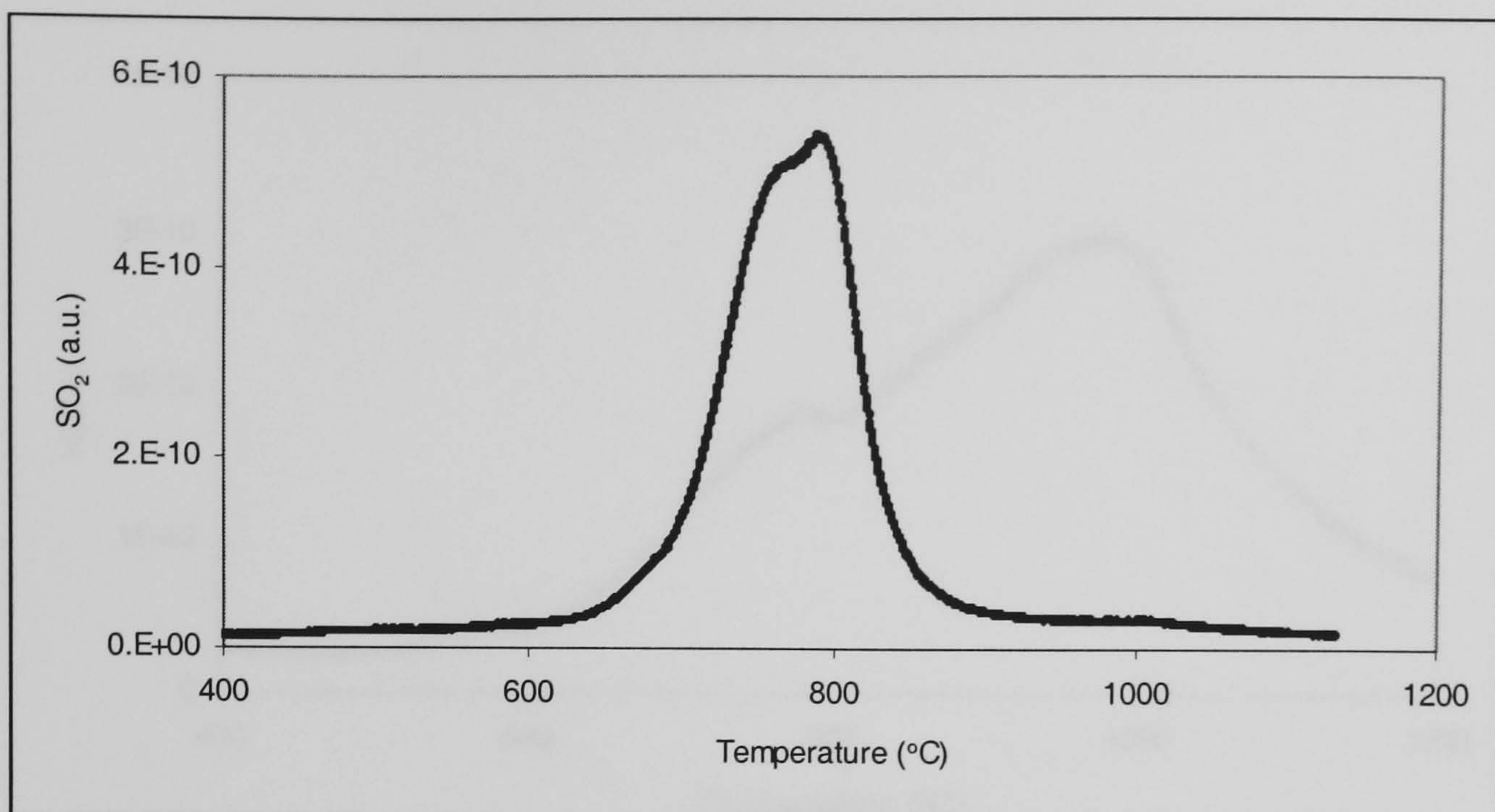


Figure 6-25 TPO of $\text{Ba}_3\text{Zr}_2\text{S}_7$ using $10^\circ\text{C}/\text{min}$ heating rate

Table 6.11. Onset temperatures and Unit Cell Lattice Parameters for $\text{Ba}_2\text{In}_2\text{S}_5$, $\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$, and $\text{Ba}_3\text{Zr}_2\text{S}_7$

	Oxidation Onset Temperature ($^\circ\text{C}$)	Reduction Onset Temperature ($^\circ\text{C}$)	Lattice parameter for 'c' site Å
$\text{Ba}_2\text{In}_2\text{S}_5$	978	845	11.7805(3)
$\text{Ba}_2\text{In}_2\text{S}_5+0.2\text{ZrS}_2$	995	865	11.7732(2)
$\text{Ba}_3\text{Zr}_2\text{S}_7$	670	640	25.5301(2)

*Bracketed () number indicates the standard deviation on the fourth decimal place

Similarly the TPR plot of $\text{Ba}_3\text{Zr}_2\text{S}_7$ has multiple peaks, which also infers a complex reaction reduction mechanism, Figure 6-26. The presence of multiple peaks in both the TPO and TPR suggests that this is related to an inherent property of material, possible due to varying lattice parameter of the unit cell. The low onset temperature, 640°C , for the reduction reaction could also be attributed to the open nature of this unit cell, Figure 6-26.

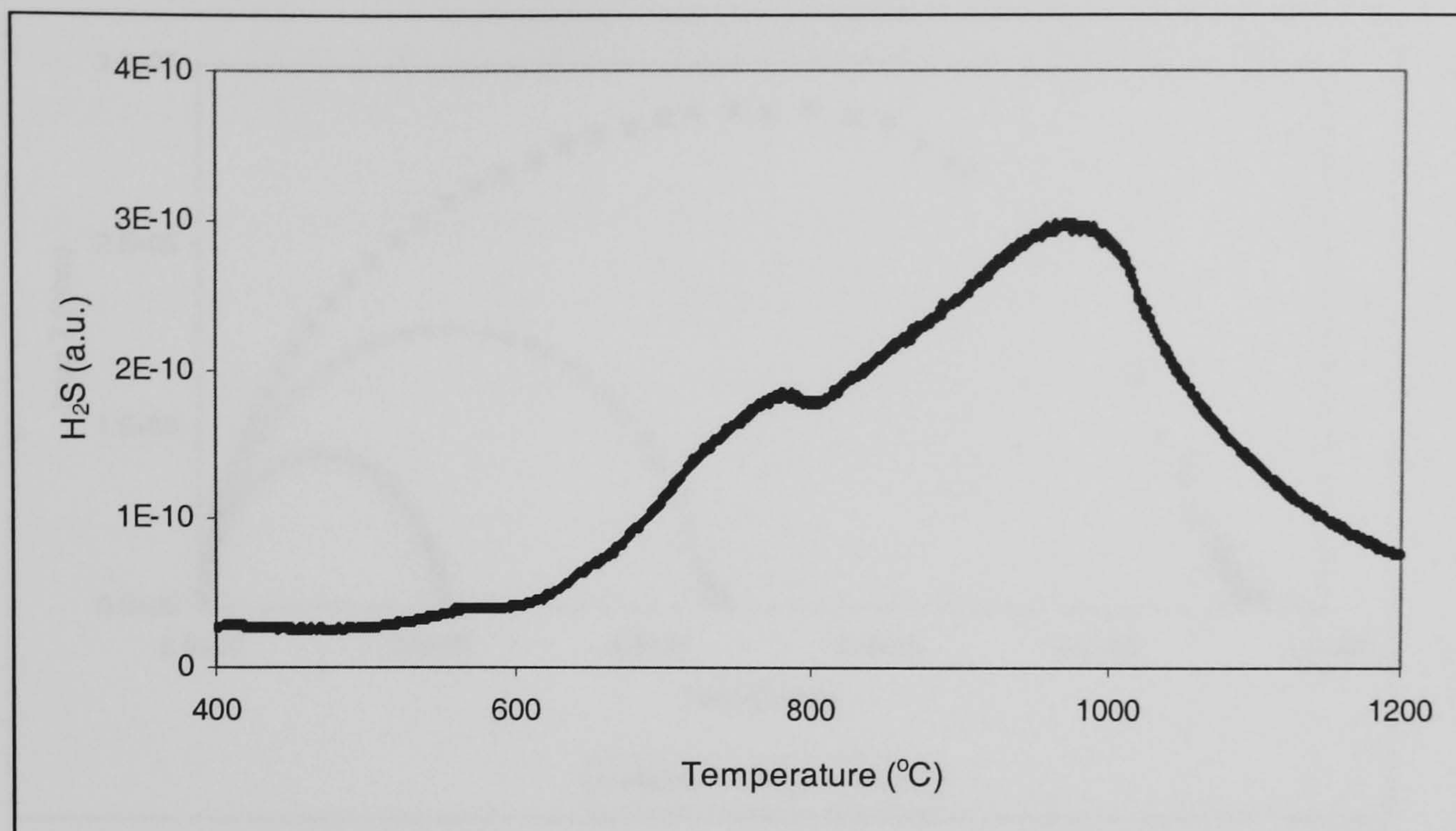


Figure 6-26. TPR of $\text{Ba}_3\text{Zr}_2\text{S}_7$ using $20^\circ\text{C}/\text{min}$ heating rate

6.2.2 Electrochemical Impedance Spectroscopy for $\text{Ba}_3\text{Zr}_2\text{S}_7$

Impedance spectroscopy of $\text{Ba}_3\text{Zr}_2\text{S}_7$ was carried out using graphite electrodes in the temperature range from 50°C to 450°C with 25°C increments with a one-hour temperature isothermal period a frequency range from $1 \times 10^6 \text{ Hz}$ to 0.1 Hz (10 points per decade) in argon atmosphere.

The Nyquist plot for $\text{Ba}_3\text{Zr}_2\text{S}_7$ appears to contain either a single arc or possibly two arcs with significant overlap, Figure 6.27. The Nyquist plot has no pronounced low frequency effect which identifies a pure ionic conductor, inferring that $\text{Ba}_3\text{Zr}_2\text{S}_7$ is at best a mixed ionic-electronic conductor, when measured in an argon atmosphere. The Nyquist plot of $\text{Ba}_3\text{Zr}_2\text{S}_7$ was adequately modelled by using the Jamnik mixed ionic-electronic equivalent circuit.

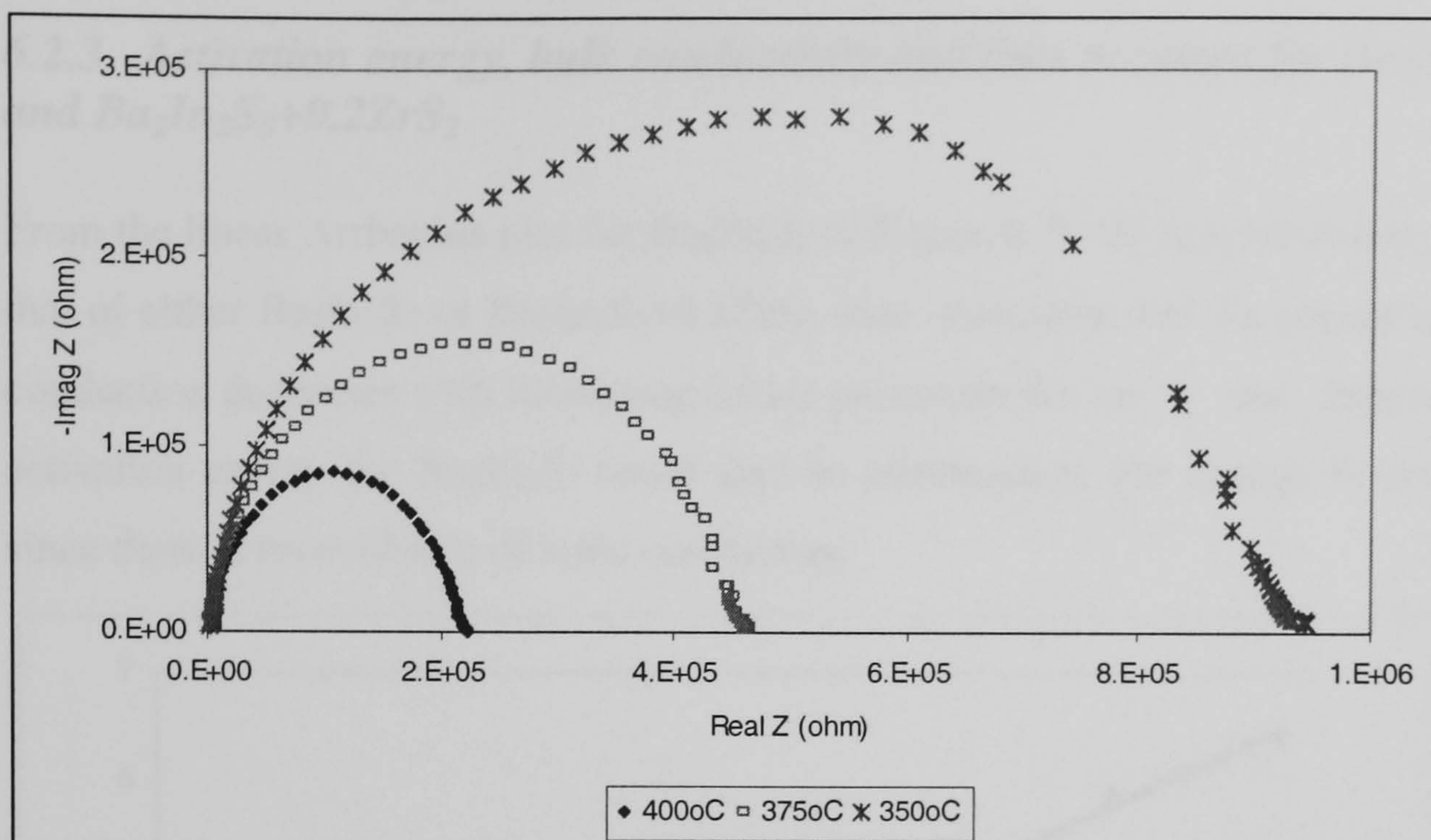


Figure 6-27. Nyquist plot of $\text{Ba}_3\text{Zr}_2\text{S}_7$ in argon at elevated temperatures

The Bode plot for $\text{Ba}_3\text{Zr}_2\text{S}_7$ also shows a phase change only at high frequencies, thereby confirming the absence of a low frequency arc that would confirm pure ionic conduction, Figure 6.28. However Jamnik calculated that the low frequency ionic blocking arc might disappear for compounds with an electronic transport number of 0.0001, Vayenas, 2003. Therefore the absence of a low frequency is not conclusive with regards to the definition of an ionic conductor. Therefore the effect of varying the partial pressure of H_2S on the bulk conductivity will determine weather this compound has significant electronic conduction.

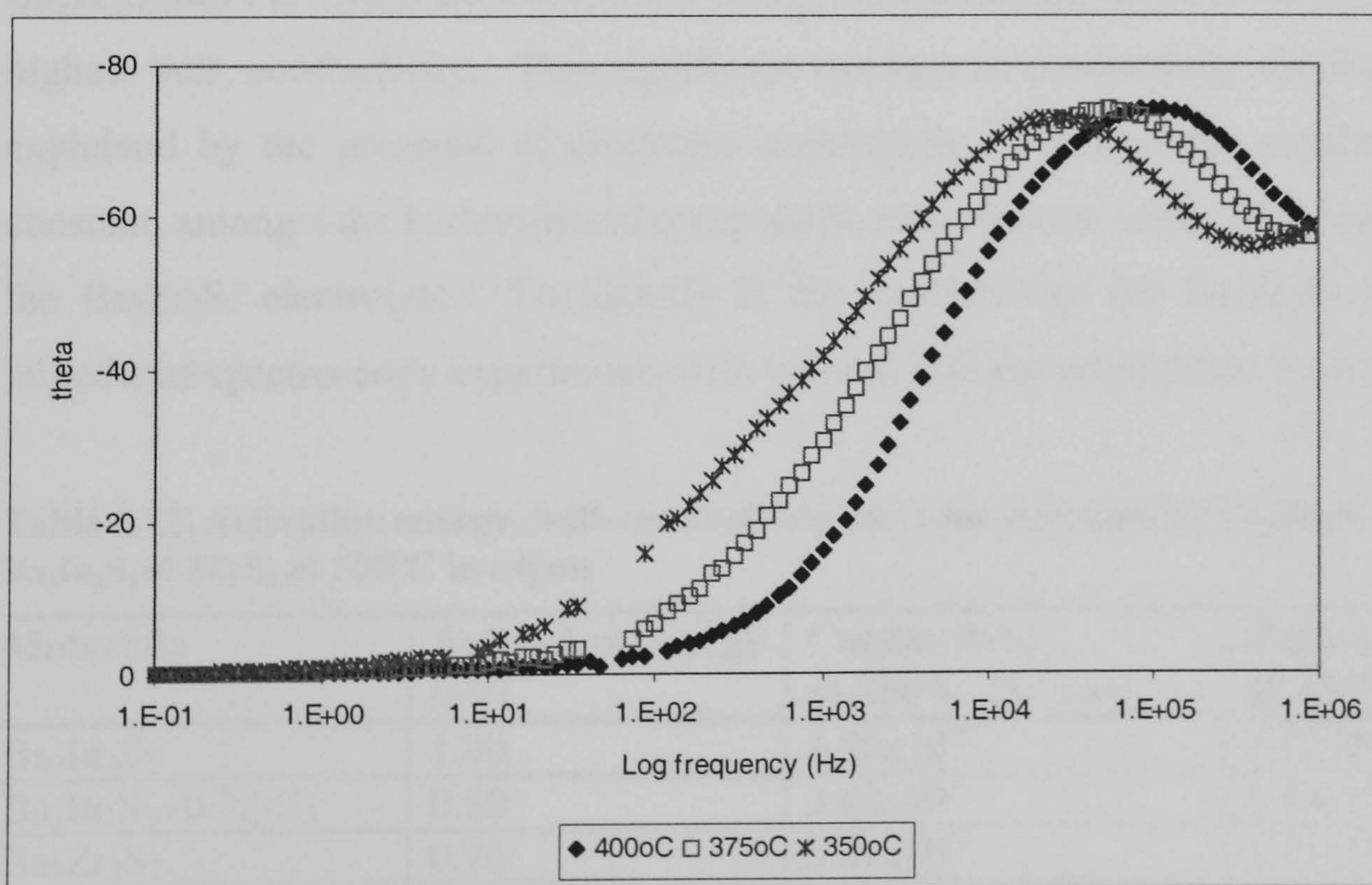


Figure 6-28. Bode plot of $\text{Ba}_3\text{Zr}_2\text{S}_7$ in argon at elevated temperatures

6.2.3 Activation energy, bulk conductivity and time constant for $Ba_3Zr_2S_7$, $Ba_2In_2S_5$ and $Ba_2In_2S_5+0.2ZrS_2$

From the linear Arrhenius plot for $Ba_3Zr_2S_7$ in Figure 6.29 the activation energy is lower than that of either $Ba_2In_2S_5$ or $Ba_2In_2S_5+0.2ZrS_2$, thus indicating that the energy required for bulk conduction decreases with increasing lattice parameter for the ‘c’ site. However, the reduced activation energy for $Ba_3Zr_2S_7$ could also be attributed to the change in conducting specie, since there is no evidence of ionic conduction.

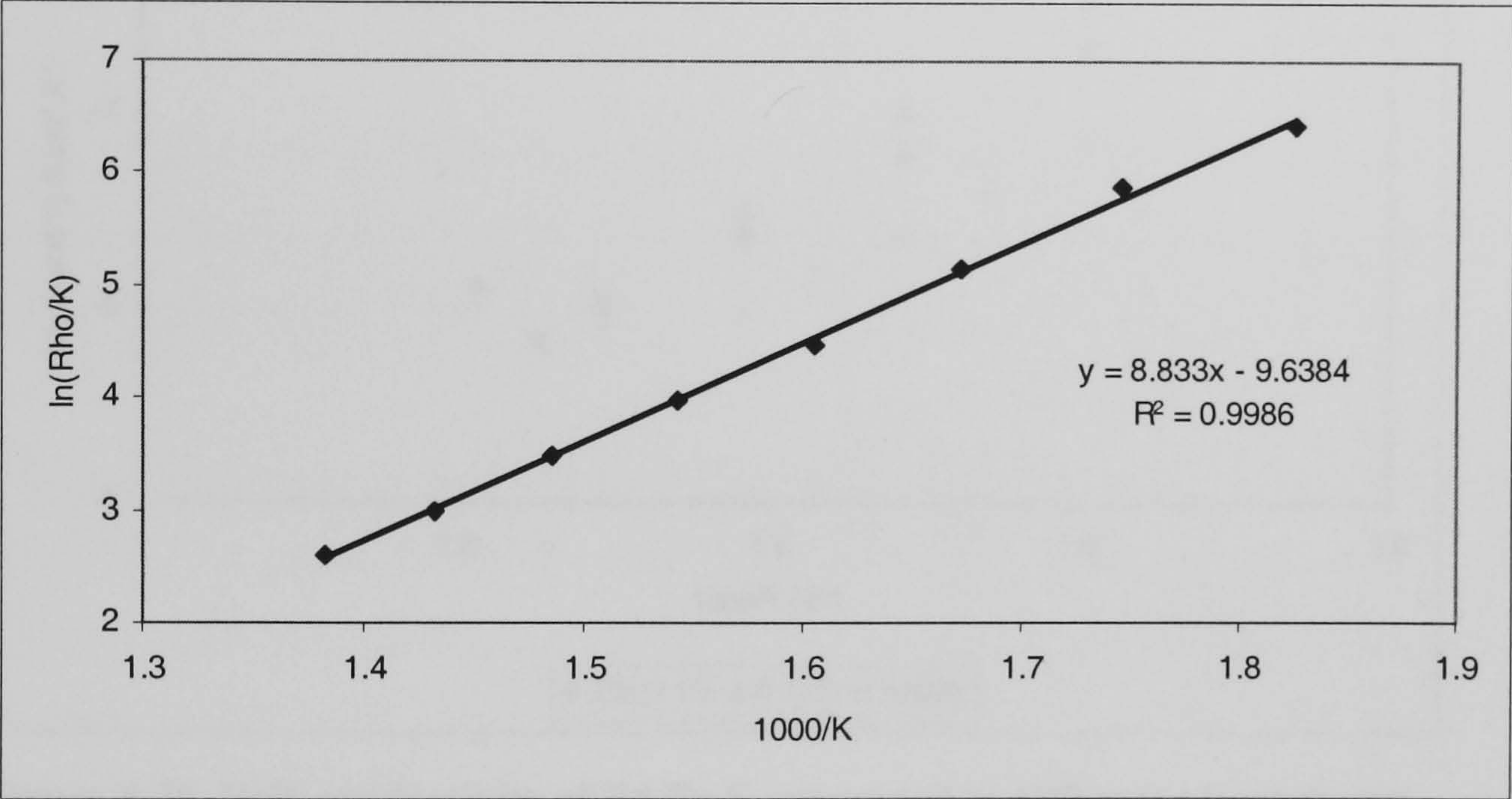


Figure 6-29 Arrhenius plot of ionic hopping activation energy for $Ba_3Zr_2S_7$

$Ba_3Zr_2S_7$ has the lowest bulk activation energy for the barium based electrolytes as well as the highest bulk conductivity. This significant increase in conductivity for $Ba_3Zr_2S_7$ could be explained by the presence of electronic conduction. However the similarity of the time constant, amongst the barium-based compounds, may indicate some ionic conductivity within the $Ba_3Zr_2S_7$ electrolyte. To identify if the conductivity for $Ba_3Zr_2S_7$ is ionic, further impedance spectroscopy experiments with varying H_2S partial pressure were done.

Table 6.12. Activation energy, bulk conductivity and time constant for $Ba_3Zr_2S_7$, $Ba_2In_2S_5$ and $Ba_2In_2S_5+0.2ZrS_2$ at 500°C in argon

Materials	Activation energy (eV)	Conductivity at 500°C (S ⁻¹ .cm)	Bulk time constant at 350°C (sec)
Ba ₂ In ₂ S ₅	1.00	3.20x10 ⁻⁶	1.77x10 ⁻⁴
Ba ₂ In ₂ S ₅ +0.2ZrS ₂	0.89	3.44x10 ⁻⁶	6.44x10 ⁻⁴
Ba ₃ Zr ₂ S ₇	0.76	5.41x10 ⁻³	1.71x10 ⁻⁴

6.2.4 H₂S Concentration dependence of bulk conductivity for Ba₃Zr₂S₇

The bulk conductivity decreased with increasing H₂S concentration indicating the presence of electronic conduction in Ba₃Zr₂S₇, Figure 6.30. Therefore the absence of the low frequency arc in the Nyquist plot and decreased conductivity with increased H₂S concentration confirms the presence of significant electronic conduction.

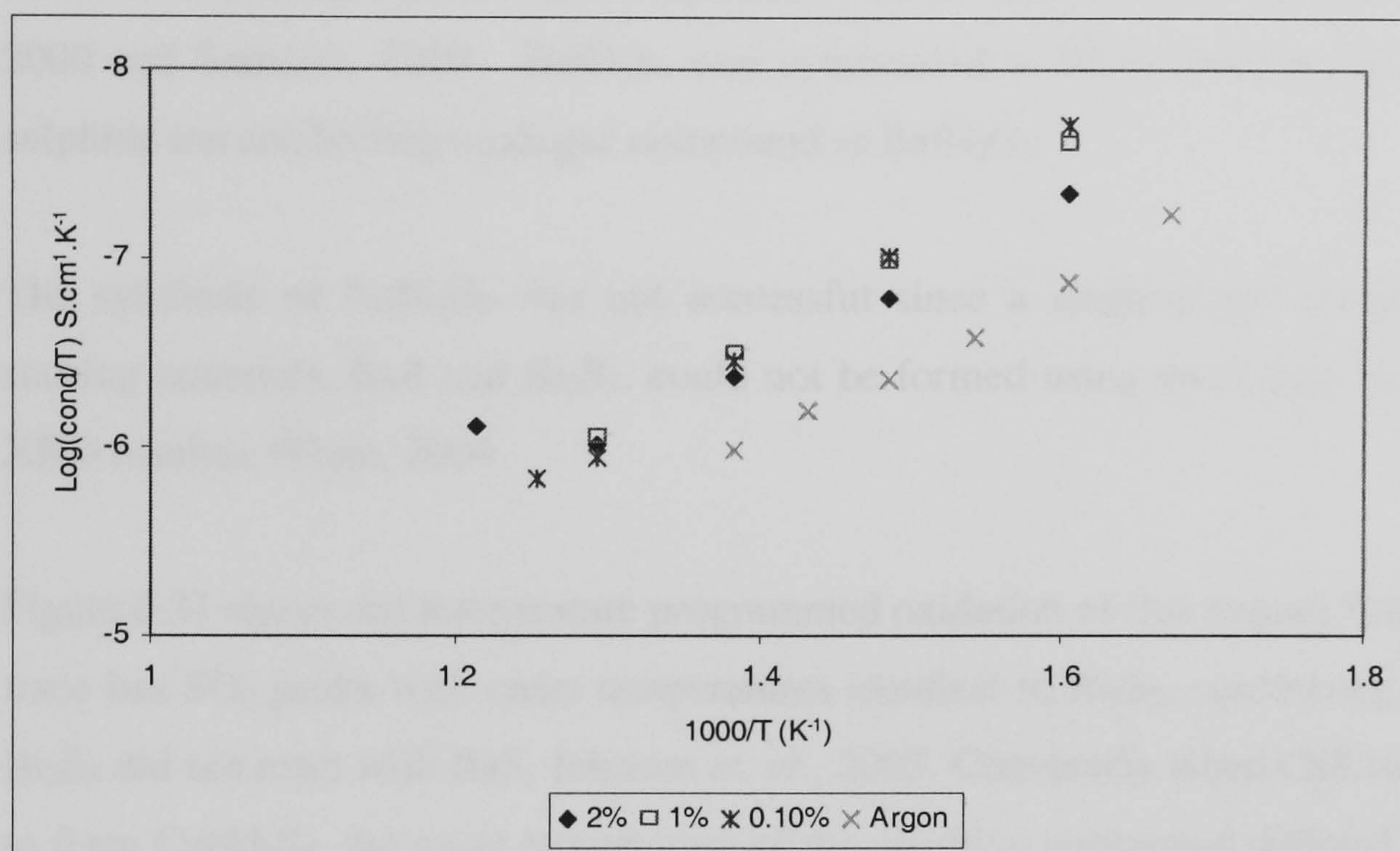


Figure 6-30. Bulk conductivity of Ba₃Zr₂S₇ measured in different atmospheres

In summary, Ba₂In₂S₅ is the most thermally stable electrolyte; hence it has potential in very high temperature applications. Also the bulk conductivity remained fairly independent of H₂S concentration from 0vol%H₂S/Ar to 2vol%H₂S/Ar, which infers excellent ionic conduction stability over this very large concentration range.

Doping of Ba₂In₂S₅ with ZrS₂ caused a slight increase in the thermal stability as well as the bulk conductivity. However the onset of hole conduction in 20mol%ZrS₂ doped Ba₂In₂S₅ at high H₂S concentrations suggest that less doping should be used to improve thermal and ionic conducting properties without introducing electronic conduction.

Ba₃Zr₂S₇ is the least stable of the barium-based electrolytes. It has appears to have significant electronic conduction since the bulk conductivity decreased with increasing H₂S concentration.

6.3 The Failed BaBi₂S₄ Electrolyte

BaBi₂S₄ electrolyte was synthesised because Bi₂O₃ is an excellent oxide ion conductor, Boyapati. *et. al*, 2001. A phase change occurs within Bi₂O₃ when heated; heating creates defects in the unit cell thus allowing ionic conduction. However the conducting phase of Bi₂O₃ disappears as the temperature is lowered. Therefore research continues to develop methods of stabilizing the conducting phase of Bi₂O₃ at reduced temperature Yaremchenko, 2000 and Sammes, 1999. BaBi₂S₄ was synthesised to begin the research in developing a sulphide ion conducting analogue compound to BaBi₂O₄.

The synthesis of BaBi₂S₄ was not successful since a single-phase compound free of the starting materials, BaS and Bi₂S₃, could not be formed using solid-state reactions (based on XRD results), White, 2004.

Figure 6.31 shows the temperature programmed oxidation of this impure 'BaBi₂S₄'. The TPO trace has SO₂ peaks with onset temperatures identical to Bi₂S₃, confirming that much of the Bi₂S₃ did not react with BaS, Johnson *et. al.*, 2003. Conversely when CaS reacted with Nd₂S₃ to form CaNd₂S₄, the onset temperature of the resulting compound differed from the starting materials; oxidation onset temperatures were approximately: >1000°C, 620°C and 700°C for CaS, Nd₂S₃ and CaNd₂S₄ respectively.

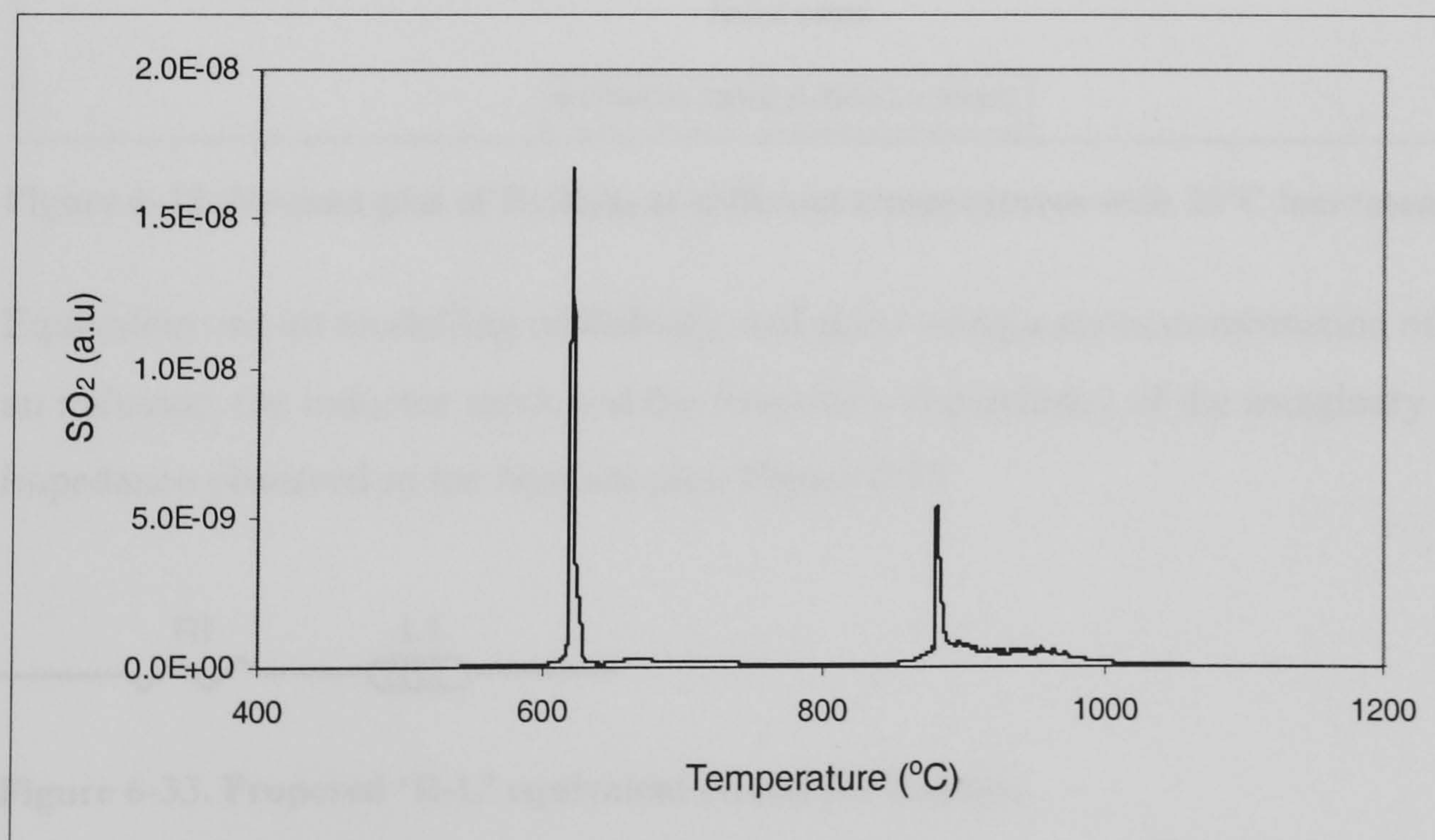


Figure 6. 6-31. Temperature programmed oxidation of BaBi₂S₄ at 10°C/min

The electrochemical characterisation of the failed BaBi₂S₄ compound has no capacitive component in its impedance, Figure 6-32. Therefore none of the physically distributed properties such as grain boundary, grain interior and the electrode-electrolyte interface that

causes a space charge collection (capacitance) that occurs in ionic conducting compounds is present for the failed BaBi_2S_4 . Rather, the Nyquist plot represents conduction that would occur for metallic electrolyte. Since the real component of impedance is almost independent of frequency, Figure 6-32. However the imaginary component of impedance is frequency dependent; this indicates that the system, graphite// BaBi_2S_4 //graphite, is more complicated than a pure metallic compound, as expected

The Bode plot for BaBi_2S_4 shows that the phase change occurs at a high frequency, therefore the non-capacitive (inductive) feature of the Nyquist and Bode plot could be related to the property of the electrolyte rather than the graphite- BaBi_2S_4 interface, Figure 6.34.

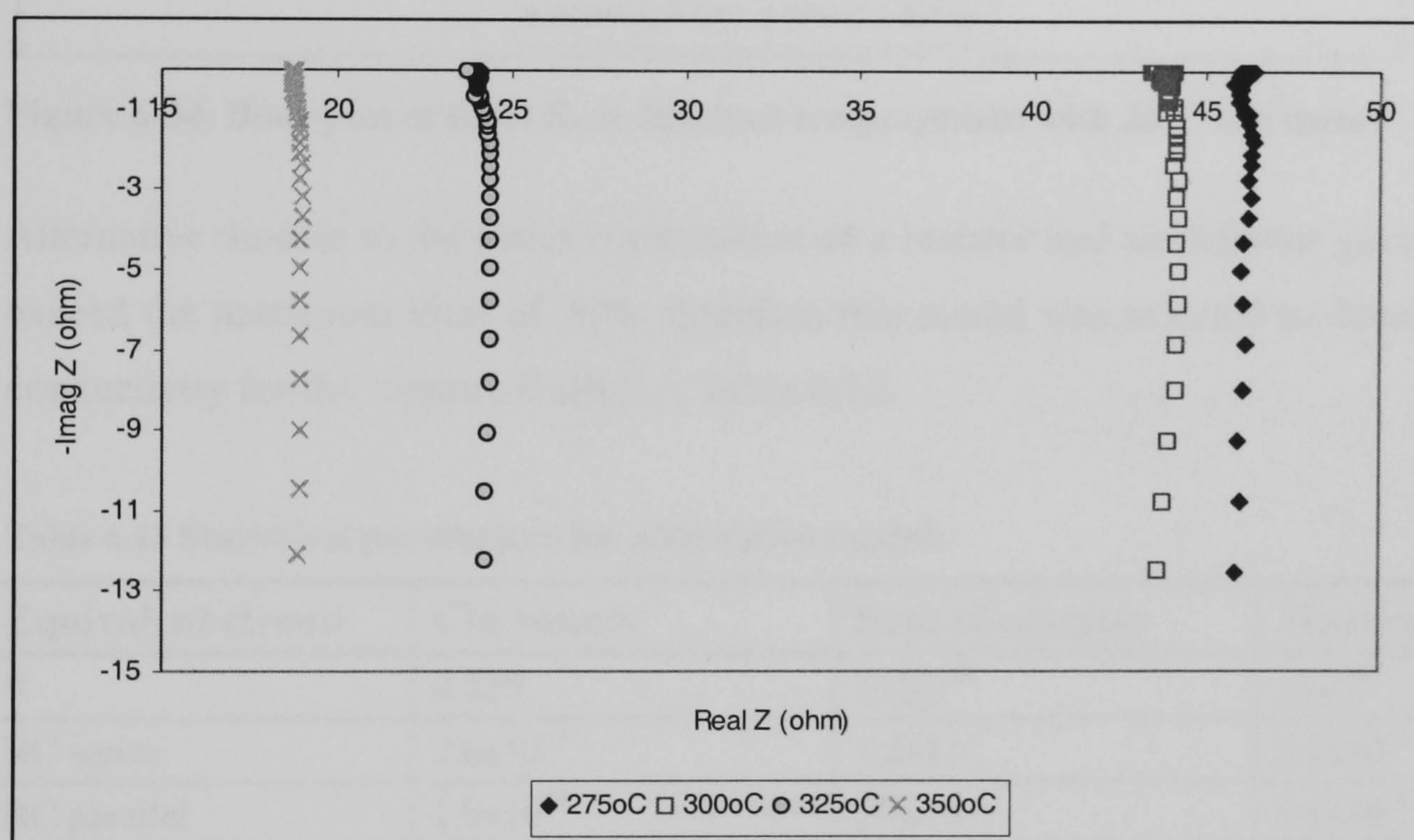


Figure 6-32. Nyquist plot of BaBi_2S_4 at different temperatures with 25°C increments

Equivalent circuit modelling of BaBi_2S_4 was done using a series combination of a resistor and an inductor; the inductor modelled the frequency dependency of the imaginary component of impedance observed in the Nyquist plot, Figure 6.33.



Figure 6-33. Proposed 'R-L' equivalent circuit for BaBi_2S_4

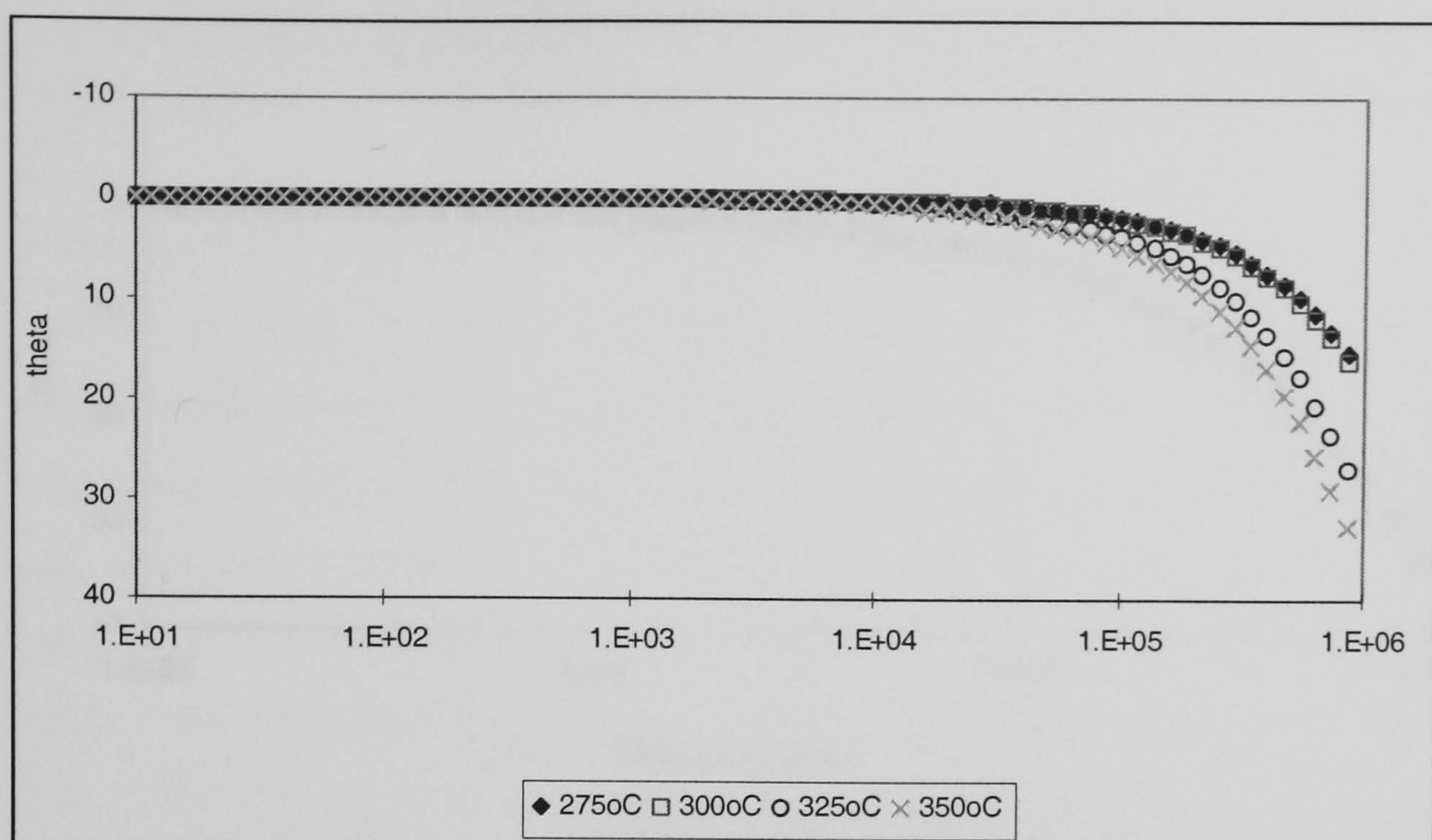


Figure 6-34. Bode plot of BaBi₂S₄ at different temperatures with 25°C increment

Alternative models to the series combination of a resistor and an inductor gave errors, which exceed the maximum limit of 30%; therefore this model was selected to determine the bulk conductivity for the ‘impure BaBi₂S₄’, Table 6.13.

Table 6.13 Statistical parameters for alternative models

Equivalent circuit	Chi-square	Sum-of-squares	Maximum error %
R	0.529	1×10^{-20}	1×10^{20}
RC series	2.6×10^{11}	3.5×10^{13}	5.3×10^{11}
RC parallel	1.9×10^{16}	2.7×10^{18}	6.1×10^{13}
L	1×10^{-20}	1×10^{-20}	1.2×10^5
RL series	0.0127	1.881	0.6456
RL parallel	1582	2.34×10^5	6036

The goodness of fit between the model and the experimental data is shown in the Bode plot of BaBi₂S₄ at 350°C, where it clearly shows an excellent agreement at all frequencies measured, Figure 6-35.

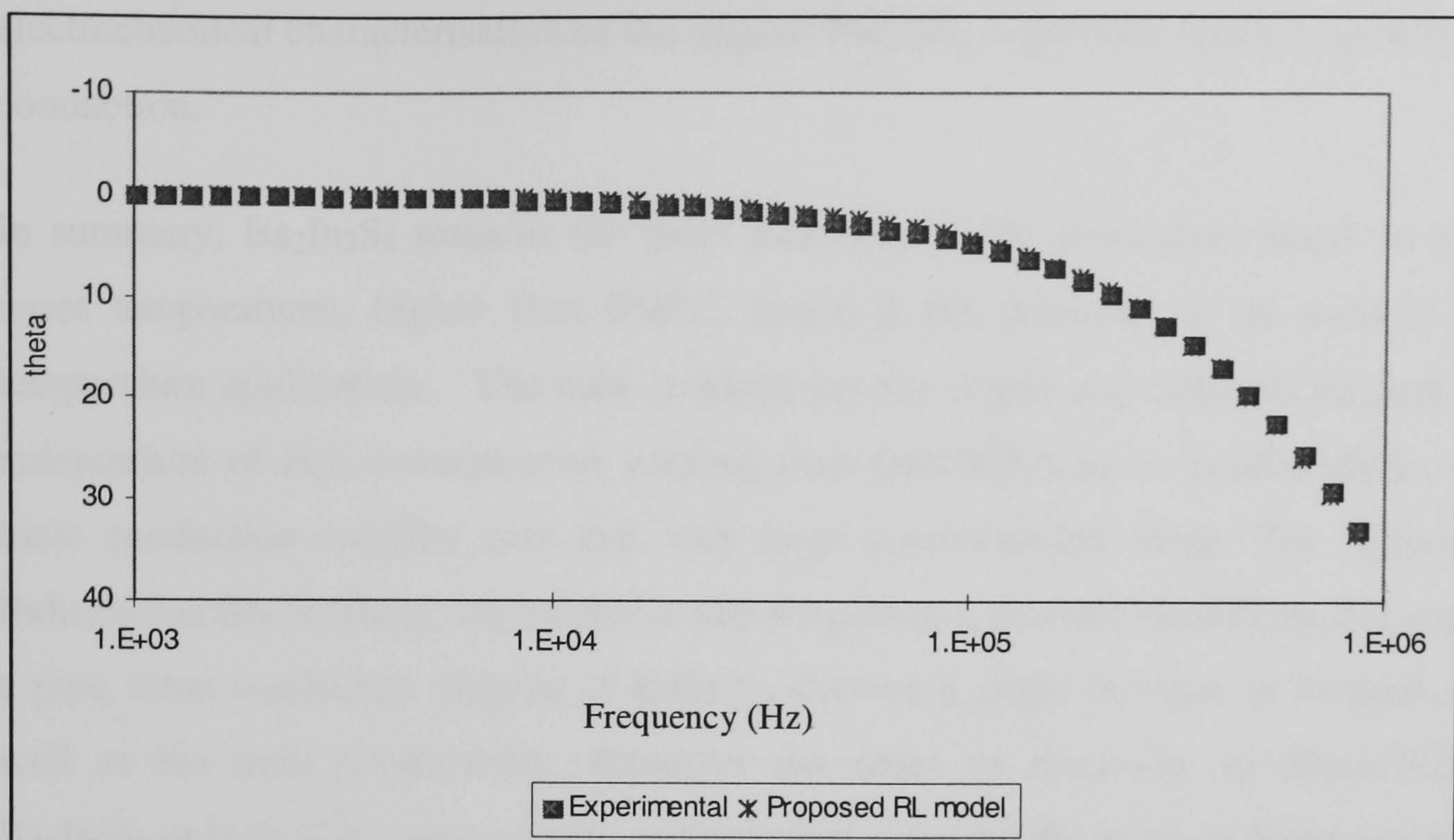


Figure 6-35. Bode plot experimental and RL model for BaBi₂S₄ at 350°C

The activation energy for bulk conductivity for BaBi₂S₄ is 1.0eV, which also remains independent of H₂S concentration, Figure 6.36. Since the bulk conductivity measured by impedance spectroscopy has no capacitive component.

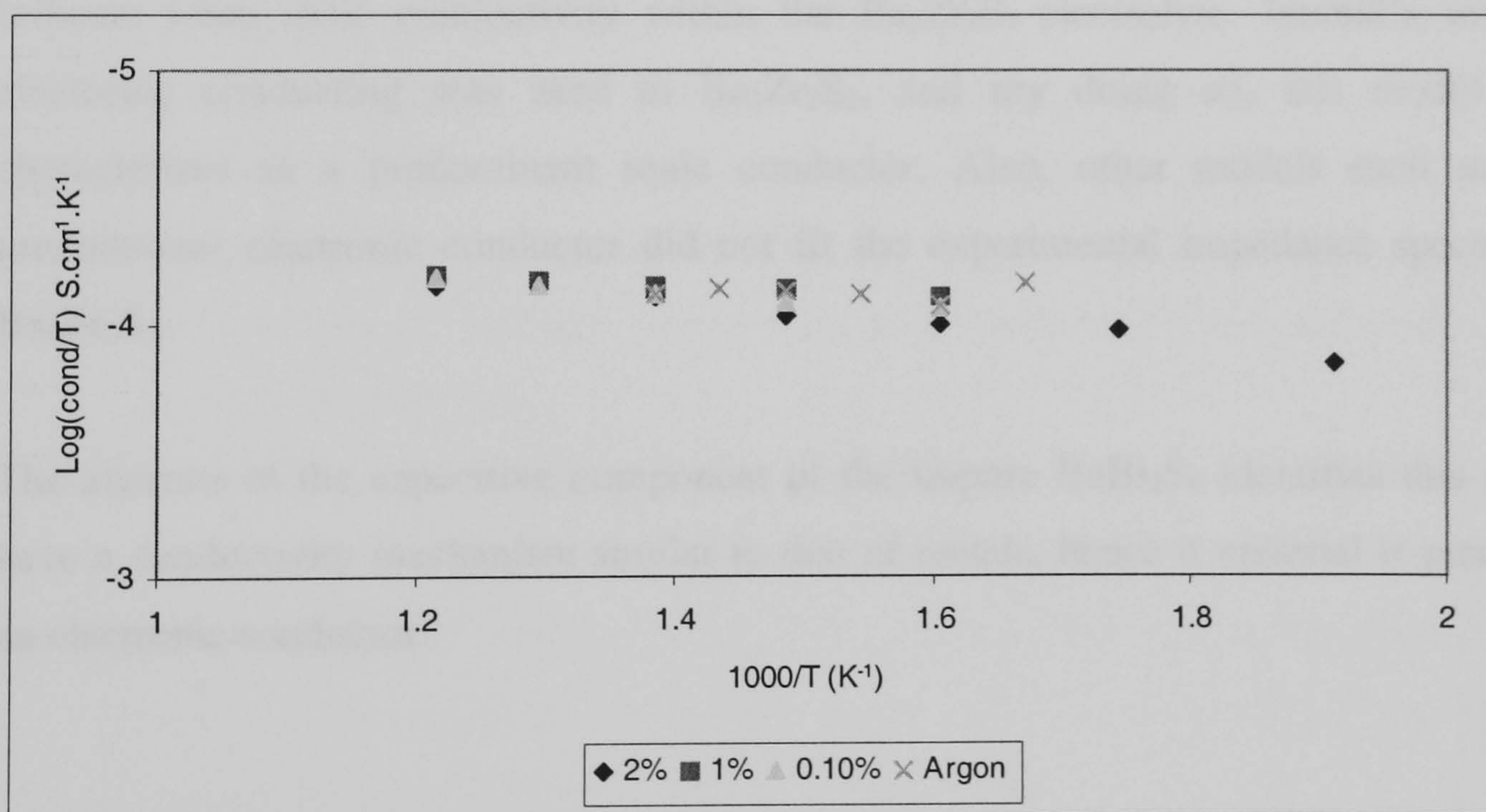


Figure 6-36. Bulk conductivity of BaBi₂S₄ measured in different atmospheres

Based on the experimental data for the impure BaBi₂S₄ electrolyte, ionic conduction apparently does not occur in compounds, which have not formed a pure phase. The multiplicity of SO₂ peaks in the TPO of BaBi₂S₄ also suggests mixed compounds. Therefore using XRD results, to discontinue and further characterisation appears to be justified since the

electrochemical characterisation of the impure BaBi_2S_4 electrolyte failed to indicate any ionic conduction.

In summary, $\text{Ba}_2\text{In}_2\text{S}_5$ remains the most thermally stable electrolyte based on its the high onset temperatures, higher than 950°C , hence it has potential to be used in very high temperature applications. The bulk conductivity for doped and undoped $\text{Ba}_2\text{In}_2\text{S}_5$ remained independent of H_2S concentration varying from 0vol% $\text{H}_2\text{S}/\text{Ar}$ to 1vol% $\text{H}_2\text{S}/\text{Ar}$, suggesting ionic conduction stability over this very large concentration range. The Nyquist plot for BaIn_2S_5 has the Warburg impedance at low frequencies, thereby identifying this electrolyte as a pure ionic conductor. Doping of BaIn_2S_5 showed a slight increase in thermal stability as well as the bulk conductivity. However the onset of electronic in 20mol% ZrS_2 doped $\text{Ba}_2\text{In}_2\text{S}_5$ at high H_2S concentration suggests that reducing the level of doping should be used to improve ionic conducting properties without introducing electronic conduction.

While $\text{Ba}_3\text{Zr}_2\text{S}_7$ has a bulk conductivity higher than $\text{Ba}_2\text{In}_2\text{S}_5$, the presence of electronic conduction was detected by the decrease in bulk conductivity with increasing H_2S concentration. However the similarity between time constants for $\text{Ba}_3\text{Zr}_2\text{S}_7$ and $\text{Ba}_2\text{In}_2\text{S}_5$ may indicate some ionic conductivity within the $\text{Ba}_3\text{Zr}_2\text{S}_7$ electrolyte. Jamnik's mixed ionic-electronic conducting was used to $\text{Ba}_3\text{Zr}_2\text{S}_7$, and by doing so, this model implicitly characterises as a predominant ionic conductor. Also, other models such as Jamnik's predominant electronic conductor did not fit the experimental impedance spectroscopy of $\text{Ba}_3\text{Zr}_2\text{S}_7$.

The absence of the capacitive component of the impure BaBi_2S_4 identifies this material to have a conductivity mechanism similar to that of metals, hence it material is predominantly an electronic conductor.

6.4 Chapter 6 References

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Chapter 7

7. Conclusions

This research applies existing experimental techniques to characterise the selected electrolytes. The generic uses and limitations of each technique applied to characterisation of sulphide electrolytes are:

- Mass Spectroscopy assisted TPO and TPR establishes the thermal stability of the electrolytes in an oxidising and reducing atmosphere.
- Mass Spectroscopy assisted TPO also gives the thermal activation energy for the oxidation reaction of electrolyte; however no correlation was established between the thermal activation energy and the activation energy for ionic hopping/conduction.
- Determination of the thermal activation energy using Mass Spectroscopy assisted TPO requires less than 5°C accuracy in defining the peak temperature. This translates into more than 99% accuracy for the peak temperature. The accuracy of the peak temperature was improved by reducing the volume of the reactor, so the distance between the thermocouple and the sample is minimised, to allow easy and repeatable location of the sample. Reducing the reactor volume also leads to a sharp and narrow TPO trace, which facilitates easy interpretation of the peak temperatures.
- Integration of the SO₂ and O₂ peaks of the Mass Spectroscopy assisted TPO allows for the complete mass balance of the oxidation process, thereby establishing the extent of oxidation of the electrolyte at 1000°C, which is the maximum temperature of the Mass Spectroscopy TPO. This leads to the general observation that some sulphides oxidises to form a mixture of sulphates and oxides.
- No clear relationship was observed between the extent of oxidation and the ionic conducting property of the electrolyte. However the sulphur and oxygen mass balance was done on the CaNd₂S₄ series identifies CaNd₂S₄+0.1Nd₂S₃ as the electrolyte that released the highest percentage of sulphur which formed SO₂ in the TPO; this electrolyte was previously reported as having the highest ionic conductivity in the series of doped CaNd₂S₄ compounds.
- Electrochemical impedance spectroscopy was successful in determining the bulk conductivity under the following experimental conditions:
 - Using platinum electrodes and current collectors in an inert atmosphere such as argon
 - Using a graphite electrodes in various concentrations of H₂S in Ar mixture
- The use of gold electrodes in an argon atmosphere failed due to an apparent reaction with the electrolyte. This was presumed to be the formation of a covalent gold

sulphide, AuS_2 because the gold electrode sputtered onto the electrolyte changed colour from gold to reddish-brown. Also the surface resistance of the electrode increased from less than 10Ω (before EIS experiments) to more than $2\text{M}\Omega$ (after EIS experiments). The sputtered gold electrode changed colour and resistance either after an EIS experiments by using a maximum temperature of 400°C or after several weeks at room temperature in air. Since electrolytes sputtered with gold forms stable reaction products, their use as electrodes were discontinued.

- Published experimental results of impedance characterisation of oxide ion conducting materials have used either argon or an oxygen rich atmospheres, therefore EIS of sulphide electrolytes were done in both H_2S rich atmosphere and argon which led to the following conclusions:
 - EIS of sulphide electrolytes with a $\text{H}_2\text{S}/\text{H}_2$ atmosphere using a platinum electrodes lead to unstable results seen as severe scattering of data and the data were also unrepeatable. This could have been due to an electrochemical reaction between the platinum and H_2 or platinum and H_2S , therefore the gas was changed to an inert gas.
 - EIS of sulphide electrolytes with argon and platinum electrodes gave stable and repeatable results at lower temperatures. For temperatures in excess of 250°C , the EIS results were not repeatable. This was attributed to an electrochemical reaction between the platinum and sulphide electrolyte rather than to the thermal decomposition of the electrolyte. The oxidation and reduction onset temperatures previously established were in excess of 200°C of the EIS experiment temperature. Therefore platinum electrodes were changed to the inert graphite plates.
 - EIS of sulphide electrolytes with graphite electrodes gives stable and repeatable results in both argon and $\text{H}_2\text{S}/\text{Ar}$ mixtures.
- The frequency range from 0.01Hz to $1 \times 10^6\text{Hz}$ is suitable to observe all the phase changes associated with the conduction mechanism in the electrolyte and the electrode-electrolyte interface. Measurement at a lower frequency than 0.01Hz does not lead to any further phase angle change. Using a perturbation signal of 0.1V_{rms} is sufficient to cause the excitement of mobile ions, while reducing the signal to $0.01\text{V}_{\text{rms}}$ leads to significant scattering of the resulting impedance data, suggesting that the amplitude of the perturbation signal is insufficient.

- The choice of the suitable equivalent circuit differentiates pure ionic conducting electrolytes from mixed ionic-electronic conducting to electronic conducting electrolytes.
 - The Bauerle equivalent circuit is suitable to model sulphide electrolytes which exhibit pure ionic conduction which leads to the low frequency arc that indicates ionic blocking at the electrolyte-electrode interface.
 - Sulphide electrolyte which have capacitive components to their impedance but not phase angle change at low frequencies are suitably modelled using Jamnik equivalent circuit for mixed ionic-electronic conduction with predominant ionic conduction. However the derived parameters, conductivity, time constants and activation energies, have not been verified independently by alternative characterisation methods.
 - Sulphide electrolytes without a capacitive component and no phase angle change at low frequencies are best modelled by using a series combination a resistor and an inductor that infers predominant electronic conduction.
- The measurement of the resistivity using the 4-point DC Danbridge Resistance meters gives unstable and unrepeatable results. This is possibly because the Danbridge resistance meter selects the appropriate voltage by pulsing (1-10 V/sec) various voltages, which makes the applied DC voltage frequency dependent. This applied DC voltage could be considered pseudo AC voltage, which may cause ionic conduction resulting in scattering of the DC resistance. Therefore the scattering of the DC current could be due to ionic motion. The Danbridge resistance meter was not useful to measure the DC resistivity of sulphides. The resistivity, cross-sectional, was measured by using a 2-point DC multi-meter. This identifies electrolytes with significant electronic conduction.
- Electrochemical pumping experiments can detect the presence or absence of sulphide ion conduction by using $\text{H}_2\text{S}/\text{Ar}/\text{electrolyte}/\text{Ar}$. Changing the carrier gas from argon, i.e. $\text{H}_2\text{S}/\text{H}_2/\text{Pt}/\text{electrolyte}/\text{Pt}/\text{H}_2$ does not differentiate sulphide ion conduction from hydrogen ion conduction, assuming no electronic conduction. Hydrogen ion conduction is a common feature for perovskite structure, which is the structure that many of the electrolytes adopt. Many electrochemical-pumping experiments had short-circuiting because of either the method of applying the electrode or the cementing of the reactor. Either source of short-circuiting was mitigated by modification to the experimental procedure; hence the successful identification of the presence or absence sulphide ion conduction is possible.

- Applying a voltage of 1-2V and using an operating temperature of 100°C lower than the onset temperature for reduction leads to repeatable experiments, thereby confirming the stability of the electrolyte under these conditions. Increasing the applied volts to 5-10V introduces the possibility of an electrochemical reduction of the electrolyte.
- The open circuit voltage, OCV, of the concentration cell should be measured, since this parameter can be used to determine the transport number for the electrolyte. It can also indicate if the concentration is leaking, since this would lead to the OCV tending to zero, because of the disappearance of a concentration difference.

This research investigated selected sulphide electrolytes based on the electrochemical properties of the oxide ion conducting properties of their oxide analogues. Improving the conduction of these selected sulphides by doping was attempted when possible. The thermal and electrochemical characterisation for series of compounds led to the following conclusions:

- TPO and TPR of doped CaNd_2S_4 compounds are stable up to 700°C in an oxidising and reducing atmosphere. Three electrodes, gold, platinum and graphite were used in EIS experiments; only the graphite electrode gives stable and repeatable EIS results. The presence of an ionic blocking arc is detected only for $\text{CaNd}_2\text{S}_4+10\text{mol}\%\text{Nd}_2\text{S}_3$; it means that this compound is a pure ionic conductor. Both Bauerle and Jamnik equivalent circuits for pure ionic conductors or mixed ionic-electronic conductors are suitable to model EIS data for $\text{CaNd}_2\text{S}_4+10\text{mol}\%\text{Nd}_2\text{S}_3$. However only Jamnik equivalent circuit for mixed ionic-electronic conductor is suitable to model all the compounds in this series of compounds, except for $\text{CaNd}_2\text{S}_4+10\text{mol}\%\text{Nd}_2\text{S}_3$, therefore they are at best mixed ionic-electronic conductors. The Jamnik mixed ionic-electronic equivalent circuit identifies $\text{CaNd}_2\text{S}_4+10.0\text{mole}\%\text{Nd}_2\text{S}_3$ with a bulk conductivity of $1.09 \times 10^{-6} \text{S.cm}^{-1}$ agreeing with Kalinina bulk conductivity determined through galvanic cells. However all other bulk conductivities were several orders of magnitude larger than the ones obtained by Kalinina galvanic cell method. This increased conductivity with increased doping results from the onset of electronic type conduction. EIS experiments in varying H_2S concentration from 0vol% $\text{H}_2\text{S}/\text{Ar}$ to 2vol% $\text{H}_2\text{S}/\text{Ar}$ confirm the following:
 - Undoped CaNd_2S_4 exhibits hole conduction
 - $\text{CaNd}_2\text{S}_4+10\text{mol}\%\text{Nd}_2\text{S}_3$ exhibits ionic conduction
 - $\text{CaNd}_2\text{S}_4+20\text{mol}\%\text{Nd}_2\text{S}_3$ exhibits electronic conduction

- $\text{CaNd}_2\text{S}_4+30\text{mol}\%\text{Nd}_2\text{S}_3$ exhibits ionic conduction only at elevated temperatures.
- Electrochemical pumping of the type compound $\text{CaNd}_2\text{S}_4+x\text{Nd}_2\text{S}_3$ using the cell $\text{H}_2\text{S}/\text{H}_2/\text{Pt}/\text{electrolyte}/\text{Pt}/\text{H}_2$ had inherent experimental limitations in terms of short circuiting of system as well as possible by H_2S by passing through the electrolyte in to the argon chamber. Therefore the results from these experiments do not supersede previously established data. Electrochemical pumping experiments supports the previously attained results as follows:
 - Undoped CaNd_2S_4 exhibits ionic – electronic conduction and possibly cationic conduction
 - $\text{CaNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ indicates predominant electronic conduction

Absolute conclusions on differentiating cationic, anionic from electronic conduction were not possible due to possible experimental errors leading to short-circuiting of the resulting cell.

- TPO and TPR of doped SrNd_2S_4 compounds are stable up to 700°C in an oxidising and reducing atmosphere. Only Jamnik equivalent circuit for mixed ionic-electronic conductor is suitable to model all the compounds in this series, therefore they are at best mixed ionic-electronic conductors. The Jamnik mixed ionic-electronic equivalent circuit identifies $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ with a bulk conductivity of $3.39 \times 10^{-3} \text{S.cm}^{-1}$ at 500°C , which is three orders of magnitude greater than the calcium sulphide analogue compound. Similarly, all other bulk conductivities of SrNd_2S_4 type compounds were several orders of magnitude larger than their equivalent CaNd_2S_4 type. This increased conductivity with increased doping results from the onset of electronic type conduction. EIS experiments in varying H_2S partial pressure from $0\text{vol}\%\text{H}_2\text{S}/\text{Ar}$ to $2\text{vol}\%\text{H}_2\text{S}/\text{Ar}$ confirm the following:
 - Undoped SrNd_2S_4 exhibits ionic conduction at elevated temperatures
 - $\text{SrNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ exhibits electronic conduction
 - $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ exhibits ionic conduction
 - $\text{SrNd}_2\text{S}_4+0.3\text{Nd}_2\text{S}_3$ exhibits electronic conduction with possible ionic conduction at elevated temperatures.
- Electrochemical pumping of the type compound $\text{SrNd}_2\text{S}_4+x\text{Nd}_2\text{S}_3$ by using the $\text{H}_2\text{S}/\text{H}_2/\text{Pt}/\text{electrolyte}/\text{Pt}/\text{H}_2$ had inherent experimental limitations, therefore the data cannot be used conclusively, led to following possibilities:
 - Undoped SrNd_2S_4 exhibits ionic – electronic conduction; possibly cationic conduction

- $\text{SrNd}_2\text{S}_4+0.2\text{Nd}_2\text{S}_3$ exhibits electronic conduction at low temperatures; possibly anionic conduction at elevated temperatures.

Absolute conclusions on differentiating cationic, anionic from electronic conduction were not possible due to possible experimental errors leading to short-circuiting of the resulting cell.

- TPO and TPR of doped CaSm_2S_4 compounds are stable up to 720°C in an oxidising and reducing atmosphere. McDonald's model consisting of five series connection of RC elements which models perfectly ionic conducting electrolytes, fitted experimental impedance spectroscopy in the frequency range of 10^{-1}Hz to 10^{-6}Hz . The McDonald's model for pure ionic conductors identifies $\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ with a bulk conductivity of $3.51 \times 10^{-4}\text{S.cm}^{-1}$, at 500°C , which is two orders of magnitude greater than the $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ analogue compound. A further increase in doping leads to a reduction in bulk conductivity, therefore the optimum doping for maximum conductivity is less than 10mol%. EIS experiments in varying H_2S partial pressure from 0vol% $\text{H}_2\text{S}/\text{Ar}$ to 2vol% $\text{H}_2\text{S}/\text{Ar}$ confirm the following:
 - Undoped CaSm_2S_4 exhibits ionic conduction up to 1vol% $\text{H}_2\text{S}/\text{Ar}$, 2vol% $\text{H}_2\text{S}/\text{Ar}$ causes hole conduction
 - $\text{CaSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ shows ionic electronic conduction up to 1vol% $\text{H}_2\text{S}/\text{Ar}$; at 2vol% $\text{H}_2\text{S}/\text{Ar}$ it shows electronic conduction
 - $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ and $\text{CaSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ exhibit hole conduction.
- Electrochemical pumping of the type compound $\text{CaSm}_2\text{S}_4+x\text{Sm}_2\text{S}_3$ by using the $\text{H}_2\text{S}/\text{H}_2/\text{Pt}/\text{electrolyte}/\text{Pt}/\text{H}_2$ had inherent experimental limitations, therefore the data cannot be used conclusively, led to following possibilities:
 - Undoped CaSm_2S_4 exhibits ionic – electronic conduction; possibly cationic conduction
 - $\text{CaSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ exhibits anionic conduction at elevated temperatures.

Differentiating cationic, anionic from electronic conduction was not possible due to possible experimental errors leading to shorting circuiting of the resulting cell.
- TPO and TPR of doped SrSm_2S_4 compounds are stable up to 800°C in an oxidising atmosphere and at 690°C in a reducing atmosphere. Bauerle equivalent circuit for pure ionic conductors fits experimental impedance spectroscopy in the frequency range of 10^{-1}Hz to 10^6Hz . The Bauerle model for pure ionic conductors identifies $\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ with a bulk conductivity of $6.12 \times 10^{-6}\text{S.cm}^{-1}$, at 500°C , which is six times greater than the $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ analogue compound. A further increase in doping leads to 30mol% and it causes a reduction in bulk conductivity, therefore the optimum doping for maximum conductivity is less than 10mol%. EIS experiments in varying H_2S concentration from 0vol% $\text{H}_2\text{S}/\text{Ar}$ to 2vol% $\text{H}_2\text{S}/\text{Ar}$ confirm the following:
 - Undoped SrSm_2S_4 exhibits predominant ionic conduction

- $\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ exhibits predominant ionic conduction but with the onset of hole conduction at high H_2S concentrations
- $\text{SrSm}_2\text{S}_4+0.2\text{Sm}_2\text{S}_3$ exhibits ionic conduction
- $\text{SrSm}_2\text{S}_4+0.3\text{Sm}_2\text{S}_3$ exhibits electronic conduction
- Electrochemical pumping of the type compound $\text{SrSm}_2\text{S}_4+x\text{Sm}_2\text{S}_3$ using the $\text{H}_2\text{S}/\text{H}_2/\text{Pt}/\text{electrolyte}/\text{Pt}/\text{H}_2$ had inherent experimental limitations, therefore the data cannot be used conclusively, led to following possibilities:
 - $\text{SrSm}_2\text{S}_4+0.1\text{Sm}_2\text{S}_3$ and $\text{SrSm}_2\text{S}_4+30\text{mol}\%\text{Sm}_2\text{S}_3$ exhibit sulphide ion conduction; these electrolytes are not stable at 550°C and 650°C with the application of 1Vdc without a positive pressure of H_2S .

Differentiating cationic, anionic from electronic conduction was not possible due to possible experimental errors leading to shorting circuiting of the resulting cell as instability of the electrolyte.

- Several barium containing compounds were synthesised and characterised; namely the doped and undoped analogues to the orthorhombic fast ion conducting $\text{Ba}_2\text{In}_2\text{O}_5$; $\text{Ba}_3\text{Zr}_2\text{S}_7$ with a Ruddlesden-Popper crystal having open structure which favours anionic conduction. Also a BaBi_2S_4 electrolyte, which is the analogue to Bi_2O_3 , the excellent oxide ion conductor, was attempted but it failed to form the desired BaBi_2S_4 . TPO of $\text{Ba}_2\text{In}_2\text{S}_5$, $\text{Ba}_3\text{Zr}_2\text{S}_7$ and BaBi_2S_4 varied from 950°C , 670°C and 620°C respectively. TPR of these compounds showed that they were less stable in a reducing atmosphere. Bauerle equivalent circuit for pure ionic conductors fits experimental impedance spectroscopy for BaIn_2S_5 and ZrS_2 doped $\text{Ba}_2\text{In}_2\text{S}_5$ while Jamnik model fits the EIS data of $\text{Ba}_3\text{Zr}_2\text{S}_7$. Impure BaSi_2S_4 exhibited metallic type conduction. The Bauerle model for pure ionic conductors identifies BaIn_2S_5 with a bulk conductivity of $2.61 \times 10^{-6} \text{S.cm}^{-1}$, at 500°C , which is two times greater than the $\text{CaNd}_2\text{S}_4+0.1\text{Nd}_2\text{S}_3$ reference compound. Doping with 20mol% ZrS_2 causes a marginal improvement in conductivity at this temperature. $\text{Ba}_3\text{Zr}_2\text{S}_7$ has a bulk conductivity of $5.41 \times 10^{-3} \text{S.cm}^{-1}$, at 500°C . EIS experiments in varying H_2S partial pressure from 0vol% $\text{H}_2\text{S}/\text{Ar}$ to 2vol% $\text{H}_2\text{S}/\text{Ar}$ confirms the following:
 - Undoped $\text{Ba}_2\text{In}_2\text{S}_5$ exhibits ionic conduction up to 1vol% $\text{H}_2\text{S}/\text{Ar}$ but with the onset of hole conduction at high H_2S concentrations
 - $\text{BaIn}_2\text{S}_5+0.2\text{ZrS}_2$ exhibits ionic conduction up to 1vol% $\text{H}_2\text{S}/\text{Ar}$ but with the onset of electronic conduction at high H_2S concentrations
 - $\text{Ba}_3\text{Zr}_2\text{S}_7$ exhibits the presence of significant electronic conduction.

- Electrochemical pumping of $\text{Ba}_2\text{In}_2\text{S}_5$ by using the $\text{H}_2\text{S}/\text{Ar}/\text{Pt}/\text{electrolyte}/\text{Ar}_2$ leads to following:
 - BaIn_2S_5 exhibits sulphide ion conduction from 600°C up to 700°C with the application of 1Vdc.

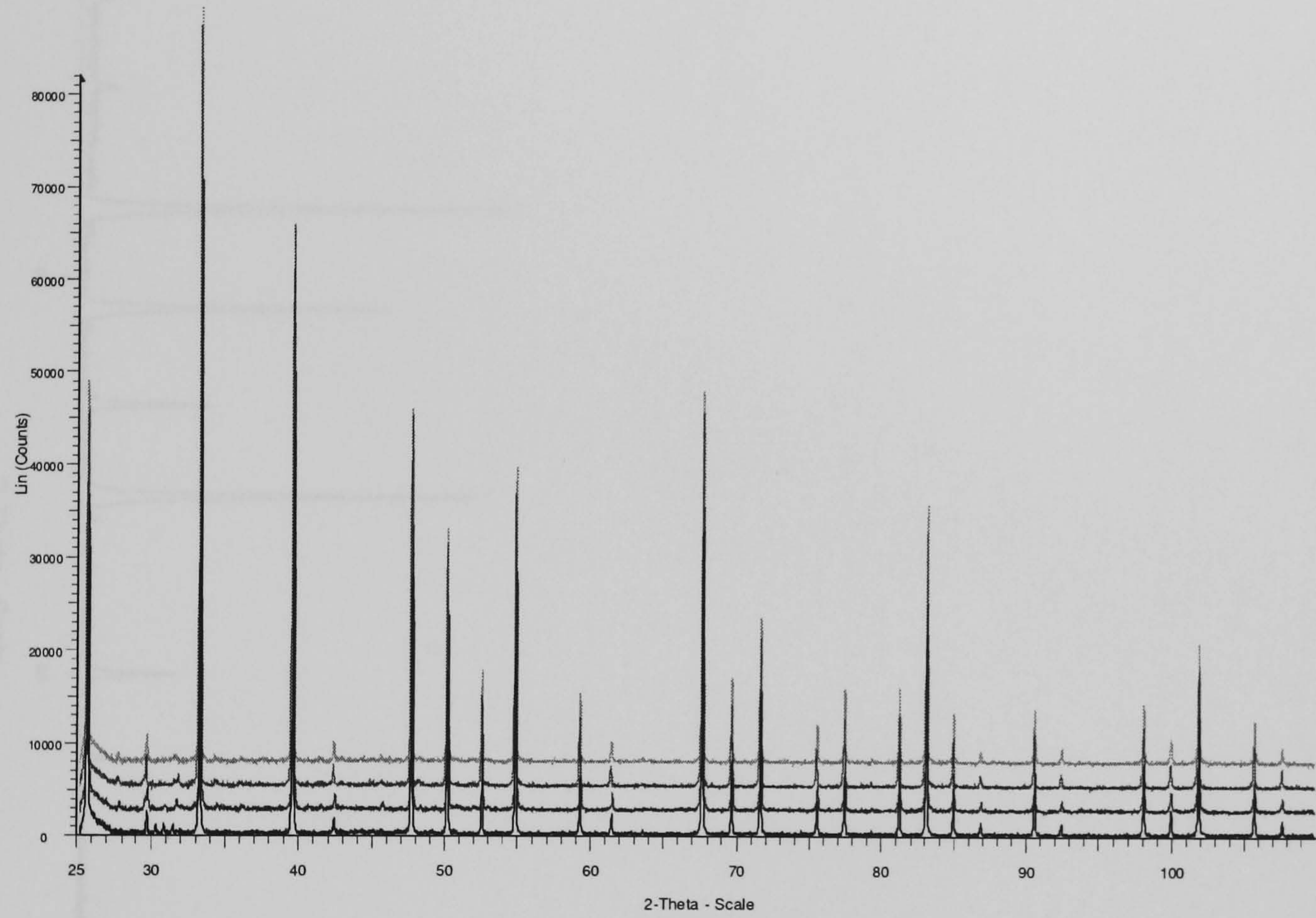
Chapter 8

8. Recommendations and Future Work

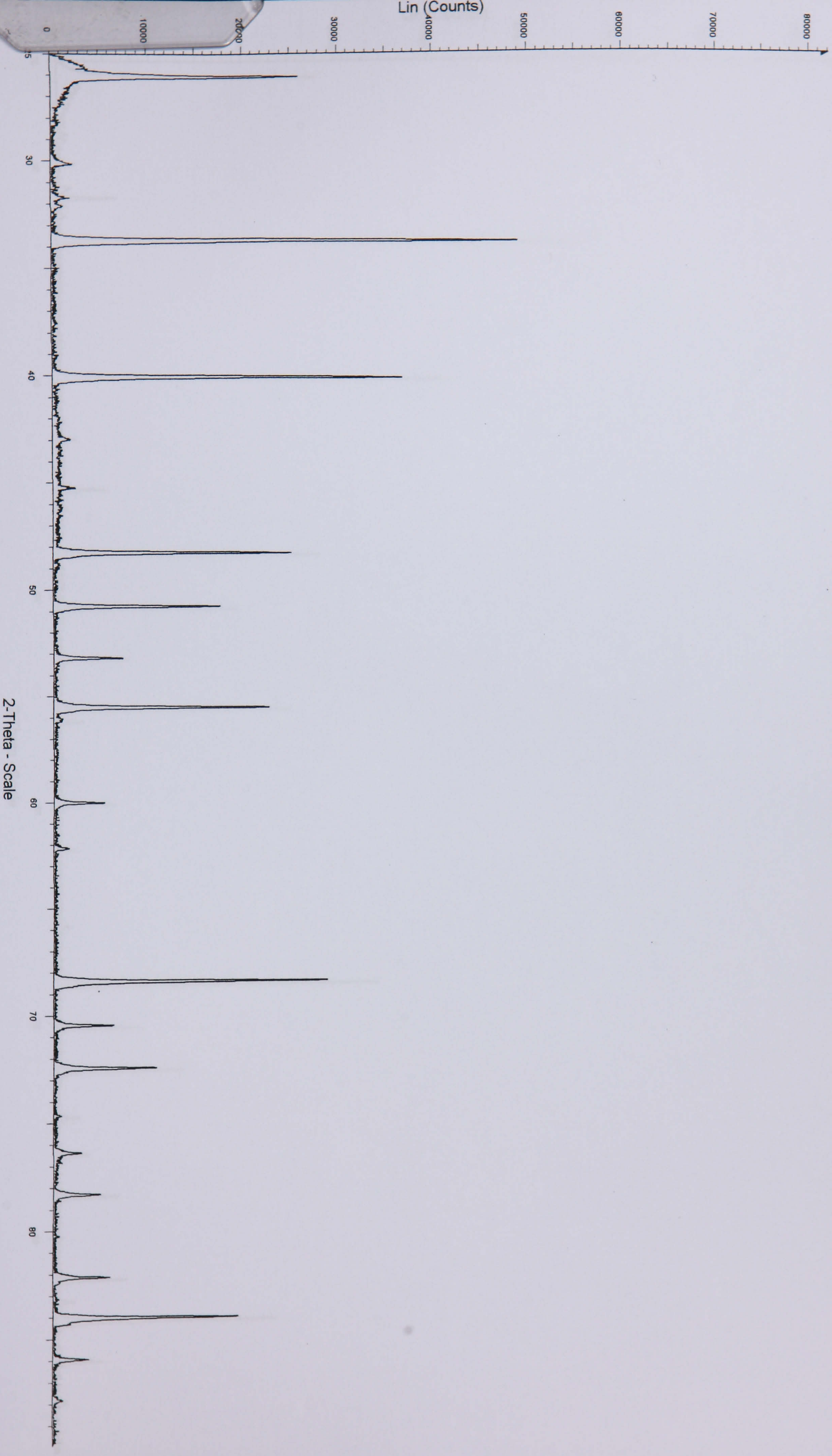
1. Applying the established experimental procedure, TPO and TPR to novel compounds allows for quick and reliable determination of thermal properties. Therefore the technique should be used to complement the electrochemical characterisation of CaSm_2S_4 , SrSm_2S_4 and BaIn_2S_5 (doped and un-doped) materials.
2. Applying ambient 4-point-d.c measurement to ionic conducting material, may give unrepeatable results and as such this method has the potential to be used as a screening tool to differentiate ionic conductors from electronic conductors. Therefore this technique may be used to screening method.
3. EIS should be carried out in an inert atmosphere with un-reactive electrodes accurately characterise the electrolyte. Therefore gold electrodes should not be used with sulphide electrolytes. Platinum electrodes maybe used with sulphide electrolytes, however gases that react with platinum should be avoided, such as H_2 or H_2S but use inert gases such as Ar or He. Graphite electrodes are compatible with sulphide electrolytes as well as reactive gases such as H_2S . Future EIS characterisation should be carried out ionic conducting electrolytes in varying H_2 partial pressure to establish proton ion conduction.
4. CaNd_2S_4 series should ionic conduction at 10mol% Nd_2S_3 doping; increasing beyond this level did not lead to any significant improvement in ionic conductivity. Therefore reducing the dopant to less then 10mol% Nd_2S_3 should be done to optimise the ionic conductivity of the series of compounds
5. SrNd_2S_4 series does appear to be ionic conducting; therefore these materials should be examined as electrode materials.
6. CaSm_2S_4 exhibits peculiar impedance spectra, therefore future electrochemical characterisation in terms of, EIS with various H_2 partial pressures, should be established.
7. SrSm_2S_4 appears to exhibited pure ionic conduction, therefore these materials could be characterised by developing sensor type experiments.
8. Similarly, both $\text{Ba}_2\text{In}_2\text{S}_5$ and $\text{BaIn}_2\text{S}_5+0.2\text{ZrS}_2$ appears to be a sulphide ion conductor and therefore application experiments, such sensors, should be developed for this compound.

9. APPENDIX A

SrNd2S4-Nd2S3 Series

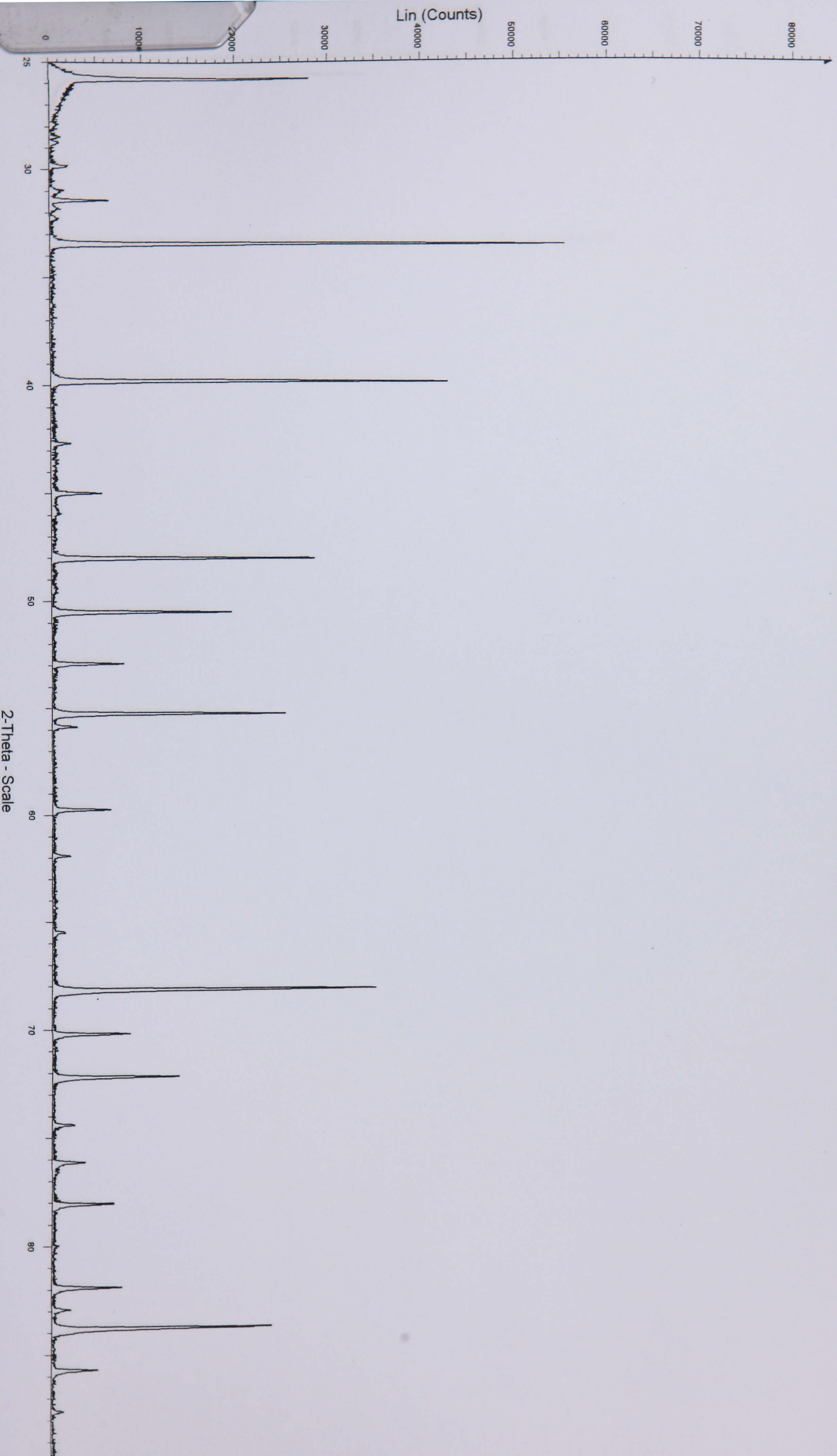


CaSm2S4-0%



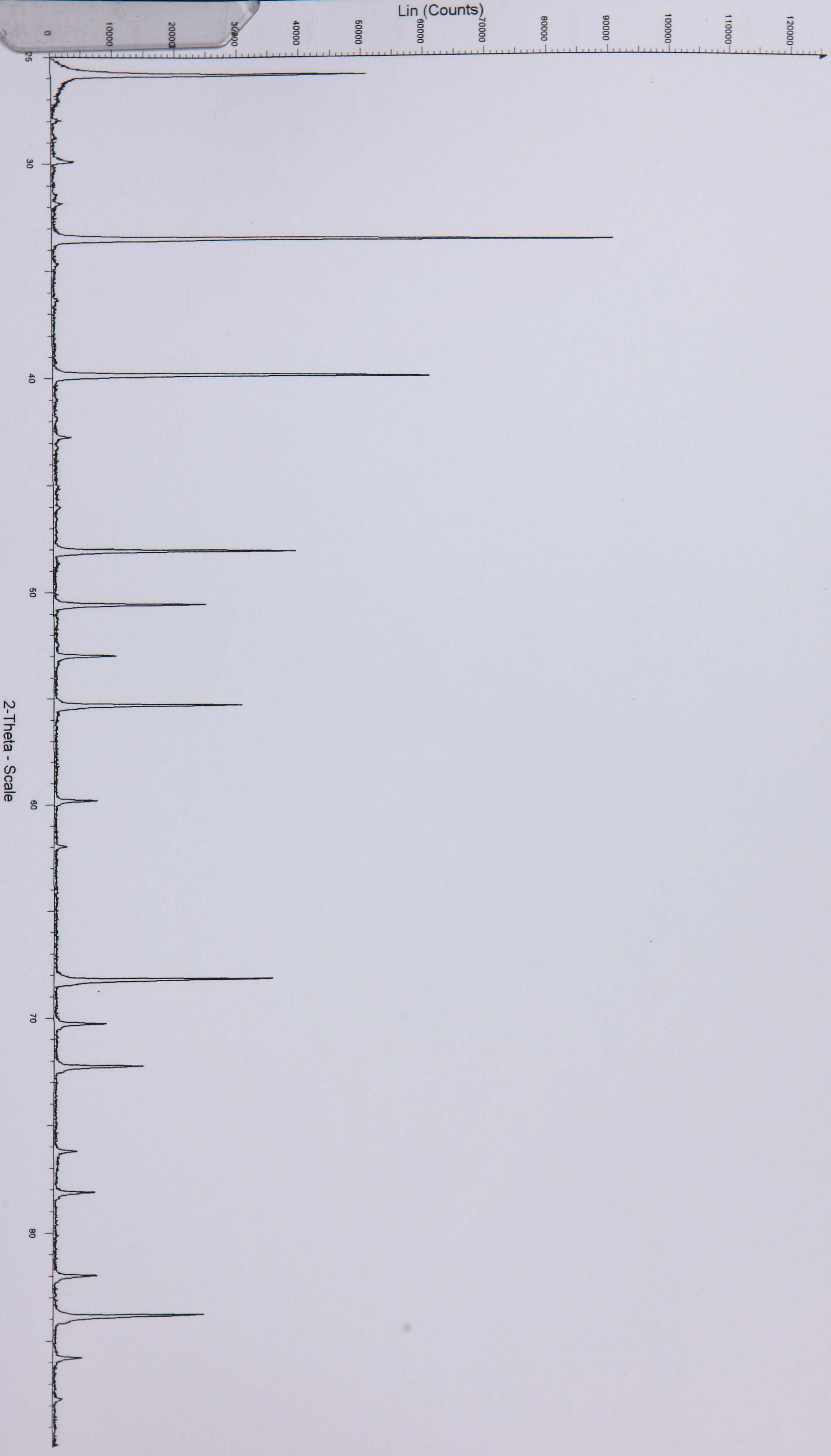
CaSm2S4-0% - File: CaSm2S4 0%.RAW - Type: PSD fast-scan - Start: 25.000 ° - End: 89.930 ° - Step: 0.014 ° - Step time: 12.7 s - Temp.: 25 °C (Room) - Time Started: 1 s - 2-Theta: 25.000 ° - Theta: 12.500 ° - Phi: 0.00 ° - Operations: Background 1.000,1.000 | Import

10%CaSm2S4



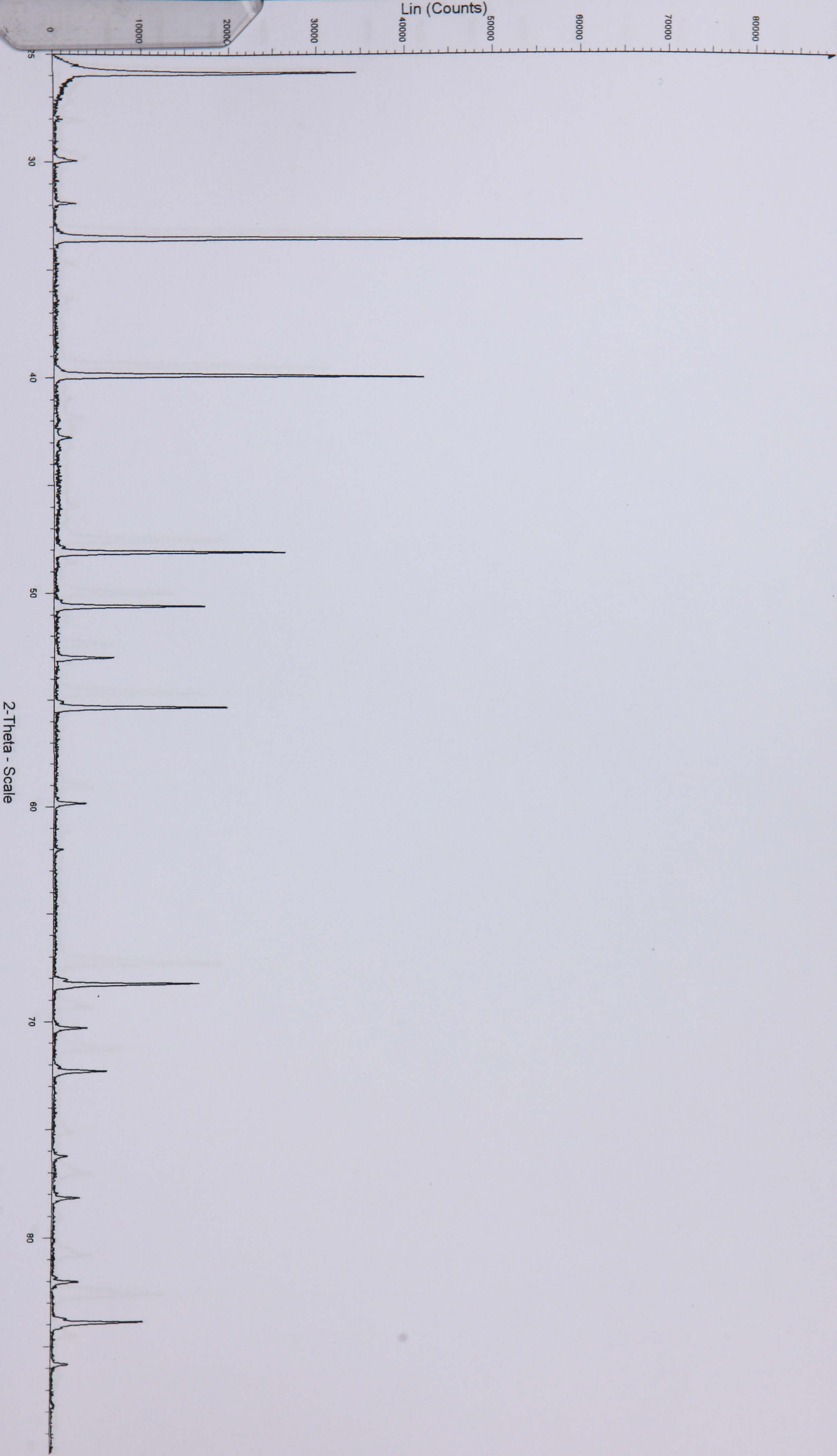
10%CaSm2S4 - File: CaSm2S4 10%.RAW - Type: PSD fast-scan - Start: 25.000 ° - End: 89.930 ° - Step: 0.014 ° - Step time: 12.7 s - Temp.: 25 °C (Room) - Time Started: 1 s - 2-Theta: 25.000 ° - Theta: 12.500 ° - Phi: 0.00 °
Operations: Background 1.000,1.000 | Import

CaSm2S4-20%1



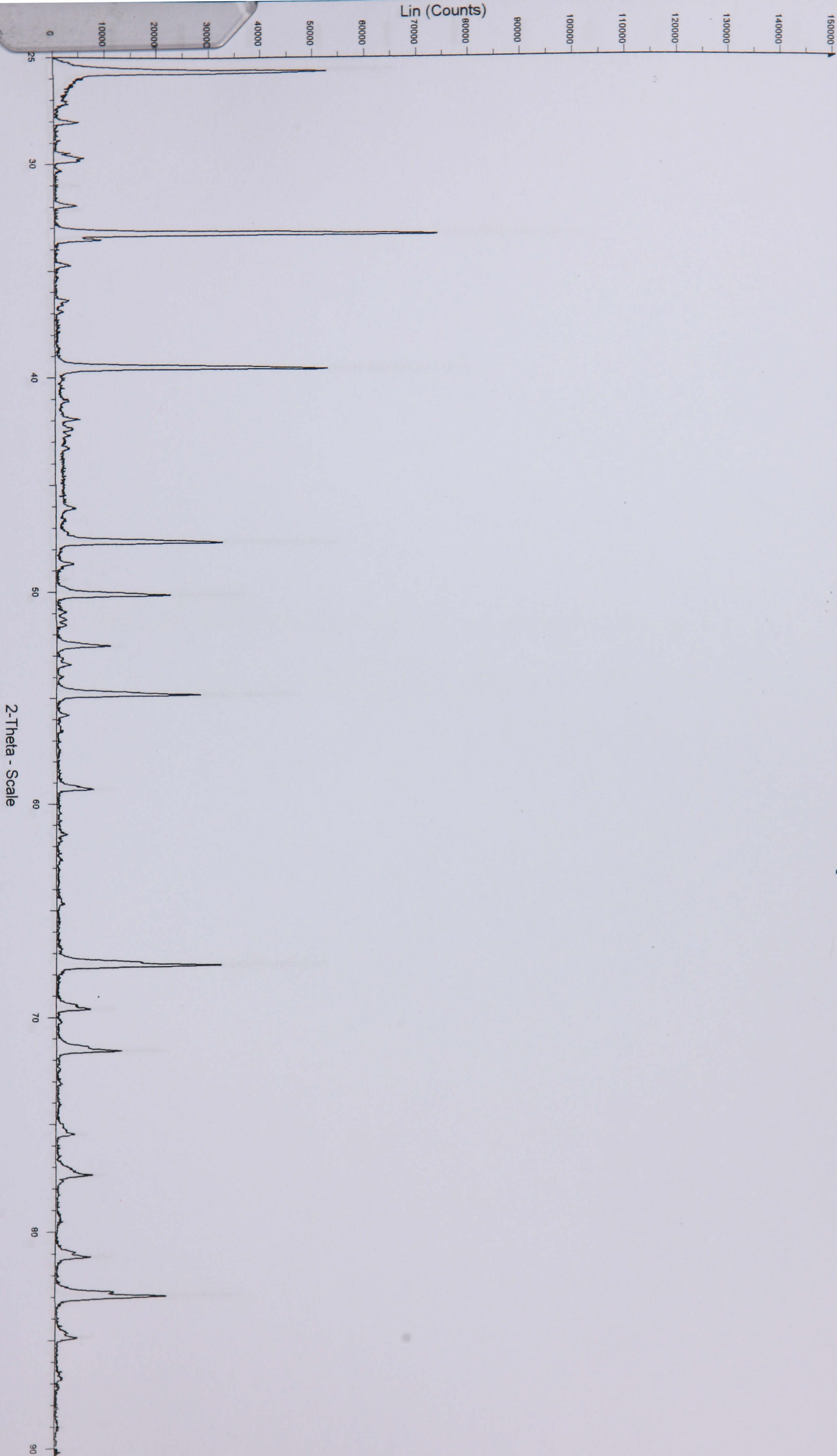
CaSm2S4-20%1 - File: CaSm2S4 20%1.RAW - Type: PSD fast-scan - Start: 25.000 ° - End: 89.930 ° - Step: 0.014 ° - Step time: 12.7 s - Temp.: 25 °C (Room) - Time Started: 3 s - 2-Theta: 25.000 ° - Theta: 12.500 ° - Phi: 0.0
Operations: Background 1.000,1.000 | Import

30% CaSm2S4



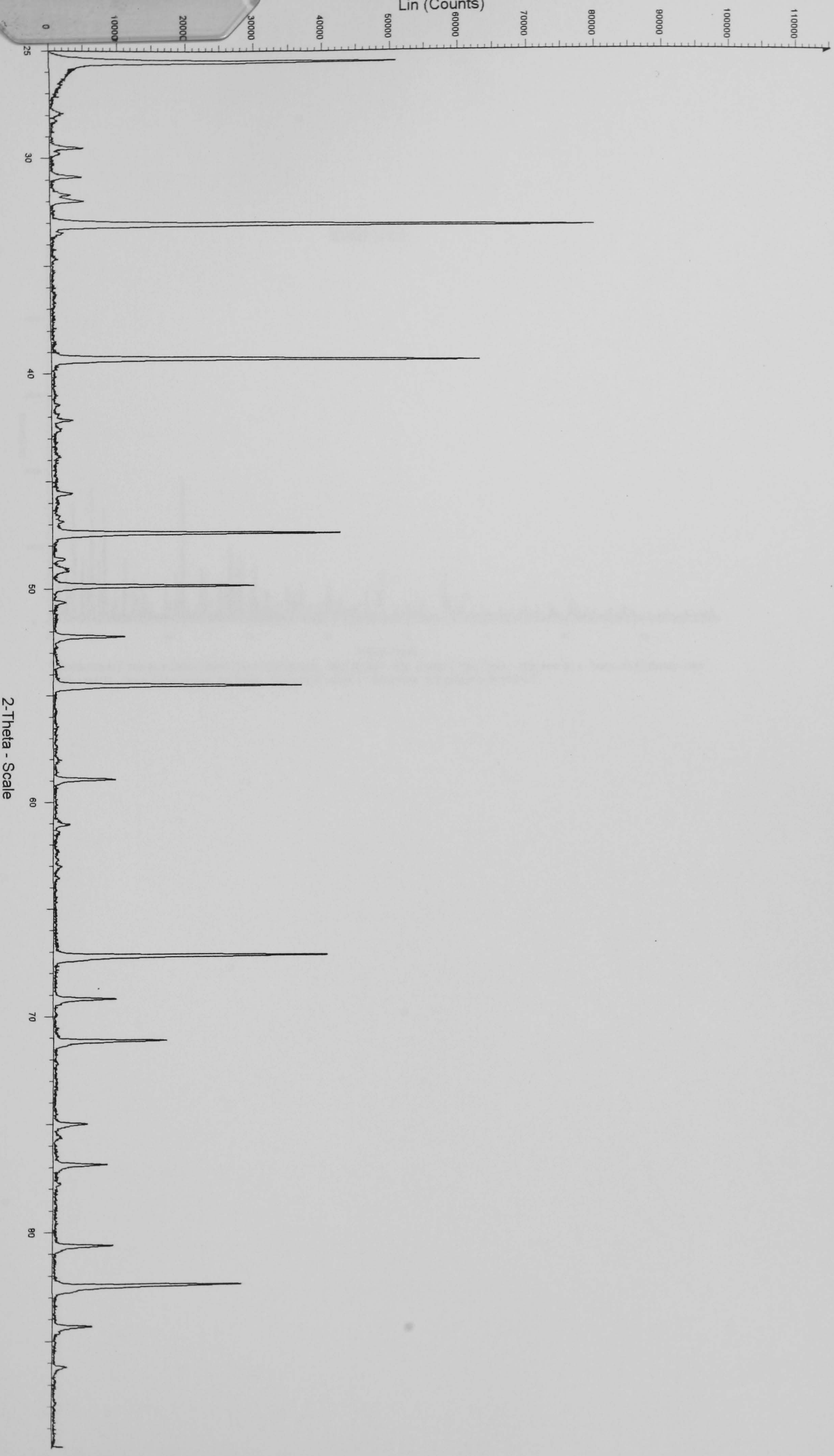
30% CaSm2S4 - File: CaSm2S4 30%.RAW - Type: PSD fast-scan - Start: 25.000 ° - End: 89.930 ° - Step: 0.014 ° - Step time: 12.7 s - Temp.: 25 °C (Room) - Time Started: 1 s - 2-Theta: 25.000 ° - Phi: 0.00 °
Operations: Background 1.000,1.000 | Import

SrSm2S4-20%doped



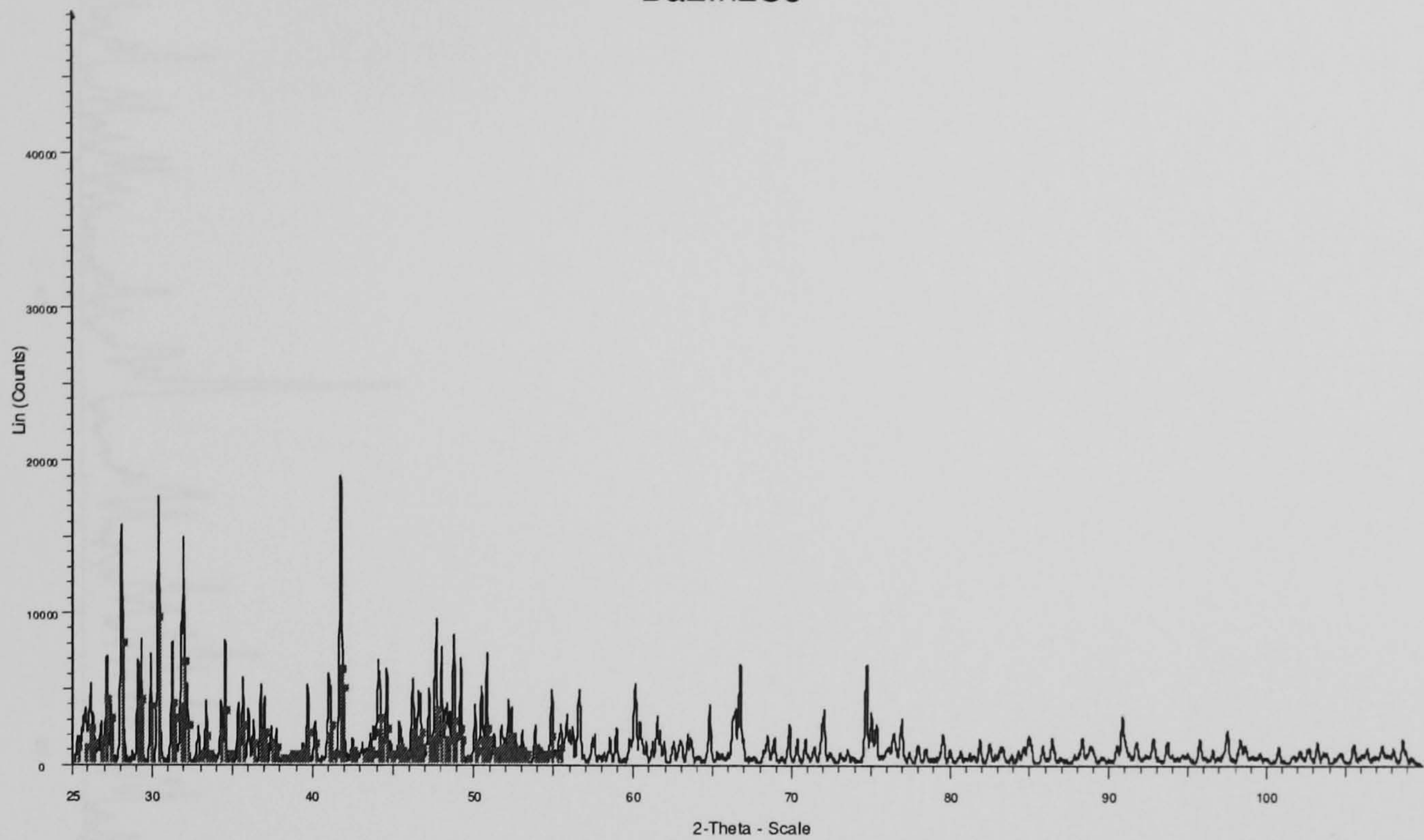
⌵ SrSm₂S₄-20%doped - File: SrSm₂S₄ 20%doped.RAW - Type: PSD fast-scan - Start: 25.000 ° - End: 90.393 ° - Step: 0.014 ° - Step time: 12.7 s - Temp.: 25 °C (Room) - Time Started: 3 s - 2-Theta: 25.000 ° - Theta: 12.500 ° - Operations: Background 1.000,1.000 | Import

SrSm2S4-30%



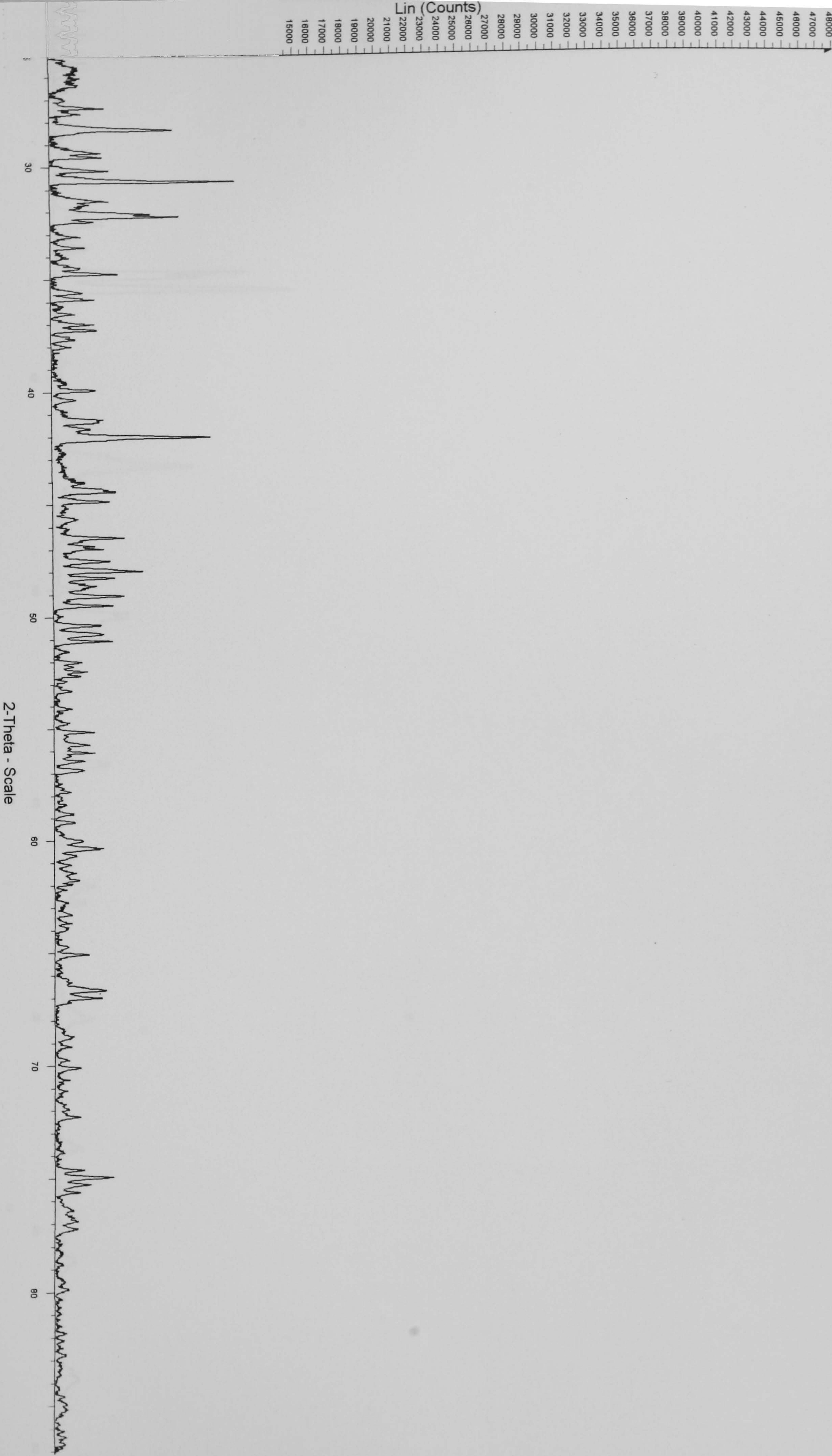
Operations: Background 1.000, 1.000 | Import

Ba2In2S5



■ Ba2In2S5(A1) - File: Ba2In2S5(A1).RAW - Type: PSD fast-scan - Start: 25.000 ° - End: 109.932 ° - Step: 0.014 ° - Step time: 9.1 s - Temp.: 25 °C (Room) - Time
■ 79-1956 (C) - Barium Indium Sulfide - Ba2(In2S5) - Y: 129.66 % - d x by: 1. - WL: 1.5406 - Orthorhombic - I/c PDF 3.7 -

doped Ba2In2S5



doped Ba₂In₂S₅ - File: Ba2In2S5doped.RAW - Type: PSD fast-scan - Start: 25.000 ° - End: 87.101 ° - Step: 0.014 ° - Step time: 12.7 s - Temp.: 25 °C (Room) - Time Started: 3 s - 2-Theta: 25.000 ° - Phi: 0.00
Operations: Background 1.000,1.000 | Import

Ba3Zr2S7+flux



Ba3Zr2S7+flux - File: Ba3Zr2S7+flux.RAW - Type: PSD fast-scan - Start: 25.000 ° - End: 90.393 ° - Step: 0.014 ° - Step time: 12.7 s - Temp.: 25 °C (Room) - Time Started: 3 s - 2-Theta: 25.000 ° - Theta: 12.500 ° - Phi: 0.00 ° - Operations: Background 1.000,1.000 | Import

10. APPENDIX B

Calibration Compounds for TPO/TPR

Bismuth sulphide (Bi_2S_3) was selected as the calibration compound, because it is known to be completely reduce in the presence of hydrogen at elevated temperatures. This is the main method of producing the metal commercially. Through experimenting, Neodymium Sulphide, Nd_2S_3 , was found to react completely with oxygen (at least the same extent as Bismuth Sulphide based on the peak_area:molar_sulphur ratio), hence its selection as a reference compound. The oxidation of Nd_2S_3 and Bi_2S_3 resulted in similar peak areas (based on the same molar sulphide calibration), even though the shapes of the oxidation curves were completely different.

SO_2 Calibration

The material used for SO_2 calibration was Bi_2S_3 , a typical TPO-S is shown in Figure 1A. Complete oxidation of Bi_2S_3 was assumed. The varying experimental conditions used are given below.

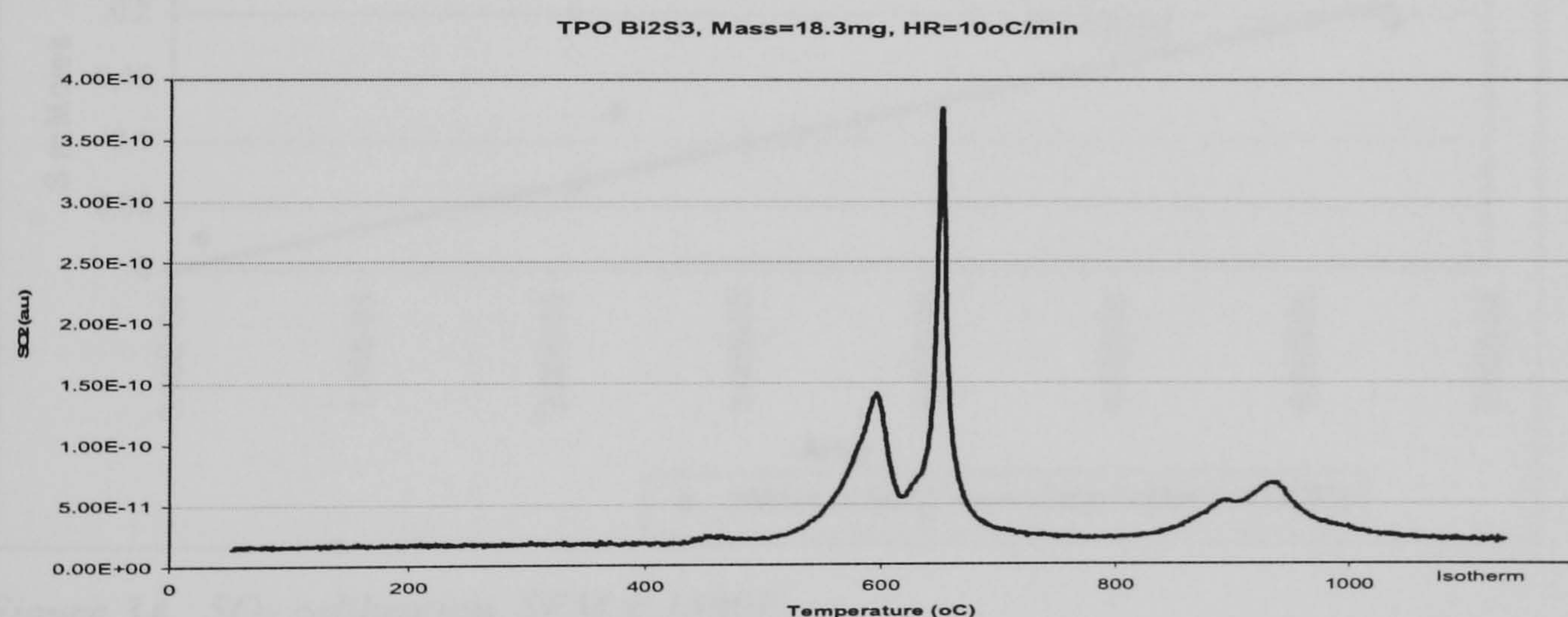


Figure 1A. TPO-S of Bi_2S_3

SEM VOLTAGE EFFECT

Calibration at different voltages was done in order to overcome technical difficulties with the software. It was noted that an increase in the electron multiplier voltage leads to a reduction in the moles-of-sulphur per area ratio (gradient of graph), Figure 3A.,

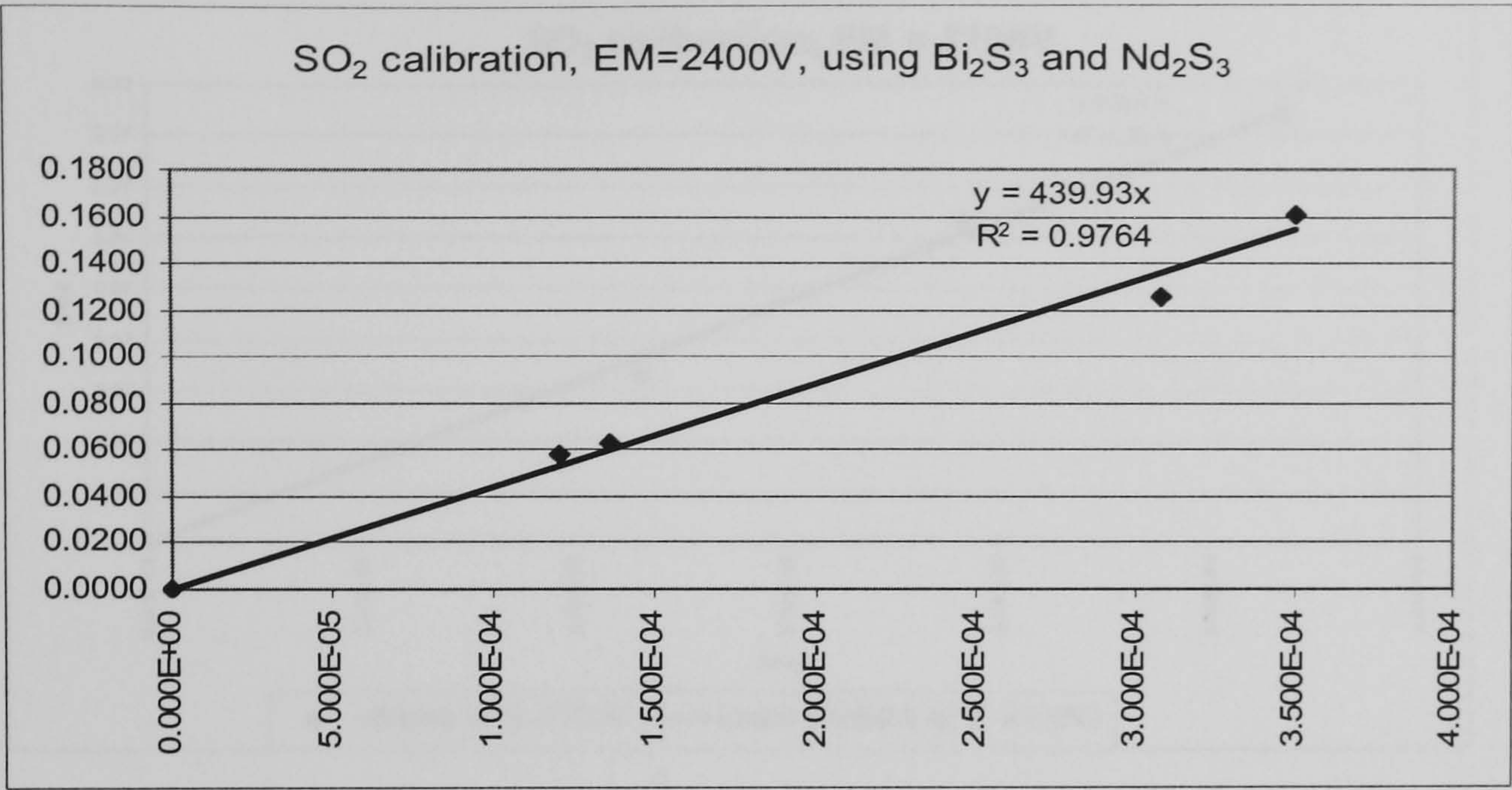


Figure 2A.. SO₂ calibration, SEM = 2400V

SO₂ calibration s at 1800V and 2100V is shown in Figures 3A and 4A below.

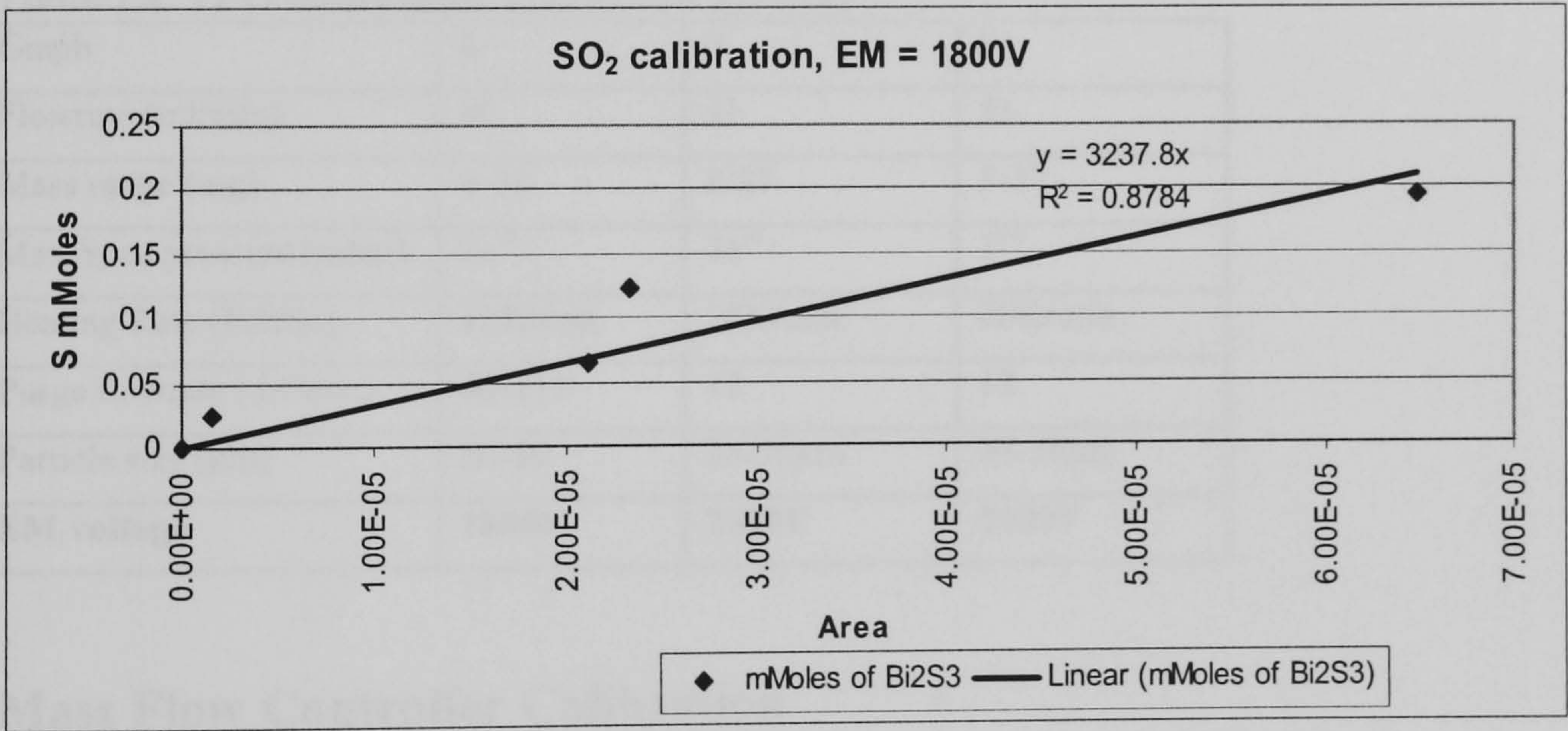


Figure 3A.. SO₂ calibration, SEM = 1800V

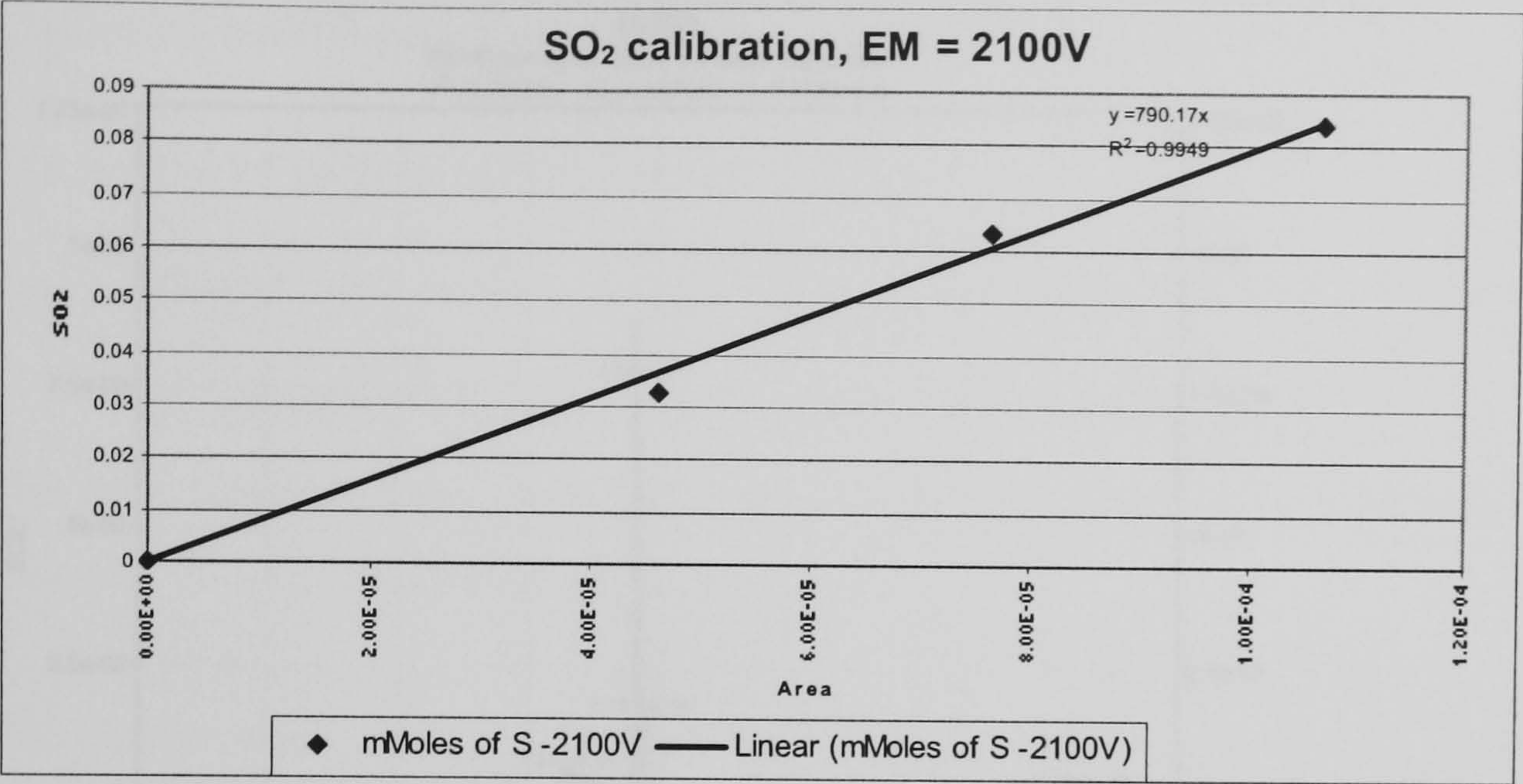


Figure 4A.. SO_2 calibration, SEM = 1800V

TPO Experimental condictioncs used in the calibration experiment are as follows:

Table 1A. TPO calibration conditions for SO_2

Graph	6	7	8
Flowrate (ml/min)	40	51	51
Mass range (mg)	4-33	8-27	5-27
MassSpec pressure (mbar)	$2e^{-6}$	$3e^{-6}$	$3e^{-6}$
Heating Rate (K/min)	15K/min	20K/min	20K/min
Purge flowrate (ml/min)	40-115	12	12
Particle size (μ m)	38-50	38-50 μ m	38-50 μ m
EM voltage	1800V	2400V	2100V

Mass Flow Controller Calibration

Mass flow controllers were calibrated for, argon, helium, hydrogen and air, using a bubble flow meter and a stop watch. The results are presented below.

$Flow_rate_{Ar}(ml/s) = 0.0245 \times MFCS, R^2 = 0.998$

$Flow_rate_{Air}(ml/s) = 0.018 \times MFCS, R^2 = 0.994$

$Flow_rate_{H_2}(ml/s) = 0.0172 \times MFCS, R^2 = 0.9972$

Where MFCS = Mass Flow Controller Setting

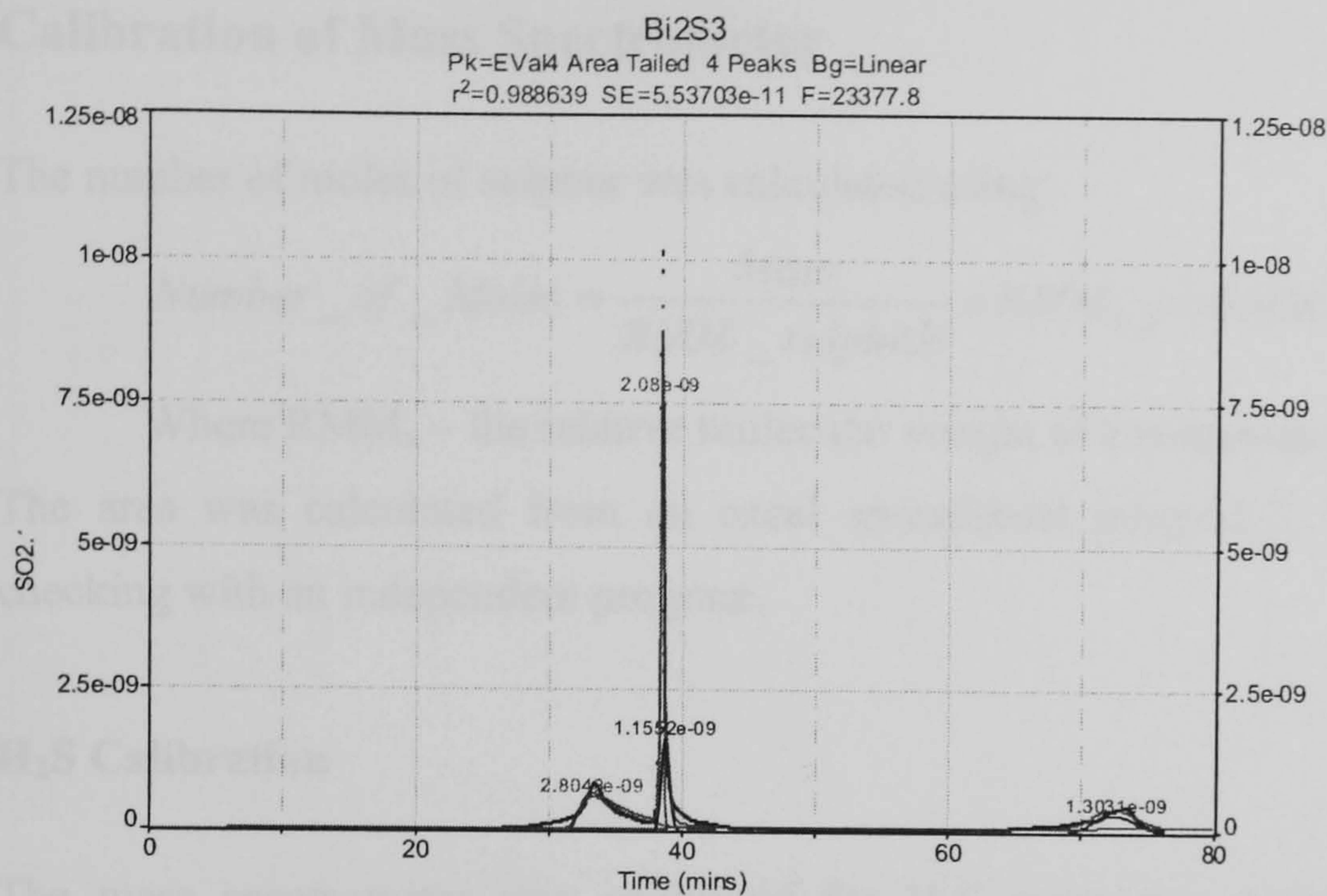


Figure 5A. Deconvoluted SO_2 signal from Mass Spectrometer Oxidation and de-convolution of Bi_2S_3

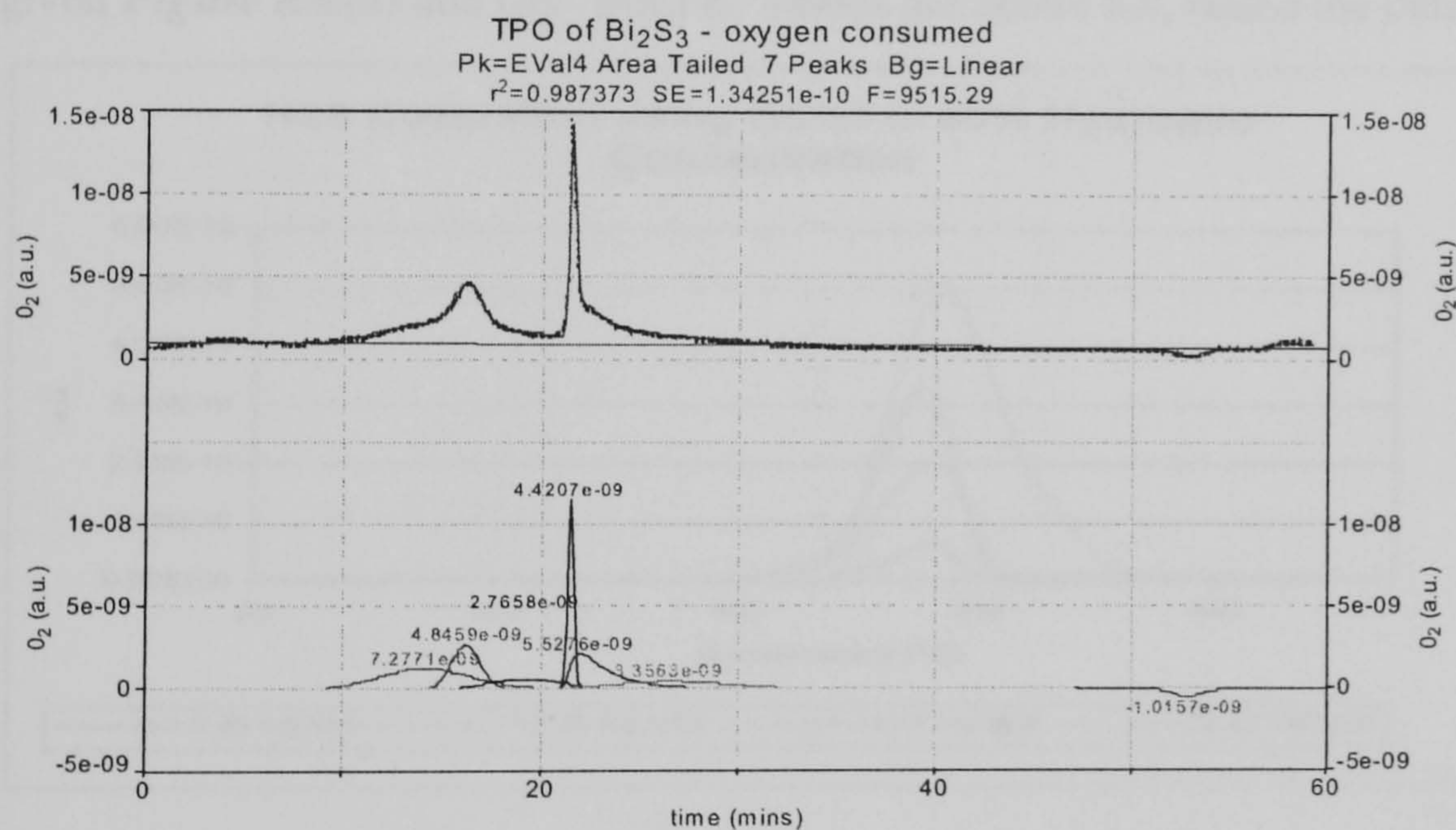


Figure 6A. Deconvoluted O_2 signal from Mass Spectrometer Oxidation and de-convolution of Bi_2S_3

Table 2A. Area for Nd_2S_3 and Bi_2S_3 oxidation deconvoluted peaks

	Area located @ starting temperature ($^{\circ}\text{C}$)	
	Nd_2S_3	Bi_2S_3
1	3.8724e-8 625	<u>1.608e-8@500</u>
2	1.608e-8@650	<u>5.0637e-9@625</u>
3		<u>6.1476e-9@780</u>

Calibration of Mass Spectrometer

The number of moles of sulphur was calculated using:

$$\text{Number_of_Moles} = \frac{\text{Mass}}{\text{RMM_sulphide}} \times \text{RMM}_{\text{H}_2\text{S}} \text{ or } \text{RMM}_{\text{SO}_2}$$

Where RMM_x – the relative molecular weight of a compound

The area was calculated from an excel spreadsheet_integra2.2, which was validated by checking with an independent program.

H₂S Calibration

The mass spectrometer was calibrated for H₂S using two concentrations namely, 20% hydrogen and 80% Hydrogen in Argon. The sample of Bi₂S₃ was varied between 4-30mg of Bi₂S₃. The TPR-S results of Bi₂S₃ are shown in Figure 7A and the derived calibration line is given **Figure 8A**.(a) and (b). Both R^2 values are above 0.9, hence the calibrations are useful.

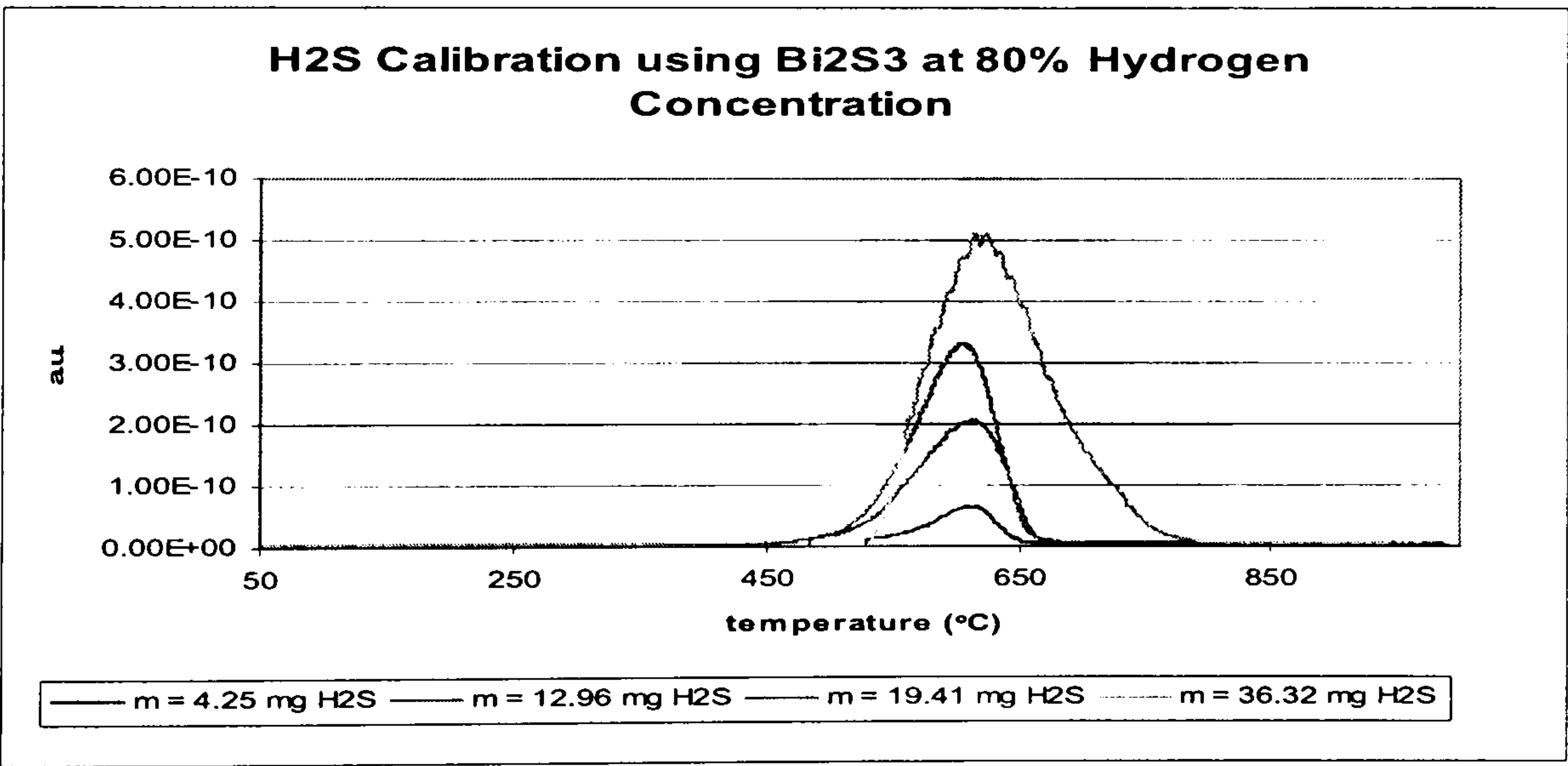


Figure 7A. TPR-S of Bi₂S₃ at 80wt%Hydrogen

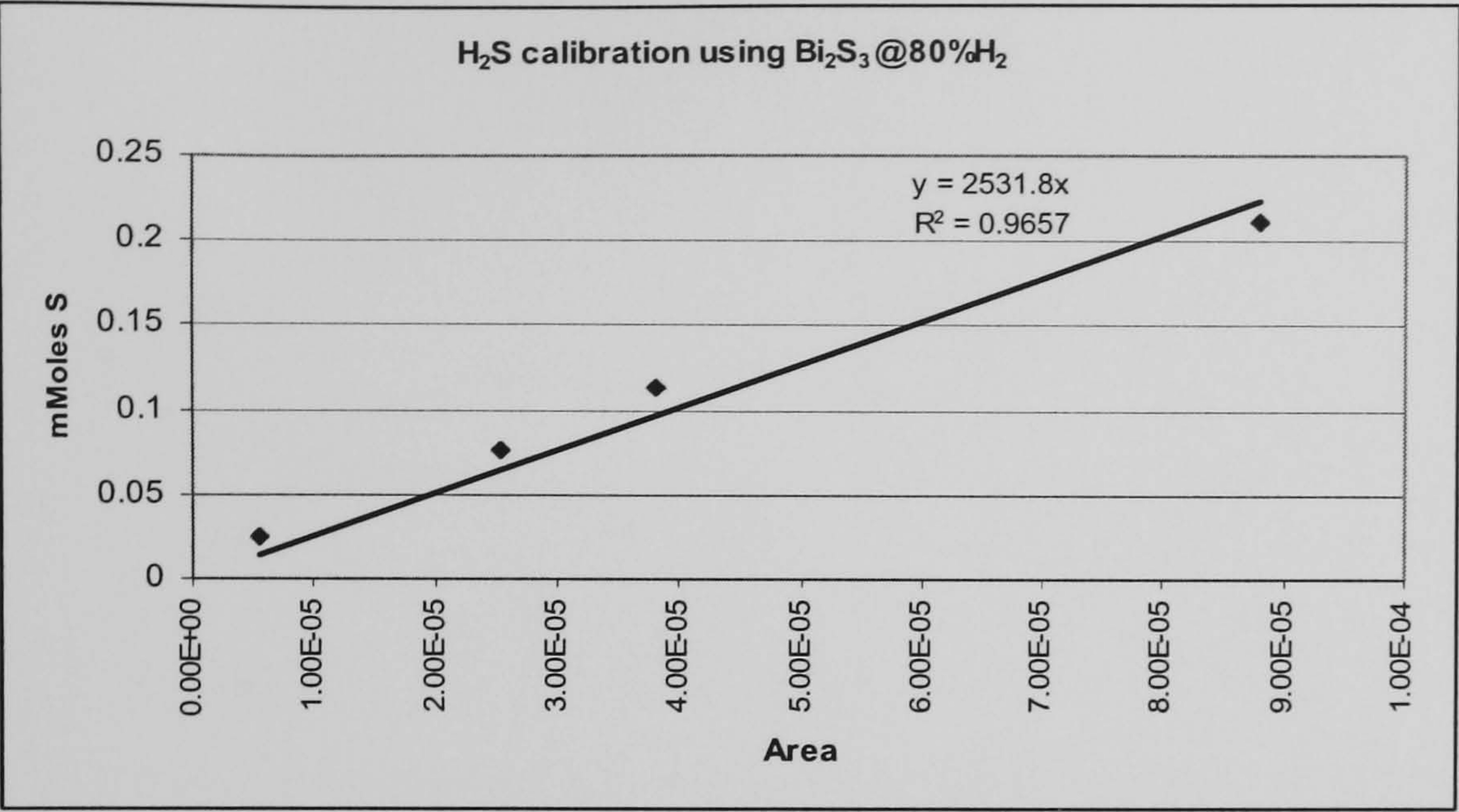


Figure 8A.. H₂S Calibration at different concentration

Table 3A Experimental conditions for H₂S Calibration

	80% H ₂ calibration
Flowrate	40ml/min
Mass range	5-36mg
MassSpec pressure	6-8e ⁻⁶ mbar
Argon pressure	52 psi
Air pressure	50psi
Heating Rate	15K/min
Purge Flow rate	40-60 ml/min
Particle size	38-50μm

11. APPENDIX C

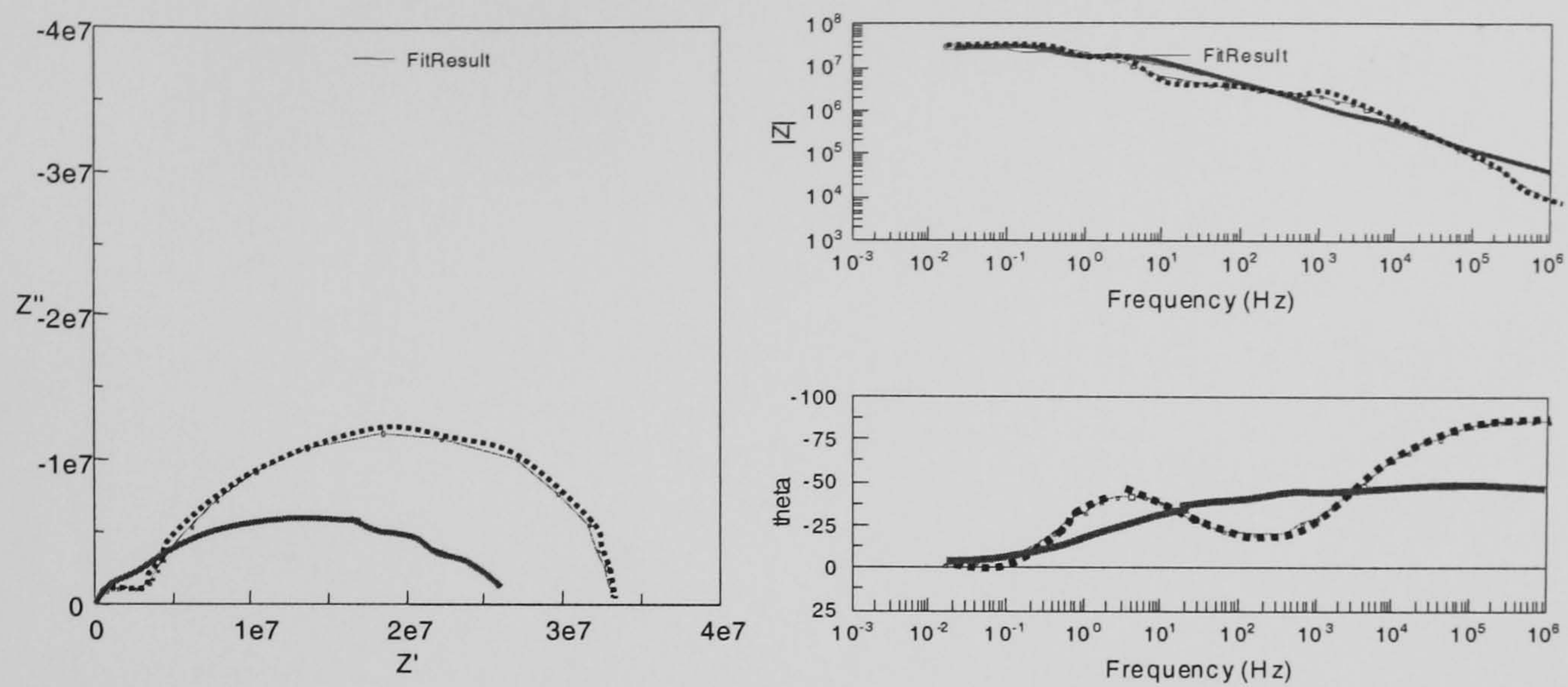


Figure.1 Typical experimental and modelling results for one R-CPE circuit element, weighted sum of squares of 32.67

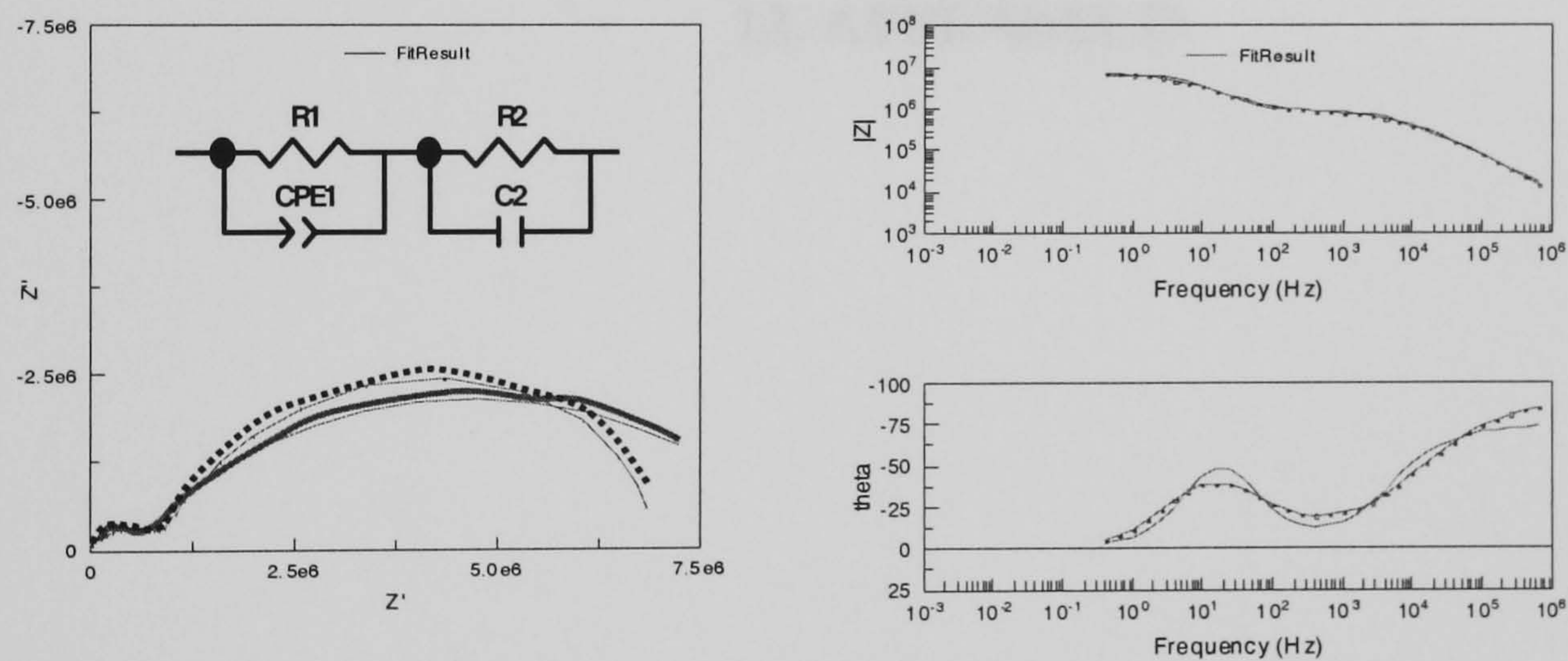


Figure.2 Typical modelling results for R-CPE and R-C circuit element, weighted sum of squares of 1.869

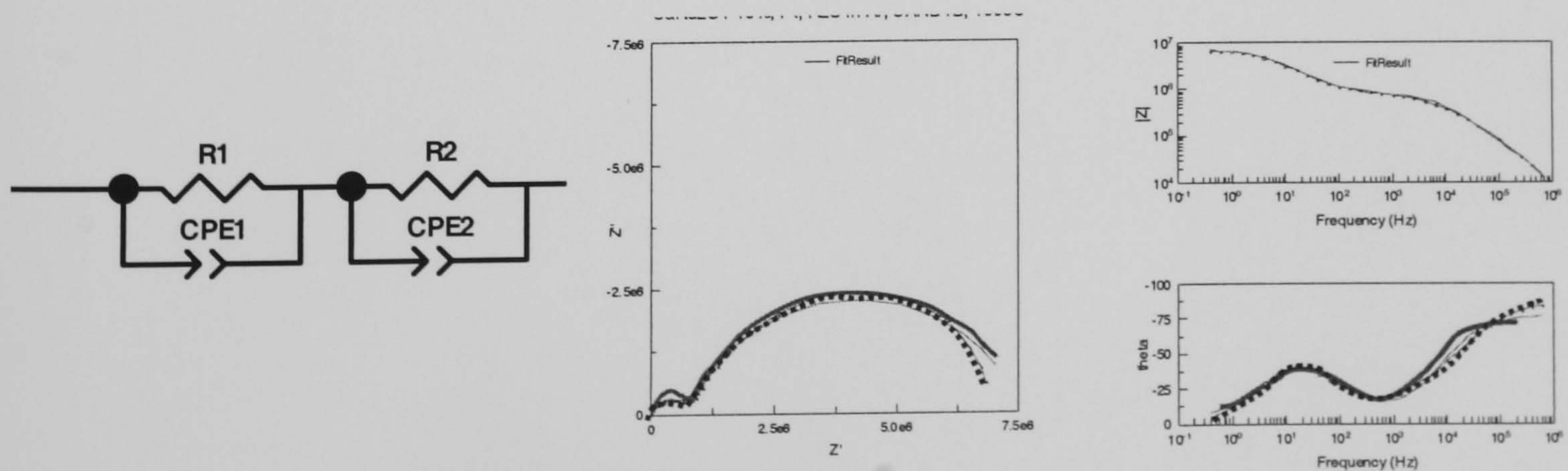


Figure.3. Typical modelling results for two R-CPE circuit element, weighted sum of squares of 0.4659

12. APPENDIX D

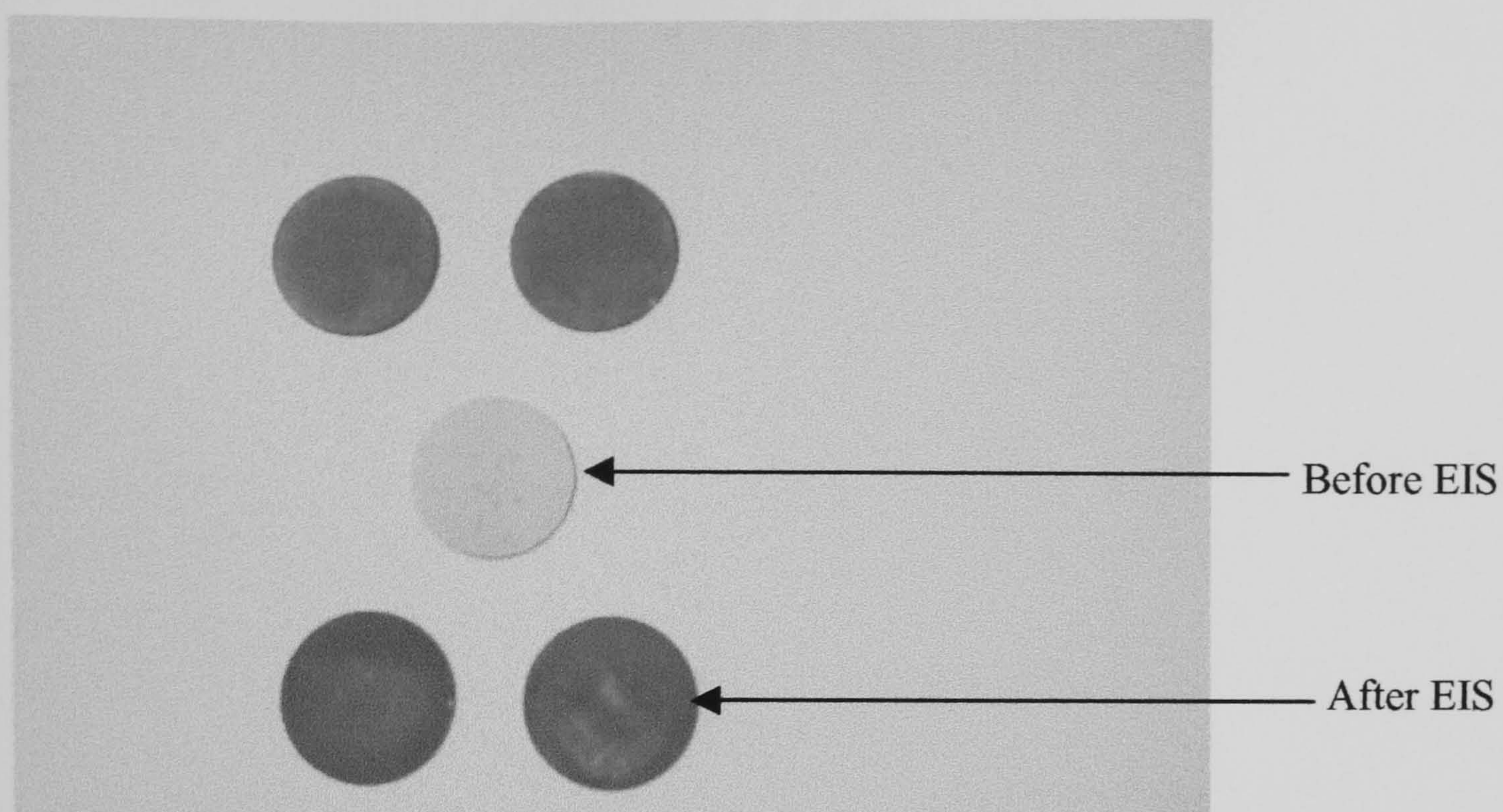
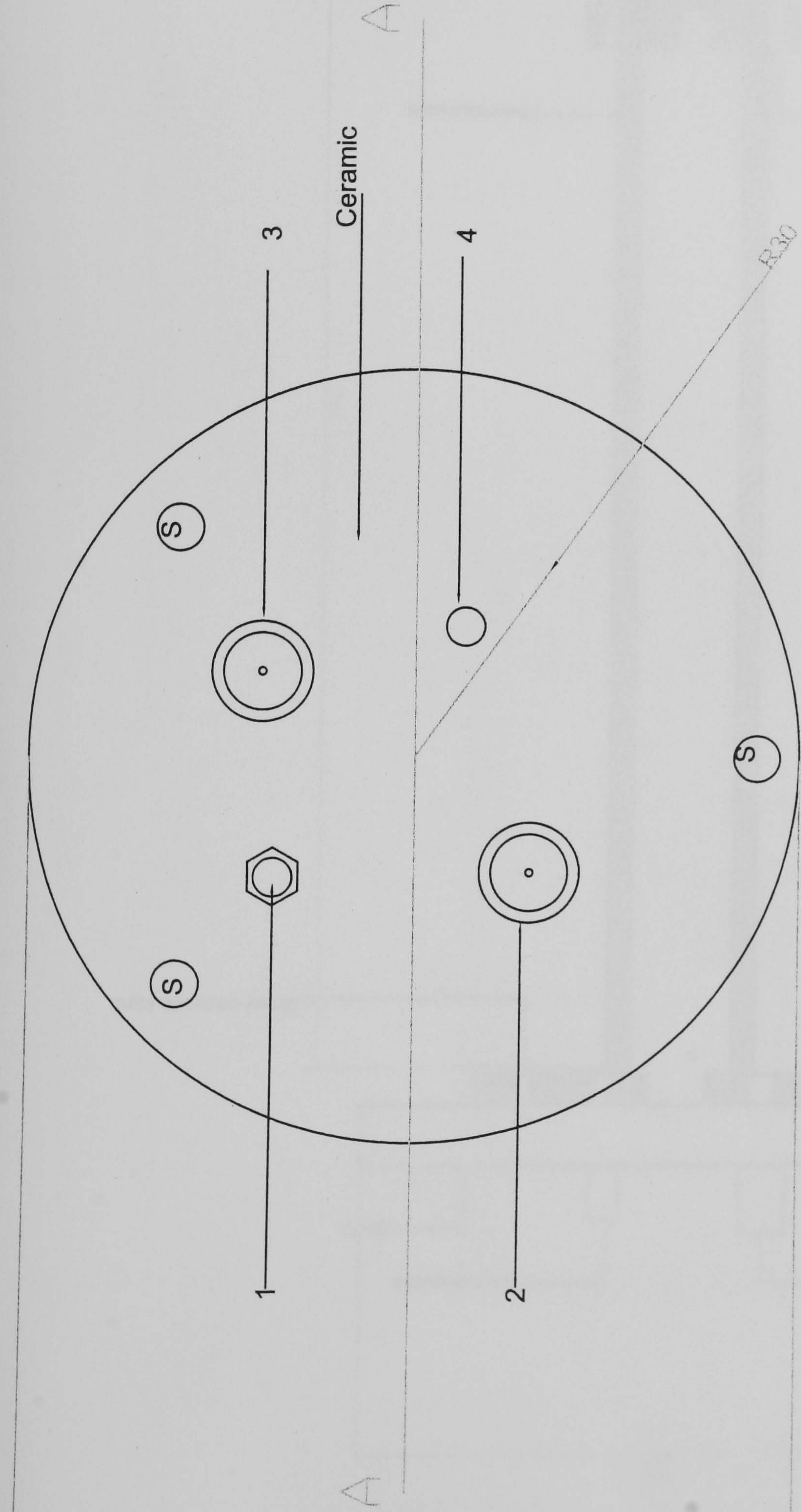
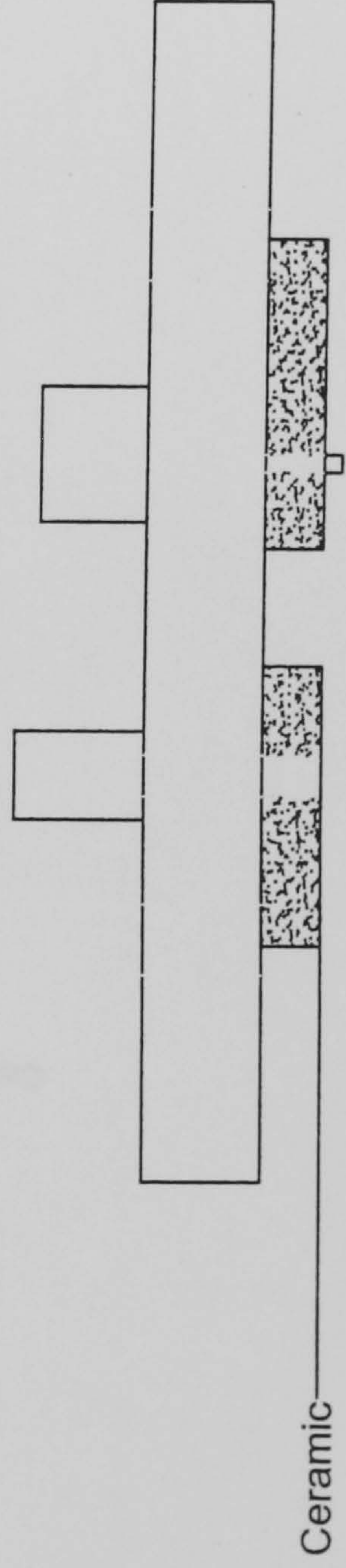


Figure B1. Gold electrodes on CaNd_2S_4 and SrNd_2S_4 compounds (before and after EIS experiments)

13. APPENDIX E



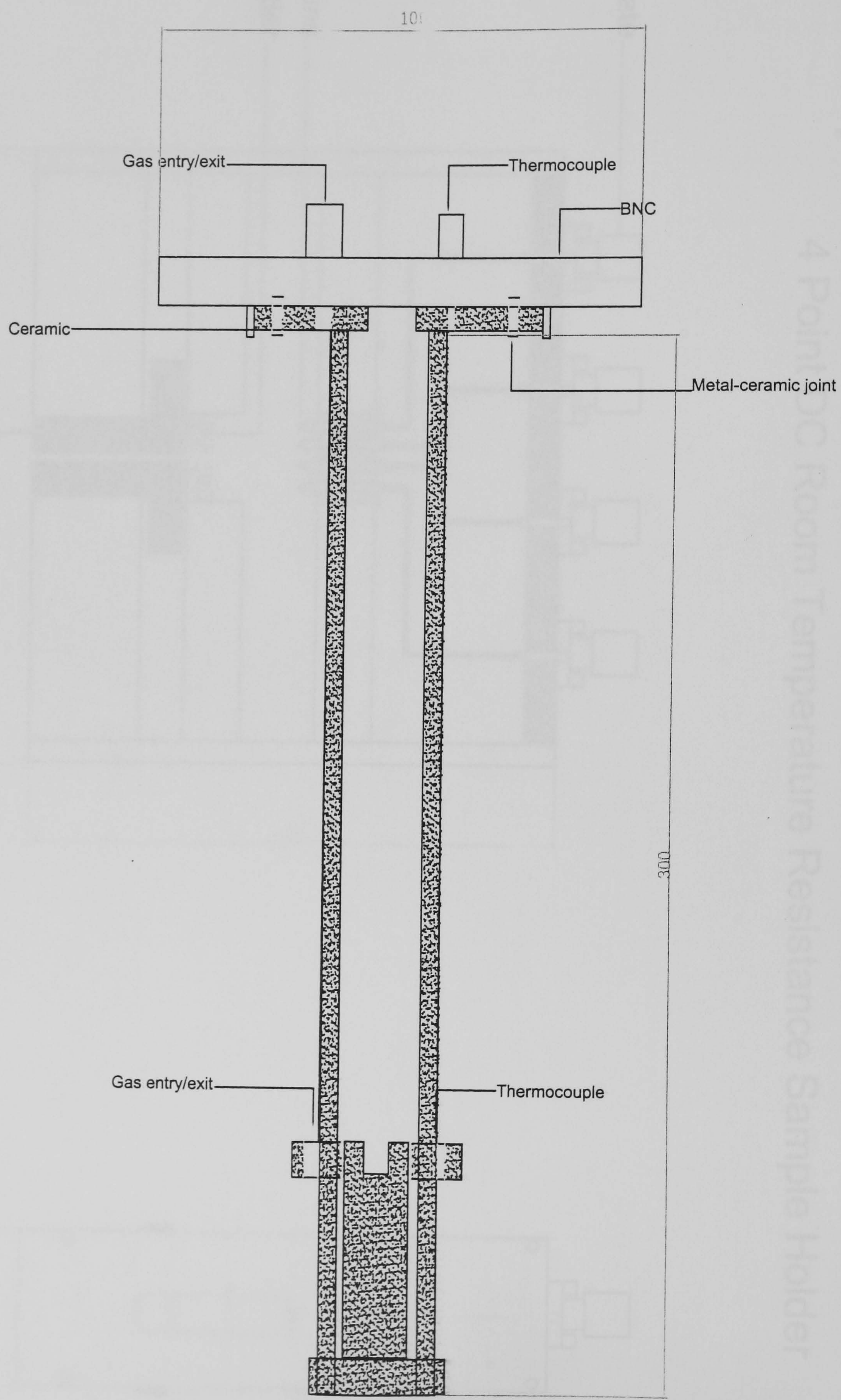
Cross section A-A



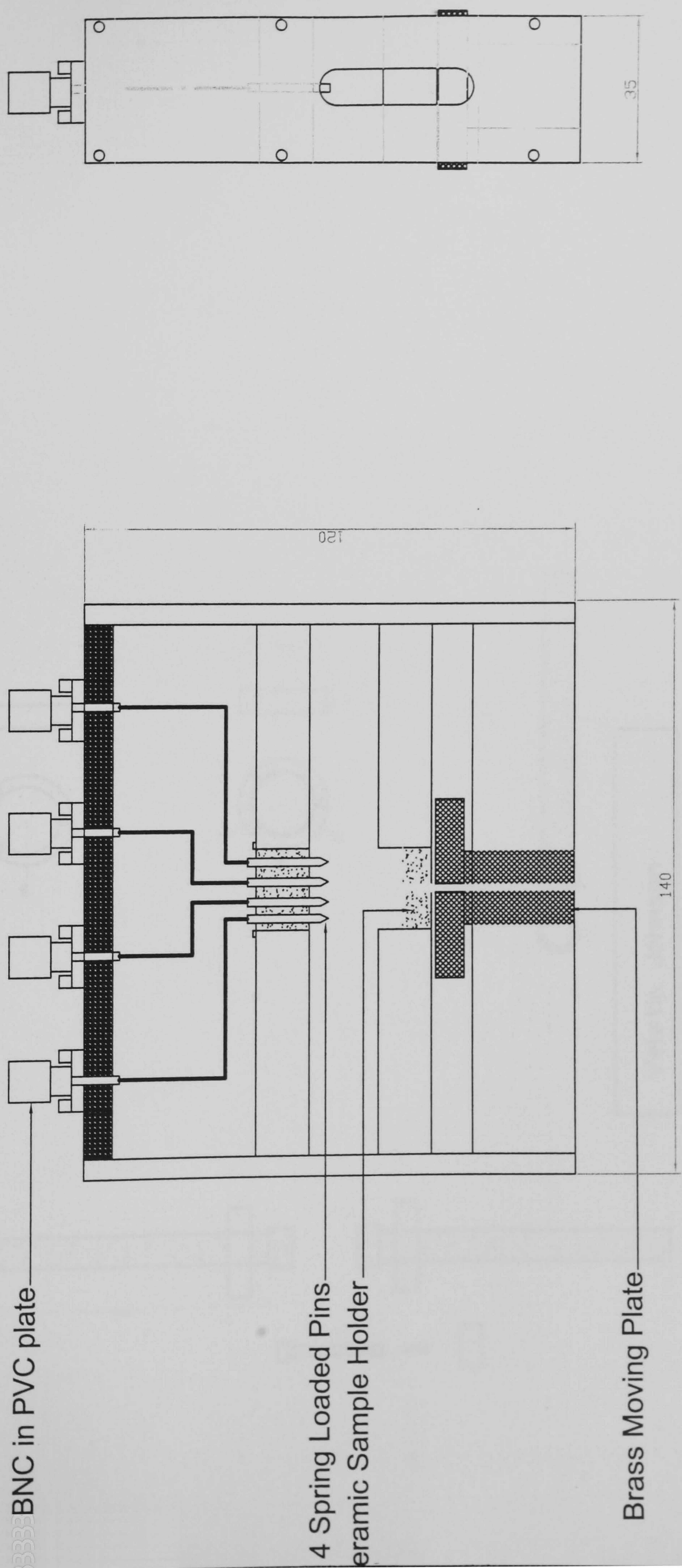
Key

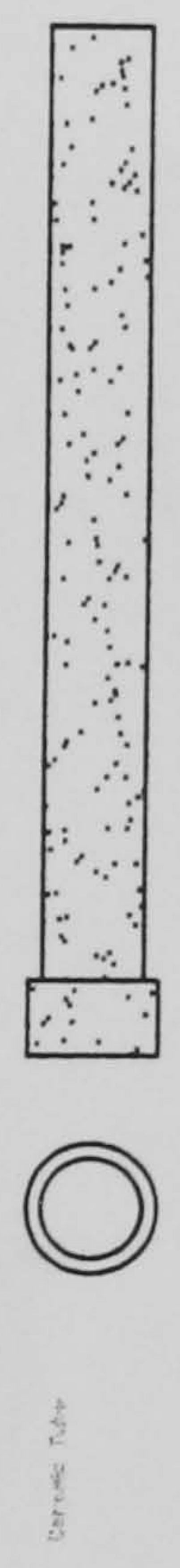
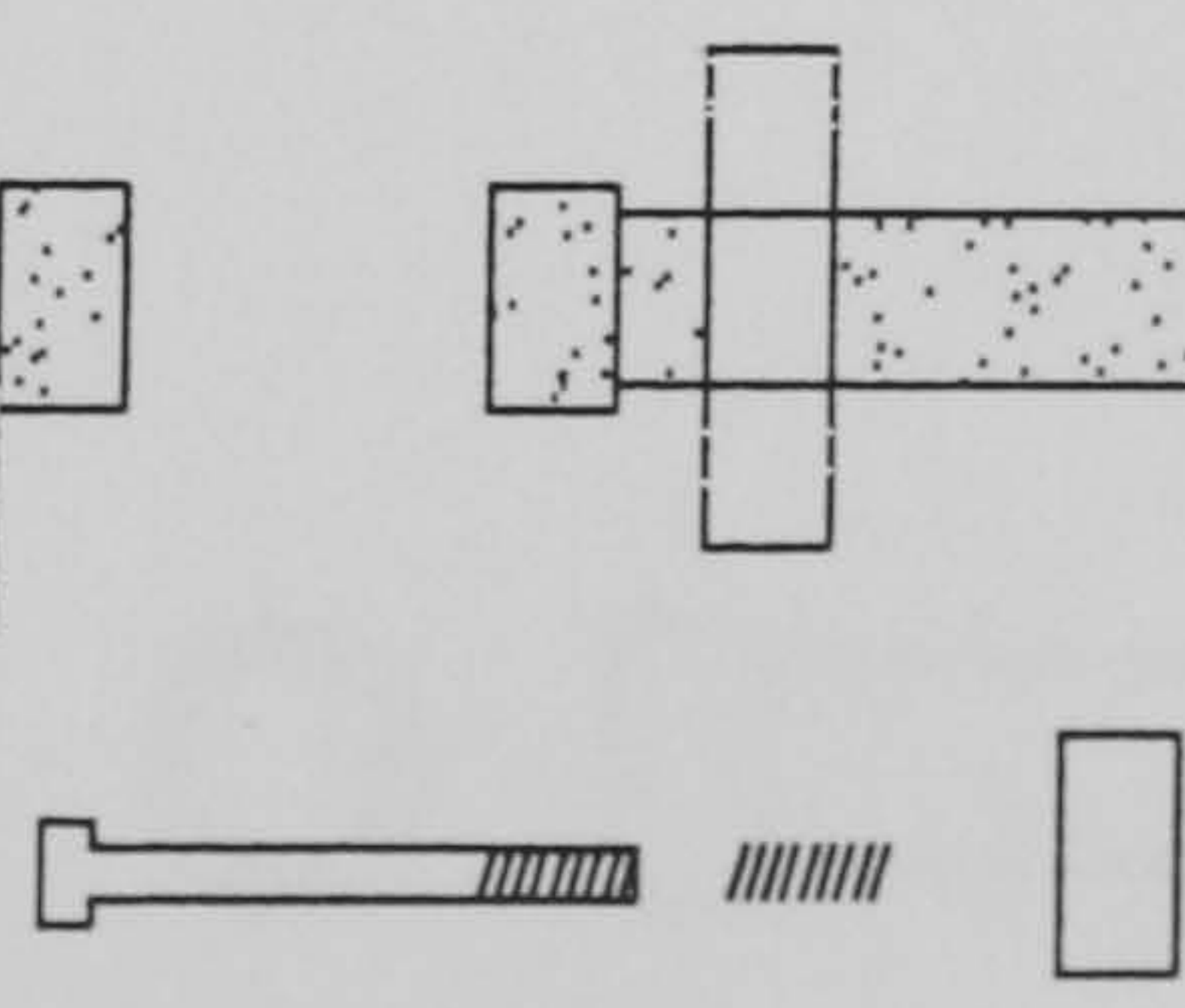
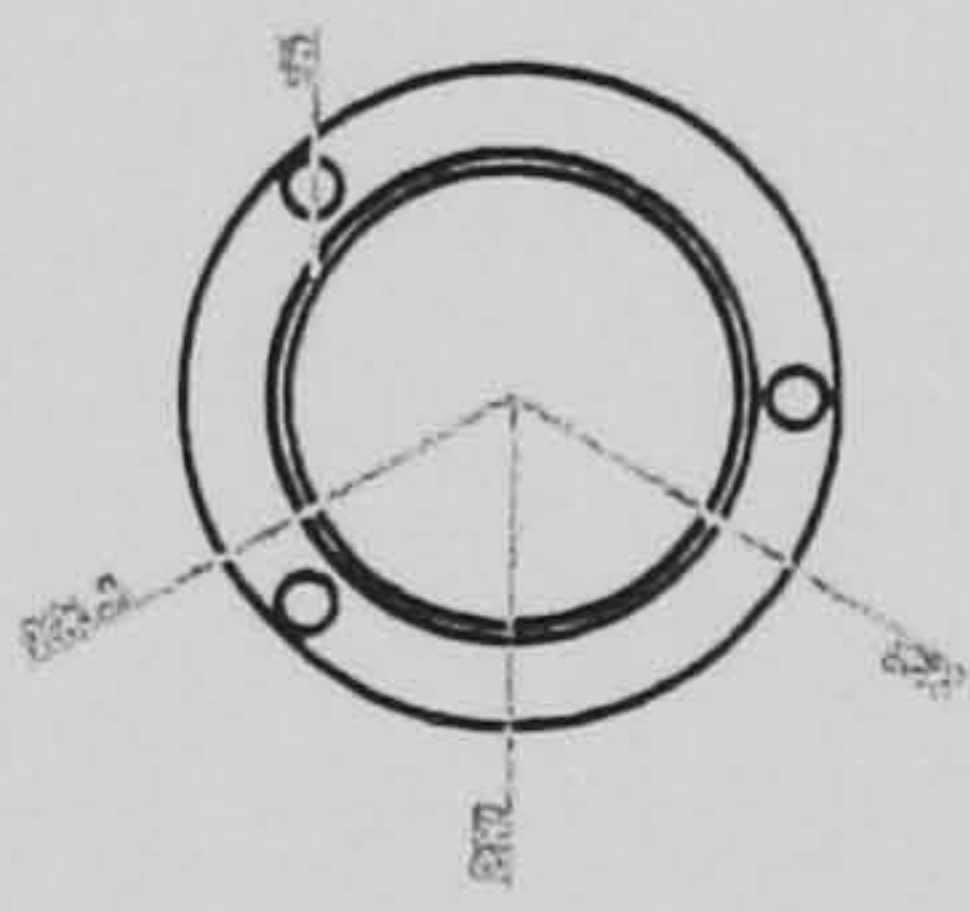
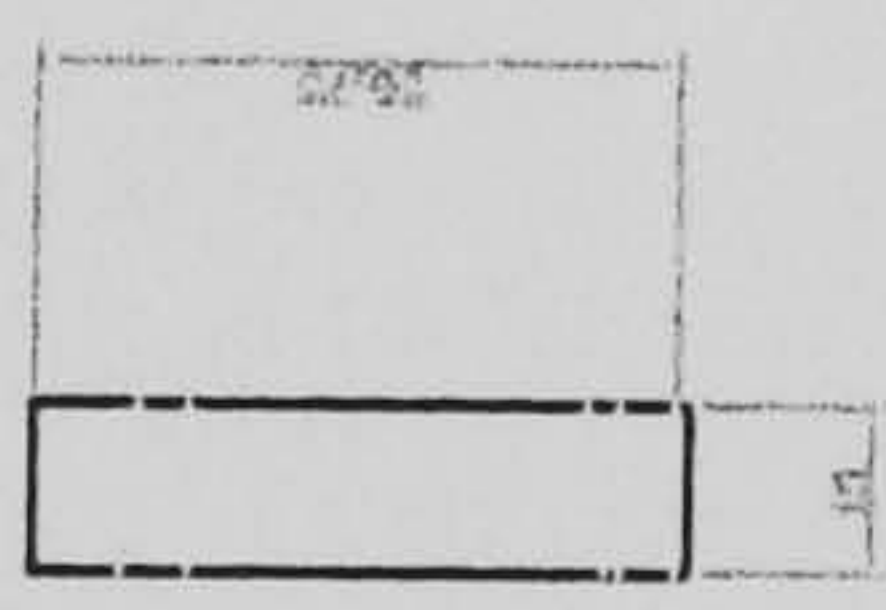
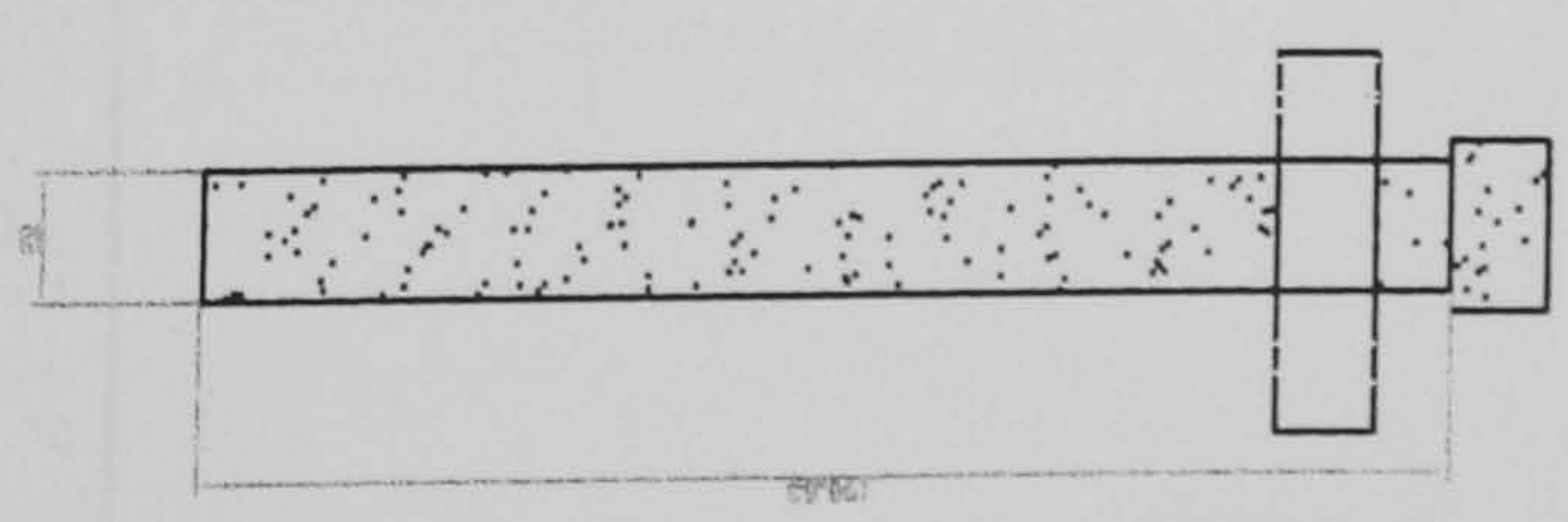
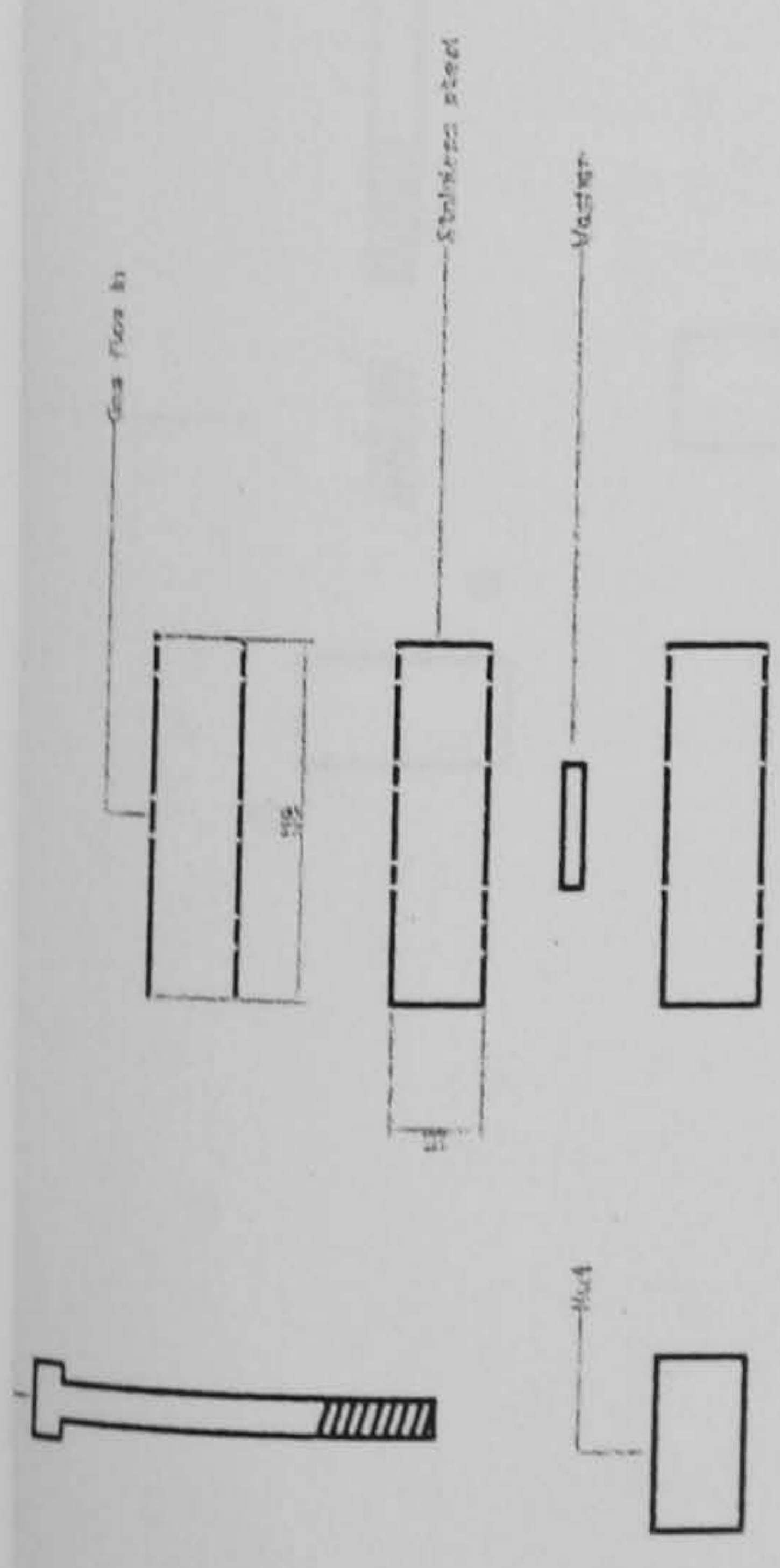
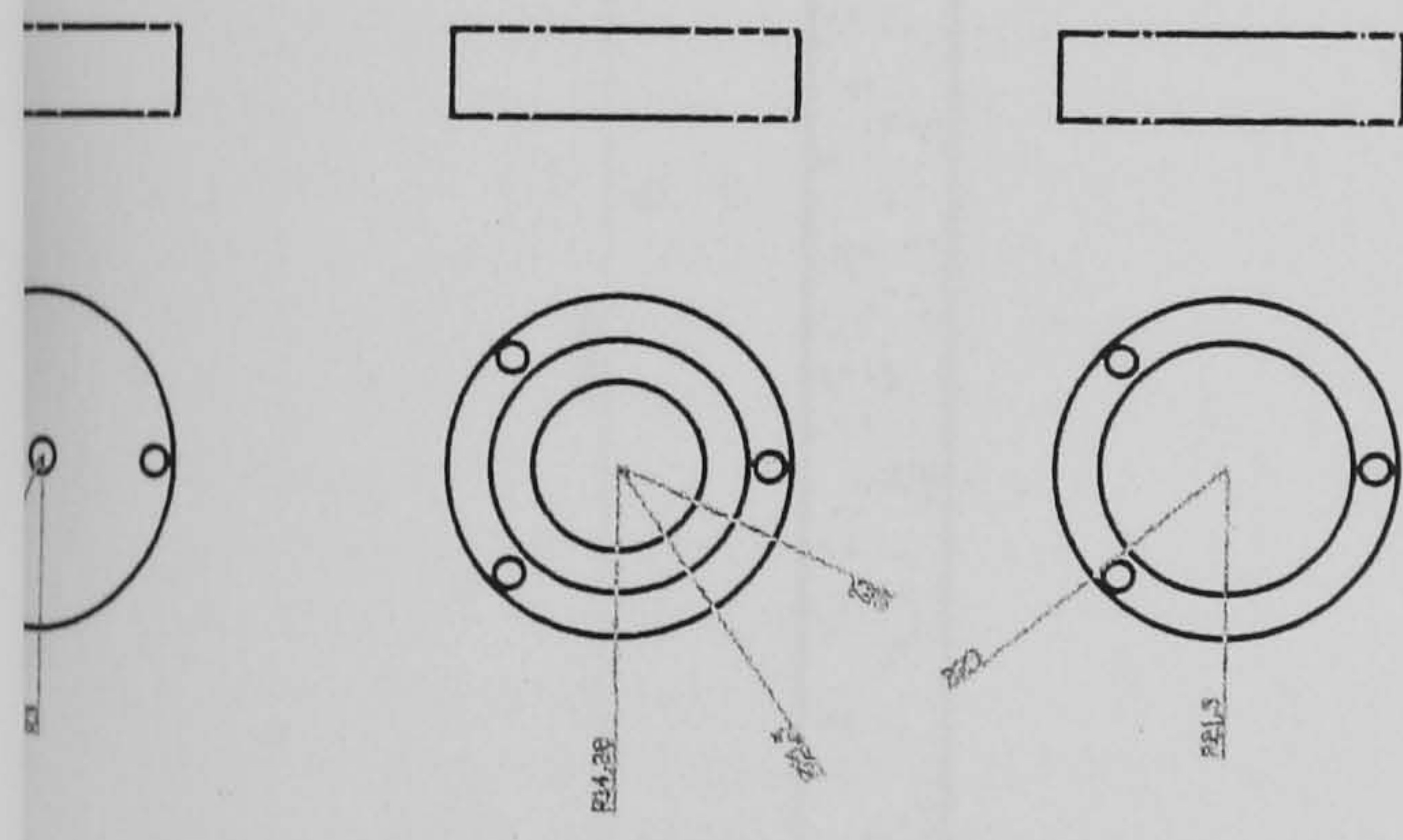
- 1 Gas entry and exit
- 2 BNC #1
- 3 BNC #2
- 4 Thermocouple
- S Screws

Ceramic holder #1



4 Point DC Room Temperature Resistance Sample Holder



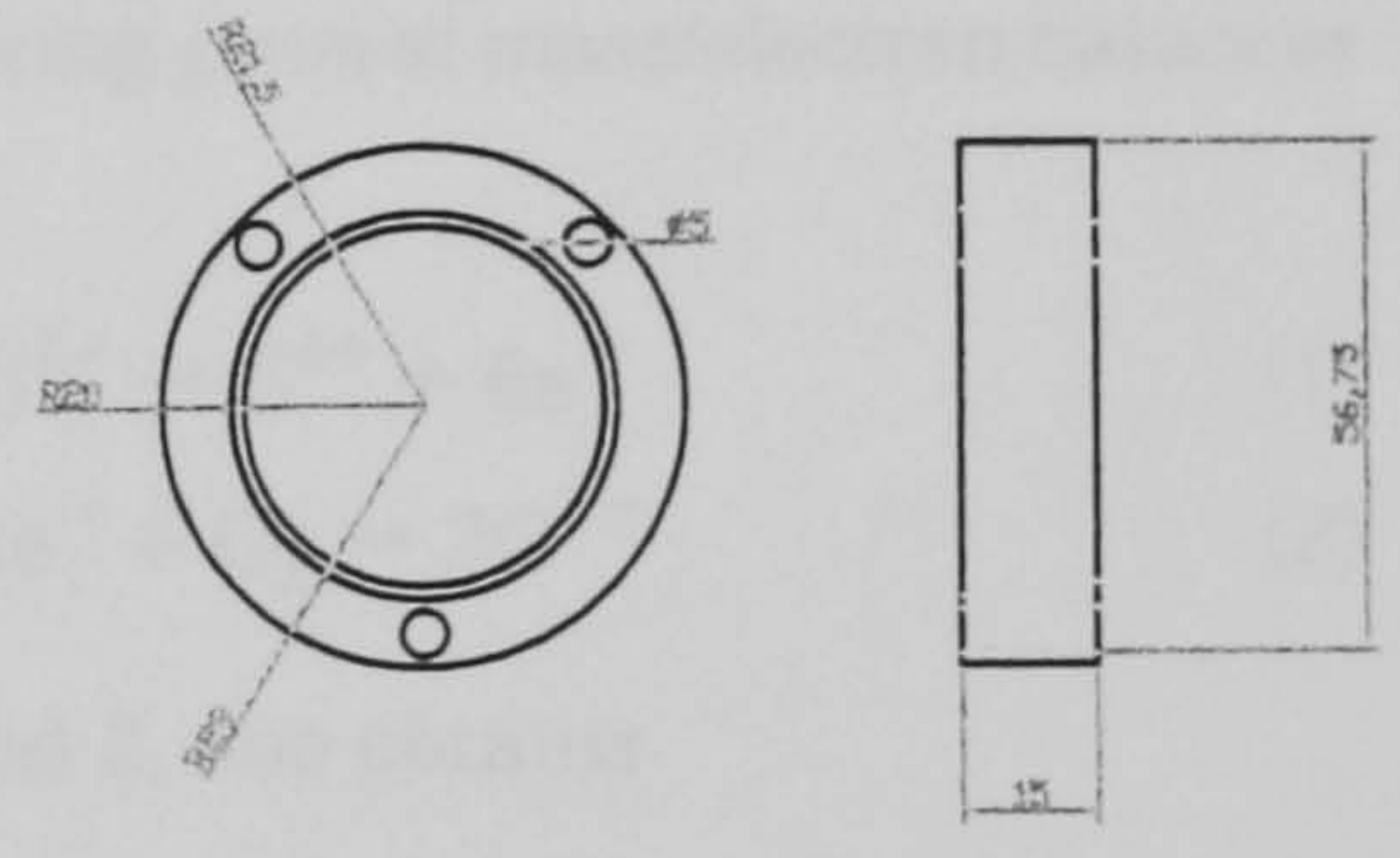
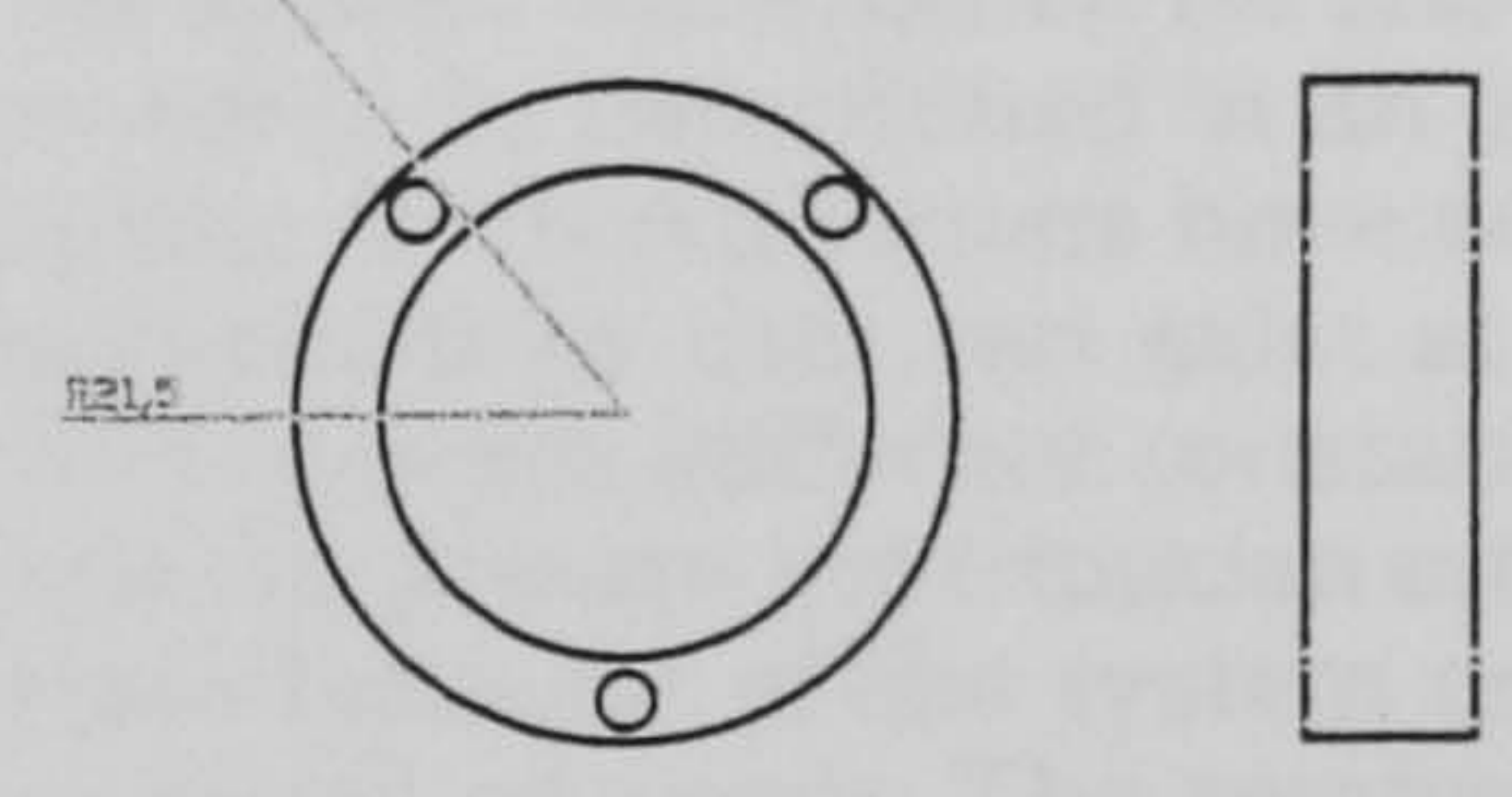
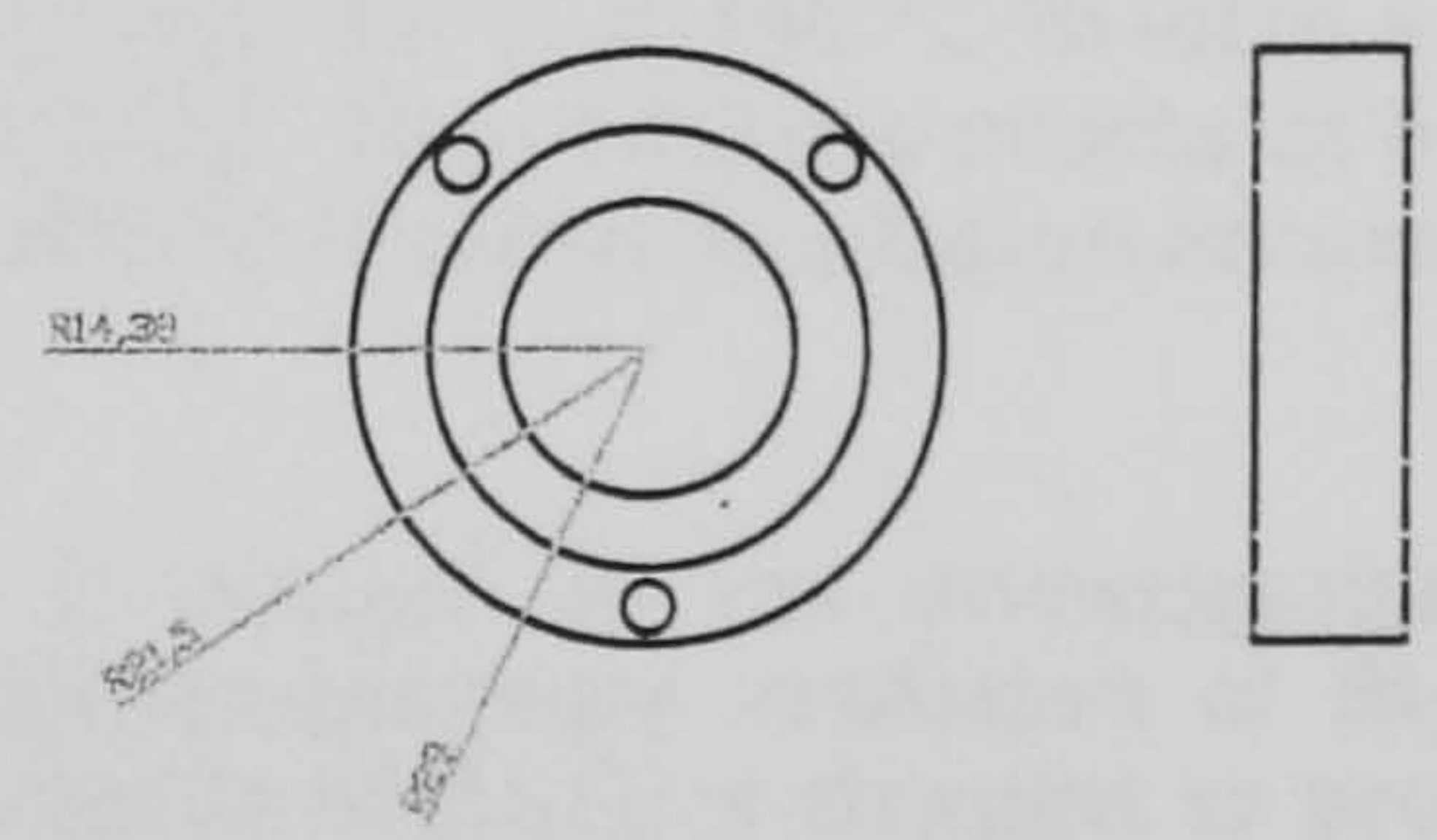
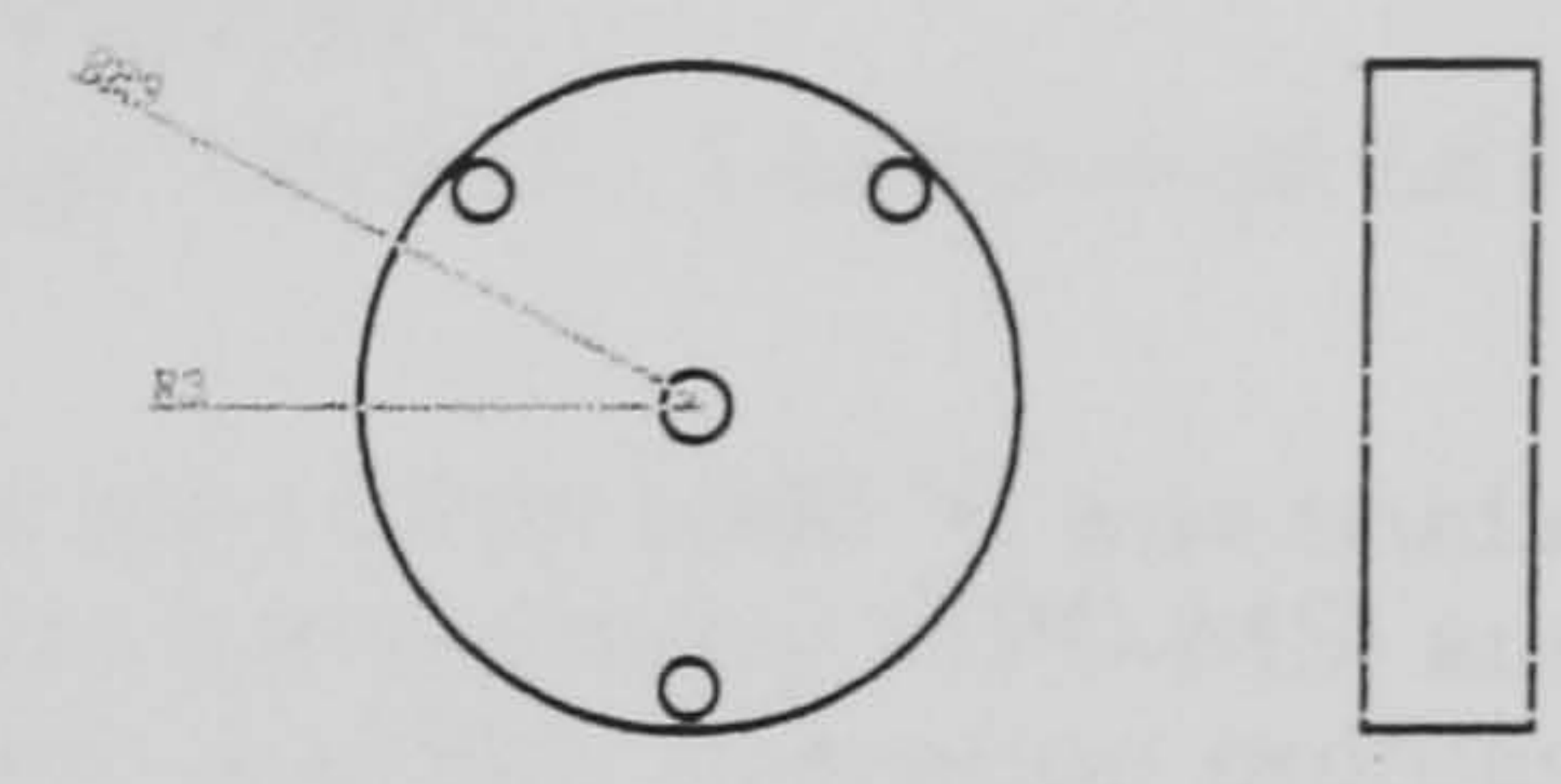
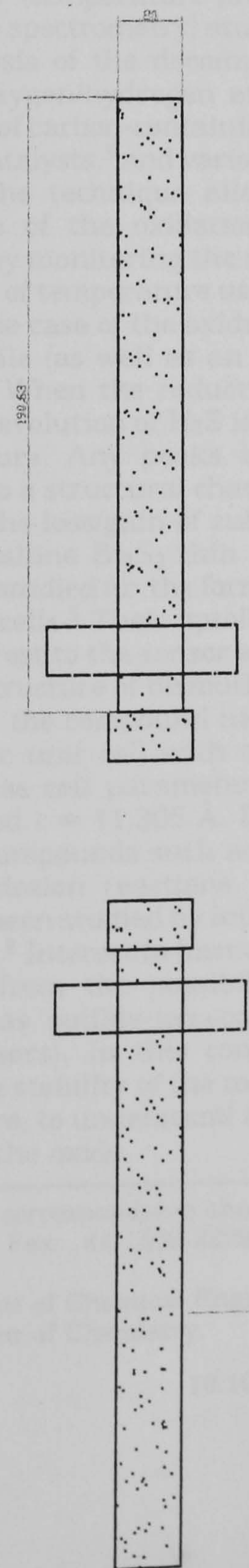
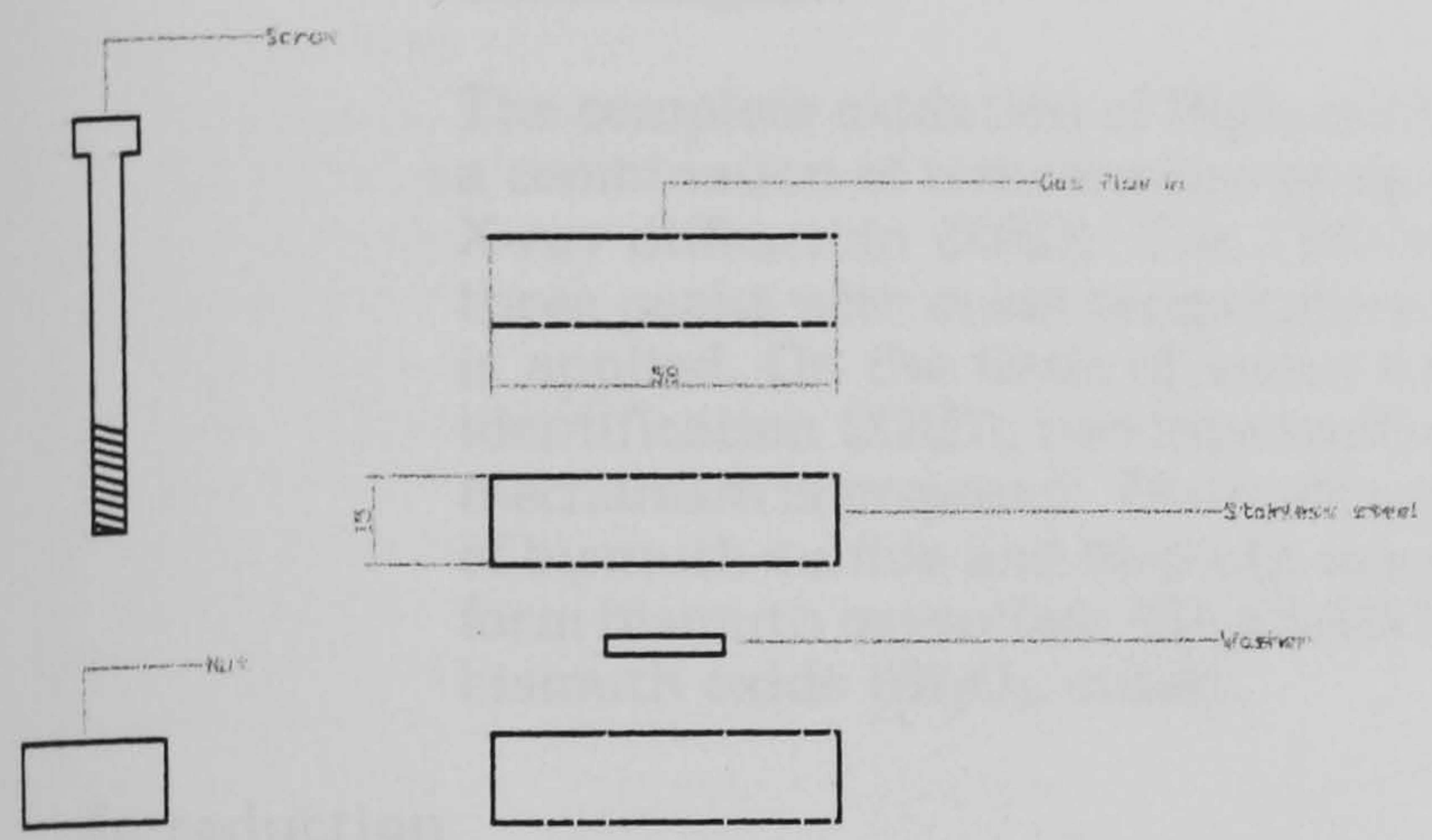


Ceramic Tube

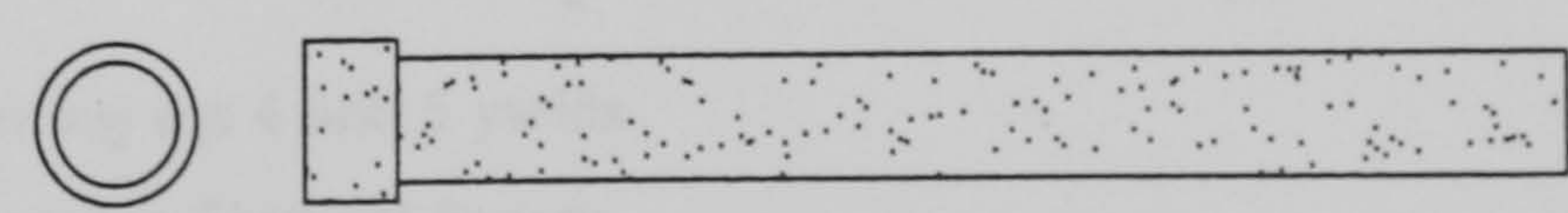
Veletia Johnson

Structural Investigation of the High Temperature
Aluminum Sulfate Decomposition
Techniques

Electrochemical Reactor



Ceramic Tube



Veletia Johnson

Structural Investigation of the High-Temperature Oxidation of Bismuth Sulfide Using TPO-MS and in Situ X-ray Diffraction Techniques

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The complete oxidation of Bi_2S_3 in the temperature range from 50 to 1000 °C was studied using a combination of temperature-programmed oxidation mass spectrometry (TPO-MS) and in situ X-ray diffraction (XRD). The TPO-MS oxygen consumption and SO_2 liberation profiles exhibit three peaks with onset temperatures at 440, 612, and 800 °C, when a heating rate of 10 °C/min is applied. On the basis of sulfur and oxygen molar balance (TPO-MS) augmented by species identification (XRD), two intermediate sulfates were determined. The following Bi_2S_3 oxidation mechanism is proposed: Bismuth sulfide (Bi_2S_3 , orthorhombic) reacts at 440 °C to form a mixture of bismuth sulfide and bismuth oxysulfate ($\text{Bi}_2\text{S}_3 + \text{Bi}_2\text{O}_2\text{SO}_4$). This mixture reacts at 612 °C to form bismuth oxysulfate [$\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$, monoclinic]. At 800 °C, further oxidation occurs to yield bismuth oxide (Bi_2O_3 , cubic).

Introduction

TPO/R-MS (temperature-programmed oxidation/reduction mass spectrometry) studies have been employed in the analysis of the decomposition of various compounds in oxygen/hydrogen atmospheres, such as investigations of carbon-containing compounds,^{1,2} sulfide-containing catalysts,³ and various metal-sulfide-containing ores.⁴ The technique allows for a quasi in situ investigation of the oxidation/reduction behavior of compounds by monitoring the reactant/product profiles as a function of temperature using a mass spectrometer. That is, in the case of the oxidation of a sulfide, an SO_2 product profile (as well as an O_2 consumption profile) is observed. When the reduction of a sulfide is being studied, the evolution of H_2S is monitored as a function of temperature. Any peaks in the observed profiles correspond to a structural change caused by a chemical reaction or the loss/gain of sulfur.

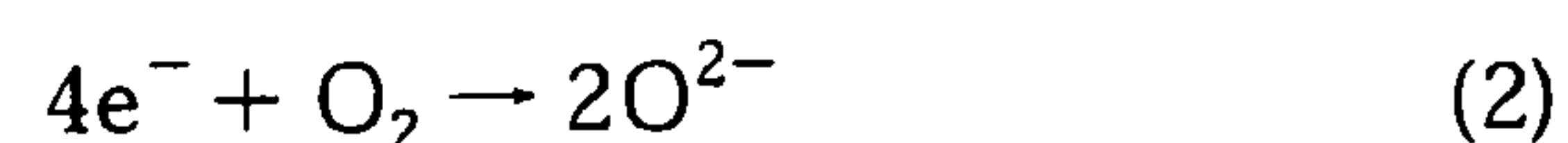
Nanocrystalline Bi_2S_3 thin film structures are currently being studied for the formation of novel photoelectrochemical cells.⁵ Their optoelectronic properties are of great interest to the sensor and semiconductor industries.⁶ The structure of bismuth sulfide has been widely studied, and the compound has been found to have an orthorhombic unit cell with space group $Pm\bar{c}n$.⁷ The compound has cell parameters of $a = 3.9811 \text{ \AA}$, $b = 11.147 \text{ \AA}$, and $c = 11.305 \text{ \AA}$. Bi_2S_3 has been combined with other compounds such as InP and GaAs, and the thermal oxidation reactions of such semiconducting layers have been studied by infrared and X-ray emission spectroscopy.⁸ Interest in bismuth sulfide based systems also stems from the possibility of employing these compounds as sulfide-ion-conducting materials (fuel cells or sensors). In this context, it is important to establish the stability of the material against oxidation and, therefore, to understand the transformation of the sulfide into the oxide.

This study is focused on the investigation of the process of high-temperature oxidation of Bi_2S_3 . The process of oxidation of Bi_2S_3 is thought to proceed via the path bismuth sulfide \rightarrow sulfate \rightarrow oxysulfate \rightarrow oxide; however, the specific stoichiometries and reaction temperatures remain to be determined in an engineering context. A number of investigations have dealt with the different stoichiometries that can exist at equilibrium in the Bi–S–O system (different constant partial pressures), whereas the present contribution establishes the non-steady-state behavior of the system under one constant oxygen partial pressure. The combination of two in situ techniques (TPO/R-MS and X-ray powder diffraction) is employed in this work to elucidate the dynamic oxidation mechanism of Bi_2S_3 and, thereby, to show how powerful this methodology can be for the analysis of such systems.

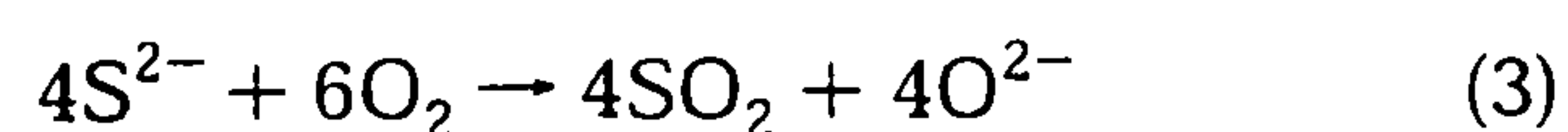
Oxidation Chemistry

The oxidation of Bi_2S_3 can produce an oxide or a sulfate via the following general mass/electron balances

Oxide formation

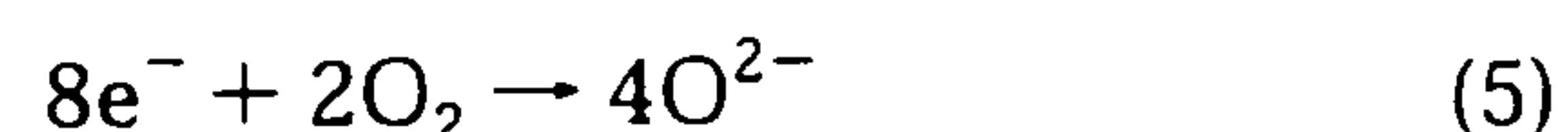
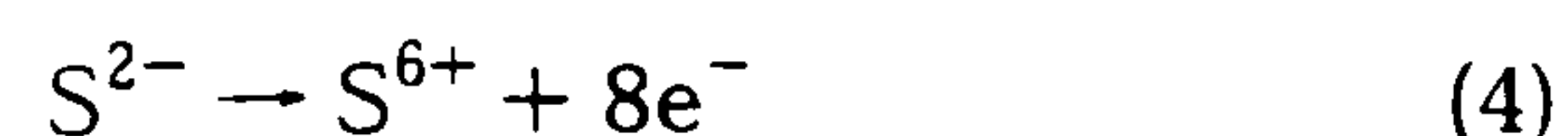


Combining eqs 1 and 2, one obtains



Hence, in the formation of an oxide from a sulfide, 1.5 mol of oxygen is required per mole of sulfur, and 1 mol of sulfur dioxide is liberated.

Sulfate formation and decomposition

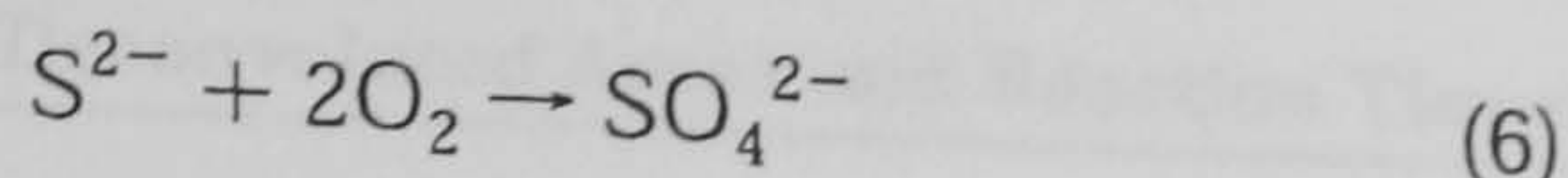


Combining eqs 4 and 5 yields

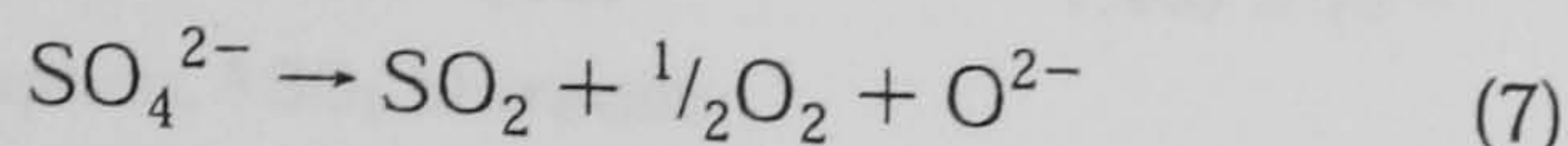
* To whom correspondence should be addressed. Tel.: 44-1509-222518. Fax: 44-1509-223932. E-mail: k. hellgardt@lboro.ac.uk.

[†] Department of Chemical Engineering.

[‡] Department of Chemistry.



Therefore, 2 mol of oxygen is needed to form 1 mol of the sulfate without the liberation of oxygen. If, subsequently, the sulfate decomposes, the following reaction occurs



Experimental Section

Chemicals. Bi_2S_3 was obtained from three sources: STREM Chemicals U.K. (purity 99.99% metal basis), Aldrich Chemicals (99.9%), and through stoichiometric synthesis from the elements (99%).

Argon and air were supplied by BOC, and their purities exceeded 99.9 vol %. Hydrogen was supplied via a hydrogen generator (electrolysis of water), and its purity exceeded 99.99 vol %.

Experimental Procedure. Bi_2S_3 was heated at a rate of 10 °C/min in a 20-mm-i.d. quartz furnace. A reactor (length = 300 mm, inside diameter = 3.8 mm, thickness = 2.5 mm, and volume = 6 mL) containing approximately 10–20 mg of Bi_2S_3 (particle size range = 38–52 μm) was heated either in the presence of a 14 vol % hydrogen/argon mixture (45 mL/min) or a 6 vol % of air/argon mixture (60 mL/min). The gas enters and leaves the reactor through 1/4-in. Swagelok fittings with graphite ferrules producing airtight seals, the Bi_2S_3 being supported by quartz wool as illustrated in Figure 1.

The above concentrations were selected such that the mass spectrometer signal was not saturated with the reactant gas, and the flow rates were chosen to optimize the response of the system (resolution of the peaks). All gases were controlled by Aalborg 0–200 mL/min mass flow controllers, which were calibrated using a bubble flow meter. The heating rate was controlled by a West 6400 temperature controller, the power to the furnace being supplied by a Wayne Kerr 0–70 V, 0–60 A dc power supply. This allowed for precise and accurate temperature ramping. The reactant and product gases were monitored by a quadrupole mass spectrometer (Vacuum Generators). The mass spectrometer collects data in arbitrary units (au). Therefore, calibrations were performed whereby the signal for a known flow rate of O_2 was recorded for 1 min, and a correction for the background O_2 concentration was obtained. Air from BOC was used as the calibration gas for oxygen (21% air, 79% nitrogen). The signal (in au·min) for SO_2 was converted into moles according to the masses and stoichiometries of reference compounds such as Nd_2S_3 and CuS that were oxidized at the same heating rate. The exhaust gases were scrubbed using sodium hydroxide solution before being discharged into a fume cupboard, Figure 2. The profiles of the monitored gas concentrations from the mass spectrometer were deconvoluted using nonlinear regression fitting of Gaussian peaks (Peakfit 4.1).

The oxidation profiles obtained from the TPO-MS experiments were used to designate nine temperature stages to record a series of in situ X-ray diffraction patterns. Powder X-ray diffraction was performed on a Bruker D8 powder diffractometer fitted with a PSD detector, using $\text{Cu K}\alpha_1$ radiation. High-quality X-ray data were collected across a 2θ range of 10–90° over a period of 24 h using a 2θ step size of 0.015°. In situ high-temperature X-ray diffraction was performed on the Bi_2S_3 sample as it was being oxidized, the temperature

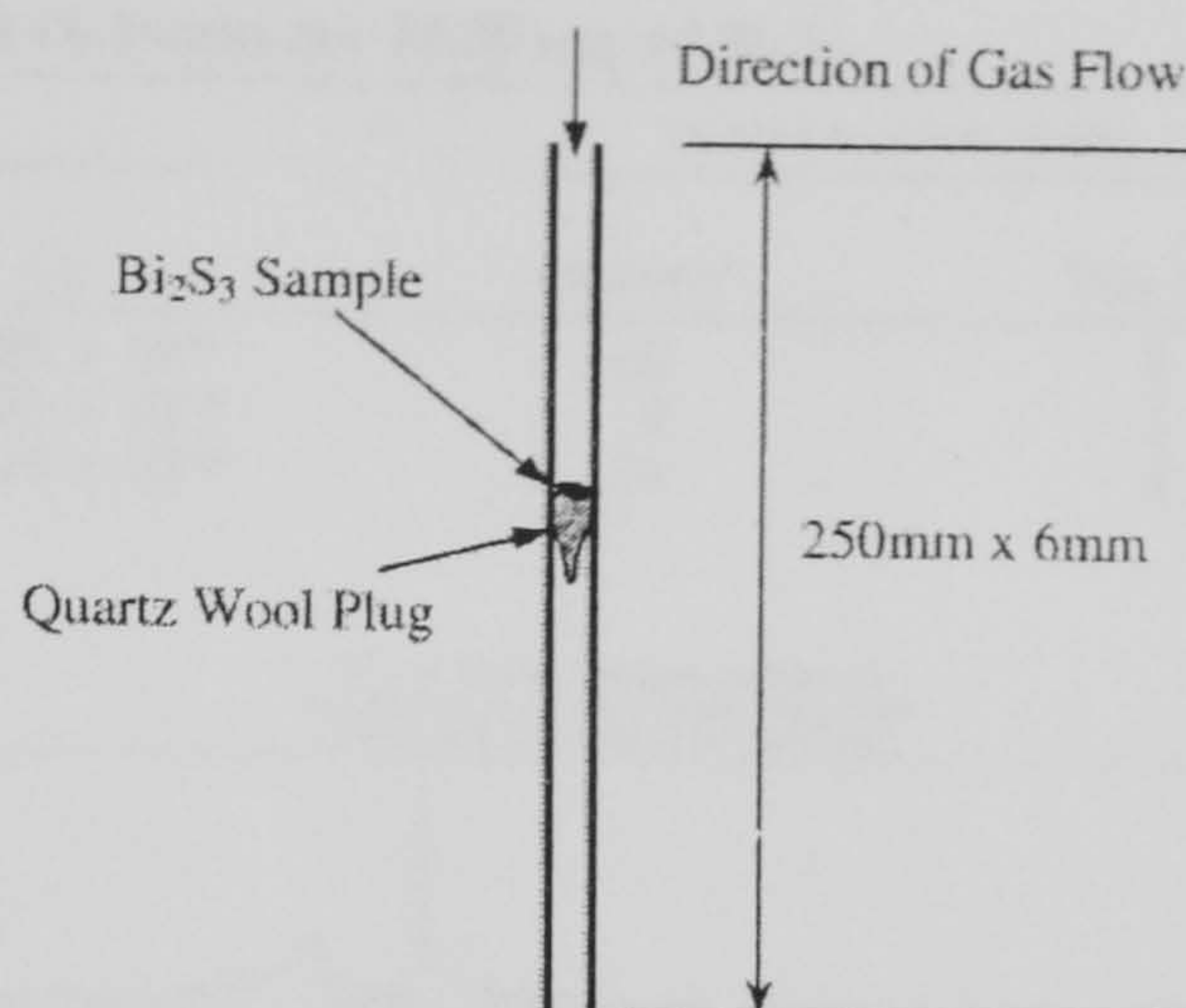


Figure 1. Temperature-programmed oxidation/reduction reactor.

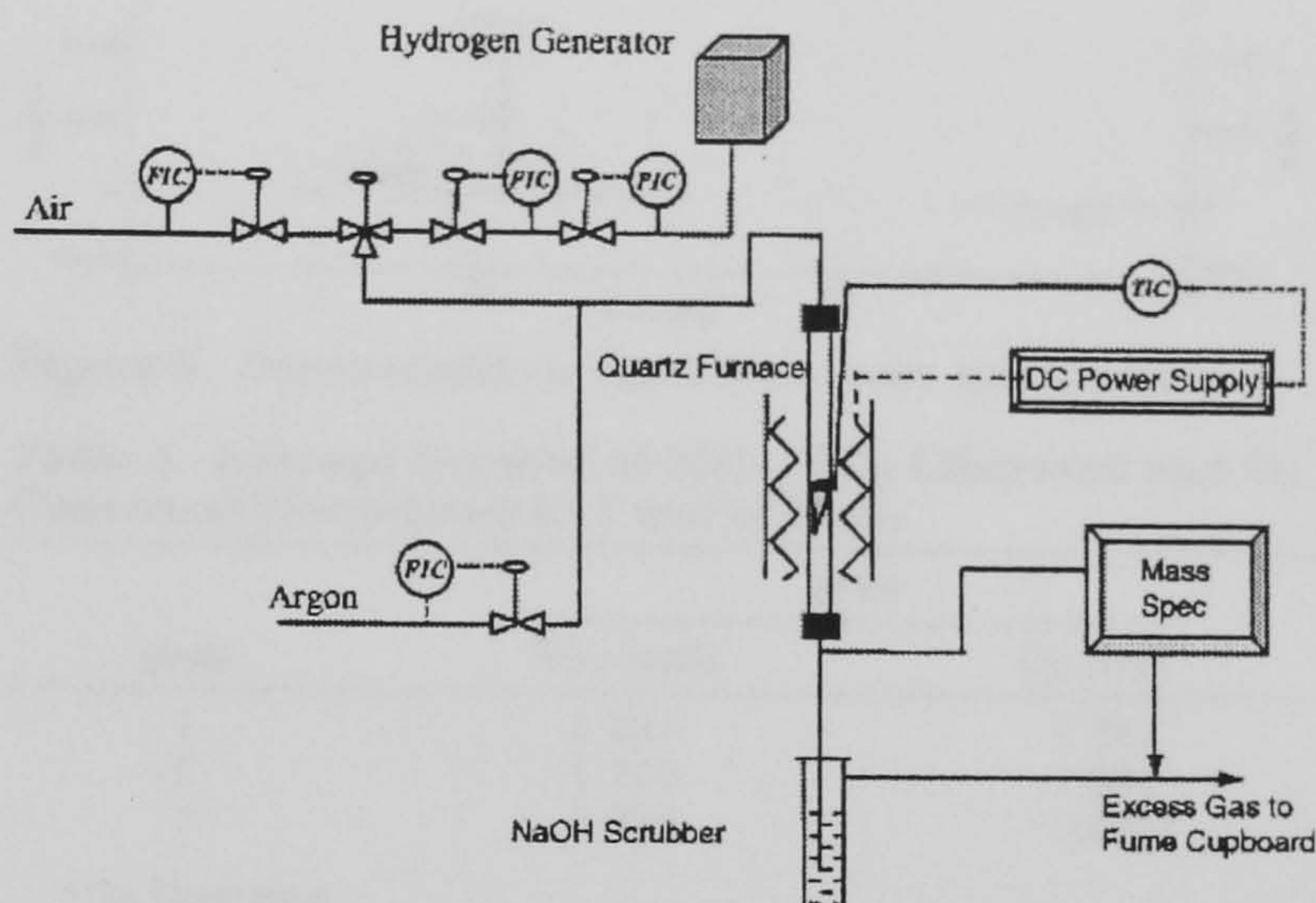


Figure 2. Experimental setup of TP apparatus.

being raised at 0.33 °C/min over a temperature range of 27–1000 °C. X-ray diffraction patterns were obtained over 4-h periods at 27, 400, 440, 490, 520, 570, 620, 800, and 910 °C.

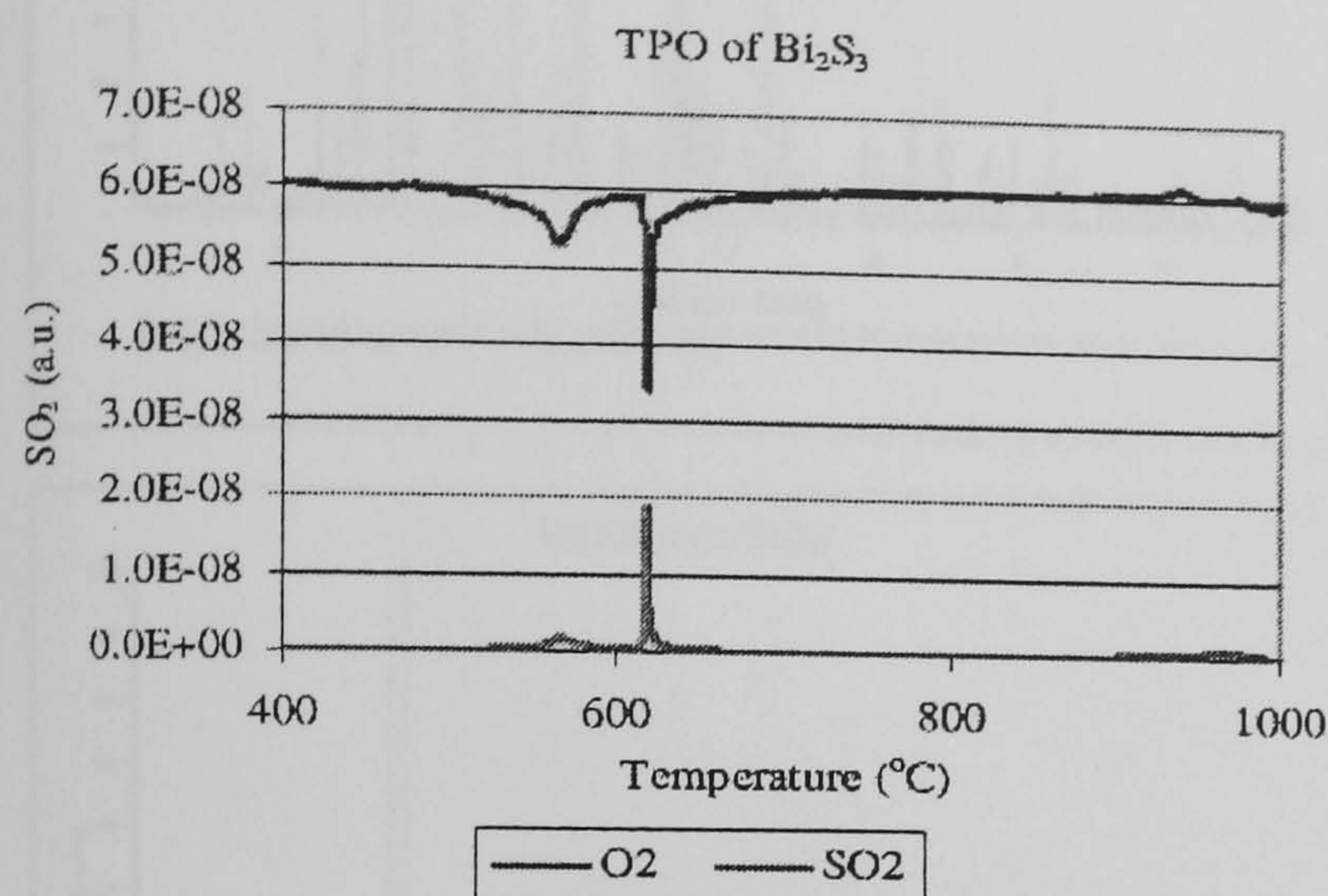
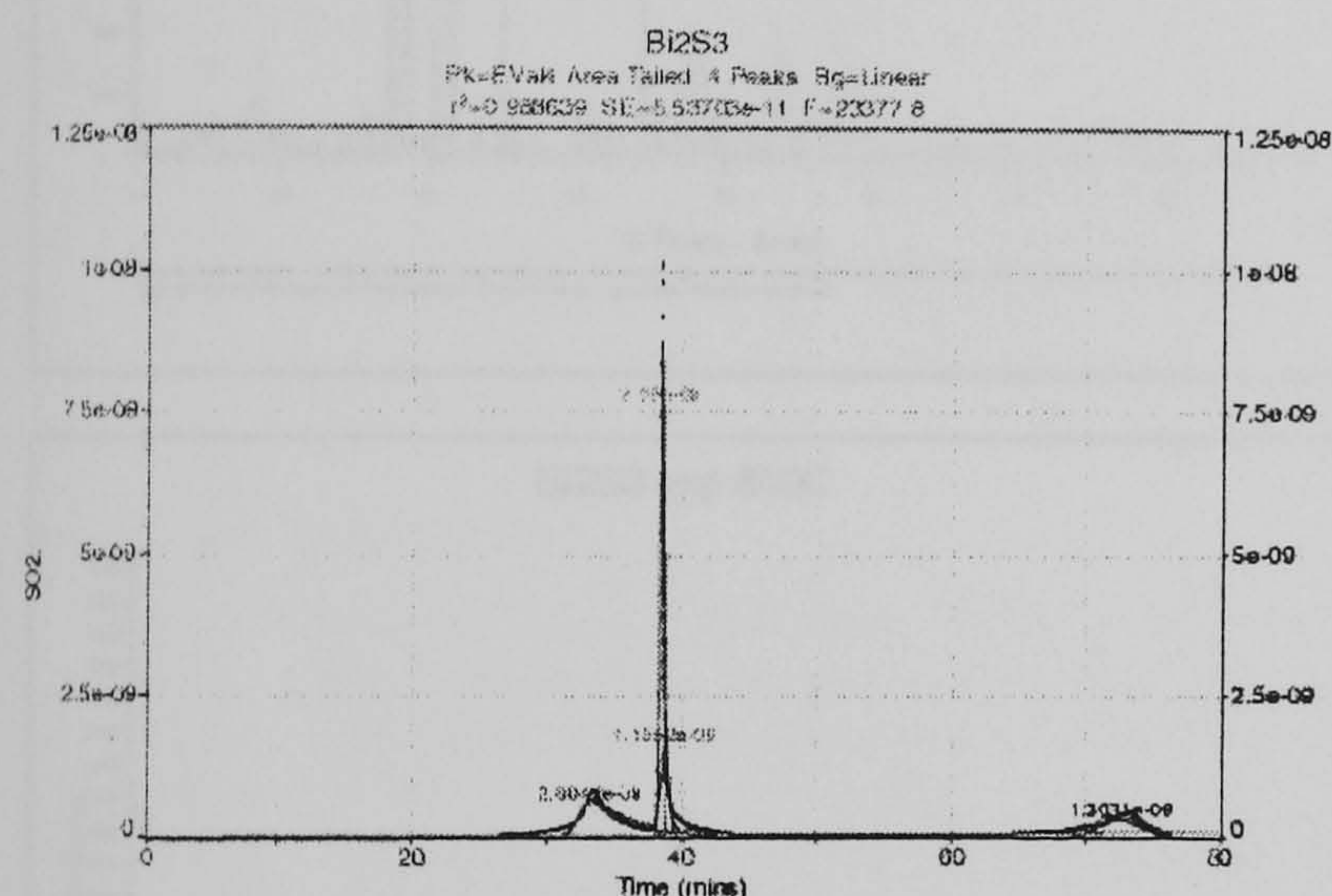
Results and Discussion

Temperature Programmed Oxidation/Reduction. All three Bi_2S_3 samples showed very similar SO_2/O_2 profiles (Figure 3). Three SO_2 peaks were observed with the following onset temperatures: 440 °C (± 3 °C), 612 °C (± 3 °C), and 800 °C (± 10 °C). Three peaks were also observed in the corresponding O_2 profile, the first two peaks representing consumption reactions (depicted as negative peaks) and the third peak representing a liberation (positive peak). The concentration of O_2 is apparently much higher than that of the SO_2 . The reason for this is that mass spectrometers always operate with some background oxygen present within the vacuum system (constant leak rate). The onset temperatures of the O_2 peaks were 410 °C (± 30 °C), 610 °C (± 3 °C), and 905 °C (± 100 °C). The onset temperatures of the first and third peaks were difficult to determine as these peaks appear to have long tails (not sharp as the second peak). The oxygen substitution reaction appears to be complete at 988 °C.

Previous literature reports concerning the liberation of $\text{H}_2\text{S}/\text{SO}_2$ from sulfides suggest that different peaks appearing in the TPO/R-MS profile can be associated with different sulfur bond strengths, typical sulfur species being described as excess sulfur, stoichiometric sulfur, and nonstoichiometric sulfur.⁹ Excess sulfur is usually liberated at low temperature, i.e., much less

Table 1. Typical Deconvoluted Areas and Reaction Times for SO₂ and O₂ Peaks for 25.29 mg of Bi₂S₃

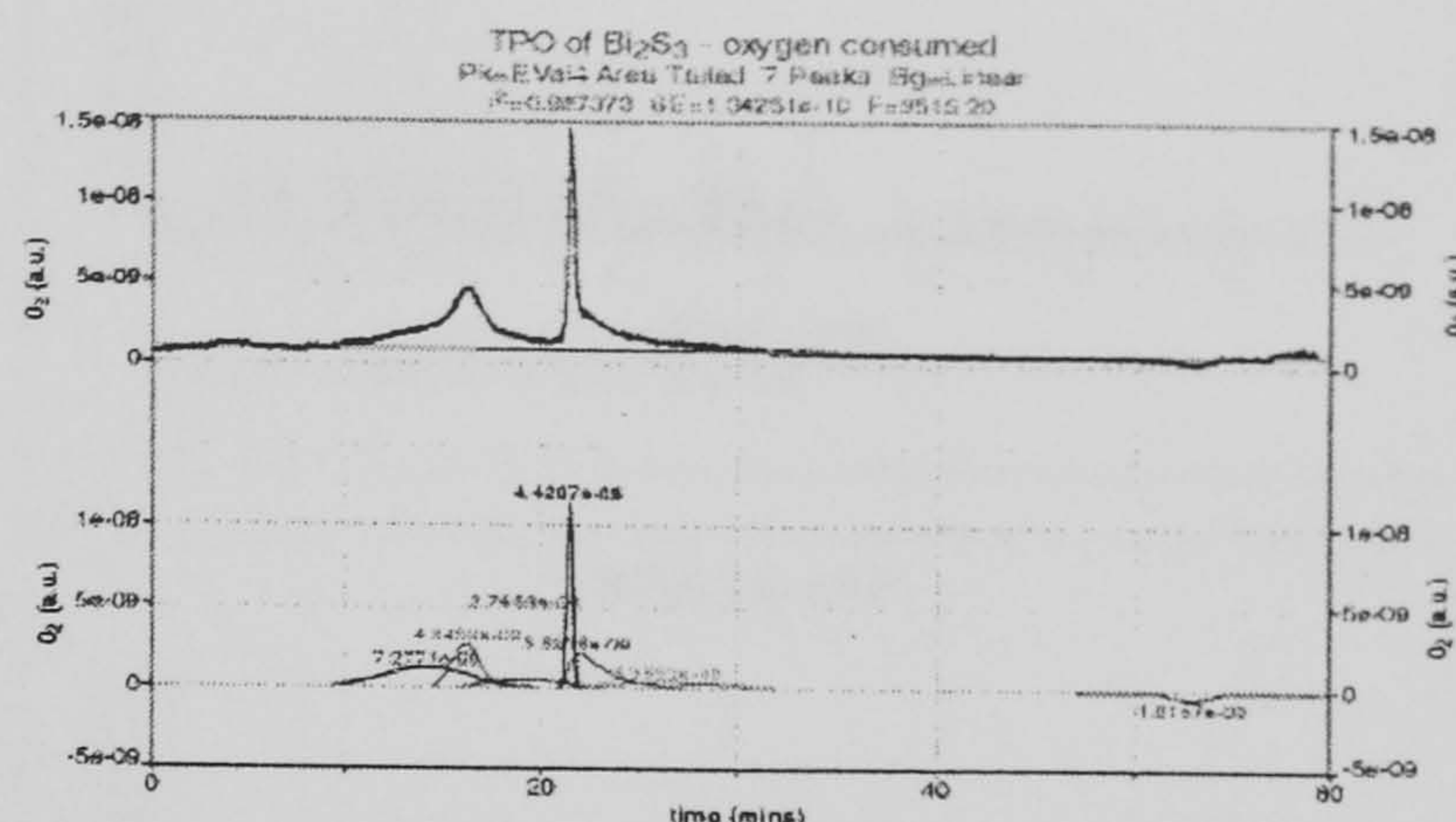
peak	approximate temperature range (°C)	area (au·min)		reaction time (min)	
		SO ₂	O ₂	O ₂ cons ^a	SO ₂ lib ^b
1	440–600	2.186×10^{-9}	1.489×10^{-8}	12	8
2	600–690	3.803×10^{-9}	1.331×10^{-8}	9	5
3	800–1000	1.440×10^{-9}	-1.026×10^{-9}	14	8

^a O₂ consumption. ^b SO₂ liberationFigure 3. Temperature-programmed oxidation of Bi₂S₃ at 10 °C/min, showing oxygen consumed and SO₂ liberated.Figure 4. Deconvoluted SO₂ signal from mass spectrometer.

than 400 °C. To investigate whether the first peak seen in the TPO-MS profile is due to excess sulfur, temperature-programmed reduction (TPR-MS) was carried out. In this case, only one broad peak was observed, which exhibited an onset temperature of 504 °C, similar to the onset temperature in the TPO-MS experiment. The reduction was complete at 904 °C. These results clearly indicate that the first peak in the TPO profile could not result from the oxidation of excess amorphous sulfur, which is not detectable by XRD. Excess sulfur would have reacted at a much lower temperature to form H₂S.

The TPO/TPR-MS data were deconvoluted using Peakfit 4.1. The deconvolution of the SO₂ signal (Figure 4) was possible with four peaks, with an R^2 value of 0.994. The second peak was deconvoluted into two peaks because it was very narrow and had a tail toward the higher temperature; this additional peak could not be attributed to a physical/chemical phenomenon and was combined with the major peak for peak area calculations.

The O₂ consumption profile from Figure 3 was inverted (Figure 5), because the Peakfit 4.1 software

Figure 5. Deconvoluted O₂ signal from mass spectrometer.Table 2. Average Number of Moles SO₂ Liberated and O₂ Consumed Normalized to 1 mol of Bi₂S₃

peak	area	
	SO ₂ (mol)	O ₂ (mol)
1	1.091	2.762
2	1.274	1.981
3	0.635	-0.243 ^a

^a O₂ liberated.

allows for more efficient data analysis when the major peaks identified are positive. Deconvolution gave six peaks, (the number of peaks affects the R^2 value), to give an R^2 value of 0.988, which is still lower than what was achieved in the deconvolution of the SO₂ profile. The lower R^2 value was expected because the background concentration of O₂ in the mass spectrometer is high. The first and second peaks were deconvoluted into three contributing peaks, because these peaks exhibited shoulders to either side. The third O₂ peak, where O₂ is liberated, represented by the negative area, could be fitted by one peak (symmetrical). The time required for each sequential reaction was estimated from the widths of the deconvoluted peaks (this also accounts for the shoulders), and the data are presented in Table 1. All areas were converted into moles (sulfur or oxygen) to elucidate on the intermediates and the mechanism involved in the oxidation process. The average results of five temperature-programmed experiments are given in Table 2.

In Situ X-ray Diffraction. Nine temperature stages were identified during the course of the TPO-MS experiments where the identification of the phases during the oxidation process would be of interest. The obtained X-ray diffraction patterns are shown sequentially in Figure 6. The XRD patterns obtained for each temperature stage were cross-referenced to the JCPDS powder diffraction pattern database¹⁰ and other literature sources,^{11–13} and each phase was assigned accordingly (Table 3).

The X-ray diffraction data show that complete oxidation occurs to Bi₂O₃ by the final heating stage.

The TPO-MS profile was obtained at a heating rate of 10 °C/min, whereas the XRD patterns were all

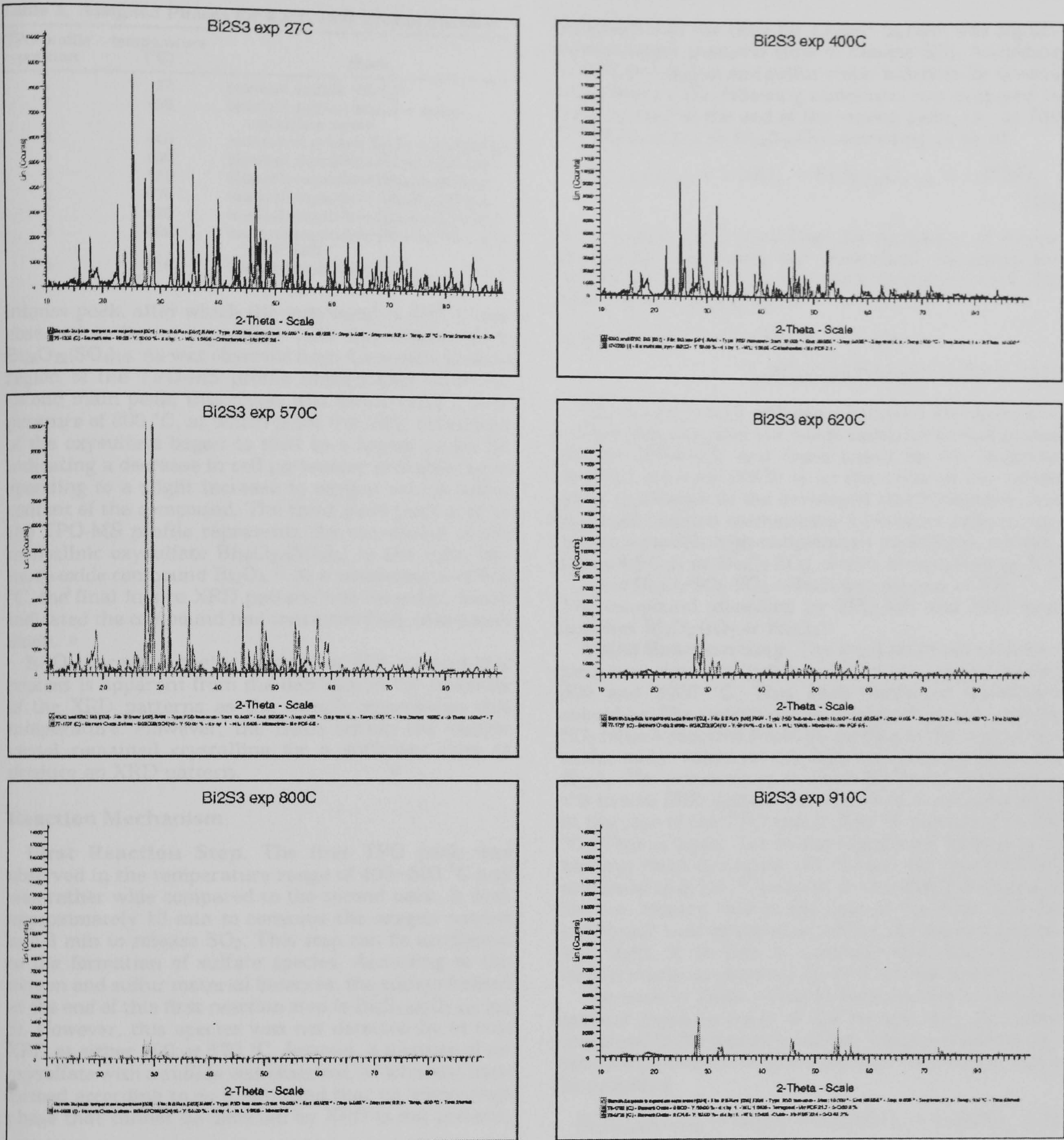


Figure 6. In situ X-ray diffraction patterns observed at different temperatures.

obtained at a heating rate of 0.333 °C/min. This difference in heating rate caused the onset temperature of the reflections to be shifted, with the first sign of oxidation appearing in the XRD patterns at 400 °C whereas the onset of the first reflection in the TPO-MS profile occurred at 520 °C; this difference was predicted because of the different heating rates used in the two experiments.

The first absorption of oxygen in the TPO-MS profile is a very minor peak, occurring just before the first main peak in the profile. The corresponding reflection was seen in the XRD pattern at 400 °C as the very first emergence of nonsulfide reflections at 30° and 51° (2θ), which correspond to an oxysulfate ($\text{Bi}_2\text{O}_2\text{SO}_4$), emerging

within the Bi_2S_3 pattern. The fact that the XRD reflections do not correspond to the pattern of the sulfate suggests a disordered transition from the sulfide to the oxysulfate, as was observed in the pattern at 440 °C, rather than a smooth progression through the sulfate. The mass balance alone suggests a sulfate, which has been identified in the literature as the intermediate; however, a sulfate and (sulfide + oxysulfate) could not be distinguished from the mass balance alone.

Hence, the first relatively broad peak in the TPO-MS pattern corresponds to the initial structural transformation from the sulfide, with an orthorhombic structure, to a mixture of phases $\text{Bi}_2\text{S}_3 + \text{Bi}_2\text{O}_2\text{SO}_4$ at 440 °C. This first peak is followed immediately by a sharper more

Table 3. Assigned Phases for Each TPO Profile Position

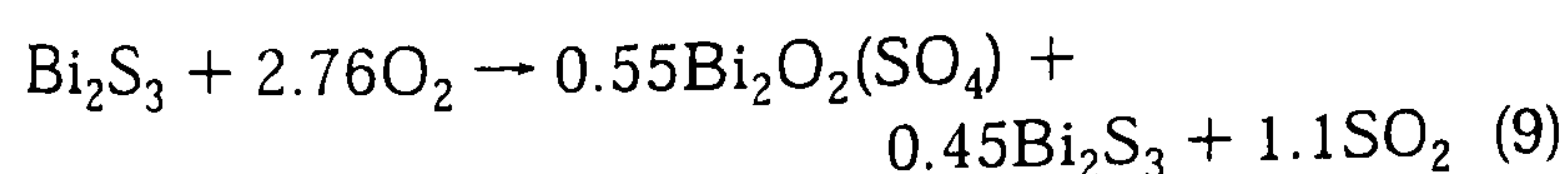
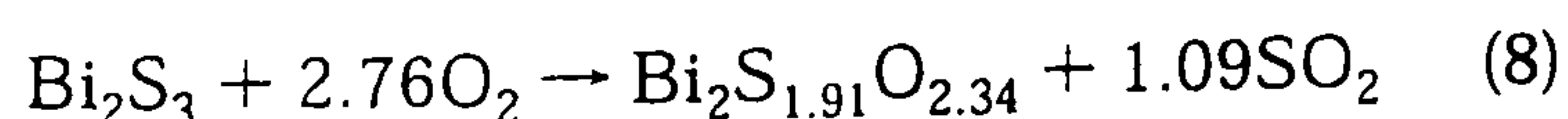
TPO profile position	temperature (°C)	phase
1	27	bismuth sulfide (Bi ₂ S ₃) ¹¹
2	400	bismuth sulfide (Bi ₂ S ₃) + minor oxysulfate peaks
3	440	mixture of phases (Bi ₂ S ₃ + Bi ₂ O ₂ SO ₄)
4	490	bismuth oxysulfate [Bi ₂₈ O ₃₂ (SO ₄) ₁₀] ¹²
5	520	bismuth oxysulfate [Bi ₂₈ O ₃₂ (SO ₄) ₁₀]
6	570	bismuth oxysulfate [Bi ₂₈ O ₃₂ (SO ₄) ₁₀]
7	620	bismuth oxysulfate [Bi ₂₈ O ₃₂ (SO ₄) ₁₀]
8	800	bismuth oxysulfate [Bi ₂₈ O ₃₂ (SO ₄) ₁₀] + peak shift
9	910	bismuth oxide (Bi ₂ O ₃) ¹³

intense peak, after which the compound at 490 °C was observed to be an oxysulfate with the stoichiometry Bi₂₈O₃₂(SO₄)₁₀. As was observed from the second plateau region of the TPO-MS profile immediately after the second main peak, this phase was stable until a temperature of 800 °C, at which point the XRD reflections of the oxysulfate began to shift to a higher angle 2θ, indicating a decrease in cell parameter probably corresponding to a slight increase in oxygen versus sulfur content of the compound. The third main peak area in the TPO-MS profile represents the conversion of the monoclinic oxysulfate Bi₂₈O₃₂(SO₄)₁₀ to the cubic bismuth oxide compound Bi₂O₃.¹³ At a temperature of 910 °C, the final in situ XRD pattern was recorded, which indicated the compound had converted fully to bismuth oxide.

Bi₂O₃ normally begins to melt at 860 °C, and this process is apparent from the decrease in the intensity of the XRD patterns as the sample approaches this temperature. However, the Bi₂O₃ within the sample vessel remained crystalline for a sufficient time to produce an XRD pattern.

Reaction Mechanism

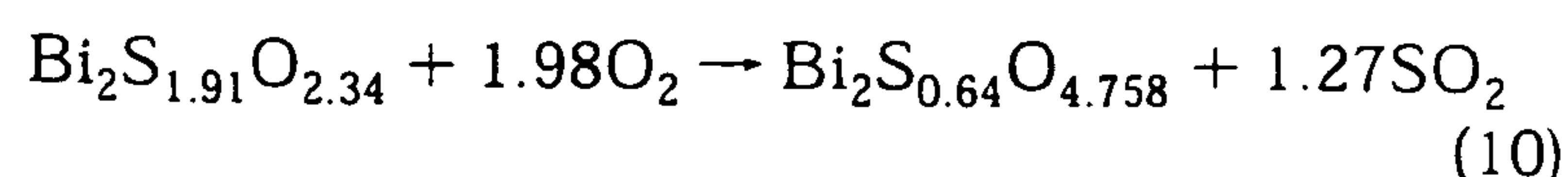
First Reaction Step. The first TPO peak was observed in the temperature range of 400–600 °C and was rather wide compared to the second peak. It took approximately 13 min to consume the oxygen needed and 8 min to release SO₂. This step can be attributed to the formation of sulfate species. According to the oxygen and sulfur material balances, the sulfate formed at the end of this first reaction step is Bi₂S_{1.909}O_{3.342} (eq 8). However, this species was not detected by in situ XRD at either 400 or 570 °C. Instead, a mixture of an oxysulfate with a sulfide was observed, which must have formed according to eq 9, provided that an amorphous phase that cannot be detected by XRD is not present.



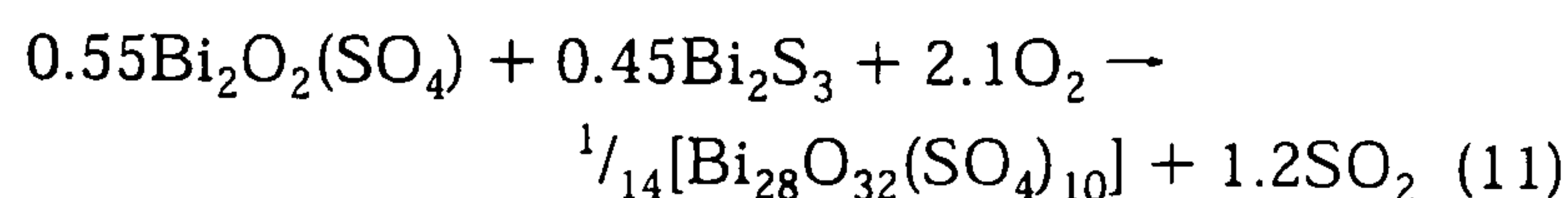
Reports in the literature suggest that the low-temperature oxysulfate produced might be either Bi₂(SO₄)₃, which decomposes at 405–418 °C,¹⁴ or Bi₂O₆S, which forms at 390–405 °C¹⁵ and can be represented as Bi₂O₂(SO₄).

Second Reaction Step. The second TPO peak, observed in the temperature range of 600–690 °C, is very narrow, in both the oxygen consumption and SO₂ liberation profiles. The oxygen consumption took 9 min, whereas the SO₂ liberation took 5 min. Again, it was

observed that the time for oxygen uptake was significantly longer than the time to release SO₂. According to both the oxygen and sulfur molar balances for several experiments, the following compound was proposed to have formed at the end of the second peak, i.e., at 700 °C, Bi₂S_{0.64}O_{5.16} or Bi₂₈S₁₀O₇₂, according to eq 10.



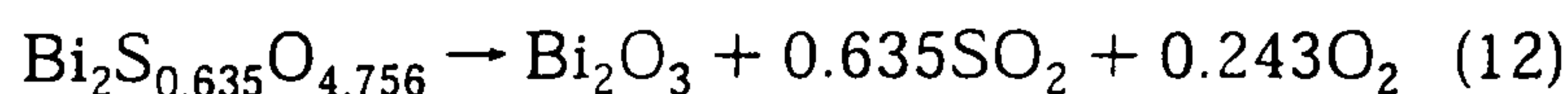
In this case, XRD identified the formation of a new oxysulfide, and using the theoretical equations for sulfate formation, eq 3, and oxide formation, eq 6, the mass balance yields eq 11.



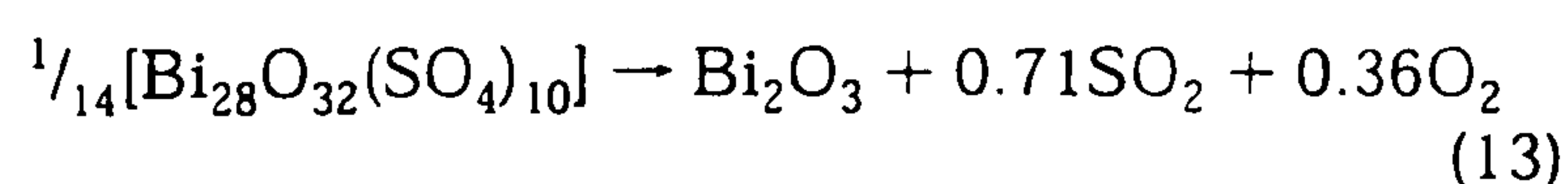
The stoichiometric difference between the equations/compounds proposed via molar balances on sulfur and oxygen (TPO-MS) and those based on the observed reaction products (XRD) is on the order of 5%, which gives confidence in the developed stoichiometries and proposed reaction mechanisms. Literature reports suggest two possible high-temperature oxysulfates, namely, Bi₂O₃·4(SO₃)₃ or Bi₂O₃·SO₃, which decomposes at 870 °C, and Bi₂O₃·SO₃·SO₃, which decomposes at 975 °C.¹⁶ The compound identified by TPO-MS and XRD best matches Bi₂O₃·SO₃ or Bi₂O₆S.

Third Reaction Step. The third and final oxidation peak was observed in the temperature range between 800 and 1000 °C. This peak exhibited significant shoulders. The oxygen release required 14 min, and the SO₂ release required 8 min. According to the oxygen and sulfur molar balances, the final compound produced is Bi₂O₃. The temperature at which Bi₂O₃ was produced in the in situ XRD system was observed to be lower than in the case of the TPO result (910 °C compared to 980 °C). This is again due to the significant difference in heating rates employed (10 °C/min for the TPO-MS compared to 0.333 °C/min for in situ XRD). Because of the low heating rate in the case of the XRD and the significant time required to collect the powder diffraction data, it is safe to conclude that the reaction temperatures as observed by TPO are the correct ones.

The data in Table 2 clearly indicate that a complete account could be made of the oxygen and the sulfur contained in the bismuth–sulfur–oxygen system at any time/temperature. The following final reaction can hence be proposed



Using eq 6, we obtain



The stoichiometries of the intermediate sulfates identified in the above mechanism assume that all of the liberated sulfur was converted to SO₂ and detected by the mass spectrometer. This is a reasonable assumption given that, at these elevated temperatures, SO₂ is thermodynamically the most stable S–O compound.

Conclusions

TPO-MS data show that Bi₂S₃ has moderately good oxygen stability, being stable in the sulfide form up to

a temperature of around 440 °C, at which point it begins to oxidize. Judging from overall and individual molar balances, Bi_2S_3 undergoes a three-step oxidation process to form Bi_2O_3 during which sulfate intermediates $\text{Bi}_2\text{O}_2(\text{SO}_4)$ and $\text{Bi}_{28}\text{S}_{10}\text{O}_{72}$ are produced. The proposed sulfate intermediates are consistent with suggestions from the literature (with regard to stoichiometry) and corresponding X-ray diffraction patterns.

Molar balances alone cannot establish which intermediate compounds are formed during the solid-state transformation of Bi_2S_3 ; however, the combination of TPO-MS and XRD proves to be a powerful tool in detailing the reaction mechanisms of the dynamic oxidation process:

Bismuth sulfide (Bi_2S_3), orthorhombic, reacts at 440 °C to form a mixture of bismuth sulfide and bismuth oxysulfate ($\text{Bi}_2\text{S}_3 + \text{Bi}_2\text{O}_2\text{SO}_4$). This mixture reacts at 612 °C to form bismuth oxysulfate [$\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$], monoclinic. At 800 °C, further oxidation occurs to finally yield bismuth oxide (Bi_2O_3), cubic.

Acknowledgment

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