**Microstructure and ionic conductivities of NASICON-type Li1.3Al0.3Ti1.7(PO4)3 solid electrolytes produced by cold sintering assisted process**

Hong Caia,b, Tong Yua, Dongrui Xiea, Benshuang Sunc, Jiang Chengd, Lu Lid, Xujin Bao a\*, Hongtao Zhanga\*

a Department of Materials, Loughborough University, Epinal Way, Loughborough, LE11 3TU, UK

b Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, UK

c Henan Province Industrial Technology Research Institute of Resources and Materials, Zhengzhou University, Zhengzhou, Henan, 450001, P. R. China

d School of Material Science and Engineering, Chongqing University of Arts and Sciences, Chongqing 402160, P. R. China

\* Corresponding authors

Email address: x.bao@lboro.ac.uk; h.zhang3@lboro.ac.uk

Table S1. Calculated room-temperature bulk (*σ*b), grain boundary (*σ*gb), and total (*σ*t) conductivities for LATP electrolytes produced by CSP / dry-pressing and subsequently annealing at different temperatures

|  |  |  |  |
| --- | --- | --- | --- |
| Processing condition | *σ*b (S/cm) | *σg*b (S/cm) | *σ*t (S/cm) |
| CSP + post-annealing | As-CSPed | 6.40 × 10-4 | 2.02 × 10-6 | 2.01 × 10-6 |
| 700 ℃ | 5.85 × 10-4 | 3.89 × 10-6 | 3.86 × 10-6 |
| 800 ℃ | 3.61 × 10-4 | 3.10 × 10-5 | 2.86 × 10-5 |
| 900 ℃ | 1.14 × 10-3 | 6.86 × 10-4 | 4.29 × 10-4 |
| 1000 ℃ | 6.66 × 10-4 | 1.87 × 10-4 | 1.46 × 10-4 |
| 1100 ℃ | 6.99 × 10-4 | 2.30 × 10-5 | 2.23 × 10-5 |
| Dry-pressing + annealing | 700 ℃ | 5.11 × 10-4 | 2.19 × 10-5 | 2.10 × 10-5 |
| 800 ℃ | 9.72 × 10-4 | 4.97 × 10-5 | 4.73 × 10-5 |
| 900 ℃ | 1.36 × 10-3 | 6.58 × 10-5 | 6.28 × 10-5 |
| 1000 ℃ | 1.24 × 10-3 | 9.14 × 10-5 | 8.51 × 10-5 |
| 1100 ℃ | 1.21 × 10-3 | 6.56 × 10-5 | 6.22 × 10-5 |

Table S2. Summary of relative density (ρ) and conductivity (σ) versus sintering temperature of LATP ceramics produced by various sintering routes from earlier and current work

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| CompositionLi1+xAlxTi2-x(PO4)3 | Powder synthesis route | Sintering method | Sintering temperature (ºC) | Sintering time | ρ (%) | σ (S/cm) | Ref |
| *x* = 0.3 | Solid-state reaction | CS | 1000 | 2 h | × | 3.35×10-4 | [1] |
| *x* = 0.3 | Solid-state reaction | CS | 1000 | 12 h | 97.3 | 4.81×10-4 | [2] |
| *x* = 0.3 | Sol-gel | CS | 1100 | × | 94.2 | 1.88×10-4 | [3] |
| *x* = 0.3 | Hydrothermal | CS | 1200 | 3 h | 98.06 | 2.44×10-4 | [4] |
| *x* = 0.3 | Sol-gel | CS | 1100 | 8 h | 94.2 | 1.0×10-4 | [5] |
| *x* = 0.3 | Sol-gel | CS | 1000 | 1 h | 86-90 | 3-4×10-4 | [6] |
| *x* = 0.3 | Solid-state reaction | CS | 1200 | 2 h | 91.8 | 1.34×10-6 | [7] |
| *x* = 0.3 | Sol-gel | CS | 1000 | 12 h | 71 | 7.3×10-5 | [8] |
| *x* = 0.3 | Solid-state reaction | CS | 1200 | 2 h | 95.9 | 7×10-4 | [9] |
| *x* = 0.3 | Solid-state reaction | UHS | 960 | 100 s | 90.2 | 4.67×10-4 | [10] |
| *x* = 0.3 | Solid-state reaction | UHS | 1200 | 60 s | > 90 | × | [11] |
| *x* = 0.3 | Sol-gel | SPS | 900 | 0 | 99 | 6.8×10-5 | [8] |
| *x* = 0.3 | Melt quenching | SPS | 1000 | 5 min | 96.7 | 1.2×10-4 | [12] |
| *x* = 0.4 | Sol-gel | SPS | 650 | 8 min | 100 | 1.12×10-3 | [13] |
| *x* = 0.3 | Melt quenching | SPS | 1000 | 5 min | 99.4 | 1×10-3 | [14] |
| *x* = 0.3 | Coprecipitation | SPS | 900 | 5 min | 97 | 1.6×10-4 | [15] |
| *x* = 0.4 | Sol-gel | SPS | 900 | 1 min | 97 | 5×10-4 | [16] |
| *x* = 0 | Solid-state reaction | SPS | 1100 | 10 min | ~ 94 | 1.4×10-5 | [17] |
| *x* = 0.3 | Solid-state reaction | SPS | 1100 | 10 min | ~ 96 | ~ 1×10-4 | [17] |
| *x* = 0.3 | Melt quenching | SPS | 1000 | 5 min | 98.9 | 4×10-4 | [18] |
| *x* = 0.3 | Sol-gel | SPS | 1100 | 15 min | 98 | 1×10-3 | [19] |
| *x* = 0.4 | Melt quenching | MW | 1000 | 30 s | × | 5.33×10-4 | [20] |
| *x* = 0.3 | Solid-state reaction | MW | 890 | 10 min | 90 | 3.15×10-4 | [21] |
| *x* = 0.3 | Solid-state reaction | FAST | 900 | 3 h | 86 | 4.76×10-4 | [22] |
| *x* = 0.3 | Sol-gel | HP | 1100 | × | 96.7 | 1.83×10-4 | [23] |
| *x* = 0 | × | HP | 1050 | 1 h | 88 | 2×10-7 | [24] |
| *x* = 0.3 | Solid-state reaction | CSP | 200 | 30 min | × | 3.0×10-4 | [25] |
| *x* = 0.3 | Sol-gel | CSP | 200 | 1 h | 94 | 1.26×10-5 | [26] |
| Annealed @ 800 | 1 h | 95 | 1.55×10-4 |
| *x* = 0.3 | Sol-gel | CSP | 120 | 1 h  | × | × | [27] |
| Annealed @ 650 | 2 h | 93 | 8.04×10-5 |
| *x* = 0.3 | Solid-state reaction | CSP-assisted process | 250 | 1 h | 83.0 | 2.01×10-6 | This work |
| Annealed @ 900 | 1 h | 87.4 | 4.29×10-4 |
| Annealed @ 1000 | 1 h | 96.0 | 1.46×10-4 |

CS = conventional sintering; CSP = cold sintering process; FAST = field-assisted sintering technique; HP = hot pressing; MW = microwave sintering; SPS = spark plasma sintering; UHS = ultrafast high-temperature sintering; × = no reported data.

****

Figure S1. XRD patterns of the starting LATP powders for CSP and pellets produced by CSP at different temperatures, along with the reference LiTi2(PO4)3 pattern (JCPDS card: 35-0754).

****

Figure S2. The relationship between relative density and CSP temperature for LATPsamples produced by CSP under 250 MPa for 1 h.

**References**

[1] S. Wang, Y. Ding, G. Zhou, G. Yu, A. Manthiram, Durability of the Li1+xTi2-xAlx(PO4)3 solid electrolyte in lithium-sulfur batteries, ACS Energy Lett. 1 (2016) 1080–1085. doi:10.1021/acsenergylett.6b00481.

[2] S. He, Y. Xu, B. Zhang, X. Sun, Y. Chen, Y. Jin, Unique rhombus-like precursor for synthesis of Li1.3Al0.3Ti1.7(PO4)3 solid electrolyte with high ionic conductivity, Chemical Engineering J. 345 (2018) 483-491. doi:10.1016/j.cej.2018.03.151.

[3] S. Yu, A. Mertens, X. Gao, D.C. Gunduz, R. Schierholz, S. Benning, F. Hausen, J. Mertens, H. Kungl, H. Tempel, R. Eichel, Influence of microstructure and AlPO4 secondary-phase on the ionic conductivity of Li1.3Al0.3Ti1.7(PO4)3 solid-state electrolyte, Funct. Mater. Lett. 09 (2016) 1650066. doi:10.1142/S1793604716500661.

[4] P.Y. Yen, M.L. Lee, D.H. Gregory, W.R. Liu, Optimization of sintering process on Li1+xAlxTi2-x(PO4)3 solid electrolytes for all-solid-state lithium-ion batteries, Ceram. Int. 46 (2020) 20529–20536. doi:10.1016/j.ceramint.2020.05.162

[5] A. Mertens, S. Yu, N. Schön, D.C. Gunduz, H. Tempel, R. Schierholz, F. Hausen, H. Kungl, J. Granwehr, R.A. Eichel, Superionic bulk conductivity in Li1.3Al0.3Ti1.7(PO4)3 solid electrolyte, Solid State Ionics. 309 (2017) 180–186. doi: 10.1016/j.ssi.2017.07.023.

[6] G.B. Kunshina, O.G. Gromov, E.P. Lokshin, V.T. Kalinnikov, Sol-gel synthesis of Li1.3Al0.3Ti1.7(PO4)3 solid electrolyte, Russ. J. Inorg. Chem. 59 (2014) 424–430. doi:10.1134/S0036023614050118.

[7] A. Belous, G. Kolbasov, L. Kovalenko, E. Boldyrev, S. Kobylianska, B. Liniova, All solid-state battery based on ceramic oxide electrolytes with perovskite and NASICON structure, J. Solid State Electrochem. 22 (2018) 2315–2320. doi:10.1007/s10008-018-3943-x.

[8] M. Pérez-Estébanez, J. Isasi-Marín, A. Rivera-Calzada, C. León, M. Nygren, Spark plasma versus conventional sintering in the electrical properties of NASICON-type materials, J. Alloys Compd. 651 (2015) 636–642. doi:10.1016/j.jallcom.2015.08.126.

[9] H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, G.Y. Adachi, Ionic conductivity of solid electrolytes based on lithium titanium phosphate, J. Electrochem. Soc. 137 (1990) 1023–1027. doi:10.1149/1.2086597.

[10] Y. Lin, N. Luo, E. Quattrocchi, F. Ciucci, J. Wu, M. Kermani, J. Dong, C. Hu, S. Grasso, Ultrafast high-temperature sintering (UHS) of Li1.3Al0.3Ti1.7(PO4)3, Ceram. Int. 47 (2021) 21982–21987. doi:10.1016/j.ceramint.2021.04.216.

[11] C. Wang, W. Ping, Q. Bai, H. Cui, R. Hensleigh, R. Wang, A.H. Brozena, Z. Xu, J. Dai, Y. Pei, C. Zheng, G. Pastel, J. Gao, X. Wang, H. Wang, J. Zhao, B. Yang, X. (Rayne) Zheng, J. Luo, Y. Mo, B. Dunn, L. Hu, A general method to synthesize and sinter bulk ceramics in seconds, Science. 368 (2020) 521–526. doi:10.1126/science.aaz7681.

[12] K. Waetzig, A. Rost, U. Langklotz, B. Matthey, J. Schilm, An explanation of the microcrack formation in Li1.3Al0.3Ti1.7(PO4)3 ceramics, J. Eur. Ceram. Soc. 36 (2016) 1995–2001. doi:10.1016/j.jeurceramsoc.2016.02.042.

[13] X. Xu, Z. Wen, X. Yang, L. Chen, Dense nanostructured solid electrolyte with high Li-ion conductivity by spark plasma sintering technique, Mater. Res. Bull. 43 (2008) 2334–2341. doi:10.1016/j.materresbull.2007.08.007.

[14] K. Waetzig, A. Rost, C. Heubner, M. Coeler, K. Nikolowski, M. Wolter, J. Schilm, Synthesis and sintering of Li1.3Al0.3Ti1.7(PO4)3 (LATP) electrolyte for ceramics with improved Li+ conductivity, J. Alloys Compd. 818 (2020) 153237. doi:10.1016/j.jallcom.2019.153237.

[15] S. Duluard, A. Paillassa, L. Puech, P. Vinatier, V. Turq, P. Rozier, P. Lenormand, P.-L. Taberna, P. Simon, F. Ansart, Lithium conducting solid electrolyte Li1.3Al0.3Ti1.7(PO4)3 obtained via solution chemistry, J. Eur. Ceram. Soc. 33 (2013) 1145–1153. doi:10.1016/j.jeurceramsoc.2012.08.005.

[16] G. Lancel, P. Stevens, G. Toussaint, M. Maréchal, N. Krins, D. Bregiroux, C. Laberty-Robert, Hybrid Li ion conducting membrane as protection for the Li anode in an aqueous Li-air battery: Coupling sol-gel chemistry and electrospinning, Langmuir. 33 (2017) 9288–9297. doi:10.1021/acs.langmuir.7b00675.

[17] C.M. Chang, Y. Lee, S.H. Hong, H.M. Park, Spark plasma sintering of Li1.3Ti2(PO4)3-based solid electrolytes, J. Am. Ceram. Soc. 88 (2005) 1803–1807. doi:10.1111/j.1551-2916.2005.00246.x.

[18] E.C. Bucharsky, K.G. Schell, T. Hupfer, M.J. Hoffmann, M. Rohde, H.J. Seifert, Thermal properties and ionic conductivity of Li1.3Al0.3Ti1.7(PO4)3 solid electrolytes sintered by field-assisted sintering, Ionics (Kiel). 22 (2016) 1043–1049. doi:10.1007/s11581-015-1628-3.

[19] E.C. Bucharsky, K.G. Schell, A. Hintennach, M.J. Hoffmann, Preparation and characterization of sol-gel derived high lithium ion conductive NZP-type ceramics Li1+xAlxTi2-x(PO4)3, Solid State Ionics. 274 (2015) 77–82. doi:10.1016/j.ssi.2015.03.009.

[20] C. Davis, J.C. Nino, Microwave processing for improved ionic conductivity in Li2O-Al2O3-TiO2-P2O5 glass-ceramics, J. Am. Ceram. Soc. 98 (2015) 2422–2427. doi:10.1111/jace.13638.

[21] L. Hallopeau, D. Bregiroux, G. Rousse, D. Portehault, P. Stevens, G. Toussaint, C. Laberty-Robert, Microwave-assisted reactive sintering and lithium ion conductivity of Li1.3Al0.3Ti1.7(PO4)3 solid electrolyte, J. Power Sources. 378 (2018) 48–52. doi:10.1016/j.jpowsour.2017.12.021.

[22] A. Rosenberger, Y. Gao, L. Stanciu, Field-assisted sintering of Li1.3Al0.3Ti1.7(PO4)3 solid-state electrolyte, Solid State Ionics. 278 (2015) 217–221. doi:10.1016/j.ssi.2015.06.012.

[23] G. Yan, S. Yu, J.F. Nonemacher, H. Tempel, H. Kungl, J. Malzbender, R.A. Eichel, M. Krüger, Influence of sintering temperature on conductivity and mechanical behavior of the solid electrolyte LATP, Ceram. Int. 45 (2019) 14697–14703. doi:10.1016/j.ceramint.2019.04.191.

[24] J. Wolfenstine, J.L. Allen, J. Sumner, J. Sakamoto, Electrical and mechanical properties of hot-pressed versus sintered LiTi2(PO4)3, Solid State Ionics. 180 (2009) 961–967. doi: 10.1016/j.ssi.2009.03.021.

[25] N. Hamao, Y. Yamaguchi, K. Hamamoto, Densification of a NASICON-type LATP electrolyte sheet by a cold-sintering process, Materials (Basel). 14 (2021) 4737. doi:10.3390/ma14164737.

[26] M. Vinnichenko, K. Waetzig, A. Aurich, C. Baumgaertner, M. Herrmann, C.W. Ho, M. Kusnezoff, C.W. Lee, Li-ion conductive Li1.3Al0.3Ti1.7(PO4)3 (LATP) solid electrolyte prepared by cold sintering process with various sintering additives, Nanomaterials. 12 (2022) 3178. doi: 10.3390/nano12183178.

[27] Y. Liu, J. Liu, Q. Sun, D. Wang, K.R. Adair, J. Liang, C. Zhang, L. Zhang, S. Lu, H. Huang, X. Song, X. Sun, Insight into the microstructure and ionic conductivity of cold sintered NASICON solid electrolyte for solid-state batteries, ACS Appl. Mater. Interfaces. 11 (2019) 27890–27896. doi:10.1021/acsami.9b08132.