Preparation and Characterization of Ta-substituted $\text{Li}_7\text{La}_3\text{Zr}_{2-x}\text{O}_{12}$ Garnet Solid Electrolyte by Sol-Gel Processing

Sang A Yoon, Nu Ri Oh, Ae Ri Yoo, Hee Gyun Lee, and Hee Chul Lee[†]

Department of Advanced Materials Engineering, Korea Polytechnic University, Siheung 15073, Korea

(Received April 10, 2017; Revised June 9, 2017; Accepted June 19, 2017)

ABSTRACT

In this work, Ta-substituted $\text{Li}_7\text{La}_3\text{Zr}_{2-x}\text{O}_{12}$ (LLZTO) powder and pellets with garnet cubic structure were fabricated and characterized by modified and optimized sol-gel synthesis. Ta-substituted LLZO powder with the smallest grain size and pure cubic structure with little pyrochlore phase was obtained by synthesis method in which Li and La sources in propanol solvent were mixed together with Zr and Ta sources in 2-methoxy ethanol. The LLZTO pellets made with the prepared powder showed cubic garnet structure for all conditions when the amount of Li addition was varied from 6.2 to 7.4 mol. All the X-ray peaks of the pyrochlore phase disappeared when the Li addition was increased above 7.0 mol. When the final sintering temperature was varied, the LLZTO pellet had a pyrochlore-mixed cubic phase above 1000°C. However, the surface morphology became much denser when the final sintering temperature was increased. The sol-gel-driven LLZTO pellet with a sintering temperature of 1100°C showed a lithium ionic conductivity of 0.21 mS/cm when Au was adopted as electrode material for the blocking capacitor. The results of this study suggest that modified sol-gel synthesis is the optimum method to obtain cubic phase of LLZTO powder for highly dense and conductive solid electrolyte ceramics.

Key words : Li ion battery, Solid electrolyte, Garnet, Sol-gel, LLZO

1. Introduction

Lithium ion batteries, due to their high energy density and reasonable price, are seeing a gradual extension of applications from small mobile devices to electric vehicles and high-capacity energy storage devices. However, since the stability issue involving leakage of the liquid electrolyte is coming to the fore, relevant studies are drawing attention to this flaw. Among studies to improve battery stability, some research groups have found that the ignition of an electrolyte can be inhibited by replacing a liquid electrolyte with a solid one. Currently, solid electrolytes that are being investigated for all-solid-state batteries include perovskite titanates, NASICON phosphates, LISICON sulfides, and cubic garnets.¹⁻⁵⁾

Among these materials, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) ceramic of cubic garnet structure has a lithium ion conductivity of 10^{-4} S/cm or higher at room temperature and a thermally and chemically stable interface with Li metal; this is the most promising electrode.⁶⁾ LLZO may also have a tetragonal structure, wherein the ion conductivity in the tetragonal structure is significantly lower, by two orders of magnitude, than that of the cubic structure.^{7,8)} Long-duration high-temperature sintering, which suppresses the tetragonal structure, is a process that allows a cubic structure to be obtain-

ed. However, as lithium components are volatilized during the high-temperature sintering process, the porosity may increase and the Li ion conductivity may decrease. In such a case, an efficient method of obtaining a cubic structure is to substitute with such elements as Al, Ta, Nb, and Sb.⁹⁻¹³⁾

At present, the easiest way of preparing LLZO powder is a solid-state reaction. However, since the solid-state reaction requires a too-high sintering temperature, the lithium volatilization may result in a porous surface and an unstable stoichiometry. Recently, sol-gel synthesis is drawing attention because of its various advantages, including relatively low process temperature, high purity, and high stoichiometry controllability.¹⁴⁻¹⁶⁾

In the present study, an optimized sol-gel method was investigated by applying various solutions and mixing orders in the synthesis of Ta-substituted LLZO powder. In addition, in the formation of a ceramic material, the effects of the sintering temperature and of Li addition on the phase formation and the surface morphology were investigated using optimized Ta-substituted LLZO powder. Finally, blocking capacitors were formed by using Au and Pt electrodes; then, the applicability of the prepared ceramic material as a solid electrolyte for an all-solid-state lithium battery was evaluated.

2. Experimental Procedure

The starting raw materials that were used for the sol-gel method preparation of the Ta-substituted LLZO powder

[†]Corresponding author : Hee Chul Lee

E-mail : eechul@kpu.ac.kr

Tel : +82-31-8041-0589 Fax : +82-31-8041-0599

included lithium nitrate hydrate ($\text{LiNO}_3 \cdot x\text{H}_2\text{O}$, 99.999%, Alfa Aesar), lanthanum nitrate hydrate ($\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.9%, Sigma Aldrich), zirconium (IV) propoxide ($\text{Zr}(\text{OC}_3\text{H}_7)_4$, 70 wt.% in 1-propanol, Sigma Aldrich), and tantalum (V) ethoxide ($\text{Ta}(\text{OC}_2\text{H}_5)_5$, 99.98%, Sigma Aldrich). 1-propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, anhydrous 99.7%, Sigma Aldrich), 2-methoxyethanol (2-MOE, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, anhydrous 99.8%, Sigma Aldrich), and other solvents were used to effectively dissolve the raw materials. Acetic acid (AC, 1.0 M CH_3COOH , Fluka) was added as a chelating agent to help sol-gel formation. To achieve the desired final stoichiometry of the sol-gel powder, the raw materials were mixed according to the molar ratios in the chemical formula of $\text{Li}_x\text{-La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$; the “x” in the formula, representing the quantity of Li, was varied from 6.2 to 7.4 mol.

Figure 1 is a schematic diagram showing the preparation LLZTO solutions by four different methods. In the individual methods, the mixing order, use of a solvent, and the type of solvent used were varied. In all four methods, the Ta-doped raw materials, which are not well dissolved in 1-propanol, were dissolved in 2-MOE. In Method 1, the Li and La raw materials in their own solutions, the Zr raw material and AC dissolved in 1-propanol, and the Ta material dissolved in 2-MOE were mixed together and dissolved by stirring. In Method 2, the mixture solution of Li and La and the mixture solution of Zr and AC in Method 1 were mixed together; then, the Ta raw material was mixed later (Method 2). In Method 3, Li and La were dissolved in 2-MOE, Zr and Ta material were separately dissolved in 2-MOE with AC, and then the two resulting solutions were mixed to form the final LLZTO sol solution. Finally, Method 4 was the same as Method 3 except that the Li and La raw materials were dissolved in 1-propanol.

Figure 2 is a schematic diagram showing the preparation

of the LLZTO powder through sequential gelation of the LLZTO solutions; also shown in the preparation of LLZTO pellets through sintering of the powder. First, the prepared LLZTO sol solution underwent gelation through aging for

Fig. 2. Process flow diagram for sol-gel LLZTO powder and pellet.

Fig. 1. Process flow diagrams for the Ta-substituted LLZO (LLZTO) sol with four different synthesis methods.

12 h. The resulting gel was dried for nine hours and underwent pre-calcination at 450°C for 4 h to remove the organics. Using an oil-hydraulic press, the resulting powder was pressurized in a pellet mold having a diameter of 20 mm at 8.3 MPa; then, powder was calcinated at 950°C for 4 h. Subsequently, to prepare the raw material powder for the LLZTO pellet, the pellet was ground in a mortar and underwent ball-milling at 250 rpm for 24 h using general zirconia balls. The raw material powder was pressurized at 8.3 MPa and eventually, using a Cold Isostatic Press (CIP) at 130 MPa, prepared as a pellet. In the final sintering process at high temperature, isotropic pressurization was performed to make the residual stress distribution uniform and to prevent bending or cracking of the pellet. The final sintering process for pellet preparation was performed in a temperature range of 900 to 1100°C for 4 h. To prevent lithium loss at high temperature as much as possible, the pellet was covered with powder having the same composition; this is called a mother powder.

To observe the thermal behavior of the LLZTO material and to determine the temperature of phase transformation to a cubic phase, analyses were performed using a thermogravimetry and differential thermal analyzer (TG and DTA, Netzsch DSC200F3) with the previously prepared LLZTO gel. The crystallographic structures of the LLZTO powder and the pellet were determined using an X-ray diffractometer (XRD, Rigaku D/MAX-2200/PC) in Bragg-Brentano geometry (θ - 2θ) mode with Cu K α radiation. The crystal grain size was estimated on the basis of the width of the XRD pattern peak. The relation between the crystal grain size and

the XRD peak width is determined using the Debye-Scherrer equation, shown in Equation (1):

$$d = k\lambda/\beta \cdot \cos\theta \quad (1)$$

wherein d denotes the average size of the crystal grain, k the Debye-Scherrer constant (0.89), λ the X-ray wavelength, β the line broadening in radians obtained from the full width at half maximum, and θ the Bragg diffraction angle. Surface images of the powder and the pellet were obtained using a field emission scanning electron microscope (FESEM, Hitachi S-4700). The pellet density was calculated as the weight, measured using an electronic scale, divided by the measured volume. The relative density was obtained by dividing the calculated density value by the theoretical density. The lithium ion conductivity of the prepared LLZTO pellet was measured at room temperature by Electrochemical Impedance Spectroscopy (EIS, VersaSTAT 3, Princeton Applied Research). To form a stable interface, both sides of the LLZTO pellet were polished using sand paper up to 2000 grits, and finalized using 1 μ m diamond paste (Allied High Tech Products). To make the measurement samples into blocking capacitors, a precious metal, such as Pt or Au, was deposited on both sides of the pellet to a thickness of 100 nm. The impedance of the fabricated cells was measured in the frequency range of 10 Hz to 1 MHz with a perturbation amplitude of 100 mV.

3. Results and Discussion

Figure 3 shows the results of the TG and DTA analyses

Fig. 3. TG and DTA curves of the LLZTO gels synthesized by four different methods according to temperature.

performed in the atmosphere with the prepared LLZTO gel to determine the optimal sintering temperature and the final sintering temperature for the LLZTO powder and pellet. In the measurement range of room temperature to 1200°C, the TG curve shows two instances of drastic weight decrease of all the samples; the DTA curve shows two significant endothermic reaction peaks around the temperatures at which the weight decreases occurred. The first peak, found at around 600°C, is considered to be relevant to the process in which the LLZTO lattice is formed as Li_2CO_3 melts. The TG analysis results indicate that the weight loss was enhanced as the carbon components diffused as gases. The second peak, found between 700°C and 800°C, is assumed to be relevant to the transformation of the LLZTO lattice from a tetragonal phase to a cubic phase.¹⁷⁾ Neither a particular peak on the DTA curve nor a significant weight loss on the TG curve was found at a temperature higher than 900°C. The LLZTO gels prepared by Method 1 and Method 2 showed a small first peak, with little weight loss around 600°C, while the LLZTO gels prepared by Method 3 and Method 4 showed a sharp first peak with drastic weight loss. This may be because most LLZTO lattices in the LLZTO gels prepared by Method 3 and Method 4 may be transformed to a cubic phase immediately after being produced at the first peak temperature.

Figure 4 shows the XRD curves of the LLZTO powders prepared using the LLZTO solutions prepared via the different synthetic methods shown in Fig. 1. Regardless of the preparation method, all the LLZTO powders had a cubic phase, not a tetragonal phase, as verified by the XRD standard peaks of JCPDS 45-109 (cubic LLZO, ICSD data), which are shown together for comparison. The tiny peaks commonly observed at the diffraction angles of 23° and 40° may correspond to the Ta_2O_5 and La_2O_3 phases, respectively. However, the samples prepared by Methods 1 to 3 included peaks corresponding to a Li-deficient $\text{La}_2\text{Zr}_2\text{O}_7$ pyrochlore

Fig. 4. XRD patterns of the LLZTO powder prepared by different synthesis methods of LLZTO solution. Conditions: Pre-calcination temperature, 450°C; Calcination temperature, 950°C.

phase, although the peak size was small.

The lattice plane spacing and the lattice constant of the LLZTO cubic phase were calculated using the 2θ value of the diffraction angle of the (211) plane corresponding to one of the major peaks in the XRD pattern. As shown in Fig. 4, the lattice constants of the LLZTO powders prepared by Methods 1 to 4 were 12.90 Å, 12.85 Å, 12.87 Å, and 12.71 Å, respectively, indicating that the lattice constant of Method 4 was the smallest. This may be because the lattice constant of Method 4 showed the largest decrease because the Ta^{5+} ions ($r_{\text{ion}} \sim 0.068$ Å) that had a smaller ionic radius efficiently occupied the lattice sites of Zr ions ($r_{\text{ion}} \sim 0.087$ Å).

Table 1 shows the crystal grain size depending on the solution synthesis method, wherein the crystal grain size was calculated from the XRD pattern shown in Fig. 3 using the Debye-Scherrer equation, representing the relation between the crystal size and the XRD peak width. Although the grain size was not significantly dependent on the solution synthesis method, the grain size was smallest in the powder prepared by Method 4.

Figure 5 shows 10,000 times magnified SEM images of the surface of the LLZTO powders prepared by different LLZTO solution synthesis methods. The shape of the powder surface was found not to be significantly dependent on the synthesis method.

Table 1. Grain Size of LLZTO Powder According to Synthesis Method of LLZTO Solution from XRD Peak Broadening and Debye-Scherrer Equation

Solution Synthesis Method	1	2	3	4
Grain size (nm)	86	88	84	82

Fig. 5. Planar SEM images of the LLZTO powder prepared by different synthesis methods of LLZTO solution. Conditions: Pre-calcination temperature, 450°C; Calcination temperature, 950°C.

Fig. 6. XRD patterns of LLZTO pellets with Li addition. Conditions: Solution preparation, Method 4; Calcination temperature, 950°C; Sintering temperature, 950°C.

Considering the generation of Li-deficient $\text{La}_2\text{Zr}_2\text{O}_7$ phase, the analyzed lattice constant, and the crystal grain size, Method 4 was chosen as the most appropriate LLZTO solution synthesis method and was applied to the subsequent LLZTO pellet preparation.

Figure 6 shows the XRD patterns of the LLZTO pellets prepared by varying the quantity of added lithium from 6.2 to 7.4 mol. The LLZTO solution was prepared by Method 4 and the final sintering temperature was 950°C. All the pellets, from the Li-deficient (6.2 mol) pellet to the Li-excessive (7.4 mol) pellet, showed a dominant cubic garnet structure. However, the Li-deficient LLZTO pellet included a slight amount of $\text{La}_2\text{Zr}_2\text{O}_7$ phase. This result implies that, in comparison with the conventional solid-state reaction that was studied previously, LLZTO pellet preparation by sol-gel method, depending on the quantity of Li addition, has a very wide process window for the formation of a pure cubic phase.¹⁸⁾

Figure 7 shows the XRD pattern of the LLZTO pellets depending on the final sintering temperature. The LLZTO solution was prepared by Method 4; the quantity of Li addition was 7.4 mol. Tetragonal phases were included in the pellets only when the final sintering temperature was as low as 800°C, at which point tetragonal phases were identified by the split and seemingly overlapped tips of the peaks in the XRD pattern. When the final sintering temperature was high (over 1000°C), an Li-deficient $\text{La}_2\text{Zr}_2\text{O}_7$ peak was found due to lithium loss, although the pellet surface was covered with the mother LLZTO powder of the same composition. At the highest sintering temperature of 1100°C, a strong peak corresponding the $\text{La}_2\text{Zr}_2\text{O}_7$ phase was found. Although it was presumed that the cubic phase could be stabilized at the high temperature via Li vacancies generated by the replacement of Zr with the Ta added to LLZO, the results showed that the stabilization did not effectively take place at the high temperature. Therefore, in future studies, powders will be synthesized via sol-gel method by adding a

Fig. 7. XRD patterns of LLZTO pellets sintered at various temperatures. Conditions: Solution synthesis, Method 4; Calcination temperature, 950°C; Li addition, 7.4 mol.

doping element other than Ta, and solid electrolyte ceramic pellets having excellent properties will be prepared using the powders as raw materials.

Figure 8 shows 50,000 times magnified SEM images of the surfaces of the pellet samples shown in Fig. 7. The sample surface became more compact as the final sintering temperature was increased. As indicated in the figure caption for Fig. 8, the actually-measured density also gradually increased from 4.0 g/cm³ to 4.8 g/cm³ as the final sintering temperature increased from 800 to 1100°C. The density of 4.8 g/cm³ obtained at the final sintering temperature of 1100°C corresponds to a relative density of 89%, which was higher than the relative density of 84% obtained in a previous solid-state reaction study¹⁹⁾ in which, with a similar composition, the sintering was performed for 24 h at the

Fig. 8. SEM images of LLZTO pellets sintered at various temperatures: (a) 800°C (density, $d = 4.0 \text{ g/cm}^3$), (b) 900°C ($d = 4.1 \text{ g/cm}^3$), (c) 1000°C ($d = 4.5 \text{ g/cm}^3$), and (d) 1100°C ($d = 4.8 \text{ g/cm}^3$)

Fig. 9. Nyquist plots (at room temperature and frequency range of 10 Hz ~ 1 MHz) of the LLZTO pellets sintered at 1100°C: Pt/LLZTO/Pt (Li ionic conductivity, $\sigma_{\text{Li}} = 0.14$ mS/cm) and Au/LLZTO/Au ($\sigma_{\text{Li}} = 0.21$ mS/cm).

temperature of 1200°C. Despite the lower sintering temperature and the shorter sintering duration, the pellets produced in the present study showed a relative density higher than that of the previous study, probably because the raw material powder used for pellet preparation was synthesized by sol-gel method to have a smaller particle size. However, for accurate comparison of the density between ceramic pellets, there should be almost no pyrochlore phase, which has a relatively high density.

Figure 9 shows the room temperature EIS results of the blocking capacitors prepared by depositing a Pt or Au electrode on both sides of the LLZTO pellets, sintered at 1100°C, having the highest density. The calculated values of overall lithium ion conductivity were 0.14 mS/cm when Pt was used as the electrode and 0.21 mS/cm when Au was used as the electrode. The overall ion conductivity consists of the ion conductivity inside the grains, that across the grain boundary, and that at the interface between the electrode and the solid electrolyte. The overall ion conductivity was higher when Au was used as the electrode, probably because the contact resistance between the Au electrode and the solid electrolyte was lower. The lithium ion conductivity of 0.21 mS/cm is an excellent value in comparison with those obtained in previous studies, but is not the world's highest level.⁹⁾ While the increase of the ion conductivity via Li vacancies obtained by substituting Zr with Ta, and the high relative density obtained by the sol-gel method used in the preparation, had positive effects, the second phase of the Li-deficient pyrochlore might have imparted a negative effect at the same time. Therefore, future studies will be conducted to prepare a solid electrolyte ceramic of pure cubic phase and high density by suppressing the formation of the pyrochlore phase as much as possible through appropriate substitution and processing.

4. Conclusions

In the present study, LLZTO ($\text{Li}_x\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$) solid electrolyte powders and pellets having a cubic garnet structure were successfully prepared by an improved sol-gel method. In the synthesis of the LLZTO solutions for the sol-gel process, relatively good properties were obtained by first dissolving Zr and Ta raw materials together in 2-MOE. In the sol-gel method preparation of the LLZTO pellets, a cubic garnet structure was obtained for all the pellets prepared by varying the quantity of lithium addition from 6.2 to 7.4 mol, indicating that LLZTO pellet preparation by sol-gel method has a very wide process window. When the final sintering temperature was as low as 800°C, a slight amount of tetragonal phase was included because the driving energy of the transformation to the cubic phase was not sufficiently high. When the final sintering temperature was 1000°C or higher, Li-deficient $\text{La}_2\text{Zr}_2\text{O}_7$ was formed due to lithium loss. A very strong $\text{La}_2\text{Zr}_2\text{O}_7$ peak was found at the sintering temperature of 1100°C. However, when the sintering temperature was as high as 1100°C, LLZTO pellets having a high density and a compact shape were prepared. EIS analysis of the blocking capacitor prepared by depositing an Au electrode showed an excellent lithium ion conductivity of 0.21 mS/cm.

Acknowledgments

This work was supported by a National Research Foundation (NRF) grant funded by the Korean government (Ministry of Science, ICT and Future Planning) (Grant code: 2017R1A2B1009993).

REFERENCES

1. K. B. Dermenci, E. Cekic, and S. Turan, "Al Stabilized $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolytes for All-Solid State Li-Ion Batteries," *Int. J. Hydrogen Energy*, **41** [23] 9860-67 (2016).
2. Y. Zhang, J. Cai, F. Chen, R. Tu, Q. Shen, X. Zhang, and L. Zhang, "Preparation of Cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolyte Using a Nano-Sized Core-Shell Structured Precursor," *J. Alloys Compd.*, **644** 793-98 (2015).
3. J. Wolfenstine, E. Rangasamy, J. L. Allen, and J. Sakamoto, "High Conductivity of Dense Tetragonal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$," *J. Power Sources*, **208** 193-96 (2012).
4. Y. Zhang, F. Chen, R. Tu, Q. Shen, and L. Zhang, "Field Assisted Sintering of Dense Al-Substituted Cubic Phase $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolytes," *J. Power Sources*, **268** 960-64 (2014).
5. J. Wolfenstine, J. Ratchford, E. Rangasamy, J. Sakamoto, and J. L. Allen, "Synthesis and High Li-Ion Conductivity of Ga-Stabilized Cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$," *Mater. Chem. Phys.*, **134** [2] 571-75 (2012).
6. E. J. Cussen, "Structure and Ionic Conductivity in Lithium Garnets," *J. Mater. Chem.*, **20** [25] 5167-73 (2010).

7. I. Quinzeni, D. Capsoni, V. Berbenni, P. Mustarelli, M. Sturini, and M. Bini, "Stability of Low-Temperature $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Cubic Phase: The Role of Temperature and Atmosphere," *Mater. Chem. Phys.*, **185** 55-64 (2017).
8. J. Awaka, N. Kijima, H. Hayakawa, and J. Akimoto, "Synthesis and Structure Analysis of Tetragonal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ with the Garnet-Related Type Structure," *J. Solid State Chem.*, **182** [8] 2046-52 (2009).
9. K. Liu, J. T. Ma, and C. A. Wang, "Excess Lithium Salt Functions More than Compensating for Lithium Loss when Synthesizing $\text{Li}_{6.5}\text{La}_3\text{Ta}_{0.3}\text{Zr}_{1.5}\text{O}_{12}$ in Alumina Crucible," *J. Power Sources*, **260** 109-14 (2014).
10. T. Liu, Y. Ren, Y. Shen, S. X. Zhao, Y. Lin, and C. W. Nan, "Achieving High Capacity in Bulk-Type Solid-State Lithium Ion Battery Based on $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ Electrolyte: Interfacial Resistance," *J. Power Sources*, **324** 349-57 (2016).
11. K. C. Santosh, C. L. Roberto, K. Xiong, and K. Cho, "Point Defects in Garnet-Type Solid Electrolyte ($\text{c-Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$) for Li-Ion Batteries," *Solid State Ionics*, **261** 100-5 (2014).
12. K. Tadanaga, N. C. Rosero-Navarro, T. Yamashita, A. Miura, and M. Higuchi, "Preparation of $\text{Li}_7\text{La}_3(\text{Zr}_{2-x}\text{Nb}_x)\text{O}_{12}$ ($x = 0 - 1.5$) and $\text{Li}_3\text{BO}_3/\text{LiBO}_2$ Composites at Low Temperatures Using a Sol-Gel Process," *Solid State Ionics*, **285** 6-12 (2016).
13. A. R. Yoo, S. A. Yoon, Y. S. Kim, J. Sakamoto, and H. C. Lee, "A Comparative Study on the Synthesis of Al-Doped $\text{Li}_{6.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ Powder as a Solid Electrolyte Using Sol-Gel Synthesis and Solid-State Processing," *J. Nanosci. Nanotechnol.*, **16** [11] 11662-68 (2016).
14. N. Rosenkiewitz, J. Schuhmacher, M. Bockmeyer, and J. Deubener, "Nitrogen-Free Sol-Gel Synthesis of Al-Substituted Cubic Garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)," *J. Power Sources*, **278** 104-8 (2015).
15. E. Rangasamy, J. Wolfenstine, J. Allen, and J. Sakamoto, "The Effect of 24c-site (A) Cation Substitution on the Tetragonal-Cubic Phase Transition in $\text{Li}_{7-x}\text{La}_{3-x}\text{A}_x\text{Zr}_2\text{O}_{12}$ Garnet-Based Ceramic Electrolyte," *J. Power Sources*, **230** 261-66 (2013).
16. T. Thompson, J. Wolfenstine, J. L. Allen, M. Johannes, A. Huq, I. N. David, and J. Sakamoto, "Tetragonal vs. Cubic Phase Stability in Al-Free Ta Doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)," *J. Mater. Chem. A*, **2** [33] 13431-36 (2014).
17. J. Sakamoto, E. Rangasamy, H. Kim, Y. Kim, and J. Wolfenstine, "Synthesis of Nano-Scale Fast Ion Conducting Cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$," *Nanotechnology*, **24** [42] 424005-12 (2013).
18. I. Kokal, M. Somer, P. H. L. Notten, and H. T. Hintzen, "Sol-Gel Synthesis and Lithium Ion Conductivity of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ with Garnet-Related Type Structure," *Solid State Ionics*, **185** [1] 42-6 (2011).
19. N. Janani, S. Ramakumar, S. Kannan, and R. Murugan, "Optimization of Lithium Content and Sintering Aid for Maximized Li^+ Conductivity and Density in Ta-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$," *J. Am. Ceram. Soc.*, **98** [7] 2039-46 (2015).