Phase formation of a garnet-type lithium-ion conductor $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$

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Abstract

The phase formation of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ was investigated by high temperature X-ray diffraction measurements. The tetragonal phase was obtained in the range of $x = 0$ to 0.20 and the cubic phase was formed at $x = 0.25$ at room temperature. A linear change of the lattice parameters was observed from $x = 0$ to 0.20, which is in good agreement with the systematic composition change. The solubility limit of Al^{3+} was determined to be $x = 0.25$. The reversible phase transition between the tetragonal phase and the cubic phase was observed at 640 °C for $x = 0$. The marked increase of ionic conductivity at the phase transition temperature is consistent with the structural change of the ordering/disordering of lithium ions. In addition, the phase transition temperature decreased with increasing x , and the cubic phase was stabilized at $x = 0.25$ from room temperature to 900 °C. The ionic conductivity increased with x and the highest ionic conductivity of $3.1 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C was obtained for $x = 0.25$. Al^{3+} substitution introduces lithium vacancies, which has a strong influence on the phase transition between the tetragonal and cubic phases. The results obtained here suggest that control of the lithium vacancies is the key to obtain a fast lithium-conducting phase.

Introduction

The fast lithium-ion conducting electrolytes with chemical and electrochemical stability in contact with lithium metal is key to the development of next generation energy storage systems such as all-solid-state lithium secondary batteries and lithium-air secondary batteries [1-3]. The practical solid-state electrolyte requires not only high lithium-ion conductivity, but also chemical and electrochemical stability with lithium metal. Many lithium-ion conducting oxides have been investigated [3,4]; however, most are excluded from application as an electrolyte due to their poor stability with lithium metal.

Among the lithium-ion conductors, the garnet-like conductors are considered to be one of the most promising materials for application as an electrolyte of all-solid-state lithium secondary batteries. In 2003, the garnet-like compounds of $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($M = \text{Nb}$ and Ta) were reported as lithium-ion conductors that have excellent chemical stability with lithium metal [5]. However, the ionic conductivity of these materials was low at around $10^{-6} \text{ S cm}^{-1}$ at 25°C . Therefore, extensive studies have been pursued to improve the ionic conductivity of these systems [6-8]. Garnet-like $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) was discovered by Murugan et al. [8] and exhibits a high bulk conductivity of $\text{ca } 5 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C in addition to electrochemical stability with lithium metal.

Three phases have been reported for LLZ; a fast lithium-conduction cubic phase prepared at high temperature (H.T.)-cubic phase, a tetragonal phase obtained at around 1000°C , and a low temperature (L.T.)-cubic phase formed by reaction with moisture and CO_2 [8-10]. The garnet compounds are generally described as $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$, where A , B and C are eight, six and four oxygen coordinated cation sites in the cubic structure. The LLZ structure has La^{3+} at A -sites, Zr^{4+} at B -sites, and lithium ions at C sites and interstitial sites [9,11-13]. The H.T.-cubic phase forms a disordered lithium arrangement [13], whereas the tetragonal phase forms an ordered lithium arrangement [9]. The structure of the L.T.-cubic phase has yet to be clarified. Although the H.T.-cubic phase exhibits high ionic conductivity, the other phases have low ionic conductivity of $\text{ca. } 10^{-6} \text{ S cm}^{-1}$ at 25°C .

To obtain a phase that exhibits fast lithium conductivity, the phase relationships in the stoichiometric $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ system have been investigated [14,15]. Recent studies suggest that the thermodynamically stable phase at room temperature is

the tetragonal phase [14,16]. The reversible phase transition between the tetragonal and H.T.-cubic phases proceeds very fast at 650 °C; therefore, the H.T.-cubic phase with stoichiometric composition cannot be quenched at room temperature [14]. It has been considered that the H.T.-cubic LLZ with the lithium-disordered structure could be stabilized at room temperature by the replacement of Li^+ for Al^{3+} , which originated as contamination from the aluminum crucible used during the high temperature sintering period [14,17,18]. The H.T.-cubic phase was successfully stabilized at room temperature by the addition of Al_2O_3 sources and Rangasamy et al. suggested that at least 0.204 mole of Al^{3+} is required to obtain the H.T.-cubic phase of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ at room temperature [16]. In addition, the presence of Al^{3+} at lithium sites was suggested by from a nuclear magnetic resonance spectroscopy (NMR) study [19]. Such research suggests that the $\text{Li}^+/\text{Al}^{3+}$ composition influence the phase stability of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$. However, the details of the phase formation and ionic conductivity of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ are still unclear.

Furthermore, LLZ reacts with H_2O and/or CO_2 in air below 400 °C (even at room temperature) to form the L.T.-cubic phase, which exhibits low ionic conductivity [10,14]. The L.T.-cubic phase has similar X-ray diffraction (XRD) patterns to that of H.T.-cubic phase, except for a slightly larger lattice parameter. Therefore, an investigation on the phase relationships and characteristics of the tetragonal and H.T.-cubic phases should be conducted under CO_2 -free conditions to avoid formation of the L.T.-cubic phase.

In the present study, the phase formation, structure and ionic conductivity of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ were investigated. To obtain CO_2 -free samples, $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ was annealed in an inert atmosphere prior to measurements. The phase formation of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ was investigated using high temperature XRD in an inert atmosphere. The phase transition behavior was confirmed by thermogravimetry/differential thermal analysis (TG/DTA). In addition, the relationship between the structure and ionic conductivity is discussed.

Experimental

The garnet-like lithium ion conductor $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ was synthesized by conventional solid state methods. Appropriate amounts of Li_2CO_3 (Nacalai Tesque, 99%), $\text{La}(\text{OH})_3$ (Aldrich, 99.9%), ZrO_2 (Tosoh), and Al_2O_3 (Alfa Aesar, 99.997%) were ball-milled in hexane for 2 h with zirconia milling media. The mixed powder was isostatically pressed into pellets, which were placed on a gold sheet in a magnesia crucible and then calcined at 950 °C for 5 h in a N_2 gas flow. The samples were then ground, pelletized and sintered at 1300 °C for 1 h in air. For the $x = 0$ sample, a magnesia crucible was used to obtain an Al^{3+} -free sample, while the $x > 0$ samples were fired in an alumina crucible. To compensate for Li evaporation during the high temperature synthesis, a 5% excess of lithium was added and the powder bed method was applied. For the Al^{3+} doped samples, extra pellets with the same composition were placed between the alumina crucible and the sample pellet to prevent Al^{3+} contamination from the crucible. The sintered pellets were quenched from above 400 °C to prevent reaction with CO_2 and H_2O .

Phase identification was performed using a powder X-ray diffractometer (Bulker D8 and Rigaku RINT 2500) with Cu K α radiation. The diffraction data were collected at each 0.02° step width in the 2θ range from 10 to 80°. Structural parameters were refined using Topas Ver. 4 [20]. The high temperature XRD measurement was conducted using the Bulker D8 diffractometer with a high temperature furnace attachment and an inert gas flow. The measured samples were annealed in the high temperature XRD apparatus, by which it was expected to eliminate the presence of impurity phases caused by reaction with CO_2 and H_2O in the air. XRD measurements were performed up to 900 °C with a heating rate of 30 K min⁻¹. TG/DTA analysis (Thermo Plus TG 8120, Rigaku) was employed to measure the heat flow and the mass increase/decrease during the heating process.

The Li, La, Zr and Al compositions were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent Technologies ICP-OES 710). The ionic conductivity of the sintered pellets with sputtered gold electrodes was measured by the AC impedance method using a frequency response analyzer (Solartron 1260) in the frequency range of 0.1 Hz to 1 MHz from 25 to 800 °C in an inert gas atmosphere.

Results and discussion

Figure 1 shows XRD patterns for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ samples measured at room temperature. Diffraction peaks of the samples with $x = 0-0.20$ could be indexed according to the tetragonal garnet-like structure with the space group $I41/acd$ [9]. For $x = 0.20$, diffraction peaks corresponding to the cubic garnet-like structure with the space group $Ia-3d$ [21] were also observed. The quenching from 400°C may be insufficient to convert the cubic phase to tetragonal phase complete. The 422 peak observed at 33.7° for the tetragonal phase was shifted to a higher angle with increasing x , whereas the 224 peak observed at 34.4° was shifted to a lower angle. These peaks then merged into a single strong intensity peak at $x = 0.25$. The peaks of the samples with $x = 0.25$ and 0.26 could be assigned to the cubic garnet-like structure with the space group $Ia-3d$ [21]. At $x = 0.267$, the small amount of impurity peaks corresponding to LaAlO_3 coexisted with the garnet phase, and whose garnet phase showed no peak shift. These results suggest that the solubility limit is at around $x = 0.25$. The phase formation of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ at room temperature is consistent with the previous reports [16,17]. Cubic phase LLZ was stabilized at room temperature by the change in the lithium composition caused by Al^{3+} substitution.

The chemical composition was analyzed using ICP-OES and the results are summarized in Table 1, where the ratios are normalized with respect to the Zr content. The measured atomic ratio of Li and Al approximately coincides with that of the formula unit $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$. The Li and Al^{3+} contents were slightly smaller than those of the starting mixture for all samples. This may be due to the difficulty in precise analysis of the garnet-like compounds by ICP-OES measurement [17,18,22].

Rietveld refinements of XRD data for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ were conducted based on a garnet-like structure with the space group $Ia-3d$ for cubic samples [13] and the space group $I41/acd$ for tetragonal samples [9]. The occupancy values of Li were fixed and were not taken into account for the Rietveld refinement analysis. The position of Al was fixed at $24d$ sites. Figure 2 shows the final XRD Rietveld pattern for the sample with $x = 0.25$. The atomic coordinates are listed in Table 2. The $K\beta$ peaks observed in the 2θ range of $30.4 - 30.6$, $14.8 - 15.4$, $23.0 - 23.4$, $24.6 - 25.0$, $27.7 - 27.9$, $29.4 - 29.6$, $38.6 - 38.8$ and that due to the presence of an impurity phase were excluded from the refinement cycles. The profile fitting provided good agreement factors; R_{wp} of 12.12 %, R_p of 8.97 %, R_B of 5.73 %, and GOF 1.67 for $x = 0.25$.

Figure 3 shows the change in lattice parameters with x for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$. A linear decrease of a and linear increase of c were observed from $x = 0$ to 0.20. The cubic phase was formed at $x = 0.25$, where a became constant. The linear change of the lattice parameters from $x = 0$ to 0.20 is in good agreement with the systematic compositional change of the tetragonal LLZ. The solubility limit of Al^{3+} was confirmed to be at $x = 0.25$ in $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$. The c/a ratio of the tetragonal cell approached 1.0 with an increase in x within the composition range of $0 \leq x \leq 0.20$, which suggests the tetragonal garnet structure transforms to the cubic structure by the introduction of the lithium vacancies. The tetragonal garnet structure forms an ordered lithium arrangement with a Li–Li distance of $>2.5 \text{ \AA}$ [9], which is longer than those of the cubic garnet structure [13] and reflects the increase in the electric repulsion energy between adjacent lithium ions with an excess of lithium ions in the tetragonal structure. The decrease of tetragonality against x may correspond to a decrease of the electric repulsion energy between adjacent lithium ions by the introduction of lithium vacancies in the tetragonal garnet structure. The location of the solubility limit at the composition where the cubic phase appears suggests the instability of the tetragonal structural causes Al^{3+} substitution to stabilize the cubic structure.

To confirm the phase stability and phase transition behavior of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ at high temperature, TG/DTA measurement and H.T.-XRD measurement were conducted in an inert gas flow from 25 to 900 °C. The samples were annealed in an inert gas flow at 900 °C in the equipment before measurement to prevent phase transformation to the L.T.-cubic phase induced by CO_2 and/or moisture. No weight change was observed in TG profiles measured for all samples, which suggests that the reaction of LLZ with CO_2 and/or moisture could be prevented during the measurement. Figure 4 shows DTA curves for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ samples with (a) $x = 0$, (b) $x = 0.066$ and (c) $x = 0.133$ during heating and cooling processes. The endothermic/exothermic peaks observed at 640 °C for $x = 0$ is attributed to the reversible phase transition between the tetragonal and cubic phases [14]. The endothermic/exothermic peaks were observed at lower temperature and became smaller for the sample with $x = 0.067$. However, these broadened peaks were scarcely observed for $x = 0.133$. The introduction of lithium vacancies decreases the latent heat of the phase transition; therefore, the endothermic/exothermic peaks corresponding to

the phase transition of the samples with $x = 0.133$ – 0.20 were not observed due to the low latent heat and the detection limit of the TG/DTA apparatus.

Figure 5 shows H.T.-XRD patterns for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ with (a) $x = 0$, (b) $x = 0.133$, and (c) $x = 0.25$ as representative data. For the sample with $x = 0$, the tetragonal phase was observed in the low temperature region. The phase transition from the tetragonal to cubic phase was observed at a temperature corresponding to the endothermic peak observed in the DTA measurements. The diffraction patterns for the cooling process were in good agreement with those for the heating process. The small peak deviation observed in the DTA curves during the heating/cooling process suggests that the H.T.-cubic phase is difficult to obtain by quenching for $x = 0$. In the XRD pattern for the sample with $x = 0.133$, the diffraction peaks of the tetragonal phase merged into a single peak in the range of 400 – 450 °C and the cubic phase was observed up to 900 °C. The general tendency of the phase transitions that accompany atomic rearrangement indicate the rate of the phase transition gradually decreased with the phase transition temperature in this system. The cubic phase was observed for the sample with $x = 0.25$ over all measurement temperatures.

Figure 6 shows the lattice parameter change of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ as a function of temperature. For $x = 0$, both a and c lattice parameters showed a linear increase with the temperature, which reflects the thermal activation of the lattice vibration. The a parameter decreased and the c parameter increased just below the phase transition temperature, and became equivalent within a narrow temperature range. The lattice parameter change for the cooling process showed good agreement with that of the heating process. The lattice parameter change corresponding to the phase transition was observed at 400 – 450 °C for $x = 0.133$. The tetragonality of the tetragonal phase decreased in the temperature range of 400 – 450 °C, where the similarity between a and c suggests the formation of the cubic phase was completed at 450 °C. The lattice parameter for the $x = 0.25$ sample changed linearly with the temperature, which is in good agreement with the formation of the cubic phase for all measurement temperatures. The introduction of lithium vacancies enhances the formation of the cubic structure with the disordered lithium arrangement.

Figure 7 shows impedance plots for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ measured in an inert atmosphere. Two semicircles were observed for the sample with (a) $x = 0$ and (b) 0.25 in the high frequency range with a spike in the low-frequency range, the latter of which

is due to electrode contribution. The semicircles were interpreted as parallel combinations of resistance and capacitance. The part of the semicircle at higher frequency is attributed to the bulk resistance and that at the lower side is attributed to the grain boundary resistance. The intercept of the semicircle on the real axis at high frequency is attributed to the bulk resistance and that at the low frequency side is attributed to the total resistance of the bulk and grain boundaries. In contrast, only one semicircle was observed for the sample with $x = 0.133$ in the high frequency range with a spike in the low-frequency range. The bulk and grain boundary contributions could not be separated clearly from the impedance data. The sum of the bulk and grain boundary resistivity was obtained from the intercepts of the semicircle on the real axis.

Figure 8 shows the temperature dependence of the ionic conductivity for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$. The ionic conductivity increased linearly against the temperature, and then jumped between 620 and 650 °C for the sample with $x = 0$, which is in good agreement with the phase transition confirmed by TG/DTA and H.T.-XRD measurements. This indicates the formation of the fast conduction phase above the phase transition temperature [14]. A small jump of conductivity was observed between 550 and 600 °C for the sample with $x = 0.067$. The change of conductivity at the phase transition temperature became gradual with increasing x , which is consistent with the structural change confirmed by the H.T.-XRD measurements. The sample with $x = 0.25$ exhibited high ionic conductivity above $10^{-4} \text{ S cm}^{-1}$ at 25 °C. The high ionic conductivity of $x = 0.25$ is in good agreement with stabilization of the cubic phase, which exhibits fast lithium ion conduction. The increase of ionic conductivity for the $x = 0.25$ sample became gradual above 400 °C, which is often observed for conventional superionic conductors [3,23].

Figure 9 shows the phase diagram of the $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ system. For the stoichiometric $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ($x = 0$), the tetragonal phase is thermodynamically stable up to 640 °C, and then transforms to the cubic phase. The phase transition temperature decreases from $x = 0$ to 0.20. The rate of the phase transition gradually decreased with the phase transition temperature in this system. The quenching above the phase transition temperature of $x = 0.20$ stabilized the cubic phase at room temperature and two phase region was observed at low temperature. The cubic phase was stabilized from room temperature to 900 °C at $x = 0.25$. The phase formation of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ is dependent on the lithium content. The lithium ions in the

stoichiometric $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ are fully occupied at Li1, Li2 and Li3 sites and form a complete ordered arrangement in the tetragonal structure with the space group $I41/acd$ (no. 142) [9]. Thermal activation of the lattice vibration enhances lithium migration, which causes the phase transition from the lithium-ordered tetragonal phase to the lithium-disordered cubic phase. Thus, the increase of conductivity at the phase transition temperature is in good agreement with the rearrangement of lithium ions. The formation of the tetragonal structure for the lithium rich composition suggests that the ordered arrangement of lithium ions with long Li–Li distances is caused by the electric repulsion energy between adjacent lithium ions. When the thermal vibration energy overcomes the large electrostatic energy, the phase transition occurred at 640 °C for $x = 0$. The decrease of the phase transition temperature against x suggests that the phase transition occurs with lower thermal energy by the introduction of lithium vacancies. The decrease of lithium ions decreases the electrostatic energy in the structure, so that the ordered lithium arrangement becomes unstable. The order-disorder transition temperature of Li ions gradually decreased with the Al^{3+} content, i.e., the lithium vacancies and the cubic phase with disordered Li arrangement was stabilized at room temperature for $x = 0.25$. This suggests that > 0.4 mol of lithium vacancies are necessary to stabilize the cubic phase, which is in good agreement with the calculated result [24]. A discontinuous change from the tetragonal phase to the cubic phase was observed between $x = 0.20$ and 0.25 , and the discontinuity is similar to the structural change at the phase transition temperature of tetragonal LLZ. The phase transition between the tetragonal and cubic phases is predominantly determined by the arrangement of lithium ions [25] and occurs without a significant change of the framework. The details of the Li^+ and Al^{3+} distributions at lithium sites should thus be investigated further by a combination of neutron diffraction and NMR measurements.

Figure 10 shows the temperature dependence of ionic conductivity for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ from 25 to 100 °C. The ionic conductivities at 25 °C and the activation energies are summarized in Table 3. The activation energy was calculated by the slope in the temperature range of 25–100 °C. The ionic conductivity increased and the activation energy decreased from $x = 0$ to 0.20 . The ionic conductivity jumped at $x = 0.25$, which corresponds to stabilization of the cubic phase with the lithium disordered arrangement. The highest conductivity of $3.1 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C and an

activation energy of 0.33 eV were observed for $x = 0.25$, which are comparable to that previously reported [8,26]. The conductivity of the garnet-type lithium ionic conductors generally shows a positive tendency against the lithium content due to the increase of excess lithium ions that occupy 96h interstitial sites in the cubic structure [27]. However, $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ exhibits an opposite tendency against the lithium content. The different tendency of the ionic conductivity against the lithium content of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ may correspond to the difference in the lithium arrangements between the tetragonal and cubic structures. The lithium ions in stoichiometric $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ form a completely ordered arrangement with full occupation at lithium sites [9]. The high activation energy suggests that the complete ordering of the lithium ions disturbs lithium migration, so that stoichiometric $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ exhibits low ionic conductivity. The introduction of lithium vacancies increased ionic conductivity; however, the activation energy of Al-doped LLZ with the tetragonal structure was still high, which suggests that tetragonal structure is not suitable for the fast diffusion of lithium ions. In contrast, the cubic phase with the disordered lithium structure exhibits high ionic conductivity above $10^{-4} \text{ S cm}^{-1}$ with a low activation energy. The low activation energy of the cubic phase suggests that there is low electrostatic repulsion energy between lithium ions and the increase of equivalent lithium sites enhances the mobility of lithium ions, which enables fast lithium diffusion in the structure. Therefore, an increase of the carrier concentration may influence the ionic conductivity of the cubic garnet compounds. The present results suggest that the phase formation of the garnet-type lithium conductor, $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$, is dependent on the lithium content. Thus, control of the lithium vacancies is a key to obtain a fast lithium-ion conducting phase.

Conclusion

The phase formation, structure and ionic conductivity of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ were investigated. The tetragonal phase was obtained from $x = 0$ to 0.20 and the H.T.-cubic phase was stabilized for $x = 0.25$ at room temperature. A linear decrease of the a -axis and a linear increase of the c -axis from $x = 0$ to 0.20 was in good agreement with the systematic compositional change of tetragonal LLZ. The cubic structure was formed at $x = 0.25$, where the a lattice parameter became constant, which suggests the solubility limit of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ is $x = 0.25$. The fast phase transition between the

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3 tetragonal and cubic phases was observed at 640 °C for the sample with $x = 0$, which
4 suggests that the fast conduction phase of stoichiometric $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ is stable at high
5 temperature and difficult to obtain at room temperature. The phase transition
6 temperature decreased with increasing x and the cubic phase was stabilized at room
7 temperature for $x = 0.25$. The introduction of lithium vacancies by Al^{3+} substitution
8 stabilized the cubic phase and the highest ionic conductivity of $3.1 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C
9 was obtained at $x = 0.25$ with an activation energy of 0.33 eV.
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FIGURES

Fig. 1. (a) XRD patterns for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ samples measured at room temperature and (b) 422 and 224 peak shifts.

Fig. 2. XRD Rietveld pattern for the $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ sample.

Fig. 3. Lattice parameter change against x in $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$.

Fig. 4. DTA curves for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ samples with (a) $x = 0$, (b) $x = 0.066$ and (c) $x = 0.133$ measured in an inert atmosphere with a heating rate of 20 K min^{-1} .

Fig. 5. H.T. XRD patterns for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ with $x = 0, 0.133$ and 0.25 during the heating and cooling processes between 25 and 900 °C in an inert gas flow with a heating/cooling rate of 30 K min⁻¹.

Fig. 6. Lattice parameter change of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ as a function of temperature.

Fig. 7. Impedance plots for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ with (a) $x = 0$ and (b) $x = 0.25$ measured at 30°C under an inert gas atmosphere.

Fig. 8. Temperature dependence of conductivity for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ in the range of 400–700 °C.

Fig. 9. Phase diagram for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$.

Fig. 10. Temperature dependence of conductivity for $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ in the temperature range of 25–100 °C.

TABLES

Table 1 Li content in $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$.

Composition, x	Li content	Al content
0	6.38	0
0.067	6.237	0.036
0.133	5.989	0.087
0.20	5.87	0.146
0.25	5.837	0.196
0.26	5.72	0.204

Table 2 Rietveld refinement results for $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$.

Atom	Site	g	x	y	z	$U / \text{\AA}^2$
Li1	24d	0.69	3/8	0	1/4	0.021
Al	24d	0.08	$= x(\text{Li1})$	$= y(\text{Li1})$	$= z(\text{Li1})$	0.021
Li2	96h	0.349	0.0959	0.6922	0.5731	0.021
La	24c	1	1/8	0	1/4	0.0097
Zr	16a	1	0	0	0	0.0064
O	96h	1	-0.03196(3)	0.05370(4)	0.15070(4)	0.0107

Unit cell : cubic $Ia-3d$ (230): $a = 12.96328$ (5) $\text{\AA}$, $R_{\text{wp}} = 12.12$, $R_{\text{p}} = 8.97$, $R_{\text{B}} = 5.73$, $R_{\text{e}} = 7.24$, GOF = 1.67.

Table 3 Conductivity at 25 °C and activation energy of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$.

x	$\sigma_{\text{Bulk}} / \text{S cm}^{-1}$	$\sigma_{\text{Total}} / \text{S cm}^{-1}$	E_a / eV
0	2.80×10^{-7}	2.0×10^{-7}	0.58
0.067		9.7×10^{-7}	0.46
0.133		2.09×10^{-6}	0.44
0.20		3.24×10^{-6}	0.42
0.25	3.13×10^{-4}	2.1×10^{-4}	0.33