Oxide single crystals with high lithium-ion conductivity as solid electrolytes for all-solid-state lithium secondary battery applications

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Li₆.₅La₃Zr₁.₅Nb₀.₅O₁₂ and Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂ single-crystal rods were grown by floating zone melting. A typical single-crystal rod is 8 mm in diameter and 70 mm in length. Crystallized Li₆.₅La₃Zr₁.₅Nb₀.₅O₁₂ and Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂ have cubic structures in the I₄₁d space group. The crystal structures of Li₆.₅La₃Zr₁.₅Nb₀.₅O₁₂ and Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂ belong to the cubic I₄₁3 space group, while the final structure refinements were performed based on an approximate space group Ia3d. The lattice parameter (a) of Li₆.₅La₃Zr₁.₅Nb₀.₅O₁₂ was 12.9130(8) Å (1 Å = 0.1 nm), while that of Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂ was 12.9455(6) Å. The crystallographic reliability factors (R-values) of the Li₆.₅La₃Zr₁.₅Nb₀.₅O₁₂ and Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂ crystal structures were 7.09% (wR = 7.94%) and 8.82% (wR = 7.45%), respectively, based on the single-crystal neutron diffraction data. Li ions in the crystal structures occupied both distorted tetrahedral 96i sites and distorted octahedral 96j sites. From the results of alternating current impedance measurements, we estimated the total Li-ion conductivity of Li₆.₅La₃Zr₁.₅Nb₀.₅O₁₂ and Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂ at 298 K to be 1.39 × 10⁻³ and 1.27 × 10⁻³ S cm⁻¹, respectively. These are the highest conductivities reported to date for Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂ members. The bulk properties of garnet-type electrolyte single crystals were advantageous for bulk conductivity and lacked the grain boundaries characteristic of sintered polycrystalline bodies. These solid electrolytes represent a game-changing technology for realizing advanced battery systems with strong safety features.

Key-words: Solid electrolyte, Garnet-type lithium ion conductor, Crystal structure analysis, Single crystal, FZ method, All-solid-state lithium secondary battery

1. Introduction

1.1 All-solid-state lithium (Li) secondary batteries

Scientists in many countries have recently begun researching all-solid-state Li batteries and developing them as next-generation energy devices. Since these batteries can be fabricated using high-voltage positive electrodes and metallic Li, all-solid-state Li batteries with high energy densities can be obtained.1–3 All-solid-state Li batteries have three main components: a positive electrode, a negative electrode, and a solid electrolyte that contains Li. The key material in all-solid-state Li secondary batteries is the solid electrolyte, which exhibits high Li-ion conductivity. Solid electrolytes can be roughly divided into two types, sulfides and oxides, each with its own advantages and disadvantages. Among inorganic solid electrolyte materials, glass and crystalline sulfides are good Li-ion conductors.4,5 However, the generation of hydrogen sulfide poses a risk if these materials are exposed to the air. Metallic Li cannot be used as an anode because it is highly reactive with sulfide-based solid electrolytes. In contrast, oxide solid electrolytes are relatively stable in the atmosphere. However, their Li-ion conductivity is low (10⁻⁴ S cm⁻¹), and they often lack plasticity, which makes it difficult to form an interface between the solid electrode and the solid electrolyte.

Our research and development efforts have been focused on improving the safety of solid electrolytes. Herein, we describe the growth, crystallographic characterization, and electrochemical characterization of garnet-type single crystals.

1.2 Garnet-type solid electrolytes

Oxide solid electrolytes are further classified into glass, glass ceramics, or crystalline type. Crystalline solid electrolytes include NASICON,6 perovskite,7 Na⁺/Li⁺ ion-exchanging β-alumina,8 and garnet type.9–24 As their name implies, garnet-type Li solid electrolytes have crystal structures that are very similar to those of the precious stone garnet or yttrium-aluminum-gallium garnet that is used as an optical crystal. The general formula of garnet is C₃A₂B₃O₁₂. The C, A, and B sites in the crystal contain...
oxygen with dodecahedral, octahedral, and tetrahedral coordination, respectively. In contrast, Li atoms take the place of oxygen in the octahedrally coordinated sites of garnet-type Li solid electrolytes.

In a garnet-type Li solid electrolyte with the composition Li$_7$La$_3$Zr$_2$O$_{12}$, lanthanum occupies the C-sites, zirconium occupies the A-sites, and Li occupies the B-sites and voids. Various elements in garnet-type Li solid electrolytes can be substituted. Substitution with calcium, strontium, and barium at C-sites has been reported. Substitution with niobium, tantalum, tin, and hafnium can occur at A-sites, whereas aluminum and gallium can occupy B-sites.\(^{10-25}\)

The quantity of Li in solid electrolytes varies with the substituent elements, and the Li-ion conductivity depends on the arrangement and occupancy rate of Li. Several garnet-type Li solid electrolytes have been reported to have Li-ion conductivity on the order of $10^{-4}$ S cm$^{-1}$.\(^{1-22}\) Making them excellent Li$^+$ conductors among oxide Li solid electrolytes. Among garnet-type oxide compounds, Li$_{7-x}$La$_3$Zr$_{2-x}$Nb$_x$O$_{12}$\(^{10,11,24,25}\) and Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$\(^{12-14,16,26}\) exhibit especially high Li-ion conductivity and wide potential windows. In these compounds, niobium and tantalum are substitutes for atoms in Li$_7$La$_3$Zr$_2$O$_{12}$.\(^{17-19}\)

1.3 Problems associated with garnet-type solid electrolytes

It has been shown in several recent reports on garnet-type solid electrolytes that partial substitution with Ga and/or Sc and Al in the Li$_7$La$_3$Zr$_2$O$_{12}$ structure can yield ionic conductivity on the order of $10^{-3}$ S cm$^{-1}$.\(^{21-23}\) However, these materials have some major shortcomings. Li-ion conductivity at room temperature must be improved, and internal short-circuiting can occur during charging.\(^3,13,15,16\)

Internal short-circuiting between the positive and negative electrodes of an all-solid-state Li secondary battery is due to the precipitation of Li metal. Of course, combustion does not occur in an all-solid-state Li secondary battery as it does in a conventional Li secondary battery. However, the battery function gets impaired by short-circuiting. Internal short circuits in all-solid-state Li secondary batteries are caused by the growth of Li metal dendrites along the grain boundaries of the Li solid electrolytes. Internal short-circuiting has been reported at low currents and could not be eliminated, even after component densification by various methods. We hypothesized that short-circuiting could be prevented using either a Li solid electrolyte without grain boundaries or a single crystal. We, thus, began developing large single crystals of garnet-type Li solid electrolytes.

1.4 Growth of garnet-type solid electrolyte single crystals

In order to improve the conductivity of Li$^+$ at room temperature and prevent short-circuiting in solid electrolytes, the sintered density of the polycrystalline body must be increased. Ultimately, a single-crystal body is most desirable. This is because the relative density of a single crystal is 100%, meaning that it contains no voids. Since there are no voids or grain boundaries in a logical single-crystal body, it is possible to produce an electrolyte that exhibits only bulk conductivity. However, only very small Li$_{7-3x}$Al$_x$La$_3$Zr$_2$O$_{12}$ single crystals (<1 mm) have been prepared via flux-based methods or high-temperature heating, and the bulk electrochemical properties of garnet-type oxides have not yet been determined.\(^{18-20}\) Furthermore, garnet-type solid electrolytes are unstable in water, so water cannot be used to remove the solvent used during synthesis. This makes flux-based methods unsuitable for the growth of single crystals. Large single crystals of inorganic functional materials can be manufactured with melt growth techniques, such as the Czochralski method and floating zone (FZ) methods. No crucible is used in the FZ method, so no impurities are mixed into the crystal. Since the melting zone is localized, single crystals can be grown with highly volatile materials. However, no high-temperature phase diagrams have been reported for garnet-type solid electrolytes. Moreover, preventing the decomposition of the garnet structure via volatilization of Li from the melt requires special care. Therefore, we used the zone melting method to grow giant single crystals of the garnet-type solid electrolytes Li$_6.5$La$_3$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ and Li$_6.5$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ in an FZ apparatus.\(^{24-26}\) Single crystal growth was supported by Ms. Kayoko Yamaguchi, Mr. Ei suke Bannai, and Dr. Junji Akimoto, who belong to National Institute of Advanced Industrial Science and Technology, AIST. We used single crystals to investigate the detailed chemical, structural, and electrochemical properties of Li$_6.5$La$_3$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ and Li$_6.5$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$. Electrochemical measurement was supported by Dr. Hiroshi Nagata, who belongs to AIST. Single crystal neutron diffraction measurement was supported by Dr. Takashi Ohara and Dr. Ryoji Kinagi who belong to National Institute of Japan Atomic Energy Agency. Finally, we evaluated the performance of an all-solid-state Li secondary battery with each of the single-crystal electrolytes. The manufacture of the all-solid-state Li secondary battery was supported by Mr. Haruo Ishizaki, who belongs to AIST.

2. Experimental

2.1 Growth of single crystals

Polycrystalline feedstocks were first prepared via a conventional solid-state reaction. Li$_2$CO$_3$ (99.99%), La$_2$O$_3$ (99.99%), ZrO$_2$ (99.99%), and either Nb$_2$O$_5$ (99.99%) or Ta$_2$O$_5$ (99.99%) were mixed in a 3.9:1.5:1.5:0.25 molar ratio and heated at 1,123 K for 60 h in the air. The nominal compositions of the feedstocks were Li$_7$La$_3$Zr$_2$O$_{12}$ and Li$_7$La$_3$Zr$_2$Ta$_2$O$_{12}$, whereas the target compositions were Li$_6.5$La$_3$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ and Li$_6.5$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$. Li was added to the feedstocks in an excess of 20% to prevent compositional deviation due to the volatilization of Li during crystal growth. Each sample was then reground by placing it in a zirconia pot with isopropanol and a 4 mm zirconia ball and rotating the vessel at 200 rpm for 120 min in a planetary ball mill (p7; Fritsch GmbH, Idar-Oberstein, Germany). The powdered feedstocks were inserted into
rubber tubes and formed into cylinders 12 mm in diameter and 80 mm in length by isostatic pressing. The feedstock rods were subsequently sintered at 1,423 K for 4 h in the air. Single-crystal growth experiments were performed under air flow using the FZ method in an optical image furnace (Crystal Systems, Inc., Japan) equipped with four 1,000 W halogen lamps.\(^{24,26}\)

**2.2 Characterization of the single crystals**

The orientations of the as-grown single crystals were measured using monochromatized Cu K\(_\alpha\) radiation (40 kV, 30 mA) at 295 K on a two-axis X-ray diffractometer (Rigaku SmartLab, Japan) equipped with a charge-coupled device detector and a Johansson’s Ge(111) curved crystal.\(^{26}\) The surface of the single-crystal plate was observed using a scanning electron microscope (SEM; JEOL JCM-6000, Japan).\(^{26}\) An energy dispersive X-ray spectrometry (EDS, JEOL JCM-6000, Japan) was used to investigate the uniformity of the surface elements.\(^{27}\) Each pulverized single crystal was dissolved in hydrofluoric acid at 93 K in an autoclave to prepare a solution. The chemical compositions of the crystals were then analyzed with inductively coupled plasma atomic emission spectroscopy (ICP-AES; Thermo Jarrell Ash Corp., IRIS Advantage, USA).\(^{24,26}\)

**2.3 Crystal structure analysis**

In order to analyze their crystal structures, small transparent crystals were processed into 0.2 mm (\(\phi\)) spheres for single-crystal X-ray diffraction (XRD) and 0.5 mm (\(\phi\)) spheres for single-crystal neutron diffraction measurements. In order to determine their space group, the single-crystal XRD intensities of Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) and Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) were measured at 295 K on a four-circle diffractometer (Rigaku AFC-7S, Japan) equipped with a Mo K\(_\alpha\) radiation source (50 kV, 30 mA) and a graphite monochromator.\(^{24,26}\) For structural refinement, the XRD intensities of the Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) and Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) single crystals were recorded on a 2D diffractometer (Rigaku R-AXIS RAPID-II, Japan) equipped with an imaging plate detector, a graphite monochromator, and a Mo K\(_\alpha\) radiation source (50 kV, 30 mA) at 295 K.\(^{24,26}\) The neutron diffraction intensities of the Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) and Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) single crystals were measured using a time-of-flight neutron diffractometer equipped with a 2D detector (BL18 SENCU; J-PARC, Japan)\(^{21}\) using a poisoned decoupled hydrogen moderator (100 kW) at 295 K.\(^{24,26}\) Structural refinement was performed using the Jana2006 program.\(^{29}\)

**2.4 Li-ion conductivity and diffusion**

Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) and Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) single-crystal alternating current (AC) impedance measurements were conducted with an impedance analyzer (Solartron 1260, AMETEK, USA) at an applied AC amplitude of 10 mV and frequencies from 13 MHz to 10 Hz. Measurements were performed under flowing N\(_2\) gas at 253, 263, 273, 283, 293, 298, 303, and 313 K. For measurement, thin plates, approximately 8 mm in diameter and 0.8 mm thick, were cut from the single-crystal rods. A 2 mm (\(\phi\)) gold blocking electrode was deposited with a magnetron sputterer.\(^{24,26}\)

Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) and Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) direct current (DC) polarization measurements were performed using an electrochemical analyzer (Solartron Modulab) using 2 mm (\(\phi\)) gold blocking electrodes at room temperature. The blocking electrodes were deposited onto an 8 mm (\(\phi\)) × 0.7 mm thick plate of single-crystal Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) and Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\). Measurements with the Au/Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) and Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\)/Au structures were performed in a symmetric two-electrode flat cell. The contribution from electron conduction was investigated while applying a 200 mV polarization voltage.\(^{24,26}\)

Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) DC polarization measurements were performed using the electrochemical analyzer at 298 K using 2 mm (\(\phi\)) Li foils as nonblocking electrodes. The nonblocking electrodes were fabricated on an 8 mm (\(\phi\)) × 3.5 mm thick plate of the Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) single crystal.\(^{24}\)

The Li-ion diffusion coefficients were determined with solid-state \(^7\)Li pulsed-field-gradient nuclear magnetic resonance (\(^7\)Li-PFG-NMR) spectroscopy.\(^{26,27}\) Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) and Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) were crushed into particles several millimeters in diameter. The crushed samples were added to sample tubes in a glove box filled with N\(_2\) gas. \(^7\)Li-PFG-NMR analysis was performed at 155.583 MHz on a Bruker BioSpin Avance III HD 400 spectrometer at 298 and 333 K using the stimulated echo method. The spectral width was 7.763975 kHz, the pulse width was 10 μs (\(\pi\)/2 pulse), and the diffusion time was 0.8 s. The magnetic field strength gradients were 0–2,000 Gauss cm\(^{-1}\) at 298 K and 0–800 Gauss cm\(^{-1}\) at 333 K. We calculated the Li-ion diffusion coefficients from the slopes of the Stejskal and Tanner diffusion plots\(^{30}\) obtained from Eqs. (1) and (2).

\[
I = I_0 \exp ( - bD ),
\]

where \(I\) is the NMR signal strength, \(I_0\) is the initial strength of the NMR signal, and \(D\) is the diffusion coefficient (m\(^2\)/s\(^{-1}\)). The \(b\)-value (s m\(^{-2}\)) is defined as

\[
b = \gamma^2 g^2 \delta^2 [\Delta - (\delta/3)],
\]

where \(\gamma\) is the gyromagnetic ratio (Hz G\(^{-1}\)), \(g\) is the magnetic field strength gradient (G cm\(^{-1}\)), \(\delta\) is the magnetic field gradient application time (s), and \(\Delta\) is the magnetic field gradient pulse interval or diffusion time (s).

**2.5 Charge–discharge measurements with an all-solid-state secondary battery**

Electrochemical charge and discharge tests of the all-solid-state secondary Li battery were performed with a two-electrode flat cell. A 6 mm (\(\phi\)) × 0.7 mm thick plate of Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) was cut from a single-crystal rod and used as the solid electrolyte. A positive LiCoO\(_2\) electrode was formed on the solid electrolyte by the sol–gel
A 0.02 mol kg\(^{-1}\) precursor solution was prepared by dissolving Li acetate and cobalt acetate in ethylene glycol in a 1:1 molar ratio. The precursor solution (10 \(\mu\)L) was then spin-coated onto the solid electrolyte. This was repeated for a total of five times, followed by heating at 1,123 K for 10 min in the air. Li foil (5 mm \(\phi\)) served as the negative electrode. The cells were constructed in an argon-filled glove box. After standing in an open-circuit configuration for 24 h, electrochemical measurements were carried out at a constant current density of 8.8 \(\text{Ac m}^{-2}\) at voltages between 3.1 and 4.0 V at 353 K.24)

3. Results and discussion

3.1 Growth and characterization of Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) and Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) single crystals

Using the obtained centimeter-sized Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) and Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) single-crystal rods, we optimized the growth conditions for FZ melting. Based on the crystal growth experiment, a 20\% excess of the Li raw material was used in the feed rod. Excess Li was added to compensate for the significant Li volatilization at the high growth temperature. Typical single-crystal Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) and Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) rods, approximately 8 mm in diameter and 70 mm in length, are shown in Figs. 1(a) and 1(b). Figure 2 shows the surface and periphery of a polished Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) single-crystal plate after it was sliced from the single-crystal rod. The inner bulk of the single crystal was colorless and transparent. The XRD pattern of the Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) single-crystal plate collected with a biaxial diffractometer (Fig. 3) indicated that crystal growth occurred in the (332) direction. The results of structural refinement clearly showed that the [332] lattice plane traversed the diffusion path of Li ions in the garnet structure. A similar orientation was confirmed in the single-crystal plate of Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\). An SEM image of the single-crystal Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) plate surface (Fig. 4) revealed only scratches from polishing. No voids or grain boundaries were visible. Figure 5 shows the results of elemental analysis of the surface of Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) by EDS. It can be seen that La, Zr, Ta and O are uniformly distributed. A plate of single-crystal Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) exhibited a similar orientation and surface appearance. The atomic ratios in a \(~50\) mg sample of Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) crystals determined with ICP-AES were Li/La/Zr/Ta = 6.499(1):2.987(3):1.500(1):0.501(2). Similarly, the atomic ratios in Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) were Li/La/Zr/Nb = 6.488(3):2.992(4):1.489(2):0.505(3).

3.2 Crystal structures of Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) and Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\)

The cubic garnet structure is known to be in the \(Ia\bar{3}d\) space group. However, the weak reflections in the single-crystal XRD patterns (Fig. 6) did not obey the \(Ia\bar{3}d\) space group extinction rule. The space group of the indices that did not follow the extinction rule was determined with the detailed intensity data collected from the Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) single crystal on a four-circle diffractometer with a scintillation counter. The 00\(l\) line scan obtained by scanning \(h\) from 0 to 17 in steps of 0.05 is shown in Fig. 6(a). The 0\(kl\) line scan obtained by scanning \(h\) and \(k\) from 0 to 8.5, where \(k = l\), is shown in Fig. 6(b). Weak reflections were observed when the \(Ia\bar{3}d\) extinction rule was \(l = 4n\) at 00\(l\), \(k = l\), and both \(k\) and \(l\) were even at 0\(kl\). For the peaks

![Fig. 1. (a) As-grown Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Nb\(_{0.5}\)O\(_{12}\) single-crystal rod and (b) as-grown Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) single-crystal rod.](Image)

![Fig. 2. A polished Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) single-crystal plate. The plate was approximately 8 mm in diameter and 0.8 mm thick.](Image)

![Fig. 3. XRD pattern of the Li\(_{6.5}\)La\(_{3}\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{12}\) single-crystal plate collected on a two-axis XRD.](Image)
marked with asterisks in Fig. 5, the reflections appeared at \( l = 2n \) at 001 and \( k + l = 2n \) at 0kl (Fig. 6). These reflections also appeared in the single-crystal neutron diffraction data. The space group that accounted for all of the reflections in the single-crystal specimen was \( I2_13 \). The crystal structure of garnet \( Li_5La_3Ta_2O_{12} \) has been assigned to the \( I2_13 \) space group.20) Interestingly, the \( Li_6.5La_3Zr_{1.5}Ta_{0.5}O_{12} \) single crystal described in that report was also synthesized at a high temperature (1,673 K). The crystal structures of \( Li_6.5La_3Zr_{1.5}Nb_{0.5}O_{12} \) and \( Li_6.5La_3Zr_{1.5}Ta_{0.5}O_{12} \) belong to the cubic \( I2_13 \) space group, while the final structure refinements were performed based on an approximate space group \( Ia3d \). Because the intensities of the additional reflections were very low: only 1/1,000 the intensity of the main reflections. For example, the 004 reflection produced 500,000 counts, whereas the 002 reflection generated only 200. Additionally, not all of the peaks could be accounted for by the \( I43d \) space group, in which Ga atoms in the
crystal structure are replaced. We, thus, attributed the very weak intensities to diffuse scattering, and Ia3d was refined to determine the precise crystal structure. Considering that the weak reflections were due to diffuse scattering, we plan to analyze the local structure in future work. A similar behavior was observed with Li6.5La3Zr1.5Nb0.5O12. The structure in Li6.5La3Zr1.5Nb0.5O12 and Li6.5La3Zr1.5Ta0.5O12 comprised of LaO8 and (Zr, Nb, or Ta)O6 polyhedra was refined using the single-crystal XRD data and the reported garnet-type atomic coordinates.\(^{18}\) The Li sites in Li6.5La3Zr1.5Ta0.5O12 were determined from the single-crystal XRD and neutron diffraction data using a differential Fourier synthesis map (Fig. 7). The reliability values of the single-crystal XRD data obtained from Li6.5La3Zr1.5Nb0.5O12 were 4.25% (R) and 5.82% (wR). R and wR of the single-crystal neutron diffraction were 7.09 and 7.94%, respectively. The R and wR values of the single-crystal neutron diffraction data from Li6.5La3Zr1.5Ta0.5O12 were 3.32 and 4.45%, respectively. The reliability values of the single-crystal neutron diffraction data were 8.82% (R) and 7.45% (wR). Even when the XRD and neutron diffraction data were used complementarily for refinement, it was difficult to determine the occupancy ratios of Zr and Nb or Ta. We, therefore, refined the crystal structure using fixed values obtained from the ICP-AES analysis. The Li6.5La3Zr1.5Nb0.5O12 and Li6.5La3Zr1.5Ta0.5 crystal lattice parameter (a) was refined by the least-squares method using the single-crystal XRD data. In Li6.5La3Zr1.5Nb0.5O12, \(a = 12.9130(8)\) Å (1 Å = 0.1 nm), whereas \(a = 12.9455(6)\) Å in Li6.5La3Zr1.5Ta0.5O12. The crystal structure refinement data are summarized in Table 1. The final atomic coordinates in Li6.5La3Zr1.5Nb0.5O12 and its atomic displacement parameters determined from the single-crystal neutron diffraction data are shown in Tables 2 and 3, respectively. The atomic coordinates and atomic displacement parameters of Li6.5La3Zr1.5Ta0.5O12 are shown in Tables 4 and 5, respectively. Occupancy was refined only for Li atoms. The crystal structure parameters determined by single
crystal XRD are listed in Tables SI1–SI4 in the supporting information. Comparing the results of refinement of XRD data and neutron diffraction data, the atomic displacement parameters are smaller in the results using neutron diffraction data.

**Figure 8** shows the refined crystal structure of Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂. A similar crystal structure was constructed for Li₆.₅La₃Zr₁.₅Nb₀.₅O₁₂. Based on these structural refinements, we determined the chemical composition of Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂ to be Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂. The chemical composition of Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂ was Li₆.₅La₃Zr₁.₅Nb₀.₅O₁₂. Li ions occupied two interconnected sites in the framework structure. Li₁ and Li₂ ions were located in distorted tetrahedral and octahedral 96h sites, respectively. In the (La₃Zr₁.₅Ta₀.₅O₁₂)₆.₅⁻ and (La₃Zr₁.₅Nb₀.₅O₁₂)₆.₅⁻ garnet solid electrolyte framework structures, Li⁺ occupied the A-sites formed by (Zr, Ta, or Nb)O₆ and the C-sites formed by LaO₈. The 96h sites were split from 24d sites, where Li ions formed tetrahedrons. However, other 96h sites were split from 48g sites, where Li ions formed octahedrons. The conductivity of Li⁺ seems to have been improved by splitting because the distance between Li sites was shortened. Li ions in ordered, disordered, and partially disordered arrangements are shown in **Fig. 9**. Our results suggested that the arrangement of Li ions in the garnet structure differed from the previously reported arrangement. In previous studies, Li ions in a crystal structure within the Iₐ₃d space group were reported to occupy the tetrahedral 24d and distorted octahedral 96h sites. Thus, the Li–Li distances in our structures were shorter than those reported previously.

### Table 1. Crystal structure refinement data

| Composition          | Li₆.₅La₃Zr₁.₅Nb₀.₅O₁₂ | Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂ |
|----------------------|------------------------|------------------------|
| Lattice constant a (Å) | 12.931(8)              | 12.945(6)              |
| Lattice volume V (Å³)  | 2153.2(2)              | 2169.48(17)            |
| Space group           | Iₐ₃d                  |                        |
| Dx (g/cm⁻³)           | 5.1626                 | 5.395                  |
| F (000)               | 770.094                | 770.631                |
| Radiation used        | TOF neutron            |                        |
| Moderator             | Unbound poison type hydrogen |                |
| Crystal size (diam., mm) | 0.50                 | 0.50                   |
| Absorption correction | empirical method       |                        |
| Extinction factor     | none                   | none                   |
| Diffractometer        | J-Parc SENU            |                        |
| 2θ range (deg.)       | 3.59–55.94             | 3.5–79.99              |
| No. of measured reflections | 7168                 | 4948                   |
| No. of observed reflections | 1081                | 1669                   |
| after averaging with |                        |                        |
| |                        |                        |
| k min/max             | –18/32                 | –36/37                 |
| k min/max             | –29/31                 | –16/26                 |
| l min/max             | –32/20                 | –33/23                 |
| Maximum shift         | 0.0493                 | 0.0498                 |
| Δρ Max./Δρ Min. (e/Å³) | 0.38/–0.26             | 0.39/–0.28             |
| R (%)                 | 7.09                   | 8.82                   |
| wR (%)                | 7.94                   | 7.45                   |
| Weighting scheme      | 1/σ²(Fo)               |                        |
| GOF                   | 1.45                   | 2.42                   |

*Fixed to the chemical analysis result by ICP-AES. **Restriction of Ueq(Nb1) = Ueq(Zr1).

### Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å²) of Li₆.₅La₃Zr₁.₅Nb₀.₅O₁₂ determined from the single-crystal neutron diffraction data. The bond valence sum (BVS) for each site is shown

| Atom | Site | Occ. | x   | y   | z   | Ueq | BVS |
|------|------|------|-----|-----|-----|-----|-----|
| Li1  | 96h  | 0.117(7) | 0.759(6) | 0.112(5) | –0.019(8) | 0.036(14) | 0.590 |
| Li2  | 96h  | 0.419(9) | 0.6542(5) | 0.1724(5) | 0.0617(5) | 0.0169(18) | 0.380 |
| La1  | 24c  | 1     | 0.25 | 0.125 | 0   | 0.00409(17) | 3.00 |
| Zr1  | 16a  | 0.75(5) | 0.25 | 0.25 | 0.25 | 0.002377(11)** | 3.82 |
| Nb1  | 16a  | 0.25(5) | 0.25 | 0.25 | 0.25 | 0.002377(11)** | 3.24 |
| O1   | 96h  | 1     | 0.19626(6) | 0.28124(5) | 0.10137(6) | 0.00741(18) | 1.84 |

*Fixed to the chemical analysis result by ICP-AES. **Restriction of Ueq(Nb1) = Ueq(Zr1).

### Table 3. Anisotropic displacement parameters (Å²) of Li₆.₅La₃Zr₁.₅Nb₀.₅O₁₂ determined from the single-crystal neutron diffraction data

| Atom | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|------|------|------|------|------|------|------|
| La1  | 0.0022(2) | 0.0079(4) | 0.0022(2) | 0   | 0.0014(3) | 0   |
| Zr1  | 0.0024(2)* | 0.0024(2)* | 0.0024(2)* | 0.0000(3)* | 0.0000(3)* | 0.0000(3)* |
| Ta1  | 0.0024(2)* | 0.0024(2)* | 0.0024(2)* | 0.0000(3)* | 0.0000(3)* | 0.0000(3)* |
| O1   | 0.0073(3) | 0.0093(3) | 0.0054(3) | 0.0011(3) | –0.0001(3) | 0.0011(3) |

*Restriction of U₁₂(Nb1) = U₁₂(Zr1).

### Table 4. Atomic coordinates, equivalent isotropic displacement parameters (Å²), of Li₆.₅La₃Zr₁.₅Ta₀.₅O₁₂ determined from the single-crystal neutron diffraction data. The bond valence sum (BVS) for each site is shown

| Atom | Site | Occ. | x   | y   | z   | Ueq | BVS |
|------|------|------|-----|-----|-----|-----|-----|
| Li1  | 96h  | 0.104(9) | 0.764(5) | 0.132(8) | 0.00(2) | 0.014(3) | 0.545 |
| Li2  | 96h  | 0.422(10) | 0.6531(4) | 0.1731(5) | 0.0617(4) | 0.022(2) | 0.366 |
| La1  | 24c  | 1     | 0.25 | 0.125 | 0   | 0.00497(15) | 2.95 |
| Zr1  | 16a  | 0.75(5) | 0   | 0   | 0   | 0.00319(10)** | 3.80 |
| Ta1  | 16a  | 0.25(5) | 0   | 0   | 0   | 0.00319(10)** | 3.83 |
| O1   | 96h  | 1     | 0.1966(5) | 0.2812(5) | 0.10143(6) | 0.00869(16) | 1.83 |

*Fixed to the chemical analysis result by ICP-AES. **Restriction of U₁₂(Ta1) = U₁₂(Zr1).
A short Li–Li distance, disordering of Li sites, and partial occupation by Li atoms are thought to be key for Li$^{+}$ diffusion in the garnet structure. Accordingly, we speculated that Li ions might have diffused more rapidly in our single crystals than they did in the reported polycrystalline samples.\(^{12)\text{–}14)\)

### 3.3 Electrochemical measurements with the Li$_{6.5}$La$_{3}$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ single crystal

Figure 10(a) shows the Nyquist plots for the Li$_{6.5}$La$_{3}$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_{3}$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ single-crystal plates constructed from AC impedance data collected at 298 K under flowing N$_2$ gas. The measured orientation is (332). The tails on the low-frequency sides of the Nyquist plots indicate electrode blocking of mobile Li ions. Single semicircles were observed on the high-frequency sides of the Nyquist plots. Thus, we were not able to separate conductivity into bulk and grain boundary components. The total Li$^{+}$ conductivity in Li$_{6.5}$La$_{3}$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ was 1.27 × 10$^{-3}$ S cm$^{-1}$ at 298 K. Using the same measurement method, the conductivity of Li$_{6.5}$La$_{3}$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ was found to be 1.39 × 10$^{-3}$ S cm$^{-1}$ at 298 K. This was comparable to the bulk Li$^{+}$ conductivity measured in the sintered Li$_{6.5}$La$_{3}$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ sample, although the total conductivity of a sintered sample at room temperature has been reported to be 8.4 × 10$^{-4}$ S cm$^{-1}$.\(^{12)\) Therefore, the conductivity values measured in this study were the highest among those reported for Li$_{6.5}$La$_{3}$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ members. This indicated that the conductivity of Li$^{+}$ in our single-crystal samples had only a bulk component and that the grain boundaries characteristic of polycrystalline materials were absent. The relationship between Li$^{+}$ conductivity and temperature in the Li$_{6.5}$La$_{3}$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_{3}$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ single-crystal plates from 253 to 313 K is shown in Fig. 10(b). An activation energy of 0.44 eV was determined from the average rate of change in the Arrhenius plot \[\ln(\sigma T) \text{ versus } 1/T\]. The activation energies of Li$_{6.5}$La$_{3}$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_{3}$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ were in good agreement with this value at approximately 0.44 eV.

![Crystal structure of Li$_{6.5}$La$_{3}$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$](image)

**Table 5.** Anisotropic displacement parameters (Å$^2$) of Li$_{6.5}$La$_{3}$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ determined from the single-crystal neutron diffraction data

| Atom | $U_{11}$   | $U_{22}$   | $U_{33}$   | $U_{12}$   | $U_{13}$   | $U_{23}$   |
|------|------------|------------|------------|------------|------------|------------|
| La1  | 0.0035(2)  | 0.0079(3)  | 0.0035(2)  | 0          | 0.0023(3)  | 0          |
| Zr1  | 0.00319(17)* | 0.00319(17)* | 0.00319(17)* | -0.0002(2)* | -0.0002(2)* | -0.0002(2)* |
| Ta1  | 0.00319(17)* | 0.00319(17)* | 0.00319(17)* | -0.0002(2)* | -0.0002(2)* | -0.0002(2)* |
| O1   | 0.0089(3)  | 0.0061(3)  | 0.011(3)   | 0.0002(2)  | 0.0017(2)  | 0.0007(2)  |

*Restriction of $U_{ij}(\text{Ta1}) = U_{ij}(\text{Zr1})$. 

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Kataoka: Oxide single crystals with high lithium-ion conductivity as solid electrolytes for all-solid-state lithium secondary battery applications
The DC polarization measurements performed with \( \text{Li}_{6.5}\text{La}_{3}\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12} \) and \( \text{Li}_{6.5}\text{La}_{3}\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12} \) single-crystal plates with two gold blocking electrodes at 298 K are plotted in Fig. 11. When the gold blocking electrodes were used, the current initially decreased over time because of polarization but then became almost constant. Based on these measurements, the electronic conductivity of \( \text{Li}_{6.5}\text{La}_{3}\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12} \) was estimated to be \( 1.11 \times 10^{-7} \text{ Sc m}^{-1} \). Electron conductivity in the crystal was, thus, very low, and the transport rate was estimated to be 0.00877\%.

Similarly, the electron conductivity measured in \( \text{Li}_{6.5}\text{La}_{3}\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12} \) was \( 7.1 \times 10^{-6} \text{ Sc m}^{-1} \), which represented a contribution of approximately 0.55\%.

### 3.4 Internal short-circuiting in the \( \text{Li}_{6.5}\text{La}_{3}\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12} \) single crystal

The experimental short-circuit data obtained from the DC polarization measurements with the symmetric Li/\( \text{Li}_{6.5}\text{La}_{3}\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12} \)/Li cell at 298 K are shown in Fig. 12. The measured orientation is (332). The results suggested that the \( \text{Li}_{6.5}\text{La}_{3}\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12} \) single-crystal plate served as both a solid electrolyte and a separator without short-circuiting up to 0.5 mA cm\(^{-2}\). They also indicated that the dissolution and deposition of Li metal were reversible. This meant that the dendrites formed did not penetrate the solid electrolyte because the single-crystal plate was very dense. As shown in Fig. 12, no short-circuiting was observed. However, the voltage was unstable at current densities of 0.4 mA cm\(^{-2}\) or higher. This instability may have been caused by interfacial contact due to Li deposition and desorption. Furthermore, the conductivity estimated from the DC polarization at 0.1 mA cm\(^{-2}\) was \( 1.0 \times 10^{-3} \text{ Sc m}^{-1} \). This was higher than the total conductivity of \( 1.3 \times 10^{-3} \text{ Sc m}^{-1} \) obtained from the AC impedance measurement. Figure 13 shows the results of the AC impedance measurements performed with the symmetric Li/\( \text{Li}_{6.5}\text{La}_{3}\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12} \)/Li cell before and after the DC polarization measurement at 298 K. The total resistance of the symmetric Li/\( \text{Li}_{6.5}\text{La}_{3}\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12} \)/Li cell increased by approximately 600 \( \Omega \) cm before the DC polarization and by about 800 \( \Omega \) cm after the DC polarization. Resistance would have been low if the symmet-
rical cell short-circuited and the arc of the AC impedance plot were smaller.

3.5 Li diffusion in Li$_{6.5}$La$_3$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ single crystals

The Stejskal and Tanner diffusion plots of Li$_{6.5}$La$_3$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ are shown in Figs. 14(a) and 14(b) at 298 and 333 K. The Li$^+$ diffusion coefficients of Li$_{6.5}$La$_3$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ were 1.58 × 10$^{-13}$ and 9.77 × 10$^{-13}$ m$^2$ s$^{-1}$, respectively. The Li$^+$ diffusion coefficients of Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ at 298 and 333 K were 1.57 × 10$^{-13}$ and 7.96 × 10$^{-13}$ m$^2$ s$^{-1}$, respectively. These values were comparable to a previously reported value for a polycrystalline sample of Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$, which was 6.5 × 10$^{-13}$ m$^2$ s$^{-1}$ at 353 K. The diffusion coefficient reported for a Li$_{6.5}$La$_3$ZrTaO$_{12}$ single crystal was 10$^{-14}$ m$^2$ s$^{-1}$.

The diffusion coefficients obtained in our study were, thus, higher than the values reported in the literature. The Li-ion conductivity based on our AC impedance measurements was 1.27 × 10$^{-3}$ S cm$^{-1}$, which was also higher than the previously reported value of 3 × 10$^{-4}$ S cm$^{-1}$. We believe that conductivity depends on the degree of tantalum substitution and the Li–Li distance. Compared to previously reported results, the Li–Li distance determined in this study was shorter, as the arrangement of Li ions in our crystal structures was more disordered.

3.6 Charge–discharge measurements with an all-solid-state secondary battery

The cycling performance of the Li/Li$_{6.5}$La$_3$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$/LiCoO$_2$ cell during charge and discharge tests at voltages between 3.1 and 4.0 V at a constant current density of 8.8 µA cm$^{-2}$ at 333 K is shown in Fig. 15. The Coulombic efficiencies of the first, second, third, fourth, fifth, and sixth cycles were 98.4, 88.7, 92.0, 93.5, 94.1, and 95.3%, respectively. It was thought that the battery capacity was small because of the upper limit of the cutoff voltage (4.0 V). The positive electrode in the battery currently consists entirely of active material, which is the source of many problems. However, we believe that combining the solid electrolyte with a conductive material can resolve these problems.

![AC impedance measured in the symmetric Li/Li$_{6.5}$La$_3$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$/Li cell before and after the DC polarization measurement at 298 K.](image)

![Stejskal and Tanner diffusion plots at 298 and 333 K. (a) Li$_{6.5}$La$_3$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ and (b) Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$.](image)

![Charge–discharge cycling performance of the Li/Li$_{6.5}$La$_3$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$/LiCoO$_2$ all-solid-state secondary Li battery at voltages from 3.1 to 4.0 V (versus Li/Li$^+$) at a current density of 8.8 µA cm$^{-2}$ at 353 K.](image)
4. Conclusion

In this study, we grew centimeter-sized single crystals of garnet-type Li$_{6.5}$La$_2$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_2$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ via the FZ melting method. The XRD and neutron diffraction analysis of their crystal structures revealed that Li ions occupied two distinct 96h sites in the interstices of the garnet structure. This split resulted in shorter Li–Li distances and a disordered arrangement of Li sites along the conduction pathways. The Li$^+$ conductivity values measured in this study were the highest reported among already existing single-crystal specimens. In fact, the Li$^+$ conductivity of Li$_{6.5}$La$_2$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_2$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ at 298 K determined with the AC impedance measurements exceeded $1.00 \times 10^{-3}$ S cm$^{-1}$. These are the highest values reported for materials with the same chemical compositions. The Li$^+$ diffusion coefficients of the Li$_{6.5}$La$_2$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ single crystal as revealed by $^7$Li-NMR analysis were $1.57 \times 10^{-12}$ m$^2$ s$^{-1}$ at 298 K and $7.96 \times 10^{-12}$ m$^2$ s$^{-1}$ at 333 K. Those of the Li$_{6.5}$La$_2$Zr$_{1.5}$Nb$_{0.5}$O$_{12}$ single crystal were $1.58 \times 10^{-12}$ m$^2$ s$^{-1}$ at 298 K and $9.77 \times 10^{-13}$ m$^2$ s$^{-1}$ at 333 K. These values, which were related to Li-ion migration, exceeded those reported for polycrystalline samples. Based on the results of the chemical and structural characterization, garnet-type single-crystal samples exhibited excellent bulk properties, which allowed the realization of bulk conductivity without the grain boundaries found in sintered polycrystals. Finally, an all-solid-state Li secondary battery was prepared using a single crystal as a substrate, and we demonstrated reversible cycling. The basic physical properties of the single-crystal samples were advantageous, and the samples served as battery components that resolved the problem of internal short-circuiting.

Acknowledgment  Dr. Hiroshi Nagata (National Institute of Advanced Industrial Science and Technology, AIST) carried out the electrochemical characterization. I would also like to thank Dr. Junji Akimoto (AIST) for his sported in the single-crystal growth and electrochemical characterization. I would like to thank Mr. Haruo Ishizaki, Ms. Kayoko Yamaguchi and Mr. Eisuake Bannai (AIST) for their assistance in single-crystal growth and manufacture of all-solid-state Li secondary battery. I would also like to thank Dr. Takashi Ohhara and Dr. Ryouji Kiyanagi (National Institute of Japan Atomic Energy Agency) for their assistance in the single-crystal neutron diffraction experiments (Proposal No. 2015A0147 and 2016A0235). Part of this research was supported by the Advanced Low Carbon Technology Research and Development Program (ALCA-SPRING) of the Japan Science and Technology Agency (JST). The author would like to thank Enago (www.enago.jp) for the English language review.

References

1) J. B. Goodenough and Y. Kim, Chem. Mater., 22, 587–603 (2010).
2) M. Armand and J. M. Tarascon, Nature, 451, 652–657 (2008).
3) J. Janek and W. G. Zeier, Nature Energy, 1, 1–4 (2016).
4) N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kata, S. Hama, K. Kawamoto and A. Mitsui, Nat. Mater., 10, 682–686 (2011).
5) Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba and R. Kanno, Nature Energy, 1, 16030 (2016).
6) M. Weiss, D. A. Weber, A. Senyshyn, J. Janek and W. G. Zeier, Appl. Mater. Interfaces, 10, 10935–10944 (2018).
7) Y. Inaguma, C. Liquan, M. Itoh and T. Nakamura, Solid State Commun., 86, 689–693 (1993).
8) M. T. Chowdhury, R. Takekawa, Y. Iwai, N. Kuwata and J. Kawamura, J. Chem. Phys., 140, 124590 (2014).
9) E. Rangasamy, J. Wolfenstine and J. Sakamoto, Solid State Ionics, 206, 28–32 (2012).
10) S. Ohta, T. Kobayashi and T. Asoaka, J. Power Sources, 196, 3342–3345 (2011).
11) K. Ishiguro, Y. Nakata, I. Uechi, Y. Takeda, O. Yamamoto and N. Imanishi, J. Electrochem. Soc., 160, A1690–A1693 (2013).
12) N. Hamao, K. Kataoka, N. Kijima and J. Akimoto, J. Ceram. Soc. Jpn., 124, 678–683 (2016).
13) H. Yamada, T. Ito and R. H. Basappa, Electrochim. Acta, 220, 648–656 (2016).
14) K. Hayamizu, Y. Matsuda, M. Matsui and N. Imanishi, Solid State Nucl. Mag., 70, 21–27 (2015).
15) Y. Takeda, O. Yamamoto and N. Imanishi, Electrochemistry, 84, 210–218 (2016).
16) C. L. Tsai, V. Roddatis, C. Chandran, Q. Ma, S. Uhltenbruck, M. Bram, P. Heitjans and O. Guillon, Appl. Mater. Interfaces, 8, 10617–10626 (2016).
17) R. Murugan, V. Thangadurai and W. Weppner, Angew. Chem. Int. Edit., 46, 7778–7781 (2007).
18) J. Awaka, A. Takashima, K. Kataoka, N. Kijima, Y. Idenmoto and J. Akimoto, Chem. Lett., 40, 60–62 (2011).
19) C. A. Geiger, E. Alekseev, B. Lazic, M. Fisch, T. Armbruster, R. Langner, M. Fechthalikov, N. Kim, T. Pettke and W. Weppner, Inorg. Chem., 50, 1089–1097 (2011).
20) H. Hyooma and K. Hayashi, Mater. Res. Bull., 23, 1299–1407 (1988).
21) C. Bernuy-Lopez, W. J. Manalastas, J. M. L. D. Amo, A. Aguadero, F. Aguesse and J. A. Kilner, Chem. Mater., 26, 3610–3617 (2014).
22) D. Rettenwander, G. Redlhammer, F. Preishuber-Pflügl, L. Cheng, L. Miara, R. Wagner, A. Welzl, E. Saard, M. M. Doeff, M. Wilkening, M. Fisch, T. Armbruster, R. Langner, M. Fechthalikov, N. Kim, T. Pettke and W. Weppner, Chem. Mater., 28, 3234–3292 (2016).
23) L. Buannic, B. Orayech, J. M. L. D. Amo, J. Carrasso, N. A. Kato, F. Aguesse, W. Manalastas, W. Zhang, J. Kilner and A. Lordès, Chem. Mater., 29, 1769–1778 (2017).
24) K. Kataoka, H. Nagata and J. Akimoto, Sci. Rep., 8, 9965 (2018).
25) K. Kataoka, T. Akao, H. Nagata, H. Nagai, J. Akimoto and J. Akedo, Synthetiology, 12, 38–39 (2019).
26) K. Kataoka and J. Akimoto, ChemElectroChem, 5, 2551–2557 (2018).
27) Private Communication.
28) T. Ohhara, R. Kiyanagi, K. Okikawa, K. Kaneko, T. Kawasaka, I. Tamura, A. Nakao, T. Hanashima, K.
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