Lithium-ion conductivity and crystal structure of garnet-type solid electrolyte Li$_{7-x}$La$_x$Zr$_{2-x}$Ta$_x$O$_{12}$ using single-crystal

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Single-crystal rods of Li$_{7-x}$La$_x$Zr$_{2-x}$Ta$_x$O$_{12}$ ($X = 0.2, 0.4, 0.5, 0.6, 0.8$) were grown by floating zone melting. The typical size of the single-crystal rod was 8 mm in diameter and 70 mm in length. Li$_{7-x}$La$_x$Zr$_{2-x}$Ta$_x$O$_{12}$ ($X = 0.2, 0.4, 0.5, 0.6, 0.8$) crystallizes in a cubic structure with an Ia-3d space group. Single crystal structure analysis was performed for all single crystals. How the lithium ion conductivity varies with the substitution amount of tantalum was investigated using a single crystal. Analyzing the results of AC impedance measurements, we estimated the total Li-ion conductivity of member in Li$_{7-x}$La$_x$Zr$_{2-x}$Ta$_x$O$_{12}$ single-crystal. As a result, when $X = 0.4$, the lithium ion conductivity became the maximum, and it was $1.10 \times 10^{-3}$ S cm$^{-1}$ at 298 K. The activation energy ticked up with increasing tantalum substitution.

Key-words : Solid electrolyte, Garnet-type lithium ion conductor, Crystal structure analysis, Single crystal, FZ method

1. Introduction

Recently, R&D of all-solid-state lithium battery as one of next generation energy devices is being conducted in many countries. In all-solid-state lithium batteries, there is a possibility that high voltage positive electrodes and metallic lithium can be used, so batteries with high energy density are expected.$^{1-3}$ In addition, all-solid-state lithium batteries may be able to solve problems with organic electrolyte, such as high temperature and low temperature operation. The all-solid-state lithium battery is composed of three members, a positive electrode, a negative electrode, and a solid electrolyte, as main members. In order to realize an all-solid-state lithium battery, development of solid electrolyte is important. The solid electrolyte has a sulfide-base$^{4,5}$ and an oxide-base, but from the viewpoint of safety, we are studying an oxide-type lithium solid electrolyte. Oxide-base solid electrolytes are also classified into glass-type, glass-ceramics-type and crystalline-type. Among crystalline solid electrolytes, NASICON-type Li$_1$Al$_{0.5}$Ge$_{1.5}$PO$_4$, perovskite-type La$_2$Ti$_4$O$_{12}$, $\beta$-alumina with Na+/Li+ ion-exchange type,$^8$ garnet-type Li$_3$La$_2$Zr$_2$O$_{12}$ and the like are also reported.$^9-27$ A garnet-type lithium solid electrolyte possesses, as the name implies, a very similar crystal structure as garnet used as a precious stone, or yttrium-aluminum-gallium (YAG) garnet used as optical crystals,$^{28}$ or yttrium-Iron-Gallium garnet used as magnetic materials.$^{29}$ The original garnet is expressed by the general equation C$_3$A$_2$B$_3$O$_{12}$, in which the C site has oxygen and dodecahedral coordination, the A site has oxygen and octahedral coordination, and the B site has oxygen and tetrahedral coordination. On the other hand, in garnet-type lithium solid electrolytes, lithium is present in the interspace where oxygen and octahedral coordination are present in an ordinary garnet structure. For example, in a garnet-type lithium solid electrolyte with Li$_3$La$_2$Zr$_2$O$_{12}$ composition, the C site is occupied by lanthanum, the A site by zirconium, and the B site and interspace are occupied by lithium. For a garnet-type lithium solid electrolyte, it is known that various elements are substituted, and it has been reported that at the C site calcium, strontium, barium substitute; at the A site, niobium, tantalum, tin, and hafnium; and at the B site, aluminum and gallium.$^{9-27}$ The amount of lithium changes according to the substituent element, and Li-ion conductivity changes with the changes of arrangement and occupancy rate of lithium. For garnet-type lithium solid electrolytes, there are several reports of Li-ion conductivity of $10^{-3}$ S/cm order, and it has excellent lithium ion conductivity among oxide-base solid electrolytes.$^9,20$ Especially, it has been reported that a garnet-type solid electrolyte in which a part of zirconium site is substituted with tantalum or niobium has high ionic conductivity.$^9,12,20,24-27$ Recently, we succeeded in growing bulk single crystal of garnet type solid electrolyte by floating zone method (FZ method).$^{24,25}$ With respect to Li$_{7-x}$La$_x$Zr$_{2-x}$Nb$_x$O$_{12}$ in which zirconium was partially substituted by niobium, the change in the substitution amount and the change in the lithium ion conductivity was examined for the single crystal.

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When \( X = 0.5 \), the lithium ion conductivity became the maximum.\(^{24}\) Furthermore, the single crystal and the aerosol deposition method were combined to form an all-solid-state lithium battery.\(^ {26} \) In addition, we have successfully grown a single crystal of Li\(_{6}\)La\(_{9}\)Zr\(_{2}\)Ta\(_{0.5}\)O\(_{12}\) with a tantalum substitution amount of 0.5.\(^ {25} \) Detailed diffusion coefficients are investigated by PNG-nuclear magnetic resonance measurement using a single crystal.\(^ {25} \) In present study, we report about the amount of tantalum substitution and Li-ion conductivity using single crystals for Li\(_{7-x}\)La\(_{3}\)Zr\(_{2-x}\)Ta\(_{x}\)O\(_{12}\) \((X = 0.2, 0.4, 0.5, 0.6, 0.8)\).

2. Experimental

2.1 Sample preparation

In the present study, sample synthesis was carried out in two steps. The first step is to adjust the powder. The feedstock polycrystalline materials were first prepared by a conventional solid-state reaction. A mixture of Li\(_2\)CO\(_3\) (99.9% pure), La\(_2\)O\(_3\) (99% pure), ZrO\(_2\) (98% pure), and Ta\(_2\)O\(_5\) (99% pure) at a molar ratio of 4.2–0.6x:1.5:2–x:x was heated at 1123 K for 60 h in air. Here, \( x \) represents the substitution amount of tantalum. For this time, \( X = 0.2, 0.4, 0.6, 0.8 \). The nominal feedstock composition is Li\(_{8-x-2}\)La\(_{2}\)Zr\(_{2-x}\)Ta\(_{x}\)O\(_{12}\), which is 20% lithium excess composition of the objective Li\(_{7-x}\)La\(_{3}\)Zr\(_{2-x}\)Ta\(_{x}\)O\(_{12}\), so as to prevent the compositional deviation due to volatilization during lithium by crystal growth. The sample was reground at 200 rpm for 120 min by filling a sample, isopropanol and 4 mm zirconia ball in a zirconia pot using a planetary ball mill (P-7, Fritsch GmbH). The feedstock powder filled a rubber tube and formed a cylindrical shape 10 mm in diameter and 80 mm long by isostatic pressing. The rods were subsequently sintered at 1423 K for 4 h in air. The second step is to grow crystal. The single-crystal growth experiments were performed in air-flow atmosphere using the FZ method in an optical image furnace (Crystal System, Inc.) equipped with four 1000 W halogen lamps.

2.2 Characterization of sample

To examine the space group and refine the crystal structure, the single-crystal X-ray diffraction (XRD) intensity data was measured by a single-crystal X-ray with a IP detector (Rigaku R-AXIS RAPID II) using graphite-monochromatized Mo K\(_\alpha\) radiation (50 kV, 30 mA) at 295 K. XRD measurement were performed on the same sample processed into a spherical shape with a diameter of 100 micrometers. The structure was refined using computer program Jana2006.\(^ {30} \) The program VESTA was used to draw the crystal structure and the electron density distribution.\(^ {31} \)

2.3 Electrochemical properties

The AC impedance for Li\(_{7-x}\)La\(_{3}\)Zr\(_{2-x}\)Ta\(_{x}\)O\(_{12}\) \((X = 0.2, 0.4, 0.6, 0.8)\) single crystals was measured using a Solartron 1260 impedance analyzer operating at 10 mV applied AC amplitude at 13 MHz–10 Hz frequencies at temperature intervals (253, 263, 273, 283, 293, 298, 303, and 313 K) in N\(_2\) gas flow. The present study, the measurement was carried using a thin-plate specimen having a diameter of 6 mm and a thickness of 1.3 mm obtained by cutting a single-crystal rod. The blocking electrode was 6 mm diameter sputtered gold formed by magnetron sputter deposition.

3. Results and discussion

Using the obtained centimeter-sized single-crystal rod of Li\(_{7-x}\)La\(_{3}\)Zr\(_{2-x}\)Ta\(_{x}\)O\(_{12}\), we optimized the growth conditions of FZ melting method. Based on the crystal growth experiment, we put 20% excess of Li raw material in the feed rod. The excess lithium was added because of the significant lithium volatilization at high temperature. Figure 1(a) shows a typical single-crystal rod of Li\(_{6.6}\)La\(_{3}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) about 8 mm in diameter and 80 mm length. Figure 1(b) shows a typical polished single-crystal plate, both the surface and outer periphery, after slicing from the single-crystal rod. The plate size was about 8 mm in diameter and 0.8 mm in thickness. The bulk part of the single crystal was colorless and transparent on the inside. Figure 2 shows the surface of a single-crystal plate, captured with a scanning electron microscope (SEM), revealing only polishing scratches and no voids or grain boundaries.

A structure consisting of La\(_2\)O\(_3\) and (Zr,Ta)O\(_6\) polyhedra in Li\(_{7-x}\)La\(_{3}\)Zr\(_{2-x}\)Ta\(_{x}\)O\(_{12}\) \((X = 0.2, 0.4, 0.5, 0.6, 0.8)\) was refined using the single-crystal XRD data and the reported garnet-type atomic coordinates.\(^ {25} \) The Li sites were then determined using a difference Fourier synthesis map, with the single-crystal X-ray. Figure 3 shows the difference Fourier map of Li\(_{6.8}\)La\(_{3}\)Zr\(_{1.8}\)Ta\(_{0.2}\)O\(_{12}\) as a representative example. Since the occupation rate of lithium could not be refined, we occupied lithium so that the R factor would be the best value. The difference Fourier syntheses using the final atomic parameters revealed no significant residual peaks. The resultant reliability values were \( R = 5.04\% \) and \( wR = 6.32\% \) (Li\(_{6.8}\)La\(_{3}\)Zr\(_{1.8}\)Ta\(_{0.2}\)O\(_{12}\)), \( R = 3.68\% \) and \( wR = 5.36\% \) (Li\(_{6.6}\)La\(_{3}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\)), \( R = 3.13\% \) and \( wR = \)}
3.77\% (Li_{6.5}La_{3}Zr_{1.5}Ta_{0.5}O_{12}), R = 3.10\% and wR = 3.98\% (Li_{6.4}La_{3}Zr_{1.4}Ta_{0.6}O_{12}), R = 3.41\% and wR = 4.14\% (Li_{6.2}La_{3}Zr_{1.2}Ta_{0.8}O_{12}), for the single-crystal XRD data. The lattice parameter for the Li_{7-\delta}La_{3}Zr_{2-\delta}Ta_{\delta}O_{12} (\delta = 0.2, 0.4, 0.5, 0.6, 0.8) crystal was refined by the least-squares method using the single-crystal XRD data. Each lattice constant is 

\[ a = 1.29448(4) \text{ nm for Li}_{6.2}La_{3}Zr_{1.8}Ta_{0.2}O_{12}, \]

\[ a = 1.29375(4) \text{ nm for Li}_{6.4}La_{3}Zr_{1.6}Ta_{0.4}O_{12}, \]

\[ a = 1.29216(6) \text{ nm for Li}_{6.5}La_{3}Zr_{1.5}Ta_{0.5}O_{12}, \]

\[ a = 1.29101(2) \text{ nm for Li}_{6.6}La_{3}Zr_{1.6}Ta_{0.4}O_{12}, \]

\[ a = 1.29071(3) \text{ nm for Li}_{6.2}La_{3}Zr_{1.2}Ta_{0.8}O_{12}. \]

Table 1 summarizes the crystal structure refinement data. Table 2 lists the final atomic coordinates and atomic displacement parameters of each material determined by the single-crystal XRD data. Since it was analysis by X-ray, we have not refined occupation ratio of Li. Figure 4 shows the refined crystal structure for Li_{6.8}La_{3}Zr_{1.6}Ta_{0.4}O_{12}. The Li ions occupied two interstitial sites constructed by the framework structure. The Li1 was located in the distorted octahedral 96h site and Li2 was located in the tetrahedral 24d site. In a garnet solid electrolyte, the Li site is occupied in the (La_{3}Zr_{2-\delta}Ta_{\delta}O_{12})^{7-\delta} framework structure, which consists the A site formed by (Zr, Ta)O_{6} and the C site formed by the LaO_{8}. The 96h site is the position split from the 24d site where Li ions form a tetrahedron. The Li ion conductivity seems to have improved because all the lithium splitting shortened the lithium distance. The distance between Li1 and Li2 is 0.164 nm for Li_{6.8}La_{3}Zr_{1.8}Ta_{0.2}O_{12}, 0.159 nm for Li_{6.6}La_{3}Zr_{1.6}Ta_{0.4}O_{12}, 0.159 nm for Li_{6.5}La_{3}Zr_{1.5}Ta_{0.5}O_{12}, 0.167 nm for Li_{6.4}La_{3}Zr_{1.6}Ta_{0.4}O_{12}, 0.166 nm for Li_{6.2}La_{3}Zr_{1.2}Ta_{0.8}O_{12}.

Fig. 2. Photograph of the surface of a single-crystal plate by SEM.

![Fig. 2. Photograph of the surface of a single-crystal plate by SEM.](image)

Fig. 3. Shows three-dimensional difference Fourier synthesis maps and the (La_{3}Zr_{1.6}Ta_{0.4}O_{12})^{6.6} framework structure in Li_{6.6}La_{3}Zr_{1.6}Ta_{0.4}O_{12}. The solid box indicates the unit cell. Shows the electron density distributions of the threshold value of 0.0012 nm\(^{-3}\) in the map prepared from the XRD measurement data.

Table 1. Crystal structure refinement data

| Composition       | X = 0.2 | X = 0.4 | X = 0.5 | X = 0.6 | X = 0.8 |
|-------------------|---------|---------|---------|---------|---------|
| Lattice constant \( a \text{ nm} \) | 1.29448(4) | 1.29375(4) | 1.29216(6) | 1.29101(2) | 1.29071(3) |
| Lattice volume \( V \text{ nm}^3 \) | 2.16915(20) | 2.16547(13) | 2.15799(10) | 2.15170(9) | 2.15021(9) |
| Space group       | \( Ia-3d \) |
| Dx (mg m\(^{-1}\)) | 5.244   | 5.355   | 5.425   | 5.491   | 5.597   |
| \( F(000) \)      | 2992    | 3040    | 3064    | 3088    | 3136    |
| Radiation used    | MoK\(\alpha\) |
| Monochromator     | graphite |
| Crystal size (diam., mm) | 0.30   | 0.25    | 0.25    | 0.30    | 0.30    |
| Absorption correction | 0.0384 | 0.0213  | 0.0306  | 0.0747  | 0.0375  |
| Extinction factor (Becker and coppens type I) | 0.0306 |
| Diffractometer    | Rigaku R-AXIS RAPID II |
| 2\(\theta\) range (deg.) | 3.86\textendash27.45 |
| No. of measured reflections | 17427 |
| No. of observed reflections after averaging with | 180 |
| \( |F| > 3\sigma(F) \) | 180 |
| \( R_{int} \) (%) | 7.69    | 3.76    | 5.77    | 3.15    | 4.00    |
| \( R \) (%)       | 5.04    | 3.68    | 3.13    | 3.10    | 3.41    |
| \( wR \) (%)      | 6.32    | 5.36    | 3.77    | 3.98    | 4.14    |
| Weighting scheme  | \( 1/\sigma^2 \) (Fo) |
| GOF               | 2.10    | 2.61    | 1.58    | 2.17    | 1.98    |
Ta$_{0.8}$O$_{12}$. When the replacement amount of Ta is around 0.5, the distance of Li$_1$–Li$_2$ tends to be short. The short Li–Li distance, Li site disordering, and partial occupation of the Li atoms were reported as key to Li ion diffusion in the garnet-type structure.

Figure 5 shows a normalized AC impedance Nyquist plot of the Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ ($x = 0.2$, 0.4, 0.5, 0.6, 0.8) single-crystal plate specimen at 298 K in an N$_2$ atmosphere.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (nm$^2$) for Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ ($x = 0.2$, 0.4, 0.5, 0.6, 0.8) determined using the single-crystal XRD data.

| Composition | Wyckoff Positions | atom | x     | y     | z     | Ueq     | Occupancy parameters |
|-------------|-------------------|------|-------|-------|-------|---------|----------------------|
| $x = 0.2$   | $96h$             | Li    | 0.652(4) | 0.172(5) | 0.065(4) | 0.00015(10) | 0.327 |
|            | $24d$             | Li    | 0.65(3) | 0.17(3) | 0.059(3) | 0.00008(6) | 0.310 |
|            | $24c$             | La    | 0.0539(6) | 0.1493(6) | -0.0316(6) | 0.00010(2) | 0.310 |
| $x = 0.4$   | $96h$             | Li    | 0.654(2) | 0.176(3) | 0.058(3) | 0.00010(8) | 0.302 |
|            | $24d$             | Li    | 0.650(2) | 0.179(3) | 0.062(3) | 0.00008(9) | 0.293 |
| $x = 0.5$   | $96h$             | Li    | 0.653(4) | 0.1493(4) | -0.0315(4) | 0.000149(17) | 0.75  |
| $x = 0.6$   | $96h$             | Li    | 0.650(4) | 0.1493(4) | -0.0316(4) | 0.000128(14) | 0.277 |
| $x = 0.8$   | $96h$             | Li    | 0.653(4) | 0.1477(4) | -0.0310(4) | 0.000126(16) | 0.6  |

Figure 5. AC impedance Nyquist plot of the Li$_{7-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ with $x = 0.2$, 0.4, 0.5, 0.6, 0.8 single-crystal plate specimen at 298 K in an N$_2$ atmosphere.
Li7.4La3Zr2.4Ta0.8O12 with x = 0.2, 0.4, 0.5, 0.6 and 0.8.

From this figure, it can be understood that the lithium-ion conductivity was maximum the Ta content of x = 0.4. Even with data using past sintered bodies, it is reported that the maximum is obtained when the tantalum substitution amount is 0.5.10) This result was similar for the niobium substitution product.24) The composition is probably shifted due to the growth of a single crystal, and it is considered that when x = 0.4, the composition is close to Li6.4La3Zr2.5Ta0.5O12. From these results, it was reconfirmed using a single crystal that the Li-ion conductivity becomes maximum around the substitution amount of tantalum X' = 0.5. Figure 7 presents a graph of the relationship between Li-ion conductivity and temperature of the Li7.4La3Zr2.4Ta0.8O12 with x = 0.2, 0.4, 0.5, 0.6, and 0.8 single-crystal plate samples in the temperature range from 253 to 313 K. The activation energy was calculated from the average rate of change of the Arrhenius plot [Ln (σT) vs. 1/T]. Even in the single-crystal samples with different amounts of tantalum substitution, measured activation energy ranged from 0.39 to 0.47 eV. This value well agreed with the data of the sintered body.18) The activation energy was the lowest at 0.39 eV when the substitution amount of tantalum was X' = 0.2, and ticked up with the increase of the substitution amount of tantalum, and became 0.47 eV when the substitution amount of tantalum was X' = 0.8. The factor is considered that the smaller the tantalum substitution amount, the longer the lattice constant and bigger the volume of the path in which the lithium ions are present, and hence the energy for transferring the lithium ions to the adjacent site decreases.

4. Conclusion

We grew centimeter-sized single crystals of garnet-type solid electrolyte Li7-xLa3Zr2-xTa12 with x = 0.2, 0.4, 0.5, 0.6 and 0.8 by FZ melting. Crystal structure of each composition were determined by single crystal XRD measurement. As a result, the shorter the distance between lithium, the better the lithium ion conductivity. The distance between lithium ions was the shortest when the amount of tantalum substitution was around 0.4. In fact, as a result of AC impedance measurement, the Li-ion conductivity became the highest at the chemical composition Li6.4La3Zr1.6Ta0.4O12, and the value was $1.10 \times 10^{-3}$ S cm$^{-1}$ at 298 K. The activation energy ticked up with increasing tantalum substitution.

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