Wide range lattice parameter control by aliovalent substitution to the rare-earth site in cubic garnet Li$_{6.75}$($La_{1-x}Sm_x$)$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$

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Garnet-type Li-ion conductor Li$_{6.75}$($La_{1-x}Sm_x$)$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ powders were synthesized with $0 \leq x \leq 1$ using solid-state reaction method. Almost single-phased garnet phase was obtained by synthesis at 900 °C for all Sm contents. The lattice parameters decrease linearly, concomitantly with increasing Sm content, following Vegard’s law. Results of X-ray diffraction and Raman spectroscopy show that Sm is substituted to the rare-earth element site and that the cubic structure of garnet is stable at a main phase at room temperature. Therefore, this study demonstrates that Sm substitution to La site in the garnet-type Li-ion conductor provides continuous lattice parameter control in a wide range up to $a = 1.27170(8)$ nm. It is noteworthy that the wavenumber shifts of Raman mode related to the four-coordinated Li–O bond are observed only slightly in spite of the large lattice contraction and clear observation of peak-top shifts of other cation-oxygen modes, implying that Li-ion conductivity would be less affected by aliovalent substitution to the rare-earth site.

Key-words: Li-ion battery, LLZO, Solid state electrolyte, Rare-earth element substitution

1. Introduction

All-solid-state Li-ion batteries have attracted much attention for development of next-generation batteries with long lifetime, high safety, and highly powdered contents. Among all materials of which the entire solid-state Li-ion battery consist, solid-state electrolytes are extremely important for assessing battery properties. Particularly, Li-ion conductive oxides are desirable materials for solid-state electrolyte because of their high chemical stability in ambient atmosphere, which enables easier fabrication processing and safer operation. Recently, several studies examining garnet-type Li$_3$La$_2$Zr$_2$O$_{12}$ (LLZO) has been reported, investigating their wide potential window and high ionic conductivity with $10^{-4}$–$10^{-3}$ S/cm, even at room temperature (around 25 °C).\textsuperscript{1,2}

The ionic conductivity of garnet-type Li-ion conductor has been improved by optimization of the concentration and by enhanced mobility of mobile Li ion, as described below.\textsuperscript{3} The Li ion concentration in the garnet-type Li-ion conductor can be improved by increasing $X$ of Li$_3$RE$_3$-M$_2$O$_{12}$, where RE stands for a rare earth element, and $M$ can be Te$^{6+}$, Ta$^{5+}$, Zr$^{4+}$, etc. with reduction of the valence of the M element. However, the tetragonal garnet phase, in which Li–Li repulsion is enhanced by greater Li content and lattice distortion, becomes stable at room temperature in stoichiometric LLZO, giving low ionic conductivity. Many studies have been undertaken to assess suppression of the tetragonal transition with supervalent substitutions to stoichiometric LLZO. For example, Ta$^{5+}$ partial substitution to the Zr$^{4+}$ site introduces vacancies in the Li site, so that the highly ion-conductive cubic garnet phase becomes stable. Combined with the idea of increasing Li-ion concentration, the supervalent substitution to LLZO can be expected to have optimal contents for achieving high ionic conductivity.

Another strategy, that of optimizing the local structure such as lattice parameter, is also important because the ion mobility would be affected by bond lengths between mobile ions and surrounding ions. For example, for one well-known oxide-ion conductor (Zr$_{0.75}$Ce$_{0.08}$RE$_{0.17}$)O$_{1.92}$, where RE stands for rare earth, ionic conductivity improvement without changing the oxygen vacancy has reportedly been achieved by decreasing the lattice parameter: substituting an RE element with a smaller ionic radius.\textsuperscript{3} In LLZO, supervalent substitution such as that of Ta$^{5+}$ ion to the Zr$^{4+}$ site changes the amount of Li vacancy, but it also alters the lattice parameter of the garnet structure.\textsuperscript{4} From earlier studies, Murugan et al. reported a
lattice parameter effect on ionic conductivity without changing the Li concentration achieved by isovalent substitution with changing ionic radii in Li$_x$La$_{3M-O_12}$, where $M$ can be Ta, Nb, Sb, or Bi, and Li$_x$AE$La_2$Ta$_2$O$_{12}$, where AE stands for alkali earth. As a result, the increase of the lattice parameter engenders decreased ionic conductivity. In contrast, tetragonal garnet Li$_x$RESr$_2$Ta$_2$O$_{12}$, where $RE$ stands for La-Gd, in which the lattice parameter decreases with the ionic radius of $RE$ element, showed higher ionic conductivity for $RE = Pr$ and Sm than for La, indicating that the tendency of the ionic conductivity is not straightforwardly dependent on the lattice parameter. Similarly, the optimal lattice parameter for the activation energy of Li-ion conduction was suggested by Zhang et al. in the study of co-substitution of Ca$^{2+}$ and Ta$^{5+}$ to LLZO, which also provides lattice parameter constriction without Li concentration.

This study was conducted for specimen preparation with continuous control of the lattice parameter of LLZO by single isovalent substitution only to La site substitution, not by the aliovalent co-substitution to two sites. The rare-earth ($RE$) element enables the isovalent substitution to the La site. Early studies of garnet-type Li-ion conductors have explored Li$_x$RESr$_2$Ta$_2$O$_{12}$ for RE of Y, Pr, Nd, and Sm-Lu and have examined Li$_x$RESr$_2$O$_{12}$ for $RE = La$, Pr, and Nd. However, only $RE = Nd$ has been reported from studies of the Li$_x$RESr$_2$O$_{12}$ system. For this study, we specifically examined specimen preparation of Sm partial and whole substitution to La in LLZO because Sm ion is expected to be stable in the trivalent state for LLZO. Greater constriction of the lattice parameter is expected from substitution of Sm$^{3+}$ to the La$^{3+}$ site than that of Nd$^{3+}$ because of its smaller ionic radius: La$^{3+}$, 1.16 Å; Nd$^{3+}$, 1.109 Å; and Sm$^{3+}$, 1.079 Å. The Sm$^{3+}$ substitution to La$^{3+}$ site likely occurs in the theoretical simulation. This report is the first to describe synthesis and structural analysis of Li$_x$$_{1-x}$Ta$_2$O$_{12}$ ($RE = La_{1−x}$Sm$_x$) LREZTO powders using the conventional solid-state reaction. To do so, Ta was substituted to the Zr site for stabilizing the cubic garnet structure ($lu$-3$d$), which possesses higher ionic conductivity, at least for $RE = La$. The amount of Ta substitution was fixed to 0.25 for comparison of the same Li contents. Results indicate that the almost single-phased LREZTO powders were synthesized successfully for any Sm content. The main phase in the obtained powders was confirmed to be the cubic garnet phase for all Sm contents. The tendencies of lattice parameters and Raman spectra indicate that Sm is substituted correctly to the La site. Furthermore, the compositional tendency of Raman spectra implies that the bond length of four-coordinated Li-O is unaffected by lattice parameter constriction that occurs with the rare-earth substitution.

2. Experimental procedure

Li$_{x}$Ta$_{2}$O$_{12}$ ($RE = La_{1−x}$Sm$_x$) were synthesized using conventional solid-state reaction with various Sm contents: $x = 0$, 0.25, 0.50, 0.75, and 1. The Li$_2$CO$_3$, La$_2$O$_3$, Sm$_2$O$_3$, ZrO$_2$, and Ta$_2$O$_5$ powders were wet-mixed by hand-milling in an alumina mortar to have the molar ratio of Li$_x$La$_{3-x}$Sm$_x$Zr$_{10}$Ta$_{25}$O$_{12}$: Li$= 8.4(3 - 3)x$: 1.75:0.25, in which the Li nominal content is 25 mol.% excess of the target composition to compensate for Li loss from Li volatilization during annealing at high temperatures. After mixture of the starting materials in an alumina crucible was annealed at 700 °C for 5 h, continuous annealing was conducted at 900 °C for 10 h. The initial step at 700 °C was applied for promotion of the pre-reaction and for suppression of the reaction between the alumina crucible and the molten of Li$_2$CO$_3$ or Li$_2$O decomposed from Li$_2$CO$_3$. Moreover, 900 °C was used as the maximum temperature of the annealing process because the reaction between powders and the alumina crucible was observed after annealing at temperatures higher than 1000 °C. The powder obtained after annealing was ground by hand-milling and was annealed again in the same sequence without additional Li$_2$CO$_3$. The crystalline information of the powder obtained after twice-annealing was evaluated using X-ray diffraction (XRD) and Raman spectroscopy. XRD patterns were measured using Cu-Kα radiation (D8 Advance; Bruker Ltd.). The scan step, speed and range were, respectively, 0.02°, 0.3 s/step and 15°-65°.

The Rietveld refinements for obtained XRD patterns were carried out with using the software TOPAS (Bruker AXS, version 4.1). Raman spectra were obtained by irradiating a green laser ($λ = 532$ nm, NRS-7100; JASCO Corp.).

3. Results and discussion

Figure 1 depicts XRD patterns of the powders with $RE = (La_{1−x}$Sm$_x$), where $x = 0$, 0.25, 0.50, 0.75, and 1. For all compositions, almost all XRD peaks are assigned...
which implies that $L$ to the indices of the garnet phase without peak splitting, a cubic garnet structure ($RE$$_2$Zr$_2$O$_7$), presumably formed because of inhomogeneity of the composition and lower reactivity of Sm than La. The secondary phase is expected to be suppressed by an additional solid-state reaction, or by using a combination of mechanochemical processing and subsequent heating, as reported previously. It is noteworthy that we found during measurement processes that LSMZTO powders displayed in Fig. 1: (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$, (e) $x = 1$. The observed (+), calculated (red curve), and their difference patterns (blue curve) are shown. The green and black vertical lines lie at the Bragg angles of LREZTO with refined lattice parameters by Rietveld analyses and Sm$_2$Zr$_2$O$_7$, respectively. $R_{wp}$ is weighted-profile $R$ value with the contribution of background. $R_c$ is expected value and reflects the quality of the data. $R_p$ is profile fitting $R$ value. GOF is $R_{wp}/R_c$ (goodness-of-fit).

to the indices of the garnet phase without peak splitting, which implies that LREZTO with all compositions shows a cubic garnet structure ($La$-3$d$). For $x = 1$, a tiny peak was detected at $2\theta \sim 30^\circ$. It was assigned to the pyrochlore phase (Sm$_2$Zr$_2$O$_7$), presumably formed because of inhomogeneity of the composition and lower reactivity of Sm than La. The secondary phase is expected to be suppressed by an additional solid-state reaction, or by using a combination of mechanochemical processing and subsequent heating, as reported previously. It is noteworthy that we found during measurement processes that LSMZTO powders were likely to be less hygroscopic than LaZTO, which might be meaningful for battery fabrication with prevention of the formation of LiOH and Li$_2$CO$_3$ surface resistive layers.

As reported from an earlier study of Sm$^{3+}$ substitution to pentavalent $M$ sites ($M = Nb, Ta$) in Li$_{5+x}$La$_{3-x}$M$_2$O$_{12}$, Sm$^{3+}$ can be substituted to the Zr$^{4+}$ site. As presented in Fig. 1, detection of almost no impurity, even at higher Sm contents, supports Sm substitution to the La site. That Sm substitution to the Zr site is expected to result in the detection of many impurity phases because of composition loss at the La site and excess at the Zr site, which contrasts to the impurity increase with Sm content in the report on Li$_{5.5}$La$_{3}Nb$_2$_3$Sm$_{0.5}$O$_{12}$. More clearly, Sm substitution to the Zr site is expected to increase the lattice parameter with Sm content because the ionic radius of Sm$^{3+}$ is much greater than that of Zr$^{4+}$, as reported for Li$_{5.5}$La$_3$M$_2$$_2$Sm$_{0.5}$O$_{12}$, where the following apply: Zr$^{4+}$, 0.72 Å; Nb$^{5+}$, 0.64 Å; Ta$^{5+}$, 0.64 Å; and Sm$^{3+}$, 0.958 Å for six-coordination. Therefore, one can confirm whether Sm is substituted to the La site or to the Zr site by investigating the Sm-content-dependence of the lattice parameter.

Figure 2 shows the Rietveld refinements for the XRD patterns of LREZTO powders displayed in Fig. 1. The lattice parameters of LREZTO for all compositions were found using the Rietveld analyses: $1.29682(6)$ nm for $x = 0$, $1.28926(3)$ nm for $x = 0.25$, $1.28397(5)$ nm for $x = 0.50$, $1.27746(7)$ nm for $x = 0.75$, and $1.27170(8)$ nm for $x = 1$. They are all presented in Fig. 3. The lattice parameter of the obtained LREZTO decreases concomitantly with increasing Sm contents; it lies on the line, which is consistent with Vegard’s law. In addition, the ionic radius is displayed along the upper horizontal axis of Fig. 3, which is converted from the bottom axis by consideration of the ionic radii and molar ratio of eight-coordinated La$^{3+}$ and Sm$^{3+}$ ions. The lattice parameter of Li$_{5.4}$Al$_{0.5}$Nd$_{2}$Zr$_2$O$_{12}$ reported by Howard et al. is also depicted in Fig. 2 as a function of the ionic radius, which is almost on the line obtained in this study. This near matching indicates that the lattice constriction tendency of the LREZTO obtained in this work is consistent with that of $RE = Nd$. Collectively, these results imply that Sm$^{3+}$ is substituted correctly to the La$^{3+}$ site in all compositions.

Figure 4 presents the constriction ratios of lattice parameter dependences on $RE$ ionic radius for the reported cubic-garnet-type compounds: $RE_3M_2$O$_{12}$ ($M = Al, Ga,$

![Figure 2](image-url)
Fe),18) Li₃RE₃Te₂O₁₂,⁹) and Li₅RE₃Ta₂O₁₂,¹⁰) in addition to this work on Lₐ₃Z₃TO. The constriction ratio is represented by \( \frac{a_{RE}}{a_{La}} \), where \( a_{RE} \) is the lattice parameter in \( \text{RE} = \text{rare-earth element} \) and where \( a_{La} \) is the lattice parameter in \( \text{RE} = \text{La} \). Because only Li₃La₃Te₂O₁₂ has not been reported, the \( a_{La} \) of Li₅RE₃Te₂O₁₂ is estimated by extrapolation of the fitting line for the lattice parameter dependence on the ionic radius. A universal line can be found for cubic-garnet type compounds, as shown by the broken line in Fig. 4, implying that constriction of the RE ionic radius results in a common lattice constriction in cubic garnets. The data of Lₐ₃Z₃TO obtained from this study also lie on the same line, which demonstrates that Sm³⁺ is substituted correctly to the La³⁺ site in the cubic garnet structure. Therefore, we synthesized the cubic-garnet-type Lₐ₃Z₃TO with Sm substitution to the La site. The lattice parameter can be controlled by the amount of the Sm substitution. It is noteworthy that the obtained lattice parameter in \( x = 1 \) [\( a = 1.271170(8) \text{nm} \)] is the smallest value among the LLZO systems reported to date.¹) Consequently, this study is meaningful because the wide-range change of a parameter supports a good understanding of dominant factors affecting Li-ion conductivity. 

Raman spectra of the synthesized Lₐ₃Z₃TO powders with \( 0 \leq x \leq 1 \) are exhibited in Fig. 5. A narrow band near 120 cm⁻¹ corresponds to the vibration mode of \( \text{RE}^{3⁺} \) ions in the \( \text{REO}_8 \) dodecahedra, according to the reported assignment of each band in the Li garnet structure.¹⁹)-²¹) The stronger band near 650 cm⁻¹ and the weaker band near 750 cm⁻¹ are related, respectively, to breathing modes of octahedral Zr-O and Ta-O bonds.²⁰),²¹) The LLZO structure has four-coordinated and six-coordinated Li-O bonds, which are respectively designated in this paper as Li(4)-O and Li(6)-O bonds, respectively. Inverted triangles denote peak-tops of each mode band.

The wavenumbers at the peak-top of the Raman mode bands corresponding to each bond are shown as a function of the Sm content in Fig. 6. The Zr–O, Ta–O, and Li(6)–O modes show a blue shift with increasing Sm content. When the bond strength increases, a blue shift of Raman mode is generally observed. Consequently, the blue shifts of the three modes indicate bond-length contractions in the Zr–O, Ta–O, and Li(6)–O bonds because of the decrease of the lattice parameter. However, a red shift with increasing Sm content is observed for the modes related to RE–O. An increase of the atomic weight results in a red shift of Raman mode. When a harmonic oscillator of a simple one-dimensional chain is constructed using atoms of two kinds such as \( \text{RE} \) and O, the wavenumber of the acoustic mode is proportional to 

\[
\mu^* = (m_1 + m_2)^{-1/2},
\]
with high-density or single crystals have been fabricated. The Li-ion conductivity of RE element substituted LLZO will be investigated in future works to assess the role of the local structure on ion conductivity in garnet-type Li-ion conductors.

4. Conclusions

Garnet-type Li-ion conductor LREZTO powders were synthesized for \(0 \leq x \leq 1\) in \(RE = (La_{1-x}Sm_x)\) using a conventional solid-state reaction method. XRD profiles and Raman spectra indicate that almost single-phased cubic-garnet phase was obtained for all \(Sm\) contents through synthesis at 900 °C. The smallest lattice parameter among the LLZO systems reported to date was obtained for \(x = 1\). The lattice parameter decreases linearly following Vegard’s law, concomitantly with increasing \(Sm\) content. The lattice constriiction ratio of LREZTO by \(RE\) element substitution is consistent with that of other garnet compounds. Red shifting was observed for the Raman mode related to the \(RE-O\) bond. These results demonstrate that \(Sm^{3+}\) ions are substituted correctly to the \(La^{3+}\) site in the LLZO structure. Although clear blue shifts of Ta-O, Zr-O, and Li(6)-O modes are observed, we observed very little or no shift of the Li(4)-O mode in spite of the large lattice constriction, implying that the bond length in the LiO4 tetrahedron, which is most important for ionic conductivity, would be affected only slightly by \(Sm\) substitution to the \(RE\) site in spite of the large decrease of the lattice parameter.

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