Li-ion conductivity and crystal structure of garnet-type 
Li$_{6.5}$La$_3$M$_{1.5}$Ta$_{0.5}$O$_{12}$ (M = Hf, Sn) oxides

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We investigated the Li-ion conductivity and crystal structure of the Ta-doped Li$_{6.5}$La$_3$M$_{1.5}$Ta$_{0.5}$O$_{12}$ (M = Hf, Sn) samples. All of the Ta-doped samples exhibited a relatively high conductivity of $\sim 10^{-4}$ S cm$^{-1}$ at room temperature, and the activation energies of Li$_{6.5}$La$_3$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_3$Sn$_{1.5}$Ta$_{0.5}$O$_{12}$, which were determined from the Arrhenius plots in measured temperature range, are $E_a = 0.40(6)$ and $0.45(1)$ eV, respectively. The crystal structure was analyzed by Rietveld method using powder X-ray diffraction data. From a view point of the Li-O polyhedral volume in unit cell, Li$_{6.5}$La$_3$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ has a most suitable Li-ion environment among the Li$_{6.5}$La$_3$M$_{1.5}$Ta$_{0.5}$O$_{12}$ (M = Zr, Hf, Sn) compounds.

Key-words : Garnet-type oxide, Li-ion conductor

1. Introduction

Li-ion rechargeable batteries are required improvement in safety and high energy density, because of wide application from small-size electrical devices to large-size power sources. Especially, all-solid-state Li-ion batteries using solid oxide electrolyte have attracted attention as next-generation batteries without inflammable organic liquid electrolytes.1–4 There are many candidates of Li-ion conductive oxides as solid electrolyte for all-solid-state Li-ion batteries,5–9 the garnet-type oxide with a general formula of Li$_7$La$_3$M$_2$O$_{12}$ (M = Zr, Hf, Sn) has been extensively investigated on the Li-ion conductivity and crystal structure of garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$, which was first reported by Murugan et al.,5 both has high Li-ion conductivity and wide electrochemical potential window. In order to improve the Li-ion conductive properties of the garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$, a large number of studies on the chemical substitution using various cation species has been reported.10–17 Among them, Ta-doped Li$_7$La$_3$Zr$_2$O$_{12}$ exhibits a relatively higher Li-ion conductivity ($\sim 10^{-4}$ S cm$^{-1}$ at room temperature).18–21 Consequently, Li$_{6.5}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ has been extensively investigated on the Li-ion conductivity, detailed crystal structure and synthetic process including optimization of the amount of Ta substitution. On the other hand, a similar Ta substitution for the garnet-type Li$_7$La$_3$Hf$_2$O$_{12}$ has been reported.22 As a result of the optimization of Ta content, Li$_{6.5}$La$_3$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ also shows a relatively higher Li-ion conductivity of $3.45 \times 10^{-4}$ S cm$^{-1}$ at room temperature.23

As previously demonstrated, Ta is one of the most effective dopant for the garnet-type oxide, and the optimum Ta-content is nearly 0.5 mol%. Therefore, we focused on the composition of 0.5 mol% Ta per unit formula of garnet-type oxide having the cubic structure. As is well known, Li$_7$La$_3$Sn$_2$O$_{12}$ also has tetragonal system.24 Although the optimized dopant for Li$_7$La$_3$Sn$_2$O$_{12}$ was not examined yet including the amount of substitution. It can be expected that the Li-ion conductivity of Li$_7$La$_3$Sn$_2$O$_{12}$ also was improved by Ta substitution for Sn site.

Furthermore, the chemical stability of garnet related type Li$_7$La$_3$M$_2$O$_{12}$ (M = Zr, Hf, Sn) to carbonate and hydroxide was recently reported by first-principle calculation using DFT calculation.25 As from the reports, Li$_7$La$_3$Sn$_2$O$_{12}$ showed higher chemical stability than the other two materials. So, the Li$_7$La$_3$Sn$_2$O$_{12}$ could be expected for solid electrolyte as all-solid-state Li-ion batteries. However, Li-ion conductive properties and crystal structure parameters of Li$_7$La$_3$Sn$_2$O$_{12}$, which has cubic system by substitution has not been clarified yet.

In this study, we synthesized the garnet-type Li$_{6.5}$La$_3$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_3$Sn$_{1.5}$Ta$_{0.5}$O$_{12}$ by the conventional solid-state synthesis method under Al-free conditions. In addition, we investigated the difference of electrochemical properties from M cation in Li$_{6.5}$La$_3$M$_{1.5}$O$_{12}$ (M = Zr, Hf, Sn), and examined the origin of difference of their conductive properties using crystal structure analysis in comparison with those in Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$.

2. Experimental

The garnet-type oxide Li$_{6.5}$La$_3$M$_{1.5}$Ta$_{0.5}$O$_{12}$ (M = Hf, Sn) samples were prepared by conventional solid state reaction method using HfO$_2$ (99.99%, Rare Metallic Co., Ltd.) and SnO$_2$ (99.99%, Rare Metallic Co., Ltd.) according to the reported procedure as we previously described.26

The phase purity and identification of prepared samples were performed by powder X-ray diffraction (Rigaku, SmartLab) using Cu K$_\alpha$ radiation with 2θ range from 10 to 90° at an interval step of 0.02°. The chemical compositions and morphology of cross-section of sintered samples was analyzed using SEM-EDS (JEOL, JCM-6000) at an acceleration voltage of 15 kV.

The electrical conductivity was measured by AC impedance method using a Solartron 1260 impedance analyzer. The measurement was carried out in a temperature range from 253 to 313 K at 100 mV applied AC amplitude, at 32 MHz to 100 Hz frequencies. To measure the Li-ion conductivity, the both sides of measured pellet were coated by Au as Li-ion blocking electrodes using Au sputtering.

The crystal structure analysis of the obtained samples was performed by Rietveld method using XRD data. For the Rietveld analysis of collected XRD patterns, the space group of Ia-3d was...
used for the cubic phases.

3. Results and discussion

3.1 Sample characterizations

Figure 1 shows the powder X-ray diffraction patterns of Li$_{6.5}$La$_{3}$M$_{1.5}$Ta$_{0.5}$O$_{12}$ ($M$ = Hf, Sn). As from XRD patterns, no impurity was detected, and the all diffraction peaks of Li$_{6.5}$La$_{3}$M$_{1.5}$Ta$_{0.5}$O$_{12}$ ($M$ = Hf, Sn) were attributed to single phase of cubic (S.G.: Ia-3d) structures. The lattice parameters of Li$_{6.5}$La$_{3}$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_{3}$Sn$_{1.5}$Ta$_{0.5}$O$_{12}$ samples, calculated by least-squares method, were $a = 12.9334(1)$ Å and $a = 12.9023(1)$ Å, respectively. The lattice parameter of Li$_{6.5}$La$_{3}$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ was larger than that of Li$_{6.5}$La$_{3}$Sn$_{1.5}$Ta$_{0.5}$O$_{12}$ because of larger average ionic radii of cations occupied at octahedral site [Hf$^{4+}$: 0.71 Å, Sn$^{4+}$: 0.69 Å, Ta$^{5+}$: 0.64 Å].28

Figure 2 shows the cross-sectional morphology of Li$_{6.5}$La$_{3}$M$_{1.5}$Ta$_{0.5}$O$_{12}$ ($M$ = Hf, Sn) after sintering at 1150°C. Those sintering samples has a high relative density (above 90% of the theoretical density) which is enough to measure the Li-ion conductivity. The grain size of Li$_{6.5}$La$_{3}$Sn$_{1.5}$Ta$_{0.5}$O$_{12}$ was slightly larger than that of Li$_{6.5}$La$_{3}$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$. This fact may suggest a difference in the grain growth rate of these materials at 1150°C. Chemical compositions of Li$_{6.5}$La$_{3}$M$_{1.5}$Ta$_{0.5}$O$_{12}$ ($M$ = Hf, Sn) were determined to be La:Hf:Ta = 3:1.50:0.51 and La:Sn:Ta = 3:1.52:0.54 by EDX analyses, respectively, which agrees well with the structural formula of Li$_{6.5}$La$_{3}$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_{3}$Sn$_{1.5}$Ta$_{0.5}$O$_{12}$.

3.2 Conductive properties

Figure 3(a) shows the Cole–Cole plots of Li$_{6.5}$La$_{3}$M$_{1.5}$Ta$_{0.5}$O$_{12}$ ($M$ = Hf, Sn). The impedance plots of samples indicates one semicircle for bulk and grain boundary resistance. Since the spectrums could not be well separated to bulk and grain-boundary elements, we considered uniformly the total conductivity as a function of temperature. The temperature dependence of total Li-ion conductivity for the Li$_{6.5}$La$_{3}$M$_{1.5}$Ta$_{0.5}$O$_{12}$ ($M$ = Hf, Sn) samples are compared with that25) for Li$_{6.5}$La$_{3}$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ in Fig. 3(b). The activation energies ($E_a$) of Li$_{6.5}$La$_{3}$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_{3}$Sn$_{1.5}$Ta$_{0.5}$O$_{12}$, which were determined from the Arrhenius plots in measured temperature range, were $E_a = 0.400(6)$ and 0.451(1) eV, respectively. On the other hand, the values of Li-ion conductivity at room temperature for Li$_{6.5}$La$_{3}$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_{3}$Sn$_{1.5}$Ta$_{0.5}$O$_{12}$ were measured to be $4.0 \times 10^{-4}$ and $1.9 \times 10^{-4}$ S cm$^{-1}$, respectively. In the present

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Fig. 1. Powder X-ray diffraction patterns of Li$_{6.5}$La$_{3}$M$_{1.5}$Ta$_{0.5}$O$_{12}$ ($M$ = Hf, Sn) sintered at 1150°C for 4 h.

Fig. 2. SEM images of the cross-section morphology of (a) Li$_{6.5}$La$_{3}$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ and (b) Li$_{6.5}$La$_{3}$Sn$_{1.5}$Ta$_{0.5}$O$_{12}$.

Fig. 3(a). Nyquist plots of Li$_{6.5}$La$_{3}$M$_{1.5}$Ta$_{0.5}$O$_{12}$ ($M$ = Hf, Sn) at 297 K.

Fig. 3(b). Arrhenius plots of total conductivities of Li$_{6.5}$La$_{3}$M$_{1.5}$Ta$_{0.5}$O$_{12}$ ($M$ = Zr, Hf, Sn).
study, Li₆₅La₃Hf₁₅Ta₀₅O₁₂ has a lower activation energy than those of Li₆₅La₃Zr₁₅Ta₀₅O₁₂ and Li₆₅La₃Sn₁₅Ta₀₅O₁₂, although the Li-ion conductivity of Li₆₅La₃Zr₁₅Ta₀₅O₁₂ is highest among them at room temperature.

3.3 Crystal structure analysis

To clarify the difference in the Li-ion conductivity among the Ta-0.5 substituted garnet-type oxides Li₆₅La₃M₁₅Ta₀₅O₁₂ (M = Zr, Hf, Sn) from a crystallographic viewpoint, the crystal structure analysis was performed by the Rietveld analysis using powder XRD data. The structure parameters were refined using the reported atomic coordinates using the cubic Ia-3d (No. 230) space group. Figure 4 shows the Rietveld refinement patterns of Li₆₅La₃M₁₅Ta₀₅O₁₂ (M = Hf, Sn), and the refined parameters are given in Tables 1 and 2, respectively. The ratio of occupancy for the octahedral M/Ta site was fixed to the nominal composition. In the garnet-type Li-ion conductors, it is well known that the Li occupancy of both the tetrahedral 24d and octahedral 96h sites has a huge effect on their Li-ion conductive properties.²⁹,³⁰ Here, the Li1 and Li2 atoms occupied at tetrahedral 24d site and octahedral 96h site, respectively. The tendency of Li occupation at the 24d and 96h sites, g(Li1) = 0.60 and g(Li2) = 0.39, determined in the present Li₆₅La₃M₁₅Ta₀₅O₁₂ (M = Hf, Sn) was very similar to that in Li₆₅La₃Zr₁₅Ta₀₅O₁₂.²⁵ Hence, the difference in Li-ion conductivity among Li₆₅La₃M₁₅Ta₀₅O₁₂ (M = Zr, Hf, Sn) is due to another structural view point. Additionally, the atomic displacement parameters of Li²⁴d and 96h site for Li₆₅La₃Hf₁₅Ta₀₅O₁₂ was larger value than other Li₆₅La₃Sn₁₅Ta₀₅O₁₂. So, the diffusion of Li-ion in Li₆₅La₃Hf₁₅Ta₀₅O₁₂ between 24d and 96h is relatively easy owing to their larger atomic displacement parameters.

Polyhedral volumes constructed by surrounding oxygen coordination around central cations for Li₆₅La₃Hf₁₅Ta₀₅O₁₂ and Li₆₅La₃Sn₁₅Ta₀₅O₁₂, respectively, were given as shown in Figure 4. Li₁ and Li₂ have tetrahedral and octahedral polyhedra, respectively. It is expected that the lithium ions in the octahedral sites play a role as a carrier for the Li-ion conductivity. The cubic crystal system, space group Ia-3d, lattice parameter a = 12.93341(9) Å.

Table 1. Structure parameters of Li₆₅La₃Hf₁₅Ta₀₅O₁₂ refined using the powder X-ray diffraction data. R-values: Rp = 8.30%, Rp = 5.91% and R = 6.01%. Cubic crystal system, space group Ia-3d, lattice parameter a = 12.93341(9) Å.

| Atom | Site | g | x | y | z | U (Å²) |
|------|------|---|---|---|---|--------|
| La   | 24d  | 1 | 1/8 | 0 | 1/4 | 0.0040(2) |
| Hf/Ta| 16c  | 0.75/0.25 | 0 | 0 | 0 | 0.0035(2) |
| Li1  | 24d  | 0.596(6) | 3/8 | 0 | 1/4 | 0.071(1) |
| Li2  | 96h  | 0.39(4) | -0.063(2) | 0.637(3) | 0.647(3) | 0.051(1) |
| O    | 96h  | 1  | -0.032(8) | 0.0352(3) | 0.1496(3) | 0.001(1) |

a) g(Li2) = 52/96 - 24/96 × g(Li1).

Table 2. Structure parameters of Li₆₅La₃Sn₁₅Ta₀₅O₁₂ refined using the powder X-ray diffraction data. R-values: Rp = 8.96%, Rp = 6.43% and R = 6.50%. Cubic crystal system, space group Ia-3d, lattice parameter a = 12.90227(9) Å.

| Atom | Site | g | x | y | z | U (Å²) |
|------|------|---|---|---|---|--------|
| La   | 24c  | 1 | 1/8 | 0 | 1/4 | 0.0040(2) |
| Sn/Ta| 16c  | 0.75/0.25 | 0 | 0 | 0 | 0.0014(2) |
| Li1  | 24d  | 0.60(5) | 3/8 | 0 | 1/4 | 0.022(8) |
| Li2  | 96h  | 0.39(4) | 0.158(3) | 0.671(2) | 0.574(2) | 0.019(9) |
| O    | 96h  | 1  | -0.035(2) | 0.0515(3) | 0.1489(2) | 0.002(1) |

a) g(Li2) = 52/96 - 24/96 × g(Li1).

Table 3. Volume of polyhedral constructed by surrounding oxygen atoms around central cations for Li₆₅La₃M₁₅Ta₀₅O₁₂ (M = Hf, Sn, Zr).

| L₆₅La₃M₁₅Ta₀₅O₁₂ | Li₆₅La₃Sn₁₅Ta₀₅O₁₂ | Li₆₅La₃Zr₁₅Ta₀₅O₁₂ |
|------------------|---------------------|---------------------|
| Lattice parameter a (Å) | 12.93341(9) | 12.90227(9) | 12.94809(3) |
| Cell volume V (Å³) | 2163.41(3) | 2147.82(3) | 2170.79(1) |
| Li₁O₄, tetrahedron (Å³) | 3.43 | 3.32 | 3.42 |
| Li₂O₆, octahedron (Å³) | 14.50 | 14.12 | 14.44 |
| La₂O₆, dodecahedron (Å³) | 28.45 | 29.02 | 28.81 |
| (M, Ta)O₆, octahedron (Å³) | 12.25 | 12.02 | 12.26 |
although the Li-ion conductivity of Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ is respectively. Li$_{6.5}$La$_3$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ has a lower activation energy.

Li$_{6.5}$La$_3$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ was synthesized by conventional solid-state method. The X-ray diffraction patterns of Li$_{6.5}$La$_3$M$_1$Ta$_{0.5}$O$_{12}$ (M = Hf, Sn) samples were assigned to be single phases of (S.G.:$Ia$-3d) structures. As from conductivity measurement, their Li-ion conductivity at room temperature for Li$_{6.5}$La$_3$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_3$Sn$_{1.5}$Ta$_{0.5}$O$_{12}$ were $\sigma$$_{\text{Li-ion}}$ = $4.0 \times 10^{-4}$ and $1.9 \times 10^{-4}$ S cm$^{-1}$, respectively. Li$_{6.5}$La$_3$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ has a lower activation energy than those of Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ and Li$_{6.5}$La$_3$Sn$_{1.5}$Ta$_{0.5}$O$_{12}$, although the Li-ion conductivity of Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ is highest among them at room temperature.

To reveal the difference in the Li-ion conductivity among the Ta-0.5 substituted garnet-type oxides Li$_{6.5}$La$_3$M$_1$Ta$_{0.5}$O$_{12}$ (M = Zr, Hf, Sn) from a crystallographic view point, the crystal structure analysis was performed by the Rietveld analysis using powder XRD data. As from results, the polyhedral volumes of Li$_1$O$_4$ and Li$_2$O$_6$ in Li$_{6.5}$La$_3$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ is largest among these Li$_{6.5}$La$_3$M$_1$Ta$_{0.5}$O$_{12}$ compounds. This fact may suggest the lowest activation energy observed in the Li$_{6.5}$La$_3$Hf$_{1.5}$Ta$_{0.5}$O$_{12}$ sample.

Acknowledgements: A part of this work was supported by the Advanced Low Carbon Technology Research and Development Program (ALCA-SPRING) from Japan Science and Technology Agency (JST).

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