Synthesis, Crystal Structure, and the Ionic Conductivity of New Lithium Ion Conductors, \( M \)-Doped LiScO\(_2\) (\( M = \text{Zr, Nb, Ta} \))\(^{1,2}\)

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New lithium ion conductors of \( M \)-doped LiScO\(_2\) (\( M = \text{Zr, Nb, Ta} \)) were synthesized by a solid-state reaction method. Peak shifts of the X-ray diffraction patterns revealed the formation of solid solutions with aliovalent cation doping. In addition, increase in the ionic conductivity by \( M \) doping is indicated. The highest total conductivity of \( 7.94 \times 10^{-8} \text{ S cm}^{-1} \) at 623 K with an activation energy of 88 ± 5 kJ mol\(^{-1} \) was observed for the Zr\(^{4+} \) doped sample in the systems. The Zr\(^{4+} \) doped system showed the largest solid solution limit in Li\(_{1-x}\)Sc\(_x\)ZrO\(_2\) (\( x = 0.1 \)) and continuous increase of the conductivity with increasing \( x \). Structural analysis by Rietveld refinement indicated that the lattice expansion and lithium-ion vacancy formation by the Zr doping in the structure, which could contribute to the increase in the ionic conductivity.


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1. Introduction

Lithium ion conductive solids are expected to serve as solid electrolytes for all-solid-state batteries because they could address the safety issues in current lithium batteries. Higher stability, reliability and energy density could be provided by replacing the organic flammable liquid electrolytes by the solid electrolytes.

Therefore, many studies focusing on solid lithium ion conductors have been reported. Among these reports, sulfide-based lithium ion conductors have attracted considerable attention. In particular, the lithium superionic conductor Li\(_{10}\)GeP\(_2\)S\(_{12}\) exhibits an extremely high conductivity of \( 1.2 \times 10^{-2} \text{ S cm}^{-1} \) at room temperature. Its conductivity is comparable to or exceeds that of the organic liquid electrolytes. In addition, it maintains excellent conductive properties even at low temperatures\(^1\). However, sulfide-based materials have serious problems that remain unsolved. For instance, a high-resistance interface layer is easily formed in contact with the electrodes, and sulfides are unstable in ambient air because of their high reactivity with moisture\(^2\).

On the other hand, oxide-based materials are relatively stable in air; thus, various synthesis methods can be applied and facile fabrication processes are expected for all-solid-state batteries\(^3\). Among oxide-based solid electrolytes, perovskite-type Li\(_{1-x}\)La\(_x\)(Ti\(_2\)O\(_3\))\(_y\)TiO\(_3\) is considered as one of the most promising candidates because of its high ionic conductivity (greater than \( 10^{-3} \text{ S cm}^{-1} \) at room temperature)\(^4\). However, a serious reduction of Ti\(^{4+} \) to Ti\(^{3+} \) at the interface between the low-potential anodes during the electrochemical process gives rise to undesirable electronic conduction\(^5\). Therefore, the practical use of Li\(_{1-x}\)La\(_{x}\)(Ti\(_2\)O\(_3\))\(_y\)TiO\(_3\) in all-solid-state batteries is still difficult. A material that satisfies all the conditions required for using lithium ion conductors as solid electrolytes for battery applications (i.e., high ionic conductivity at room temperature, chemical stability, electrochemical stability, thermal stability, and low cost) has not been discovered yet. Therefore, it is necessary to investigate new solid lithium ion conductors. In this study, we focus on LiScO\(_2\), which has an ionic conductivity of \( 4 \times 10^{-3} \text{ S cm}^{-1} \) at 573 K. Although the ionic conductivity is not incredibly high, this material is attractive because it has better thermodynamic stability when placed in contact with lithium metal\(^6\).

LiScO\(_2\) has a fractional cationic ordered rock-salt structure with tetragonal \( I4_{1}/amd \) symmetry\(^7\). The related cationic structure has the potential to partially rearrange based on the synthesis conditions and the doped element\(^8\). Element doping is an effective method to increase the ionic conductivities of solid lithium ion conductors. Further, LiScO\(_2\) shows the possibility of increasing its ionic conductivity by doping; however, no subsequent investigations have been reported for the same. Thus, in an attempt to improve the ionic conductivity of LiScO\(_2\) by introducing lithium vacancies in the structure, aliovalent cations Zr\(^{4+} \), Nb\(^{5+} \), and Ta\(^{5+} \) were doped into LiScO\(_2\). The doped Li\(_{1-x}\)Sc\(_x\)\(_{1-y}\)M\(_y\)O\(_2\) were synthesized, and their crystal structures and ionic conductivities were evaluated.

2. Experimental Procedure

LiScO\(_2\) and aliovalent cation-doped Li\(_{1-x}\)Sc\(_x\)\(_{1-y}\)M\(_y\)O\(_2\) were synthesized by a solid-state reaction method. Li\(_2\)CO\(_3\) (Wako Pure Chemical Industries, Ltd., 99.0% purity), Sc\(_2\)O\(_3\) (Wako Pure Chemical Industries, Ltd., 99.0% purity), ZrO\(_2\) (Kanto Chemical Co., Inc., 99.0% purity), Nb\(_2\)O\(_5\) (Wako Pure Chemical Industries, Ltd., 99.9% purity), and Ta\(_2\)O\(_5\) (Kanto Chemical Co., Inc., 99.95% purity) were used as starting materials. To compensate Li loss during the synthesis process at high temperature, excess lithium (20% in mol.% scale) was used for the synthesis. The starting materials were weighted in ap-
propriate molar ratios and mixed in an agate mortar with acetone. After volatilization of the acetone, the specimens were pressed into pellets (diameter = 5–10 mm) at 400–600 MPa using a uniaxial press machine (RIKEN KIKI Co., LTD, P–6). The pellets were heated at reaction temperatures of 1073–1623 K for 1–12 h in air and then slowly cooled to room temperature. The synthesized pellets were crushed into powders and characterized using an X-ray diffractometer (XRD; SmartLab, Rigaku) with Cu Kα1 radiation (λ = 1.541 Å). The tube voltage and tube electric current of the XRD were 45 kV and 200 mA, respectively. Diffraction data were collected over the 20 range of 10° to 70° with a step interval of 0.02°.

Ionic conductivity was measured by an ac impedance method (Solartron, 1260). The crushed powders were pressed into disc-shaped pellets (diameter = ~5 mm; thickness = ~2 mm) under a pressure of 1620 MPa. Au paste (Nilaco Corporation, Au-176010, 99.5%, Resistivity < 1 × 10^{-4} Ω cm) was painted on both faces of the pellets. The Au/Sample/Au cells were heated to 773 K for 12 h before measuring the ionic conductivity. The ac impedances of the Au/Sample/Au cells were measured between 298 and 673 K in a dry Ar atmosphere in the frequency range of 1–10^6 Hz at 500 mV. After keeping the cells at each test temperature for 30 min, the ionic conductivity was measured, and the measured data was analyzed using ZPLOT and ZVIEW softwares\(^9\).

Synchrotron X-ray diffraction data was obtained using a synchrotron X-ray source at the BL02B2 or BL19B2 beamline at SPring-8. A Debye–Scherrer diffraction camera was used for the measurements at room temperature with an X-ray wavelength of 0.5 Å. For the XRD measurements, the powder samples were sealed in Lindermann glass capillaries (approximately 0.3 mm in diameter). The incident-beam wavelength was calibrated using CeO\(_2\) (NIST SRM Ceria 640b). The crystal structure parameters were refined by the Rietveld method using the RIETAN-FP program\(^{10}\).

### 3. Results and Discussions

Figure 1(a) shows the XRD patterns for the LiScO\(_2\) and Li\(_{1+y}\)Sc\(_{1−y}\)M\(_{0.1}\)O\(_2\) (y = 0.1). Almost the diffraction peaks in the patterns was indexed to the tetragonal crystal structure of LiScO\(_2\) (space group P\(_4_1\)/amd (141)). This indicates that all the synthesized samples might have the same crystal structure as LiScO\(_2\). The peaks in the diffraction patterns at approximately 0.3 mm in diameter). The incident-beam wavelength was calibrated using CeO\(_2\) (NIST SRM Ceria 640b). The crystal structure parameters were refined by the Rietveld method using the RIETAN-FP program\(^{10}\).

![Representative impedance spectra at 623 K (a) and the conductivity presented by the Arrhenius plots (b) for doped Li\(_{1−x}\)Sc\(_x\)M\(_{0.1}\)O\(_2\) (M = Zr\(^{4+}\), Nb\(^{5+}\), or Ta\(^{5+}\)).](image)

Figure 2 shows the impedance spectra (Fig. 2(a)) and the temperature dependence of the conductivity presented by the Arrhenius plots (Fig. 2(b)) for the Li\(_{1−x}\)Sc\(_x\)M\(_{0.1}\)O\(_2\) (x = 0.1). The conductivities were calculated from the impedance spectra shown in Fig. 2(a), which are characteristic of pure ionic conductors. These plots consist of a semicircle and a spike, which correspond to the contributions from the bulk/grain boundary and the electrode, respectively. The bulk and grain boundary contribution could not be separated from the impedance spectra and therefore, the conductivity values were calculated as the sum of both contributions. The semicircle shape was not detected for the impedance spectra of the undoped LiScO\(_2\) in the temperature range of 298–627 K because the resistance of LiScO\(_2\) may be out of the limitation range of the apparatus (>100 MΩ). Resistance values were calculated from the diameters of the semicircles in the impedance spectra. The conductivity values were calculated from the resistance values. The diameters of the semicircles in the impedance spectra decrease by the doping, indicating that it is possible to survey and evaluate the ionic conductivities. The observed capacitance values for the semicircles were in mately 50° (peak 211) shifted to lower angles upon doping with Zr\(^{4+}\) and to higher angles upon doping with Nb\(^{5+}\) and Ta\(^{5+}\), as shown in Fig. 1(b). This indicates the formation of solid solutions for Li\(_{1−x}\)Sc\(_x\)M\(_{0.1}\)O\(_2\) (x = 0.1, M = Zr\(^{4+}\), Nb\(^{5+}\), and Ta\(^{5+}\)) via aliovalent cation doping while maintaining the basic structure of LiScO\(_2\). Lithium vacancies might be introduced into the structures upon the partial substitution of Sc\(^{3+}\) with higher aliovalent cations (Zr\(^{4+}\), Nb\(^{5+}\), and Ta\(^{5+}\)). On the other hand, an interstitial oxygen formation was possible to compensate charge neutrality in the crystal lattice instead of the lithium vacancy formation. However, no significant lattice parameter change due to the cation doping and small interstitial space for additional oxygen atoms in the lattice deny that possibility. The small peaks at approximately 32° along with those in the region below 23° for the Nb\(^{5+}\)- and Ta\(^{5+}\)-doped samples are due to the generated impurity phases. Although their intensities were extremely low compared to those of the main phase peaks, slight impurity peaks were also observed for the Zr\(^{4+}\)-doped samples. In contrast to doping with higher-valent cations Nb\(^{5+}\) and Ta\(^{5+}\), doping with the lower-valent cation Zr\(^{4+}\) introduces fewer lithium vacancies into the structure. However, because of the similar ionic radii of Zr\(^{4+}\) (0.72 nm) and Sc\(^{3+}\) (0.745 nm) at the six-coordinated octahedral position in the structure of LiScO\(_2\), the doping range of the generated solid solution is wider for Zr\(^{4+}\) doping.
LiScO$_2$ lattice reduces the energy barrier for lithium diffusion also decreased more than 10% by the aliovalent cation doping. Furthermore, the activation energies improved through the formation of solid solutions via aliovalent cation doping. This demonstrates that the ionic conductivity was dramatically improved.

<table>
<thead>
<tr>
<th>Doped element</th>
<th>Composition</th>
<th>Total conductivity $\sigma$, S cm$^{-1}$ @573 K</th>
<th>Activation energy $E_a$, kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>–</td>
<td>LiScO$_2$</td>
<td>$4.2 \times 10^{-9}$ [ref]</td>
<td>101 [ref]</td>
</tr>
<tr>
<td>Ta</td>
<td>Li$<em>{0.8}$Sc$</em>{0.9}$Ta$_{0.1}$O$_2$</td>
<td>$5.79 \times 10^{-7}$</td>
<td>$57 \pm 11$</td>
</tr>
<tr>
<td>Nb</td>
<td>Li$<em>{0.8}$Sc$</em>{0.9}$Nb$_{0.1}$O$_2$</td>
<td>$6.01 \times 10^{-7}$</td>
<td>$85 \pm 3$</td>
</tr>
<tr>
<td>Zr</td>
<td>Li$<em>{0.8}$Sc$</em>{0.9}$Zr$_{0.1}$O$_2$</td>
<td>$9.73 \times 10^{-7}$</td>
<td>$88 \pm 5$</td>
</tr>
</tbody>
</table>

Table 1 Ionic conductivities at 573 K and activation energies of doped Li$_{1-x}$Sc$_{1-x}$M$_x$O$_2$ ($M = $Zr$^{4+}$, Nb$^{5+}$, or Ta$^{5+}$). Previously reported values of LiScO$_2$ are also included.

Figure 3 shows the ionic conductivities of Li$_{1-x}$Sc$_{1-x}$Zr$_x$O$_2$ at 573 K as a function of the composition $x$. The LiScO$_2$ ($x = 0$) value is plotted from previous report.

The range of $10^{-10}$-$10^{-12}$ F. The activation energy values of the ionic conduction were calculated from the slopes of the Arrhenius plots shown in Fig. 2b. Table 1 summarizes the ionic conductivities at 573 K and activation energies for Li$_{1-x}$Sc$_{1-x}$M$_x$O$_2$ ($x = 0.1$) along with previously reported values for LiScO$_2$.

Comparing to the previous data about the conductivity of LiScO$_2$, the ionic conductivities of Li$_{1-x}$Sc$_{1-x}$M$_x$O$_2$ were improved by two orders of magnitude. This demonstrates that the ionic conductivity was dramatically improved through the formation of solid solutions via aliovalent cation doping. Furthermore, the activation energies also decreased more than 10% by the aliovalent cation doping, indicating that the formation of the lithium vacancy in the LiScO$_2$ lattice reduces the energy barrier for lithium diffusion. Zr$^{4+}$-doped samples show the highest values of ionic conductivity; an ionic conductivity of 9.73 $\times 10^{-7}$ S cm$^{-1}$ was observed at 573 K. In order to verify the changes in the ionic conductivities caused by Zr$^{4+}$ doping, Li$_{1-x}$Sc$_{1-x}$Zr$_x$O$_2$ with different Zr$^{4+}$ doping amounts ($x$: 0–0.2) were synthesized, and the ionic conductivities and crystal structures were evaluated.

Figure 3 shows the ionic conductivities of Li$_{1-x}$Sc$_{1-x}$Zr$_x$O$_2$ with varying composition $x$ at 573 K. The ionic conductivity continuously increased with increasing $x$ from 0 to 0.1. The concentration of lithium vacancies also increases with increasing Zr content. The ionic conductivity of the sample with $x = 0.2$ was slightly lower than that of the sample with $x = 0.1$ because of the increase in resistance caused by the additional impurity formations. From the aforementioned results, we can conclude that the solid solution region of Li$_{1-x}$Sc$_{1-x}$Zr$_x$O$_2$ is 0 $\leq x \leq 0.1$ and that the ionic conductivity continuously increases in this region.

Figure 4 shows the results of the Rietveld refinement for the samples with $x = 0$ (Fig. 4a) and 0.1 (Fig. 4b). Tables 2 and 3 summarize the structural parameters determined by the refinement process for $x = 0.0$ and 0.1, respectively. Since there is a strong correlation between occupancy and atomic
displacement parameters for the structure refinement, the atomic displacement parameter of the Sc was firstly refined with fixing of its occupancy value as the nominal composition. After that the occupancy was refined using the refined atomic displacement parameter to obtain better fitting results. The agreement factors of $R_{wp}=11.55$ and 7.28 for $x=0.0$ and 0.1, respectively, show that the refined parameters are reliable. All the diffraction peaks are indexed to the space group $I4_1/amd (141)$ with tetragonal symmetry, with the exceptions of the reflections of impurities. The lattice parameters of LiScO$_2$ were $a = b = 4.1791(18)$ Å and $c = 9.3610(4)$ Å, which are nearly identical to the reported parameters ($a = b = 4.182$ Å, $c = 9.318$ Å$^3$). The lattice parameters of the sample with $x = 0.1$ are $a = b = 4.1804(16)$ Å and $c = 9.4186(3)$ Å; thus, doping with Zr$^{4+}$ increased the lattice parameters. The refinement results show that 10% Zr$^{4+}$ was doped at Sc$^{3+}$ sites in the structure, which is consistent with the nominal composition. Lithium vacancies may be formed to maintain the charge conservation in LiScO$_2$ because the Zr$^{4+}$ ion which has relatively higher valence compared to the Sc$^{3+}$ ion was partially substituted to the Sc site. The above results demonstrate that the ionic conductivity of LiScO$_2$ was improved by substitution with higher-aliovalent cations and that the lattice expansion and formation of lithium vacancies due to Zr$^{4+}$ doping contributed to the increase in the ionic conductivity of the LiScO$_2$ system.

4. Conclusion

LiScO$_2$ and Li$_{1-x}$Sc$_{1-x}$M$_x$O$_2$ (Zr$^{4+}$, Nb$^{5+}$, and Ta$^{5+}$) were synthesized by a solid-state reaction method, and the changes of ionic conductivities due to doping were evaluated. The ionic conductivities of Li$_{1-x}$Sc$_{1-x}$M$_x$O$_2$ were improved by two orders of magnitude, and the activation energies decreased. The highest ionic conductivity of $7.94 \times 10^{-6}$ S cm$^{-1}$ at 623 K was observed for the sample doped with 10% Zr$^{4+}$. The results of the crystal structure analysis and ionic conductivity measurements showed that the ionic conductivities of Li$_{1-x}$Sc$_{1-x}$M$_x$O$_2$ were improved because of the introduction of lithium vacancies in the structure by doping with higher-aliovalent cations. This revealed that the ionic conductivities of LiScO$_2$-based materials, which exhibit high chemical stabilities and are thermodynamically stable when placed in contact with pure Li, can be greatly improved by doping. Optimizing the solid solution formation region with suitable substitution element(s) and synthesis method(s), it is highly possible to develop new groups of solid lithium ion conductors that can be used in practical applications as solid electrolytes for all-solid-state lithium batteries.

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