Introduction

Solid electrolytes, one of the key materials for realizing all-solid-state batteries, are required to have high ionic conductivity, suitable deformability, and high chemical/electrochemical stability. A number of previous studies have suggested that sulfide-based electrolytes meet these requirements. In particular, the ionic conductivities of sulfide electrolytes reach $10^{-2}$ S cm$^{-1}$ at 25 °C, a value comparable to that of the organic liquid electrolytes used in commercial lithium-ion batteries.$^{1,12}$

Moreover, sulfide electrolytes have better deformability for densification than oxide electrolytes.$^{9}$ So far, various sulfides, such as Li$_2$S-P$_2$S$_5$ glass-based electrolytes,$^{4,5}$ thio-LISICON-type crystals,$^{10-14}$ Li$_4$GeP$_2$S$_{12}$-type crystals,$^{1,2,15,16}$ and argyrodite-type crystals,$^{17-20}$ have been reported as solid electrolytes. These solid electrolytes have been prepared with a wide range of compositions. For example, the thio-LISICON series have been prepared in the form of Li$_4$GeS$_4$-Li$_2$PS$_4$, Li$_4$GeS$_4$-Li$_5$GaS$_4$, Li$_5$PS$_4$-Li$_5$SiS$_4$, etc.$^{12,14,21}$ Further, the crystal structures and conductivities at room temperature of Li$_4$GeS$_4$, Li$_2$PS$_4$, and Li$_5$SiS$_4$, which are the terminal compositions in binary systems, have been reported. As the other terminal composition, Li$_5$GaS$_4$ has been reported to have a low conductivity of $5.1 \times 10^{-8}$ S cm$^{-1}$ at 100 °C$^{14}$ however, its crystal structure has not been reported. The Li$_5$GaS$_4$ crystals are stable at room temperature and can be readily prepared by heating a mixture of the starting materials. On the other hand, glassy and amorphous electrolytes are prepared by melt quenching or a mechanochemical process.$^{4,6}$ In general, glassy and amorphous electrolytes have higher conductivities than the corresponding crystalline phases, because of their higher free volumes. Such glasses are notable precursors for metastable superionic conductive crystals. For example, when the 70Li$_2$S-30P$_2$S$_5$ glass is heated to 240 °C, the superionic conductive phase of Li$_5$P$_2$S$_{11}$ precipitates as a metastable phase in the amorphous matrix.$^{6,8,22}$

In addition, metastable crystalline phases can be prepared directly via mechanochemistry,$^{31-24}$ and metastable crystalline phases often exhibit higher conductivities than the stable crystalline phases. For instance, Li$_7$Sn$_3$ prepared by heating a mixture of the starting materials has a stable orthorhombic crystal structure,$^{25,26}$ while the Li$_7$Sn$_3$ sample prepared by the mechanochemical process has the metastable hexagonal crystal structure.$^{24}$ Further, the metastable hexagonal Li$_7$Sn$_3$ has higher ionic conductivity than the stable orthorhombic Li$_7$Sn$_3$.

In this study, we focused on the thio-LISICON composition of Li$_5$GaS$_4$, whose crystal structure has not yet been clarified. In particular, the formation of the metastable phase of Li$_5$GaS$_4$ by a mechanochemical process (ball milling) was investigated. Subsequently, crystalline phases were obtained by heating the milled metastable Li$_5$GaS$_4$ sample at different temperatures. The structures of the different crystalline phases were analyzed by X-ray diffraction (XRD) and Raman spectral analyses, and the conductivities of the stable and metastable phases were also examined.

Experimental section

Li$_2$S (Mitsuwa Chemical Co., Ltd., 99.9%) and Ga$_2$S$_3$ (Kojundo Chemical Lab. Co., Ltd., 99.99%) powders were used as the
starting materials for the mechanochemical synthesis of the Li$_5$GaS$_4$ solid electrolyte. A stoichiometric mixture of 5Li$_2$S·1Ga$_2$S$_3$ (= Li$_5$GaS$_4$) was mechanochemically processed at 510 rpm for 100 h using a planetary ball mill apparatus (Pulverisette 7; Fritsch GmbH). In this process, 0.5 g of the mixture of the starting materials was milled in a 45 mL zirconia pot with 250 zirconia balls (diameter: 4 mm). After the mechanochemical process, the Li$_5$GaS$_4$ powder was collected; this sample is hereafter referred to as milled Li$_5$GaS$_4$. The milled powder was subsequently heated at 420 or 600 °C for 2 h in a dry argon atmosphere; the heat-treated Li$_5$GaS$_4$ samples are referred to as HT-420 °C or HT-600 °C, respectively. All the steps in the synthesis were carried out in a dry argon atmosphere.

X-ray diffraction (XRD) of the powder was performed on an X-ray diffractometer (SmartLab, Rigaku Corporation) using Cu-Kα radiation. The diffraction patterns were obtained in steps of 0.02° in the 2θ range of 10–80° at a scan rate of 10° min$^{-1}$. Rietveld refinement of the XRD patterns was performed using the RIETAN-FP software. The diffraction data for the Rietveld refinement were collected in steps of 0.02° in the 2θ range of 10–130° at a scan rate of 1° min$^{-1}$ using monochromatic Cu-Kα$_1$ radiation. For the Rietveld refinement, first, the peak shape, background coefficient, scale factor, and lattice constants were refined. Then, the occupancy was fixed at the stoichiometric composition, and the isotropic displacement parameters of sulfur and gallium were refined. The crystal models were obtained using the VESTA software.

Raman spectroscopic analysis to identify the local structural units in the solid electrolytes was carried out using a Raman spectrophotometer (LabRAM HR-800, HORIBA Ltd.) equipped with a 532 nm diode-pumped solid-state laser.

The ionic conductivity of the solid electrolyte was determined through electrochemical impedance spectroscopy. The impedance data were obtained in the frequency range of 10$^{-7}$ to 10$^{-1}$ Hz using an impedance analyzer (SI-1260, Solartron) at an applied AC voltage of 50 mV. The prepared electrolyte powders were pressed at 360 MPa to form pellets at room temperature (~25 °C). The diameter and thickness of the pellets were approximately 10 mm and 1 mm, respectively. Thin gold films were coated onto the entire surface of the pellets on both the sides to serve as current collectors. The ionic conductivity was measured in the temperature range of approximately 30–75 °C. Activation energies ($E_a$) were calculated from the slopes of the Arrhenius plots and then the conductivities at 25 °C ($\sigma_{25°C}$) was obtained by extrapolation.

Results

First, the solid electrolyte, milled Li$_5$GaS$_4$ was prepared by a mechanochemical process. Then, the milled sample was heated at 420 or 600 °C to obtain heated samples (HT-420 °C or HT-600 °C). The milled and heat-treated samples were white powders. Fig. 1 shows the powder XRD patterns of the as-milled and heated Li$_5$GaS$_4$ samples, along with those of the starting materials. The XRD patterns of the prepared Li$_5$GaS$_4$ samples contain peaks of unknown phases, as indicated by blue circles or red stars (Fig. 1). The peaks marked by blue circles are similar to those of Li$_2$S with an antifluorite-type structure belonging to the cubic system. The XRD pattern of the milled sample only
contains the set of peaks marked by blue circles. When the milled sample was heated at 420 °C, two sets of peaks (both the peaks marked by blue circles and by red stars) appeared in the XRD pattern. The peaks marked by red stars could be indexed to the monoclinic structure. Upon heating at a higher temperature of 600 °C, only the peaks marked by red stars were observed. Thus, as the heat-treatment temperature was increased, the peaks indexed to the cubic structure disappeared, while the peaks indexed to the monoclinic structure appeared. These results suggest that the cubic structure is the metastable phase, while the monoclinic structure is the stable phase.

Fig. 2 shows the Raman spectra of as-milled Li₅GaS₄ and the heated samples. The spectrum of the milled sample shows a broad peak centered at ~335 cm⁻¹. This peak may contain multiple peaks, but the peak separation is difficult. The peak does not include the component of Ga₂S₃ used as the starting material, because its main peak appears at a different wavenumber. Upon heating the sample, the Raman spectrum changed; an asymmetric peak appeared at ~345 cm⁻¹ in the spectrum of HT-420 °C, while two strong peaks appeared at ~310 and 340 cm⁻¹ for HT-600 °C. Note that the bands at ~310 and 340 cm⁻¹ have not been attributed to any units in glasses containing Ga₃S₃ in previous studies. Based on the X-ray crystal structure results of HT-600 °C, which will be discussed later, the Raman bands at 310 and 340 cm⁻¹ observed for HT-600 °C are assigned to isolated GaS₄ tetrahedral units.

To date, only the conductivity of Li₅GaS₄ has been reported, but not its crystal structure. Among the materials with the composition of Li₅MS₄ (M = B, Al, Ga, In, and Tl), only the crystal structure of Li₅AlS₄ has been analyzed in detail. The similarity of the XRD patterns of Li₅AlS₄ and Li₅GaS₄ was exploited to identify the crystal structure of Li₅GaS₄. The Rietveld refinement results for Li₅GaS₄ are presented in Fig. 3 and Table 1, and the crystal structure of Li₅GaS₄ is shown in Fig. 4. Li₅GaS₄ has the tetrahedral sites of lithium and gallium, and the octahedral site of lithium. In the Rietveld refinement of the XRD pattern of the HT-600 °C sample, the parameters reported for Li₅AlS₄ (P2₁/m [space group No. 11], α = 6.2488 Å, b = 7.8369 Å, c = 6.6853 Å, β = 90.333°) were used as the initial structural parameters, and then the parameters were refined using the Le Bail method. In the Rietveld refinement, the occupancy of all atoms and the atomic displacement parameters of Li were not refined. The full profile and Rietveld fitting of Li₅GaS₄ clearly reveal that the refined structure is almost accurate except for the difference in peak intensity at about 28°, which is probably due to the partial occupancy of gallium at the lithium site. Further analysis by neutron diffraction or single crystal X-ray diffraction is required to determine the lithium and gallium occupancy in detail.

Fig. 5 shows the temperature-dependence of the conductivities of the three Li₅GaS₄ samples. At the composition of Li₅GaS₄, the conductivities differed according to the heating temperature. The milled sample showed the highest conductivity of 2.2 × 10⁻⁵ S cm⁻¹ at 25 °C among the three prepared samples. The ionic conductivities of HT-420 °C and HT-600 °C at 25 °C were 8.1 × 10⁻⁷ and 2.1 × 10⁻⁸ S cm⁻¹, respectively.

Table 1  Crystallographic data of stable monoclinic Li₅GaS₄ obtained by the Rietveld refinement of the X-ray (Cu-Kα₂ radiation) diffraction. Fractional coordinates and occupancies for Li₅GaS₄: mW denotes the integrated combination of the multiplicity and Wyckoff letter.

<table>
<thead>
<tr>
<th>Site</th>
<th>mW</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occ.</th>
<th>U Å²</th>
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<tr>
<td>S1</td>
<td>2e</td>
<td>0.7539 (5)</td>
<td>1/4</td>
<td>0.8549 (6)</td>
<td>1</td>
<td>0.0120 (15)</td>
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<tr>
<td>S2</td>
<td>2e</td>
<td>0.2651 (5)</td>
<td>1/4</td>
<td>0.1749 (6)</td>
<td>1</td>
<td>0.0042 (11)</td>
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<tr>
<td>S3</td>
<td>4f</td>
<td>0.7557 (3)</td>
<td>0.0101 (3)</td>
<td>0.3322 (4)</td>
<td>1</td>
<td>0.0096 (9)</td>
</tr>
<tr>
<td>Ga</td>
<td>2e</td>
<td>0.6326 (3)</td>
<td>1/4</td>
<td>0.1706 (3)</td>
<td>1</td>
<td>0.0087 (7)</td>
</tr>
<tr>
<td>Li1</td>
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<td>0.3290 (27)</td>
<td>1</td>
<td>0.0127</td>
</tr>
<tr>
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<td>0.8413 (44)</td>
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<td>0.0127</td>
</tr>
<tr>
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<td>0.4967 (36)</td>
<td>1</td>
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<td>1</td>
<td>0.0127</td>
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</table>

The activation energies of the milled sample, HT-420 °C, and HT-600 °C were calculated to be 37, 44, and 47 kJ mol⁻¹, respectively.

Discussion

In the XRD patterns of the prepared Li₅GaS₄ samples (Fig. 1), the peaks of the milled sample are comparable to those of Li₂S, one of the two starting materials. However, the Raman band of crystalline LiS at ~370 cm⁻¹ was not clearly observed in the Raman spectrum of the milled Li₅GaS₄ sample. Thus, the peaks marked by blue circles in the XRD patterns were assigned to the antifluorite-type crystal structure, and not to the starting material Li₂S. Although a detailed analysis of the metastable crystal phase is difficult because of the broad XRD peaks, the observed XRD peaks can be attributed to a new metastable phase with the antifluorite-type crystal structure, which has eight tetrahedral sites for the cation surrounded by four anions in a unit cell. In general, in a cation-disordered crystal structure, the cation sites are randomly occupied by cations or defects. In the case of antifluorite-type Li₅GaS₄, lithium cations, gallium cations, and defects randomly occupy the eight cation sites. The metastable antifluorite-type Li₅GaS₄ has a similar structure to the monoclinic Li₅GaS₄ (Fig. 4) because both phases are composed of isolated GaS₄ tetrahedra. The ionic radii of lithium and gallium cations in the antifluorite-type crystal are however significantly different; the sizes of Li⁺ and Ga³⁺ are 0.59 Å and 0.47 Å under tetrahedral coordination (n = 4; n is the coordination number), respectively. The cation sites of the antifluorite-type structure seem to have a high tolerance to the size of the cations. Such a cation-disordered phase has been previously reported for Li₄SnS₄ and Li₂TiS₃. In the crystal structure of hexagonal Li₄SnS₄, the tetrahedral sites are occupied by Li⁺ (rionic (n = 4): 0.59 Å) and Sn⁴⁺ (rionic (n = 4): 0.55 Å). In the mechanochemically synthesized Li₅TiS₄, the octahedral sites are occupied by cations of different sizes, viz., Li⁺ (rionic (n = 6): 0.76 Å) and Ti⁴⁺ (rionic (n = 6): 0.605 Å). These results indicate that cation disorder is possible not only in a structure with cations of similar sizes but also in structures containing cations of different sizes prepared by the mechanochemical process. Thus, the mechanochemical process is effective in the preparation of disordered structures, and the obtained disordered structures are metastable and have faster ionic conduction than the thermodynamically stable phases. The milled Li₅GaS₄ sample with a metastable crystal structure has higher...
conductive carriers are important for fast ionic conduction. Considering those of Li₅AlS₄ (9.7 × 10⁻⁸ S cm⁻¹) and Li₅SbS₄ (4.8 × 10⁻⁸ S cm⁻¹), the conductivity of HT-600 °C is much higher than that of the heated sample with the stable monoclinic crystal phase. This results from the precipitation of the metastable phase. Thus, among the three samples prepared in this study, the as-milled sample with the metastable antifluorite-type crystal phase has the highest conductivity, while the HT-600 °C sample with the stable monoclinic crystal phase has the lowest conductivity. The results clearly indicate that the antifluorite-type crystal is more suitable for ionic conduction than the monoclinic crystal.

Conclusions

In this study, sulfide antifluorite-type structure is proposed as a new framework for ionic conduction. A metastable Li₅GaS₄ solid electrolyte was prepared by a mechanochemical process and subsequently transformed into a stable Li₅GaS₄ solid electrolyte by heat treatment. The mechanochemically processed sample had the metastable antifluorite-type phase. When heated at 600 °C, the phase transformed to the stable monoclinic one, similar to that of Li₅AlS₄. The conductivity of the milled sample (metastable antifluorite-type phase) was determined to be 2.1 × 10⁻⁸ S cm⁻¹ at 25 °C, which is three orders of magnitude higher than that of the heated sample with the stable phase. Thus, it is concluded that the metastable phase is a more suitable structure for ionic conduction than the stable phase at the composition of Li₅GaS₄. The results of this study extend research toward understanding sulfide electrolytes with cation-disordered metastable phases and cation-ordered stable phases, and contribute to the development of solid electrolytes with high ionic conductivity.

Author contributions

T. K., A. S., and A. H. designed the experiments and wrote the paper. T. K. synthesized and characterized the electrolytes. T. K. and C. H. performed the crystal analysis. A. S., T. M., and A. H. supervised the study. All of the authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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References