Solid electrolytes Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ prepared via a mechanochemical process

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Solid electrolytes are important materials for enhancing the performance of all-solid-state sodium rechargeable batteries. Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ (0 ≤ x ≤ 1.2) samples were prepared using a mechanochemical process, followed by heat treatment and their structures and ionic conductivities were investigated. Glassy samples were obtained via the mechanochemical process; the samples with the Na$_{11}$Sn$_2$PS$_{12}$ type crystal structure were obtained for all the prepared compositions through the heat treatment of the glasses. The Na$_{11}$Sn$_2$PS$_{12}$ (x = 1) sample obtained by heat treatment at 300 °C exhibited an ionic conductivity of 2.6 × 10$^{-4}$ S cm$^{-1}$ at 25 °C, which was the highest conductivity observed among all the samples with Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ (0 ≤ x ≤ 1.2) compositions.

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1. Introduction

All-solid-state sodium rechargeable batteries have attracted significant attention as promising next-generation large-scale energy storage systems because they are expected to show superior safety and performance at low cost. The inexpensiveness is attributed to the abundance of sodium. Moreover, some electrochemical characteristics, such as standard reduction potential, of sodium are similar to those of lithium.\textsuperscript{1–3} The primary materials used in these batteries are solid electrolytes with high ionic conductivities.

We reported in a previous study that the Na$_3$PS$_4$ solid electrolyte with metastable cubic phase has a sodium ionic conductivity of 4.6 × 10$^{-4}$ S cm$^{-1}$ at 25 °C,\textsuperscript{6,7} which was higher than that of the stable tetragonal Na$_3$PS$_4$ crystal (1 × 10$^{-5}$ S cm$^{-1}$).\textsuperscript{8} The Na$_3$PS$_4$ solid electrolyte was prepared via a mechanochemical technique and subsequent heat treatment. Moreover, the all-solid-state cells (Na$_3$Sn$_4$ alloy/Na$_3$PS$_4$ solid electrolyte/TiS$_2$) were successfully operated as rechargeable batteries at room temperature.\textsuperscript{8} After the discovery of the cubic Na$_3$PS$_4$, some sodium sulfides such as Na$_3$SbS$_4$ have been found to exhibit high ionic conductivities exceeding 1 mS cm$^{-1}$ at room temperature.\textsuperscript{9–11} The cubic Na$_3$PS$_4$ has the Na$_3$Sn$_2$PS$_{12}$ phase, which has a sodium ionic conductivity of 4.6 × 10$^{-4}$ S cm$^{-1}$ at 25 °C,\textsuperscript{12} which was the highest conductivity observed among all the samples with Na$_3$PS$_4$ (0 ≤ x ≤ 1.2) compositions.\textsuperscript{13–15}

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Na$_{10}$GeP$_2$S$_{12}$ (2Na$_3$PS$_4$Na$_4$GeS$_4$) is a solid electrolyte that comprises a larger number of sodium ions than Na$_3$PS$_4$.\textsuperscript{13} Although Kandagal et al. have reported the ionic conductivity of the Na$_{10}$GeP$_2$S$_{12}$ solid electrolyte to be 10$^{-3}$ S cm$^{-1}$ from AIMD simulations,\textsuperscript{14} the experimental ionic conductivity was found to be 2.4 × 10$^{-5}$ S cm$^{-1}$.\textsuperscript{11–13} Na$_{11}$Sn$_2$PS$_{12}$, with an ionic conductivity of over 10$^{-4}$ S cm$^{-1}$,\textsuperscript{15,16} and Na$_{11}$Sn$_2$PS$_{12}$, with an ionic conductivity of over 10$^{-3}$ S cm$^{-1}$,\textsuperscript{16,17} were reported in 2016 and 2018, respectively. The Na$_{11}$Sn$_2$PS$_{12}$ was synthesized by the solid-state method. However, materials with compositions between Na$_{10}$Sn$_2$PS$_{12}$ and Na$_{11}$Sn$_2$PS$_{12}$ have not been reported. Therefore, the structures and ionic conductivities of these materials are worth investigating. Moreover, the materials enriched with additional sodium and tin have also been focused on in this study.

In this study, Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ (0 ≤ x ≤ 1.2) solid electrolytes were synthesized using a mechanochemical technique and consecutive heat treatment. Metastable phases are often obtained by the crystallization of the glasses. Therefore, we first prepared the glasses with the composition of Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ (0 ≤ x ≤ 1.2) via a mechanochemical process, following which the crystal phases were obtained by the heat treatment of the prepared glasses. The structure of Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ was investigated by X-ray diffraction (XRD) and Raman spectroscopy. The thermal stabilities were measured by differential thermal analysis (DTA). The ionic conductivities of...
Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ were evaluated through the AC impedance method.

2. Experimental procedure

Stoichiometric mixtures of Na$_2$S (> 99.1%; Nagao), P$_2$S$_5$ (> 99%; Sigma-Aldrich), and SnS$_2$ (> 99.5%; Mitsuwa Chem.) were weighed based on the chemical formula of Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ (0 ≤ x ≤ 1.2) and mechanochemically processed using a planetary ball mill (Pulverisette 7; Fritsch GmbH) with a 45 mL zirconia pot and 500 zirconia balls (4 mm in diameter). The total mass of the starting materials, rotation speed, and milling duration were 1.0 g, 380 rpm, and 17 h, respectively. The rotation speed and milling duration are the same as those reported for the synthesis of Na$_{10}$SnP$_2$S$_{12}$.$^{15}$ All the processes were performed in a dry Ar atmosphere. The report ed Na$_{10}$SnP$_2$S$_{12}$ solid electrolyte was heat-treated at 700 °C for 12 h in an evacuated quartz tube,$^{15}$ while the milled Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ (0 ≤ x ≤ 1.2) powders were heated for 1 h in an electric furnace in this study. Na$_{11}$Sn$_2$PS$_{12}$ was also prepared by the solid-state method under similar conditions as mentioned in Ref. 17. The hand grinded powder was placed in a carbon crucible, sealed in a quartz tube under vacuum, and subsequently heated at 700 °C for 5 h.

XRD measurements of the prepared materials were carried out using CuKα radiation with a diffractometer (SmartLab; Rigaku) at room temperature. The diffraction data were collected in steps of 0.01° in the 2θ range of 10.0–80.0°. DTA was performed using a thermal analyzer (Thermo Plus TG8110; Rigaku Corp.) at the heating rate of 10 °C min$^{-1}$. Raman spectroscopy was performed using a Raman spectrophotometer (LabRAM HR-800; Horiba) with a 532 nm solid-state laser to identify the structural units. The solid electrolytes were placed in an airtight vessel filled with dry Ar gas.

The ionic conductivities of the prepared Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ solid electrolytes were measured by electrochemical impedance spectroscopy (EIS). The data were collected in the frequency range from 10 Hz to 1 MHz using an impedance analyzer (1260, Solartron) with an applied AC voltage of 50 mV. The temperature range for the conductivity measurements was between 25 to 100 °C and the samples were left for 1.5 to 2 h until they reached the preset temperatures. The measurements were carried out using pellets (10 mmφ) cold-pressed at 360 MPa. The Na$_{11}$Sn$_2$PS$_{12}$ pellet for comparison was sintered at 480 °C for 1 h after cold pressing the powder which was heated at 700 °C for 5 h. As ion-blocking electrodes, gold thin films (10 mmφ) were deposited on both faces of the pellets with a quick coater (Quick Coater SC-701; Sanyu Electron). To prevent air exposure, each pellet was sealed in a laminate-type pouch cell.

3. Results and discussion

Figure 1 shows the XRD patterns of the as-milled Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ (0 ≤ x ≤ 1.2) samples. All the obtained samples showed halo XRD patterns, suggesting that all the starting materials underwent reaction, resulting in samples with amorphous phases. This tendency was similar to the one reported for Na$_{10}$GeP$_2$S$_{12}$.$^{13}$ The DTA curves of the as-milled Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ (0 ≤ x ≤ 1.2) samples are shown in Fig. 2. Glass transition behavior was slightly observed below the exothermic peaks corresponding to the crystallization. For example, the glass transition temperature (T$_g$) of the x = 0.3 sample was 240 °C, as shown in Fig. S1. Therefore, the as-milled samples were defined as glass electrolytes.
Hereafter, the structure and ionic conductivity with respect to different heat treatment temperatures are discussed for the Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ ($x = 0.3$) sample as a representative.

The Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ glass was heated at 200, 260, 300, and 400 °C as indicated by the red arrows in Fig. S1. The XRD patterns of the Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ samples prepared at different heat treatment temperatures are shown in Fig. 3. Even after heating at 200 °C, an amorphous phase was observed. It is because the sample was not crystalized at 200 °C as the $T_g$ of the Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ glass is 240 °C. After heating at 260 and 300 °C, the samples with XRD patterns similar to that of the reported Na$_{11}$Sn$_2$PS$_{12}$ were obtained. The sample heated at 300 °C has higher crystallinity than that heated at 260 °C. In contrast, when the glass was heated at 400 °C, a second phase Na$_3$PS$_4$ was obtained along with the Na$_{11}$Sn$_2$PS$_{12}$ phase. In the DTA curve, a broad exothermic peak was observed at 315 °C. It is evident from the XRD patterns that the exothermic peak can be attributed to the crystallization of Na$_3$PS$_4$.

The conductivities $\sigma$ of the pelletized Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ samples were measured using EIS. The temperature dependence of the ionic conductivities of the Na$_{10.3}$Sn$_{1.3}$-P$_{1.7}$S$_{12}$ glass is shown in Fig. 4(a). The inset in Fig. 4(a) is the Nyquist plot of the Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ glass at 30 °C. A semicircle in the higher-frequency region and a spike in the lower-frequency region were observed. Because the bulk and grain boundary components were difficult to separate, the total conductivity was determined from the total resistance $(R)$, shown as a black arrow in Fig. 4(a). The temperature dependence of the ionic conductivities obeyed the Arrhenius equation [$\sigma = \sigma_0 \exp(-E_a/RT)$], where $\sigma_0$ and $E_a$ are the pre-exponential factor and activation energy for conduction, respectively. The ionic conductivities at 25 °C ($\sigma_{25}$) of the Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ samples heated at different temperatures are shown in Fig. 4(b). Moreover, the ionic conductivities at 25 °C ($\sigma_{25}$) and activation energies of the Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ glass and heated samples are shown in Table 1. The ionic conductivity of the Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ glass was $1.7 \times 10^{-5}$ S cm$^{-1}$ at 25 °C. The ionic conductivity of the Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ sample heated at 200 °C was $2.5 \times 10^{-5}$ S cm$^{-1}$, which was close to that of the glass because of the presence of the glass phase in the Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ sample heated at 200 °C. The Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ sample heated at 260 °C showed the ionic conductivity of $7.5 \times 10^{-5}$ S cm$^{-1}$. It was higher than that of glass electrolyte, suggesting that the obtained crystal phase exhibited a high ionic conductivity. The ionic conductivity of Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ heated at 300 °C was $1.1 \times 10^{-4}$ S cm$^{-1}$, which became higher than that of the sample heated at 260 °C, owing to higher crystallinity. When heated at 400 °C, the sample showed a higher ionic conductivity of $3.0 \times 10^{-4}$ S cm$^{-1}$.

### Table 1. Ionic conductivities and activation energy of the milled Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ samples heated under different temperatures

| HT temp. | $\sigma_{25}$/S cm$^{-1}$ | $E_a$/kJ mol$^{-1}$ |
|----------|--------------------------|---------------------|
| not heated | $1.7 \times 10^{-5}$ | 42 |
| 200 | $2.5 \times 10^{-5}$ | 41 |
| 260 | $7.5 \times 10^{-5}$ | 35 |
| 300 | $1.1 \times 10^{-4}$ | 34 |
| 400 | $3.0 \times 10^{-4}$ | 30 |

Fig. 3. XRD patterns of the heated Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ samples.

Fig. 4. (a) Temperature dependence of the ionic conductivities for Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ glass. (Inset): Nyquist plots of Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ glass at 30 °C. (b) Ionic conductivities of the Na$_{10.3}$Sn$_{1.3}$P$_{1.7}$S$_{12}$ heated samples at 25 °C.
The conductivity enhancement was mainly owing to a higher crystallinity of Na$_{11}$Sn$_2$PS$_{12}$ phase compared to the sample heated at 300 °C. In order to avoid the contribution of Na$_3$PS$_4$ by-products to the conductivity of the Na$_{10}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ samples, the other Na$_{10}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ (0 ≤ x ≤ 1.2) glassy electrolytes were heated at 300 °C for crystallization.

The XRD patterns of Na$_{10}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ samples heated at 300 °C are shown in Fig. 5. All the heated samples mainly exhibited the Na$_{11}$Sn$_2$PS$_{12}$ phase. Meanwhile, the secondary Na$_3$PS$_4$ phase was observed in the x = 0 and 0.2 compositions. The reported Na$_{10}$Sn$_2$PS$_{12}$ (x = 0), which was prepared by ball milling, heating at 700 °C in an evacuated quartz tube, and slow cooling to room temperature, included Na$_2$S, P$_2$S$_5$, and Na$_3$PS$_4$ as impurities. These results suggest that it is challenging to synthesize the single Na$_{10}$Sn$_{2+x}$P$_{2-x}$S$_{12}$ phase in the range of 0 ≤ x ≤ 0.2 via a mechanochemical process. In addition, the existence of unknown phases was observed in the XRD patterns of x = 1.1 and 1.2. There is a possibility that the range of 1 < x is outside the solid solution formation region. The single Na$_{11}$Sn$_2$PS$_{12}$-type crystals were obtained only in the range of x = 0.3 to 1. Moreover, as shown by aligning the diffraction peaks at 2θ = 37.5° (marked with a blue dashed line in Fig. S2), the peaks of Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ samples inclined to shift to lower angles with increasing x. Meanwhile, the lattice parameter increased with increasing x. Theionic radii of four-coordinated P and Sn are 0.17 and 0.55 Å, respectively. Thus, the lattice parameter expanded because of the successful substitution of P to Sn.

To investigate the difference of the local structure, the Raman spectra of Na$_{10+x}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ (0 ≤ x ≤ 1.2) were measured (Fig. 6). The intensity ratio of PS$_{4-}^{3-}$ to SnS$_4^{4-}$ decreased with increasing x, corresponding to their compositions, suggesting that P was successfully substituted with Sn. Moreover, the SnS$_4^{4-}$ band of the x = 1.2 composition shifted to a lower wavenumber compared with those of other compositions, suggesting that the x = 1.2 composition was outside the solid solution formation range. This is also evident from the results of XRD patterns, as shown in Fig. 5. The Sn$_2$S$_7^{6-}$ units, which could not be included in the Na$_{11}$Sn$_2$PS$_{12}$ crystal structure, would be included in the amorphous phase.

The ionic conductivities of the Na$_{10}$Sn$_{1+x}$P$_{2-x}$S$_{12}$ (0 ≤ x ≤ 1.2) glasses and heated samples are shown in Fig. 7. All the samples were heated at 300 °C. Measurements were carried out for pelletized milled or heated powders.
The ionic conductivities of the milled samples slightly increased with increasing $x$. However, they had almost the same value of 10^{-3} S cm^{-1} at 25 °C. The slight increase in the ionic conductivities was attributed to the increase of the sodium-ion content in the glass phase. From $x = 0$ to 1, the ionic conductivities of the heated samples increased with increasing $x$. This could be because the lattice volume became larger and the number of sodium ions increased. In contrast, over $x = 1$, the conductivities decreased with increasing $x$. The decreased ionic conductivities could be attributed to the unknown phases interrupting the ion conduction. These results suggest that the observed phase and their structure are correlated with ionic conductivity. The ionic conductivities and activation energy of the Na_{10+x}Sn_{1+x}P_{2-x}S_{12} (0 ≤ x ≤ 1.2) milled and heated samples are listed in Tables S1 and S2, respectively.

The Na_{11}Sn_{2}PS_{12} $(x = 1)$ heated sample showed the highest ionic conductivity of 2.6 × 10^{-4} S cm^{-1} at 25 °C. However, the reported Na_{11}Sn_{2}PS_{12} samples exhibited ionic conductivities over 10^{-3} S cm^{-1} [16,17]. One of the reasons is that they are sintered bodies, while our pellets were prepared by cold pressing for the heated powder sample. Therefore, the structures and ionic conductivities of the Na_{11}Sn_{2}PS_{12} samples prepared under different heating conditions were investigated. The milled Na_{11}Sn_{2}PS_{12} powder was heated using the same conditions as those employed in Ref. 17. The obtained powder was pressed at 360 MPa and heated at 480 °C for 1 h to prepare a sintered body. The sample is denoted as sintered sample in this paper. The XRD patterns of the Na_{11}Sn_{2}PS_{12} glass, heated sample, and sintered sample are displayed in Fig. S3. The phase of sintered sample was a single Na_{11}Sn_{2}PS_{12} phase, and was the same as the heated sample. The crystallinity of the phase of sintered sample was higher than that of the heated sample phase, because of its higher and longer heating temperature. The ionic conductivity of the sintered sample was similar to those of reported for the Na_{11}Sn_{2}PS_{12} crystal. It suggests that the composition dependence of ionic conductivities is similar for the samples prepared by the solid-state method and the mechanochemical process. From these results, the Na_{11}Sn_{2}PS_{12} sample was found to have the best composition for application as a sodium-ion conductor, among samples with the Na_{10+x}Sn_{1+x}P_{2-x}S_{12} (0 ≤ x ≤ 1.2) composition. It was superior pertaining to the easy preparation of the single phase, large lattice parameter, and large number of sodium ions.

4. Conclusions

Glassy and crystalline Na_{10+x}Sn_{1+x}P_{2-x}S_{12} (0 ≤ x ≤ 1.2) samples were prepared using a mechanochemical process, followed by heat treatment on some samples. The glass samples were obtained following the mechanochemical process. Meanwhile, samples with the Na_{11}Sn_{2}PS_{12} crystal phase were obtained by heating the glasses at 300 °C. The range for the formation of the single phase was 0.3 ≤ x ≤ 1. Although the frame structure was almost the same among the Na_{10+x}Sn_{1+x}P_{2-x}S_{12} (0 ≤ x ≤ 1.2) samples, the ratio of PS_{4}^{3-} to SnS_{4}^{2-} changed with increasing x, corresponding to their compositions. The ionic conductivity of Na_{10+x}Sn_{1+x}P_{2-x}S_{12} glass remained nearly the same, i.e., 10^{-3} S cm^{-1} at 25 °C. In contrast, the ionic conductivities of the heated samples increased with increasing x at 0 ≤ x ≤ 1. In contrast, the conductivities decreased at x > 1. The Na_{11}Sn_{2}PS_{12} $(x = 1)$ heated sample showed the highest ionic conductivity of 2.6 × 10^{-4} S cm^{-1} at 25 °C. The sintered body of the Na_{11}Sn_{2}PS_{12} sintered sample showed 1.1 × 10^{-3} S cm^{-1}, which was the same as that reported for the Na_{11}Sn_{2}PS_{12} crystal prepared by the solid-state method. From these results, the range of formation of single-phase Na_{10+x}Sn_{1+x}P_{2-x}S_{12} and the composition for obtaining the highest ionic conductivity were found.

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