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Preparation and characterization of highly sodium ion conducting 
Na$_3$PS$_4$-Na$_4$SiS$_4$ solid electrolytes

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Abstract

This study investigated electrical and electrochemical properties of (100-x)Na3PS4•xNa4SiS4 (mol%) glass-ceramics prepared using mechanical milling and consecutive heat treatment. Glass-ceramics at the compositions of 0 ≤ x ≤ 10 exhibited higher conductivity than 10⁻⁴ S cm⁻¹ at room temperature, which was achieved by precipitation of cubic Na₃PS₄ crystal with high sodium ion conductivity. The conductivity increased concomitantly with increasing Na₄SiS₄ contents at compositions of 0 ≤ x ≤ 6. The glass-ceramic with 6 mol% Na₄SiS₄ exhibited conductivity of 7.4×10⁻⁴ S cm⁻¹ at room temperature, which is the highest value reported for Na⁺ ion conducting sulfides to date. The conductivities of the glass-ceramics in the composition range of 25 ≤ x ≤ 100, where unknown phases are crystallized, were 10⁻⁷ – 10⁻⁵ S cm⁻¹. These were lower than the conductivities of the corresponding glasses before heat treatment. The 90Na₃PS₄•10Na₄SiS₄ electrolyte showed a wide electrochemical window of 5 V.
1. Introduction

Rechargeable batteries capable of storing renewable energy generated from solar and wind power sources are a key technology in the effort to reduce greenhouse gas emissions. Rechargeable lithium batteries are widely used today in portable power storage applications. However, flammable organic liquid electrolytes present safety concerns. Moreover, lithium resources are limited and are present in remote or in politically sensitive areas. Increasing demand for large lithium-ion batteries in electric vehicles will engender rising costs of lithium resources. Further development of safe, low-cost lithium batteries is necessary for widespread popularization of large rechargeable batteries for use in vehicles and distributed power applications. All-solid-state batteries are safe because they do not suffer from leakage, volatilization, or flammability of electrolytes. They employ inorganic solid electrolytes instead of organic liquid electrolytes.1–2 Rechargeable sodium-ion batteries are more suitable than lithium-ion batteries for use in energy storage systems from the viewpoint of production costs based on abundant sodium sources.3–6 Therefore, all-solid-state sodium secondary batteries are anticipated for use as next-generation batteries providing high safety and low cost for use with distributed energy sources.

Very recently, we reported that all-solid-state sodium batteries with a Na₃PS₄ glass–ceramic electrolyte operated successfully as rechargeable batteries at room temperature.7 The high conductivity of the Na₃PS₄ glass–ceramic was 4.6×10⁻⁴ S cm⁻¹ at room temperature,8 which was achieved by precipitation of the cubic Na₃PS₄ crystal with high Na⁺ ion conductivity. To improve all-solid-state sodium battery performance, solid electrolytes with higher Na⁺ ion conductivity must be developed.

For lithium ion conductors, Kanno et al. reported that Li₃PS₄-based crystals, where Li₄GeS₄ was partially substituted for Li₃PS₄, showed higher conductivity than Li₃PS₄ and Li₄GeS₄ crystals.9 Recently, Li₁₀GeP₂S₁₂ crystal showed extremely high lithium ion conductivity of more than 10⁻² S cm⁻¹ at room temperature.10 We also reported that the partial substitution of Li₄SiS₄ for Li₃PS₄ was effective for increasing the conductivity of Li₃PS₄ glass–ceramics.11 To increase the conductivity of Na₃PS₄
glass–ceramics, we have particularly studied partial substitution of Na₄SiS₄ for Na₃PS₄ because the introduction of Si element is effective for increasing conductivity of the Li₃PS₄ glass–ceramic system.

For this study, (100-x)Na₃PS₄•xNa₄SiS₄ (mol%) glass–ceramics were prepared using mechanical milling and heat treatment (HT). The relation between crystals precipitated in the (100-x)Na₃PS₄•xNa₄SiS₄ glass–ceramics and their ionic conductivities was investigated. Thermal and electrochemical properties of glass–ceramics were also evaluated.

2. Experimental

A mixture of Na₂S (> 99.1%; Nagao Co.), P₂S₅ (> 99%; Aldrich Chemical Co. Inc.), and SiS₂ (> 99.9%; Furuuchi Chemical Co.) powders at the composition of (100-x)Na₃PS₄•xNa₄SiS₄ (mol%) was mechanically milled at ambient temperature using a planetary ball mill apparatus (Pulverisette 7; Fritsch GmbH) with a zirconia pot (45 ml) and 500 zirconia balls (4 mm diameter). The rotation speed was 510 rpm. Milling durations were 1.5–25 hours. After mechanical milling, the powdered samples were compressed with a conventional uniaxial cold press to prepare 10-mm-diameter, 1–1.5-mm-thick pellets. To obtain the glass–ceramics, the milled sample pellets were crystallized by heating at an appropriate temperature between 220°C and 360°C in an electric furnace for 2 h. The heating temperature was selected based on crystallization temperatures determined using differential thermal analysis (DTA). All processes were performed in a dry Ar atmosphere. The XRD measurements of the prepared materials were performed using Cu Kα with a diffractometer (Ultima IV; Rigaku Corp.). Diffraction data were collected in 0.01° steps from 10.0° to 60.0° in 2θ. DTA was performed using a thermal analyzer (thermo Plus TG8110; Rigaku Corp.). The heating rate was 10°C min⁻¹.

Ionic conductivities of the pelletized (100-x)Na₃PS₄•xNa₄SiS₄ milled samples and the heated samples prepared at various temperatures were evaluated using AC impedance measurements. The pellets were then coated with carbon paste on both faces to form ion-blocking electrodes. Two stainless steel
disks coupled with Pt wires were attached to the pellets as current collectors. AC impedance measurements were conducted for the cell using dry Ar gas flow with an impedance analyzer (1260; Solartron Analytical) at frequencies of 10 Hz to 8 MHz. Cyclic voltammetry measurements were conducted to investigate the electrochemical properties of the solid electrolytes. A stainless-steel disk as the working electrode and a sodium foil as the counter and reference electrode were attached to each face of the pellet. Cyclic voltammograms of the 90Na3PS4•10Na4SiS4 glass–ceramic were obtained with a scan rate of 5 mV s\(^{-1}\) between −0.5 and 5.0 V (vs. Na\(^+/\)Na) at 25 °C. A stainless-steel disk as the working electrode and a sodium foil as the counter and reference electrode were attached to each pellet face.

3. Results and Discussion

Figure 1 presents XRD patterns of the (100-\(x\))Na3PS4•\(x\)Na4SiS4 samples prepared using mechanical milling. A cubic Na3PS4 phase was crystallized using a milling process in the samples at the composition range of 0 ≤ \(x\) ≤ 10. We recently reported the cubic Na3PS4 phase that was obtained directly at the composition \(x=0\) using Na2S (Nagao Co.) as a starting sodium source,\(^8\) while a Na3PS4 glass was prepared using Na2S (Aldrich Co.).\(^7\) Halo patterns were observed for samples between 25 ≤ \(x\) ≤ 100, suggesting that glass samples were obtained.

Figure 2 shows DTA curves of the (100-\(x\))Na3PS4•\(x\)Na4SiS4 milled samples. An exothermic peak attributable to crystallization was observed for the glass samples (\(x=67\) and 100). A broad exothermic peak was also observed for the samples (\(x=0\) and 10) where the cubic Na3PS4 phase was precipitated directly using a milling process. A glassy component partially remaining in the milled samples was crystallized. The pelletized samples were thus heat treated at over those crystallization temperatures as shown in Figure 2. The heat-treated samples are described as “glass–ceramics”.

Figure 3 shows XRD patterns of the (100-\(x\))Na3PS4•\(x\)Na4SiS4 glass–ceramics. Silicon was used as an internal standard in XRD measurements. In the composition range of 0 ≤ \(x\) ≤ 10, the intensity of the
peaks attributable to the cubic Na₃PS₄ increased. No new peaks attributable to other crystalline phases appeared. The crystallite size of cubic Na₃PS₄ at the composition of x=0 was determined by the Scherrer equation from the full width of half maximum of the peak with the highest intensity; the size of cubic Na₃PS₄ increased from ca. 13 nm to ca. 22 nm by the heat treatment. At the composition of x=25, new peaks in addition to the peaks of the cubic Na₃PS₄ were observed. Only new peaks appeared at the composition of x=67. The pattern at the composition of x=100 differed completely from that of x=67, indicating that a different unknown phase was precipitated in the glass–ceramic of x=100. Unfortunately, we have not identified these two unknown phases at the present stage. In the following discussion, we describe the unknown phases observed at the composition of x=67 and x=100 as “unknown I” and “unknown II” phases, respectively.

The temperature dependence of conductivity of the 94Na₃PS₄•6Na₄SiS₄ glass–ceramic pellets is portrayed in Figure 4. The inset shows a complex impedance plot of the glass–ceramic measured at 25°C. In the plot, a part of a semicircle in the higher-frequency region and a spike in the lower-frequency region were observed, suggesting that the glass–ceramic behaves as a typical ionic conductor. The former component was attributed to bulk and grain boundary contributions, which were not separated distinctly. The total conductivity, which includes bulk and grain-boundary components, was determined from the total resistance (Rₜotal) at the cross-section of the semicircle and the spike on the x-axis. The total conductivity obeys the Arrhenius equation, σ = σ₀ exp (-Eₐ / RT). Therefore, activation energy (Eₐ) for conduction was calculated from the slope in the temperature dependence of conductivity.

Figure 5(a) shows the composition dependence of ambient temperature conductivities of the (100-x)Na₃PS₄•xNa₄SiS₄ samples. Open circles denote the conductivity for the as-prepared samples by milling. In the composition range of 25 ≤ x ≤ 100, where amorphous samples were obtained, the conductivities of the as-prepared samples were about 10⁻⁵ S cm⁻¹. In the composition range of 0 ≤ x ≤ 10, where the samples included the cubic Na₃PS₄ phase, the conductivities were 10⁻⁵ – 10⁻⁴ S cm⁻¹. Closed
circles denote conductivity for the heat-treated samples (glass–ceramics). In the composition range of $25 \leq x \leq 100$, where the unknown I or II phase was precipitated, the conductivities of the glass–ceramics were $10^{-7} - 10^{-5}$ S cm$^{-1}$; the conductivities were lower than those of as-prepared samples. Conductivities of the unknown I or II crystals are expected to be lower than those of the amorphous samples. In the composition range of $0 \leq x \leq 10$, where the cubic Na$_3$PS$_4$ phase was mainly crystallized, the conductivities increased to more than $10^{-4}$ S cm$^{-1}$ by heat treatment. All the glass–ceramics in the composition range were prepared by heat-treatment at 220°C. Figure 5(b) shows the composition dependence of ambient temperature conductivities and activation energies for conduction of the (100-x)Na$_3$PS$_4$$\cdot$$x$Na$_4$SiS$_4$ ($0 \leq x \leq 10$) glass–ceramics. The conductivity increased with an increase of the $x$ content from $x=0$ to 6 in the (100-x)Na$_3$PS$_4$$\cdot$$x$Na$_4$SiS$_4$, whereas the activation energies were similar in the composition range. Improvement of the conductivities would be attributed to the increase of pre-exponential factor ($\sigma_0$). The 94Na$_3$PS$_4$$\cdot$$6$Na$_4$SiS$_4$ glass–ceramic showed the highest conductivity of $7.4\times10^{-4}$ S cm$^{-1}$, which was 1.7 times higher than the conductivity of the Na$_3$PS$_4$ glass–ceramic ($x=0$). The conductivity of glass-ceramics is affected by both precipitated crystalline phases and glass compositions. Although the conductivity of the Na$_4$SiS$_4$ glass ($2\times10^{-5}$ S cm$^{-1}$ as shown in Fig. 5(a)) is higher than that of the Na$_3$PS$_4$ glass ($6\times10^{-6}$ S cm$^{-1}$), the conductivity of the 94 Na$_3$PS$_4$$\cdot$$6$ Na$_4$SiS$_4$ glass–ceramic is two orders of magnitude higher than that of the Na$_4$SiS$_4$ glass. Thus, the contribution of glass composition to the conductivity enhancement of glass–ceramic ($x=6$) would be small. The origin of the conductivity enhancement is investigated by XRD measurement as shown in Fig. 3. Neither a clear shift of peak positions nor an increase in peak intensities of the cubic Na$_3$PS$_4$ was observed from partial substitution of Na$_4$SiS$_4$ for Na$_3$PS$_4$. To examine a possible formation of solid-solution, the Rietvelt analysis for the XRD data of the glass-ceramics is now in progress. In addition, detailed structural analyses of the glass–ceramics using neutron and/or synchrotron X-ray diffraction are necessary for further discussion.
The electrochemical window of the 90Na$_3$PS$_4$•10Na$_4$SiS$_4$ glass–ceramic electrolyte was examined using cyclic voltammetry. As depicted in Figure 6, cathodic and anodic currents that are respectively attributable to sodium deposition and dissolution were observed at about 0 V vs. Na$^+$/Na. No significant current attributable to electrolyte decomposition was detected up to 5 V vs. Na$^+$/Na. These results suggest that the Na$_3$PS$_4$-Na$_4$SiS$_4$ glass–ceramic electrolyte exhibited a wide electrochemical window of 5 V and that it was electrochemically stable against Na metal.

4. Conclusions

For this study, (100-x)Na$_3$PS$_4$•xNa$_4$SiS$_4$ milled samples were prepared using a planetary ball mill apparatus. The cubic Na$_3$PS$_4$ phase was crystallized directly in as-prepared samples at the composition range of 0 ≤ x ≤ 10. Amorphous materials were obtained for samples between 25 ≤ x ≤ 100. All as-prepared samples showed conductivities of about 10$^{-5}$ S cm$^{-1}$ at 25°C.

The (100-x)Na$_3$PS$_4$•xNa$_4$SiS$_4$ glass–ceramics were prepared by heat treatment of the milled samples. Unknown crystals were precipitated in glass–ceramics at the compositions of x=25, 67, and 100. The conductivities of the glass–ceramics were lower than those of the milled samples. In the composition range of 0 ≤ x ≤ 10, the cubic Na$_3$PS$_4$ phase was only crystallized in the glass–ceramics. Their conductivities were greater than 10$^{-4}$ S cm$^{-1}$ at 25°C. Glass–ceramics with 6 mol% Na$_4$SiS$_4$ showed the highest conductivity of 7.4×10$^{-4}$ S cm$^{-1}$, which is higher than that of Na$_3$PS$_4$ glass–ceramic without Na$_4$SiS$_4$. Cyclic voltammetry showed that the 90Na$_3$PS$_4$•10Na$_4$SiS$_4$ glass–ceramic electrolyte exhibited a wide electrochemical window of 5 V. The Na$_3$PS$_4$-Na$_4$SiS$_4$ glass–ceramic electrolytes showed not only high ionic conductivity but also high electrochemical stability. Therefore, this electrolyte system presents benefits for improving all-solid-state sodium secondary batteries.

Acknowledgements
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References


Figure caption

Figure 1 XRD patterns of the (100-x)Na₃PS₄·xNa₄SiS₄ (mol%) mechanically milled samples. The numbers in brackets are milling period of time. Inverted triangle denotes the diffraction peaks attributable to the cubic Na₃PS₄ phase.⁷

Figure 2 DTA curves of the (100-x)Na₃PS₄·xNa₄SiS₄ mechanically milled samples.

Figure 3 XRD patterns of the (100-x)Na₃PS₄·xNa₄SiS₄ heat-treated (glass-ceramic) samples. A silicon powder as an internal standard was added to the glass-ceramic powders in the composition range of 0 ≤ x ≤ 5.

Figure 4 Temperature dependence of the conductivities of the 94Na₃PS₄·6Na₄SiS₄ (mol%) glass-ceramic sample. Inset is a complex impedance plot of the glass-ceramic sample at room temperature.

Figure 5 (a) Composition dependence of the room temperature conductivities for the (100-x)Na₃PS₄·xNa₄SiS₄ samples. Open and closed circles denote the conductivities for the as-prepared samples and heat-treated (glass-ceramic) samples, respectively. (b) Composition dependence of the room temperature conductivities and the activation energies for conduction of the (100-x)Na₃PS₄·xNa₄SiS₄ (0 ≤ x ≤ 10) glass-ceramic samples. Circles and triangles denote the conductivities and the activation energies, respectively.

Figure 6 Cyclic voltammogram of the 90Na₃PS₄·10Na₄SiS₄ glass-ceramic sample.
Fig. 1

Intensity (arb. unit)

2θ /° (CuKα)

x=0 (1.5 h)
x=5 (15 h)
x=10 (15 h)
x=25 (20 h)
x=67 (25 h)
x=100 (20 h)

△: cubic Na₃PS₄[7]
Fig. 2

Temperature / °C

Heat treatment

Exo.

Endo.

x=0

x=10

x=67

x=100

Tc

Tc

Tc

Tc

100 150 200 250 300 350 400
Fig. 3
\( \sigma = \sigma_0 \exp \left( -\frac{E_a}{RT} \right) \)

Fig. 4
Fig. 5(a)
Fig. 5(b)

\[
\sigma_{25} / \text{S cm}^{-1}
\]

\[
\text{Ea / kJ mol}^{-1}
\]

\[
\text{Mol}\% \text{ Na}_4\text{SiS}_4
\]

\[
7 \times 10^{-4}
\]

\[
3 \times 10^{-4}
\]

\[
1 \times 10^{-4}
\]
Na → Na⁺ + e⁻

Potential / V (vs. Na⁺ / Na)

Current / μA

5 mV s⁻¹
25°C

1st
2nd

Na⁺ + e⁻ → Na

Fig. 6