Preparation of sodium ion conducting $\text{Na}_3\text{PS}_4\text{-NaI}$ glasses
by a mechanochemical technique

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Abstract

Structures and ionic conductivities of the $(100-x)\text{Na}_3\text{PS}_4 \cdot x\text{NaI}$ ($0 \leq x \text{ (mol\%)} \leq 33$) glasses and glass-ceramics were investigated. In the XRD patterns, halo patterns were observed in the composition range of $0 \leq x \leq 29$. The glass-ceramics were prepared by a heat treatment of the glasses. In the glass-ceramics with NaI, an unknown phase which has not been reported was mainly precipitated. The Raman spectra of the glasses and glass-ceramics indicated that all samples included the PS_4^{3-} units. The conductivities of glasses increased with increasing the NaI content, and the $71\text{Na}_3\text{PS}_4 \cdot 29\text{NaI}$ glass showed the highest conductivity of $1.4 \times 10^{-5} \text{ S cm}^{-1}$. The conductivities of the glass-ceramics at all composition were over $10^{-4} \text{ S cm}^{-1}$.

Keywords : Solid electrolyte, Glass, Glass-ceramic, Sodium ion conductor, Sodium iodide, Sulfide

1. Introduction

Lithium ion batteries are used for one of rechargeable batteries at various scenes, for example, cellular phones, electric vehicles, personal computer and so on. However, they use flammable organic liquid electrolytes and thus the safety improvement is required especially for large scale applications. All-solid-state batteries are expected to remove safety hazards because these use inorganic electrolytes [1-3]. Moreover, sodium secondary batteries have been attracted for application to distributed power systems because they can use abundant sodium source [4,5]. Recently, we have found that all-solid-state sodium batteries with a Na_3PS_4 glass-ceramic electrolyte successfully operated as a secondary battery at 25 °C [6]. The Na_3PS_4 glass-ceramic exhibited the high conductivity of over $10^{-4} \text{ S cm}^{-1}$ at room temperature, which was achieved by precipitation of the cubic Na_3PS_4 crystal with high sodium ion conductivity. To improve the performance of the all-solid-state batteries, solid electrolytes with higher sodium ion conductivity are needed. Glasses are expected to form favorable contacts between electrode and electrolyte by hot-press at above glass transition temperature [7]. For lithium ion conductors, glasses are a precursor for obtaining highly lithium ion

conductive glass-ceramics with super ionic conducting crystals [8,9]. It is well known that the addition of lithium halides to glasses is effective in increasing the conductivities of the glasses. For example, the addition of LiI to $\text{Li}_2\text{S-P}_2\text{S}_5$ glasses is known to increase conductivity for electrolytes [10]. The lithium ion conductivity of $67\text{Li}_2\text{S} \cdot 33\text{P}_2\text{S}_5$ glass increased from $10^{-4} \text{ S cm}^{-1}$ to $10^{-3} \text{ S cm}^{-1}$ by adding 45 mol% LiI by melt quench. Recently, $\text{Li}_2\text{S-P}_2\text{S}_5\text{-LiI}$ electrolytes were prepared by mechanochemical technique and these electrolytes showed higher conductivity than the mother $\text{Li}_2\text{S-P}_2\text{S}_5$ glasses [11,12].

In this study, glasses in the system $\text{Na}_2\text{S-P}_2\text{S}_5\text{-NaI}$ were prepared by a mechanochemical technique. To our knowledge, the addition of NaI to $\text{Na}_2\text{S-P}_2\text{S}_5$ glasses has not been reported. The composition of Na_3PS_4 ($75\text{Na}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol%)) was selected because its glass-ceramic showed a high conductivity of more than $10^{-4} \text{ S cm}^{-1}$. The effects of the NaI addition on conductivity and structure of the $\text{Na}_2\text{S-P}_2\text{S}_5$ glasses and glass-ceramics were examined.

2. Experimental

Solid electrolytes $(100-x)\text{Na}_3\text{PS}_4 \cdot x\text{NaI}$ ($0 \leq x \text{ (mol\%)} \leq 33$) glasses were prepared by a mechanochemical technique using a planetary ball mill apparatus. Reagent-grade Na_2S (Nagao, 99.1%), P_2S_5 (Aldrich, 99%) and NaI (Aldrich, 99.999%) were used as starting materials. They were mixed in an agate mortar and then put into a 45ml ZrO_2 pot with 500 ZrO_2 balls (diameter: 4mm). The pot was set in a planetary ball mill apparatus (Fritsch, Pulverisette 7) and mechanochemical treatment was performed to prepare glasses at the rotation speed of 510 rpm for 1.5 ~ 8 hours. The glass-ceramics were prepared by a heat treatment of the glasses at 200 ~ 270°C for 2 hours. All the processes were carried out in a dry Ar atmosphere.

X-ray diffraction (XRD) measurements ($\text{CuK}\alpha$) were performed using a diffractometer (Rigaku, UltimaIV) to identify crystal phases of the glasses and glass-ceramics. Differential thermal analyses (DTA) were performed for the glasses using a thermal analyzer (Rigaku, Thermo-plus 8120) to observe crystallization temperatures. The glasses were sealed in Al pans in an Ar-filled glove box and heated at 10 °C min⁻¹ under N_2 gas flow up to 550 °C. Raman spectra of the glasses and glass-ceramics were measured using a Raman spectrometer (Jasco, RMP-210) with 532

nm YAG laser. Ionic conductivities of the glasses were measured for the pellets with 10 mm in diameter and about 1.5 mm in thickness pressed under 360MPa. Carbon paste was painted on both faces of the pellets and stainless steel disks were attached to the pellets as current collectors. AC impedance measurements were carried out in a dry Ar atmosphere using an impedance analyzer (Solartron, 1260). The frequency range and the applied voltage were 0.1Hz to 8MHz and 50mV, respectively.

3. Results and discussion

The XRD patterns of the $(100-x)\text{Na}_3\text{PS}_4 \cdot x\text{NaI}$ samples after mechanical milling are shown in Fig.1. Halo patterns were observed in the range from $x=0$ to $x=29$. The pattern of the glass at $x=10$ showed a small peak at about $2\theta=31^\circ$, attributed to cubic- Na_3PS_4 ; a glass sample partially including cubic- Na_3PS_4 was prepared by milling at the composition. A weak peak attributable to the NaI crystal remained for the sample at $x=33$. In the composition of $x=0$, cubic Na_3PS_4 phase was directly crystallized by a milling process at 510 rpm for 1.5 ~ 8 hours. On the other hand, a halo pattern was observed by changing milling condition of rotation speed from 510 rpm to 230 rpm for

70 hours. Both the patterns are shown and the rotation speeds are denoted in Fig.1.

Figure 2 shows the Raman spectra of the prepared glasses. A band at 410 cm^{-1} was observed for the glasses of $x=0$ (510rpm) and 10, while a band at 420 cm^{-1} was observed for $x=0$ (230rpm), 18, 26 and 29, respectively. The band at 420 cm^{-1} is attributable to the PS_4^{3-} unit in the sulfide glasses and the crystallized Na_3PS_4 glass showed the band at about 412 cm^{-1} [13]. The reason why the vibration frequencies of PS_4^{3-} in glass and crystal are different has not been clarified yet. The small band at 380 cm^{-1} is attributable to the $\text{P}_2\text{S}_6^{4-}$ unit [13]. In this study, the crystalized sample ($x=0$ (510 rpm)) showed the band at 410 cm^{-1} and thus the band is attributable to the PS_4^{3-} unit in the cubic Na_3PS_4 crystal. The $x=10$ glass also showed a band at 410 cm^{-1} in addition to that at 420 cm^{-1} , suggesting that cubic Na_3PS_4 is partially present in the glass.

DTA curves of the milled samples are shown in Fig.3. Glass transition phenomena were observed between 170°C and 190°C , suggesting that the obtained amorphous samples are glasses. The glass transition temperatures (T_g) shifted to the lower temperature side with increasing the NaI content. It suggests that NaI is introduced into

the glass matrix. Two exothermic peaks were observed between 170 °C and 270 °C for the glasses of at $x=0$ and 5. The peaks at the higher temperature side disappeared for the glasses of at $x=18$, 26 and 29. To prepare glass-ceramics, the glasses were heated just above crystallization temperatures at the lower exothermic peak. In the composition of $x=0$, the glass-ceramic prepared by milling at 510 rpm for 1.5 h and consecutive heat treatment showed the highest conductivity[14]. Therefore, in order to compare to the effect of adding NaI to glass-ceramic, the glass-ceramic at the composition of $x=0$ prepared by milling at 510 rpm was used.

Figure 4 shows the XRD patterns of the glass-ceramics prepared by a heat treatment of the glasses. Silicon was used as an internal standard in XRD measurements. The cubic Na_3PS_4 crystal with a high sodium ion conductivity was precipitated in $(100-x)\text{Na}_3\text{PS}_4 \cdot \text{NaI}$ ($x=0$ and 10) glass-ceramics. In the composition range of $10 \leq x \leq 29$, new peaks appeared, and the peaks have not been reported and identified at the present stage; the peaks are denoted as unknown phase in this figure. The XRD pattern of the glass-ceramic at $x=18$ showed only unknown phase. In the range of $18 < x$, unknown phase and NaI were crystalized. The Rietveld analysis for the unknown phase is now in

progress and detailed structure will be reported elsewhere in the near future.

Figure 5 shows the Raman spectra of the glass-ceramics. The glass-ceramics at $x=0$ and 10 had a peak at 410 cm^{-1} , which is attributable to the PS_4^{3-} units in the cubic Na_3PS_4 phase. The FWHM of the peak is smaller than that of the milled samples ($x=0$ and 10) because crystallization of cubic Na_3PS_4 phase proceeded by a heat treatment as shown in Fig.4. The glass-ceramics at $x=18, 26$ and 29 had a peak at about 410 cm^{-1} and weak shoulder at about 420 cm^{-1} . The peak at 410 cm^{-1} became broad compared with the composition of $x=0$. The peak position at about 410 cm^{-1} was shifted to the low wavenumber side with increasing the NaI content. We have not identified the unknown phases at the present stage, but suggesting that an unknown phase (showed in Fig.4) consisted of the PS_4^{3-} units from the peak position in Raman spectra.

The conductivities at room temperature for $(100-x)\text{Na}_3\text{PS}_4 \cdot x\text{NaI}$ glasses and glass-ceramics are shown in Fig.6. Closed circles denote the conductivity for the glasses prepared by milling. The frequency dependence of the absolute values of impedance $|Z|$ for the $74\text{Na}_3\text{PS}_4 \cdot 26\text{NaI}$ glass and glass-ceramic electrolytes at various temperatures from 25 to 120°C are shown in Fig. S1 (supporting information). The conductivities of

glass and glass-ceramic were determined from the $|Z|$ values in the frequency range from 10^4 to 10^7 Hz. The conductivity of the Na_3PS_4 glass ($x=0$) was $6.0 \times 10^{-6} \text{ S cm}^{-1}$. The conductivities of glasses increased with increasing the NaI content. The $71\text{Na}_3\text{PS}_4 \cdot 29\text{NaI}$ glass showed the highest conductivity of $1.4 \times 10^{-5} \text{ S cm}^{-1}$. A similar enhancement of the conductivity was reported for the $67\text{Li}_2\text{S} \cdot 33\text{P}_2\text{S}_5$ glass by the addition of LiI [10], but the significant enhancement in conductivity observed in the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5\text{-LiI}$ system was not observed in the $\text{Na}_2\text{S}-\text{P}_2\text{S}_5\text{-NaI}$ system. Na_3PS_4 ($75\text{Na}_2\text{S} \cdot 25\text{P}_2\text{S}_5$) is orthothiophosphate composition, while $67\text{Li}_2\text{S} \cdot 33\text{P}_2\text{S}_5$ is pyrothiophosphate composition. In this study, NaI was added to the glass with higher alkali concentration, and thus the magnitude of the effects of the increase of cation concentration on conductivity would be small.

On the other hand, the conductivity of glass-ceramics was affected by precipitated crystals. The conductivity of the Na_3PS_4 ($x=0$) glass-ceramic was $4.6 \times 10^{-4} \text{ S cm}^{-1}$. Although the cubic Na_3PS_4 crystal remained in the glass-ceramics with 10 mol% NaI, the conductivity of the glass-ceramics was decreased with increasing the NaI content; the unknown phase precipitated from the glasses of $10 \leq x$ would have a lower

conductivity than that of cubic Na_3PS_4 phase. The conductivities of over $10^{-4} \text{ S cm}^{-1}$ were obtained at the all compositions for glass-ceramics.

4. Conclusions

The $(100-x)\text{Na}_3\text{PS}_4 \cdot x\text{NaI}$ glasses were prepared by a mechanochemical technique. In the XRD patterns, halo patterns were observed in the range from $x=0$ to $x=29$. An unknown phase which has not been reported was mainly precipitated in the glass-ceramics with NaI. The glasses added with NaI exhibited higher conductivities than that of the mother Na_3PS_4 glass and the conductivities of the glasses increased with increasing the NaI content. The glass at the composition of $x=29$ showed the highest conductivity of $1.4 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. Glass-ceramics prepared by a heat treatment of the glasses showed a higher conductivity of over $10^{-4} \text{ S cm}^{-1}$.

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Figure captions

Fig.1 XRD patterns of $(100-x)\text{Na}_3\text{PS}_4 \cdot x\text{NaI}$ (mol%) glasses prepared at the rotation speed of 510 rpm. The pattern of the glass($x=0$) prepared at the rotation speed of 230 rpm was also shown..

Fig.2 Raman spectra of $(100-x)\text{Na}_3\text{PS}_4 \cdot x\text{NaI}$ (mol%) glasses.

Fig.3 DTA curves of $(100-x)\text{Na}_3\text{PS}_4 \cdot x\text{NaI}$ (mol%) glasses.

Fig.4 XRD patterns of $(100-x)\text{Na}_3\text{PS}_4 \cdot x\text{NaI}$ (mol%) glass-ceramics.

Fig.5 Raman spectra of $(100-x)\text{Na}_3\text{PS}_4 \cdot x\text{NaI}$ (mol %) glass-ceramics.

Fig.6 Composition dependence of the room temperature conductivities for the $(100-x)\text{Na}_3\text{PS}_4 \cdot x\text{NaI}$ glasses and glass-ceramics. Closed and open symbols denote the conductivities for the glasses and glass-ceramics, respectively.

Fig.1

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Fig.6