



Short communication

Structure and properties of $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{P}_2\text{S}_3$ glass and glass–ceramic electrolytesKeiichi Minami^a, Akitoshi Hayashi^{a,*}, Satoshi Ujiie^b, Masahiro Tatsumisago^a^a Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuencho, Naka-ku, Sakai, Osaka 599-8531, Japan^b The Kansai Electric Power Co., Inc., Amagasaki, Hyogo 661-0974, Japan

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ABSTRACT

High lithium ion conducting $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$ (mol%) glasses and glass–ceramics were prepared by the mechanical milling method. Glasses were obtained in the composition range of $0 \leq x \leq 10$. The substitution of P_2S_3 for P_2S_5 promoted the formation of the $\text{P}_2\text{S}_6^{4-}$ units in the glasses. The conductivity of the glass increased with an increase in P_2S_3 contents up to 5 mol% and the glass with 5 mol% of P_2S_3 showed the conductivity of $1 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. In the case of glass–ceramics, the conductivity increased with an increase in P_2S_3 contents up to 1 mol%, and the superionic conducting $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal was precipitated in the glass–ceramic. The glass–ceramic with 1 mol% of P_2S_3 showed the highest conductivity of $3.9 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature.

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1. Introduction

High lithium ion conductive solid electrolytes have been researched for many years. In a lot of lithium ion conductive solid electrolytes, sulfide-based solid electrolytes show high conductivity more than $10^{-4} \text{ S cm}^{-1}$ at room temperature [1,2]. We have investigated structure and properties of the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ solid electrolytes which were prepared by the mechanical milling [3] and the melt quenching techniques [4]. Recently, the $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ (mol%) glass–ceramic electrolyte has attracted much attention because of its high lithium ion conductivity. The conductivity of $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ mechanically milled glass was $5.4 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. Superionic conductive $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal [5] was precipitated by crystallization of the glass and the obtained glass–ceramic showed the high conductivity of $3.2 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature [3].

We reported that the substitution of a small amount of P_2O_5 for P_2S_5 at the composition $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ is effective in enhancing the conductivity of glass and glass–ceramic [6]. Moreover, electrochemical stability of the glass–ceramic against lithium metal was improved by the P_2O_5 substitution [7]. The improvement of the properties for the glass–ceramic would be due to the incorporation of oxygen into the $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal. Machida et al. have

reported that the substitution of a small amount of P_2S_3 for P_2S_5 increased the conductivity of the $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ glass [8]; the obtained glass with 5 mol% of P_2S_3 showed the highest conductivity of $6.2 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. Enhancement of conductivity of both glass and glass–ceramic electrolytes is expected by substituting P_2S_3 for P_2S_5 at the composition of $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$.

In this work, the $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$ (mol%) glasses and glass–ceramics were prepared by mechanical milling. Effects of substitution of P_2S_3 for P_2S_5 on the structure and properties of the glass and glass–ceramic electrolytes were investigated.

2. Experimental

The $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$ (mol%) glasses were prepared by the mechanical milling method. Reagent-grade Li_2S (Idemitsu Kosan, 99.9%), P_2S_5 (Aldrich, 99%) and P_2S_3 (Aldrich, >99%) crystalline powders were used as starting materials. The mixture of these materials was mechanically milled at room temperature by a planetary ball mill apparatus (Fritsch Pulverisette 7) using an alumina pot (volume of 45 ml) with 10 alumina balls (10 mm in diameter). A rotating speed was 370 rpm and the milling time was 20 h. The glass–ceramics were prepared by heating the glasses at above crystallization temperatures. All processes were performed in a dry Ar atmosphere. XRD measurements ($\text{Cu K}\alpha$) were conducted using a diffractometer (Bruker AXS, M18XHF²²-SRA). Raman spectra of the glasses were measured with a Jasco NR-1000 Raman spectrophotometer using the 514 nm line of an Ar^+ laser

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beam. Differential thermal analyses (DTA) were performed by using a Rigaku thermal analyzer (Rigaku, Thermo-plus 8110). The heating rate was $10^{\circ}\text{C min}^{-1}$.

Ionic conductivities were measured for the pelletized samples with 10 mm in diameter and about 1 mm in thickness. Carbon paste was painted as electrodes on the both faces of the pellets. Two stainless steel disks coupled with gold wires were attached to the pellets as a current collector. The obtained 2-probe cell was packed in a glass tube and then the tube was sealed with a silicone stopcock equipped with needle valves, platinum electrodes and a thermocouple. Ac impedance measurements were carried out for the cell using dry Ar gas flow by an impedance analyzer (Solartron, 1260) in the frequency range of 10 Hz to 8 MHz. The temperature range of the measurements was from 25°C to above the first crystallization temperature of glass samples.

3. Results and discussion

Fig. 1 shows the XRD patterns of mechanically milled samples. Halo patterns were observed for the samples in the composition range $0 \leq x \text{ (mol\%)} \leq 10$ in the system $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$, indicating that the amorphous samples were obtained. On the other hand, the diffraction peaks attributable to the Li_2S crystal remained at the compositions with 20 and 30 mol% of P_2S_3 although halo patterns were basically observed. The peak intensities of Li_2S crystal increased with increasing P_2S_3 contents. Glass transition phenomena were observed from the DTA analysis in Fig. 3 of obtained amorphous samples and thus they are in glassy state.

Raman spectra of the $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$ glasses are shown in Fig. 2. Two peaks were observed at 407 and 420 cm^{-1}

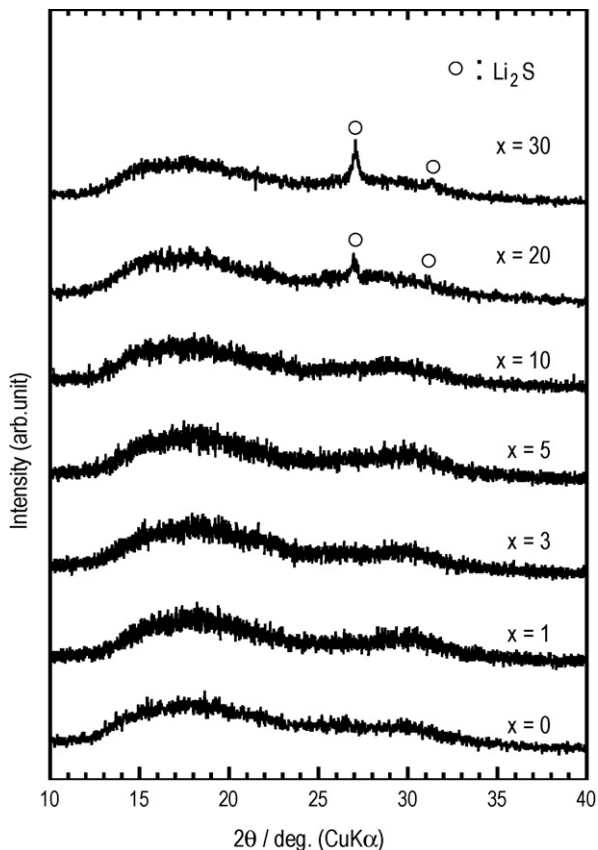


Fig. 1. XRD patterns of the $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$ samples prepared by mechanical milling for 20 h.

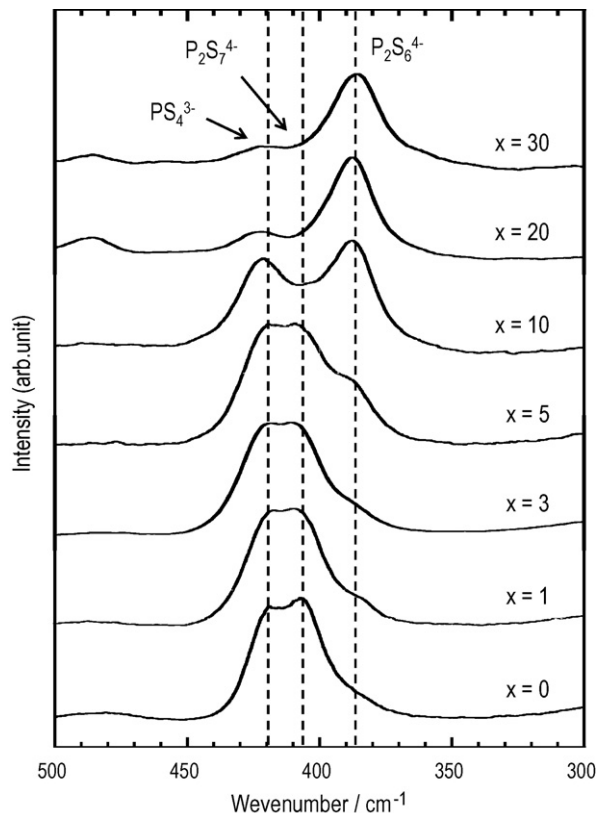


Fig. 2. Raman spectra of the $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$ glasses prepared by mechanical milling for 20 h.

in the spectrum of the $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ glass ($x=0$). Tachez et al. reported that the two peaks are attributed to the $\text{P}_2\text{S}_7^{4-}$ units and the PS_4^{3-} units, respectively [9]. The $\text{P}_2\text{S}_7^{4-}$ units gradually disappeared and $\text{P}_2\text{S}_6^{4-}$ units (382 cm^{-1}) with P–P bond were produced by substituting P_2S_3 for P_2S_5 . It was revealed that the increase of the P_2S_3 content led to the decrease of $\text{P}_2\text{S}_7^{4-}$ units and the formation of $\text{P}_2\text{S}_6^{4-}$ units.

DTA curves of obtained glasses are shown in Fig. 3. Two exothermic peaks were observed in the curve of the $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ glass ($x=0$). The peak at around 240°C is attributable to the crystallization of the superionic conductor $\text{Li}_7\text{P}_3\text{S}_{11}$ and that at around 420°C is attributable to the transformation of the $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal to the $\text{Li}_4\text{P}_2\text{S}_6$ and thio-LISICONIII analog crystal [10]. By substituting P_2S_3 for P_2S_5 , the crystallization peak at around 240°C gradually disappeared and a new crystallization peak at around 280°C attributable to the crystallization of thio-LISICONIII analog crystal appeared. In addition, the transformation peak at around 420°C was shifted to the lower temperature region at the compositions $x < 10$, suggesting that the $\text{Li}_4\text{P}_2\text{S}_6$ crystal was easily produced in the glass-ceramics.

Fig. 4 shows the XRD patterns of the $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$ glass-ceramics prepared by heating the glasses at temperatures higher than the first crystallization temperature by 30°C . The superionic conductive $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal was precipitated in the glass-ceramics at the compositions up to 5 mol% of P_2S_3 contents. However, peak intensity of the $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal decreased with increasing the P_2S_3 contents and almost all the peaks of $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal disappeared in the glass-ceramic with 10 mol% of P_2S_3 . The crystal analogous to the thio-LISICONIII phase in the $\text{Li}_4\text{GeS}_4\text{--Li}_3\text{PS}_4$ solid solution [11] was also observed in the glass-ceramics with more than 1 mol% of P_2S_3 . The exothermic peak at around 280°C as shown in Fig. 3 is therefore attributable to the crystallization of

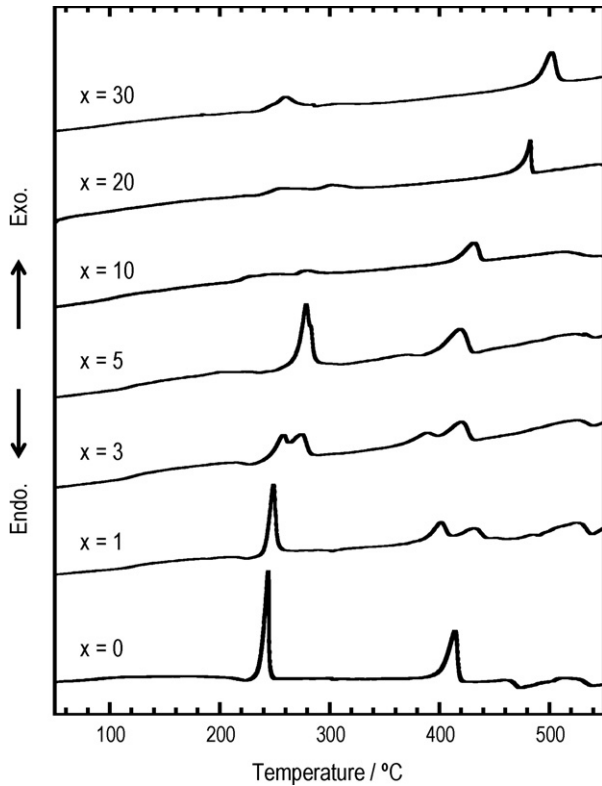


Fig. 3. DTA curves of the $70\text{Li}_2\text{S} \cdot (30 - x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$ glasses prepared by mechanical milling for 20 h.

thio-LISICONIII analogue crystal as mentioned above. Peak intensity of low lithium ion conducting $\text{Li}_4\text{P}_2\text{S}_6$ crystal increased with increasing P_2S_3 contents because of increase of the $\text{P}_2\text{S}_6^{4-}$ units in mother glass and decrease of precipitation temperature of the $\text{Li}_4\text{P}_2\text{S}_6$ crystal. Decrease of the $\text{P}_2\text{S}_7^{4-}$ units and increase of the $\text{P}_2\text{S}_6^{4-}$ units in the glass would cause disappearance of the $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal and appearance of the $\text{Li}_4\text{P}_2\text{S}_6$ crystal and thio-LISICONIII analog crystals.

Fig. 5 shows the composition dependence of the ambient temperature conductivity and activation energy for conduction of the $70\text{Li}_2\text{S} \cdot (30 - x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$ glasses and glass-ceramics. In the case of glass, the conductivity increased with an increase in P_2S_3 contents up to 5 mol% and the glass with 5 mol% of P_2S_3 showed the highest conductivity of $1.0 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. The enhancement of conductivity would be due to the “mixed anion effect” which is observed in the glasses containing two or more kinds of anion species [8,12]. The $70\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5 \cdot 5\text{P}_2\text{S}_3$ glass consisted of the $\text{P}_2\text{S}_6^{4-}$ anion in addition to the $\text{P}_2\text{S}_7^{4-}$ and PS_4^{3-} anions, and thus the glass showed higher conductivity than the $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ glass. In the case of glass-ceramics, the conductivity of all the glass-ceramics increased by crystallization of the glasses. The conductivity increased with an addition of 1 mol% P_2S_3 , and the glass-ceramic with 1 mol% of P_2S_3 showed the highest conductivity of $3.9 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. The conductivity gradually decreased with further increasing P_2S_3 contents. Conductivity of the glass-ceramic mainly depends on the precipitated crystal and then the decrease of the conductivity is due to the precipitation of the $\text{Li}_4\text{P}_2\text{S}_6$ crystal in the glass-ceramics. On the other hand, the superionic conducting $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal was precipitated in the glass-ceramics with a small amount of P_2S_3 and therefore the glass-ceramics showed high conductivity of over $10^{-3} \text{ S cm}^{-1}$. It has not been clarified the reason why the glass-ceramic with 1 mol% of P_2S_3 exhibited higher conductivity

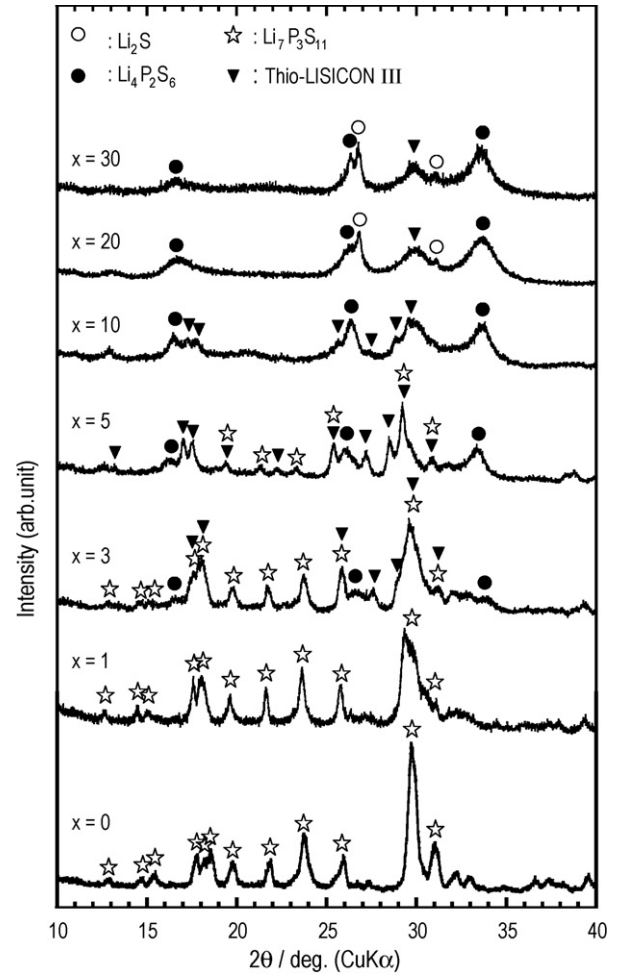


Fig. 4. XRD patterns of the $70\text{Li}_2\text{S} \cdot (30 - x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$ glass-ceramics prepared by heat treatment of the glass at above crystallization temperature.

than the $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ glass-ceramic. Incorporation of the trivalent phosphorus into the $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal is a possible reason for the conductivity enhancement; detailed structural analysis of the glass-ceramics is needed for further discussion.

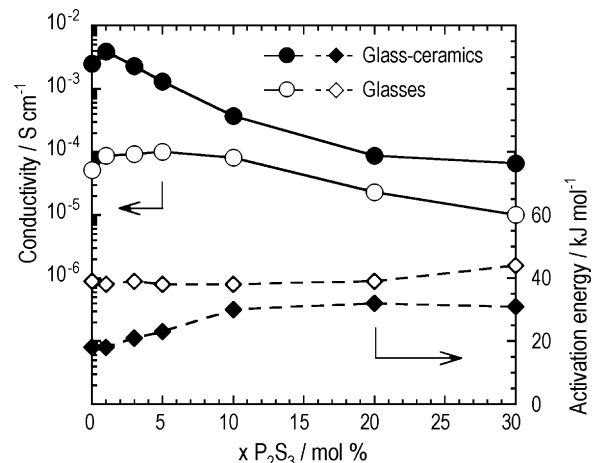


Fig. 5. Composition dependence of room temperature conductivity and activation energy for conduction of the $70\text{Li}_2\text{S} \cdot (30 - x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$ glasses and glass-ceramics.

4. Conclusions

The $70\text{Li}_2\text{S} \cdot (30 - x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$ glasses in the composition range $0 \leq x \leq 10$ were prepared by the mechanical milling method. The $\text{P}_2\text{S}_7^{4-}$ units gradually disappeared and the $\text{P}_2\text{S}_6^{4-}$ units were formed by substituting P_2S_3 for P_2S_5 . The substitution of P_2S_3 for P_2S_5 promoted the formation of the $\text{P}_2\text{S}_6^{4-}$ units in the glasses. Conductivity of the glass increased with increasing P_2S_3 contents and the glass with 5 mol% of P_2S_3 showed the conductivity of $1 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. The glass–ceramics were obtained by heating the glasses at above crystallization temperature. The glass–ceramics with up to 5 mol% of P_2S_3 showed high conductivity of over $10^{-3} \text{ S cm}^{-1}$ because of the precipitation of the superionic conducting $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal. The $\text{Li}_4\text{P}_2\text{S}_6$ crystal instead of the $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal was precipitated by substituting further amounts of P_2S_3 for P_2S_5 . The glass–ceramic with 1 mol% of P_2S_3 showed the highest conductivity of $3.9 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. It was found that the substituting a small amount of P_2S_3

for P_2S_5 is effective in enhancing conductivity of the glass and glass–ceramic electrolytes.

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