

# Preparation and ionic conductivity of $\text{Li}_7\text{P}_3\text{S}_{11-z}$ glass-ceramic electrolytes

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## ABSTRACT

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%) glass and glass-ceramic electrolytes were prepared via mechanochemical route using a planetary ball mill apparatus. Ball-milling condition and glass composition for achieving high  $\text{Li}^+$  ion conductivity in glass-ceramic electrolytes were investigated. The glass-ceramics prepared using  $\text{ZrO}_2$  media (500 balls, 4 mm in diameter) exhibited higher conductivity than those prepared using  $\text{Al}_2\text{O}_3$  media (10 balls, 10 mm in diameter). The former experiment condition was appropriate for preparing homogeneous glasses. The substitution of 1 mol% of  $\text{P}_2\text{S}_3$  for  $\text{P}_2\text{S}_5$  enhanced the conductivity of the glass-ceramics and the maximum conductivity was  $5.4 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature. The  $\text{Li}_7\text{P}_3\text{S}_{11}$  analogous phase,  $\text{Li}_7\text{P}_3\text{S}_{11-z}$ , was formed at the composition with 1 mol%  $\text{P}_2\text{S}_3$  and the  $\text{Li}_7\text{P}_3\text{S}_{11-z}$  phase would have higher conductivity than the  $\text{Li}_7\text{P}_3\text{S}_{11}$  crystal without substitution.

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## 1. Introduction

Sulfide glass-ceramics in the system  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  are a strong candidate of solid electrolytes for all-solid-state lithium rechargeable batteries because of their high  $\text{Li}^+$  ion conductivity and wide electrochemical window [1–6]. The  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  glass-ceramics were prepared by careful heat treatment of the corresponding mother glasses, and superionic crystals were precipitated in the glass-ceramics. In particular, the superionic  $\text{Li}_7\text{P}_3\text{S}_{11}$  crystal [7] was formed by heating the  $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$  (mol%) glass and the prepared glass-ceramic at the composition exhibited high conductivity of  $3.2 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature [3,5]. The  $\text{Li}_7\text{P}_3\text{S}_{11}$  crystal was not synthesized by a conventional solid-state reaction and thus the glass electrolyte is important as a precursor for forming the superionic crystal.

In general, the  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  sulfide glasses are prepared by melt quenching [8,9]. We have developed the preparation of the sulfide glasses via mechanochemical route using a planetary ball mill apparatus [10–12]. Thermal and electrical properties and local structure of the milled glasses are affected by several ball-milling parameters such as material of pot and ball, number and size of ball, and rotation speed of the apparatus. The use of appropriate experiment conditions is important for developing superior glass and glass-ceramic electrolytes.

The glass composition also has an influence on character of glass-ceramics. In the ternary system  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{P}_2\text{S}_3$ , the incorporation of a small amount of  $\text{P}_2\text{S}_3$  to the  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  system enhanced the conductivity of glass-ceramics [13].

Here we show a further increase in conductivity of the  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{P}_2\text{S}_3$  glass-ceramic electrolytes by examining milling parameters for preparation of mother glass electrolytes. In the present study,  $\text{Li}_7\text{P}_3\text{S}_{11}$ -based glass-ceramic electrolytes were prepared by crystallization of the  $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$  (mol%) glasses. The mother sulfide glasses were synthesized by mechanical milling with  $\text{ZrO}_2$  pot and balls instead of  $\text{Al}_2\text{O}_3$  media previously used. The effects of milling condition and glass composition on thermal and electrical properties and precipitated crystalline phases of the electrolytes were investigated.

## 2. Experimental

Mechanical milling conditions for preparing 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 electrolytes were investigated. Reagent-grade  $\text{Li}_2\text{S}$  (Idemitsu Kosan, 99.9%),  $\text{P}_2\text{S}_5$  (Aldrich, 99%), and  $\text{P}_2\text{S}_3$  (Aldrich, 99%) crystalline powders were used as starting materials. Ball milling was carried out using a planetary ball mill apparatus (Fritsch Pulverisette 7). The mixture of starting materials was put into a  $\text{ZrO}_2$  pot (volume of 45 ml) with 500  $\text{ZrO}_2$  balls with the size of 4 mm in diameter and then ball-milled at a rotation speed of 510 rpm for 8–12 h under room temperature. The glasses were also prepared with a conventional milling condition using an  $\text{Al}_2\text{O}_3$  pot (volume of 45 ml) with 10  $\text{Al}_2\text{O}_3$  balls with the size of 10 mm in diameter at a rotation speed of 370 rpm for 20 h [11]. The glass-ceramics were prepared by heating the glasses at 280 and 360 °C, which were above the temperature of the first crystallization peak on a thermal analysis curve. All processes were performed in a dry Ar atmosphere.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were performed by using thermal analyzers (Rigaku, Thermo-plus 8110 and SII, DSC6200). The prepared glass powder was sealed in an Al pan in an Ar-filled glove box, and then DTA

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measurements were carried out at the heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under  $\text{N}_2$  gas flow. Ionic conductivities were measured for the powder-compressed pellets by ac impedance method using an impedance analyzer (Solartron, 1260). The measurements were carried out in the frequency range of 10 Hz to 8 MHz under a dry Ar atmosphere. XRD measurements ( $\text{CuK}\alpha$ ) were conducted using a diffractometer (Bruker AXS, M18XHF<sup>22</sup>-SRA). Solid-state  $^{31}\text{P}$  MAS-NMR measurements were carried out using a spectrometer (Varian, Unity Inova 300). The spectra were recorded at the observed frequency of 121.43 MHz, the  $90^\circ$  pulse length of  $2.0\ \mu\text{s}$ , and the recycle pulse delay of 5.0 s. Those structural analyses were done in a dry Ar atmosphere.

### 3. Results and discussion

#### 3.1. Milling condition for preparing the $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ glass

Fig. 1 shows DTA curves of the  $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$  (mol%) glasses prepared by mechanical milling with two different experiment conditions. The curve of the  $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$  glass prepared by melt quenching [9] is also shown as comparison. Agglomerated particles with the size of a few micrometers were used for DTA measurements in each case; an influence of particle size on thermal behavior would not be considered.

The glass prepared by milling with a previous experiment condition using an  $\text{Al}_2\text{O}_3$  pot and 10  $\text{Al}_2\text{O}_3$  balls (10 mm in diameter) [11] showed the glass transition temperature ( $T_g$ ) of  $200\text{ }^{\circ}\text{C}$  and the crystallization temperature ( $T_c$ ) of  $235\text{ }^{\circ}\text{C}$ . These temperatures are somewhat lower than those of the glass prepared by melt quenching [9]. On the other hand, the glass prepared by milling with a  $\text{ZrO}_2$  pot and 500  $\text{ZrO}_2$  balls (4 mm in diameter) exhibited the  $T_g$  of  $218\text{ }^{\circ}\text{C}$  and the  $T_c$  of  $255\text{ }^{\circ}\text{C}$ , which are almost the same as those of the glass prepared by melt quenching. The glass prepared with the  $\text{ZrO}_2$  media showed clearer glass transition and crystallization than the glass prepared with the  $\text{Al}_2\text{O}_3$  media, suggesting that a homogeneous glass with narrowly-distributed  $T_g$  was obtained by using the  $\text{ZrO}_2$  media.

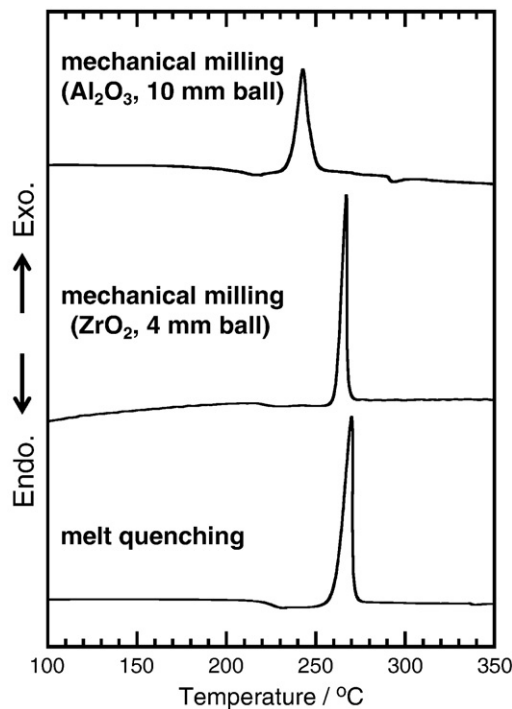


Fig. 1. DTA curves of the  $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$  (mol%) glasses prepared by milling with two different experiment conditions. The curve of the melt quenched glass [9] is also shown as comparison.

The milling period of time to obtain glasses in the former case was 8 h, which was shorter than that in the latter case of 20 h.

The  $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$  glass-ceramics were prepared by heating the milled glasses at over the crystallization temperature. In the previous study using the  $\text{Al}_2\text{O}_3$  media, the glass-ceramic prepared by heating the glass at  $360\text{ }^{\circ}\text{C}$  exhibited the conductivity of  $3.2 \times 10^{-3}\ \text{Scm}^{-1}$  at room temperature [3,5]. In the case using the  $\text{ZrO}_2$  media, the glass-ceramic prepared by heating the glass at  $360\text{ }^{\circ}\text{C}$  showed the higher conductivity of  $5.4 \times 10^{-3}\ \text{Scm}^{-1}$  at room temperature. The  $\text{Li}_7\text{P}_3\text{S}_{11}$  crystal was precipitated from both glasses; the increase in degree of crystallinity is a possible reason for the conductivity enhancement. It is revealed that the mechanical milling with smaller  $\text{ZrO}_2$  balls is effective in preparing glass-ceramics with high conductivity.

#### 3.2. Characterization 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 our previous report, conductivity enhancement for glass-ceramics was achieved by substituting 1 mol% of  $\text{P}_2\text{S}_3$  for  $\text{P}_2\text{S}_5$  [13]. The  $\text{Al}_2\text{O}_3$  media was used for preparation of glasses in the report. In the present study, the glass-ceramics with the substitution of a small amount of  $\text{P}_2\text{S}_3$  (below 3 mol%) were characterized in detail. 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 milling with a  $\text{ZrO}_2$  pot and 500  $\text{ZrO}_2$  balls (4 mm in diameter). The milling time for preparation of glasses was dependent on the starting compositions and the milling for 8–12 h was needed at a rotation speed of 510 rpm.

Fig. 2 shows the DSC curves of the  $70\text{Li}_2\text{S}\cdot (30-x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{S}_3$  ( $x=0, 0.5, 1, 2,$  and  $3$ ) glasses. The DTA curve of the  $x=0$  glass was already shown in Fig. 1. The crystallization peak temperature on the DSC curve was somewhat lower than that on the DTA curve; this would be caused by using different apparatuses for thermal analysis. The DSC curves of the glasses with  $x=0.5$  and 1 showed one crystallization peak and were similar to the curve of the glass with  $x=0$ . The first crystallization peak slightly shifted to the higher temperature side and the second crystallization peak appeared on the DSC curves of the glasses with  $x=2$  and 3. The temperature difference between two crystallization peaks was very small and it was thus difficult that a crystalline phase corresponding to the first crystallization peak was separately identified by XRD measurements. The

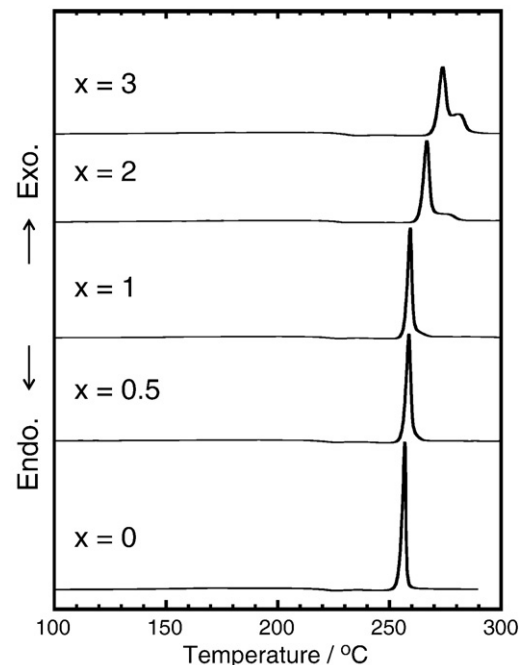


Fig. 2. DSC curves of the  $70\text{Li}_2\text{S}\cdot (30-x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{S}_3$  (mol%) glasses prepared by milling.

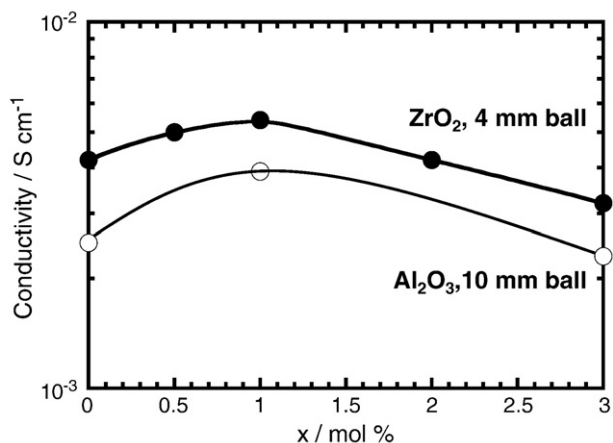


Fig. 3. Composition dependence of room temperature conductivities for the  $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$  glass-ceramics prepared with the  $\text{ZrO}_2$  media. The conductivities of the glass-ceramics prepared with the  $\text{Al}_2\text{O}_3$  media [13] are also shown as comparison.

glass-ceramics at all the compositions were prepared by heating the glasses at  $280^\circ\text{C}$ , which is just over the second crystallization peak temperature.

Fig. 3 shows the composition dependence of room temperature conductivities for 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. The conductivities of the glass-ceramics prepared with the  $\text{Al}_2\text{O}_3$  media [13] are also shown as comparison. The  $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$  glass-ceramic showed the conductivity of  $4.2 \times 10^{-3} \text{ S cm}^{-1}$ . The conductivity was increased with an increase in  $x$  up to 1 mol% and then the conductivity was decreased. The highest conductivity of  $5.4 \times 10^{-3} \text{ S cm}^{-1}$  was obtained at the composition  $x = 1$ . The composition dependence of conductivity of glass-ceramics was almost the same as that in the previous study using the  $\text{Al}_2\text{O}_3$  media [13], but the conductivities in the present study were higher in all the compositions than those in the previous study. The enhancement in conductivity of the glass-ceramics was caused by improving the milling conditions as mentioned above.

To discuss the composition dependence of conductivity, structural analyses of glass-ceramics were investigated by  $^{31}\text{P}$  MAS-NMR and X-ray diffraction measurements. Fig. 4 shows  $^{31}\text{P}$  MAS-NMR spectra of the

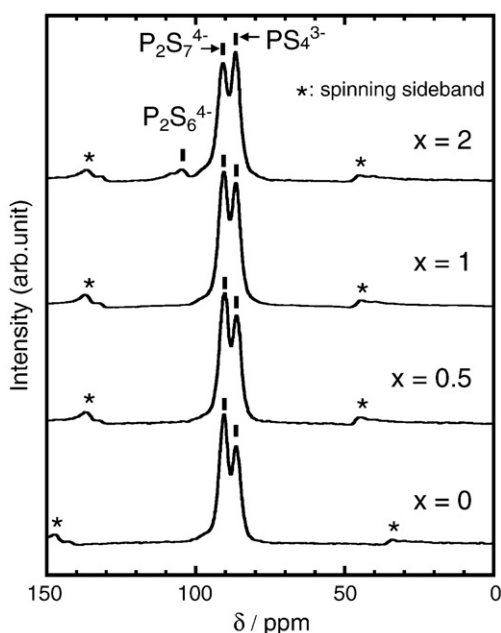


Fig. 4.  $^{31}\text{P}$  MAS-NMR spectra of the  $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$  glass-ceramics.

$70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$  glass-ceramics. Two peaks at 87 and 90 ppm were observed in all the compositions. The peak intensity at 87 ppm was gradually increased with an increase in  $x$ . A small peak at 105 ppm appeared in the glass-ceramic with  $x = 2$ . Eckert et al. reported that the peak at 87 ppm was assigned to the  $\text{PS}_4^{3-}$  ion in the  $\text{Li}_3\text{PS}_4$  crystalline phase [14]. The peaks at 90 and 105 ppm were respectively attributable to the  $\text{P}_2\text{S}_7^{4-}$  and  $\text{P}_2\text{S}_6^{4-}$  ions. The  $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$  glass-ceramic ( $x = 0$ ), where the  $\text{Li}_7\text{P}_3\text{S}_{11}$  crystal was precipitated as a single phase, consisted of the  $\text{PS}_4^{3-}$  and  $\text{P}_2\text{S}_7^{4-}$  ions. The ratio of the  $\text{PS}_4^{3-}$  ion to the  $\text{P}_2\text{S}_7^{4-}$  ion in the glass-ceramics was somewhat increased with an increase in the  $\text{P}_2\text{S}_3$  content. The  $\text{P}_2\text{S}_6^{4-}$  ion was slightly formed in the glass-ceramic  $x = 2$  and the conductivity degradation would be caused by the formation of the  $\text{P}_2\text{S}_6^{4-}$  ion.

Fig. 5 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 (a) in the  $2\theta$  range from  $10^\circ$  to  $40^\circ$  and (b) in the magnified  $2\theta$  range from  $19^\circ$  to  $29^\circ$ . A silicon powder as an external standard was added to the glass-ceramic powders for XRD measurements. The XRD peaks of the  $x = 0$  glass-ceramic as shown in figure (a) have smaller FWHM (Full Width at Half Maximum) than the peaks of the  $x = 0$  glass-ceramic prepared using the  $\text{Al}_2\text{O}_3$  media previously reported [13]; a heat treatment condition was almost the same in both samples. This suggests that the degree of crystallinity of the  $\text{Li}_7\text{P}_3\text{S}_{11}$  phase in the present glass-ceramic is larger than that in the previous study. All the XRD peaks for the  $x = 1$  and 3 glass-ceramics were basically assigned to

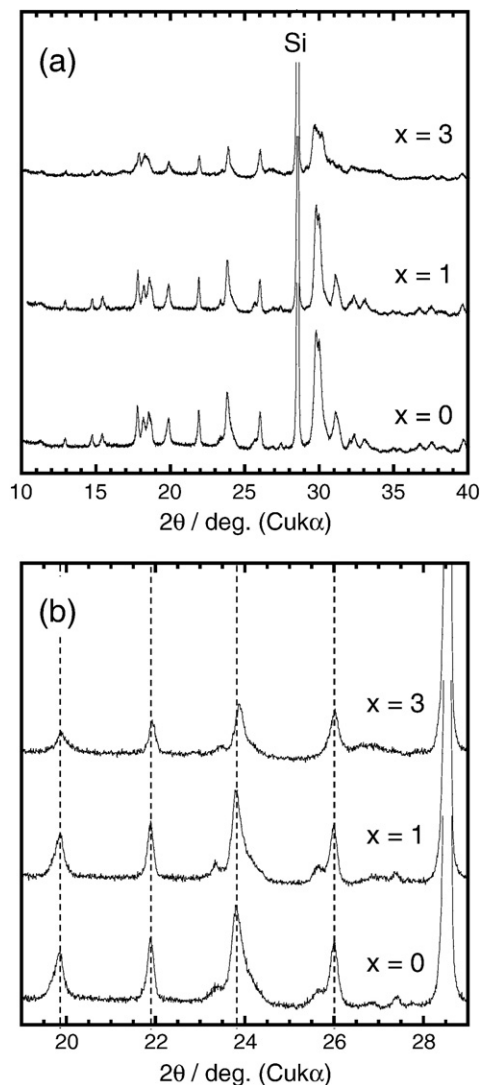


Fig. 5. XRD patterns of the  $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{S}_3$  glass-ceramics (a) in the  $2\theta$  range from  $10^\circ$  to  $40^\circ$  and (b) in the magnified  $2\theta$  range from  $19^\circ$  to  $29^\circ$ .

the  $\text{Li}_7\text{P}_3\text{S}_{11}$  crystal. In the magnified figure (b), no peak shift was observed for the glass-ceramics with  $x=1$  and 3. The trivalent phosphorus ion ( $\text{P}^{3+}$ , 58 pm) in  $\text{P}_2\text{S}_3$  has a similar ionic radius to the pentavalent phosphorus ion ( $\text{P}^{5+}$ , 52 pm) in  $\text{P}_2\text{S}_5$  [15] and thus the peak shift was not observed. The partial substitution of  $\text{P}_2\text{S}_3$  for  $\text{P}_2\text{S}_5$  brings about a lack of sulfur in the  $\text{Li}_7\text{P}_3\text{S}_{11}$  crystal, and therefore a  $\text{Li}_7\text{P}_3\text{S}_{11-z}$  crystal would be formed and it would enhance the conductivity of glass-ceramics with 1 mol%  $\text{P}_2\text{S}_3$ .

#### 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 and glass-ceramics were prepared by mechanical milling using the  $\text{ZrO}_2$  media (500 balls, 4 mm in diameter). The prepared glass-ceramics exhibited higher conductivity than those prepared using the  $\text{Al}_2\text{O}_3$  media (10 balls, 10 mm in diameter). The former experiment condition was appropriate for preparing homogeneous glasses and the superionic  $\text{Li}_7\text{P}_3\text{S}_{11}$  with high crystallinity was precipitated from the glasses. The substitution of 1 mol% of  $\text{P}_2\text{S}_3$  for  $\text{P}_2\text{S}_5$  enhanced the conductivity of the glass-ceramics and the maximum conductivity was  $5.4 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature. The  $\text{Li}_7\text{P}_3\text{S}_{11}$  analogous phase,  $\text{Li}_7\text{P}_3\text{S}_{11-z}$ , was formed at the composition with 1 mol%  $\text{P}_2\text{S}_3$  and the  $\text{Li}_7\text{P}_3\text{S}_{11-z}$  phase would have higher conductivity than the  $\text{Li}_7\text{P}_3\text{S}_{11}$  crystal without substitution.

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