Structure and Ionic Conductivity of Li$_2$S-P$_2$S$_5$-P$_2$O$_5$ Glasses and Glass-Ceramics Prepared by Mechanical Milling

Fuminori MIZUNO, Takamasa OHTOMO, Akitoshi HAYASHI, Kiyoharu TADANAGA, Tsutomu MINAMI and Masahiro TATSUMISAGO

Department of Applied Materials Science, Graduate School of Engineering, Osaka Prefecture University, I-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

Lithium ion conducting Li$_2$S-P$_2$S$_5$-based solid electrolytes with P$_2$O$_5$ and Li$_2$O as an oxygen source were synthesized by the mechanical milling method. P$_2$O$_5$ effectively reacted with Li$_2$S-P$_2$S$_5$ compared to Li$_2$O. $^{31}$P MAS-NMR spectroscopy revealed that the 80Li$_2$S·18P$_2$S$_5$·2P$_2$O$_5$ (mol%) glass included PO$_2$S$_{1-n}$ (n = 1, 2, 3) tetrahedral units where phosphorus was coordinated with both sulfurs and oxygens. The 80Li$_2$S·19P$_2$S$_5$·1P$_2$O$_5$ (mol%) glass attained a minimum value of the glass transition and crystallization temperatures. In addition, the glass exhibited high ambient temperature conductivity of 1.7×10$^{-4}$ S cm$^{-1}$ and low activation energy of 36 kJ mol$^{-1}$ for conduction which were comparable to the glass without P$_2$O$_5$. Further increase in P$_2$O$_5$ to the Li$_2$S-P$_2$S$_5$-P$_2$O$_5$ glasses led to a decrease in conductivities at room temperature and an increase in activation energies. The higher conductivity and lower activation energy for conduction of the 80Li$_2$S·(20−x)P$_2$S$_5$·xP$_2$O$_5$ (mol%) glass-ceramics compared to those of the corresponding glasses were caused by the fact that the highly conductive thio-LISICON analog phase was precipitated by heating of the glass over the crystallization temperature.

[Received August 8, 2003; Accepted January 16, 2004]

Key-words: Solid electrolyte, Lithium ion, Mechanical milling, Sulfide, Glass, Glass-ceramic

1. Introduction

Solid electrolytes with high lithium ion conductivities have been intensively investigated for the application to all-solid-state lithium secondary batteries. 1) Lithium ion conductive solid electrolytes, which have a wide variation of materials such as gel, polymer, crystal and glass, require high conductivities at room temperature, wide electrochemical windows, unity of lithium ion transport number, nonflammability and so on. Sulfide-based lithium ion conducting glasses are one of the most promising solid electrolyte materials with these superior properties. 2)−6)

A variety of sulfide-based glasses have been prepared by the melt quenching method. 2)−6) The mechanical milling technique has been recently utilized as a new technique to prepare glassy solid electrolyte powders. 7) This technique has several advantages in preparation as compared with the melt quenching technique. For example, the syntheses of glassy materials can be carried out at room temperature under an atmospheric pressure. Mechanically milled fine powders can be directly used for solid electrolytes in all-solid-state cells. We have succeeded in preparation of glassy powders in the systems Li$_2$S−SiS$_2$, 7) Li$_2$S−SiS$_2$−Li$_2$MoO$_3$, 8,9) Li$_2$MoO$_3$−Li$_2$PO$_4$, 10) Li$_2$SiO$_4$ etc.). 8,9) Li$_2$N−SiS$_2$, 10) Li$_2$S−P$_2$S$_5$, 11) and Li$_2$S−P$_2$S$_5$−SiS$_2$ 12) by mechanical milling using a high-energy ball mill apparatus. These glasses have high lithium ion conductivities over 10$^{-4}$ S cm$^{-1}$ at room temperature.

Li$_2$S−P$_2$S$_5$ glasses have attracted much interest because the glass-ceramics in the system Li$_2$S−P$_2$S$_5$ obtained by the heat treatment of the glasses over their crystallization temperatures exhibit higher lithium ion conductivities at room temperature than the pristine glasses; 13) the conductivity of the 80Li$_2$S·20P$_2$S$_5$ (mol%) glass-ceramic is about 10$^{-4}$ S cm$^{-1}$. The enhancement of conductivity in the system Li$_2$S−P$_2$S$_5$ proved to be caused by the precipitation of high lithium ion conducting crystals and the decrease of grain boundaries due to the softening of powders by the heat treatment around glass transition temperatures. 14,15) We have confirmed that an all-solid-state cell using the 80Li$_2$S·20P$_2$S$_5$ glass-ceramic as a solid electrolyte works as lithium secondary batteries and exhibits excellent cycling performances over 200 cycles. 16) On the other hand, we have reported that the Li$_2$S−SiS$_2$ glasses with small amounts of ortho-oxosalts such as Li$_2$SiO$_4$ exhibited not only high lithium ion conductivities at room temperature but also high thermal stability as compared with pure sulfide glasses. 6,17) NMR and XPS measurements showed that SiOS$_4$ tetrahedral units with non-bridging sulfurs and a bridging oxygen, which do not strongly trap lithium ions, were mainly present in activation energies. 17) Very recently, Yoneda et al. have reported that Li$_2$S−P$_2$S$_5$ mechanically milled glasses with small amounts of Li$_2$O exhibited twice as high ambient temperature conductivity as the glasses without Li$_2$O; 18) the conductivity of the 67.5Li$_2$S·7.5Li$_2$O·25P$_2$S$_5$ (mol%) glass is 2.7×10$^{-4}$ S cm$^{-1}$ at room temperature. Thus, the addition of small amounts of oxide to pure sulfide glasses is one of effective ways to increase ionic conductivity. However, the local structures of the Li$_2$S−P$_2$S$_5$ milled glasses doped with small amounts of oxide have not been examined yet. Local structure is very important in order to consider the conduction mechanism as mentioned above. Furthermore, to investigate the effect of the addition of oxide on the structure and properties of the Li$_2$S−P$_2$S$_5$ glass-ceramics is also of great interest in order to obtain highly conductive glass-ceramics.

In the present study, Li$_2$S−P$_2$S$_5$-based glasses with small amounts of oxide were prepared by mechanical milling. P$_2$O$_5$ and Li$_2$O were used as an oxygen source because the structure and properties of mechanically milled products would depend on the starting materials. Thermal properties and electrical conductivities for the obtained glasses were investigated. The local structures of the glasses were analyzed using $^{31}$P MAS-NMR measurements. Furthermore, we discuss the compositional dependences of ionic conductivities of the glasses and glass-ceramics obtained by the heat treatment of the glasses.
2. Experimental

Li$_2$S-P$_2$S$_5$-based glasses were prepared by using the mechanical milling technique. Reagent-grade Li$_2$S (Furuuchi, 99.9%), P$_2$S$_5$ (Alirdich, 99.9%), Li$_2$O (Kishida, 99.5%), and P$_2$O$_5$ (Alirdich, 99.99%) crystalline powders were used as starting materials to prepare the 80Li$_2$S·(20 – x)P$_2$S$_5$·xP$_2$O$_5$ (mol%) and the (80 – y) Li$_2$S·yLi$_2$O·20P$_2$S$_5$ (mol%) glasses. The content of lithium compounds (Li$_2$S + Li$_2$O) in these glasses was fixed to be 80 mol%, because the 80Li$_2$S·20P$_2$S$_5$ glass-ceramic exhibited the highest conductivity at room temperature in the binary glass-ceramics. The mixture of these materials was mechanically milled at room temperature by a planetary ball mill apparatus (Fritsch Pulsver-sette 7) using an alumina pot (volume of 45 mL) with ten alumina balls (10 mm in diameter); the milling time was 20 h and a rotating speed was 370 rpm. All the processes were performed in a dry Ar-filled glove box ( [H$_2$O] ≈ 1 ppm).

X-ray diffraction (XRD) measurements (CuK$_\alpha$) were performed using a diffractometer (XRD-6000, Shimadzu). Differential thermal analyses (DTA) were carried out using a thermal analyzer (Thermo-plus 8110, Rigaku) for the obtained powder samples sealed in an Al pan in a dry N$_2$ atmosphere; the heating rate was 10°C·min$^{-1}$. Electrical conductivities were measured for the pelletized samples obtained by cold press under 3700 kg·cm$^{-2}$; the diameter and thickness of the pellets were 10 mm and about 1 mm, respectively. AC impedance measurements were carried out in dry Ar atmosphere using an impedance analyzer (SI1260, Solartron) in the frequency range of 100 Hz to 15 MHz. Solid-state $^{31}$P MAS–NMR spectra were recorded at 121.43 MHz on a nuclear magnetic resonance (NMR) spectrometer (UNITY INOVA 300, Varian). The powdered samples were packed into a zirconia spinner with a sealant in a dry Ar-filled glove box. Detailed conditions for NMR measurements were described in a previous paper.

3. Results and discussion

First, two starting materials of P$_2$O$_5$ and Li$_2$O were compared from a point of view of an effective oxygen source. Figure 1 shows the XRD patterns of the 80Li$_2$S·16P$_2$S$_5$·4P$_2$O$_5$ (mol%) and 60Li$_2$S·20Li$_2$O·20P$_2$S$_5$ (mol%) samples prepared by mechanical milling for 20 h. Both samples contain equal molar contents of oxygens in nominal composition. In the system Li$_2$S-P$_2$S$_5$-P$_2$O$_5$, the diffraction peak of P$_2$O$_5$ rapidly disappeared after mechanical milling for a few hours, while the intensity of the diffraction peak of Li$_2$O gradually decreased with an increase in milling time in the system Li$_2$S-Li$_2$O-P$_2$S$_5$. The glass with P$_2$O$_5$ after milling for 20 h shows a halo pattern. Although the diffraction peak due to Li$_2$S is still present, the peak due to P$_2$O$_5$ completely disappears. The glass with Li$_2$O after milling for 20 h also shows a halo pattern. However, the diffraction peak due to Li$_2$S is not present and the peak due to Li$_2$O remains a little. In our previous report, the XRD peaks due to Li$_2$S crystal were slightly observed for the 80Li$_2$S·20P$_2$S$_5$ (mol%) glass in the binary system after mechanical milling for 20 h. Thus, it is found that P$_2$O$_5$ reacts with Li$_2$S-P$_2$S$_5$ more effectively compared to Li$_2$O. In this paper, the mechanically milled samples in the system Li$_2$S-P$_2$S$_5$-P$_2$O$_5$ were examined in detail.

Figure 2 shows the XRD patterns of the mechanically milled 80Li$_2$S·(20 – x)P$_2$S$_5$·xP$_2$O$_5$ (mol%) samples. Although the diffraction peaks due to Li$_2$S slightly remain, halo patterns are basically observed for all the compositions, indicating that these samples become almost amorphous after milling for 20 h.

Figure 3 shows the $^{31}$P MAS–NMR spectra of the mechanically milled 80Li$_2$S·(20 – x)P$_2$S$_5$·xP$_2$O$_5$ (mol%) amorphous samples with x = 0 and x = 2. A peak at 83 ppm is observed for the glass without P$_2$O$_5$. Two peaks at 83 and 35 ppm are observed for the glass with 2 mol% P$_2$O$_5$, and the peak at 83 ppm is broadened at the upfield side in comparison with the spectrum of x = 0, suggesting that a broad peak at around 65 ppm is present. The peak at 83 ppm is assigned to phosphorus coordinated with four sulfurs, which is represented as a PS$_4$ tetrahedral unit. The component of a POS$_4$ tetrahedral unit in

![Fig. 1. XRD patterns of the 80Li$_2$S·16P$_2$S$_5$·4P$_2$O$_5$ (mol%) and the 60Li$_2$S·20Li$_2$O·20P$_2$S$_5$ (mol%) samples prepared by mechanical milling for 20 h.](image1)

![Fig. 2. XRD patterns of the 80Li$_2$S·(20–x)P$_2$S$_5$·xP$_2$O$_5$ (mol%) samples prepared by mechanical milling for 20 h.](image2)

![Fig. 3. $^{31}$P MAS–NMR spectra of the mechanically milled 80Li$_2$S·(20–x)P$_2$S$_5$·xP$_2$O$_5$ (mol%) amorphous samples.](image3)
which phosphorus is coordinated with one oxygen and three sulfur also overlaps on the 83 ppm.\textsuperscript{16} The peaks at 65 and 35 ppm are respectively assigned to PO\textsubscript{2}S\textsubscript{2} and PO\textsubscript{2}S tetrahedral units.\textsuperscript{19} Since the peaks due to PO\textsubscript{2}S\textsubscript{2−n} (n = 1, 2, 3) units are much stronger than the peak due to PO\textsubscript{2} unit (8 ppm), the oxygen atoms are apparently incorporated into the Li\textsubscript{2}S-P\textsubscript{2}S\textsubscript{5} glass-network.

Figure 4 shows the DTA curves of the mechanically milled 80Li\textsubscript{2}S(20 − x)P\textsubscript{2}S\textsubscript{5}·xP\textsubscript{2}O\textsubscript{5} (mol%) amorphous samples. Sharp exothermic peaks at around 200°C due to the crystallization (T\textsubscript{c}) and slight endothermic changes at around 170°C due to the glass transition (T\textsubscript{g}) are observed in all the amorphous samples, indicating that these samples are in a glassy state. The values of T\textsubscript{c} and T\textsubscript{g} do not monotonically increase with an increase in the P\textsubscript{2}O\textsubscript{5} content but exhibit a minimum at the composition of x = 1.

Figure 5 shows the temperature dependence of electrical conductivities of the mechanically milled 80Li\textsubscript{2}S·19P\textsubscript{2}S\textsubscript{5}·1P\textsubscript{2}O\textsubscript{5} (mol%) glass. The glass was heated up to 230°C over the crystallization temperature and then cooled down to room temperature. Open and filled circles denote heating and cooling processes, respectively. The conductivity of the glass before heating is 1.7 × 10\textsuperscript{-4} S·cm\textsuperscript{-1} at room temperature. This value is as high as those of mechanically milled amorphous materials such as Li\textsubscript{2}S-SiS\textsubscript{2},\textsuperscript{7} Li\textsubscript{2}S-SiS\textsubscript{2}-Li\textsubscript{2}SiO\textsubscript{4},\textsuperscript{9} and Li\textsubscript{2}N-SiS\textsubscript{2}·xP\textsubscript{2}O\textsubscript{5} (mol%) glass.\textsuperscript{10} The conductivity of the glass-ceramic in the cooling process exhibits a higher value in the whole temperature region than the pristine glass in the heating process; the conductivity of the glass-ceramic at room temperature is 7.3 × 10\textsuperscript{-4} S·cm\textsuperscript{-1}. The activation energy for conduction was calculated from a slope of the line using the Arrhenius equation. The activation energy of 36 kJ·mol\textsuperscript{-1} for conduction in the heating process decreases to 34 kJ·mol\textsuperscript{-1} in the cooling process. Thus, it is found that the glass-ceramic with higher conductivity and lower activation energy than the mother glass is obtained by heating of the glass over the crystallization temperature.

Figure 6 shows the composition dependences of the conductivity at 25°C (\sigma\textsubscript{25}) and activation energy (E\textsubscript{a}) for conduction of the mechanically milled 80Li\textsubscript{2}S(20 − x)P\textsubscript{2}S\textsubscript{5}·xP\textsubscript{2}O\textsubscript{5} (mol%) glasses and glass-ceramics. Open and filled marks denote glasses and glass-ceramics, respectively. Circles and triangles denote \sigma\textsubscript{25} and E\textsubscript{a}, respectively. The glass with 1 mol% P\textsubscript{2}O\textsubscript{5} exhibits similar \sigma\textsubscript{25} and E\textsubscript{a} compared to the glass without P\textsubscript{2}O\textsubscript{5}. Further increase in x results in both a decrease in \sigma\textsubscript{25} and an increase in E\textsubscript{a}. In general, lower T\textsubscript{c} of glassy materials tends to bring about the higher ionic conductivity at room temperature. In this case, the glass with 1 mol% P\textsubscript{2}O\textsubscript{5} keeps high \sigma\textsubscript{25} and exhibits lower E\textsubscript{a}, suggesting that small amounts of P\textsubscript{2}O\textsubscript{5} play a significant role to move lithium ions smoothly in the Li\textsubscript{2}S-P\textsubscript{2}S\textsubscript{5} glasses. Furthermore, the similar composition dependence was observed in melt-quenched Li\textsubscript{2}S-SiS\textsubscript{2}-Li\textsubscript{2}MO\textsubscript{3} (Li\textsubscript{2}MO\textsubscript{3} = Li\textsubscript{2}PO\textsubscript{3}, Li\textsubscript{2}SiO\textsubscript{4} etc.) oxysulfide glasses,\textsuperscript{6,17} The addition of small amounts of Li\textsubscript{2}SiO\textsubscript{4} to the Li\textsubscript{2}S-SiS\textsubscript{2} glasses did not monotonously decrease \sigma\textsubscript{25} but retained high conductivities comparable to pure sulfide glasses. This non-monotonous change on \sigma\textsubscript{25} is understood by the fact that the oxygen atoms added were mainly present as bridging oxygen atoms which worked as weaker traps of lithium ions compared to non-bridging ones.\textsuperscript{17} The addition of large amounts of Li\textsubscript{2}SiO\textsubscript{4} decreased \sigma\textsubscript{25} and increased E\textsubscript{a}, because SiO\textsubscript{2}S and SiO\textsubscript{2} tetrahedral units with more than two oxygen atoms increased, and non-bridging oxygen atoms which worked as stronger traps of lithium ions also increased.\textsuperscript{17} Yoneda et al. have also reported that the similar composition dependence in mechanically milled (75 − x)Li\textsubscript{2}S·xLi\textsubscript{2}O·25P\textsubscript{2}S\textsubscript{5} (mol%) glasses was observed because two kinds of anions consisting of sulfurs and oxgens were coexistent.\textsuperscript{18} Thus, the change on the composition dependences of \sigma\textsubscript{25} and E\textsubscript{a} in the 80Li\textsubscript{2}S(20 − x)P\textsubscript{2}S\textsubscript{5}·xP\textsubscript{2}O\textsubscript{5} (mol%) glasses is presumed as follows. The addition of small amounts of P\textsubscript{2}O\textsubscript{5} keeps high \sigma\textsubscript{25} and decreases E\textsubscript{a},
because a POS₄ tetrahedral unit with a bridging oxygen is formed. The addition of large amounts of P₂O₅ decreases σ₂₅ and increases Eₐ because PO₄ and PO₄ tetrahedral units with non-bridging oxygens are formed. On the other hand, the 80Li₂S·(20−x)P₂S₅·xP₂O₅ (mol%) glass-ceramics exhibit higher σ₂₅ and lower Eₐ than the mother glasses at all the compositions. The composition dependences of σ₂₅ and Eₐ are very similar to that of the mother glasses.

Figure 7 shows the XRD patterns of the 80Li₂S·(20−x)P₂S₅·xP₂O₅ (mol%) glass-ceramics (x = 0 and x = 1) obtained after the conductivity measurements. The diffraction patterns of both glass-ceramics almost correspond to that of highly conductive crystal thio-LISICON Li₃₂Ge₆S₂₂P₆.75S₄, which exhibits the highest ambient temperature conductivity in a series of sulfide crystalline solid electrolytes reported by Kanno et al. The conductivities of the glass-ceramics in the system Li₂S–P₂S₅–SIS₂ monotonically increased with an increase in crystallinity of the precipitated thio-LISICON phase. This result suggests that the enhancement of σ₂₅ in the glass-ceramics shown in Fig. 6 is due to the precipitation of the thio-LISICON analog phase obtained by crystallization of the glasses. Furthermore, almost all peaks shown in the pattern for the glass-ceramic with 1 mol% P₂O₅, except for Li₂S, slightly shift toward larger diffraction angles and are broadened in comparison with the peaks shown in the pattern for the glass-ceramic without P₂O₅; this shift and broadening imply that part of sulfur atoms in the glass-ceramic with 1 mol% P₂O₅ are replaced with oxygen atoms. ³¹P MAS-NMR measurements revealed that the components of PO₄S₄₋ₓ (n = 1, 2, 3) tetrahedral units, where phosphorus is coordinated with both sulfurs and oxygens, were observed in the glass-ceramics with P₂O₅. Thus, it is suggested that the thio-LISICON analog, in which part of sulfur atoms in the crystal lattice are replaced with oxygen atoms, would be obtained in the Li₂S–P₂S₅–P₂O₅ glass-ceramics.

4. Conclusions
Li₂S–P₂S₅–P₂O₅-based solid electrolytes with small amounts of oxide such as P₂O₅ and Li₂O were synthesized by the mechanochemical milling method. XRD patterns suggested that P₂O₅ as an oxygen source reacted with Li₂S–P₂S₅ more effectively. ³¹P MAS-NMR spectra showed the presence of PO₄S₄₋ₓ (n = 1, 2, 3) tetrahedral units where phosphorus was coordinated with both sulfurs and oxygens, indicating that oxygens were incorporated into the Li₂S–P₂S₅ glass-network. The 80Li₂S·19P₂S₅·1P₂O₅ (mol%) glass attained a minimum value of Tₑ and Tₑ, and then showed similar σ₂₅ and lower Eₐ compared to the 80Li₂S·20P₂S₅ (mol%) glass. The Li₂S–P₂S₅–P₂O₅ glass-ceramics also exhibited almost the same composition dependences of σ₂₅ and Eₐ as the mother glasses. In particular, 80Li₂S·19P₂S₅·1P₂O₅ (mol%) glass-ceramic showed high lithium ion conductivity of 7.3×10⁻⁴ S·cm⁻¹ at room temperature. It was found that the highly conductive thio-LISICON analog crystal was also precipitated from the Li₂S–P₂S₅ glasses containing oxide such as P₂O₅.

Acknowledgement This work was supported by the Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References