

Mechanochemical Synthesis of Fast Lithium Ion Conducting Solid Electrolytes in the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{SiS}_2-\text{Al}_2\text{S}_3$ System

YU. SHIBUTANI, F. MIZUNO, A. HAYASHI and M. TATSUMISAGO

Department of Applied Chemistry, Graduate School of Engineering,
Osaka Prefecture University, Sakai, Osaka 599-8531 (Japan)

E-mail: hayashi@chem.osakafu-u.ac.jp

Abstract

Glassy solid electrolytes with higher Li_2S content were mechanochemically prepared in the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ based multicomponent system, and showed high conductivity by the addition of glass formers SiS_2 and Al_2S_3 . The $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 1.1\text{SiS}_2 \cdot 1.1\text{Al}_2\text{S}_3$ (mol. %) glass exhibited the conductivity of $1.2 \cdot 10^{-4}$ S/cm at room temperature, which was twice as high as the conductivity of the $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 2.2\text{SiS}_2$ glass without Al_2S_3 . The glass ceramics obtained by crystallization of the glasses showed the same XRD patterns as superionic crystals called thio-LISICON II phase of $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$, which is one of the best Li^+ ion conducting crystals with very high conductivity over 10^{-3} S/cm at ambient temperature. The conductivity of the glass ceramic prepared by heating the glass at 230 °C was $1.2 \cdot 10^{-3}$ S/cm, which was one order of magnitude higher than that of the corresponding glass. The precipitated thio-LISICON II analogs are responsible for the high conductivity of the glass ceramics.

INTRODUCTION

All-solid-state lithium rechargeable batteries attract much attention because of their high safety and reliability. Solid electrolytes with high lithium ion conductivity are the key materials developing all-solid-state batteries. Sulphide glassy materials in the systems $\text{Li}_2\text{S}-\text{SiS}_2$ and $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ prepared by the melt quenching method are strong candidates of solid electrolytes. These glasses are well known as lithium ion conductors with high conductivities of over 10^{-4} S/cm at room temperature [1, 2].

Recently, sulphide crystalline materials with superionic conduction have also been developed, which are called thio-LISICON [3, 4]. The best ion conductor in a series of thio-LISICONs is the solid solution $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$. The $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ crystals have a similar structure to $\gamma\text{-Li}_3\text{PO}_4$ and the system is divided into three composition regions depending on monoclinic superstructures with different types of cation ordering: the region I ($0 < x \leq 0.6$) has a monoclinic superlattice cell of $a \times 3b \times 2c$ which is related to the orthorhombic Li_4GeS_4 , and the region II ($0.6 < x < 0.8$) and region III ($0.8 \leq x < 1.0$)

have different monoclinic cells with $a \times 3b \times 3c$ and $a \times 3b \times 2c$, respectively. The thio-LISICON phase in region II is reported to show the highest conductivity of $2.2 \cdot 10^{-3}$ S/cm at room temperature among three regions [3].

Another candidate for solid electrolytes is a glass ceramic material. We succeeded in enhancing conductivity by crystallization of mechanochemically prepared $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glassy electrolytes [5–7]. The glass ceramics obtained by crystallization of the glasses showed the same XRD patterns as thio-LISICON phase in region II (thio-LISICON II, a representative composition: $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$). This thio-LISICON II analogous phase was not synthesized by conventional solid-state reaction in the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ binary system [7]. The precipitated metastable thio-LISICON II analog is responsible for the high conductivity of the glass ceramics.

Conductivity of the glass ceramics depends on the precipitated crystalline phases. In order to obtain thio-LISICON II analog with very high conductivity, increasing Li^+ concentration of glass matrix is important. For instance, thio-LISICON II analog was precipitated from the $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ (mol. %) glass, while less con-

ductive thio-LISICON III (a representative composition: $\text{Li}_{3.2}\text{Ge}_{0.2}\text{P}_{0.8}\text{S}_4$) analog was precipitated from the $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol. %) glass [7]. Because the glasses with Li_2S content over 75 mol. % partially included unreacted Li_2S crystal, further amorphization in the higher Li_2S composition range leads to highly conductive glass ceramic materials with thio-LISICON II analog. The incorporation of additional glass formers is known to be an effective way to promote amorphization.

In the present study, the glasses with high Li^+ concentrations in the multicomponent system $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{SiS}_2-\text{Al}_2\text{S}_3$ were mechanochemically synthesized using a planetary ball mill apparatus. The glass ceramic materials were prepared by heating the glasses at several temperatures over the crystallization temperature. The effects of the addition of glass network formers (SiS_2 and/or Al_2S_3) to the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ binary system on precipitated crystals and conductivity were investigated.

EXPERIMENTAL

Reagent grade Li_2S (Furuuchi Chem., 99.9 %), P_2S_5 (Aldrich, 99 %), SiS_2 (Furuuchi Chem., 99.9 %) and Al_2S_3 (Koujundo Chem., 98 %) crystalline powders were used as starting materials for sample preparation. The mechanical milling treatment was carried out for the batch (1 g) of the mixed materials placed into an alumina pot (volume of 45 ml) with 10 alumina balls (10 mm in diameter) using a high-energy planetary ball mill apparatus (Fritsch Pulverisette 7) [8, 9]. The rotation speed was fixed at 370 rpm and all processes were conducted at room temperature in a dry Ar-filled glove box.

X-ray diffraction (XRD) measurements were carried out using a Mac-Science M18XHF²²-SRA diffractometer with $\text{CuK}\alpha$ radiation for the obtained materials. The sample was sealed in an Ar-filled container with the beryllium windows. Differential thermal analysis (DTA) was carried out using a Rigaku thermal analyzer (Thermo Plus 8110) for the obtained powder samples sealed in an Al pan in a dry Ar atmosphere.

The electrical conductivity of the samples was measured by using AC impedance meth-

ods. The powder samples were pelletized by cold pressing at 3700 kg/cm^2 and carbon paste was painted on both sides of the pellet to serve as electrodes. The pellet size was 10 mm in diameter and 1.5 mm in thickness. The electrical conductivity of the pellet was measured in a dry Ar atmosphere from 10 Hz to 8 MHz with an impedance analyzer (Model 1260, Solartron) in the temperature range of 25–230 °C.

RESULTS AND DISCUSSION

Amorphous materials in the $x\text{Li}_2\text{S} \cdot (100 - x)\text{P}_2\text{S}_5$ (mol. %) binary system were prepared by mechanical milling for 20 h. The sample at the composition $x = 75$ was completely amorphous, while those at the compositions $x > 75$ ($x = 76, 78$ and 80) were partially amorphous with Li_2S crystals remaining. The obtained amorphous materials exhibited glass transition phenomena in DTA measurement, suggesting that they are in glassy state.

Glass ceramics were prepared by heating the mechanically milled glasses over the crystallization temperature. The first crystal phase from the composition $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ was the crystal analogous to thio-LISICON II, while the crystal analogous to thio-LISICON III was precipitated from the composition $78\text{Li}_2\text{S} \cdot 22\text{P}_2\text{S}_5$. The thio-LISICON II phase exhibits higher Li^+ conductivity than the thio-LISICON III phase [3], and the precipitation of thio-LISICON II is an effective way to improve conductivity of glass-ceramic materials. The thio-LISICON II phase

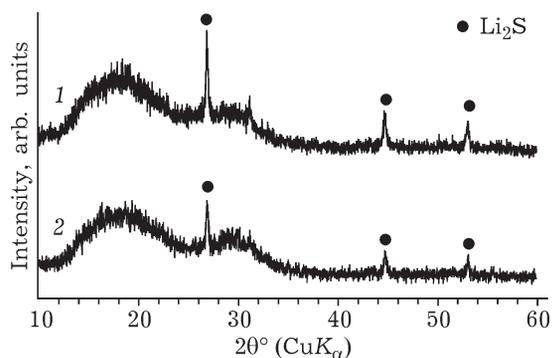


Fig. 1. X-ray diffraction patterns of the $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 2.2\text{SiS}_2$ (1) and $78\text{Li}_2\text{S} \cdot 17.6\text{P}_2\text{S}_5 \cdot 4.4\text{SiS}_2$ (mol. %) (2) glasses prepared by mechanical milling for 20 h: 1 - $x = 2.2$, $\text{P}_2\text{S}_5/\text{SiS}_2 = 9/1$; 2 - $x = 4.4$, $\text{P}_2\text{S}_5/\text{SiS}_2 = 8/2$.

has a higher lithium content than the thio-LISICON III phase, and therefore thio-LISICON II analog would not be formed from the $78\text{Li}_2\text{S} \cdot 22\text{P}_2\text{S}_5$ glass because of insufficient Li concentration in the glass matrix.

In order to prepare glassy materials with higher Li concentration, the mixed former system of $78\text{Li}_2\text{S} \cdot (22 - x)\text{P}_2\text{S}_5 \cdot x\text{SiS}_2$ was investigated. Figure 1 shows the XRD patterns of the $78\text{Li}_2\text{S} \cdot (22 - x)\text{P}_2\text{S}_5 \cdot x\text{SiS}_2$ samples prepared by mechanical milling for 20 h. Halo patterns are basically observed in both samples, whereas the diffraction peaks due to Li_2S are present. The intensity of the Li_2S peaks for the sample (1) is smaller than that for sample (2), suggesting that amorphization effectively proceeds in the former case.

Figure 2 shows the XRD patterns of the $78\text{Li}_2\text{S} \cdot (22 - x)\text{P}_2\text{S}_5 \cdot x\text{SiS}_2$ glass ceramics. The glass ceramics were prepared by heating the glass up to 230 °C over the crystallization temperature. Thio-LISICON II analog is formed from the glass (curve 1), while thio-LISICON III analog is mainly formed from the glass (curve 2). The precipitated crystal phases are different in spite of the constant Li_2S composition of 78 mol. %. The difference would be caused by the degree of amorphization. Although the ratio of Li to (P + Si) in the glass (curve 2) with $x = 4.4$ is larger than that in the glass (curve 1) with $x = 2.2$, the Li concentration of glass matrix in the latter case would be

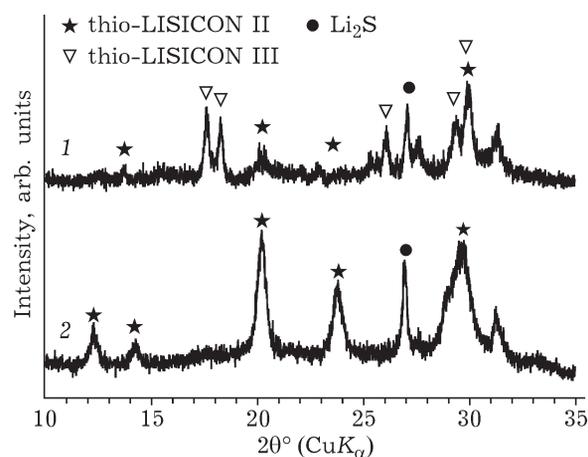


Fig. 2. X-ray diffraction patterns of the $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 2.2\text{SiS}_2$ (1) and $78\text{Li}_2\text{S} \cdot 17.6\text{P}_2\text{S}_5 \cdot 4.4\text{SiS}_2$ (mol. %) (2) glass ceramics.

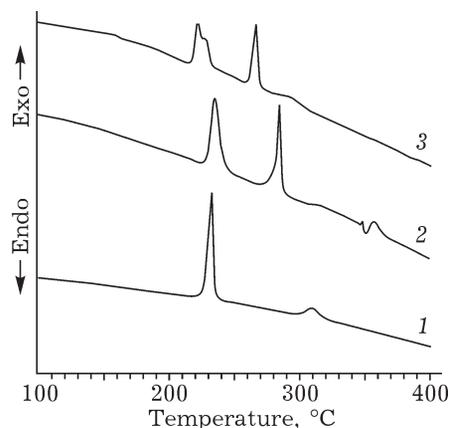


Fig. 3. Differential thermal analysis curves of the $78\text{Li}_2\text{S} \cdot 22\text{P}_2\text{S}_5$ (1), $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 2.2\text{SiS}_2$ (2), and $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 1.1\text{SiS}_2 \cdot 1.1\text{Al}_2\text{S}_3$ (3) glasses prepared by mechanical milling for 20 h. The heating rate is 10 °C/min.

higher than that in the former case, where large amounts of Li_2S crystals remain. Thio-LISICON II analog is easily precipitated from Li-rich glass matrix (curve 1). Since thio-LISICON III analog was formed from the $78\text{Li}_2\text{S} \cdot 22\text{P}_2\text{S}_5$ glass, thio-LISICON II analog is successfully obtained by adding 2.2 mol. % SiS_2 to the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ binary system.

The fourth component Al_2S_3 was added to the above ternary composition in order to achieve further amorphization. Figure 3 shows DTA curves of the $78\text{Li}_2\text{S} \cdot 22\text{P}_2\text{S}_5$, $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 2.2\text{SiS}_2$ and $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 1.1\text{SiS}_2 \cdot 1.1\text{Al}_2\text{S}_3$ glasses. The heating rate was fixed at 10 °C/min. Several sharp exothermic peaks due to crystallization are observed. The first crystallization temperatures are observed at around 230 °C for all the samples. The second crystallization temperatures decrease by adding the third and the fourth glass formers to the composition $78\text{Li}_2\text{S} \cdot 22\text{P}_2\text{S}_5$.

Figure 4 shows XRD patterns of glass and glass ceramic at the composition $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 1.1\text{SiS}_2 \cdot 1.1\text{Al}_2\text{S}_3$. The glass ceramic was prepared by heating the glass up to 230 °C. Although a broad peak due to Li_2S still remains, amorphization surely proceeds by adding Al_2S_3 to the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{SiS}_2$ ternary system in terms of the comparison of the XRD pattern of the ternary glass (curve 1) as shown in Fig. 1. The formation of glass matrix with higher Li concentration in the quaternary system would decrease the crystallization temper-

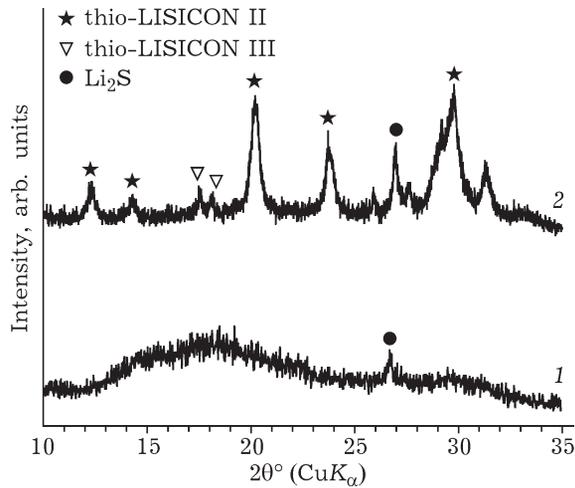


Fig. 4. X-ray diffraction patterns of the glass (1) and glass ceramic (2) with the composition $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 1.1\text{SiS}_2 \cdot 1.1\text{Al}_2\text{S}_3$ (mol. %).

ature as shown in Fig. 3. Thio-LISICON II analog is mainly formed and thio-LISICON III analog is also partially precipitated in the glass ceramic (curve 2). Thio-LISICON III analog was mainly present after the glass heated at over the second crystallization peak on the DTA curve as shown in Fig. 3.

Figure 5 shows the temperature dependence of conductivities for the $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot (2.2 - y)\text{SiS}_2 \cdot y\text{Al}_2\text{S}_3$ ($y = 0, 1.1$) glasses and glass ceramics. The conductivity was measured during a heating and cooling cycle; the glasses were heated up to 230 °C (the first

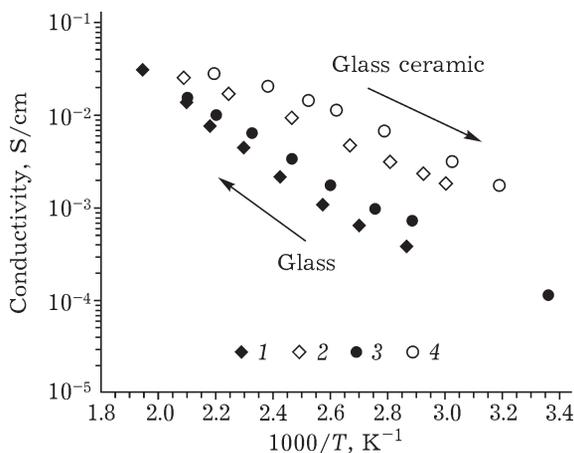


Fig. 5. Temperature dependence of conductivity for the $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot (2.2 - y)\text{SiS}_2 \cdot y\text{Al}_2\text{S}_3$ (mol. %) ($y = 0, 1.1$) glasses and glass ceramics: 1, 2 - $y = 0$, heating runs; 3, 4 - $y = 1.1$, cooling runs.

crystallization temperature) and then the obtained glass ceramics were cooled down. Crystallization of glass concurrently occurs during conductivity measurements on the heating process and then the temperature dependence of conductivity of the glasses tends to be nonlinear.

The $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 1.1\text{SiS}_2 \cdot 1.1\text{Al}_2\text{S}_3$ glass exhibits the conductivity of $1.2 \cdot 10^{-4}$ S/cm at room temperature, which is almost twice as high as the conductivity of the $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 2.2\text{SiS}_2$ glass without Al_2S_3 . This is because a higher Li concentration and larger volume fraction of glass matrix are achieved in the former system with Al_2S_3 . The conductivity of the glass ceramic was $1.2 \cdot 10^{-3}$ S/cm at room temperature (extrapolated value), which was one order of magnitude higher than that of the corresponding glass. The precipitated thio-LISICON II analog is responsible for the high conductivity of the glass ceramics. The glass ceramic with the fourth component Al_2S_3 exhibits higher conductivity than the glass ceramic without Al_2S_3 . Thio-LISICON II analog with higher crystallinity is obtained in the former case as shown in Fig. 4, and therefore the glass-ceramic material with Al_2S_3 achieves an excellent conductivity of 10^{-3} S/cm at room temperature. This conductivity is also higher than that for the $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass ceramic ($7.2 \cdot 10^{-4}$ S/cm) with thio-LISICON II analog prepared by heating at the same temperature of 230 °C [7].

CONCLUSIONS

The $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{SiS}_2-\text{Al}_2\text{S}_3$ multicomponent glassy materials were prepared by the mechanical milling method. Amorphization was promoted by adding glass formers of SiS_2 and Al_2S_3 to the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ binary system. Two phases of thio-LISICON II and III analogs were present in the multicomponent glass ceramics and in particular thio-LISICON II analog with higher conductivity was preferentially precipitated from the Li-rich multicomponent glassy matrix.

The $78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 1.1\text{SiS}_2 \cdot 1.1\text{Al}_2\text{S}_3$ glass exhibited the conductivity of $1.2 \cdot 10^{-4}$ S/cm at room temperature, which was twice as high as the conductivity of the

$78\text{Li}_2\text{S} \cdot 19.8\text{P}_2\text{S}_5 \cdot 2.2\text{SiS}_2$ glass without Al_2S_3 . The conductivity of the glass-ceramic prepared by heating the glass at 230 °C was $1.2 \cdot 10^{-3} \text{ S/cm}$ at room temperature. The formation of thio-LISICON II analog and the improvement of its crystallinity are key points to develop glass ceramic solid electrolytes with high Li^+ conductivity.

Acknowledgements

This work was supported by the Grant-in-Aid for Scientific Research on Section (B) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and the Industrial Technology Research Grant Program in 2005 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

REFERENCES

- 1 R. Mercier, J. P. Malugani, B. Fahys and G. Robert, *Solid State Ionics*, 5 (1981) 663.
- 2 A. Pradel and M. Ribes, *Ibid.*, 18/19 (1986) 351.
- 3 R. Kanno and M. Murayama, *J. Electrochem. Soc.*, 148 (2001) A742.
- 4 M. Murayama, R. Kanno, M. Irie *et al.*, *J. Solid State Chem.*, 168 (2002) 140.
- 5 A. Hayashi, S. Hama, H. Morimoto *et al.*, *Chem. Lett.*, (2001) 872.
- 6 M. Tatsumisago, S. Hama, A. Hayashi *et al.*, *Solid State Ionics*, 154–155 (2002) 635.
- 7 A. Hayashi, S. Hama, T. Minami and M. Tatsumisago, *Electrochem. Commun.*, 5 (2003) 111.
- 8 H. Morimoto, H. Yamashita, M. Tatsumisago and T. Minami, *J. Am. Ceram. Soc.*, 82 (1999) 1352.
- 9 A. Hayashi, S. Hama, H. Morimoto *et al.*, *Ibid.*, 84 (2001) 477.