Superionic Conduction in Rapidly Quenched $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{PO}_4$ Glasses

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 $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{PO}_4$ 系超急冷ガラスの超イオン伝導

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Lithium ion conducting glasses were prepared in the system $(0.6\text{Li}_2\text{S}\cdot0.4\text{SiS}_2)-\text{Li}_3\text{PO}_4$ by twin-roller rapid quenching. The temperatures of glass transition (T_g) and crystallization (T_c) were determined for the glassy samples with 0–40 mol% Li_3PO_4 . The conductivity values at 25°C (σ_{25}) were maximized and the activation energies (E_a) for conduction were minimized at the composition with 5 mol% Li_3PO_4 ; the maximum σ_{25} value was as high as $9 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$. Since the difference between T_g and T_c was also maximized at the same composition, it was concluded that the doping of small amounts of Li_3PO_4 improved both the glass stability against crystallization and the lithium ion conductivities.

Key-words: Superionic conductor, Rapid quenching, Lithium ion conduction, Lithium thiosilicate, Glassy electrolyte

1. Introduction

Lithium ion-based solid electrolytes are promising for utilization in high voltage and high energy density solid-state battery systems.¹⁾ Lithium thiosilicate $\text{Li}_2\text{S}-\text{SiS}_2$ glasses are one of the best candidates because of their high conductivities of about $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at room temperature and the high stability against the chemical reaction with lithium metals.^{2),3)} Kennedy et al. reported that the doping of lithium halides to the $\text{Li}_2\text{S}-\text{SiS}_2$ glasses improved the ion conductivity in one order of magnitude. However, such a doping was also found to lower the stability against lithium metals.^{4),5)} One of the groups of the present authors reported that the doping of lithium orthophosphate Li_3PO_4 to the $\text{Li}_2\text{S}-\text{SiS}_2$ system improved the stability against the lithium metal as well as the conductivity values.^{6),7)} Such a dopant like Li_3PO_4 was also found to improve the stability against electrochemical reduction.

On the other hand, another group of the present authors have demonstrated that the rapid quenching technique of melts is very useful to obtain lithium ion conducting oxide glasses with high concentration of Li_2O .⁸⁾ We have developed a variety of rapidly quenched oxide glasses with high Li^+ ion conduction and

also showed that rapidly quenched oxysulfide glasses are the best candidate of lithium ion conductors with high conductivities and stability.⁹⁾

In the present study we applied the twin-roller rapid quenching in the preparation of oxysulfide glasses in the system $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{PO}_4$. Glass formation and thermal and electrical properties are reported in the paper. Compositional variation of conductivity is discussed for the data obtained for bulk samples, in which the grain boundary effect can be eliminated, although most researchers have used the pelletized samples made of pulverized glass samples for conductivity measurements.

2. Experimental

Reagent-grade Li_3PO_4 , Li_2S , and SiS_2 were used as starting materials. The mixture in a vitreous carbon crucible was heated using an electric furnace at 1000°C for 1 h. The molten mixture was poured into the rotating twin-roller to obtain flake-like samples with a thickness of about 20 μm .

The differential thermal analyses (DTA) were performed for the glassy samples sealed in an Al pan using a Mac-Science thermal analyzer. The conductivity was measured for the flakes, on which two parallel electrodes of carbon paste were painted 0.5 mm apart on one surface. The measurement was carried out in dry Ar atmosphere using an impedance analyzer (HP 4192A) in the temperature range 25–200°C.

3. Results and discussion

A composition of $0.6\text{Li}_2\text{S}\cdot0.4\text{SiS}_2$ was selected as a base glass composition and several amounts of Li_3PO_4 were doped. For the composition $(100-x)(0.6\text{Li}_2\text{S}\cdot0.4\text{SiS}_2)\cdot x\text{Li}_3\text{PO}_4$, brownish-orange, transparent glasses were obtained in the range $x < 40$ mol%; the samples showed halo patterns in X-ray diffraction measurements and exhibited glass transition phenomena in thermal analyses. Glasses could not be obtained for the composition range $x > 40$ because the starting mixtures did not completely melt at 1000°C in this composition range.

Figure 1 shows the composition dependence of glass transition temperature T_g and crystallization

Fig. 1. Composition dependence of T_g and T_c for the system $(100-x)(0.6\text{Li}_2\text{S}\cdot 0.4\text{SiS}_2)\cdot x\text{Li}_3\text{PO}_4$. The values of T_c-T_g are also shown.

temperature T_c for the $(100-x)(0.6\text{Li}_2\text{S}\cdot 0.4\text{SiS}_2)\cdot x\text{Li}_3\text{PO}_4$ glasses. The difference between T_g and T_c , which is one of the measures of the glass stability, is also plotted in this figure. The values of T_g and T_c , which ranged from 290 to 340°C and from 350 to 425°C, respectively, made a complex change with compositions. While the doping of Li_3PO_4 apparently decreases T_g when x is less than 10 mol%, further doping of Li_3PO_4 brings about the increase of T_g . Although the doping of 5 mol% Li_3PO_4 does not change the T_c value, further doping of Li_3PO_4 tends to decrease the T_c value. The value of T_c-T_g , which ranges from 40 to 110°C, exhibits a maximum value at the composition with 5 mol% Li_3PO_4 . In other words, the doping of 5 mol% Li_3PO_4 is most effective to stabilize the glassy state against crystallization.

Figure 2 shows the results of the frequency-dependent complex impedance measurements of the 95 $(0.6\text{Li}_2\text{S}\cdot 0.4\text{SiS}_2)\cdot 5\text{Li}_3\text{PO}_4$ glass as an example at several temperatures. The bulk impedance is attributable to the semicircle which was observed at each temperature. The bulk resistance was obtained

Fig. 2. Complex impedance plots for a rapidly quenched $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{PO}_4$ glass $(95(0.6\text{Li}_2\text{S}\cdot 0.4\text{SiS}_2)\cdot 5\text{Li}_3\text{PO}_4)$ at 34 and 133°C.

from the intersecting point of the semicircle with the real axis. Conductivity data for the entire composition range are shown in Fig. 3 as $\log \sigma$ vs. reciprocal absolute temperature. The data are a good fit to the Arrhenius type equation:

$$\sigma = \sigma_0 \exp(-E_a/RT),$$

where E_a is the activation energy for conduction, σ_0 is a preexponential factor, and R is the gas constant.

Figure 4 shows the composition dependence of conductivity at 25°C, σ_{25} , and the activation energy E_a for conduction. The error bars are mainly due to the uncertainties of sample thickness and distance between electrodes. The σ_{25} values range from 5×10^{-6} to $9 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$. The value for the $0.6\text{Li}_2\text{S}\cdot 0.4\text{SiS}_2$ glass, which is about $4 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, is very similar to the values for pelletized samples obtained by the present authors, Kennedy et al., and Pradel et al.^{(3),(6),(10)} Such a result means that the influence of grain boundaries or packing densities on conductivity measurements for pelletized samples is negligible.

The σ_{25} values maximize at the composition with 5 mol% Li_3PO_4 , as already shown for the pelletized glass samples prepared by liquid N_2 cooling,⁽⁶⁾ indicating that the doping of a small amount of Li_3PO_4 apparently enhances conductivities. The maximum value of $9 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ is the highest one in the

Fig. 3. Temperature dependence of conductivity for the rapidly quenched $(100-x)(0.6\text{Li}_2\text{S}\cdot 0.4\text{SiS}_2)\cdot x\text{Li}_3\text{PO}_4$ glasses.

Fig. 4. Composition dependence of σ_{25} and E_a for the rapidly quenched $(100-x)(0.6\text{Li}_2\text{S}\cdot 0.4\text{SiS}_2)\cdot x\text{Li}_3\text{PO}_4$ glasses.

lithium ion conducting glasses without any halide ions. The E_a values range 36–53 kJ/mol. A minimum of E_a is observed at the same composition where the maximum of σ_{25} is observed. Since the preexponential factors scatter around 1×10^6 S·cm⁻¹ and do not change with composition, the enhancement of conductivity is concluded to relate to the decrease in E_a with a doping of Li₃PO₄.

It is noteworthy that the σ_{25} values were maximized at the composition with 5 mol% Li₃PO₄, at which the T_c - T_g values were also maximized as shown in Fig. 1. Figure 5 shows the relation between the σ_{25} values and the T_c - T_g values for

Fig. 5. Relation between σ_{25} and T_c - T_g for the rapidly quenched $(100-x)(0.6\text{Li}_2\text{S} \cdot 0.4\text{SiS}_2) \cdot x\text{Li}_3\text{PO}_4$ glasses.

$(100-x)(0.6\text{Li}_2\text{S} \cdot 0.4\text{SiS}_2) \cdot x\text{Li}_3\text{PO}_4$ glasses. A good correlation holds between the σ_{25} values and the T_c - T_g values; the more the stability of the glasses, the higher the conductivity for the present glass system. It is thus concluded that the doping of small amounts of Li₃PO₄ improved the stability of glass against crystallization and, at the same time, enhanced the ion conductivities up to 9×10^{-4} S·cm⁻¹.

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