Structure of Li_2S-P_2S_5 sulfide glasses

Sulfide glasses are materials of interest for solid electrolytes in lithium ion batteries (LIBs) [1], because the realization of an all-solid-state battery will enable the miniaturization of battery packages and reduce safety issues compared with those of LIBs with an organic electrolyte. Significant progress has been made so far with the discovery of numerous sulfide compounds with high ionic conductivities such as $Li_7P_3S_{11}$ [2], $Li_{10}GeP_2S_{12}$ [3], $Li_{10}SnP_2S_{12}$ [4], and $Li_7P_2S_8I$ [5]. All these materials are derived from Li_2S-P_2S_5 sulfide glasses. Therefore, the nature of Li_2S-P_2S_5 glasses must be clarified in detail to continue the development of advanced Li ionic conductors targeted at the realization of all-solid-state batteries.

To clarify the origin of the ionic conduction, we present a comparative fundamental study of the structures of the $67Li_2S$-$33P_2S_5$ ($67Li_2S$), $70Li_2S$-$30P_2S_5$ ($70Li_2S$), and $75Li_2S$-$25P_2S_5$ ($75Li_2S$) glasses. The lithium ionic conductivities of $67Li_2S$, $70Li_2S$, and $75Li_2S$ were found to be $5.6{\times}10^{-5}$ S/cm, $1.4{\times}10^{-4}$ S/cm, and $3.0{\times}10^{-4}$ S/cm, respectively. We performed high energy X-ray diffraction measurements at SPring-8 **BL04B2**, and analyzed the environment of the Li^+ ions by structural analyses combining X-ray and neutron diffraction measurements with the aid of density functional theory (DFT), reverse Monte Carlo (RMC) simulation, and Raman spectroscopy to reveal the relationship between structural properties and Li ionic conduction. Binary Li_2S-P_2S_5 glasses, which consist of PS_x polyhedral anions, are well-known superionic conductors. To quantitatively evaluate the fraction of PS_x polyhedral anions, the Raman spectra of the $67Li_2S$, $70Li_2S$, and $75Li_2S$ glasses were obtained,

as shown in Fig. 1(a). It is known that bands in the frequency range of $330-480$ cm^{-1} are sensitive to the S-P-S bond angle. We assigned the three bands at approximately 425 cm^{-1}, 410 cm^{-1}, and 390 cm^{-1} to the stretching vibration of the P-S bonds in the PS_4^{3-} (*ortho*-thiophosphate) ion, $P_2S_7^{4-}$ (*pyro*-thiophosphate) ion, and $P_2S_6^{4-}$ (an ethanelike structure with a P-P bond) ion, respectively. The ratios of the PS_4^{3-}, $P_2S_7^{4-}$, and $P_2S_6^{4-}$ ions were estimated using a Lorentzian function, shown as dotted lines in Fig. 1(b), and are summarized as open circles, open triangles, and open squares in Fig. 1(c), respectively. It is clear that the ratio of PS_4^{3-} ions increases with the Li_2S content, while the ratios of $P_2S_7^{4-}$ and $P_2S_6^{4-}$ ions decrease. Intriguingly, it was found that $P_2S_6^{4-}$ ions exist in these glasses with ratios of approximately 33.0%, 18.3%, and 4.4% in $67Li_2S$, $70Li_2S$, and $75Li_2S$, respectively, whereas they should not be contained in the stoichiometric compositions ($0PS_4$:$100P_2S_7$ in $67Li_2S$, $50PS_4$:$50P_2S_7$ in $70Li_2S$, and $100PS_4$:$0P_2S_7$ in $75Li_2S$). This means that there is a sulfur deficiency in these glasses.

Figure 2 shows experimental X-ray total structure factors, $S^X(Q)$, for the $67Li_2S$, $70Li_2S$, and $75Li_2S$ glasses. Oscillations in $S^X(Q)$ remain up to the high Q region, which is evidence for well-defined short-range order in the formation of P-S bonds. The difference between the three compositions is not significant in both sets of diffraction data. To uncover the relationship between the glassy structure and the high ionic conductivity for these glasses, we modeled the atomic structure of the Li_2S-P_2S_5 glasses by DFT/RMC simulation using X-ray and neutron diffraction data,
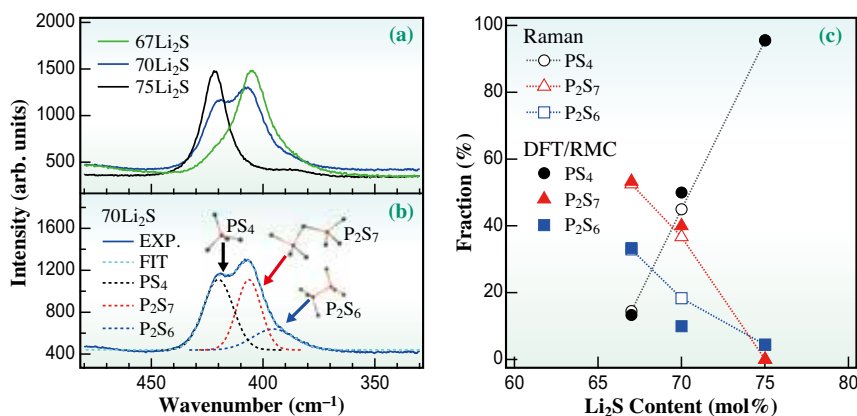

Fig. 1. **(a)** Raman spectra in the range of $330-480$ cm^{-1} for Li_2S-P_2S5 glasses. Black, blue, and green lines represent $75Li_2S$, $70Li_2S$, and $67Li_2S$ glasses, respectively. **(b)** Spectral decomposition of Raman spectrum for $70Li_2S$ glass. Blue line, experimental data; dotted lines, fitting result for all PS polyhedral anions (light blue), PS_4 (black), P_2S_7 (red), and P_2S_6 (blue). **(c)** PS*x* polyhedral fractions for Li_2S-P_2S_5 glasses derived from Raman spectra (open marks) and DFT/RMC model (filled marks).

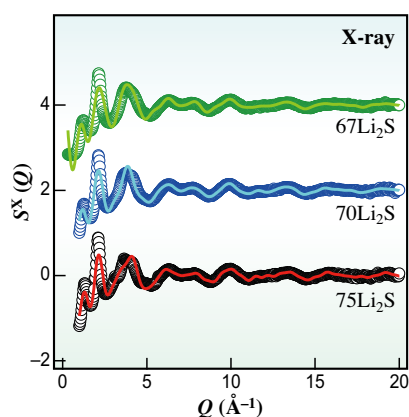Fig. 2. Total structure factors $S(Q)$ at room temperature for Li_2S-P_2S_5 glasses derived from X-ray diffraction. Circles, experimental data; lines, DFT/RMC model.

fixing the ratios of the PS_4^{3-}, $P_2S_7^{4-}$, and $P_2S_6^{4-}$ ions on the basis of Raman spectroscopy measurements to reproduce the plausible glassy structures. The total structure factors $S^X(Q)$ of the Li_2S-P_2S_5 glasses derived from the DFT/RMC model are shown in Fig. 2 as lines. The DFT/RMC model is consistent with the experimental data.

The DFT/RMC structure is consistent with both the diffraction data and the Raman data, and we compared the electronic structure in terms of each PS_x polyhedral anion for the $70Li_2S$ glass. Figures 3(a) and 3(b) show the partial density of states (p-DOS) of the $70Li_2S$ glass for the S $3p$-orbital and P $3p$-orbital, respectively. It is apparent that the orbitals form a hybrid orbital between the phosphorus and sulfur; the highest occupied

molecular orbital (HOMO) is located at -4.0 to -0.5 eV and the lowest unoccupied molecular orbital (LUMO) is located at 1.5 to 5.0 eV. The positive charge of the P ion is large owing to the hybrid orbital. However, the p-DOS plots of the P ion reveal that the P_2S_7 anion only differs from the PS_4 and P_2S_6 anions as follows (Fig. 3(b)). A shallow level appears near the bottom of the LUMO at approximately 2.0 eV in the P_2S_7 anion, which is related to a covalent bond between the P ion and the bridging sulfur (BS) ion in the P_2S_7 anion. This electron transfer is expected to weaken the positive charge of the P ions, which attract Li^+ ions to the P_2S_7 anions more strongly than the other PS_x polyhedral anions. Furthermore, it is easy for the attracted Li^+ ions to remain around the P_2S_7 anions, which may suppress the lithium ionic conduction in solid electrolytes.

In this study, we found that $P_2S_6^{4-}$ ions as well as PS_4^{3-} and $P_2S_7^{4-}$ ions are present in $67Li_2S$, $70Li_2S$, and $75Li_2S$ glasses on the basis of Raman spectroscopy measurement. Density functional theory and reverse Monte Carlo simulations (DFT/RMC) quantitatively reproduced the results of high-energy X-ray diffraction, neutron diffraction, and Raman spectroscopy, fixing the ratios of PS_4^{3-}, $P_2S_7^{4-}$, and $P_2S_6^{4-}$ ions. The electronic structure of the DFT/RMC model suggests that the existence of the P_2S_7 anion may suppress lithium ionic conduction. Thus, the control of the edge sharing between PS_x anions and Li ions without electron transfer between the P ion and the BS ion is expected to facilitate lithium ionic conduction in a solid electrolyte, which should contribute to the development of all-solid batteries.
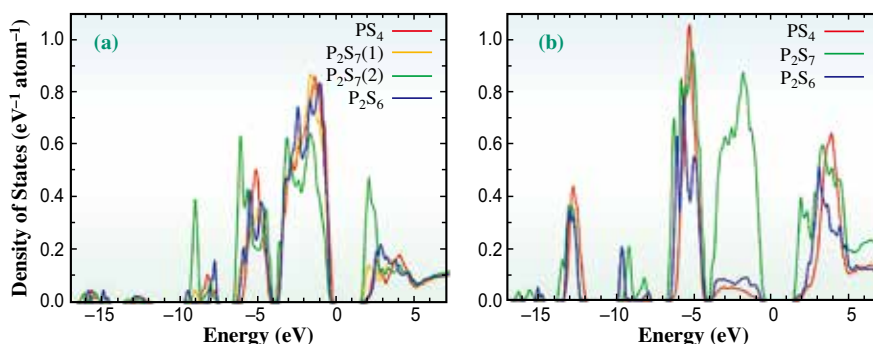

Fig. 3. Partial DOS for (a) S $3p$-orbital and (b) P $3p$-orbital of $70Li_2S$ glass.

K. Ohara[a,b,*], A. Mitsui[a,c], Y. Uchimoto[a] and Z. Ogumi[a]

[a] Kyoto University
[b] Japan Synchrotron Radiation Research Institute (JASRI)
[c] Toyota Motor Corporation

*Email: ohara@spring8.or.jp

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