The solid-electrolytes (SEs) are a key component in all-solid-state Li-ion batteries (LIBs). The sulfide SEs are the promising candidates for all-solid-state LIBs in its property; intermediate Young's moduli, high Li-ion conductivity, and the stability of electrochemical reaction. It is well known that a 75Li$_2$S·25P$_2$S$_5$ (mol%) glass, which is one of the most famous sulfide SEs, shows the phase transition from glass to crystal around $T = 473$ K. However, there are few studies on the local structural changes during crystallization process due to the lack of a unified local structural analysis method applicable to both glassy and crystalline states. Recently, we have developed a method to evaluate the local structural changes during the phase transition by using X-ray total scattering profiles combined with a reverse Monte-Carlo (RMC) modeling.

Figure 1 shows the experimental and RMC results for both the glassy and crystalline states. We have successfully constructed structural models consistent with the experimental total scattering profiles. The angular histograms of S-(P)-S and S-(S)-S respectively had peaks at $S$-(P)-$S = 109.5$ and $S$-(S)-$S = 60^\circ$ and the results indicated that the PS$_4$ clusters remain the tetrahedral structure over the wide range from glass to crystal. We also calculated the average spatial distribution maps of P and S atoms. Figure 2 shows the experimentally obtained $G_{obs}(r)$ and the average spatial distribution maps of S and P atoms of the PS$_4$ cluster. S atom has a wider distribution between the corner of PS$_4$ tetrahedra at the higher temperature of the glassy state and then to be narrow distribution due to the crystallization. The S-Li correlation at $r = 2.5$ Å shown in $G_{obs}(r)$ show little change at any temperature, indicating that the motion of Li-ion is followed to the libration of PS$_4$ clusters. The trend is in good agreement with the Li-ion conductivity obtained in the previous study. The RMC results suggest that the PS$_4$ cluster motion plays an important role in the Li-ion migration in 75Li$_2$S·25P$_2$S$_5$ (mol%) glass and crystals. We will also discuss about local structure changes during the crystallization process.

Figure 1. Observed (black solid line) and calculated (red broken line) structure factor, corresponding residual curve (green solid line) of 75Li$_2$S·25P$_2$S$_5$. (a) glass and (b) crystal

Figure 2. Experimentally obtained $G(r)$ and spatial distribution of P (purple) and S (yellow) atom of each state.