ESRF	**Experiment title:** Network structure in fast-ion conducting glass AgI-As_2Se_3	**Experiment number:** HD63
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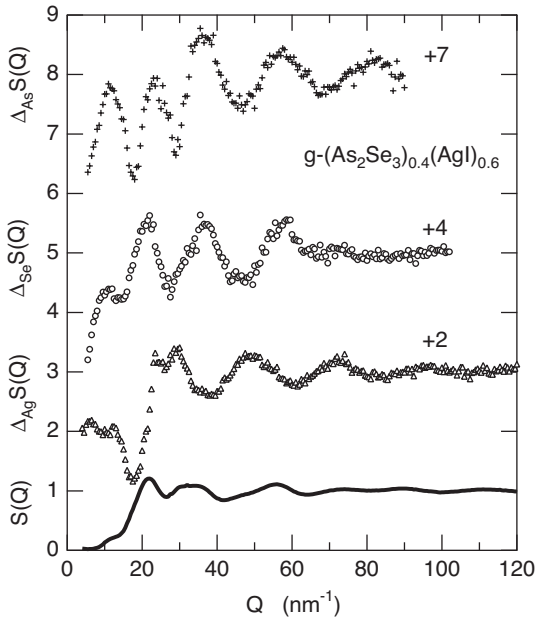
Report:

Glassy mixture of chalcogenides and Ag halides behaves as a superionic conductor even at room temperature. Thus it has received much attention due to the fundamental interest on the conduction mechanism as well as the application to solid-state electrochemical devices. In case of $(As_2Se_3)_{1-x}(AgI)_x$ mixtures, glassy phases can be obtained over a wide concentration range of $0 \leq x \leq 0.6$. Usuki and coworkers [1] have investigated electrical, thermodynamic, and structural properties of glassy $(As_2Se_3)_{1-x}(AgI)_x$ mixtures, such as electrical conductivity, magnetic susceptibility, density, Raman scattering, XAFS, diffraction using both X-rays and neutrons. All of these experimental results do not contradict a model of a pseudo-binary mixture of the As_2Se_3 network matrix and AgI-related ionic conduction pathways. This structural model has, however, not been confirmed by any partial structural experiments covering the intermediate-range order (IRO), such as neutron scattering using isotope substituted sample or anomalous X-ray scattering (AXS). Thus, the conduction mechanism of this room-temperature superionic glass is still open to question.

In this project, we have carried out an AXS experiment on glassy $(As_2Se_3)_{0.4}(AgI)_{0.6}$ mixture close to the As, Se, and Ag K edges. The glassy sample was obtained by simple iced-water quenching the sample in a fused silica ampoule after heating and rocking the melt for at least 48 hours. A pellet with a flat surface was made for the AXS experiment with a pressing tool. The concentration and the homogeneity of the

sample were examined by measuring conventional X-ray diffraction and differential thermal analysis at several positions of the quenched sample. The AXS experiment was carried out at two energies below the K edges of As and Se (-20 and -200 eV), or Ag (-30 and -200 eV) at BM02/ESRF. For the diffraction experiment, we used a graphite crystal energy analyser together with a scintillation counter on a long (45 cm) detector arm, which we developed for the AXS experiment. The differential structure factors $\Delta_i S(Q)$ can be obtained by taking the difference of two scattering spectra, and the i-th element related partial structure factors $S_{ij}(Q)$ dominate the $\Delta_i S(Q)$.
Figure shows the $\Delta_i S(Q)$ spectra close to the As (crosses), Se (circles), and Ag (triangles) K edges. For the comparison, the total structure factor $S(Q)$ is also given by the solid curve. Clear contrasts are observed among the $\Delta_i S(Q)$ and $S(Q)$ spectra. Differences from the other spectra are prominent in $\Delta_{\mathrm{Ag}} S(Q)$: the oscillations are almost out phase of the others. Another difference is observed in the pre-shoulder in $S(Q)$ near $Q = 12$ nm^{-1}, which is the clear evidence of the IRO in this glass. The $\Delta_{\mathrm{As}} S(Q)$ spectrum has a large prepeak at about 12 nm^{-1}, where the small pre-shoulder locates in $S(Q)$. The $\Delta_{\mathrm{Se}} S(Q)$ spectrum also shows a small peak at the same Q position. However, $\Delta_{\mathrm{Ag}} S(Q)$ shows almost no indication of the prepeak or pre-shoulder. It should be noted that both the $\Delta_{\mathrm{As}} S(Q)$ and $\Delta_{\mathrm{Se}} S(Q)$ results surprisingly look very similar to those of glassy As_2Se_3 [2], although their $S(Q)$ spectra are very different from each other. Thus the local structure around the As and Se atoms is very similar to that in glassy As_2Se_3. Although there has not been no experiment that obtained partial information on the structure of molten AgI, Shimojo et al. [3] have recently carried out a first principles molecular dynamic simulation of this salt which reproduce well the $S(Q)$ spectrum. The $\Delta_{\mathrm{Ag}} S(Q)$ spectrum obtained from this simulation surprisingly coincides well with that of glassy $(As_2Se_3)_{0.4}(AgI)_{0.6}$ mixture. Thus, it is concluded that the local environment around the Ag atoms in $(As_2Se_3)_{0.4}(AgI)_{0.6}$ superionic glass is absolutely molten AgI-like. Therefore, the pseudo-binary mixture of the As_2Se_3 network matrix and AgI-related ionic conduction pathway is a good structural model for this room-temperature superionic glass. The present results were obtained during two beamtimes (HS2798 and HD63).



[1] T. Usuki et al., J. Non-Cryst. Solids **312-314**, 570 (2002).
[2] S. Hosokawa et al., J. Non-Cryst. Solids **352**, 1517 (2006).
[3] F. Shimojo et al., J. Phys. Soc. Jpn. **75**, 114602 (2006).