



	Experiment title: Ion conducting mechanism in superionic conducting glass AgBr-As ₂ Se ₃	Experiment number: HD3
Beamline: BM02	Date of experiment: from: 04 Sept. 2006 to: 11 Sept. 2006	Date of report: 25 February 2008
Shifts: 18	Local contact(s): Dr. J.-F. Bézar	<i>Received at ESRF:</i>
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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. Even though crystal AgBr does not have a superionic phase at any temperatures, a room-temperature superionic phenomena appear in AgBr-doped As₂Se₃ systems similar to AgI-doped As₂Se₃ mixtures.

Onodera et al. [1] have measured electrical conductivity, density, and differential thermal analysis. As in glassy (As₂Se₃)_{1-x}(AgI)_x mixtures [2], (As₂Se₃)_{1-x}(AgBr)_x has glassy phases in a wide concentration range of $0 \leq x \leq 0.6$. Although this glassy systems are expected to have a similar structure which describes a model of a pseudo-binary mixture of the As₂Se₃ network matrix and AgBr-related ionic conduction pathways as in glassy (As₂Se₃)_{1-x}(AgI)_x mixtures, there has been no structural study. Thus, the conduction mechanism of this room-temperature superionic glass is still open to question.

In this project, we have carried out an anomalous X-ray scattering (AXS) experiment on glassy (As₂Se₃)_{0.4}(AgBr)_{0.6} mixture close to the As, Se, Ag, and Br 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, Se, Br (-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), Ag (triangles), and Br (squares) 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. Both the $\Delta_{\text{As}} S(Q)$ and $\Delta_{\text{Se}} S(Q)$ results surprisingly look very similar to those of glassy As_2Se_3 [3] and $(\text{As}_2\text{Se}_3)_{0.4}(\text{AgI})_{0.6}$. Thus the local structure around the As and Se atoms is very similar to that in glassy As_2Se_3 . The $\Delta_{\text{Ag}} S(Q)$ spectrum shows a quite different feature from that in glassy $(\text{As}_2\text{Se}_3)_{0.4}(\text{AgI})_{0.6}$: the large oscillations almost disappear and no negative dip remains near the first peak position in $S(Q)$. The $\Delta_{\text{Br}} S(Q)$ spectrum has a peak near the Q position of the first peak in $S(Q)$. It is worth noting that the $\Delta_{\text{Br}} S(Q)$ shows a shoulder at about 13 nm^{-1} , which contribute the pre-shoulder in $S(Q)$. The partial structure factors $S_{ij}(Q)$ of molten AgBr has experimentally been obtained by a combined experiments of AXS and neutron diffraction by Saito et al. [4]. It should be noted that both the $\Delta_{\text{Ag}} S(Q)$ and $\Delta_{\text{Br}} S(Q)$ spectra are very different from those of molten AgBr calculated from $S_{ij}(Q)$ up to the first peak position. Unlike the AgI-doped glass, thus, the intermediate-range structure around the Ag and Br atoms in glassy $(\text{As}_2\text{Se}_3)_{0.4}(\text{AgBr})_{0.6}$ would not be molten AgBr-like, which may reflect those in the crystal structures between AgI and AgBr. This is in detail discussed elsewhere [5].

[1] Y. Onodera et al., Solid State Ionics **177**, 2597 (2006).

[2] T. Usuki et al., J. Non-Cryst. Solids **312-314**, 570 (2002).

[3] S. Hosokawa et al., J. Non-Cryst. Solids **352**, 1517 (2006).

[4] M. Saito et al., J. Phys. Soc. Jpn. **68**, 1932 (1999).

[5] S. Hosokawa et al., Phys. Rev. B, submitted.

