Experiment title: Ion conduction mechanism in room temperature superionic glasses $Ag_x(GeSe_3)_{1-x}$ by anomalous x-ray scattering		**Experiment number:** HD540
Beamline: BM02	**Date of experiment:** from: 10 July 2012 to: 17 July 2012	**Date of report:** 06 March 2014
Shifts: 18	**Local contact(s):** Dr. Jean-François Bérar	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
S. Hosokawa*, J. Stellhorn*, A. Nierobisch*, and W.-C. Pilgrim
Philipps University of Marburg, Department of Chemistry, Physical Chemistry, D-35032 Marburg, Germany
Y. Kawakita*
J-PARC Center, Japan Atomic Energy Agency, Tokai 319-1195, Japan
K. Hayashi*
Tohoku University, Institute for Materials Research, Sendai 980-8577, Japan

Report:

Recently, much attention has been paid to investigate superionic conductors, which can be used as solid electrolytes for solid state batteries. Superionic glasses with high ionic conductivity of $10^{-6} - 10^{-2}$ S/cm are promising materials for such applications. It is well-known that superionic behavior in Ag-containing chalcogenide glasses, such as $Ag_x(GeSe_3)_{1-x}$, is observed at room temperature in contrast to high temperatures needed in crystalline superionic conductors, such as AgI and Ag_2Se. Another advantage of these glasses as electrolytes is that the glassy state can easily be obtained in a wide concentration range by simple water or even air-quenching.

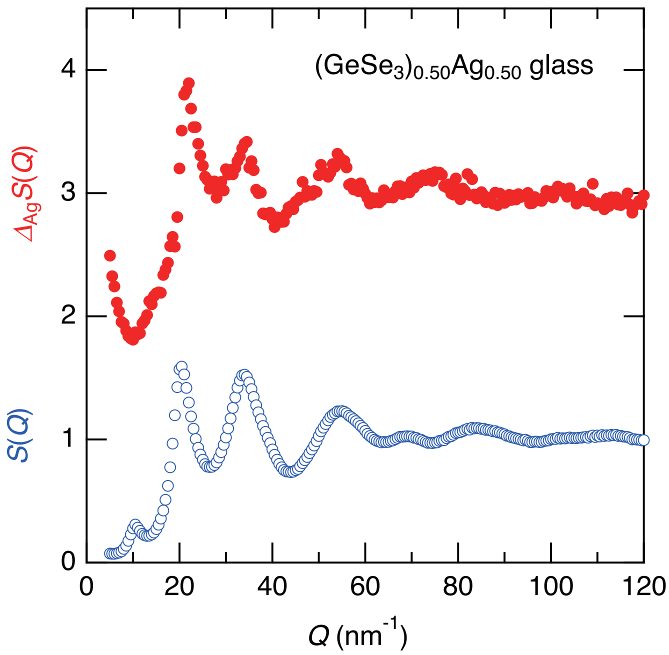
Kumara et al. [1] performed structural experiments on $Ag_x(GeSe_3)_{1-x}$ glasses, such as high-energy x-ray scattering, neutron diffraction, and XAFS. These data were analyzed using reverse Monte Carlo (RMC) modeling, and three-dimensional atomic configurations were obtained, where chain-like fragments of Ag atoms were clearly observed. However, intrinsic experimental difficulties prevented the discriminations between the Ge and Se elements, and the further understandings of the role of the Ge-Se network were still lacking.

In this beamtime, we have carried out anomalous x-ray scattering (AXS) experiments on $Ag_{0.50}(GeSe_3)_{0.50}$, $Ag_{0.33}(GeSe_3)_{0.67}$, and $Ag_{0.15}(GeSe_3)_{0.85}$ glasses close to the Ag K edge (25.514 keV) to confirm the findings by Kumara et al. [1]. The glassy samples were prepared by water-quenching from molten mixtures of Ag, Se, and $GeSe_2$ sealed in silica ampoules under vacuum condition. After quenching pellets with flat surfaces of 13 mmϕ were produced using a pressing tool. The concentrations and homogeneity were examined by x-ray diffraction and differential thermal analysis

at several positions of the quenched samples. The AXS experiments were carried out in reflection geometry using a normal $\omega - 2\theta$ diffractometer installed at BM02 at two incident x-ray energies (-30 and -300 eV) below the Ag K edge. A bent graphite crystal analyzer was mounted on a 1 m-long detector arm for discriminating the elastic signal from fluorescence and Compton scattering contributions. The experimental details are given elsewhere [2,3].

Figure shows the differential structure factor around the Ag K edge, $\Delta_{\rm Ag}S(Q)$, and the total structure, $S(Q)$, of the $Ag_{0.5}(GeSe_3)_{0.5}$ glass. As clearly seen in the figure, prominent differences are observed between the $\Delta_{\rm Ag}S(Q)$ and $S(Q)$, i.e., $\Delta_{\rm Ag}S(Q)$ shows a phase separation tendency at the low Q and no indication of the prepeak at about 10 nm^{-1}, which are consistent with the previous RMC results with x-ray and neutron scattering and XAFS. In addition, the first peak at 21 nm^{-1} in $\Delta_{\rm Ag}S(Q)$ is much higher than that in $S(Q)$.

In the next beamtime in next April, we will measure AXS close to the Ge and Se K edges, and full sets of partial structural information will be obtained in combination with these AXS data close to the Ge and Se K edges and RMC modeling. On this basis, we will explain the structural information on the ion conduction mechanism in the $Ag_x(GeSe_3)_{1-x}$ glasses.



[1] L. S. R. Kumara et al., Eur. Phys. J. Web Conf. **15**, 02007 (2011).
[2] S. Hosokawa et al., Phys. Rev. B **84**, 014201 (2011).
[3] S. Hosokawa et al., Eur Phys. J. Special Topics **208**, 291 (2012).