ESRF	**Experiment title:** Ion conduction mechanism in room-temperature superionic glass Ag-GeSe3	**Experiment number**: HC-1137
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Report:

Superionic conducting materials are of growing interest in fundamental and applied materials science, as they can e.g. be employed as solid electrolytes in solid-state batteries. Superionic glasses with a 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 is observed at room temperature, such as for Ag-$GeSe_3$ alloys, in contrast to high temperatures needed in crystalline superionic conductors. 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 $Ag_{0.50}(GeSe_3)_{0.50}$ and $Ag_{0.15}(GeSe_3)_{0.85}$ glasses close to the Ge and Se *K* edge (11.104 and 12.658 keV, respectively), thus completing our datasets from experiment HD-540, during which we measured the corresponding Ag absorption edges (25.514 keV).

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 mm in diameter 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 standardard ω-2Θ diffractometer installed at BM02 at two incident x-ray energies (-20 and -200 eV) below the Ge and Se *K* edges. 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 1 a) displays the differential structure factors around the Ge, Se and Ag *K* edge and the total structure factor *S(Q)* of the $Ag_{0.5}(GeSe_3)_{0.5}$ glass together with the results of an RMC simulation using the complete set of three differential and one total structure factor. We can confirm that the first sharp diffraction peak (FSDP) around 1.05 $Å^{-1}$ is majorly comprised of Ge-Se and Ge-Ge correlations, indicating a $GeSe_4$ background network structure in the glass. In front of this network, a phase separation tendency of the Ag atoms is visible in the $S_{AgAg}(Q)$, thus confirming the view of Ag conduction pathways, which are supposed to form in the material above the superconductivity threshold of x = 0.3 ([1, 4]). For the $Ag_{0.15}(GeSe_3)_{0.85}$ material, we can observe that the FSDP is also present in the $\Delta_{Ag}S(Q)$, confirming the view that Ag atoms are homogenously incorporated into the background glassy network below x = 0.3 .

Our results as well point to a breakdown of the "8-N" rule in the superconducting phase, as Se is highly over-coordinated with a coordination number of N(Se)=2.93 (note that this rule is fulfilled in the pure $GeSe_3$ material [2]). However, we are planning to confirm this view by completing also the structural data on $Ag_{0.33}(GeSe_3)_{0.67}$ on the Ge and Se *K* edge in a subsequent AXS experiment, which was not possible during the experiment at hand. This will provide us with information about the structure directly at the superconductivity threshold.

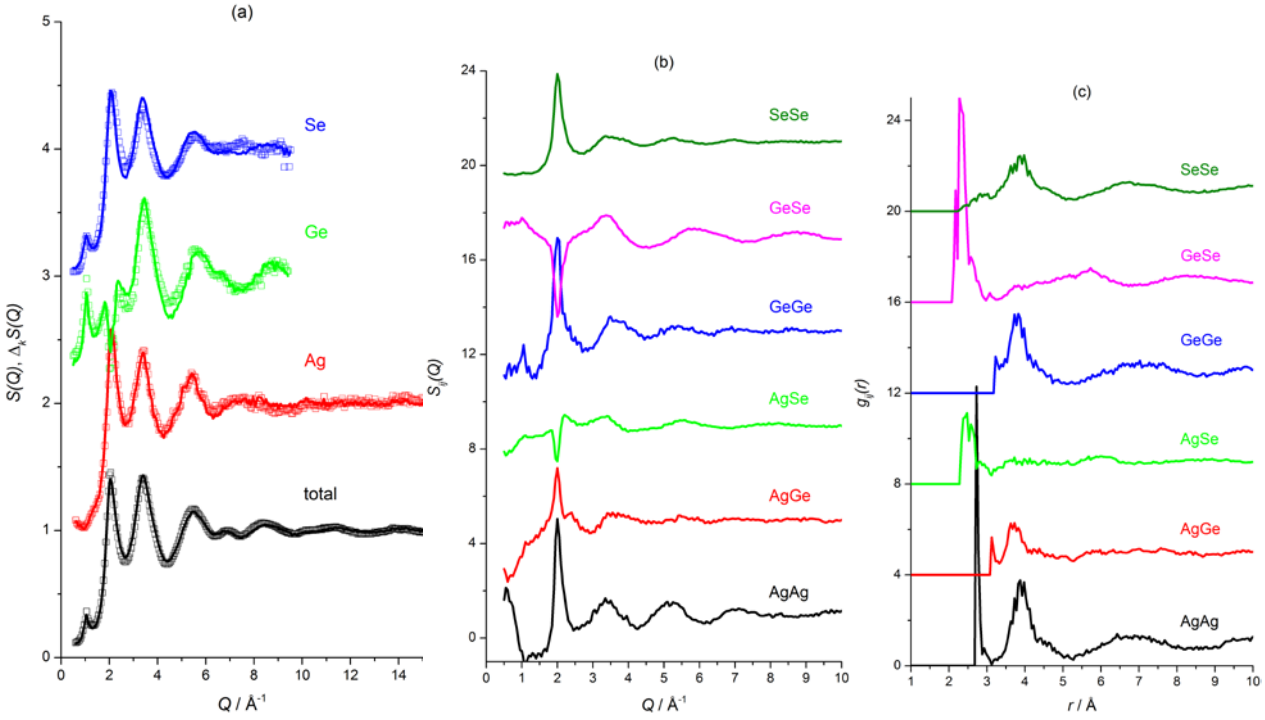

Figure 1: (a) *S(Q)* at 25.214 keV and $\Delta_k S(Q)$ around the Ag, Ge and Se *K* edges. Squares indicate data obtained from the AXS experiments, and solid curves denote the best fits by RMC modeling. (b) Partial structure factors obtained by RMC. (c) Partial pair correlation functions obtained by RMC. Datasets are displaced upwards for clarity.

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[2] S. Hosokawa et al., Phys. Rev. B **84**, 014201 (2011).
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[4] K. Ohara et al., J. Phys. Soc. Jpn. **79** (2010) Suppl. A 141-144.