

## Experiment Report for Prefectural Beamline

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Beamline no.: BL15
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### **Local- and intermediate-range structures of As-Se glasses below the stiffness transition region**

**J.R. Stellhorn and S. Hosokawa**

**Kumamoto University**

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#### **1 . Summary** (Note: Please include conclusions)

We conducted a first experiment of anomalous x-ray scattering (AXS) at BL15. The aim of our research project is the investigation of As-Se glasses in the floppy glass-forming region. In this experiment, we obtained the differential structure factor of the As K edge of  $\text{As}_{25}\text{Se}_{75}$ . Using this AXS data, element-specific contributions can be determined in this material even though As and Se possess very similar atomic numbers ( $Z = 33$  and  $34$ ). These data will help to understand the relation between the structure and the stiffness transition of As-Se glasses.

## 2. Purpose of experiment and background

Mean-field constraint theory [1, 2] for network glasses provides a powerful tool to explain numerous anomalies around the critical composition of rigidity percolation threshold at an average coordination number  $\langle r \rangle = 2.4$ , where the number of constraints per atom is equal to the degree of freedom. The character of the network glass undergoes a first-order-like transition from floppy at  $\langle r \rangle < 2.4$  to rigid at  $\langle r \rangle > 2.4$ . In case of glassy (g-)As<sub>x</sub>Se<sub>1-x</sub> systems, this corresponds to  $x = 0.40$ , i.e. the stoichiometric compound As<sub>2</sub>Se<sub>3</sub>, because the coordination numbers of As and Se are believed to be 3 and 2, respectively. Temperature modulated differential scanning calorimetry (MDSC) measurements on bulk As<sub>x</sub>Se<sub>1-x</sub> glasses provide evidence for a multiplicity of stiffness transitions from floppy to rigid glasses: an onset point at  $x = 0.29$ , and a completion point at  $x = 0.37$ . [3, 4] The intermediate phase represents an unstressed rigid glass phase.

We have previously carried out partial structure analyses for g-As<sub>x</sub>Se<sub>1-x</sub> around the stiffness transition region by the AXS method. It was found that the prepeak at  $1.2 \text{ \AA}^{-1}$  in the structure factor  $S(Q)$  is mainly composed of the As-As correlation, but there is a contribution of the As-Se correlation as well.[5, 6] The  $x$  dependence of the position and width of the prepeak in  $S_{\text{AsSe}}(Q)$  is inconsistent with the results of ab-initio MD simulations by Bauchy et al. [7], while that of the As-As wrong bond fractions is consistent with this theory. To confirm these results, experimental data in the floppy region of  $x < 0.29$  are necessary.

Therefore, we have carried out an AXS experiment on an As<sub>25</sub>Se<sub>75</sub> sample. A major problems to analyze the structure of these compounds with usual x-ray techniques is that the elements possess very similar atomic numbers ( $Z = 33$  and  $34$ ), and also have similar backscattering intensities in x-ray absorption spectroscopy. The proximity of the absorption edges is another difficulty for an extended x-ray absorption fine structure investigation. Anomalous x-ray scattering, however, can distinguish these element-specific contributions. For example, the relative weighting of the As-As correlation is only 5% in the normal  $S(Q)$ , but enhanced to about 17% in  $\Delta_{\text{As}}S(Q)$ .

## 3. Experimental (Note: Description of sample, method of experiment and analysis, etc.)

The AXS experiment was carried out using a standard diffractometer installed at BL15. An energy-dispersive SDD detector was used to discriminate the elastic scattering signal from spurious contributions of fluorescence lines and inelastic contributions. The energy resolution of the detector was about 220 eV near 10 keV. We also used a second SDD detector to monitor the fluorescence signals independently during the entire experiment, which greatly facilitates the data analysis.

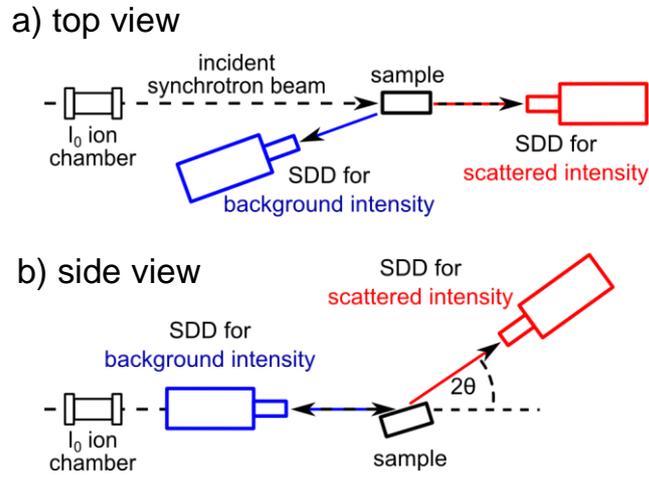


Fig. 1: Schematic view of the setup for the AXS experiment from the top (a) and from the side (b).

One SDD detector is used to collect the scattered intensity in a  $2\theta$  range, the other detector is fixed in a backscattering position and mainly monitors the fluorescence signals during the entire measurement.

The experiment itself was conducted at two incident x-rays energies of about 20 eV (**near** edge) and 200 eV (**far** edge) below the  $K$  absorption edge of As (11.686 keV). The scattering intensity was measured by a SDD detector in an angular range of about  $2\theta = 2^\circ \sim 140^\circ$ , in constant steps in  $Q$  space of about  $0.05 \text{ \AA}^{-1}$ .

The data were corrected for absorption effects and Compton scattering, and normalized using the Norman-Krogh-Moe method [8,9]. Further details on the theoretical and experimental background of AXS can be found elsewhere [10-14].

#### 4. Results and Discussions

In this experiment, we investigated the  $\text{As}_{25}\text{Se}_{75}$  glass by AXS. The experiment is an important step to demonstrate feasibility of the current AXS setup at BL15, to test the simplified data analysis possible because of the special setup, and to prove the possibility to gain element-specific information.

The total and differential structure factor of As are displayed in Fig. 2 along with the corresponding pair correlation functions obtained by Fourier transform. The  $\Delta_{\text{As}}S(Q)$  function in general has a form similar to the total  $S(Q)$ , but there are notable differences in certain peak intensities and forms, e.g. the first sharp diffraction peak (FSDP) around  $1.2 \text{ \AA}^{-1}$  becomes distinct and well separated from the "main" peak around  $2.2 \text{ \AA}^{-1}$ . The peak at  $2.2 \text{ \AA}^{-1}$  is smaller than in the total  $S(Q)$ . These graphs confirm trends in the relative peak intensities also observed for larger As contents as discussed in refs. [5, 6], which shows that the main peak intensity is growing as a function of the As content. This is related to a minimum in the As-Se partial structure factor around  $2 \text{ \AA}^{-1}$ . A first interpretation of the data can be gained by a Fourier transform of the total and differential pair correlation functions, as shown in Fig. 5 b). Both functions exhibit similar features, but the  $\Delta_{\text{As}}g(r)$  shows a larger signal in the first coordination shell around  $2.4 \text{ \AA}$ . According to ref. [6], this is due to the larger contribution of the As-Se correlation.

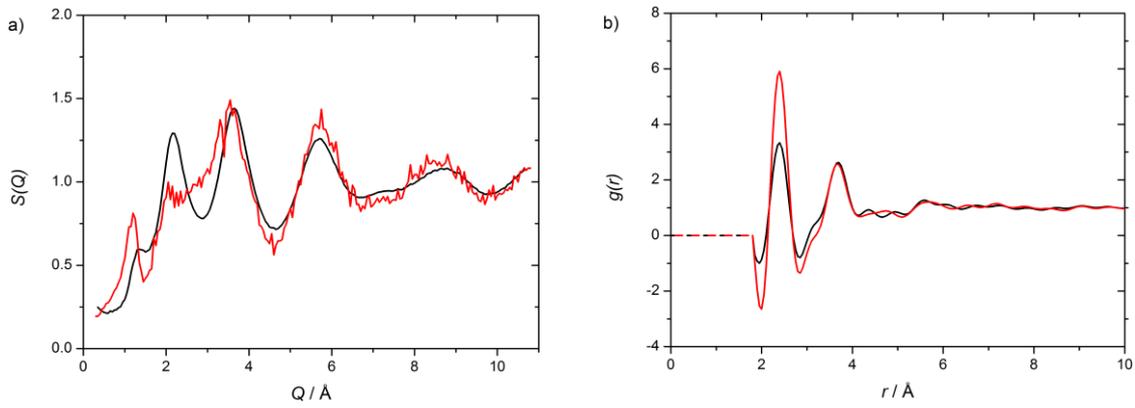


Fig. 2: Experimental scattering data of the  $\text{As}_{25}\text{Se}_{75}$  glass collected at the As edge. (a) total (black) and differential (red) structure factors, and (b) total (black) and differential (red) pair correlation functions.

## 5. Future issues

In subsequent experiment, we expect to derive partial structural data for several  $g\text{-As}_x\text{Se}_{1-x}$  glasses, which has yet almost exclusively been the domain of the neutron scattering using isotope enriched samples. From the  $S_{ij}(Q)$  results across the rigidity percolation threshold composition, the concentration variation of the short- and intermediate-range order in  $g\text{-As}_x\text{Se}_{1-x}$  can be discussed in detail, for example the conformation of the quasi-tetrahedral units can be visualized, and their role for the floppy-rigid transition in this network glasses can be clarified.

## 6. References

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**7. Publications, patents** (Note: Typical deliverables related to this proposal.)

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**8. Keywords** (Note: 2-3 words about samples and experimental methods.)

As-Se, chalcogenide glass, anomalous x-ray scattering, stiffness transition

**9. About the publication of research results**

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