	Experiment title: Rigidity transitions and molecular structure of As-Se glasses	**Experiment number**: HS-1860
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Report:

Mean-field constraint theory [1,2] for network glasses provides a powerful tool to explain experimentally observed numerous anomalies around the critical composition of the 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 As_xSe_{1-x} systems, this corresponds to $x = 0.40$. Recently, Boolchand and coworkers measured *T*-modulated differential scanning calorimetry (MDSC) on As_xSe_{1-x} glasses. The results clearly provide evidence for a multiplicity of stiffness transitions; an onset point at $x = 0.29$ ($\langle r \rangle = 2.29$), significantly lower than the mean-field value of $\langle r \rangle = 2.40$, and a completion point at $x = 0.37$. The intermediate phase in between represents an *unstressed rigid* glass phase. The MDSC results show that the compositional width of the intermediate phase is larger in glassy As_xSe_{1-x} than in glassy Ge_xSe_{1-x} [4]. These thermal results led them to conclude that in addition to pyramidal $As(Se_{1/2})_3$ units, 30 % of quasitetrahedral $Se{=}As(Se_{1/2})_3$ units also serve to cross-link Se_n chains at $x < 0.40$. Generally, one expects a glass structure in the intermediate different from the *floppy* or *rigid* phases, which would account for the *unstressed* nature of the backbone. However, we know little about the structure of this glass system [5] that would permit to understand the observed thermal behaviour.

Anomalous x-ray scattering (AXS) experiments were carried out at two energies (–20 and –200 eV) below the K edge of each element using a normal ω–2θ diffractometer. To obtain a sufficient energy resolution (to discriminate the elastic signal from the K_β

fluorescence and Compton scattering contributions) and enough counts in a reasonable data acquisition time, we chose a graphite analyser crystal with a 40 cm detector arm [6], providing an energy resolution of about 55 eV. The samples were prepared by quenching the melts after rocking a quartz ampoule containing the mixed compound. The measurements were performed at room temperature with reflectance geometry.

We measured three samples (x = 0.20, 0.29, and 0.40) in steps ΔQ of 0.05 Å^{-1}. As an example of our results, differential structure factors $\Delta_i S(Q)$ for glassy $As_{40}Se_{60}$ close to the As and Se K edges are shown in the figure by crosses and circles, respectively. Also given is the total structure factor $S(Q)$ (solid line) measured at the incident x-ray energy of 11664 eV (200 eV below the As K edge). Apparently, the statistical quality of the $\Delta_i S(Q)$s is excellent and easily allows an interpretation of underlying information. $\Delta_{As}S(Q)$ has a larger prepeak at 1.2 Å^{-1} than the $S(Q)$ at the same Q position, whereas the first peak becomes smaller and shifts towards the higher Q position. On the other hand, $\Delta_{Se}S(Q)$ has a small shoulder around Q = 1.45 Å^{-1}, which would produce an asymmetric shape for the prepeak in $S(Q)$. Since $\Delta_{As}S(Q)$ originates from partial structure factors $S_{ij}(Q)$ of about 33 % $S_{AsAs}(Q)$, 60 % $S_{AsSe}(Q)$, and 7 % $S_{SeSe}(Q)$, while $\Delta_{Se}S(Q)$ results from about –3 % $S_{AsAs}(Q)$, 40 % $S_{AsSe}(Q)$, and 63 % $S_{SeSe}(Q)$, it is obvious that the prepeak at 1.2 Å^{-1} is a result of the As-As correlation and the signal around 1.45 Å^{-1} is composed of the Se-Se contribution. Very similar results are also obtained at the other two compositions. In order to confirm the above speculation on a quantitative basis, it is essential to obtain complete sets of $S_{ij}(Q)$s from the present results. Such analyses are now in progress. Still needed are experiments for the other concentrations x = 0.25, 0.33, and 0.37, to discuss the relation between the structure and the stiffness transition, especially exploring quasitetrahedral $Se{=}As(Se_{1/2})_3$ units. These experiments will be applied in the next proposal.

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