ESRF	**Experiment title:** Partial structural analysis on superionic conducting glass $(As_2Se_3)_{1-x}(CuI)_x$	**Experiment number:** HS2348
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Report:

Glassy mixture of chalcogenide and CuI (or AgI) behaves as a superionic conductor at room temperature. Thus it has recently received much attention due to the basic interest on the conduction mechanism as well as the application to solid state electrochemical devices. In case of $(As_2Se_3)_{1-x}(CuI)_x$, a glassy phase can be obtained over a wide concentration range up to $x \sim 0.7$, and the conductivity exponentially increases with increasing CuI concentration x [1].

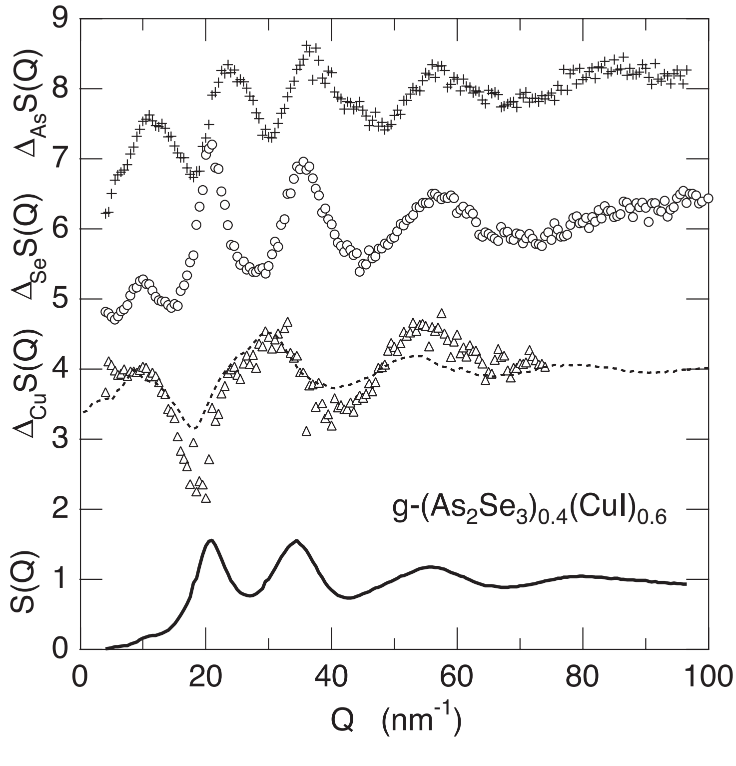
Usuki et al. [1] investigated electrical, thermodynamic, and structural properties of this exotic glass system. From XAFS and X-ray scattering experiments, they concluded that the structure of As_2Se_3-CuI glasses can be modelled as a pseudo-binary mixture of a network matrix of $As(Se_{1/2})_3$ pyramidal units and CuI-related conduction pathways. On the contrary, Bychkov et al. [2] obtained a different result from an XAFS experiment where a significant Cu-Se correlation is seen in the first shell around the Cu^+ ions (40-70 %), which can be considered to be unfavourable for the ionic conduction. This serious controversy may result from the different procedures between the XAFS analyses. Usuki et al. [1] applied a two-subshell model including the Cu-I and Cu-Cu correlations as in α-CuI, and Bychkov et al. [2] approximated the Cu-I and Cu-Se correlations. Therefore, it is essential to perform another local structure analysis using a different technique.

The AXS experiments were performed at two incident x-ray energies (-20 and -200 eV) below the K edges of As, Se, or Cu, using a normal ω-2θ diffractometer. In order to obtain differential structure factors, $\Delta_i S(Q)$, with high statistical quality, two requirements should be fulfilled: 1) A good energy resolution to discriminate the elastic signal from the fluorescence and Compton contributions, and 2) a sufficient number of scattered X-ray photons within a reasonable data collection time. We chose a graphite crystal analyzer providing a good Bragg reflection, which was placed on a 40-cm-long arm to obtain an energy resolution of 60 eV. The glassy $(As_2Se_3)_{0.4}(CuI)_{0.6}$ sample was prepared by quenching the melts after rocking the quartz ampoule of the mixed compounds.

Figure shows $\Delta_i S(Q)$ spectra of glassy $(As_2Se_3)_{0.4}(CuI)_{0.6}$ measured at energies close to the As (crosses), Se (circles), and Cu (triangles) K edges. For the comparison, $S(Q)$ measured at E = 11667 eV (200 eV below the As K edge) is also shown by the solid curve in the figure. Contrasts between $\Delta_i S(Q)$s and $S(Q)$ are very prominent at the prepeak position of Q = 12 nm^{-1}, the prepeak being the clear evidence of the existence of intermediate-range order in this glass. $\Delta_{As}S(Q)$ has a distinct prepeak, while a small shoulder locates in $S(Q)$. $\Delta_{Se}S(Q)$ also has a small peak at the same Q position.

Surprisingly, both $\Delta_{As}S(Q)$ and $\Delta_{Se}S(Q)$ are very similar to those of the parent glassy As_2Se_3 carried out recently using the same diffractometer [3], except in the prepeak region, although their $S(Q)$s are very different from each other. Therefore it is plausible that the short-range order of this glassy superionic conductor around the As and Se atoms are very similar to that in glassy As_2Se_3, and the intermediate-range order around the As and Se elements would be modified by mixing with the CuI component.

The dashed curve on the $\Delta_{Cu}S(Q)$ data shows $\Delta_{Cu}S(Q)$ of liquid CuI calculated using partial structure factors obtained by a combination of AXS and neutron scattering [4]. The feature of $\Delta_{Cu}S(Q)$ for this glass is very similar to that for liquid CuI except the amplitude. This discrepancy would come from the difference of the temperature. From the Fourier transform of this $\Delta_{Cu}S(Q)$ spectrum, the nearest-neighbour distance was obtained to be ~0.26 nm, which is very similar to that in CuI crystals, but far longer than that of Cu-Se estimated by Bychkov et al. [2] using the XAFS experiment. From these findings, it can be concluded that a pseudo-binary mixture of the As_2Se_3 network matrix and CuI-related conduction pathways would be a good structural model for this superionic glass.



[1] T. Usuki et al, unpublished. Similar results were obtained for glassy $(As_2Se_3)_{1-x}(AgI)_x$ systems, T. Usuki et al., J. Non-Cryst. Solids 312-314 (2002) 570.
[2] E. Bychkov et al., J. Non-Cryst. Solids 232-234 (1998) 314.
[3] S. Hosokawa et al., Proc. 20th Int. Cong. on Glass (Kyoto, 26 Sept.-1 Oct. 2004), submitted.
[4] Y. Waseda et al., J. Phys.: Condens. Matter 12 (2000) A195.