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Report:

The stiffness transition [1,2] is a simple and attractive idea for describing physical properties of network glasses using the averaged coordination number of systems. This idea was substantially developed experimentally by Boolchand and coworkers [3] as the so-called intermediate phase (IP) examined by thermodynamic and Raman scattering measurements. In As_xSe_{1-x} glasses [4], they expressed an opposition to the so-called $8-N$ bonding rule proposed by Mott [5] experimentally based on the stiffness transition theory. It was found that non-reserving heat flow obtained from temperature-modulated differential calorimetry almost vanishes in the $0.29 < x < 0.37$ composition range, separating the floppy glasses from the stressed rigid ones. Since the ideal boundary is $x = 0.40$ if the $8-N$ bonding rule was strictly valid, they proposed a breakdown of this rule and suggested that 28.6% of Se=As$(Se_{1/2})_3$ quasi-tetrahedral units should exist in addition to the normal As$(Se_{1/2})_3$ pyramidal units around the As atoms.

We have carried out anomalous x-ray scattering (AXS) experiments on the As_xSe_{1-x} glasses at $x = 0.40$ [6], 0.33, and 0.29 [7], including the IP concentration, and the obtained differential structure factors $\Delta_k S(Q)$ were analyzed using reverse Monte Carlo (RMC) modeling for evaluating the partial structure factors $S_{ij}(Q)$ and the corresponding partial pair distribution functions $g_{ij}(r)$. In this report, we discuss the local- and intermediate-range partial structures in relation to the stiffness transition, the $8-N$ bonding rule, and the existence of wrong As-As homopolar bonds.

The bulk As_xSe_{1-x} glassy samples were obtained by quenching the melts in quartz

ampoules containing the mixed compound. The melts were homogenized at 600°C for at least 48 h before the samples were slowly quenched in air.

The AXS measurements were carried out at BM02 at two incident x-ray energies of 20 and 200 eV below the As (11.868 keV) and Se (12.658 keV) K edges. The measurements were performed in reflectance mode using a standard $\omega - 2\theta$ diffractometer installed at the beamline.

The RMC simulations were carried out using two $\Delta_k S(Q)$s and the total structure factor $S(Q)$. To avoid unphysical atomic configurations, three constraints were applied to the RMC modeling. Firstly the cut-off values were determined to be 0.235, 0.230, and 0.225 nm for the As-As, As-Se, and Se-Se atomic pairs. Secondly weak bond angle constrains were applied for each type to be about 100°. Finally a constraint of Se-Se bond fractions was applied around the Se atoms. These fractions were chosen from the results of an *ab initio* molecular dynamics (MD) simulation by Bauchy et al. [8].

Figure shows $g_{\mathrm{AsAs}}(r)$ (left), $g_{\mathrm{AsSe}}(r)$ (center), and $g_{\mathrm{SeSe}}(r)$ (right) at $x = 0.29$ (top), 0.33 (middle), and 0.40 (bottom) obtained from the RMC modeling. The figure is taken from Ref. [7]. At $x = 0.40$, a small peak is observed at $r \sim 0.23$ nm in $g_{\mathrm{AsAs}}(r)$ [6]. The existence of such homopolar wrong bonds were discussed in detail by Bauchy et al. [8] using *ab initio* MD simulation. With decreasing x, the As-As wrong bonds rapidly decreases in the IP concentration range, which is in good agreement with the *ab initio* MD data [8]. For the further discussion, the AXS experiment should be performed in the wider concentration range including the floppy glasses, which are now in progress.

[1] J. C. Phillips, J. Non-Cryst. Solids **34**, 153 (1979).
[2] M. F. Thorpe, J. Non-Cryst. Solids **57**, 355 (1983).
[3] D. Selvanatham et al., Phys. Rev. B **61**, 15061 (2000).
[4] D. G. Georgiev et al., Phys. Rev. B **62**, R9228 (2000).
[5] N. F. Mott, Philos. Mag. **19**, 835 (1969).
[6] S. Hosokawa et al., Europhys. Lett. **102**, 66008 (2013).
[7] S. Hosokawa et al., J. Non-Cryst. Solids, submitted.
[8] M. Bauchy et al., Phys. Rev. Lett. **110**, 165501 (2013).