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The structure of permanently densified $GeSe_2$ glasses

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$GeSe_2$ is an archetypal tetrahedral glass that differs from both vitreous silica and germania in that it forms a network of both edge and corner sharing tetrahedra with a substantial number of homopolar bonds at normal pressure. A combination of high energy diffraction measurements and Raman spectroscopy have been performed on glassy $GeSe_2$ samples with densities of 3 and 4% greater than the normal glass. The samples were pressurised in a multi-anvil cell and recovered to ambient pressure for the experiments. The higher density samples show a dramatic decrease in the first sharp diffraction peak height and shift to higher Q-values on densification. This is related to a breakdown of intermediate range order arising from the Ge–Ge interactions. X-ray difference functions suggest there is a small increase in the number of Se–Se 'wrong' bonds and an increase in Ge–Ge corner sharing tetrahedra for the 4% denser glass compared to the normal glass. The Raman data also show a decrease in ratio of edge sharing:corner sharing tetrahedra indicating a change in the distribution of large ring structures that form the glassy network.

It has been suggested that during compression the connectivity of liquid $GeSe_2$ changes in character from a two to three dimensional network, on the basis of synchrotron x-ray measurements at high temperature and pressure,[1,3] the transformation being analogous to the monoclinic to tetragonal transition observed in the crystal phase. Furthermore it has been postulated that the observed breakdown of intermediate range order, characterised by the loss of the first sharp diffraction peak (FSDP) in the liquid at high pressure, may develop into a first order liquid-liquid transition in the supercooled regime.[11] An abrupt amorphous–amorphous transition may also appear in glassy state at high pressures.[3] 'Polyamorphic' behaviour of this type surrounds the controversial sharp transformation observed between high and low density amorphous ice,[14] and the tetrahedral to octahedral transformation that occurs in vitreous silica and germania at high pressure.[5,6]

The first sharp diffraction peak has been related to real space intermediate range ordering in many network glasses, e.g.[17] and has been shown to arise predominantly from Ge–Ge correlations in glassy $GeSe_2$.[8] A full set of partial structure factors measured using the method of isotopic substitution in neutron diffraction has shown that the structure of liquid $GeSe_2$ at ambient pressure comprises of $Ge(Se_{1/2})_4$ tetrahedra linked by both edge (34%) and corner sharing configurations.[8] However these results also showed evidence for a substantial number of defects in the glass such as Ge–Ge and Se–Se homopolar bonds. Molecular dynamics simulations suggest that the main contributions to the FSDP arise from Ge–Ge correlations between 4–8 Å[9,10] and the connectivity of the $Ge(Se_{1/2})_4$ tetrahedra can be attributed to different distributions of n-fold rings. Most of these rings being three, six, seven and eight fold in number.

In this study we have characterised local and intermediate range structural changes in permanently densified $GeSe_2$ glasses, corresponding to 3 and 4% increases in density compared to the normal glass, using x-ray diffraction and Raman spectroscopy.

Experimental

A natural sample of several grams was made from pure elements (Ge 99·99%, Se 99·99% Aldrich Chemicals Ltd.) and a isotopically enriched ^{76}Se sample of ~240 mg (99% ^{76}Se Cambridge Isotopes Ltd.) were produced in an identical manner by quenching from the melt at a temperature of 850°C into water at the University of Littoral. Approximately 200 mg of the each glass was wrapped in foil and compressed to 9±0·3 GPa (natural $GeSe_2$) and 10±0·4 GPa ($Ge^{76}Se_2$) in a multi-anvil device at the high pressure laboratory, University of Arizona. Density measurements of the

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