

In situ neutron diffraction studies of frameworks and their response to changes in P, T and composition

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Pressure (P) is an excellent variable for the study of frameworks since it allows isochemical variation of network geometry. High temperature on the other hand, especially under low confining P can lead to large changes associated with loss of volatiles. This is especially the case for zeolitic materials, or materials subject to oxidation. The changes induced at high P also tend to be more drastic as the relatively soft M-X-M bonds connecting primary building units (PBU) show greater variation over easily obtained P than they do up to the melting or decomposition point of the framework.

For a particular chemistry, the geometry adopted in either nano-crystalline and glassy forms of networks may be quite different from the crystalline counterpart. For example glassy GeSe₂ which comprises of both edge and corner sharing tetrahedral PBU, arranged in a distribution of ring sizes is an archetypal network glass. However, unlike oxide glasses the glassy GeSe₂ network contains a significant number of 'wrong' or homopolar bonds enabling a variety of (defect) local packing arrangements. The coherent scattering cross-section for neutrons, unlike that for X-ray scattering, is independent of Q and varies from isotope to isotope. This allows the collection of total scattering from samples where the scattering length for particular sites can be varied, including being made null for appropriate combinations of isotopes. A signature of the intermediate range order in glassy GeSe₂ is indicated by the presence of a first sharp diffraction peak (FSDP) in the measured structure factor (at a momentum transfer of $Q \sim 1.0 \text{ \AA}^{-1}$), although chemical ordering (associated with the principal peak at $Q \sim 2 \text{ \AA}^{-1}$) has also been associated with extended range ordering in real space. Synchrotron x-ray experiments on the high pressure liquid report a breakdown of the intermediate range order at high pressure (signified by the disappearance of the FSDP), and have led to the suggestion that GeSe₂ may undergo a (first order) polyamorphic liquid-liquid transition at high pressure from a 3D network to a 2D network. We performed neutron and high energy x-ray diffraction experiments to investigate the effect of pressure on the structure of GeSe₂ glass, and find clear evidence for a high pressure structure where the PBU changes to one of higher coordination and where significant collapse of the SBU occurs. Some of these changes, in the densified glasses are retained to room pressure. In situ joint ultrasonic and diffraction studies show a significant shear mode softening at pressures corresponding to changes in the PMU and SBU geometry.