Formation of a Dense Octahedral Glass

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Introduction

We have performed in-situ x-ray diffraction measurements of GeO_2, an archetypal network-forming glass under pressure. Below 5 GPa, additional atoms encroaching on the first tetrahedral shell are seen to be a precursor of local coordination change. Between 6 and 10 GPa, we observe structures with a constant average coordination of ~5, indicating a new metastable, intermediate form of the glass. At 15 GPa, the structure of a fully octahedral glass has been measured. This structure is not retained upon decompression and, therefore, must be studied *in situ*.

Methods and Materials

X-ray data were collected at the Sector 11 ID-C diffractometer at the Advanced Photon Source using a high-energy (115 keV) monochromatic beam. As the constituent atoms in the sample scatter each radiation differently, the x-ray data more strongly represent the Ge-Ge and Ge-O correlations. The x-ray samples had a volume of 1.1 mm^3 and were loaded as powders, without a pressure medium, into a novel large-volume moissanite anvil cell. The effects of pressure gradients were minimized by using a beam significantly smaller than the diameter of the anvil tip. Pressures were measured using a ruby-fluorescence technique, and are accurate to +/- 0.2 GPa.

Results

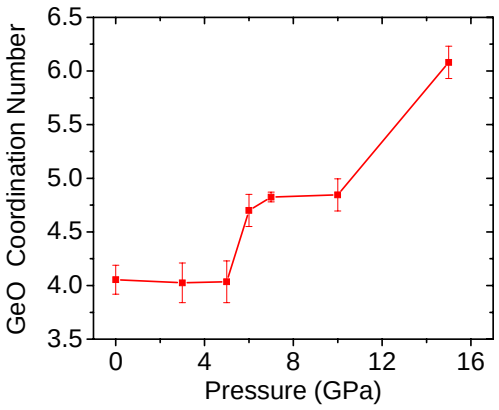

Fig.1. Ge-O coordination number as a function of pressure.

Below 6 GPa, we observe a reduction in Ge-O bond length and concurrent peak broadening indicating increasing distortion of the polyhedra with pressure. A narrowing Ge-O peak width at 6GPa, concurrent with a constant coordination number of nearly five, is consistent with the formation of pentahedra: first as highly-distorted tetrahedra with non-bonded oxygen atoms forced into the close proximity, but becoming progressively regular at higher pressure.

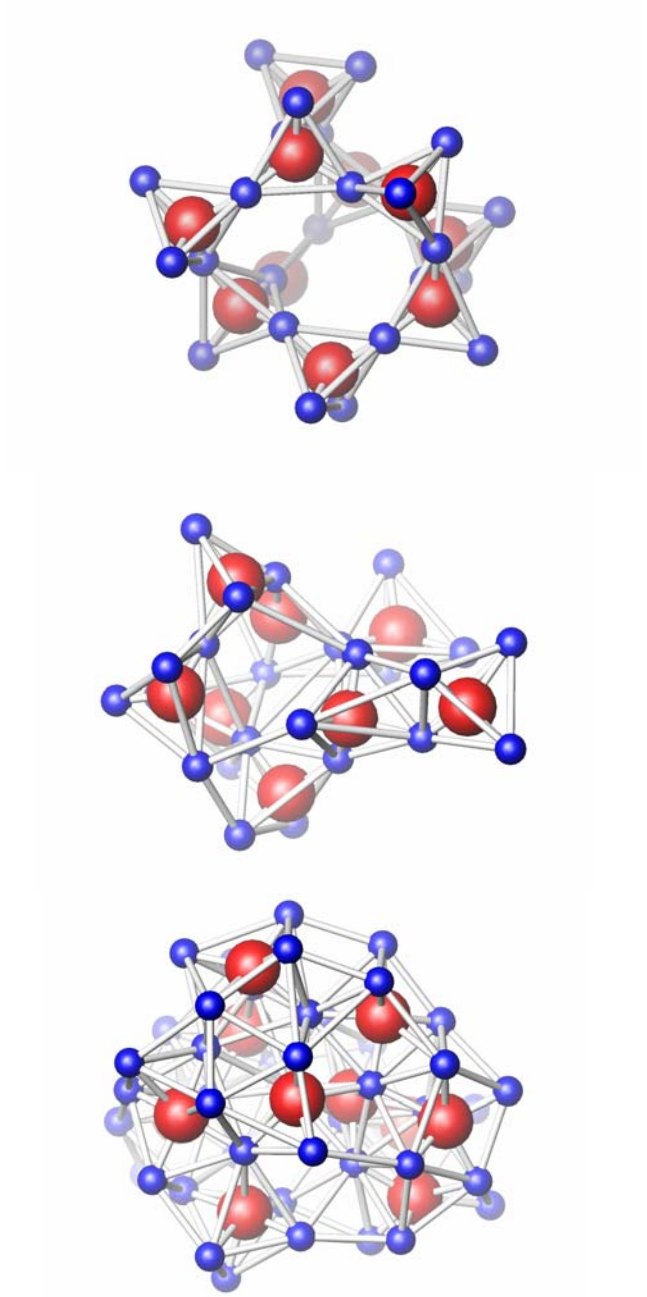

Fig.2. Reverse Monte Carlo fits to the diffraction data showing (top) The 'cage' network in normal tetrahedral glass (middle) cage collapse & the'Germanate anomaly' (five fold coordinated Ge (bottom) the formation of a dense octahedral glass.

At 15 GPa, the local coordination has increased to six, indicating fully octahedral units. This implies further structural change between 10 and 15 GPa, specifically, additional oxygen must enter the first coordination shell. The octahedral pattern is characterized by several pronounced peaks, and is very distinct from the tetrahedral form. The Ge-O peak in the octahedral glass is centered on 1.91(2) Å, consistent with that found within planes of edge-shared octahedra in the crystalline rutile phase of 1.87 Å (at 16 GPa).

Discussion

Using these novel techniques, we have performed detailed structural characterization, including the *direct* measurement of local coordination and the extended structure of a high pressure glass. These new methods facilitate the detailed study of structural transformations in amorphous solids and, in the case of GeO_2, we observe significant changes in intermediate range order and stable intermediately-coordinated structures, which are seen over a broad pressure range.

Acknowledgments

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References

[1] The formation and Structure of a dense Octahedral Glass. M. Guthrie, C.A. Tulk, C.J. Benmore *et al.*, *Physical Review Letters* 93, **2004**, 115502.