

Structural Transformations in Permanently Densified ν -GeO₂

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Introduction

Pressure-induced amorphous transformations are known to occur in several tetrahedral systems and can result in permanently densified glasses (PDGs) upon the release of pressure [1-3]. *In situ* studies on ν -SiO₂ and ν -GeO₂ indicate that there is a reversible change in the cation coordination with pressure. In PDGs, evidence of an irreversible effect suggests retention of the high-pressure phase. We report a high-energy x-ray diffraction measurement on densified GeO₂ (10 GPa) from which information on all three nearest neighbor (NN) correlations has been obtained.

Methods and Materials

The glass samples were contained in a 4-mm-wide aluminum frame with thin-walled (10- μ m thick) Mylar windows, such that only the glassy beads and amorphous Mylar windows were in the path of the 1 \times 1-mm square x-ray beam. Background measurements on the same part of the Mylar window without the sample were made to eliminate the container scattering contribution. It should be noted that recent developments in high energy x-ray instrumentation have some advantages over conventional methods (e.g., lower attenuation and multiple scattering factors and higher achievable momentum transfer range). The measurements were performed by using an x-ray energy of 100 keV.

For the data analysis, a software code ISOMer-X was developed by our group at IPNS [4]. Corrections were made for detector dead time, container scattering, and Compton scattering. The software program ISOMer-X was used to reduce the data. At these high energies, the x-rays act as a bulk probe, and attenuation and multiple scattering effects were estimated to be negligible. The relativistic corrections were applied at high Q by using the Klein Nishina formula, and the atomic form factors and Compton scattering were obtained from the tabulated values of Hubbell [5].

Results

Figure 1 shows the experimental structure $S_X(Q)$ for the densified GeO₂ glass along with that of the normal GeO₂ glass for comparison. The first sharp diffraction peak (FSDP) position shifts to lower Q , and its intensity decreases on densification. Figure 2 shows the $T(r)$ for

both the normal and densified glass. The x-ray scattering is dominated by the Ge correlations. The Ge-O₁ and Ge-Ge₁ distances are well-discerned from a Gaussian fit in the undensified glass. In the densified case, as seen from the figure, there is a broadening of the Ge-Ge peak around 3 \AA and a change in the sloping background. The position of the peak does not appear to change much, however; because of the broadening of the peak, the center of mass of the peak position extracted from the fit shows a shift toward a slightly higher r .

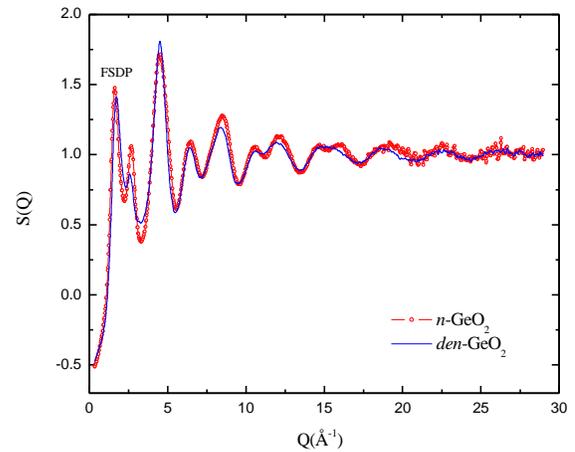


FIG. 1. $S(Q)$ for normal and densified GeO₂ glass.

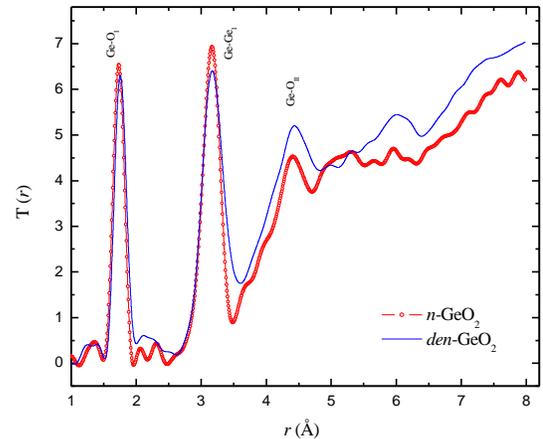


FIG. 2. $T(r)$ for normal and densified GeO₂ glass.

By combining these results with those obtained from neutron diffraction done on the same sample at the glass, liquids, and amorphous materials diffractometer (GLAD) at IPNS in the same Q range, we have been able to obtain information about all three partials: Ge-O, Ge-Ge, and O-O.

Discussion

Our results elucidate structural changes in both the short-range order (SRO) and intermediate-range order (IRO) of GeO₂ glass. Pressurization results in a reduction in the inter-tetrahedral Ge-O-Ge and the intra-tetrahedral O-Ge-O angles. The frustration caused is accommodated as a decrease in the next-nearest neighbor (NNN) Ge-O_{II} and O-O_{II} distances and an increase in the Ge-O_I and O-O_I and Ge-Ge NN distances. Structural changes induced by densification are brought about primarily by the reconfiguration in the NNN oxygen correlations, thereby reducing the IRO. This leads to a bending of the Ge-O-Ge angle and a subsequent distortion of the GeO₄ tetrahedra. We propose that it is the NNN O-O_{II} packing that determines the high-pressure structure of the GeO₂ glass. The manuscript for publication of the results is being prepared. Measurements on amorphous BeH₂ and BeD₂ have also been performed in the same beamline, and data analysis is underway.

Acknowledgments

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