Intermediate-Range Order in Permanently Densified GeO$_2$ Glass

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Information about the partial structure factors of densified GeO$_2$ glass has been obtained from neutron and x-ray diffraction measurements. Densification causes a reduction in the length scale of the intermediate range order (IRO). The difference structure factors obtained by combining the x-ray and neutron data so as to eliminate one partial structure factor at a time shows the greatest effects when the Ge-Ge correlations are eliminated and least when O-O correlations are eliminated. This implies that the reduced length scale results from a decrease in the next-nearest neighbor Ge-O and O-O distance caused by a rotation about the Ge-O-Ge bonds and a distortion of the GeO$_4$ tetrahedra.

Two contiguous length scales describe the amount of residual structural organization in a topologically disordered system. First, the short-range order (SRO) refers to correlations existing between nearest neighbors and is a common feature of most amorphous materials. Second, intermediate range order (IRO) is defined as the level of structural organization involving distances significantly longer than nearest-neighbor bonds. Networking-forming liquids and glasses of AX_2 stoichiometry exhibit IRO through the appearance of a first sharp diffraction peak (FSDP) in the static neutron or x-ray scattering structure factor, typically in the range of $k \sim 0.5$–1.5 Å^{-1}. Structural changes associated with densification of tetrahedral network glasses, such as GeO$_2$ and SiO$_2$, has been the subject of debate in recent years [1–5]. Changes are observed in both the SRO, described by the bond lengths and angles of the local structural units, in the case of GeO$_2$ and SiO$_2$ tetrahedra, and in the IRO, describing the manner in which these units are assembled into the 3D network of the glass. The changes in SRO are relatively straightforward and consist of a slight increase in the mean Ge-O or Si-O bond length and a decrease in the mean O-O distance, the two effects combine to increase the distortion of the structural unit from a perfect tetrahedron. The changes in the IRO, on the other hand, are more complicated and have been the subject of considerable debate.

Many network glasses have been shown to undergo a gradual structural transition at high pressure, in which the underlying thermodynamic driving force is still not well established [6]. In GeO$_2$ glass, a gradual coordination change from fourfold to sixfold under applied pressures is well established [7]. Upon decompression, the glasses appear to return to fourfold coordination but with a permanent increase in density [8]. Recently, a series of GeO$_2$ glasses densified at different pressures up to 6 GPa were investigated by high resolution neutron scattering [9]. The authors find a decrease in the length scale of the IRO on densification and attribute this to the reduction in the size of the network cages, wherein the mean Ge-O bond length changes only very slightly in the densified glasses and there is a decrease in the mean Ge-O-Ge bond angle. However, it was not possible to extract the Ge-Ge distance exactly due to overlapping correlations from the O-O and Ge-Ge correlations in the neutron spectra. Recently, a technique has been developed for obtaining all three partial structure factors for normal GeO$_2$ glass through the combination of neutron and x-ray scattering techniques [10]. This approach is limited to Q values below 10 Å^{-1} and therefore poor resolution in real space. In this Letter, we report the results of a combination of neutron and x-ray diffraction measurements on normal and densified GeO$_2$ glass from which information about the partial structure factor $S_{ij}(Q)$ for different element pairs (i, j) have been obtained. We find the greatest effects when the Ge-Ge correlations are eliminated and least when O-O correlations are eliminated. This result is surprising since previous discussions on IRO in network glasses have focused on cation-cation correlations.

Amorphous GeO$_2$ was synthesized using a standard room temperature sol-gel method: tetraethoxygermane (Gelest, Inc.) was added to water. The resulting precipitate was filtered and rinsed with methanol. The amorphous GeO$_2$ material was then put into a Pt capsule and placed inside a 1400 °C oven for 12 h. The material was removed from the oven and allowed to air cool, resulting in a large piece of GeO$_2$ glass. This GeO$_2$ glass was densified to 10 GPa at room temperature using a multianvil press in the high-pressure facility at Arizona State University. The density of the glass increased by 11% in agreement with previous work [8]. Pulsed neutron diffraction measurements were made on the GLAD facility at the Intense Pulsed Neutron Source at Argonne National Laboratory (ANL) and x-ray measurements were performed on the

high-energy beam line ID-11-C at the Advanced Photon
Source at ANL using an energy of 115 keV. Measurements
were made on the densified glass over a period of
two years and no detectable structural relaxation was
observed.

Average structure factors $S(Q)$ were extracted from the
x-ray and neutron data using the formula

$$S(Q) = \frac{I(Q)}{[\sum_i c_i W_i(Q)]^2}$$
$$= \frac{1}{[\sum_i c_i W_i(Q)]^2} \sum_{i,j} c_i W_i(Q) c_j W_j(Q)[S_{i,j}(Q) - 1], \quad (1)$$

where c_i is the concentration of species i and W_i is the
coherent scattering length, b_i, for the neutrons and the
atomic form factor $f_i(Q)$ for x rays.

Figures 1(a) and 1(b) show the experimentally deter-
mined neutron and x-ray average structure factors $S_N(Q)$
and $S_X(Q)$ for the normal and densified GeO_2 glass. The
peak at 1.6 Å^{-1}, often called the first sharp diffraction
peak (FSDP), is generally taken as a signature of IRO. On
densification it shifts towards higher Q, broadens, and
becomes less intense. The second peak is also reduced but
without any significant shift. These observations agree
well with previous neutron measurements on GeO_2 [9]
and SiO_2 [1].

The neutron and x-ray structure factors represent dif-
ferent combinations of partial structure factors $S_{ij}(Q)$,
where the indices i, j refer to the atom type, Ge or O
[Eq. (1) and Table I]. If three independent combinations
could be measured, all three partials could be obtained
[10]. In our case, two independent combinations were
measured and difference structure factors may be ob-
tained using the following relation:

$$\Delta_k S(Q) = \frac{\alpha_k S_N(Q)\overline{b}^2 - \beta_k S_X(Q)\overline{f(Q)}^2}{\alpha\overline{b}^2 - \beta\overline{f(Q)}^2}, \quad (2)$$

each eliminating one of the partials $S_{Ge-Ge}(Q)$ $(k = 1)$,
$S_{GeO}(Q)$ $(k = 2)$, and $S_{OO}(Q)$ $(k = 3)$, shown in
Figs. 2(a)–2(c). The percentages of each partial in
$S_N(Q)$, $S_X(Q)$, and the $\Delta_K S(Q)$ are given in Table I.

The difference correlation functions, $\Delta_K T(r)$, obtained
by the Fourier transformation of the corresponding
$\Delta_K S(Q)$, are shown in Fig. 3. The changes in the short-
range structure can be determined accurately, since the
Ge-Ge and the O-O peaks are resolved in the difference
functions. By fitting Gaussian functions, we find that the
nearest-neighbor Ge-O distance is increased by $0.005 \pm$
0.001 Å while the O-O and Ge-Ge distances are de-
creased by 0.023 ± 0.002 Å and 0.019 ± 0.002 Å, respec-
tively. These changes imply an increased distortion of a
regular tetrahedron $[(r_{OO}/r_{GeO}) = \sqrt{8/3} = 1.633]$ in the
densified glass and are consistent with the correlation
between the bond length and bond angle observed by
Gibbs et al. [11]. The O-O peak is broadened in the
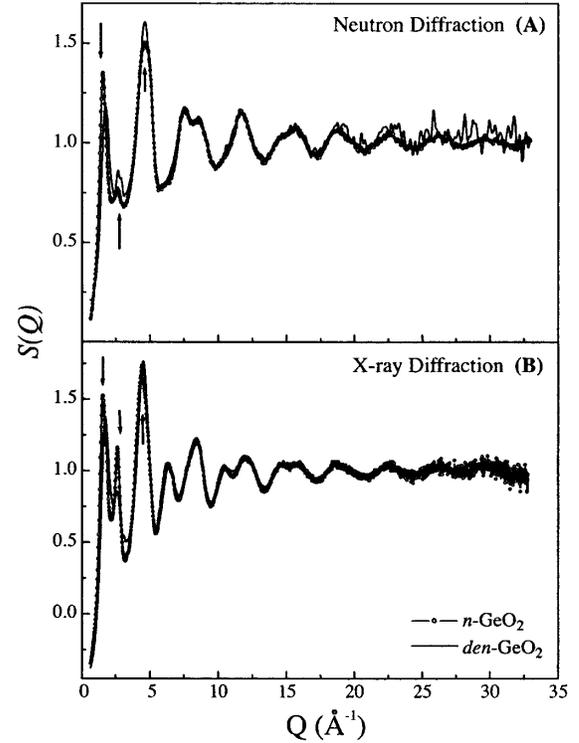
FIG. 1. Measured structure factors of normal and densified
GeO_2 glass by (a) neutron and (b) x-ray diffraction. The arrows
indicate the shift in peak coordinates in the densified glass.

densified glass, and was best fit using two Gaussian func-
tions. Features in the $\Delta_K T(r)$ at larger r can be ascribed to
second-neighbor Ge-O and Ge-Ge correlations, but can-
not be determined very accurately, so we rely on the
reciprocal space data to obtain information about the
changes in IRO.

The nature of IRO in network glasses and its relation to
FSDP has been a controversial topic since the earliest days
of x-ray diffraction. A comprehensive review of the vari-
ous interpretations has been given by Wright et al. [12] in
connection with SiO_2. The picture now generally ac-
cepted is that the FSDP reflects a periodic arrangement
of structural elements whose nature depends on the glass
in question [13,14]. The periodicity decays after a finite
number of periods, leading to a peak of finite width in
contrast with the Bragg peaks observed in crystalline
solids. In the case of chalcogenide glasses such as

TABLE I. Coefficients of the partial $S_{ij}(Q)$ in each difference
spectrum for $Q = 0$.

	S_{Ge-Ge}	S_{Ge-O}	S_{O-O}
$S_N(Q)$	0.1832	0.2448	0.3272
$S_X(Q)$	0.4607	0.2180	0.1032
$\Delta_1 S(Q)$	0	0.36	0.64
$\Delta_2 S(Q)$	0.61	0	−0.39
$\Delta_3 S(Q)$	0.74	0.26	0
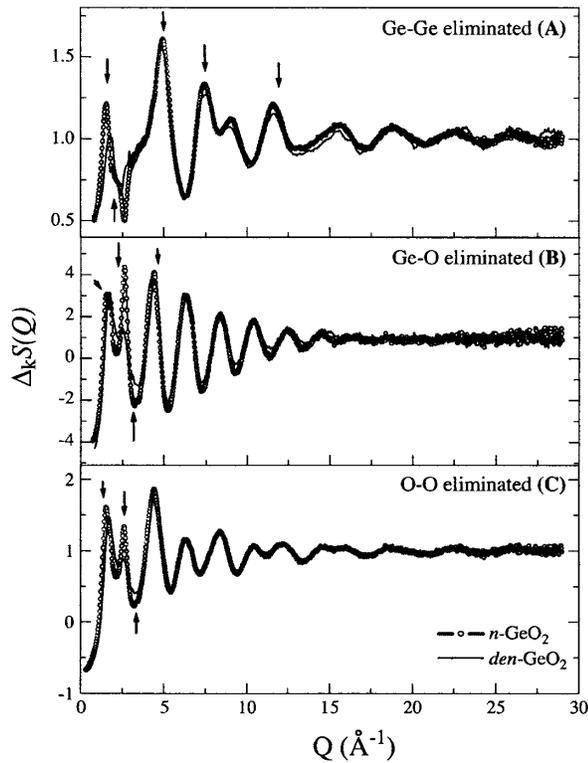
FIG. 2. Difference structure factors, $\Delta_K S(Q)$, of normal and densified GeO_2 obtained from neutron and x-ray $S(Q)$'s, by eliminating one partial. The arrows indicate the shift in peak coordinates in the densified glass. (a) Ge-Ge eliminated, (b) Ge-O eliminated, and (c) O-O eliminated.

FIG. 3. The difference correlation function, $\Delta_K T(r)$, obtained by the Fourier transformation of the corresponding $\Delta_K S(Q)$. (a) Ge-Ge eliminated, (b) Ge-O eliminated, and (c) O-O eliminated.

As_2Se_3, Wright et al. [15] associated the structural elements with the boundaries of the cages of the 3D covalent network (irregular groups of 10–20 atoms enclosing the open region of the network), and this concept applies equally well to other network glasses and GeO_2 in particular. More recently, Elliot et al. [16] associated the FSDP with holes in the network, which can be identified with the centers of the cages and thus have the same periodicity. Further support for this molecular picture just given comes from the diffraction pattern of alkali silicates [17] and germanate [18] glasses, where the large alkali ions require larger cages and give rise to a diffraction peak at even lower Q.

The structure of normal GeO_2 glass comprises a network of corner-shared GeO_4 tetrahedra [8]. From the diffraction data shown in Figs. 1 and 2, the length scale of the periodicity is given by $2\pi/Q_P$ where Q_P is the peak position. The peak height reflects both the degree of periodicity and is also a function of the packing of the structural elements. Denser packing leads to a reduction in the height of the FSDP leading, for example, to the anomalous temperature dependence of the FSDP in chalcogenide glasses [19]. In the present study, changes in the position and the height of the FSDP in compacted GeO_2 glass are observed as a result of the density increase of 11%: Q_p also increases by 11% and the peak height

decreases, whereas a uniform compression would lead to an increase in Q_p of just 4% and no change in height (elastic compression) [4]. This implies that the reduction in cage size is not commensurate with density increase and that the cages are becoming more densely packed.

In previous work on densified GeO_2 [9] and SiO_2 [1], it was proposed that it is the Ge-Ge or Si-Si correlation length that decreases on densification, associated with the reduction of the intertetrahedral Ge-O-Ge or Si-O-Si angles, respectively. The decrease in the length scale of the IRO evidenced from the FSDP shift in the total structure factors from our results and those of Stone et al. [9] is a cumulative effect produced by all three partial correlations. The difference structure factors, obtained by eliminating the contribution of one partial at a time, makes the scenario more clear. From Figs. 2(a)–2(c) it is seen that, upon densification, the shift in the first peak to higher Q and the reduction in the peak intensity are greatest in the case where the Ge-Ge correlations are eliminated and least when the O-O correlations are eliminated. This implies that the change in structure on densification in GeO_2 glass is dominated by the oxygen correlations.

These results lead to the following interpretation for the structural transformation in permanently densified GeO_2 glass. As densification proceeds at lower pressures, the network connectivity is reduced by a decrease in the cage size, associated with a closer packing of the
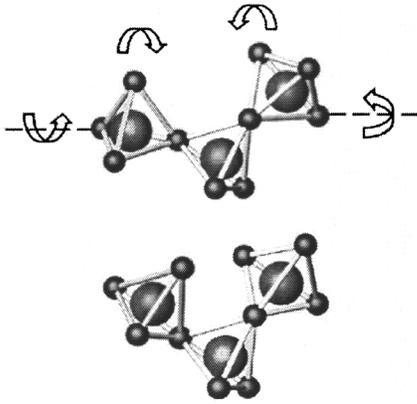
FIG. 4. Schematic of the tetrahedral network of the GeO_2 glass with corner shared GeO_4 tetrahedral units. The arrows show the bending of the Ge-O-Ge angles and rotation of the tetrahedra used to produce the densified structure discussed in the text.

relatively rigid GeO_4 tetrahedra. Further increase of pressure results in a reconfiguration of the next-nearest neighbor oxygen packing caused by a rotation of the tetrahedra around the Ge-O-Ge bonds and a deformation of the O-O network. This frustration is propagated to smaller length scales resulting in the distortion of the GeO_4 tetrahedra themselves. The system acquires a structure with a more efficient packing of the oxygen ions to fill in the lesser volume available to it. This scenario is illustrated by the difference structure factors $\Delta_K S(Q)$ where, upon eliminating all the Ge-Ge correlations and retaining only the oxygen correlations [Fig. 2(a)], the change in the FSDP is relatively drastic, while in the other extreme eliminating all the O-O correlations [Fig. 2(c)] produces a much smaller change in the FSDP. Thus, it is the next-nearest neighbor oxygen Ge_1-O_2 and O_1-O_2 packing (Fig. 4) that governs the high-pressure structure of the GeO_2 glass.

Our conclusion is supported by the trend observed in the Si-O-Si angle distribution in densified SiO_2 glass deduced from MAS NMR spectroscopy by Devine *et al.* [20] and that in radiation densified SiO_2 glass determined from neutron diffraction measurements by A. C. Wright *et al.* [21]. These authors conclude that the shift in the Si-O-Si angle brought about by densification is due to a decrease in the next-nearest neighbor oxygen O_1-O_2 distance, in agreement with that calculated from a steric hindrance model [22]. It has been demonstrated in Refs. [22,23] that by including steric hindrance criteria, which impose a restriction on the O_1-O_2 next-nearest neighbor distance, the most important modification brought about by densification is a reduction in the distance of closest approach of these atoms. Moreover, the hysteresis observed in the *in situ* reversible transition of GeO_2 glass [7] has been ascribed to the slow transformation kinetics, from a densely packed high-pressure state to one with less efficient oxygen packing.

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