High-Pressure X-Ray Diffraction of SiO_2 Glass

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We have measured the x-ray structure factor $S(Q)$ for SiO_2 glass to 42 GPa in the diamond-anvil cell using new experimental techniques for studying amorphous materials at high pressures. Large changes in the first sharp diffraction peak of $S(Q)$ with increasing pressure provide evidence for changes in the medium-range order of the glass (length scales of ~4–10 Å). Average pair correlation functions at high pressure reveal significant changes in the nearest-neighbor geometry of the glass with compression. Between 8 and 28 GPa the coordination of Si increases, and at 42 GPa the value is close to six.

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Measurements of liquid and glass structures have important applications throughout the physical sciences [1]. In particular, high-pressure studies are critical for identifying new equilibrium and metastable states that can be accessed as amorphous materials as compressed to smaller volumes and for providing experimental tests for structural models of liquids and glasses. Such work is motivated by recent experiments that have documented changes in the nearest-neighbor geometry and vibrational spectra of inorganic liquids and glasses under compression [2–7], thereby suggesting that amorphous materials may undergo structural transitions, just as crystalline compounds are modified by high-pressure phase transformations. Moreover, there is great current interest in identifying intermediate-range order in amorphous materials [8] and in developing new empirical constraints for structural models [9–12]. At present, our understanding of these issues is incomplete because of the few structural probes that are available for characterizing noncrystalline compounds at high pressures.

To this end, diffraction techniques provide the best measure of amorphous structures. In the case of x-ray experiments, one obtains an unambiguous description of atomic correlations between 0.5 and 10 Å averaged over length scales of 100–1000 Å. For structural studies, these techniques are preferable to spectroscopic methods which probe vibrational and electronic properties over a more limited range of distances and that generally require *a priori* structural models to interpret the measurements. Also, compared to studies on quenched materials at ambient conditions [13], *in situ* high-pressure diffraction experiments allow direct measurements on novel structures that may be unstable on decompression. Despite these advantages, high-pressure diffraction measurements on liquids and glasses have been limited to date by the poor scattering power of amorphous materials and the small sample size in high-pressure experiments ($\sim 10^{-13}$ m^3). Specifically, the diffuse scattering from the small amount of sample is overwhelmed by the broad Compton scattering from the pressure transmitting anvils (e.g., in diamond-cell experiments).

Recently, we have overcome these problems by the use of high-brightness, low-divergence synchrotron radiation. By collimating the radiation to dimensions on the order of 10 μm and spatially filtering the diffracted beam, we significantly damp the Compton scattering from the components of the high-pressure cell. And, by using energy dispersive diffraction and the high critical energy from a wiggler source, we can probe a wide range of reciprocal space for weakly scattering amorphous materials [$Q = 4\pi \sin(\theta)/\lambda$; $1 < Q < 16.5$ Å^{-1}] [14]. Here we apply these new techniques to measurements of the x-ray diffraction from SiO_2 glass to pressures of 42 GPa. This material is an archetypal network-forming glass, and its properties are of great importance in wide areas of condensed matter physics and the Earth and materials sciences. Recently, there has been a large effort to identify structural transitions in SiO_2 glass and structurally related compounds at high pressures with spectroscopic [2–6] and theoretical studies [15–18]. Moreover, there is intense interest in using diffraction techniques to study the medium-range order of silica glass and to quantify its variation with pressure [13] and temperature [19].

We measured energy dispersive x-ray diffraction spectra from SiO_2 glass in air and in the diamond-anvil cell at 8, 28, and 42 GPa at the superconducting wiggler beam line of the National Synchrotron Light Source (X-17C). Samples of SiO_2 glass (Herasil) were compressed in a diamond-anvil cell without a pressure medium to minimize unwanted background diffraction and Compton scattering. Energy dispersive diffraction spectra were measured at 5–7 scattering angles in the range $6° < 2\theta < 33°$. For each measurement, the contribution from the diamond Compton scattering was subtracted and the intensities were normalized to the source spectrum for the synchrotron. The individual measurements at each 2θ were then combined and averaged to form a single x-ray spectrum in the range $1 < Q < 16.5$ Å^{-1}. Further details will be presented elsewhere [20]. The pressures were measured with either the ruby fluorescence [21] or diamond Raman scales [22]. We estimate the maximum pressure variation over the x-rayed sample (~30 μm in length) to be less than ±0.25 GPa at the highest pressures. Spectroscopic measurements on SiO_2

glass indicate that the effects of nonhydrostatic stresses in the present study are similar to those in crystalline diffraction experiments: Anisotropic compression and pressure variations tend to broaden the distribution of bond lengths; however, they have little effect on the general structure [23].

The x-ray structure factor $S(Q)$ for SiO_2 glass is shown for a series of pressures in Fig. 1. At ambient conditions, our data are in excellent agreement with previous studies [24,25]. With increasing pressure, we find that there are particularly dramatic changes in the positions and intensities of all the peaks in $S(Q)$ at $Q \lesssim 5.0$ Å^{-1}. Pressure has a large effect on the structure of SiO_2 glass, and thus our results contrast the relatively small changes in $S(Q)$ that have been documented with increasing temperature [19]. For example, to 8 GPa the first sharp diffraction peak shifts from $Q \sim 1.55$ to 1.92 Å^{-1}, while its intensity remains approximately constant. Over the same range of pressure, the width of the broad peak at 5.0 Å decreases by ~50%. The largest changes in $S(Q)$ occur between 8 and 28 GPa. The intensity of the first diffraction peak decreases by ~50% while its position shifts from 1.92 to 2.29 Å^{-1}; a new peak appears at 3.18 Å^{-1}; and the peak at 5.0 Å^{-1} shifts to lower values of Q (~4.9 Å^{-1}). Between 28 and 42 GPa, the changes in $S(Q)$ are relatively small: There are small outward shifts in the first two peaks (from 2.29 to 2.37 Å^{-1} and from 3.18 to 3.38 Å^{-1}), the broad peak near 4.9 Å^{-1} continues to shift to longer wavelengths (~4.8 Å^{-1}), and there is a continued decrease in the intensity of the first diffraction peak.

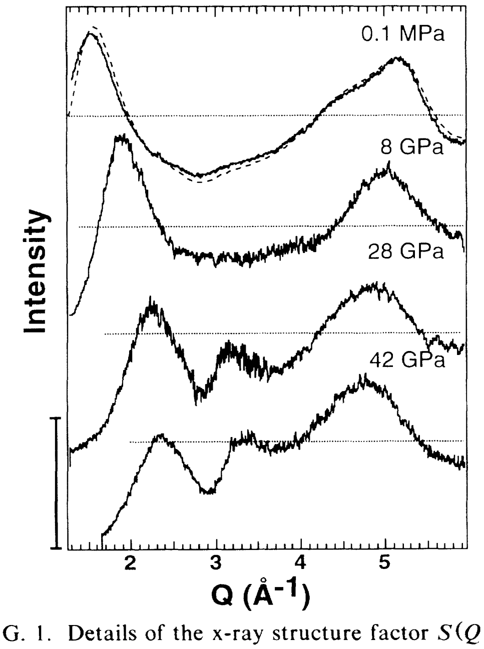

FIG. 1. Details of the x-ray structure factor $S(Q)$ measured for silica glass between 0.1 MPa and 42 GPa. At ambient pressure, the data of [25] (dashed line) are shown for comparison. The termination of our data near $Q = 1$-1.5 Å^{-1} reflects the minimum diffraction angles and energies for these experiments. The horizontal lines correspond to $S(Q) = 1$ for each experiment. The vertical scale bar at the left indicates one unit for $S(Q)$.

The relationship between $S(Q)$ and individual structural features remains a fundamental question for the study of glasses [9-12]. Here we compare the change in the position of the first diffraction peak (Q_1), to the linear strain (d/d_0) associated with elastic compression of the glass. Given a decrease in the volume (V) without structural modifications, changes in Q_1 can be described by $(V/V_0)^{1/3} = d/d_0 \sim Q_{01}/Q_1$, where $d \sim 2\pi/Q_1$ and the subscript 0 refers to values at ambient pressure. Examining the changes between 0.1 MPa and 8 GPa for SiO_2 glass, we find $Q_{01}/Q_1 = 0.81$ while the linear elastic compression to this pressure is significantly smaller, $d/d_0 \sim 0.93$ [26]. Similarly, at 28 and 42 GPa the increase in Q_1 is approximately 3 times larger than would be expected from the elastic strain alone. Thus, the shift of the first diffraction peak with pressure is inconsistent with simple elastic compression of SiO_2 glass. We believe that this discrepancy cannot be caused by anisotropic compression and that it must reflect pressure-induced structural transitions in the medium-scale order (~4-10 Å) that is described by the first diffraction peak in $S(Q)$ [9].

These observations have important implications for models of the first sharp diffraction peak [9-12]. This peak is a characteristic feature of the diffraction pattern for a large class of network structured glasses which have medium-range order beyond nearest-neighbor distances [9] (~4.2 Å for SiO_2 glass). By comparison, the first peak in $S(Q)$ for randomly packed materials occurs at length scales that are comparable to nearest-neighbor separations [1]. We find that there is no change in the intensity of the first diffraction peak up to 8 GPa, and thus we expect that the degree of intermediate-scale ordering is preserved in SiO_2 glass over the range of elastic compression ($0 < P < 10$ GPa [26]). These results contrast diffraction measurements on glassy chalcogenides [27], pressure densified SiO_2 glass [13], and models that predict a decrease in the intensity of the first diffraction peak with increasing pressure [10]. At higher pressures, however, the response of SiO_2 glass changes significantly. Above 28 GPa, the erosion of the first diffraction peak and the emergence of a new peak at nearest-neighbor length scales ($Q \sim 3.18$ Å^{-1}, $d \sim 1.9$ Å) are consistent with a large decrease in the medium-range ordering of the glass.

One obtains an estimate of the real space correlations in the glass at high pressure from the Fourier sine transform of the structure factor (Fig. 2):

$$G(r) = \frac{2}{\pi} \int M(Q) Q [S(Q) - 1] \sin(Qr) dQ ,$$

where $M(Q)$ is a high-frequency filter that removes the finite truncation effects in the transform [13]. Because

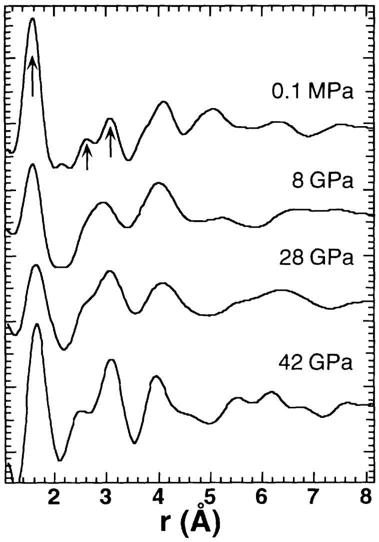

FIG. 2. Average pair correlation functions $G(r)$ for SiO_2 glass with increasing pressure. At ambient pressure, the Si-O, O-O, and Si-Si peaks are indicated at 1.59, 2.61, and 3.07 Å, respectively.

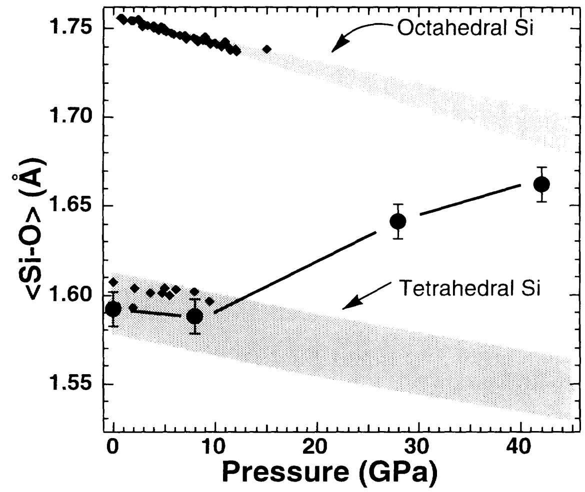

FIG. 3. Comparison between the most probable Si-O distance in silica glass measured in this study (●) and the Si-O bond length in crystalline SiO_2 polymorphs with tetrahedral and octahedral coordination (shaded curves and ◆). For tetrahedral SiO_2, the bond length at high pressures is calculated assuming an effective bulk modulus of 400 GPa, and accounting for the variability due to changes in the Si-O-Si angle [31]. The Si-O bond length for octahedral SiO_2 is derived from the equation of state of stishovite [34]. For comparison, measured values of the shortest Si-O bond are plotted (◆) for *α*-quartz [29,30] and stishovite [35-37] at high pressures.

SiO_2 glass contains more than one type of atom, $G(r)$ is a convolution of all the Si-O, O-O, and Si-Si correlations. Consequently, integration of $G(r)$ does not provide a measure of the coordination state, though $G(r)$ does describe near-neighbor bond lengths. For x-ray diffraction measurements, the Si-O correlations have the strongest weight in $G(r)$, and the Si-O peak is an unambiguous feature. At ambient conditions, we attribute the peaks at 1.59, 2.61, and 3.07 Å to the Si-O, O-O, and Si-Si pairs, respectively (cf. [19,24,25,28]). These represent most probable values for the individual bonds, and they can be used to estimate the most likely bond angles (e.g., Si-O-Si and O-Si-O). We estimate the uncertainty in the most probable bond lengths and angles in this study to be ~ ±0.01 Å and ±2°, respectively.

Between 0.1 MPa and 8 GPa, there is little change in the Si-O separation within our resolution (Fig. 3), and the Si-Si distance appears to decrease. Qualitatively, these observations are consistent with the elastic compression mechanisms that have been observed in crystalline SiO_2 polymorphs over a similar range of pressure (e.g., [29,30]). Below ~10 GPa, volume compression occurs through bending of the Si-O-Si intertetrahedral angles (i.e., decreasing Si-Si separations), with little change in the dimensions of the individual SiO_4 tetrahedra.

With compression to 28 GPa, the Si-O peak increases from 1.59(1) to 1.64(1) Å, and the Si-Si separation seems to increase. Although nearest-neighbor bond lengthening under pressure is unusual, studies of the crystalline SiO_2 phases show that the Si-O separation increases with compression of the Si-O-Si angle [31] and with increases in Si coordination. At this pressure, we find that the most probable Si-O distance is significantly larger than the value that would be expected for tetrahedrally coordinated SiO_2 [1.64(1) compared to 1.57(2) Å]. Thus, our data indicate that the coordination of the glass increases between 8 and 28 GPa.

By 42 GPa, the Si-O peak shifts to 1.66(1) Å. Compared to the ambient pressure value [2.61(1) Å], the O-O peak decreases to 2.50(1) Å. Thus, first-neighbor separations increase while second-neighbor distances decrease over this range of pressure. Similar changes in bond lengths are observed in the transformation from the tetrahedral to the octahedral polymorphs of crystalline silicates. Using the values of the Si-O and O-O peaks, we find a most probable intrapolyhedral O-Si-O angle of 96(2)° for the glass at 42 GPa. This value is intermediate between the tetrahedral and octahedral values of 109.5° and 90°, respectively. At 42 GPa, there is only a small difference between the most probable Si-O separation in the glass [1.66(1) Å] and the Si-O bond length in stishovite [1.69(1) Å], the octahedrally coordinated crystalline polymorph of SiO_2. Broadly, these data indicate that there are large and continuous changes in the structure of SiO_2 glass over a wide range of pressure. At the highest pressures of this study, we conclude that the polymerized tetrahedral structure of SiO_2 glass is eliminated and that the average coordination is close to six. Thus, we find an inverse correlation between the coordination of the glass and the intensity of the first diffraction peak. This supports models that attribute this feature in $S(Q)$

to medium-scale correlations in the structure of linked SiO_4 tetrahedra [11]. Our results are also consistent with the loss of tetrahedral Raman and infrared vibrations that have been documented above 28 GPa in SiO_2 glass [2,4] and with changes in the rheology of silica that have been measured to 80 GPa [32]. By comparison, recent EXAFS measurements on amorphous GeO_2 show an increase from fourfold to sixfold coordination at significantly lower pressures (7–9 GPa [5]), consistent with the behavior of the corresponding silicate and germanium crystalline phases.

In conclusion, we report the first direct structural measurements on a glass at elevated pressures. These measurements of bond lengths and angles should provide a new empirical basis for studies of silica glass at high pressures. We note that even further detailed structural information (e.g., individual pair correlations, estimates of sample densities) can be obtained from our data by fitting the measured $S(Q)$ with reverse Monte Carlo simulations [33]. These results will be reported elsewhere.

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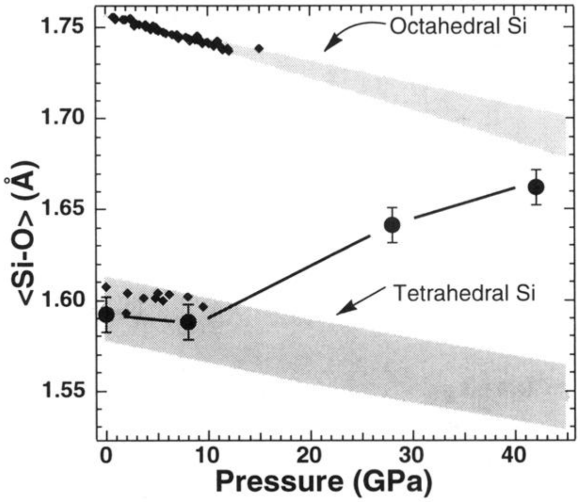

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