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Structural and topological changes in silica glass at pressure

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The effects of high pressures on the structure of silica glass have been elucidated using high-energy x-ray diffraction up to 43.5 GPa. A decrease in the first two peak positions in the real-space pair-distribution functions up to 15 GPa indicates an initial shrinkage of the tetrahedral units. Above this threshold pressure the Si-O bond peak shape becomes asymmetric and the average Si-O bond length and coordination number both increase linearly with pressure. Also, strained geometries in the O-O correlations lead a pronounced topological rearrangement of the second and third nearest neighbors.

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I. INTRODUCTION

Silica is the base component for a large part of the earth's mantle as well as most commercial glasses. At ambient pressure silica glass has an open three-dimensional network structure, comprising of corner-shared SiO_4 tetrahedra.[1] There are two topological transformations associated with SiO_2 glass at high pressure. The first is a compression of the tetrahedral network which has been investigated by many groups[2,3] and results in a permanent densification of the recovered glass with little change in the tetrahedral units. The second less studied transition is hysteretic but reversible, and characterized by the transformation from an amorphous tetrahedral framework to a dense amorphous octahedral network material at higher pressures. This transformation is believed to take place gradually somewhere over the pressure range from 10–40 GPa, but many of the structural details associated with the coordination change are still a matter of debate.[4–6] The compression mechanisms in this pressure range most likely play an important role in the structure of natural magmas in the earth's mantle region.[7] The tetrahedral crystalline phases of silica, i.e., cristobalite, tridymite, quartz, and coesite, are all known to undergo pressure-induced amorphorization at room temperature to what is presumed to be the high-density octahedral amorphous phase of silica.[8–10] Upon heating, the high-pressure amorphous phase devitrifies into the stishovite phase comprising of edge-shared SiO_6 octahedra.[10]

Experimental insights into the mechanisms behind the densification of silica glass were pioneered by Bridgman[11] in the 1950s. Later, Williams and Jeanloz[12] suggested a tetrahedral-to-octahedral silicon coordination change occurred in SiO_2 glass, starting around 17–25 GPa, based on infrared spectroscopy data. Hemley *et al.*[13] reported that the Raman spectrum of glassy SiO_2 between 8 and 30 GPa was consistent with a shift in ring statistics toward more three- and four-membered rings of tetrahedra. The first reported high-pressure structure factor of SiO_2 glass was measured using energy dispersive x-ray diffraction, suggesting that the Si-O bond distance shifts toward that observed in stishovite above 40 GPa.[14] This was confirmed recently by Sato and Funamori[4] at 50 GPa. Upon decompression the octahedra revert back to a densified tetrahedral form, underlining the importance of studying the transition *in situ*. In this study we have observed the tetrahedra shrink up to 15 GPa and above this threshold the Si-O coordination number increases linearly with pressure, concomitant with the onset of edge sharing. The network topology is also found to undergo changes, primarily in a narrow 5–7 Å region involving the second and third nearest neighbors.

II. EXPERIMENTAL

High-pressure x-ray diffraction experiments on SiO_2 glass were performed on beamline 1-ID at the Advanced Photon Source, Argonne National Laboratory, USA using a cylindrical diamond anvil cell (DAC) with perforated diamonds. The measurements used a focused high-energy x-ray beam of dimensions $20\times 20\ \mu m^2$ (Ref. 15) and an incident wavelength 0.1241 Å (100 keV). A cylindrical-type DAC was fitted with 300 μm culet diamonds and the anvil on the downstream side of the cell was perforated to reduce the Compton scattering signal from diamond.[16,17] The SiO_2 glass was packed together with a few pieces of ruby smaller than 1 μm in a 90 μm diameter, 20-μm-thick hole, electroeroded in a rhenium gasket by using an electric discharge machine (Hylozoic Products) without a pressure transmitting medium. The pressure was determined by using the ruby fluorescence technique. The scattered x-ray intensity was measured using a GE Revolution amorphous-Si area detector situated at a distance of 245 mm from the sample. The Q scale was calibrated using the diffraction pattern from crystalline CeO_2. The two-dimensional data were radially integrated using MATLAB and processed in the same software using the methods previously described.[16] Ten x-ray structure factors, $S(Q)$, were measured over a pressure range 1.5–43.5 GPa covering a momentum-transfer range from 0.6 to 16 Å^{-1}. We note that using the Bhatia-Thornton formalism[18] the x-ray $S(Q)$ for SiO_2 glass is dominated by the number-number structure factor which describes the topology of the glassy network.

III. RESULTS

The Faber-Ziman[19] x-ray structure factors measured up to 43.5 GPa in this study are presented in Fig. 1. The first sharp

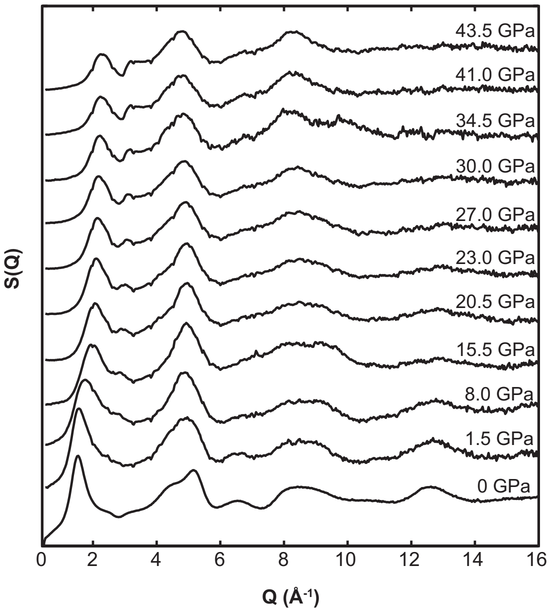

FIG. 1. X-ray structure factors $S(Q)$ measured during the compression of SiO_2 glass in a DAC over the pressure range from ambient to 43.5 GPa.

diffraction peak (FSDP) in our study shows a dramatic reduction in height and a linear shift toward larger momentum transfers up to pressures of ~15 GPa, in agreement with previous studies, see Fig. 2. The changes in the FSDP can be interpreted as a contraction of cages surrounding open regions of the glass network as the density is increased.[20] The appearance of a new peak on the high-Q side of the FSDP around 3 $Å^{-1}$ observed in our 15.5 GPa $S(Q)$ has previously been associated with the presence of SiO_6 octahedra.[14]

Density is an important parameter in interpreting x-ray diffraction data from amorphous materials and in developing realistic models. Recently, x-ray absorption methods were used to measure the density of silica glass to 50 GPa under static pressure at room temperature.[4,21] These density data are consistent with shock-wave measurements[22] and were subsequently used in the analysis of our x-ray data. The Fourier transformation of our Faber-Ziman[19] $S(Q)$ data gives the real-space pair-distribution function, $G(r)$, which directly quantifies the Si-O bond length and coordination changes with pressure. This operation was performed using a Lorch modification function.[23] The differential distribution function $D(r)=4\pi\rho r[G(r)-1]$ with the bulk density ρ removed, highlights the changes at higher r.[24] The average Si-O bond length was determined from the position of the maximum of the first physical peak in real space, between 1.6–1.7 Å in $D(r)$, and is shown in Fig. 3. At ambient pressure, the partial pair distribution functions [Ref. 1] show that the peak at ~2.6 Å corresponds to the O-O distance and the peak at ~3.1 Å corresponds to the Si-Si distance. The Si-O bond distance is plotted as a function of pressure in Fig. 4 and is in good agreement with previously reported measurements.[4,14] The data indicate a slight compression in the average Si-O distance up to 15 GPa followed by a linear increase with pressure up to 43.5 GPa. The same behavior is more pronounced in the second peak position in $D(r)$, which is dominated by the O-O correlations, indicating the tetrahedra shrink up to 15 GPa. A minimum in the second peak position in $D(r)$ occurs around 15 GPa above which the Si-O peak can no longer be approximated by a single Gaussian peak and tends toward the longer bond lengths in stishovite (although at 43.5 GPa the average Si-O bond length remains significantly shorter than the crystal). Upon decompression the average Si-O bond length at 27 GPa is longer than observed on compression, but it reverts back to a similar (tetrahedral) value by 14 GPa.

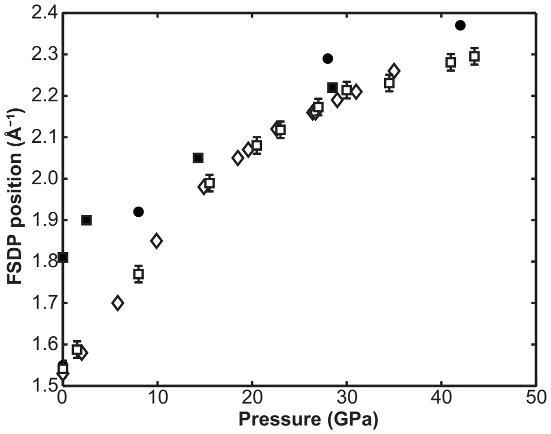

FIG. 2. The pressure dependence of the position of the FSDP. The squares are from DAC compression (open) and decompression (solid) in this study. The open diamonds are the data from Sato and Funamori (Ref. 21) the solid circles are the data from Meade *et al.* (Ref. 14).

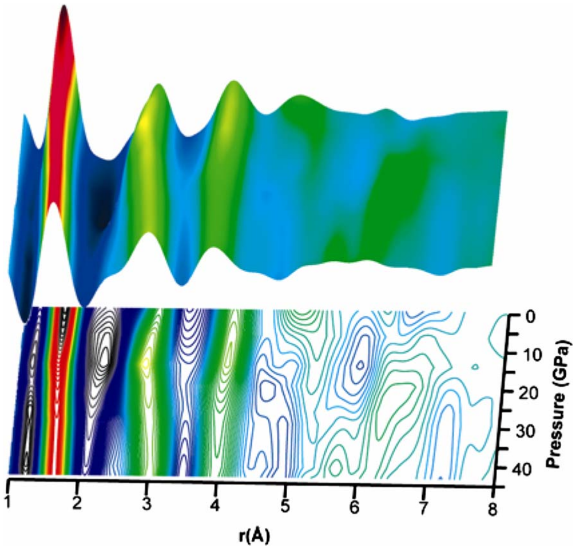

FIG. 3. (Color online) The x-ray differential distribution functions, $D(r)$ measured for glassy SiO_2 up to a pressure of 43.5 GPa.

IV. DISCUSSION

Early molecular-dynamics (MD) simulations by Stixrude and Bukowinski,[7] found that topological changes in tetrahedra up to 20 GPa occur via an increase in the characteristic

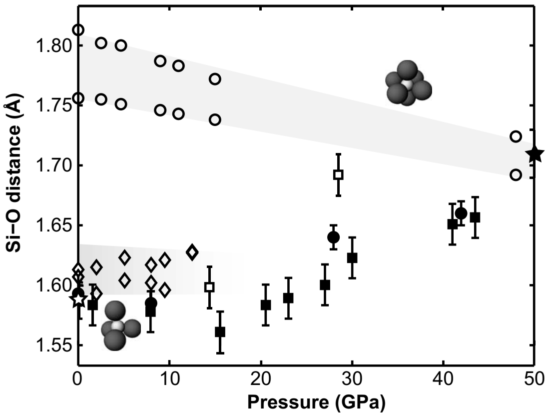

FIG. 4. The pressure dependence of the Si-O bond distance in SiO_2 glass upon compression (solid squares) and decompression (open squares) measured using high-energy x-ray diffraction. These data are compared to the Si-O bond distances published for quartz (open diamonds) and stishovite (open circles) as a function of pressure (Refs. 9 and 10). The two series of bond distances plotted for quartz and stishovite correspond to the shortest and longest Si-O bond distances within the structure. The solid circles represent the Si-O distances reported by Meade *et al.* (Ref. 14) for SiO_2 glass. Previous studies at ambient pressure (Ref. 1) (open star) and 50 GPa (Ref. 4) (solid star).

ring size with increasing density. Vashishta *et al.*[25] performed MD simulations including three-body covalent interactions on glassy SiO_2 up to 42.3 GPa at a density the same as crystalline stishovite, concluding that elastic compression cannot account for the observed shift in the FSDP and at high-pressure distorted octahedra share both edges and corners. MD simulations by Tse *et al.*[26] indicate that a coordination change in glassy SiO_2 occurs at pressures above 14–17 GPa, with the system gradually reaching a Si-O coordination number of ~6 by 30 GPa. The importance of obtaining high-accuracy data of the Si-O coordination number throughout the entire pressure range of the transition has recently been stressed.[5] The Si-O coordination numbers were calculated by fitting two-Gaussians in Q space, to account for the asymmetric peak at 15 GPa and above as illustrated in Fig. 5, and Fourier transforming at the same Q maximum as the data with the identical Lorch function. The error bars were estimated by evaluating the coordination number by direct integration up to the minimum after the Si-O peak. The x-ray results show an essentially linear increase in Si-O coordination number from 4 to 6 above a pressure of ~15 GPa (see Fig. 6). This change is similar to that predicted by using MD simulations[26] but shifted to higher pressure by ~10 GPa. The Si-O coordination number is also in agreement with the value of 5.8 predicted by MD at 42.3 GPa.[25]

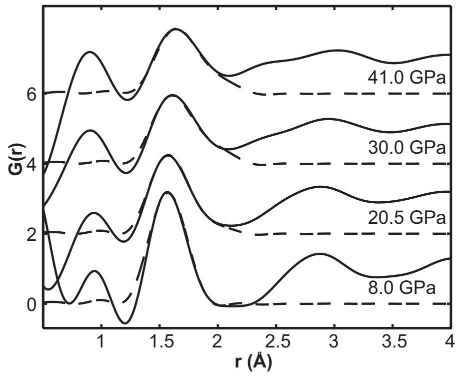

FIG. 5. Single and two Gaussian fits (dashed lines) to the pair-distribution function, $G(r)$, Fourier transformed at the same maximum Q value as the data (solid lines).

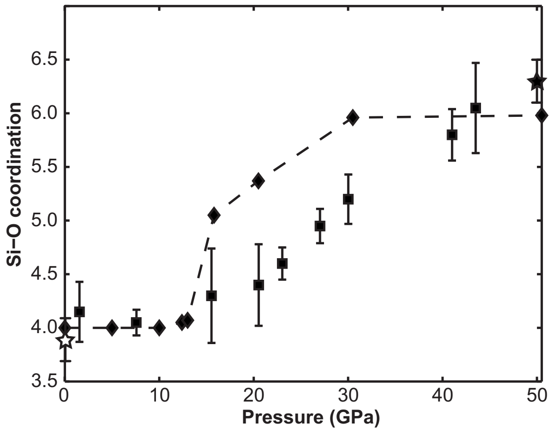

FIG. 6. Comparison of the Si-O coordination number pressure dependence obtained from this study upon compression (solid squares) and those calculated by Tse *et al.* (Ref. 26) from a molecular-dynamics simulation (solid diamonds). Previous studies at ambient pressure (Ref. 1) (open star) and 50 GPa (Ref. 4) (solid star) are also shown.

Glassy GeO_2 is often used as an analog for high-pressure studies on SiO_2 since the full transformation occurs at lower pressures. High-pressure measurements have previously been performed on the glassy GeO_2 by Guthrie *et al.*[27] using x-ray diffraction. Below 5 GPa additional atoms approaching the first coordination shell were observed prior to the coordination change and between 6–10 GPa an average coordination number of ~5 was obtained and interpreted as a mixture of distorted fourfold, fivefold, and sixfold polyhedra on the basis of molecular-dynamics simulations.[27] At 15 GPa GeO_2 glass was found to be fully octahedral. A similar trend has been observed from accurate high-pressure neutron-diffraction measurements on glassy GeO_2 up to 8.6 GPa,[28] although the coordination number increase was found to be not as sharp and qualitatively similar to the results found in this study.

The $D(r)$ curves in Fig. 3 show the compression of the tetrahedral structure at low pressures (<15 GPa) is associated with a shortening of the second peak at 3 Å and considerable rearrangements in the second and third nearest-neighbor region. The peak at ~5 Å, which has large contributions from the second nearest-neighbor O-O and Si-Si interactions, decreases in intensity with pressure, in qualitative agreement with the simulations of Tse *et al.*[26] A comparison of the experimental data with the predicted pair-distribution functions for SiO_2 glass at 42.3 GPa from MD simulations by Vashishta *et al.*[25] in the octahedral form show that the shoulder at 2.5 Å above 23 GPa is due to O-O interactions, indicating that neighboring polyhedra participate in edge sharing. An outward shift of the second peak in $D(r)$ from 2.93 to 3.04 Å may be due to a combination of the growth of the second Si-O peak and a splitting of the first Si-Si peak at high pressure. It is also consistent with an increase in the nearest-neighbor Si-Si intensity, due to a higher population of three-membered rings, which have been identified in compressed SiO_2 glass using Raman spectroscopy.[13]

The predicted increase in ring size at pressures around 20 GPa (Refs. 2 and 7) and observed increase in two-, three-, and four-membered rings at higher pressures,[13] suggests there is a dramatic change in glass topology. As the average Si-O coordination number increases, large rearrangements are observed in the x-ray pair-distribution function in the 5–7 Å region, which are associated with polyhedral connectivity. In the dense tetrahedral network, there is a maximum in intensity in $D(r)$ between 6–7 Å at 20 GPa, which persists at higher pressures. An increase in intensity occurs around 5.8 Å above 23 GPa, forming a broad peak which is most likely due to changes in the oxygen interactions based on comparison with MD simulations.[25] However, the experimental 43.5 GPa data show a considerably broader first O-O peak than simulations,[25] indicating that the octahedra are more heavily distorted. We note that in crystalline stishovite two-, three-, and four-membered rings dominate. In Fig. 7 we show a possible configuration in the distorted octahedral glass comprising of two- and three-membered rings. The longest O-O distances in this cluster lie in the 5–7 Å region. The strained local geometries and topological changes observed experimentally are in agreement with *ab initio* MD simulations on liquid silica, which predict an increase in network connectivity caused by coordination defects and formation of SiO_5.[29] It is anticipated that these x-ray results will provide a testbed for the idea that densification of glassy SiO_2 may be related to the appearance of both smaller and larger rings at high pressure.[2,30]

For glassy SiO_2 we observe a linear change in the position of the FSDP with pressure up to ~15 GPa followed by a gradual curvature (Fig. 2), implying a continuous change in intermediate-range order is associated with the changes in topology and Si-O coordination number. This agrees with the high-pressure and high-temperature measurements of the FSDP in SiO_2 glass.[31] It has been suggested that the densification of SiO_2 glass is similar to that of α quartz based on changes in the large distribution of intertetrahedral angles.[26] Since in the amorphous state the transition to sixfold Si-O coordination is much more gradual than in the crystal, the disordered packing of the SiO_4 polyhedra appears to inhibit the formation of an ordered edge-shared structure. This results in a heavily distorted octahedral high-pressure glass through which densification also occurs through changes in polyhedral connectivity.

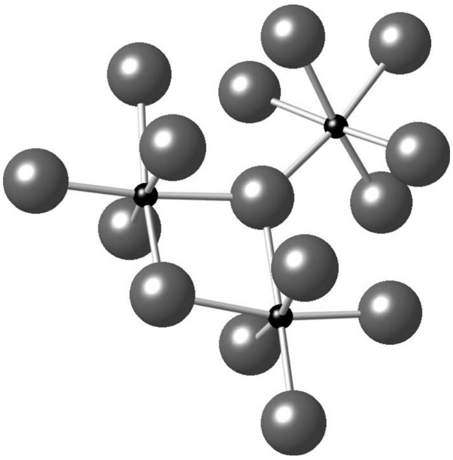

FIG. 7. A possible configuration for two- and three-membered rings in the high-pressure octahedral SiO_2 glass. A significant population of four-membered rings are also expected (Ref. 13). The small black spheres represent silicon atoms and the large gray spheres represent oxygen atoms.

V. CONCLUSIONS

Accurate x-ray structure factors of SiO_2 have been measured from ambient pressure to 43.5 GPa using a perforated diamond anvil cell. The data are in good agreement with previous measurements at either extreme of our experimental pressure range. Our data show that the SiO_4 tetrahedra shrink slightly upon compression up to ~15 GPa, and above 15 GPa the average Si-O bond length and coordination number increases linearly with pressure, eventually forming a distorted octahedral glass. At longer distances significant rearrangements in polyhedral connectivity are observed, primarily in the 5–7 Å region, which are attributed to the formation of two-, three-, and four-membered rings.

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