Sixfold-Coordinated Amorphous Polymorph of SiO_2 under High Pressure

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We have developed synchrotron x-ray absorption and diffraction techniques for measuring the density and structure of noncrystalline materials at high pressures and have applied them to studying the behavior of SiO_2 glass. The density, coordination number, and Si-O bond length at a pressure of 50 GPa were measured to be 4.63 g/cm^3, 6.3, and 1.71 Å, respectively. Based on the density data measured in this study and the sound velocity data available in the literature, the bulk modulus at 50 GPa was estimated to be 390 GPa, which is consistent with the pressure dependence of the density in the vicinity of 50 GPa. These results, together with the knowledge from our exploratory study, suggest that SiO_2 glass behaves as a single amorphous polymorph having a sixfold-coordinated structure at pressures above 40–45 GPa up to at least 100 GPa.

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Pressure-induced change in the structure and properties of noncrystalline materials, such as liquids and glasses, is an important and challenging issue in condensed-matter physics. In particular, the behavior of SiO_2 glass has attracted considerable attention because of its importance not only in high-pressure physics but also in geophysics and materials science [1]. Numerous theoretical and experimental studies have revealed that SiO_2 glass shows anomalous behavior such as elastic softening with increasing pressure up to 2–3 GPa [2–7] and permanent densification by applying a pressure more than 10 GPa [4–6,8,9]. Molecular dynamics simulations have suggested the occurrence of a structural transformation accompanied by the increase in coordination number, i.e., the number of oxygen atoms around a silicon atom, from four to six at higher pressures [10]. However, the results obtained by different experimental techniques are controversial. X-ray diffraction measurements suggested that the coordination number remains four at least up to 20 GPa [9] and then increases from four to six at higher pressures [11]. The results of Raman scattering [12] and infrared absorption [13] are consistent with those of x-ray diffraction. However, x-ray Raman scattering (O *K*-edge) suggested that the change in the coordination number occurs between 10 and 20 GPa [14]. Brillouin scattering showed a drastic increase in sound velocities over the similar range of pressure [6]. On the other hand, x-ray Raman scattering (Si *L*-edge) suggested that the change to six does not occur even at 70 GPa [15].

The most serious problem in understanding the transformation from a fourfold- to a sixfold-coordinated structure may be the lack of density data under high pressure. The pressure dependence of density is one of the most fundamental and important pieces of information in high-pressure physics. However, density measurements of SiO_2 glass were limited to pressures up to about 10 GPa because of experimental difficulties [2,5,7,16]. Our exploratory x-ray diffraction measurements have suggested that SiO_2 glass may behave as a single amorphous polymorph, i.e., which shows elastic behavior with change in pressure, at least between 50 and 100 GPa [17]. Therefore, we have developed new experimental techniques and have measured the density of SiO_2 glass as a function of pressure up to above 50 GPa, where the amorphous polymorph is expected to appear. We have also measured the x-ray structure factor (and pair distribution function) of SiO_2 glass at 50 GPa. In this Letter, we report on the results of density and structure measurements of SiO_2 glass, and discuss the structure and properties of the amorphous polymorph and the transformation from a fourfold- to a sixfold-coordinated structure.

All experiments were conducted with a diamond-anvil cell at room temperature without a pressure transmitting medium. Density measurements were carried out for the sample compressed together with two reference materials

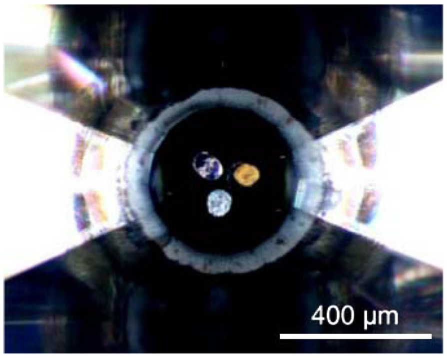

FIG. 1 (color online). An optical-microscope image taken at 50 GPa through the diamond anvil with both dark-field and transmitted illuminations in run 3 of density measurements. The sample, SiO_2 glass (upper right), and the two reference materials, beryllium (lower) and aluminum (upper left), were compressed together in the *c*-BN gasket.

with a known density by using an x-ray absorption method with monochromatic x rays at BL-18C of Photon Factory (Tsukuba, Japan). The density of the sample was determined from the intensities of transmitted x rays measured for the sample and the reference materials by assuming that the thicknesses of the three materials were the same. Three independent runs were carried out with x rays at 10 keV. In runs 1 and 2, because a conventional rhenium gasket was used, the thickness of the sample became too thin to accurately determine the density at pressures above 35 GPa. In order to overcome this problem, in run 3, a cubic boron nitride (*c*-BN) gasket was used and the density was successfully determined at pressures up to above 50 GPa. A photograph taken at 50 GPa in run 3, in which anvils having a 400 μm culet were used, is shown in Fig. 1 [18]. A 25 μm collimator was used to reduce the size of the incident x-ray beam in this run. The technical details of the density measurement (including the experimental settings of runs 1 and 2) and the *c*-BN gasket have been reported elsewhere [17,19]. Structure measurements were carried out by using an x-ray diffraction method with white x rays at BL-14C2 of Photon Factory. The x-ray structure factor $S(Q)$ and pair distribution function $g(r)$ were measured at 50 GPa as discussed above, with anvils having a 350 μm culet and the *c*-BN gasket. The sample geometry was the same as that for typical experiments with the *c*-BN gasket [17]. The method used in this study was basically the same as that with a multianvil press [20,21], but some modifications were made for a tiny sample in a diamond-anvil cell as follows. (i) The incident x-ray beam was well collimated by tungsten carbide of 10 mm thickness having a hole of 30 μm diameter [22], which was placed at a distance of 20 mm from the sample, and then irradiated the sample. (ii) The profiles of x rays scattered by the anvils (e.g., Compton and Laue scatterings) were measured for corrections. In this study, $S(Q)$ was obtained by combining x-ray diffraction profiles collected at diffraction angles $2\theta = 5 \sim 28°$ with x rays at $20 \sim 60$ keV [23]. $g(r)$ is related with $S(Q)$ via Fourier transform as

$$g(r) = 1 + \frac{1}{2\pi^2 rn} \int_0^\infty Q\{S(Q) - 1\} \sin(Qr) dQ, \qquad (1)$$

where n is the average number density. Pressure was determined by the Raman shift of the diamond anvil [24] (or the position of the first sharp diffraction peak, i.e., FSDP, of the sample below 25 GPa in runs 1 and 2 of density measurements [19]).

The results of density measurements are shown in Fig. 2. The density of SiO_2 glass increased greatly and almost linearly from 10 to 40 GPa, and then relatively slightly above 40 GPa. No discontinuous changes like the first-order transition in crystalline materials were observed. The density of SiO_2 glass exceeded those of the fourfold-coordinated crystalline polymorphs of SiO_2, quartz and coesite, at around 20 GPa. This seems to be consistent with the findings of previous studies that these crystalline polymorphs amorphize above 20–25 GPa [25]. The bulk modulus can be estimated based on the relation $K = \rho V_B{}^2$, by using the density measured in this study and the bulk sound velocity measured by Brillouin scattering [6]. Here, K, ρ, and V_B are the bulk modulus, density, and bulk sound velocity, respectively. The great increase in density between 10 and 40 GPa cannot be explained by the estimated bulk modulus. This suggests that SiO_2 glass does not behave as a single amorphous polymorph, but its structure irreversibly changes with increasing pressure between 10 and 40 GPa. On the other hand, the estimated bulk modulus is consistent with the pressure dependence of the density, suggesting that SiO_2 glass behaves as a single amorphous polymorph above about 40 GPa. The bulk modulus below 10 GPa has also been reported to be consistent with the increase in density [6]. The zero-pressure parameters for the amorphous polymorph were determined to be $\rho_0 = 3.88$ g/cm^3, $K_0 = 190$ GPa, and $K_0' = 4.5$ (fixed) by fitting the third-order Birch-Murnaghan equation of state [26] to the density data with the constraint from bulk sound velocity data [27]. Here, K' is the pressure derivative of bulk modulus. A small difference between the isothermal and adiabatic moduli was ignored in this study. The parameters were determined to be $\rho_0 = 3.93$ g/cm^3 and $K_0 = 241$ GPa by assuming $K_0' = 3$, and $\rho_0 = 3.84$ g/cm^3 and $K_0 = 153$ GPa by assuming $K_0' = 6$. In all three cases, the density and bulk modulus at 50 GPa are 4.63 g/cm^3 and 390 GPa, respectively. These three equations of state are identical within the uncertainties of density measurements at pressures all the way to at least

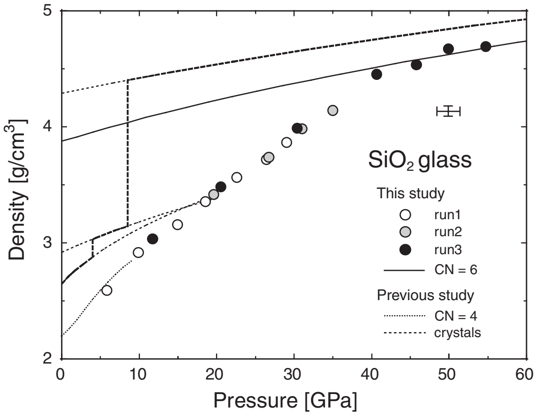

FIG. 2. Pressure dependence of the density of SiO_2 glass. Uncertainties have been estimated as indicated by the error bar [19]. The solid line represents the equation of state for the sixfold-coordinated amorphous polymorph of SiO_2 ($\rho_0 = 3.88$ g/cm^3, $K_0 = 190$ GPa, $K_0' = 4.5$) which was determined by using the densities in this study and the sound velocities in the literature [6]. The thick broken line represents the pressure dependence of the density of thermodynamically stable crystalline polymorphs of SiO_2 (i.e., quartz [34] transforms to coesite [35] and then to stishovite [28] with increasing pressure).

100 GPa. As shown in Fig. 2, the equation of state for this amorphous polymorph is almost parallel to that for the sixfold-coordinated crystalline polymorph, stishovite ($\rho_0 = 4.29\ \mathrm{g/cm^3}$, $K_0 = 310$ GPa, and $K_0' = 4.6$ [28]), suggesting that the density of SiO_2 glass does not exceed that of crystalline polymorphs even at 100 GPa. It is worth pointing out that the density of GeO_2 glass may exceed that of the crystalline polymorph of GeO_2 under high pressure [29].

$S(Q)$ and $g(r)$ at 50 GPa are shown in Fig. 3. n in Eq. (1) was determined to be 0.139 Å^{-3} directly from the density, i.e., 4.63 $\mathrm{g/cm^3}$, measured in this study. As to the FSDP of $S(Q)$, the position significantly shifted to a higher Q and the intensity significantly decreased by applying a pressure of 50 GPa. The second peak (at around 4.8 Å^{-1}) slightly shifted to a lower Q and became much higher than the FSDP. Moreover, a new peak appeared at around 3.3 Å^{-1}. These features are consistent with the previous study up to about 40 GPa [11]. The position of the FSDP at 50 GPa was determined to be 2.39 Å^{-1} in this study. On the other hand, it was 2.34 Å^{-1} in our exploratory x-ray diffraction study [17]. This small difference may be a systematic error since the experimental settings, including analytical procedures, of the two studies were quite different. Otherwise, the irradiation of white x rays may have affected the kinetics and/or stress state of the sample. While no changes in pressure were observed before and after the irradiation of monochromatic x rays (in both density measurements and exploratory x-ray diffraction measurements), the pressure decreased from 52 to 49 GPa in this measurement. The position and area of a peak in $g(r)$ provide the information of the interatomic distance and coordination number. The first peak of $g(r)$ corresponds to the Si-O pair [11,21,30]. The Si-O bond length and the coordination number were determined to be 1.71 Å [31] and 6.3, respectively, with a root mean square displacement of 0.13 Å, by using a pair-function method [30]. The Si-O bond length of stishovite is estimated to be 1.71 Å at 50 GPa [32] and is coincident with that of the glass. Similarly, for stishovite at 50 GPa, the mode of the O-O distances (distribution) is estimated to be 2.4 Å, and those of the Si-Si and the second-neighbor Si-O distances are both estimated to be 3.1 Å. They are in good agreement with the positions of the second and the third peak. As shown in Fig. 3, $S(Q)$ at $Q > 10\ \text{Å}^{-1}$ was not precisely determined since the intensity of coherent scattering decreases and that of incoherent scattering increases with Q. Nevertheless, the errors in the Si-O bond length and the coordination number due to this source are estimated to be ±0.02 Å and ±0.2, respectively. Errors due to density measurements are smaller. Therefore, it is concluded that SiO_2 glass has a sixfold-coordinated stishovite-like local structure at 50 GPa.

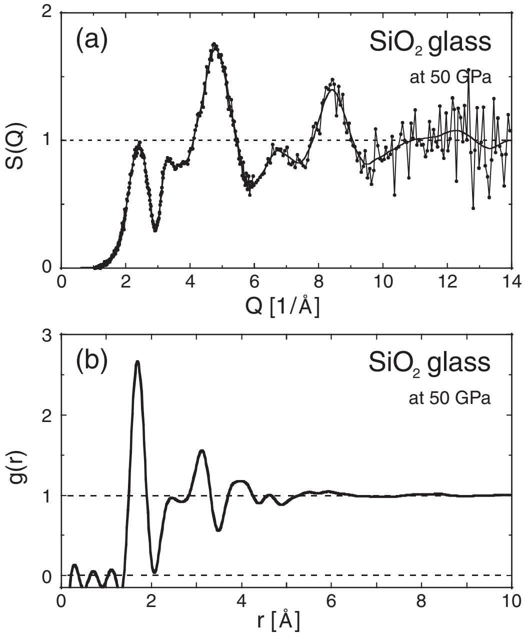

FIG. 3. (a) Structure factor and (b) pair distribution function of SiO_2 glass at 50 GPa.

The experimental results of this study, together with those of exploratory x-ray diffraction study up to 100 GPa [17], and considering the uncertainties of both studies, suggest that SiO_2 glass behaves as a single amorphous polymorph having a sixfold-coordinated stishovite-like local structure at pressures above 40–45 GPa up to at least 100 GPa. As discussed in the first paragraph, x-ray Raman scattering (Si L-edge) suggested that the coordination number does not become six even at 70 GPa [15]. However, this interpretation is based solely on the comparison of spectra between SiO_2 glass under high pressure and stishovite at ambient pressure, and therefore other possibilities cannot be ruled out. The results of our density measurements are also important to understand the behavior of SiO_2 glass at pressures between 10 and 40–45 GPa. X-ray Raman scattering (O K-edge) suggested that the change in the coordination number occurs between 10 and 20 GPa [14]. Brillouin scattering showed a drastic increase in sound velocities over the similar range of pressure [6]. The change in the coordination number, however, is unlikely to occur between 10 and 20 GPa since the density of SiO_2 glass is smaller than those of the fourfold-coordinated crystalline polymorphs below 20 GPa. The anomalies observed by x-ray Raman scattering (O K-edge) and Brillouin scattering may be attributed to irreversible changes in the intermediate-range order. On the other hand, our results support the proposal that the yield strength of SiO_2 glass decreases at around 25 GPa due to the transformation from a fourfold- to a sixfold-coordinated structure [33]. The yield strength would be underestimated if the relaxation of stresses could occur in the sample due to a sudden decrease in volume (as in the case of the first-order transition of crystalline materials). This possibility can be eliminated since no discontinuous increase in density was observed in SiO_2 glass at around 25 GPa.

In summary, the behavior of SiO_2 glass under high pressure can be described as follows. (i) SiO_2 glass behaves as a single amorphous polymorph having a fourfold-coordinated structure below 10 GPa. (ii) Irreversible changes in the intermediate-range order begin at around 10 GPa. (iii) Irreversible changes in the short-range order begin at around 25 GPa and the coordination number continuously increases from four to six with increasing pressure. (iv) The changes in the short-range order end at 40–45 GPa, and SiO_2 glass behaves as a single amorphous polymorph having a sixfold-coordinated structure at higher pressures at least up to 100 GPa.

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