



High-pressure structural transformation of SiO₂ glass up to 100 GPa

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We have conducted structure measurements of SiO₂ glass under high pressure up to 100 GPa by an energy-dispersive x-ray diffraction method with synchrotron white x rays. X-ray diffraction data indicate that SiO₂ glass transforms from a fourfold- to a sixfold-coordinated structure at pressures between 20 and 35 GPa, and then behaves as an amorphous polymorph having a sixfold-coordinated structure at least up to 100 GPa. These results are consistent with those of density measurements by an x-ray absorption method with monochromatic x rays, except for the slight difference in the pressure range where the transformation from a fourfold- to a sixfold-coordinated structure is completed. They are also mostly consistent with those of structure measurements by an x-ray diffraction method with monochromatic x rays but some aspects are quantitatively different. It is presumed that the irradiation of white x rays may have relaxed the structure and deviatoric stresses of SiO₂ glass in this study.

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I. INTRODUCTION

Pressure-induced change in the structure and properties of noncrystalline materials, such as liquids and glasses, is an important issue in condensed-matter physics. In particular, the behavior of SiO₂ glass has attracted considerable attention because of its importance not only in high-pressure physics but also in geophysics and materials science. Numerous theoretical and experimental studies have revealed its anomalous behavior since the pioneering study by Bridgman¹ in the middle of the 20th century. By analogy with its crystalline equivalents, the structural transformation of SiO₂ glass in the short-range order, i.e., the change in the coordination number from 4 to 6, is expected to occur under high pressure. Details of this structural transformation have been revealed gradually. By comprehensively considering the results of Raman scattering,² infrared absorption,³ density measurement,^{4,5} and x-ray diffraction,⁵⁻⁷ it is suggested that the transformation from a fourfold- to a sixfold-coordinated structure may occur at pressures between 20 and 40–45 GPa. This suggestion is in fairly good agreement with predictions of molecular-dynamics simulations conducted by using different types of interatomic potentials, based on *ab initio* calculations,⁸ experimental data,^{9,10} and a combination of both.^{11,12} It is also in good agreement with the result of x-ray diffraction measurements up to above 40 GPa, which have most recently been reported.¹³

However, some problems such as effects of transformation kinetics still remain unclear.^{7,14-16} Moreover, only a few studies have been conducted at pressures above 50 GPa. Our exploratory x-ray diffraction measurements up to 100 GPa have suggested that the pressure dependence of the position of the first sharp diffraction peak (FSDP) shows no evidence for another structural transformation.¹⁷ Most recently, sound-velocity measurements up to 200 GPa have suggested that a sixfold-coordinated structure may eventually transform to a higher-coordinated structure at above 140 GPa.¹⁸ However, these measurements are not sufficient to discuss the structure of SiO₂ glass. We have succeeded in measuring the structure factor of SiO₂ glass up to 100 GPa by using recently devel-

oped experimental techniques.^{5,19} In this paper, we discuss the structural transformation of SiO₂ glass up to 100 GPa in detail, including effects of transformation kinetics.

II. EXPERIMENT

All experiments were conducted with a diamond-anvil cell at room temperature without a pressure transmitting medium. X-ray diffraction measurements were carried out by using the energy-dispersive method with slits and solid-state detector systems at the vertical-wiggler beamline BL-14C2 of Photon Factory (Tsukuba, Japan). Measurements were conducted at seven different pressures up to 100 GPa. Anvils having a 350 and 250 μm flat culet were used in measurements at lower five pressures and higher two pressures, respectively. A cubic boron nitride gasket¹⁷ was used to increase the sample thickness for improving the data quality. Pressure was determined by the Raman shift of the diamond anvil.²⁰ The data at 74 GPa were obtained during decompression and all the other data were obtained during compression. Scattered x rays were collected at diffraction angles $2\theta=5^\circ-28^\circ$ ($E=20-60$ keV) at lower five pressures and $2\theta=5^\circ-25^\circ$ ($E=20-67$ keV) at higher two pressures. An entrance collimator with a hole of 30 μm in diameter was used for all measurements. Structure factor $S(Q)$ was determined by combining all the data collected at several diffraction angles. Pair distribution function $g(r)$ is related to $S(Q)$ via the Fourier transform. As discussed in our previous study,¹⁹ a correction procedure with a termination function $M(Q)=1/[1+\exp\{(Q-Q_F)/a\}]$, where $Q_F=10 \text{ \AA}^{-1}$ and $a=1 \text{ \AA}^{-1}$, was used to obtain reliable sets of $S(Q)$ and $g(r)$. The number density, which appears in the relation between $S(Q)$ and $g(r)$, was estimated based on the results of density measurements by an x-ray absorption method.^{4,5} The number density at 35 GPa was estimated based on the equation of state for a sixfold-coordinated amorphous polymorph, and the reason for which will be discussed later (cf. the transformation to a sixfold-coordinated structure was completed at 40–45 GPa in density measurements⁵). The data at 51 GPa

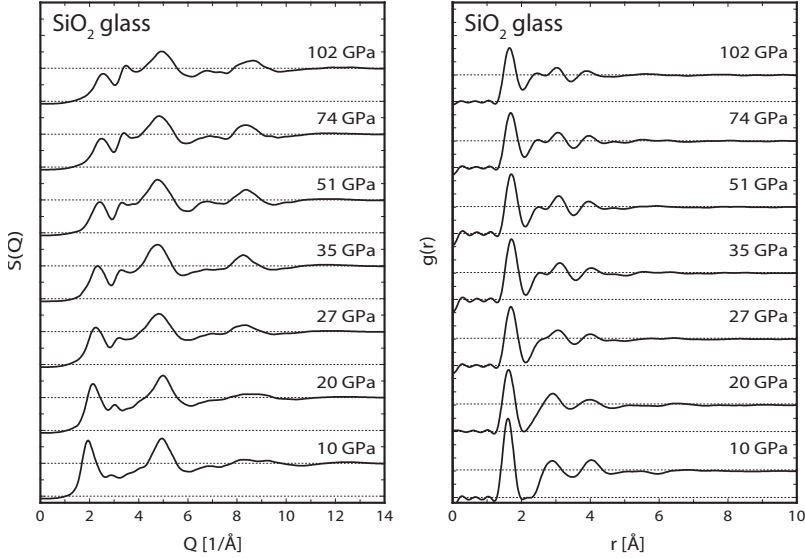


FIG. 1. Pressure dependence of $S(Q)$ and $g(r)$ of SiO_2 glass.

were the same as those reported in our previous study⁵ but they were reanalyzed with an improved method. Technical details for pressure generation¹⁷ and experimental and analytical methods of x-ray diffraction measurements¹⁹ are described elsewhere.

III. RESULTS AND DISCUSSION

A. $S(Q)$ and $g(r)$ up to 100 GPa

$S(Q)$ and $g(r)$ of SiO_2 glass measured up to 100 GPa are shown in Fig. 1. Experimental results, including the information on the first peaks of $S(Q)$ and $g(r)$, i.e., the FSDP and the Si-O bond, are summarized in Table I. As clearly shown

in Fig. 1, shapes of $S(Q)$ and $g(r)$ are significantly different below and above 27 GPa. $S(Q)$ and $g(r)$ at 27 GPa show intermediate features between those at 20 and 35 GPa. Above 35 GPa, $S(Q)$ and $g(r)$ show no significant changes, suggesting that no major structural transformations occur at this pressure range. As to the FSDP, its intensity decreases and its position shifts to a higher Q significantly with increasing pressure up to 35 GPa, and these changes become small at pressures above 35 GPa. A new peak, which is not observed at ambient pressure, appears at around $Q \sim 3 \text{ \AA}^{-1}$ and it becomes prominent above 35 GPa. The peak at around $Q \sim 9 \text{ \AA}^{-1}$ also becomes prominent above 35 GPa. The second peak shifts to a lower Q slightly with in-

TABLE I. Summary of experimental results.

Pressure ^a (GPa)	FSDP ($1/\text{\AA}$)	r_{SiO} ^b (\AA)	CN_{SiO} ^b	σ_{SiO} ^b (\AA)	n ^c ($1/\text{\AA}^3$)	Run ^d
10.2 (10.6 → 9.8)	1.94	1.62	4.1	0.135	0.088	5
20.0 (20.5 → 19.5)	2.14	1.64	4.3	0.152	0.104	4-1
26.9 (27.6 → 26.1)	2.26	1.71	5.0	0.155	0.113	4-2
35.2 (36.2 → 34.1)	2.33	1.73	6.1	0.152	0.134	3
50.6 (52.2 → 49.0)	2.40 ^{e,f}	1.72 ^c	6.1 ^c	0.152 ^c	0.139	1
73.8 (75.5 → 72.1)	2.49	1.71	6.1	0.158	0.147	2-2
101.5 (103.3 → 99.6)	2.56 ^f	1.67	6.0	0.158	0.154	2-1

^aPressures measured before and after x-ray diffraction measurements are shown in parentheses.

^bFor Si-O bond, the interatomic distance r_{SiO} , coordination number CN_{SiO} , and root-mean-square displacement σ_{SiO} were estimated by using a pair-function method with uncertainties of about $\pm 0.02 \text{ \AA}$, ± 0.4 , and $\pm 0.1 \text{ \AA}$, respectively (Ref. 19).

^cNumber densities were estimated based on density measurements by an x-ray absorption method (Ref. 5).

^dFive independent runs were conducted. In runs 2 and 4, x-ray diffraction measurements were carried out at two different pressures in numerical order.

^eThe same x-ray diffraction data reported in a previous paper (Ref. 5) have been reanalyzed by using a modified procedure (Ref. 19). The position of FSDP, r_{SiO} , CN_{SiO} , and σ_{SiO} were reported to be 2.39 \AA^{-1} , 1.71 \AA , 6.3 , and 0.13 \AA , respectively, in the previous paper.

^fAfter energy-dispersive x-ray diffraction measurements, angle-dispersive x-ray diffraction measurements were carried out and the positions of FSDP at 49 and 100 GPa were measured to be 2.39 and 2.52 \AA^{-1} , respectively.

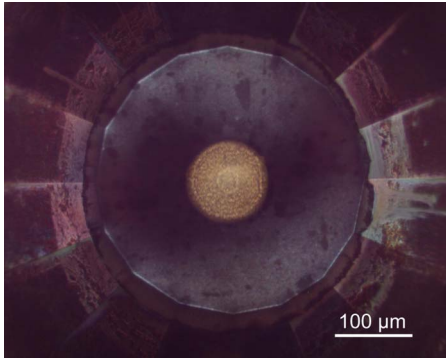


FIG. 2. (Color online) An optical-microscope image of the sample taken with both bright-field and transmitted illuminations after x-ray diffraction measurements in run 5. The culet of the anvil was 350 μm in diameter. The cubic boron nitride gasket was used. Optically distinct area of about 30 μm in diameter, which is the same size as the x-ray beam, can be seen at the center of the sample. This contrast became significant upon decompression. The image was taken at 5 GPa during decompression.

creasing pressure below 35 GPa. The first peak of $g(r)$ shifts to a higher r significantly with increasing pressure between 20 and 35 GPa. A new peak appears inside the second peak above 35 GPa. All these features are qualitatively consistent with previous x-ray diffraction studies.^{6,7,13}

B. Structure and stress relaxations

It is highly possible that the irradiation of white x rays had relaxed the structure and stress of the sample in this study. Decrease in pressure was observed before and after the x-ray diffraction measurements. After the measurements, the boundary of the area irradiated by white x rays was clearly observed by using an optical microscope (Fig. 2). These phenomena were not observed before and after the irradiation of monochromatic x rays (in both density and x-ray diffraction measurements). Density measurements with monochromatic x rays have suggested that the transformation to a sixfold-coordinated structure is completed at 40–45 GPa. This is not consistent with the fact that no significant changes in $S(Q)$ and $g(r)$ were observed above 35 GPa (Fig. 1). This inconsistency may be explained by assuming that white x rays had relaxed the structure of the sample. It was reported that the pressure interval of the structural transformation of SiO_2 glass was narrowed (i.e., the high-pressure phase was synthesized at a lower pressure) by annealing the sample in the case of the structural transformation in the intermediate-range order, which are observed at a low-pressure range and related to the permanent densification.^{7,14,15} The effect of irradiating with white x rays may be similar to that of annealing in the case of SiO_2 glass.

The pressure dependence of the position of the FSDP, which is mainly related to the intermediate-range order,^{21–23} is shown in Fig. 3. The positions and shapes of the peaks in $S(Q)$, not only the FSDP but also a new peak and the second peak, are in excellent agreement with those by Meade *et al.*⁶ [i.e., $S(Q)$'s agree very well with each other]. In both this study and Meade *et al.*,⁶ measurements were conducted with

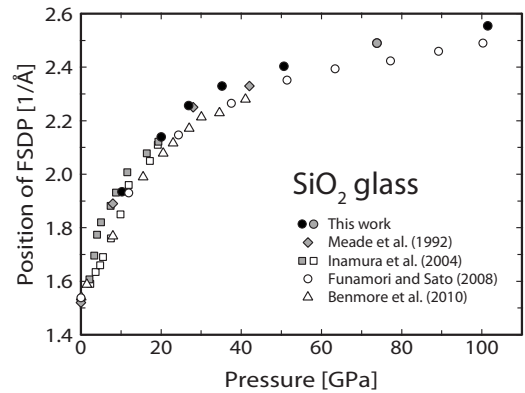


FIG. 3. Pressure dependence of the position of the FSDP of SiO_2 glass. Black and gray data of this work were measured during compression and during decompression, respectively. Gray and white data of Inamura *et al.* (Ref. 7) were measured at high temperature, where the shift of the FSDP finished, and at room temperature, respectively. The other data were measured during compression at room temperature.

a combination of a diamond-anvil cell and white x rays, therefore the effect of the irradiation of white x rays is expected to be similar. Our $S(Q)$ is also in good agreement with that reported by Inamura *et al.*⁷ obtained with a combination of a large-volume press and white x rays. However, the shape of our FSDP is in better agreement with that of their FSDP at high temperature (where the structure and stress of the sample have been relaxed) than that at room temperature. In large-volume press experiments, most of low-energy x rays are thought to be absorbed by the pressure mediums and not to reach the sample, and therefore the structural relaxation of the sample may not occur sufficiently by the irradiation of white x rays.

On the other hand, the positions of the peaks in our $S(Q)$ are obviously different from those reported by Benmore *et al.*¹³ with a combination of a perforated diamond-anvil cell and high-energy monochromatic x rays. The results by Benmore *et al.*¹³ are in good agreement with the pressure dependence of the position of the FSDP determined by our exploratory x-ray diffraction measurements with monochromatic x rays.¹⁷ However, the difference in the x-ray diffraction methods (i.e., angle-dispersive versus energy-dispersive) does not so much affect the result [e.g., see Funamori *et al.*²⁴ to compare $S(Q)$'s of SiO_2 glass measured with an angle-dispersive method by Waseda and Toguri²⁵ and an energy-dispersive method by Funamori *et al.*;²⁴ also see caption f of Table I]. Therefore, this discrepancy should be ascribed to differences in the state of the sample. In x-ray diffraction measurements of crystalline samples, deviatoric stresses such as a uniaxial stress significantly affect the positions and shapes of diffraction peaks.^{26,27} It is expected that $S(Q)$ is also affected by deviatoric stresses in x-ray diffraction measurements of non-crystalline solids. Assuming that the effect of the irradiation of white x rays is similar to that of annealing, it is highly possible that the irradiation of white x rays had relaxed not only the structure but also the stress of the sample.

C. Si-O bond length and coordination number

The pressure dependence of the Si-O bond length and the coordination number is shown in Figs. 4 and 5. These two

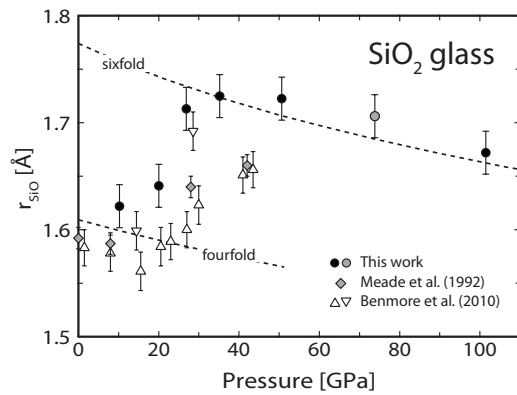


FIG. 4. Pressure dependence of r_{SiO} of SiO_2 glass. Symbols are the same as in Fig. 3. Inverted-triangle data of Benmore *et al.* (Ref. 13) were measured during decompression. Estimated bond lengths of fourfold- and sixfold-coordinated crystalline phases are shown as dotted lines for comparison (see Ref. 16).

figures strongly suggest that the coordination number of SiO_2 glass increases from 4 to 6 at pressures between 20 and 35 GPa, and remains 6 up to at least 100 GPa. As described in the previous section, density measurements with monochromatic x rays suggest that the structural transformation in the short-range order ends at 40–45 GPa.⁵ In this study, however, it is suggested that SiO_2 glass has already transformed to a sixfold-coordinated structure at 35 GPa because of the structural relaxation caused by the irradiation of white x rays. Therefore, the data at 35 GPa were analyzed with the number density estimated based on the equation of state for the sixfold-coordinated amorphous polymorph.

The pressure dependence of the Si-O bond length does not agree very well with that of previous studies (Fig. 4). As described above, $S(Q)$ of this study is in excellent agreement with that of Meade *et al.*⁶ In Meade *et al.*,⁶ however, $S(Q)$ was shown only at $Q < 6 \text{ \AA}^{-1}$ and the detail of the analysis was not described. Therefore, the reason of the discrepancy is not clear. On the other hand, our $S(Q)$ is relatively largely different from that by Benmore *et al.*¹³ This may be attributed to the fact that structure and stress relaxations did not occur in their measurements. The definition of the Si-O bond length in Benmore *et al.*¹³ is not the same as that in this study. However, even if their definition is applied to our data, resultant bond lengths become smaller only by $\sim 0.01 \text{ \AA}$, and therefore the discrepancy cannot be explained. It is worth noting that the two data points during decompression are not in agreement with those during compression in Benmore *et al.*¹³ In particular, the difference at around 30 GPa is quite large, and this suggests that there is hysteresis in the transformation from a fourfold- to a sixfold-coordinated structure in measurements with monochromatic x rays. It may also be due to the difference in the stress state during compression and decompression.

The pressure dependence of the coordination number is in relatively good agreement with Benmore *et al.*¹³ (Fig. 5). The effect of deviatoric stresses may be large on the bond length, i.e., peak positions in $g(r)$, and may be small on the coordination number, i.e., peak areas in $g(r)$. The estimated coordination number is dependent on the number density

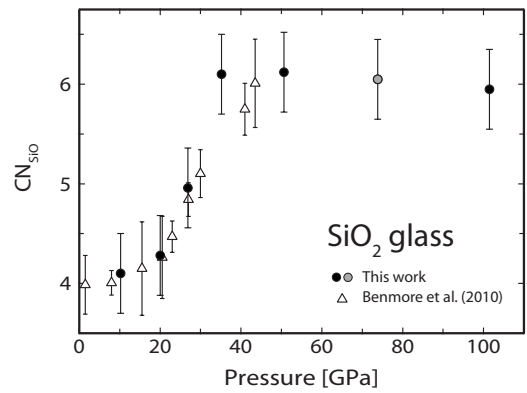


FIG. 5. Pressure dependence of CN_{SiO} of SiO_2 glass. Symbols are the same as in Fig. 3.

used in the analysis. Deviatoric stresses do not affect the density measurement by an x-ray absorption method.⁴ The result of density measurements by an x-ray absorption method was also used in Benmore *et al.*,¹³ and this may partly be responsible for the relatively good agreement.

The coordination number at 27 GPa was calculated to be 5. It is difficult to judge whether SiO_2 glass at 27 GPa has a mixed state of fourfold- and sixfold-coordinated structures or a single fivefold-coordinated structure, based solely on measurements in this study. However, it is unlikely that fourfold- and sixfold-coordinated structures coexist due to kinetic barriers because the irradiation of white x rays may have relaxed the structure. Therefore, the transformation from a fourfold- to a sixfold-coordinated structure may not be the first-order-like at room temperature. Assuming that the contribution of entropy (i.e., the contribution of the $-TS$ term, where T and S are temperature and entropy, respectively) to the Gibbs free energy is not so large at room temperature, it might be probable that SiO_2 glass has a single structure rather than has a mixed state of the two structures.^{28,29}

The pressure dependence of the Si-O bond length of sixfold-coordinated SiO_2 glass is similar to that of sixfold-coordinated crystalline polymorphs (Fig. 4). The data at 74 GPa were measured during decompression but both the Si-O bond length and the coordination number are consistent with those during compression, and the hysteresis is small (within the margin of error) in this pressure range. These results strongly suggest that SiO_2 glass behaves as a single amorphous polymorph having a local structure similar to sixfold-coordinated crystalline polymorphs, from 35 GPa to at least 100 GPa. This conclusion supports our speculation in previous studies^{5,17} and does not contradict with the result of recent sound-velocity measurements.¹⁸

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