

Transformations in the Intermediate-Range Structure of SiO₂ Glass under High Pressure and Temperature

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The temperature dependence of the x-ray structure factor for SiO₂ glass was measured at several pressures up to 19.2 GPa. The position of the first sharp diffraction peak moved to a higher momentum transfer as the temperature increased in a specific pressure-temperature range. The intermediate range structure was thermally relaxed to a denser one. Around 7 GPa, the temperature-induced shift saturated and the crystallization temperature drastically increased. These results support the existence of a relatively stable high-pressure form of SiO₂ glass. A sudden transformation was not observed.

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There is an increasing interest on polymorphism of glasses and liquids, and the possibility of a first-order phase transition. Different structures of SiO₂ glass have been recognized, but the existence of a first-order phase transition between the structures is controversial. Bridgman reported a permanent increase in density for SiO₂ glass after being subjected to pressure above 10 GPa at room temperature [1]. At a given applied pressure, the compacting effect increased as the temperature increased [1,2]. Approximately a 20% increase in density was achieved by treating at 7.4 GPa and 700 °C [3]. Since drastic changes in elastic and vibrational properties accompanied, it has been suggested that the highly densified SiO₂ glass is an “amorphous polymorph” [4].

In spite of the large change in density, changes in the short-range order of the densified SiO₂ glass were small [3,5–8]. The basic structural units, SiO₄ tetrahedra, were preserved and the change in the Si-O bond length was negligible. The large increase in density was attributed to a significant modification in the intermediate range order, which was manifested by a drastic change in the first sharp diffraction peak (FSDP) of the structure factor, $S(Q)$ [3,7]. The FSDP was observed in numerous types of glass [9] and appeared at 1.55 \AA^{-1} for SiO₂ glass at normal pressure, which suggests that Fourier components of period $\approx 2\pi/Q \approx 4 \text{ \AA}$ are involved. As the density increased, the position moved almost linearly to higher Q [3]. Several experimental and simulation studies demonstrated that the densification is accompanied by a reduction in the ring sizes and a collapse of void space [6,8,10–12].

Although *in situ* experiments at room temperature have revealed that the pressure-induced structural change in SiO₂ glass is gradual and continuous [4,13,14], some groups have proposed that the transformation occurs via a first-order amorphous-amorphous phase transition at high temperature [15] similar to that between low- and high-density amorphous ices [16]. They argue that the

glass transition temperature of SiO₂ glass is high so that the transition is kinetically hindered at room temperature [15]. Following their prediction, it has recently been reported that the volume suddenly decreased by 20% at 680 °C and 3.6 GPa [17]. However, other experimental and simulation studies have revealed a continuous decrease of volume at elevated temperatures and high pressures [12,18–20]. To determine whether a first-order amorphous-amorphous transition exists, we conducted *in situ* x-ray diffraction experiments at elevated temperatures and at several pressures up to 19.2 GPa. The result at 17.2 GPa was previously reported [21].

A cubic-type multianvil apparatus (SMAP2) installed on the BL14B1 beam line at the SPring-8 synchrotron radiation facility was used for measurements below 9.9 GPa [22]. A rod of SiO₂ glass with a 2.0 or 1.5 mm diameter, a tube-type graphite heater, and a cube made of boron-epoxy mixture were used. The temperature was monitored by an alumel-chromel thermocouple, while the pressure was determined by an internal NaCl marker [23]. A Kawai-type double stage press (SPEED1500) on BL04B1 at SPring-8 was used for measurements at and above 11.9 GPa [22]. For these experiments, a rod of SiO₂ glass with a 1.5 mm diameter, a W₉₇Re₃-W₇₅Re₂₅ thermocouple, a NaCl pressure marker, and an MgO gasket were used. The x-ray diffraction pattern was measured by an energy-dispersive method. To obtain structure factor, $S(Q)$, diffraction data at different 2θ angles were combined by an empirical method [24,25]. Some crystallization temperatures were determined on the BL11XU beam line with a cubic-type apparatus.

Figure 1 shows the P - T points where the measurements were performed. Initially the pressure was increased at room temperature, and then the sample was heated at a constant applied load. Typically, as the temperature increased, the pressure slightly decreased. Crystallization began at temperatures indicated by + and was almost completed at the temperatures indicated by ×. The

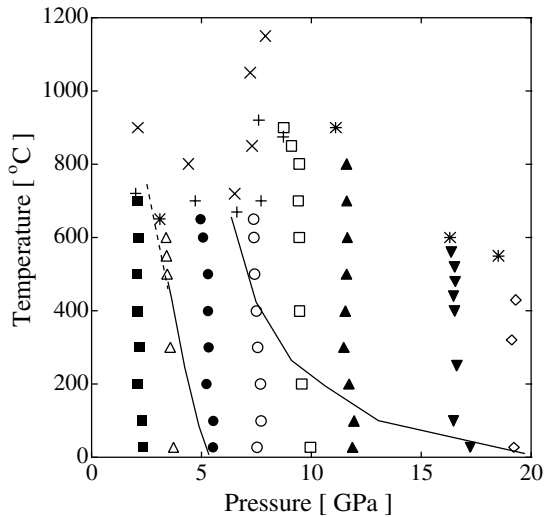


FIG. 1. The pressure and temperature points where the measurements were performed. The SiO_2 sample partially crystallized at the points indicated by + and fully crystallized at points indicated by \times . The lines are explained in the text.

sample crystallized to quartz ($P \leq 4.4$ GPa), coesite ($4.4 \leq P \leq 11.1$ GPa), or stishovite ($11.1 \leq P \leq 19.2$ GPa). The mixtures of two crystalline phases were observed at 4.4 and 11.1 GPa. The crystallization temperature decreased up to 3.7 GPa. Above 7 GPa it rapidly increased from about 700 °C to about 1000 °C and then gradually decreased above 10 GPa.

Figure 2 shows the room-temperature pressure dependence of $S(Q)$ for SiO_2 glass up to 19.2 GPa. The position of the FSDP at ambient pressure, 1.55 \AA^{-1} , was consistent with the previous reports [13]. The FSDP moved to higher Q and became broad as the pressure increased. On the other hand, the shifts of peak positions in the region $Q > 4 \text{ \AA}^{-1}$ were relatively small. The small change in the

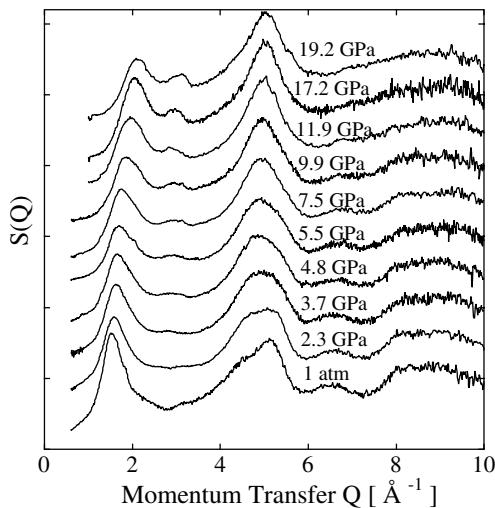


FIG. 2. The pressure dependence of $S(Q)$ at room temperature.

high- Q region indicates that the short-range order was mostly preserved. In fact, the radial distribution functions obtained by the Fourier transform of $S(Q)$ revealed that the Si-O bond length was almost constant [21]. Above 4.8 GPa, a new peak appeared at about 3 \AA^{-1} . The intensity of this new peak increased as the pressure increased. The small peak around 6.5 \AA^{-1} disappeared at high pressures. The overall tendency agreed with the previous study [13].

Figure 3 plots the temperature dependence of $S(Q)$ at 3.7 GPa and that at 9.9 GPa. The change of FSDP at 3.7 GPa was small. The intensity of FSDP barely increased with temperature, and its position slightly shifted to higher Q . On the other hand, a large change in FSDP was obvious at 9.9 GPa. The FSDP became sharper and its position moved to higher Q as the temperature increased. The change was small above 400 °C. The shift to higher Q indicates that the characteristic distance in real space was reduced. The direction of the shift was contrary to that expected from the normal thermal expansion. Thus, it is highly probable that the density of SiO_2 glass increased with temperature due to the relaxation of the intermediate range structure. The sharpening of the FSDP was also anomalous since peak broadening at high temperature was expected due to an increase in the thermal vibration. It suggests an increase in the correlation length or a more ordered, homogeneous structure at high temperature, which supports thermal relaxation in the intermediate range structure. This sharpening continued even after the shift of the FSDP stopped. The new peak at about 3 \AA^{-1} became small as the temperature increased.

Figure 4 summarizes the typical temperature dependence of the position of the FSDP at several pressures. It was reported that the position of FSDP was not dependent on temperature at atmospheric pressure [26]. Our result at 2.3 GPa did not show significant temperature dependence either. The shift to higher Q started above 300 °C at 3.7 GPa. At 5.5 GPa, the shift of the FSDP continued from room temperature to the highest temperature. At

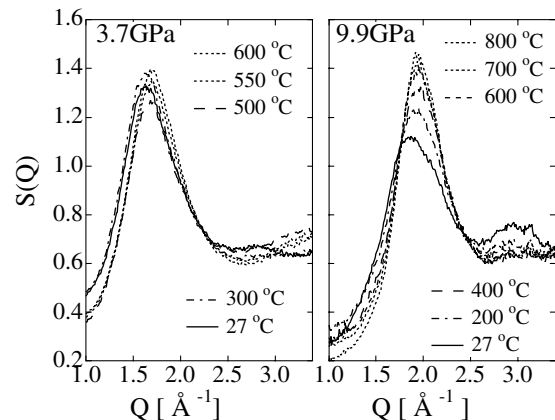


FIG. 3. Temperature dependence of $S(Q)$ at 3.7 and at 9.9 GPa.

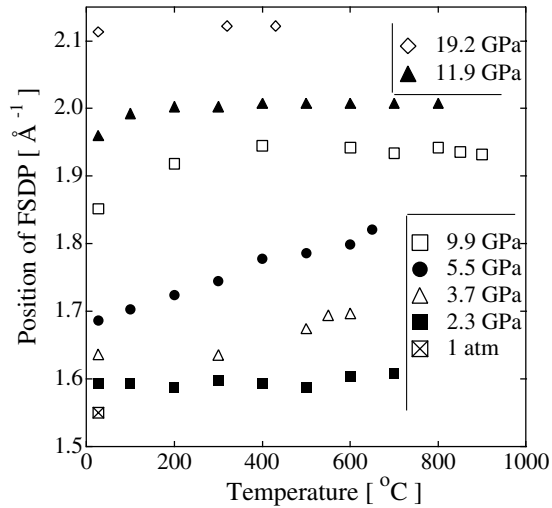


FIG. 4. The temperature dependence of the FSDP position.

9.9 GPa, the shift stopped at 400 °C, and the temperature where the shift terminated decreased as the pressure increased. At 11.9 GPa, the shift stopped at 200 °C and the total range of the shift was small. These results clearly indicate that there is a P - T region where the intermediate range structure relaxed to a denser one, which was induced by the heating. The absence of relaxation in the high-pressure, high-temperature region implied that a relatively stable high-pressure form of SiO_2 glass exists. The rapid increase of the crystallization temperature above 7 GPa as shown in Fig. 1 is also evidence for an increased stability. A sudden change in the position of the FSDP was not observed when heating.

In Fig. 1, the area surrounded by two solid lines indicates the transformation region where the temperature-induced shift of the position of the FSDP occurred. The region coincided with the threshold region where the permanent densification was induced by high-pressure high-temperature treatments [2]. Heat treatment above a threshold temperature, which decreased as the pressure increased, induced a permanent densification. The density of the recovered sample at a certain pressure increased with temperature, but it approached saturation at high temperature and high pressure [2]. El'kin *et al.* speculated a similar transformation region based on their volume measurements of SiO_2 glass at moderate temperatures [18]. The region was consistent with our findings.

The transformation region is also evident in a plot of the FSDP position as a function of pressure. In Fig. 5, the closed circles indicate the position of FSDP at room temperature, and the open circles indicate the position at a given temperature where the shift caused by the heating was terminated by either crystallization or the saturation at each pressure. At room temperature, the FSDP position moved to a higher Q as the pressure increased. It had a small positive curvature up to 10 GPa. Then the slope sharply decreased and moved almost

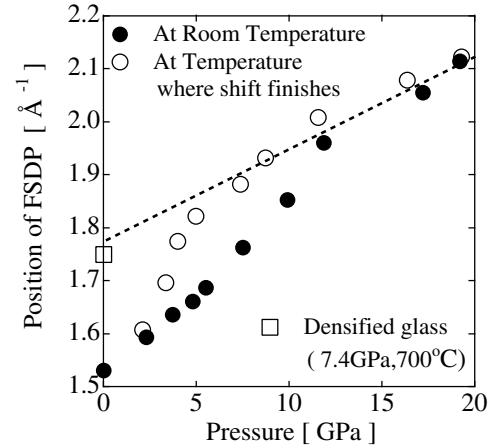


FIG. 5. The position of FSDP at room temperature and the temperature where the peak is through shifting. Dashed line is a guide for eyes.

linearly with pressure above 10 GPa. The sharp change in the slope indicates that the compression mechanism changed around this pressure, which pressure coincided with the threshold of the permanent densification at room temperature. On the other hand, the position of the FSDP at high temperatures started to deviate from that at room temperature around 3 GPa and rapidly increased with pressure. Above 7 GPa, it had the same slope for the high-pressure part of the room-temperature curve.

In Fig. 5, the open square indicates the position of the FSDP for a 20% densified glass obtained by a heat treatment at 7.4 GPa and 700 °C [3]. The position was very similar to the extrapolated relationship between the FSDP position and the pressure in the high-pressure region. Highly densified glass can be considered a quenched high-pressure form. This relationship explained why densification above 20% was difficult to achieve.

As shown in Figs. 1 and 5, the transformation region became narrower at high temperatures, but the width remained even near the crystallization temperature. Crystallization seems to hinder the amorphous-amorphous first-order phase transition, if it exists.

The existence of intermediate states between the normal and the highly densified glass also suppressed the sudden amorphous-amorphous transition. Reported $S(Q)$ for moderately densified glass [3] cannot be reproduced by combining those of the normal and the highly densified glasses, which implies that intermediate structures between the two forms are possible. The continuously observed change of FSDP in our *in situ* experiments confirms the existence of intermediate states.

Previous diffraction measurements on densified glasses revealed a linear relationship between the position of the FSDP and the density [3]. If this relationship holds for the intermediate structure at high pressures, then the density change from heating can be roughly estimated. The shift induced by heating reached a maximum, 0.13 \AA^{-1} , at

5.5 GPa. The estimated corresponding change in density was 0.20 g/cm^3 , which was approximately 9.5% of the density for the normal glass and 8% of the density at 5.5 GPa and room temperature [27]. The amount of density change is supposed to be sufficient to produce highly densified glass since the glass is already compressed about 20% at room temperature and because the high-pressure form has a smaller compressibility [18].

Mukherjee *et al.* reported that at 680°C and 3.6 GPa a sudden decrease in volume by 20% in the amorphous state occurred before crystallization. In our measurements, crystallization started at 650°C and 3.1 GPa. The difference in the crystallization temperatures may be due to the different high-pressure generation methods. Yet, a volume change of 20% is inconsistent with our estimated density change from heating.

The fact that heating induced the structural change in the intermediate range order suggests that a thermally activated process such as rebonding, i.e., breaking of the original bonds and forming of new ones, accompanies the changes. Simulation studies have shown such events and the resultant changes in the topology of tetrahedron connectivity. Trachenko *et al.* reported that tetrahedral topology did not break below 3 GPa [11,19]. The rebonding at room temperature began above 3 GPa and the number of rebonding events remarkably increased above 5 GPa. At elevated temperatures, the number of rebonding events increased. The transformation region was consistent with our results. They reported a gradual decrease of 7% in volume up to 927°C and 3.6 GPa [12]. This volume change was consistent to our estimates. Furthermore, the changes in the topology of tetrahedron connectivity toward more efficient packing of the tetrahedra were supported by our diffraction data. A preliminary reverse Monte Carlo analysis on $S(Q)$ revealed that the number of small rings increased as the densification progressed. The change of the ring statistics probably decreases the number and/or the size of interstitial voids and hence contributes to the large shift of the FSDP. Detailed analysis on $S(Q)$ and radial distribution functions will be presented elsewhere [28]. Trachenko *et al.* also pointed out that overcoordinated Si atoms appeared above 3 GPa [12]. The appearance of the new peak at 3 \AA^{-1} , which became prominent at pressures where the sixfold structure was dominant [13], and the disappearance of it by heating may indicate creation and thermal relaxation of such defects, respectively.

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- [1] P.W. Bridgman and I. Šimon, *J. Appl. Phys.* **24**, 405 (1953).
 - [2] J. Arndt and D. Stöffler, *Phys. Chem. Glasses* **10**, 117 (1969).
 - [3] Y. Inamura *et al.*, *Physica (Amsterdam)* **241–243B**, 903 (1998).
 - [4] M. Grimsditch, *Phys. Rev. Lett.* **52**, 2379 (1984).
 - [5] P. McMillan, B. Piriou, and R. Couty, *J. Chem. Phys.* **81**, 4234 (1984).
 - [6] R. A. B. Devine and J. Arndt, *Phys. Rev. B* **35**, 9376 (1987).
 - [7] S. Susman *et al.*, *Phys. Rev. B* **43**, 1194 (1991).
 - [8] Y. Inamura *et al.*, *J. Non-Cryst. Solids* **293–295**, 389 (2001).
 - [9] S. R. Elliott, *J. Phys. Condens. Matter* **4**, 7661 (1992).
 - [10] W. Jin, R. K. Kalia, P. Vashishta, and J. P. Rino, *Phys. Rev. B* **50**, 118 (1994).
 - [11] K. Trachenko and M.T. Dove, *J. Phys. Condens. Matter* **14**, 7449 (2002).
 - [12] K. Trachenko and M.T. Dove, *Phys. Rev. B* **67**, 064107 (2003).
 - [13] C. Meade, R. J. Hemley, and H. K. Mao, *Phys. Rev. Lett.* **69**, 1387 (1992).
 - [14] R. J. Hemley, H. K. Mao, P. M. Bell, and B. O. Mysen, *Phys. Rev. Lett.* **57**, 747 (1986).
 - [15] D. J. Lacks, *Phys. Rev. Lett.* **84**, 4629 (2000).
 - [16] O. Mishima, L. D. Calvert, and E. Whalley, *Nature (London)* **314**, 76 (1985).
 - [17] G. D. Mukherjee, S. N. Vaidya, and V. Sugandhi, *Phys. Rev. Lett.* **87**, 195501 (2001).
 - [18] F. S. El'kin *et al.*, *JETP Lett.* **75**, 342 (2002).
 - [19] K. Trachenko and M.T. Dove, *Phys. Rev. B* **67**, 212203 (2003).
 - [20] V. G. Karpov and M. Grimsditch, *Phys. Rev. B* **48**, 6941 (1993).
 - [21] Y. Katayama and Y. Inamura, *J. Phys. Condens. Matter* **15**, S343 (2003).
 - [22] W. Ustumi *et al.*, *J. Phys. Condens. Matter* **14**, 10497 (2002).
 - [23] D. L. Decker, *J. Appl. Phys.* **36**, 157 (1965).
 - [24] K. Tsuji *et al.*, *Rev. Sci. Instrum.* **60**, 2425 (1989).
 - [25] K. Funakoshi, Ph.D. thesis, Tokyo Institute of Technology, 1997.
 - [26] S. Susman, K. J. Volin, D. G. Montague, and D. L. Price, *Phys. Rev. B* **43**, 11076 (1991).
 - [27] O. B. Tsiok, V. V. Brazhkin, A. G. Lyapin, and L. G. Khvostantsev, *Phys. Rev. Lett.* **80**, 999 (1998).
 - [28] Y. Inamura, S. Kohara, and Y. Katayama (to be published).