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Abstract
The pressure dependence of the structure factor for vitreous silica was measured
up to 8.3 GPa at 500 °C by means of an *in situ* x-ray diffraction method. The
position of the first sharp diffraction peak (FSDP) moved to a higher momentum
transfer as the pressure increased. It moved rapidly between 3.3 and 5.8 GPa,
and then the slope of the FSDP position as a function of pressure decreased.
The pressure dependence of the position is the same as that for a sample heated
to 500 °C after room-temperature compression. On decompression at 500 °C,
the position of the FSDP showed hysteresis. The pressure dependence of the
FSDP position suggests that the permanent densification of vitreous silica is
realized due to preservation of the intermediate-range structure stabilized at high
pressure and temperature.

1. Introduction

The idea of 'polyamorphism', polymorphism of glasses and liquids, has recently attracted
wide attention, and the possibility of a first-order phase transition between the polymorphs has
been discussed [1–4]. Highly densified vitreous silica may be an example of an 'amorphous
polymorph' [5–7]. Vitreous silica was permanently densified after being subjected to pressure
above 10 GPa at room temperature [5]. The densification occurred at lower pressures when
the sample was heated under pressure [5, 6]. An approximately 20% increase in density was
achieved by treatment at 7.4 GPa and 700 °C [8]. In spite of the large change in density,
changes in the short-range order of the densified vitreous silica were small [8–12]. The large
increase of density was attributed to a significant modification of intermediate-range order,
which was manifested by a drastic change in the first sharp diffraction peak (FSDP) of the
structure factor [8, 11]. The FSDP was observed in numerous types of glass [13], and appeared
at $Q = 1.55 \, \text{Å}^{-1}$ for vitreous silica at normal pressure, which suggests that Fourier components

of period $\approx 2\pi/Q \approx 4$ Å are involved. The position of the FSDP moved almost linearly to higher Q as the density increased [8].

Although the pressure-induced structural change in vitreous silica is gradual and continuous at room temperature [7, 14, 15], some groups have proposed that the transformation occurs via a first-order amorphous–amorphous phase transition [16]. They argue that the glass transition temperature of vitreous silica is high so that the transition is kinetically hindered at room temperature. After the prediction, a sudden decrease in volume by 20% at 680 °C and 3.6 GPa has been reported [17]. However, other experimental and theoretical studies have revealed a continuous decrease of volume at elevated temperatures under high pressure [18–22].

To determine whether a first-order amorphous–amorphous transition exists, we have recently conducted *in situ* x-ray diffraction experiments on vitreous silica at elevated temperatures and at several pressures up to 19.2 GPa [23–25]. The results are summarized as follows. The position of the FSDP moved to a higher momentum transfer as the temperature increased in a specific pressure–temperature range. The direction of the temperature-induced shift indicated that 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 vitreous silica. A sudden transformation which corresponds to a 20% decrease of volume was not observed. The transformation region became narrower at high temperatures, but the width remained even near the crystallization temperature.

Since glass is not an equilibrium state, it is expected that the structure of a glass at a certain pressure–temperature point depends on the path to the point in the pressure–temperature plane. In this respect, the absence of a sudden transformation at elevated temperature does not exclude a possibility of such transformation on different paths. To investigate the possibility of the sudden transformation further, we have measured x-ray diffraction patterns of vitreous silica at elevated pressures up to 8.3 GPa and at 500 °C. The pressure dependence of the x-ray diffraction pattern on decompression was also measured.

2. Experimental procedure

In situ x-ray diffraction experiments were carried out using a cubic-type multi-anvil apparatus (SMAP2) installed on the BL14B1 beamline at the SPring-8 synchrotron radiation facility [26]. A rod of vitreous silica with a 1.5 mm diameter was used as a sample. It was inserted into a tube-type graphite heater. A cube made of boron–epoxy mixture was used as the pressure-transmitting medium. The temperature was monitored by an alumel–chromel thermocouple. The pressure was determined by an internal NaCl marker [27]. The x-ray diffraction pattern was measured by an energy-dispersive x-ray diffraction method using white x-rays. To obtain the structure factor, $S(Q)$, diffraction data at $2\theta = 4, 5, 6, 8, 10, 13$ and $18°$ were measured and combined by an empirical method [28, 29]. It took about 2 h to measure the set of diffraction data. To monitor the position of the FSDP, the diffraction pattern at $2\theta = 5°$ alone was measured at additional pressure points.

3. Results

Figure 1 shows the experimental path in a pressure–temperature diagram. The crosses indicate crystallization temperatures determined by previous experiments [24]. At elevated temperatures, the vitreous sample partially crystallized at the points indicated by $+$ and fully crystallized at the points indicated by $\times$. To avoid crystallization, the sample was compressed
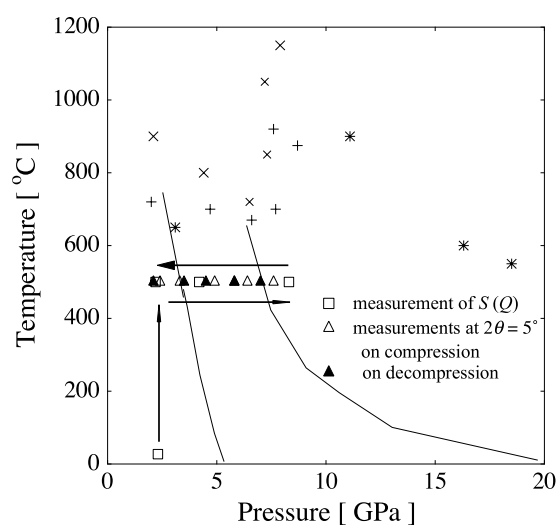
Figure 1. Experimental path in a pressure–temperature diagram. See text for details.

below the crystallization temperatures. The pressure was increased to 2.4 GPa at room temperature and then the temperature was increased to 500 °C because the temperature cannot be stably increased at low pressures in the present high-pressure apparatus. The pressure slightly decreased to 2.2 GPa as the temperature increased. The pressure was then increased to 8.3 GPa at 500 °C. The open squares indicate the points where a set of diffraction patterns at different 2θ angles was measured, and the open triangles indicate the points where a pattern at $2\theta = 5°$ was measured on compression. The sample was then decompressed to 2.1 GPa. The closed triangles indicate the points where a pattern at $2\theta = 5°$ was measured on decompression. The area surrounded by the two solid lines is a transformation region where the position of the FSDP moved to a higher momentum transfer as the temperature increased [24]. The experimental path crossed the transformation region as shown by the two arrows.

Figure 2 shows x-ray diffraction patterns measured at $2\theta = 5°$. The first broad maximum corresponds to the FSDP. A small peak around 43 keV is a diffraction peak from a graphite heater which surrounds the sample. Above 4.2 GPa, new peaks appeared, and they were attributed to diffraction lines of quartz and coesite. The vitreous silica started to crystallize even below the crystallization temperatures determined by the measurements at elevated temperatures under high pressure. Although the intensities of the peaks increased with increasing pressure, the broad amorphous pattern still dominated up to 8.3 GPa. The position of the first maximum moved to a higher momentum transfer as the pressure increased.

Figure 3 shows the x-ray structure factor for vitreous silica at various pressures on compression at 500 °C. The diffraction peaks of crystals were removed. The position of the FSDP moved to a higher momentum transfer while the positions of other peaks remained the same. The small change in the high-Q region indicated that the Si–O distance is almost constant. In fact, the position of the first peak in the pair correlation function, which is obtained by a Fourier transform of $S(Q)$, stays constant at $r = 1.60$ Å. Therefore the densification cannot be attributed to uniform compression. This peak position is unfavourable to the existence of six-fold coordinated Si because the Si–O distance for four-fold coordinated SiO_2 is about 1.61 Å and that for six-fold coordinated SiO_2 is about 1.75 Å in this pressure range [14]. The width and the height of the FSDP did not change significantly.
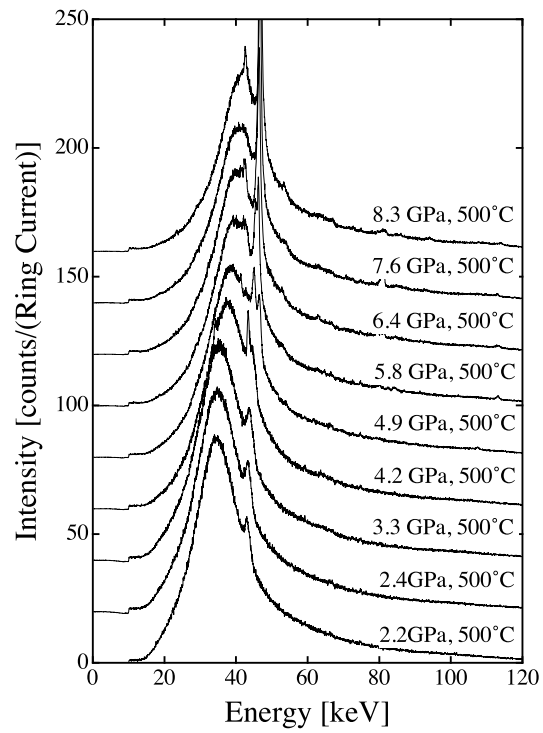
Figure 2. Pressure dependence of x-ray diffraction pattern taken at $2\theta = 5°$ on compression at 500 °C. The data acquisition time was 300 s.
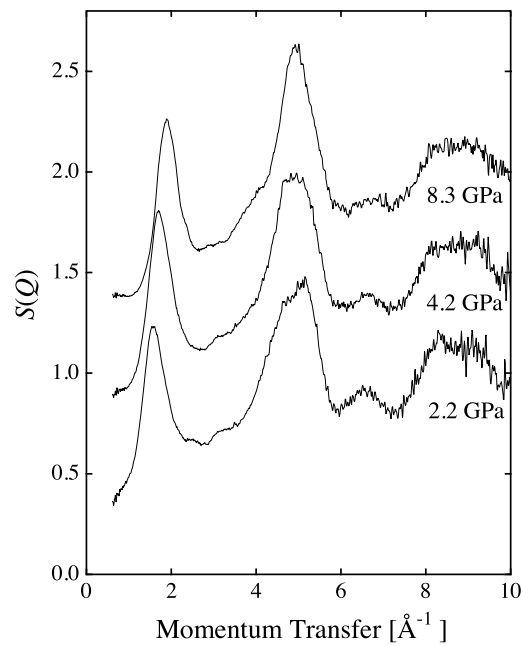

Figure 3. Structure factor, $S(Q)$, measured at 500 °C and at 2.2, 4.2 and 8.3 GPa on compression.
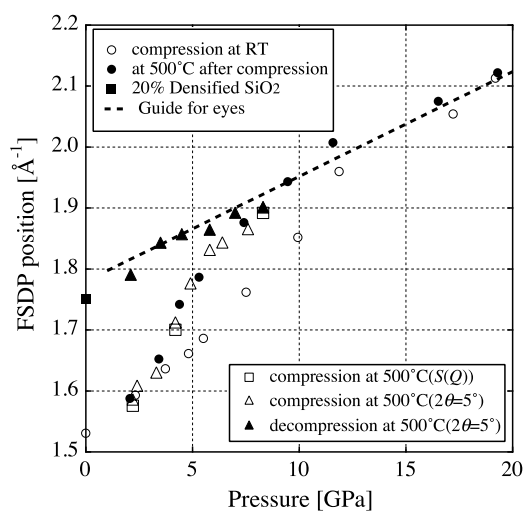
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Figure 4. The position of the FSDP at 500 °C on compression (open squares and open triangles) and decompression (closed triangles) together with that at room temperature (open circles) and that at 500 °C after room-temperature compression (closed circles). The closed circles at 9.5, 16.5 and 19.3 GPa are the average of the FSDP positions at 400 °C and 600 °C, average of those at 480 °C and 520 °C, and position at 430 °C, respectively. The closed square indicates the position for 20% densified glass recovered from a heat treatment at 7.4 GPa and 700 °C. The dashed line is a guide for the eyes.

4. Discussion

In figure 4, the position of the FSDP at 500 °C is plotted as a function of pressure. The open squares indicate the positions determined by $S(Q)$ measured on compression. The positions of the triangles were determined from a diffraction pattern at $2\theta = 5°$ after a correction using a normalization function obtained through the analysis of a set of diffraction patterns at different 2θ angles. The open triangles indicate the positions measured on compression and the closed triangles indicate the positions measured on decompression. The agreement between the value obtained from $S(Q)$ and that obtained from the diffraction data at $2\theta = 5°$ is good. The position of the FSDP measured on compression at room temperature (open circle) and that at 500 °C for the sample heated after room-temperature compression (solid circle) are also plotted [24]. The position on compression at 500 °C started to deviate from that at room temperature above 3.3 GPa, and rapidly moved to higher momentum transfer with increasing pressure. The change became small above 5.8 GPa, and it gradually approached the extrapolated line of the high-pressure part ($P > 12$ GPa) of the room-temperature curve. This pressure dependence is the same as that for the sample heated to 500 °C after room-temperature compression. The coincidence indicates that the path dependence of the FSDP position is negligibly small in the present experimental conditions.

As shown in figure 4, the position of the FSDP showed large hysteresis on decompression at 500 °C. It moved to a lower momentum transfer along an extrapolated relationship between the FSDP position and the pressure in the high-pressure region ($P > 12$ GPa at room temperature). In this high-pressure region, the pressure dependence of position of FSDP was small, and the FSDP moved slightly at elevated temperatures. These results suggest that a relatively stable form of vitreous silica exists in this region. The fact that the pressure dependence of the FSDP position on decompression roughly obeys the relation in the

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high-pressure region suggests that the intermediate-range structure at high pressures is preserved on decompression. It approached the value for a 20% densified glass at 0 GPa indicated by the closed square. Thus the highly densified glass can be regarded as a quenched high-pressure form.

Although the FSDP position shows large pressure dependence at 500 °C, the width and the height of the FSDP do not show any significant changes, as shown in figure 3. In contrast to these results, the width of the FSDP became wide and the height of the FSDP became small when the vitreous silica was compressed at room temperature [24]. In addition, a new peak appeared at around $Q = 3 \text{ Å}^{-1}$ at room temperature. The FSDP became sharp when the sample was heated under high pressure. At the same time the intensity of the new peak decreased. In other words, the shape of the FSDP of the sample compressed after heating was similar to that of the sample heated after compression. The path dependence of the shape of the FSDP was also small.

The difference between the room-temperature and high-temperature compression, i.e. the more rapid shift of the position of the FSDP at high-temperature, clearly demonstrates the importance of thermally activated processes in the transformation to the denser form. Molecular dynamics simulation studies showed that the transformation to the denser form is caused by rebonding, i.e. breaking of the original bonds and forming of new ones [20, 22]. Such processes realize denser packing of SiO_4 tetrahedra and therefore affect the position of the FSDP. There are potential barriers for rebonding and they are hindered at room temperature. The present results support this scenario.

There are few reports on the pressure dependence of the structure of vitreous silica at high temperatures. El'kin *et al* reported a change in volume of silica glass in the compression and unloading cycles at 202 and 272 °C [19]. They reported that the volume reduction is irreversible due to the high bulk modulus of the densified glass. Larger permanent densification was achieved at higher temperature, and they speculated a similar transformation region based on their measurements. Huang and Kieffer carried out molecular dynamics simulations of silica glass for compression and decompression cycles at high temperatures [22]. They reported a rapid increase of density due to a decrease of bulk modulus on compression and a large hysteresis on decompression. They attributed the permanent densification to irreversible changes in the intermediate-range order, especially in the ring statistics. The reported pressure dependence of the density on both compression and decompression paths is remarkably similar to that of the FSDP position in the present study. All these studies agree with each other and indicate that the permanent densification occurs without sudden change of density.

5. Conclusion

The pressure dependence of the structure factor for vitreous silica was measured up to 8.3 GPa at 500 °C by means of an *in situ* x-ray diffraction method. The pressure dependence of the position of the FSDP was the same as that for the sample heated to 500 °C after compression, indicating that the path dependence was negligibly small. Although the width of the region where the FSDP rapidly shifts to higher momentum transfer with increasing pressure is narrower than that at room temperature, no sudden change was observed. The narrower width shows the importance of thermally activated processes in the transformation to the denser structure. On decompression at 500 °C, the position of the FSDP showed hysteresis. The pressure dependence of the position of the FSDP on both compression and decompression is remarkably similar to that of the volume reported in the previous experimental and theoretical studies [19, 22]. This coincidence indicates that the permanent densification of vitreous silica

is realized due to a preservation of the intermediate-range structure at high pressure and high temperature.

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