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Anelastic compression of nanometer-sized silica particles under high pressure: A high-energy x-ray diffraction measurement

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We compressed nanometer-sized silica particles, fumed silica, using a cubic-anvil-type apparatus up to pressures of 8 GPa at room temperature. The high-energy (61.7 keV) x-ray diffraction measurements of the recovered samples were carried out to determine the x-ray structure factor and in the real space correlation functions. These results indicate that anelastic compression occurs in silica nanoparticles in the pressure range from 4 to 8 GPa, which is well below the pressure regime of the anelastic compression (~10 to ~20 GPa) observed for bulk amorphous silica.

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Nanometer-sized silica particles (diameter $d = 10-100$ nm) have attracted considerable interest because of their widespread applications, including heterogeneous catalysis, technical adsorbents, silicate sources of mesoporous materials, fillers, and carriers of drugs. One of the commonly used silica nanoparticles is fumed silica, which is a synthetic amorphous silicon dioxide. Fumed silica is produced at high temperatures of about 1200–1600 °C by the hydrolysis of silicon tetrachloride vapor in an oxygen-hydrogen flame. The amorphous nature of fumed silica results from an extremely rapid cooling of highly viscous droplets of silicon dioxide, forming so-called primary particles. The size of primary particles ranges from 5–50 nm. The primary particles collide and are fused together to form stable aggregates having a mean size of about 200–500 nm. These aggregates then stick together to form loosely bonded agglomerates, resulting in a white fluffy powder with an extremely low bulk density down to 0.03 g/cm^3. The true density of the primary particles is 2.20 g/cm^3,[1] which is the same as that of the corresponding bulk material, namely, amorphous SiO_2 (a-SiO_2). This indicates that each nanoparticle in the aggregate is a nonporous material similar to bulk a-SiO_2. However, because of its extremely small particle sizes and high surface area (50–400 m^2/g), it is expected that the structure and physical, chemical, and optical properties of fumed silica are different from those of the corresponding bulk materials. Thus far, a number of studies have been carried out to understand the nature and properties of fumed silica and its related nanoparticles.[1–10] In particular, the surface properties and reactivity of fumed silica, which depend substantially on the quantity and structural environments of its surface hydroxyl groups, have been extensively studied.[1,11]

In this paper, we concentrate our interest on the structural characteristics of fumed silica after compression at high pressure. Previously, intense experimental and theoretical effort has gone into understanding the effect of pressure on the structure and properties of bulk a-SiO_2, revealing some interesting and anomalous behaviors.[12–22] It has been demonstrated that below ~10 GPa at room temperature, the compression of bulk a-SiO_2 is elastic and reversible. An irreversible densification is then observed in the range between ~10 and ~20 GPa. Beyond this anelastic regime, compression is again reversible and no further densification is observed. It is hence interesting to investigate whether these compressional regimes of bulk a-SiO_2 can also be applied to nanometer-sized silica particles such as fumed silica. It will give a clue to understand how scales of distance, namely, short, intermediate, and long-range scales of distance, determine the high-pressure behavior of a-SiO_2. In the present study we, therefore, compressed fumed silica between 4 and 8 GPa, in which compression is completely reversible for bulk a-SiO_2, and the structure of the samples recovered from high pressures was investigated by using high-energy x rays from a synchrotron. Since the wavelength of the photons used in the experiments is quite short, the resulting photo-electrical absorption is significantly decreased.[23] High-energy x-ray diffraction has additional further advantages, e.g. the wide accessible Q range, the small scattering angles, and the diminishing correlation terms.[23] These specific characteristics of high energy x-ray measurements enable us to obtain the sufficiently high resolution in the real-space correlation functions, which can be comparable to those obtained from a typical neutron diffraction experiment. Furthermore, the weighting factor of the Si-Si correlation is larger for x-rays than for neutrons, indicating that the high-energy x-ray experiments are especially suitable for analyzing a possible change in the distribution of Si-O-Si bond angles. Neutron elastic and inelastic scattering measurements on as-prepared fumed silica has been reported previously,[2,4,5] to our knowledge, however, the atomic structure of the fumed silica samples compressed over 4 GPa has not been investigated by any diffraction experiments.

The fumed silica used in this work was Sigma *S*-5130 from Sigma Chemical Co. (nominal particle size: 7 nm; specific surface area: 390 ± 40 m^2/g). Adsorbed H_2O and CO_2 along with surface hydroxyl groups were removed by calcining at 1000 °C in air before compression. The sample filled in a boron nitride cell was pressurized at room temperature nearly isostatically at 4, 6, and 8 GPa for 30 min using a cubic-anvil-type apparatus. Dimensions of the compressed

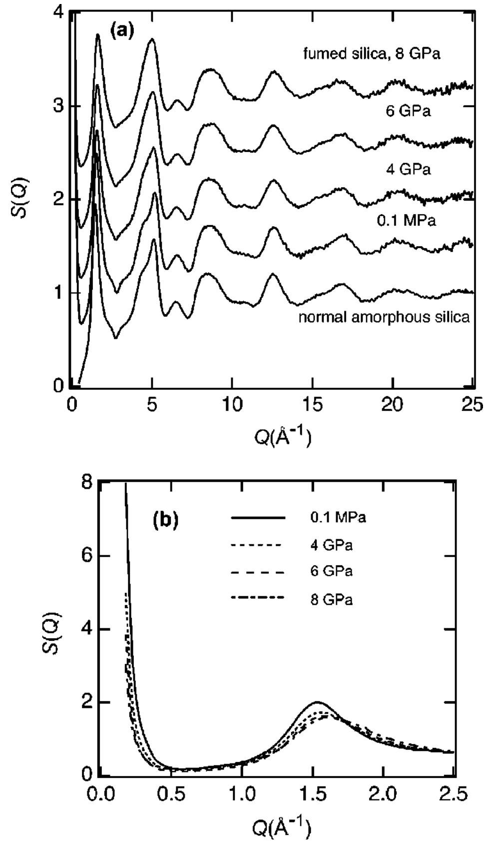

FIG. 1. (a) The x-ray structure factors $S(Q)$ of normal bulk amorphous SiO_2 and fumed silica retrieved from the indicated pressures. Successive curves are displaced upward by 1 for clarity. (b) The expand plot of the x-ray structure factors $S(Q)$.

samples are 2–5 mm in diameter and 0.3–2 mm thick depending on the applied pressure. The sample compressed at 4 GPa is opaque, whereas the samples compressed at 6 and 8 GPa are almost transparent. This transformation from opaque to transparent samples probably results from the pressure-induced reaction of the fumed silica surface, suggesting the formation of the interparticle Si-O-Si linkages even at room temperature.

The x-ray diffraction experiments of the recovered decompressed samples were performed in transmission geometry using an incident photon energy of 61.7 keV at the bending magnet beamline BL04B2 (Ref. 24) of SPring-8, Hyogo, Japan, with a horizontal two-axis diffractometer.[25] In this work, x-ray diffraction data were measured up to $Q_{\max} = 25$ Å^{-1} for all the noncompressed and compressed fumed silica samples as well as normal bulk a-SiO_2.

The total Faber-Ziman structure factor,[26] $S(Q)$, for fumed silica is shown in Fig. 1 for a series of pressures. We see from Fig. 1 that $S(Q)$ of noncompressed fumed silica is essentially identical with that of bulk a-SiO_2 at $1 < Q < 25$ Å^{-1}, in agreement with previous neutron scattering measurements on fumed silica.[5] These results indicate that the microscopic structure inside the primary particles of fumed silica is very similar to that of bulk a-SiO_2. We also notice from Fig. 1 that noncompressed fumed silica shows an abrupt increase in $S(Q)$ in the Q range below ~0.5 Å^{-1}, in accord with previous small-angle neutron scattering measurements.[2,5] Such a peculiar x-ray scattering in the low-Q region probably results from the structural fluctuation or the aggregated structure formed from the nanometer-sized primary particles.[5]

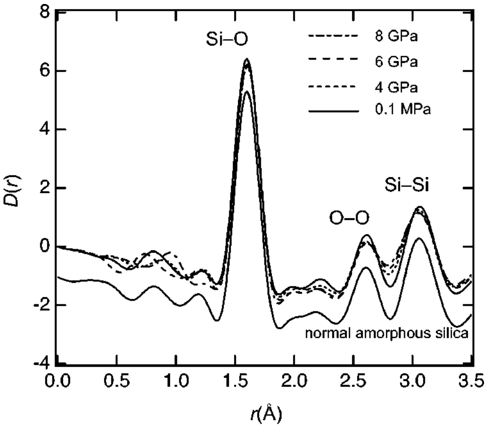

FIG. 2. Differential correlation functions $D(r)$ of normal bulk amorphous SiO_2 and fumed silica retrieved from the indicated pressures. The data of bulk amorphous SiO_2 are displaced downward by 1 for clarity.

Information in real space can be obtained by performing the appropriate Fourier transform of $S(Q)$; one such function is the differential correlation function $D(r)$, which is defined as[27]

$$D(r) = \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} M(Q) Q [S(Q) - 1] \sin(Qr) dQ,$$

where $M(Q)$ is a Lorch modification function[28] to reduce termination effects resulting from the finite upper limit of Q. As shown in Fig. 2, there is no apparent difference in $D(r)$ between noncompressed fumed silica and normal a-SiO_2 as in the case of $S(Q)$.[29]

As for the compressed fumed silica samples, however, there are systematic changes in the positions and intensities of the peaks in $S(Q)$ with increasing pressure. For example, the first sharp diffraction peak in $S(Q)$ shifts from $Q \sim 1.53$ to 1.63 Å^{-1} with increasing pressure up to 8 GPa, and accordingly the intensity of this peak decreases by ~20% [see Fig. 1(b)]. On the other hand, the peak at ~5.2 Å^{-1} shifts to lower values of Q (~5.0 Å^{-1}) from ambient pressure to 8 GPa. These results strongly suggest that the intermediate-range order beyond nearest-neighbor distances is not preserved in fumed silica upon compression up to 8 GPa. That is, the anelastic compression most likely occurs in the present fumed silica samples. We should also note that the strong scattering seen in the Q range below 0.5 Å^{-1} decreases in intensity with increasing pressure [see Fig. 1(b)], suggesting that the aggregated structure consisting of the fumed silica primary particles tends to become homogeneous on compression.

We next turn to changes in the real space correlations $D(r)$ with pressure (see Fig. 2). As for the Si-O (~1.6 Å) and O-O (~2.6Å) correlations, we do not see any changes in the respective interatomic bond distances. As for the Si-Si

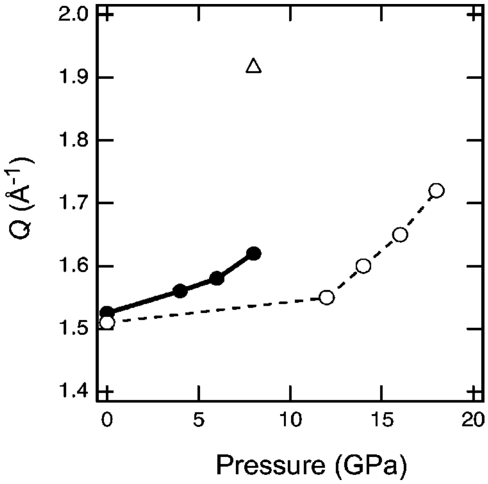

FIG. 3. Pressure dependence of the positions of the first sharp diffraction peak in $S(Q)$ measured for fumed silica (filled circle) and bulk amorphous SiO_2 (open circle, Ref. 30) retrieved from the indicated pressures. The position of the first sharp diffraction peak in $S(Q)$ of bulk amorphous SiO_2 measured *in situ* at 8 GPa (open triangle, Ref. 15) is also shown.

correlations at ~3.1 Å, however, the shorter distance side of the correlations develops appreciably with increasing pressure, and the Si-Si peak shifts slightly to lower values from ~3.07 to ~3.05 Å with compression from ambient pressure to 8 GPa. Such a decrease in the Si-Si distance has also been reported for bulk a-SiO_2 in previous *in situ* high-pressure diffraction experiments on a-SiO_2 at 8 GPa.[16] These observed changes in the real space correlations imply that the present anelastic compression observed for fumed silica results from a shift in the Si-O-Si intertetrahedral bond angle distribution to smaller angles, with little change in the configurations of the constituent SiO_4 tetrahedral units. A similar model has also been proposed to explain the mechanism of the anelastic compression of bulk a-SiO_2.[20]

We next compare the x-ray diffraction data of the present fumed silica samples with those of compressed bulk a-SiO_2 samples retrieved from high pressures[30] (see Fig. 3). As shown in Fig. 3, the first sharp diffraction peak shifts to higher Q with increasing pressure for both fumed silica and bulk a-SiO_2; however, fumed silica shows such a shift well below the lower limit (~10 GPa) of the anelastic regime observed for bulk a-SiO_2. The observed shift in the first sharp diffraction peak of fumed silica retrieved from 8 GPa is comparable to that of bulk a-SiO_2 retrieved from ~15 GPa. These results clearly indicate that the pressure onset for anelastic compression of fumed silica is much lower than that of bulk a-SiO_2, although the resultant structural changes are expected to be very similar to each other.[31]

According to *in situ* high-pressure x-ray diffraction[16] and *in situ* Raman scattering[15] measurements, bulk a-SiO_2 shows appreciable elastic deformation during compression even when the samples are compressed at pressures below ~10 GPa (also see Fig. 3). It is believed that the structural modification in bulk a-SiO_2 under pressure in the elastic regime results not from reconstruction of the Si-O bonds but from an elastic collapse of open-ring configurations to decrease the Si-O-Si intertetrahedral angles,[15,16] namely, a mechanism by which the angle distribution is altered without bond breaking. At higher pressures over ~10 GPa, however, reconstructive changes begin to occur to show anelastic compression,[12–14,20] accompanied by a shift in ring statistics toward smaller rings such as three-membered and four-membered rings of tetrahedra in the structure.[20] Considering that the pressure-induced changes observed in fumed silica are irreversible and anelastic as in the case of bulk a-SiO_2 after compression over ~10 GPa, we suggest that reconstructive changes take place in the network of fumed silica particles, accompanied by void compaction of the samples. The compressional anomalies observed in fumed silica may hence be interpreted in terms of changes in compressibility of amorphous silica with particle size. Thus far, the effect of particle size on the pressure-induced structural transitions has been investigated for several nanocrystalline materials,[32–35] showing that physical and electronic properties of crystals depend strongly on particle size. Some crystalline nanoparticles, e.g., CeO_2,[33] show that compressibility decreases with decreasing particle size, whereas others, e.g., PbS,[32] exhibit the opposite tendency depending on the factor governing the compressibility of the materials. It is hence quite likely that compressibility of fumed silica also can be dependent on the particle size. We suggest that the interatomic interactions in the long-range (>~10 nm) length scale, which may inhibit the reconstructive changes in the total SiO_2 network, will play a role in showing the elastic response in bulk a-SiO_2; however, nanometer-sized silica particles are lacking, although in part, in such long-range interactions, explaining a decreased compressibility of the present fumed silica samples.

In conclusion, we have shown that nanometer-sized fumed silica particles exhibit anelastic compression between 4 and 8 GPa, in which bulk a-SiO_2 still shows an elastic behavior upon compression. From the high-energy x-ray diffraction measurements of the retrieved fumed silica samples, it has been found that (1) the first sharp diffraction peak undergoes substantial changes in both position and intensity, (2) the nearest Si-O and O-O bond distances do not change appreciably, and (3) the Si-Si correlation at ~3.1 Å shifts to lower distances. Since these changes are very similar to those observed for bulk a-SiO_2 in the anelastic regime, we suggest that the anomalous compressive behavior of fumed silica results from a decreased compressibility of the nanometer-sized particles as compared with bulk a-SiO_2.

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