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Transformation of SiO_2 to the amorphous state by shearing at high pressure

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ABSTRACT

A natural α-quartz disc with flat surfaces perpendicular to (100) was sheared at 5 GPa in order to confirm that the sheared state at high pressure is not always the same as that obtained at high hydrostatic pressure. A transmission X-ray diffraction pattern taken from the sample that was sheared at high pressure revealed five broad halo rings; the pattern was taken about three months after the high-pressure experiment. The ratios of the interplanar spacing corresponding to the densest radius of the smallest ring to those of the other ones are 0.610, 0.514, 0.459, and 0.399, respectively. This set of rings does not appear from α-quartz. These are approximately equal to those obtained from solids with space group *Fd*3*m*. A Raman spectroscopic study also showed the structural change due to shearing at high pressure. The spectrum appears neither from α-quartz nor from coesite. These facts indicate, therefore, that the crystalline α-quartz sample transformed to the amorphous state based on a structure consistent with *Fd*3*m* space group.

INTRODUCTION

Structures sheared at high pressures sometimes remain the same at atmospheric pressure (Sakka 1975; Furuichi et al. 2001, 2002). On the other hand, we cannot deny the possibility that the solid state sheared at high pressure is not always the same as that at high hydrostatic pressure. Accordingly, we can expect to produce new industrial materials by shearing solids at high pressure. On the other hand, studies of solid structures sheared at high pressures impart fundamental knowledge to some field of physics and chemistry, because in the natural world there are cases where solids are sheared at high pressure. Their structures and state, however, have seldom been reported. Therefore, transformation of crystalline SiO_2, one of the most popular ceramics, to the amorphous state by shearing at high pressure is the subject of this paper.

EXPERIMENTAL PROCEDURE

An α-quartz plate, 1 mm thick, was cut off from a natural single crystal parallel to (100) using a diamond wheel. The surface was subsequently polished with a diamond file to form the specimen shown in Figure 1. The specimen was put between two alumina rods tapered at one end (by π/4 rad) and inserted into a magnesia octahedron as shown in Figure 2 (Lawlis et al. 1998). The pressure around the octahedron was then increased at the rate of 1 GPa per hour to 5 GPa. After maintaining this pressure for one hour, the pressure was lowered at the rate of 1 GPa per hour to the atmospheric pressure. While the pressure was increasing, the specimen was sheared in the [001] direction. After a lapse of about three months from the time of the shearing, a transmission X-ray diffraction pattern was obtained from a sheared specimen (target: Mo; filter: 0.1 mm thick Zr; collimator aperture: 1.0 mm; tube voltage: 40 kV; tube current: 40 mA; exposure time: 10 h; specimen to imaging plate distance: 50 mm) using an imaging plate.

Specimen thinning for taking the diffraction patterns was accomplished by polishing with a metal-bonded diamond (average grain size: 30 μm) board. To determine the densest radii of halo rings in the diffraction pattern, about 30 radial density distributions were taken for each one and averaged, because they were extremely faint and imperfect in spite of the fact that the pattern was taken after a long exposure time on an imaging plate that is several dozen times as sensitive as X-ray film.

To obtain further information, Raman spectra were obtained from both the sheared specimen and the original unsheared one in triple subtractive mode using a spectroscope with resolving power of 100 μm. The spectrum from the sheared specimen was made up of 10 individual spectra; the direction from which each spectrum was obtained was successively shifted by 10° in the horizontal direction. Exposure time was 30 s. An objective lens with 100 magnification was used and for excitation 514.5 nm oscillation lines of an Ar-ion laser was used at a power level of 5 mW at the specimens.

RESULTS AND DISCUSSION

The shearing largely elongated the specimen only in the sheared direction ([001] direction), resulting in reduction of the thickness to about 70% of the initial value. The color of the sample changed from transparent and colorless to opaque milk white. Figure 3 shows a transmission X-ray diffraction pattern taken from the sheared specimen. We see five broad rings, although some are very faint and only a part of them can be seen on the printed page. Only the unusually long exposure time and the high sensitivity of the imaging plate made it possible

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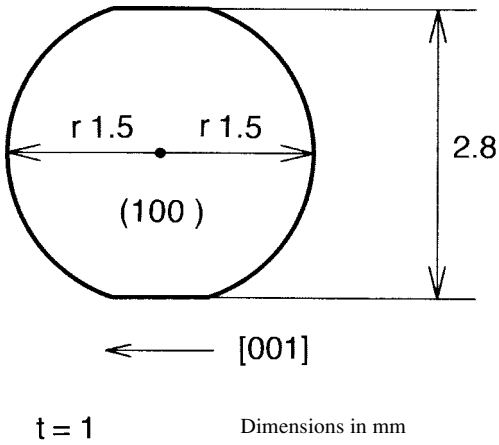

FIGURE 1. Specimen to be sheared.

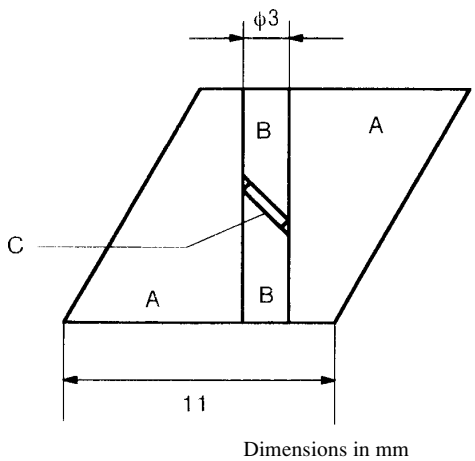

FIGURE 2. Schematic drawing showing the shearing mechanism at high pressure; A = magnesia octahedron in high hydrostatic pressure, B = alumina rod, C = specimen. ϕ signifies cylindrical hole.

to photograph them.

According to Scherrer's equation, $D = K\lambda/\beta\cos\theta$, the breadth of a ring (β) is in reverse proportion to $\cos\theta$, where θ is the Bragg angle, D is the crystallite size, λ is the X-ray wavelength, and K is a constant. In transmission X-ray diffraction patterns $\cos\theta$ decreases with θ, where $0 \leq \theta \leq \pi/4$. As clearly seen in the diffraction pattern, the third-smallest ring is much broader than the second-smallest ring. This is in conflict with Scherrer's equation. We also estimated the strain necessary to broaden the rings from the breadth of the second smallest ring; the smallest ring is very faint. The breadth of the former ring is about 2 mm, the wavelength of the X-rays used was about 70.93 pm, the interplanar spacing corresponding to the densest radius of this ring was, as mentioned below, 172.7 pm, and the specimen-imaging plate distance was 50 mm. The Bragg angle (θ) and $\Delta\theta$ calculated from these values were approximately 0.21

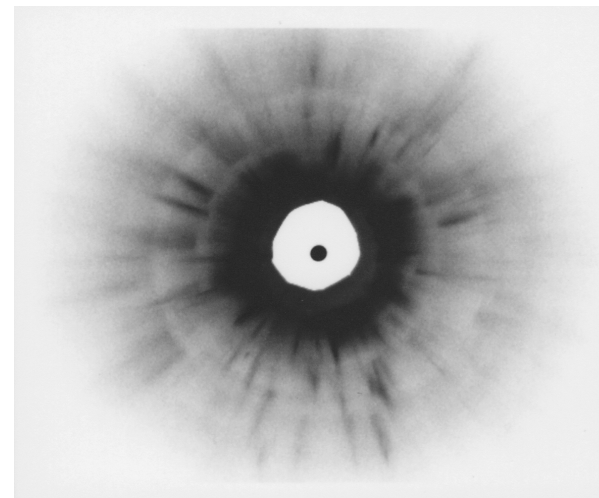

FIGURE 3. Transmission X-ray diffraction pattern.In spite of the fact that the pattern was taken after a long exposure time on an imaging plate that is much more sensitive than X-ray films, the rings in the print are extremely vague and faint, so they may not be clearly seen in this print.

and 0.03 rad, respectively. By substituting these values for $\Delta d/d = -\cot\theta * \Delta\theta$, we determined the necessary strain to be about 0.15. This value is high enough to crack SiO_2 to release residual stress. Accordingly, neither fine crystallite size nor the residual strain can be the main cause of the broad breadth of the rings.

The spacings corresponding to the densest radii of the halo rings are 283.0, 172.7, 145.6, 129.8, and 112.9 pm. The ratios of the largest spacing to the others are 0.610, 0.514, 0.459, and 0.399, respectively. They are almost equal to those of the interplanar spacing of the (111) plane to the interplanar spacings of the (220), (311), (400), and (331) planes of a cubic lattice. This set of rings appears from a solid consistent with the *Fd3m* space group. No JCPDS file of silicon oxides corresponds to Figure 3. We may, therefore, consider the state of Figure 3 different from those previously reported. These facts suggest that α-quartz transformed to a largely disordered state based on a solid structure consistent with *Fd3m* space group.

Figure 4 shows Raman spectra obtained from the original unsheared α-quartz sample and the sheared one. By comparing these spectra, we see that one of the peaks (arrow A) disappeared, the intensities of some peaks were reduced, some peaks were broadened, and a new peak (arrow B) appeared in the sheared spectrum. These changes indicate the transformation of α-quartz to another structure or state.

The main change in the Raman spectra of α-quartz and coesite with high hydrostatic pressure is a shifting of the peaks (Hemsley 1987); the disappearance of peaks as shown in Figure 4 does not occur at high hydrostatic pressure. The spectrum shown in Figure 4b is different from that of quartz glass. All the peaks in these spectra are low and wide. These facts indicate the formation of a previously unreported form of disordered SiO_2.

Atoms in ceramics irreversibly shift by severe dry rubbing

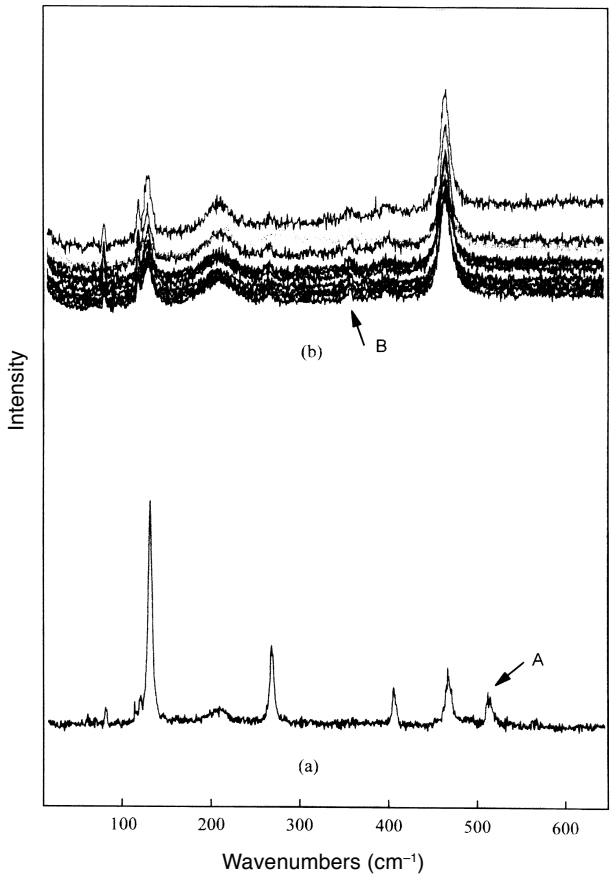

FIGURE 4. Raman spectra of SiO_2 before (**a**) and after (**b**) shearing.

(Furuichi et al. 1995). Rubbing accompanies shearing. In the process of rubbing, high pressures ought to arise when minute projections on a friction surface of a specimen make contact with those of a slider surface. We cannot deny the possibility that this kind of damage occurred in the sample sheared at high pressure. The shifting mentioned above is, in most cases, asymmetric. This brings about a lack of regularity among lattice planes. What is more, some lattice planes disappear due to the shifting. This state is too disordered to be called crystalline (Furuichi and Matsura 1997; Furuichi et al. 1997, 2000).

The term "amorphous" originated to express the disordered state of a friction surface (Finch and Quarrell 1936). Many scientists and engineers take "non-crystalline" to mean "amorphous". It may be reasonable, therefore, to think that the X-ray diffraction pattern and the Raman spectra mentioned above suggest the transformation of α-quartz to amorphous SiO_2 based on a solid structure consistent with space group $Fd3m$.

The diffraction pattern was taken about three months after the shearing. We may say that the amorphous state mentioned above remains at atmospheric pressure.

To our regret, we could not take transmission electron diffraction pattern (TEM diffraction pattern) because the sheared specimen broke into pieces during the process of sample thinning, perhaps due to residual stress.

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