New High-Pressure Transformation in $\alpha$-Quartz

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Recent experimental and theoretical studies report that quenched pressure-amorphized $\alpha$-quartz is elastically anisotropic and displays a reversal of anisotropy with respect to the original crystallographic orientation. We demonstrate that samples recovered from static compression experiments of $\alpha$-quartz exhibit an unusual pressure-induced microstructure, which arises from a new phase transformation in $\alpha$-quartz at 21 GPa. Upon decompression, the high-pressure phase reverts to a quartzlike structure in a twinned state, accounting for the previously reported elastic behavior.

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The unusual high-pressure behavior of the SiO$_2$ polymorph $\alpha$-quartz and its structural analogs has been the subject of recent experimental [1–12] and theoretical [13–20] investigations. Potentially anomalous properties of the material recovered from high pressure have been of particular interest [1–3,18,20]. Hemley [1] reported pressure-induced amorphization of $\alpha$-quartz and observed amorphous material in samples quenched from above 30 GPa. Kruger and Jeanloz [2] reported unusual behavior of pressure-quenched samples of $\alpha$-berlinite (AlPO$_4$, isostructural with $\alpha$-quartz). This material becomes x-ray amorphous at 18 GPa, but upon quenching was found to recrystallize in the structure and orientation of the original crystal. McNeil and Grimsditch [3] measured Brillouin scattering from single crystals of oriented $\alpha$-quartz to maximum pressures of 25 GPa. Upon decompression of the pressure-amorphized material, significant anisotropy was found in the frequency shifts measured parallel and perpendicular to the c axis of the original quartz crystal. Although there seemed to be a “memory” of the crystallographic orientation of the quartz, frequency shifts of longitudinal waves measured perpendicular to the original c axis after quenching were greater than the parallel values, which is the opposite of measurements made of the starting material. On the basis of these observations and Raman measurements of the quenched samples, it was inferred that an anisotropic amorphous solid had been formed by pressure for the first time, and the quenched phase exhibited a reversal of elastic “sign” with respect to the original quartz crystallographic orientation. These conjectures are of considerable theoretical interest, because the quenched material is claimed to be amorphous (lacking long-range order) (e.g., [19,20]).

For example, a recent molecular dynamics (MD) calculation appears to have found support for this proposal [20]. In this Letter, we document a new crystalline-crystalline phase transformation in $\alpha$-quartz that occurs at 21 GPa when the material is statically compressed at room temperature. We demonstrate that the anisotropy of material quenched from quasi-hydrostatic compression is controlled by this transformation and is not that of an amorphous solid.

It is now established that when pressurized well outside of its stability field at 300 K, $\alpha$-quartz gradually transforms to an amorphous state [1,3–5,7,8]. Despite the growing number of investigations, no detailed in situ structural studies near the onset of amorphization have been reported. This is essential for understanding the origin of the previously reported anomalous behavior [3]. We have examined the high-pressure behavior of $\alpha$-quartz under static compression using in situ synchrotron x-ray diffraction, as well as Raman scattering and optical microscopy. To examine the reproducibility of transitions occurring under different sample conditions and degrees of hydrostaticity, over ten powder samples and twelve single crystals of natural quartz were compressed in a Mao-Bell megabar-type diamond-anvil cell (as in previous work [17]) using a variety of pressure media, including neon, argon, and a 4:1 methanol-ethanol mixture. Samples were monitored visually during decompression, and quenched products were examined using electron diffraction and transmission electron microscopy (TEM), optical microscopy, and Raman spectroscopy.

Diffraction techniques are essential for characterizing the structural state of materials, specifically long-range translational order. Upon quasi-hydrostatic compression in a neon medium, we found that polycrystalline $\alpha$-quartz diffracts synchrotron x-ray radiation to about 20 GPa (Fig. 1). Hexagonal unit-cell parameters refined from low-angle peaks in patterns collected below this pressure agree well with other structural studies of compressed quartz [7,8,21]. With continued room-temperature compression, there is a sudden loss of the quartz 110, 210, 211, and 113 peaks, a shift of the quartz 100, 101, 102, 202, 203, and 212 interplanar spacings, and the simultaneous appearance of new peaks at 3.66, 2.66, and 1.48 Å. Similar changes are observed in this pressure range during static compression of polycrystalline quartz with no medium. We also find a sharp change in the character of the Raman spectrum at 21 GPa, marked by weakening and broadening of the $\alpha$-quartz $A_1$ modes with the simultaneous weakening and ultimate disappearance of the $E$ modes, consistent with previous results [1,4,11]. Although this has generally been interpreted as being asso-
FIG. 1. (a) Interplanar spacings \( (d) \), and (b) representative energy-dispersive synchrotron x-ray diffraction spectra from quasihydrostatic compression of polycrystalline \( \alpha \)-quartz. Open circles and Q symbols correspond to quartz diffraction, solid circles and Q' represent shifted quartzlike peaks, and solid squares and * depict new nonquartz peaks. Diffraction from neon (Ne), the pressure medium, and ruby (R) serve to calibrate pressure. Data were collected on beam line X-17C of the National Synchrotron Light Source, Brookhaven National Laboratory. The apparent increase with pressure of the interplanar spacing around 3.8 Å may arise from uncertainty associated with determining positions of diffraction peaks of the high-pressure phase. All quartz samples obtained from the U.S. National Museum of Natural History (sample R17701).

FIG. 2. Electron diffraction patterns from a recovered single-crystal sample experiencing compression to 22.8 GPa (argon medium). Extra spots are seen at (a) \( \frac{1}{2} \{122\}^* \) of a \{210\} zone axis pattern, and (b) \( \frac{1}{2} \{012\}^* \) of a \{211\} zone axis pattern. The single crystal for this experiment was obtained from a polished thin section of quartz cut parallel to \{001\}. After compression, the sample was crushed for TEM examination. All electron microscopy was performed at the Johns Hopkins high resolution TEM facilities with a Philips 420 TEM equipped with a SuperTwin objective lens and operated at 120 keV.

Distinct, nonquartz intensities are detected along various reciprocal lattice directions between primary quartz spots in patterns from some of the quenched grains (Fig. 2). Because these extra spots are sharp and correspond to integral multiples of the primary quartz translations (3 times), they are evidence of a superstructure. Such superstructures do not occur in normal, well-crystallized quartz [22].

An additional technique, complementary to diffraction, is provided by conventional polarizing light microscopy, which allows for the determination of optical character and large-scale microstructure of samples both within the diamond cell and after quenching. In each experiment, a distinct change in the character of the quartz samples preceded the changes at 21 GPa in the x-ray diffraction and Raman spectra. For the polycrystalline samples (grain size \(< 5 \mu m \) ), there was a change in contrast between the sample and the pressure medium. In single crystals, there is a similar contrast change and the sudden appearance of one or more sets of parallel birefringent planes, as reported previously [4,23]. The boundaries of these features lie parallel to rational crystallographic planes of the original quartz crystal, and the orientations are reproducible in multiple experiments, with \{100\} being most common. The planar features are quenchable,
and at ambient conditions they are found by optical microscopy to be either amorphous or crystalline lamellae (e.g., [4]). It is significant that different crystalline regions of recovered “single” crystals do not necessarily share optic axes (Fig. 3). While the crystalline lamellae of one parallel set generally have the same optical orientation, this orientation often differs from those of the bulk crystal and of other sets of lamellae. Electron diffraction reveals corresponding differences in crystallographic orientation. These observations of multiple crystallographic orientations within the once-homogeneous single quartz crystal demonstrate that the recovered sample is twinned [24].

From our single-crystal experiments, we find that varying proportions of the crystalline material in quenched samples share optic (and crystallographic) axes with the starting material. In other words, only certain areas have maintained a “memory” of the original quartz orientation upon decompression reversal of the high-pressure phase; the remaining crystalline regions differ in optical orientation. Elasticity, the manner in which a crystal deforms under stress, is described by a fourth-rank tensor, whereas the indices of refraction are described by a second-rank tensor (the optical indicatrix) [25]. The reversal of optic sign in regions of recovered samples implies a corresponding change in the elastic properties, consistent with previous observations [3].

Further compression of our samples beyond 21 GPa produces weak and broad glasslike bands in both the x-ray (Fig. 1) and Raman spectra, indicating that the new crystalline phase amorphizes, consistent with the lower-resolution x-ray studies reported previously [7]. We find that residual crystalline material is present in all samples quenched from between 15 and 30 GPa. Raman spectra of these quenched samples reveal bands originating from both amorphous and crystalline SiO₂, with frequency shifts resembling those of room-pressure quartz (Fig. 4). Only samples quenched from above 30 GPa are completely amorphous (isotropic) with respect to their properties measured by spectroscopic, optical, and TEM techniques [4,5,11]. We conclude that samples quenched from between 21 and 30 GPa experience a decompression transition from the new crystalline phase to a twinned quartz-like structure. This accounts for the previously reported anomalous elastic properties of the material and resolves the disparate measurements on quenched samples from quartz and berillium compression experiments. Both materials are crystalline, but quartz has become twinned due to the unexpected transition documented here. To explain their quenched “amorphous” SiO₂ with anisotropic elastic properties, McNeil and Grimsditch [3] suggested that coherent structural units, namely, the helical chains of SiO₄ tetrahedra that lie parallel to c of the quartz structure, are disordered in their stacking perpendicular

FIG. 3. Direct comparison of micron-scale optical observations with nanometer-scale microstructure and diffraction information obtained by TEM. Before compression, a polished thin section of [110] quartz was thinned by argon ion milling. A fragment containing a prethinned edge was optically characterized and then compressed to 23.6 GPa (neon medium). (a) An optical micrograph (crossed polars) of the recovered sample shows two orientations of large-scale (1–5 μm) lamellae; one set is parallel to (102) of the original quartz (horizontal), and the second set is at an angle to both the first set and the flat aspect of the sample. Use of an optical retardation plate indicates that crystalline and amorphous phases coexist in this sample, and the crystalline components of the two sets of lamellae differ in optical orientation (e.g., [4]). (b) A TEM micrograph obtained from the circled area in (a) shows fine-scale (10–50 nm) microstructure within a single optical lamella. The light bands are amorphous lamellae. (c) Selected-area electron-diffraction pattern from the same area indicates that the first set of crystalline lamellae are in the same crystallographic orientation as the original crystal.

FIG. 4. Raman spectrum of a single-crystal sample recovered from 25.6 GPa (argon medium) compared to spectra of SiO₂ glass and pristine quartz (intensities of the first two are magnified by a factor of 12 and 6, respectively). The samples used for the compression experiment and zero-pressure quartz measurement were obtained from a polished [110] thin section of quartz. The spectra were measured in backscattering geometry with 514.5-nm excitation using a Dilor XY spectrograph equipped with a charge-coupled-device detector.
to c, a conjecture supported by MD calculations [20]. Our study demonstrates that the effects are from microstructural changes rather than disorder on a unit-cell scale (which would not be evident in a MD simulation with finite box size). In other words, considerable long-range order exists in samples recovered from quasihydrostatic experiments, if the maximum static pressures remain below 30 GPa [26].

Finally, our study documents the existence of a metastable crystalline-crystalline transformation in quartz occurring prior to or during amorphization. Previous studies indicate that metastable transitions also occur in the silica polymorphs coesite [1,7] and cristobalite [27]. We suggest that the newly observed quartz transition is first order, perhaps involving order-disorder, and could have some parallels to the high-temperature α-β transition and the associated transition to the incommensurate phase [28]. Amorphization of the new high-pressure crystalline phase occurs with increasing pressure beyond 21 GPa, and thus the new transition may be viewed as an intermediate stage in amorphization. Additionally, the new phase most likely experiences partial decomposition amorphization. The mechanisms of these amorphization transformations may differ from that induced by large shear stresses. Thus, solid-state pressure-induced amorphization can be achieved by several pathways and may be controlled by different mechanisms.

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[22] The only reports of extra spots in quartz electron diffraction patterns are from studies of the microcrystalline variety (chalcedony), which is deposited from aqueous solution. These nonquartz spots can originate from the intersection of streak systems from planar stacking disorder, or may be true diffraction maxima, originating from a silica polymorph found to be abundant in microcrystalline quartz [G. Meihe, H. Graetch, and O. W. Florke, Phys. Chem. Minerals 10, 197 (1984); P. J. Heaney and J. E. Post, Science 255, 441 (1992); P. J. Heaney, D. R. Veblen, and J. E. Post, Am. Mineral. (to be published)].
[23] This change occurs at slightly different pressures depending upon the medium and crystal orientation. Hence, there appears to be a weak, but measurable, dependence on shear stress across the sample, even in nominally quasihydrostatic media such as rare gas solids.
[24] We conclude that twinning is not the origin of the extra nonquartz spots in electron diffraction patterns (Fig. 2) because the twinning observed is on a nanometer to micrometer scale and the nonquartz intensities are sharp with no streaking. See P. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley, and M. J. Whelan, *Electron Microscopy of Thin Crystals* (Robert E. Krieger, Malabar, FL, 1977), 2nd ed.
[26] In our quasihydrostatic experiments, sample thickness was always less than the gasket thickness to avoid bridging. This is significant because shear stresses as low as 4 GPa have been demonstrated to drive quartz amorphization [4]. The presence of shear stresses may produce a more rapid densification of amorphous material, which could give rise to anomalous sound velocities reported in previous compression experiments. The effects of uniaxial compression on the new 21 GPa phase transition are unknown.
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