A New Phase and Pressure Induced Amorphization in Silica

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Using first principles variable cell shape molecular dynamics, we predict a new structure for silica. This structure results from annealing α-quartz at pressures near a major phonon instability. The new phase is obtained by rotations of SiO_4 tetrahedra producing edge-sharing SiO_6 octahedra and SiO_5 cuboids. This type of mechanism was proposed to account for structural transitions in silicate melts and amorphous solids under pressure. Here this mechanism is observed in a crystalline to crystalline phase transformation for the first time. The diffraction pattern of the new phase compares favorably with that of the unidentified intermediate crystalline phase found in silica during the amorphization. [S0031-9007(98)05382-4]

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Although pressure induced amorphization occurs in a wide variety of solids [1], it remains a poorly understood phenomenon. Our Letter is concerned with a crystal-to-crystal phase transformation which occurs in quartz before it amorphizes at room temperature under pressure. These crystal-to-crystal and eventual amorphization transformations involve metastable phases with the nature of the intermediate crystalline phase being unknown. Diamond anvil cell experiments in quartz have shown that the amorphous phase develops out of this intermediate crystalline phase [2,3] There is great interest in clarifying the nature of this new phase and the role it might play in the amorphization process.

We show that the experimentally observed x-ray diffraction pattern of the intermediate crystalline phase compares favorably with that of a structure generated by first principles variable cell shape molecular dynamics (FP-VCS-MD) simulations of quartz near the onset of a major acoustic phonon softening. This phonon instability has been predicted by lattice dynamics calculations based on interatomic potentials [4–7] to occur at the K point of the Brillouin zone (BZ). Such calculations show a considerable softening of the *entire* lowest acoustic branch: the branch exhibits a dispersion of the order of kT when the instability occurs. Also, the softening of the acoustic branch is manifested as a shear instability in *ab initio* calculations of the Born mechanical stability criteria at similar pressures [7,8]. In pioneering molecular dynamics simulations of the quartz crystal-to-crystal transformation based on interatomic potentials, Somayazulu *et al.* [9] observed a transformation to a complex monoclinic phase; however, its x-ray diffraction pattern did not compare favorably with the experimental one. We find, instead, that a different structure which derives from the K-zone-edge phonon, and has higher symmetry, $P3_2$, quantitatively explains the experimental data on the new phase.

The stable phases of SiO_2 under pressure are quartz, coesite, and stishovite, in this order. At room temperature, the transformations to coesite (≈ 3 GPa) and stishovite (≈ 7 GPa) are kinetically inhibited. Consequently, quartz can be kept metastable up to 21 GPa [10]. This seems to be a common property of systems that have been observed to amorphize under pressure: the parent phase is driven far beyond its stability field before it amorphizes [1]. The experimental observations at the onset of amorphization in quartz are somewhat complex, but it is clear that around 21 GPa a new crystalline phase appears in a lamellar microstructure. The amorphous phase develops out of this new phase. As pressure increases, the amorphous regions grow and finally coalesce at pressures near 30 GPa [2]. Samples recovered from above 30 GPa appear to be entirely amorphous, while those recovered from below this pressure contained crystalline regions. This fact explained an amazing property of the apparently amorphous quartz: the pressure quenched phase, although amorphous as under x ray, displayed anisotropic elastic properties [11]. A closely related phenomenon also occurs in $AlPO_4$-berlinite [12,13], except that its pressure quenched phase seems to revert to the parent phase.

We note a strong parallel between experiment and theory. Experimentally, an intermediate crystalline phase appears from which the amorphous nucleates. Theoretically, the lowest acoustic state at the K point becomes unstable at a pressure around which the entire acoustic branch is characterized by soft modes. The identification of the intermediate crystalline phase, originating from the zone-edge instability, would suggest that a more generalized softening of the acoustic states is behind the gradual amorphization. The zone-edge eigenmode involves rotations of the SiO_4 tetrahedra and small distortions. As pointed out by Stolper and Ahrens [14], such rotations may provide extremely convenient paths for gradual coordination changes and densification in silicate melts, glasses, and possibly pressure induced amorphization.

We investigated this problem using FP-VCS-MD [15]. The calculations were performed within the local density approximation [16]. We used the Perdew-Zunger [17] parametrization of the Ceperley-Alder [18] exchange-correlation functional. Troullier-Martins pseudopotentials [19] were employed as in previous studies [8]. Likewise, the plane-wave energy cutoff was taken to be 64 Ry, and the Brillouin zone sampling for self-consistency included only the Γ point. Our runs started from an atomic configuration obtained after equilibrating quartz at 19 GPa and superimposing ionic displacements proportional to the normal mode amplitude of the lowest acoustic phonon at K [7]. The supercell contains 27 atoms. We optimized its geometry while compressing it to 33 GPa. The resulting structure was then annealed at 33 GPa at temperatures fluctuating between 300–600 K for 0.8 ps followed by a rapid quench to 0 K. The x-ray diffraction patterns of the structures, before and after the anneal differed (see Fig. 1) [20], suggest that considerable structural rearrangements occurred during the annealing process. Owing to the strong rearrangements, we followed this run with another anneal for an additional 0.8 ps at 300–600 K while compressing to 40 GPa and followed by another rapid quench to 0 K. The x-ray diffraction pattern after the second anneal was basically identical to the first one, which indicated that the structural rearrangement had proceeded to completion.

Before annealing the structure at 33 GPa, the resulting phase consisted of rotated and highly distorted SiO_4 tetrahedra. Alternatively, the structure could be described as containing SiO_6 octahedral and SiO_5 cuboid "embryos" inside which silicons retained four predominant nearest neighbors. This structure was 9% denser than quartz. After the anneal, silicons moved to the center of these polyhedra and became fully six- and fivefold coordinated. Its density was essentially the same, i.e., 10% denser than quartz. The final structure is contrasted to the quartz structure in Figs. 2 and 3. The final structure contains pairs of edge-sharing SiO_6 octahedra arranged in a double helix configuration with the branches of the helix touching each other and forming the triangular orange units shown in Fig. 3(b). These units are interlinked by highly distorted fivefold coordinated cuboids consisting of face-sharing tetrahedra [yellow polyhedra in Fig. 3(a)]. This type of fivefold site differs from those forming square pyramids recently found in a crystalline calcium silicate material at high temperatures and pressures [21], and obtained in simulations of quartz under nonhydrostatic pressure by Badro *et al.* [22].

The octahedral stishovite phase is the stable structure in the pressure range for which this new phase is found. Therefore, structures containing a certain fraction of silicons in octahedral sites should be more stable than phases containing silicons exclusively in tetrahedral sites. Presumably, the larger the fraction of octahedral sites, the more stable the structure is within this pressure range. Our new phase contains two-thirds (one-third) of silicons in sixfold (fivefold) sites. At 33 GPa, the enthalpy for the new structure is 0.10 eV/atom lower than for quartz; this difference increases to 0.13 eV/atom at 40 GPa.

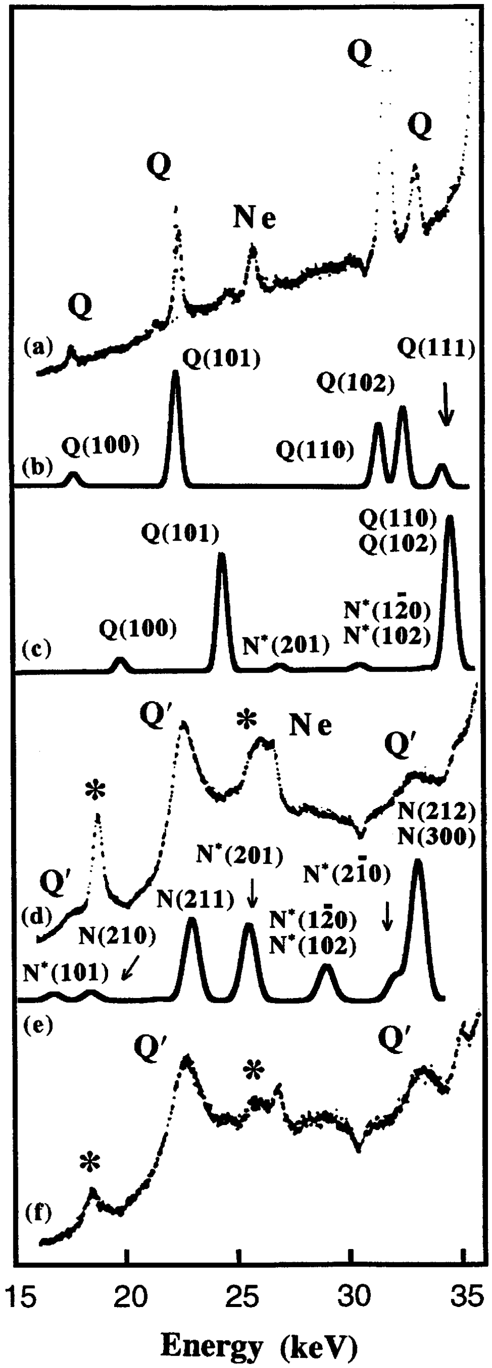

FIG. 1. Energy dispersive x-ray diffraction patterns. Quartz at 17 GPa obtained (*a*) experimentally and (*b*) in the present calculation (19 GPa). (*c*) Relaxed structure at 33 GPa after superimposing atomic displacements corresponding to the lowest acoustic phonon mode at the K point of the BZ on the structure shown in (*b*). (*d*) The intermediate crystalline phase found experimentally at 25.5 GPa. (*e*) The newly found phase obtained at 40 GPa after relaxation to 26 GPa. (*f*) The experimental spectrum at 27.4 GPa.

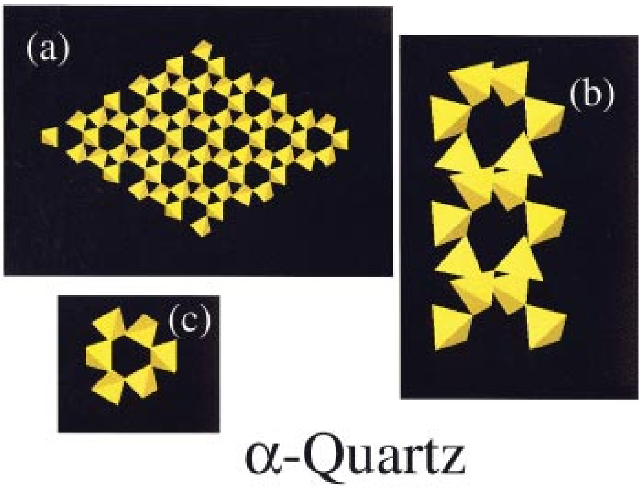

FIG. 2(color). Silica in the quartz structure at $P = 0$ GPa. (a) top view (along the **c** axis) of quartz, (b) side view of the tetrahedral double helix, and (c) its projection along the **c** axis.

Before the first anneal, the structure at 33 GPa had two-thirds of silicons fourfold coordinated inside distorted oxygen octahedra. Around these silicons, O-O separation distances varied from 2.4 to 2.9 Å. The four nearest neighbors are located at ≈1.57–1.62 Å, and the two next nearest neighbors between 2.35 and 2.53 Å. The remaining silicons had four neighbors at ≈1.59–1.62 Å and one more at 2.56 Å. The next neighbors are beyond 2.82 Å. This can be compared with quartz, which has four first neighbors at ≈1.60 Å and four second neighbors at 2.80 Å. Stishovite has six first neighbors ranging from 1.76 to 1.81 Å at zero pressure. In contrast, the final structure has sixfold Si1 and Si3 sites (see Table I) with neighbors located between 1.55 and 2.03 Å, and fivefold Si2 sites with neighbors located between 1.62 and 1.80 Å.

The predicted x-ray diffraction lines of the new phase are compared to the experimental observations at 25.5 and 27.4 GPa in Fig. 1. The comparison is made after decompressing the structure obtained at 40 GPa to 26 ± 3 GPa. Except for one peak at approximately 30 keV, we see a very good agreement between the theoretical and experimental spectra. This extra peak might exist, but it may be obscured in the experiment by the large background and low resolution within this pressure range. We have indexed the peaks with respect to the space group $P3_2$ which is a subgroup of the quartz space group $P3_121$. The only symmetry operations of quartz which remain in the new phase are the threefold screw rotations along the hexagonal c axis. The structural parameters for the phase are presented in Table I.

The number of atoms in our runs was chosen to accommodate the atomic configuration resulting from a particular phonon modulation at the K point of the BZ. Our results confirm the instability suggested by pair-potential calculations, giving evidence that the new phase derives from the zone-edge mode. It is possible that other structures might be found by considering different supercell geometries [23], as phonon instabilities occur at higher pressures across the entire lowest acoustic branch. However, the results in Fig. 1 show that the natural choice of a modulation corresponding to the soft K phonon leads to a structure which captures the main structural characteristics of the new phase.

The identification of this new crystalline phase can be interpreted as evidence that the driving force behind the amorphization in quartz is this mechanical instability, or alternatively, this major phonon softening of the entire acoustic branch (or sheet). Also, this picture provides evidence that the amorphous phase is produced by the type of mechanism that Stolper and Ahrens [14] predicted. This mechanism involves a continuous change of coordination as observed in silicate glasses and melts under pressure,

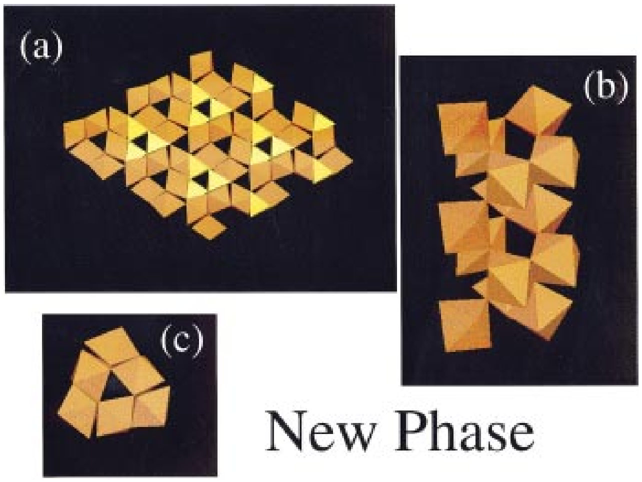

FIG. 3(color). Predicted new high pressure phase of quartz. (a) Top view of the new phase, (b) side view of the octahedral double helix, and (c) its projection along the **c** axis. Orange polyhedra correspond to oxygens in octahedral configuration. Silicons are off center and remain fourfold coordinated inside these octahedra. The tetrahedra in Fig. 2(b) and the octahedra in (b) surround the same cations (Si1 and Si3; see Table I) before and after the transformation; respectively. The remaining yellow tetrahedra in (a) are formed by oxygens surrounding Si2 sites.

TABLE I. Structural parameters of the newly found phase of silica with symmetry $P3_2$. The primitive cell vectors are, respectively, $\mathbf{a} = a/2\hat{x} - \sqrt{3}\,a/2\hat{y}$, $\mathbf{b} = a/2\hat{x} + \sqrt{3}\,a/2\hat{y}$, $\mathbf{c} = c\hat{z}$. At approximately 40 ± 3 GPa, $a = 6.84$ Å and $c = 4.81$ Å. This phase contains 9 Si atoms and 18 O atoms per unit cell located at the following Wyckoff sites: (u, v, w), $(-v, u - v, w + 2/3)$, $(-u + v, -u, w + 1/3)$.

	u	v	w
Si1	−0.301	0.131	−0.399
Si2	−0.229	−0.069	0.000
Si3	−0.634	−0.084	0.149
O1	−0.112	0.101	0.288
O2	−0.127	0.416	−0.438
O3	−0.093	0.425	0.053
O4	−0.083	0.154	−0.211
O5	0.151	−0.251	−0.641
O6	0.218	−0.253	−0.153

and possibly in pressure induced amorphization. Here we find this type of mechanism operating in a crystalline-to-crystalline phase transformation. Consistent with previous conjectures, we find that this type of transformation is initiated by rigid rotations of the tetrahedral units driven by a soft phonon that causes a volume collapse. This is followed by a structural rearrangement after annealing that involves mainly the motion of the Si atoms which lock in the final structure. To our knowledge, this is the first direct observation of a Stolper-Ahrens-type mechanism behind a phase transformation in a silicate.

The nature of this new phase suggests several tests that, in addition to further structural refinements, could verify the current picture. Change in coordination should be evident by Raman, infrared spectroscopy, or techniques that probe the local environment of silicon in the new phase. Besides, this phase is racemic and should display chiral properties. Our phase also offers an explanation for an important experimental observation: Similarly to the case of melts and glasses, the phase transformation involves mainly tetrahedral rotations and changes of coordination that proceed nearly continuously through easy paths. The backwards phase transformation should proceed as easily. The new high pressure phase should not be quenchable, as is observed [3].

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