

Structure of a New High Pressure Phase in α -Quartz Determined by Molecular Dynamics Studies

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(Received 18 January 1994)

Kingma *et al.* have recently reported the diffraction evidence of a new phase transition in α -quartz at 21 GPa. We use molecular dynamical calculations to show this phase to be the precursor on the way to amorphization. The powder x-ray patterns generated from the simulated structure show the emergence of superlattice peaks at ≈ 20 GPa. These predicted diffraction patterns are in excellent agreement with the experimental results and are indicative of a tripling of the unit cell in the **a-b** (basal) plane of α -quartz. In the pressure amorphized phase the calculated structure factor, $S(Q)$, is also in excellent agreement with the experimental results of Meade *et al.*

PACS numbers: 61.50.Ks, 61.43.Bn, 62.50.+p

The high pressure behavior of the α -quartz phase of SiO_2 has been a subject of extensive experimental [1–9] and theoretical [10–17] studies recently. α -quartz is known to transform to an amorphous phase between 20 and 30 GPa at 300 K [1, 3, 4, 6, 7]. A recent x-ray diffraction study of Kingma *et al.* [1] has shown that the pressure induced amorphization is preceded by another reversible phase transition at 21 GPa. This new phase is found to persist up to 30 GPa beyond which irreversible amorphization sets in. The transition at 21 GPa is accompanied by a loss of some of the strong diffraction lines of α -quartz and emergence of new lines at 3.66, 2.66, and 1.48 Å. Selective area transmission electron microscopy studies of samples decompressed from 22.8 GPa show extra diffraction spots at $\frac{1}{3}\langle 122 \rangle^*$ and $\frac{1}{3}\langle 012 \rangle^*$ in addition to the primary quartz reflections. The existence of this phase transformation has led one to doubt the cause of recovery of sound velocity along the *c* axis on decompression from 25 GPa as noted in the Brillouin scattering studies. Kingma *et al.* [1] attribute this to the reversibility of this new phase transformation. In this Letter, we use molecular dynamics (MD) simulations to explain the structure of this new phase.

Our present MD calculations use the pair potential parameters derived by Tsuneyuki *et al.* [10] based on the self-consistent Hartree-Fock calculations on model clusters of SiO_2 . This potential has been shown to reproduce the lattice constants of various equilibrium structures of SiO_2 within an accuracy of $\approx 5\%$, bulk modulus within 10%, and enthalpies within 1% of the experimental results [10]. The bond angles and bond lengths calculated using this potential [14] agree very well with the accurate *ab initio* calculations of Binggeli and Chelikowski [13]. In addition the calculated thermal expansion [10], the equation of state [16], as well as the phonon frequencies [18] are in excellent agreement with experimental data. In this paper we further explain two recent experimental observation using the same potential.

Present MD calculations were performed on a $3 \times 3 \times 3$ supercell of α -quartz consisting of 243 atoms. Details

of the calculations have been reported earlier [14, 16, 19]. Starting from ambient pressure, the pressure was raised in steps of 5 GPa except in the vicinity of 20 GPa, where finer steps were used. For each pressure, the simulations were performed until equilibration (≈ 1 psec). At 20 GPa the equilibration took almost 5 psec and a new structure emerged as a function of time. The coordinates of the super cell averaged over 200 time steps (for 0.002 psec) were used to generate the x-ray diffraction patterns. These were calculated using a powder diffraction program modified appropriately for an energy dispersive x-ray diffraction [20]. Standard x-ray scattering factors [21] of Si^{4+} and O were used. Our simulated diffraction profiles in the *d* range of 1–5 Å, before and after the phase transition at 20 GPa are shown in Fig. 1. The qualitative agreement of our simulation studies with the experimental observations of Kingma *et al.* [1] is excellent as is evident from Fig. 2, wherein

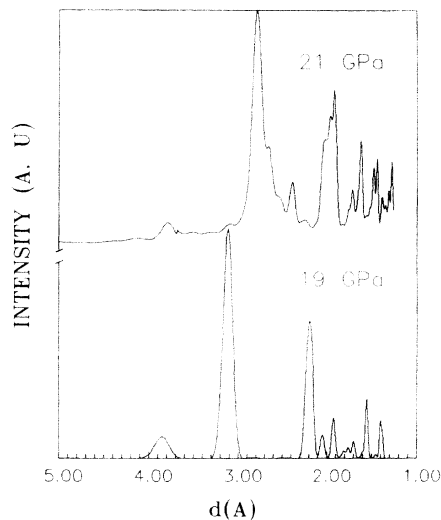


FIG. 1. Calculated diffraction patterns just before the phase transformation and immediately after, at 19 and 21 GPa, respectively.

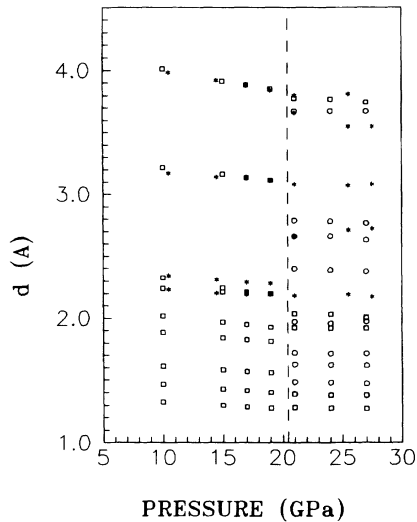


FIG. 2. Calculated variation of the d spacing of the diffraction lines in the range of 1–5 Å as a function of pressure. The α -quartz peaks are shown by \square , while the non-quartz-like peaks are shown by \circ . The data of Kingma *et al.* [1] are also shown for comparison (*). It may be noted that the diffraction data of Kingma *et al.* are restricted to the range 2–4 Å.

we have plotted the variation of d spacings with increasing pressure. Their experimental data reported for the range 2–4 Å are also presented for comparison. In addition to the diffraction lines observed by Kingma *et al.* [1], we also obtain peaks at 2.39 and 2.03 Å. The peak at 2.03 Å overlaps with the diffraction peak from the pressure transmitter [1]. The diffraction peak at 2.39 Å is expected to have an intensity which is roughly 25% of the strong peak at 2.8 Å and occurs in a region having substantially high background in the experiment of Kingma *et al.* [1]. It can also be absent because of texture effects. The reported diffraction pattern in the α -quartz phase shows effects of preferred orientations as the intensity ratio $I^{(110)}/I^{(101)}$ is greater than 1 in contrast to our calculated true powder profile. In diamond cell work, texture is known to be mostly present. In the present case, it may be affirmed by the differences in the relative intensities of the two experimental diffraction patterns for α -quartz phase reported by the same group [1,3]. Since the instrumental parameters of the synchrotron radiation employed by Kingma *et al.* are not available, we were not able to appropriately adjust the background in our powder profiles. Further experimental verification of the predicted diffraction peaks in the region 1–2 Å would be useful in testing our simulation. Table I shows the indexing of these diffraction peaks at 21 GPa based on the original quartz unit cell. All the new non-quartz-like peaks correspond to integral multiples of $(\frac{1}{3}, \frac{1}{3}, 0)$. This implies that these new diffraction lines are superlattice reflections indica-

TABLE I. Calculated d spacings at 21 GPa, and their indices with respect to the MD unit cell of α -quartz, which gets distorted to $a = 3.87$, $b = 4.31$, $c = 5.11$ Å, $\alpha = 83.2^\circ$, $\beta = 83.8^\circ$, and $\gamma = 117.4^\circ$, at this pressure. However, the pattern can also be well indexed with a monoclinic cell with $\mathbf{a}' = \mathbf{a} + 2\mathbf{b}$, $\mathbf{b}' = 3\mathbf{b}$, $\mathbf{c}' = \mathbf{c}$ (where the primed axes refer to the monoclinic cell of symmetry $P2$) and the interaxial angles approximated to $\alpha = \beta = 90^\circ$.

d (Å)	(hkl)
3.775	100
3.674	$\frac{2}{3} \frac{2}{3} 1$
2.788	101
2.664	$\frac{4}{3} \frac{2}{3} 1$
2.557	$\frac{1}{3} \frac{1}{3} 2$
2.398	$1 \frac{2}{3} 1$
2.254	$\frac{1}{3} \frac{4}{3} 1$
2.034	102
1.970	$\frac{4}{3} \frac{2}{3} 2$
1.922	020
1.720	021
1.626	$\frac{1}{3} \frac{5}{3} 2$
1.485	$\frac{5}{3} \frac{2}{3} \bar{1}$
1.445	022
1.388	113
1.312	212

tive of a cell tripling along the a_q and b_q directions of quartz. It is interesting to point out that Chaplot and Sikka [22] have recently proposed softening of a [110] mode of α -quartz at $(\frac{1}{3}, \frac{1}{3}, 0)$ (along the $K\Gamma$ direction in the Brillouin zone) and the present supercell structure is in agreement with this proposal. From the tables of Stokes and Hatch [23] for $P3_121$ (space group 144), we find that the possible subduced space group symmetries are $P3_12$, $P3_1$, $C2$, or $P1$. Inspection of the basal plane atomic positions rules out $P3_1$ therefore implying that the new structure at 20 GPa is possibly $C2$ or $P2$. In fact all the diffraction lines can be consistently indexed with $P2$. The atomic displacements of Si are found to be rather small (typically 0.1 Å) as compared to oxygen displacements (typically 0.4 Å) indicating that the structural transition is most probably brought about by rotations of the tetrahedra. As there is no change in the translational periodicity along the c_q direction, we infer that the rotations are proba-

bly restricted to the planes perpendicular to the $[001]_q$ direction. Our MD calculations also show a shearing of the basal planes normal to the c_q axis. Further, as the pressure is raised in the calculation, the diffraction peaks broaden gradually with simultaneous increase in the overall incoherent scattered part. As we are dealing with one set of coordinates of the ensemble it is not yet possible to discern the exact pressure at which these diffraction peaks become unobservable. However, from the diffraction patterns generated from three cells along the c_q axis, it is noticed that the new phase becomes "x-ray diffraction amorphous" around 28 GPa.

It is being recognized increasingly that the pressure induced phase transitions are generally displacive and could involve multistep symmetry descent and ascent. The existence of this lower symmetry phase between the (ambient) trigonal and amorphous phases is consistent with this picture [24–26]. Thus, the monoclinic phase is a step towards the ultimate descent in space group symmetry, which is the amorphous phase.

The calculated x-ray structure factor $S(Q)$ in the amorphous phase at 28 and 47 GPa is shown in Fig. 3. The appearance of the diffraction peak at 3.16 \AA^{-1} at the cost of the peak at 1.8 \AA^{-1} which shifts to $\approx 2.2 \text{ \AA}^{-1}$ is clearly seen at 28 GPa and is in complete agreement with experimental results of Meade *et al.* [2]. Further, this shift is associated with the change in Si coordination from 4 to 6. It is interesting to note that this $S(Q)$ for fused silica has been reproduced by Jin *et al.* [17] also. It should be noted that Jin

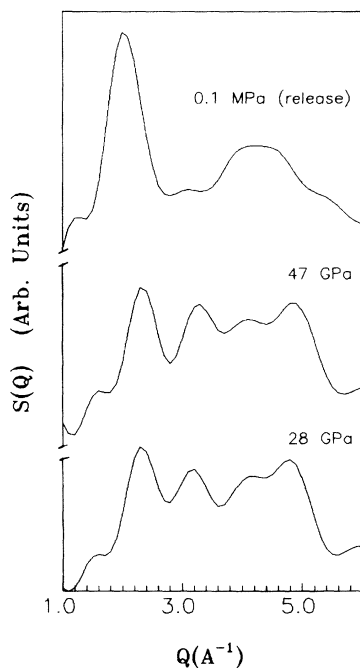


FIG. 3. Calculated $S(Q)$ at 28 and 47 GPa, and after the pressure release.

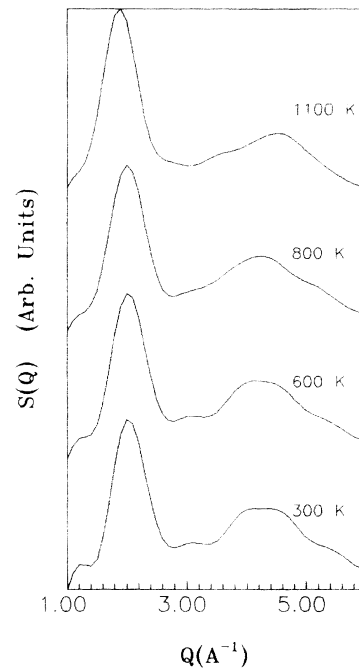


FIG. 4. Calculated $S(Q)$ of the retrieved glass as a function of temperature.

et al. have simulated an isotropic silica glass while our simulation gives anisotropic glass from the crystalline quartz. This similarity in the $S(Q)$ of the isotropic and the anisotropic amorphous phases implies that the mechanism of coordination change under pressure is similar in both cases. Our MD calculations [16] indicate that this anisotropy is retained even on complete release of pressure. However, if the temperature is raised to above 1100 K in this retrieved glass the anisotropy is completely destroyed. We have also calculated the $S(Q)$ of the retrieved amorphous phase as a function of increasing temperature and is shown in Fig. 4. The shift of the first diffraction peak back to 1.8 from 2.15 \AA^{-1} at $\approx 1100 \text{ K}$ is found to be coincident with the reversal in Si coordination from 6 to 4.

In conclusion, our MD studies on α -quartz are consistent with the x-ray diffraction results of Kingma *et al.* [1] and Meade *et al.* [4] and provide a possible structural model of the new phase. Also this Letter shows the utility of MD simulations to determine the structure when it is not easily determinable from a limited diffraction data set.

The authors acknowledge useful discussions with Dr. S. L. Chaplot.

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