Dynamical instabilities in α -quartz and α -berlinite: A mechanism for amorphization

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Elastic instabilities have been used to explain the occurrence of amorphization in both α -quartz (SiO₂) and α -berlinite (AlPO₄). However, there is a dynamical instability at $(\frac{1}{3}, \frac{1}{3}, 0)$ in the Brillouin zone preceding the elastic instability for both structures which implies that distortion of a $3 \times 3 \times 1$ supercell will form a more stable crystal structure. Simulations of distorted supercells of size $3 \times 3 \times 1$ resulted in the collapse of the structures below the elastic instability pressures for both α -quartz and α -berlinite. A subtle difference between them was that the eigenvectors for phosphorus were smaller than those of silicon or aluminum and on "amorphization" the PO₄ units in α -berlinite remained completely intact with only the aluminum changing coordination. This resulted in amorphization around the PO₄ units with no P-O-P links formed and a return to a crystalline phase on the release of pressure for α -berlinite, which was not found in the simulations of α -quartz.

I. INTRODUCTION

Pressure-induced amorphization has been observed for a number of materials, although much of the work has focused on α -quartz. α -quartz amorphizes between 15 and 25 GPa,^{1,2} as shown by broad peaks in both Raman³ and x-ray diffraction studies,^{1,2} which are indistinguishable from measurements on fused silica.⁴ It does, however, remain anisotropic after amorphization.⁵

Kingma *et al.*⁶ observed superlattice reflections just prior to amorphization at 21 GPa, which is consistent with softmode phonons observed in computer simulations.^{7–9} Simulations have also observed an elastic instability^{8,10} indicated by a violation in the Born stability criteria,¹¹ and it has been suggested that the elastic instability is the driving force for amorphization. Molecular dynamics (MD) simulations have observed a different elastic instability, which has also been attributed to the amorphization.¹²

Transmission electron microscopy (TEM) studies have indicated that amorphization can occur via more than one mechanism.^{13,14} These show that amorphization can occur along planar defect features (PDF's) such as those observed in shock metamorphized quartz¹⁵ or as bulk amorphization. The precise mechanism depends on the extent to which the pressure is hydrostatic, bulk amorphization occurs with hydrostatic compression,¹⁶ and PDF amorphization occurs at lower pressure under non-hydrostatic conditions.^{1,13,16}

Materials isostructural with α -quartz, namely α -berlinite and α -GeO₂, have also been shown to amorphize at high pressure.^{13,17} However, α -berlinite behaves rather differently on the release of pressure. It not only recrystallizes but returns to the same crystallographic orientation,^{6,18} indicating that there must be some order in the amorphous phase not present in α -quartz.¹⁹

Static simulations of AlPO₄ have shown the same dynamical and elastic instability as observed for α -quartz.^{7,20} In addition, MD simulations have been able to observe amorphization and recrystallization^{7,21} in which the PO₄ units remain intact after amorphization.

However, there is still controversy surrounding the

mechanism of amorphization. The role of the dynamical and different elastic instabilities is confused, and the differences in the mechanism between α -quartz and α -berlinite have not been established. In this paper we use lattice dynamics to compare and contrast the dynamical instabilities and amorphization of α -quartz and α -berlinite to investigate these problems.

II. SIMULATION METHODS

The computer simulations presented were based on the Born model of solids in which potential models were used to simulate the forces acting between ions. The potentials used for both SiO_2 and $AIPO_4$ were derived by van Beest, Kramer, and van Santen²² using a combination of ab initio calculations on clusters of H_4XO_4 and experimental data on the structures and elastic properties.

We have performed a comparison of the dynamical instabilities of α -quartz and α -berlinite using the lattice dynamical code PARAPOCS.²³ This method has advantages over MD, which include the unambiguous identification of the point in the Brillouin zone where a vibrational mode softens and, hence, if the mode is away from the zone center, the supercell through which the transition will pass. When a soft mode was identified away from the zone center, the appropriate supercell, identified from the soft mode, was simulated and the mode analyzed by displacing the atoms along the eigenvectors. Energy minimization of the structures was performed, displacing the atoms and breaking the symmetry by applying small (<0.005) strains to the lattice vectors. The breaking of the symmetry was required to allow the ions to relax independently.

III. RESULTS AND DISCUSSION

 α -quartz and α -berlinite both show elastic instabilities when pressure is applied, violating the third Born stability criteria, at 25 GPa and 40 GPa, respectively, in agreement with Chelikowsky and Binggeli¹⁰ and Keskar, Chelikowsky, and Wentzcovitch.²⁰ In addition, preceding this we observe a dynamical instability at $(\frac{1}{3}, \frac{1}{3}, 0)$ in the Brillioun zone at 21.5

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FIG. 1. Phonon dispersion curves showing (a) the soft mode for α -quartz at 21.5 GPa, (b) the soft mode for α -berlinite at 29 GPa, (c) the imaginary phonon branch for α -quartz at 25 GPa, and (d) the imaginary phonon branch for α -berlinite at 40 GPa.

GPa and 29 GPa [Figs. 1(a) and 1(b)] for α -quartz and α -berlinite, respectively, with the frequency of the modes becoming imaginary at 21.7 GPa and 29.5 GPa, respectively. The calculated elastic instability is the result of the soft acoustic mode becoming imaginary across the whole phonon branch [Figs. 1(c) and 1(d)], i.e., the slope of the branch is negative at the γ point. However, the occurrence of a dynamical instability, where one of the phonon branches softens at one point in K space also indicates an unstable crystal structure. Indeed simulations of this type of unstable crystal structure are possible by constraining the size or symmetry of the simulation cell to prevent removal of this soft mode via relaxation. For example, molecular dynamics simulations on cells that are not multiples of the $3 \times 3 \times 1$ supercell identified here cannot access the soft mode at $(\frac{1}{3}, \frac{1}{3}, 0)$. In this case, amorphization will occur only when an accessible phonon point becomes soft, which happens at higher pressure, and, hence, the amorphization pressure will be overestimated. This will not be very significant for α -quartz because the relevant soft mode at 21.5 GPa reduces rapidly, becoming imaginary across the whole branch by 25 GPa (e.g., the amorphization pressure of 21.5 GPa obtained by Binggeli, Chelikowsky, and Wentzcovitch.24

In contrast, the soft mode for α -berlinite, which appears at 29 GPa, reduces mode slowly and only becomes negative across the whole branch at 40 GPa. There will thus be a more noticeable shift in the simulated amorphization pressure if the simulation cell is not a multiple of $3 \times 3 \times 1$. This is illustrated by the MD study of Tse and Klug,²¹ where the amorphization pressure is calculated to be 31 GPa for the $4 \times 4 \times 2$ cell used. This can be compared to the closest accessible K point $(\frac{1}{4}, \frac{1}{4}, 0)$, which becomes imaginary at 31.8 GPa.

The dynamically unstable mode at $(\frac{1}{3}, \frac{1}{3}, 0)$ indicates that the crystal may lower its energy by distorting its structure in a $3 \times 3 \times 1$ supercell, which is consistent with superlattice



FIG. 2. Structure of (a) crystalline α -quartz, (b) crystalline α -berlinite, (c) amorphized α -quartz, and (d) amorphized α -berlinite.

reflections observed by Kingma *et al.*⁶ in α -quartz. Animation of the vibrational mode in a $3 \times 3 \times 1$ supercell showed that the eigenvectors for the motion of the ions within this mode were similar for both structures. Both show rotation of the double chains forming the channels. A subtle difference between the eigenvectors for the two systems is that the phosphorus motion is smaller than that of the silicon or aluminum.

Simulations on the $3 \times 3 \times 1$ supercells with lowered symmetry resulted in collapse of the crystal structures and gave rise to amorphous cells (within the constraint of the simulation cell dimensions) for both α -quartz and α -berlinite. Very slightly different starting configurations results in the different pseudo amorphous cells. The crystalline structures of α -quartz and α -berlinite are shown in Figs. 2(a) and 2(b). Figure 2(c) shows a typical amorphous structure obtained after the collapse of α -quartz to an amorphous solid. In this case the remains of two of the initial four main channels can be seen. α -berlinite amorphized typically with more of the channel structure still visible with the remains of three of the four channels shown in a typical structure obtained [Fig. 2(d)]. The remains of the channel structure may give rise to the anisotropic behavior observed by McNeil and Grimsditch⁵ for α -quartz and by Itie *et al.*¹⁷ for α -belinite. The "amorphous" SiO₂ is typically 16% smaller than the crystalline cell, while the AlPO₄ is only 7% smaller, which is consistent with MD data^{7,21} and indicates that the volume reduction for ALPO₄ is smaller than that for SiO₂. Analysis of the static radial distribution functions (RDF's) showed differences for phosphorus compared to aluminum and silicon (Fig. 3). The phosphorus RDF shows a well-defined first coordination shell unlike silicon and aluminum, although all show a loss of long-range order. This was further demonstrated when the coordination of the atoms was considered. Silicon had a variety of high coordination with the majority 6 coordinate [Fig. 4(a)]. The aluminum had a wider variety of coordination, from 2 to 6, which on average (4.6) showed an increase over the initial 4 coordination. Phosphorus, however, showed only 4 coordination and had not changed on amorphization, although an extra long (approximately 2.00 Å) fifth oxygen atom can be observed for a few phosphorus atoms. In addition, it is noticeable that not only are the PO₄ intact but that they remain bonded to the same oxygen



FIG. 3. Static radial distribution functions for the amorphous cells, (a) silicon-oxygen, (b) aluminum-oxygen, and (c) phosphorus-oxygen.

atoms with no P-O-P links formed. This result is consistent with the MD work of Tse and Klug²¹ and Chaplot and Sikka⁷ and explains the observed sharper peaks in the phosphorus RDF.

The pressure on a typical quartz cell was raised to 30 GPa and then released in stages to monitor the energy and struc-



FIG. 4. Distribution of coordination numbers for (a) silicon and (b) aluminum.



FIG. 5. Energy as a function of release of pressure for (a) amorphized α -quartz and (b) amorphized α -berlinite.

ture as a function of release of pressure [Fig. 5(a)]. The lattice energy of the amorphous phases was less than that of the crystalline structure at the same pressure. However, the reduction in the volume on amorphization leads to a smaller pressure-volume (PV) term, and hence the enthalpy (lattice energy + PV) of the amorphous phase is more stable at high pressure [Figs. 5(a) and 5(b)]. On release of pressure the amorphous SiO₂ did not return to the α -quartz structure, although the amorphous phase was metastable with respect to α -quartz. This shows that above 9 GPa the amorphous cell is more stable than α -quartz, although it is not formed until the crystal structure can access the dynamical instability and does not return to the thermodynamically more stable α -quartz structure on release of this pressure but remains amorphous (Fig. 6).

The AlPO₄ behaved completely differently on the release of pressure. The structure remained amorphous down to 25 GPa, but the majority of simulation cells did not converge between 22.5 and 17.5 GPa. One cell did minimize and this produced an almost crystalline phase that only differed from pure AlPO₄ by a single Al interstitial. The activation energy for diffusing back to its lattice site was calculated to be approximately equal to the average kinetic energy available at 300 K. However, if the cells were minimized directly to 15 GPa, they returned to crystalline AlPO₄, indicated by the discontinuity in the energy on reduction of pressure [Fig. 5(b)]. This pressure range (22.5–17.5 GPa) matches closely the amorphous to crystalline transformation found on release of pressure using MD.⁷

The simulations showed a clear difference between the behavior of SiO_2 and $AIPO_4$ and the ability of $AIPO_4$ to



FIG. 6. Structure of amorphized α -quartz after the release of pressure.

return to its original crystal structure on release of pressure. It is likely that the preservation of the PO_4 tetrahedra combined with the lack of P-O-P bond formation on amorphization enabled the structure to return to the crystalline phase on the release of pressure.

IV. CONCLUSIONS

Soft vibrational modes were calculated for both α -quartz and α -berlinite at $(\frac{1}{3}, \frac{1}{3}, 0)$ in the Brillouin zone at 21.5 GPa and 29 GPa, respectively. The simulation results suggest that amorphization of both α -quartz and α -berlinite is the result of this dynamical instability rather than the elastic instabilities,^{8,10} which occurs at higher pressure as a consequence of the soft mode becoming imaginary across the

whole Brillouin zone. This is further demonstrated by the MD simulations of Tse and Klug²¹ using a $4 \times 4 \times 2$ supercell of AlPO₄ with the same potential model employed in this study. They found that amorphization occurred at 31 GPa, well below the elastic instability and slightly above the dynamical instability. The slightly higher pressure is the result of their simulation cell not being of the optimum size to access the soft mode at $(\frac{1}{3}, \frac{1}{3}, 0)$ and accessing instead the soft mode when it reached $(\frac{1}{4}, \frac{1}{4}, 0)$ at approximately 31 GPa.

Simulations on the $3 \times 3 \times 1$ supercells result in unit cells of amorphous character with increased and variable coordination number and bond length for silicon and aluminum. The eigenvectors of the vibrational mode differ in α -berlinite in that the phosphorus motion is much reduced in comparison with the silicon and aluminum and the amorphization. This resulted in the amorphous cells produced all having 4 coordinate phosphorus, while the silicon and aluminum vary up to 6 coordinate.

The simulation results indicated that, while the amorphization of α -quartz and α -berlinite are closely linked, they differed in that the phosphorus showed no coordination change and that this was responsible for the return of the structure to the crystalline phase as it effectively pinned the amorphous phase. This was demonstrated by the lack of P–O–P bonds indicating that the structure essentially amorphized around the PO₄ tetrahedron.

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