On finite-size effects in the simulation of high-pressure, quartz-like structures

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The stability of two recently suggested crystalline structures arising from compressing quartz is investigated. One phase, called quartz II, is obtained by compressing a model of quartz to pressures P slightly above 22 GPa. The second phase is obtained by shock compressing the quartz II sample to $P = 50$ GPa. The new structure is a modulated structure of quartz II and the corresponding phase is called quartz II_m. We observe strong size effects or compatibility effects above 26 GPa. If the initial system consists of 360 or 720 SiO_2 units, an 'ideal' quartz II structure remains stable up to 30 GPa, while a larger system of 864 SiO_2 units shows modulations of the quartz II structure when compressed above 28 GPa. On decompression from the 50 GPa sample, the larger system appears to be more stable than the smaller system, for which the incompatibility of the intrinsic modulation with the box geometry apparently leads to large fluctuations of the cell geometry.

I. INTRODUCTION

Pressure-induced phase transformations in silica, SiO_2, have been widely studied by fundamental solid state physicists and chemists and are of great interest because of its importance in material science and technology. As a result, experimental observations of a number of different high-pressure silica polymorphs yet unidentified have been reported within the last decade[1–7]. Despite its simple chemical composition, silica shows rich polymorphism at elevated pressures and temperatures. The details of the silicon distribution among free positions in the oxygen network strongly depends on the starting sample and the conditions of treatment, but a general trend is that at pressures above 40-45 GPa most of the silicon atoms occupy octahedral positions while the oxygen atoms form hcp sublattices. On the other side at ambient to moderate pressures, i.e. 9 GPa or less, silicon is typically tetrahedrally coordinated by oxygen. The first of the two cases mentioned above could be described as a concentration modulation of the silicon sublattice over the monoclinically distorted hcp oxygen sublattice. The existence of high kinetic barriers related to the transformations to octahedrally coordinated stable silica phases arise the coexistence of metastable low and high-pressure crystalline phases with amorphous forms[8–16].

Three years ago Haines et al.[5] found experimentally after fast compression of an initial α-quartz sample to 45 GPa the presence of a new crystalline phase later characterized by the symmetry group $P2_1/c$. Almost at the same time Dubrovinsky et al.[4] by compressing cristobalite XI at ambient temperatures obtained an α-PbO_2-type silica made of 2 x 2 kinked chains of SiO_6 octahedra with a very similar structure to the one reported by Haines et al.[5]. In a recent paper[17], the current and additional authors reported, after performing molecular dynamics simulations (MD) of quartz II under fast compression at 50 GPa, a new phase which was similar to quartz II but appeared to be modulated in a non-systematic fashion. This phase was called quartz II_m and

the speculation was that the system might want to have an incommensurate modulation of the lattice. These calculations are certainly very speculative, since they were based on model potentials that have been optimized for low-pressure SiO_2 (see discussion below). However, the analysis of the phase behaviour of a model potential often has an interest in its own right, among other reasons, because similar behaviour might be observed in systems with related coordination changes.

As stated, this new phase seems to be a modulated version of quartz II that was interpreted as a probably incommensurate modulation of the lattice, which is pinned. The long wavelength associated with the lattice modulation makes it unfeasible for ab-initio calculations to tackle the stability of quartz II_m. In the present manuscript a more extensive description of this new phase will be offered by analyzing the structure factor $S(E)$ and its mechanical stability by applying the Born criterion at finite pressures[18]. MD simulations based on the model potential proposed by van Beest, Kramer and van Santen (BKS)[19] were performed. While not being perfect, BKS shows good agreement when comparing the high-pressure structures generated by this simple potential to sophisticated potentials[20–22] and ab-initio simulations[11].

Since we speculated that the modulation in quartz II_m is incommensurate, it is necessary to analyze the effect of system size. Initial runs did not show any size dependence, but increasing the original quartz sample in the z direction revealed qualitative changes in the simulation results. The difference between runs of different system size is the subject of this paper. In the next section, we will quickly review the methods used and provide some details of the simulation runs. Section III presents the results and the conclusions can be found in section IV.

II. METHODS

In this study, standard MD techniques were implemented with the aid of the BKS model potential op-

timized for four-coordinate silicon. All the simulations were performed at constant external isotropic stress, kept constant within the Parinello-Rahman method[23] for the box dynamics. Small values of the box inertia were chosen to guarantee that the fluctuations of the box shape occurred on a barely larger time scale than those of the atoms. Moreover, the phase transformations reported here can only be observed if the box geometry is allowed to adjust quickly, because large box inertia lead to amorphization of the sample. We also want to note that a Langevin thermostat was used in order to always quickly find the next available energy minimum.

All 'samples' start out originally as α-quartz. In previous papers[17,18,22], the size of the boxes was typically chosen to be $6a$, $4\sqrt{3}a$, $5c$ in x, y, and z direction, respectively, or alternatively $5a$, $3\sqrt{3}a$, $4c$. Here a and c denote the two independent lattice constants of α-quartz. Between the two system sizes, no discrepancies in the simulations could be observed other than the 'typical' size effects, i.e., smaller systems smear out phase transitions more strongly than larger systems[24]. Here, we will also analyze a system with the initial size of $6a$, $4\sqrt{3}a$, $6c$, for which new behaviour is observed. In the following, we will only compare the $(6 \times 4 \times 5)$ box containing 2160 atoms and the $(6 \times 4 \times 6)$ cell containing 2592 atoms.

As was mentioned before constant temperature was maintained via a Langevin thermostat with coupling $\gamma = 4$ THz. The time step was chosen to be 1 fs and 10,000 steps used to equilibrate a sample after a pressure or temperature change. For more details, we refer to Ref. 24. The structure factor $S(E)$ was calculated following the definition that appears in the classical literature[25] capable of fitting the data reported within the International Tables for X-Ray Crystallography[26]. We tested our results by first reproducing some of those published by Wentzcovitch et al.[27].

III.   RESULTS

In a first step, using values for the temperature within the range 200K-300K, different α-quartz cells were exposed to high pressures following the path described by the current authors in a previous work[17] and an initial set of quartz II configurations was obtained at $P = 24$ GPa. Snapshots resulting from these runs are shown in Fig. 1. We want to note the small difference in the structure between the small system shown in part (a) and the large system shown in part (c). However, it seems to us, that these subtle differences cannot be resolved experimentally. The difference in the $S(E)$, which is shown in Fig. 2, is so small that we cannot resolve the difference graphically between the 28 GPa small system and the 28 GPa large system in its initial compression run.

After equilibration, a shock compression up to 50GPa was applied to each one of the quartz II configurations in a second step. As noted before, increasing the pressure quasi-adiabatically would have led to irreversible amor-
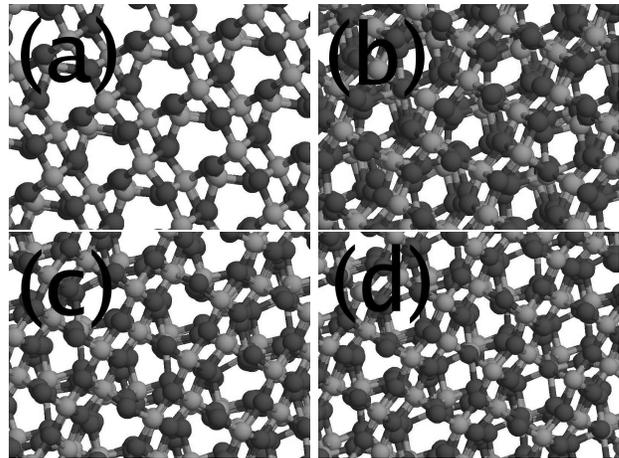
FIG. 1: (a) Snapshot of small system during compression or decompression at 28 GPa. (b) Small system after compression at 50 GPa. (c) Large system during compression at 28 GPa. (d) Large system at decompression from 50 GPa.

phization of the samples. The newly obtaining crystalline configuration were named quartz II_m type polymorphs in a previous paper[17]. They appear to be a local modulation of the quartz II structure. Their configurations at 50 GPa are shown in parts (b) and (d) of Fig. 1, each showing a fraction of the small and the large simulation cell, respectively.

There are no apparent, systematic differences in the structure visible to the eye, which can be seen more clearly when the full system is shown. We do not intend to show the full systems here for reasons of space. However, there are clear differences between the $S(E)$ for the small system at $P = 28$ GPa and the $S(E)$ of the large system after decompression at the same pressure. The differences show in particular at small wave vectors. Again, in the initial compression run coming from the α-quartz phase, the $S(E)$'s related to the small and the large system are almost identical to each other, while the structures differ slightly as evidenced in Fig. 1 (a) and (c). We want to note that at 50 GPa, the $S(E)$ of the two system sizes resemble each other very closely (and so do the radial distribution functions, which are not shown here). However, there is one characteristic discrepancy, namely the peaks related to a momentum transfer expressed as 3.0 keV and 6.0 keV don't show in the small system.

When calculating also the coordination of the silicon atoms by the oxygen atoms for each one of the phases new differences arise. While the initial quartz II samples for both systems are 1/3 four-coordinated, 2/3 six-coordinated, the quartz II_m systems at 50 GPa show a 1/9 five-coordination, 8/9 six-coordination. This coordination ratio changes after decompressing the former samples to 28 GPa, being the new relation 1/9 four-coordinated, 8/9 six-coordinated for the big system and 1/3 four-coordinated, 2/3 six-coordinated for the smaller
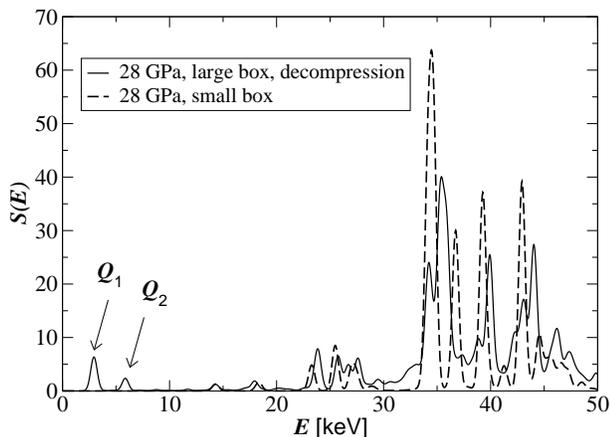
FIG. 2: Structure factor $S(E)$ for the small box (identical for compression and decompression run) and for the large box on decompression. Upon initial compression, $S(E)$ of the large system is almost identical to that of the small system. The peaks indicated with $\mathbf{Q}_1$ and $\mathbf{Q}_2$ correspond to the reciprocal lattice vectors $(0.0465, 0.0271, 0.2522)\mathring{A}^{-1}$ and $(0.5152, -0.0765, -0.0881)\mathring{A}^{-1}$ respectively.

FIG. 3: Equation of state for large box and small box. Both runs are decompression runs.

FIG. 4: Minimum eigenvalue of the Birch coefficients for the large and the small simulation cell as a function of pressure. Error bars are in the order of symbol size.

one.

Even though the difference in (free) enthalpy per atom $H = F + PV$ between the large and the small system is relatively small, i.e., in the order of 0.01 eV at 50 GPa, and much less different in the vicinity of 28 GPa, same with the Helmholtz free energy F, the volume V and the elastic properties show more striking effects. The $P(V)$ diagram is shown in Fig. 3 for the two system sizes. Apparently, the larger system is denser than the smaller one, however, the gain in PV is essentially compensated by an extra expense in additional potential energy. Note that the small system shows the transition back to quartz II at about 30 GPa, which can be tested also by checking the coordination numbers for the silicon atoms reported before; while the large system has a similar transition, also to quartz II, at a pressure that is about 6 GPa lower.

As discussed in a previous paper[17] by the current authors and collaborators, even when the molar volume of the decompressed quartz II at ambient conditions (17.8 $\pm$ 0.2 cm^3/mol) is similar to the molar volume of the $P2_1/c$ crystal reported by Haines et al.[5] (14.02 $\pm$ 0.12 cm^3/mol), the $S(E)$ are quite different for both cases. After performing the required comparison, it was shown that the quartz II obtained in our simulations reproduces the phase reported by Kingma et al.[6] instead of the one reported by Haines et al.

Lastly, we wish to discuss the elastic stability of the various samples. A sample is mechanically stable at zero pressure if the matrix of the elastic constants is positive definite, which is called the Born stability criterion. At finite pressures, the definition of elastic constants is not unique and the proper generalization of the Born crite-

rion is to require the positive definiteness of the matrix of the Birch coefficients. The smallest eigenvalue $B_{\min}$ of that matrix thus indicates whether the sample becomes mechanically unstable. Between the large and the small system, clear differences can be observed in Fig. 4. In particular, both systems show a dip near the transition, i.e., where the quartz II$_m$ structure reverts to the ideal quartz II structure. A final feature comes out when analyzing the $P(V)$ and $B_{\min}(P)$ diagrams simultaneously. As can be noticed whenever a discontinuity (jump) appears in the first graph a softening (dip) shows up in the second one for the same value of P.

IV. CONCLUSIONS

The stability of two recently suggested crystalline structures arising from compressing quartz-like structures was investigated by molecular dynamics (MD) simulations. One phase, called quartz II, is obtained by compressing adiabatically a model of quartz to P slightly above 22 GPa. The second phase is obtained by shock compressing quartz II to $P = 50$ GPa. The new phase has a slightly modulated structure, which we call quartz II_m. Two system sizes were compared in this study, i.e., one in which the original α-quartz simulation cell was chosen to be $6a$, $4\sqrt{3}a$, $5c$, where a and c are the two independent lattice constants of α-quartz, and another cell of length $6a$, $4\sqrt{3}a$, $6c$ along the x, y, and z axis, respectively. The first choice is referred to as the small system, the second choice as the large system. Smaller system sizes than the ones used here all show the same behaviour as that of the $6 \times 4 \times 5$ box. We conclude that any (dramatic) effect in the simulation results between the small and the large system can only be due to a compatibility issue, i.e., a modulation that the system wants to undergo intrinsically in the small system is prevented due to the interplay of periodic boundary conditions and system size.

Strong size effects are observed at P above 26 GPa. While both systems undergo the transition from α-quartz to quartz II at a similar pressure, the large system is starting to deform at approximately 28 GPa. The observed structure modulations are irreversible when the system is decompressed to smaller pressures. In both cases, it is not possible to increase P slowly from 30 GPa to higher values, because the samples amorphisize above 34 GPa. However, it is possible to shock compress the samples up to 50 GPa without loss of long-range periodic order. These structures can be decompressed adiabatically. While snapshots of the large and the small box look very similar, the small box misses two diffraction peaks at $\mathbf{Q}_1 = (0.0465, 0.0271, 0.2522)\mathring{A}^{-1}$ and $\mathbf{Q}_2 = (0.5152, -0.0765, -0.0881)\mathring{A}^{-1}$. The first wave vector would be parallel to the z axis, if the cell were not sheared with respect to the original α-quartz configuration. The associated wavelength is too long in order to fit into the small cell. Apparently, the mode associated with $\mathbf{Q}_1$ couples relatively strongly to the center of the Brillouin zone, because the equation of state as well as $B_{\min}$ show relatively strong differences between the small and the large system.

While we regard the analysis of the 50 GPa simulations more as a generic analysis than as a realistic simulation of SiO_2, we believe that the modulations of the structure seen up to 28 GPa may be realistic as they could be caused by electrostatic interactions. The former assumption is based on the results of an independent study able to show that BKS reproduces piezoelectric properties rather well[22], thus giving confidence to the choices of the effective charges associated with the silicon and oxygen ions.

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