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Orthorhombic quartzlike polymorph of silica: A molecular-dynamics simulation study

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Using molecular-dynamics simulations we have examined a quartzlike polymorph of silica, the structural analog of ice XII recently found in applied-field computer simulations of water [I. M. Svishchev and P. G. Kusalik, Phys. Rev. B **53**, 8815 (1996)]. This form of silica is built from continuous zig-zag chains of the SiO_4 tetrahedra similar to those found in the familiar hexagonal quartz structure and it retains the same valent Si-O distance as in hexagonal quartz, roughly 1.7 Å. Yet, the linkage pattern of the coordination polyhedra in the structure is such that it results in an orthorhombic, $Pnc2$, symmetry with 12 SiO_2 per unit cell. Under ambient conditions the density of the orthorhombic phase is roughly 5% higher than that of hexagonal quartz. This orthorhombic form of silica is found to be stable over a wide range of temperatures and pressures, up to 1500 K and 10 GPa, respectively. [S0163-1829(97)00802-3]

I. INTRODUCTION

Water and silica can be found in a variety of crystalline and amorphous forms which share the same linkage pattern of tetrahedrally coordinated oxygen or silicon atoms.[1,2] The familiar hexagonal and the metastable cubic modifications of ice I are isostructural, respectively, with tridymite and crystobalite, the low-density modifications of silica, while ice III is structurally similar to keatite. The crystalline structures of the high-density polymorphs of ice VI and VII, can be described as two interpenetrating tetrahedral networks of edingtonite and crystobalite type, respectively.
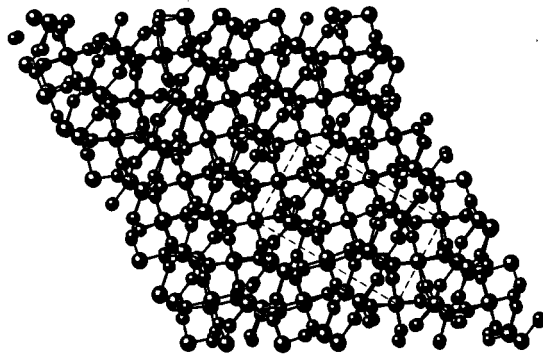
Among the crystalline forms of silica, quartz is the most common and important polymorph; its field of stability dominates the phase diagram for SiO_2 at low and moderate pressures.[3] Bernal and Fowler[4] originally proposed that quartzlike arrangements of H_2O molecules may occur among denser ice polymorphs and suggested that this may also account for some of the unusual physical-chemical properties of liquid water. Their hypothesis has never been confirmed experimentally; however, very recently the crystallization of a quartzlike form of ice (referred to as ice XII) has been observed in computer simulations of liquid water under pressure and subject to a static electric field.[5,6] One of the most interesting structural features of this form of ice is that it is built from continuous zig-zag chains of tetrahedrally coordinated oxygen atoms similar to those found for silica atoms in high quartz,[2] but their linkage pattern is such that it results in orthorhombic symmetry with 12 water molecules per unit cell.[5]

The purpose of this study is to investigate, using molecular-dynamics simulations, a SiO_2 polymorph with orthorhombic symmetry that is the structural analog of ice XII. In recent years computer simulations have been widely used to probe various silica structures, usually through the calculation of their mechanical stabilities with respect to temperature and pressure.[7–13] Research interest in this area
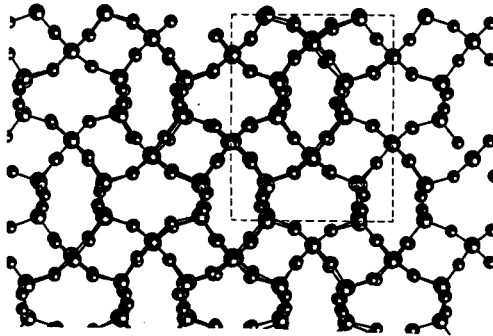
includes studies of the pressure-induced transformations of quartz. Despite numerous investigations, the details of these transitions and, in particular, the nature of the intermediate crystalline phase[14] which is believed to emerge during the pressure-induced amorphization of quartz, are still unclear and remain the subject of intense speculation.[8,11,13–15] Unfortunately, one of the major problems in these studies is that existing computer simulation methodology, while being a powerful tool in modeling solid-solid transformations of the displacive type (such as of high-to-low quartz), is not yet adequately equipped to mimic directly transformations of the reconstructive type, for instance between various ice polymorphs or between quartz and its neighbors on the SiO_2 phase diagram (such as tridymite, etc.). To bypass these limitations one can use structural analogy, the approach we exploit in this work, in designing and probing new phases.

II. SIMULATION DETAILS

Our observations are based on molecular-dynamics simulations performed with the interatomic potentials of van Beest and co-workers.[16] We have worked under constant pressure conditions (Nosè barostat) using variable shape simulation cells[17] containing 192 SiO_2 units. The Ewald method was employed to calculate the long-range electrostatic interactions. A fourth-order Gear algorithm with a time step of 1.0 fsec was used to integrate our Gaussian isokinetic equations of motion. At each state point the systems were equilibrated for approximately 10 psec, and averages were collected over subsequent 20 psec trajectories. In some cases longer simulation runs spanning 150–200 psec were carried out in order to accumulate the velocity autocorrelation functions. In constructing the initial configuration of orthorhombic SiO_2 we placed the Si atoms at lattice sites corresponding to the oxygen positions in the ice XII structure;[5] the O atoms were initially ordered as in hexagonal high quartz.[2]
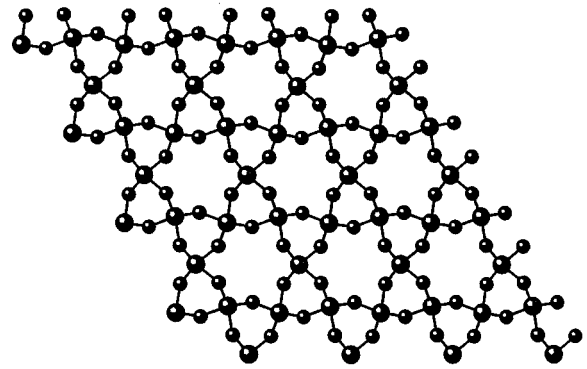
(a)

(b)

FIG. 1. The structure of the orthorhombic polymorph at a temperature of 300 K and a pressure of 2 GPa. The crystallographic projections 001 (a) and 100 (b) are shown. The gray and the black spheres represent, respectively, the silicon and the oxygen atoms. The dashed line marks the unit cell.
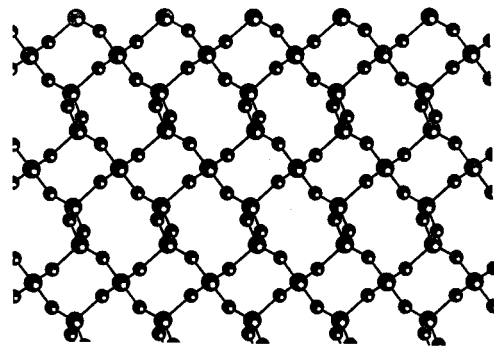
III. RESULTS

The crystal structure of our orthorhombic SiO_2 polymorph in its minimum energy configuration at 300 K is shown in Fig. 1. We identified its space-group symmetry as $Pnc2$, with 12 SiO_2 per unit cell. Table I lists the unit-cell parameters

TABLE I. The calculated structural data for the orthorhombic phase of SiO_2 (300 K, 0.1 GPa).

Atom	Site	x	y	z
		Space group $Pnc2$		
	Cell parameters $\alpha=4.888(1)$ Å, $b=8.68(1)$ Å, $c=10.31(1)$ Å			
		Density $\rho=2.737$ g/cm^3		
Si(1)	2a	0	0	0.705(1)
Si(2)	2b	1/2	0	0.290(1)
Si(3)	4c	0.181(5)	0.801(3)	0.083(1)
Si(4)	4c	0.319(3)	0.300(2)	0.412(2)
O(1)	4c	0.125(5)	0.165(5)	0.034(2)
O(2)	4c	0.376(2)	0.669(4)	0.460(1)
O(3)	4c	0.202(5)	0.397(2)	0.292(1)
O(4)	4c	0.324(9)	0.121(2)	0.372(3)
O(5)	4c	0.172(3)	0.623(3)	0.122(1)
O(6)	4c	0.302(9)	0.896(3)	0.203(1)

(a)

(b)

FIG. 2. The structure of the hexagonal quartz at a temperature of 300 K and a pressure of 2 GPa. The crystallographic projections 0001 (a) and $11\bar{2}0$ (b) are shown. The gray and the black spheres represent, respectively, the silicon and the oxygen atoms.

and the atomic site coordinates. This arrangement can be described as a bipartite structure derived from the familiar hexagonal quartz framework, hence we will refer to it as being ''quartzlike.'' The crystal structure of hexagonal quartz is displayed in Fig. 2. Both structures are similarly built from continuous zig-zag chains of corner-shared SiO_4 tetrahedra;[2] their characteristic linkage patterns are depicted schematically in Fig. 3. We emphasize that in hexagonal quartz the SiO_4 tetrahedra running along the $11\bar{2}0$ axis alternate their orientations (''up and down''), as shown in Fig. 3(a). In our structure these tetrahedra have their vertices pointing in the same direction, as shown in Fig. 3(b), hence two kinds of distorted hexagonal channels are evident along its 100 direction [see Fig. 1(b)]. In comparison, the traditional hexagonal packing features only one repeating motif of hexagonal channels [see Fig. 2(b)].

The atom-atom radial distribution functions (RDF) at 300 K are displayed in Fig. 4. These results indicate essentially the same valent Si-O bond distance, about 1.7 Å, in both the orthorhombic and the hexagonal modifications; the respective silicon-oxygen distributions exhibit nearly identical first maxima at this separation [Fig. 4(a)]. The Si-Si RDF [Fig. 4(b)] for the orthorhombic phase features a split first maximum, suggestive of a strained local configuration of silicon atoms, and a new peak at about 3.9 Å.

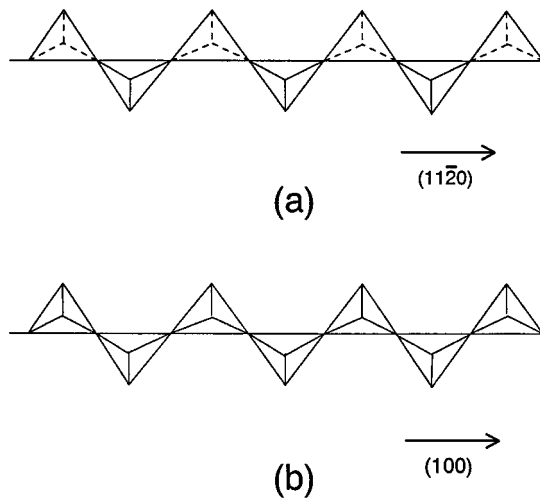The distributions of the local interatomic angles at 300 K

FIG. 3. The linkage pattern of the corner-shared SiO_4 units in the crystal structure of the hexagonal (a) quartz and of the orthorhombic (b) form.

are shown in Fig. 5. As we might expect,[18] both the valent O-Si-O [Fig. 5(a)] and the Si-O-Si [Fig. 5(b)] angle distributions for the hexagonal quartz are highly symmetric and are peaked around 109° and 144°, respectively. The Si-O-Si
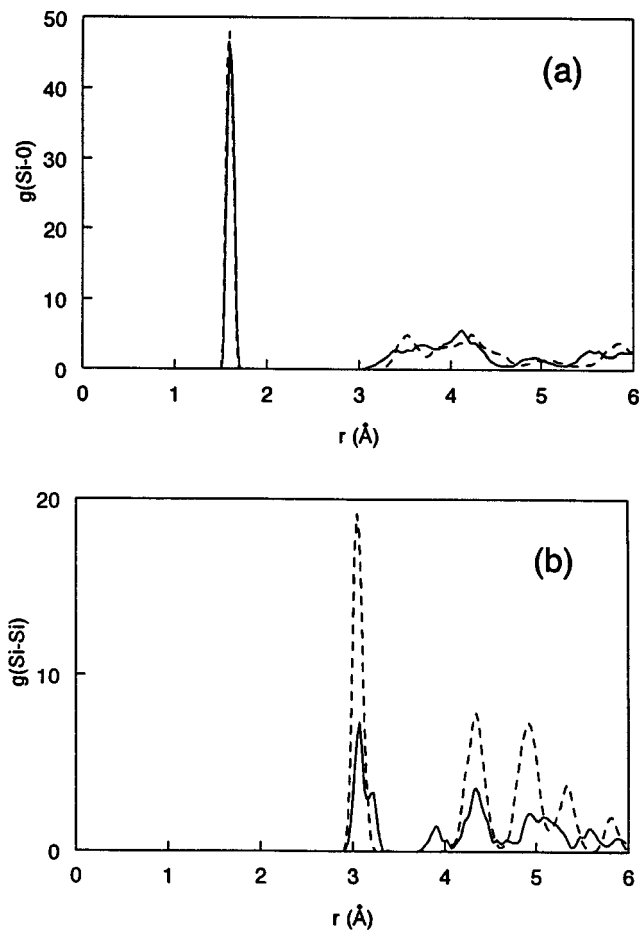

FIG. 4. The radial distribution functions for Si-O (a) and Si-Si (b) pairs. The solid and the dotted lines represent, respectively, the orthorhombic and the hexagonal structures at $T=300$ K and $P=2$ GPa.
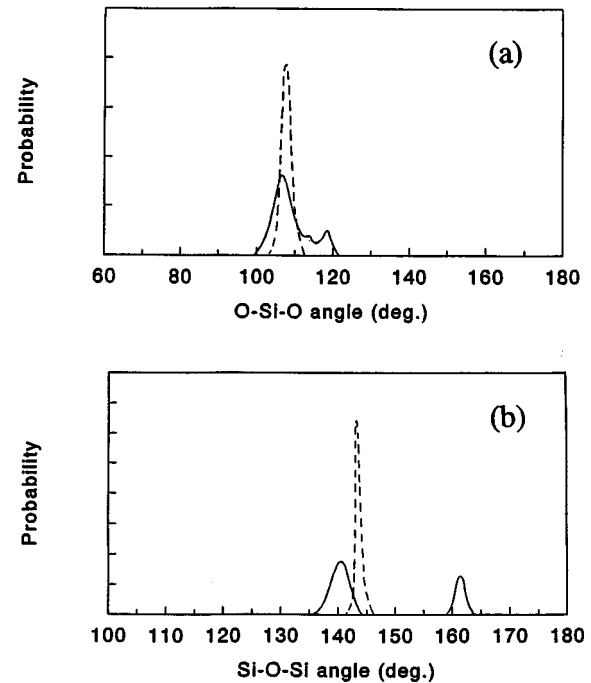

FIG. 5. The distributions of O-Si-O (a) and Si-O-Si (b) angles. The solid and the dotted lines represent, respectively, the orthorhombic and the hexagonal structures at $T=300$ K and $P=2$ GPa.

angle distribution for the orthorhombic modification is clearly bimodal, with the maxima at approximately 141° and 162°, which can be seen in Fig. 5(b). Its O-Si-O angle distribution [Fig. 5(a)] also appears to have two distinct maxima, at about 108° and 119°, (and a small shoulder at about 114°) indicating nontrivial deformations of the coordination polyhedra from the ideal tetrahedral shape.

The phonon density of states at 300 K is analyzed in Fig. 6; the power spectra of the velocity autocorrelation functions for silicon and oxygen atoms are shown. These spectra are similar to those obtained previously for the crystobalite modification.[19] It is interesting to note that the low-lying acoustic modes in the orthorhombic structure propagate at higher frequencies than those in the hexagonal structure. We may recall that these low-frequency modes are usually attributed to a torsion and bending of the tetrahedral framework.[9,19] This stiffer collective response of the orthorhombic structure is accompanied, on the other hand, by a greater degree of flexibility within the SiO_4 coordination units as revealed in the shift of its high-intensity mode at about 1100 cm^{-1} (corresponding to the antisymmetric stretching of the Si-O bond) toward lower frequencies.

The temperature and the pressure dependences for the configurational energy and the density are shown in Fig. 7. We have examined a wide range of pressures, from -4 to 10 GPa, and temperatures, from 50 to 1500 K. No reconstructive phase transition or the amorphization was detected. The lattice energy of the orthorhombic phase is a minimum at approximately 2 GPa over the temperature range examined [Fig. 7(a)]. Under ambient conditions ($P=0$ GPa and $T=300$ K) the density of the orthorhombic phase is roughly 5% higher than that of hexagonal quartz. The lattice energy of the orthorhombic polymorph is essentially a linear function of temperature, however the density variation seems to
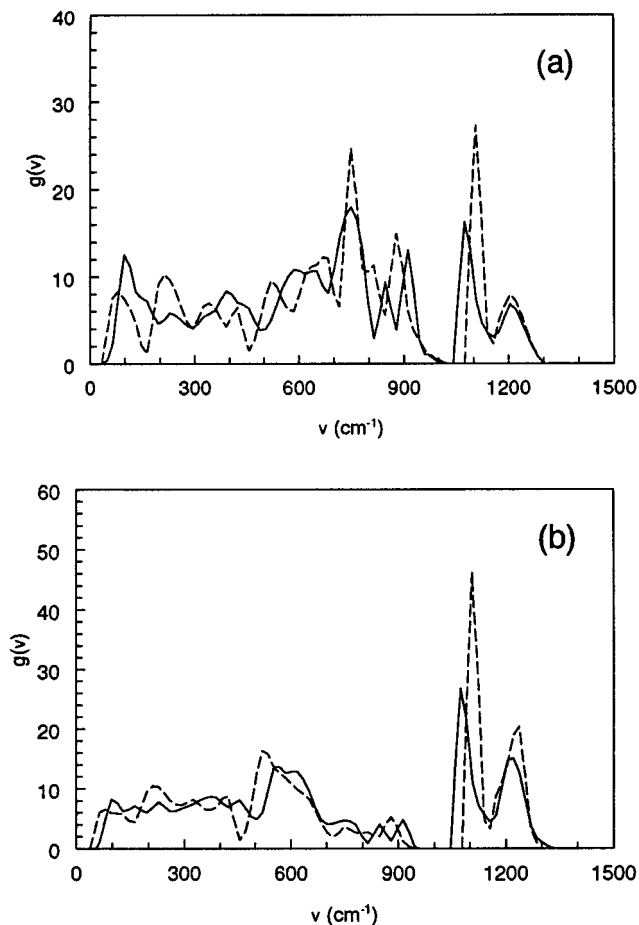
FIG. 6. The power spectra of the velocity autocorrelation functions for the silicon (a) and the oxygen (b) atoms. The solid and the dotted lines represent, respectively, the orthorhombic and the hexagonal structures at $T = 300$ K and $P = 2$ GPa.
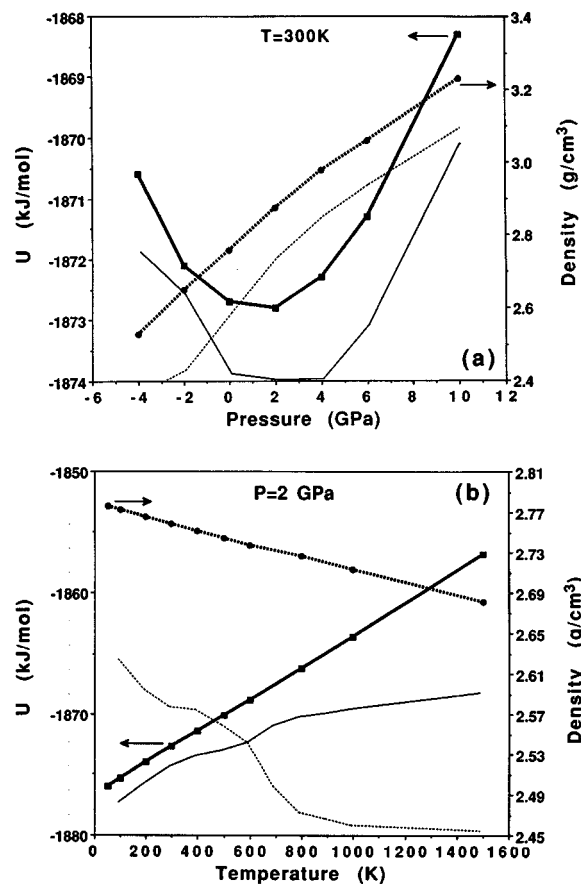

FIG. 7. The pressure (a) and the temperature (b) dependences for the configurational energy (the solid lines) and the density (the dotted lines). The thick lines with symbols are for the orthorhombic structure and the thin lines are for the hexagonal structure.

suggest a vague structural transformation (which becomes more evident when the unit-cell parameter a is plotted against temperature) gradually taking place at temperatures between 600 and 800 K, as might be seen in Fig. 7(b). This structural transformation does not appear to affect the space-group symmetry of the orthorhombic modification. In contrast, hexagonal quartz exhibits a rather pronounced change in its energy and density [see Fig. 7(b)], and a reduction in the crystal symmetry, upon its thermally induced high-to-low transformation. One possible explanation for this is that the two-fold screw axis of tetrahedra rotation (which, among other factors, makes this transformation possible in hexagonal quartz[20]) is absent in the orthorhombic structure, where a regular twofold axis is found instead (see. Fig. 3). We remark that these axes lie along the directions of the tetrahedra chains depicted in Fig. 3.

Due to its higher density compared with hexagonal quartz, the orthorhombic structure of SiO_2 might be expected to appear during pressure-induced transformations of low-density crystalline forms of silica, such as tridymite, crystobalite, and quartz. We remark that such crystal-crystal transformations would probably require drastic reconstruction of the SiO_4 packing pattern and are unlikely to be induced in a standard computer simulation. At this point we can offer only indirect evidence for its possible formation during

(static) pressure-induced transformations of quartz. We have simulated the x-ray powder-diffraction spectrum for our orthorhombic structure. This spectrum retains all the major lines characteristic of the hexagonal α-quartz structure. At the same time, three of the most intense peaks are found to approximately correspond with the peaks experimentally ob-
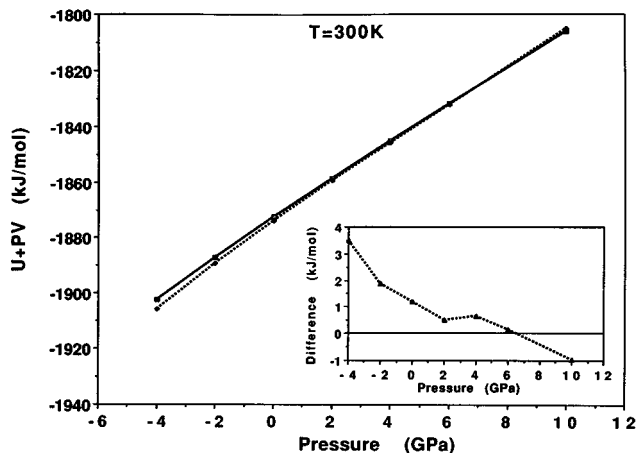

FIG. 8. The pressure dependence for the enthalpy. The solid and the dotted lines represent, respectively, the orthorhombic and the hexagonal structures at $T = 300$ K. The inset shows their enthalpy difference, defined as $(U + PV)_{\text{ortho}} - (U + PV)_{\text{hex}}$.

served during the compression of α quartz (notably, at 3.66, 2.66, and 1.48 Å) and attributed to the formation of an intermediate crystalline phase.[14]

We have also determined the enthalpies $(U+PV)$ for the hexagonal and the orthorhombic structures which are shown in Fig. 8. Their difference, defined as $(U+PV)_{ortho}$ $(U+PV)_{hex}$, is negative above 6 GPa (see inset in Fig. 8). This suggests that under pressure (above 6 PGa) the orthorhombic structure in quartz may become the more stable, prior to the amorphization [above 20 GPa (Refs. 8, 13, and 14)].

IV. CONCLUDING REMARKS

Using MD simulations we have examined a quartzlike SiO_2 modification with an orthorhombic symmetry, the structural analog of ice XII recently found in computer simulations of water under applied electric fields. We have found this crystalline form of silica to be mechanically stable over a wide range of temperatures, from 50 to 1500 K, and pressures, from -4 to 10 GPa, with a minimum lattice energy at about 2 GPa. One of its most interesting features is that it does not exhibit a marked high-to-low transformation characteristic of familiar hexagonal quartz. Under ambient conditions ($P=O$ GPa and $T=300$ K) the density of the orthorhombic phase is roughly 5% higher than that of hexagonal quartz.

Given our observations, further experimental efforts are clearly warranted to examine whether this form of silica can be synthesized in the laboratory. We may suggest that nonhydrostatic (shock-wave) conditions[10,21] which can yield a variety of metastable phases are particularly worth exploring. From a theoretical standpoint, simulating the amorphization process of the orthorhombic phase may provide important microscopic information about the relative mechanical stabilities of silica frameworks.

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