

Influence of Temperature and Anisotropic Pressure on the Phase Transitions in α -Cristobalite

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The role of temperature and anisotropy of the applied load in the pressure-induced transformations of α -cristobalite is investigated by means of first principles molecular dynamics combined with the metadynamics algorithm for the study of solid-solid phase transitions. We reproduce the transition to α -PbO₂ as found in experiments and we observe that the transition paths are qualitatively different and yield different products when a nonhydrostatic load is applied, giving rise to a new class of metastable structures with mixed tetrahedral and octahedral coordination.

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Silica is the main component of Earth's crust and a technologically very important material. Its phase diagram is characterized by the appearance of many metastable phases and marked hysteresis [1–4]. An understanding of its transition mechanisms offers the key to its complex behavior and properties. The phase transitions of α -cristobalite under pressure are still an unresolved puzzle in the physics of silica. Experiments conducted at pressures between 370 and 450 kbar, i.e., well in the range of stability of stishovite at room temperature, have failed to see the transformation to stishovite and report instead a transition to the α -PbO₂ poststishovite phase via the intermediate formation of a cristobalite-XI phase [5,6]. Several theoretical studies which employed classical force fields [7–9] or density functional theory [10,11] have also been performed. While the mechanism of formation of cristobalite-XI has been identified in Ref. [11] and its structure resolved, none of the above-mentioned simulations has ever revealed a transition to poststishovite phases. The cause of such failure may be due to the limitations of the theoretical methods used so far for simulating such a complex event as pressure-induced phase transitions. In addition it has been hypothesized that nonisotropic stresses might be responsible for such discrepancy, and for this reason α -cristobalite appears a natural candidate for studying the effect of nonisotropic load. In this Letter we report the results of a number of *ab initio* metadynamics simulations [12–14] of the pressure-induced transformation of α -cristobalite, at different temperatures and in hydrostatic and nonhydrostatic conditions, which allow for simulating the experimental transition to the α -PbO₂ phase and explaining the discrepancy between theory and experiments. We also show how the elastic response of the system can be used to engineer stresses able to steer transitions in different directions.

We apply an improved version of the metadynamics algorithm for the study of structural phase transitions in

crystals [14] as reported in [15,16], in combination with the Car-Parrinello scheme for first principles molecular dynamics (MD) [12]. The simulations are performed at the density-functional theory level and exploit the generalized gradient exchange and correlation functional by Perdew, Burke, and Ernzerhof [17]. Norm-conserving pseudopotentials in the Troullier-Martins form [18] are used, the Kohn-Sham orbitals are expanded in a plane wave basis set with a cutoff of 80 Ry and the first Brillouin zone is sampled in the Γ point only. This simulation protocol reproduces the correct sequence of the known stable crystalline phases of silica [19] and yields a range of stability of stishovite between 80 and \sim 520 kbar. The α -PbO₂ phase turns stable above 850 kbar [16]. Supercells containing 16 and 32 SiO₂ units, obtained by replicating the tetragonal unit cell of α -cristobalite, are used as initial structures. Classical MD simulations using the force field by van Beest, Kramer, and van Santen (BKS) [20] on a supercell containing 108 f.u. have also been performed to rule out artifacts due to the small size of the simulation cells used here. The shape of the cell described by the three vectors of the cell matrix \mathbf{h} is used as set of collective coordinates [14]. We further eliminate rotations by taking an upper triangular \mathbf{h} whose components we arrange to form the vector $\tilde{\mathbf{h}} = (h_{11}, h_{22}, h_{33}, h_{12}, h_{13}, h_{23})^T$. The forces that guide the evolution of $\tilde{\mathbf{h}}$ are the sum of a thermodynamic component $-\frac{\partial \mathcal{G}}{\partial \mathbf{h}}$ where \mathcal{G} is the Gibbs free energy and a history-dependent term that pushes the system out of local minima and forces it to explore other basins. In the anisotropic case if we decompose the external stress tensor in the anisotropic and hydrostatic part $\mathbf{P}_{\text{ext}} = \boldsymbol{\Sigma} + P$ with $P = \text{Tr}(\mathbf{P}_{\text{ext}})/3$ one has (similarly to Ref. [21]):

$$-\frac{\partial \mathcal{G}}{\partial h_{ij}} = V[\mathbf{h}^{-1}(\mathbf{p} - P)]_{ji} + V_0[\mathbf{h}_0^{-1}\boldsymbol{\Sigma}\mathbf{h}_0^T - \mathbf{h}]_{ji}, \quad (1)$$

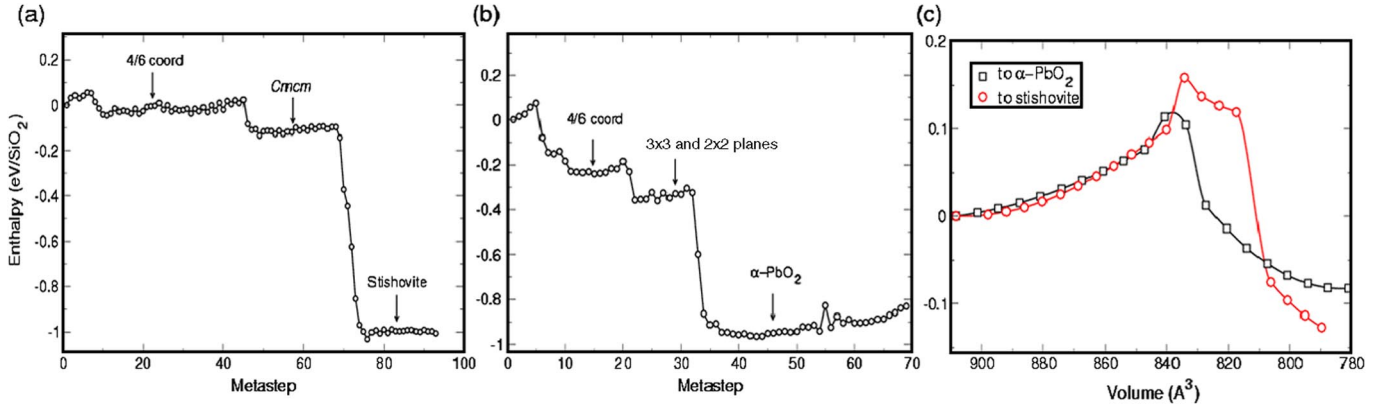


FIG. 1 (color online). Evolution of the enthalpy during the transitions at 260 kbar and 600 K from cristobalite-XI to stishovite (a) and to α -PbO₂ (b). The activation barriers of the first step of the mechanisms (c) have been computed by optimizations of the atomic positions at fixed h matrix. h values are determined by linear interpolation from cristobalite-XI to the first intermediates.

where \mathbf{p} is the internal pressure tensor, obtained by averaging over a MD run in the canonical ensemble and \mathbf{h}_0 is the reference value of \mathbf{h} . It has been shown [15,16] that it is numerically convenient to evaluate the elastic response matrix

$$A_{ij} = \partial^2 \mathcal{G}(\tilde{\mathbf{h}}) / \partial \tilde{h}_i \partial \tilde{h}_j |_{\tilde{\mathbf{h}}_0} \quad (2)$$

and replace \mathbf{h} with the scaled variables s_i , which are expressed as functions of the eigenvalues λ_i and the eigenvector matrix O_{ji} of A_{ij} : $s_i = \sqrt{\lambda^i} \sum_j O_{ji} (\tilde{h}_j - \tilde{h}_j^0)$. This change of variables also makes it easier to describe transitions, since typically only few s components are active. The history-dependent potential in the metadynamics simulations is made of Gaussians with a width of 100 (kbar bohr³)^{1/2} and a height of 10⁴ kbar bohr³ for the 32 f.u. cell, and 70 (kbar bohr³)^{1/2} and 5000 kbar bohr³ for the 16 f.u. system. The Gaussian heights correspond to 29 meV per formula unit.

We first consider the case of hydrostatic compression of α -cristobalite at 260 kbar [22], at room temperature and at 600 K. This pressure is well within the range of the thermodynamic stability of stishovite for the theoretical model considered here [16,23]. At first α -cristobalite transforms into a tetragonal four-coordinated phase with $P4_12_12$ symmetry, previously observed in experiments and dubbed cristobalite-XI [5,6]. This is a displacive transition that involves only a lattice distortion, and can be simply achieved by a straight minimization of the enthalpy even at zero temperature.

When the metadynamics is switched on, cristobalite-XI may undergo different transitions. At room temperature the transition to α -PbO₂ is observed, as found in experiments, while at 600 K cristobalite-XI transforms either into stishovite or into α -PbO₂, depending on the initial conditions and on the parameters of the history-dependent potential. Both transitions evolve through stepwise mechanisms, in which mixed 4- and 6-coordinated metastable intermedi-

ates occur [Figs. 1(a) and 1(b)]. The fact that both transition paths are observed at the relatively low temperature of 600 K suggests that similar activation barriers are involved. To verify this hypothesis we have computed the enthalpy of the transitions from cristobalite-XI to the first intermediate found along each path [Fig. 1(c)] and we found that the barrier to be crossed in the transition to α -PbO₂ is slightly smaller, which explains why such transition occurs more easily at lower temperature.

In Fig. 2 the phase transition to α -PbO₂ is shown. We first note that cristobalite-XI can be seen as formed by planes of tetrahedral chains stacked in the (11 $\bar{2}$) direction [Fig. 2(a)]. This structure evolves into an intermediate made of fully octahedral planes with 2 \times 2 chains, as in α -PbO₂, alternated by planes made of tetrahedra and octahedra [Fig. 2(b)]. In the following step the remaining four-coordinated silicon atoms achieve sixfold coordination and the formerly mixed planes display chains of octahedra with a 3 \times 3 pattern (Fig. 2c), which eventually rearrange into 2 \times 2 chains to form a perfect α -PbO₂ crystal [Fig. 2(d)],

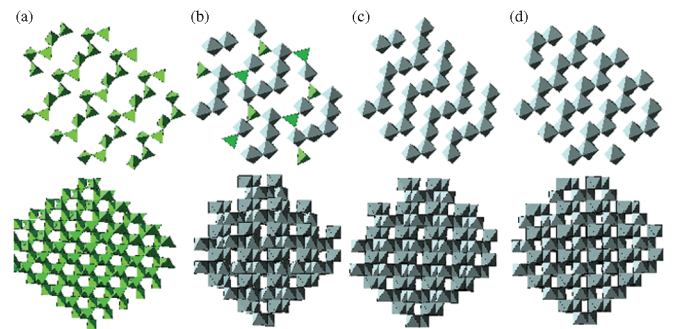


FIG. 2 (color). Section of a (11 $\bar{2}$) plane (top row) and side view (bottom row) of the metastable structures encountered in the transition from cristobalite-XI (a) to α -PbO₂ (d). The transition occurs via the formation of a mixed tetrahedral and octahedral structure (b) and of a defective octahedral structure made of alternating 2 \times 2 and 3 \times 3 planes (c).

TABLE I. Eigenvalues (in units of [Mbar · bohr]) and the corresponding normalized eigenvectors of the Hessian matrix (2) for a sample of cristobalite-XI at a pressure $p = 220$ kbar at zero temperature.

Eigenvalue	s_1	s_2	s_3	s_4	s_5	s_6
	7.23	9.24	13.9	13.9	35.8	77.9
Eigenvector						
h_{11}	-0.005	-0.330	0.001	-0.001	0.716	0.6160
h_{22}	-0.004	-0.303	0.003	-0.002	-0.698	0.6485
h_{33}	0.022	0.894	-0.007	0.004	0.026	0.4471
h_{12}	-0.999	0.022	-0.001	-0.003	-0.001	0.0046
h_{13}	-0.002	0.005	0.916	0.401	0.001	0.0007
h_{23}	-0.002	-0.007	-0.401	0.916	-0.001	0.0001

through a bond-switching mechanism similar to that described in Ref. [16].

A set of classical metadynamics simulations on a larger supercell confirms the above-mentioned *ab initio* results. Such simulations have been performed at room temperature and $P = 100$ kbar, due to the well-known pressure shift in the phase diagram of the BKS potential, which overstabilizes dense octahedral phases with respect to tetrahedral structures [24]. We found transitions to both stishovite and α -PbO₂-type structures. Also in this set of simulations the final structure is achieved by stepwise mechanisms, where the coordination turns from fourfold to sixfold. The larger size of the supercells augments the chances of obtaining defective structures with stacking faults, that are eventually fixed by continuing the metadynamics runs.

In order to understand better these transitions we analyze the eigenvalues and eigenvectors of the elastic response matrix A (Table I). As usual [16] the mode corresponding to the largest eigenvalue s_6 is related to

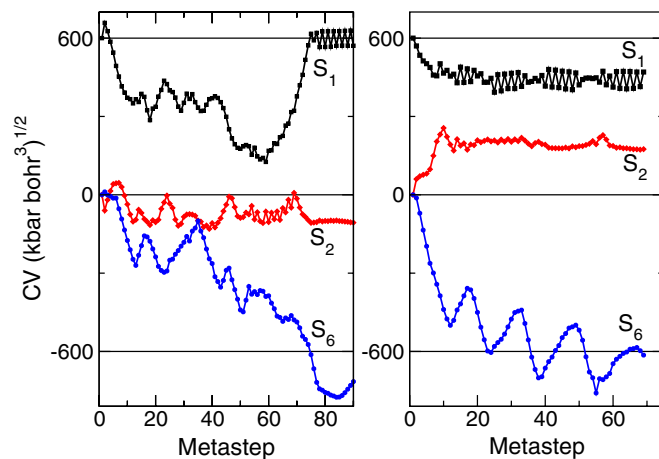


FIG. 3 (color online). Evolution of the relevant collective variables during the transition at 260 kbar from cristobalite-XI to stishovite at 600 K (left panel) and to the α -PbO₂ poststishovite phase at room temperature (right panel).

the volume change. It is also worth noting that there are two close low lying modes. One, s_1 , is a shear with a change in the off-diagonal term h_{12} , the other one, s_2 , is an orthorhombic deformation in which a compression in the xy plane is accompanied by a dilatation along z . In Fig. 3 we report only the evolution of s_1 , s_2 , and s_6 at $P = 260$ kbar. In the transition to stishovite, significant variations in s_1 and s_6 are seen, while s_2 remains inactive as do all the other variables, not shown in Fig. 3. In fact the tetragonal structure undergoes first a shear which reaches its maximum when the $Cmcm$ structure [25] is formed; later, when the tetragonal stishovite is formed, s_1 returns approximately to its original zero value. On the other hand, the transition to α -PbO₂ seems to be triggered by the activation of the s_2 mode, together with s_6 , which is related to the volume contraction.

From these considerations we argue that activating different elastic modes may favor different transition paths. First we apply a stress that would facilitate or inhibit the activation of s_2 at the expenses of s_1 in order to devise how possible experimental nonhydrostatic conditions may produce new structures or inhibit the transition to stishovite. Thus we apply a nonisotropic stress of the type $P_{11} = P_{22} = P_{33} + \Delta P$ and $P = \text{Tr}(\mathbf{P})/3$ is the applied pressure in Eq. (1). P is set to 260 kbar and ΔP to 40 kbar. First we note that for negative ΔP only transitions to stishovite qualitatively similar to those observed under hydrostatic pressure are observed. When an external pressure with positive ΔP is applied, we discover a new polymorph of symmetry $P4_122$. This structure is only partially octahedral since 8 of the 32 silicon atoms retain a tetrahedral coordination. This structure is made of planes stacked in the (111) direction, containing sequences of 2×2 chains of octahedra, as for α -PbO₂ [26], interrupted by the presence of 4-coordinated silicon atoms (see Fig. 4). Continuing the run we did not observe any new transition and the structure remained stable also upon decompression to 0 kbar. While they have never been observed experi-

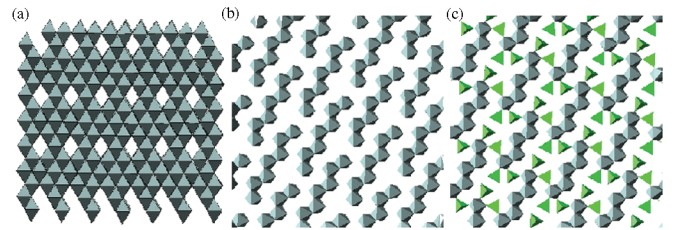


FIG. 4 (color). Views of the newly found $P4_122$ structure obtained from nonhydrostatic compression of cristobalite-XI at 260 kbar. Panel (a) displays a side view showing the stacking of the octahedral (111) planes, while the two types of planes are shown in panels (b) and (c). The transition to this structure involves a smaller densification than when stishovite is formed. At 260 kbar the equilibrium density of cristobalite-XI is $\rho = 3.2$ g/cm³, the one of stishovite is 4.65 g/cm³ and the one of the $P4_122$ structure is 4.3 g/cm³.

mentally in silica, mixed 4 and 6-coordinated phases have been found in AlPO_4 under pressure [27]. In SiO_2 such phases usually display only limited stability and are likely to occur for very short times as intermediates. We suggest that a nonisotropic load may lead to the formation of much more stable tetrahedral-octahedral mixed phases also in SiO_2 , that can be detected by Raman spectroscopy or angle-dispersive x-ray diffraction, as in [27]. Simulations at $P = 420$ kbar give an enthalpy barrier for the $P4_122$ phase to transform into more stable structures of 0.4 eV/ SiO_2 . Within transition state theory, assuming a rate prefactor of 1 THz, such barrier implies a lifetime at least of the order of few μs , which is accessible to present day time-resolved crystallography. In order to induce further transitions we increase the pressure to 420 kbar and for simplicity we revert to hydrostatic conditions. The 4-coordinated silicon atoms are eliminated in two steps. The first transition produces a structure where all the silicon atoms are sixfold coordinated but there are also 8 overcoordinated (fourfold) and 8 undercoordinated (two-fold) oxygens. The symmetry of this structure is $P2_12_12_1$ and its unit cell is orthorhombic. Also this structure is metastable at 420 kbar and does not transform upon decompression to 0 kbar. A second transition yields a lower enthalpy octahedral structure with a smaller number of coordination defects (6 pairs of under- or overcoordinated oxygens), made of layers of stishovite alternated to layers of α - PbO_2 .

In conclusion, we have elucidated the path from α -cristobalite to α - PbO_2 from dynamical simulations. In addition our results illustrate clearly the fact that although crystal structure transitions are first order, and therefore they cannot be in general described as elastic instabilities, nonetheless the elastic response of the system plays a major role. Indeed by appropriately selecting the external stress one can generate new pathways and new structures.

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