

Ab Initio Molecular Dynamics Study of the Pressure Induced Phase Transformations in Cristobalite

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ABSTRACT

The mechanism for the pressure induced transformation of cristobalite to stishovite and post-stishovite phases has been obtained from constant pressure ab initio molecular dynamics simulations. The cristobalite to stishovite transformation is found to be a two step process where SiO_4 tetrahedra first rotate followed by a lattice distortion to yield the 6-coordinated stishovite structure. Further compression of stishovite yields the CaCl_2 structure and is followed by another 6-coordinated structure with symmetry $P2_1/n$ (at 11 Mbar) which remains stable to a pressure of about 14 Mbar and then transforms into a 9-coordinated $P2_1/m$ structure.

Keywords: High-pressure, Ab Initio calculations, Car-Parrinello, SiO_2 .

1 INTRODUCTION

Pressure induced phase transitions in SiO_2 have been studied by many methods [1-6]. Several studies focussed on the search for possible phases of SiO_2 that may exist at pressures beyond the stability range of the well established CaCl_2 structure [2]. Experimental and theoretical studies provided evidence for the existence of $\alpha\text{-PbO}_2$ -like and other structures [1,3,4,7] at high pressures. However, the stability regions of these latter phases and the conditions for their preparation are still a matter of debate. The mechanism itself for the formation of the high pressure phases from those stable at ambient conditions are basically unknown. For example, experimental studies on the transformation of cristobalite to stishovite reported several intermediate phases [8,9] whose appearance were strongly dependent on the degree of deviation from purely hydrostatic conditions [8]. In fact, the role of non-hydrostatic conditions can not easily be assessed in high pressure experiments. In this respect, theoretical modeling by ab initio calculations can be of great help in providing reliable predictions on the relative stability of different phases under purely hydrostatic pressure.

At present, with the exception of the rutile to CaCl_2 transformation[3,5], first-principles theoretical studies have relied mainly on comparing the energies of calculated equations-of-state (EOS) for individual structures.

Although a given structure may be predicted to be thermodynamically stable over a pressure range, there may be no energetically favored path for the transformation to be kinetically allowed. In other words, the formation of a new structure may be very dependent on the choice of the starting phase as well as on the exact conditions of stress and temperature required to overcome the free energies barriers along the transformation path. A transformation path for the cristobalite to stishovite transition has been proposed by O'Keefe and Hyde[10] based on crystallographic considerations and later shown by Hartree-Fock calculations [11] to have a reasonably low enthalpy barrier. However, the latter results do not exclude the possibility that other more favorable paths may exist. Ab initio constant pressure molecular dynamics [12] allows us to surmount this difficulty by providing a more reliable sampling of the configurational space accessible and thus provides predictions on the stability and formation mechanisms of high-pressure structures. In this work, we report on the simulation of pressure-induced transformations of α -cristobalite silica under hydrostatic conditions which allowed us to characterize the transformation path to stishovite and to predict the structures of post-stishovite phases.

2 THEORETICAL METHODS

Ab initio constant pressure Car-Parrinello simulations [12-14] were performed using a gradient corrected [15] density functional approach and norm-conserving pseudopotentials [16]. The Kohn-Sham orbitals are expanded in a plane wave basis set with an energy cutoff of 80-90-Ry and periodic boundary conditions are imposed. Brillouin Zone (BZ) integration was restricted to the supercell Γ point. Simulations were performed with time steps of 1-2 a.u. with a fictitious electron mass of 800 a.u. Constant pressure simulations were carried out by slowly increasing the pressure in 10 GPa or 100 GPa increments for pressures below or above 100 GPa, respectively. Structures were equilibrated at a temperature of 300 K (all pressures) and 3000 K (for pressures in the range 60-700 GPa) with simulations at both temperatures yielding the same number and sequence of phases. Statistical averages were taken over a 0.5 ps duration after a 0.2 ps equilibration time at each pressure. Geometry refinement of new structures emerging from the dynamical simulations and

calculation of the EOS [17] were obtained employing the local density approximation, a larger energy cutoff of 100 Ry, and 6X6X6 Monkhorst-Pack [18] k-point mesh for BZ integration. The relative stability of the phases at the higher pressures as further verified by FLAPW calculations [19].

3 RESULTS AND DISCUSSION

The simulations were started with a 48-atom 2X2X1 supercell of α -cristobalite (space group $P4_12_12$) which is commensurate with a 2X2X2 stishovite supercell (space group $P4_2/mnm$). On raising the pressure to 50 GPa the system transformed spontaneously into a very well formed stishovite phase with no sizeable volume discontinuity. The average structures at different pressures across the transformation is reported in Fig. 1. Note that the $P4_12_12$ space group of α -cristobalite is a sub-group of the $P4_1/mnm$ space group of stishovite where the unit cells of the two structures are related by a doubling of the c-axis. The transformation is irreversible, with the stishovite phase being retained at ambient conditions upon release of the pressure from 60~GPa in the simulation. By analyzing the atomic trajectories we verified that the transformation path is very similar to the mechanism proposed by O'Keefe and Hyde[10]. The mechanism, sketched in Fig. 1, is identified by monitoring the evolution of the fractional atomic coordinates (with respect to the α -cristobalite unit cell), as a function of pressure, Fig. 2. In α -cristobalite the O and Si atoms occupy the $8b(x,y,z)$ and $4a(x,x,0)$ sites, respectively. Under pressure, a continuous evolution occurs, with each fractional coordinate smoothly approaching the values of the stishovite structure: limiting values of these parameters are $y_o=x_o$, $z_o=0$ and $x_{Si}=1/2$. The smooth structural evolution fits well with the description of Ref. [10] with the exception that the simulated transformation occurs in a stepwise fashion: the tetrahedra rotate first and then distort producing an abrupt change in the coordination number as demonstrated by the analysis of the coordination number of Si and the twist angle $\theta = \cos^{-1}(\langle z_o \rangle \langle c \rangle / \langle r_{Si-O} \rangle)$ (where $\langle z_o \rangle$, $\langle c \rangle$ and $\langle r_{Si-O} \rangle$, are the average values of the z_o , the c-axis and Si-O bond lengths respectively). First, there is a change, between $P=0.2$ -- 30 GPa, in θ which gradually approaches the limiting value of 90° for the stishovite structure. After rotation, the tetrahedra undergo a distortion which is reflected in a change in slope of the x_{Si} fractional coordinate as a function of pressure at 40 GPa. This is followed by an abrupt jump in the coordination number of Si at $P=50$ GPa where the Si atom moves to the ideal position ($x_{Si}=1/2$) for stishovite. The relative simplicity of this transition suggests that stishovite may be cleanly formed from α -cristobalite and the formation of lower symmetry phases seen experimentally may be, in part, due to non-hydrostatic conditions.

The stishovite structure is stable over only a small pressure range and transforms into the $CaCl_2$ phase as the pressure is increased from 70 to 80 GPa in our simulation.

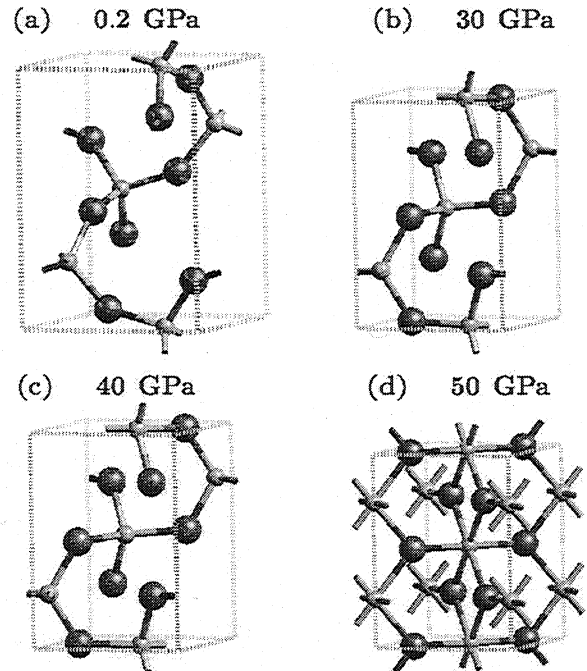


Figure 1: Average structures obtained from constant pressure simulations for the α -cristobalite to stishovite transformation. (a) 0.2 GPa (b) 30 GPa (c) 40 GPa (d) 50 GPa.

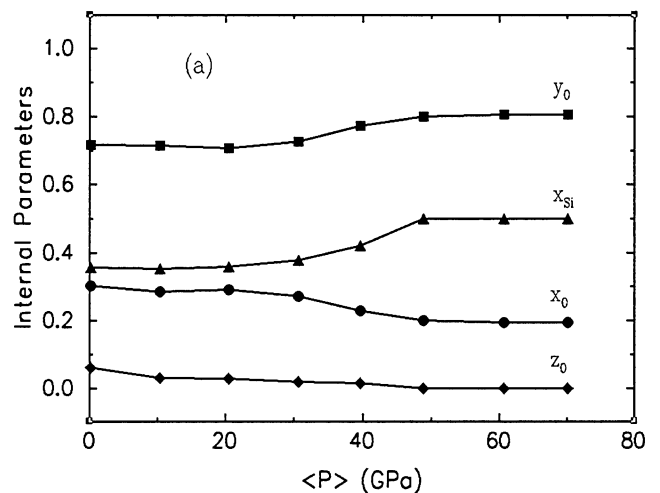


FIGURE 2: Symmetry independent fractional coordinates (with respect to α -cristobalite unit cell) as a function of pressure; x_o (square), y_o (circle), z_o (diamond) and x_{Si} (triangle). Limiting values of these parameters in a 1X1X2 supercell of stishovite are $y_o=x_o$, $z_o=0$ and $x_{Si}=1/2$.

This transformation is in good agreement both with experiment[2] and previous theoretical studies [3]. The $CaCl_2$ phase is extremely robust and survives compression up to an applied pressure of 11 Mbar where a slight monoclinic distortion into a lower symmetry $P2_1/n$ structure is observed. This new phase is only a small variation of $CaCl_2$, the Si atoms remain sixfold coordinated.

The same transformation at the same pressure was detected in a second simulation with a larger cell containing 96 atoms. By further increasing the pressure in this latter cell, a more dramatic transition is seen at 14 Mbar where a monoclinic $P2_1/m$ phase is formed (Fig. 3). Both transformations occur without a sizeable volume discontinuity. The transition is most prominently seen in the Si-O and O-O radial distribution functions (RDF), $g(r)$ (Fig 3a). The Si-O RDF of both CaCl_2 and $P2_1/n$ structures have only one sharp first nearest neighbor peak at around 1.4 Å which integrates to 6 nearest neighbors. This is transformed at 14 Mbar into a broad peak that integrates to 2 bonds at 1.4 Å, six bonds at about 1.5-1.6 Å and a broad flat region between 1.6-1.8 Å which integrates to one leading to a total coordination number of nine. This is mirrored by a change in the O-O RDF. The double peak structure in the O-O RDF of CaCl_2 and $P2_1/n$, which corresponds to a total coordination number of 12 nearest neighbors, transforms into a broad and highly structured peak in $P2_1/m$ which integrates to 11 nearest neighbors. The decrease in O-O coordination number suggests that the $P2_1/m$ phase is formed by collapsing the octahedra in order to minimize the repulsive interactions between O^{2-} anions. This interpretation is also supported by the fact that upon reducing pressure from 14 Mbar back down to 11 Mbar the structure reverts to the $P2_1/n$ phase unlike stishovite which is retained upon releasing the pressure.

To test this hypothesis and further confirm these findings we compared the enthalpies of the new structures obtained from the simulations with static calculations similar to those of previous studies[1-6]. We have computed the EOS for the stishovite, $P2_1/n$ and $P2_1/m$ phases as well as for $\alpha\text{-PbO}_2$ and Pa3 phases which are believed to be competitive structures at high pressure. We optimize all the structural parameters of the different phases at several volumes resulting in the EOS reported in Fig. 4. As expected, stishovite is the most stable phase and $P2_1/m$ the least for volumes larger than 17 \AA^3 . Conversely, at volumes below 11 \AA^3 the $P2_1/m$ phase is the lowest in energy [19]. This is a larger volume than the $\sim 10 \text{ \AA}^3$ found for the reversible $P2_1/m \rightarrow P2_1/n$ in the constant pressure simulations and likely reflects the lack of proper BZ integration in the latter. For volumes between $11\text{-}17 \text{ \AA}^3$, the Pa3 phase is lowest in energy followed closely by $\alpha\text{-PbO}_2$ neither of which is seen in the constant pressure simulations. Analysis of the relationship between the crystal structures of Pa3, $\alpha\text{-PbO}_2$ and stishovite shows that the unit cells of these phases are commensurate with the 96 atom supercell used in the simulations. The fact that these phases were not observed neither in the 300 K nor in the 3000 K simulations suggests that large energy barriers might be present and hinder their formation from stishovite. The existence of a large energy barrier for the $\text{CaCl}_2 \rightarrow \alpha\text{-PbO}_2$ transition is also expected by considering the substantial rearrangement of atoms which would be required for such a transformation, as opposed to the relatively simple path for the formation of the novel $P2_1/m$ structure. The formation of a $\alpha\text{-PbO}_2$ -like

structures has been observed experimentally near metal particles after laser heating (2000 K) amorphous silica or silica gel [7] at high pressures in diamond anvil cells. The current results suggest that the metal may act not only as a local hot site as a result of absorption of the laser energy but possibly also as a catalyst.

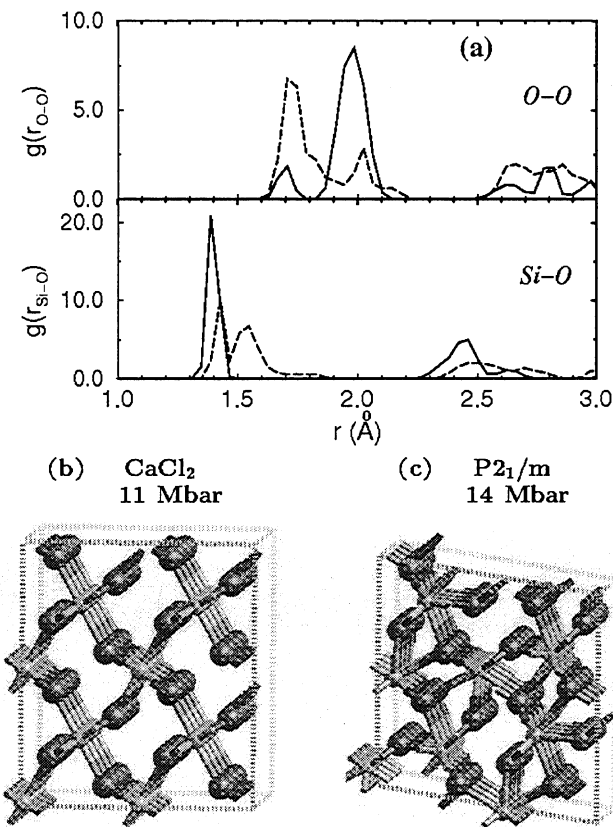


FIGURE 3: Radial distribution functions (RDF), $g(r)$, for (a) Si--O and O--O distances of SiO_2 : (solid line) CaCl_2 (dashed line) $P2_1/m$ at 11 and 14 Mbar respectively. Structures of SiO_2 : (a) CaCl_2 11 MBar (b) $P2_1/m$ 14 MBar. Si is represented by small grey sphere and O by large black sphere.

4 CONCLUSIONS

In conclusion, we have simulated by constant pressure ab initio MD a spontaneous transformation of CaCl_2 silica into a monoclinic phase ($P2_1/n$) at 11 Mbar which in turn transforms into a second monoclinic phase ($P2_1/m$) with 9-fold coordinated silicon. This pressure range is achievable only in laser-driven shock wave experiments which would inevitably involve considerable heating, limiting the identification of the predicted new phases. The lack of proper BZ sampling in the dynamical simulations is responsible for an overestimation of the pressure at which the $P2_1/n$ phase becomes thermodynamically more stable than the $P2_1/m$ phase. In fact, although in the simulation the

$P2_1/m$ phase reverts back to the $P2_1/n$ at 11 Mbar, in the EOS (Fig. 4) at full convergence in the BZ sampling, the transition back to the $P2_1/n$ phase is predicted at 7 Mbar. Therefore, it is likely that also the value of 14 Mbar found for a barrierless transformation from $P2_1/n$ to $P2_1/m$ upon compression, represents a large overestimation of the real transition pressure. The present work further highlights the importance of constant pressure dynamical simulations to uncover a phase diagram at high pressure and its advantages with respect to conventional static EOS calculations. First, the new phase appears spontaneously in the dynamical run without any initial guess of its geometry. To our knowledge the $P2_1/m$ structure is unprecedented and thus an educated guess based on known phases would not have yielded this phase. Second, although one may propose thermodynamically stable structures at a given pressure, based on a static EOS, there is no guarantee that they may be reached by a kinetically accessible path. As long as a structure is restricted by high enthalpy barriers, it can remain metastable at normal temperature and hydrostatic pressure. Ab initio constant pressure simulations may provide access to the conditions for local instability and be employed to predict the ultimate phase a system would reach if not preempted by transformations activated either by catalytic agents or non-hydrostatic conditions.

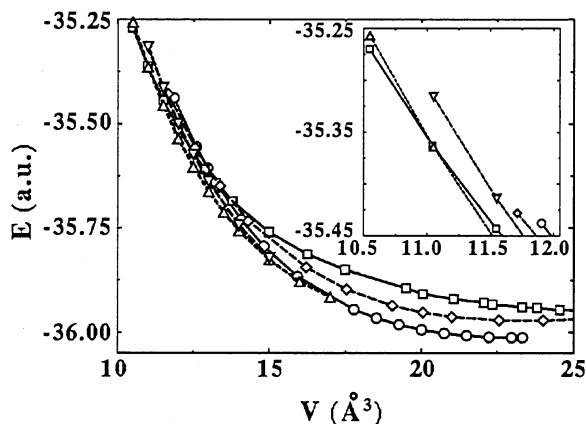


Figure 4: Energy as a function of volume of the stishovite (circles), $P2_1/m$ (square) $P2_1/n$ (diamond), Pa3 (triangle) and a-PbO₂ (inverted triangle) phases of SiO₂. Insert shows a blow up of high density region. Energies and volumes are given per SiO₂ unit.

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 [18] To verify that this is not an artifact of our pseudopotential calculation we have verified this conclusion using FLAPW. For a volume of 10Å³/SiO₂ the $P2_1/m$ phase is more stable by 0.10a.u./SiO₂ (GGA), 0.11a.u./SiO₂. (LDA) than Pa3.