A new high-pressure silica phase obtained by molecular dynamics

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ABSTRACT

A molecular dynamics study with analytical and ab initio interatomic potentials revealed the possibility of a new silica phase with \( Pnc2 \) structure, which is more stable than stishovite and its \( CaCl_2 \)-like modification at pressures above approximately 120 GPa over a wide range of temperature. Our analysis of simulated X-ray diffraction patterns of various hypothetical post-stishovite phases shows that this new phase should be considered in the treatment of high-pressure experiments involving silica. The new phase might be responsible for the seismic discontinuity at 2728 km depth and should be treated as potentially stable at the pressures and temperatures of the lowermost mantle.

INTRODUCTION

Silica is one of the most studied materials. It attracts special attention in earth science because in the chondritic model \( SiO_2 \) accounts for about 50% of the composition of the Earth. Since the discovery of stishovite in 1962 by Stishov and Popova, various experimental and theoretical studies have suggested the possible existence of another, so-called “post-stishovite” phase.

Possible post-stishovite phases can be separated into two groups. Experimentally observed crystal-chemical analogs of \( AX_2 \)-type oxides such as \( \alpha-PbO_2 \), fluorspar (\( CaF_2 \)), crottine (\( \alpha-PbCl_2 \)), and baddeleyite (\( ZrO_2 \)) (Ming and Manghnani 1982; Sato et al. 1991; Tang and Endo 1993) belong to the first group, and the phases proposed for explaining the results of high-pressure experiments on \( SiO_2 \), \( \alpha-PbO_2 \), Fe, N, disordered nyceline NiAs, and \( CaCl_2 \) structures (Altshuler and Podurec 1973; Hemley 1987; Liu 1982; Simakov 1973; Sekine et al. 1987; Tsushima and Yagi 1989) belong to the second group. However, the reliability of the interpretations of experimental data is questionable (Lacks and Gordon 1993; Tse et al. 1992). Despite several attempts, and with the exception of the transition to \( CaCl_2 \)-like structure, which is likely a second-order transition, none of the other possible post-stishovite phases with energy lower than that of stishovite was simulated at pressures up to 150 GPa.

We investigated all the suggested post-stishovite phases up to 150 GPa on a systematic basis using molecular dynamics (MD) and lattice dynamics simulation methods with our new analytical (Belonoshko and Dubrovinsky 1995) and previously developed ab initio (RTAM, Tsuneyuki et al. 1988) interatomic potentials (IP), starting from various reasonable post-stishovite structural types. The selection of structural types for our calculations required systematization of data on high-pressure \( SiO_2 \) phases. Based on the basis of our analysis of possible structures, we restricted starting structures to fluorite, \( \alpha-PbO_2 \), modified \( \alpha-PbO_2 \) (with space group \( I2/a \)), \( \alpha-PbCl_2 \), and baddeleyite \( ZrO_2 \) structural types.

METHOD AND RESULTS

We used the Parrinello-Rahman (Parrinello and Rahman 1981) modification of the MD method, which allows simulations at constant pressure and the possibility to change the shape and size of the computational cell, an important consideration in the simulation of phase transitions. Coulombic interaction was calculated using the Ewald method. Because there are no a priori good or bad methods, we thoroughly checked the method used in this study against well-established experimental data. We succeeded in reproducing thermoelastic properties of the \( \alpha \)-quartz, coesite, and stishovite as well as the quartz-coesite, coesite-stishovite, and stishovite-melt phase transitions in close agreement with experiment (Belonoshko and Dubrovinsky 1995; Dubrovinsky et al. 1996). This provided us with confidence in the method.

We obtained the following results starting from all the structural types described above and considered to be reasonable high-pressure modifications of \( SiO_2 \).

First, fluorite, modified fluorite (with space group \( Pa3 \)), \( \alpha-PbO_2 \), modified \( \alpha-PbO_2 \) (space group \( I2/a \)), and \( \alpha-PbCl_2 \)-like phases of \( SiO_2 \) are unstable with respect to stishovite at pressures up to 150 GPa and 300 K. This is in agreement with theoretical (Bukowinski and Wolf 1986; Sherman 1993) and experimental (Hemley et al. 1995) studies. The phase closest to stishovite in stability is modified \( \alpha-PbO_2 \) (space group \( I2/a \)). Stishovite and \( \alpha-PbO_2 \) energies at 300 K and 150 GPa are \(-4352\) and \(-4332\) kJ/mol, respectively. This result is in perfect agreement with that obtained by Tse et al. (1992).

Second, at pressures near 100 GPa, orthorhombic distortion of the stishovite unit cell gradually increases and may be interpreted as a transition from stishovite to a \( CaCl_2 \)-like structure. The value of the distortion increases smoothly with pressure. This possible phase transition, stishovite–to–\( CaCl_2 \)-like modification of \( SiO_2 \), is probably second order. Calculation of elastic constants shows that \( c_{11} - c_{12} = 0 \) at 83 GPa and 300 K and indicates that at this pressure stishovite becomes unstable. The transi-
Figure 1. Projection along the b axis of the new SiO$_2$ structure (space group C$_2$ $–$ Pnc2) simulated with MD at 100 GPa and 300 K ($a$ = 4.2275, $b$ = 3.8900, $c$ = 4.7225 Å, $Z$ = 4, Si1 (0.0, 0.0, 0.1450), Si2 (0.5, 0.0, 0.8271), O1 (0.8322, 0.2636, 0.3680), O2 (0.6672, 0.7586, 0.1050)). The numbers indicate the positions of atoms along the vertical axis. This structure (which we call “SBAD”) can be considered as intermediate between $\alpha$-PbO$_2$ ($Pbcn$) and baddeleyite ($P2_1/c$).

Thin lines show octahedra with an arrangement similar to the $\alpha$-PbO$_2$ structure.

The transition to CaCl$_2$-like structure is subtle, and changes of $a/b$ ratio indicating the transition is observable in MD simulations occur above 90 GPa ($a/b = 1.053$ at 100 GPa).

Third, starting from the baddeleyite structure, we obtained a structure with the $Pnc2$ space group (Fig. 1). This structure (which we term “SBAD”) can be considered as intermediate between $\alpha$-PbO$_2$ ($Pbcn$) and baddeleyite ($P2_1/c$). Indeed, the octahedra of this structure are gradually distorted and transformed to seven-apex polyhedra (characteristic of baddeleyite) during pressure decrease to 10 GPa. Figure 2 shows that at pressures higher than 70 GPa, the density of SBAD becomes greater than that of stishovite and that at 150 GPa and 300 K the difference is 0.8%. At 300 K and 100 GPa, the total energies of SBAD and stishovite are $-4437.88$ and $-4446.35$ kJ/mol, respectively, and at 150 GPa the corresponding energies are $-4344.69$ and $-4352.19$ kJ/mol. Taking into account the $P\text{AV}$ term and additional simulations with a pressure step of 10 GPa, we found that at pressures of about 120 GPa and higher, stishovite (or rather CaCl$_2$-like silica) becomes less stable than the SBAD phase. In summary, at 300 K and from ambient pressure up to 150 GPa the sequence of change of SiO$_2$ phases is as follows: $\alpha$-quartz, coesite, stishovite, CaCl$_2$-type SiO$_2$, SBAD. The transition to the SBAD structure does not depend on temperature within the precision of our pressure step, as shown by the simulations at 3000 K. Therefore, we conclude that the SBAD phase is the best candidate structure to represent the silica phase in the Earth’s mantle close to the core-mantle boundary.

Fourth, Table 1 shows X-ray diffraction patterns (MoK$_\alpha$, radiation) of some SiO$_2$ phases (including the new phase SBAD, Fig. 1) obtained in this study at 100 GPa and 300 K. Table 1 shows that the shift (or even splitting) of reflections with respect to the stishovite pattern can be easily interpreted as transformation of stishovite to any post-stishovite SiO$_2$ phase, including the CaCl$_2$-like modification, as noted by Tsuchida and Yagi (1989). Tse et al. (1992) also noted that the four diffraction peaks observed by Tsuchida and Yagi (1989) and attributed to the CaCl$_2$-like structure are in common with the ideal and modified $\alpha$-PbO$_2$ structures.

Fifth, the calculations were repeated using the ab initio TTAM potential, and a semiquantitative agreement with the results computed using our potential was obtained. This is especially compelling because these two potentials are derived from completely different methods. This proves that the simulated phase does not depend on a particular potential. Therefore, we suggest that it is necessary to consider the SBAD phase for the reliable interpretation of high-pressure experimental data on phase transformations of SiO$_2$.

### DISCUSSION

Several high-pressure silica phases have been suggested, and many of them are predicted over a broad pressure range. For example, Cohen (1992) and Park et al. (1988) predicted $Pa3$ phase stability above 150 and 60 GPa, respectively, using the same LAPW method; recent experimental studies (Hemley et al. 1995) have ruled out the existence of this phase up to at least 2 Mbar. Therefore, we did not analyze available theoretical predictions of high-pressure silica phases. Such detailed analysis would go far beyond the scope of this paper.

Two experimental studies have predicted stishovite-CaCl$_2$-like phase transition at 100 GPa (Tsuchida and Yagi 1989) and 45 GPa (Kingma et al. 1995). The interpretation provided by Tsuchida and Yagi (1989) is not the only possible (Tse et al. 1992; see also Table 1). Kingma et al. (1995) experimentated in quasi-hydrostatic conditions; in other words, the pressure was not absolutely hydrostatic. Because the pressure at which structural changes were observed depends on the rheology of the pressurizing medium (Kingma et al. 1995; H.-K. Mao, personal communication) and is subject to large hysteresis (40–58 GPa, Hemley et al. 1995), we do not know whether the observed change of Raman spectra (Kingma et al. 1995) is an indication of a phase transition or the activation of inactive modes owing to distortion of stishovite caused by stress. Therefore, the experimental studies do not contradict our prediction of a new phase.

As one can see in Figure 2a, the volume of stishovite at ambient conditions is overestimated by 4%. The volume effect of the suggested transition is about 0.8%.
TABLE 1. Calculated X-ray patterns (MoKα radiation) of different crystal structures of SiO₂ obtained by MD simulations at 100 GPa and 300 K

<table>
<thead>
<tr>
<th></th>
<th>Stishovite</th>
<th>CaCl₂</th>
<th>α-PbO₂</th>
<th>SBAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (Å)</td>
<td>l (%)</td>
<td>d (Å)</td>
<td>l (%)</td>
<td>d (Å)</td>
</tr>
<tr>
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<td>100</td>
<td>2.7591</td>
<td>100</td>
<td>2.0905</td>
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<tr>
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<td>5</td>
<td>1.7959</td>
</tr>
<tr>
<td>1.7407</td>
<td>11</td>
<td>1.7068</td>
<td>21</td>
<td>1.7284</td>
</tr>
</tbody>
</table>

SBAD phase also appears to be stable according to ab initio TTAM IP, we are confident that this discovery is not potential-specific. Because the character of the chemical bonding does not change up to at least 110 GPa (Sherman 1993), it is possible that the IP correctly describes interaction in the range of pressures of SBAD stability.

If there is free silica in the mantle, the transition to the denser SBAD phase should produce seismic discontinuity at depth corresponding to the pressure of the transition (~120–130 GPa corresponds to ~2600–2800 km depth according to Preliminary Reference Earth Model, Dziewonski and Anderson 1981). In fact, there is a sharp increase in velocity of ~2.8% at 2728 km (Weber and Davis 1990; Wright et al. 1985), which corresponds to the top of D* layer. This suggests either that there is also free silica above 2728 km or that free silica appears as the result of the breakdown of MgSiO₃ perovskite (Hu et al. 1994), either because of the higher stability of MgO (periclase) and SiO₂ (SBAD) in comparison with MgSiO₃ perovskite or because of chemical reactions at the core-mantle boundary (Goarant et al. 1992; Knittle and Jeanloz 1989).

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