Structural stability of silica at high pressures and temperatures

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The high-pressure phase diagram of SiO₂ has been calculated using density-functional perturbation theory. We find that phase transitions of silica do not correspond to any observed seismic discontinuities within the Earth. We analyze the breakdown of close packing occurring in SiO₂ above 200 GPa and conclude that it is due to asphericity and deformability of ions, which can generally lead to the formation on non-close-packed structures at high pressure. Our calculations indicate that pyrite-structured SiO₂, stable above 200 GPa, has no soft modes down to ambient pressure and could, therefore, be quenchable. Above 750 GPa a cotunnite-type phase is stable.

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I. INTRODUCTION

Silica (SiO₂) polymorphs are of great importance in solid state physics, technology, and Earth sciences. Understanding their high-pressure behavior can provide many useful ideas—especially for crystal chemistry of silicates that make up most of the Earth’s mantle. For example, the discovery of stishovite, a rutile-structured silica polymorph [Fig. 1(a)], has revolutionized the understanding of the deep Earth’s interior by suggesting that in deep-mantle silicates Si atoms are octahedrally (rather than tetrahedrally) coordinated. The transition from the fourfold to sixfold coordination, at least in liquids, may proceed via an intermediate exotic fivefold coordination. Many years after the discovery of stishovite, two post-stishovite phases were identified: those with the CaCl₂-type structures [for brevity we denote here as SiO₂-I, Fig. 1(b) and α-PbO₂-type (SiO₂-II, Fig. 1(c))]; theoretical studies suggested that at still higher pressures a pyrite-type phase [SiO₂-III, Fig. 1(c)] is stable. The pressure-temperature stability fields of these phases remain poorly known.

It is well established that at ~50 GPa and 298 K stishovite undergoes a second-order transition to SiO₂-I, although recently this transition was argued to be first order due to strain-order parameter coupling. This transition was proposed as the cause of the seismic anomaly observed in the Earth at the depth of 1200 km. Above ~90 GPa an α-PbO₂ structured phase (SiO₂-II) becomes stable, having space group Pbnm (Refs. 6 and 7) or its polar subgroup Pnc2₁,8,13.

The structures of stishovite SiO₂-I and SiO₂-II are based on the hexagonal close packing of oxygens with Si atoms filling half of the octahedral voids; there are many energetically similar metastable structures differing only in the distribution of cations over the octahedral voids. At high temperatures a disordered distribution is possible—as in the Fe₂N-type structure, experimentally found to be metastable for SiO₂ (Ref. 14).

According to theory, SiO₂-II is stable up to ~200 GPa, when it transforms to a pyrite-type phase (SiO₂-III). Silica has not yet been studied experimentally at conditions appropriate for synthesis of SiO₂-III, but pyrite-type phases are known for analogous materials at high pressure: RuO₂, PbO₂, GeO₂ (Ref. 15), and SnO₂ (Ref. 16). The pyrite structure (SiO₂-III) marks a new twist in structural chemistry of silica: it is not close packed, yet much denser than close-packed structures of stishovite, SiO₂-I, and SiO₂-II. Two additional features make this structure especially interesting: unusual 6+2 coordination of Si, and relatively short O-O contacts with a possibility of O-O bonds. Indeed, typical pyrites MX₂ do have X-X covalent bonds. Here we focus on two issues: (1) high-pressure phase diagram of SiO₂ and its geophysical significance and (2) investigation of the pressure-induced breakdown of structural close packing associated with the formation of SiO₂-III.

II. COMPUTATIONAL METHODOLOGY

Our calculations are based on density-functional perturbation theory (for a review, see Ref. 17) within the local density approximation (LDA) and pseudopotential plane wave method as implemented in the ABINIT code. We used non-local Troullier-Martins pseudopotentials with partial core corrections and plane wave basis sets with a 40 Ha cutoff. The pseudopotential core radii are 0.766 Å for O (1s²2s²2p⁶ core) and 1.105 Å for Si (1s²2s²2p⁶ core). The Brillouin zone was sampled with 4×4×6 (for stishovite and SiO₂-I) and 4×4×4 (for SiO₂-II and SiO₂-III) Monkhorst-Pack meshes. Electronic self-consistency was performed until forces converged to within 10⁻⁶ Ha/Bohr; crystal structures were optimized by steepest descent until forces on atoms were below 10⁻⁵ Ha/Bohr. With our computational settings, the total energies, energy differences between polymorphs, pressure, and phonon frequencies are converged to within 14×10⁻³ eV/atom, 2×10⁻³ eV/atom, 0.3 GPa, and 1 cm⁻¹, respectively. Dynamical matrices were calculated on a 2×2×3 (stishovite and SiO₂-I) and 2×2×2 (SiO₂-II and SiO₂-III) grids and then interpolated throughout the Brillouin zone using the technique, explicitly accounting for the long-range electrostatic contributions. The interpolation er-
rors are within 12 cm\(^{-1}\) in stishovite and SiO\(_2\)-I, and within 5 cm\(^{-1}\) in SiO\(_2\)-II and SiO\(_2\)-III.

Our calculations clearly confirm the second-order nature of the stishovite-SiO\(_2\)-I transition with mechanical instability \(C_{11} - C_{12} = 0\) precisely within 1 GPa at the thermodynamic transition pressure, and we see no hysteresis in this transition. For SiO\(_2\)-II we find that the true symmetry is Pbcn: starting with a distorted Pnc\(_2\) structure we obtained Pbcn after structural optimisation, in agreement with findings of Ref. 7. We note that the Pbcn structure has no soft modes.

Diagonalizing the dynamical matrices at a large number of wave vectors, we obtain the phonon density of states \(g(\omega)\) and can evaluate thermodynamic functions, e.g., heat capacity \(C_V\), entropy \(S\), and Helmholtz free energy \(F\), as a function of temperature:

\[
C_V(T) = k_B \int_0^{\omega_{\text{max}}} \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{\exp \left( \frac{\hbar \omega}{k_B T} \right)}{\left[ \exp \left( \frac{\hbar \omega}{k_B T} \right) - 1 \right]^2} g(\omega) d\omega, \tag{1}
\]

\[
S(T) = \int_0^{\omega_{\text{max}}} \left\{ -k_B \ln \left[ 1 - \exp \left( -\frac{\hbar \omega}{k_B T} \right) \right] \right. \\
\left. + \frac{1}{T} \frac{\hbar \omega}{\exp \left( \frac{\hbar \omega}{k_B T} \right) - 1} \right\} g(\omega) d\omega, \tag{2}
\]

\[
F(T) = E_0 + \int_0^{\omega_{\text{max}}} \left( \frac{\hbar \omega}{2} + k_B T \ln \left[ 1 - \exp \left( -\frac{\hbar \omega}{k_B T} \right) \right] \right) g(\omega) d\omega, \tag{3}
\]

where \(E_0\) is the energy of the static lattice, \(\hbar\) the Planck constant, and \(k_B\) the Boltzmann constant. Examples of calculated phonon densities of states are given in Fig. 2. As Table I shows, such calculations are able to reproduce experimental data for SiO\(_2\) and other materials rather accurately.

Within the quasiharmonic approximation, we have explored both thermodynamic and dynamical stability of SiO\(_2\) polymorphs; mechanical stability was studied separately by calculating the elastic constants from nonlinear stress-strain relations. We calculate the Gibbs free energy via the Helm-

![FIG. 1. Calculated structures of SiO\(_2\) phases. (a) stishovite at 20 GPa, (b) SiO\(_2\)-I at 70 GPa, (c) SiO\(_2\)-II at 120 GPa, (d) SiO\(_2\)-III at 220 GPa.](image)

![FIG. 2. (Color online) Calculated phonon densities of states of stishovite (bottom), SiO\(_2\)-II (middle) and SiO\(_2\)-III (top) at \(P=0\).](image)
TABLE II. Static equations of state. SiO$_2$-I is unquenchable, its zero-pressure properties are only fitted parameters. Total energy and volume (values per formula unit), bulk modulus and its pressure derivative are given.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$E_0$, a.u.</th>
<th>$V_0$, Å$^3$</th>
<th>$K_0$, GPa</th>
<th>$K'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stishovite</td>
<td>$-37.798568$</td>
<td>23.1559</td>
<td>318.326</td>
<td>4.3726</td>
</tr>
<tr>
<td>SiO$_2$-I</td>
<td>$(-37.796067)$</td>
<td>(23.5751)</td>
<td>(258.354)</td>
<td>(4.6135)</td>
</tr>
<tr>
<td>SiO$_2$-II</td>
<td>$-37.7925485$</td>
<td>22.7805</td>
<td>324.426</td>
<td>4.2327</td>
</tr>
<tr>
<td>SiO$_2$-III</td>
<td>$-37.7597881$</td>
<td>21.7481</td>
<td>344.806</td>
<td>4.3130</td>
</tr>
</tbody>
</table>

$^a$Third-order Birch-Murnaghan equation of state from experiment (Ref. 9): $V_0=23.315$ Å$^3$, $K_0=291$ GPa, $K'_0=4.29$.

The static part of $F(V,T)$ was represented by the Vinet equation of state$^{28}$ (Table II), the vibrational part was well fitted by third-order polynomial functions of volume at each temperature. Since the stishovite-(SiO$_2$-I) phase transition is due to the onset of a mechanical instability of stishovite, the corresponding phase equilibrium line was found as a set of $P,T$ points at which stishovite becomes mechanically unstable. All other equilibrium lines were found by examining free energy differences. Methodology used here is very similar to that of our recent works.$^{23,26,29}$

For the analysis of chemical bonding in SiO$_2$ polymorphs we employ topological analysis of electron density,$^{30}$ electron localization function,$^{31}$ and localized orbital locator.$^{32}$ For topological analysis, the total density was restored by adding atomic core electron density to the valence density obtained in our pseudopotential calculations. As shown by Bader,$^{30}$ the total electron density can be uniquely partitioned into atomic basins with well-defined, additive, and transferable properties, such as atomic volumes and charges. There are different types of critical points at boundaries between atomic basins; $(3,-1)$ points can be used to define atomic coordination. The density Laplacian $(\nabla^2 \rho)$ indicates regions of electronic concentration ($\nabla^2 \rho < 0$) or depletion ($\nabla^2 \rho > 0$); $\nabla^2 \rho < 0$ in the bonding region shows a shared (covalent) interaction as opposed to closed-shell interactions. Our calculations suggest that chemical bonding in stishovite and phases I–III is similar: at all pressures studied here these phases are wide-gap insulators, predominantly ionic with a covalent component for Si–O bonds (see also Bader and Born atomic charges in Table III). Si in the octahedral coordination, and similar parameters of Si–O bond critical points. The six $(3,-1)$ bond critical points between Si and O in SiO$_2$-III are characterized by low electron density (0.70 e Å$^{-3}$ at zero pressure) and positive Laplacian $\nabla^2 \rho$ (8.12 e Å$^{-5}$), suggesting that Si–O interaction is closed shell. From atomic volumes (Table III) we see that crystal volume is dominated by O atoms.

TABLE III. Bader volumes and charges at 0 GPa. For comparison, tetrahedral Si in sillimanite (Al$_2$SiO$_5$) has $Z_{Si}=3.164$ (3.191) $|e|$, $V_{Si}=3.223$ Å$^3$.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$Z_{Si}$</th>
<th>$V_{Si}$ Å$^3$</th>
<th>$Z_{O}$</th>
<th>$V_{O}$ Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stishovite</td>
<td>3.216</td>
<td>(3.865)$^a$</td>
<td>-2.702</td>
<td>10.239</td>
</tr>
<tr>
<td>SiO$_2$-II</td>
<td>3.202</td>
<td>(3.903)$^a$</td>
<td>-2.777</td>
<td>10.000</td>
</tr>
<tr>
<td>SiO$_2$-III</td>
<td>3.170</td>
<td>(4.020)$^a$</td>
<td>-2.950</td>
<td>9.396</td>
</tr>
</tbody>
</table>

$^a$In parentheses: spherically averaged Born dynamical charges.

The calculated phase diagram (Fig. 3) is very simple and agrees remarkably well with the diagram sketched by Akins and Ahrens$^{33}$ on the basis of their shock compression data and reasonably well with (Ref. 34). Recent theoretical work$^{34}$ also gives similar results. However, experiments of Ref. 13 do not agree with our results for the (SiO$_2$-I)-(SiO$_2$-II) transition.
-II) equilibrium line. In Ref. 13, SiO$_2$-II was obtained not by compression of SiO$_2$-I, but by pressurising cristobalite structure in the region of its metastability and therefore what the authors of Ref. 13 observed was probably a thermally activated metastable transition cristobalite-(SiO$_2$-II), facilitated by temperature and therefore having a negative Clapeyron slope. This is not too surprising, given the multitude of known metastable phases and transitions in SiO$_2$ (see, e.g., Refs. 7 and 14).

There has been some experimental evidence$^{36}$ that at pressures 62–100 GPa and temperatures 1900–3200 K, MgSiO$_3$ perovskite breaks down into the mixture of oxides, MgO and post-stishovite phase of SiO$_2$ identified$^{36}$ as SiO$_2$-II. An implication of these results would be that SiO$_2$-II is a major mineral phase of the lower mantle. From our phase diagram (Fig. 3) we see, however, that most of the $P,T$ conditions indicated in Ref. 36 correspond to stability of SiO$_2$-I. Moreover, most experiments (e.g., Ref. 38 and 39) and recent $ab$ initio calculations$^{28}$ show that MgSiO$_3$ perovskite does not decompose into MgO+SiO$_2$ at lower mantle conditions.

This implies that pure SiO$_2$ phases in the lower mantle can exist only in SiO$_2$-rich regions associated with subduction of relatively cold lithospheric slabs [in the rest of the lower mantle MgO/SiO$_2$ > 1, and any free SiO$_2$ would react with MgO (Ref. 26)]. Using our calculated phase diagram one can predict the depths of seismic discontinuities that could occur due to phase transitions of SiO$_2$ inside the Earth’s mantle. If SiO$_2$ phases were abundant in areas of subduction, one would expect two seismic discontinuities [Fig. 3(b)], one between 1350 km (55 GPa, 1630 K) and 1410 km (58 GPa, 2130 K) associated with the stishovite-(SiO$_2$-I) transition and the other between 2145 km (94 GPa, 1830 K) and 2210 km (90 GPa, 2440 K) due to the (SiO$_2$-I)-(SiO$_2$-II) transition. The LDA typically underestimates transition pressures by several GPa, so in reality these phase transitions could occur 100–200 km deeper. Still, these depths (~1500 and ~2300 km) do not correspond to any observed seismic discontinuities. Reference 35 relates the (SiO$_2$-I)-(SiO$_2$-II) transition to the so-called $D''$ discontinuity at 2700 km,$^{40}$ but this is inconsistent with present results: the depth of transition does not agree with our results and the transition itself, involving only minor changes in shear wave velocity, cannot explain the observed large shear wave discontinuity. In addition, the (SiO$_2$-I)-(SiO$_2$-II) transition is associated with a large decrease in elastic anisotropy$^{41}$ that is inconsistent with large seismic anisotropy below 2700 km.$^{42}$ In fact, seismic velocity jumps due to the (SiO$_2$-I)-(SiO$_2$-II) transition are small [~1% in pure SiO$_2$ (Ref. 41)] and for all realistic compositions (amount of SiO$_2$ phases below 30 vol. %) it would be undetectable with current seismological techniques. However, the effect of the stishovite-(SiO$_2$-I) transition on seismic velocities is much larger [~60% for shear waves (Ref. 41)] and should be observable if any significant amount (>2 vol. %) of SiO$_2$ phases were present in the lower mantle. Since no discontinuity is known at 1500 km, we conclude SiO$_2$ polymorphs do not exist in significant amounts in any extended regions of the Earth’s lower mantle.

![Phonon dispersion curves for SiO$_2$-III at P=0, showing no soft modes.](image)

**FIG. 4.** Phonon dispersion curves for SiO$_2$-III at $P=0$, showing no soft modes.

**IV. PYRITE-TYPE PHASE (SiO$_2$-III) AND BREAKDOWN OF CLOSE PACKING**

It is known that stishovite and SiO$_2$-II possess remarkably high hardnesses,$^{43}$ but SiO$_2$-III may be even harder, since this cubic phase has a significantly higher bulk modulus (at zero pressure $344\pm3$ GPa, as found from the elastic constants and the equation of state, Table II). We find that SiO$_2$-III is dynamically and mechanically stable at least in the range 0–260 GPa (see Fig. 4), and therefore could be decompressed to ambient conditions.

SiO$_2$-III is very interesting from the crystal-chemical point of view: its structure is unusual for an oxide and suggests (by analogy with pyrite-type chalcogenides) that there could be O-O bonds. Structures of stishovite, SiO$_2$-I, and SiO$_2$-II are based on the increasingly regular hexagonal close packing of O atoms. The question is why SiO$_2$-III, in spite of lack of anion close packing, is much denser than these phases and becomes more stable at extreme pressures. We remind the reader that density is a crucial factor for high-pressure stability.

First, we argue that there are no O-O bonds in the structure. The structure of SiO$_2$-III has only two independent variables—the oxygen coordinate $x_0$ and the unit cell parameter. At $x_0=0.10$–0.15 one has the molecular CO$_2$-type structure, at $x_0=0.25$ the fluorite structure. By increasing $x_0$ to above 0.345 one arrives at the normal pyrite structure with
distinct O–O “dumbells,” at $x_O=0.345$ the “dumbell” O–O distance becomes equal to six other O–O distances, and at $x_O<0.345$ “dumbells” dissociate. Although SiO$_2$-III is just on the border ($x_O=0.344$ at $P=0, 0.350$ at 260 GPa), topological analysis shows a critical point in the middle of each O–O “dumbell” in this structure at all pressures, as in typical pyrite structures. However, this is not a bonding interaction: the O–O interatomic distance is much longer than the usual distances of 1.4–1.5 Å of peroxide bonds and more similar to nonbonding O–O distances in ionic oxides (2.2 Å at $P=0$). Although there is a critical point between these atoms, the corresponding electron density is low and “$r^2$ is positive” suggestive of a closed-shell interaction, probably repulsive between like atoms. Figure 5 shows maps of the total electron density, its Laplacian, the electron localization function, and localized orbital locator in the (110) plane of SiO$_2$-III. These maps indicate mixed ionic-covalent character of Si—O bonds, but no covalent bonding between the O atoms. In particular, between these atoms one sees no peak in the electron localization function or the localized orbital locator, and $\nabla^2 \rho$ is positive. It is clear from Fig. 5 that oxygen atoms are highly aspherical in SiO$_2$-III.

For the breakdown of close packing under pressure, two mechanisms are well known: (1) increase of the cation/anion size ratio with pressure that leads to high (>6) coordination numbers incompatible with close packing, and (2) complex electronic reorganisation within the solid. Neither applies to our case. As discussed in Sec. II, in all considered structures Si atoms are 6-coordinated, and there are no major differences in bonding between SiO$_2$-III and other silica phases.

In the present case, the high density of SiO$_2$-III and its stability at high pressure are explained by the asphericity of oxygen atoms in its structure (visible in Fig. 5): indeed, packing of aspherical atoms can be denser than close packing of hard spheres. The asphericity itself is due to partial covalency of Si—O bonds and steric deformations of atoms in the structure. According to our ab initio results, SiO$_2$-III is 5% denser than close-packed SiO$_2$-II at zero pressure, whereas the hard-sphere model incorrectly predicts 19% lower density.

Among simple models alternative to the traditional “hard-sphere” thinking, there are “deformable sphere” models (e.g., pair potential models, which correctly predict SiO$_2$-III to be denser than SiO$_2$-II) and “bond network” models that focus on bond lengths (which show only modest variations in crystals) rather than on radii of atoms (which are allowed to be aspherical). The best of the latter models, Brown’s bond...
valence model,\textsuperscript{47} allows one to predict bond lengths for each topology by solving bond-valence balance equations. Within this model, SiO\textsubscript{2}-III is correctly predicted to be 6\% denser than undistorted close-packed polymorphs. The dramatic failure of the hard-sphere model and success of even the simplest models that are able to account for deformability of atoms leads us to conclude that deformability of atoms is a key factor in the breakdown of close packing under pressure. There can, in principle, be many structures that are denser than their close-packed counterparts; in these structures, atoms are not spherical and experience “squeezing” at short distances (e.g., in SiO\textsubscript{2}-III O atoms are “squeezed” at short O-O contacts). Though energetically costly, this may enable greater density and, thus, stability at high pressure.

Figure 6 shows an \textit{ab initio} zero-pressure unit cell volume of SiO\textsubscript{2}-III as a function of $x_0$ (line 1), in comparison with two simple models: Brown’s model (line 2) and hard-sphere model (line 3). Even the shape of this line cannot be reproduced by a simple hard-sphere model (line 3). Brown’s model is rather successful, its difference from \textit{ab initio} results being mainly due to steric O-O repulsion,\textsuperscript{47} which is greatest in the fluorite structure ($x_0=0.25$) and $x_0>0.375$ (pyrite structure with very close O-O contacts) and smallest at $x_0=0.34$ (cf. our \textit{ab initio} structure with $x_0=0.344$). Thus, the structure of SiO\textsubscript{2}-III found in \textit{ab initio} calculations combines high density and only modest anion-anion repulsion.

\section*{V. POST-PYRITE PHASES}

For the reasons discussed above, SiO\textsubscript{2}-III appears to be a remarkably stable phase. As possible post-pyrite phases, we have considered the baddeleyite (space group $P2_1/c$, 12 atoms per unit cell), cotunnite ($Pnma$, 12 atoms per cell), and the OI structure ($Pbca$, 24 atoms per cell) recently found in TiO\textsubscript{2};\textsuperscript{48} these structures are shown in Fig. 7. For these phases, the Brillouin zone was sampled by $4\times4\times4$, $4\times8\times4$, and $2\times4\times4$, respectively; all other computational settings are the same as described in Sec. II. At zero K, only the cotunnite structure has a region of stability—it becomes more stable than SiO\textsubscript{2}-III above 750 GPa (Fig. 8). In this non-close-packed structure Si atoms are in the ninefold coordination, which is incompatible with close packing. The OI-type structure is only marginally less stable at zero K, and cannot be ruled out as a possible stable phase at high temperatures and pressures $\sim700$–$800$ GPa.

\section*{VI. SUMMARY}

Silica (SiO\textsubscript{2}) undergoes a series of post-stishovite structural phase transitions: first into a CaCl\textsubscript{2}-type phase ($\sim50$ GPa), then into an $\alpha$-PbO\textsubscript{2}-type ($\sim90$ GPa), pyrite-type ($\sim200$ GPa), and cotunnite-type (750 GPa) phases. Using density-functional perturbation theory, we have calculated the high-pressure phase diagram of SiO\textsubscript{2}. We conclude that it is unlikely that SiO\textsubscript{2} polymorphs exist in significant amounts in any large portion of the Earth’s lower mantle. Pressure-induced breakdown of close packing in SiO\textsubscript{2}, predicted to occur at 200 GPa, has been examined in detail and explained by deformability of atoms enabling high density for non-close-packed structures: for a system of deformable ions, non-close-packed structures may turn out to be denser and more stable at high pressure. This mechanism for pressure-induced breakdown of close packing is expected to be very common. One of further examples is provided by Al\textsubscript{2}O\textsubscript{3}, where close-packed corundum phase transforms at $\sim90$ GPa into a non-close-packed Rh\textsubscript{2}O\textsubscript{3}(II) structure (Ref. 49, and references therein) without changes in the electronic structure or atomic coordination numbers. We expect that appearance of non-close-packed phases at high pressure should be a general feature of many materials, including silicates and oxides.

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