CaSiO₃ perovskite at lower mantle pressures

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We investigate by first-principles the structural behavior of CaSiO₃ perovskite up to lower mantle pressures. We confirm that the cubic perovskite modification is unstable at all pressures. The zero Kelvin structure is stabilized by SiO₆ octahedral rotations that lower the symmetry to tetragonal, orthorhombic, rhombohedral, or to a cubic supercell. The resulting structures have comparable energies and equation of state parameters. This suggests that relatively small deviatoric/shear stresses might induce phase transformations between these various structures softening some elastic moduli, primarily the shear modulus. The seismic signature accompanying a local increase in CaSiO₃ content should be a positive density anomaly and a negative Vₚ anomaly.


1. Introduction

[2] The lower mantle is generally believed to consist mainly of (Mg,Fe)SiO₃ perovskite and (Mg,Fe)O magnesiowüstite, with CaSiO₃ perovskite, maybe, up to 7–8 volume % [Ringwood, 1975; O'Neill and Jeanloz, 1990; Ito and Stixrude, 1992; Hellfrich and Wood, 2001; Irifune, 1994] or 9 weight % [Kesson et al., 1998]. Despite its importance, there are many unanswered questions about the structure, the stability, the equation of state and the properties of CaSiO₃ under pressure and temperature, that complicates any attempt to model the lower mantle [Stacey and Isaak, 2001].

[3] At ambient conditions, CaSiO₃ forms the mineral wollastonite, which has a pyroxenoid structure. Under pressure, it transforms to walstromite, then to a mixture of larnite (Ca₂SiO₄) and titanite-structured CaSiO₃ [Gasparik et al., 1994; Swamy and Dubrovinsky, 1997; Shim et al., 2000a]. The perovskite structure appears at about 10 GPa and 1100 K, the phase boundary having a positive Clausius-Clapeyron slope of about 2.7 MPa/K (as estimated from the phase diagrams published in the papers cited above). At lower mantle conditions CaSiO₃ has an ideal cubic perovskite structure, while at lower temperatures it is distorted. The small amplitude of the distortions is hardly observable by current high-temperature and high-pressure X-ray techniques and several orthorhombic and tetragonal structures have been proposed, based on experimental measurements [Shim et al., 2002; Kurashina et al., 2004, Ono et al., 2004] or theoretical calculations [Stixrude et al., 1996; Chizmeshya et al., 1996; Akber-Knutson et al., 2002; Magyari-Köpe et al., 2002]. CaSiO₃ perovskite is unquenchable at ambient conditions [e.g., Liu and Ringwood, 1975; Wang and Weidner, 1994].

[5] The equation of state (EOS) of the cubic perovskite phase of CaSiO₃ has been measured up to core-mantle boundary pressures by different groups [e.g., Mao et al., 1989; Tanimoto and Yagi, 1989; Wang and Weidner, 1994; Wang et al., 1996; Shim et al., 2000a, 2000b, 2002; Kurashina et al., 2004; Ono et al., 2004; Shieh et al., 2004]. The average of the published fits of the experimental results by third order Birch-Murnighan EOS, yields a unit cell volume, V₀ = 45.542 Å³, bulk modulus, K₀, ranging from 232 to 288 GPa, and its pressure derivative, K', within 3.9–4.5. In most of the experimental studies, K' was fixed to 4.0. A variety of techniques were also employed in theoretical studies of CaSiO₃ [e.g., Wentzcovitch et al., 1995; Chizmeshya et al., 1996; Stixrude et al., 1996; Swamy and Dubrovinsky, 1997; Karki and Crain, 1998; Hama and Suito, 1998; Akber-Knutson et al., 2002], ranging from empirical interatomic potentials fitted on experimental thermodynamic data to pure first-principles calculations. The average of the theoretical results is similar to the one obtained for the experimental data: V₀ = 45.728 Å³, K₀ = 246–305 GPa and K' = 3.5–4.3. Many of these studies, both experimental and theoretical, focus on the behavior of the cubic modification of CaSiO₃ under pressure.

[6] In the present study we perform a detailed investigation of the major symmetry-allowed modifications of CaSiO₃, obtained as distortions from the parent cubic phase. We discuss the stability and the equation of state of these phases and demonstrate that the I4/mcm phase is the most likely stable static atomic configuration.

2. Computational Details

[6] We perform first-principles calculations based on density functional theory (DFT) with plane waves and pseudopotentials. We use Troullier-Martins pseudopotentials, previously tested for Ca [Karki and Wentzcovitch, 2003], and for Si and O [Wentzcovitch et al., 2004] with an 85 Rydberg (1 Rydberg = 13.605 eV) cutoff for the plane waves kinetic energy. We determine the crystal structure using damped variable-cell shape molecular dynamics
3. Various Structural Constructions

The phonon dispersion relations of the Pm$\overline{3}$m cubic phase computed at several pressures show lattice instabilities in the R ($1/2$, $1/2$, $1/2$) and M {$1/2$, $1/2$, $0$} points of the reciprocal space (Figure 1). All the instabilities correspond to octahedral rotations. The instability in R increases with pressure, while the one in M slightly decreases with pressure. These results are consistent with a previous theoretical investigation [Stixrude et al., 1996]. We build the candidate low-temperature structures by superposing these unstable octahedral rotations into the Pm$\overline{3}$m cubic structure up to 160 GPa.

The unstable phonon modes in R, three-fold degenerated, correspond to nearly rigid out-of-phase rotations of the SiO$_6$ octahedra around the cartesian axes. Following the notation proposed by Glazer [Glazer, 1972, 1975], these rotations correspond to a$^-$, b$^-$ or c$^-$, if the rotation axis is parallel to [100], [010] or [001], respectively. The unstable phonon modes in M, one-fold degenerated, correspond to rigid in-phase rotations of the octahedra around the cartesian axis. Their notation is a$^+$, b$^+$ or c$^+$ if the corresponding rotation axis is parallel to [100], [010] or [001], respectively. The absence of the octahedral rotation around a certain axis is denoted by a$^0$, b$^0$ or c$^0$. Rotations along different cartesian axis, but with the same amplitude are denoted with the same letter, for example, a a$^+$ means in-phase rotations along the [100] and [010] cartesian axis, with the same amplitude and an out-of-phase rotation along the [001] cartesian axis with a different amplitude.

Glazer [1972, 1975] obtained all the 26 possible lower-symmetry structures by adding up to three rotations, one around each cartesian axis. Later, Darlington [2002] reduced the number of structures (Table 1), by taking into account only those generated by rotations of same magnitude around equivalent axis. We consider in our analysis the structures generated by the latter approach.

<table>
<thead>
<tr>
<th>Space Group</th>
<th>Glazer Notation</th>
<th>Unstable Phonon Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pm$\overline{3}$m</td>
<td>a a$^+$</td>
<td>-</td>
</tr>
<tr>
<td>I4/mcm</td>
<td>a a$^+$</td>
<td>R</td>
</tr>
<tr>
<td>Im$\overline{3}$a</td>
<td>a b$^+$</td>
<td>R_R</td>
</tr>
<tr>
<td>R$\overline{3}$c</td>
<td>a a$^+$</td>
<td>R_R_R</td>
</tr>
<tr>
<td>P4/mmb</td>
<td>a b$^+$</td>
<td>M</td>
</tr>
<tr>
<td>I4/mmm</td>
<td>a b$^+$</td>
<td>M,M</td>
</tr>
<tr>
<td>Im$\overline{3}$</td>
<td>a a$^+$</td>
<td>M,M,M</td>
</tr>
<tr>
<td>P4/mmc</td>
<td>a a$^+$</td>
<td>M,M,R</td>
</tr>
<tr>
<td>Pmna</td>
<td>a b$^+$</td>
<td>R,R,M</td>
</tr>
</tbody>
</table>

4. Results and Discussion

The properties of the lower-symmetry structures are very similar in terms of enthalpy, density and equation-of-state parameters. With the exception of the R$\overline{3}$c structure (obtained from the addition of the three unstable R modes), all the other structures have lower energy than the cubic one.

The relative energy differences between all phases are very small, as shown in Figure 2 and Table 2. They are computed based on fits with third-order polynomial expansions of the energy as a function of the compression $f$ [Poirier, 2000]:

$$f = \frac{1}{2} \left( \frac{V_0}{V} \right)^{2/3} - 1.$$  (1)

In general, the tetragonal structures are energetically preferred to the orthorhombic ones, the lowest in energy being the I4/mcm phase (obtained from one R mode). The energy difference between the cubic and the tetragonal I4/mcm structure is on the order of 43 meV/molecule at low pressure and 100 meV/molecule at high pressure. In order of increasing energy, after the I4/mcm phase we find the P4$_2$/nmc, Pnma and I4/mmm (whose energy difference is on the order of the accuracy of the calculation), I4/mmm and Im$\overline{3}$ (again with very small energy differences) and the cubic Pm$\overline{3}$m phase. Our results are different from those obtained considering only the octahedral tilt [Magyari-Köpe et al., 2002] due to the absence of further structural
relaxation in the cited study. They are also different with respect to those obtained in a density-functional-based Variationally Induced Breathing model study [Akber-Knutson et al., 2002], who considered only Pm3m, I4/mcm, Pnma and P1 structures and where the orthorhombic one is energetically preferred at high pressure. The differences are perhaps not surprising given the subtlety of the problem and the more empirical approach used in the above study (where the electron density is obtained as a superposition of spherical ionic charge densities, thus not taking into account effects like polarization).

In general our calculated c/a ratio is larger than 1.0, while the experimental measurements [Shim et al., 2002] showed a slightly smaller than 1.0 c/a ratio. With the exception of the P4/mmbm structure, the c/a ratio exhibited by the tetragonal and the orthorhombic structures, is about 1.03, slightly increasing with pressure. The P4/mmbm structure presents a c/a ratio on the order of 1.08 at 0 GPa, that decreases with pressure to about 1.07 at 160 GPa. The I4/mcm and the P4/nmc structures have c/a ratios about 1.02 at 0 GPa and about 1.03 at 160 GPa. The two orthorhombic structures, Imma and Pnma have the b/a ratio about 1.005 at low pressure and about 1.01 at high pressure, and the c/a ratio about 0.995 at all pressures. The I4/mmm structure, exhibits a c/a ratio of about 0.995 at all pressures. A possible alternative explanation to the c/a ratio lower than unity invokes distortions in octahedra instead of octahedral tilting [Shim et al., 2002], resulting in a tetragonal P4/mmm structure, but this has not been considered in our study.

These differences in the c/a ratio between our theoretical results and the experimental data account also for differences in the diffraction peaks (when compared to Shim et al. [2002], Kurashina et al. [2004], and Ono et al. [2004]). Except for the P4/mmbm theoretical structure, all the other have hardly observable splittings of the corresponding cubic (200) peak, and with very similar intensities.

All the structures have very similar densities, ranging within about 0.02 g/cm^3 at all pressures. The density of the cubic modification is 4.32 g/cm^3 at 0 GPa and 5.77 g/cm^3 at 130 GPa. The R3c structure has the smallest density, while the I4/mcm structure has the largest density, 4.33 g/cm^3 at 0 GPa and 5.78 g/cm^3 at 130 GPa. The density of CaSiO_3 is about 0.25 g/cm^3 larger than PREM's [Dziewonski and Anderson, 1981], with a relatively constant difference at all pressures. Obviously, the temperature will decrease these differences.

As expected from the variation of the energy and density with pressure, the pressure-volume relations are similar for all the studied phases. We fit third-order (BM3) and forth-order (BM4) Birch-Murnagham equations of state to first-principles results in all polymorphs. The

![Figure 2. Energy difference between the polymorphs of CaSiO_3.](image)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Pm3m</th>
<th>I4/mcm</th>
<th>Imma</th>
<th>R3c</th>
<th>P4/mmbm</th>
<th>I4/mmm</th>
<th>Im3</th>
<th>P4/nmc</th>
<th>Pnma</th>
</tr>
</thead>
<tbody>
<tr>
<td>V (Å^3)</td>
<td>44.579</td>
<td>44.537</td>
<td>44.567</td>
<td>44.821</td>
<td>44.629</td>
<td>44.599</td>
<td>44.600</td>
<td>44.576</td>
<td>44.576</td>
</tr>
<tr>
<td>K (GPa)</td>
<td>250</td>
<td>249</td>
<td>249</td>
<td>247</td>
<td>247</td>
<td>250</td>
<td>250</td>
<td>248</td>
<td>249</td>
</tr>
</tbody>
</table>

| V (Å^3)  | 44.588| 44.547| 44.576| 44.832| 44.641  | 44.609 | 44.610| 44.566 | 44.588|
| K (GPa)  | 248  | 247   | 247  | 244  | 244     | 248    | 247  | 251    | 246  |
| K''''    | -0.002| -0.002| -0.002| -0.002| -0.002  | -0.002 | -0.002| -0.001 | -0.002|

Energy, meV/molecule

<table>
<thead>
<tr>
<th>Energy</th>
<th>32.5 Å^3</th>
<th>43 Å^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>-10</td>
<td>-10</td>
</tr>
<tr>
<td>-68</td>
<td>-8</td>
<td>-8</td>
</tr>
<tr>
<td>483</td>
<td>10</td>
<td>357</td>
</tr>
<tr>
<td>-10</td>
<td>-5</td>
<td>-8</td>
</tr>
<tr>
<td>-8</td>
<td>-8</td>
<td>-37</td>
</tr>
</tbody>
</table>

*The EOS parameters are derived from third- (BM3) and forth-order (BM4) Birch-Murnagham fits to the first-principles results. The uncertainty of the calculations is on the order of 20 meV/molecule.
results of the fits are summarized in Table 2. The values for
the specific volume, \( V_\text{p}/Z \), where \( Z \) is the number of
molecules in the unit cell, range in a narrow interval,
44.5–46.0 \( \text{Å}^3 \). The bulk modulus within BM3 is about
250 GPa for all the structures, with the exception of R3c,
and slightly smaller in BM4, where the spread of the value
is somewhat larger: 246–251 GPa.

This study has considered only \( 2 \times 2 \times 2 \) super-
structures resulting from unstable phonons at M and R. They
all have similar energies and it is anticipated that structures
with larger primitive cells but similar octahedral rotation
patterns will have similar energies as well. Since along any
M-R line an entire optical branch is unstable, it is expected
that different and larger superstructures result from other
frozen commensurate and/or incommensurate phonons. The
resulting structures will have tetragonal symmetry if the
frozen phonons reside along the same MR line. Unstable
phonons belonging to different MR lines will generate
orthorhombic or tetragonal structures.

[19] This multitude of structural instabilities has two
main consequences. From the structural point of view, the
high temperature stabilization of the cubic structure may
occur by two different processes: anharmonic fluctuations
between these structures, or static disorder of octahedral
rotations. At the moment, without knowledge of the energy
barriers between these structures, this remains an open
point. This question should be properly investigated by first
principles molecular dynamics simulations.

[20] Second, since CaSiO\(_3\) is permanently on the verge
of structural transformations between these phases, it is
likely to display giant responses to deviatoric or shear
stresses. These stresses caused by seismic waves might
induce phase transformations (actually symmetry trans-
formations), regardless of temperature. Therefore, the
seismic signature accompanying local increase in CaSiO\(_3\)
content should be a positive density anomaly and a
simultaneous negative anomaly in \( V_\text{p} \). The \( V_\text{p} \) anomaly
is less certain due to the relatively large bulk modulus of
CaSiO\(_3\) at high pressure (125–145 GPa larger than
PREM’s at 135 GPa and \( T = 0 \) K). Temperature effects
on the elasticity of CaSiO\(_3\) are expected to be quite
dramatic due to these subtle phase transitions and molec-
ular dynamics calculations are expected to provide the
magnitude of all these effects. Although still controver-
sial, anti-correlation between density and shear velocity
appears to be detected by seismic tomography in places
such as beneath the Central Pacific [Ishii and Tromp,
1999]. Excess iron [Humayun et al., 2004] is expected
to be related to such anomaly, however, CaSiO\(_3\) might be
associated with it as well.

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