Theoretical determination of the structures of CaSiO₃ perovskites

Density functional theory is used to determine the possible crystal structure of the CaSiO₃ perovskites and their evolution under pressure. The ideal cubic perovskite is considered as a starting point for studying several possible lower-symmetry distorted structures. The theoretical lattice parameters and the atomic coordinates for all the structures are determined, and the results are discussed with respect to experimental data.

1. Introduction

CaSiO₃ is the third most important component of the Earth’s lower mantle, where, according to the current geophysical models, it can account for as much as 7% in volume (Ringwood, 1975; O’Neill & Jeanloz, 1990; Ita & Stixrude, 1992). Above 10 GPa and 1100 K, CaSiO₃ has the ideal cubic perovskite structure (Gasparik et al., 1994; Swamy & Dubrovinsky, 1997; Shim et al., 2000) with Pm̅3m symmetry.

This phase is unquenchable, and at ambient conditions of temperature and pressure it becomes amorphous (e.g. Liu & Ringwood, 1975; Wang & Weidner, 1994). According to different experimental studies (Shim et al., 2002) and theoretical calculations (Stixrude et al., 1996; Chizmeshya et al., 1996; Akber-Knutson et al., 2002; Magyari-Köpe et al., 2002; Jung & Oganov, 2005), at low temperature, CaSiO₃ has a distorted-perovskite structure, several tetragonal and orthorhombic candidates being proposed. However, no structural refinement of these possible modifications has been performed to date, and there are still controversies related to the symmetry of these phases.

In our previous paper (Caracas et al., 2005), we reported on the implications of CaSiO₃ in modeling the Earth’s lower mantle, while in the present study we present a detailed analysis of the crystallochemistry of CaSiO₃ perovskites. We start our analysis with the investigation of the phonon band dispersions in the cubic phase at different pressures. We find that the cubic structure exhibits unstable phonon modes at the zone boundary, appearing between the high-symmetry points $R \{1/2, 1/2, 1/2\}$ and $M \{1/2, 1/2, 0\}$. The instability of the cubic phase increases with pressure, the frequency of the unstable phonon at $R$ decreasing from 150i cm⁻¹ at ~5 GPa to 22i cm⁻¹ at 164 GPa. The frequency of the LO (longitudinal optic) unstable phonon at $M$ slightly increases from 109i cm⁻¹ at ~5 GPa to 99i cm⁻¹ at 164 GPa. These unstable modes are characterized by rotations of octahedra in columns parallel to the Cartesian axes. The unstable mode at $M$ corresponds to in-phase rotations, where all the octahedra in one column rotate in the same direction, while the unstable mode at $R$ corresponds to out-of-phase rotations, where each octahedron rotates contrary to all its neighbors. According to Glazer’s (1972, 1975) notation, the first type of rotation, in-phase, is...
designated by a plus sign, and the second, out-of-phase, by a minus sign. Consequently, the \(a^+b^-c^+\) notation represents the superposition of an in-phase rotation around the \(a\) axis and an out-of-phase rotation around the \(b\) axis, with different amplitudes. There is no rotation around the \(c\) axis. This notation corresponds to a structure derived by the simultaneous condensation of one unstable phonon at \(R\) and one at \(M\). Glazer (1972, 1975) built all the possible distorted perovskite structures based on such rigid octahedral rotations, obtaining 26 structures by combining up to three out-of-phase and/or in-phase rotations.

Further improvements of Glazer’s model were realized by taking into account the group–subgroup relations between the distorted structures (Howard & Stokes, 1998), or by considering only those generated by rotations of the same magnitude around equivalent axes (Darlington, 2002). We base our exploration of the distorted structures of CaSiO₃ perovskite on the approach proposed by Darlington (2002). Our analysis is thus limited only to the structures that may result from the condensation of the unstable phonon modes at \(R\) and \(M\), the largest distorted cell being a \(2 \times 2 \times 2\) supercell (\(Z = 8\)) of the cubic structure (Table 1). All the theoretical structures listed in Table 1 are energetically competitive and at high pressure slightly lower than the cubic \(Pm3\) phase. Condensations of unstable phonon modes at points other than \(R\) and \(M\) are certainly possible at arbitrary commensurate and/or incommensurate points on the \(MR\) line. However, based on our results, we do not expect a major energy lowering due to such condensations.

### Table 2

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Space group</th>
<th>Ca</th>
<th>Si</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pm\bar{3}m)</td>
<td>221</td>
<td>((0,0.5,0.5))</td>
<td>((0,0.0))</td>
<td>((0.5,0.0))</td>
</tr>
<tr>
<td>(I4/mcm)</td>
<td>140</td>
<td>((0,0.5,0.25))</td>
<td>((0,0.0))</td>
<td>((0.0,0.25))</td>
</tr>
<tr>
<td>(Imma)</td>
<td>74</td>
<td>((0,0.25,0))</td>
<td>((0,0.0))</td>
<td>((0.25,0.25))</td>
</tr>
<tr>
<td>(P4/mbm)</td>
<td>127</td>
<td>((0,0.0,0.5))</td>
<td>((0,0.0))</td>
<td>((0.0,0.5))</td>
</tr>
<tr>
<td>(I4/mmm)</td>
<td>139</td>
<td>((0,0.0,0))</td>
<td>((0,0.5))</td>
<td>((0.25,0.25,0.25))</td>
</tr>
<tr>
<td>(I43)</td>
<td>204</td>
<td>((0,0.0,0))</td>
<td>((0,0.5))</td>
<td>((0.25,0.25,0.25))</td>
</tr>
<tr>
<td>(P42/nmc)</td>
<td>137</td>
<td>((0,0.75,0.75))</td>
<td>((0,0.0))</td>
<td>((0.75,0.75,0.75))</td>
</tr>
<tr>
<td>(Pnma)</td>
<td>62</td>
<td>((0,0.25,0))</td>
<td>((0,0.0))</td>
<td>((0.25,0.25,0.25))</td>
</tr>
</tbody>
</table>

### 2. Computational details

All the calculations are based on the local density approximation of the density functional theory (Hohenberg & Kohn, 1964; Kohn & Sham, 1965), as implemented in the PWSCF code (Baroni et al., 2001). The PWSCF code is based on plane waves and pseudopotentials. Within this approach, the wavefunctions describe only the valence and conduction electrons, while the core electrons are taken into account using pseudopotentials. We use Troullier–Martins pseudopotentials, whose construction details and reference electronic configurations are published elsewhere (Karki & Wentzcovitch, 2003).

We determine the crystal structures using variable-cell-shape molecular dynamics (Wentzcovitch, 1991). This method allows the simultaneous determination of both the unit-cell parameters and the internal degrees of freedom (atomic coordinates) within an \(ab\) \(initio\) approach. A fictitious mass is attributed to the unit cell in order to apply the molecular dynamics technique to both the cell and the atoms. Here these dynamics are used in the damped form to search for the lowest enthalpy configurations. We fully relax the lattice parameters and the atomic positions. The initially chosen space-group symmetries are naturally preserved during the relaxation process leading to the final lattice parameter and Wyckoff coordinates.

We use an 85 Rydberg (1 Rydberg = 13.605 eV) cut-off radius for the plane-wave kinetic energy. The sampling of the parent cubic Brillouin zone (BZ) is achieved by using a primitive \(4 \times 4 \times 4\) grid of special \(k\) points (Monkhorst & Pack, 1976). These parameters ensure an accuracy of the calculations of better than 5 kbar in pressure and of the order of 10 meV per molecule in energy. As we study different structures, all derived from the cubic one, we use in all our calculations BZ sampling schemes that are equivalent to the \(4 \times 4 \times 4\) grid of \(k\) points of the parent cubic structure. The relation between the BZs follows the group–subgroup relation.
that exists between the parent cubic and each of these low-
symmetry structures. As they represent superstructures of
the cubic lattice, their BZ will be smaller than the parent cubic
one. Some of the k points from the first cubic BZ will find
themselves in the second BZ of the superstructure. Conse-
sequently, these points will be folded back to the first BZ of the
superstructure. The high symmetry of the starting grid that
samples the parent cubic structure and the position of the BZs
of the superstructures with respect to the cubic one ensure the
superposition of the k points during folding, and thus a smaller
number of k points in the superstructure is needed. The result-
ning k-point grids in the superstructures may be described
as several superposed grids, a common technique that allows a
maximum sampling of the BZ with a minimum cost (Froyen,
1992). This procedure also guarantees the accuracy and the
meaningfulness of the comparison between the different
polymorphs, as the reciprocal space is equally well sampled in
all the structures. The k-point grids used for each structure and
their shifts with respect to Γ are given in Table 1, while Fig. 1
presents a simplified model of their reduction.

3. Results and discussion

All the cubic, tetragonal and orthorhombic structures
obtained from condensation of the unstable phonon modes in
R and M have energy lower than or comparable to the ideal
cubic perovskite phase (at 160 GPa, the energy of the 14/mcm
structure that is the most stable is about 90 meV per mole-
cule below the energy of the cubic structure). These structures
are characterized by slight distortions, induced by the almost rigid
rotating octahedra. The structural resemblance of these
structures with the parent cubic phase, together with inherent
kinetic factors, made their experimental identification a diffi-
cult task (Shim et al., 2002).

Figure 1
Simple two-dimensional model of the relations between the Brillouin
zones of a parent structure and a derived superstructure, and the folding
of the k points from the second to the first BZ of the superstructure.

Our theoretical results are summarized in Tables 2 and 3.
Table 2 lists the Wyckoff positions occupied by Ca, Si and O
atoms in each of the analyzed structures, while the evolution
with pressure of the internal degrees of freedom (positions not
fixed by symmetry) and of the lattice parameters is given in
Table 3. As an example, the crystal structures of the lowest-
energy polymorphs, I4/mcm, P42\(\text{\textit{j}}\)nnm and Pnma, are
presented in Fig. 2.

The experimental measurements (Shim et al., 2002) show
lattice distortions corresponding to tetragonal structures
associated with c/a ratios slightly smaller than 1.0. According
to our theoretical results, all tetragonal structures, except
I4/mnnm, have c/a ratios slightly larger than 1.0. The origin of

Figure 2
Crystal structure of the lowest-energy distorted modifications of CaSiO\(_3\).
The structures in the top row are viewed along the b axis, with a
horizontal, and those in the lower row along the a axis, with c horizontal.
From left to right, the structures of the I4/mcm, P42\(\text{\textit{j}}\)nnm and Pnma
phases are shown.

Figure 3
Range of Si—O bond lengths in the cubic, tetragonal and orthorhombic
modifications of CaSiO\(_3\). The bonds in the cubic Pm3m and tetragonal
I4/mcm phases are plotted for comparison.
Table 3
Lattice parameters (in Å) and the general atomic coordinates for the analyzed CaSiO₃ perovskites, as determined at different pressures.

<table>
<thead>
<tr>
<th>Phase</th>
<th>P (GPa)</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>80</th>
<th>130</th>
<th>160</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pn3m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0.2043</td>
<td>0.2039</td>
<td>0.2035</td>
<td>0.2030</td>
<td>0.2025</td>
<td>0.2023</td>
<td>0.2018</td>
<td>0.2015</td>
<td></td>
</tr>
<tr>
<td>Imma</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>7.6234</td>
<td>7.5609</td>
<td>7.6138</td>
<td>7.6623</td>
<td>7.7765</td>
<td>7.8586</td>
<td>7.9894</td>
<td>7.9854</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0.2043</td>
<td>0.2043</td>
<td>0.2043</td>
<td>0.2043</td>
<td>0.2043</td>
<td>0.2043</td>
<td>0.2043</td>
<td>0.2043</td>
<td></td>
</tr>
<tr>
<td>P4/mmb</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>0.2072</td>
<td>0.2065</td>
<td>0.2059</td>
<td>0.2053</td>
<td>0.2043</td>
<td>0.2030</td>
<td>0.2013</td>
<td>0.2005</td>
<td></td>
</tr>
</tbody>
</table>

Table 4
The positions of the most intense powder diffraction peaks as simulated based on the theoretical structures at 50 GPa.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>110</th>
<th>111</th>
<th>200</th>
<th>210</th>
<th>211</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pn3m</td>
<td>17.1</td>
<td>21.0</td>
<td>24.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I4/mcm</td>
<td>17.0</td>
<td>21.0</td>
<td>24.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Imma</td>
<td>17.0</td>
<td>20.0</td>
<td>24.2</td>
<td>26.3</td>
<td>29.7</td>
</tr>
<tr>
<td>P4/mmb</td>
<td>16.9</td>
<td>19.6</td>
<td>23.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I4/mmm</td>
<td>17.1</td>
<td>21.0</td>
<td>24.4</td>
<td>27.2</td>
<td>29.6</td>
</tr>
</tbody>
</table>

The discrepancy could be due to 0 K calculations, as at finite T the structure might be partially disordered.

The Si—O bond lengths lie in the range 1.75–1.87 Å at 0 GPa and 1.58–1.67 Å at 160 GPa, as shown in Fig. 3. Both maximum and minimum bonds are recorded in P4/mmb. Fig. 3 also plots the position of the bonds in Pn3m and I4/mcm with respect to the whole range of computed Si—O lengths. It is interesting to note that even if the tetragonal I4/mcm modification has a density larger than the cubic Pn3m, the Si—O bonds in the former structure are longer than those in the latter. Thus, the higher compaction of the tetragonal phase is realized through octahedral rotations. The difference in bond lengths that reflects an octahedral deformation is about 0.02 Å in I4/mcm.

The evolution with pressure of the Si—O—Si angles in the distorted structures is shown in Fig. 4. All the angles lie above

![Figure 4](image-url)

Pressure evolution of the Si—O—Si interatomic angles.
155°, with the relatively weak pressure dependence. The smallest Si—O—Si angles are obtained in \textit{P}4/\textit{mmb} and \textit{I}4/\textit{mcm}, both with a decreasing trend under pressure. The Si—O—Si angles are directly related to the octahedral rotations induced by the phonon instabilities only for pure in-phase and pure out-of-phase rotations in the \textit{P}4/\textit{mmb} and \textit{I}4/\textit{mcm} structures, respectively. In the other cases, the coupling between the unstable phonon modes as well as the lattice deformations allow us only to estimate the octahedral rotations to less than 8°.

Based on the theoretically determined crystal structures we may simulate the powder diffraction pattern and compare it with the experimental data. The experimental powder diffraction pattern (Shim et al., 2002) recorded at 45.8 GPa shows weak splittings of the 110, 200 and 211 cubic peaks occurring around \(2\theta \approx 17.4, 24.6\) and 30.3°, respectively. Fig. 5 shows the simulated powder diffraction patterns for 20 ranging between 15 and 32.5° at 50 GPa for all the studied structures, while Table 4 details the positions of the most intense peaks. The \textit{I}4/\textit{mmm} structure shows the most complex diffraction pattern, while the cubic \textit{Im}3 phase, because of the symmetry, does not show any splitting. The \textit{P}4/\textit{mmb} tetragonal phase exhibits a large splitting of the cubic 200 peak. In the orthorhombic phases, \textit{Pnma} and \textit{Imma}, the peak splittings are small and they contribute mainly to the peak broadening. The other tetragonal phases, \textit{I}4/\textit{mcm}, \textit{P}4/\textit{mmb} and \textit{P}4/\textit{mnc}, exhibit large splittings.

In general, with respect to the experimental pattern we observe various differences in the splitting magnitude and the peak intensity for all the theoretical structures. These discrepancies are associated with theoretical distortions from the ideal cubic symmetry that are larger than the experimental ones, owing to the neglect of the thermal effects in our calculations and the presence of dynamical or static disorder exhibited by the SiO\textsubscript{6} octahedra in the real structure of CaSiO\textsubscript{3}. However, the theoretical structures we report in this study can be used as starting points in the structural refinements of the CaSiO\textsubscript{3} perovskite structure. The detailed theoretical analysis of the different possible space groups and of the distortions associated with these represent an important input for experimentalists attempting to solve the structures of CaSiO\textsubscript{3} perovskites at high pressures and temperatures from diffraction data.

![Figure 5](image_url)

**Figure 5**
Theoretical powder diffraction patterns for different polymorphs of the CaSiO\textsubscript{3} perovskite.
Calculations were performed using the PWSCF package, http://www.pwscf.org, which is now part of the Quantum-ESPRESSO package (open-source Package for Research in Electronic Structure, Simulation, and Optimization; http://www.quantumespresso.org). This is an initiative of the DEMOCRITOS National Simulation Centre (http://www.democritos.it) for the development of open-source scientific software. This research was supported by the NSF grants EAR-0135533 and EAR-0230319, and the Minnesota Supercomputing Institute. We thank B. B. Karki for the pseudopotentials and A. Darlington for fruitful discussions related to the lower-symmetry phases.

References


