A molecular dynamics study of structural and dynamical correlations of CaTiO$_3$

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Abstract

An effective interatomic potential which can be used to describe perovskite-type CaTiO$_3$ in molecular dynamics (MD) simulations is proposed. The potential proposed consists of two-body interactions, which include steric repulsions due to atomic sizes, Coulomb interactions resulting from charge transfer between particles, and charge-induced dipole interactions due to the electronic polarizability of ions and dipole–dipole (van der Waals) attraction. The energetics of the three crystalline forms of CaTiO$_3$ were calculated: the orthorhombic-Pbnm structure had the lowest energy, followed by the tetragonal-I4/mcm and cubic-Pm3m structures. The two phase transitions induced by temperature change were characterized through anomalies in the lattice parameters, elastic constants, bulk modulus, bond-angle distribution and the intensity of the first peak of the partial pair distribution function, $g_{\text{Ca-O}}(r)$. Analysis of the pair distribution function is a sensitive means of detecting structural transformation in materials caused by small distortions. It is shown that the rise in structural symmetry with temperature is actually due to the tilting of the TiO$_6$ polyhedra. The response of the system to external pressure was also analyzed. Extremely high pressure, up to 300 GPa, was applied and no significant modification attributable to a major structural change was observed. The proposed interatomic potential is in good agreement with experimental data, predicting the melting point, phonon vibrational density of states, thermal expansion coefficient and specific heat at constant volume. The recrystallized polycrystalline CaTiO$_3$ was reproduced in the simulation by cooling the liquid. It is shown that the presence of grain boundaries in the material is essential to reproduce the experimental data correctly.

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Keywords: CaTiO$_3$; Molecular dynamics calculations; Phase transition; Mechanical properties; Recrystallization

1. Introduction

Ceramics are inorganic solids used in a wide variety of fields, in both crystalline and amorphous forms, and are considered, along with metals and polymers, one of the three primary classes of solid materials. Owing to their versatile electrical and optical properties, ceramics have many high-technology applications, being used as insulators, resistors, capacitors, electronics-packaging materials and high-temperature superconductors [1]. Perovskite oxides are ceramics of great scientific and technological interest for their ferroelectric, pyroelectric, piezoelectric, dielectric and catalytic properties. The commonest are ternary ABO$_3$ oxides, where atom A is typically Ba, Ca, Pb, Sr, Na or K, and atom B is typically Nb, Ti or Zr. The structures, classification and correlations between structure and physical properties of the perovskite-type compounds have been studied by many authors [2–5]. Although the exact nature of the structure of many materials is still in doubt, the basic perovskite structure is a simple cubic system, in which the A ions are at the corners of the unit cell, B ions are at the center, and the O$^{2-}$ ions occupy the centers of the cubic cell faces, forming an octahedral oxygen-coordinated site. Very few ternary oxides have this simple cubic structure at room temperature, although many of them assume this structure at high temperatures. This structure can be transformed into a number of distorted polymorphs. The precise structure depends on chemical composition, temperature and stress. The A$^{2+}$B$^{4+}$O$_3$ perovskites, with the
relatively small B$^{3+}$ and larger A$^{2+}$ ions, include the well-known mineral perovskite, CaTiO$_3$, after which they are named. This material will be the focus of attention in this paper.

Calcium titanate exhibits orthorhombic-$Pbnm$ symmetry at 300 K, but shows a decrease in its orthorhombic distortion with increasing temperature, to attain progressively higher symmetry, eventually reaching the cubic structure described above. Several studies have been reported in the literature on the structural phase transitions of CaTiO$_3$ that occur with changing temperature and pressure [6–13]. In many fields, including physics, chemistry, biology, geoscience and materials science, structural phase transition is one of the most important phenomena [14]. It is very important to determine the transition temperature (pressure) accurately because, near the transition, many materials exhibit interesting and useful properties. Besides the large volume of experimental data, there are a number of unsolved problems related to the microscopic mechanisms of phase transitions. An understanding of the origins of these mechanisms would be useful for optimizing the properties of solid solutions. CaTiO$_3$ is an interesting material with which to explore these features.

There are some contradictions and misunderstandings regarding the crystallographic space group of CaTiO$_3$ and the number of phases observed as the temperature is raised to 1720 K [9]. Ali and Yashima [12,13] reported that the sequence of phase transitions induced by temperature rise in this material goes from orthorhombic-$Pbnm$, through tetragonal-$I4/mcm$, finally to cubic-$Pm3m$, after which it melts. Gillet et al. [7] reported that, under pressure, no significant changes in the structure of CaTiO$_3$ are observed at pressures up to 22 GPa at room temperature. Beyond the particular interest to materials science of the crystal structure and phase transitions of calcium titanate, it is also very important in earth science. More detailed knowledge of the properties of CaTiO$_3$ perovskite could be very helpful in understanding pyrope and related materials, which are analogous materials and have similar phase diagrams. (Mg,Fe)SiO$_3$ is probably the most abundant mineral in the Earth’s mantle but, being unstable at atmospheric pressure, it is very hard to analyze experimentally, unlike CaTiO$_3$.

Molecular dynamics (MD) simulation of materials is a valuable technique in the analysis of equilibrium configurations of crystals and liquids, melting and crystallization phenomena, phase transitions, diffusion, conductivity and thermodynamic properties of inorganic materials at the atomic level. A MD study of a system of 10,240 particles interacting via a pairwise potential was conducted. The structural and dynamical correlations of the crystalline state of CaTiO$_3$ and their behavior under varying temperature and pressure were investigated. Using the proposed interaction potential, properties such as the energies of crystal structures, phase transitions under heating, melting, mechanical properties, thermal expansion, vibrational density of states (VDOS), behavior of the system under pressure and recrystallization were analyzed.

Simulations show that the system has two phase transitions induced by a rise in temperature, where the three phases orthorhombic, tetragonal and cubic are identified by anomalies in the lattice parameters, elastic constants and bulk modulus. It was found that the transitions are marked by the tilt angles of CaTiO$_3$ oxygen polyhedra, in agreement with experimental data. The simulations found no evidence of phase transitions with pressure. A polycrystalline solid was also obtained by cooling the melt, and it was verified that the presence of defects, such as grain boundaries, are necessary to fit the experimental data well.

2. Interaction potential

In principle, a full description of the properties of a given material should be given in quantum mechanical terms. However, the inherent complexity of quantum calculations makes it necessary to search for phenomenological interatomic potentials which can lead to analytical solutions for the properties of materials. These potentials are based on some of the chemical and physical trends in given classes of crystalline material, such as metals, semiconductors or alkali halides, in which similar bonding mechanisms dominate.

Ceramics are inorganic solids held together by bonds that are either ionic or partially ionic and partially covalent. In spite of the partially covalent character of the Ti–O bond, the system is modeled by a two-body central force interatomic potential, based on the form of the Vashishta and Rahman [15] interatomic potential, which has been used successfully for many different systems [16–21]. The total potential energy of the system is written as

$$U = \sum_{i<j} U_{ij}$$

$$U_{ij} = \frac{Z_i Z_j e^2}{r_{ij}} \exp\left(-\frac{r_{ij}}{\xi}ight) + \frac{H_{ij}}{r_{ij}^{6/2}} - \frac{D_{ij}}{2 r_{ij}^{3}} e^{-\eta_{ij} r_{ij}} - W_{ij}$$

The first term represents the Coulomb interaction, which is a function of the effective charges on the ions, $Z_{i} = Z_{j}$ (in units of the electron charge $|e|$) and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, the interatomic distance between ions $i$ and $j$. The second term represents the steric effects of the sizes of the ions, where $H_{ij}$ and $\eta_{ij}$ are the strength and exponent of steric repulsion, respectively. The third term represents the charge-induced dipole interaction, to include the electronic polarizabilities of the atoms. Here, $D_{ij}$ is the strength of the charge–dipole attraction. This is an important term in the interaction potential, since O$^{2-}$ is highly polarizable. The last term represents the induced dipole–dipole potential based on the van der Waals interaction, where $W_{ij}$ is its strength. Parameters $\lambda$ and $\xi$ are the screening lengths for Coulomb and charge–dipole terms, respectively.
The values of all the parameters in the interaction potential were determined from some selected physical properties, such as cohesive energy, bulk modulus, elastic constant and lattice parameters for the orthorhombic structure. The fitted parameters are summarized in Table 1. Fig. 1 plots each two-body $U_{ij}$ interaction potential as a function of distance. The lattice parameters, bulk modulus, cohesive energy, elastic constant and melting temperature calculated from the interaction potential and the corresponding experimental values for CaTiO$_3$ in the orthorhombic-Pbnm structure are listed in Table 2.

3. MD calculation

3.1. MD method

MD calculations were performed in the micro-canonical ($N$, $V$, $E$) and isenthalpic–isobaric ($N$, $P$, $H$) ensembles with periodic boundary conditions. The ($N$, $P$, $H$) ensemble, due to Parrinello and Rahman [26], allows the simulation box to vary in size and shape. This is imperative to observe structural phase transitions in solids. The equations of motion were integrated with the velocity Verlet algorithm [27], with a time step of $2 \times 10^{-15}$ s. The total energy of the system was conserved to better than 1 part in 10$^5$ over the entire simulation. The system was investigated for the effects of temperature and pressure. The temperature was slowly increased at zero (atmospheric) pressure by scaling the velocity of particles by a few per cent at each 1000 time steps. In the study of pressure effects, the initial temperature of the system was $T = 300$ K. The external pressure was raised at a rate of 2 GPa per 50,000 time steps up to 22 GPa and then at a rate of 20 GPa per 70,000 time steps, up to 300 GPa.

3.2. Structural correlation functions

The phase space trajectory obtained from MD provides complete information on structural correlations. This study examined two-body structural correlations through partial and total pair distribution functions and three-body correlations through bond-angle distribution.

Table 1
Parameter set for the two-body interaction potential used in the MD simulation of structural, dynamical and mechanical properties of CaTiO$_3$.

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Ti</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z_{j(c)}$</td>
<td>0.9697</td>
<td>1.9394</td>
<td>-0.9697</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Two-body</th>
<th>Ca–Ca</th>
<th>Ca–Ti</th>
<th>Ca–O</th>
<th>Ti–Ti</th>
<th>Ti–O</th>
<th>O–O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{ij}$</td>
<td>11</td>
<td>9</td>
<td>9</td>
<td>11</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>$H_{ij}$ (eV Å$^2$)</td>
<td>8223.57981</td>
<td>216.64756</td>
<td>2365.84091</td>
<td>25.22251</td>
<td>374.99707</td>
<td>684.09897</td>
</tr>
<tr>
<td>$D_{ij}$ (eV Å$^3$)</td>
<td>2.0687</td>
<td>1.0343</td>
<td>2.1627</td>
<td>0</td>
<td>1.1284</td>
<td>2.2568</td>
</tr>
<tr>
<td>$W_{ij}$ (eV Å$^6$)</td>
<td>0</td>
<td>0</td>
<td>242.6390</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\lambda = 5.5$ Å</td>
<td>$\xi = 3.25$ Å</td>
<td>$r_{\text{cut}} = 8.0$ Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Two-body interaction potential as a function of distance. The total interaction potential is the sum of all two-body potentials, as described in Eq. (1).

Table 2
Calculated and experimental values for a selection of physical properties of CaTiO$_3$ in the orthorhombic-Pbnm structure.

<table>
<thead>
<tr>
<th>Lattice parameter (Å)</th>
<th>Exp.</th>
<th>MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>5.3789 (2)$^a$</td>
<td>5.37888</td>
</tr>
<tr>
<td>$B$</td>
<td>5.4361 (2)$^a$</td>
<td>5.43613</td>
</tr>
<tr>
<td>$C$</td>
<td>7.6388 (3)$^a$</td>
<td>7.63875</td>
</tr>
<tr>
<td>Density (g cm$^{-3}$)</td>
<td>3.978–4.04$^b$$^c$</td>
<td>4.043</td>
</tr>
<tr>
<td>Cohesive energy (eV)</td>
<td>$-6.34^d$$^e$</td>
<td>$-6.33983$</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>$C_{11}$</td>
<td>203.5</td>
</tr>
<tr>
<td>$C_{12}$ (GPa)</td>
<td>$-352.6$</td>
<td>$-124.9$</td>
</tr>
<tr>
<td>Melting temperature (K)</td>
<td>2262$^g$</td>
<td>2550 (50)</td>
</tr>
</tbody>
</table>

$^a$ Ref. [12].
$^b$ Ref. [4].
$^c$ Ref. [22].
$^d$ Ref. [5].
$^e$ Ref. [23].
$^f$ Ref. [24].
$^g$ Ref. [25].
Partial distribution functions, \( g_{\alpha\beta}(r) \), are calculated from the definition [28]:

\[
\langle n_{\alpha\beta}(r) \rangle \Delta r = 4\pi r^2 \Delta r \rho c_{\beta} g_{\alpha\beta}(r)
\]

(2)

where \( n_{\alpha\beta} \Delta r \) denotes the number of particles of species \( \beta \) in a shell between \( r \) and \( r + \Delta r \) around a particle of species \( \alpha \). The angular brackets represent the ensemble average as well as the average over all species \( \alpha \) particles. The total number density is \( \rho = N/\Omega \) (where \( N = N_{\alpha} + N_{\beta} \)) and the fraction of \( \beta \) particles is \( c_{\beta} = N_{\beta}/N \). The total pair distribution function \( g(r) \) is defined as

\[
g(r) = \sum_{\alpha\beta} c_{\alpha} c_{\beta} g_{\alpha\beta}(r)
\]

(3)

The partial distribution functions are extremely useful in the study of phase transitions in solids. Structural phase transitions in perovskites involve small atomic displacements and are associated with very small volume changes. Transitions from orthorhombic to tetragonal and then to cubic phases in CaTiO\(_3\) occur through tilting of the TiO\(_6\) polyhedra [13]. This means that practically no significant change in particle positions occurs. Analysis of the appropriate pair distribution function can show the increase in symmetry of a material with temperature. Structural changes are also observed by analyzing three-body correlations through bond-angle distributions.

Generally, as the temperature rises, the peaks in \( g(r) \) broaden and decrease in intensity owing to thermal agitation of the particles. However, when the symmetry increases in a structural phase transition, there is a merging of close peaks to form one peak of higher intensity, even when the temperature rises. This is illustrated in Fig. 2.

For CaTiO\(_3\), the most appropriate partial pair distribution function in which to observe this increase in symmetry is the Ca–O function, because the transitions occur through tilting of the TiO\(_6\) polyhedra and therefore involve no change in the first interatomic distance between Ti and O particles. A change in the intensity of the second peak of \( g_{\text{Ti-Ti}}(r) \) can also be observed, but the changes in intensity of \( g_{\text{Ca-O}}(r) \) are more marked. Therefore, in the case of materials in which the phase transition occurs with very small distortions, an increase in symmetry can be analyzed by observing the increase in the intensity of the first peak of the appropriate \( g_{\alpha\beta}(r) \), as well as changes in the bond-angle distribution.

3.3. Dynamical correlation functions

The dynamical properties of the system were investigated through the VDOS. The VDOS was calculated by Fourier transformation of the velocity auto-correlation function, defined as [29]

\[
Z_s(t) = \frac{\langle v_{i}(0) \cdot v_{i}(t) \rangle}{\langle v_{i}(0)^2 \rangle}
\]

(4)

where \( v_{i}(t) \) is the velocity of the \( i \)th particle of species \( \alpha \) (Ca, Ti or O) at time \( t \), and the angular brackets denote ensemble averages over particles and time origins. The velocity auto-correlation function was generated after the system had been very well thermalized at 300 K. The partial VDOS was then calculated as

\[
G_s(\omega) = \frac{6N_s}{\pi} \int_0^\infty Z_s(t) \cos(\omega t) dt
\]

(5)

and the total VDOS

\[
G(\omega) = \sum_x G_s(\omega)
\]

(6)

was obtained.

From the resulting MD simulations, one can obtain the temperature and pressure dependence of the maxima of the VDOS. A linear approximation gives the temperature coefficient of frequency at constant pressure \( \left( \frac{\partial \omega}{\partial T} \right)_P \), at zero pressure, and the pressure coefficient of frequency at constant temperature \( \left( \frac{\partial \omega}{\partial P} \right)_T \), at \( T = 300 \) K.

Another important property of the system which can be obtained from VDOS is the specific heat at constant volume. This can be calculated as [30]

\[
C_V = \frac{3Nk_B}{\pi^2} \int_0^\infty \frac{\omega e^\omega}{(e^\omega - 1)^2} G(\omega) d\omega
\]

(7)

where \( u = \hbar \omega/k_B T \), and \( k_B \) is the Boltzmann constant. From \( C_V \), it is possible to derive the Debye temperature \( \Theta_D \) by the expression [30]

\[
C_V = \frac{12}{5} \pi^4 Nk_B \left( \frac{T}{\Theta_D} \right)^3
\]

(8)

which holds at low temperatures.

3.4. Elastic properties

Experimental difficulties have certainly restricted investigation of the variation in the elastic constants of CaTiO\(_3\) with temperature. In the case of conventional ultrasonic measurements, crystals of natural material are not readily available with the required size and perfection. If the
crystalline material has low symmetry, comparable difficulties may arise with Brillouin scattering [31] techniques. Single crystals of CaTiO$_3$ are very hard to obtain, because this material inevitably twins during formation [32].

The present authors have made predictions about the behavior of the elastic constants of crystalline CaTiO$_3$ as a function of temperature. The linear elastic constants were calculated from the generalized Hooke’s Law, written as

$$\sigma_{ij} = C_{ij} \epsilon_{ij} \quad (i, j = 1, 2, \ldots, 6)$$  \hspace{1cm} (9)

For each temperature, the system was first thermalized for 20,000 time steps. The elastic constants were then calculated as the average value of $C_{ij}$ computed every 50 time steps over an additional 90,000 time-step run.

The isothermal bulk modulus was computed from the second derivative of the potential with respect to the system volume, which is written as

$$B = \left< \frac{1}{9V} \sum_i r_i^2 \frac{\partial^2 U}{\partial r_i^2} \right>$$  \hspace{1cm} (10)

where $r_i$ is the position of the $i$th particle.

4. Results and discussion

The MD calculations were performed on a system of 10,240 particles (2048Ca + 2048Ti + 6144O), initially in an orthorhombic-Pbnm structure. The orthorhombic MD box had edges $L_x = 43.022$ Å, $L_y = 43.494$ Å and $L_z = 61.107$ Å, which provided a density matching the experimental value of $\rho = 4.043$ g cm$^{-3}$. The lattice constants and atomic coordinates for the Pbnm CaTiO$_3$ structure were taken from Ali and Yashima [12]. Starting with this structure and using the proposed interatomic potential, the MD system stabilizes at $T = 85$ K in its initial configuration.

4.1. Energies of crystal structures

With the proposed interaction potential (Eq. (1)), the lattice energies per particle were computed for the three common crystalline forms of CaTiO$_3$, as a function of volume per particle. These calculations allowed the prediction of the most stable structure, its equilibrium energy, unit cell volume, bulk modulus and its derivative, and estimation of the pressure necessary to induce a structural transition. In Fig. 3, the computed energies of the orthorhombic-Pbnm, tetragonal-I4/mcm and cubic-Pm3m structures are plotted against volume per particle. The energies were obtained by hydrostatic compression/dilatation of the molecular dynamics box edges. The dashed lines in Fig. 3 show the Murnagahan equation of state fitted to the MD data [34]:

$$E(V) = \frac{B_0 V}{B'_0 (B'_0 - 1)} \left[ B'_0 \left( 1 - \frac{V}{V_0} \right) + \frac{V}{V_1} \right] - 1 + E(V_0)$$  \hspace{1cm} (11)

The essential information about the structures is summarized in Table 3, together with the values obtained from MD at zero pressure.

The lowest-energy structure is the orthorhombic-Pbnm, followed by tetragonal-I4/mcm and then cubic-Pm3m. Experimentally, these structures are found to be in the same order of energy. From the Murnagahan equation of state, it was found that the unit cell volume for the orthorhombic-Pbnm crystal structure is $V_0 = 223.38$ Å$^3$, which corresponds to unit cell dimensions of $a = 5.3790$ Å, $b = 5.4364$ Å and $c = 7.6390$ Å. These results are in excellent agreement with the experimental values [12], $a = 5.3789(2)$ Å, $b = 5.4361(2)$ Å and $c = 7.6388(3)$ Å. The tetragonal-I4/mcm structure has the unit cell volume $V_0 = 227.86$ Å$^3$, which corresponds to the lattice constants $a = 5.437$ Å, $c = 7.708$ Å, with a $c/a$ ratio of 1.418, in very good agreement with experiment, which gives $c/a = 1.415(3)$. For the cubic structure, it was found that $V_0 = 57.45$ Å$^3$ and the lattice constant $a = 3.8586$ Å, while experiment gives $V_0 = 59.167$ Å$^3$ and $a = 3.8967(1)$ Å. From both MD and Murnagahan equation of state calculations, the minimum energies agree well for all structures. The results show that the CaTiO$_3$ unit cell volume increases with increasing lattice energy. However, the magnitude of the bulk modulus decreases. This indicates that the compressibility of the system increases, i.e., the system actually expands into the tetragonal and cubic structures. From these results and the profiles of energies exhibited in Fig. 3, it can be inferred that it would be very hard to induce a structural phase transition by pressure, since the pressure of the transition should be obtainable from a common tangent to the $E$ vs. $V$ curves for the orthorhombic-Pbnm and the other two structures. Note that the CaTiO$_3$ structures are almost degenerate in volume per particle. This agrees with the experimental fact that the structural phase transitions induced by changing temperature, in this mineral, occur through very small structural distortions.

4.2. Structural transformation by temperature rise and melting

The system was heated by scaling up the velocity of particles by 1% each 1000 time steps at constant pressure. At each temperature, the system was thermalized for 20,000
time steps before further heating. Fig. 4 shows the partial pair distribution functions at $T = 300$ K for the $Pbnm$–CaTiO$_3$ structure, obtained by MD. The orthorhombic structure is stable, and the peak positions in $g_{ab}(r)$ resemble the experimental distances in the $Pbnm$ structure (arrows) [12].

Table 3
MD results, Murnaghan equation of state (11) fitted to the MD data and experimental data for minimum energy per particle, volume per particle, bulk modulus ($B_0$) and first derivative of the bulk modulus ($B_0'$), for orthorhombic-$Pbnm$, tetragonal-$I4/mcm$ and cubic-$Pm3m$ structures at zero pressure.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Properties</th>
<th>MD</th>
<th>Murnaghan</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthorhombic-$Pbnm$</td>
<td>$E/N$ (eV)</td>
<td>-6.33983</td>
<td>-6.340</td>
<td>-6.34$^{a,b}$</td>
</tr>
<tr>
<td></td>
<td>$V/N$ ($\text{Å}^3$)</td>
<td>11.1663</td>
<td>11.169</td>
<td>11.17</td>
</tr>
<tr>
<td></td>
<td>$B_0$ (GPa)</td>
<td>203.5</td>
<td>183.9</td>
<td>177–212$^{d,e}$</td>
</tr>
<tr>
<td></td>
<td>$B_0'$</td>
<td>-</td>
<td>5.7</td>
<td>5.10–5.6$^{e}$</td>
</tr>
<tr>
<td>Tetragonal-$I4/mcm$</td>
<td>$E/N$ (eV)</td>
<td>-6.26967</td>
<td>-6.271</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$V/N$ ($\text{Å}^3$)</td>
<td>11.3145</td>
<td>11.393</td>
<td>11.76$^{c}$</td>
</tr>
<tr>
<td></td>
<td>$B_0$ (GPa)</td>
<td>188.4</td>
<td>159.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$B_0'$</td>
<td>-</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>Cubic-$Pm3m$</td>
<td>$E/N$ (eV)</td>
<td>-6.23965</td>
<td>-6.241</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$V/N$ ($\text{Å}^3$)</td>
<td>11.3878</td>
<td>11.490</td>
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<tr>
<td></td>
<td>$B_0$ (GPa)</td>
<td>185.2</td>
<td>136.6</td>
<td>-</td>
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<tr>
<td></td>
<td>$B_0'$</td>
<td>-</td>
<td>3.5</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Ref. [5].
$^b$ Ref. [23].
$^c$ Ref. [12].
$^d$ Ref. [4].
$^e$ Ref. [24].

Fig. 4. Partial pair distribution functions $g_{ab}(r)$ vs. $r$ in $Pbnm$–CaTiO$_3$ obtained by MD at $T = 300$ K, in comparison with the average experimental distances (arrows) between particles at $T = 296$ K [12].

[35,36], which agrees well with the reported experimental melting temperature of $T = 2262$ K [25] (dash-dotted line). Despite the MD melting temperature being higher than the experimental temperature by almost 300 K, this is a good result because, in the simulation, one is dealing with a perfect crystal without surface effects and defects. When the surface is suppressed by periodic boundary conditions, the system can be superheated to temperatures well above the equilibrium melting point. The presence of defects and surfaces diminishes the extent of system superheating.
and lowers the melting temperature, owing to the formation of melt nucleation sites [37]. The analysis of the structure obtained by cooling the system (open circles) is discussed in Section 4.5.

During heating (see Fig. 5a), there is a change in the slope of the $V$ vs. $T$ curve around $T = 2100$ K (arrow). Fig. 5b shows this change in detail, indicating a structural phase transition. Experimentally, two structural phase transitions are observed in CaTiO$_3$ [12], induced by temperature. A first-order transformation from orthorhombic to tetragonal occurs at $1498 \pm 25$ K, and a second-order transformation, from tetragonal to cubic phase, occurs at $1634 \pm 13$ K. The first transition predicted by MD occurs at $2141 \pm 6$ K, a temperature well above that observed experimentally. As in the case of the melting temperature, this happens because a perfect crystal is being modeled. Such a system has great structural stability, so that a higher temperature is necessary to enable the transition. Fig. 6 shows the lattice parameters, which are defined for the pseudo-cubic cell $\sqrt{2}a \times \sqrt{2}b \times 2c$, plotted against relative temperature ($T/T_T$), obtained by MD and experimental data. $T_T$ is the temperature at the ortho-tetra phase transition. Similarly to the experimental data, these results show that the first transition is of first order, and the second is of either second or higher order. The dashed lines in Fig. 6 delimit the range of existence of the experimental tetragonal phase. Fig. 7a displays the lattice parameters (relative to those at room temperature) obtained from MD simulations and reported experimental values [25], plotted against temperature, for both the experimental and MD simulation data. Note that the thermal expansion coefficients of CaTiO$_3$ show a considerable anisotropy. The MD linear thermal expansion coefficients for the orthorhombic-Phmm structure are in the order $a > b > c$, as observed experimentally (see Table 4). The thermal expansion coefficients for $a$ and $c$ are higher than the experimental values [6,25], while that for $b$ is in very good agreement. Consequently, at the orthorhombic to tetragonal phase transition, an increase in volume of 0.38% is observed, which is higher than that of 0.088% observed experimentally [13]. In a perfect crystal, the predominant effect in thermal expansion is the increase in distance between neighboring particles, while in imperfect systems there are also other effects, such as poor thermal conductivity across...
grain boundaries or expansion of the grains and movement of domain walls, which can influence the thermal expansion of the bulk material. The good agreement of the thermal expansions for all lattice parameters at low temperature is an important result which validates the binding forces described in the interatomic potential, since the thermal expansion of solids is one of the physical properties that depend on the nature of the binding forces between the constituent atoms.

The anisotropy in the thermal expansion of CaTiO$_3$ can be seen in the MD results. Fig. 7b shows the (0 1 0) plane, which contains the a and c axes and has lower symmetry than the (1 0 0) plane, where the b axis is seen. The system favors greater expansion of parameters a and c than of b, since its symmetry tends to increase with increasing temperature.

The plots of tetragonality ($c/a$) and the intensity of the first peak of the partial pair distribution function $g_{\text{Ca-O}(r)}$ against relative temperature, depicted in Fig. 8, confirm the existence of the two MD phase transitions exhibited in Fig. 6. The Ti–Ti–O bond-angle distributions shown in Fig. 9a merge at 90° when going from the orthorhombic to the cubic phase. The angles $\Theta_1 < 90^\circ$ and $\Theta_2 > 90^\circ$ for the orthorhombic structure are displayed on the image of the lattice in Fig. 9b. This result is clarified by the image of the (0 0 1) plane of the system in the three phases, shown in Fig. 9b together with their unit cells. Note that there is a clear alignment among the oxygen polyhedra in this plane.

In order to visualize the tilt angle at high temperatures, an average particle position was first obtained for each phase and temperature, from which pictures were created. From these pictures, it was possible to visualize the projections of the crystal structures along the [1 0 0] and [0 0 1] directions. Experimental tilt angles were determined by Ali and Yashima [13], in agreement with the classification of tilted octahedra in perovskites due to Glazer [3]. The present results are compared with the experiments in Fig. 10. Since the effects of periodic boundary conditions are more relevant at high temperatures, where the phase transitions were observed by MD, it was necessary to consider only the internal part of the simulation box for the calculations of the projected pictures, in order to determine the tilted angles.

In the orthorhombic-$Pbnm$ structure, there is the $\Phi_x, \Phi_y, \Phi_z$ tilting system (where $\Phi_x = \Phi_y$), while in the tetragonal-$I4/mcm$ and cubic-$Pm3m$ structures, one has $\Phi^0_x, \Phi^0_y, \Phi^0_z$ and $\Phi^1_x, \Phi^1_y, \Phi^1_z$ tilting systems, respectively. The subscripts $x, y, z$ refer to tilts about the [1 0 0], [0 1 0] and [0 0 1] directions.

Table 4

<table>
<thead>
<tr>
<th></th>
<th>$a_0$</th>
<th>$b_0$</th>
<th>$c_0$</th>
<th>$a_V$</th>
</tr>
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<tbody>
<tr>
<td>MD</td>
<td>24(4)</td>
<td>6.8(1)</td>
<td>9(2)</td>
<td>50.9(7)</td>
</tr>
<tr>
<td>Exp.</td>
<td>15.5–16.8</td>
<td>6.3–7.5</td>
<td>12.9–14.4</td>
<td>35.1–38.7</td>
</tr>
</tbody>
</table>
axes, and the superscripts +, − and 0 indicate whether successive octahedra along an axis have the same tilt (in-phase), opposite tilt (out-of-phase) or no tilt about that axis, respectively [3]. In Fig. 10, note that MD tilts follow the same trends as those determined experimentally. The $\Phi_z$ and $\Phi_z^+$ tilt angles of the orthorhombic-\textit{Pbnm} phase decrease steadily with increasing temperature up to first transition, where both $\Phi_z$ and $\Phi_z^+$ tilt angles decrease discontinuously to $\Phi_z^-$ and to $0^\circ$, respectively. These discontinuous changes indicate a first-order phase transition, as shown by the behavior of lattice parameters in Fig. 6 at the orthorhombic–tetragonal transition. In contrast, $\Phi_z^-$ decreases continuously to zero, suggesting that the second phase transition, tetragonal–cubic, is continuous.

4.3. Elastic properties of CaTiO$_3$

Minerals such as CaTiO$_3$, which undergo phase transitions, can show dramatic variations in their elastic properties. The molecular dynamics results allow one to predict the behavior of the elastic constants in the vicinity of the phase transitions of CaTiO$_3$.

The elastic properties of a material with orthorhombic structure are completely specified by nine elastic or stiffness constants, for all classes of this system [33]. These constants were computed at $T = 300$ K and are presented in Table 5. The MD results are compared with \textit{ab initio} calculations [38], showing good agreement. When the material becomes tetragonal, six elastic constants are needed and, in the cubic structure, only three elastic constants survive. $C_{11}$, $C_{22}$, $C_{33}$, $C_{13}$ and $C_{23}$ were computed as functions of temperature. At the phase transition, their values can change significantly for a given material.

The small change in lattice parameters (Fig. 6) is contrasted with substantial anomalies in the bulk modulus and elastic constants $C_0$, displayed respectively in Figs. 11 and 12 (lines are only to guide the eye), in the vicinity...
of the transitions. Three different types of behavior are observed in these figures, a clear signature of different crystalline phases. In Fig. 11, note that the bulk modulus decreases up to the first transition and remains apparently stable in the tetragonal phase, after a small rise at $T_T$, until the next transition, where its magnitude decreases again with rising temperature. In contrast, in Fig. 12, the stiffness constant $C_{11}$ decreases in the tetragonal phase, suggesting a softening of the short-range repulsive forces. The important result here is that $C_{11} = C_{22}$ and $C_{13} = C_{23}$ from $T = T_T$, which indicates that a phase transition from orthorhombic to tetragonal structure is actually predicted. The phase transition from tetragonal to cubic is marked by anomalies in these elastic constants, such as the significant increase in $C_{11}$. Note that in the cubic structure $C_{11} = C_{22} = C_{33}$, as would be expected in an isotropic crystal. Not much can be said about the anomalies of constants $C_{13}$ and $C_{23}$, on account of the error in the calculations caused by thermal fluctuation in the system, since these properties are computed at temperatures well above 2000 K. An interesting feature of the results is the similar behavior of $C_{11}$ and $C_{44}$ at the transition from tetragonal to cubic structure, in both the MD results for CaTiO$_3$ and experimental results reported for SrTiO$_3$ [39]. This may be evidence of isomechanical analogues in the two perovskite structures.

4.4. Vibrational density of states and pressure effect

The VDOS for CaTiO$_3$ was calculated at 300 K and zero pressure for the orthorhombic-Pbnm structure and compared with the results obtained from ab initio studies by Parlinski et al. [40], at zero temperature and zero pressure, for the same structure. In Fig. 13, the total and partial VDOS are shown for Ca, Ti and O atoms. Note that the Ca atom vibration profile agrees very well in both calculations, the atoms vibrating preferentially at lower frequencies. Owing to the stronger coupling in the TiO$_6$ octahedron, the Ti and O atoms vibrate at higher frequencies. Note that the distribution profile calculated by MD for the Ti atoms is approximately the same as that for the Ca atoms. This is due to their masses being almost the same. Although Ti atoms vibrate in the same frequency range in both studies, in the MD calculations there is a peak in the distribution around 9 THz, while in the ab initio calculations there is no preferential frequency of vibration. These differences are related to the force fields. In ab initio calculations, there is a more detailed force field which can describe all the bonding elements around the atoms, while in the MD calculations one has a simple two-body force field, strictly ionic. These results are interesting because they show that the Ti and O bondings really have other characteristics, such as covalence, explaining the discrepancy between the MD and ab initio calculations of the VDOS for oxygen and titanium. The good agreement in the VDOS of calcium indicates that Ca bonding has no

<table>
<thead>
<tr>
<th>$C_{ij}$ (GPa)</th>
<th>MD</th>
<th>Ab initio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>293(6)</td>
<td>299</td>
</tr>
<tr>
<td>$C_{22}$</td>
<td>327(5)</td>
<td>302</td>
</tr>
<tr>
<td>$C_{33}$</td>
<td>322(4)</td>
<td>319</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>141(4)</td>
<td>119</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>104(4)</td>
<td>106</td>
</tr>
<tr>
<td>$C_{23}$</td>
<td>124(4)</td>
<td>102</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>120(3)</td>
<td>114</td>
</tr>
<tr>
<td>$C_{55}$</td>
<td>73(5)</td>
<td>103</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>103(5)</td>
<td>104</td>
</tr>
</tbody>
</table>

Table 5: Elastic constants $C_{ij}$ (GPa) of Pbnm–CaTiO$_3$ calculated by MD at $T = 300$ K and ab initio studies [38].
covalent character, i.e., the force field is almost purely ionic. Despite the force fields adopted being very different in the \textit{ab initio} and MD calculations, the total VDOS are in quite good agreement.

The effects of temperature and pressure on the VDOS were also studied. Fig. 14a and b shows the results obtained by MD for temperature and pressure dependence of some peaks in the VDOS profiles, in comparison with Raman frequencies of first- and second-order bands, obtained experimentally by Gillet et al. [7]. Experimentally, the frequencies of vibration decrease linearly with rising temperature, with values of $\frac{\partial \omega}{\partial T}$ ranging from $-0.018(3)$ to $-0.033(1)$ cm$^{-1}$ K$^{-1}$, while the slopes obtained by MD range from $-0.014(1)$ to $-0.039(1)$ cm$^{-1}$ K$^{-1}$ for all bands except the one at 450 cm$^{-1}$, in which $\frac{\partial \omega}{\partial T} = -0.052(2)$ cm$^{-1}$ K$^{-1}$. However, the experimental frequencies of bands between 150 and 550 cm$^{-1}$ increase linearly with pressure, with values of $\frac{\partial \omega}{\partial P}$ ranging from 1 to 3 cm$^{-1}$ GPa$^{-1}$, while the MD slopes vary from 1 to 4.2(2) cm$^{-1}$ GPa$^{-1}$ for the same frequency range. Experimentally, near 500 cm$^{-1}$, $\frac{\partial \omega}{\partial P} = 5.1$ cm$^{-1}$ GPa$^{-1}$, while the MD result was $\frac{\partial \omega}{\partial P} = 5.7(2)$ cm$^{-1}$ GPa$^{-1}$. All these results are in very good agreement. It was not possible to observe anomalies such as shifts or the appearance of new peaks in the VDOS in the vicinity of phase transitions, because all the distribution peaks broaden as the anharmonicities increase at high temperatures $>2000$ K.

From the MD density of states, the specific heat at constant volume for CaTiO$_3$ was calculated. Fig. 15 shows the specific heat and the Debye temperature (inset) vs. temperature. The variation in the specific heat with temperature is in agreement with that expected from the Debye interpolation formula (Eq. (8)), with $C_V$ tending to $3Nk_B$ at high temperatures. The minimum in the $(\Theta_D, T)$ curve occurs at 34 K, which is approximately the same (35 K) as that
observed experimentally for strontium titanate SrTiO$_3$ [41], a similar material with perovskite structure. Unfortunately, the authors have no experimental data for CaTiO$_3$ to compare with the MD results.

Regarding the analysis of the system under pressure, the relative volume was calculated as a function of pressure and compared, in Fig. 16, with experimental data reported by Ross and Angel [11]. The results are in very good agreement with the experimental data, and there is no evidence of a phase transition induced by pressure up to 10 GPa. No significant change in the structure was observed experimentally up to 22 GPa [7]. The solid line in Fig. 16 was obtained by fitting a third-order Birch–Murnaghan equation of state [34]

$$P = \frac{B_0}{B'_0} \left\{ \left( \frac{V_0}{V} \right)^{\frac{4}{3}} - 1 \right\}$$

(12)

where $B_0$ is the bulk modulus at zero pressure, $B'_0$ its corresponding pressure derivative, and $V_0$ the atomic volume of the system at zero pressure and $T = 300$ K. The best fit to the present data was obtained with the values of these properties shown in Table 6, alongside MD and experimental results.

With the good result shown in Fig. 16, the authors were encouraged to study the behavior of the system under extremely high pressures. The applied pressure was raised to 300 GPa at a constant temperature of 300 K. The pseudo-cubic lattice parameters, bulk modulus and density of CaTiO$_3$ are shown in Fig. 17a and b. Note that all three lattice parameters decrease up to 100 GPa. At this point, parameter $b$ stabilizes, while parameters $a$ and $c$ continue decreasing. Above 180 GPa, $b$ starts to increase, the system expanding in the [0 1 0] direction. The bulk modulus has a strong dependence on the pressure applied to the system and increases almost linearly with it. The mass density was

<table>
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<th>Properties</th>
<th>MD</th>
<th>Murnaghan</th>
<th>Exp.</th>
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<td>$V_0$ ($\text{Å}^3$)</td>
<td>11.2</td>
<td>11.195</td>
<td>11.17$^a$</td>
</tr>
<tr>
<td>$B_0$ (GPa)</td>
<td>200.4(4)</td>
<td>189.8(3)</td>
<td>177–212$^b,c$</td>
</tr>
<tr>
<td>$B'_0$</td>
<td>–</td>
<td>5.27(7)</td>
<td>5.10–5.6$^b$</td>
</tr>
</tbody>
</table>

$^a$ Ref. [12].

$^b$ Ref. [4].

$^c$ Ref. [24].
fitted to the function \( \rho = \rho_0 + \xi \sqrt{P} \), where \( \rho_0 = 3.78 \text{ g cm}^{-3} \) and \( \xi = 0.143(1) \text{ g (cm}^3 \text{ GPa}^{1/2})^{-1} \).

To check for any evidence of a phase transition in this range of pressure (0–300 GPa), all the elastic constants \( C_{ij} \) \((j = 1, \ldots, 6)\), \( C_{22} \) and \( C_{23} \) were computed as functions of pressure (Fig. 18). The non-zero elastic constants at 300 K, calculated for the orthorhombic structure of CaTiO\(_3\), are presented in Table 5, while the other \( C_{ij} \) have values \( C_{14} = 0(2) \text{ GPa}, C_{15} = 0(4) \text{ GPa}, \) and \( C_{16} = 0(6) \text{ GPa} \). If a phase transition from orthorhombic to tetragonal occurred, some anomaly in the elastic constants such as \( C_{11} \) should occur, as observed for temperature-related transitions in Section 4.3. The most important feature in the orthorhombic–tetragonal transition induced by temperature is that \( C_{11} = C_{22} \) and \( C_{13} = C_{23} \). However, one can see in Fig. 18 that the values of these constants diverge with rising pressure, and no anomaly is observed. In other words, the degree of orthorhombic distortion increases with pressure. If a phase transition from orthorhombic to another phase with less symmetry were induced by pressure, such as monoclinic, triclinic or even the tetragonal \( 4/m \) phase, some of the elastic constants \( C_{14}, C_{15} \) and \( C_{16} \) would become non-zero, but this is not the case, confirming the initial hypothesis in Section 4.1 that a phase transition induced by pressure in CaTiO\(_3\) is very unlikely, if not impossible. Note that, above \( P = 120 \text{ GPa}, C_{11} \approx C_{12} \). This means that the response of the material by a deformation in the \([0 0 1]\) direction is approximately isotropic in the plane \((0 0 1)\) above 120 GPa. The behavior of the system under pressure was also analyzed at 2000 K, the pressure again being raised to 300 GPa. No significant change was observed that could be attributed to a major structural transformation.

### 4.5. Obtaining a polycrystalline solid

Here, the recrystallization of the CaTiO\(_3\) by cooling the melt is discussed. The volume and energy per particle are plotted as functions of temperature during cooling in Fig. 5. The system was cooled at the same rate as that used for heating. The structure of the recrystallized material was characterized in terms of two-body correlations. Fig. 19 compares the total pair distribution function at 300 K for a CaTiO\(_3\) single crystal with that for the recrystallized solid and with the melt at 2570 K. Note that the peaks for almost all correlations in the polycrystalline solid resemble the peaks observed in the single crystal, indicating that the recrystallization occurs in the orthorhombic structure. The decreased intensity in \( g_{\text{Total}}(r) \) is due to amorphous regions formed during the cooling procedure. A snapshot of the recrystallized material is shown in Fig. 20, where the crystalline domains from different points of view are clearly visible.

The bulk moduli of CaTiO\(_3\) at constant temperature (300 K), calculated by MD, are plotted against pressure for the single crystal and the polycrystalline solid in Fig. 21, together with the experimental results [4]. Note that the absence of defects such as grain boundaries in the single crystal actually influences the magnitude of the bulk modulus. The results obtained by MD for the polycrystalline material are nearer the experimental values than those for the single crystal. The density of the MD polycrystal is \( \sim 10\% \) less than that observed experimentally. At \( T = 1720 \text{ K}, \) the experimental density [12] for the cubic-\( Pm3m \) phase is \( \rho = 3.82 \text{ g cm}^{-3} \), while the polycrystal at \( T = 300 \text{ K} \) has \( \rho = 3.57 \text{ g cm}^{-3} \). The experimental and MD data were fitted by a linear function \( B = B_0 + xP \), and the results are presented in Table 7. Note that the slope \( x \) of the B vs. \( P \) curve is larger for the polycrystal (see Fig. 21), owing to its lower density \( \rho \), a consequence of the many amorphous regions formed during the recrystallization of the material. It is seen that below 2 GPa, \( B_{MD} > B_{Exp} \), while above that pressure \( B_{MD} < B_{Exp} \). The system recrystallized at zero pressure has some free volume which disappears as the pressure rises to

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Fig. 18. Variation in elastic constants \( C_{ij} \) with pressure at constant temperature (300 K), calculated by MD for CaTiO\(_3\).

Fig. 19. Comparison of the total pair distribution functions for a single crystal of CaTiO\(_3\) at 300 K, the melt at 2570 K and polycrystal at 300 K.
2 GPa. Therefore, in this pressure range, the system is more compressible. Above 2 GPa, the system is stiffer, becoming less compressible as a consequence of many defects, due to amorphous regions. Other properties of the polycrystal as a function of temperature, such as the phase transitions, were not checked because the low density of the polycrystal has too great an effect on the thermal expansion of the system, which can disguise whether the comparison with experimental data is related to the presence of defects or to the greater distance between atoms at high temperatures. Studies are being conducted to optimize the solidification of a good polycrystal.

5. Conclusions

The interatomic interaction potential proposed to describe CaTiO$_3$ in molecular dynamics simulations proved very effective. With this interatomic potential, it was possible to describe two structural phase transitions induced by temperature change, similar to those observed experimentally. These structural transitions could be described in terms of expansion of the system and the tilt of the TiO$_6$ octahedra. The orthorhombic to tetragonal transition was found to be of first order, and the tetragonal to cubic of second order. These transitions could also be characterized in terms of elastic constants and bulk moduli. The phonon vibrational densities of states derived by MD are in good agreement with \textit{ab initio} results, and the pressure dependence of the vibrational modes is very well reproduced. The equation of state, up to 10 GPa, is correctly obtained. Cooling from the melt results in a recrystallized polycrystalline system. The results for CaTiO$_3$ polycrystal and single crystal show that it is undoubtedly relevant to include defects in the crystal in order to reproduce properties satisfactorily. The computed bulk modulus for the recrystallized polycrystalline sample simulation can represent experimental data more adequately.

The results show that the interatomic potential proposed for the system analyzed describes the temperature and pressure effects very well and can be recommended for the study of other interesting similar materials, in particular (Fe,Mg)SiO$_3$ silicate perovskite, which is the dominant material in the Earth’s lower mantle and of interest in

<table>
<thead>
<tr>
<th>Properties</th>
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<th>Polycrystal</th>
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</tr>
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<td>$A$ (GPa)</td>
<td>5.3(1)</td>
<td>5.9(1)</td>
<td>4.5(1)</td>
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<td>$B_0$ (GPa)</td>
<td>200.7(2)</td>
<td>175.7(2)</td>
<td>178.3(2)</td>
</tr>
<tr>
<td>$\rho$ (g cm$^{-3}$)</td>
<td>4.03</td>
<td>3.57</td>
<td>3.978–4.04$^{a,b}$</td>
</tr>
</tbody>
</table>

$^a$ Ref. [4].
$^b$ Ref. [22].
high-pressure mineral physics, seismology and geodynamics of the Earth’s interior.

Acknowledgments

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