First-principles study of structural and vibrational properties of SrHfO$_3$ compared to SrZrO$_3$

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**Abstract**

The structural and vibrational properties of SrHfO$_3$ compared to those of the SrZrO$_3$ were investigated using first-principles calculations. The phonon dispersion curves, reported in the high-symmetry cubic perovskite phase, point out the coexistence of structural antiferrodistortive instabilities at the R and M zone-boundary points and a ferroelectric instability at the zone center. Different possible intermediate phases are characterized by comparing their internal energies, giving the same hierarchy of phases as for the SrZrO$_3$. The main features of the ferroelectric instability are also discussed, and, contrary to what was found for SrZrO$_3$, it seems very unlikely to induce the ferroelectricity in the SrHfO$_3$ Pnma ground state either by compressive or tensile epitaxial strain.

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1. Introduction

The oxide perovskites compounds (ABO$_3$) exhibit a variety of interesting physical properties, which can be exploited in a wide range of applications such as optoelectronic, spintronic, thermoelectric, high-dielectric, ferroelectric/piezoelectric and multiferroic materials [1]. Among them, strontium hafnium oxide (SrHfO$_3$) is a most promising candidate due to their large dielectric constant and sufficient band offsets for electrons and holes which can be use as a high-k gate dielectric material for use in memories, capacitors, complementary metal-oxide-semiconductor (CMOS) and metal-oxide semiconductor field-effect transistor (MOSFET) technology [2–4]. Subject of several experimental [2–8] and theoretical [9–15] studies, various structural phase transitions are reported in this compound (Table 1).

Since SrHfO$_3$ is supposed having an identical crystal structure as SrZrO$_3$ [17], in this paper, we systematically present a first-principles study of the structural, dielectric and dynamical properties of the different phases of SrHfO$_3$, as has not yet been done to our knowledge, compared to the study of SrZrO$_3$ [18]. In the cubic phase, our calculations highlight the coexistence of both antiferrodistortive (AFD) and ferroelectric (FE) structural instabilities, previously founded by Vali [10] and Sinha [19] but overlooked by Yangthaissong [20]. We then characterize the orthorhombic ground state as well as many possible intermediate phases and compare their internal energies. We finally discuss the main features of the FE instability and conclude that it is not possible to induce FE ground state either by compressive or tensile epitaxial strain. Our comparative study between the two perovskites will serve to give a deeper understanding of underlying physics of this compound.

This paper is organized as follows. Section II summarizes the technical details of the calculations. Section III presents the lattice constant, the Born effective charges and phonon dispersion curves of the cubic perovskite phase. Section IV discusses the AFD instabilities and the relative stability of different possible phases arising from the condensation of these instabilities. Section V discusses the FE instability and the possibility to induce the ferroelectric instability in the Pnma ground state. Section VI concludes the paper.

2. Technical details

The first-principles calculations presented in this work were performed in the framework of density functional theory (DFT) thanks to the ABINIT package [21,22]. The exchange-correlation term is described by adopting generalized gradient approximation using the Perdew-Burke-Ernzerhof of revised for solids functional (GGA–PBESol) [23]. We adopted a plane-wave pseudopotential approach, with optimized pseudopotentials generated using the ONCVPSP code [24,25]. The 4s, 4p, and 5s levels of Sr, 5s, 5p, 5d, and 6s levels of Hf, and 2s and 2p levels of O were considered as valence states. Some results have been checked at the LDA level using Slater exchange [26]. Convergence was reached for
an energy cutoff of 45 hartrees for the plane-wave expansion and a 8 × 8 × 8 grid of k-points for the Brillouin zone sampling of the single perovskite cell with five atoms. When condensing the AFD instabilities, either we considered a 20-atom supercell corresponding to 2A0, 2B0, and 2O0, and a sampling of 6 × 4 × 6 k-points or, for the Cmcm phase, a 40-atom supercell corresponding to 2A0, 2B0, and 2O0 and a sampling of 4 × 4 × 4 k-points. We explicitly checked that the relative energy of the different phases is well converged and independent of the choice of the supercell. Structural relaxations were performed until the forces and stresses were smaller than 10−7 hartrees/bohr and 10−7 hartrees/bohr3 respectively. The phonon frequencies, Born effective charges, and electronic dielectric tensor were calculated according to density functional perturbation theory (DFPT) [27]. The Space Group Symmetry were checked by FINDSYM program [28] and the phonon modes were analysed by AMPLIMODES code [29].

3. Cubic perovskite structure

First, we report the properties of the highly-symmetric cubic perovskite structure of SrHfO3. In this cubic phase, the atomic positions are fixed by symmetry and the only structural parameter to be relaxed is the lattice constant a0. Our results are reported in Table 2 compared to SrZrO3, SrTiO3 and CaTiO3, and other theoretical and experimental values. We report also the Born effective charges (Z') and the optical dielectric constant (εω) of cubic SrHfO3, SrZrO3, SrTiO3 and CaTiO3. In the cubic structure, Z' of A (A = Sr; Ca) and B (B = Hf; Zr; Ti) atoms are isotropic while, for O, two distinct values have to be considered depending if the O atom is displaced along the B–O chain (O⊥) or perpendicularly to it (O∥).

Our relaxed lattice constant (a0 = 4.093 Å) is in good agreement with those reported experimentally and other theoretical results. Note that the experimental lattice constant reported varies from 4.069 Å to 4.117 Å [2–8]. All of the present ab initio calculations were performed using our calculated theoretical lattice constants. The Born effective charges of B (B = Hf; Zr; Ti) and O∥ are strongly anomalous, 5.72/6.15/7.28/7.36e and −4.57/−4.99/−5.76/−5.87e instead of the nominal charges of respectively +4e and −2e. These anomalous Born effective charges are known as a common feature of ABO3 compounds and were related to dynamical transfer of charge between the B d and O 2p orbitals [31]. Z'Sr/Ca and Z'O are also anomalous but to a much lower extent. We notice the trend for the Born effective charges of larger beings in titanates (ATiO3) than in zirconates (AZrO3) and hafnates (AHfO3). The Z' of SrHfO3 are in fact closer to those of SrZrO3 than to those of SrTiO3 and CaTiO3 [18]. The calculated optical dielectric constant is of 4.38, near to that for SrZrO3 (4.71). It is smaller than for ATiO3 (A = Sr, 6.24; Ca, 6.39), coherently with the larger bandgap of SrZr−HfO3.

Within our calculations SrHfO3 is described as a good insulator with an indirect bandgap of 3.76 eV between R and Γ points, which is closer to that of SrZrO3 (3.42 eV) and consistent with other results (3.74 eV [11], 3.61 eV [20], 3.7 eV [32]) but wider than that of SrTiO3 (1.88 eV). The feature of the GGA is, among others, to underestimate from about 30 to 40%, the experimental band gap, which is 6.1 eV [30] but correctly reproduces the insulating nature of this compound. Note, however, that the hybrid functionals, like B3PW and B3LYP give a bandgap value much better agreement with the experiment, as demonstrated by Egilis et al. on the SrZrO3 (Exp: 5.60; B3PW: 5.30; B3LYP: 5.31) [33,34].

In Fig. 1, we report the phonon dispersion curves of cubic SrHfO3. The Γ–X, Γ–M, and Γ–R lines are along the [100], [110], and [111] directions, respectively. Negative values in the graph correspond to

Table 1

<table>
<thead>
<tr>
<th>SrHfO3</th>
<th>SrZrO3</th>
<th>SrTiO3</th>
<th>CaTiO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pm3m</td>
<td>Pm3m (1000 K)</td>
<td>Pm3m (1360 K)</td>
<td>Pm3m (1170 °C)</td>
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<tr>
<td>I4/mcm</td>
<td>Imma (700 K)</td>
<td>I4/mcm (1023 K)</td>
<td>I4/mcm (830 °C)</td>
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<tr>
<td>Imma</td>
<td>Pnma</td>
<td>Cmcm (873 K)</td>
<td>Imma (700 °C)</td>
</tr>
<tr>
<td>Pnma</td>
<td>Pnma</td>
<td>Pnma</td>
<td>Pnma</td>
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Table 2

<table>
<thead>
<tr>
<th>Lattice parameter (Å) of SrHfO3 at relaxed volume compared to SrZrO3 and SrTiO3, and other theoretical and experimental values. a: GGA–PBESol, b: LDA, c: GGA–WC. Born effective charges (Z'), optical dielectric tensor and GAP of cubic SrHfO3 and SrZrO3. The nominal charge are +2e, +4e, and −2e for A, B and O ions respectively.</th>
<th>SrHfO3</th>
<th>SrZrO3</th>
<th>SrTiO3</th>
<th>CaTiO3</th>
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<td>6.1 [2,30]</td>
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Fig. 1. (Color online) Calculated phonon dispersion curves of cubic (a) SrHfO3 and (b) SrZrO3 [18] at the GGA–PBESol and GGA-WC volumes respectively along the path Γ–X – M – R – Γ – M of the cubic Brillouin zone.
imaginary phonon frequencies and are related to unstable modes. By condensing these unstable modes, it is theoretically possible to find the possible intermediate phases and the stable phase of a compound. Frequencies and types ferroic unstable modes are summarized in Table 3.

We see in Fig. 1 and Table 3 that there are strong AFD instabilities at the R point (M 3173 cm−1, triply degenerated) and at the M point (M 3 160i cm−1, not degenerated). These modes correspond to rotations of oxygen octahedra as it will be discussed in the next Section. The present calculation of zone center phonons of cubic SrHfO3 shows an unstable TO mode as an imaginary frequency mode with the value of 49i cm −1, in agreement with what has been predicted by Stachiotti et al. [9] (76i cm −1), Vali [10] (61i cm −1), Hou [11] (66.9i cm −1) and Sinha [19] (75i cm −1). This M 3 unstable mode was not observed by Yangtaihsong [20] who worked within the LDA–PZ and GGA–PBE. Our LDA calculation reveals an additional instability at the point M (M 3 i 5i cm −1, twice degenerated), in agreement with the phonon curves presented by Vali [10] but very weak compared to the same instability shown in SrZrO3 [18] (M 3 i 50i cm −1). The I mode is a polar TO mode that involves the motions of Sr, Hf and O atoms while the M 3 unstable mode involves the anti-polar motion of Sr and O atoms. Comparatively to the phonon dispersion curves of cubic SrZrO3, which exhibits the same Pnma orthorhombic antiferrodistorted ground state, we notice that the phonon dispersion curves of SrHfO3 are similar to those of SrZrO3, particularly for AFD modes: they show an AFD instability extending from M to R as well as I G 3 unstable mode. The only important difference is the amplitudes of the instabilities that are larger in SrZrO3 (I G 3 871 cm −1; I G 3 179i cm −1; M 3 167i cm −1; M 3 50i cm −1) than in SrHfO3 especially for the I mode (4% for AFD and 44% for FE). This result will be useful later in the text.

Let’s now analyse in the next two Sections the AFD instabilities and the related orthorhombic ground-state structure. We will then discuss the FE instability.

4. Antiferrodistortive instabilities

The AFD R 3 and M 3 modes were observed in the phonon dispersion curves of SrHfO3 cubic phase (Fig. 1), with more larger amplitudes imaginary frequencies (1731 cm−1 and 160i cm−1, respectively, Table 3) than FE mode (I G 3 491 cm−1). R 3 and M 3 define unstable modes that are associated to tilts of the oxygen octahedra along one of the three cubic directions, with consequent octahedra along that direction moving either “in phase” (M 3 tilts) or “out-of-phase” (R 3 tilts). These motions correspond to the tilt components identified by Glazer [35,36] and that can be combined to generate more complex tilted structures. So, what phase stabilize the SrHfO3 it was only AFD? In order to identify the AFD ground state of SrHfO3, we computed the energy gains arising from the competitive appearance of different tilts in the reference cubic perovskite structure belongs to the space group Pm3m, wich is described in Glazer’s notations as a0a0a0. Of course, as we can see in Fig. 3, the full relaxation of distortions combining the three rotation modes M 3 and R 3 favor the appearance of several additional modes, even though they are not unstable by themselves [37,38]. Although the different relaxed structures can consequently only be described in first approximation as arising from a combination of perfect tilts, we will still refer to them below through the well-know Glazer’s notations for convenience.

In Fig. 2, we report for the AFD phases the energy gain calculated with two functional, GGA–PBEsol and LDA, compared to the high symmetry cubic phase. To analyse the effect of the functional, the strain and the cation displacement on energy gain for Imma, Cmcm and Pnma phases, we did three calculations: The first calculation, we’ll call the current calculation (cal. 1), in GGA–PBEsol and LDA, was to allow the relaxation of the strain, i.e. by making a complete relaxation lattice parameters and atomic positions, in the second calculation (cal. 2) we were relaxing only atomic positions in the cubic volume (cubic lattice parameter fixed), i.e. by not allowing the strain to relax, and the third type of calculation (cal. 3), meanwhile, was to also relax the lattice parameters and atomic positions, as for the calculation (cal. 1), but by setting the cations to their high symmetry positions. The calculations (cal. 2) and (cal. 3) were done only using the functional GGA–PBEsol.

Comparing the energy gains of the two separate AFD modes (R 3 and M 3), we note that the M 3 instability is energetically disadvantaged compared to the ones of R 3 in the SrHfO3. The relaxation of the M 3 mode is more favorable when it is condensed around a single direction (a0a0c+, P4/mmm, −138 meV/f.u.) than in three directions (a0a0a+, Im3, −134 meV/f.u.), whereas for the R 3 mode, our calculations show that it is more favored when it is condensed simultaneously around two directions. The Imma phase (a0a0c−, −195 meV/f.u.) is indeed lower in energy than the phases I4/mcm (a0a0c−, −176 meV/f.u.), “out-of-phase” rotation around a single direction, and K3c (a0a0a−, −185 meV/f.u.), “out-of-phase” rotation around three directions. Even by adding a FE motion in the last phase, which gives K3c (a0a0a−), whatever the functional used (red, GGA–PBEsol, and blue, LDA, columns), we still do not observe any additional energy gain (−185 meV/f.u.).

By now combining the two modes of rotation M 3 and R 3, we note, in agreement with the analyzes of the previous individual condensations, the unfavorable character of the condensation of “in phase” rotations (M 3 2) in two directions, with the Pnnm phase (a0b0b+, −183 meV/f.u.) slightly higher in energy than the Cmcm phase (a0b0c−, −185 meV/f.u.). The R 3 mode contribution can be seen when compared Im3, with “in phase” rotations in three directions (a0a0a+), and Pnnm, replacing only one “in phase” by an “out-of-phase” rotation (a0b0b+), that produce a gain of energy about −50 meV/f.u. So, whatever the functional used (red, GGA–PBEsol, and blue, LDA, columns), we notice that Cmcm phase (a0b0c−, −185 meV/f.u.) appear to be more favorable in SrHfO3 than Im3 (a0a0a+, −134 meV/f.u.), Pnnm (a0b0b+, −183 meV/f.u.), K3c (a0a0a−, −185 meV/f.u.) and K3c (a0a0a−, −185 meV/f.u.) phases. Let’s put aside the last four phases, since they are unlikely, and continue our analysis about the other more favorable phases in

### Table 3

<table>
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<tr>
<th>k-points</th>
<th>Mode</th>
<th>Type</th>
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<td>I 3</td>
<td>(FE)</td>
<td>3 × 40i</td>
</tr>
<tr>
<td>M</td>
<td>M 3</td>
<td>(AP)</td>
<td>1 × 160i</td>
</tr>
<tr>
<td>R</td>
<td>R 3</td>
<td>(AFD)</td>
<td>3 × 173i</td>
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SrHfO3

<table>
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<th>GGA–PBEsol</th>
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<th>GGA–WC</th>
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<td>3 × 40i</td>
<td>3 × 55i</td>
<td>3 × 87i</td>
</tr>
<tr>
<td>1 × 160i</td>
<td>1 × 169i</td>
<td>1 × 167i</td>
</tr>
<tr>
<td>2 × 5i</td>
<td>2 × 50i</td>
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SrZrO3

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</tr>
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<td>3 × 179i</td>
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AP – antipolar mode.
SrHfO$_3$ (I4/mcm, Imma, Cnmn, and Pnma).

Similarly to what was found in the SrZrO$_3$, the Cnmn and Imma phases have similar internal energy, with only a difference of $\sim 10$ meV/f.u. to the advantage of the Imma phase. Comparing the first two calculations (cal. 1), making a complete relaxation lattice parameters and atomic positions (red columns), and (cal. 2), not allowing the strain to relax (cyan columns), we can observe a sizeable contribution of strain relaxation: $\sim 30$ meV/f.u. in I4/mcm and about $\sim 20$ meV/f.u. in Cmcm, Imma and Pnma phases. Considering the third type of calculation (cal. 3), by setting the cations to their high symmetry positions (green columns), we find that the two phases Imma and Pnma, with equal energy ($\sim 184$ meV/f.u.) are energetically more favorable in SrHfO$_3$ than Cmcm ($\sim 158$ meV/f.u.) phase, thus giving the Imma phase a not insignificant position. The Imma phase is not yet observed experimentally but it seems to be more favorable in SrHfO$_3$ than that Cmcm experimentally reported [6,8]. The contribution of cations relaxation is more observed in Pnma ($\sim 29$ meV/f.u.) and Cnmn ($\sim 27$ meV/f.u.) than in Imma ($\sim 11$ meV/f.u.). According to the energy gain obtained in each of the AFD phases presented in Fig. 2, it turns out that, whatever the functional used, the purely low-energy AFD state in SrHfO$_3$ is in the orthorhombic phase Pnma ($a^+ b^- c^-$), combined two “out-of-phase” rotations ($R_x$) and an “in-phase” rotation ($R_y$). The coupling of these two modes of rotation has the effect inter alia of reducing their amplitudes of octahedral rotations: $c^+ = 11.68^\circ$ in P4/mmb, $c^- = 12.24^\circ$ in I4/mcm, whereas $b^+ = 7.19^\circ$ and $a^- = 8.05^\circ$ in the Pnma phase.

Our result (Fig. 2) shows the sequence Pn3m>P4mm>P4/mmb>I4/mcm>Cmcm>Imma>Pnma in agreement with that (Pn3m > I4/mcm > Cmcm > Pnma) found by Kennedy et al. [6] and Murata et al. [13]. We note here a remarkable similarity between the two compounds SrHfO$_3$ and SrZrO$_3$ as regards the hierarchy of the distortions as a function of the internal energy [18]. It is interesting that this hierarchy is different from that reported by Vali [10], in which Pm3m>Cmcm>I4/mcm>Pnma, reporting Cmcm less stable than I4/mcm, and by Cherlad et al. [39], in which Pm3m>I4/mcm>Imma>Cmcm>Pnma, reporting Cmcm less stable than Imma. To quantify the distortions that appear in the main phases we project the structural distortions onto symmetry adapted modes of the cubic phase using AMPLIMODE software [29].

The results in Fig. 3 show the amplitudes of the modes in the fully relaxed phases from the calculations.

In the P4mm, P4/mmb, and I4/mcm phases the mode decomposition shows only the primary modes we have condensed: $G_4$ (blue column), $M_3^i$ (yellow columns), and $R_2^i$ (magenta columns) respectively (Fig. 3). This is different for the Imma, Cmcm, and Pnma phase in which the additional modes $R_2^i$ (green columns), $X_5^i$ (cyan columns), $M_2^i$ and $M_4^i$ (red column) appears, through trilinear couplings with antipolar modes type $\lambda Q_{M_1}Q_{R_2}Q_{X_5}$ or $\lambda Q_{M_1}Q_{R_2}Q_{R_2}$ [18], with a small amplitude in the mode projections while we have condensed only the primary $R_2^i$ and $M_3^i$ modes. In the Imma phase the coupling, allowed by the (cal. 1) with respect to the (cal. 3), is done with the $R_2^i$ mode and allow substantial additional energy gain ($\sim 11$ meV/f.u., Fig. 2). In the Cmcm and Pnma phases, coupling with the $R_2^i$ mode is also allowed, but it is mainly a coupling with the $X_5^i$ mode (Fig. 3) which becomes dominant and stabilizes these phases through additional energy gain of respectively $\sim 27$ and $\sim 29$ meV/f.u. (Fig. 2). The Pnma structure allows the $R_2^i$, $X_5^i$ and $M_3^i$ (with a very low amplitude for the last) modes, and the Cmcm structure allows the $R_2^i$, $X_5^i$ and $M_4^i$ modes. In the Pnma phase, the atoms Hf ($B$ in general case) remain fixed at their high symmetry positions. The $X_5^i$ mode stabilizing Cmcm and Pnma phase consist of an antipolar distortion of Sr and O atoms, with a double

Fig. 2. (Color online) Calculated energy gain (in meV/f.u.) with respect to the cubic phase of different phases of SrHfO$_3$. Relative total energies are shown with Pm3m phase as the reference. The energies were calculated with two functional, GGA-PBEsol and LDA, and consist here of three calculations, (cal. 1: red columns for GGA-PBEsol, and blue columns for LDA), (cal. 2: cyan columns) and (cal. 3: green columns), as described in the text. For clarity, the exact value of the energy gain is written in each case. The two functional ones show the same sequence for all phases.

Fig. 3. (Color online) Modes contributing to the condensation of relaxed main phases in SrHfO$_3$. Associated amplitudes (in Å) were calculated by AMPLIMODES [29]. The main modes consist of FE displacement ($T_2^i$) and oxygen octahedron rotation ($R_y^i$ and $M_3^i$), whereas the additional modes consist of couplings with cations ($R_x^i$ and $X_5^i$) or oxygen ($M_2^i$ and $M_4^i$) displacements. At the scale of this diagram, the contribution of the mode $M_3^i$, in Pnma phase, is insignificant.

\[ \text{Imma} \]
contribution of Sr, in the b and a orthorhombic plane respectively, while R_2^+ mode stabilizing the Imma phase also consist of an antipolar displacement of Sr and O atoms, again with a double contribution of Sr, but in the orthorhombic c direction for Sr and O, plus the motion of O in the orthorhombic a direction.

In Table 4 we report the lattice parameters and atomic positions (in reduced coordinates) of the different possible intermediate phases. The amplitudes of the rotation angles of the oxygen octahedra are also reported. As previously mentioned, due to anharmonic couplings, some of these structures cannot be described using rigid oxygen tilts only but can involve other types of oxygen or cationic motions. The amplitudes of the rotation angles are therefore only indicative and were estimated from the amplitudes of the overlaps of the atomic distortion with rigid oxygen tilt motions. Going from single condensation (P4/mmbm and I4/mcm phases) to the combination of both oxygen rotation modes R_4^+ and M_3^+ (Cmcm and Pnma), we observe that the amplitude of M_3^+ slightly decreases (−8% and −13% respectively) while the amplitude of R_4^+ increases (+16% and +32% respectively).

The sequence of the phases found in the SrHfO_3 is the same as that found in the SrZrO_3 [18]. The I4/mcm phase has a tetragonality of 1.023, slightly similar to that 1.025 for SrZrO_3, in good agreement with the experimental observations of Kennedy et al. [6] (c_0/a_0 > 1). The hierarchy of the amplitudes of the rotations is the same in the two compounds when we go from an AFD phase with one rotation towards phases with several rotations. No experimental data are available for the Imma phase, but the pseudotetragonality of 0.993, equal to that found in SrZrO_3, is in agreement with other theoretical results [10,39]. It’s in the orthorhombic Pnma ground state that the reduction of the amplitudes of the rotations is greatest (a' = 8.21° and b' = 7.20°), just as it was found in the SrZrO_3 (a' = 8.48° and b' = 7.62°).

### 5. Ferroelectric instability

In the phonon dispersion curves of the cubic phase (Fig. 1), we have identified a small FE instability at the zone center (Γ', 49i cm⁻¹). Although this instability does not play any role in the ground state, it is inherent to the material and will compete with the AFD. In this Section, we better characterize this FE instability and report how SrHfO_3 would behaves in absence of AFD instabilities. In Table 5 we report the tolerance factor [40] (t), normalized

<table>
<thead>
<tr>
<th>Table 4</th>
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<tr>
<td>Calculated cell parameters and atomic positions of different phases of SrHfO_3 in agreement with the energy gain hierarchy observed previously. The values in bracket correspond to the experimental measurements from Ref. 6.</td>
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<th>d³a³b³ (Pn3m)</th>
<th>cell (Å)</th>
<th>a</th>
<th>b</th>
<th>c</th>
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<th>Rotation Angle</th>
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<tr>
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<th>d³b³c⁺ (P4/mmbm)</th>
<th>cell (Å)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Distortion amplitude</th>
<th>Rotation Angle</th>
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<tr>
<td>Sr</td>
<td>5.7055</td>
<td>5.7055</td>
<td>4.1273</td>
<td>0.006 (0.002)</td>
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<tr>
<td>Hf</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.010 (0.001)</td>
<td>7.19°</td>
<td></td>
</tr>
<tr>
<td>O_1</td>
<td>1/4</td>
<td>1/4</td>
<td>1/4</td>
<td>0.036 (0.004)</td>
<td>7.19°</td>
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<tr>
<td>O_2</td>
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<td>0</td>
<td>0</td>
<td>0.034 (0.009)</td>
<td>7.19°</td>
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<th>d³b³c⁻ (I4/mcm)</th>
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<td>0</td>
<td>0.004 (0.016)</td>
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<tr>
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<td>1/4</td>
<td>1/4</td>
<td>0.045 (0.045)</td>
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<td>0</td>
<td>0.047 (0.031)</td>
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<td>1/4</td>
<td>1/4</td>
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<td>0</td>
<td>0.034 (0.009)</td>
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<th>c</th>
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<td>5.7621</td>
<td>5.7621</td>
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<td>0</td>
<td>0</td>
<td>0.004 (0.004)</td>
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<tr>
<td>O_1</td>
<td>1/4</td>
<td>1/4</td>
<td>1/4</td>
<td>0.016 (0.014)</td>
<td>a' = 8.05°</td>
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<tr>
<td>O_2</td>
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<td>0</td>
<td>0</td>
<td>0.072 (0.063)</td>
<td>a' = 8.05°</td>
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eigendisplacement in real space for FE unstable mode at Γ point (polarization along z) and TO modes effective charge associated (as defined in Ref. 27).

When consider the ATO3 perovskites (ferroelectrics PbTiO3 and BaTiO3, and incipient ferroelectric SrTiO3) in the cubic phase, the eigendisplacement vector of the Γ polar instability is dominated by opposite displacements of B and O atoms (O1 and O2), while for AFD perovskites SrTiO3 (B = Zr; Hf), the B and O1 displacement contribution become smaller and the Γ polar instability is relatively dominated by opposite displacements of A and O1 atoms. In the SrTiO3 (B = Zr; Hf), contrary to what is observed in the ATO3 perovskites, the B now appears to move not against but with the oxygens but with a much smaller amplitude. The weak Sr−Hf displacements contribution in SrHfO3, compared to Sr-Zr contributions in SrZrO3, can be explained by the fact that the atomic weight of Hf is approximately twice that of Zr, 178.5 vs 91.2 amu. The mode effective charge associated with this unstable mode is 4.15e, close to that in SrZrO3 (4.38e), while this value increase in ATO3.

From the analysis of Table 5, we see that the balance of A or B sites in the condensation of pure FE mode and the intensity of modes effective charge vary with the Goldschmidt tolerance factor t. The ATO3 compounds all have a tolerance factor t > 1 and 0 eigenvalue dominated by the B cation (AB for PbTiO3), while in the SrTiO3 (B = Zr; Hf) AFD compounds with a tolerance factor t ≪ 1, the instabilities are more dominated by the A cation (AB for SrHfO3). In terms of the tolerance factor, SrTiO3 (1.001) is in between the ferroelectric BaTiO3 (1.063) and SrHfO3 (0.949), which exhibits octahedral rotations, showing that the crystal is on the borderline of being AFD or FE. Indeed SrTiO3 is known to be an incipient ferroelectric [41]. The compound with a strong A-site dominance is rather AFD at low energy state, such as SrHfO3 and SrZrO3 which stabilize the AFD orthorhombic phase Pnma with small mode effective charge. The O1 displacement is low in AFD compounds, and relatively beyond the triple in ATO3, which is characteristic of oxygen rotations in the former.

In the cubic symmetry, FE unstable mode is three times degenerate. We then compared the energies of phases with the polarization along three different directions in order to identify the FE polar phase lowest energy: FEy (P4mm) phase with a polarization oriented in the [100] direction, FEy (Amma2) phase with a polarization oriented in [110] direction and FEy (R3m) with a polarization along the diagonal [111]. We present in Fig. 4 energy gains from the cubic phase high symmetry and polarization of the three FE polar phases related in SrHfO3, respectively. To analyse the effect of the strain on energy gain for polar phases, we did two calculations: The (cal. 1), for GGA–PBEsol and LDA, and the (cal. 2) as previously explained.

From the energies, similarly to that found in SrZrO3 [18], the SrHfO3 FE phase is the most stable, meaning that in the absence of AFD instabilities the resulting ground state would be a ferroelectric P4mm tetragonal phase, as predicted by Sinha [19] and Murata et al. [13]. Whatever the type of calculation carried out, LDA and GGA–PBEsol, (cal. 1) and (cal. 2), the P4mm trend remains confirmed. While in the SrZrO3 strain relaxation favors the stable FE tetragonal state [18], in the SrHfO3 the strain does not seem to play a significant role in stabilizing the same stable FE tetragonal state. Vali [10] has conclude that P4mm and Cmcm phases of SrHfO3 cannot possibly occur.

The possibility of inducing ferroelectricity by strain engineering in the Pnma ground state of the SrZrO3 has been demonstrated by Amisi et al. [18]. What about SrHfO3? Using the same methodology as that was done in SrZrO3, we suppose a cubic perovskite substrate imposing to the Pnma phase of SrHfO3 an epixtal constraint a = c = 2√2a_{substrate}, limiting also ourselves to epitaxial strains of ±4% (with respect to the pseudocubic cell parameter) which typically correspond to the largest values accessible experimentally on this type of system. For each calculation, the cell parameter b is relaxed together with the atomic positions. Two cases was considered: the case of a compressive epitaxial strain of −4% (a_{substrate} = 3.899 Å), and the one of a tensile epitaxial strain of +4% (a_{substrate} = 4.224 Å).

According to our calculations, the structure stays in the a−b−c− phase, confirmed by the absence of any further phonon instability, with just a modification of the amplitude of the AFD distortions and an expansion or contraction of the cell along the b direction. It therefore appears that, contrary to SrZrO3, it is not possible to induce a FE-Pnma ground state in SrHfO3 by imposing either a compressive or a tensile epitaxial strain.

6. Conclusions

In this paper, we reported a first-principles study of the structural and dynamical properties of SrHfO3. We pointed out that, in its cubic phase, SrHfO3 exhibits both antiferrodistortive and ferroelectric instabilities. The antiferrodistrotive instabilities are responsible for the Pnma ground-state, that arises from the successive condensation of three rotational modes and further prevent the appearance of a ferroelectric distortion. Our results showed that the Imma and Cmcm phases have a very similar internal energy but it is the Imma phase which is the most stable. We have highlighted that in absence of AFD distortions, SrHfO3 would be a P4mm tetragonal ferroelectric with a spontaneous polarization of 23 μC/cm2, smaller than in SrZrO3 (42 μC/cm2). The hierarchy of phases with respect to the internal energy of the SrHfO3 is the same as in the SrZrO3, but contrary to what was found for last, it seems to us very unlikely to induce the ferroelectricity in the SrHfO3 Pnma ground state either by compressive or tensile epitaxial strain.
Acknowledgments

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References


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