Electronic structure of cubic SrHfO$_3$: Ferroelectric stability and detailed comparison with SrTiO$_3$

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Electronic structure calculations of cubic SrTiO$_3$ and SrHfO$_3$ are presented. The full-potential linear augmented-plane-wave method is used and exchange-correlation effects are treated by the local-density approximation. The tendency to ferroelectricity of both compounds is explored and compared by displacing the transition metal atom (Ti or Hf) towards one of the oxygens (001 direction). The calculations show that ferroelectricity is favored in SrTiO$_3$ with respect to SrHfO$_3$ and that this fact may be correlated with the degree of hybridization between transition metal d-O p bands as has been found for other related systems. Also a detailed discussion of the calculated electric field gradients is presented. [S0163-1829(97)03201-3]

INTRODUCTION

The $A$BO$_3$ compounds exhibit a variety of interesting properties which are dependent on which particular $A$ and $B$ elements are forming them. In particular, we are interested in those where $A$ is an alkaline earth (Ca, Sr, or Ba) and $B$ is a tetravalent metal (Hf or Ti). Usually they form cubic, tetragonal, orthorhombic, or rhombohedral lattices and exhibit a rich phase diagram. Anions form a regular octahedron in the cubic symmetry surrounding $B$ atoms or distorted octahedrons in crystals with lower symmetries. It is basically this $B$-metal–oxygen octahedron complex that determines the different characteristics of these compounds, resulting in distinct electron distributions associated with the $B$-metal–oxygen covalent bonds. These systems have been extensively studied because of their possible technological applications, such as ferroelectricity, but there is also interest in the understanding of the physics underlying their phase transitions. In this work we have concentrated on a parallel study of the electronic structure of SrTiO$_3$ and SrHfO$_3$.

Although SrHfO$_3$ is a compound that has been well known for a long time, still there is no consensus about its crystalline structure. A cubic structure was determined by Hoffman$^1$ using x-ray diffraction with $a=4.069$ Å at room temperature. Andrade et al. studied SrHfO$_3$ by perturbed angular correlation spectroscopy (PAC) and determined only the strongest component of the electric field gradient (EFG) tensor to be $2.32 \times 10^{17}$ V/cm$^2$ at $^{181}$Ta probes measured at Hf sites.$^2$ The presence of an EFG suggests a noncubic structure. More recently, Cuffini et al.$^3$ have determined by x-ray diffraction that SrHfO$_3$ is cubic at high temperatures, but suffers a phase transition around 600 °C to an orthorhombic structure. At the lowest temperature where the cubic phase is well defined (700 °C), the lattice parameter was found to be 4.117 Å. For the samples in the orthorhombic phase, de la Presa et al. obtained by PAC a value of $2.02 \times 10^{17}$ V/cm$^2$ for the EFG at $^{181}$Ta probes at room temperature.$^4$

SrTiO$_3$ has the simple cubic perovskite structure at high temperature, suffers an antiferrodistortive transition at 105 K, and goes to a tetragonal phase in which the oxygen octahedra have rotated in opposite senses in neighboring unit cells. In the range 50–100 K, there is a softening of the ferroelectric (FE) polar phonons that appears to extrapolate to a FE transition close to 20 K. It is believed that quantum fluctuations suppress long-range ferroelectric order at low temperatures since no FE transition is observed.$^5$ SrTiO$_3$ is therefore referred to as an incipient ferroelectric.

In the present work we study the electronic structure of SrTiO$_3$ and SrHfO$_3$ in the cubic phase. To our knowledge no other study of the electronic structure of SrHfO$_3$ exists in the literature, and so our first-principles study represents an important contribution. Other first-principles calculations$^6,7$ exist for SrTiO$_3$, but our comparative study between the two perovskites will serve to give a deeper understanding of underlying physics. We also study the tendency of SrTiO$_3$ and SrHfO$_3$ to suffer a FE transition when the $B$ atom is displaced in the 001 direction and discuss the EFG that appears at the $A$ and $B$ sites when such a distortion from the cubic symmetry is performed. This pattern for the atom distortions is not the actual ferroelectric mode, which will most probably involve not only z-axis displacements of the $B$ cation, but will include the oxygens and $A$ cations as well [as, for example, in the case of KTaO$_3$ (Ref. 8)]. Anyhow, a qualitative sensing of possible instabilities will be reflected by this restricted pattern movement. We find in the case of SrTiO$_3$ a clear tendency to ferroelectricity which is not present in SrHfO$_3$. Our calculations support the idea that the tendency to ferroelectricity is more important for perovskites that have a greater hybridization between $B$-d and O-p bands as other authors have suggested for related systems.$^8$ Our present cal-

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calculations will serve as a basis for future studies of the exact displacement pattern of the ferroelectric mode of SrHfO$_3$ and its relation to the most stable phase at low temperatures.

**APPRAOCH**

The calculations presented in this work were performed within the local density approximation (LDA) to density functional theory, using the full-potential (FP) linear augmented-plane-wave (LAPW) method. In this method no shape approximation on either the potential or the electronic charge density is made. We use the WIEN95 implementation of the method, which allows the inclusion of local orbitals (LO’s) in the basis, improving upon linearization and making possible a consistent treatment of semicore and valence states in one energy window, hence ensuring proper orthogonality. The Hedin-Lundqvist parametrization for the exchange-correlation potential is used.

The atomic sphere radii ($R_i$) were used for Sr, O, Ti, and Hf, respectively, in SrTiO$_3$ and SrHfO$_3$ calculations. We take for the parameter $R K_{\text{max}}$, which controls the size of the basis sets in these calculations, the value of 8 for both systems studied. This gives well-converged basis sets consisting of approximately 739 and 895 LAPW functions plus local orbitals for SrTiO$_3$ and SrHfO$_3$, respectively. The correctness of the choice of these parameters was checked by performing calculations for other $R_i$ ($R_{\text{Hf}}=2$ a.u., $R_{\text{Ti}}=1.9$ a.u., and $R_{\text{Sr}}=2$ a.u.) and with increased values of $R K_{\text{max}}$. Even when changes in $R K_{\text{max}}$ from 8 to 9 give no significant differences for most of physical properties we studied (bulk modulus, EFG, partial charges), to obtain a well-converged absolute value of total energy it is necessary to increase further $R K_{\text{max}}$. For example, to obtain a precision of 1 mRy in the cohesive energy it is necessary to take $R K_{\text{max}}=10$ for our choice of $R_i$. We introduce LO’s to include the following orbitals in the basis set: Ti $3s$ and $3p$, Hf $5s$ and $5p$, Sr $4s$ and $4p$, and O $2s$.

Integrations in reciprocal space were performed using the special points method. We used $7\times7\times7$ meshes which represent 400 $k$ points in the first Brillouin zone. In the case of displacement of the $B$ ion in the (001) direction where the cubic symmetry is broken, we used less dense meshes of $5\times5\times5$, which made our calculations less expensive, still giving the precision required.

**RESULTS AND DISCUSSION**

We first performed calculations for SrTiO$_3$ and SrHfO$_3$ in the cubic perovskite structure as a function of the lattice parameter. Evaluating the energy as a function of volume, we obtain the theoretical value of the lattice parameter in the cubic structure and the corresponding bulk modulus. These quantities and the cohesive energy are shown in Table I and compared with available experimental values. For SrTiO$_3$ we obtain a lattice parameter which is 1% smaller than the experimental value as usually occurs in LDA calculations. The bulk modulus is also in good agreement with experimental determinations as well as with other LDA ab initio calculations. In brackets is the bulk modulus obtained at the experimental lattice parameter, normally quoted as a more reliable evaluation from a LDA calculation. For SrHfO$_3$ our value of the lattice parameter coincides with the one obtained experimentally by Hoffman at room temperature and is approximately 1% smaller than that obtained by Cuffini et al. for the cubic phase at 700 °C. Anyhow, recent experimental evidence seems to point out that the most stable phase at room temperature is not the cubic one, but one of orthorhombic symmetry. This suggests that the previous experimental value at room temperature taken as corresponding to a cubic phase may be in fact an averaged lattice parameter from the orthorhombic one.

In Fig. 1 we show the band structure for SrTiO$_3$ and SrHfO$_3$ at our predicted values of lattice parameters. The valence band structures of both systems are very similar: They consist essentially of nine O $2p$-derived bands which are hybridized with Ti or Hf $d$ orbitals. The conduction band structure presents more pronounced differences because the Hf $d$ states lie higher in energy and therefore hybridize with Sr $d$ orbitals much more than those of Ti. The size of the indirect $R$–$\Gamma$ gap is the most remarkable difference between the two band structures. These are 3.67 eV for SrHfO$_3$ and 1.84 eV for SrTiO$_3$. Blazey obtained by wavelength-modulation spectroscopy a gap of 3.34 eV for SrTiO$_3$. Hybridization between O $p$ and B cation $d$ bands can be observed looking at the sphere-projected density of states (DOS) shown in Fig. 2. The Ti $d$ component of the DOS in the valence band region is greater than the Hf $d$ component, and this implies that Ti 3$d$–O 2$p$ covalency is more important than that of Hf 5$d$–O 2$p$. The magnitude of the sphere-projected DOS is, of course, somewhat dependent on the choice made for the $R_i$’s. The question is then open whether the remarks made above about covalency remain true under changes in the sphere size radii. To check this point we calculate the sphere-projected DOS for SrHfO$_3$ for $R_{\text{Hf}}=2$ a.u. and integrate it in the valence band region to obtain the amount of Hf $d$ charge. We obtain 0.66e in this case, 0.18e more than when $R_{\text{Hf}}=1.78$ is used, but still quite less than the 0.99e obtained for the $d$ charge in the Ti sphere in SrTiO$_3$. We have checked, performing the calculation of the electronic structure of SrTiO$_3$ at the equilibrium volume.

### Table I. Lattice parameter (in $\text{a.u.}$), bulk modulus (in $\text{GPa}$) and cohesive energy (in $\text{Ry/cell}$) obtained in the present calculation and compared with available experimental results. In brackets is the bulk modulus at the experimental equilibrium volume.

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice parameter</th>
<th>Bulk modulus</th>
<th>Cohesive energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$</td>
<td>a 7.30</td>
<td>7.38$^a$</td>
<td>$E_{\text{coh}}$ 3.17</td>
</tr>
<tr>
<td>B 203(165)</td>
<td>174–183$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrHfO$_3$</td>
<td>a 7.69</td>
<td>7.69$^b$</td>
<td>$E_{\text{coh}}$ 2.98</td>
</tr>
<tr>
<td>B 184</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference 14.

$^b$Reference 1.
of SrHfO$_3$, that the electronic-structure-related differences of both compounds mentioned in this paragraph are not due to the 5% greater lattice parameter of SrHfO$_3$. The effect of greater $B\ d-O\ p$ covalency for Ti than for Hf as well as the larger gap obtained for SrHfO$_3$ than for SrTiO$_3$ may be attributed to the much smaller binding energy of $d$ orbitals in Hf (8.14 eV) than in Ti (11.04 eV).\cite{17} On the other hand, the larger Hf-5$d$ orbital radius compared with that of Ti-3$d$ would favor greater covalency in SrHfO$_3$. From our results it is evident that the effect of the binding energies is dominant. We would like to stress that our comparative analyses of the band structure of SrTiO$_3$ and SrHfO$_3$ shows the same relevant features than those made by Singh\cite{8} for KNbO$_3$ and KTaO$_3$, although the differences found between the electronic structures of the Sr-based compounds are more pronounced.

To study the tendency of the SrTiO$_3$ and SrHfO$_3$ cubic perovskites to suffer a ferroelectric transition, we performed calculations of electronic properties of these systems for different displacements of the B ion in the 001 direction. In Fig. 3 we plot the total energy as a function of the B-ion displace-
ELECTRONIC STRUCTURE OF CUBIC SrHfO$_3$: ...  

ment for different volumes. At the experimental equilibrium volume, neither of the two systems is energetically favored with the proposed ferroelectric transition, but energy differences with respect to the undisplaced ($\Delta \varepsilon = 0$) case are much smaller in the case of SrTiO$_3$. In fact when we repeat the calculation for a volume expansion greater than 5%, SrTiO$_3$ shows an instability and would undergo a ferroelectric transition. In particular, for a 10% volume expansion SrTiO$_3$ presents a shallow, but well-defined double well, while in SrHfO$_3$ the ferroelectric transition is still far away. We can then conclude from our calculations the existence of a tendency to ferroelectricity of cubic SrTiO$_3$ which is not present at all in the case of SrHfO$_3$. Our results for SrTiO$_3$ are in agreement with the present experimental and theoretical understanding that points out that SrTiO$_3$ is an incipient ferroelectric. For SrHfO$_3$ there is much less work done, but the existing experimental results seem to show that no ferroelectric transition is favored in this system. Our electronic structure calculations for both SrTiO$_3$ and SrHfO$_3$ support the idea that the existence of a ferroelectric phase is to be associated to the degree of hybridization of the $B\ d$ bands with $O\ p$ bands.  

Once the B atom is separated from its cubic site, an electronic field gradient (EFG) appears at its nuclear position and at that of Sr with principal axis in the 001 direction. In Table II we show the EFG as a function of the displacement $\Delta \varepsilon$ at the different atomic sites for two volumes. The behavior of the EFG is quite different at the O sites since these have noncubic symmetry and so a sizable EFG appears even when $\Delta \varepsilon = 0$. Also, at the O sites the EFG has a different sign in SrTiO$_3$ and SrHfO$_3$ when $\Delta \varepsilon = 0$ and varies strongly with volume. The EFG at the Hf site in SrHfO$_3$ has the same sign as at the Ti site in SrTiO$_3$, but the magnitude is almost 6 times larger and in both cases almost independent of volume. To understand the origin of the sign and magnitude of the EFG, it is usually useful to separate the contribution coming from inside the muffin-tin (MT) sphere of the atom under consideration and those arising from the rest of the lattice. In FPLAPW calculations, the contribution coming from the MT sphere may be expressed as

$$V_{zz}^{MT} = -\left(\frac{4\pi}{5}\right)^{1/2} \int_0^{r_{MT}} \rho(r) r^2 dr,$$

where $\rho(r)$ is the $L=2$, $M=0$ radial component of the charge density when it is expanded in symmetrized spherical harmonics $Y_{LM}(\hat{r})$ (Ref. 18) and it is assumed that the principal axis points in the $z$ direction. 

Let us now concentrate on the B-ion sites where we find that more than 93% of the contribution to the EFG comes from the interior of the B sphere. The origin of the sign of the EFG may be understood by looking at the charge asymmetries $\Delta n_p = 1/2(n_{p_z} + n_{p_y}) - n_{p_z}$, and $\Delta n_d = (n_{d_{z^2}} + n_{d_{xy}} - 1/2(n_{d_{z^2}} + n_{d_{xy}})) - n_{d_{z^2}}$, where $n_i$ is the charge of $i$ character inside the MT sphere.  

The valence charge inside the B sphere originates in the hybridization of valence orbitals of B atom with $O\ p$ orbitals. Displacing the B atom in the 001 direction increases hybridization of orbitals that have their charge pointing along the $z$ direction, and so $\Delta n_p$ and $\Delta n_d$ (which are zero for $\Delta \varepsilon = 0$) become negative numbers and a negative contribution to the EFG is also obtained. The opposite holds for the contribution from sem-

![FIG. 3. Total energy of cubic SrTiO$_3$ (a) and SrHfO$_3$ (b) as a function of the displacement $\Delta \varepsilon$ of the B atom in the 001 direction for different volumes. Energies are referred to the undisplaced cases at the corresponding volumes. $V_0$ is the corresponding experimental equilibrium volume. The solid line shows the fourth-degree polynomial interpolation.](image-url)
core states because hybridization is associated with their de-
population and then a positive contribution to the EFG
results. However, we obtained that the valence contribution
is clearly dominant in these cases and then it determines the
sign of the EFG. Concerning the different magnitude of the
EFG in SrTiO$_3$ and SrHfO$_3$, it is clear that it is not related to
the difference in the lattice parameters of the two systems
since Table II shows little dependence of the EFG with vol-
ume. Then, to investigate this point, we looked at the contribu-
tions to $p_{20}(r)$ coming from the different orbital symme-
tries and, we obtain, as in Ref. 19, the $p$ and $d$ contributions
to $V_{zz}^{MT}$. For the case $\Delta z = 0.04$, we obtain for $V_{zz}^{MT}(p)$ and $V_{zz}^{MT}(d)$ the values of $-0.29$ and $-0.48$ for SrTiO$_3$ and
$-2.21$ and $-1.57$ for SrHfO$_3$. This is an interesting result
because looking at the $d$ contribution, for example, one may
think, in principle, that as Ti $d$–O $p$ hybridization is greater
than Hf $d$–O $p$ hybridization the Ti atom would have to
“feel” the asymmetry of the oxygen neighbors in SrTiO$_3$
more than the Hf in SrHfO$_3$. However, $V_{zz}^{MT}(d)$ for Hf is 3
times $V_{zz}^{MT}(d)$ for Ti. In fact, if we look at the charge asym-
metry $\Delta n_{d}$, it is greater for the Ti in SrTiO$_3$ ($-0.037$) than
for Hf in SrHfO$_3$ ($-0.025$). But even when the EFG is
related to the charge asymmetries $\Delta n_p$ and $\Delta n_d$, the factor
$1/r^3$ in expression (1) strongly enhances the anisotropic con-
tributions for very short distances. In the case of Hf the main
contribution to integral (1) comes from $r \approx 0.1$ a.u., while in
the case of Ti it is distributed up to $r = 0.5$ a.u. This is related
to the fact that Hf the $5d$ radial function has more weight
near the origin than the Ti $3d$ nodeless radial function. This
magnification of the charge asymmetry is even more drastic
when comparing $d$ to $p$ contribution for the Hf site. $\Delta n_p$’s
for Hf valence and semiconductor states are less than 0.001 in
both cases and, as we mentioned, they have different signs. How-
ever, $V_{zz}^{MT}(p) > V_{zz}^{MT}(d)$ for Hf in SrHfO$_3$.

Our calculated value of the EFG in SrHfO$_3$ for $\Delta z$ be-
tween 0.02 and 0.04 in units of the lattice parameter is of the
same order of magnitude as the measured value for the ortho-
 rhombic phase at the $^{19}$F probe. However, although we find this
agreement, we must remark that the experimentally observed
orthorhombic distortion is quite different from the one we
studied and that the experimental value is obtained at Ta.
Still, the magnitudes of the Hf-O distance variations are of
the same order in both cases.

SUMMARY AND CONCLUSIONS

Within the LDA we have analyzed the electronic structure
of SrHfO$_3$ in the cubic phase with a direct comparison to
SrTiO$_3$. We could identify the O $p$–B atom $d$ hybridization
as the main factor determining tendency to ferroelectricity.
We find that SrTiO$_3$ has a pronounced facility to a ferroelec-
tric instability, while SrHfO$_3$ has not. This is in agreement
with the actual understanding of SrTiO$_3$ as an incipient
ferroelectric and a nonobservation of ferroelectricity in the
Hf compound. The detailed analysis of the EFG, which ap-
pears with the $z$-axis $B$-atom distortion, allows us to compare
the microscopic interplay of $p$ and $d$ contributions in both
compounds. The present study serves as a starting point for
the study of the orthorhombic phase and its associated EFG
measured with PAC at the Ta- (Hf-) replaced site.

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