Electronic Structure and Ferroelectric Behavior of Lanthanum Substituted Bismuth Titanate

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The effect of substituting La for Bi atoms in Bi₄Ti₃O₁₂ is investigated from first-principles calculations using the full-potential linearized augmented plane wave (LAPW) method. A comparative study of the electronic structure and lattice-dynamics properties of Bi₄Ti₃O₁₂ and La₂Bi₂Ti₃O₁₂ shows the role of covalent bonding in the ferroelectric instabilities. The displacement patterns displayed by unstable zone-center phonon modes and a detailed analysis of the orbital contribution to the valence band illustrate the importance of Bi (La)-O interactions for the ferroelectric behavior of the doped material.

Keywords: Aurivillius; BIT; first-principles

Introduction

In recent years, Aurivillius compounds have emerged as important candidates for the development of non-volatile ferroelectric random access memories (NV-FRAMs) due to its relatively low voltage operation, low leakage current, fast switching and good fatigue resistance with Pt bottom electrodes [1, 2]. Strontium Bismuth Tantalate (SBT) films were the first of the Aurivillius to show promise for FRAMs applications [3]. However, SBT films have critical problems such as high processing temperatures to be applied to semiconductor process and a low remanent polarization which is insufficient for the high density integration of FRAMs.

To overcome these problems, different preparation conditions and/or the use of new ferroelectric materials have been explored. Bismuth titanate, Bi₄Ti₃O₁₂ (BIT), may be a good candidate material for FRAMs, since its bulk value of remanent polarization is about 30 µC/cm². However, BIT thin films showed fatigue and low values of polarization (~4–8 µC/cm²). Park et al. [4] showed that lanthanum substituted bismuth titanate, Bi₄₋ₓLaₓTi₃O₁₂ (BLT) thin films provide a promising alternative for FRAMs applications. BLT films are fatigue-free on metal electrodes, can be deposited at lower temperatures and show a higher remanent polarization (~12 µC/cm²) than SBT. Recently, Chon et al. [5] reported very high values of remanent polarization in Nd-modified bismuth titanate (BNdT) thin films, with a remanent polarization value as high as 50 µC/cm², which was attributed to the development of the polarization vector along the c-axis (in undoped BIT the polarization...
is almost exclusively along the a-axis). However, Garg et al. [6] found that while (118) and (104)-oriented BNdT films displayed polarization values of 6 µC/cm² and 20 µC/cm², respectively; (001)-oriented films do not show ferroelectric activity.

BLT films present a similar controversial situation. Yau et al. [7] stated that the polarization in c-oriented BIT films significantly increases with added La. In this way, the higher polarization observed in BLT films could be attributed to microscopic changes involving a polarization tilt towards the c axis, caused by the doping with the electronically less active ion (La) onto the A-sites in the BIT structure. On the other hand, Lee and Hesse [8] found that while (118) and (104)-oriented Bi₃₋₂₅La₀.₇₅Ti₃O₁₂ films displayed polarization values of 10 µC/cm² and 16 µC/cm², respectively; (001)-oriented films revealed only a small polarization component (∼0.5 µC/cm²). So, there is a need for the application of highly precise first-principles methods in order to clarify the microscopic changes caused by the substitution of Bi ions in BIT by lanthanide (La, Nd, Ce, Pr, Sm, Eu). In this work we investigate the effects of substituting Bi for La atoms by calculating the electronic structure and the ferroelectric instabilities of the paraelectric phase of Bi₂La₂Ti₃O₁₂, where all Bi atoms in the perovskite A site are replaced by La atoms.

**Approach**

The calculations presented in this work were performed using the full-potential linearized augmented plane-wave (LAPW) method with the addition of local-orbital basis functions as implemented in the WIEN code [9]. Exchange and correlation effects were treated within the local density approximation (LDA). The muffin-tin sphere radii Rᵢ = 1.7, 2.3 and 1.5 a.u. were used for Ti, Bi (La) and O, respectively. The value of the parameter Rₖₘₐₓ, which controls the size of the basis set for the wavefunctions, was chosen to be 7.0, which resulted in well converged basis sets. For the Ti-3s and 3p, Bi-6s and 5d, La- 5s and 5p, and O-2s states local orbitals were chosen in addition. Integrations in reciprocal space were performed using the tetrahedron method with 30 k-points in the irreducible Brillouin zone. Convergence tests indicate that only small changes result from going to a denser k-mesh or to a larger value of Rₖₘₐₓ.

To search for the presence of ferroelectric instabilities in the tetragonal paraelectric structure, we determined the phonon frequencies and eigenvectors of the infrared-active Eₐ and A₂u modes, which are polarized perpendicular and parallel to the c axis, respectively. To this end, we calculated atomic forces for several small displacements consistent with the symmetry of the mode. From the force as a function of displacement, the dynamical matrix was constructed and diagonalized. Once the eigenvectors have been determined, we evaluate the total energy as a function of the displacement pattern of the unstable (imaginary frequency) modes. This curve will provide the ferroelectric instability energy associated with a particular phonon mode.

The calculations were performed at the experimental lattice constants of BIT: a = 3.85 Å and c = 32.832 Å [10]. The internal atomic positions for each material were determined using a damped Newton dynamics method. The final force on each atom was less than 1 mRy/a.u.

**Results and Discussion**

Aurivillius compounds have a general formula (Bi₂O₂)(ₐₘ₋₁BₘO₃ₘ₊₁). They consist of an intergrowth between (Bi₂O₂)²⁺ sheets and (ₐₘ₋₁BₘO₃ₘ₊₁)²⁻ perovskite-like layers, with m being the number of octahedra stacked along the direction perpendicular to the sheets,
and A and B the two types of cations that enter the perovskite unit. The structure of BIT, shown in Fig. 1, consists of Bi$_2$O$_2$ layers and perovskite-type units with m = 3 and A-site Bi atoms.

Raman spectroscopy measurements [7, 11] have clearly indicated that La is entering into the lattice replacing Bi at the A site (see Fig. 1).

Recently, we have investigated the microscopic origin of ferroelectric instabilities in Aurivillius compounds from first-principles calculations [12]. A comparative study of the ferroelectric instabilities of the tetragonal paraelectric phase showed that while SBT presents only one unstable E$_u$ mode, which mainly involves movements of the Bi$_2$O$_2$ planes relative to the SrTa$_2$O$_7$ perovskite-like layers (rigid layer mode), BIT displays, besides an unstable rigid-layer mode, another imaginary-frequency mode with a displacement pattern involving movements of the Bi ions in the perovskite A site with respect to the TiO$_6$ octahedra (A-site mode). As an aid to visualization of the unstable polar modes of BIT, illustrations of their displacement patterns are shown in Fig. 2.

We showed that the A-site mode has a larger imaginary frequency and a deeper energy well compared with the rigid-layer mode, suggesting that the A-site mode is the relevant one for the ferroelectric transition in BIT. This picture is fully consistent with crystal structure refinements of the ferroelectric ground-state structure which attributed the large spontaneous polarization of BIT to large a-axis displacements of Bi ions in the perovskite A site with respect to the chains of corner-connected TiO$_6$ octahedra [13, 14]. Regarding c axis polarization, we have not obtained any ferroelectric instabilities along the [001] direction, although an A$_{2u}$ mode is very close to instability.
BLT is an A-site substituted BIT, so the inclusion of La in the perovskite block is expected to influence the ferroelectric properties of BIT. The band structure of the optimized tetragonal structures for BIT and BLT are shown in Fig. 3. Both materials presents two bands centered at $\sim 10$ eV which are derived from 6 s orbitals of Bi atoms which belong to the Bi$_2$O$_2$ planes, and a manifold of 36 valence bands which are derived from O(2p) orbitals. The conduction bands are derived mainly from Ti(3d) and Bi(6p) orbitals in BIT, and from Ti(3d), La(5d), La(6s) and Bi(6p) orbitals in BLT. In the case of BIT, two low-dispersion additional bands centered at $-10$ eV are derived from 6s orbitals of Bi atoms at the perovskite A site (Bi(A)). In BLT, the manifold of 6 bands centered at $-13.5$ eV are derived from La(5p) orbitals. The fundamental band gaps are indirect, with the conduction band minimum at the Brillouin zone center and the valence band maximum at a zone border. For BIT, the theoretical band gap is $\sim 1.2$ eV. This is increased to $\sim 2$ eV by the inclusion of La in the perovskite block, which could explain the decreases of the leakage current in BLT capacitor devices. We note, however, that LDA calculations underestimate the band gap in semiconductors.

From a chemical point of view, it is often postulated that since a La$^{3+}$ ion has no outer electron, in contrast to a Bi$^{3+}$ ion, which has a lone pair of 6s electrons, less hybridization with O(2p) should lead to less structural distortion of the perovskite block and wider band gaps. To analyze in detail the hybridization of the O(2p) valence states with the electronic states of the ions at the perovskite A site (Bi in BIT and La in BLT), we show in Fig. 4 the total and sphere-projected density of states (DOS) for the valence band.

Although the valence band presents mainly O(2p) character, there is a quite strong hybridization. For the case of BIT, the Bi contribution has both s-like (mainly in the upper part of the valence band) and p-like (mainly in the lower part) character. These contributions arise from a strong hybridization between O(2p) valence band states with Bi 6s (fully

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**Figure 2.** Illustrations of the displacement patterns of the unstable $E_u$ modes in BIT. The structures are projected in the ac plane.
occupied) and Bi 6p (conduction) bands. In BLT, the La contribution has s-like and d-like character, both uniformly distributed along the valence band. These contributions arise from hybridizations between O(2p) valence band states with La(5p) bands (fully occupied) and La(5d) conduction bands.

We have determined the presence of ferroelectric instabilities along the [110] axis in the paraelectric tetragonal structure of BLT by the calculation of phonon frequencies and eigenvectors of the infrared-active $E_u$ modes. A similar calculation for BIT accounted for the presence of two unstable modes in this material, a rigid-layer mode ($\omega = i48 \text{ cm}^{-1}$) and an A-site mode ($\omega = i145 \text{ cm}^{-1}$) [12]. For the case of BLT, we have obtained only one unstable mode ($\omega = i47 \text{ cm}^{-1}$) which involves movements of the Bi$_2$O$_2$ planes relative

**Figure 3.** Band structure of tetragonal BLT and BIT along several high-symmetry lines in the Brillouin zone.
to the $\text{La}_2\text{Ti}_3\text{O}_{10}$ perovskite-like layers (rigid-layer mode). The A-site, which was found relevant for the ferroelectric transition in BIT, is stable in BLT ($\omega = 30 \text{ cm}^{-1}$). The corresponding total energy calculations to compare the energy gains of the modes are shown in Fig. 5.

The rigid-layer modes of the two materials display ferroelectric instabilities with similar energy gains ($\sim 4 \text{ mRy/cell}$). While LDA yields to an unstable A-site mode in BIT, with an energy gain of 13 mRy/cell, the A-site mode is stable in BLT. This result provides a microscopic interpretation of the a-axis polarization decrease with the increase of La content.

Regarding ferroelectric instabilities along the [001] direction, we have determined phonon frequencies and eigenvectors of the infrared-active $A_{2u}$ modes. For BIT, we obtained that the $A_{2u}$ modes are all stable (real frequency), and the lowest frequency mode ($\omega = 34 \text{ cm}^{-1}$) involves movements of the $\text{Bi}_2\text{O}_2$ planes relative to the $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ perovskite-like layers along the c axis [12]. A similar calculation for BLT shows that the $A_{2u}$ modes are stable in this material as well, with frequencies larger than BIT. In fact, the lowest frequency $A_{2u}$ mode in BLT, which involves movements of the $\text{Bi}_2\text{O}_2$ planes relative to the $\text{La}_2\text{Ti}_3\text{O}_{10}$ perovskite-like layers, has a frequency of $\sim 47 \text{ cm}^{-1}$. These results indicate that the c-axis ferroelectric instability in BIT does not increase with added La.

Recently, Perez-Mato et al. showed that the experimental distortion associated to the ferroelectric phase in SBT is a superposition of contribution from polar and non-polar modes, and the independent freezing of a tilting mode at the Brillouin zone border would be responsible of an intermediate phase experimentally observed in SBT [15]. In BIT,
Figure 5. Total energy as a function of the ferroelectric distortion amplitude for the rigid-layer and A-sites modes in BLT and BIT. The displacements were performed along the [110] direction. The energies are with respect to that of the perfect tetragonal structure.

however, a direct transition between the tetragonal and the ferroelectric phase has been reported. Consequently, Perez-Mato et al. pointed out that the energetic interplay of polar and tilting modes, which plays an important role in the stabilization of ferroelectric phase in SBT, may change drastically in Aurivillius compounds with odd number of octahedra. We remark that we have investigated here the effects of La substitution on the polar instabilities of the paraelectric phase. Although this approach allowed us to provide a clear microscopic picture about the suppression of ferroelectric instabilities in BLT, further investigations of the effects of La substitution on the tilting modes would be desirable.

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