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Electronic structures and lattice dynamics of

**BaTiO_3** and **BiFeO_3** : a comparative

first-principles study

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Abstract

First-principles calculations were performed to investigate the ferroelectric properties of barium titanate and bismuth ferrite, as well as phonon dispersion of BaTiO_3, using density functional theory and density functional perturbation theory. Results show that the strong hybridization of Ti-O and Bi-O lead to the corresponding mechanisms for stabilizing the distorted structure. The spontaneous polarization of 59.4 µC/cm² and 27.6 µC/cm² were calculated for BiFeO_3 and BaTiO_3 respectively, using berry phase method within the modern theory of polarization. The stereochemical activity of Bi-6s long-pair, which was the driven mechanism for ferroelectricity in BiFeO_3, was able to produce greater polarization than the Ti off-centring displacement in BaTiO_3. New multiferroic perovskite type materials combined with these two ferroelectric instabilities were predicted to have a better ferromagnetic ordering in comparison with BiFeO_3.

**Key words:** Density functional perturbation theory; Band structure; Density of states

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1 Introduction

Barium titanate (BTO) is a classical example of ferroelectric material which was widely used in electronic devices as high permittivity capacitors, infrared detectors or transducers due to its particular characteristics [1-6]. The perovskite structure materials have been intensively investigated for half a century. Much experimental works have been conducted to analyze the properties of the perovskites type ferroelectric materials in order to push forward the applied progress. Meanwhile numerous theoretical works have been employed to discover the driven mechanism of the ferroelectric properties in BTO, which is caused by the Ti off-centring displacement.

First principles calculation has been used to describe the electronic structure of materials, and one of the first theoretical investigations of ferroelectric transition in BTO has been done by Cohen and Krakouer in the early 1990s using the first principles calculations based on density functional theory (DFT) with local density approximation (LDA) method [7,8].

In recent years, magnetoelectric materials have attracted much interests again due to the large electric polarization and saturated magnetization measured in BiFeO$_3$ thin film. Previous works have shown that the magnetoelectric properties have been originating from the coupling between ferroelectric and ferromagnetic order parameters[9-13]. BiFeO$_3$ has long been known to be ferroelectric with a Curie temperature of about 1103 K and antiferromagnetic with a Néel temperature of 643 K. The Fe magnetic moments were coupled ferromagnetically in the (111) plane and antiferromagnetically in the adjacent plane along [111] crystalline direction, which is called the G-type antiferromagnetism. It also has a rhombohedral distorted perovskite structure with space group $R3c$. The ten-atom rhombohedral unit cell can been seen arising from
a distortion of a reference Pm\(\overline{3}\)m cubic perovskite structure, which has been considered as the probable paraelectric(PE) phase. The symmetry permits a canting of antiferromagnetic sublattice resulting in a weak ferromagnetism. However, there is a spiral structure in which the antiferromagnetic axis rotates through crystal with a long-wavelength period of 620\(\AA\)[14]. Therefore, the linear magnetoelectric effect was reduced with the cancellation of magnetization due to this long spiral structure. This cancellation can be suppressed in thin film as a large saturation magnetization\((\sim 1\ \mu_B\) per unit cell) have been observed in epitaxial BiFeO\(_3\) thin film of 70 nm [15].

We have previously investigated the coupling of the weak ferromagnetism and ferroelectricity, and the ferroelectric mechanism in bulk BiFeO\(_3\), which is achieved by the Bi-6s stereochemical activity of long-pair. The ferroelectric mechanisms for these two perovskite type materials are different, which were mainly achieved by the different A and B cite in the perovskite structures. Although different works have been performed to specify the electronic structures and ferroelectric behaviors of ABO\(_3\) perovskites materials, unfortunately fewer literatures can be found on the comparison of the ferroelectric mechanisms in these two materials with different ferroelectric mechanisms. In this paper, we mainly focused on the calculations of orbital-resolved density of states (DOS), the band structure, and the charge density of these two materials, in order to gain an clear understanding on these two driving mechanisms in perovskite type ferroelectrics. Moreover phonon dispersion of BaTiO\(_3\) was reported here to give a further understanding on the destabilizing modes, which related deeply with the ferroelectric behaviors. We hope that the macroscopic magnetization of BiFeO\(_3\) can be improved by doping with Ti. Doping of Ti in BiFeO\(_3\) would generate the coexistence of excellent ferromagnetic and ferroelectric properties in the same phase.
The remainder of this article is structured as follows: In section II, we presented the computational details of our calculations. We provided the calculated results and discussions in section III. In section IV, the conclusion based on our calculation were given.

2 Computational details

2.1 Methodology

Calculations in this work have been done using the Quantum-ESPRESSO package[16], which is based on the density functional theory (DFT) and density functional perturbation theory (DFPT) using the plane-wave pseudopotential formalism. We used our self-interaction-corrected ultrasoft pseudopotential implementation with the Perdew Burke Ernzerhof (PBE) exchange correlation functional, as the common local density approximation failed to obtain a band gap in the transitional metal oxides. In our DFT computations, plane-wave basis set with kinetic energy cut-off of 40 Ry was employed, and it has shown that the results are well converged at this cutoff. Bi 5d, 6s, and 6p electrons, Fe 3s, 3p, and 3d electrons, Ba 5p, and 6s electrons, Ti 3s, 3p, and 3d electrons, and O 2s and O 2p electrons have been treated as valence states. We used up to $6 \times 6 \times 6$ grids of special k points in total energy calculation. In the local spin density approximation plus U (LSDA+U) framework, the strong Coulomb repulsion was treated by adding a Hubbard-like term to the effective potential, leading to an improved description of the interaction in the transitional metal oxides. The Hubbard parameter U in the range $U = 0 \text{ eV} - 8 \text{ eV}$ were used in this work. The band gap of BiFeO$_3$ was opened significantly when U was equal to 7 eV, while the insulated property has not been improved as U was
increasing further. We used this value in the following sections. The phonon
dispersion curves were computed within a variational formulation of density
functional perturbation theory (DFPT) [17].

2.2 Structure optimization

For BaTiO₃, the lattice parameters, ranging from 3.69 to 4.29 Å, was evalu-
ated with respect to the lowest total energy, which covered the average
value (a = 3.9904 Å, c = 4.0689 Å) calculated from our experimental samples,
BaTiO₃ powder. Meanwhile the tetragonality maintained unchanged under
P4mm symmetry, as tetragonal phase is known experimentally to be stable
at room temperature. The calculated lattice constant value was plotted with
respect to energy and fitted to the Murnaghan equation of states, permitting
to give the bulk modulus [18]. The atomic positions were relaxed afterward by
minimization of the Hellman-Feynman forces within a convergency threshold
of 10⁻³ Ry/Bohr, using Broyden-Fletcher-Goldfarb-Shanno (BFGS) variable
metric method, as cell shape and volume were fixed. For BiFeO₃, the lattice
parameters and atomic positions were taken from the corresponding value of
BiFeO₃ in Ref. [15]. There were smaller deviations from the original values
after relaxation.

2.3 Spontaneous polarization

In the modern theory of polarization approach [19-21], the total polarization
P for given crystalline geometry can be calculated as the sum of ionic and
electronic contributions. The ionic contribution is calculated by summing the
product of the position of each ion in the unit cell with the nominal charge
of its rigid core. The electronic contribution is determined by evaluating the
phase of the product of overlaps between cell-periodic Bolch functions along a densely-sampled string of neighboring points in k-space.

3 Results and discussion

For BaTiO$_3$, the lattice parameters covering the experimental value (a=3.990 Å, c=4.069 Å) was evaluated with respect to the lowest total energy. The optimization of volume was performed with lattice constant varying from 3.69 to 4.29 Å, and the volume plotted versus energy was shown in Fig.1. The calculated value was fitted to the Murnaghan equation of states, permitting to evaluate the bulk modulus. The normal parabolic curve gave the optimal value of 4.013 Å, a little bit larger compared with the corresponding experimental value of 3.990 Å for BaTiO$_3$.

The calculated band structure of BaTiO$_3$ was shown in Fig. 2 so as to understand the role of ferroelectric distortions on the electronic structures and bonding behaviors. The band gap was 1.92 eV within our approach, and this was in good agreement with the fact that the band gap was underestimated by a factor of 2 within the DFT-LDA method. The Band structure was separated into three portions in the valence band. The narrow band positioned at -17eV was derived from O-2s states, and the one positioned at -10eV was originated from the Ba-5p states. There is a manifold in the valence band near Fermi level which was attributed to the hybridization of Ti-3d and O-2p states. Moreover, the conduction band near Fermi level have a strong Ti-3d characteristic, indicating the $d^0$ configuration. There was fewer Ba states in these two regions, which can be confirmed by the orbital-resolved density of states (DOS) of Ba 6p, Ti 3d, and O 2p shown in Fig.3. In conduction band, the Ti-3d states distributing mainly in the energy region from 1.8 ev to 7.8
eV, overlapped deeply with the O-2p states in the same energy region with slightly Ba 6s involved. The strong Ti-O bonding under the ligand field can be observed from the charge density along (110) plane containing the Ti and O atoms shown in Fig.4. Along the displaced direction, Ti was deeply involved in the bonding with O to produce the covalent bonding, which was sensitive to the ferroelectric displacements. The strong covalent bonding characteristic favored the Ti off-centering displacement along the polarized direction, which clearly confirmed the destabilizing ferroelectric modes, while the slightly Ba involving feature tend to produce the ionic characteristic of Ba-O bonding, which can be seen from the charge density along (001) plane shown in Fig.5. It is clear that the long-distance ionic Ba-O bonding is slightly participating in the ferroelectric distortions.

In order to gain more insight into the role of ferroelectric distortions on electronic structure and bonding behavior in BiFeO₃, a classic multiferroic with rhombohedral perovskite structure under $R3c$ space group, in which the weak ferromagnetism and ferroelectricity coexist. We reported the band structure of BiFeO₃ in Fig.6. The excellent magnetoelectric properties in this fascinating materials have attracted more interests in recent years in terms of the excellent polarization measured in epitaxial grown thin film[15]. The ferroelectricity is mainly attributed to the Bi-6s activity of stereochemical long-pair, which can only occur if the cation ionic site does not have inversion symmetry. The valence bands in the vicinity of the Fermi energy was originated from hybridization of Bi-6p electrons and O-2p electrons, unlike the case in BaTiO₃, which was caused mainly by the B cite transitional metal ion hybridizing with O. Moreover, the strong overlapping bands in this energy region definitely confirmed the long-pair feature of Bi-6s electrons, which can create greater ferroelectric distortions in the perovskite materials in comparison with that driven by the B-site off-centring in the BaTiO₃. The orbital-resolved DOS of
Bi-6p states, Fe-3d states, and O-2p states were illustrated in Fig. 7. Fe-3d states were pushed away from the mixing energy region of Bi-O in this rhombohedral structure, with fewer states taking part in the overlapping. That is equivalent to saying that the Fe directly connecting ferroelectricity and ferromagnetism were excluded from the role of ferroelectric distortions in BiFeO$_3$, which preclude the possibility of direct linear magnetoelectric effect.

The spontaneous polarization was evaluated using the berry phase method based on modern theory of polarization. Born effective charges (BECs) were estimated by computing the Cartesian components of the polarization with respect to the atomic displacements, i.e.:

$$\Delta P_\alpha \approx \sum_{j\beta} \frac{\partial P_\alpha}{\partial \mu_{j\beta}} (\mu_{j\beta} - \mu_{0j\beta}) = \frac{e}{\Omega} \sum_{j\beta} Z'_{j\alpha\beta} \Delta \mu_{j\beta}$$

(1)

where $\Delta \mu_{j\beta}$ is the displacement of ion $j$ in Cartesian direction $\beta$, $Z'_{j\alpha\beta}$ is its BECs tensor, and $\Omega$ is the unit cell volume. The $P$ is calculated from berry phase method by considering a specific structural pathway parametrized by the change in atomic displacement connecting a centrosymmetric reference structure and the displaced structure. The displacements along [001] for BaTiO$_3$ and [111] for BiFeO$_3$ direction were chosen smaller (2% lattice constant) enough to ensure the validity of the linear treatment in Eq.(1). The BECs was also calculated based on the density functional perturbation theory[17] as follows:

The general quadratic expression of the energy as a function of the phonon optic coordinates $u$ and the electrical degrees of freedom (i.e., the field, $E$) is

$$E(u, E) = \frac{1}{2} M \omega_0^2 u^2 - \frac{\Omega}{8\pi} \varepsilon_{\infty} E^2 - e Z^* u \cdot E,$$

(2)

Where $M$ is the nuclear reduced mass, $\Omega$ is the volume of the unit cell, $\varepsilon_{\infty}$ the electronic dielectric constant of the crystal, $Z^*$ is the born effective charge of
the ions. The electrical induction \( \mathbf{D} \) is defined as:

\[
\mathbf{D} = -\frac{4\pi}{\Omega} \frac{\partial \mathbf{E}}{\partial \mathbf{E}} = \frac{4\pi}{\Omega} e \mathbf{Z}^* \mathbf{u} + \epsilon_\infty \mathbf{E}
\]

(3)

Born effective charge tensor of the \( s \)th ion is the partial derivative of the macroscopic polarization with respect to a periodic displacement of all the ions of the \( s \) species at zero macroscopic electric field:

\[
e \mathbf{Z}^*_{\alpha\beta} = \Omega \frac{\partial P^\alpha_{\beta}}{\partial \mathbf{u}^\alpha_{\beta}(\mathbf{q} = 0) \mid_{E=0}}
\]

(4)

The BECs based on these two different schemes were listed in table I. They yield the results in the same magnitude. It can be found that the Ti, O\(_T\) (on the top of Ti), and Bi are all having anomalous high value in comparison with the nominal charges. These results agree well with the fact that the Ti off-centring ferroelectric distortions in BaTiO\(_3\) and stereochemical activity of Bi-6s long-pair in BiFeO\(_3\) lead to the ferroelectric instability. The large O\(_T\) also reflect that the destabilizing ferroelectric mode of Ti is along [001] direction in the tetragonal BaTiO\(_3\), which is moving together with O\(_T\), while O\(_P\) (in the TiO\(_2\) termination) were slightly involved. The spontaneous polarization were 59.4 \( \mu \)C/cm\(^2\) and 27.6 \( \mu \)C/cm\(^2\) for BiFeO\(_3\) and BaTiO\(_3\) respectively, which are in good agreement with the previous calculated values. The relative large polarization of BiFeO\(_3\) indicate that the stereochemical long-pair of Bi 6s tend to yield a greater ferroelectric distortions than the Ti off-centring in BaTiO\(_3\).

The calculated phonon dispersion curves along the high symmetry lines of the tetragonal Brillouin zone are shown in Fig.8. The unstable modes, which determine the nature of the phase transitions and the dielectric and piezoelectric responses of the compounds, have imaginary frequencies. Their dispersion is shown below the zero-frequency line. The most unstable mode is at \( \Gamma \), and this mode, dominated by the Ti displacement against the oxygens, is the one that
freezes in to give the ferroelectric phases. However, the instability is not only restricted to the Γ points. Branches of Ti-dominated unstable modes extend over much of the Brillouin zone. The dispersions of the transverse optic mode mode are flat from X to M points, and stiffened rapid towards R point in the Brillouin zone. This point reflect that the instability was confined to three quasi-two-dimensional slabs of reciprocal space, which were intersecting at Γ. This indicate a chain-like unstable localized distortions for the Ti displacements in real space, and agree well with the charge density of BaTiO$_3$ along (110) plane shown in Fig.4.

The macroscopic magnetization of BiFeO$_3$ were canceled by the antiferromagnetic G-type structure and the spiral structure, in which the antiferromagnetic axis rotates through the crystal in a long-wavelength period of 620 Å. This drawback can be overcome partly by doping with Ti. Therefore, the new multiferroic combined with these two mechanisms of ferroelectricity (Bi-6s long-pair and Ti off-centring displacement) were expected to have excellent ferroelectric and ferromagnetic properties in comparison with BiFeO$_3$.

4 Conclusion

Different chemical mechanisms of ferroelectric distortions in BaTiO$_3$ and BiFeO$_3$ have been analyzed using density functional theory and density functional perturbation theory. The stereochemical activity of Bi-6s long-pair, which was the driven mechanism for ferroelectricity in BiFeO$_3$, was able to produce greater polarization than the Ti off-centring displacement in BaTiO$_3$. The chain-like Ti-O displacement, which was determined by the strong hybridization of Ti-O$_T$, was confirmed again by the phonon dispersion curves along the high symmetry points in the reciprocal space. The different A and B-cites ele-
ments, and structures lead to these two mechanisms of ferroelectricity. The Ti-doping BiFeO$_3$ was expected to be a potential multiferroic having excellent ferromagnetic and ferroelectric characteristics.

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**Figure captions:**

Figure 1: Volume vs. total energy per formula unit for BaTiO$_3$.

Figure 2: Electronic band dispersion for BaTiO$_3$. The Fermi level was set to zero.

Figure 3: Orbital-resolved DOS for Ba,Ti, and O in BaTiO$_3$. (a),(b), and (c) show the DOS for Ba-5p, Ba-6s, Ti-3d, and O-2p states respectively. Spin-up states are shown in the upper portions and spin-down states in the lower portions in all panels. The Fermi level was set to zero.

Figure 4: Charge density (in arbitrary units) in (110) plane for BaTiO$_3$.

Figure 5: Charge density (in arbitrary units) in (001) plane for BaTiO$_3$.

Figure 6: Electronic band dispersion for BiFeO$_3$. The Fermi level was set to zero.

Figure 7: Orbital-resolved DOS for Bi,Fe, and O, and total DOS in BiFeO$_3$. (a),(b),(c), and (d) show Bi-6p states, Fe-3d states, O-2p states, and total DOS respectively. Spin-up states are shown in the upper portions and spin-down states in the lower portions in all panels. The Fermi level was set to zero.

Figure 8: Phonon dispersion curves for BaTiO$_3$ along the high symmetry lines in reciprocal space.
Table 1

The polarization (P) and BECs (Z*) for BiFeO$_3$ along [111] and BaTiO$_3$ along [001]. The subscript AP and DFPT refer to values calculated from the approximation and DFPT approach respectively.

|          | Bi | Fe | O  | Ba | Ti  | O$_T$ | O$_P$ |
|----------|----|----|-----|----|-----|-------|-------|
| Z$_{AP}$ | 4.41 | 3.32 | -2.58 | 2.48 | 6.85 | -5.38 | -1.98 |
| Z$_{DFPT}$ | 5.04 | 3.16 | -2.20 | 2.51 | 7.10 | -5.56 | -2.08 |

P(µC/cm$^2$) | 59.4 | 27.6
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