Optik 127 (2016) 1503–1506

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

The study of the electronical properties of $BiTiO_3$ crystal by substitution of Na atom

J. Baedi*, F. Mircholi

Physics Department, Hakim Sabzevari University, Sabsevar, Iran

ARTICLE INFO

Article history:
Received 28 December 2014
Accepted 12 October 2015

Keywords:
Electronical properties
$BiTiO_3$
BNT
Density of states

ABSTRACT

We studied the electronic properties of $Bi_{0.5}Na_{0.5}TiO_3$ (BNT), $BiTiO_3$ compounds in the framework of density functional theory (DFT), using the full-potential linearized augmented plane wave (FP-LAPW) method with generalized gradient approximation (GGA) for correlation potential. The result shows that there is a remarkable difference between energy gap of $BiTiO_3$ compound by BNT compound. Energy gap of $BiTiO_3$ and BNT is about 1.9 and 2.6 eV, respectively, which is comparable with experimental results. The space group for our supercell was chosen to be P4bm for tetragonal phase. We have calculated the electron charge density in real space and found the kind of chemical bonds between the different atoms in these two compounds. The result show that kind of bonds are comparable with direct calculation method of chemical bonds. The calculated density states and crystal structure show that there is a stronger hybridization between orbitals of O and Ti in energy of near Fermi energy.

1. Introduction

$Bi_{0.5}Na_{0.5}TiO_3$ (BNT) was first synthesized by Smolenskii and Agranovskaya [1] in 1959. A few years later, it was found to be ferroelectric from the polarization–electric field hysteresis loops [2]. In 1974, Sakata and Masuda [3] reported an antiferroelectric phase, which is existed at 220 °C from dielectric measurement with an applied DC field. However, the optical and X-ray investigations [3,4] did not show any structural changes from the ferroelectric to the antiferroelectric phases. The maximum of dielectric permittivity [2,3,5,6] appeared around 325–335 °C and its value at a frequency of 10 kHz was 2600 [6]. BNT is a perovskite ferroelectric material that has a relatively large remnant polarization ($Pr = 34\ \mu C/cm^2$) at room temperature and a relatively high Curie temperature $T_c = 320\ °C$. Its relatively high coercive field $Ec = 7.3$ MV/m makes the problem of poling BNT. In addition, because Na_2O in the BNT absorbs the moisture facilely, the relative density of BNT is lowered substantially. In order to solve the aforementioned problems, the additive (such as Eu_2O_3 [7], $MnCO_3$ [8], Nd_2O_3 [9,10], La_2O_3 [10], Sm_2O_3 [10], or Nb_2O_5 [10]) was added in BNT to modify and enhance the relative properties of BNT. Beside $BiTiO_3$ compound has perovskite structure that two $BiTiO_3$ unit cells of hypothetic perovskite structure constitute $Bi_2Ti_3O_{12}$ (BIT) compound. The BIT is as a layer-type compound, $Bi_2Ti_3O_{12}$ layer. Compound of BIT is a ferroelectric material with wide applications in the electronic industry as capacitors, transducers, memory devices, and sensors [11,12].

2. Method of calculations

The calculations were performed in the framework of density functional theory (DFT) [13], using the full-potential linearized augmented plane wave (FP-LAPW) method as implemented in Wien2K codes [14]. The generalized gradient approximation (GGA) of Perdew et al. was selected for the exchange-correlation energy in our calculation. The wave functions were expanded into spherical harmonics within atomic muffin-tin (MT) spheres and in the form of plane wave in the remaining space. The MT spheres are supposed not to overlap with each other. The chosen radii of MT spheres for atoms are R_{MT} (Bi) = 2.48 Å, R_{MT} (Na) = 2.48 Å, R_{MT} (Ti) = 1.89 Å, and R_{MT} (O) = 1.67 Å. The cutoff energy, which defines the separation of the valence and core state, was chosen to be about −0.5 Ryd. The $BiTiO_3$ compounds have 20 atoms, i.e., four Bi, four Ti, and 12 O atoms, while the supercell used in our calculations has 40 atoms, i.e., four Bi, four Na, eight Ti, and 24 O atoms. Because the atomic size of Bi is incomparable to Na, we need to optimize all of lattice parameters in the BNT compound.

---

[*] Corresponding author. Tel.: +985144013220.
E-mail addresses: j_baedi1@yahoo.com (J. Baedi), mircholyfateme@yahoo.com (F. Mircholi).

http://dx.doi.org/10.1016/j.ijleo.2015.10.073

Table 1
Lesser value of optimized permanents for BNT supercell.

Compound	Preliminary permanents [15]) (Å)		Optimized permanents(Å)	
BNT	$a = b = 5.5191$	$c = 7.8170$	$a = b = 5.4256$	$c = 7.6844$

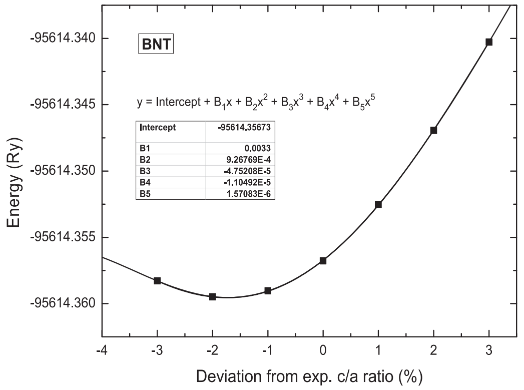

Fig. 1. Variations of energy to variation ratio %c/a for volume optimization BNT supercell.

Table 2
Parameters of BNT crystal.

Crystal	Space group	Phase	$a = b$ Å Unit cell	c Å unit cell	$\alpha = \beta = \gamma$
BNT [16]	P4bm	Tetragonal	5.5191	7.8170	90

3. Result and discussion

3.1. Optimization of lattice parameters

One of the important parameters of calculations is the lattice permanent. The preliminary permanents for preliminary cells of crystal are brought in Table 1. To ensure that we have a suit crystal lattice, the crystal lattice constant must be optimized on base the lowest energy, secondly. The volume optimization for BNT supercell in base variation percent of c/a ratio is shown in Fig. 1. The lesser values of preliminary permanents and the optimized permanents for BNT supercell in the tetragonal phase are shown in Table 1. Also, other values of lattice parameters are brought in Table 2.

3.2. Bond length

The length of a chemical bond is the distance between the centers of the two bonded atoms (the internuclear distance.) Bond lengths have traditionally been expressed in Angstrom units, but picometers are now preferred ($1\,\text{Å} = 10^{-8}\,\text{cm} = 100\,\text{pm}$). Bond lengths are typically in the range 1–2 Å or 100–200 pm. Even though the bond is vibrating, equilibrium bond lengths can be determined experimentally to within ±1 pm. Bond lengths depend mainly on the sizes of the atoms, and secondarily on the bond strengths, the stronger bonds tending to be shorter.

An ionic bond is the force of attraction between oppositely charged ions in a compound. We can compare ionic bonds with length bonds in these compounds and assess those ionic scales. The bond length accounts for ionic bond exactly by the sum of the ionic radii for the two atoms and relevant correction in N coordination number. These values with different N are brought in Table 2.

$$D_N = R_C + R_A + D_N.$$

Table 3
Values of Δ_N for different neighbors' numbers.

Δ_N (Å)	The first neighbor number (N)
−0.5	1
−0.31	2
0	6
+0.04	7
+0.19	12

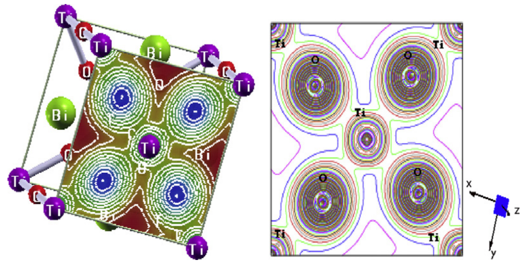

Fig. 2. Contours of electron charge density in (0 0 1) surface of $BiTiO_3$ crystal at real space.

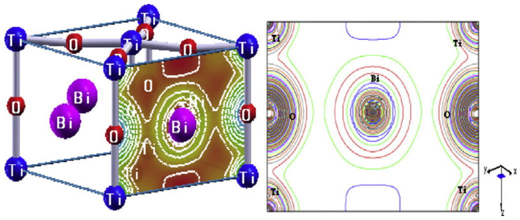

Fig. 3. Contours of electron charge density in (1 0 0) surface of $BiTiO_3$ crystal at real space.

The values for the ionic radii of Ti^{3+} and O^{2-} ions are 0.69 and 1.40, respectively. According to up frame,

$$\text{Ti-O}: \quad D_6 = 0.69 + 1.40 + 0 = 2.09\,\overset{\circ}{\text{A}},$$

where $N = 6$ and $\Delta_N = 0$ (Table 3).

While the TAuthor: Please check the sentence "Because of the atoms.." for clarity. Ti—O bond length is 1.96 Å in BNT, which is shorter than ionic bond. It is evident that Ti—O bond in these compounds is not ionic though rather, there are covalent bonds, too. This may be due to the stronger covalent bond.

The values for the ionic radii of Bi^{2+} and O^{2-} ions in $BiTiO_3$ compound are 0.96 and 1.40, respectively.

$$\text{Bi-O}: \quad D_6 = 0.96 + 1.40 + 0 = 2.36\,\overset{\circ}{\text{A}}.$$

The calculated Bi—O bond in this compound is 2.36 Å, and on the other hand, the Bi—O bond in $BiTiO_3$ compound is detected to be 2.75 Å, which is rather than necessary bond length for ionic band.

By the incorporation of Na in $BiTiO_3$, a Na atom is substitute of a Bi atom in similar position. The Bi—O bond has less ionic tendency than the Na—O bond, this is shown in Fig. 4.

3.3. Electron charge density

Contours of the electric charge density for $BiTiO_3$ and BNT crystals at real space are shown in Figs. 2–4. The electric charge density in the (0 0 1) and (1 0 0) surfaces of $BiTiO_3$ crystal are shown in Figs. 2 and 3.

It is true that the Ti—O bonds, are more ionic but due electric charge density to other atoms in this compound, Ti—O bonds are less covalent. On the other hand, the bond between the O atoms is covalent.