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Ceramics International 39 (2013) S283–S286

CERAMICS INTERNATIONAL

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First principle study on structural, elastic and electronic properties of cubic $BiFeO_3$

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Available online 16 October 2012

Abstract

We present the first principle studies of the structural and electronic properties in high temperature cubic phase (Pm3m) of $BiFeO_3$ based on Density Functional Theory (DFT). All calculations are performed within Local Density Approximation (LDA) functional and Generalized Gradient Approximation (GGA) functional with Ultrasoft Pseudopotentials (USP). It shows that the calculated structural parameters of cubic $BiFeO_3$ are in a good agreement with previous literatures. Based on the calculated of elastic properties of cubic $BiFeO_3$, this material shows a stable mechanical structure. In electronic band structure, the electron wave propagates through Brillouin zone X–R–M–G–R points where the highest valence band overlap with the lowest conduction band to give zero energy band gaps. The Density of States (DOS) demonstrated the significant hybridization between Bi6p, Fe3d and O2p in the range of −5 eV–5 eV. Thus, it can be implied that multiferroic $BiFeO_3$ are metallic at cubic phase and the metal–insulator transition in this material obeys the band theory.

Keywords: Multiferroic; $BiFeO_3$; Density Functional Theory (DFT)

1. Introduction

Multiferroic $BiFeO_3$ (BFO) has attracted a new interest in fundamental sciences and has shown great potential for a new application due to its ability to exhibit both ferromagnetic (G-type antiferromagnetic) and ferroelectric properties at room temperature [1]. In recent year, the first principle and experimental studies focus on this essential multiferroic material due to their superior in ferroelectric properties and room temperature magnetoelectric effect have been carried out [2–4]. However, there are very few literature studies on high temperature phase transition (paraelectric γ-phase) [5,6]. As BFO decomposed at high temperature, the study on phase and metal–insulator transitions at high temperature become almost impossible [1]. Moreover, there is very little report on first principle study of cubic Pm3m $BiFeO_3$. Therefore, the paraelectric–ferroelectric transition and metal–insulator transition in this material are still not fully understood.

In this work, we study on structural, elastic and electronic properties of BFO in paraelectric Pm3m cubic phase by First Principle method (which can only be experimentally obtained at high temperature). The origin and metal–insulator transition of multiferroic BFO materials will be discussed in detail using electronic ground states calculation.

2. First principle method

The first principle calculations of paraelectric cubic (Pm3m space) $BiFeO_3$ materials (shown in Fig. 1) have been performed by using the Cambridge Serial Total

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http://dx.doi.org/10.1016/j.ceramint.2012.10.078

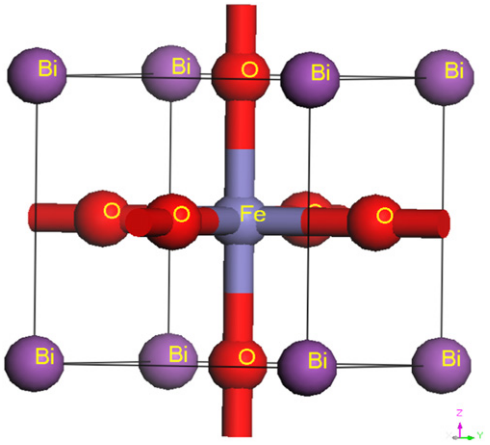

Fig. 1. Schematic diagram of cubic (Pm3m space group) $BiFeO_3$ with perovskite structure.

Energy Package (CASTEP) package [7,8] with Plane Wave Basis sets and Vanderbilt Ultrasoft Pseudopotentials (USP) [9]. This first principle calculation is based on Density Functional Theory (DFT) within Local Density Approximation (LDA) [10] and Generalized Gradient Approximation (GGA) [11] with and without of spin polarized. In this work, the geometry optimization calculation is achieved using convergence thresholds of 5.0×10^{-6} eV/atom for total energy, 0.01 eV/Å for maximum force, 0.02 GPa for pressure and 5.0×10^{-4} Å for displacement. The electronic properties calculation were performed with and without Hubbard U interaction LDA and corrected LSDA+U (U=3 eV) functionals.

3. Results and discussion

In this work, geometry optimization of Pm3m cubic phase BFO was performed within LDA and different GGA (PBE, PW91 and WC) functional with and without of spin polarized. The comparison is listed in Table 1 and it shows that the calculated lattice parameter is comparable to the other previous first principle study [4] and in good agreement with experimental data [6,12]. The different between the calculation data and experimental data is believed to have come from the defects and the limitation in high temperature measurement of the experimental study. From the comparison, the geometrical optimization calculation of cubic BFO with spin polarized show better results than without spin polarized.

Table 2 shows the calculated Single-crystal elastic constant (C_{ij}), Bulk modulus (B_0), optimum volume (V_0), Young modulus (E) and polycrystalline aggregate properties of cubic BFO. The calculations are performed within LDA and GGA-PBE functional with spin polarized. The elastic study of material is important for both fundamental and application of materials science. From our calculated result, it clearly shows that the elastic properties of cubic BFO increased with decreasing of the optimum volume. In cubic materials, the mechanical stability of the crystal is presented

Table 1
Structural lattice parameter of cubic $BiFeO_3$ calculated from LDA and different GGA functional. Previous theoretical and experimental data also included for comparison.

	a (Å)	
	Spin polarized	Non-spin polarized
LDA	3.844	3.699
GGA-PBE	3.946	3.804
GGA-PW91	3.943	3.805
GGA-WC	3.907	3.770
Exp.	3.9916[a]3.93[b]	
Theoretical	3.75(LDA)[c]4.21(GGA)[c]	

[a]Reference [6].
[b]Reference [12].
[c]Reference [4].

Table 2
Single-crystal elastic constant (C_{ij}), Bulk modulus (B_0), optimum volume (V_0), Young modulus (E), polycrystalline aggregate properties of bulk modulus (B), shear modulus (G) in Voigt–Reuss–Hill approaches of cubic $BiFeO_3$ calculated from local (LDA) and non-local (GGA) functional with spin polarized.

Property	With spin polarized	
	LDA	GGA-PBE
V_0 (Å^3)	56.79	61.44
C_{11} (GPa)	296.4 ± 5.3	238.5 ± 10.6
C_{12} (GPa)	111.9 ± 11.2	104.7 ± 1.4
C_{44} (GPa)	62.2 ± 0.9	62.0 ± 3.7
B_0 (GPa)	173.4 ± 7.7	149.3 ± 3.6
B_V (GPa)	173.4	149.3
B_R (GPa)	173.4	149.3
B_H (GPa)	173.4	149.3
E (GPa)	235.1	174.6
G_V (GPa)	74.3	64.0
G_R (GPa)	71.6	63.9
G_H (GPa)	72.9	63.9

by several criteria [13]: $(C_{11}-C_{12})>0$; $(C_{11}+2C_{12})>0$; $C_{44}>0$. The calculated elastic constants of cubic BFO show positive values and it is suggested to have a stable mechanical structure. The bulk modulus ($B_{V,R,H}$) and shear modulus ($G_{V,R,H}$) represent the calculated results pertaining to Voigt–Reuss–Hill approaches [14]. It is noted that for any cubic phase, the Voigt–Reuss–Hill bulk moduli are identical. This elastic properties study also can provide valuable theoretical information on mechanical properties of the material. For deeper understanding on the origin and metal–insulator transition in BFO material, we carried out the electronic ground states properties calculation by using first principle method within LDA (non-spin paramagnetic) and LSDA+U (U=2 eV). Based on the first principle study [16], energy U=2 eV is efficient to give rhombohedral R3c BFO in insulator with correct electron occupied orbitals.

The electron waves propagate in band structure through Brillouin zone X–R–M–G–R points and density of states

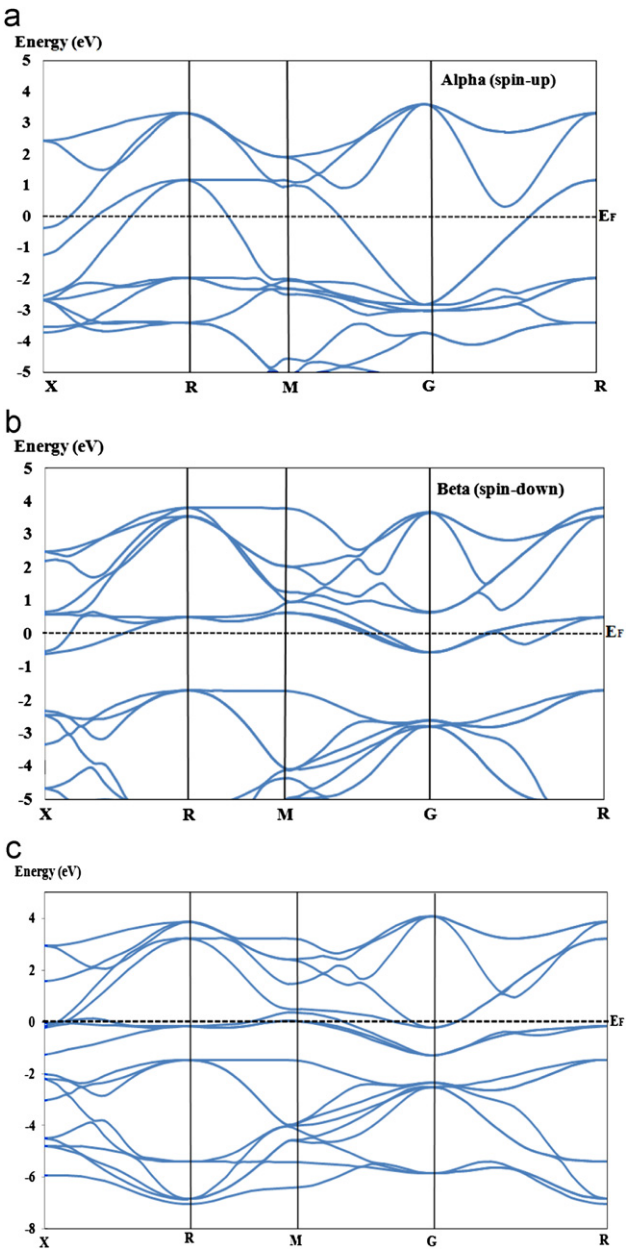

Fig. 2. Electronic band structure for alpha states (spin-up) (a), beta states (spin-down) (b) and non-magnetic and (c) of cubic $BiFeO_3$ along the high symmetry axes of the Brillouin zone.

(DOS) of cubic BFO is shown in Figs. 2 and 3 respectively. The Fermi energy in this calculation is set to zero energy. From the calculated band structure (LDA and LSDA + U), BFO in Pm3m cubic phase has zero energy band gaps (metallic) which the highest valence band overlaps with the lowest conduction band.

It is obviously shown that electron waves propagate from the highest valence band through X–R–M–G points and overlap with the lowest conduction band to leave BFO metallic material in cubic phase. Thus, the metal–insulator in this material obeys the band theory instead of Mott theory due to its transition that is related to the change in their structure [6,15]. The correlation between

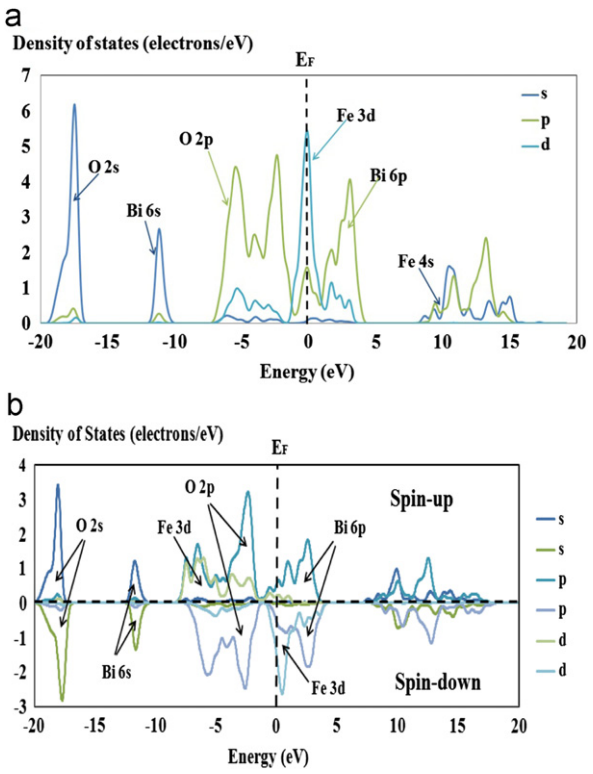

Fig. 3. Density of states (DOS) for LDA calculation (a) and LSDA (spin-up and spin-down states) calculation and (b) of cubic Pm3m $BiFeO_3$.

electron occupied orbital with the band structure (valence band and conduction band) is illustrated by DOS calculation (see Fig. 2). Our DOS calculation shows that the valence band and conduction band are occupied with O2p, Fe3d and Bi6p states respectively with significant hybridization between Bi6p, Fe3d and O2p states in the range of −5 eV–5 eV. Hence, the hybridization of Bi6p–O2p states in addition of Bi6s states in DOS demonstrated the lone-pair of Bi^{3+} cation (stereochemically active $6s^2$ lone-pair) that has possibly contributed to the large ferroelectric polarization in the BFO material [16,17].

4. Conclusion

The structural and electronic properties of multiferroic BFO at high temperature cubic phase are systematically studied by first principle study based on DFT (in CASTEP package). The calculated structural properties with LDA and GGA (PBE, PW91 and WC) calculations are in good agreement to the other previous experiment and first principle studies. Based on our first principle investigation, BFO is a metallic material in Pm3m cubic phase which corresponds to the zero band gap in band structure calculation. The results obtained are in agreement with experimental study by Palai et al. [6]. We suggest that the metal–insulator transition in BFO material obeys the band theory instead of Mott theory. The strong Coulomb repulsive force due to the hybridization of Bi6p–O2p states

has contributed large ferroelectric polarization in this multiferroic material.

Acknowledgment

This work is supported by the Fundamental Research Grant Scheme [Grant no. 600-RMI/ST/FRGS 5/3/Fst (4/2010)] provided by the Ministry of Higher Education and the Institute of Science (IOS), Universiti Teknologi MARA, Malaysia.

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