A comprehensive review of First Principle Study on Bismuth Ferrite

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Abstract

First Principle Method have been successfully used to explain various properties of multiferroic materials and to predict novel effects and new systems that exhibit multiferroic properties. In this study we review recent theoretical studies of the $BiFeO_3$ (BFO) using Density Functional Theory (DFT). DFT is a computational method that derives properties of molecules based on a determination of electron density of molecules. The most significant advantage of DFT method is the significant increase in computational accuracy without the additional increase in computing time. In this review we discuss the different aspects of the electronic structure, magnetic and electrical properties as well as the lattice stability and density of states of BFO. Finally, we report on recent investigations of direct bandgap in the electronic structure and also the change in Fe-O-Fe bond angles that controls the local magnetization of domain walls with different type of doping.

Keywords: First Principle method, Density-functional theory (DFT), $BiFeO_3$, Crystal structure, Electronic structure.

1.1 Introduction

Recent years have seen a tremendous progress in explore movement in the field of multiferroic materials and magneto-electric compounds. In December 2007 Science Magazine listed multiferroic materials as one out of ten 'Areas to watch in 2008', the only entry from the materials science/condensed matter area that was included in this list [1]. First principles calculations using density-functional theory (DFT) [2-4] have played an important role in this 'Renaissance of Magneto-electric Multiferroics' [5]. In the present paper we will give a brief summary of the current status of research on multiferroic materials and highlight some of the contributions that have been made using first principles electronic structure calculations. According to the original definition put forward by Schmid [6], multiferroic materials are materials that combine two or more of the primary forms of ferroic order, i.e. ferroelasticity, ferroelectricity, ferromagnetism, and ferrotoroidicity. In practice, most of the recent research has focused on materials that combine some form of magnetic order (ferromagnetic, antiferromagnetic, non-collinear) with ferroelectricity. Therefore, the term multiferroics is nowadays often used synonymous with magnetic ferroelectrics.

1.1 Structure of BFO: $BiFeO_3$ is a rhombohedral perovskite with space group R3c. The ground-state structure is reached from the ideal cubic perovskite Pm3m by imposing two symmetry adapted lattice modes: (a) a nonpolar *R*-point mode which rotates successive oxygen octahedra in opposite sense around the [111] direction and (b) a polar distortion, consisting of polar displacements along the [111] direction as well as symmetric breathing of adjacent oxygen triangles. The rhombohedral lattice constant is 5.63 Å with corresponding pseudocubic lattice constant, a_0 =3.89 Å and the rhombohedral angle, α=59.35°, is close to the ideal value of 60° [7]. First-principles density-functional calculations have been shown to accurately reproduce these values [8].

1.2 What is First Principal Study?: As this review is about First principle study of BFO, it helps us to provide at least a brief description of the current state of First principle methodological development. However, the literature on first-principles methods is vast and provide a comprehensive overview about outside the scope of this review. A calculation is said to be or from of first-principles if it relies on the fundamental laws of quantum physics without additional assumptions or special models. For the prediction of many materials properties, such a calculation generally involves studying a system of N electrons in an external potential and finding the solution

to the many-body time-independent Schrodinger equation [9]. Moreover, First principles calculation provides us to get the experimental results without performing any experimental procedure and thus very time efficient and cost effective, especially in countries of Third world. There are many theories of First principle study. Amongst those the DFT or Density Functional Theory is the most popular.

2. Electronic structure method of modeling materials

The properties of each materials start with its bonding. This fundamental description of bonding needs the calculation of the electronic distribution. The method that provides such data and information is known as the *electronic structure method* [10].

The basis for all quantum mechanical calculations of the electronic structure of a material is the Schrodinger equation,

$$H\Psi = E\Psi \dots\dots\dots\dots (1)$$

Where H is the Hamiltonian operator, E is the energy, and ψ the wave function. A key point of quantum mechanics is that. H is an operator and thus behaves quite differently than an equivalent function in classical systems.

2.1 Density Functional Theory: DFT has its foundation in the Hohenberg–Kohn (H–K) theorem [2], which states that (i) all ground-state properties of a system, including the total energy, are some functional of the ground-state charge density; and (ii) the correct ground-state charge density minimizes the energy functional

$$E[n] = T[n] + U[n] + \int V(r)n(r)d^3r$$

where n is the charge density, r is the position, E is the total energy, T is the kinetic energy, V is the potential energy from the external field (typically due to the positively charged nuclei of the crystal), and U is the electron–electron interaction energy. The H–K theorem implies that the ground-state for any system can be determined by varying the charge density until the global minimum in the energy functional is found. Thus, the complex problem of solving the many-body Schrodinger equation of N electrons with 3N spatial coordinates is reduced to a simpler (though still difficult) problem based on the charge density of 3 spatial coordinates. However, while the H–K theorem guarantees in principle a correspondence between the ground-state charge density and energy, the true functional relating the charge density to the energy is unknown [9].

There are many DFT calculation processes such as Local density Approximation (LDA), Generalised Gradient Approximation (GGA), Perdew–Burke–Ernzerhof functional (PBE), Perdew–Wang functional (PW91) etc. Amongst all these GGA and LDA is the most popular and GGA gives very accurate results.

3. Review of Properties:

3.1. Structural Property: The lattice parameters obtained from First principle study of BFO are recorded in Table 1.The values obtained from different methods are compared with the experimental values.

Source	Lattice parameter	Volume	α	Fe (x,x,x)	O (x,y,z)
Exp a[11]	5.634	124.6	59.348	0.221	0.528, 0.395, 0.933
Exp b[12]	5.637	124.8	59.344	0.221	0.524, 0.397, 0.934
Exp c[13]	5.630	124.3	59.343	0.221	0.523, 0.422, 0.939
CASTEP-GGA[14]	5.669	124.0	58.349	0.222	0.368, 0.551, 0.929
VASP-LDA	5.459	116	60.360	0.231	0.542,0.943,0.398
VASP-GGA	5.687	128.5	59.235	0.223	0.534,0.936,0.387
ABINIT-LDA	5.500	115	60.180	0.231	0.399, 0.541, 0.946
PWSCF-LDA	5.660	120.4	57.320	0.221	0.530, 0.936, 0.390
WIEN2K-GGA	5.672	127.7	59.240	0.224	0.535, 0.937, 0.388

Table 1 : Comparison of experimental data and first principle calculations

It is seen that the outcomes are in better concurrence with experimental data, which have as it were a 0.56% accuracy of the experimental value. But the length and angle of the lattice vector are a little longer and smaller than the experimental mean values, respectively. It is indicated that there is a more serious inner structural distortion in geometry optimization in our simulation than the experimental [12, 13, 15]. This is attributed to no

defect in ideal crystal, which is different from the practical crystal. There is approximately 2.4% overestimation by using DFT calculation [14].

3.2. Electronic Properties:
DFT calculated energy band structure of BFO along the high symmetry directions in the Brillouin zone is shown in Fig. 1. The top of valence is set as zero energy level for BFO. To repair the systematic error, the scissors made a rigid upward shift of conductive bands by 1.4 eV to represent the experimental band gap [16].
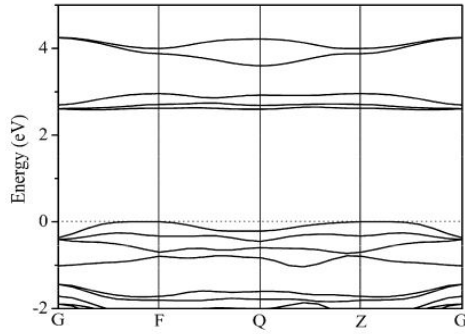

Figure 1: Calculated energy band structure of $BiFeO_3$. The energy of the top of the valence band (EF) is set to zero [14].

Explaining the nature of the electronic band structure, the total and atomic site partial densities of states (PDOS) of BFO have been calculated shown in Fig. 2. The angular momentum character of the different structures can be identified from the PDOS. From the Fig. 2, the lower bands in the range of −11 to −9 eV are provided by Bi-6s states and the lone pair lying off centre for this site is difficult to be infected by other atoms. Thus, the origin of ferroelectricity in BFO is better described as originating from dynamic O p–Bi p hybridization [17]. The top of the valence bands in the range of −6.5–0 eV is shown to be of predominantly O-p states character with minor contributions of Bi-p states and Fe-d states. At the lower conduction bands (2.5–4 eV), Fe-d states provide mostly and O-p states provide only a little. The middle conduction bands (6–8 eV) are occupied dominantly by Bi-p states, Fe-s states take over the range of 10–11 eV in the top of the conduction bands. From the Fig. 2, there are covalent bonding contributions between Fe and O atoms and between Bi and O atoms
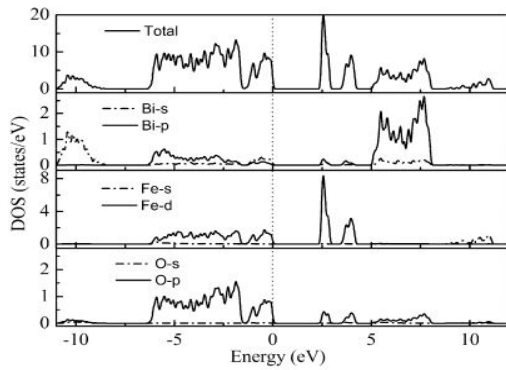

Figure 2: The calculated total and partial densities of states in $BiFeO_3$ (only show spin up). From the top down, it is shown total density, the density of Bi, Fe, O atom in turn. [14]

3.3 Magnetic Properties:
Dependence of magnetization on Fe-O-Fe bond angle: Fe-O-Fe in each layer of BFO supercell are plotted. The bond angles change by up to 4° in the wall region to compensate for the changes in structure associated with polarization orientation. It should be noted that the Fe-O-Fe angles remain far from the ideal 180° in all cases, indicating that the structure within the walls is far from an ideal cubic perovskite structure. It is represented in the following figure. In the next figure, we show the net local magnetization resulting from the canting of the Fe magnetic moments in each layer across the 109° domain wall. We see that the local canting increases the net magnetization by 33% in the wall layer, consistent with the larger deviation of the Fe-O-Fe angles from 180°. From **Figure 3(c)**, it is seen that Fe-O-Fe bond angle for 109° domain wall deviates more in the domain wall region. Again from **Figure 3,** it is noted that magnetization increases in the same region for 109° domain wall.

Thus, changes in structure at the domain walls cause slight changes in Fe-O-Fe bond angle, which result in changes in canting of the Fe magnetic moments, which can enhance the local magnetization at the domain walls.
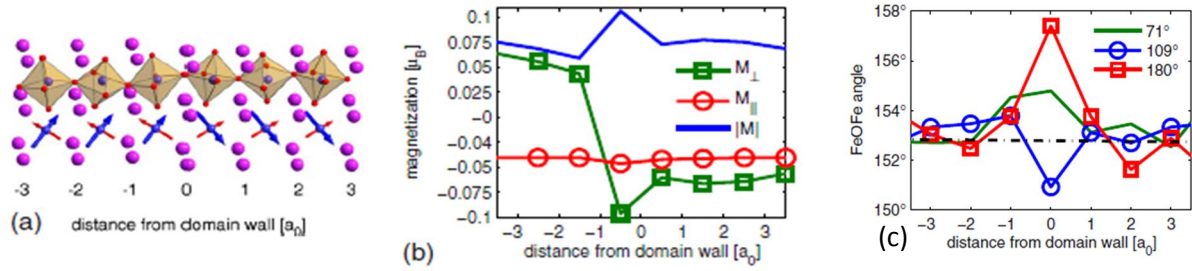
Figure 3: Layer-by-layer local magnetic moment across the 109° domain boundary. (a) shows the local magnetization vectors small red arrows resulting from the canting of the Fe magnetic moments in each layer, which is perpendicular to the local electric polarization (big blue arrows), (b) shows the local component of the magnetization projected parallel and perpendicular to the wall plane and the local magnitude. (c) Fe-O-Fe angles in each layer of the super-cell. The bulk value of 152.9° is indicated by the dashed line. The angle changes significantly in the domain wall region [18]

4. Effects of doping on the properties of BFO

For practical applications of $BiFeO_3$, the impurities, large leakage current, antiferromagnetic nature and large dielectric loss are main barriers. Doping is considered best way to enhance multiferroic properties of BFO [19]. Several research groups have reported that when BFO is single doped or co-doped, the superior ferroelectric property can be obtained through reduction of leakage current due to suppression of oxygen vacancies [20]. Considerable experimental works have been made to adjust the band structure of $BiFeO_3$ by doping. In addition to, the magnetization property can be enhanced by rare earth due to change in Fe-O-Fe bond angle [21]. In this review, we will discuss A-site, B-site and oxygen substitution with specific examples for each.

4.1. A-site substitution: Perovskite (ABO_3) Bismuth Ferrite has Bi^{3+} ions at A-site, so replacing the Bi3+ ions by other transition metal ions makes A-site substitutions. It is well established that the ferroelectricity in BFO originates from Bi^{3+} $6s^2$ lone pair electrons [22], whereas ferromagnetism is related to the partially filled d orbital of Fe and Fe-O-Fe angle change [23]. Several experimental works have been made to alter the Bi site through various alkaline and rare earth metals such as Ca, Ba, Sr, La, Pr, Nd, Sm, Ho, Gd, Ru etc. Substitution of Bi^{3+} ions by alkaline ions resulting in the appearance of oxygen vacancies that in turn increases the electrical conductivity of the materials [24]. On the other hand, when Bi^{3+} is substituted by rare earth trivalent ions which ionic radii are smaller than Bi^{3+} ions, it results in enhancement of magnetization with more electrical insulating behavior [25].

4.2. B-site substitution: B-site substitution refers the case that the Fe^{3+} ions are substituted by others ions. B-site doping affects physical properties i.e. by enhancing magnetic property by changing Fe-O-Fe super-exchange interactions and modifying the electronic structure near the Fermi level [26]. Various attempts have been made on doping at Fe site in BFO with a number of transition ions such as Ti, Cr, Mn, Co, Ni, Zn etc. Among them, Ti^{4+} is very effective dopant to improve the electrical properties of BFO. Some research groups have reported that Fe-site doping by Ti^{4+} ions reduces leakage current by over three orders of magnitude. Similarly, doping with Mn and Cr are also considered to reduce the leakage current [27, 28]. Wei Cai et al reported that the band gap of BFO changes with the amount of Ti content by following manner

Titanium content (at %)	0	2	4	8
Band gap (eV)	2.58	2.49	2.43	2.38

4.3. Oxygen-site substitution: Doping with certain foreign metal ions in BFO system might introduce surface defects such as oxygen vacancies. The presence of such oxygen vacancies changes both the chemical and electronic properties of BFO and consequently, the performance of BFO devices [29]. In addition to, the magnetization of BFO is affected by the presence of oxygen vacancies, which mainly depend on the precise position of oxygen vacancies [30]. Many research groups have confirmed that high leakage current for BFO results from the generation of a number of oxygen vacancies [31]. In all cases, oxygen vacancies lead to the

formation of Fe^{2+} ions from Fe^{3+}. Therefore, it is fundamentally important to control oxygen vacancies and their kinetic behavior. Addition of 4+ ions e.g. Ti^{4+} to BFO at Fe^{3+} site leads to reduction of oxygen vacancies, where 2+ ions increase the oxygen vacancies [32]. N is a very effective dopant to enhance magnetic property. It is suggested that, $1\mu_B$ total magnetic moment is produced by adding one N atom at O site compared with no magnetic moment in the perfect BFO [32].

5. Conclusion: First principle calculation based on the density functional theory for a multiferroic system was reviewed in this paper. Results from different works on this material regarding magnetic, electric and the effect of dopants from different works and calculation were presented. Computational methods help in the synthesis and characterization of materials before experimental work can be undertaken. This helps to minimise the experimental trial and error technique and saves time, cost and give better results. However further research is needed to engineer more efficient algorithm and functional for more precise results that can deliver better results for the already established models.

6. References

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