

Multiferroic BiFeO₃ for Photovoltaic Applications : A First-principles Study

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Abstract. *Ferroelectric materials are new candidates for photovoltaic materials. Ferroelectrics can produce photocurrents without using p-n junction which is necessary for conventional photovoltaic devices. BiFeO₃ is one of the most promising multiferroic materials having band gap of 2.5 eV. This band gap is too wide to be used as photovoltaic devices, therefore lower band gap is necessary. In order to reduce BiFeO₃ band gap, we carry out a first-principles calculation. We study Cu substitution impurities. We introduce a single Cu atom in the 2x2x2 supercell and we find that the band gap is reduced by 0.039 eV. We expect the existence of optical transition energy between valence and impurity band with energy value 1.232 eV lower than the band gap of BiFeO₃.*

Keywords: BiFeO₃, Cu substitution impurities, photovoltaics, band gap.

1 Introduction

Bismuth ferrite (BiFeO₃) is a promising room temperature single-phase multiferroic material [1]. It has ability to exhibit both ferromagnetic (G-type antiferromagnetic) under the Neel temperature (T_N) of 640 K and ferroelectric properties under the Curie temperature (T_C) of 1120 K [2, 3]. Those two orders are coupled so that by changing the magnitude or direction of one type of order, the other is also changed [4]. At ambient condition, BiFeO₃ has a rhombohedral symmetry belonging to the R3c space group [7]. It permits the development of spontaneous polarization along [111] direction of the highly distorted perovskite [8]. The primitive unit cell contains two formula units with ten atoms [9] as shown in Fig. 1. The perovskite structure has the general stoichiometry ABX₃ [10]. Where "A" is large cation, "B" is smaller cation, and "X" is anion. In BiFeO₃ case, both A and B cations are trivalent states.

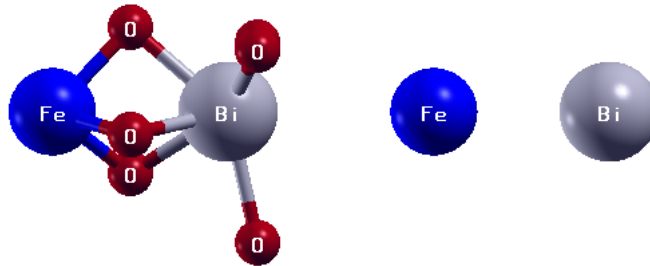


Figure 1: Schematic view of BiFeO₃ unit cells.

Recently the photovoltaic effect in ferroelectric materials has attracted enormous interest. Ferroelectrics can generate photocurrents without using p-n junction which is necessary for conventional photovoltaic devices. Ferroelectrics do not need separation of electrons and holes by internal field et all, photocurrent and photovoltage can be observed in pure homogeneous single crystals [5, 6]. This ability leads ferroelectrics as one of the candidates for next generation photovoltaic devices. Experimentally multiferroic BiFeO₃ materials having band gap of 2.5 eV as reported by Gao et al.[12]. Unfortunately, these band gap is too large to be used for photovoltaic application. Material with band gap 1.3–2.0 eV have the greatest potential to make an efficient cell [13]. A wider band gap would be unable to absorb low-energy photons and a narrower band gap would lose many high-energy photon to heat. This band gap problem become our concern in this study.

2 Calculation Details

To perform the first-principles electronic-structure calculations we use density functional theory (DFT) as implemented in OpenMX code [14]. All calculations in this study performed by local spin density approximation (LSDA) exchange correlation form [15] plus U [16] approach with $U=4$ eV for Fe and Cu 3d electrons, norm-conserving pseudopotentials [17] are used. Wavefunctions are expanded by linear combination of multiple pseudoatomic orbitals (LCPAO) [18, 19]. The orbitals are specified as Bi10.0-s3p3d2, Fe8.0S-s3p3d3, Cu8.0S-s3p3d3, and O6.0-s3p3. The former numbers written after atomic symbols are cut off radii of the confinement potential. Whereas the latter parts (s3p3d2, etc) are number of orbitals for s, p, and d composed. These calculations are performed with a $8 \times 8 \times 8$ uniform \mathbf{k} -point mesh centered at Γ and the convergence criteria for energy is 10^{-7} Hartree. G -type antiferromagnetic order is assumed for all calculations with collinear spin arrangement (does not consider spin orbit coupling).

3 Results and Discussion

3.1 Structural parameters

BiFeO₃ has rhombohedral structure with space group R3c, where the Bi atom is placed at the origin. The calculation results of full structural optimization of G-type antiferromagnetic BiFeO₃ are collected in Table 1. Our results are in better agreement with both experimental [20] and previous calculations [21]. Fractional coordinates of atomic positions presented in Wyckoff positions, 2a for Bi and Fe and 6b for O are referred to the rhombohedral system. The lattice constant of the primitive unit cell a_{rh} and the rhombohedral angle α are also listed. Both calculated and experimental rhombohedral angle are very close to 60° which would appropriate to perfect cubic lattice vectors.

Table 1. Calculated and experimental parameters for BiFeO₃ in R3c structure.

		Present calc.	Prev. calc.	Expt.
Bi (2a)	x	0	0	0
Fe (2a)	x	0.214	0.227	0.221
O (6b)	x	0.536	0.542	0.538
	y	0.938	0.943	0.933
	z	0.392	0.397	0.395
a_{rh} (Å)		5.59	5.52	5.63
α (°)		59.37	59.84	59.35

In the R3c structure, the Fe site has two types of bonds with different bond length. Three oxygen neighbors have bond lengths of 1.94 Å and the others have 2.11 Å, which results in the distortion of FeO₆ octahedra. The ideal cubic perovskite structure has O-Fe-O bond angle of 180°, which is changed in this system by 165.07° because of its distortion.

3.2 Electronic properties

We calculate the electronic structures of BiFeO₃ in R3c structure. For BiFeO₃ unit cell, the structure has indirect band gap of 1.77 eV. We did a comparison with previous calculation performed by Neaton et al.[21] as listed in Table 2.

Table 2. BiFeO₃ unit cell band gap of present and previous calculations (in eV).

	$U=4$ eV
Present Calc.	1.8
Previous Calc.	1.9

In order to reduce BiFeO₃ band gap, we introduce Cu substitution impurities with concentration about 6.25%. So that we need to enlarge BiFeO₃ system from unit cell to $2 \times 2 \times 2$ supercell. The supercell system consists of 80 atoms: 16 Bi, 16 Fe, and 48 O atoms, where a Fe atom is replaced with a Cu atom as an impurity as shown in Fig. 2. After adding Cu impurities, then we relax the position of all atoms until the absolute deviation between the eigenvalue energy at the current and previous SCF step is less than convergence criterion.

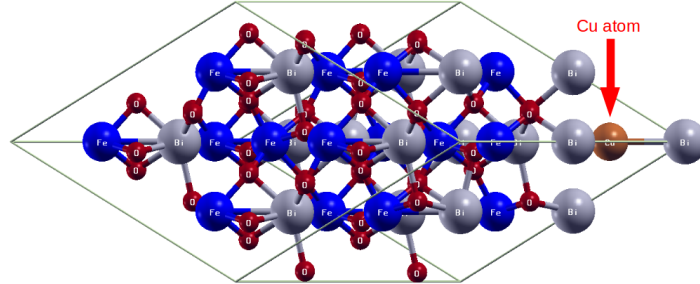


Figure 2: A $2 \times 2 \times 2$ BiFeO₃ supercell with Cu substitution impurities. Grey ball is Bi, blue ball is Fe, red ball is O, and brown ball is Cu.

The calculated energy band structure of BiFeO₃ supercell along high-symmetry directions in Brillouin zone for system without impurities (called perfect system) and system with Cu impurities (called impurity system) are given in Figs. 3(a) and 3(b). Red and green structures for the up- and down-spin states, respectively. Up- and down-spin states in perfect system have exactly same value, therefore this system has no net magnetic value. Both perfect and impurity systems have indirect band gap, with the top of the valence band located at F point and the bottom of the conduction band at γ point.

For perfect system, we can find energy band gap E_g about 1.834 eV. Some states appear between valence and conduction band for impurity system case. These states come from Cu impurities (called impurity band). So, in order to perform band gap calculation we have to neglect these states. Then we can find impurity system has band gap E_g^{Cu} about 1.795 eV, only 0.039 eV reduced from perfect system band gap. This band gap is still too wide for photovoltaic applications. We

expect the existence of optical transition energy E_{Opt}^{Cu} between valence and impurity band. This optical transition energy has value about 0.602 eV, 1.232 eV different with the band gap of perfect system. Unfortunately this optical transition energy value also still not favorable for photovoltaic applications. In addition, the calculated Fe magnetic moment is $3.67 \mu_B$, in a good agreement with experimental value [20] ($3.75 \mu_B$) and theoretical value [22] ($3.65 \mu_B$).

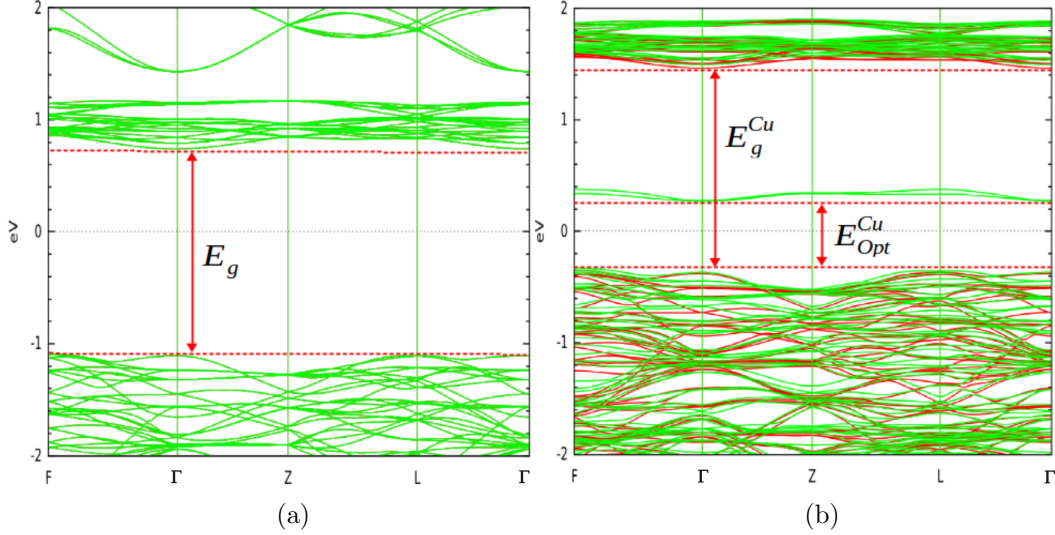


Figure 3: Band structures of BiFeO₃ supercell along high-symmetry directions, the Fermi level is located at 0 eV. The valence, conduction, and impurity band edges are indicated by the red dashed horizontal lines. (a) BiFeO₃ supercell system without impurities, (b) BiFeO₃ supercell system with Cu impurities.

4 Conclusion

In summary, we have investigated the effect of Cu substitution impurities in BiFeO₃ system. We find that Cu impurities reduce BiFeO₃ band gap by 0.039 eV. We expect there is optical transition energy between valence and impurity band, which has value 1.232 eV lower than the band gap of BiFeO₃ perfect system.

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