Multiferroic $SrTiO_3$/ $BiFeO_3$ Superlattice: A First-principles Study

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ABSTRACT

We present the results of the first principles density functional theory based calculations for structural, electrical and magnetic properties of $SrTiO_3$/ $BiFeO_3$ (STO/BFO) multilayer using local spin density approximation (LSDA+U). Our calculations predict that the ground state structure comprises of tetragonal *P4mm* symmetry with G-type antiferromagnetic spin structure having in-plane lattice parameters, $a = b = 3.8856$ Å. The electronic band structure and density of states show that the material has a band gap ~ 1.69 eV. Magnetic moment per Fe site was found to be ~ 4.09 μ_B. Spontaneous polarization, calculated using Berry phase method showed large polarization (~ 19.5 $\mu C/cm^2$) in the out of plane direction. Ti and O ions were identified as the primary contributors toward polarization.

Keywords: Multiferroic, strontium titanate, bismuth ferrite, multilayer, density functional theory.

1. INTRODUCTION

Material designing based on of artificial layered structures has pioneered a new field of process engineering owing to the possibility of developing unusual and novel functional properties which are often not found in the respective bulk systems.[1-5] Multilayers of ferroelectric and multiferroic have been probed quite extensively in order to study improved and novel properties.

Barium titanate-strontium titanate superlattice structure has been found to demonstrate improved polarization and dielectric properties. Both experiments [3] and first principles studies [2] conclude that interfacial strain as well as local asymmetries in this system cause symmmetry lowering which in turn improves the physical properties. Similar studies showing improved ferroelectric properties were made in other systems such as $KNbO_3$/$KTaO_3$,[6] $PbTiO_3$/$SrTiO_3$,[1] $SrTiO_3$/$BaTiO_3$,[7] $PbTiO_3$/$PbZrO_3$,[8] etc.

Multiferroic systems, especially bismuth ferrite has attracted tremendous attention due its large polarization [9] and high ferroelectric (T_c) and magnetic (T_N) transition temperatures. However, its use is largely restricted due to the poor leakage characteristics, primarily because of valence fluctuation of Fe ions. Solid solution [10] and doping at both Bi [11] and Fe [12] sites have been found to be benifacial to improve leakage behavior. Heterostructure, particularly lead titanate based multilayers [13] was also found to improve leakage behavior, significantly. Strontium titanate having large dielectric constant could be a viable alternative to replace hazardous lead. There are, infact, experimental evidence[14] of improved ferroelectric and leakage characteristics in strotium titanate- bismuth ferrite (STO/BFO) heterostructure. However, the origin of such improved ferroelectric properties has not been explored, particularly, at the first principles level. To our knowledge, the crystal structure and magnetic characteristics have not been studied even at the experimental level. In this work, we, therefore, present our first principles density functional theory based calculations of the ground state crystal and electronic structures, magnetic behavior and spontaneous polarization.

2. CALCULATION DETAILS

Our entire calculation is based on the first principles density functional theory.[15] Vienna ab-initio simulation package (VASP)[16] was used with projector augmented wave method (PAW).[17] The Kohn-Sham equation[18] was solved using local spin density approximation (LSDA+U)[19] with Hubbard parameter, U = 4.5 eV for Fe 3d states only. We included 10 valence electrons of Sr ($4s^2 4p^6 5s^2$), 4 for Ti ($3d^3 4s^1$), 5 for Bi ($6s^2 6p^3$), 8 for Fe ($3d^7 4s^1$) and 6 for O ($2s^2 2p^4$) ions. Conjugate gradient algorithm was used for the structural optimization. All the calculations were performed at 0 K. Structural optimization and calculation of the electronic band structure and density of states were carried out using Monkhorst-Pack 9×9×3 mesh.[20]

3. RESULTS AND DISCUSSION

3.1 Structural Optimization

We started our calculations with the experimental lattice parameters of cubic strontium titanate (STO). [4] Keeping the constant lattice parameters and ionic positions of STO and allowing bismuth ferrite (BFO) to assume identical lattice parameters and ionic positions, we stacked alternate layers of STO and BFO as shown in Fig. 1(a) and (b). In order to consider all possible spin configurations, we constructed a bigger ($\sqrt{2} \times \sqrt{2} \times 2$) supercell (Fig. 1(c)) out of the one shown in Fig. 1(b). Four possible spin

configurations were considered *viz.* ferromagnetic, A, C and G-type antiferromagnetic. Structures with difference spin configurations were subsequently relaxed (shape, size and ionic positions) such that thre pressure on the cell is close to zero and forces on the ions are less than 0.005 eV/Å.

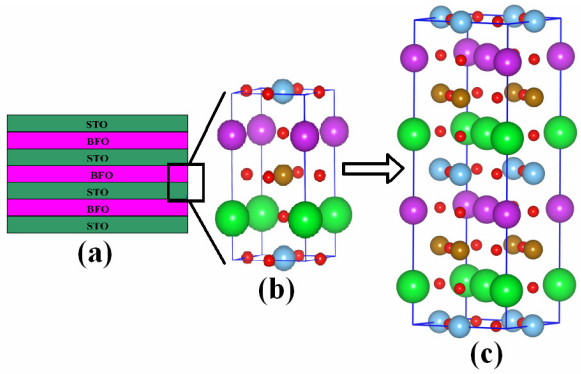

Fig. 1- (a) schematic diagram showing alternate stacking of STO and BFO layers, (b) Schematic diagram of the supercell constructed by stacking alternate unit cells of STO and BFO, (c) $\sqrt{2} \times \sqrt{2} \times 2$ supercell constructed from the one shown in Fig. 1(b). In Fig. 1(b) and (c) green spheres indicate Sr ions, blue represents Ti ions, violet spheres are for Bi ions, brown, Fe and red shperes indicate O ions.

Fig. 2 plots the total energies of the relaxed structures of different spin configurations mentioned above. Fig.2 shows that while ferromagnetic and A-type antiferromagnetic structures have higher energies, C and G-type antiferromagnetic structures have comparable energies with the G-AFM structure has 15.02 meV lower energies than the C-type structure.

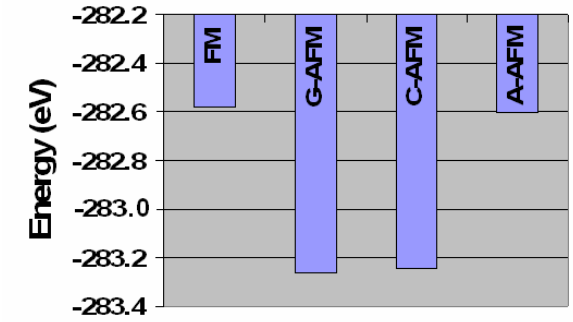

Fig. 2 – Total energy of STO/BFO superlattice structure with different spin configurations showing G-type antiferromagnetic structure with lowest energy is the ground state structure.

We, therefore, conclude that the ground state structure of STO-BFO superlattice is G-type antiferroimagnetic. It was also found that the ground state structure possesses tetragonal P4mm symmetry with in-plance lattice parameters $a = b = 3.8848$ Å and $c/a = 2.066$.

3.2 Electronic Structure and Magnetic Behavior

Fig. 3(a) shows electronic band structure of STO/BFO super-lattice structure along high symmetry directions.

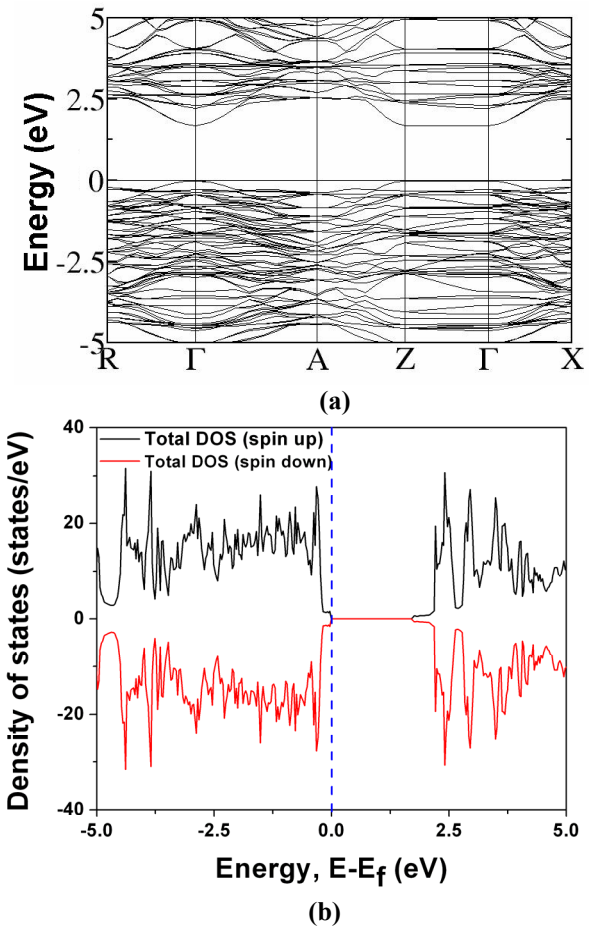

Fig. 3- (a) Electronic band structure along high symmetry directions, (b) Total density of states of STO/BFO superlattice structure.

It was found that the bands are quite flat in certain direction. As a result, the estimated band gap, ~ 1.69 eV, is equal for direct and indirect cases. Fig. 3 (b) plots the total density of states. From the partial desnity of states we determined the angular momentum charcters of different states. It was found that the uppermost part (-7.06 eV- 0 eV) comprises mainly of Fe 3d, Ti 3d and O 2p states. Beyond the fermi level, the conduction band is also consisted of Fe 3d, Ti 3d and O 2p. Presence of noticeable amount of Bi 6p states was also found here. Therefore, from the density of states we predict hybridization among Fe 3d, Ti 3d and O 2p states which would significantly impart covalency in Fe-O bond and Ti-O bond.

Calculated Fe magnetic moment in the ground state structure is ~ 4.09 μ_B which is comparable to the value of Fe moment in $BiFeO_3$. It was also found that O ions at SrO layer have moment of ~ 0.13 μ_B while O at BiO layer have

moment ~ 0.03 μ_B indicating existance of superexchange interaction.

3.3 Chemical Bonding

Fig. 4 plots the electronic charge densities on (001) and (010) planes at different layers. Considerable charge sharing was observed between Ti 3d and O 2p and Fe 3d and O 2p states at TiO_2 and FeO_2 layers, respectively, on (001) plane indicating existance of covalent character of Ti-O and Fe-O bond as indicated by density of states. Charge densities of Bi and Sr ions are largely symmetric predicting no significant charge sharing with the surrounding O ions. In other words, Sr and Bi ions do not take part in the formation of covalent bonding with O ions in STO/BFO superlattice. Combining density of states and charge density plots we conclude that ferroelectricity in STO/BFO superlattice would primarily be due to Ti, Fe and O ions which in contrast with the case of multiferroic BiFeO3 where ferroelectricity originates from the lonepair electrons of Bi ions. [21]

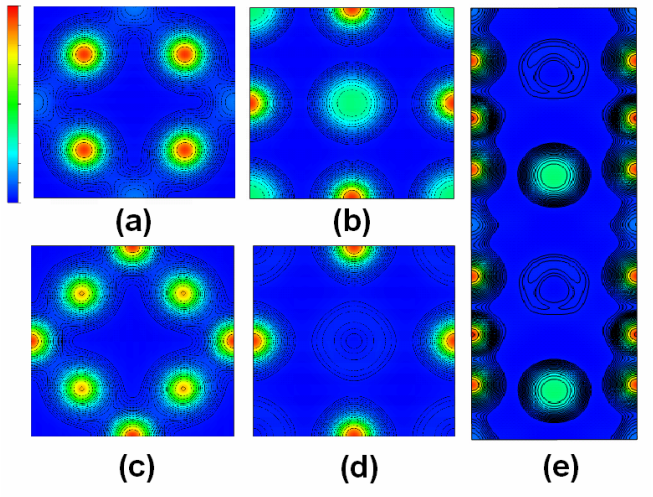

Fig. 4 – Electronic charge densities plotted on (001) planes for (a) TiO_2, (b) SrO, (c) FeO_2 and (d) BiO layers, (e) charge density on (010) plane.

3.4 Spontaneous Polarization and Origin of Ferroelectricy

Spontaneous polarization (P_s) in ferroelectric materials can be defined as:

$$P_s = [\mathrm{P}(u)\text{-}\mathrm{P}(0)] = \int_0^u Z^*(u)du = uZ(u) \qquad (1)$$

where, P (u) and P(0) are the polarization of the ferroelectric and paraelectric states, Z*(u) is the Born effective charges of the constituent ions and du is the relative displacement vectors of ions across the ferroelectric-paraelectric transition temperature (T_c). Calculating the displacement vectors and considering the Born effective charges of constituent ions of STO/BFO superlattice, we estimated spontaneous polarization in STO/BFO superlattice to be ~ 19.54 $\mu C/cm^2$. The conponents of polarization along three principal directions are: 0.012 $\mu C/cm^2$, 1.69 $\mu C/cm^2$ and 19.47 $\mu C/cm^2$ for [100], [010] and [001], respectively, indicating the spontaneous polarization lies almost along [001] direction. Experimental results at room temperature predicts $P_s \approx 2P_r \approx 17\ \mu C/cm^2$ in the out of plane ([001]) direction [14] is in good agreement with our calculation. In order to know the origin of ferroelectricity we estimated individual contribution of ions along [001] direction as listed in Table 1.

It is observed that Ti and O ions primarily contribute to the spontaneous polarization which is in sharp contrast of $BiFeO_3$ where polarization originates from Bi and O ions [21].

Table 1: Partial Polarization showing contribution of individual of the ions along [001] direction

P ($\mu C/cm^2$)				
P_{Sr}	P_{Ti}	P_{Bi}	P_{Fe}	P_O
-2.02	27.51	-3.76	2.35	-43.55

CONCLUSION

We performed first principles density functional theory based calculations for structural, electrical and magnetic properties of $SrTiO_3$/ $BiFeO_3$ (STO/BFO) superlattice using local spin density approximation (LSDA+U). Our results indicate that the ground state structure is G-type antiferromagnetic with tetragonal *P4mm* symmetry. Electronic structure calculation shows both direct and indirect band gaps are identical and ~ 1.69 eV. Density of states predicts significant hybridization of Ti 3d, Fe 3d and O 2p states which is further substantiated by charge sharing between Ti-O and Fe–O at TiO2 and FeO2 planes, respectively. Calculated value of spontaneous polarization ~ 19.54 $\mu C/cm^2$, is in agreement with experimental observation. It was found that ferroelectricity in STO/BFO superlattice originates from Ti and O ions.

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