Physics Letters A 373 (2009) 2374–2381

Contents lists available at ScienceDirect

Physics Letters A

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# Stability and electronic structure of $BiFeO_3$ (111) polar surfaces by first-principle calculations

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ARTICLE INFO

*Article history:*
Received 3 February 2009
Received in revised form 11 April 2009
Accepted 29 April 2009
Available online 8 May 2009
Communicated by R. Wu

*PACS:*
68.35.Bs
68.47.Gh
68.35.Md
73.20.At

*Keywords:*
Multiferroic materials
Surface
DFT
Electronic structure

ABSTRACT

The structural and electronic properties of $R3c$ phase $BiFeO_3$ (111) surface were calculated by the full-potential augmented plane wave method within the LSDA + $U$. It is found that the (111)-Bi/$O_3$/Fe-terminated surface is more stable than the O- and Fe-terminated surfaces at the O-poor environment, and (111)-$O_3$/Fe/Bi-terminated surface is more stable than the Bi- and Fe-terminated surfaces at the O-rich environment. Indeed, the (111)-Fe/Bi/$O_3$-terminated surface cannot be stabilized, after relaxation it will turn to the Bi-terminated surface. The density of states (DOS) of the relaxed $BiFeO_3$ (111) surface were calculated and compared with that of the bulk $BiFeO_3$. The ground-state electronic property of ferroelectric $BiFeO_3$ is found to be insulating and antiferromagnetic, but the $BiFeO_3$ (111) surface all have metallic properties, and the Fe magnetic moments are coupled ferromagnetically (F) within the pseudocubic (111) planes and antiferromagnetically (AF) between adjacent planes.

## 1. Introduction

Multiferroic materials have attracted extensive attention due to their potential usage in information, the emerging of spintronics and sensors [1–3]. Multiferroic materials are rare in nature because the physical/structural/chemical conditions for a material to be simultaneously magnetic and ferroelectric are generally difficult to be achieved [4,5]. Especially, ferroelectricity requires that the crystal structure be noncentrosymmetric and the ferroelectric transition is directly related to the structural phase transformation. Therefore, in such intriguing multiferroics, structural characterizations are extremely important. Currently there is a great deal of effort being expended to develop nanoscale devices. If nanoscale systems based on ferroelectricity are to be feasible, then the polar instabilities must remain dominant down to the nanoscale. In systems of reduced dimensionality, such as thin films or nanoparticles, a substantial fraction of the material is found in proximity to a surface, and surface effects may become important. The surface can affect the material behavior by modifying the strength of the various instabilities and their interactions leading to phases not present in bulk systems. With the rapidly advancing miniaturization of ferroelectric devices and the use of thin films, attention is focusing on the role played by surfaces and interfaces in the overall performance of the materials.

The ferroelectric $ABO_3$ perovskites have been investigated extensively by experimental and theoretical researchers because they have many technological applications such as high-capacity memory cells or optical waveguides. In such devices, the perovskites are typically used in the form of thin films. Therefore, it is important to investigate how the physical properties are affected by surfaces. In recent years, first-principles studies on the surface of ferroelectrics have deeply enhanced the understanding of surface effects on their ferroelectricities and other properties [6–11]. In spite of the renewed experimental interest for the polar terminations of the $BiFeO_3$, no theoretical study of either the (111) surface of $BiFeO_3$ has been performed so far, to our knowledge. It is the aim of this work to analyze the electronic properties and the stability of these surfaces. Considering the large number of degrees of freedom of the surface configurations (such as the termination, the stoichiometry, the type of the reconstruction and the atomic geometry within the two-dimensional unit cell), and the lack of firm

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doi:10.1016/j.physleta.2009.04.067

experimental grounds to choose among various structural models, we restrict our study to a few configurations of the surfaces, which show a variety of surface stoichiometries.

In the present Letter, we focus on the (111) polar surfaces of $R3c$ structure $BiFeO_3$ (BFO), which is one of the most extensively studied multiferroics, and exhibits magnetic with ferroelectric order at room temperature [12]. $BiFeO_3$ is ferroelectric with relatively high Curie temperature $T_C = 1103$ K and exhibits antiferromagnetic behavior with high Néel temperature $T_N = 643$ K [13–15]. The Fe magnetic moments are coupled ferromagnetically (F) within the pseudocubic (111) planes and antiferromagnetically (AF) between adjacent planes. The structure of the ferroelectric phase has highly distorted perovskite in rhombohedral cell with space group $R3$ [16,17]. The absence of centrosymmetry in $R3c$ permits the relative displacements of the atomic sublattices along [111] [18], most notably those of Bi with respect to the distorted $FeO_6$ cages.

## 2. Computational method

The calculations were performed in the framework of density functional theory. We used the CASTEP computer code [19] to optimize the lattice constants and calculate the Mulliken charge, and the generalized gradient approximation (GGA) [20] was used with the ultrasoft pseudopotential [21]. The total energy calculation and the analysis of the electronic structure are all calculated by the full-potential augmented plane wave (FP-APW) method in the WIEN2k package [22] with the LSDA + $U$ method [23,24], and in the LSDA + $U$ calculation we use $U_{\mathrm{eff}} = 4$ eV, since this value gives an insulating solution for all systems of bulk $BiFeO_3$. Higher values of $U_{\mathrm{eff}}$ would result only in small quantitative changes. These $U_{\mathrm{eff}}$ values also have been used for Fe ions in bulk $BiFeO_3$ by J.B. Neaton et al. [25], and they got a good result.

In this Letter, the self-consistent field calculations are based on the following parameters: the atomic-sphere radii $R_{\mathrm{mt}}$ are chosen as 2.5, 2.5 and 1.0 a.u. for the Fe, Bi and O atoms, respectively. Inside the muffin tins (MTs) the wave functions are expanded in spherical harmonics up to $l_{\max}^{\mathrm{wf}} = 10$, and the nonspherical contributions to the electron density and potential are considered up to $l_{\max}^{\mathrm{pot}} = 6$. The charge density Fourier expansion cutoff $G_{\max} = 18$ in the muffin tins, three hundred $k$-points in the first Brillouin zone were adopted in the calculations (242 points in the irreducible part of the surface Brillouin zone) with 174 677 plane waves at the equilibrium lattice constant. The cut-off parameter $R_{\mathrm{mt}}K_{\max}$ limiting the number of the plane waves is equal to 5.0, where $K_{\max}$ is the maximal value of the reciprocal lattice vector used in the plane wave expansion, and $R_{\mathrm{mt}}$ is the smallest atomic sphere radius in the surface cell, so the plane-wave cut off energy is 340 eV. With these cutoff parameters an accuracy of energy differences better than 0.1 meV has been achieved.

## 3. Results of surface calculations

We first investigated the bulk rhombohedral phase by optimizing the structural parameters of $BiFeO_3$ in a 10-atom unit cell with space group $R3c$. The structure can be described as a distorted perovskite. The ground state was found to be an antiferromagnetic insulator with a lattice constant of 5.52 Å and a rhombohedral angle of 59.84°, as compared with the experimental values 5.63 Å and 59.35° [17], which are within the deviations typical of the LSDA.

Because the (111) surface of $R3c$ phase $BiFeO_3$ is a tri-layer stacking sequence $\ldots Bi/O_3/Fe/Bi\ldots$, the compositions of the adopted slabs are not symmetric upon inversion along the surface normal. In order to achieve the appropriate electro-static boundary conditions and make the slab stoichiometry identical to the bulk, the two terminations of the slabs are generally different. Schematically, the (111) ideal surface of $R3c$ phase $BiFeO_3$ can be represented by sequences of charged layers $Bi/O_3/Fe\ldots Bi/O_3/Fe$, $O_3/Fe/Bi\ldots O_3/Fe/Bi$ and $Fe/Bi/O_3\ldots Fe/Bi/O_3$, respectively (Fig. 1). When a stoichiometric $BiFeO_3$ slab is ideally cut and the two parts are put apart, two complementary surface terminations are created. In our case, they are the (111)-$Bi/O_3/Fe\ldots$, (111)-$O_3/Fe/Bi\ldots$ and the (111)-$Fe/Bi/O_3\ldots$ terminations on one hand, and the (111)-$Fe/O_3/Bi\ldots$, (111)-$Bi/Fe/O_3$ and the (111)-$O_3/Bi/Fe$ ones on the other, respectively. Since the surface stoichiometry is equal to that in the bulk, polarity can be suppressed only by internal electron redistribution. The vacuum was also used in the simulations, and the vacuum between the repeated slabs amounts to 10 Å. In the (111) orientation of $R3c$ phase $BiFeO_3$, crystal planes with the stacking sequence of atomic layers $\ldots Bi/O_3/Fe/Bi\ldots$ orientations are not electrically neutral, regardless of whether atomic charges are calculated using Mulliken population analysis or estimated with formal ionic charges. Therefore, the creation of these surfaces introduces polarity, which tends to create instability due to surplus surface charges or dipole moments and resultant spurious electric fields. Assuming that the ionic charges of O, Bi, and Fe are equal to formal charges ($Q_{\mathrm{O}} = -2e$, $Q_{\mathrm{Bi}} = +3e$, and $Q_{\mathrm{Fe}} = +3e$), the $O_3$ layers would bear a charge of $\sigma_{\mathrm{O}} = -6e$ per unit cell area, while the Bi (Fe) planes would bear a charge with density $\sigma_{\mathrm{Bi}} = +3e$ ($\sigma_{\mathrm{Fe}} = +3e$) per unit cell area. Such surfaces can become stable if the surface charge density is adequately reduced to prevent the appearance of infinite potentials and spurious electric fields.

A good agreement in the surface rumpling parameters of $SrTiO_3$ between the DFT calculations [26,27] and the experimental results [28,29] has shown that density functional theory (DFT) calculations can predict well the surface structure of perovskite materials. Table 1 illustrates our calculated atomic relaxations for the $BiFeO_3$ (111) surface. Large relaxation occurs in the four outermost layers. As for Fe-terminated surface we also find that the surface layer is rearranged, as shown in Table 1. The reconstruction induces a switch in the upper three or two layers. Therefore, the ordering of the layers $Fe/O_3/Bi\ldots$ and $Fe/Bi/O_3\ldots$ from the surface toward the bulk is $O_3/Fe/Bi\ldots$ and $Bi/O_3/Fe/Fe\ldots$, respectively, as is shown in Fig. 2(b) and (d). When we chose the $(2 \times 2)$ supercell, we found almost the same reconstruction of these two Fe-terminated surfaces, but did not find the reconstruction of the other four surfaces.

We now discuss the stability of the $BiFeO_3$ polar faces. Firstly, we focus on the surface energy $E_s$ averaged over the two slab terminations. Then, we take into account the fact that the surfaces are open systems, which can exchange atoms with the surroundings. The stability of *each* termination is therefore discussed in terms of the surface grand potential. $2E_s$ is the energy required to split a massive material and produce two distinct terminations. Conversely, it is equal to the work of adhesion of the two terminations, when they approach each other to produce bulk $BiFeO_3$. This quantity is thus an indication of the overall stability of the split crystal, as a function of the different orientations. Since the slabs that we consider have an integer number of formula units, the surface energy averaged over the two terminations $E_s$ is obtained from the total energy, by subtracting the energy of an equal number of formula units of bulk $BiFeO_3$. In Table 2 we summarize the values obtained for $E_s$ in the six slabs studied. The lowest value is obtained for the $Bi/O_3/Fe$–$Fe/O_3/Bi$ slab. These values are not much higher than the typical surface energies of non-polar surfaces. For the sake of comparison, they are much less than the surface energy found in a previous study for the stoichiometric, $(1 \times 1)$ polar MgO (111) surface [30], within the same method ($\tilde{E}_s = 7.2\ \mathrm{J/m^2}$).

Although the values of $E_s$ are indicative of the overall stability of the split crystal, they give no information as to which termi-