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Density functional theory plus U study of vacancy formations in bismuth ferrite

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First-principles density functional theory plus U study on the formation enthalpy of BiFeO₃ and the intrinsic vacancies was performed. The formation enthalpy of BiFeO₃ from oxides is only -0.2 eV, indicating that BiFeO₃ could easily decompose into Bi₂O₃ and Fe₂O₃ under thermal or electrical stresses. It is found that the vacancy induced local distortions have insignificant effect on the ferroelectric property, thanks to the high stability of the ferroelectric configuration in BiFeO₃. Moreover, Bi and Fe vacancies have comparable formation energies, and become dominant in the oxygen rich conditions, leading to p-type conductivity. © 2010 American Institute of Physics. [doi:10.1063/1.3447369]

The current interest in multiferroic materials is largely driven by the possible large magnetoelectric effect in compounds and/or heterostructures that possess both magnetic and ferroelectric orders, which may find applications in multistate random access memory and spintronic devices.^{1,2} Bismuth ferrite (BiFeO₃) is the most studied single-phase multiferroic material, which has high ferroelectric Curie temperature ($T_c=1103$ K) and antiferromagnetic Neel temperature ($T_N=643$ K).²

A great number of experiments have indicated that stoichiometric BiFeO₃ samples are difficult to obtain due to the small processing window.^{3–5} Moreover, properties of BiFeO₃, such as remnant polarizations, coercive field, dielectric constant, magnetization, and leakage current, are very sensitive to defects (e.g., secondary phases and intrinsic vacancies).^{2,6–9} Despite the extensive experimental studies, theoretical investigation of the phase stability of and defects formation in BiFeO₃ is still lacking, though studies on the oxygen vacancy have been reported recently.¹⁰ In this study, we investigated the formation enthalpy of BiFeO₃ and intrinsic vacancies in BiFeO₃ under different thermochemistry conditions using first principles density functional theory (DFT) calculations.

First-principles DFT calculations within the projector augmented wave (PAW) method were implemented in the VASP.¹¹ We used the semiempirical LSDA+U method, where the strong Coulomb repulsion between localized *d* states is treated by adding a Hubbard-type term (*U*) to the effective potential. The LSDA+U method has been recognized to accurately describe the structural and electronic property of BiFeO₃.^{6,12,13} In this study, we used a value of $U_{\text{eff}}=6$ eV ($U=6$ eV and $J=0$ eV) in the framework of Dudarev's approach, which has been shown to give a good description of bulk and electronic properties of BiFeO₃.^{12,13} The pseudopotential approach was adopted and Bi $5d^{10}6s^26p^3$, Fe $3p^63d^64s^2$, and O $2s^22p^4$ are treated in the basis. All the calculations were performed with an energy cutoff of 500 eV for the plane wave expansion of the PAW, and the Gaussian-smearing for the Brillouin zone integrations. Convergence

tests on the cutoff energy and *k* point sampling were conducted before any structure relaxation, and it is found that the convergence error is less than 0.03% of the total energy.¹⁴

The unit cell of BiFeO₃ is consisted of two formula units in order to accommodate the rock-salt (G-type) antiferromagnetic ordering. The canting of antiferromagnetic sublattices and the spiral spin structure are ignored in this study. The ground state structural parameters of the *R3c* BiFeO₃ was determined by relaxing the lattice parameters and ionic positions while keeping the unit cell volume and β at the experimental values ($124.32 \text{ \AA}^3$ and 59.35°),¹⁵ in view of the well known deficiency of LSDA in calculating the lattice parameters of perovskite ferroelectrics.¹⁶ Besides, total energies (chemical potentials) were calculated for Fe(*Im* $\bar{3}m$), Bi(*R* $\bar{3}m$), Bi₂O₃ (α phase, *P21/c*), and Fe₂O₃ (α phase, *R* $\bar{3}c$) as the reference materials. The chemical potential of oxygen was considered as the energy of an isolated spin-polarized molecule, storing in a $25 \times 25 \times 25 \text{ \AA}^3$ box; and the numerical integration was carried out by gamma point only. The calculated lattice parameters and ion positions reproduced well the experimental values.^{17,18}

We then estimated the formation enthalpy of BiFeO₃ by considering the reaction ($\text{Bi}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \rightarrow 2\text{BiFeO}_3$) at atmosphere pressure (the small $P\Delta V$ term is neglected), which could be calculated as:

$$\Delta H_f = E(\text{BiFeO}_3) - 0.5E(\text{Bi}_2\text{O}_3) - 0.5E(\text{Fe}_2\text{O}_3), \quad (1)$$

where *E* is the total energy after structure relaxation. The calculated formation enthalpy of BiFeO₃ from oxides shows a very small value of -0.20 eV, close to that from experimental report,¹⁹ which indicates that BiFeO₃ is thermodynamically not very stable in air without contact with Bi₂O₃/Fe₂O₃ flux.²⁰ Experimentally, it has been reported that BiFeO₃ decomposes easily under thermal or electrical stresses.²¹

The formation of vacancies was investigated by removing one atom from a $3 \times 3 \times 3$ supercell (270 atoms), which corresponds to very small defect concentrations of 1.85% for V_{Bi} and V_{Fe} , and 0.62% for V_{O} , in order to minimize the effects of the spurious interactions between the vacancy and its mirror images. All the defective structures were relaxed while keeping the lattice parameters fixed until the Hellman–

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TABLE I. Calculated displacements of the ions in the NN position with the vacancy; and the induced polarization estimated by Born effective charges.

	Defect concentration (%)	Displacement (Å)			Polarization ($\mu\text{C}/\text{cm}^2$)
		Bi	Fe	O	
Perfect	...	0	0	0	103.3
V_{Bi}	1.85	0.11 (NNN)	0.20	0.32	110.2
V_{Fe}	1.85	0.22	0.09	0.29	111.5
V_{O}	0.62	0.20	0.20	0.17	110.4

Feynman forces are less than $0.05 \text{ eV}/\text{\AA}$ and energies converge within 0.01 eV . The Brillouin zone sampling was conducted by a $2 \times 2 \times 2$ Monkhorst Pack grid of k points. We have also calculated the defect structure using different U values, and found that changing the U values has little effect on the calculated structures. Our calculations show that significant atomic relaxations around the vacancies take place for the atoms that are less than $\sim 5.6 \text{ \AA}$ from the defect. For the cation vacancies (V_{Bi} and V_{Fe}), the surrounding cations move inwards and oxygen move outwards, simply as a result of Columbic interaction. On the other hand, oxygen vacancy leads to expanded lattice as the cations are pushed outwards. The magnitude of the largest displacements of the Bi, Fe, and O from the defect-free positions in the presence of a Bi vacancy is 0.11 , 0.20 , and $0.32 \text{ \AA}$ (Table I). Fe vacancy induces displacements of $0.22 \text{ \AA}$, $0.09 \text{ \AA}$, $0.29 \text{ \AA}$ for Bi, Fe, and O atoms, and O vacancy causes that of $0.20 \text{ \AA}$, $0.20 \text{ \AA}$, and $0.17 \text{ \AA}$, respectively. All the ions experiencing the most significant movement are in the nearest-neighbor (NN) position to the vacancy, except that the next-nearest-neighbor (NNN) Bi cation in the presence of Bi vacancy.

The electrical polarizations of the structures with and without vacancy were estimated by summing over the Born effective charge multiplied by the displacements of the ions from the centrosymmetric cubic perovskite. The polarization of the perfect BiFeO_3 is calculated to be $103.3 \mu\text{C}/\text{cm}^2$ along $[111]$ directions, which is close to the experimental and calculated value in the previous studies.⁶ It is also found that the lattice distortion caused by the existence of intrinsic vacancies (at the calculated concentrations) in the BiFeO_3 lat-

tice does not significantly affect the polarization, which has been attributable to the high stability of the ferroelectric configuration in BiFeO_3 .⁶

The formation energies of the intrinsic vacancies in BiFeO_3 at the charge state q (E_F^q) can be calculated using the equation below:

$$E_F^q = (E_D^q - E_P^q) - \mu_v + q(E_f + E_{\text{VBM}}) \quad (2)$$

where E_D^q and E_P^q are the total energies of the defective and perfect supercells, respectively, in the charged state q , μ_v denotes the corresponding atomic chemical potential, E_f is the Fermi energy, and E_{VBM} is the position of the valence band maximum (VBM). In our LSDA+ U calculations, the fairly large U of 6 eV produces a large band gap (2.5 eV) closest to the experimental data.²² We also apply a monopole correction $e^2 Q^2 \alpha / a \epsilon$ to the total energy of the charged systems, where α is the Madelung constant, a is the lattice constant, and ϵ is the experimental dielectric constant of the bismuth ferrite (~ 6.25). Defect formation energies as a function of Fermi level were calculated under two thermochemistry conditions. (1) Oxygen-rich condition: $\text{O}_2/\text{Bi}_2\text{O}_3/\text{BiFeO}_3$ equilibrium, and (2) Oxygen-poor: $\text{Bi}/\text{Bi}_2\text{O}_3/\text{BiFeO}_3$ equilibrium.

The calculated formation energies of all intrinsic vacancies in BiFeO_3 as a function of Fermi level are shown in Fig. 1. The figure is drawn in a way that the formation energy of a vacancy at a particular charge state is only shown if the charge state has the lowest energy. So the change in slope indicates a transition between different charged states of the

FIG. 1. (Color online) Calculated defect formation energy for vacancies as a function of the Fermi level in (a) oxygen-rich and (b) oxygen poor condition. Only the vacancies among the lowest formation energies are shown. The zero of the Fermi level is set to the top of the valence band.

FIG. 2. Variation in dominant defect in $R3c$ BiFeO_3 as a function of chemical potential of oxygen and Fermi level in the equilibrium of $\text{Bi}_2\text{O}_3/\text{O}_2/\text{BiFeO}_3$. The dashed lines indicate the ionization levels of the most stable vacancies, and dotted line denotes the ionization levels of the metastable vacancies.

vacancy. Under oxygen rich condition [Fig. 1(a)], Bi and Fe vacancies have comparable formation energies, which are negative for most part of the band gap, indicating that the formation of Bi and Fe vacancies is exothermic and spontaneous. Under oxygen poor condition, the most abundant intrinsic vacancy in BiFeO_3 is oxygen vacancies, though Bi and Fe vacancies dominate near the conduction band. The 0/+1 transition of oxygen vacancy occurs at 1.33 eV below the conduction band, which is indeed a deep donor level.

The above results lead to two interesting conclusions. First, the calculated formation energies of Bi and Fe vacancies are comparable. And there is possibly a transition between Bi vacancy rich and Fe vacancy rich in BiFeO_3 if the Fermi level lies at 0.17 eV from the VBM in the band gap (Fig. 2). This is different from the usual assumption that Bi vacancies are the easiest to form in BiFeO_3 because of the high volatility of Bi. Indeed, experimentally it is possible to obtain Bi or Fe rich BiFeO_3 films by changing the deposition conditions.³ Second, BiFeO_3 is likely a p-type semiconductor under normal (oxygen rich) processing conditions. As shown in Fig. 2, both Bi and Fe vacancies have two shallow defect levels. Bi vacancy shows the 0/-1 and -1/-2 transitions 0.13 eV and 0.56 eV above the VBM, respectively. And our calculations locate the 0/-1 and -1/-2 transitions of Fe vacancy 0.21 eV and 0.67 eV above the VBM, respectively. Under oxygen rich conditions, these levels lead to p-type conduction. Similar scenarios have been confirmed in many ferroelectric oxides such as PbTiO_3 , which has a p-type character due to the PbO loss during fabrication.^{23,24} However, definitive experimental confirmation of the conduction type of BiFeO_3 has not been reported, even though many studies assumed that oxygen vacancies are the cause of high leakage current under the Pool-Frenkel mechanism.¹⁰ To better understand the leakage behavior of BiFeO_3 , it is crucial to first determine the dominating defects, thus the conduction type, in BiFeO_3 . Unfortunately, only few experimental studies on

BiFeO₃ touch the topic but several researchers did report a p-type behavior in bulk and BiFeO₃ thin films.^{25,26}

In summary, we performed a LSDA+U study on the formation enthalpy of BiFeO_3 and formation energies of vacancies in BiFeO_3 . Consistent with experimental observations, it is found that BiFeO_3 could easily decompose into Bi_2O_3 and Fe_2O_3 under thermal and/or electrical stresses. It is also found that Bi and Fe vacancies have comparable formation energies, and p-type conductivity might be the character of BiFeO_3 synthesized under normal (oxygen rich) processing conditions, in contrast to the usual assumptions that oxygen vacancies are responsible for the leakage current. We hope that this study could lead to more research attention on this topic, and enhance our understanding about the leakage mechanism of BiFeO_3 .

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