First-Principles Investigation of Morphotropic Transitions and Phase-Change Functional Responses in $BiFeO_3$-$BiCoO_3$ Multiferroic Solid Solutions

Oswaldo Diéguez and Jorge Íñiguez
Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain

(Received 10 May 2011; published 26 July 2011)

We present an *ab initio* study of the BFCO solid solution formed by multiferroics $BiFeO_3$ (BFO) and $BiFeO_3$ (BCO). We find that BFCO presents a strongly discontinuous morphotropic transition between BFO-like and BCO-like ferroelectric phases. Further, for all compositions such phases remain (meta) stable and retain well-differentiated properties. Our results thus suggest that an electric field can be used to switch between these structures and show that such a switching involves large phase-change effects of various types, including piezoelectric, electric, and magnetoelectric ones.

DOI: 10.1103/PhysRevLett.107.057601 PACS numbers: 77.84.−s, 64.75.Nx, 71.15.Mb, 75.85.+t

Functional oxides attract attention because of their potential for designing materials tailored for specific applications. A lot of work focuses on $BiFeO_3$ (BFO), one of the few compounds that is magnetoelectric (ME) multiferroic—i.e., displays coupled electric and magnetic orders—at room temperature [1]. Interest in BFO has been recently refueled by the discovery that an electric field $\mathcal{E}$ can be used to switch between two different ferroelectric (FE) phases of epitaxially compressed films [2]. Such a $\mathcal{E}$ switching has a number of functional effects associated to it, as the phases involved are markedly dissimilar in terms of cell shape (the switching thus implies a large piezoelectric effect) and magnetism (ME effect). Hence, BFO films offer the appealing possibility of obtaining *phase-change* functional responses of various kinds. Here we propose that some BFO-based solid solutions are ideally suited to this end, and present illustrative first-principles results for $BiFe_{1-x}Co_xO_3$.

Materials-design aspects.—The $\mathcal{E}$ switching in BFO films involves two phases [3]: one that is similar to the rhombohedral structure of bulk BFO and has a polarization $\boldsymbol{P}$ roughly along the [111] pseudocubic direction (R phase in the following), and a phase with a unit cell of very large aspect ratio ($c/a \sim 1.25$) and $\boldsymbol{P}$ roughly parallel to [001] (*supertetragonal* or T phase). First-principles work has shown that these phases revert their relative stability as a function of epitaxial strain [3,4], and that there is a strain range in which both can exist [4]. It has also been predicted that, even in absence of stabilizing fields, BFO presents many T phases that are local energy minima [5]. The theory is thus compatible with the observation that $\mathcal{E}$ fields can be used to switch between different FE phases of BFO.

These results suggest that, to find materials in which the $\mathcal{E}$ switching is possible, one must look for compounds displaying a strongly discontinuous transition between two FE phases; further, the FE phases should be robustly stable and their polarizations point along markedly different directions, so that it is easy to switch between them by applying properly oriented fields. An obvious strategy is to look for chemical substitutions of BFO that may result in a morphotropic phase boundary (MPB) between the R phase of the pure compound and a second FE structure. Among many possibilities, the $BiFe_{1-x}Co_xO_3$ (BFCO) solid solution seems particularly promising. Note that bulk $BiCoO_3$ (BCO) is a ME multiferroic that presents a supertetragonal FE phase [6]; thus, BFCO is likely to display a R-T morphotropic transition analogous to the one induced by epitaxial compression in BFO films.

The x-ray experiments of Azuma *et al.* [7] confirmed that, as the Co content grows, BFCO moves from R to T traversing a narrow region of presumably monoclinic (M) symmetry. (Similar results have been obtained for thin films [8].) This is reminiscent of what occurs in prototype piezoelectric $PbZr_{1-x}Ti_xO_3$ (PZT), where the M phase found at the MPB [9] is characterized by its structural softness and large electromechanical responses [10]. However, as far as we know, no enhanced response has been observed in BFCO, which questions the existence of a PZT-like M phase in this compound [11]. Note that this is encouraging in the present context: For $\mathcal{E}$-switching purposes, we would like BFCO's R and T phases to be relatively stiff (as opposed to soft) and stable.

BFCO's morphotropic transitions.—We used the generalized gradient approximation plus Hubbard U (GGA + U) approach to density functional theory (DFT) as implemented in the VASP package [12], the calculation details being essentially identical as in previous studies of similar materials [13]. We worked with the 40-atom cell depicted in the insets of Fig. 1(b), which allows us to describe the R and T phases of interest [5] and vary the ratio of Co atoms x in steps of 1/8. Figure 1(a) shows the formation energy of the phases investigated as a function of composition; this is defined as $E_f = E - (1-x)E_{\text{BFO}} - xE_{\text{BCO}}$, where E is the energy of a particular BFCO structure of composition x, and E_{BFO} and E_{BCO} are the ground-state energies of the pure compounds. Figure 1 also shows the polarization of selected structures [1(b)] and the cell parameters [1(c) and 1(d)].

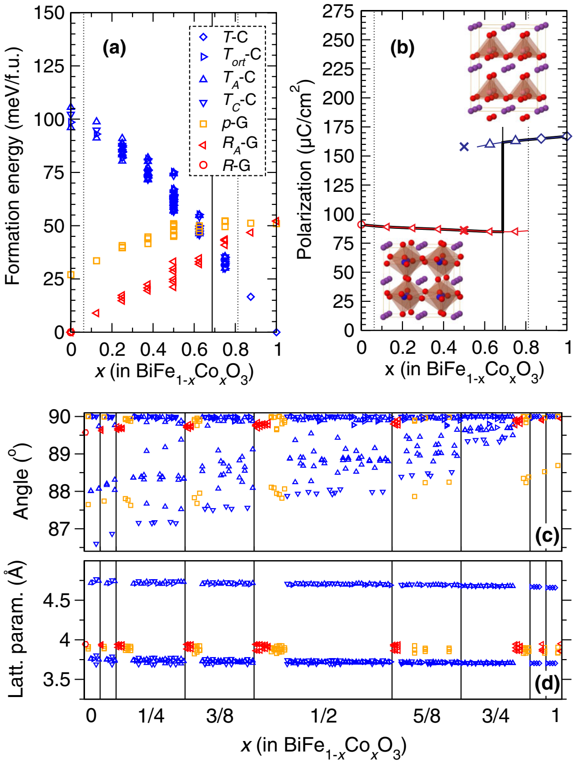

FIG. 1 (color online). (a) Formation energy versus composition for all studied phases. Labels as in Table I; various instances of the same symbol at a given x correspond to different Fe-Co arrangements. (b) Polarization magnitude for the most stable structures (joined by thick line); a few others shown for comparison; crosses correspond to rocksalt-ordered T_A and R_A structures. Insets: BFO (R-G) and BCO (T-C) structures. (c) Pseudocubic lattice constants and (d) angles of the structures in (a); same x configurations given in order of increasing energy. Dotted vertical lines mark second-order R-R and T-T transitions (see text); solid line marks the first-order R-T transition.

The six points at $x = 0$ in Fig. 1(a) correspond to the stable BFO phases described in Ref. [5], whose properties are summarized in Table I. The ground state is the well-known FE phase of the compound; we call it R-G, noting its G-type antiferromagnetic (AFM) spin order (i.e., nearest-neighboring irons have antiparallel spins). We also considered four FE T phases with C-AFM order (i.e., parallel spins along the stretched lattice vector and antiparallel in plane). We label these phases according to their symmetry, which is not tetragonal for any of them: We have an orthorhombic phase ($T_{\rm ort}$), two monoclinic phases of type M_A [i.e., with $\boldsymbol{P}$ in the $(1\bar{1}0)$ plane [14]; we call them T_A], and a monoclinic M_C phase [i.e., with $\boldsymbol{P}$ in the (100) plane; we call it T_C]. Finally, we also considered the paraelectric phase p-G.

To search for BCO phases, we substituted irons by cobalts in the six structures just described; then, for each of them we ran a short molecular dynamics (with random initial velocities to break all symmetries) followed by a full relaxation. We thus obtained the three solutions listed in Table I. All four T structures relaxed to the T-C phase known to be BCO's ground state [6]; our computed structure ($a = b = 3.70$ Å and $c/a = 1.26$) is in reasonable agreement with experiment ($a = b = 3.729$ Å and $c/a = 1.267$ [6]) and previous DFT results [15,16]. The optimization starting from BFO's R-G phase led to a structure in which the $R3c$ symmetry is slightly broken to monoclinic M_A [faces of O_6 octahedra lying on (111) planes form isosceles, instead of equilateral, triangles]; we call it R_A-G. Finally, BCO's p-G phase is analogous to BFO's. For intermediate compositions, we considered BFO's stable phases and studied all the inequivalent Fe-Co arrangements at the perovskite B sites. In all cases we ran a molecular dynamics followed by a full structural relaxation; the result of each such optimization renders a data point in Fig. 1(a).

TABLE I. Stable phases considered for BFO and BCO. We show the label for each phase (see text), space group (SG), polarization magnitude (μC/cm^2) and angle (relative to the perpendicular to the plane defined by the two shortest pseudocubic lattice vectors for the T phases, and to the pseudocubic [111] for the R phases), and energy (meV/f.u.) above that of the most stable phase.

Material	Phase	SG	Polarization	ΔE
BFO	T_A-C	Pc	120 (23°)	106
	T_C-C	Cm	150 (20°)	103
	$T_{\rm ort}$-C	$Pna2_1$	139 (0°)	99
	T_A-C	Cc	145 (19°)	96
	p-G	$Pnma$	0	27
	R-G	$R3c$	91 (0°)	0
BCO	R_A-G	Pc	82 (5°)	52
	p-G	$Pnma$	0	51
	T-C	$P4mm$	167 (0°)	0

Many conclusions can be drawn from Fig. 1. Most importantly, we found that BFCO undergoes a strongly discontinuous transition between a R phase ($c/a \sim 1$) and a T phase ($c/a \sim 1.25$) at $x \approx 0.7$. We also found that the R and T phases (as well as the p phase) are stable for all compositions [17], a feature likely related to Bi's peculiar bonding properties [5]. Note also that the R and T phases retain their main features—i.e., values of polarization and structural parameters—for all considered compositions and Fe-Co arrangements. Hence, according to our results, BFCO may allow for an $\mathcal{E}$-controlled switching between two distinct FE phases in a wide composition range around the R-T transition [18]. Further, the robustly stable character observed for the R and T phases suggests there may be a relatively large experimental freedom to tune BFCO (e.g., by varying the composition or epitaxial conditions of a film) and optimize the switching.

As regards the structure of the R phases, Figs. 1(b)–1(d) show no major changes occur when moving from BFO's R-G to BCO's R_A-G. Nevertheless, we identified a distinct effect: For $x > 0$ all the R structures present the distortion of the oxygen-octahedron faces described above for pure

BCO. By inspecting the cases in which the Fe-Co arrangement is compatible with the rhombohedral threefold axis, we found this symmetry breaking renders a M_A structure, as in pure BCO. We thus label these phases as R_A-G in Fig. 1, where a dotted line at $x \approx 0.07$ marks a continuous transition between R-G and R_A-G.

As for the T phases, Figs. 1(c) and 1(d) show they evolve continuously as the Co content increases, and become truly tetragonal (i.e., the pseudocubic lattice constants a and b become equal, and the angles turn 90°) for $x \approx 0.8$; this second-order transition to BCO's T-C phase is marked by a dotted line in Fig. 1.

Our results thus confirm the R-T MPB reported by Azuma *et al.* [7]; yet, the agreement between theory and experiment is far from perfect. At a quantitative level, our calculations place the MPB at $x \approx 0.7$, at variance with the value of $x \approx 0.35$ obtained by extrapolating the data of Ref. [7] to low temperatures. We think this deviation can be partly related to DFT's limitations to predict accurately the relative stability of the R and T phases, as recently discussed for BFO [5]. The simulations, on the other hand, seem reliable when they predict that BFCO displays no PZT-like M phase acting as a bridge between the R and T structures at the MPB; rather, our results would be compatible with a R-T phase coexistence at the MPB region [19]. Finally, more structural measurements are needed to determine which T phase(s) occur in BFCO and confirm the monoclinic-orthorhombic symmetries predicted at intermediate compositions.

BFCO's phase-change properties.—The R-T switching involves a large change in BFCO's unit cell, which results in a phase-change piezoelectric effect. It also involves a large change in polarization: We may switch between $P_z \approx 53\ \mu\mathrm{C/cm^2}$ (R phase) and $P_z \approx 165\ \mu\mathrm{C/cm^2}$ (T phase), which may prove useful in the design of field-effect and other devices. Additionally, the R and T phases present very different dielectric and piezoelectric responses: For example, for $x = 1/2$ and a rocksalt Fe-Co order, we obtained an approximately diagonal static dielectric tensor for the R_A-G phase, with $\epsilon_{xx}^{\mathrm{latt}} \approx 46$; in contrast, the analogous T_C-C phase presents an anisotropic response with $\epsilon_{xx}^{\mathrm{latt}} \approx 259$, $\epsilon_{yy}^{\mathrm{latt}} \approx 122$, and $\epsilon_{zz}^{\mathrm{latt}} \approx 16$. (We observed similar trends for piezoelectricity. These results reflect a well-known fact for FE perovskite oxides: making $\boldsymbol{P}$ rotate is energetically less costly than changing its magnitude [10].) Hence, the R-T switching also allows for a large dielectric and piezoelectric tunability [20].

The R-T switching also involves a change in the spin order, which moves from G-AFM to C-AFM. If any, the net magnetization of such AFM structures will be a small one arising from spin canting (see Ref. [4] for representative results for BFO); thus, the associated phase-change effect will be tiny. On the other hand, work on BFO [3,5] shows that the magnitude of the exchange interactions varies considerably between the R and T phases. We found that such a differentiated behavior also occurs in BFCO, resulting in markedly different Nèel temperatures (T_N's) and response properties.

To investigate BFCO's magnetic properties, we considered the most stable R and T configurations at $x = 0$, $1/8$, $7/8$, and 1, as well as the lowest-energy structures with a rocksalt Fe-Co arrangement at $x = 1/2$ [21]. We computed the energies of the following spin orders: ferromagnetic (FM), C-AFM, G-AFM, and A-AFM (as obtained from G-AFM by making spins parallel in plane); the results are shown in Figs. 2(a) and 2(b). Most notably, we found that the structure type determines the hierarchy of spin arrangements: Independently of the Co content, all the R phases have the G-AFM order as the most stable one, followed by C-AFM, A-AFM, and FM; in turn, C-AFM is the ground state of all the T phases, followed by G-AFM, A-AFM, and FM. From a model Hamiltonian perspective, this implies that the magnetic couplings will depend strongly on the atomic structure (R or T) and weakly on the chemical details (Fe/Co ratio and spatial arrangement). Indeed, we were able to capture the essence of our DFT results in the

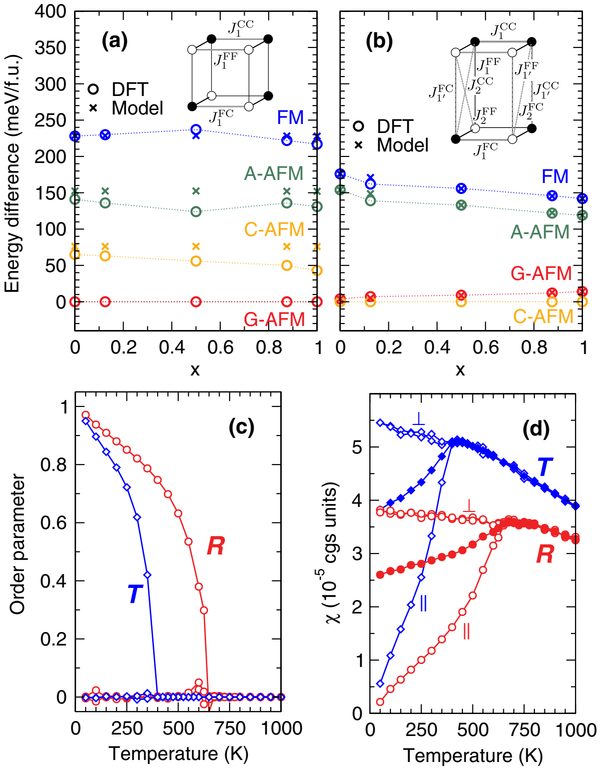

FIG. 2 (color online). (a),(b) Energy differences between spin orders for representative BFCO structures (see text); R phases in (a) and T phases in (b). Circles show DFT results; crosses correspond to model Hamiltonians including the J couplings defined in insets (see text). (c) Temperature dependence of AFM order parameter (G type for R and C type for T). (d) Temperature dependence of the total magnetic susceptibility (solid symbols), and of its components [parallel (∥) and perpendicular (⊥); open symbols] with respect to the direction of the AFM order parameter.

two simple Heisenberg models, one for all the R phases and one for all the T phases, described in the following.

We write the energy of a spin configuration as $E = E^0 + \frac{1}{2}\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$, where E^0 is a reference energy, J_{ij} is the exchange coupling between Fe-Co atoms i and j, and $\mathbf{S}_i$ is the three-dimensional spin of atom i. For simplicity, here we assume $|\mathbf{S}_i| = 1$; the reported J_{ij} values have been calculated accordingly.

In the R phases, any Fe/Co atom has six Fe/Co first nearest neighbors (FNNs) that are roughly equivalent (they are equivalent if the symmetry is exactly rhombohedral). Thus, we can tentatively take $J_{ij} = J_1$ as our single FNN interaction, and also neglect further couplings. From our results for the pure compounds, we obtained $J_1^{\mathrm{FF}} = 38.0$ meV and $J_1^{\mathrm{CC}} = 38.1$ meV, and from the results at $x = 1/2$ we got $J_1^{\mathrm{FC}} = 38.1$ meV. The minimal Hamiltonian thus defined predicts the energies shown as crosses in Fig. 2(a); it clearly captures the essential magnetic interactions in BFCO's R phases.

For the T phases, we take advantage of the (approximate) tetragonal symmetry and consider only two FNN couplings: in plane J_1 and out of plane $J_{1'}$. Note that by choosing $J_1 > 0$ and $J_{1'} < 0$ we would correctly reproduce the C-AFM ground state but wrongly predict the A-AFM order as the least favorable one. Hence, we need to introduce a new interaction J_2 between second nearest neighbors [see inset in Fig. 2(b)]. With this model we obtained the results shown as crosses in Fig. 2(b); the computed parameters are (in meV) $J_1^{\mathrm{CC}} = 30.9$, $J_1^{\mathrm{FC}} = 35.0$, $J_1^{\mathrm{FF}} = 40.8$, $J_{1'}^{\mathrm{CC}} = 2.3$, $J_{1'}^{\mathrm{FC}} = 3.3$, $J_{1'}^{\mathrm{FF}} = 4.5$, $J_2^{\mathrm{CC}} = 2.3$, $J_2^{\mathrm{FC}} = 2.0$, and $J_2^{\mathrm{FF}} = 1.6$. Note that all the computed $J_{1'}$ and J_2 constants are positive, implying that all the out-of-plane interactions are antiferromagnetic in the T phases of BFCO. Ultimately, the J_2 couplings prevail and render the out-of-plane parallel spin alignment of the C-AFM ground state.

We solved these Hamiltonians using standard Monte Carlo techniques. Figures 2(c) and 2(d) show representative results obtained for $x = 1/2$ systems with Fe and Co atoms randomly distributed in a $20 \times 20 \times 20$ periodically repeated simulation box. We found that the R and T cases present markedly different T_N's of about 650 and 400 K, respectively. These results are compatible with the experimental values for BFO (643 K) [1] and BCO (470 K) [6], and reflect the weak out-of-plane interactions that result in a lower T_N in the T case. Figure 2(d) shows the magnetic susceptibility: At room temperature, the total susceptibility of the T phase almost doubles the result for the R phase; hence, we predict that the R-T switching will have a clear magnetic signature.

We have thus shown that the $\mathrm{BiFe}_{1-x}\mathrm{Co}_x\mathrm{O}_3$ solid solutions are likely to present large electric-field-driven phase-change effects of various types (piezoelectric, electric, magnetoelectric). We hope our predictions will attract interest towards such promising materials and effects.

Supported by MICINN-Spain [Grants No. MAT2010-18113, No. MAT2010-10093-E, and No. CSD2007-00041; *Ramón y Cajal* program (OD)]. Computing facilities provided by RES and CESGA. Discussions with M. Bibes, J. Fontcuberta, and F. Sánchez are acknowledged.

[1] G. Catalan and J.F. Scott, Adv. Mater. **21**, 2463 (2009).

[2] R.J. Zeches *et al.*, Science **326**, 977 (2009).

[3] A.J. Hatt, N.A. Spaldin, and C. Ederer, Phys. Rev. B **81**, 054109 (2010).

[4] J.C. Wojdeł and J. Íñiguez, Phys. Rev. Lett. **105**, 037208 (2010).

[5] O. Diéguez, O.E. González-Vázquez, J.C. Wojdeł, and J. Íñiguez, Phys. Rev. B **83**, 094105 (2011).

[6] A.A. Belik *et al.*, Chem. Mater. **18**, 798 (2006).

[7] M. Azuma *et al.*, Jpn. J. Appl. Phys. **47**, 7579 (2008).

[8] S. Yasui *et al.*, Appl. Phys. **105**, 061620 (2009); S. Yasui *et al.*, Jpn. J. Appl. Phys. **48**, 09KD06 (2009).

[9] B. Noheda *et al.*, Appl. Phys. Lett. **74**, 2059 (1999).

[10] L. Bellaiche, A. García, and D. Vanderbilt, Phys. Rev. Lett. **84**, 5427 (2000); H. Fu and R.E. Cohen, Nature (London) **403**, 281 (2000).

[11] K. Miura, M. Kubota, M. Azuma, and H. Funakubo, Jpn. J. Appl. Phys. **49**, 09ME07 (2010).

[12] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11 169 (1996); G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[13] We used the so-called "PBEsol" approximation, J.P. Perdew *et al.*, Phys. Rev. Lett. **100**, 136406 (2008), which describes well the relative stability of BFO's R and T phases [5].We used the "Hubbard U" correction of S.L. Dudarev *et al.*, Phys. Rev. B **57**, 1505 (1998), with U_{eff} values of 4 and 6 eV for the $3d$ electrons of Fe and Co, respectively; these choices, which are common in the literature, affect the composition at which the MPB is obtained, but not our qualitative results.We used the "projector augmented wave" method, P.E. Blochl, Phys. Rev. B **50**, 17953 (1994), to represent the ionic cores, solving for the following electrons: Fe's $3p$, $3d$, and $4s$; Co's $3d$, and $4s$; Bi's $5d$, $6s$, and $6p$; and O's $2s$ and $2p$. Other details as in [5].

[14] We follow the notation for the M phases introduced by D. Vanderbilt and M.H. Cohen, Phys. Rev. B **63**, 094108 (2001).

[15] M.-Q. Cai *et al.*, J. Chem. Phys. **126**, 154708 (2007).

[16] P. Ravindran, R. Vidya, O. Eriksson, and H. Fjellvåg, Adv. Mater. **20**, 1353 (2008).

[17] Our structural optimizations were designed to render energy minima; we confirmed the stability of selected structures. We estimated the energy barrier separating R and T phases near the MPB, obtaining values ($\sim$100 meV/f.u) comparable with the barrier associated to the Landau limit for FE switching in typical materials.

[18] The p-G phase will not be stable in the presence of an electric field, and its only influence on the switching might be regarding its path.

[19] The coexistence of small R and T regions might be seen in some experiments as an averaged M phase, which would explain the results of Ref. [7].

[20] The computed electronic band gaps present a large spread of about 1 eV; we did not observe any distinct band-gap change associated to the R-T switching.

[21] At $x = 1/2$, an ordered Fe-Co arrangement might result in *ferrimagnetism* (e.g., if a G-AFM spin structure is combined with rocksalt Fe-Co order). However, we obtained a very weak dependence of BFCO's energy on the Fe-Co arrangement; thus, such ordered structures seem unlikely.