Epitaxial Phases of BiMnO$_3$ from First Principles

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Bulk BiMnO$_3$ is the only transition-metal perovskite oxide that is insulating and shows strong ferromagnetism. This distinctive behavior would make it a promising candidate as a magnetoelectric multiferroic if it was also a polar material, but experiments have shown that bulk BiMnO$_3$ has either a very small polarization (below 0.1 $\mu$C/cm$^2$) or, most likely, that it is a paraelectric. There is also experimental evidence that the polarization in BiMnO$_3$ films grown on SrTiO$_3$ can be as high as 20 $\mu$C/cm$^2$. Despite of the interest of these behaviors, the diagram of BiMnO$_3$ as a function of epitaxial strain has remained largely unexplored. In this article, we use first-principles to predict that both under enough compressive and tensile epitaxial strain BiMnO$_3$ films are ferroelectric with a giant polarization around 100 $\mu$C/cm$^2$. The phases displayed by the films are similar to those experimentally found for BiFeO$_3$ in similar conditions—at compressive strains, the film is supertetragonal with a large component of the polarization pointing out of plane, while at tensile strains the polarization points mostly in plane. Like in BiFeO$_3$ films, these phases are antiferromagnetic—the orbital ordering responsible for ferromagnetism in BiMnO$_3$ is absent in the polar phases. Our calculations also show that the band gap of some of these BiMnO$_3$ films is substantially smaller than gaps typically found in ferroelectric oxides, suggesting it may be a suitable material for photovoltaic applications.

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I. INTRODUCTION

BiMnO$_3$ is the only strong ferromagnetic insulator among the transition-metal perovskite oxides, a family of functional materials whose members display many different properties of technological interest. The Curie temperature of BiMnO$_3$ is around 105 K$^{12}$ below which several groups have reported measurements of its magnetic moment close to 4 $\mu_B$ per Mn atom.$^{3,4}$ The unique ferromagnetic behaviour of BiMnO$_3$ is related to the presence of orbital ordering of the Mn$^{3+}$ ions ($3d^4$)—elongated half-filled $d_{x^2}$ orbital points towards empty $d_{x^2-y^2}$ orbitals of neighboring Mn cations.$^8$ For many years BiMnO$_3$ was supposed to have also a weak switchable polarization (below 0.1 $\mu$C/cm$^2$), and the polar space group $C2$ was assigned to its crystal structure.$^8$ However, recent electron diffraction experiments by Belik and coworkers$^8$ point to a $C2/c$ space group, which is not polar; these results have been confirmed by neutron powder diffraction experiments$^8$ Despite of this, when BiMnO$_3$ is grown as an epitaxial film on SrTiO$_3$ it develops a strong polarization, which Jeen and coworkers$^{9,10}$ measured to be 23 $\mu$C/cm$^2$; other groups reported similar results—a polarization between 9 and 16 $\mu$C/cm$^2$ and signatures of ferroelectricity.$^{10,11}$

Perovskite oxides display dramatic changes in their properties when grown as epitaxial films on a substrate, with the misfit strain imposed by the substrate playing a major role in these changes.$^{11}$ Given that non-polar perovskites develop ferroelectricity under epitaxial strain, it is somewhat surprising that the epitaxial phase diagram of BiMnO$_3$ is largely unexplored in the search for possible coexistence of magnetic and polar orderings. Using first-principles calculations, Hatt and Spaldin$^{12}$ concluded that BiMnO$_3$ remains non-polar when compressive or tensile strain is applied to the film; they used the $C2/c$ bulk phase as the starting point of their calculations, subjecting the simulation cell to constraints that mimic the strained film. No other phases seem to have been studied using computational approaches, although earlier calculations by Hill and Rabola$^{13}$ and by Seshadri and Hill$^{14}$ pointed to the existence of ferroelectric instabilities in this material. In this study we explore structures that are good candidates to become the ground state of epitaxial BiMnO$_3$ films. At high compressive strains, we have looked at the supertetragonal phases...
with giant polarization that are found in BiFeO$_3$ films$^{15}$ and in BiCoO$_3$ bulk and films$^{20}$ these phases are called supertetragonal, or $T$, because they have a large $c/a$ ratio (some of them have lower symmetry than tetragonal). At high tensile strains, we have explored phases of low energy in BiFeO$_3$ (including the $Pnma$ structure of both bulk BiFeO$_3$ and bulk BiMnO$_3$ under pressure$^{17}$ and epitaxial polar phases of BiFeO$_3$ under tensile strains). We have found that BiMnO$_3$ and BiFeO$_3$ films display similar structures under high tensile and compressive strains; therefore, we predict that BiMnO$_3$ has a strong polarization when grown in these conditions.

II. METHODS

Our first-principles calculations are based on density-functional theory (DFT)$^{18,19}$ However, BiMnO$_3$ contains highly localized $d$ orbitals that are not described accurately within pure DFT. One approach towards a better description of the electronic properties of these solids is to add a “Hubbard $U$” term to the energy of the system that favors localization on those electrons; this requires picking a value of $U$ that reproduces some set of experimental or more accurate theory results. Another approach is to use a hybrid density functional that includes a portion of exact Hartree-Fock exchange$^{20}$ this in general ameliorates the problems with $d$ or $f$ electron delocalization, predicts band gaps for solids that are much closer to experimental results than those of pure DFT$^{21}$ and performs better than the “Hubbard $U$” approach in perovskite oxides such as BiFeO$_3$. Both approaches are implemented in VASP$^{22}$ the first-principles code that we have used to carry out the calculations presented in this work. To optimize our typical structures with VASP the second approach requires a hundred times more computer time than the first one, so we have used the code in the following way: for our exploratory calculations we applied a Hubbard $U$ following the rotationally invariant method described in Ref. $^{21}$ and for our final results we used a hybrid functional according to the HSE06 prescription$^{23}$. As in our previous article on BiFeO$_3$ we worked with the Perdew-Burke-Ernzerhof DFT exchange-correlation functional adapted to solids (PBEsol)$^{22}$ We used the projector augmented-wave method to represent the ionic cores solving for the following electrons: Mn’s 3$p$, 3$d$, and 4$s$; Bi’s 5$d$, 6$s$, and 6$p$; and O’s 2$s$ and 2$p$. We represented wave functions in a plane-wave basis set truncated at 500 eV. We performed integrations within the Brillouin zone by using $k$-point grids with densities similar to that of a 6 $\times$ 6 $\times$ 6 grid for a 5-atom perovskite unit cell.

III. RESULTS AND DISCUSSION

A. Metastable Phases of Bulk BiMnO$_3$

We started our search for metastable phases of BiMnO$_3$ by doing PBEsol+$U$ ionic relaxations for the seven lowest-energy crystal structures found for bulk BiFeO$_3$ in our previous work$^{18}$ (which can accommodate to a $2 \times 2 \times 2$ pseudocubic 40-atom cell) and for the experimental $C2/c$ ground state configuration of BiMnO$_3$ (using 40-atom cells that are not pseudocubic). For each of these eight configurations we prepared four types of magnetic arrangements, as in Ref. $^{27}$—ferromagnetic (FM), and antiferromagnetic of the A, C, and G types (A-AFM, C-AFM, G-AFM, respectively). We then did three types of searches for local minima of the energy: (1) we directly relaxed the structures until forces and stresses were close to zero; (2) we did a few steps of molecular dynamics in order to break possible spurious symmetries, and then we relaxed the resulting structures until forces and stresses were close to zero; and (3) we took the lowest-energy magnetic ordering found so far for each structure type and relaxed the atoms imposing each of the other three magnetic orderings. At the end, we chose the lowest-energy phase for each type of structure found and for each type of magnetic ordering. In all the optimization calculations of this work the final forces were below 0.015 eV/$\AA$ and the final stresses are below 0.0005 eV/$\AA^3$.

The process just described lead to the identification of the configurations whose energies are given in Fig. 1 (top). The corresponding phases are labeled in the following way (directions are given in the pseudocubic setting): the ground state with $C2/c$ symmetry is labeled as GS; the paraelectric phase with $Pnma$ symmetry is labeled as $p$; the ferroelectric phase derived from the $R3c$ phase that is the ground state of BiFeO$_3$ is labeled as $R_{aac}$ (since Mn$^{3+}$ is a $d^4$ Jahn-Teller active ion, the original $R3c$ phase distorts into this one, which has a polarization with a component along [110] and another one along [001], corresponding to the $Cc$ monoclinic space group); the other phases are supertetragonal $T$ phases like the ones mentioned earlier. Three of these $T$ phases are local minima of the energy according to our analysis of the corresponding force-constant matrices: $T_{aac}$ (originating from the $Cc$ phase, with a small component of the polarization along [110] and a large one along [001]), $T_c$ (originating from the $Pna2_1$ phase, with polarization along [001]), and $T_{aac}$ (originating from the $Pc$ phase, with a small component of the polarization along [110] and a large one along [001]). We also found that two of these $T$ phases are not local minima of the energy: $T_{ac}$ (originating from the $Cm$ phase, with a small component of the polarization along [010] and a large one along [001]) and $T_c'$ (the simplest $P4/mnm$ tetragonal configuration with polarization along [001]).

The calculations mentioned in the previous paragraph were done using $U = 4$ eV and $J = 1$ eV, since these val-
FIG. 1. (Color online.) Energies of the bulk BiMnO$_3$ phases found to be either saddle points of the energy surface ($T'_c$ and $T_{ac}$) or local minima (the rest), computed using PBEsol+$U$ (top) and HSE06 (bottom), for each of four magnetic orderings.

![Graph showing energy differences for BiMnO$_3$ phases](image)

TABLE I. Properties of the bulk BiMnO$_3$ phases corresponding to minima of the energy found in this work: name given to the phase (and most favorable magnetic ordering), space group, energy (in meV per formula unit with respect to the ground state), band gap (in eV), $c/a$ ratio, and polarization vector (in $\mu C/cm^2$).

| Phase       | S.G.  | $\Delta E$ | Gap      | $P$      |
|-------------|-------|------------|----------|----------|
| $T'_{ac}$ (A-AFM) | $Pc$ | 138        | 2.1      | (42, 42, 95) |
| $T_c$ (A-AFM)       | $Pna2_1$ | 102       | 1.8      | (0, 0, 75)  |
| $T_{ac}$ (A-AFM)      | $Cc$  | 93         | 1.8      | (43, 43, 73) |
| $R_{ac}$ (A-AFM)     | $Cc$  | 26         | 2.7      | (61, 61, 39) |
| $p$ (A-AFM)          | $Pnma$ | 15         | 2.7      | (0, 0, 0)   |
| SG (FM)              | $C2/c$ | 0          | 1.7      | (0, 0, 0)   |

Note: The $T$ phases have similar characteristics to those found for BiFeO$_3$ (an analysis of most of their atomic displacement patterns can be found in Ref. 23); the most stable one has also a $Cc$ space group, a large $c/a$ ratio (1.17), and a large macroscopic polarization (94 $\mu C/cm^2$). Magnetic arrangements other than those shown in these Tables display similar structural configurations, differences in their lattice parameters being always below 1%. The band gaps are always smallest for the FM ordering, and largest for the G-AFM orderings, the difference for a given structure going up to 1.5 eV.

B. Structures of BiMnO$_3$ Epitaxial Films

The bulk phases described here can be made stable by growing the material as a coherent epitaxial thin film. Like in BiFeO$_3$, the supertetragonal phases are expected to be favored at compressive strains; at tensile strains, the large in-plane lattice parameters of the $p$ and $R_{ac}$ phases hint that these might be more stable than the GS phase. To check these hypothesis we have done structural optimizations for the four lowest-energy phases, where the epitaxial effect is simulated by constraining the in-plane lattice vectors to be equal in length and to form a 90° angle. Figure 2 shows how the properties of these films change with the in-plane lattice constant. At lattice constants around 3.90 Å the epitaxial distortion on the GS film breaks the $C2/c$ symmetry, but it is otherwise very small, so the corresponding film is still the favored one. As we compress the film, the $T_{aac}$ phase becomes competitive, and below around 3.75 Å it is expected to be the stable state of the material. For tensile strains at in-plane lattice parameters above 4 Å we expect the $R_{aac}$ film to be the ground state, displaying a large polarization with components both in plane and out of plane. The $p$ phase is, by far, the one that has to be most distorted to fit the square symmetry of the substrate, and this renders it energetically not competitive with the other ones. The films are always insulating and display magnetic moments of around 4 $\mu_B$ localized in the
TABLE II. Lattice parameters and Wickoff positions of the bulk BiMnO$_3$ phases found to be a minimum of the energy in this work.

| Phase | Structure |
|-------|-----------|
| $T_{aa}$ | $a = 4.597$ Å, $b = 5.230$ Å, $c = 5.256$ Å<br>$\alpha = 90^\circ$, $\beta = 91.3^\circ$, $\gamma = 90^\circ$ | |
| Mn 2a | 0.5667 | 0.2552 | -0.0557 |
| Bi 2a | 0 | 0.7709 | 0 |
| O 2a | 0.1270 | 0.8051 | 0.4122 |
| O 2a | 0.6226 | 0.5461 | 0.1486 |
| O 2a | 0.6709 | -0.0276 | 0.7141 |
| $T_a$ | $a = 5.315$ Å, $b = 5.214$ Å, $c = 8.764$ Å<br>$\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ | |
| Mn 4a | 0 | -0.0046 | 0.2788 |
| Bi 4a | 0.5556 | -0.0111 | 0 |
| O 4a | -0.0303 | -0.0750 | 0.0429 |
| O 4a | 0.8105 | 0.3081 | 0.2885 |
| O 4a | 0.7120 | 0.7921 | 0.3282 |
| $T_{aa}$ | $a = 10.235$ Å, $b = 5.233$ Å, $c = 5.310$ Å<br>$\alpha = 90^\circ$, $\beta = 121.2^\circ$, $\gamma = 90^\circ$ | |
| Mn 4a | 0.2210 | 0.2546 | 0.1668 |
| Bi 4a | 1/2 | 0.2602 | 0 |
| O 4a | 0.4572 | 0.3218 | 0.3688 |
| O 4a | 0.7124 | 0.4440 | 0.3471 |
| O 4a | 0.1703 | 0.4634 | 0.3953 |
| $R_{aa}$ | $a = 9.266$ Å, $b = 5.720$ Å, $c = 5.675$ Å<br>$\alpha = 90^\circ$, $\beta = 125.7^\circ$, $\gamma = 90^\circ$ | |
| Mn 4a | 0.5233 | 0.2458 | 0.3328 |
| Bi 4a | 0.2422 | 0.2422 | 0.4844 |
| O 4a | 0.2744 | 0.3161 | 0.1236 |
| O 4a | -0.0039 | 0.4427 | 0.0890 |
| O 4a | 0.5754 | 0.4725 | 0.1539 |
| $p$ | $a = 5.928$ Å, $b = 7.440$ Å, $c = 5.372$ Å<br>$\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ | |
| Mn 4b | 0 | 0 | 1/2 |
| Bi 4c | 0.07245 | 1/4 | 0.01010 |
| O 4c | -0.02765 | 1/4 | 0.59634 |
| O 8d | 0.82708 | 0.45595 | 0.20851 |
| GS | $a = 9.544$ Å, $b = 5.592$ Å, $c = 9.852$ Å<br>$\alpha = 90^\circ$, $\beta = 110.8^\circ$, $\gamma = 90^\circ$ | |
| Mn 4e | 0 | 0.2921 | 1/4 |
| Mn 4c | 1/4 | 0.1455 | 0.3737 |
| Bi 8f | 0.6353 | 0.2270 | 0.1215 |
| O 8f | 0.5977 | 0.1733 | 0.5804 |
| O 8f | 0.1455 | 0.0718 | 0.3737 |
| O 8f | 0.3518 | 0.0472 | 0.1652 |

Mn ions. Their c/a ratios grow markedly as the strain becomes more compressive, and this translates partially into larger out-of-plane polarizations. Most of the Mn–O bonds stay at values of around 1.9 Å, but we can also see in Fig. 2 much longer bonds; those arise due to the orbital ordering in the GS phase, and in the out-of-plane directions of the $T$ phases.

FIG. 2. (Color online.) Properties of BiMnO$_3$ films as a function of the in-plane lattice parameter: (a) energy relative to the bulk ground state; (b) band gap; (c) magnetic moment of the Mn ions; (d) macroscopic polarization; (e) c/a ratio; and (f) Mn–O distances. The four structures mentioned in the legend of (c) have been considered in their favored magnetic ordering (FM for GS and A-AFM for the rest).

C. Magnetic Properties

The different magnetic orderings of a particular BiMnO$_3$ structure are within around 50 meV/f.u., both in bulk (Fig. 1) and in films (Fig. 3a), top panels). The A-AFM ordering is favored both for the $T_{aa}$ and for the $R_{aa}$ phases. These phases cannot accommodate the orbital ordering of the bulk, so the ferromagnetic ordering is not the preferred one any more.

To estimate the Néel temperature for the $T_{aa}$ and $R_{aa}$ phases we used a Heisenberg model with energy $E = E_0 + 1/2 \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$; $E_0$ is a reference energy, and $J_{ij}$ is the exchange coupling constant between the spins localized at Mn ions $i$ and $j$, given by $\mathbf{S}_i$ and $\mathbf{S}_j$ (taken as unit vectors). We restrict ourselves to first-neighbour Mn–Mn interactions in plane (described by $J_a$) and out of plane (described by $J_c$). Fitting our first-principles results to this simple model we obtain the values for those constants that are displayed in Fig. 3a (bottom panels): the energies given by the model are represented by lines in the top panel, and they show reasonable agreement with the first-principle data. The exchange coupling constants for BiMnO$_3$ are very different from those of BiFeO$_3$, reflecting the different natures of Fe$^{3+}$ (with a $d^5$ electronic configuration of half-filled orbitals, leading to strong antiferromagnetic interactions according to the Goodenough–Kanamori rules of superexchange) and
Mn\textsuperscript{+3} (with a $d^{4}$ configuration that includes an empty $e_g$ orbital, favoring in-plane ferromagnetism—the Mn–O–Mn angles in the $T_{aac}$ and $R_{aac}$ phases are between 150° and 160°). We then used a Monte Carlo method to solve our Heisenberg model in a periodically-repeated box with $20 \times 20 \times 20$ spins; the results obtained for the order parameter that describes the A-AFM alignment and for the magnetic susceptibility are shown in Fig. 3(b). Bulk BiMnO\textsubscript{3} orders magnetically below around 105 K \cite{5} and the Néel temperatures of our simulated films are similarly low—around 80 K for the $T_{aac}$ film with lattice parameter $a_{in} = 3.70$ Å, and around 90 K for the $R_{aac}$ film with $a_{in} = 4.08$ Å. The exchange coupling constants do not change much in the ranges of epitaxial strains where the $T_{aac}$ and $R_{aac}$ are expected to be stable, so the Néel temperature will be similar in these ranges.

### D. Optical Properties

BiMnO\textsubscript{3} is a particular perovskite oxide not only in its ferromagnetic properties, but also in its small band gap—typically, band gaps are above 3 eV for these materials \cite{32} but they are around 2 eV or less for some of the phases of BiMnO\textsubscript{3} according to our calculations and to the few experiments available.\cite{41} In order to further investigate the optical properties of BiMnO\textsubscript{3}, we used the independent particle approximation implemented in Vasp to compute the frequency-dependent dielectric matrix, and the related absorption coefficient. Since no experimental data for comparison are available for BiMnO\textsubscript{3}, we did a initial test on BiFeO\textsubscript{3}—we compared the absorption coefficient of bulk BiFeO\textsubscript{3} computed following this methodology with the one measured by Chen et al.\cite{33} for a film with a very similar structure.\cite{34} Our BiFeO\textsubscript{3} results in Fig. 3(a) show good agreement between theory and experiment, if we correct a shift associated to the overestimation of the band gap by the theoretical method. (This band gap for BiFeO\textsubscript{3} (3.4 eV) is the same reported earlier by Stroppa and Picozzi who performed a calculation similar to ours.) For the BiMnO\textsubscript{3} $T_{aac}$ film expected to be stable when grown on a substrate of around 3.70 Å, we find an absorption spectra that matches the solar range better than what is typical in other perovskite oxides, as shown in Fig. 3(b). We found a band gap of around 2 eV, but this could be even smaller if the HSE06 hybrid method is again overestimating it. This makes supertetragonal BiMnO\textsubscript{3} films interesting in the framework of materials for photovoltaic devices where light absorption can be coupled to other functional properties.

![Fig. 3](image-url) (Color online.) (a) Top panels: energy of different magnetic arrangements with respect to the most stable one (A-AFM), for the $T_{aac}$ (left) and $R_{aac}$ (right) phases. Bottom panels: exchange constants $J$ from fitting those energies to a simple Heisenberg model, for the $T_{aac}$ (left) and $R_{aac}$ (right) phases. (b) Top panels: A-AFM order parameter as a function of temperature for a $T_{aac}$ film of in-plane lattice constant of 3.70 Å (left) and for a $R_{aac}$ film of in-plane lattice constant of 4.08 Å (right). Bottom panels: total magnetic susceptibilities for the same films (filled symbols) and their partial contributions, parallel ($\parallel$) and perpendicular ($\perp$) to the direction of the A-AFM order parameter (empty symbols).

### IV. CONCLUSIONS

In this article we have explored the epitaxial phase diagram of BiMnO\textsubscript{3} films with the help of first-principles calculations. While bulk BiMnO\textsubscript{3} is a paraelectric, we predict that it will transform to a supertetragonal phase with a polarization of around 100 $\mu$C/cm\textsuperscript{2} when grown on substrates that compress its in-plane lattice constant to about 3.75 Å (for example, YAlO\textsubscript{3} or LaSrAlO\textsubscript{4}). This polarization will point mostly out of plane, but it is also possible for BiMnO\textsubscript{3} films to develop a polarization of similar size laying mostly in plane by growing it at tensile strains on top of substrates that expand its lat-
Values for BiFeO$_3$ are needed for stabilizing the supertetragonal phase according to our calculations, these films show in experiments nonuniform strain distributions which could be the signature of a co-existence of different (polar and non-polar) phases of BiMnO$_3$ films.

The supertetragonal phase that we have found is very similar to that of BiFeO$_3$ films grown on LaAlO$_3$ (a$_{in}$ ≈ 3.79 Å) and of BiCoO$_3$, where it is the ground state even in bulk (a$_{in}$ ≈ 3.73 Å). This kind of phases with giant polarization might be ubiquitous in transition-metal perovskite oxides containing bismuth, whose lone electron pair can be easily accommodated in this kind of structures note that previous calculations for BiScO$_3$ provide a hint that this might be yet another material displaying the same behaviour. Since BiMnO$_3$ is the only strong ferromagnet among the insulating transition-metal perovskite oxides, our results are also relevant in the context of discovery of new multiferroics; we have found that A-AFM ordering is energetically favored, but the FM ordering is competitive (especially for the R$_{aac}$ phase). It might thus be possible to engineer ferroelectric ferromagnets by combining these new film phases of BiMnO$_3$ with other transition-metals oxides in superlattices or solid solutions. Finally, in addition to this functional properties, some of these phases of BiMnO$_3$ show band gaps that are smaller than those found typically in perovskite oxides, which makes this material interesting also from the point of view of photovoltaic applications.

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FIG. 4. (Color online.) Imaginary component of the average of the diagonal elements of the dielectric matrix (left) and absorption coefficient (right) for (a) bulk BiFeO$_3$, and (b) a T$_{aac}$ film of BiMnO$_3$ (a$_{in}$ = 3.70 Å). The experimental values for BiFeO$_3$ were taken from Ref. [24]. The shaded area corresponds to the solar spectrum.
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