Epitaxial phases of BiMnO₃ from first principles

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BiMnO₃ is the only transition-metal perovskite oxide that is insulating and shows strong ferromagnetism in bulk. 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 BiMnO₃ has either a very small polarization (below 0.1 μ C/cm²) or, most likely, that it is a paraelectric. There is also experimental evidence that the polarization in BiMnO₃ *films* grown on SrTiO₃ can be as high as 20 μ C/cm². Despite the interest in these behaviors, the diagram of BiMnO₃ as a function of epitaxial strain has remained largely unexplored. Here, we use first-principles to predict that, both under enough compressive and tensile epitaxial strain, BiMnO₃ films are ferroelectric with a giant polarization around 100 μ C/cm². The phases displayed by the films are similar to those experimentally found for BiFeO₃ 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. As in BiFeO₃ films, these phases are antiferromagnetic—the orbital ordering responsible for ferromagnetism in BiMnO₃ is absent in the polar phases. Our calculations also show that the band gap of some of these BiMnO₃ 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

BiMnO₃ is the only strong ferromagnetic insulator in bulk among the transition-metal perovskite oxides, a family of functional materials whose members display many different properties of technological interest. The Curie temperature of BiMnO₃ is around 105 K [1,2], below which several groups have reported measurements of its magnetic moment close to $4 \mu_{\rm B}$ per Mn atom [3,4]. The unique ferromagnetic behavior of BiMnO₃ is related to the presence of orbital ordering of the Mn⁺³ ions (3d⁴)—elongated half-filled d_z^2 orbitals point towards empty $d_{x^2-y^2}$ orbitals of neighboring Mn cations [3]. For many years BiMnO₃ was supposed to have also a weak switchable polarization (below 0.1 μ C/cm²), and the polar space group C2 was assigned to its crystal structure [3,5]. However, recent electron diffraction experiments by Belik and co-workers [6] point to a C2/c space group that is not polar; these results have been confirmed by neutron powder diffraction experiments [7]. Despite this, when BiMnO₃ is grown as a epitaxial film on SrTiO₃, it develops a strong polarization, which Jeen and co-workers [8] measured to be 23 μ C/cm²; other groups reported similar results—a polarization between 9 and 16 μ C/cm² [9], and signatures of ferroelectricity [10].

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 other nonpolar perovskites develop ferroelectricity under epitaxial strain, it is somewhat surprising that the epitaxial phase diagram of BiMnO₃ is largely unexplored in the search for the possible coexistence of magnetic and polar orderings. Using first-principles calculations, Hatt and Spaldin [12] concluded that BiMnO₃ remains nonpolar 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 Rabe [13] and by Seshadri and Hill [14] pointed to the existence of ferroelectric instabilities in this material. In this paper we explore structures that are good candidates to become the ground state of epitaxial BiMnO₃ films. At high compressive strains, we have looked at the supertetragonal phases with giant polarization that are found in BiFeO₃ films [15] and in BiCoO₃ bulk and films [16]; 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 BiFeO₃ (including the Pnma structure of both bulk BiFeO₃ and bulk BiMnO₃ under pressure [17] and epitaxial polar phases of BiFeO₃ under tensile strains). We have found that BiMnO₃ and BiFeO₃ films display similar structures under high tensile and compressive strains; therefore, we predict that BiMnO₃ has a strong polarization when grown in these conditions.

II. METHODS

Our first-principles calculations are based on densityfunctional theory (DFT) [18,19]. However, BiMnO₃ 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 BiFeO₃ [22]. Both approaches are implemented in VASP [23], 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. [24], and for our final results we used a hybrid functional according to the Heyd-Scuseria-Ernzerhof (HSE06) prescription [21]. As in our previous article on BiFeO₃ [25], we worked with the Perdew-Burke-Ernzerhof DFT exchange-correlation functional adapted to solids (PBEsol) [26]. We used the projector augmented-wave method to represent the ionic cores [27], solving for the following electrons: Mn's 3p, 3d, and 4s; Bi's 5d, 6s, and 6p; and O's 2s and 2p. 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 those of a $6 \times 6 \times 6$ grid for a 5-atom perovskite unit cell.

III. RESULTS AND DISCUSSION

A. Metastable phases of bulk BiMnO₃

We started our search for metastable phases of BiMnO₃ by doing PBEsol+U ionic relaxations for the seven lowest-energy crystal structures found for bulk BiFeO₃ in our previous work [25] (which can accommodate to a $2 \times 2 \times 2$ pseudocubic 40-atom cell) and for the experimental C2/c ground state configuration of BiMnO₃ (using 40-atom cells that are not pseudocubic). For each of these eight configurations we prepared four types of magnetic arrangements, as in Ref. [25]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 $0.015 \text{ eV}/\text{\AA}$ and the final stresses are below 0.0005 eV/Å^3 .

The process just described leads 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 BiFeO₃ is labeled as R_{aac} (since Mn⁺³ is a d⁴ Jahn-Teller active



FIG. 1. (Color online) Energies of the bulk BiMnO₃ 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.

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 such as 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 P4mm tetragonal configuration with polarization along [001]).

The calculations mentioned above were done using U = 4 eV and J = 1 eV, since these values gave good agreement between the structural parameters computed for the bulk ground state and the experimental results; however, the obtained band gap was close to zero, and reasonable variations of U and J could not get the band gap to open above 0.5 eV (the experimental gap of FM BiMnO₃ is 0.9 eV [28], but it is expected to be larger for antiferromagnetic configurations). Because of this failure to open band gaps, in many cases when optimizing FM structures we would get a spurious metallic state; this is the reason why in Fig. 1 (top) many of the FM states are absent. Another spurious result obtained when using PBEsol+U is that the experimental ground state of BiMnO₃ is predicted to have higher energy than the p phases.

We then used the more computationally demanding HSE06 hybrid method to reoptimize the structures reported in Fig. 1 (top), and similar FM structures; for all structures but some of the GS ones it is possible to do this with 20-atom unit cells. All phases were found to be robust insulators, and the C2/c (GS) structure was accurately predicted as the one with the lowest energy. Otherwise, the energy differences between

TABLE I. Properties of the bulk BiMnO₃ 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 μ C/cm²).

Phase	SG	ΔE	Gap	Р
$\overline{T'_{aac}}$ (A-AFM)	Рс	138	2.1	(42,42,95)
T_c (A-AFM)	$Pna2_1$	102	1.8	(0,0,75)
T_{aac} (A-AFM)	Cc	93	1.8	(43, 43, 73)
R_{aac} (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)

most phases are similar to those obtained using PBEsol+U. This is in line with the previous finding for BiFeO₃ in which we reported that energy differences between similar structures are independent of the exchange-correlation functional used due to error cancellation [25]. In particular, PBEsol+U and HSE06 predict very similar energy differences between different magnetic arrangements of the same structure; this is why we have not recomputed other magnetic orderings of the GS phase (some of them require one to double the unit cell, making these calculations computationally expensive). For each of the geometries that are local minima of the energy, Tables I and II list in detail the properties of the structure having the favored magnetic ordering; in particular, the lattice parameters predicted for the C2/c phase are within 0.4% of the experimental values [6]. The T phases have similar characteristics to those found for BiFeO3 (an analysis of most of their atomic displacement patterns can be found in Ref. [25]; 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, with differences in their lattice parameters 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 BiMnO₃ epitaxial films

The bulk phases described here can be made stable by growing the material as a coherent epitaxial thin film. As in BiFeO₃ [25], the supertetragonal phases are expected to be favored at compressive strains; at tensile strains, the large inplane lattice parameters of the p and R_{aac} phases hint that these might be more stable than the GS phase. To check these hypotheses 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 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'_{aac}	a = 4.597 Å, $b = 5.230$ Å, $c = 5.256$ Å							
		($\alpha = 90^\circ, \beta = 90^\circ$	$\gamma 1.3^\circ, \gamma = 90^\circ$				
	Mn	2a	0.5667	0.2552	-0.0557			
	Bi	2a	0	0.7799	0			
	0	2a	0.1270	0.8051	0.4122			
	0	2a	0.6226	0.5461	0.1486			
	0	2a	0.6709	-0.0276	0.7141			
T_a	a = 5.315 Å, b = 5.214 Å, c = 8.764 Å							
	Mn	4a	$\alpha = 90, p = 0$	$90, \gamma = 90$	0 2788			
	Ri I	4a	0 5556	-0.0040	0.2788			
		4a	0.0303	-0.0111	0.0420			
	0	4a	-0.0303	-0.0750	0.0429			
	0	4a	0.8105	0.3081	0.2885			
-	0	<i>+u</i>	0.7120	0.7921	0.5262			
T_{aac}	a = 10.235 Å, b = 5.233 Å, c = 5.310 Å							
		a	$a = 90^\circ, \beta = 12$	$21.2^{\circ}, \gamma = 90^{\circ}$	0.4440			
	Mn	4a	0.2210	0.2546	0.1668			
	Bi	4a	1/2	0.2602	0			
	0	4a	0.4572	0.3218	0.3688			
	0	4a	0.7124	0.4440	0.3471			
	0	4a	0.1703	0.4634	0.3953			
R_{aac}	a = 9.266 Å, $b = 5.720$ Å, $c = 5.675$ Å							
		۵	$a = 90^\circ, \beta = 12$	$25.7^\circ, \gamma = 90^\circ$				
	Mn	4a	0.5233	0.2458	0.3328			
	Bi	4a	0.2422	0.2422	0.4844			
	0	4a	0.2744	0.3161	0.1236			
	0	4a	-0.0039	0.4427	0.0890			
	0	4a	0.5754	0.4725	0.1539			
р	a = 5.928 Å, $b = 7.440$ Å, $c = 5.372$ Å							
	$lpha=90^\circ,eta=90^\circ,\gamma=90^\circ$							
	Mn	4b	0	0	1/2			
	Bi	4c	0.07245	1/4	0.01010			
	0	4c	-0.02765	1/4	0.59634			
	0	8d	0.82708	0.45595	0.20851			
GS		a = 9	0.544 Å, $b = 5$.	592 Å, c = 9.85	52 Å			
	$lpha=90^\circ,eta=110.8^\circ,\gamma=90^\circ$							
	Mn	4e	0	0.2921	1/4			
	Mn	4c	1/4	1/4	0			
	Bi	8f	0.6353	0.2270	0.1215			
	0	8f	0.5977	0.1733	0.5804			
	0	8f	0.1455	0.0718	0.3737			
	0	8f	0.3518	0.0472	0.1652			

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 μ_B localized in the 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 much longer bonds in Fig. 2; those arise due to



FIG. 2. (Color online) Properties of BiMnO₃ 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) magnitude of the total 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).

the orbital ordering in the GS phase, and in the out-of-plane directions of the T phases.

C. Magnetic properties

The different magnetic orderings of a particular BiMnO₃ structure are within around 50 meV/f.u., both in bulk (Fig. 1) and in films [Fig. 3(a), top panels]. The A-AFM ordering is favored both for the T_{acc} and for the R_{aac} phases. These phases cannot accommodate the orbital ordering of the bulk, so the ferromagnetic ordering is no longer the preferred one.

To estimate the Néel temperature for the T_{aac} and R_{aac} 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 S_i and S_j (taken as unit vectors). We restrict ourselves to first neighbor 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. 3(a) (bottom panels); the energies given by the model are represented by lines in the top panel, and they show reasonable agreement with the first-principles data. The exchange coupling constants for BiMnO₃ are very different from those of BiFeO₃ [29], 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 [30,31]) and Mn^{+3} (with a d^4 configuration that includes an empty



FIG. 3. (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 an in-plane lattice constant of 3.70 Å (left) and for a R_{aac} film of an in-plane lattice constant of 4.08 Å (right). Bottom panels: Total magnetic susceptibilities for the same films (solid symbols) and their partial contributions, parallel (||) and perpendicular (\perp) to the direction of the A-AFM order parameter (open symbols).

 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 × 20 × 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 BiMnO₃ orders magnetically below around 105 K [1,2], 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

BiMnO₃ 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 [32], but they are around 2 eV or less for some of the phases of BiMnO₃, according to our calculations and to the few experiments available [28]. In order to further investigate the optical properties of BiMnO₃, we used the independent particle approximation implemented in VASP [33] to compute the frequency-dependent dielectric matrix, and the related absorption coefficient. Since experimental data for comparison are missing for BiMnO₃, we did a initial test on BiFeO₃—we compared the absorption coefficient of bulk BiFeO₃ computed following this methodology with the one measured by Chen *et al.* for a film with a very similar structure [34]. Our BiFeO₃



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 BiFeO₃, and (b) a T_{aac} film of BiMnO₃ ($a_{in} = 3.70 \text{ Å}$). The experimental values for BiFeO₃ were taken from Ref. [34]. The shaded area corresponds to the solar spectrum irradiance in arbitrary units [35].

results in Fig. 4(a) show good agreement between theory and experiment, if we correct a shift associated with the overestimation of the band gap by the theoretical method. [This band gap for BiFeO₃ (3.4 eV) is the same reported earlier by Stroppa and Picozzi [22], who performed a calculation similar to ours.] For the BiMnO₃ 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. 4(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 BiMnO₃ films interesting in the framework of materials for photovoltaic devices where light absorption can be coupled to other functional properties.

IV. CONCLUSIONS

In this article we have explored the epitaxial phase diagram of BiMnO₃ films with the help of first-principles calculations. While bulk BiMnO₃ is a paraelectric, we predict that it will transform to a supertetragonal phase with a polarization of around 100 μ C/cm² when grown on substrates that compress its in-plane lattice constant to about 3.75 Å (for example, YAlO₃ or LaSrAlO₄ [11]). This polarization will point mostly out of plane, but it is also possible for BiMnO₃ films to develop a polarization of similar size lying mostly in plane by growing it at tensile strains on top of substrates that expand its lattice constant beyond 4 Å [such as $BaTiO_3$ or $Pb(Zr,Ti)O_3$ (PZT) [11]]. Our findings might explain the experimental reports of ferroelectricity in BiMnO₃ films grown on SrTiO₃ and LaAlO₃ with relatively large remnant polarization [8-10]; even if SrTiO₃ and LaAlO₃ have a larger lattice constant than the one needed for stabilizing the supertetragonal phase according to our calculations, in experiments these films show nonuniform strain distributions [8], which could be the signature of a coexistence of different (polar and nonpolar) phases of BiMnO₃ films.

The supertetragonal phase that we have found is very similar to that of BiFeO₃ films grown on LaAlO₃ [15] $(a_{\rm in} \approx 3.79 \,\text{\AA})$ and of BiCoO₃, where it is the ground state even in bulk ($a_{in} \approx 3.73 \text{ Å}$ [16]). This kind of phase 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 structure [25]; note that previous calculations for $BiScO_3$ [36] provide a hint that this might be yet another material displaying the same behavior. Since BiMnO₃ is the only strong ferromagnet among the insulating transition-metal perovskite oxides in bulk, our results are also relevant in the context of the discovery of different multiferroics; we have found that A-AFM ordering is energetically favored, but the FM ordering is competitive (especially for the R_{aac} phase). Thus it might be possible to engineer ferroelectric ferromagnets by combining these film phases of BiMnO₃ with other transition-metal oxides in superlattices or solid solutions. Finally, in addition to these functional properties, some of these phases of BiMnO₃ 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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