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Creating multiferroics with large tunable electrical polarization from paraelectric rare-earth orthoferrites

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Abstract

The quest for materials possessing both a magnetic ordering temperature above room temperature and a large electrical polarization is an important research direction in order to design novel spintronic and memory devices. Up to now, BiFeO₃ and related systems are the only known compounds simultaneously possessing such characteristics. Here, first-principles calculations predict that another family of materials, namely epitaxial films made of rare-earth orthoferrites (RFeO₃), can also exhibit such desired features. As a matter of fact, applying a large enough strain to these compounds, which are nominally paraelectric and have a high magnetic transition temperature, is predicted to render them ferroelectric, and thus multiferroic. At high compressive strain, the resulting ferroelectric phase of RFeO₃ systems having large rare-earth ions is even a tetragonal state characterized by a giant polarization and axial ratio. For large tensile strain, two striking inhomogenous ferroelectric phases—including one never observed before in any perovskite—are further predicted as having significant polarization. A multiphase boundary also occurs, which may lead to optimization of properties or unusual features. Finally, many quantities, including electrical polarization and magnetic ordering temperature, are tunable by varying the epitaxial strain and/or chemical pressure.

Keywords: multiferroics, rare-earth orthoferrites, strain effect, magnetic ordered temperature, ferroelectric phases

(Some figures may appear in colour only in the online journal)

1. Introduction

BiFeO₃ [1, 2] and a few other compounds, such as Aurivillus-phase materials [3], mixed perovskites of PbFe₁₊₂Ta₁₋₂O₉ and PbZr₁₋ₓTiₓO₃ [4, 5], and GaFeO₃ [6], have received a lot of attention, mostly because they possess an electrical polarization and a magnetic ordering transition temperature above 300 K. However, they have their own detrimental features such as large coercive fields and high leakage currents [7], which explains the current important research direction...
aimed at finding other room-temperature multiferroics via, for example, the application of epitaxial misfit strain. As a matter of fact, such strain can affect many physical properties of perovskite oxide films including structural, ferroelectric and magnetic behaviors [8–14]. Recently, using such strain to induce ferroelectricity in nominally paraelectric magnetic perovskite oxides, and thus create new multiferroic materials, has become a major research topic. For instance, first-principles investigations have predicted that EuTiO$_3$ [9,15], CaMnO$_3$ [10], SrMnO$_3$ [11], and SrCoO$_3$ [12], should become ferroelectric under appropriate epitaxial misfit strain. However, such compounds have their own limitations. For instance, epitaxial CaMnO$_3$ films with 2.3% strain were experimentally reported to be incipient ferroelectric (below 25 K) rather than truly ferroelectric [16]. While epitaxial EuTiO$_3$ films were indeed observed to be ferroelectric under appropriate misfit strain [15], its magnetic ordering temperature is too small (namely, of the order of 5 K) [15] to make EuTiO$_3$ of practical use.

The quest for materials possessing a large electrical polarization and magnetic transition temperature above 300 K as a result of epitaxial strain, is therefore mostly unresolved [17]. Interestingly, rare-earth orthoferrites (RFeO$_3$, where R is a rare-earth ion) are perovskite compounds that exhibit a rather high Néel (paramagnetic-to-antiferromagnetic) transition temperature, namely, $T_N$ ranges between 623 and 740 K [18, 19], and for which several physical properties are known to be tunable by chemical pressure (that is, the size of the different rare-earth ions’ radii) [20, 21]. However, RFeO$_3$ systems crystallize in the $Pbnm$ space group in their bulk form, and are thus paraelectric rather than ferroelectric—although weak electrical polarization, probably of improper origin and induced by magnetic order, has been recently reported in GdFeO$_3$ and SmFeO$_3$ ($\sim$0.12 $\mu$C cm$^{-2}$ for GdFeO$_3$ and $\sim$0.0093 $\mu$C cm$^{-2}$ for SmFeO$_3$) [22, 23]. It is therefore particularly relevant to the quest for novel and tunable room-temperature multiferroics to determine if epitaxial misfit strain (1) can induce ferroelectric phases with large proper polarization in rare-earth orthoferrites, and (2) preserves the high magnetic transition temperature of these materials. To the best of our knowledge, these determinations are missing both from the theoretical and experimental literature.

Here, we report first-principles calculations predicting that rare-earth orthoferrites do possess a large polarization and a Néel temperature well above room temperature when under large enough misfit strain. In fact, a large compressive strain applied to RFeO$_3$ materials having large rare-earth ions (Ce, Pr, Nd and Sm) is predicted to generate a tetragonal ferroelectric state having a giant electrical polarization. Moreover, for large tensile strain, two other ferroelectric phases arise, both being inhomogeneous in nature and exhibiting a significant electrical polarization. Physical properties (including electrical polarization and Néel temperature) of all these ferroelectric phases are not only tunable by the magnitude of the misfit strain but also by chemical pressure. Finally, an original phase diagram correlating the critical in-plane lattice parameter associated with structural phase transitions with the rare-earth ions’ radii is shown here, and further hints towards the existence of a multiphase boundary, inside which several states having similar energy can coexist. Such a multiphase boundary may yield optimization of several physical responses when applying a small stimulus or even the occurrence of striking phenomena, such as non-ergodicity or formation of unusual multidomains—as was found in other materials known to possess different phases with close energy (see, e.g., [9, 24–29]).

2. Computational details

The calculations are performed using the VASP code within the framework of projected augmented wave (PAW) method [30]. The generalized gradient approximation GGA + U method with the Perdew and Wang (PW91) parameterization is used in this work [31, 32]. The on-site Coulomb interaction $U$ is selected to be 3.8 eV for Fe$^{3+}$, as commonly done in the literature [13, 14, 33]. We treat the valence-electron configuration as follows: $5s^25p^65d^16s^2$ for Ce, Pr, Nd, Sm, $5p^65d^16s^2$ for Gd, Tb, Dy, Ho, Er, $3d^4s^1$ for Fe and $2s^22p^4$ for O. The 4f electrons of R ions are thus kept as core electrons. The reasons behind this choice are that (1) density-functional-theory computations are usually rather difficult to converge when partially filled 4f electrons are considered in the valence, and (2) physical properties considered in the present work, such as crystal structures and magnetic-ordered temperatures of rare-earth-based perovskites, can be reproduced rather well when keeping these 4f electrons in the core (see, e.g., [20, 34]). The plane wave energy cutoff is selected to be 500 eV, and the Hellmann–Feynman force convergence criteria is 0.005 eV Å$^{-1}$, in order to obtain well-converged results on relaxed configurations. The supercells considered in the present work contain 20 or 40 atoms. During the structural optimization, the G-type antiferromagnetic order is adopted for all phases, as consistent with the magnetic ground state of RFeO$_3$ bulks [19, 20] and since we also numerically found it of lower energy than the ferromagnetic order. We also typically consider collinear magnetism and therefore neglect spin–orbital coupling when performing structural optimization, since this latter coupling is not expected to have much influence on the total energy of different structural phases. Moreover, the Néel temperature of RFeO$_3$ is estimated by mean-field approximations (MFAs), that is $T_N = (E_{FM} − E_{AFM-G})/3k_B$ where $k_B$ is the Boltzmann constant, $E_{FM}$ and $E_{AFM-G}$ are the total energy (per formula unit) of the ferromagnetic and G-type antiferromagnetic orders, respectively. The calculated Néel temperatures at MFA level for RFeO$_3$ bulks are numerically found to be 938, 913, 895, 867, 846, 836, 831, 823 and 819 K for $R$ = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er, respectively. As expected for MFA (that neglects fluctuations) [34, 35], these theoretical values are overestimated with respect to measurements [19]. However, it is quite remarkable to realize that this overestimation is systematic and always of the order of 1.29 when comparing the predicted MFA critical temperatures with the observed values of 707, 687, 674, 657, 647, 645, 639 and 636 for
Figure 1. Schematic description of the P21am(I) and P21am(II) phases of RFeO₃ films. Panels (a) and (c) are the top view of P21am(I) and P21am(II), respectively. The displacements of all the cations are shown by arrows in panel (a), with dashed and solid lines representing Fe and R ions, respectively. On the other hand and for simplicity, only the displacements of the R ions along the a-axis are shown by arrows in panel (c). Panels (b) and (d) schematize the oxygen octahedral tilting by means of curled arrows. R, Fe and O ions are shown via blue, green and red spheres, respectively. R = Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er, respectively. In the following, we will therefore divide our predicted $T_N$ by this ratio of 1.29 in order to provide realistic predictions for RFeO₃ thin films, and denote the resulting temperature as the (rescaled) Néel temperature. The resulting remarkable agreement obtained between theory and experiments for $T_N$ explains why we use (and validates) such rescaling and the aforementioned GGA + U approach with $U = 3.8$ eV. The space group of the different phases encountered in the present work is determined by the FINDSYM software [36], while the electric polarization is calculated by the Berry-phase method [37]. Finally, the VESTA [38] package is used to draw figure 1.

3. Results and discussion

3.1. Systems under investigation

Nine RFeO₃ rare-earth orthoferrites are considered here. They correspond to $R =$ Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er, respectively (note that we did not include La in our studied list of rare-earth ions because it does not possess f electrons). We simulate RFeO₃ films being epitaxially grown on (0 0 1) cubic substrates, implying that their in-plane lattice constant is frozen (i.e., it can not relax once chosen) and identical to the lattice parameter of the substrate. We allow this in-plane lattice constant, $a_{IP}$, to typically vary from 3.5 to 4.3 Å in order to mimic different substrates. The aforementioned first-principles techniques are used to investigate such two-dimensional systems.

3.2. Symmetry of structural phases

Five phases are typically found in the simulations of these RFeO₃ epitaxial films: they are the $c$-$e$Pbnm, $ab$-$e$Pbnm (note that we use here the notations employed in [39, 40] for $c$-$e$Pbnm and $ab$-$e$Pbnm) and P4nm phases and two other states that we denote here as P2₁/am(I) and P2₁/am(II). Interestingly, while $c$-$e$Pbnm and $ab$-$e$Pbnm are found to be paraelectric (similar to the case of the Pbnm ground state of RFeO₃ bulks) and are known to exist in films made of rare-earth orthoferrites, P4nm as well as P2₁/am(I) and P2₁/am(II) all exhibit an electrical polarization and it has never been proposed that they occur in RFeO₃ systems, to the best of our knowledge. In fact, we are not aware of any previous prediction of a spontaneous polarization in epitaxially strained films made of rare-earth orthoferrites. In other words, playing with epitaxial strain in RFeO₃ can indeed lead to the occurrence of novel phases and render such important systems ferroelectric and thus also multiferroic (since they naturally possess magnetic ordering at high temperature). The atomic coordinates and lattice vectors of $ab$-$e$Pbnm, $c$-$e$Pbnm, P4nm, P2₁/am(I) and P2₁/am(II) are all provided in table 1 in the case of PrFeO₃ films.

3.3. Structural characteristics of the phases

Let us now discuss in detail such phases. The $c$-$e$Pbnm phase has the same orthorhombic (paraelectric) Pbnm space group as RFeO₃ bulks, and possesses an $a' - a'' - c'$ oxygen octahedral tilting pattern (using Glazer’s notation) [41] with the in-phase tilting axis being parallel to the c-axis (which is the growth
Table 1. Lattice vectors and atomic coordinates of the \( ab-ePbnm \), \( cePbnm \), \( P4mm \), \( P2_1am(I) \), \( P2_1am(II) \) state in case of PrFeO\(_3\) films for a given in-plane lattice constant.

| Phase          | Atoms | Wyck. | Coordinates                  |
|----------------|-------|-------|------------------------------|
| \( ab-ePbnm \) | Pr    | 2e    | \((-0.02535, -0.04601, 0.25000)\) |
| \( a_p = 4.168 ~\text{Å} \) | Pr    | 2e    | \((0.50937, 0.44778, 0.25000)\) |
| \( P2_1/m, \text{No. 11} \) | Fe    | 2b    | \((0.00000, 0.50000, 0.00000)\) |
| \( a = 5.53734 \text{Å} \) | Fe    | 2c    | \((0.50000, 0.00000, 0.00000)\) |
| \( b = 5.71543 \text{Å} \) | O     | 2e    | \((0.09018, 0.53087, 0.25000)\) |
| \( c = 8.33651 \text{Å} \) | O     | 2e    | \((0.40451, 0.02517, 0.25000)\) |
| \( \alpha = \beta = \gamma = 90^\circ \) | O     | 4f    | \((0.71177, 0.71091, 0.44997)\) |
| \( P_4mm \) | Atoms | Wyck. | Coordinates                  |
| \( a_p = 4.168 ~\text{Å} \) | Pr    | 1a    | \((0.00000, 0.00000, 0.16315)\) |
| \( P4mm, \text{No. 99} \) | Fe    | 1b    | \((0.50000, 0.50000, 0.61446)\) |
| \( a = b = 3.54946 \text{Å} \) | O     | 1b    | \((0.50000, 0.50000, -0.06644)\) |
| \( c = 5.09174 \text{Å} \) | O     | 2c    | \((0.50000, 0.00000, 0.47255)\) |
| \( P2_1am(I) \) | Atoms | Wyck. | Coordinates                  |
| \( a_p = 4.168 ~\text{Å} \) | Pr    | 2a    | \((-0.03353, 0.32815, 0.00000)\) |
| \( P2_1am, \text{No. 26} \) | Fe    | 2b    | \((0.50000, 0.44778, 0.25000)\) |
| \( a = 5.89480 \text{Å} \) | O     | 2b    | \((0.84997, 0.08396, 0.50000)\) |
| \( b = 5.89480 \text{Å} \) | O     | 2b    | \((0.78668, 0.14576, 0.50000)\) |
| \( c = 3.73686 \text{Å} \) | O     | 2b    | \((0.75353, 0.57351, 0.50000)\) |
| \( \alpha = \beta = \gamma = 90^\circ \) | O     | 2a    | \((0.55758, 0.26514, 0.00000)\) |
| \( P2_1am(II) \) | Atoms | Wyck. | Coordinates                  |
| \( a_p = 4.168 ~\text{Å} \) | Pr    | 4c    | \((0.28524, 0.30170, 0.24951)\) |
| \( P2_1am, \text{No. 26} \) | Fe    | 4c    | \((0.18134, 0.29137, 0.50000)\) |
| \( a = 5.89480 \text{Å} \) | O     | 4c    | \((0.81399, 0.67470, 0.00000)\) |
| \( b = 5.89480 \text{Å} \) | O     | 4c    | \((0.27048, 0.79299, 0.37470)\) |
| \( c = 14.97629 \text{Å} \) | O     | 4c    | \((0.73104, 0.20079, 0.37470)\) |
| \( \alpha = \beta = 90^\circ \) | O     | 4c    | \((0.56354, -0.02841, 0.39540)\) |
| \( \gamma = 90^\circ \) | O     | 4c    | \((0.03118, 0.42234, 0.11862)\) |
| \( \alpha = \beta = \gamma = 90^\circ \) | O     | 4c    | \((0.56354, -0.02841, 0.39540)\) |

\( \text{direction}) [39, 40] \). \( ab-ePbnm \) adopts a different space group, namely monoclinic \( P2_1/m \), but is also paraelectric. Moreover, the \( ab-ePbnm \) has a different growth direction as compared to the \( cePbnm \). More precisely, in the \( ab-ePbnm \) case, the epitaxial plane coincides with the (1 1 0) or (1 \( \overline{1} \) 0) plane of the orthorhombic \( Pbnm \) phase of \( RFeO_3 \) bulk [39, 40]. In that case, the in-phase oxygen octahedral tilting continues to be about the \( c \)-axis, but this axis now lies inside the epitaxial plane. Furthermore, \( P4mm \) is a tetragonal phase that possesses a homogenous electrical polarization being oriented along the pseudo-cubic \( [0 0 1] \) growth direction (note that \( P4mm \) does not exhibit any tilting of the oxygen octahedra). On the other hand, \( P2_1am(I) \) has the orthorhombic \( P2_1am \) space group, and is the \( \text{inhomogeneous} \) phase (resulting in zig-zag motions of its cations) that has been recently predicted to occur in a variety of perovskite films under large enough tensile strain [13] (note that \( P2_1am \) can become \( Pmc2_1 \) depending on the adopted setting). As shown in figure 1(a), it thus has a polarization lying along the in-plane \( a \)-axis together with a C-type antiferroelectric vector being directed along the in-plane \( b \)-axis. It also possesses an \( a^a b^a c^+ \) tilting pattern in Glazer’s notation [41], which is an in-phase tilting about the out-of-plane direction (see figure 1(b)). Note that \( P2_1am(II) \) has also been predicted to exhibit a novel magnetoelectric effect
in BiFeO$_3$ [42], which further emphasizes its importance. Finally, P$_2$$_1$am(II) also adopts P$_2$$_1$am as its space group but presents significant structural differences with P$_2$$_1$am(I)—as one can see by comparing figures 1(a) and (b) with 1(c) and 1(d). For instance, its polarization (that also lies along the in-plane $a$-axis) mostly originates from inhomogeneous displacements of the $R$ ions contained in the unit cell of P$_2$$_1$am(II). More precisely, only four of these $R$ ions mainly contribute to this polarization since the displacements of the other four $R$ ions of the supercell nearly cancel each other (because two of these latter ions significantly displace along the $a$-axis while the remaining two $R$ ions also significantly move from their ideal positions but in an opposite manner). Moreover and as schematized in figure 1(d), the oxygen
Figure 3. In-plane lattice parameter versus rare-earth ionic radius in RFeO$_3$ films. Note that P2$_1$am(I), P2$_1$am(II) and $abc$-ePbnm all have similar energy in the white region of the phase diagram.

3.4. Energetics of the phases and resulting phase diagram

Figures 2(a)–(j) show the calculated total energy of these five different phases as a function of $a_{IP}$ for the nine investigated RFeO$_3$ films. Figure 2(j) reports the comparison between the average experimental lattice parameters [19] and our calculated average lattice parameters for the different RFeO$_3$ bulks (note that, by average lattice parameter, we mean the pseudo-cubic lattice constant defined by $a = \sqrt{a^2 + b^2 + c^2}/\sqrt{2}$, where $a$, $b$ and $c$ are the lattice parameters of the orthorhombic Pbnm ground state). One can see that our GGA calculations result in a lattice constant being systematically but weakly overestimated (of the order of 0.6%) compared to experiment, which is a measure of the accuracy of the simulations. Figure 3 organizes the main findings of figure 2 in the form of a phase diagram reporting the critical in-plane lattice parameter associated with the different phase transitions as a function of the rare-earth ions’ radii, $r_R$ (that is, as a function of chemical pressure). The major conclusions arising from figures 2 and 3 are as follows. First of all, the $ab$-ePbnm phase of RFeO$_3$ is stable over a large range of in-plane lattice constants for any rare-earth orthoferrite. The only RFeO$_3$ films for which $ab$-ePbnm may be destabilized in favor of $c$-ePbnm are CeFeO$_3$ and PrFeO$_3$, but this only occurs in a relatively small lattice-constant region in which $a_{IP}$ is larger than 4.0 and smaller than 4.2 Å. Interestingly and as shown in figures 2(a) and (b), the energy difference between $ab$-ePbnm and $c$-ePbnm in these two latter films is rather small for any in-plane lattice constant, which suggests that $ab$-ePbnm and $c$-ePbnm may in fact coexist (especially in the aforementioned narrow range extending from 4.0 to 4.2 Å). Secondly, for the considered range of the in-plane lattice constant, the P4mm phase appears for relatively small $a_{IP}$ for the four largest R elements mimicked here, namely Ce, Pr, Nd and Sm, indicating that the corresponding four films become polar at large enough compressive strain ($\sim$–7.1% for $R$ = Ce, $\sim$–7.3% for Pr, $\sim$–7.6% for Nd and $\sim$–8.4% for Sm). Thirdly, P2$_1$am(I) exists for large enough in-plane lattice constant for any considered R element (namely, larger than 4.19 Å when $R$ = Ce to larger than 4.11 Å for $R$ = Er), indicating that all RFeO$_3$ films are also polar but now at relatively high tensile strain (that is above $\sim$5.9 to $\sim$7.1%). Finally, in-between the two regions of stability of the $ab$-ePbnm (or $c$-ePbnm) and P2$_1$am(I) phases, respectively, there is a small range of in-plane lattice constants for which P2$_1$am(II) is the ground state (note that the lattice constant corresponding to the central value of this range decreases as $r_R$ diminishes, similar to the chemical-pressure-induced decrease of the critical $a_{IP}$ delimiting the $ab$-ePbnm and P4mm phases, see figure 3). It is also important to realize that this range can, in fact, be considered as a multiphase boundary of RFeO$_3$ films, since the $ab$-ePbnm (and $c$-ePbnm for $R$ = Ce and Pr), P2$_1$am(I) and P2$_1$am(II) phases all have very similar energy there. Consistent with previous works on other materials (see, e.g., [9, 29]), the coexistence of all these phases may generate interesting behaviors that are typically associated with non-ergodicity [46–49]—since the system may continuously vary from one phase to another. It may also lead to an optimization of physical responses, since a small change in stimulus (such as a weak applied electric field) can favor one phase over the others and may thus result in a significant structural, electric or magnetic modification if these different phases possess rather distinct characteristics—as previously evidenced in other compounds [24–28].

3.5. Properties in the multiphase boundary

Let us thus pay more attention to this multiphase boundary and the properties of its phases. For that, figure 4 reports some physical quantities of the RFeO$_3$ epitaxial films as a function of the chemical pressure for a value of the in-plane lattice constant for which the $ab$-ePbnm (and $c$-ePbnm for $R$ = Ce and Pr), P2$_1$am(I) and P2$_1$am(II) phases are all very close to each other in energy, that is $a_{IP} = 4.186$, 4.168, 4.155, 4.137, 4.121, 4.117, 4.114, 4.110 and 4.110 Å for $R$ = Ce,
Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er, respectively. (Note that these $a_p$ correspond to tensile strains equal to 5.79%, 5.86%, 5.90%, 6.06%, 6.41%, 6.60%, 6.77%, 6.96%, 7.09% for these RFeO$_3$ films, respectively. The multiphase boundary therefore corresponds to a smaller lattice constant but larger tensile misfit strain when decreasing $r_R$). More precisely, figure 4(a) displays the electrical polarization associated with the polar P2$_1$am(I) and P2$_1$am(II) phases, while figure 4(b) shows the rescaled Néel temperature of the different ferroelectric and paraelectric stable phases considered here. One can see that the electric polarization of P2$_1$am(I) increases from ∼67 to ∼87 $\mu$C cm$^{-2}$ when $R$ changes from Ce to Er, which can be thought to reflect the fact that the tensile misfit strain associated with the multiphase boundary of RFeO$_3$ films increases during that change and that increasing the strength of the tensile misfit strain typically enlarges the polarization because of the coupling between strain and polarization [50, 51]. On the other hand, the polarization of P2$_1$am(II) is much smaller (consistent with the fact that it mostly ‘solely’ arises from the contribution of a few R ions) and only slightly increases from ∼13.5 to ∼22.3 $\mu$C cm$^{-2}$ during this variation of $R$. Moreover, the Néel temperature of any phase is reduced when $R$ changes from Ce to Er. We numerically found that such reduction is correlated with the fact that oxygen octahedral tilting strengthens when $r_R$ decreases. Furthermore, P2$_1$am(I) presents a higher $T_N$ than those of P2$_1$am(II) and ab-ePbnm (and/or c-ePbnm for $R = $ Ce and Pr) phases for any RFeO$_3$ film at its multiphase boundary—which may be related to its rather inhomogenous cation displacements and resulting orbital ordering [13]. As a result, a phase transition from the P2$_1$am(I) to P2$_1$am(II) state within the multiphase boundary of ErFeO$_3$ would not only result in an enhancement of the magnitude of the polarization by a factor of 3.9 but also in an increase of the Néel temperature by 45 K. Such changes demonstrate the possibility of significantly affecting physical quantities in RFeO$_3$ film under some specific tensile strain near or at the multiphase boundary when applying some stimulus. Another interesting possibility related to this multiphase boundary is the formation of nanodomains made of different phases (having similar energy) alternating along some specific direction. In that case and as shown in [24–26, 28], this formation can result in an enhancement of physical properties or even the occurrence of striking features. Note that we also conducted further computations incorporating spin–orbit interactions and non-collinear magnetism. These computations (not shown here) indicate that a rather weak magnetization (of the order of 0.007 Bohr magneton per formula unit) can occur in the P2$_1$am(II) state of the RFeO$_3$ films at their multiphase boundary. Such weak magnetization is oriented along the c-axis (respectively, b-axis) if the strong antiferromagnetic vector lies along the b-axis (respectively, c-axis), as consistent with the general rule given in [52] involving the direction of the axis about which the antiphase oxygen octahedral tilt together with the directions of the G-type antiferromagnetic vector and magnetization.

3.6. Dependence of physical properties on misfit strain

It is also worthwhile to demonstrate that properties of any RFeO$_3$ film can be altered by the misfit strain. For that, let us now concentrate on figure 5 which reports some calculated physical properties of CeFeO$_3$ films as a function of the in-plane lattice parameter $a_{IP}$ in their ground states (note that, for CeFeO$_3$ films and consistent with figure 2(a), P2$_1$am(II) is never a ground-state and therefore does not appear in figure 5). For instance, figure 5(a) shows that the ratio between the out-of-plane lattice parameter and the in-plane lattice parameter $c_{OP}/a_{IP}$ continuously increases as $a_{IP}$ varies between ∼4.2 and ∼3.5 Å, with the noticeable exception of a spectacular jump from 1.16 to 1.34 at the ab-ePbnm-to-P4mm phase transition. In fact, this latter phase can be considered to be a tetragonal phase since figure 5(b) also reveals that it possesses a very large electrical polarization (varying between 123 and 133 $\mu$C cm$^{-2}$ when changing $a_{IP}$ from ∼3.68 to ∼3.55 Å), in addition to exhibiting a giant axial ratio. The P4mm phase of RFeO$_3$ films therefore bears a resemblance to the so-called ‘T-phase’ of BiFeO$_3$ films appearing under similar compressive misfit strain [13, 24]. Figure 5(b) further reveals that the transition from c-ePbnm to P2$_1$am(I) is also accompanied by a discontinuity in $c_{OP}/a_{IP}$ and the formation of a significant polarization, but with smaller magnitudes than at the ab-ePbnm-to-P4mm transition. For instance, $c_{OP}/a_{IP}$ only decreases by 0.47%
and the polarization becomes equal to \( \sim 67 \, \mu \text{Ccm}^{-2} \) when the \( c \)-\( e \)-Pbnm transforms into \( P2_1\text{am}(I) \). Further, increasing \( a_{IP} \) from \( \sim 4.20 \) to \( \sim 4.26 \, \text{Å} \) within the \( P2_1\text{am}(I) \) state results in a tunable electric polarization increasing from \( \sim 68.2 \) to \( 73.7 \, \mu \text{Ccm}^{-2} \). Large discontinuities can also be seen in figure 5(c) for the magnetic ordering temperature \( T_N \) at the \( ab \)-\( e \)-Pbnm-to-P4mm transition, (with respectively small discontinuities for the \( c \)-\( e \)-Pbnm-to-\( P2_1\text{am}(I) \) transition), while a rather significant and continuous decrease of \( T_N \) from 905 to 631 K is predicted when \( a_{IP} \) increases from \( \sim 3.68 \) to \( \sim 4.2 \, \text{Å} \) within the \( ab \)-\( e \)-Pbnm and \( c \)-\( e \)-Pbnm phases (we numerically found that this decrease is accompanied by an increase of the in-phase oxygen octahedral tilting angle).

4. Conclusion

In conclusion, we have simulated properties of epitaxial (0 0 1) films made of rare-earth orthoferrites RFeO\(_3\). Several ferroelectric phases under large enough compressive strain (the tetragonal P4mm state) and tensile strain (the strongly inhomogeneous \( P2_1\text{am}(I) \) phase and the novel \( P2_1\text{am}(II) \) state) are predicted. Physical properties of these phases, including electric polarization and magnetic-ordered temperatures, are tunable not only by the magnitude of the misfit strain experienced by the films but also by chemical pressure. Moreover, under tensile strain, there exists a multiphase boundary for all investigated RFeO\(_3\) perovskites at which \( ab \)-\( e \)-Pbnm (and/or \( c \)-\( e \)-Pbnm), \( P2_1\text{am}(I) \) and \( P2_1\text{am}(II) \) can all coexist. Such a multiphase boundary can therefore result in a dramatic change of physical properties when applying a small stimulus, or even the occurrence of striking effects (such as non-ergodicity and formation of alternating nanodomains having different structures)—based on previous works conducted on other materials known to possess different types of perovskite phases (we numerically found that this decrease is accompanied by an increase of the in-phase oxygen octahedral tilting angle).

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