

# Ferroelectricity in corundum derivatives

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The search for new ferroelectric (FE) materials holds promise for broadening our understanding of FE mechanisms and extending the range of application of FE materials. Here we investigate a class of  $ABO_3$  and  $A_2BB'O_6$  materials that can be derived from the  $X_2O_3$  corundum structure by mixing two or three ordered cations on the  $X$  site. Most such corundum derivatives have a polar structure, but it is unclear whether the polarization is reversible, which is a requirement for a FE material. In this paper, we propose a method to study the FE reversal path of materials in the corundum derivative family. We first categorize the corundum derivatives into four classes and show that only two of these allow for the possibility of FE reversal. We then calculate the energy profile and energy barrier of the FE reversal path using first-principles density functional methods with a structural constraint. Furthermore, we identify several empirical measures that can provide a rule of thumb for estimating the energy barriers. Finally, the conditions under which the magnetic ordering is compatible with ferroelectricity are determined. These results lead us to predict several potentially new FE materials.

## I. INTRODUCTION

Ferroelectricity requires a material to have a spontaneous electric polarization that can be reversed by an external electric field.<sup>1</sup> The search for new ferroelectric (FE) materials holds promise for broadening our understanding of FE mechanisms and extending the range of application of FE materials. A switchable spontaneous polarization implies a hysteresis effect that can be used in memory devices.<sup>2</sup> FE materials also exhibit high and tunable electric permittivity, which can be used in capacitors to increase the capacitance and reduce the size of devices. In addition, FE materials are piezoelectric and pyroelectric, according to symmetry considerations. These combined properties make FE materials ideal for electric, mechanical and thermal sensors. Recently, research on multiferroics, in which FE and ferromagnetic orders coexist in the same material, has further extended the range of application of FE materials.<sup>3–9</sup>

The most intensively studied family of FE oxides is that of the perovskite oxides such as  $BaTiO_3$ .<sup>10,11</sup> Perovskite oxides have the chemical formula  $ABO_3$  with the  $A$  cation much larger than the  $B$  cation. The FE distortion is usually driven by  $B$ -site off-centering and typically requires an empty  $d$  shell on the  $B$  cation, which is not compatible with magnetism. Recently, rocksalt-ordered  $A_2BB'O_6$  double perovskites (and more complex  $AA'BB'O_6$  materials) have also attracted great interest.<sup>12,13</sup>

The corundum derivatives  $ABO_3$  and  $A_2BB'O_6$  make up a family of oxides that can be derived from the corundum structure with cation ordering. Most corundum derivatives are polar and thus can potentially be new FE oxides.<sup>17–32</sup>  $LiNbO_3$  (LNO) is a well-known example of a FE corundum derivative.<sup>14–16</sup> Despite the similar chemical formula, corundum derivatives are different from perovskites in many aspects. The high-symmetry parent structure is rhombohedral for corundum derivatives but cubic for perovskites. The polar-

ization reversal mechanisms are also distinct. In corundum derivatives, the polarization reversal is driven by the small  $A$  or  $B$  cations migrating between oxygen octahedra,<sup>15,16</sup> so that  $d^0$  configuration is not required. This is in contrast to the off-centering displacement of  $d^0$   $B$  cations in the oxygen octahedra in most perovskites. The huge number of potential combinations of  $A$ ,  $B$  and  $B'$  cations in the corundum-derivative family opens the possibility to achieve not only ferroelectricity but also multiferroicity.<sup>18,19</sup>

In this paper, we use first-principles density functional methods to systematically study the polar structure and the coherent FE reversal paths for a variety of corundum derivatives. First, the structures of corundum derivatives are introduced in Sec. II A. Then the structural criteria for corundum derivatives to be FE are discussed in Sec. II B. In Sec. II C, we propose a systematic method to analyze the coherent FE barrier and energy profile. Lastly, the new method is applied to several corundum derivatives, and empirical measures that can provide a rule of thumb for estimating the reversal barrier are summarized in Sec. III.

## II. PRELIMINARY

### A. Structure

The corundum derivatives  $ABO_3$  and  $A_2BB'O_6$  can be derived from the corundum structure  $X_2O_3$  with cation ordering as shown in Fig. 1. In the 10-atom rhombohedral unit cell, the cations are spaced along the three-fold rotation axis and each one is surrounded by a distorted oxygen octahedron. Two thirds of the oxygen octahedra are filled with cations, while one third of them are cation-vacant.

Based on the combinations and arrangements of cations, the corundum derivatives can be classified into four types, which we denote as follows. An oxygen oc-

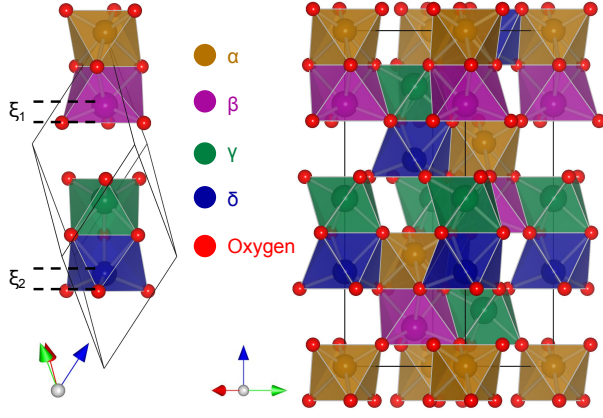


FIG. 1. Structure of corundum derivatives. The unit cell in the rhombohedral setting is shown at the left; an enlarged hexagonal-setting view is shown at right. The cations  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  are all identical in the  $X_2O_3$  corundum structure. For the LNO-type  $ABO_3$ ,  $\beta = \delta = A$ ,  $\alpha = \gamma = B$ ; for the ilmenite  $ABO_3$ ,  $\beta = \gamma = A$ ,  $\alpha = \delta = B$ ; for the ordered-LNO  $A_2BB'O_6$ ,  $\beta = \delta = A$ ,  $\gamma = B$ ,  $\alpha = B'$ ; for the ordered-ilmenite  $A_2BB'O_6$ ,  $\beta = \gamma = A$ ,  $\delta = B$ ,  $\alpha = B'$ . At left,  $\xi_1$  (or  $\xi_2$ ) is the distance between  $\beta$  (or  $\delta$ ) and the oxygen plane that it penetrates during the polarization reversal.

tahedron with an  $A$  or  $B$  cation inside is written as “ $A$ ” or “ $B$ ”, and if an oxygen octahedron is cation-vacant, the octahedron is denoted by “ $-$ ”. This notation is then used to represent the column of six face-sharing oxygen octahedra in the unit cell for each of the four different types of corundum derivatives. Thus, the LNO-type  $ABO_3$  is  $AB-AB-$ , the ilmenite  $ABO_3$  is  $AB-BA-$ , the ordered-LNO  $A_2BB'O_6$  is  $AB-AB'-$ , and the ordered-ilmenite  $A_2BB'O_6$  is  $AB-B'A-$ . Other combinations, such as  $AA-BB-$ , are connected to the four existing types as explained in Sec. II B.

### B. Coherent FE polarization reversal

Experimentally, the FE polarization reversal process is a complicated one that typically proceeds by nucleation and motion of domain walls, involving both intrinsic atomic motion and extrinsic pinning by defects. In this paper we have chosen to focus only on coherent FE domain reversal, in which every unit cell undergoes the polarization reversal simultaneously. This coherent reversal process is clearly highly oversimplified, but previous studies of perovskite oxides have shown that the coherent barrier provides a figure of merit that is often a useful indicator of the real barrier to polarization reversal.

The atomic origin of ferroelectricity in LNO is well-understood.<sup>15,16</sup> In LNO, the polarization reversal is driven by an infrared-active (IR-active) mode that is associated with the motion of Li cations along the rhombohedral axis. In the reversal process, each Li cation pene-

TABLE I. Corundum-derived structures before and after polarization reversal.

	Before	After
LNO-type	$AB-AB-$	$-BA-BA$
Ilmenite	$AB-BA-$	$-BB-AA$
Ordered-LNO	$AB-AB'-$	$-BA-B'A$
Ordered ilmenite	$AB-B'A-$	$-BB'-AA$

trates through an oxygen plane and migrates into an adjacent unoccupied oxygen octahedron. In our notation, the polarization reversal process interchanges Li with  $-$ , so that the polar structure changes from  $LiNb-LiNb-$  to its inversion image  $-NbLi-NbLi$ .

For all types of polar corundum derivatives, we assume that the polarization reversal mechanism is similar to that of LNO, i.e., that the reversal process interchanges  $A$  or  $B$  with  $-$ . The structures before and after this process are listed in Table I. Under such an operation, the LNO-type structure is transformed into its own inversion-reversed image, which is a typical FE behavior. The same is true for the ordered-LNO structure. By contrast, the ilmenite-type  $AB-BA-$  is transformed into  $BB-AA-$ , and the ordered-ilmenite  $AB-B'A-$  into  $BB'-AA-$ . These structures are not inversion-equivalent to the starting structures. Moreover, they exhibit face-sharing  $A$ -containing octahedra, making them relatively unfavorable energetically. Additionally, both the ilmenite structure and its switched partner are centrosymmetric. For these reasons, we exclude the ilmenite and ordered-ilmenite structures from further consideration as FE candidates.

### C. Energy profile calculations

For the LNO-type and the ordered-LNO FE candidates, we firstly analyze the symmetry of the reversal path. The ground state symmetry is  $R3c$  for the LNO-type materials, and  $R3$  for the ordered-LNO ones, but the symmetry of the reversal path is not straightforward. In this paper, we assume that the three-fold rotation is always preserved, so that the symmetry of the path can only be  $R3c$  or  $R3$  for the LNO-type case, and  $R3$  for the ordered-LNO case. If the structure acquires an inversion center at the midpoint of the path when the polarization is zero ( $R\bar{3}c$  or  $R\bar{3}$  for the two cases respectively), the energy profile would be symmetric. If the inversion symmetry at the midpoint is broken, as for example by magnetic ordering, the energy profile would be asymmetric.

Based on the symmetry of the reversal path, we adopt different methods to calculate the energy profile of the FE reversal. In the case when the inversion symmetry is present at the midpoint structure, the polarization reversal can be analyzed in terms of an unstable IR-active

phonon mode at the high-symmetry midpoint. In general, even if the midpoint is not in a high-symmetry reference structure, the motion of the small  $A$  cations is responsible for the polarization reversal. As illustrated in Fig. 1, we define  $\xi_1$  ( $\xi_2$ ) to be the distance between the first (second)  $A$  cation and the oxygen plane that it penetrates as this  $A$  cation moves along its path. Then  $\xi_1 + \xi_2$  is adopted as a “reaction coordinate” to describe the reversal. Finally, we use either the unstable IR-active mode at the midpoint (for the high-symmetry case) or  $\xi_1 + \xi_2$  (otherwise) as a structural constraint, and relax all other internal structural degrees of freedom while stepping through a sequence of values of this constraint. This gives us the energy profile along the path, from which the energy barrier is obtained by inspection.

#### D. First-principles methods

Our calculations are performed with plane-wave density functional theory (DFT) implemented in VASP.<sup>33</sup> The exchange-correlation functional that we use is PBEsol, a revised Perdew-Burke-Ernzerhof generalized-gradient approximation that improves equilibrium properties of densely-packed solids.<sup>34</sup> The ionic core environment is simulated by projector augmented-wave (PAW) pseudopotentials.<sup>35</sup> For transition metal elements Mn and Fe, we use a Hubbard  $U = 4.2$  eV on the  $3d$  orbitals.<sup>28,36</sup> For the Os  $5d$  orbital, we use a Hubbard  $U = 1.4$  eV.<sup>31</sup> The magnetic moments are collinear and spin-orbit coupling is neglected. The cutoff energy for all calculations is 550 eV. The energy error threshold varied slightly in different calculations, but an accuracy between  $1.0 \times 10^{-5}$  and  $1.0 \times 10^{-7}$  eV is achieved in all calculations. The forces are reduced below 0.001 eV/Å for calculations of structural relaxation. A  $6 \times 6 \times 6$  Monkhorst-Pack  $k$ -mesh is used in the calculations. Linear-response methods are used to calculate the  $\Gamma$ -point force-constant matrices. The spontaneous polarization is calculated using the Berry phase formalism.<sup>37</sup>

### III. RESULTS AND DISCUSSION

In this paper, we apply the method of calculating the energy profile described in Sec. IIC to fully analyze the coherent FE reversal path of the LNO-type corundum derivatives  $\text{LiNbO}_3$ ,<sup>14</sup>  $\text{LiTaO}_3$ ,<sup>14</sup>  $\text{ZnSnO}_3$ ,<sup>20</sup>  $\text{FeTiO}_3$ ,<sup>18,19</sup> and  $\text{MnTiO}_3$ ,<sup>18</sup> and the ordered-LNO corundum derivatives  $\text{Li}_2\text{ZrTeO}_6$ ,<sup>25</sup>  $\text{Li}_2\text{HfTeO}_6$ ,<sup>25</sup>  $\text{Mn}_2\text{FeWO}_6$ ,<sup>30</sup>  $\text{Mn}_3\text{WO}_6$ ,<sup>32</sup> and  $\text{Zn}_2\text{FeOsO}_6$ .<sup>31</sup>

#### A. Ground state structure and magnetic order

The properties of FE materials are sensitive to atomic displacements and strain, so it is essential to start our calculation with accurate structural parameters. The

TABLE II. Oxidation states of the LNO-type  $ABO_3$  and the ordered-LNO  $A_2BB'O_6$  corundum derivatives. The oxidation state of O ion is  $-2$  in all materials.

LNO-type	$A$	$B$	Ordered LNO	$A$	$B$	$B'$
$\text{LiNbO}_3$	+1	+5	$\text{Li}_2\text{ZrTeO}_6$	+1	+4	+6
$\text{LiTaO}_3$	+1	+5	$\text{Li}_2\text{HfTeO}_6$	+1	+4	+6
$\text{ZnSnO}_3$	+2	+4	$\text{Mn}_2\text{FeWO}_6$	+2	+2	+6
$\text{FeTiO}_3$	+2	+4	$\text{Mn}_3\text{WO}_6$	+2	+2	+6
$\text{MnTiO}_3$	+2	+4	$\text{Zn}_2\text{FeOsO}_6$	+2	+3	+5

lattice constants and Wyckoff positions obtained from our calculations are summarized in the Supplement, with experimental results provided for reference. Our structural parameters are very close to the experimental results. The oxidation states, obtained by rounding the integrated charge around each cation, are also displayed in Table II and are in good agreement with experimental observations.

The on-site magnetic moments are investigated for  $\text{FeTiO}_3$ ,  $\text{MnTiO}_3$ ,  $\text{Mn}_2\text{FeWO}_6$ ,  $\text{Mn}_3\text{WO}_6$  and  $\text{Zn}_2\text{FeOsO}_6$ . Our DFT+ $U$  calculation predict that the magnetic moment is about  $3.7 \mu_B$  on each  $\text{Fe}^{2+}$ ,  $4.6 \mu_B$  on each  $\text{Mn}^{2+}$ , and  $4.2 \mu_B$  on  $\text{Fe}^{3+}$ . These results are in agreement with the  $d^6$  state of  $\text{Fe}^{2+}$  and the  $d^5$  configuration of  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$ . The magnetic moment on  $\text{Os}^{5+}$  is  $2.1 \mu_B$  from our calculation, which is consistent with the high-spin  $d^3$  state after taking into account the screening of the Os moment arising from the hybridization between Os  $5d$  and O  $2p$  orbitals.

The energy of different magnetic orderings is also studied. In our calculation, we only consider magnetic structures that preserve the periodicity of the rhombohedral unit cell. Our results suggest that the ground-state magnetic ordering is anti-ferromagnetic (AFM) for  $\text{FeTiO}_3$  and  $\text{MnTiO}_3$  and ferrimagnetic (FiM) for  $\text{Zn}_2\text{FeOsO}_6$ . To investigate the magnetic structures of  $\text{Mn}_2\text{FeWO}_6$  and  $\text{Mn}_3\text{WO}_6$ , four different types of unit cell are considered in the calculation. We adopt a notation like “ $udu$ ” to describe the possible spin structure, where “ $u$ ” is spin-up, “ $d$ ” is spin-down, and the spins are given on atom  $\beta$ ,  $\delta$  and  $\gamma$ , in that order. The four possible states (not counting those that are trivially related by a global spin reversal) are  $uuu$ ,  $uud$ ,  $udu$ , and  $udd$ . The energy of each fully-relaxed magnetic structure is listed in the Supplement. Of those, the most stable state for both  $\text{Mn}_2\text{FeWO}_6$  and  $\text{Mn}_3\text{WO}_6$  is  $udu$ . However, for  $\text{Mn}_3\text{WO}_6$ , the energy difference between the  $uud$  and  $udu$  states is tiny, so we considered the polarization reversal for both magnetic states.

#### B. Symmetry of the reversal path

For the LNO-type materials, the simplest possible reversal path would be one in which the two  $A$  cations

TABLE III. The energy and the unstable phonon modes at the midpoint structure of  $\text{LiNbO}_3$ ,  $\text{LiTaO}_3$ ,  $\text{ZnSnO}_3$ ,  $\text{FeTiO}_3$  and  $\text{MnTiO}_3$  with symmetry  $R\bar{3}c$  and  $R\bar{3}$ . The energy of the ground-state structure is set to be zero as reference and the unit is meV per unit cell. The imaginary frequency of the unstable phonon is given in units of  $\text{cm}^{-1}$ .

	Energy		Unstable modes		
	$R\bar{3}c$	$R\bar{3}$	$R\bar{3}c$	$R\bar{3}$	$R\bar{3}$
			$A_{2u}$	$A_{2g}$	$A_u$
$\text{LiNbO}_3$	303	259	$216i$	$123i$	$158i$
$\text{LiTaO}_3$	163	129	$178i$	$116i$	$1i$
$\text{ZnSnO}_3$	255	241	$93i$	$30i$	$47i$
$\text{FeTiO}_3$	1014	735	$195i$	$75i$	—
$\text{MnTiO}_3$	550	468	$177i$	$73i$	$114i$

move synchronously, so that  $\xi_1 = \xi_2$  everywhere along the path. In this case the symmetry along the path is  $R\bar{3}c$ , except at the midpoint where there is an inversion center and the symmetry becomes  $R\bar{3}c$ . Another possibility is that the cations move sequentially, one after the other, so that  $\xi_1 \neq \xi_2$  for at least part of the path. In this case the symmetry is  $R\bar{3}$  except at the  $R\bar{3}$  midpoint. In order to find out which scenario occurs, we calculate the energy of the midpoint structures with symmetry  $R\bar{3}c$  and  $R\bar{3}$  respectively; the results are shown in Table III. For all LNO-type materials that we have studied, the  $R\bar{3}$  midpoint structure is energetically favored, which implies that the reversal occurs via the lower-symmetry  $R\bar{3} \rightarrow R\bar{3} \rightarrow R\bar{3}$  scenario, at least in the central portion of the path. This striking result demonstrates that the midpoint of the FE reversal path in the LNO-type FE materials is *not* identified with the high-temperature paraelectric structure,<sup>15,16</sup> but instead has lower symmetry.

The energy differences between  $R\bar{3}c$  and  $R\bar{3}$  structures can be explained by comparing their unstable phonons, for which the frequencies are listed in Table III. At  $R\bar{3}c$  symmetry, all the LNO-type candidates have *two* unstable modes along the rhombohedral axis direction, namely one  $A_{2u}$  and one  $A_{2g}$  mode. The  $A_{2u}$  mode is IR-active, and it describes the synchronous movement of  $A$  cations. The non-polar  $A_{2g}$  mode, however, is related to the out-of-phase movement of the two  $A$  cations. Comparing the unstable modes in the  $R\bar{3}c$  and  $R\bar{3}$  structures, we find that the unstable non-polar mode is absent in the  $R\bar{3}$  structure. Therefore, the unstable  $A_{2g}$  mode is responsible for the energy reduction in going from the  $R\bar{3}c$  to the  $R\bar{3}$  structure. In addition, we find an unstable  $E_u$  mode in  $\text{LiNbO}_3$  and  $\text{FeTiO}_3$  for both the  $R\bar{3}c$  and  $R\bar{3}$  structures. As the three-fold rotational symmetry is preserved in our calculation, the  $E_u$  modes are not allowed to relax and further lower the energy.

For the ordered-LNO materials, since the two  $A$  cations are not related by any symmetry even in the ground state, the two  $A$  cations move sequentially so that  $\xi_1 \neq \xi_2$ . Therefore, the reversal path adopts the  $R\bar{3}$  symmetry,

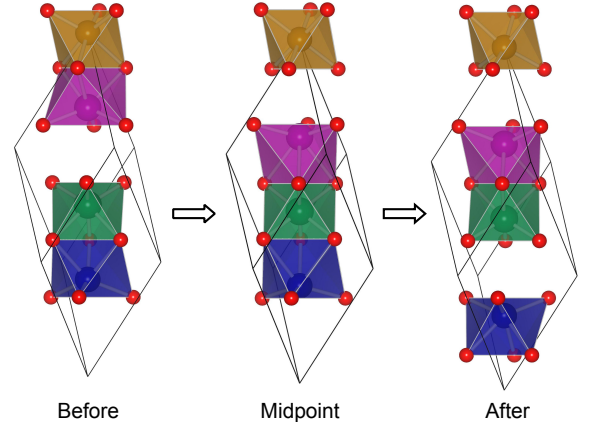


FIG. 2. Structural evolution along the polarization reversal path of the LNO-type and the ordered-LNO corundum derivatives. “Before” and “After” are the initial and final structures on the reversal path with symmetry  $R\bar{3}c$  for the LNO-type and  $R\bar{3}$  for the ordered-LNO corundum derivatives; “Midpoint” denotes the structure halfway between these and exhibits  $R\bar{3}$  structural symmetry in both cases.

except at the  $R\bar{3}$  midpoint. The only exception in our calculations is the case of the  $udu$  magnetic state in  $\text{Mn}_2\text{FeWO}_6$  and  $\text{Mn}_3\text{WO}_6$ , where the magnetic moments break inversion symmetry so that the midpoint structure slightly deviates from  $R\bar{3}$  to  $R\bar{3}c$ . Leaving aside this small distortion, the midpoint structures of the LNO-type and the ordered-LNO paths have the same structural symmetry, even though the ordered-LNO compounds have lower symmetry in their ground state.

The sequence of movements of the  $A$  cations along the FE reversal path is illustrated in Fig 2, and described quantitatively using our computed results for  $\text{LiNbO}_3$  and  $\text{Mn}_2\text{FeWO}_6$  as paradigmatic examples in Fig. 3. The “Before” and “After” structures in Fig. 2 correspond to the points at the top right and bottom left corners of Fig. 3 respectively. For the LNO-type case, the ideal  $R\bar{3}c$  “Midpoint” structure would correspond to the origin on the plot, but the reversal path does not pass through this point because of an unstable  $A_{2g}$  mode along the  $\xi_1 = -\xi_2$  direction. The “bubble” in the center confirms the significant effect of the unstable  $A_{2g}$  mode. Our “Midpoint” in Fig. 2 is thus displaced from the origin along the line  $\xi_1 = -\xi_2$ . There is a spontaneous breaking of symmetry at the point where the structure departs from the  $\xi_1 = \xi_2$  diagonal; at this point the system “randomly” makes a choice between two equivalent paths, marked by filled and open red symbols in Fig. 3.

For the ordered-LNO materials the two  $A$  cations are inequivalent, and one of them is already closer to the oxygen plane in the ground state. Let this be the one labeled by  $\xi_1$ . It is energetically favorable for this particular  $A$  cation to migrate first in the reversal path, which causes either the  $B$  or  $B'$  cation to be sandwiched between two  $A$  cations in the “Midpoint” structure as illustrated in Fig. 2. The system thus deterministically follows the

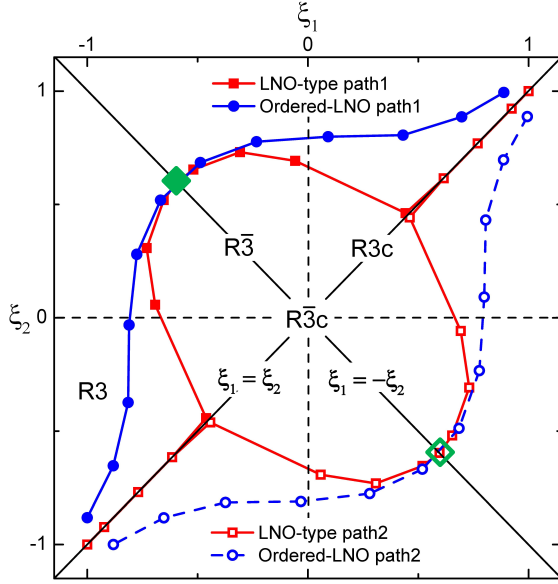


FIG. 3. Movements of  $A$  cations in LNO-type (red, here  $\text{LiNbO}_3$ ) and ordered-LNO (blue, here  $\text{Mn}_2\text{FeWO}_6$ ) corundum derivatives along the polarization reversal path.  $\xi_1$  and  $\xi_2$  are the distances from  $A$  atoms to the oxygen planes that are penetrated during the polarization reversal, here rescaled to a range between  $-1$  and  $1$ . The symmetry at an arbitrary  $(\xi_1, \xi_2)$  point is  $R3$ ; on the  $\xi_1 = \xi_2$  and  $\xi_1 = -\xi_2$  diagonals it is raised to  $R3c$  and  $R\bar{3}$  respectively; and at the origin ( $\xi_1 = \xi_2 = 0$ ) it reaches  $R\bar{3}c$ . Green diamonds denote the midpoint structure in the parameter space. In the LNO-type case “path1” and “path2” (filled and open red square symbols) are equivalent and equally probable, while the ordered-LNO system deterministically follows “path1” (full blue line), which becomes “path2” (dashed blue) under a relabeling  $\xi_1 \leftrightarrow \xi_2$ .

path indicated by the full blue line in Fig. 3, with the configuration always staying on one side of the  $\xi_1 = \xi_2$  diagonal. If we would reverse the convention on the definition of  $\xi_1$  and  $\xi_2$ , the system would be described by the dashed blue path in Fig. 3.

### C. Polarization reversal barrier

Using the methods described in Secs. II C and II D, we compute the relaxed structures and energies for a sequence of constrained values of our “reaction coordinate”  $\xi = \xi_1 + \xi_2$  for each material of interest. A selection of results for the energy along the path are presented in Fig. 4, and quantitative results for the energy barrier  $E_{\text{barrier}}$  and the spontaneous polarization  $P_S$  in the ground-state structure are reported in Table IV.

We find that the cations that are sandwiched in the midpoint structures of ordered-LNO candidates are Zr for  $\text{Li}_2\text{ZrTeO}_6$ , Hf for  $\text{Li}_2\text{HfTeO}_6$ , W for  $\text{Mn}_2\text{FeWO}_6$  and  $\text{Mn}_3\text{WO}_6$ , and Os for  $\text{Zn}_2\text{FeOsO}_6$ . These results are consistent with the analysis of  $\xi_1$  and  $\xi_2$  in the ground state, as mentioned in Sec. III B. We find that the energy differ-

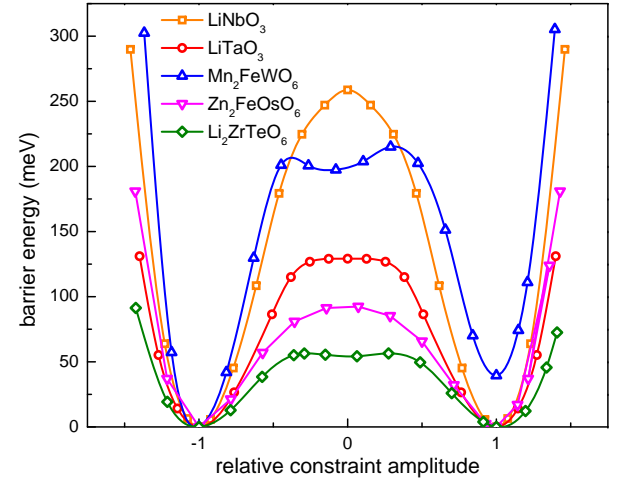


FIG. 4. The polarization reversal energy profile for  $\text{LiNbO}_3$ ,  $\text{LiTaO}_3$ ,  $\text{Mn}_2\text{FeWO}_6$ ,  $\text{Zn}_2\text{FeOsO}_6$ , and  $\text{Li}_2\text{ZrTeO}_6$ .

ence between the  $B$  and  $B'$  sandwiched midpoint structures can be attributed mainly to the Madelung energy, as shown in the Supplement. Among the computed energy barriers, those for  $\text{ZnSnO}_3$ ,  $\text{Li}_2\text{ZrTeO}_6$ ,  $\text{Li}_2\text{HfTeO}_6$ ,  $\text{Mn}_2\text{FeWO}_6$ ,  $\text{Mn}_3\text{WO}_6$ , and  $\text{Zn}_2\text{FeOsO}_6$  are lower than or comparable to those of the established FE materials  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ .

We have analyzed our calculations in an attempt to extract empirical rules of thumb that may help point in the direction of more new materials with low reversal barriers. Firstly, we have considered how the energy barriers are correlated with the spontaneous polarizations. In a FE material the energy  $E$  is often approximated as a double well of the form  $E(P) = E_0 - \mu P^2 + \nu P^4$  with positive  $\mu$  and  $\nu$ . Minimizing  $E(P)$  within this model gives the spontaneous polarization as  $P_S^2 = \mu/2\nu$  and the energy barrier  $E_{\text{barrier}} = E(0) - E(P_S) = \mu^2/4\nu$ , which can also be written as  $E_{\text{barrier}} = (\mu/2)P_S^2$ . Thus, as long as  $\mu$  can be taken as approximately constant,  $E_{\text{barrier}}$  is proportional to  $P_S^2$ . Interestingly, we find that our computed coherent barrier energies  $E_{\text{barrier}}$  roughly follow this trend with  $\mu/2 = 0.057$  as shown in Fig. 5. Therefore we suggest that FE corundum derivatives are more likely

TABLE IV. Coherent polarization reversal barrier  $E_{\text{barrier}}$  (meV) per unit cell and spontaneous polarization  $P_S$  ( $\mu\text{C}/\text{cm}^2$ ) for FE candidates.

LNO-type	$E_{\text{barrier}}$	$P_S$	Ordered-LNO	$E_{\text{barrier}}$	$P_S$
$\text{LiNbO}_3$	259	82	$\text{Li}_2\text{ZrTeO}_6$	57	33
$\text{LiTaO}_3$	129	57	$\text{Li}_2\text{HfTeO}_6$	61	32
$\text{ZnSnO}_3$	241	57	$\text{Mn}_2\text{FeWO}_6$	215	63
$\text{FeTiO}_3$	763	105	<i>uud</i> $\text{Mn}_3\text{WO}_6$	240	69
$\text{MnTiO}_3$	468	94	<i>udu</i> $\text{Mn}_3\text{WO}_6$	272	70
			$\text{Zn}_2\text{FeOsO}_6$	92	52



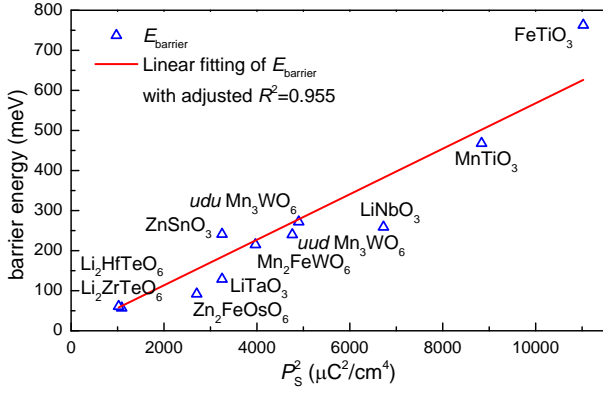


FIG. 5. Empirical proportionality between the coherent FE energy barrier and  $P_s^2$ . The red curve is the fitting polynomial  $E_{\text{barrier}} = (\mu/2)P_s^2$ , with  $\mu/2 = 0.057$ .

to be discovered in materials having a relatively low spontaneous polarization.

Furthermore, we have investigated the correlation between the spontaneous polarizations and the geometric properties of the crystals. Our results suggest that for each FE candidate, the polarization  $P$  along the reversal path is monotonically related to the reaction coordinate  $\xi$ , with the approximate relationship  $P(\xi) = m\xi + n\xi^3$ . The parameters  $m$  and  $n$  are different in each material, and they are determined by several factors that are not included in the reaction coordinate  $\xi$ , such as the displacements of the  $B$  cations and the valence states of the  $A$  cations. Despite these differences between materials, we find that the spontaneous polarizations  $P_s$  of corundum derivatives are approximately related to the reaction coordinate  $\xi_s$  in the spontaneously polarized ground state by a corresponding formula  $P_s = m\xi_s + n\xi_s^3$  with  $m = 13.3$  and  $n = 19.0$  as shown in Fig. 6. As the distance between  $A$  cations and oxygen planes can be experimentally determined, this empirical rule can provide a rough estimation of the spontaneous polarization.

#### D. Insulating vs. conducting

Our density-of-states calculations (not shown) indicate that  $\text{FeTiO}_3$  and  $\text{Mn}_2\text{FeWO}_6$  are conducting along the central portion of the polarization reversal path. A detailed analysis of the occupied  $d$  orbitals along the path reveals the reason for this metal-insulator transition. In the local octahedral environment of the ground state, the  $d$  orbitals are split into triply degenerated  $t_{2g}$  and doubly degenerated  $e_g$  orbitals. Under the threefold rotational symmetry, the  $t_{2g}$  orbitals are further split into  $a_{1g}$  and doubly degenerate  $e'_g$  irreps. The  $a_{1g}$  state has orbital character  $d_{z^2}$  with charge lobes directed along the rhombohedral axis, and since these lie closer to the neighboring cations, the energy of the  $a_{1g}$  state is lowered. Therefore, the ground-state arrangement of  $d$  or-

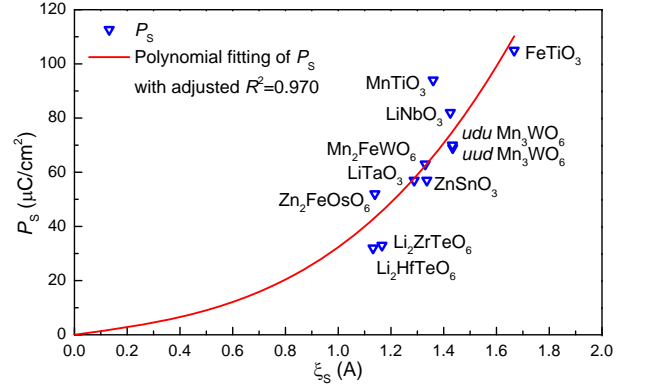


FIG. 6. Empirical correlation between the spontaneous polarization and the reaction coordinate  $\xi$  in the ground state. The red curve is the fitting polynomial  $P_s = m\xi_s + n\xi_s^3$  with  $m = 13.3$  and  $n = 19.0$ .

bitals in order of increasing energy is  $a_{1g}$  followed by  $e'_g$  and then  $e_g$ . In  $\text{FeTiO}_3$  and  $\text{Mn}_2\text{FeWO}_6$ , Fe is in the  $2+$  valence state and has a  $d^6$  configuration. In the ground state, five electrons fully occupy one spin channel and the remaining one occupies the  $a_{1g}$  orbital in the minority spin channel. However, during the polarization reversal process, the  $\text{Fe}^{2+}$  ion temporarily moves away from its neighboring cations, and as a result, the  $a_{1g}$  orbital is no longer energetically favored. Instead, the minority electron occupies the doubly degenerate  $e'_g$  orbitals, leading to a metallic state. Since a metallic state along the polarization reversal path could short out the applied bias, it may be that the switching of polarization is not possible in such cases. We propose that  $d^3$ ,  $d^5$ , and  $d^8$  orbital configurations should be much more likely to avoid this conducting problem, and are therefore more suitable targets in the search for ferroelectrically switchable magnetic corundum derivatives.

#### IV. SUMMARY

In this paper, we have proposed a method to study the coherent FE reversal path of the corundum derivative family. By analyzing the structures, we have shown that only the LNO-type and the ordered-LNO corundum derivatives can be FE in the usual sense. We have calculated the energy profiles of the reversal paths using first-principles density-functional methods. Our calculations reveal that the symmetry of the FE barrier structure is lower than that of the paraelectric phase. According to our calculations,  $\text{ZnSnO}_3$ ,  $\text{Li}_2\text{ZrTeO}_6$ ,  $\text{Li}_2\text{HfTeO}_6$ ,  $\text{Mn}_3\text{WO}_6$ , and  $\text{Zn}_2\text{FeOsO}_6$  are predicted to be possible new FE materials. We have found empirically that the energy barrier is roughly proportional to the square of the spontaneous polarization, and that the spontaneous polarization is strongly correlated with the reaction coordinate  $\xi$  in the ground state. Finally, we have also argued that magnetic corundum derivatives are unlikely

to be suitable for FE switching unless the magnetic ion is  $d^3$ ,  $d^5$  or  $d^8$ , since metallic configurations otherwise tend to appear along the FE reversal path.

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