

Ferroelectricity in Perovskites with s^0 A-Site Cations: Toward Near-Room-Temperature Multiferroics**

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Magnetic ferroelectric (FE) materials (that is, multiferroics) have received much attention and can have wide technological applications owing to the possibility of controlling their electric properties and their magnetic properties by electric fields.^[1,2] An important class of multiferroic and FE^[3] materials is based on perovskites, ABO_3 , with two different cations A and B (for example A^{2+} and B^{4+} or A^{3+} and B^{3+}), in which corner-sharing BO_6 octahedra form the three-dimensional lattice with every B_8 cube containing one A cation. An ideal cubic perovskite, in which the B–O–B bonds are linear with A located at the center of each B_8 cube (thus forming a AO_{12} polyhedron), is expected when the tolerance factor $\tau = (r_O + r_A)/\sqrt{2}(r_O + r_B)$ is unity (r_A and r_B are the ionic radii of the A and B cations, respectively, with r_O as that of the O^{2-} anion). In most cases, the A cations are small, so that $\tau < 1$ and the A–O bonds are too long to maintain the ideal cubic structure. Consequently, the A cation moves away from the center of the B_8 cube, which is accompanied by the bending of the B–O–B bonds and the rotation of the BO_6 octahedra to form a lower-coordinate AO_n polyhedron ($n < 12$) with short A–O bonds. The distortion of the ideal cubic perovskite toward a non-centrosymmetric FE structure requires another local instability apart from $\tau < 1$, namely, the second-order Jahn–Teller (SOJT) instability^[4–6] of the A-site and/or B-site cation.

As found for $PbTiO_3$,^[7] $PbVO_3$,^[8] and $BiCoO_3$,^[9] moving the A cation toward the center of one B_4 face (Figure 1a) leads to a tetragonal FE structure with space group $P4mm$. The B cations move away from the approaching A cations such that the coordinate environment of each B cation is more like a BO_5 square pyramid with shortened axial B–O

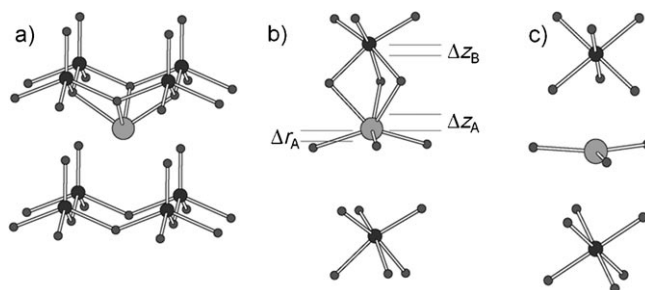


Figure 1. Perspective views of the local structures around the A cation in three perovskites ABO_3 , where the large, medium, and small circles refer to the A, B, and O atoms, respectively. a) The FE distortion in ABO_3 with space group $P4mm$. Only eight corner-sharing BO_5 square pyramids and one A cation are shown. b) The FE distortion of ABO_3 with space group $R3c$. For simplicity, only the two BO_6 octahedra at the two corners of the B_8 cube along the body-diagonal direction and the AO_3 unit lying between the two octahedra are shown. The AO_3 unit merges with the upper BO_6 octahedron to form a distorted AO_6 octahedron, which shares its face with the upper BO_6 octahedron, resulting in the face-sharing octahedral dimer ABO_9 . c) The PE structure of ABO_3 with space group $R\bar{3}c$, by which one FE structure is converted into the other FE structure with opposite polarization. The B cation in each BO_6 octahedron is located at the center of the O_6 octahedron, and the AO_3 unit lying at the midpoint between the two octahedra is planar.

bond. In $PbTiO_3$, $PbVO_3$, and $BiCoO_3$, the s^2 A-site cations Pb^{2+} and Bi^{3+} are susceptible to a SOJT distortion, which mixes the empty 6p orbital of A into the filled $6s^2$ orbital of A hence forming a lone pair on A.^[4] In $PbTiO_3$, the B-site cation Ti^{4+} (d^0) is also susceptible to a SOJT distortion, which mixes the empty Ti 3d orbitals into the filled 2p orbitals of the oxygen atom of the axial Ti–O bond.^[5,6] Thus, in $PbTiO_3$, the need to make short Pb–O bonds and the SOJT instabilities of both Pb^{2+} and Ti^{4+} ions cooperate to give rise to the observed FE distortion.^[10,11]

Another type of the A-cation displacement from the center of the B_8 cube is the movement toward one corner of the B_8 cube along the body-diagonal direction (that is, the C_3 rotational axis; Figure 1b) to form a non-centrosymmetric FE trigonal structure with space group $R3c$, as found for $BiFeO_3$.^[12] The movement of the A cation toward one corner is equivalent to that toward the opposite corner, and the two energetically-equivalent FE structures are mutually interconverted through the centrosymmetric paraelectric (PE) trigonal structure with space group $R\bar{3}c$ (Figure 1c).^[13,14] For $BiFeO_3$, the FE Curie temperature ($T_E = 1123$ K)^[15] and the three-dimensional antiferromagnetic ordering temperature ($T_N = 650$ K)^[16] are well above room temperature. For

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practical applications, it is highly desirable to find multiferroics with both T_E and T_N close to room temperature. Recently, Belik et al.^[17] have achieved a partial success toward this goal; they synthesized the indium-based multiferroics $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ ($x \approx 0.112\text{--}0.176$; $\text{M} = \text{Mn}_{0.5}\text{Fe}_{0.5}$) that have a T_N value close to room temperature; however, T_E is still high (for $x = 0.176$, $T_N \approx 270$ K and T_E is expected to be above 670 K, but the phase is transformed irreversibly to a corundum-type structure above 670 K). These multiferroics, which are isostructural with BiFeO_3 , are quite surprising in two aspects. First, magnetic ordering of a system made up of magnetic ions is generally prevented when disorder is present in the system. However, long-range magnetic ordering occurs near room temperature despite the expected disorder in the A and B sites (that is, the statistical distribution of high-spin Mn^{3+} and Fe^{3+} cations). Second, it is believed that the strong FE distortion in perovskites with s^2 A-site cations, such as BiFeO_3 , PbTiO_3 , PbVO_3 , and BiCoO_3 , arises from the need to create space for the lone pair on A. However, a strong FE distortion that is almost as strong as found for BiFeO_3 occurs in the indium-based multiferroics, although the A-site cations (In^{3+} , Mn^{3+} , and Fe^{3+}) do not possess a lone pair. Herein, we explore these puzzling observations on the basis of systematic density functional calculations for BiFeO_3 and model perovskites ABO_3 ($\text{A} = \text{Ga}, \text{In}, \text{Tl}$; $\text{B} = \text{Mn}, \text{Fe}, \text{Mn}_{0.5}\text{Fe}_{0.5}$) that simulate the indium-based multiferroics $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$.

Unless stated otherwise, our calculations were carried out for the antiferromagnetic (AFM) states of ABO_3 ($\text{A} = \text{Ga}, \text{In}, \text{Tl}$; $\text{B} = \text{Mn}, \text{Fe}, \text{Mn}_{0.5}\text{Fe}_{0.5}$) and BiFeO_3 in which all nearest-neighbor (NN) spins of the B-site cations are antiferromagnetically coupled. In the hexagonal setting of the trigonal space group $R3c$, a unit cell of these compounds has six layers of B cations perpendicular to the c axis. To simulate the random arrangement of the Mn^{3+} and Fe^{3+} ions in $\text{A}(\text{Mn}_{0.5}\text{Fe}_{0.5})\text{O}_3$, we adopted the ordered arrangement in which layers of Mn^{3+} ions alternate with layers of Fe^{3+} ions along the c direction. This arrangement is statistically most probable because each B_8 cube is given by Mn_4Fe_4 such that all NN cations are different. In our GGA + U calculations for the FE structures of ABO_3 ($\text{A} = \text{Ga}, \text{In}, \text{Tl}$; $\text{B} = \text{Mn}, \text{Fe}, \text{Mn}_{0.5}\text{Fe}_{0.5}$) and BiFeO_3 (with space group $R3c$), the positions of the atoms were fully optimized but the cell parameters were kept constant at the experimental values. The cell parameters of ABO_3 ($\text{A} = \text{Ga}, \text{In}, \text{Tl}$; $\text{B} = \text{Mn}, \text{Fe}, \text{Mn}_{0.5}\text{Fe}_{0.5}$) were fixed at those found for $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ ($x \approx 0.176$; $\text{M} = \text{Mn}_{0.5}\text{Fe}_{0.5}$).^[17]

The results of our structure optimizations for the FE structures of ABO_3 are summarized in terms of the three parameters Δr_A , Δz_A and Δz_B (Figure 1b), where Δr_A is the A-cation displacement from the center of the B_8 cube to the actual position of A in the B_8 cube; the strength of the AO_6 (BO_6) octahedron distortion is measured by the displacement Δz_A (Δz_B) from the center of the O_6 octahedron to the actual position of the A (B) cation. Given that the z axis taken along the c direction of the hexagonal setting (i.e., the body-diagonal direction of the B_8 cube; Figure 1b) shows that $\Delta z_A < 0$ and $\Delta z_B > 0$. The values of Δr_A are summarized in Table 1, and the Δz_A and Δz_B values are given in Table 2. The Δr_A values are substantial, and are largely determined by the

Table 1: Values of Δr_A calculated for ABO_3 .^[a]

A	$\text{A}(\text{Mn}_{0.5}\text{Fe}_{0.5})\text{O}_3$	AMnO_3	AFeO_3
Ga	0.588	0.550	0.593
In	0.504	0.479	0.559
Tl	0.321	0.309	0.339

[a] $\text{B} = \text{Mn}_{0.5}\text{Fe}_{0.5}$, Mn, Fe. $\Delta r_A = 0.295$ Å for BiFeO_3 .

Table 2: Values of Δz_A and Δz_B calculated for ABO_3 .^[a]

B	Parameter	GaBO_3	InBO_3	TlBO_3
$\text{Mn}_{0.5}\text{Fe}_{0.5}$	$\Delta z_B(\text{Mn})$	0.235	0.185	0.108
	$\Delta r_A(\text{Mn})$	−0.360	−0.479	−0.747
	$\Delta z_B(\text{Fe})$	0.282	0.234	0.137
	$\Delta r_A(\text{Fe})$	−0.318	−0.449	−0.720
Mn	Δz_B	0.226	0.182	0.136
	Δr_A	−0.345	−0.467	−0.745
Fe	Δz_B	0.269	0.216	0.122
	Δr_A	−0.344	−0.468	−0.732

[a] $\text{A} = \text{Ga}, \text{In}, \text{Tl}$; $\text{B} = \text{Mn}_{0.5}\text{Fe}_{0.5}$, Mn, Fe. $\Delta z_A = -0.641$ Å and $\Delta z_B = 0.193$ Å for BiFeO_3 .

A cation. For a given ABO_3 series and BiFeO_3 , the Δr_A values decrease in the order $\text{Ga}^{3+} > \text{In}^{3+} > \text{Tl}^{3+} > \text{Bi}^{3+}$, which reflects that the A-cation size increases in the order $\text{Ga}^{3+} < \text{In}^{3+} < \text{Tl}^{3+} < \text{Bi}^{3+}$. Table 2 reveals that the Δz_A and Δz_B values are substantial and are largely determined by the A cation; the $|\Delta z_A|$ values increase in the order $\text{Ga}^{3+} < \text{In}^{3+} < \text{Tl}^{3+}$, and the Δz_B values decrease with increasing $|\Delta z_A|$. The Δz_A and Δz_B values of BiFeO_3 are close to those of TlFeO_3 .

As described above, the FE distortion of the indium-based multiferroics $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ ($x \approx 0.112\text{--}0.176$; $\text{M} = \text{Mn}_{0.5}\text{Fe}_{0.5}$) is very similar in nature and magnitude to that found in BiFeO_3 , which suggests that the origin of their FE distortions is identical. The face-sharing octahedral dimer ABO_9 (Figure 1b) along the body-diagonal direction of the B_8 cube can be regarded as a result of the interaction between the BO_6 octahedron and the AO_3 pyramid (Figure 2a). As depicted in Figure 2b, the AO_3 pyramid has two hybrid orbitals ϕ_+ and ϕ_- made up of the ns and np orbitals ($n = 4, 5, 6$ for Ga^{3+} , In^{3+} , and Tl^{3+} , respectively).^[4] In the case of the s^2 cation Bi^{3+} , the ϕ_+ orbital is doubly occupied to become a lone pair, whilst the ϕ_- orbital is empty. In the case of the s^0 cations Ga^{3+} , In^{3+} and

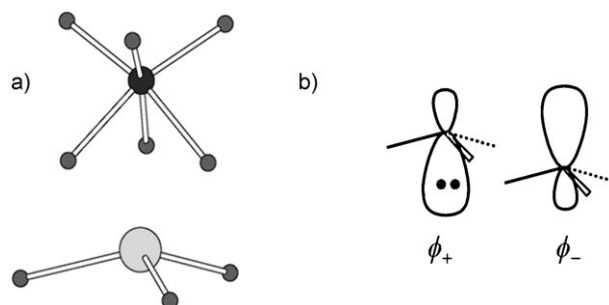


Figure 2. a) The face-sharing octahedral dimer ABO_9 in the FE structure of ABO_3 with space group $R3c$ in terms of the BO_6 octahedron and the AO_3 pyramid. b) The two hybrid orbitals ϕ_+ and ϕ_- of the AO_3 pyramid.

Ti^{3+} , both ϕ_+ and ϕ_- orbitals are empty. The energy lowering associated with the interaction of the AO_3 pyramid with the BO_6 octahedron occurs primarily from the interaction of the empty ϕ_- orbital with the filled 2p orbitals of the three oxygen atoms that form the A–O bonds. This interaction is the driving force for the SOJT distortion of the A-site cations, and is therefore independent of whether the A-site cation is an s^0 or an s^2 cation. It was shown above that the $|\Delta z_A|$ values increase in the order $\text{Ga}^{3+} < \text{In}^{3+} < \text{Tl}^{3+}$, whereas the Δz_B values decrease with increasing $|\Delta z_A|$. The extent of the A^{3+} cation displacement in the AO_6 octahedron from the center of the O_6 octahedron is related to the extension of the A^{3+} -cation np orbital ($n=4, 5$, and 6 for Ga^{3+} , In^{3+} , and Tl^{3+} , respectively); the maximum overlap of the A^{3+} cation ϕ_- orbital (hence the np orbital) with the O 2p orbitals of the three oxygen atoms forming the A–O bonds should occur at a larger $|\Delta z_A|$ value as the A cation is varied from Ga^{3+} to In^{3+} to Tl^{3+} . The involvement of the In^{3+} cation 5p orbitals in the FE distortion of the perovskite InBO_3 ($\text{B}=\text{Mn}, \text{Fe}, \text{Mn}_{0.5}\text{Fe}_{0.5}$) can be seen from the plots of the density of states (DOS) calculated for the FE and PE structures of InFeO_3 (Figure 3). The PE structure has more unoccupied

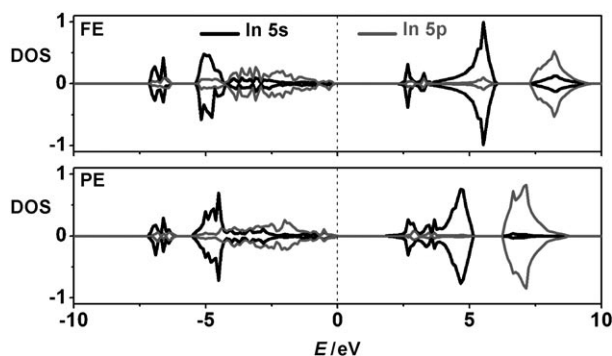


Figure 3. Plots of the projected DOS (states/eV per two formula units) calculated for the In 5s and In 5p orbitals in the FE and PE structures of InFeO_3 . The up- and down-spin densities are indicated by plus and minus DOS values, respectively.

In 5p states in a lower energy region than does the FE structure. This result means that more In 5p states are involved in bonding with the O 2p states in the FE state than in the PE state, as expected from the SOJT distortion involving the In^{3+} cation. Similar interactions should occur between the np orbitals of the A-site cation and the O 2p orbitals in the FE structure of ABO_3 with space group $P4mm$, as found for PbVO_3 .^[18]

We then examined the FE polarization of $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ ($x \approx 0.176$; $\text{M}=\text{Mn}_{0.5}\text{Fe}_{0.5}$) by considering only the perovskites AFeO_3 ($\text{A}=\text{Ga}, \text{In}, \text{Tl}$), because the FE distortion is largely determined by the A cation, as discussed above. As found for BiFeO_3 ,^[13,14] the most probable PE structure of AFeO_3 ($\text{A}=\text{Ga}, \text{In}, \text{Tl}$) has the centrosymmetric structure with space group $R\bar{3}c$.^[19] The rhombohedral setting of this structure has the positions $\text{Fe}(0,0,0)$, $\text{In}(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, and $\text{O}(x, \frac{1}{2}-x, \frac{1}{4})$. Our structure optimizations for the PE structures lead to $x=0.6023, 0.6399, 0.6405$, and 0.6707 for

GaFeO_3 , InFeO_3 , TlFeO_3 , and BiFeO_3 , respectively. Given the FE and PE structures of AFeO_3 , we calculated their FE polarizations P (along the body-diagonal direction of the B_8 cube) on the basis of the Berry phase method,^[20] which leads to 46, 74, and 139 μCcm^{-2} for GaFeO_3 , InFeO_3 , and TlFeO_3 , respectively. These values are comparable to 98.7 μCcm^{-2} calculated for BiFeO_3 .^[13,14] Experimentally, the FE polarization of $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ ^[17] is comparable in magnitude to that of BiFeO_3 ^[13,14] ($P \approx 1 \mu\text{Ccm}^{-2}$ for $x=0.143$ versus 2–6 μCcm^{-2}).

To understand why $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ ($\text{M}=\text{Mn}_{0.5}\text{Fe}_{0.5}$) has a significantly lower T_N (about 270 K for $x \approx 0.176$) than does BiFeO_3 (650 K), it is necessary to evaluate the NN spin exchange parameters J of InMO_3 ($\text{M}=\text{Mn}, \text{Fe}, \text{Mn}_{0.5}\text{Fe}_{0.5}$) and BiFeO_3 by calculating the energies of the two ordered spin states for InMO_3 and BiFeO_3 ; that is, the AFM state considered so far and the ferromagnetic (FM) state in which all NN spins are ferromagnetically coupled. By mapping the energy difference between the two states onto the corresponding energy difference expected from the spin Hamiltonian expressed in terms of J ,^[21,22] we obtain $J=-18.8, -14.6, +10.4$, and -6.1 meV for BiFeO_3 , InFeO_3 , InMnO_3 , and $\text{In}(\text{Mn}_{0.5}\text{Fe}_{0.5})\text{O}_3$, respectively. Namely, the AFM state is more stable than the FM state for InFeO_3 and $\text{In}(\text{Mn}_{0.5}\text{Fe}_{0.5})\text{O}_3$, as found for BiFeO_3 , whereas the opposite is the case for InMnO_3 .^[23,24] Note that the J value of $\text{In}(\text{Mn}_{0.5}\text{Fe}_{0.5})\text{O}_3$ is smaller than those of InFeO_3 and BiFeO_3 by a factor of about 2.5–3. In the mean field approximation,^[25] T_N scales linearly with $|J|$, so that the T_N of $\text{In}(\text{Mn}_{0.5}\text{Fe}_{0.5})\text{O}_3$ is estimated to be circa 220–260 K from $T_N=650$ K for BiFeO_3 . The latter value is quite close to that found for the indium-based multiferroics $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ ($\text{M}=\text{Mn}_{0.5}\text{Fe}_{0.5}$) (i.e., about 270 K for $x \approx 0.176$).^[17] Therefore, the three-dimensional magnetic ordering of $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ ($\text{M}=\text{Mn}_{0.5}\text{Fe}_{0.5}$) near room temperature arises from two factors: one is that the statistically most probable distribution of the Mn^{3+} and Fe^{3+} ions in the b sites leads to the three-dimensional arrangement in which the spin exchange paths between these magnetic ions are largely given by the Mn–O–Fe superexchanges; the other factor is that the Mn–O–Fe superexchange is weaker than the Fe–O–Fe superexchange by a factor of about three.

Finally, we addressed the question of how to lower T_E of perovskite multiferroics with s^0 A-site cations by considering AFeO_3 ($\text{A}=\text{Ga}, \text{In}, \text{Tl}, \text{Bi}$). It is not surprising that the indium-based multiferroics $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ ($\text{M}=\text{Mn}_{0.5}\text{Fe}_{0.5}$) have a high T_E and a high FE polarization because their FE distortion is nearly as strong as that found for BiFeO_3 . Qualitatively, T_E of AFeO_3 ($\text{A}=\text{Ga}, \text{In}, \text{Tl}, \text{Bi}$) is expected to be lowered when the stability of the FE structure with respect to the PE structure is reduced. Our calculations for the optimized FE and PE structures of AFeO_3 predict that the FE structure is more stable than the PE structure by 0.31, 0.45, 0.20, and 0.32 eV per formula unit for $\text{A}=\text{Ga}, \text{In}, \text{Tl}$, and Bi , respectively, suggesting that the tendency for the A-site cation to undergo an FE distortion should decrease in the order $\text{In}^{3+} > \text{Bi}^{3+}, \text{Ga}^{3+} > \text{Tl}^{3+}$. Therefore, TlFeO_3 would have a lower T_E value than does BiFeO_3 . It would be of interest to prepare the thallium analogue of the indium-based multi-

ferroics, such as $(\text{Ti}_{1-x}\text{M}_x)\text{MO}_3$ ($\text{M} = \text{Mn}_{0.5}\text{Fe}_{0.5}$). Another interesting compound would be $(\text{Ga}_{1-x}\text{M}_x)\text{MO}_3$ ($\text{M} = \text{Mn}_{0.5}\text{Fe}_{0.5}$), because the presence of Mn^{3+} and Fe^{3+} ions at the A-cation sites would reduce the tendency for the Ga^{3+} ions to undergo an FE distortion, thus lowering T_E .

In summary, our work explains why T_N of the indium-based multiferroic perovskites $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ ($\text{M} = \text{Mn}_{0.5}\text{Fe}_{0.5}$) is near room temperature and why the perovskites with s^0 and s^2 A-site cations have similar ferroelectric distortions. Possible perovskites with T_E lower than that of $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ are expected from $(\text{Ti}_{1-x}\text{M}_x)\text{MO}_3$ ($\text{M} = \text{Mn}_{0.5}\text{Fe}_{0.5}$) and $(\text{Ga}_{1-x}\text{M}_x)\text{MO}_3$ ($\text{M} = \text{Mn}_{0.5}\text{Fe}_{0.5}$).

Experimental Section

The calculations employed the projector-augmented wave method^[26] encoded in the Vienna ab initio simulation package,^[27] the PW91 functional form^[28] of the generalized gradient approximation (GGA), and the plane-wave cut-off energy of 400 eV. The GGA plus on-site repulsion U method^[29] (GGA + U) was used to properly describe the electron correlation associated with the Mn and Fe 3d states with several values of U for both manganese and iron. Similar results are obtained from the use of other U values, so we report only those from $U = 4.5$ eV.

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