



Above Room Temperature Ferroelectricity and Weak Ferromagnetism in $(\text{LaFeO}_3)_1/(\text{LnFeO}_3)_1$ (with Ln= Lanthanide or Y) Hybrid Improper Ferroelectrics

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Multiferroic materials

Polarization, P ↔ Magnetization, M

Where more than one ferroic properties are present in a single phase and coupled to each other.

One promising class of materials : ABO_3 perovskites

Majority of perovskite systems adopt orthorhombic Pnma structure, combining octahedral rotations about different crystallographic axes of cubic $\text{Pm}\bar{3}\text{m}$.

$\text{Pm}\bar{3}\text{m}$

M-point mode: $a^0a^0c^+$ Octahedral in-phase rotation about [001]
R-point mode: $a^+a^+c^0$ Octahedral out-of-phase rotation mode about [110]
X- point mode: Anti-polar A-site cation displacement mode

Coupling of octahedral rotation to material properties

Strong coupling with magnetic properties

Through substitution on the A-site with cations of different radii, it is possible to control the degree of rotation of BO_6 octahedra and hence the TM–O–TM bond angle that have a profound effect on the magnetic interaction between magnetic ions.

Rotation driven ferroelectricity

$\text{SrTiO}_3/\text{PbTiO}_3$ superlattice: polarization had an additional contribution due combination of two different octahedral rotations

E. Boussquet et al., Nature 452, 732 (2008)

Recent proposed design rules of octahedral rotation driven ferroelectricity

Building block
 Pnma ABO_3
Ruddlesden-Popper
N. A. Benedek et al., J. Solid State Chem. (2012) (in press)

1/1 superlattice

Double perovskite
AAB₂O₆
T-centers on both sites

(A₁A')B₂O₆
T-centers on A-sites

(A₁B')B₂O₆
T-centers on B-sites

When the inversion centers are situated only at A-sites, combination of rotation and tilt of BO_6 octahedra breaks the inversion symmetry and leads to a non-centrosymmetric structure.

J. M. Rondinelli and C. J. Fennie, Adv. Mat. 24, 1961 (2012)

The hybrid origin of ferroelectricity: "Hybrid improper ferroelectricity": $\mathcal{F} \sim Q_R Q_{1P}$

The net polarization of two consecutive AO layer along [001] direction is equal and opposite in direction, hence net polarization of the system is zero.

Inequivalent A-site displacements lead to imperfect cancellation of the layer polarization, hence generate a net polarization in the system.

Rotation driven Weak ferromagnetism and Magnetolectric effect

Breaking of inversion symmetry due to octahedral rotation turns on the Dzyaloshinskii-Moriya interaction

In Ruddlesden-Popper (CaMnO_3), CaO , one rotational mode drives the weak ferromagnetism, another manetoelctronic effect and combination of them gives ferroelectricity.

However magnetic ordering temperature ~ 115 K, which is not ideal for practical applications.

N. A. Benedek and C. J. Fennie, Phys. Rev. Lett. 106, 107204 (2011)

Present study with GGA+U: Hybrid improper ferroelectricity and weak ferromagnetism above room temperature by design

Choice of material as building block: LnFeO_3 (Ln = Lanthanide, Y): (1) Crystallize in Pnma symmetry above room temperature. (2) Order magnetically above room temperature.

$\text{LaFeO}_3/\text{YFeO}_3$:

P4/mmm ($P=0, M=0$)
 P4/mmb ($P=0, M=0$)
 Pmma ($P=0, M=0.07 \mu_B$)

Calculated phonon modes in P4/mmm structure

ω (cm^{-1})	K-point	Distortion Type	Mode
125i	Γ_5^-	FE	P_z
157i	Γ_5^-	FE	P_{xy}
252i	M_2^+	$a^0a^0c^+$	ϕ_z^-
278i	M_2^-	$a^0a^0c^+$	ϕ_z^+
277i	M_5^-	$a^+a^+c^0$	Ψ_{xy^-}

Mode Coupling: Energy Landscape

Minimum Energy Path

Mode Amplitude (Å)

$\Psi_{xy^-} \rightarrow$ Weak FM
 $\phi_z^- \rightarrow$ Linear ME coupling
 $\Psi_{xy^+} + \phi_z^+ \rightarrow$ Polarization

$\text{Pmc}2_1$ ($P=9.11 \mu\text{C}/\text{cm}^2, M=0.06 \mu_B$)

Estimated ordering temperature (T_N):
Heisenberg spin Hamiltonian: $E = E_0 - \sum_{ij} J_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j)$
 T_N within mean field: $T_N = 1/3k_B (2J_1 + 4J_2 + 8J_3 + 2J_4)$

LaYFe_2O_6	Dis. (Å)	Magnitude (meV)
J_1	3.76	5.2
J_2	3.85	5.4
J_3	5.39	0.1
J_4	5.58	0.4

Material	Computed	Experimental	Experimental: $T_N(\text{LaFeO}_3)/T_N(\text{YFeO}_3) = 1.13$
LaFeO_3 (Pnma)	1089	740	
YFeO_3 (Pnma)	968	655	Computed: $T_N(\text{LaFeO}_3)/T_N(\text{YFeO}_3) = 1.13$

Computed T_N (LaYFe_2O_6)/ T_N (LaFeO_3) = 1.044

Conclusion: Based on first principles *ab-initio* calculations we have predicted above room temperature polarization-magnetization coupling in $(\text{LaFeO}_3)_1/(\text{YFeO}_3)_1$ superlattice.

Future direction: By A-site cation mismatch in $(\text{AFeO}_3)_1/(\text{A'FeO}_3)_1$ superlattices we can gain more control over octahedral rotations and then multiferroic properties.