Strain-induced isosymmetric ferri-to-ferroelectric transition with large piezoelectricity

Gaoyang Gou$^{1,*}$ and James M. Rondinelli$^{2,†}$

$^1$Frontier Institute of Science & Technology, Xi’an Jiaotong University, Xi’an 710049, China
$^2$Department of Materials Science & Engineering, Drexel University, Philadelphia, PA 19104, USA

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We identify a first-order, isosymmetric transition between a ferrielectric (FE) and ferroelectric (FE) state in A-site ordered LaScO$_3$/BiScO$_3$ and LaInO$_3$/BiInO$_3$ superlattices. Such a previously unreported ferroic transition is driven by the easy switching of cation displacements without changing the overall polarization direction or crystallographic symmetry. Epitaxial strains less than 2% are predicted to be sufficient to transverse the phase boundary, across which we capture a $\sim$5X increase in electric polarization. In a fashion similar to classic Pb-based perovskite ceramics with a morphotropic phase boundary (MPB), we predict a large electromechanical response up to 131 pC/N in the vicinity of FiE-FE phase boundary. We propose this transition as alternative ferroic transition to obtain large piezoelectricity, with the additional advantage of operating under extreme conditions in benign chemistries and without chemical disorder.

The best piezoelectric materials belong to the functional $ABO_3$ perovskite oxide ceramic class, where a small external stimuli (mechanical stress or electric field) triggers a ferroic transition with large changes to the overall polarization. For the past few decades, the conventional approach to obtain high piezoelectricity has relied on synthesizing ferroelectric (FE) solid solutions in close proximity to a composition-induced morphotropic phase boundary (MPB). A large piezoelectric response occurs at those boundaries, across which a rotation of polarization occurs between symmetry unique polar phases. Most MPB engineering requires alloying of different FE endmembers, which introduces complexity in deciphering the microscopic origins necessary for property optimization. Therefore, identification of alternative ferroic transitions in a single-phase material suitable for generating large piezoelectricity based on new mechanisms are critical to integrating novel electroceramics into applications ranging from ultrasound imaging technology to precision actuation in micromotors.

The recent discovery of a class of hybrid improper ferroelectrics (HIF), where an electric polarization is driven by two coupled octahedral-rotation lattice modes, offer opportunities for design of ferroic materials with diverse functionalities. Typically, in A-site ordered ultra-short period 1/1 $ABO_3$/$A′BO_3$ perovskite superlattices exhibiting HIF, the electric dipoles of each cation sublattices are restricted by the symmetry of the orthorhombic $a−a−c⁺$ $BO_6$ rotation patterns in Glazer notation. Such a rotocrystalline anisotropy stabilizes a ferrielectric (FiE) state, where two of the three cation-sublattice dipoles are directed along the pseudo-cubic [110], while the third is anti-parallel to the others [110], yielding a net non-zero electric polarization. In such a layered structure, the electric polarizations of each cation-sublattice can be tuned independently—the A and B cation polarizations directly rely on the octahedral connectivity of the system. Is there a suitable way to tune the oxygen lattice topology and the polarization direction of each cation-sublattice? If answered in the affirmative, then the FiE state can be directly converted into a FE state where all cation-sublattice dipoles are in parallel alignment. Consequently, a new FiE-to-FE ferroic transition would achieve a significant polarization enhancement and large piezoelectric response in cation ordered oxides.

In this paper, we use first-principles density functional calculations to demonstrate that the polarization switching between a FiE and FE phases in HIF $ABO_3$/$A′BO_3$ perovskite superlattices is accessible with substrate-induced epitaxial strain. Specifically, we uncover a first-order isosymmetric phase transition and evaluate the feasibility of the FiE-to-FE transition through a minimum energy path (MEP) trajectory. Similar to Pb-based solid-solutions, where a large piezoelectric response occurs near the MPB driven by rotation of polarization along an easy rotation path between the rhombohedral and tetragonal FE phases, we predict a large piezoelectric response—up to 131 pC/N around the FiE-FE phase boundary, as a result of the easy polarization switching between FiE and FE phases. Lastly, the FiE-to-FE transition has the practical advantage of surviving to high temperature and at integral stoichiometry in an ordered superlattice, without introducing compositional complexity, toxicity, or a change in symmetry—features absent in conventional Pb-based piezoelectrics.

RESULTS

Models.—We select A-site ordered ultra-short period 1/1 LaMO$_3$/BiMO$_3$ perovskite superlattices, with trivalent cations $M$ = Ga, Sc and In, respectively, to guarantee the insulating behavior required to sustain an electric polarization. The 6$s^2$ stereochemical lone pair of Bi promotes structural distortions and enhanced polarizability. Lastly, each bulk $A^3+/M^{3+}O_3$ oxide forming the superlattices exhibits the targeted orthorhombic $a−a−c⁺$ octahedral rotation pattern [Fig. S1 of the Supplementary Information (SI)] reported to promote HIF.

Ground State Structures.—We search for the ground state structures by computing the phonons in the Brillouin zone of the parent $P4/mmm$ phase, i.e.,
The relative energetic stability (in meV/f.u.) with respect to the ground state [$Pmce_2|_I$] structure for various low-energy phases specified by Glazer tilt; subscripts indicate the direction of the electric polarization following the convention in Ref 21. The average tolerance factor ($\bar{\tau}$) for each perovskite superlattice is given in parentheses.

| System / Rotation | $Pmamma$ | $Pmce_2|_I$ | $Pmce_2|_II$ | $Pc$ |
|-------------------|----------|-------------|--------------|------|
| LaInO$_3$/BiInO$_3$ (0.86) | 437 | 0 | 109 | 179 |
| LaScO$_3$/BiScO$_3$ (0.89) | 338 | 0 | 57 | 170 |
| LaGaO$_3$/BiGaO$_3$ (0.94) | 97 | 0 | - | - |

We now combine the $Pnmma$ structures with the displacement vectors for $\omega_I$ and $\omega_{II}$. The symmetries of the superlattices reduce to the same polar space group $Pmc_21$ (no. 26), where the polar axis is along the pseudocubic [110] direction. Hereafter, we distinguish between the two symmetry equivalent $Pmc_21$ phases as (I) or (II), appended as a subscript to the space group label. After performing a full structural relaxation, we find that the $[Pmc_21]_I$ phase is the global ground state for all superlattices (Table I). Except for LaGaO$_3$/BiGaO$_3$, $[Pmc_21]_I$ is the next lowest energy phase, e.g., 57 meV per formula unit (f.u.) higher in energy than $[Pmc_21]_I$ in LaScO$_3$/BiScO$_3$. The small energy difference suggests transition between the two $Pmc_21$ phases may be achieved by thin film epitaxy.

To understand the energy difference between the two isosymmetric $Pmc_21$ phases, we focus on the LaScO$_3$/BiScO$_3$ superlattice, and examine its local atomic structures in more detail. Fig. 2(a) and (b) shows both polar phases projected along the [100] and [011] directions. Each possesses the same $a-\bar{a}-c^0$ rotations, but different cation displacement patterns, which become readily apparent in the layer-resolved electric polarizations [Fig. 2(c)]. $[Pmc_21]_I$ is described as a ferrielectric state, whereby a non-cancellation of anti-aligned layer dipoles ($\vec{p}_{layer}$) from the alternating LaO or BiO sublattices in the superlattice produces an overall non-zero electric polarization. In $[Pmc_21]_II$, $\vec{p}_{BiO}$ switches from anti-parallel to parallel alignment with $\vec{p}_{LaO}$. All cations displace in the same

![FIG. 1](image1.png)

(a) The $Pnmma$ paraelectric structure of the LaScO$_3$/BiScO$_3$ superlattice with the $a-\bar{a}-c^0$ rotation pattern (a). The displacement patterns of the corresponding soft phonon modes (b): $\omega_I$ with anti-parallel La-O/Bi-O in-plane displacements (left), and $\omega_{II}$ with parallel La-O/Bi-O in-plane displacements (right).

![FIG. 2](image2.png)

(a) (b) (c)

FIG. 2. Atomic structures of the two isosymmetric polar ground states ($a-\bar{a}-c^0$) with $Pmc_21$ symmetry: phase I (upper) and phase II (lower). Both top view (a) and side view (b) are shown to emphasize cation displacement directions (arrows). (c) Layer-resolved polarization $\vec{p}_{layer} = \Omega^{-1} \sum \vec{u}_i Z_i^c$, where $\Omega$ is the cell volume, $\vec{u}_i$ is the $i$ cation displacement and $Z_i^c$ is the Born effective charge. Phase I is ferrielectric (total polarization, $P = 0.12$ C/m$^2$) with anti-parallel $\vec{p}_{LaO}$ and $\vec{p}_{BiO}$, while Phase II is a normal ferroelectric ($P = 0.63$ C/m$^2$), where both $\vec{p}_{LaO}$ and $\vec{p}_{BiO}$ are oriented in the same direction.
chirality or azimuthal reorientation of molecular units served in smectic liquid-crystalline systems, 23–25 contributes less to the ground state. Connecting the octahedral rotations to the polarization to phase I [Fig. 3(c)] in the presence of a greater electrostrictive rotation amplitude that is suppressed, e.g., in ferroelectrics, displacement of \( \omega \) the polar instability occurs in the same direction, as in a conventional ferroelectric, to give a more than 5X polarization enhancement.

\[ |Pmc2_1| \] is obtained by condensation of the \( \omega_I \) soft mode, and the polar displacements are stabilized from a combination of the \( a^- a^+ e^0 \) and \( a^0 e^0 c^+ \) octahedral rotations (Fig. S1). The polarization in \[ |Pmc2_1| \] arises from the polar instability \( \omega_{1I} \) in \( Pmnn \), where cooperative displacement of all cations occur in the same direction and are opposite to the oxygen anions, as found in proper ferroelectrics, e.g., BaTiO\(_3\). Moreover, phase II has octahedral rotation amplitudes that are suppressed compared to phase I [Fig. 3(c)] in the presence of a greater electrostrictive polarization, indicating the trilinear coupling term connecting the octahedral rotations to the polarization contributes less to the ground state. 8,20

Unlike the low-temperature FiE-to-GE transitions observed in smectic liquid-crystalline systems, 23–25 where chirality or azimuthal reorientation of molecular units occurs via weak intermolecular forces, 26 in these oxide superlattices an extraordinary large energy gain derives from the steric stability of the octahedral rotations. For example, 338 eV/f.u. between the polar and paraelectric states of LaScO\(_3\)/BiScO\(_3\) viz., 48 meV/f.u. for BaTiO\(_3\), 27 which has a Curie temperature (\( T_c \)) of \( \sim 120^\circ \). As a consequence, these perovskite superlattices should have much higher ferroelectric \( T_c \)'s (\( >500^\circ \)) and persistent electric polarizations, similar to that reported for other HIF oxides. 16

**Strain-induced FiE-to-GE Transition.** The evolution of the \[ Pmc2_1 \] phases with applied epitaxial strain are examined next. Fig. 3(a) displays our calculated total energy for the two phases with respect to strain. We find in LaScO\(_3\)/BiScO\(_3\), the transition from \[ |Pmc2_1| \] to \[ |Pmc2_1| \] occurs approximately at 1.0% tensile strain. Such a transition is first-order and isosymmetric; 28 it is accompanied by a strong discontinuous increase in the overall polarization and \( c/a \) axial ratio and a reduction of the octahedral rotation amplitudes [Fig. 3(b) and (c)]. The FiE-to-GE transition also occurs in the indium superlattice, albeit at a larger strain (\( \sim 2.0\% \)), yet it is not found in the gallium compound (Fig. S5). The larger tolerance factor for the LaGaO\(_3\)/BiGaO\(_3\) reduces the energy gain between \( Pmma \) and \[ |Pmc2_1| \] (Table I), and makes the \[ |Pmc2_1| \] phase unstable. In the remainder of this paper, we focus on the strained LaScO\(_3\)/BiScO\(_3\) with an emphasis on property response enhancement near the FiE-GE transition.

The evolution of the response functions, including the dielectric permittivity and piezoelectric response, as a function of strain are computed at the DFT-level. 29 Fig. 3(d) shows that the in-plane dielectric susceptibility \( \varepsilon_{xx} \) and \( \varepsilon_{yy} \) are maximum at the FiE-to-GE transition at 1.0% tensile strain in both \[ Pmc2_1 \] phases, consistent with the first-order behavior. 30 In Fig. 3(e), we plot the piezoelectric stress constants \( \varepsilon_{ij} \), which evolve smoothly with respect to strain. The non-zero piezoelectric strain coefficients \( d_{ij} \) for the individual mono-domain FiE and FE phases at 1.0% strain are also reported in Table II. With the presence of relative small polarization and large octahedral rotation amplitudes, each polar phases displays a modest piezoelectric response, compared to...
to that of proper FE oxides without octahedral rotations (e.g., PbTiO$_3$). Similar piezoelectric responses have been reported in other hybrid-improper ferroelectric oxides as well. Despite the small piezoelectric moduli found in the individual FiE and FE phases, one should also consider the possible enhancements due to the FiE-to-FE transition in describing the macroscopic functionality.

Piezoelectricity at the FiE-to-FE Transition.—To evaluate the consequence of the FiE-to-FE transition on piezoelectricity, we first map out the energy landscape in the vicinity of the low energy phases (Fig. 4). The two-dimensional energy contours at 1.0% strain for LaScO$_3$/BiScO$_3$ are computed by varying the amplitude of the eigenvectors of the unstable Pmma phonons. We find that the FiE $[Pmc2_1]$ and FE $[Pmc2_1]_{II}$ phases are located at minima near the major axes, separated by an energy barrier. We estimate the feasibility of the FiE-to-FE transition by calculating that barrier separating the two stable structures along a MEP obtained from the NEB method [Fig. 4(b)]. We find a small, nearly strain-independent 106 meV/f.u. barrier separating the phases, and comparable to the polarization rotation barrier in piezoelectric PbTiO$_3$, suggesting the FiE-to-FE transition should be energetically accessible.

We emphasize that the change of polarization across the $[Pmc2_1] \rightarrow [Pmc2_1]_{II}$ transition [Fig. 5(a)] along the MEP is mainly due to a rigid switching in direction of Bi displacements along [110] direction above and below the ScO$_2$ layers (Fig. 2). Across the phase-transition, $\vec{p}_{BiO}$ switches from anti-parallel to parallel alignment with $\vec{p}_{LaO}$ along the polar axis by decreasing its amplitude in the (001)-plane until reaching the saddle point in the energy landscape [Fig. 5(b)]. Here, a nearly random distribution of the Bi-lone pairs within the planes emerges [Fig. 5(d)]. We find a transformation of BiO$_4$ polyhedra into highly distorted BiO$_4$ tetrahedra with enhanced Bi$^{3+}$ electron lone pair activity in $[Pmc2_1]_{II}$ (Fig. S3 and Fig. S4). After the saddle point, $\vec{p}_{BiO}$ continues to increase while $\vec{p}_{LaO}$ remains nearly unchanged.

Critically, no octahedral rotation-reversal is necessary across this unusual ferroic transition; only a moderate reduction of $\approx$25% in the rotation angle amplitude is required [Fig. 5(c)]. Specifically the MEP is dominated by a large enhancement of $\Gamma_4^{-}$ polar displacements ($>5X$), while the polarization direction remains unchanged. This behavior is unique from the polarization-rotation phenomenon commonly observed in FE oxide solid solutions with MPB, where the polarization vector aligns along different crystallographic directions. The structure evolution along the polarization-switching path indicates the FiE state is directly converted into FE state without passing through any paraelectric intermediate and large polarization enhancement can be achieved through the phase-transition. Therefore a large piezoelectric response is expected in the vicinity of the FiE-FE boundary.

Since the two phases are connected by a first-order phase transition, it is experimentally likely that both the FiE and FE phases would coexist and domain-walls separating them will be formed in tensile-strained LaScO$_3$/BiScO$_3$ films, e.g., those grown epitaxially on a (001)-terminated LaLuO$_3$ substrate with a pseudo-cubic lattice constant of 4.17 Å. Thus to realistically predict the piezoelectric response across the FiE-to-FE transition, the simulation of a multi-domain structure and various domain wall (DW) configurations are necessary. We have explored several low-Miller index planes with neutral and mechanically compatible DWs to limit the number of feasible configurations to only those that are energetically...

FIG. 4. The calculated two-dimensional energy surface contours in meV for LaScO$_3$/BiScO$_3$ with respect to the soft phonons of Pmma (a). The MEP between two polar states for LaScO$_3$/BiScO$_3$ under tensile strain (b).

FIG. 5. The calculated (a) total polarization, (b) layer-revolved polarizations and (c) major crystallographic mode amplitudes for each image along the MEP connecting phase I and II in LaScO$_3$/BiScO$_3$ at 1.0% strain. The position of the saddle point along the MEP is shown as dashed line. Electronic-localization-function (ELF) surfaces within the BiO layer for phase I, the intermediate structure at the saddle point, and phase II (d). Across the FiE-to-FE transition, the Bi lone pair alignment reverses (small lobe, arrowed).
most likely to occur (Fig. S6 and Table SVII). Owing to the enormous computational overhead, we describe next only the change in layer polarizations and enhanced piezoelectric coefficients for the lowest energy multi-domain structure.

Fig. 6(a) shows the relaxed FiE-FE multi-domain configuration for the lowest energy 0°-(001) domain wall structure. It consists of two distinct FiE and FE domains (shaded regions), which have atomic structures and layer polarizations consistent with the mono-domain FiE and FE phases described earlier. No reorientation of the overall electric polarization direction or octahedral rotation sense occurs in this multi-domain state, indicating that the simulation cell is sufficiently large to capture the multi-domain ferroelectric and piezoelectric responses.

The evolution of the layer-revolved polarizations indicates that the DW structure contributes to the overall electric polarization by favoring parallel alignment of all AO and BO$_2$ dipoles along the [110] global-polarization direction in the boundary region. The $\vec{p}_{BO}$ direction switches to align along this direction in the DW region, and remarkably, the displacement patterns in the boundary region are almost identical to that found at the saddle point along the MEP [Fig. 5(b)]. Therefore, the boundary in a multi-domain FiE-FE microstructure may act as a two-dimensional “piezoelectrically active” region under an applied electric or mechanical field.

Our simulated piezoelectric coefficients for the multi-domain structure are reported in Table II. Compared to the mono-domain FiE or FE structures, both $e_{ij}$ and $d_{ij}$ tensors are significantly enhanced in the multi-domain system (>6X). The largest piezoelectric strain coefficient $d_{15}$ reaches 131 pC/N, which is comparable or even larger than that of most single crystal perovskite oxides or digitally ordered superlattices exhibiting proper ferroelectricity. The large piezoelectric response found in the multi-domain configuration originates from the DW motion under an applied mechanical strain [Fig. 6(b)]. We find that under compressive strain ($s < 0$), $\vec{p}_{BO}$ in the domain boundary region switches from alignment along the [110] to [110] direction, whereas $\vec{p}_{layer}$ from the other AO and ScO$_2$ planes are weakly modified. This FiE domain expands and dominates, creating a state with a layer polarization gradient. The DW motion also occurs for applied tensile strains ($s > 0$), except the FE domain grows at the expense of the FiE domain [greater yellow shaded region in Fig. 6(b)]. We note that during the domain wall motion process, the cations always displace along the easy polarization-switching path as determined from the MEP between FiE and FE phases [Fig. 5]. Therefore, the isosymmetric FiE-to-FE transition with the easy polarization-switching path in the A-site ordered oxide superlattices manifests as an efficient, previously underutilized, ferroic transition to obtain large piezoelectricity in material systems beyond Pb-based piezoelectric ceramics.

**SUMMARY AND CONCLUSIONS**

We use first-principles calculations combined with group theoretical studies to uncover a first-order, isosymmetric, structural transition between a FiE and FE state in artificial A-site ordered perovskite superlattices. For LaScO$_3$/BiScO$_3$, we predict 1% tensile epitaxial strain is sufficient to induce a FiE-to-FE transition with electrical features that could enable rational technology design: A perovskite superlattice with two polar states, processing a large polarization-magnitude difference, and simultaneously large piezoelectric responses driven by easy switching of cation displacements without changes to the overall polarization direction or crystallographic symmetry—features absent in conventional ferroelectric electroceramics with MPB. Second, owing to the extraordinary large energy gain between the polar and paraelectric states, the FE-to-FiE transition should persist up to high temperature ($T > 500^\circ$C), where Pb-based piezoelectrics responses are impaired. Finally, ferrielectric materials should exhibit similar electrical switching behavior as antiferroelectrics, e.g., double hysteresis loops that improve energy density capacities, yet with the advantage of operating at much lower fields, enabling practical integration for energy harvesting devices.
METHODS

Theoretical calculations.—Our density functional theory (DFT) calculations are performed with the QUANTUM ESPRESSO code, with optimized nonlocal norm-conserving pseudopotentials, a 60 Ry plane-wave cut-off. The PBEsol exchange-correlation functional is used in the calculations; it provides an improved description of the atomic structural results over LDA or PBE (Table S1). The Brillouin zone (BZ) integrations use a $8 \times 8 \times 8$ Monkhorst-Pack $k$-point grid.

Low-energy phases are obtained by performing complete structural relaxations on soft-mode generated structures until the Hellmann-Feynman forces on the atoms are less than 0.1 meV Å$^{-1}$. For the strained films, the out-of-plane lattice constant is relaxed until the stresses are less than 0.1 kbar. The FiE-FE multi-domain supercell is constructed by combining the mono-domain FiE and FE structures and separating them by adomain walls, creating a simulation cell with a total of 60 atoms, i.e., six times of the pseudocubic unit cells. Additional details of the domain wall configurations explored are found in the SI. The electronic contribution to the polarization is calculated following the Berry phase formalism. The minimum energy path (MEP) between the stable phases is simulated using the nudged elastic band (NEB) method.

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AUTHOR CONTRIBUTIONS

G.Y.G. performed the theoretical calculations. G.Y.G. and J.M.R. conceived of the research project, contributed to the analysis of the data and writing of the article.

ADDITIONAL INFORMATION

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to G.Y.G.

COMPETING FINANCIAL INTERESTS

The authors declare no competing financial interests.
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The experimental switching path will depend on many complicated extrinsic factors, including the coexistence of two mono-domains, motion of the domain-wall. However, our calculated energy barrier of the mono-domain crystal provides a reasonable estimate for the most likely intrinsic polarization switching scenario in the strained LaScO₃/BiScO₃ superlattice.

Relevant values for comparison include: $d_{33} \approx 70$ pC/N for PbTiO₃;¹³ 36 pC/N for BaTiO₃;¹⁴ 40 pC/N for KNbO₃;¹⁷ 54 pC/N for CaTiO₃/BaTiO₃ superlattices;¹⁸ and 100 pC/N for highly strained BiFeO₃ thin films.¹⁹

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