A high-energy density antiferroelectric made by interfacial electrostatic engineering

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Dielectric capacitors hold a tremendous advantage for energy storage due to their fast charge/discharge times and stability in comparison to batteries and supercapacitors. A key limitation to today’s dielectric capacitors, however, is the low storage capacity of conventional dielectric materials. To mitigate this issue, antiferroelectric materials have been proposed1, but relatively few families of antiferroelectric materials have been identified to date2–5. Here, we propose a new design strategy for the construction of lead-free antiferroelectric materials using interfacial electrostatic engineering. We begin with a ferroelectric material with one of the highest known bulk polarizations6, BiFeO3. We show that by confining atomically-precise thin layers of BiFeO3 in a dielectric matrix that we can induce a metastable antiferroelectric structure. Application of an electric field reversibly switches between this new phase and a ferroelectric state; in addition, tuning of the dielectric layer causes coexistence of the ferroelectric and antiferroelectric states. Precise engineering of the structure generates an antiferroelectric phase with energy storage comparable to that of the best lead-based materials. The use of electrostatic confinement provides a new pathway for the design of engineered antiferroelectric materials with large and potentially coupled responses.
Antiferroelectric materials have seen a resurgence of interest due to proposed applications in a number of energy efficient technologies. These technologies exploit the electric-field-triggered phase transformation from the antipolar ground state\(^7\) to an energetically low-lying polar structure\(^4,8\). Concomitant changes in the unit cell volume, entropy and stored charge can be used for applications in transducers\(^9\), electrocaloric solid-state cooling\(^10\) and high-energy storage capacitors\(^1\). Although antiferroelectricity was first discovered in the 1950s in PbZrO\(_3\) [ref. 2,3,11], most antiferroelectric materials of interest today are alloyed compounds near a morphotropist phase boundary, which reduces the energy barrier\(^12,5\).

At such morphotropist phase boundaries, the competition between distinct, low-lying ground states can lead to colossal responses from external stimuli. Driving a system to a boundary with chemical alloying, however, fundamentally reduces the polarization of the adjacent ferroelectric phase. Here we demonstrate a new design strategy for the construction of antiferroelectrics using interfacial electrostatics that both avoids chemical substitution and, driven by environmental concerns, is in a material that is lead-free\(^13\). We start with BiFeO\(_3\), one of the strongest known ferroelectric materials with a room-temperature polarization of \(~90\) \(\mu\text{C/cm}^2\) (ref. 6). BiFeO\(_3\) can adopt other structures when subjected to large compressive\(^14\) or tensile\(^15\) strain or hydrostatic pressure\(^16\) and additional low-energy polymorphs have been identified by density functional theory (DFT) calculations\(^6,17–19\). We show that interfacial electrostatic boundary conditions imposed on a confined layer\(^20–22\) can stabilize a new antipolar phase\(^23\). An applied electric field recovers the ferroelectric state: switching field and thus the storage capacity can be tuned with the interfacial layer.

Figure 1a shows the ferroelectric BiFeO\(_3\) structure with \(R3c\) symmetry as well as several additional computed low energy non-polar structures. While some have been previously
proposed\textsuperscript{24}, we find a previously unidentified antiferroelectric state labelled “Pnma-AFE.” For in-plane lattice constants constrained to those of R3c BiFeO\textsubscript{3}, this structure lies 30 meV/f.u. (formula unit) above the R3c ground state and is the lowest energy non-polar state identified to date, lower in energy than both the LaFeO\textsubscript{3}-like structure with Pnma symmetry\textsuperscript{24} and the PbZrO\textsubscript{3}-like Pbam antiferroelectric structure found in R\textsubscript{x}Bi\textsubscript{1-x}FeO\textsubscript{3} (R = rare earth)\textsuperscript{25–29}. The Pnma-AFE phase (calculated lattice vectors \(a = 5.53\) Å, \(b = 11.15\) Å and \(c = 15.64\) Å) is characterized by antipolar “up-up/down-down” displacements of the bismuth ions and a “super-tilting” pattern of the oxygen octahedra that increases the unit cell in each direction (Fig. 1b). The tilt pattern is composed of alternating octahedral rotations of different amplitudes along the \(a\) and \(b\) axes, and a pair of identical clockwise octahedral rotations followed by a pair of identical counterclockwise rotations (where the clockwise pair has a different magnitude) along the \(c\)-axis; to our knowledge such a pattern has only been previously observed in NaNbO\textsubscript{3} (ref. 30). We extend Glazer notation\textsuperscript{31} to write the tilt pattern as \(a^\alpha\beta\gamma\delta\alpha^\epsilon\beta\gamma\delta\epsilon\epsilon\phi\phi\), where we retain the usual ‘\(a\)’, ‘\(b\)’, ‘\(c\)’ notation to indicate each lattice vector, but we replace the ‘+’ and ‘-’ superscripts by Greek superscripts to indicate the amplitude of the rotation (counterclockwise or clockwise if with an overline) of adjacent octahedra (no rotation would be indicated by a ‘0’ superscript).

We predict that the Pnma-AFE phase should be stabilized by appropriate choice of electrostatic boundary conditions, imposed through heteroepitaxy. Since the Pnma-AFE structure is non-polar, there is no electrostatic energy cost associated with forming it in thin films, with interfaces to either other non-polar dielectric materials or vacuum. In contrast, the ferroelectric polarization of R3c BiFeO\textsubscript{3} introduces a depolarizing field in such a geometry, unless free charge carriers are available to screen the large polarization discontinuity at the interface. The total energy of the BiFeO\textsubscript{3} in the heterostructure is the sum of the electrostatic
energy (higher for the R3c structure) and the internal energy (lower for the R3c structure). Since
the screening of the depolarizing fields is proportional to the interfacial area, whereas the internal
energy is proportional to the BiFeO$_3$ volume, there is a thickness-dependent crossover between
the stabilities of the two structures, with the Pnma-AFE phase becoming lower in energy in the
thin-film limit (Fig. 1c, See Supplement for full discussion).

We demonstrate experimentally that appropriate heterostructures indeed stabilize the new
antiferroelectric phase. Superlattices of $(\text{La}_x\text{Bi}_{1-x}\text{FeO}_3)_n/(\text{BiFeO}_3)_n$ for $n = 2 – 20$ were
synthesized on (001)$_{\text{pc}}$ pseudocubic (pc) TbScO$_3$ substrates using reactive molecular-beam epitaxy. Figure 2a shows simultaneously acquired high-angle annular dark field scanning
transmission electron microscopy (HAADF-STEM) and electron energy loss spectroscopy (EELS)$^{32}$ images of a $(\text{La}_{0.4}\text{Bi}_{0.6}\text{FeO}_3)_{15}/(\text{BiFeO}_3)_{15}$ film. Chemical intermixing of lanthanum is
constrained to within a unit cell of the interface. HAADF-STEM images of the adjacent
La$_{0.4}$Bi$_{0.6}$FeO$_3$ layer show a paraelectric structure, consistent with bulk crystals of this
composition$^{28}$.

High-resolution HAADF-STEM images of the confined BiFeO$_3$ layers viewed along
different projection directions show several picometre-scale distortions from the paraelectric
phase, which can be assigned to the Pnma-AFE phase as shown in Fig. 2b-d. Corresponding
mean images obtained by averaging ten equivalent regions are shown in Fig. 2e-g, respectively.
In Fig. 2b,e the bismuth atoms are displaced in an “up-up/down-down” pattern, corresponding to
the [001] projection of the Pnma-AFE structure. This deformation results in peak splitting in the
x-ray diffraction scan corresponding to the two distinct out-of-plane lattice constants.

Figure 2c shows an additional picometre-scale modulation observed in other regions, a
twin variant of the Pnma-AFE structure. Here we observe dumbbells along the bismuth columns
with alternating layers of horizontal and diagonal pairs. Figure 2d shows a region similar to that in Fig. 2c, rotated in-plane to image along the substrate [110]₀ₚc zone axis. The diagonal dumbbells correlate to a vertically oriented “up-up/down-down” displacement of successive bismuth atoms on alternate planes. Finally, neutron scattering of the superlattice suggests a G-type antiferromagnetic structure in the BiFeO₃ layers, also found in our DFT calculations.

The relative stability of the Pnma-AFE phase and the R3c phase can be tuned by adjusting the dielectric properties of the adjoining layers (or the BiFeO₃ layer thickness). Figure 3a shows a dark-field TEM image of a (La₀.₄Bi₀.₆FeO₃)₁₅/(BiFeO₃)₁₅ sample consisting of solely the Pnma-AFE phase from the same region displayed in Fig. 2b, e. Figure 3b-d shows an (La₀.₃Bi₀.₇FeO₃)₁₅/(BiFeO₃)₁₅ sample where the more polarizable dielectric layer generates phase coexistence of the R3c ferroelectric phase and Pnma-AFE phase. Here we see areas of the R3c phase with ferroelectric domains containing 109° and 180° domain boundaries along with regions of the Pnma-AFE phase in both of the orientations displayed in Fig. 2b, e and Fig. 2c, f. As shown in the piezoresponse force microscopy image in Fig. 3e, there is phase coexistence at the micrometre-scale. We also find that the BiFeO₃ fully adopts the polar R3c structure in a (BiFeO₃)₁₅/(SrTiO₃)₁₅ superlattice given the even more polarizable SrTiO₃ layers.

Finally, we demonstrate the conversion of Pnma-AFE to a ferroelectric by applying an external electric field, E_{ext}. An applied field modifies the system energy by an amount $-\vec{P} \cdot \vec{E}_{ext}$, making the R3c phase more energetically stable than Pnma-AFE for a sufficiently high field as shown in Fig. 4a. We further compute the energy pathway between the polymorphs and find a 26 meV/f.u. kinetic switching barrier (Fig. 4b) via a pathway in which the distortion modes consisting of antipolar movements of the bismuth atoms are suppressed in favour of the cooperative bismuth displacements characteristic of the R3c phase.
Polarization-electric field hysteresis loops for three \( \text{La}_{1-x}\text{Bi}_{x}\text{FeO}_3\) \(/(\text{BiFeO}_3)_{15} \) samples of varying lanthanum concentration are shown in Fig. 4c-e and Extended Data Fig. 9. At low bias, the \((\text{La}_{0.5}\text{Bi}_{0.5}\text{FeO}_3)_{15}/(\text{BiFeO}_3)_{15} \) superlattice in Fig. 4c displays the pinched double hysteresis loop characteristic of the antiferroelectric state\(^2\). The \((\text{La}_{0.3}\text{Bi}_{0.7}\text{FeO}_3)_{15}/(\text{BiFeO}_3)_{15} \) superlattice displays ferroelectric/antiferroelectric phase-coexistence\(^20\). There is a robust polarization at zero field, but two switching events are observed in the current-voltage response: a higher field switch from the antipolar state and a lower field switch from the ferroelectric state compared to Fig. 4c. Figure 4e shows a ferroelectric \((\text{La}_{0.2}\text{Bi}_{0.7}\text{FeO}_3)_{15}/(\text{BiFeO}_3)_{15} \) superlattice, displaying ferroelectric switching at the same voltage as the second switch in Fig. 4d.

We compute the stored energy from the polarization-electric field hysteresis loops. The sample in Fig. 4c has an electrical breakdown voltage of \( \approx 2.7 \text{ MV/cm} \) with a stored energy density of \( \approx 30 \text{ J/cm}^3 \). These values place our \textit{Pnma}-AFE phase among the best reported perovskite antiferroelectrics, similar to the best relaxor materials and lead-based antiferroelectrics\(^34\). Given the tunability of the switching voltage with the composition of the adjacent dielectric layer and independently high polarization of the ferroelectric parent phase, this new \textit{Pnma}-AFE structure of BiFeO\(_3\) should be a promising candidate for high-energy density capacitor applications.

In summary, we demonstrate the use of electrostatic boundary conditions to uncover a previously metastable state of BiFeO\(_3\) that displays high energy storage. Analogous electrostatic engineering could be used to uncover “hidden” ground states in other ferroic oxides with functional structural, electrical or magnetic properties. In contrast to other methods commonly used to manipulate the ground state of oxide materials including isovalent substitution (chemical pressure) or strain engineering, interfacial electrostatic engineering could achieve continuous
tuning of the phase stability/coexistence without disorder introduced through inhomogeneous dopants or dislocations. Moreover, an applied electric field can return to the bulk ground state – as shown in Fig. 4 – which could lead to large and coupled responses. In the case of our new antiferroelectric/antiferromagnetic BiFeO$_3$, an applied electric field could potentially turn on and off magnetism with the conversion to the ferroelectric/weak ferromagnetic R3c BiFeO$_3$ parent phase.

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Figure 1. Energetics of BiFeO$_3$ ground states. a, Structure and energy of the $R3c$ ferroelectric ground state, antiferroelectric “Pnma-AFE” and Pbam states and non-polar Pnma state. Energies are given for structures with the in-plane lattice constants of the $R3c$ phase. b, Decomposition of the structure of the Pnma-AFE phase into its distortions (of symmetries $\Sigma$, $\Lambda$, $R$, $S$ and $T$) relative to the ideal cubic $Pm\bar{3}m$ perovskite: i) up-up/down-down displacements of the atoms along $[010]_{pc}$ ($\Sigma$); ii) successive up-up/down-down, zero and up-up/down-down displacements of layers bismuth atoms along the $[001]_{pc}$ direction ($\Lambda$); iii) double anti-phase tilting along $[001]_{pc}$, in which two octahedra tilt in one direction with one amplitude and the next pair tilt in the opposite direction with a different rotation angle from the first pair (combination of $R$ and $T$); and iv) commensurate super-tilting along $[100]_{pc}$ and $[010]_{pc}$, with wavevector $\pi/4a$, in which each octahedron has a distinct rotation angle and consecutive octahedra are out of phase (combination of $S$ and $T$). c, Phase stability when thin films of BiFeO$_3$ are confined between dielectric layers as shown. For thin films with an appropriate dielectric layer, the Pnma-AFE polymorph is lower in energy than the ferroelectric $R3c$ polymorph. Bismuth, iron, lanthanum and oxygen are shown in red, blue, green and grey, respectively.
Figure 2 Atomic-scale characterization of the Pnma-AFE phase of BiFeO₃ in confined (La₀.₄Bi₀.₆FeO₃)ₙ/(BiFeO₃)ₙ superlattices. a, EELS spectroscopic imaging showing the atomic concentrations of bismuth, iron and lanthanum in red, blue and green, respectively. Two different atomic-scale deformations of the BiFeO₃ layer are observed as twin variants in b and c as viewed along the [010]pc zone axis of the substrate. The atomic-scale displacements in b are calculated showing an “up-up/down-down” picoscale distortion with a 45° axis. d, A similar region to that shown in c viewed along the [110]pc zone axis. Here alternate layers of the bismuth atoms in the BiFeO₃ layer show an “up-up/down-down” deformation oriented along the vertical axis. e-g, Averaged images from the BiFeO₃ layers shown in b-d, respectively. The corresponding orientation of the Pnma-AFE unit cell is shown on each image.
Figure 3. DF-TEM images of \((\text{La}_{0.4}\text{Bi}_{0.6}\text{FeO}_3)_{15}/(\text{BiFeO}_3)_{15}\) superlattices demonstrating structural tunability with altered properties of the surrounding dielectric layer. \(a\), The \((\text{La}_{0.4}\text{Bi}_{0.6}\text{FeO}_3)_{15}/(\text{BiFeO}_3)_{15}\) superlattice imaged in Fig. 2b,e showing a coherent region of the [001]_{pc}-oriented \(Pnma\)-AFE polymorph of \(\text{BiFeO}_3\). \(b-d\), A \((\text{La}_{0.3}\text{Bi}_{0.7}\text{FeO}_3)_{15}/(\text{BiFeO}_3)_{15}\) superlattice showing phase coexistence between the \(Pnma\)-AFE and \(R3c\) polymorphs of \(\text{BiFeO}_3\). As a guide to the eye, regions of the [001]-, [210]- and rotated [210]-oriented \(Pnma\)-AFE polymorph of \(\text{BiFeO}_3\) are outlined in red, purple and green, respectively. Regions with 109° and 180° domain walls of the \(R3c\) ferroelectric phase are outlined in blue. Scale bar is 15 nm. \(e\), Piezoresponse force microscopy of the sample shown in \(b-d\) demonstrating regions of high piezo-contrast coexisting with regions of low contrast. Scale bar 0.5 µm.
Figure 4. Electric-field-induced switching between the Pnma-AFE state and the ferroelectric state of BiFeO₃. a, Application of an electric field alters the relative stability of the R3c and Pnma-AFE phases in heterostructures. For a given layer thickness/dielectric, the ferroelectric R3c phase can become more stable than the antiferroelectric Pnma-AFE phase (plotted for 15 f.u.). b, Calculation of the barrier using the nudged elastic band method. There is a 26 meV/f.u. activation barrier to switch between the phases. The reaction pathway is shown, tracing the damping of the Σ and Λ antipolar distortion modes of Pnma-AFE and increase of the polar Γ mode of R3c structure. c-e, Polarization-electric field hysteresis loops for (LaₓBi₁₋ₓFeO₃)₁₅/(BiFeO₃)₁₅ superlattices with x = 0.5, 0.3 and 0.2, respectively. Tuning the lanthanum concentration in the dielectric layer converts the structure from an antiferroelectric phase as shown in c-d to a ferroelectric structure in e.
Supplemental Information: Calculation of the relative stability of polar and non-polar layers in insulating heterostructures

Here we present the derivation of the crossover in stability from the polar $R3c$ structure of BiFeO$_3$, which is the bulk ground state, to the non-polar $Pnma$-AFE structure that becomes stable in thin-film (BiFeO$_3$)$_n$/(La$_x$Bi$_{1-x}$FeO$_3$)$_n$ heterostructures, as a function of BiFeO$_3$ film thickness. This derivation provides the physics behind Figure 1c of the main text.

In a finite slab of ferroelectric material, the termination of the polarization at the surfaces of the slab results in the formation of bound charge on both surfaces. These in turn generate a depolarizing field, given by $\varepsilon_d = \frac{-P}{\varepsilon_0 \varepsilon_r}$, where the minus sign indicates that the depolarizing field acts to oppose the polarization. Here $P$ is the component of polarization perpendicular to the interface, $\varepsilon_r$ is the relative permittivity of the material in which the field is created and $\varepsilon_0$ is the permittivity of free space. (In the case of a heterostructure with multiple ferroelectric layers, each of the layers has a depolarizing field associated with it.) There is an electrostatic energy cost per unit area,

$$E_{es} = \int_0^d dz \frac{\varepsilon_0 \varepsilon_r}{2} \varepsilon_d^2 = \frac{\varepsilon_0 \varepsilon_r}{2} \varepsilon_d^2 d$$  \hspace{1cm} (S.1)

associated with the existence of the depolarizing field, which depends on the thickness, $d$, of the ferroelectric layer.

In practice the system adopts a screening mechanism to reduce the electrostatic energy cost associated with the depolarizing field. In the absence of metallic electrodes to screen the bound surface charges, here we consider a mechanism in which free charges are generated by
electron-hole pair excitation across the intrinsic band gap, $E_g$, of BiFeO$_3$. We note that this likely provides an upper bound on the screening energy cost, since free carriers will also be available from extrinsic sources such as point defects. The screening field is given by, $\varepsilon_{scr} = \frac{\sigma}{\varepsilon_0 \varepsilon_r}$, where $\sigma$ is the areal density of free charges generated by electron-hole pair excitation, so that the total electrostatic energy cost per unit area associated with the presence of the screened polarization in the slab is:

$$E_{es} = \frac{1}{2} \varepsilon_0 \varepsilon_r (\varepsilon_d + \varepsilon_{scr})^2 d + E_{scr} = \frac{1}{2} \varepsilon_0 \varepsilon_r \left(\frac{-P}{\varepsilon_0 \varepsilon_r} - \frac{\sigma}{\varepsilon_0 \varepsilon_r}\right)^2 d + E_{scr}$$  \hspace{1cm} (S.2)

Here $E_{scr} = \frac{|\sigma|}{e} E_g$ is the energy cost per unit area of creating areal charge $\pm \sigma$ simultaneously on each interface.

The amount of screening charge is determined by a balance between the energy cost of maintaining the polarization in the presence of the depolarizing field and the energy cost of creating electron-hole pairs across the gap. To determine this we minimize

$$E_{es} = \frac{P^2}{2 \varepsilon_0 \varepsilon_r} d + \frac{\sigma^2}{2 \varepsilon_0 \varepsilon_r} d - \frac{P \sigma}{\varepsilon_0 \varepsilon_r} d + \frac{\sigma}{e} E_g$$  \hspace{1cm} (S.3)

with respect to areal charge density (assuming without loss of generality that $P > 0$ and $\sigma > 0$) by setting $\frac{\partial E_{es}}{\partial \sigma} = 0$. We obtain
for the equilibrium surface density of free screening charges.

Substituting for \( \sigma \) in our expression for the electrostatic energy per unit area we obtain

\[
\sigma = \begin{cases} 
    P - \frac{e_g e_r E_g}{2d e^-} & \text{if } d \geq \frac{e_g e_r E_g}{P e^-} \\
    0 & \text{if } d < \frac{e_g e_r E_g}{P e^-}
\end{cases} \quad (S.4)
\]

This is the additional electrostatic energy per unit area associated with the formation of the polar \( R3c \) phase over the non-polar \( Pnma \)-AFE phase. The total energies per unit area of each phase are then

\[
E_{es} = \begin{cases} 
    P \frac{E_g}{e^-} - \frac{e_g e_r}{2d} \left( \frac{E_g}{e^-} \right)^2 & \text{if } d \geq \frac{e_g e_r E_g}{P e^-} \\
    \frac{1}{2} \frac{P^2}{\varepsilon_r} & \text{if } d < \frac{e_g e_r E_g}{P e^-}
\end{cases} \quad (S.5)
\]

Where \( u_{R3c} \) and \( u_{AFE} \) are the volume energy densities of the ferroelectric \( R3c \) and antiferroelectric \( Pnma \)-AFE phases respectively, where we assume that the ferroelectric polarization \( P \) to be fixed. Taking the DFT energy values of -555.93 meV/A\(^3\) (-33.553 eV/f.u) and -555.38 meV/A\(^3\) (-33.519 eV/f.u.) respectively for the \( R3c \) and \( Pnma \)-AFE phases, together with a band gap energy of \( E_g = 2 \) eV, dielectric constant \( \varepsilon_r = 55 \) and polarization \( P_z = 60 \) μC/cm\(^2\) yields the result shown in Figure 1c. of the main text. We obtain an energetic crossover at around 130 Å.
thickness (around 30 formula units of the the $R3c$ phase), where the energy density of the polar $R3c$ phase drops below that of the $Pnma$-AFE phase.

We note two other mechanisms for reducing the electrostatic energy that could occur in our insulating samples: First, polarization of the inter-layer dielectric region, which is favored by a more polarizable dielectric with large dielectric constant$^{2,3}$, and second, the formation of domains within the ferroelectric layer. Both of these effects introduce a field into the inter-layer non-ferroelectric layer.

Figure 4a of the main text is obtained by adding a term $(-\vec{P} \cdot \vec{E}_{\text{ext}})$, where $\vec{E}_{\text{ext}}$ is an external applied field to the total energy for the case of a 15 formula unit thick film in the conditions plotted in Fig. 1c. The polar phase is favoured for a field of 1.4 kV/cm.