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Artificial two-dimensional polar metal by charge transfer to a ferroelectric insulator

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Integrating multiple properties in a single system is crucial for the continuous developments in electronic devices. However, some physical properties are mutually exclusive in nature. Here, we report the coexistence of two seemingly mutually exclusive properties—polarity and two-dimensional conductivity—in ferroelectric $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ thin films at the $\text{LaAlO}_3/\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ interface at room temperature. The polarity of a ~ 3.2 nm $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ thin film is preserved with a two-dimensional mobile carrier density of ~ 0.05 electron per unit cell. We show that the electronic reconstruction resulting from the competition between the built-in electric field of LaAlO_3 and the polarization of $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ is responsible for this unusual two-dimensional conducting polar phase. The general concept of exploiting mutually exclusive properties at oxide interfaces via electronic reconstruction may be applicable to other strongly-correlated oxide interfaces, thus opening windows to new functional nanoscale materials for applications in novel nanoelectronics.

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Oxide interfaces provide a fertile ground for multi-functional integration because the delicate balance between spin, orbit, charge, and lattice degrees of freedom in oxides can be easily destabilized with relatively small stimuli^{1–4}. Ground-breaking examples are the coexistence of ferromagnetism and superconductivity at the $\text{LaAlO}_3/\text{SrTiO}_3$ (LAO/STO) interface although ferromagnetism is expected to destroy the pairing interaction responsible for superconductivity^{5,6}, and the coexistence of ferromagnetism and ferroelectricity at Fe/BaTiO_3 interface although ferroelectricity normally requires empty d orbitals while ferromagnetism is usually a result of partially filled d orbitals^{3,7}. Recently, polar metals, which possess another pair of seemingly mutually exclusive properties, ferroelectric-like polarity and conductivity, has attracted a flurry of interest. Traditionally, it was considered that introducing itinerant electrons into a ferroelectric can eliminate ferroelectricity and associated polarity as the electrons screen the long-range Coulomb forces, which favor a polar structure^{8–11}. However, recent first-principles calculations show that the charge rearrangements associated to electrostatic screening induces local lattice response, which favors polar distortions and that local off-centering can be sustained up to ~ 0.1 electron per unit cell (e/uc)^{11–13}, suggesting that there is no fundamental incompatibility between metallicity and polar distortions.

In recent decades, the research on polar metals has been mainly on three routes: (i) searching for native polar metals, such as LiOsO_3 ¹⁴, $\text{Bi}_5\text{Ti}_5\text{O}_{17}$ ¹⁵, $\text{Cd}_2\text{Re}_2\text{O}_7$ ¹⁶, and WTe_2 ¹⁷; (ii) doping charges into ferroelectric insulators, such as BaTiO_{3-x} ^{10,11} and CaTiO_{3-x} ¹²; and (iii) stabilizing a polar phase in an otherwise non-polar metal (NdNiO_3) by deliberate geometric design¹⁸. However, most of the research was focused on bulk polar metals and the question of whether such coexistence can occur in a two-dimensional system remains largely unexplored. In this report, we directly show that polarity and two-dimensional electron gas (2DEG) can coexist in a single phase by charge transfer doping to a ferroelectric insulator.

A promising candidate to study this problem is the interface between a “polar” oxide (LAO) and a ferroelectric ($\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$). In essence, ferroelectricity arises from the charge separation between positive and negative ions, which create a spontaneous polarization and an internal electric field. Similar to the charge separation in ferroelectrics, in the “polar” oxide LAO, the physically separated alternating stacking of charge-positive (LaO^+) and charge-negative (AlO_2^-) layers also creates a built-in electric field. The possible charge transfer generated by the potential across $\text{LaAlO}_3/\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ (LAO/BST) interface created by the difference between the electric fields in LAO and BST can thus serve as a useful method to dope electrons into ferroelectric BST. This charge transfer is possible because the polar-discontinuity, which generates the 2DEG at the LAO/STO interface is also present at the LAO/BST interface as BST have a stacking of charge-neutral $\text{Ti}^{4+}\text{O}_2^{2-}$ and $\text{Sr}^{2+}\text{O}^{2-}$ (or $\text{Ba}^{2+}\text{O}^{2-}$) layers similar to that of STO^{19,20}. We use ferroelectric BST thin films instead of the conventional BaTiO_3 (BTO) used in previous studies^{10,11} as we found that the Coulomb forces in BTO strongly localize electrons (see Supplementary Note 1 for more details), while doping Sr in BTO is known to weaken the ferroelectricity and hence improving electron mobility.

Results

Ferroelectricity of BST thin films on conducting Nb-doped STO substrate. We first check the ferroelectricity of the BST thin films by performing hysteresis loops, domain writing and reading experiments on a 10 uc BST/Nb:STO (001) sample using

piezoresponse force microscopy at room temperature (Fig. 1a). In its bulk form, the Curie temperature of BST is 105 K²¹. However, we find that the as-grown BST film is ferroelectric at room temperature in a single-domain state with a downward spontaneous polarization (pointing from BST to Nb:STO). This large Curie temperature enhancement is probably a result of strain²² and dimensional effects²³. The 180° phase change between 4 and -7 V (Fig. 1b, c) and the good domain writing and reading with both positive and negative voltages (Fig. 1d, e) indicate robust ferroelectricity in the BST thin film.

The -1.5 V voltage shift in the phase and amplitude hysteresis loops is due to the well-known imprint effect as commonly observed in other ferroelectric thin films^{24–26}. This could be collectively caused by the following mechanisms: (i) strain effect imposed on BST thin film by Nb:STO substrate²⁴, (ii) asymmetric electrostatic boundary condition caused by the different work functions between the two electrodes²⁵, (iii) defect dipole accumulation at the BST/Nb:STO interface due to interfacial diffusion of chemical species²⁶. Note that in Fig. 1e, some partial relaxation is observed, which is attributed to polarization relaxation, as is commonly observed in other ferroelectric ultrathin films, such as BaTiO_3 ²⁷.

Ferroelectricity modulated electronic transport properties of the 2DEG. Having observed room temperature ferroelectricity in BST thin film, we grew BST and LAO successively on atomically flat TiO_2 -terminated STO (001) substrates by pulsed laser deposition (PLD) to form a LAO/BST/STO heterostructure (see Supplementary Notes 2–4 for more details), where a 2DEG is observed at the LAO/BST interface. On one hand, the itinerant electrons introduced by the polar discontinuity at the LAO/BST interface tend to destroy the ferroelectricity and associated polarity of BST. On the other hand, the downward polarization of BST creates a downward electric field in LAO, which obstructs the polar-discontinuity-induced charge transfer from the LAO surface to the LAO/BST interface. The competition between the built-in electric field of LAO and the polarization of BST is exploited by varying the magnitude of the polarization of BST with different thicknesses. Figure 2 shows the electronic transport properties of a set of samples with fixed LAO thickness (15 uc) and different BST thicknesses. Figure 2a shows temperature-dependent sheet resistance (R_s - T) for these metallic samples. It should be noted that a single layer of BST with varying thicknesses deposited on STO substrate is insulating, indicating that a LAO layer is required to obtain conductivity in LAO/BST/STO heterostructure. Above 100 K, sheet resistance gradually increases with increasing BST thickness. However, a crossover in the R_s - T curves can be observed around 20–50 K and the sheet resistance dependence on BST thickness is reversed at low temperatures (2–20 K).

Carrier density gradually decreases with increasing BST thickness as the magnitude of the polarization increases (Fig. 2b)²⁷. Another feature in Fig. 2b is that the temperature-dependent carrier density (n - T) curves become less temperature dependent with increasing BST thickness and finally turns into (nearly) temperature independent when BST exceeds 8 uc (see Supplementary Notes 5 and 6 for more details). The decreasing carrier density with decreasing temperature in STO is attributed to freeze-out of oxygen-vacancy-induced carriers²⁰. The decreasing carrier density dependence on temperature indicates that the oxygen vacancies in our samples decrease with increasing BST thickness. This is confirmed by the decreasing photoluminescence (PL) intensity with increasing BST thickness in our PL measurements (see Supplementary Note 7 for more details), where the PL intensity is proportional to the oxygen vacancy concentration in STO. In addition, theoretical

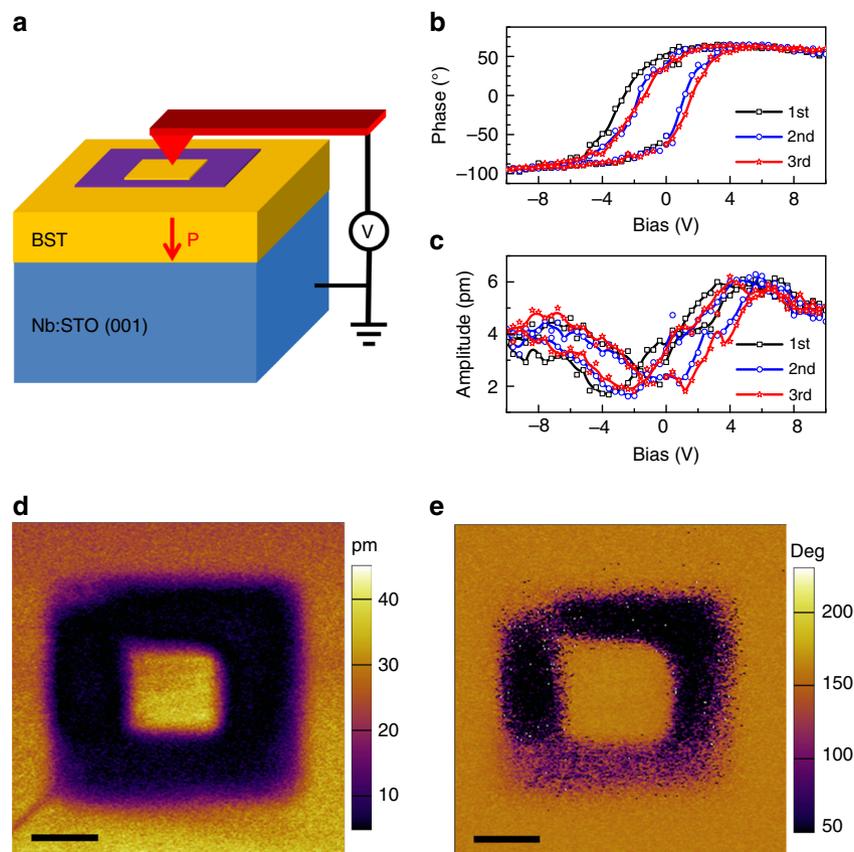


Fig. 1 Piezoresponse force microscopy characterization of a 10 unit cells of $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ thin film at room temperature. **a** Schematic diagram of the geometry for the piezoresponse force microscopy (PFM) setup, the red arrow indicates the as-grown polarization direction of $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ (BST). The Nb-doped SrTiO₃ (Nb:STO, 0.1wt% Nb doping) substrate is used as the bottom electrode. **b** Local PFM phase hysteresis loops and, **c** butterfly-like amplitude loops of the BST/Nb:STO sample, different colors stand for different voltage scans, the solid lines are guides for the eyes. **d**, **e** PFM amplitude (**d**) and phase (**e**) images ($5 \times 5 \mu\text{m}^2$) of the piezoelectric domains after application of -8 and 8 V tip bias to the 3×3 and $1 \times 1 \mu\text{m}^2$ regions, respectively. Yellow region corresponds to as-grown downward polarization, purple region represents switched upward polarization. The same color between the as-grown $5 \times 5 \mu\text{m}^2$ region and the central $1 \times 1 \mu\text{m}^2$ region indicates that the as-grown BST has a downward polarization. The scale bars in **d** and **e** are $1 \mu\text{m}$

calculations show that under reducing conditions, the oxygen vacancy formation energy in ferroelectric BTO is higher than that in STO²⁸. Hence, we conclude that the oxygen vacancy formation energy in ferroelectric BST is higher than that in paraelectric STO. When the BST thickness is below 8 uc, a 2DEG resides in both STO and BST, and a large number of oxygen-vacancy-induced carriers are present in STO. In this case, the decreasing carrier density with increasing BST thickness is a result of both the electric field effect and reduced oxygen vacancy concentration. When the BST thickness exceeds 8 uc, the 2DEG lies only in the BST and few oxygen-vacancy-induced carriers are present, leading to observation of temperature-independent carrier density. In this case, the transport properties are influenced only by the competition between the built-in electric field of LAO and the polarization of BST without the influence of oxygen vacancies, signifying the coexistence of polarity and the 2DEG above 8 uc of BST. The carrier density of the 8 uc sample is $\sim 3 \times 10^{13} \text{ cm}^{-2}$, which corresponds to ~ 0.05 e/uc. Here, we estimate the thickness of the 2DEG to be 8 uc (~ 3.2 nm). This is in good agreement with previous observations, which showed that the thickness of the 2DEG at the LAO/STO interface is around 2–4 nm^{29,30}. As discussed above, both carrier density and oxygen vacancies decrease with increasing BST thickness, leading to less electron–electron scattering and defect scattering, which consequently account for the mobility enhancement with increasing BST thickness (Fig. 2c, d).

We note the results in Fig. 2 are strikingly similar to the electric field gating experiments of LAO/STO interface^{31,32}, suggesting that the 2DEG is modulated by the electric field provided by the ferroelectric BST. We also note that the upturn of the R_s – T curve and the corresponding decreasing carrier density with decreasing temperature of the 15 uc BST sample suggest carrier localization and is consistent with Mott variable-range hopping model (see Supplementary Note 8 for more details). This behavior could be due to the strong expulsion of electrons as the BST becomes thicker, as well as increasing interfacial disorder with increasing film thickness and strain effects introduced by substrate misfit as observed in epitaxial LAO/STO systems³³.

Direct observation of the coexistence of polar displacements and 2DEG. We next turn to characterize the structural, elemental, and electronic features of a 15 uc LAO/10 uc BST/STO heterostructure with scanning transmission electron microscopy (STEM), coupled with electron energy loss spectroscopy (EELS). We detected the positions of A-site ($A = \text{La}, \text{Ba}$ or Sr), B-site ($B = \text{Al}$ or Ti), and oxygen atoms from the contrast-inverted annular-bright-field (ABF) STEM image (Fig. 3a, b and Supplementary Note 9). The BST layer shows a downward polarization, which is consistent with the as-grown BST thin film on Nb:STO (Fig. 1). The $B\text{-O}_{\text{II}}$ and $A\text{-O}_{\text{I}}$ displacements are largest at the LAO/BST interface with magnitudes as high as ~ 40 and 25 pm,

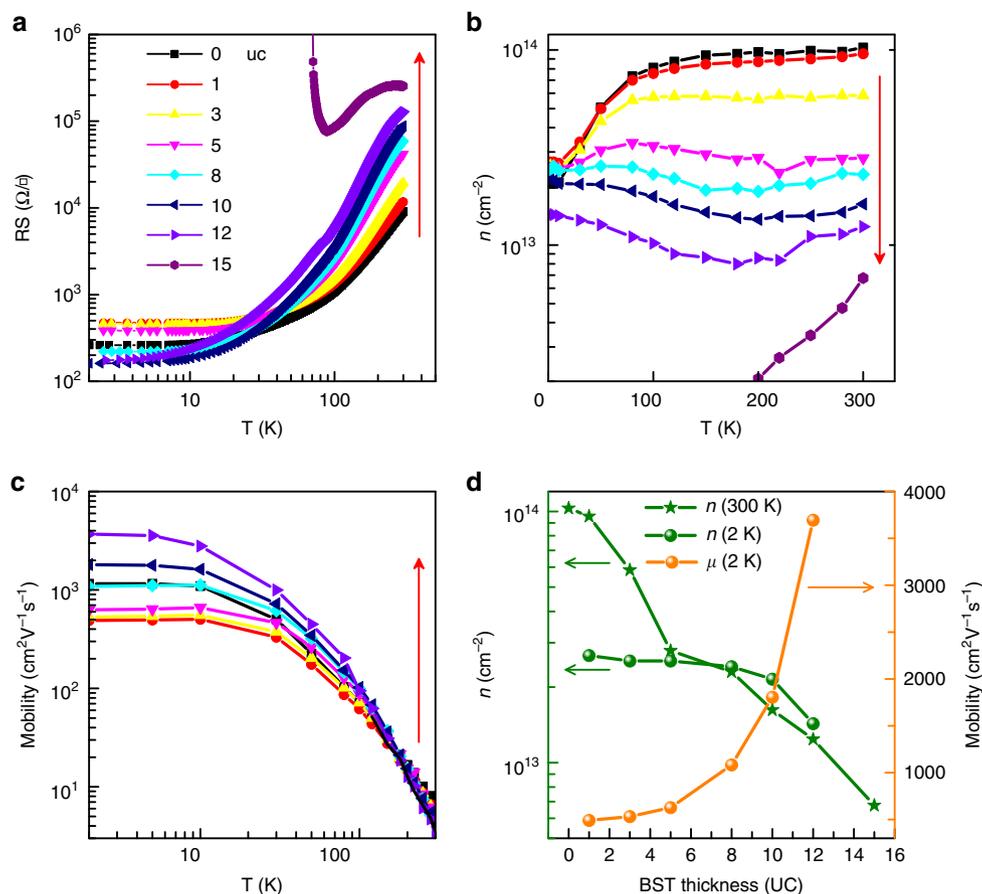


Fig. 2 Electronic transport characterization of the two-dimensional electron gas in $\text{LaAlO}_3/\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3/\text{SrTiO}_3$ heterostructure. **a–c** Temperature-dependent sheet resistance R_s (**a**), carrier density n (**b**), and mobility μ (**c**) for samples with fixed LaAlO_3 thickness (15 unit cells) and different unit cells (uc) of $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ (BST) on SrTiO_3 substrates. Different colors represent different BST thicknesses. The red arrows indicate increasing BST thickness. **d** A summary of the carrier density (at 300 and 2 K) and mobility (at 2 K) dependence on BST thickness from **b** and **c**

respectively, which are comparable to the displacements of $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films on STO substrate³⁴. The displacements gradually decrease into both LAO and STO and becomes negligibly small far away from the LAO/BST interface (Fig. 3c). The remnant displacement in LAO is probably due to BST diffusion into LAO (Fig. 4) and/or the buckling effect commonly observed in LAO/STO heterostructures^{35–37}.

STEM-EELS spectrum imaging (Fig. 3d–g) was employed to reveal the layer-by-layer elemental distribution and electronic structure by tracing the Ti $L_{2,3}$ (Fig. 3e) and O K (Fig. 3f) edges from the STO substrate to the top LAO layer. The BST/STO interface is atomically sharp, while some Ti diffusion (~ 1 uc) into the LAO layer at the LAO/BST interface is observed (Fig. 3d). The Ti valence evolution from STO and BST to the LAO/BST interface is clearly observed from the red-shift of the peak around 465 eV (Fig. 3e). In STO and BST regions far away from the LAO/BST interface, each Ti $L_{2,3}$ curve is a typical Ti^{4+} spectrum, while around the LAO/BST interface, each Ti $L_{2,3}$ curve is a mixture of Ti^{4+} and Ti^{3+} spectra. The layer-by-layer relative ratio $\text{Ti}^{3+}/(\text{Ti}^{3+} + \text{Ti}^{4+})$ grows gradually from BST to the LAO/BST interface and reaches ~ 0.2 at the interface (Fig. 3g), as evidenced via multiple linear least squares (MLLS) fitting of the experimental spectra (see Supplementary Note 10 for more details)³⁸. Another way to trace the valence state of Ti is from the O K edge, which also shows significant changes when the Ti oxidation state changes across the interface (Fig. 3f)³⁷. The energy difference between peak A and C (ΔE)

has been recognized as an accurate indicator of valence change in perovskites³⁷, the decrease of ΔE from BST to LAO/BST interface is evident in Fig. 3f–g and is related to a decrease in the Ti valence. These results unambiguously reflect a decrease of Ti valence from Ti^{4+} in BST to Ti^{3+} at the LAO/BST interface, indicating that the 2DEG lies at the LAO/BST interface and the carrier density of the 2DEG decreases away from the LAO/BST interface into the BST (Fig. 3g). The STEM and EELS results directly show that the polar displacements and Ti^{3+} (i.e. excess electrons) coexist at the LAO/BST interface in a single phase without any detectable phase separation.

First-principles calculations of the 2DEG and polar displacements in $\text{LaAlO}_3/\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3/\text{SrTiO}_3$ heterostructure. In order to investigate the relation between the charge density and polarity in LAO/BST/STO heterostructure, we performed density-functional theory (DFT)-based calculations. The profile of the conducting electron density and the displacements between anions and cations for the whole LAO/BST/STO heterostructure are shown in Fig. 4. For simplicity, instead of using a $\text{LaAlO}_3/\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3/\text{SrTiO}_3$ heterostructure as in the experiments, we used a $\text{LaAlO}_3/\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3/\text{SrTiO}_3$ heterostructure.

Our first-principles calculations were performed using DFT-based Vienna ab initio Simulation Package (VASP)^{39,40} with the local density approximation (LDA) for the exchange-correlation functional⁴¹ and the frozen-core all-electron projector-augmented wave (PAW) method^{42,43}. The cutoff energy for the

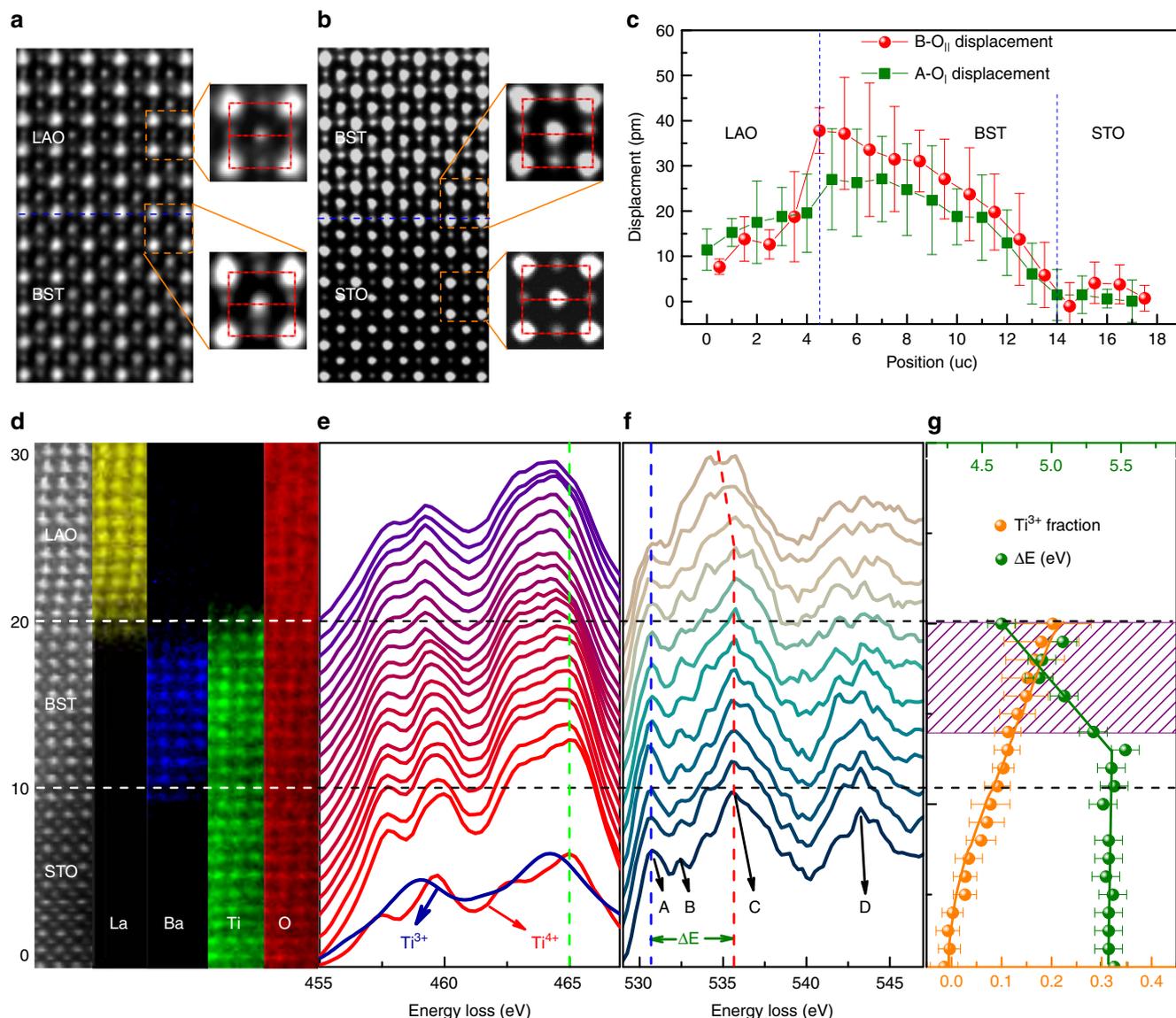


Fig. 3 Structural, elemental, and electronic characterization of a $\text{LaAlO}_3/\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3/\text{SrTiO}_3$ heterostructure. **a, b** The heterostructure has 15 unit cells (uc) of LaAlO_3 (LAO) and 10 unit cells of $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ (BST) on SrTiO_3 (STO) substrate. Atomically resolved inverted annular-bright-field scanning transmission electron microscopy (ABF-STEM) images of the LAO/BST interface (**a**) and BST/STO interface (**b**), respectively. The orange dashed squares focus on regions which are representative unit cells of LAO, the LAO/BST interface, the BST/STO interface and STO, respectively, and are enlarged for clearer view. The brighter atomic columns in the corner are A-site (Sr, Ba, La) columns and the darker columns at/near the center are B-site (Ti, Al) columns. **c** Out-of-plane B-O_{\parallel} and A-O_{\perp} displacements across the LAO/BST/STO heterostructure. **d** High-angle annular dark-field (HAADF) STEM image and electron energy loss spectroscopy (EELS) spectrum images of La $M_{4,5}$ (yellow), Ba $M_{4,5}$ (blue), Ti $L_{2,3}$ (green), and O K (red) edges. BO_2 layers are numbered from bottom to top. **e** Layer-resolved Ti $L_{2,3}$ spectra. Reference spectra for Ti^{4+} (red) and Ti^{3+} (blue) are shown at the bottom, taken from SrTiO_3 and $\text{Ti}_2\text{O}_3/\text{Al}_2\text{O}_3$, respectively. **f** Layer-resolved O K spectra, which are normalized by their respective main peaks near 535 eV. **g** Layer-resolved Ti^{3+} fraction (orange), which is defined as $\text{Ti}^{3+}/(\text{Ti}^{3+} + \text{Ti}^{4+})$, and ΔE from the O K edge (olive). The purple shaded area indicates the approximate location of the 2DEG. **e-g** are all aligned with the HAADF image and EELS spectra in **d**. The error bars show the standard deviations of the averaged measurements for each vertical atomic layer

plane wave expansion is set to 400 eV. Monkhorst-Pack k -point grids for Brillouin zone sampling are set to $6 \times 6 \times 6$ for bulk SrTiO_3 , $6 \times 6 \times 6$ for bulk LaAlO_3 , $5 \times 5 \times 6$ for bulk $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, and $5 \times 5 \times 1$ ($10 \times 10 \times 1$) for $\text{LaAlO}_3/\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3/\text{SrTiO}_3$ superlattice structure relaxation (static calculations), respectively. The structures are fully relaxed until the forces are smaller than $0.01 \text{ eV } \text{\AA}^{-1}$ for the bulk LaAlO_3 , $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, SrTiO_3 , and $0.02 \text{ eV } \text{\AA}^{-1}$ for $\text{LaAlO}_3/\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3/\text{SrTiO}_3$ superlattice structure. The equilibrium lattice constant for SrTiO_3 is 3.865 \AA . We fix the in-plane lattice constant of LaAlO_3 and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ to this number and optimize their c -axis into 3.66

and 3.96 \AA , respectively. For $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, the ratio of Ba and Sr is set to 1:1. We use $\sqrt{2} \times \sqrt{2} \times 1$ supercell for $\text{LaAlO}_3/\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3/\text{SrTiO}_3$ superlattice, which is a symmetric structure with 4.5 uc SrTiO_3 in the middle, 5 uc $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ on each of its two TiO_2 terminals, and then 3.5 LaAlO_3 on top of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$. The charge density is calculated by performing a partial charge calculation of the conduction bands below Fermi level.

The electrons mainly locate at Ti atoms in both $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ and SrTiO_3 with the largest charge density at $\text{LaAlO}_3/\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ interface (0.21 e/uc), and decays gradually from

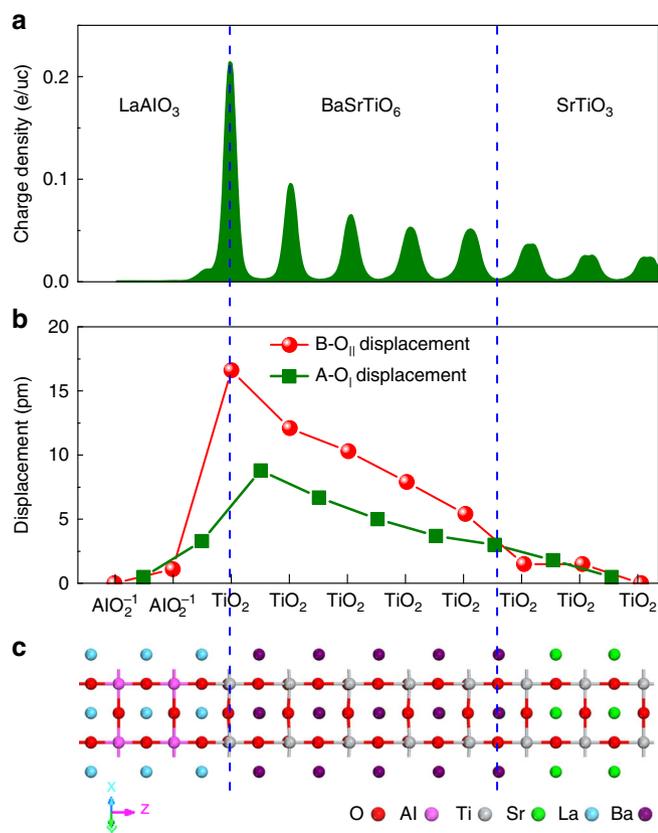


Fig. 4 First-principles calculations of the two-dimensional electron gas and polar displacements in LaAlO₃/Ba_{0.5}Sr_{0.5}TiO₃/SrTiO₃ heterostructure.

a Layer-resolved in-plane average charge density along the <001> direction. **b** Layer-resolved out-of-plane displacements of B-O_{II} (red balls) and A-O_I (green squares), respectively. **c** Structural guide of the supercell used in the calculations (only half of the structure used in the calculations is shown)

this interface into SrTiO₃ (Fig. 4a). This result agrees both qualitatively and quantitatively with the Ti³⁺ fraction analysis in Fig. 3f. The B-O_{II} and A-O_I displacements, which are in downward polarization (see Supplementary Note 11 for more details), are largest at the LaAlO₃/Ba_{0.5}Sr_{0.5}TiO₃ interface and gradually decreases into LaAlO₃ and SrTiO₃ (Fig. 4b). The trend of the calculated layer-dependent displacements well reproduces the STEM results in Fig. 3b. We note that the absolute values of the calculated displacements are around one half of those from experimental observations. This may be attributed to the underestimation of lattice constant and polarization by LDA functional, possible defects in the samples and/or measurement errors in STEM-extracted displacements. Figure 4c shows the structural guide of the supercell used in the calculations.

Discussion

Several mechanisms may contribute to the behavior of the layer-dependent displacements observed in Figs. 3 and 4: (a) A depolarizing buckling, which has been widely reported in LAO/STO heterostructure, could occur in BST to compensate the built-in electric field in LAO^{35–37}. (b) Screening of the depolarization field of BST by the insulating SrTiO₃ substrate. In an earlier report, Chisholm et al. reported that the depolarization field of PbZr_{0.2}Ti_{0.8}O₃ in PbZr_{0.2}Ti_{0.8}O₃/SrTiO₃ heterostructure could be screened by oxygen vacancies in SrTiO₃³⁴. This screening mechanism could also lead to diminishing displacement in the

first few layers of BST away from BST/STO interface. (c) Screening of ferroelectricity by itinerant electrons. As proposed by Wang et al. the critical electron density for stable polar displacement in BaTiO₃ is 0.11 e/uc¹¹. Here, we observed large Ti–O displacement (0.17 Å) at the LaAlO₃/Ba_{0.5}Sr_{0.5}TiO₃ interface with an electron density ~0.21 e/uc in Fig. 4. The discrepancy between our results and those reported by Wang et al. may be attributed to the substrate-imposed compressive strain, which has been reported to be a useful way to increase the critical electron density in BTO⁴⁴. We also note that the carrier density calculated from DFT and that extracted from EELS measurement are larger than the experimental observations (0.05 e/uc). This is probably because that some of the charges are localized in the first few layers of BST at LAO/BST interface as commonly observed at LAO/STO interface^{29,30}. To disentangle these inter-correlated mechanisms, more detailed experimental and theoretical work needs to be done. Nevertheless, the overall effect in Figs. 3 and 4 clearly suggests the coexistence of 2DEG and polarity in a single phase.

Our discoveries demonstrate a route to create a two-dimensional polar metal at oxide interface through interfacial electronic reconstruction, which is achieved by deliberately engineering the competition of the electric fields between a ferroelectric and a “polar” oxide. As coexistence of ferromagnetism and superconductivity has already been demonstrated at the LAO/STO interface^{5,6}, the integration of polarity further expands the functionality of this interface and offers new opportunities for future multifunctional devices. Moreover, the ferroelectric soft phonons could be utilized to stabilize the superconducting phase at elevated temperatures⁴⁵. We notice that during the review process of our work, a similar work by Cao et al. reported the coexistence of polarity and 2DEG in a tri-color BaTiO₃/SrTiO₃/LaTiO₃ heterostructure and we highly recommend this work to the readers of our work⁴⁶. Finally, we note that a recent publication reported an electrically switchable ferroelectric topological semimetal WTe₂¹⁷. Nevertheless, the switchability remains elusive in doped complex-oxide-based ferroelectrics, despite a previous theoretical report proposed a promising candidate Bi₅Ti₅O₁₇¹⁵.

Methods

Sample preparation. The samples were grown by PLD equipped with in situ reflection high-energy electron diffraction (RHEED). BST layer and LAO layer were successively deposited on atomically flat TiO₂-terminated STO (001) substrates at 760 °C and an oxygen pressure of 10^{−4} Torr. During the deposition, a KrF laser with a wavelength of 248 nm was used. The laser repetition was 1 Hz and the laser energy density was 1.5 J/cm². The 10 uc BST/Nb:STO (0.1 wt% Nb doped) sample was prepared under the same conditions except that no LAO was deposited. To obtain TiO₂-terminated surface, STO and Nb:STO substrates were treated with buffered hydrofluoric acid for 30 s followed by annealing at 950 °C for 1.5 h in air⁴⁷.

Piezoresponse force microscopy. Ferroelectric properties were measured using piezoresponse force microscope (PFM) and piezoresponse force spectroscopy (PFS) techniques. In this study, a commercial SPM system (MFP-3D, Asylum Research 13.03.70, USA) was used, which was controlled by a commercial software (IGOR PRO 6.34A). In the PFM measurements, amplitude (*A*) and phase (*ϕ*) images can be obtained simultaneously by applying an AC bias to the tip. The applied AC bias was 0.2 V. The amplitude image refers to piezoresponse of the material, whereas the phase image regards to the polarization direction of the material. Before the PFM measurements, DC writing processes were conducted. In these processes, dc biases of −8/8 V were sequentially applied to the conductive tip. The corresponding written areas were 3 × 3 and 1 × 1 μm², respectively. In the PFS measurement, the PFM was operated in the spectroscopy mode, the tip with a triangle-square waveform was fixed at a certain location. The frequency of the used waveform was 200 mHz, i.e., the bias-on and bias-off time was 25 ms. To exclude the electrostatic effect, the used phase hysteresis loops, *ϕ*(*E*) and amplitude loops *A*(*E*) here were obtained at bias-off state. In all the measurements, the scan rate was 1 Hz and the bottom electrode of the sample was grounded (Fig. 1a). A commercial Pt-coated Si tip (AC240TM, Olympus, Japan) with a radius of 15 nm was used in these measurements. The average spring constant is about 2 N/m, and the average resonance frequency is about 65 kHz.

Electronic transport measurements. All the electronic transport measurements (sheet resistance, carrier density, and mobility) were performed in a Van der Pauw geometry with a quantum design physical property measurement system (PPMS). The contacts of the samples were made with an aluminum wire-bonder.

Scanning transmission electron microscopy. STEM and EELS studies were conducted using a JEOL ARM200F atomic resolution analytical electron microscope equipped with a cold field-emission gun and a new ASCOR fifth-order aberration corrector and Gatan quantum ER spectrometer.

Data availability

The data that support the findings of this study are available from the corresponding author on request.

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Author contributions

W.X.Z. and A.A. conceived and designed the project. W.X.Z. and S.W.Z. prepared the samples and performed the electronic transport measurements. H.J.W., Y.Z., C.J.L. and M.S.L. performed the scanning transmission electron microscopy measurements and analysis under the supervision of S.J.P. J.Z. performed the first-principles calculations under the supervision of Y.P.F. J.X.X., R.G. and H.W. performed the piezoresponse force microscopy measurements and analysis under the supervision of K.Y.Z. and J.S.C. C.G.L. performed the photoluminescence measurements and analysis under the supervision of S.J.C. P.Y. and W.X.Z. performed the X-ray diffraction measurements and analysis. C.J.L., S.W.Z., Z.H., W.M.L., K.H., Z.S.L. and T.V. discussed the results of the project. W.X.Z., C.J.L. and A.A. prepared the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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