Article

Superfine Nanodomain Engineering Unleashing Ferroelectricity in **Incipient Ferroelectrics**

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materials owing to their potential to be engineered for exotic ferroelectric behavior, holding great promise for expanding the ferroelectric family. However, thus far, their artificially engineered ferroelectricity has fallen far short of rivaling classic ferroelectrics. In this study, we address this challenge by developing a superfine nanodomain engineering strategy. By applying this approach to representative incipient ferroelectric of SrTiO₃-based films, we achieve unprecedentedly strong ferroelectricity, not only surpassing previous records for incipient ferroelectrics but also being comparable to classic ferroelectrics. The remanent polarization of the thin film reaches up to 17.0 μ C cm⁻² with an ultrahigh Curie temperature of 973 K. Atomic-scale investigations elucidate the origin of this robust ferroelectricity in the emergent high-density superfine nanodomains spanning merely 3-10 unit cells. Combining experimental results with theoretical assessments, we unveil the underlying mechanism, where the intentionally introduced diluted foreign Fe element



creates a deeper Landau energy well and promotes a short-range ordering of polarization. Our developed strategy significantly streamlines the design of unconventional ferroelectrics, providing a versatile pathway for exploring new and superior ferroelectric materials.

1. INTRODUCTION

As essential components, ferroelectric materials are integral to the advancement of microelectronic devices, offering switchable electric dipoles and finding applications in next-generation nonvolatile memory and high-sensitivity transducers and sensors.¹⁻³ However, the stringent prerequisite for breaking the inversion symmetry limits the occurrence of ferroelectricity to a narrow range of material systems, encompassing only ten point groups.^{4,5} This constraint hampers the development and optimization of ferroelectric properties, eventually hindering their potential applications. For instance, among more than two hundred perovskite-type compounds, only a handful, such as PbTiO₃, BaTiO₃, and BiFeO₃, exhibit ferroelectric behavior.⁶ In contrast, the majority of dielectric materials (paraelectrics) lack ferroelectricity due to either their centrosymmetric crystal lattice or highly degenerate phonon structure. Consequently, addressing the challenges faced in the field of ferroelectric materials not only involves optimizing well-established ferroelectric systems but, more importantly, lies in extending ferroelectricity to numerous nonferroelectric systems. The latter endeavor holds great promise as it has the potential to significantly enrich the ferroelectric material repertoire. By exploring novel pathways to induce ferroelectric behavior in a wider range of nonferroelectric materials, we can expand the horizons of ferroelectric compounds and materials.

Incipient ferroelectrics represent a highly promising class of dielectric materials poised for engineering into ferroelectrics. This potential stems from their possession of characteristics akin to those of ferroelectric systems, such as elevation of permittivity and softening of optical phonon mode as temperature decreases.^{7,8} Although the presence of quantum fluctuation and antiferrodistortive mode in these systems often overshadow the quasi-static polar atom displacements,^{9,10} the small energy gap between the ground state and the ferroelectric state offers great opportunities to achieve a paraelectric-toferroelectric transition.¹¹⁻¹³ Exemplary instances of such incipient ferroelectric systems include SrTiO₃, KTaO₃, and CaTiO₃. To change the lattice symmetry and unlock the exotic ferroelectricity, a series of strategies, including epitaxial strain engineering,^{14,15} chemical substitution,^{16,17} defect engineering,¹⁸ and the utilization of laser excitations,^{19,20} have been utilized. However, despite these endeavors, the achieved ferroelectricity in the realm of incipient ferroelectrics still

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Figure 1. Investigations of lattice structure and chemical composition of the SrTiO₃-based epitaxial films. (a) Out-of-plane synchrotron-radiation X-ray diffraction near the (002) peak and (b) reciprocal space mapping around (103) spots of the thin film and substrate for the $x_{Fe} = 0, 0.05$, and 0.10 films. (c) Selected area electron diffraction pattern near the film–substrate interface for the $x_{Fe} = 0.05$ film along (100) zone axis. Insert is an enlarged view of the (004) and (013) spots. (d) Phi-scans of (103) spots of the film and substrate for the $x_{Fe} = 0, 0.05$, and 0.10 films. (e) Fe and Ti STEM-EELS elemental maps across the film–substrate interface, respectively. Left is the corresponding HAADF-STEM image. (f) Integrated profiles of the Fe and Ti EELS signals in (e).

falls short in the low magnitude of ferroelectric polarization within finite regions or a comparatively low Curie temperature $(T_{\rm C})$, preventing them from competing with classic ferroelectrics. Hence, developing an efficacious and generally applicable methodology to surmount these limitations and enhance the ferroelectric properties of incipient ferroelectrics can give full play to exploit the potential of these nonpolar materials.

In this study, through the development of the superfine nanodomain engineering method, we have achieved a strong room-temperature ferroelectricity in the representative incipient ferroelectric system, SrTiO₃-based thin film. This breakthrough was accomplished by simple adjustments of stoichiometry and Fe substitution. The resulting thin film exhibits a remarkable remanent polarization (P_r) of 17.0 μ C $\rm cm^{-2}$ with a high $T_{\rm C}$ up to 973 K. Such novel ferroelectricity was confirmed by systematic studies utilizing aberrationcorrected scanning transmission electron microscopy (STEM), second harmonic generation (SHG), piezoelectric force microscopy (PFM), and soft X-ray absorption spectroscopy (XAS). Through these investigations, we have uncovered the underlying mechanism responsible for this superior ferroelectric transition. The intentional induction of Ti/O point deficiency and the incorporation of Fe dopants significantly reduce the local symmetry, leading to the formation of high-density and ultrafine polar nanodots comprising only 3-10 unit cells. Consequently, the intrinsic cubic nonpolar state is transformed into a noncentrosymmetric polar state. Such a scenario is well captured by in-depth theoretical calculations. Importantly, the methodology developed in this study has broad applicability to various paraelectric materials, simplifying the design of unconventional

ferroelectrics and opening new avenues for the discovery and development of materials with superior ferroelectric properties.

2. RESULTS AND DISCUSSION

A series of thin films with varying chemical compositions $(Sr(Ti_{1-x}Fe_x)_{0.82}O_{3-\sigma})$, where $x_{Fe} = 0$, 0.05, and 0.10) were fabricated using pulsed-laser deposition (PLD). The lattice structure and chemical composition of the thin films were first investigated by synchrotron X-ray diffraction (SXRD) and scanning transmission electron microscopy (STEM). Figure 1a presents the SXRD patterns of the films. The Pendellösung fringes observed on both sides of the (002) film peak and the narrow full width at half-maximum (fwhm) ($\sim 0.05^{\circ}$) in the rocking curves (Figure S1) indicate excellent epitaxy and high crystallinity of the thin film. Notably, the (002) peak of the thin films exhibits a shift to a lower angle than that of cubic SrTiO₃ substrate, suggesting an enlarged *c* lattice constant and corresponding tetragonal distortion in the thin film. Reciprocal space mappings (RSMs) of the (103) spot and selected area electron diffraction (SAED) patterns confirm the significant tetragonality of the $x_{\text{Fe}} = 0$, 0.05, and 0.10 thin films, with a c/aratio of approximately 1.035 (Figure 1b,c). Subsequent phi scans of the (103) planes also reveal the same in-plane 4-fold symmetry in the films as that of the substrate (Figure 1d). As a comparison, the thin film with a (Ti+Fe)/Sr ratio of 1:1 shows negligible tetragonality, indicating that lattice distortion mainly originates from the deficiency state at the B site (Figures 1a, S2, and S3). The chemical composition of the thin film was analyzed using electron energy-loss spectroscopy (EELS) mapping and energy-dispersive characteristic X-ray spectroscopy (EDXS) (Figures 1e,f, S4, and S5). It can be seen that the substituted Fe elements and the concomitantly introduced Ti

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Figure 2. Ferroelectric properties of the SrTiO₃-based thin films. (a) Ferroelectric hysteresis loop of the $x_{Fe} = 0.05$ system. (b) Electrically manipulated box-in-box phase pattern using piezoelectric force microscopy. Overlaid profile represents the change in phase angle corresponding to the yellow dotted line in the phase pattern. (c) Leakage current density vs electric field curves of the $x_{Fe} = 0$, 0.05, and 0.10 films. (d) Schematic diagram of reflective SHG measurements. (e) *P*-out and (f) *S*-out SHG polar plots for the $x_{Fe} = 0$ and $x_{Fe} = 0.05$ system (dots) and fitting results (lines), respectively. (g) A comparison of P_r and SHG intensity for the $x_{Fe} = 0$ and $x_{Fe} = 0.05$ films. (h) Lattice parameters *a*, *c*, and tetragonality (*c*/*a*) plots as a function of temperature obtained from *in situ* temperature-dependent XRD. (i) Performance comparison of T_C and remanent polarization of previous representative reports with the $x_{Fe} = 0.05$ film, 17,21-23 wherein the temperature in the brackets denotes the test temperature for remanent polarization.

vacancies are uniformly distributed throughout the thickness of the film. Quantitative analysis determines that the atomic ratio of (Ti + Fe)/Sr is approximately 0.82 for $x_{Fe} = 0$, 0.05, and 0.10 films, which aligns with the initial chemical design (Figures S4 and S5). These findings indicate that by making simple adjustments to the composition, the thin films can exhibit pronounced tetragonal distortion, which serves as an important structural prerequisite for the occurrence of ferroelectricity.

The ferroelectric properties of the thin films were thoroughly characterized using various techniques. The polarization–electric field (*P*–*E*) loops clearly demonstrate the distinct ferroelectric hysteresis behavior of the films at RT (Figures 2a and S6). Notably, the *P*–*E* loop of the $x_{\rm Fe} = 0.05$ thin film exhibits a remarkable $P_{\rm r}$ of 17.0 μ C cm⁻² (Figure 2a). This polarization magnitude doubles the previous world record for SrTiO₃ and stands as the highest value among the incipient

ferroelectric materials.^{17,21-23} Moreover, it is even comparable to renowned ferroelectrics such as BaTiO₃ (P_r of 30 μ C cm⁻²) and (K,Na)NbO₃ (P_r of 25 μ C cm⁻²).^{24,25} The simultaneously acquired current-electric field curve reveals two distinct current peaks at the coercive field, serving as evidence for the presence of well-established room-temperature ferroelectric order (Figure S7).²⁶ The coercive electric field (E_c) of 0.62 MV/cm for $x_{\rm Fe} = 0.05$ film also matches the typical $E_{\rm c}$ value of 0.4-1.0 MV/cm for the BaTiO₃ epitaxial films.^{27,28} Figure 2b showcases the results from piezoelectric force microscopy (PFM), which confirm the switchability of the observed ferroelectric polarization. By altering the direction of the alternating current (ac) bias voltage applied to the conductive probe, two polarization states with a consistent phase difference of 180° between the upward and downward directions can be switched, following a box-in-box pattern (Figure 2b). The atomically flat and unchanged surface



Figure 3. Atomically resolved scanning transmission electron microscopy analysis of the thin films. Atomical scale maps of polar vectors and offcenter displacement of the Sr and Ti cations overlaid on the cross-sectional HAADF image for the $x_{Fe} = 0.05$ (a and b) and for $x_{Fe} = 0$ (d and e) along (100) zone axis. Polar clusters in the image are marked by white circles. (c) Polar plots of the spontaneous polar displacements presented in (a and b) for the $x_{Fe} = 0.05$ (top) and $x_{Fe} = 0$ systems (bottom), wherein the position of the symbol represents a polar angle and magnitude (δ_{Cation}). (f) Histogram of the integrated intensities of atomic columns for the Sr site (top) and Ti/Fe site (bottom), respectively. The red profile curve is a fitting result obtained using a Gaussian function.

morphology before and after electric manipulation attests to the high quality of the film and its intrinsic ferroelectric nature (Figure S8). To evaluate the influence of defective states in the thin film, the leakage current density versus electric field was measured (Figure 2c). Despite the presence of vacancies, the thin film exhibits a remarkably low leakage conductance, comparable to that of a perfect SrTiO₃ single crystal. This suggests that proper Fe substitution can effectively capture the free charges in the film and enhance its voltage endurance. However, excessive or insufficient Fe content ($x_{Fe} = 0.10$ and 0) both lead to a higher leakage current density, thereby deteriorating the voltage endurance and ferroelectric performance (Figures 2b and S6 and further discussed in Figure 4).

To further validate the significant magnitude of the polarization strength in the $x_{\text{Fe}} = 0.05$ thin film, optical second-harmonic generation (SHG) measurements were conducted. A typical reflective SHG configuration is depicted in Figure 2d. It is well-known that SHG signals can only be generated in a polar structure lacking inversion symmetry, which provides a distinctive signature of spontaneous polarization in ferroelectric systems.^{29,30} We find that the SHG pattern can be well fitted by a 4mm point group symmetry (Figure 2e,f), aligning with the macroscopic tetragonal distortion observed in Figure 1. Notably, archetypal ferroelectrics like PbTiO₃ and BaTiO₃ also belong to this crystalline group (Space group of P4mm), where spontaneous cation displacements dominate their ferroelectric polarizations.³¹ Since the intensity of the SHG signal ($I_{2\omega}$ where ω is the

photon frequency) is directly proportional to the magnitude of spontaneous polarization ($I_{2\omega} \propto P^2$), it can thus be used to assess the strength of ferroelectric polarization.^{32,33} It is noteworthy that the SHG intensity in the $x_{\rm Fe} = 0.05$ film is much enhanced compared to that in $x_{\rm Fe} = 0$ thin film, which shows the same tendency with P_r , as shown in the inset in Figures 2g and S9.³⁴ These results all evidence a strong ferroelectric polarization under the chemical modification of Fe in the $x_{\rm Fe} = 0.05$ system.

The robustness of this ferroelectric behavior was evaluated using temperature-dependent XRD. The temperature-dependent plots for the lattice parameters *c* and *a* and c/a ratio were obtained by analyzing the in situ XRD patterns, as shown in Figure 2h. With increasing temperature, the c/a gradually increases from RT up to 973 K and then starts to decrease beyond that temperature. This, along with the dielectric peak at the same temperature, indicates that the $T_{\rm C}$ for the robust ferroelectric phase is ~973 K (Figure S10). This level of ferroelectric stability is comparable to that of supertetragonal PbTiO₃ $(T_C \sim 998 \text{ K})^{35}$ and significantly exceeds that of BaTiO₃ $(T_C \sim 403 \text{ K})^{24}$ Based on these achievements, we compare the values of P_r and T_C of the $x_{Fe} = 0.05$ system with those in previous reports on SrTiO₃-based thin films (Figure 2i).^{17,21–23} Remarkably, the ferroelectric performance of our thin film is positioned at a significantly high level in the $P_r - T_c$ diagram, validating the effectiveness of our approach for driving strong ferroelectric transition in model incipient ferroelectrics.



Figure 4. Electronic structure analysis and density-functional-theory calculations. (a) Ti $L_{3,2}$ -edge EELS spectra collected at the substrate and film parts in the $x_{Fe} = 0.05$ STEM specimen, respectively. (b) Crystal-field splitting energy (Δ_{cf}) for SrTiO₃ single crystal, $x_{Fe} = 0$, and $x_{Fe} = 0.05$ thin films, respectively, extracted from O K-edge XAS spectra. (c) Fe $L_{2,3}$ -edge EELS map for the $x_{Fe} = 0.05$ system. (d) Fe 2*p* XPS spectrum and fitting results for the $x_{Fe} = 0.05$ system. (e) Landau energy profile of the Ti/O-defect supercell (denoted as STO) and Ti/O defective supercell with Fe substitution (denoted as Fe-STO) along (001) zone axis. (f) Calculated $3 \times 3 \times 3$ supercell overlaid with spontaneous polar vectors, wherein the Sr and O atoms are eliminated for clarity, and the Ti and Fe atoms are marked by blue and brown arrows. (g) Migration energy profile of oxygen vacancies in the calculated supercell.

To investigate the microstructural origin of the emergent strong ferroelectricity of the films, atomically resolved STEM was performed along with an in-depth quantitative analysis. A low-magnification high-angle annular dark-field (HAADF) image reveals an atomically sharp interface between the film and substrate as well as a high crystallinity of the films without any detectable impurity phases or stacking faults (Figure S11), it can be speculated that Ti/O point defects exist in the thin film which leads to this unique polar tetragonal character. Notably, many abnormal nanoregions with blurry contrast appear in the ABF-STEM image (Figures S12 and S13). Quantitative analysis demonstrates that the intensity of Ti/O atom columns decreases in these nanoregions, indicating the existence of Ti/O defect in the film (Figure S13). The Ti/Odefective unit cells thereby significantly alter the symmetry of the surrounding normal SrTiO₃ lattice, contributing to the distorted nanoregions. Given this, the unit-cell-level polar vectors, off-center displacements of cations (δ_{Cation}), and c/awere mapped simultaneously using the precise atomic positions extracted from the $x_{\text{Fe}} = 0.05$ images (Figures 3ab and S14). Intriguingly, many polar nanodots, corresponding to only 3–10 unit cells, emerge inside the $x_{\rm Fe} = 0.05$ film and are randomly positioned and embedded in a nonpolar matrix (Figure 3a). These polar nanodomains feature a large δ_{Cation} up to 15–20 pm as well as a remarkable tetragonality (c/a up to ~1.15) (Figure 3a,b). The local mean of c/a is calculated as about 1.037, being in consonance with the result $(c/a \sim 1.035)$ obtained from the RSM and SAED characterizations. Thus, these unusual polar nanodomains can be considered as the source of the tetragonality and the strong ferroelectricity of the

thin films. Moreover, through a statistical analysis of the polarization directions within these superfine nanoregions (Figure 3c), we found that instead of aligning along a single direction, the polarization directions show a broad distribution, resembling a locally monoclinic phase. This observation is reminiscent of the slush state found in relaxor ferroelectrics.

In contrast to the polar nanosheets with 2-3 monolayers in the $x_{\text{Fe}} = 0$ film (Figure 3d,e), the polar nanodots in the $x_{\text{Fe}} =$ 0.05 film possess a higher density, a smaller feature size, and a diverse polar direction, indicating an increased number of domain walls in the system. This, along with incompletely aligned polarizations, enables the Fe-substituted films to suffer a stronger dipole interaction, leading to its large hysteresis upon electric field loading. The average δ_{Cation} of the whole image increases from 5.9 pm in $x_{Fe} = 0$ to 9.8 pm in $x_{Fe} = 0.05$. Combined with high-density polar nanodomains, these results demonstrate the nature of why its ferroelectric polarization is reinforced in the $x_{\rm Fe} = 0.05$ system. Furthermore, the characters of part electric dipoles in the nanodots are analogous to the polar configurations in the monoclinic, rhombohedral, or orthorhombic ferroelectric phase, suggesting a lower symmetry rather than a perfect tetragonal structure under the modulation of Fe substitution. Furthermore, the intensities of more than 15,000 atom columns, being in proportion to $Z^{1.7-2}$ (Z is the atomic number),³⁶ are extracted from the different HAADF images inside the thin film and then normalized to the mean of each image to investigate the local atom occupancy. As illustrated in Figure 3f, the distribution of Sr-site column intensities follows a Gaussian profile with an fwhm of ~ 0.17 . In comparison, it is up to 0.32 for the Ti/Fe

sublattice due to the difference in Z between Fe ($Z_{Fe} = 22$) and Ti ($Z_{Ti} = 26$). In this case, both Ti vacancies and Fe substitution substantially broaden the distribution peak of the B-site sublattice, verifying the chemical homogeneity of the Ti/Fe sites as evidenced by EDXS and EELS characterizations (Figures S15 and S16).

To get insight into the origin of the strong ferroelectric distortion in the $x_{\rm Fe}$ = 0.05 film, we conducted detailed characterizations of the electronic structure and chemical bonding states. It is well-known that to stabilize a ferroelectric state in perovskite titanates, orbital hybridization between Ti 3d and O 2p is required as an essential prerequisite.³⁷ As shown in the O K-edge and Ti L-edge EELS and XAS spectra (Figures 4a,b), a clear shift of $3d e_g$ peak to the low energy in the Ti L-edge EELS spectrum of the Fe-substituted film was observed compared with that of the single-crystalline SrTiO₃ substrate. This indicates an orbital reconstruction induced by lattice distortion since the head-to-head σ bonding between the O 2p-Ti $3d e_g$ hybridization is more susceptible to changes in the Ti–O bonding topology (length and angle) than the π interaction of $2p-3d t_{2g}$ bonding. As a result, polar off-center displacements of Ti atoms in tetragonally distorted unit cells break the degeneracy of 3-fold t_{2g} and 2-fold e_g orbits and thereby give rise to extra energy splitting from cubic SrTiO₃, as indicated by the prominently reduced crystal-field splitting energy (Δ_{cf} , energy difference between t_{2g} and e_{g}). The change in Δ_{cf} was also in line with that in the *c*-axis tensed PbTiO₃ with an enhanced ferroelectricity.³⁵ In comparison, Δ_{cf} was extracted from the O K-edge XAS spectra of the bare SrTiO₃ single crystal, $x_{\rm Fe} = 0$, and $x_{\rm Fe} = 0.05$ thin films with a better resolution, respectively (Figure 4b). The continuous reduction in Δ_{cf} is indicative of a promoted polar distortion as well as an underlying transition from a paraelectric state in a single crystal to a ferroelectric state at $x_{Fe} = 0$ film, and finally to the superior ferroelectric state at $x_{\text{Fe}} = 0.05$ film. Furthermore, the presence of Ti³⁺ that would be detrimental to ferroelectricity can also be excluded because it will shift t_{2g} and e_g to the low-energy side simultaneously and incur the unhoped conductive behavior in the perovskite ferroelectrics.³⁸ Ti 2p XPS analysis also demonstrates that the Ti³⁺ concentration, induced by Ti/O defect, is substantially decreased from $x_{\rm Fe} = 0$ to $x_{\rm Fe} = 0.05$ (Figure S17). The introduction of excessive Fe atoms creates additional oxygen vacancies acting as acceptor dopants, which in turn increases leakage current and deteriorates ferroelectricity.^{39,40} These results unambiguously identify the role of optimal Fe substitution ($x_{Fe} = 0.05$) in lowering the leakage current and promoting ferroelectricity in the system. It can be noted that the homogeneously distributed EELS signal of Fe elements with an unchanged ratio between L_2 and L_3 indicates stable valence states for substituted Fe over the whole x_{Fe} = 0.05 film (Figure 4c). The ratio between Fe^{3+} and Fe^{2+} is determined to be 1.5:1 from the Fe 2p XPS spectrum (Figure 4d).

To investigate the role of Ti/O defects and substituted Fe atoms in the strong ferroelectricity, theoretical calculations were performed. Based on the experimental observations, a 3 × 3 × 3 supercell containing Ti/O defects and substituted Fe atom was built to stimulate the actual structure of the film. It is noteworthy that the tetragonality ($c/a \sim 1.034$) of the supercell ((Ti+Fe)/Sr = 0.89, Fe/Ti = 0.043) aligns well with the experimental values ($c/a \sim 1.035$) of the $x_{\rm Fe} = 0.05$ film ((Ti+Fe)/Sr = 0.82, Fe/Ti = 0.053). As a comparison, only Fe-substituted supercell ((Ti+Fe)/Sr = 1) does not

exhibit ferroelectric distortion $(c/a \sim 1)$. This corroborates that the Ti/O defect changes the local symmetry for the emergence of polar nanodomains. Subsequently, we compare Landau energy profiles of two $3 \times 3 \times 3$ supercells with and without Fe substitution, were constructed. It can be seen that the energy profile shows a clear double well, indicating the stabilization of the ferroelectric states in the considered supercells (Figure 4e). The polarization vectors in the Fesubstituted supercell are not solely aligned in the out-of-plane (001) direction but point to a direction between (001) and (111) directions, which forms an angle of 42° within (001) direction and are consistent with experimental observations. In this regard, the Fe substation rotates the surrounding polarization and refines the polar nanodomain within the film to minimize the local gradient energy (Figures 4f, S18, and S19), indicating its key role in the formation of ultrafine nanodomains. The effect of substituted Fe on increasing the endurance of the thin film (capturing the free charge) was assessed in the following way. We further introduced charged and charge-neutral oxygen vacancies in the SrTiO₃ supercell and Fe-substituted supercell by considering the mixed states of Fe^{2+} and Fe^{3+} in the film. Then, the migration energy barriers for the oxygen vacancies were calculated and compared. As shown in Figure 4g, in the Fe-substituted SrTiO₃ system, the migration energy barrier was significantly higher than that in the pure SrTiO₃ system, regardless of the specific moving path or the charge state of the vacancies (Figure S20). This indicates that for moderate substitution of valence-tunable transition metals like $\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+}\!,$ they can form defect complexes with oxygen vacancies, making it more difficult to move under the influence of an electric field.⁴¹ The XPS results also confirm the presence of a mixture of ions in our thin film. Consequently, the leakage current is suppressed, and the voltage endurance is greatly improved in the $x_{\rm Fe} = 0.05$ film, as demonstrated by the P-E loop and leakage measurements.

3. CONCLUSIONS

In conclusion, through superfine nanodomain engineering, we have successfully achieved strong paraelectric-to-ferroelectric transition in representative incipient ferroelectric thin films. By simply adjusting the stoichiometry and applying a simple chemical modification, we induced high-density, ultrafine polar nanodomains consisting of 3-10 unit cells, which resulted in a significant ferroelectric polarization. This methodology can be extended beyond SrTiO₃ and applied to a wide range of paraelectric perovskite oxides like CaTiO₃ (Figure S21), offering new possibilities for discovering promising ferroelectric candidates. Furthermore, this approach deepens our understanding of the coupling between lattice, charge, and polarization, opening up opportunities for exploring unconventional functionalities in these materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c05281.

Experimental procedures for thin film growth, lattice and electronic structure characterization, electrical properties measurements, theoretical calculation, details about chemical composition design, and details about chemical composition and its correlation with structure and ferroelectricity (PDF)

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Notes

The authors declare no competing financial interest.

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