Domain-Wall Enhanced Pyroelectricity

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Ferroelectric domain walls are not just static geometric boundaries between polarization domains; they are, in fact, dynamic and functional interfaces with the potential for diverse technological applications. While the roles of ferroelectric domain walls in dielectric and piezoelectric responses are better understood, their impact on pyroelectric response remains underexplored. Here, the pyroelectric response of (001)-, (101)-, and (111)-oriented epitaxial heterostructures of the tetragonal ferroelectric $PbZr_{0.2}Ti_{0.8}O_3$ is probed. These differently oriented heterostructures exhibit the same type of 90° ferroelastic domain walls, but their geometry and density vary with orientation. In turn, piezoresponse force microscopy and direct pyroelectric measurements reveal that (111)-oriented heterostructures exhibit both the highest density of domain walls and pyroelectric coefficients. By varying the thickness of these (111)-oriented heterostructures (from 100 to 280 nm), the density of domain walls can be varied, and a direct correlation between domain-wall density and pyroelectric coefficients is found. Molecular-dynamics simulations confirm these findings and reveal a novel domain-wall contribution to pyroelectric response in that the volume of the material in or near the domain walls exhibits a significantly higher pyroelectric coefficient as compared to the bulk of the domains. Analysis suggests that the domain-wall material has a higher responsivity of the polarization to both external fields and temperature. This study sheds light on the microscopic origin of domain-wall contributions to pyroelectricity and provides a pathway to controlling this effect.

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I. INTRODUCTION

Pyroelectricity is an important field of study, driven (in part) by its promising applications in waste-heat energy harvesting [1,2] and thermal sensing and imaging [3-5]. In this regard, research has been directed towards exploring

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pathways to increase the pyroelectric coefficient (π) [which is defined as $(\partial P_S/\partial T)_{E,\sigma}$ or the amount of polarization $(P_{\rm S})$ change per unit temperature (T) change at a constant electric field (E) and stress (σ)] and developing highefficiency thermal-energy conversion cycles for energy conversion [6,7]. Achieving higher π values is generally accomplished by operating a material close to its ferroelectric-to-paraelectric transition temperature (i.e., the Curie temperature $T_{\rm C}$), where the polarization change is largest for a given change in temperature. The $T_{\rm C}$ of many common ferroelectrics, however, is well above room temperature, which restricts their practicality for applications operating at or near room temperature. To address this limitation, efforts have focused on lowering $T_{\rm C}$ to enhance

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 π through various approaches such as chemical substitution [8–10] and engineering of superlattice structures [11]. For instance, substituting lanthanum for bismuth in $Bi_{0.85}La_{0.15}FeO_3$ leads to a 100% increase in the π , which is attributed to a reduction in $T_{\rm C}$. Additionally, theoretical investigations of ferroelectric-dielectric superlattices (e.g., those based on PbZr_{0.3}Ti_{0.7}O₃/SrTiO₃) suggest that periodic internal electric fields arising from polarization mismatch suppress $T_{\rm C}$ to room temperature, thus leading to enhanced pyroelectric response as compared to monolithic PbZr_{0.3}Ti_{0.7}O₃ films. While an intriguing concept, direct studies of the pyroelectric response in such superlattices remain to be completed. At the same time, advancements in the study of pyroelectricity in thin films has led to new insights, particularly in manipulating domain structures in ferroelectrics through epitaxial strain [12,13] and film composition [14,15]. For example, utilizing epitaxial strain in PbZr_{0.3}Ti_{0.7}O₃ enables the modification of out-of-plane spontaneous polarization and dielectric permittivity, thereby enhancing pyroelectric properties by exploiting variations in the fraction of different ferroelectric domain types. Additionally, compositional gradients in thin films can produce large strain gradients, thereby reducing permittivity while maintaining strong pyroelectric properties [14]. Finally, studies have probed the evolution and quantified various pyroelectric contributions (e.g., intrinsic, extrinsic, dielectric, and secondary) as a function of composition in the PbZr_{1-x}Ti_xO₃ system [15].

In general, the π (under short-circuit conditions, where E = 0) is primarily composed of three main components. The intrinsic and extrinsic contributions (the combination of which is referred to as the primary pyroelectric effect) originate from temperature-induced polarization variation within the bulk of the domains and thermally induced domain-wall motion in polydomain materials, respectively. The primary pyroelectric response can be expressed as [16]

$$\pi_{\text{primary}} = \pi_{\text{intrinsic}} + \pi_{\text{extrinsic}} = \phi \left(\frac{\partial P_s}{\partial T}\right)_{\sigma} + P_s \left(\frac{\partial \phi}{\partial T}\right)_{\sigma},$$
(1)

where ϕ is the fraction of ferroelectric domains contributing to the pyroelectric response. Additionally, there can be a secondary pyroelectric effect that arises from a temperature-induced piezoelectric effect, which, in turn, can drive changes in the polarization and can be large in thin films where there is a thermal-expansion mismatch between the pyroelectric film and substrate [13,17]. While a number of studies have explored extrinsic contributions to pyroelectricity [16,18], which are defined as $P_{\rm S}(\partial\phi/\partial T)_{\sigma}$, there have not been any studies examining other potential domain-wall contributions. For example, even in classic materials such as tetragonal PbZr_{0.2}Ti_{0.8}O₃ films, producing high-density nanotwinned domain structures can lead to significantly enhanced dielectric responses arising not just from the motion of domain walls but also from the volume of the material within the domain walls responding differently from the bulk of the material (so-called stationary or frozen domain-wall effects) [19,20]. In addition, there is increasing recognition that ferroelectric domain walls (traditionally considered simply as few unit-cell-thick interfaces separating regions of different polarization orientation) are dynamic interfaces that can offer an array of functions such as nanoscale conductivity [21] and can enhance dielectric and piezoelectric susceptibilities [16,20,22,23], thus making them potentially important for an array of applications [24-26], including nonvolatile memory [27,28] and photovoltaics [29,30]. In this spirit, the current work focuses on understanding the potential for similar contributions to pyroelectric contributions from domain walls-specifically, stationary domain-wall contributions (not motional or extrinsic contributions)-and how the polarization within domain walls responds to temperature variations.

Here, the pyroelectric responses of epitaxial, 150-nmthick (001)-, (101)-, and (111)-oriented PbZr_{0.2}Ti_{0.8}O₃ heterostructures are probed using direct pyroelectric measurements based on microfabricated electrothermal devices [1,31]. Piezoresponse force microscopy (PFM) studies reveal that all heterostructures exhibit the same type of 90° ferroelastic domain walls, but their geometry and density vary with orientation. In turn, π is found to be the largest for (111)-oriented heterostructures [approximately $-280 \ \mu\text{C} \ \text{m}^{-2} \ \text{K}^{-1}$ or around 37% and 70% higher than that in the (001)- and (101)-oriented heterostructures of the same thickness, respectively], which also have the highest density of domains or domain walls. By varying the thickness of these (111)-oriented heterostructures (from 100 to 280 nm), the density of domain walls can be varied (consistent with Kittel's law) [25,32], and a direct correlation between domain-wall density and π is found (with the maximum value changing by about 44% across this thickness range). Molecular-dynamics (MD) simulations recreate these findings and reveal a novel domain-wall contribution to pyroelectric response in that the volume of the material in or near the domain walls exhibits a significantly higher π as compared to the material in the bulk of the domains. Further analysis suggests that the domain-wall material has a higher responsivity of the polarization to both external fields and temperature. This study reveals a nonmotional, domain-wall contribution to pyroelectricity and provides a pathway to enhancing this effect in thin-film heterostructures.

II. RESULTS AND DISCUSSION

A. Domain structure evolution with orientation

To probe the role of domains and domain walls in the pyroelectric response, this work leverages a model set of materials starting with 150-nm-thick (001)-, (101)-, and (111)-oriented $PbZr_{0.2}Ti_{0.8}O_3$ heterostructures that have



FIG. 1. Structure of orientation-dependent 150-nm-thick tetragonal $PbZr_{0.2}Ti_{0.8}O_3$ heterostructures. (a),(b),(c) X-ray diffraction line scans. (d),(e),(f) Reciprocal space maps in the out-of-plane direction. (g),(h),(i) Lateral contrast [$A \cos \theta$] of PFM analysis for the as-grown state (inset), and for the poled state corresponding to (001), (101), and (111) orientations.

been produced via pulsed-laser deposition (Sec. IV). Following growth, x-ray diffraction θ -2 θ line scans are used to examine the structure of the heterostructures and confirm that, in all cases, the heterostructures are epitaxial and single phase [Figs. 1(a)-1(c)]. Additionally, x-ray reciprocal space mapping (RSM) and PFM studies (Sec. IV) are employed to evaluate the domain structure of the heterostructures with different orientations. On-axis RSM measurements are conducted about the SrTiO₃ 002-, 110-, and 111-diffraction conditions for the (001)-, (101)-, (111)-oriented heterostructures, respectively and [Figs. 1(d)–1(f)]. PFM analysis of the lateral piezoresponse contrast [amplitude (A) and phase (θ), shown here as $A\cos\theta$ of the domain structures is also completed for the three heterostructure orientations to examine both the poled state [Figs. 1(g)–1(i)] and the as-grown state [inset, Figs. 1(g)–1(i)]. The poled state is achieved after three sequential poling cycles (+8 V, -8 V, and +8 V) to ensure the heterostructures are fully switched (Sec. IV). For the (001)-oriented heterostructures, the RSMs exhibit a predominant 002-diffraction peak, along with a minority 200-diffraction peak [Fig. 1(d)]—suggesting majority out-of-plane polarized *c*-domain structure with minority in-plane polarized *a* domains. This case is supported by the PFM studies, which show that classical c/a domain structures are present in both the as-grown and poled states. In the poled state, the relative volume fractions of the *a* [lines running diagonally across the scan area, Fig. 1(g)] and *c* domains [purple background regions, Fig. 1(g)] are around 4.8% and 95.2%, respectively. Detailed analysis of



FIG. 2. Electrical and pyroelectric measurements of orientation-dependent 150-nm-thick $PbZr_{0.2}Ti_{0.8}O_3$ heterostructures. (a) Schematic illustration of pyroelectric device configuration. (b) The dc bias-dependent dielectric permittivity response measured at 1 kHz. (c) Room-temperature ferroelectric hysteresis response measured at 1 kHz. (d) The dc bias-dependent pyroelectric coefficient results for the various orientations with heating current at 1 kHz.

the domain area and domain-wall density are provided (Supplemental Material, Fig. S1) [33]. For the (101)oriented heterostructures, the RSMs contain diffraction peaks corresponding to the 101- and 110-diffraction peaks [Fig. 1(e)]—similarly suggesting the presence of majority and minority domains. This finding is further supported by the PFM studies which exhibit majority domains [yellow regions, Fig. 1(h)] with polarization oriented out of plane at an angle of approximately 43.6° from the plane of the heterostructure, and minority domains [purple regions, Fig. 1(h)], which are in-plane polarized with striplike shapes. In the poled state, the volume fractions of the majority (101)- and minority (110)-type domains are 69% and 31%, respectively. For the (111)-oriented heterostructures, the RSM contains a single, broad 111-diffraction peak [Fig. 1(f)]. PFM studies of the as-grown state [inset, Fig. 1(i)] reveal the presence of a complex domain structure that becomes more ordered after poling [Fig. 1(i)], and a nanotwinned pattern with a high density of domain walls emerges. This domain structure is made up of roughly equal fractions of three potential polarizations in the poled state. Overall, the domain-wall density (defined as the total length of domain walls in a given area) is highest in the (111)-oriented heterostructures (46.0 μ m⁻¹) as compared to that for the (001)-oriented (5.5 μ m⁻¹) and (101)-oriented (14.6 μ m⁻¹) heterostructures. These results are consistent with previous findings [20] indicating that (111)-oriented heterostructures possess domain-wall densities at least three-to-eight times higher than (001)- and (101)-oriented heterostructures. Furthermore, it has been shown that the presence of a high density of domain walls, acting as boundaries between differently polarized areas, can have a marked impact on certain properties (e.g., the dielectric response) [20].

B. (Di)electrical and pyroelectric measurements

To study the properties of the differently oriented heterostructures, microfabricated electrothermal measurement devices [Fig. 2(a)] are fabricated (Sec. IV) and used to measure the dielectric, ferroelectric, and pyroelectric response of 30 nm $La_{0.67}Sr_{0.33}MnO_3/150$ nm $PbZr_{0.2}Ti_{0.8}O_3/$ 30 nm $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3(001)$, (101), and (111) heterostructures wherein the $La_{0.67}Sr_{0.33}MnO_3$ serves as both the top and bottom electrodes (Sec. IV). Measurements of the dielectric constant [Fig. 2(b)] and dielectric loss (Supplemental Material, Fig. S2) reveal that the (111)-oriented heterostructures exhibit the highest dielectric constant-again consistent with previous studies [20] wherein stationary domain-wall contributions were reported. Conversely, the (001)-oriented heterostructures exhibit the lowest dielectric constant, which is attributed to these heterostructures being predominantly c domains with polarization aligned parallel to the applied electric field [12]. Ferroelectric polarization-electric field hysteresis loops [Fig. 2(c)] reveal that the remanent polarization is the largest for the (001)-oriented heterostructures (76 μ C cm⁻²), followed by the (101)-oriented (56 μ C cm⁻²) and (111)-oriented $(37 \ \mu C \ cm^{-2})$ heterostructures (values consistent with what is expected for the effective out-of-plane polarization values based on the projection of the polarization for each orientation). Based on the fact that the remanent polarization is largest in the (001)-oriented heterostructures, followed by that in the (101)- and (111)-oriented heterostructures, a naive assumption would be that the pyroelectric response of the three differently oriented heterostructures would follow this trend as well (i.e., for a similar change in polarization with temperature, a larger polarization along the measurement direction would produce a larger pyroelectric current). Measurements of the π [Fig. 2(d)], however, reveal that the (111)-oriented heterostructures have the largest $\pi =$ -228 to $-280 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$, followed by the (001)-oriented $(\pi = -195 \text{ to } -205 \ \mu\text{C} \text{ m}^{-2} \text{ K}^{-1})$ and (101)-oriented $(\pi = -148 \text{ to } -165 \ \mu\text{C} \text{ m}^{-2} \text{ K}^{-1})$ heterostructures. Such pyroelectric responses were also found to be stable to repeated dc bias cycles (Supplemental Material, Fig. S3) [33]. Comparing the π value after one, ten, and 100 additional cycles, the percentage difference across all cycles is generally less than 0.5%. Additional details on the pyroelectric measurements are provided, including pyroelectric-current and thermal-phase-lag measurements (Supplemental Material, Fig. S4) [33], and 3ω measurements of the temperature oscillations (Supplemental Material, Fig. S5) [33]. This trend is contrary to previous studies on exclusively (001)oriented PbZr_{0.2}Ti_{0.8}O₃ heterostructures [12,15], where it was observed that the higher the out-of-plane remanent polarization value, the higher the π . Consequently, the pyroelectricity cannot be simply explained by asserting that it is proportional to the effective out-of-plane polarization of the PbZr_{0.2}Ti_{0.8}O₃ heterostructures, which suggests that the high-density, nanotwinned domain structures in the (111)-oriented heterostructures could be contributing to the enhancement of π (as they did for the dielectric response).

C. Analysis of domain periodicity

To unravel the underlying mechanism as to why the (111)-oriented heterostructures show the highest observed π , (111)-oriented PbZr_{0.2}Ti_{0.8}O₃ heterostructures with four thicknesses (i.e., 50, 100, 150, and 280 nm) are synthesized to control the domain size and volume fraction of domain walls. Again, prior to PFM analysis, each heterostructure is subjected to three sequential poling cycles (scanning areas using a grounded scanning probe microscope tip while

applying +8 V, -8 V, and +8 V bias voltage to the bottom electrode) to ensure the heterostructures are in a fully poled state and consistent with the state measured in the pyroelectric measurements conducted after the cycling of the polarization-electric-field hysteresis loop at least three times. Lateral PFM phase images for the 50-nm-thick [Fig. 3(a)], 100-nm-thick [Fig. 3(b)], 150-nm-thick [Fig. 3(c)], and 280-nm-thick [Fig. 3(d)] heterostructures reveal the evolution of the domain size (for larger scan areas, see Supplemental Material, Fig. S7) [33]. For each thickness, high-resolution scans are completed in two different 2 μ m \times 2 μ m areas chosen at random to examine the periodicity of the nanotwinned domains (PFM images for the $2 \mu m \times 2 \mu m$ area of each heterostructure are provided; Supplemental Material, Figs. S8 and S9) [33]. One of the zoomed-in areas is shown for each heterostructure, including the PFM images of lateral piezoresponse contrast $(A \cos \theta)$ for the 50-nm-thick [Fig. 3(e)], 100-nm-thick [Fig. 3(f)], 150-nm-thick [Fig. 3(g)], and 280-nm-thick [Fig. 3(h)] heterostructures. The PFM data reveal, as expected, that by varying the thickness of the (111)-oriented heterostructures, it is possible to change the average domain size-with thinner heterostructures exhibiting smaller domain periodicities. A schematic illustration of the domain structure in the up-poled (111)-oriented heterostructures is presented [Fig. 3(i)], where the Cartesian axes are aligned along the crystallographic axes [112], [110], and [111], respectively. The domain structure consists of three types of domain bands, each separated by 120°. Within each domain band, which is further divided into two nanotwinned domain bands, only two polarization variants are present. For example, three degenerate polarization variants, denoted as P_1^+ , P_2^+ , and P_3^+ , point along [100], [010], and [001], respectively. The nanotwinned domain bands formed by P_1^+ and P_2^+ are shaded in yellow, those formed by P_2^+ and P_3^+ are shaded in purple, and those by P_1^+ and P_3^+ are shaded in blue. Ten line-profile analyses for each heterostructure are conducted, with only one representative line profile shown in the figures, for simplicity [Fig. 3(j)]. The average periodicity of the nanotwinned domains (d) in each heterostructure is measured for the ten randomly selected lines, labeled as 1 through 10. Detailed line-profile analyses of the nanotwinned domain structures for each heterostructure, corresponding to two different 2 μ m × 2 μ m areas for each thickness, are provided (Supplemental Material, Table 1) [33]. From the ensuing statistical analysis, the d values [defined as the distance across two polarization variants (e.g., P_1^+ to P_2^+ as a repeating unit)] for the 50-nm-thick, 100-nm-thick, 150-nm-thick, and 280-nm-thick heterostructures are found to be 47.6 ± 5.1 nm, 61.2 ± 7.5 nm, 68.1 ± 6.1 nm, and 85.5 ± 7.8 nm, respectively. As expected, d evolves in accordance with Kittel's law $(d \propto \sqrt{t})$ [25,32] [Fig. 3(k)], which states that d should be proportional to the square root of the heterostructure thickness (t). These results



FIG. 3. PFM analysis of the (111)-oriented domain structure as a function of thickness. (a)–(d) Lateral PFM phase images for heterostructures of varying thicknesses with a scanning area of 10 μ m × 10 μ m. (e)–(h) Zoom-in views of the same lateral PFM images [$A \cos \theta$]. (i) Schematic diagrams of the (111)-oriented inclined domain structures. (j) Example line-profile analyses of films with varying thicknesses to measure their nanodomain periodicities. (k) Kittel's law fitting of the extracted nanotwinned domain periodicities.

motivate further fabrication of these heterostructures so that their dielectric, ferroelectric, and pyroelectric responses could be tested.

D. Thickness-dependent pyroelectric measurements and MD simulations

Thickness-dependent ferroelectric polarization-electricfield hysteresis loops [Fig. 4(a)] are measured. While attempts are made to prepare the 50-nm-thick heterostructures for such measurements, the relatively large device sizes (area = 6.0×10^{-5} cm²) mean that the 50-nm-thick heterostructures have relatively large leakage currents; thus, they are excluded from further discussion. For the remaining heterostructures, the studies reveal that while all exhibit similar saturation polarizations, thinner heterostructures exhibit higher coercive fields (E_c). This finding aligns with the Janovec-Kay-Dunn law ($E_c \propto d^{-2/3}$). The dielectric constant [Fig. 4(b)] increases with decreasing film thickness, supporting the hypothesis that a greater density of domain walls enhances the dielectric response. Corresponding studies of the dielectric loss (Supplemental Material, Fig. S10) also reveal low loss values. In turn, a similar trend was noted for π [Fig. 4(c)]. At E = 0, the 100-nm-thick heterostructures have the highest $\pi(-358 \ \mu C \ m^{-2} \ K^{-1})$, followed by the 150-nm-thick



FIG. 4. Thickness-dependent studies of (111)-oriented heterostructures and MD simulations. (a) Polarization hysteresis loops, (b) dielectric constant, and (c) pyroelectric coefficient as a function of electric field for 100-, 150-, and 280-nm-thick films. (d) Simulated domain structure (top half) in (111)-oriented PbTiO₃, viewed along [111]. The domain pattern is colored based on the in-plane polarization component. Image of the ACF at 25 ps (lower half), reflecting the flexibility of local dipoles being higher at the domain walls. Polarization profiles of 90° domain walls in a (111)-oriented supercell obtained from simulated domain structures, including the polarization components along the (e) in-plane [110] (P_X) and [112] (P_Y) and (f) out-of-plane polarization along [111] (P_Z) together with the total polarization (P_{total}). (g) In-plane polarization components in panel (e) transformed into conventional Cartesian axes.

 $(-280 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1})$ and 280-nm-thick $(-249 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1})$ heterostructures. It is also observed that, for all heterostructures, upon application of an increasing E, π gradually decreases. For example, in the 100-nm-thick heterostructures, π decreases in magnitude from $-358 \ \mu C \ m^{-2} \ K^{-1}$ at E = 0 to $-227 \ \mu C \ m^{-2} K^{-1}$ at $E = 600 \ kV cm^{-1}$, indicating that the electric dipoles become less susceptible to temperature fluctuations in the presence of an external electric field. The dielectric response also exhibits a similar trend: As the magnitude of the applied *E* increases, the response decreases (Supplemental Material, Fig. S11) [33]. The PFM analysis (Fig. 3) reveals that, as the thickness of the heterostructures decreases, so does the nanotwinned domain periodicity, and this evolution is seen to inversely correlate with the increase in π (i.e., the peak value of the dc bias-dependent pyroelectric loops). These findings suggest that increasing the volume density of domain walls in (111)-oriented PbZr_{0.2}Ti_{0.8}O₃ results in an approximately 1.8-fold increase in π as compared to (001)-oriented PbZr_{0.2}Ti_{0.8}O₃, which exhibits $\pi = -200 \ \mu C \ m^{-2} \ K^{-1}$ [17].

Having established experimentally that π is enhanced with increasing domain-wall density, MD simulations are used to investigate the microscopic mechanism behind this observation. Here, the MD simulations examine the behavior of electric dipoles using two approaches: (1) extracting π under static conditions by measuring polarization values at different temperatures and (2) assessing polarization susceptibility based on the time autocorrelation function (ACF) under dynamic conditions. First, largescale MD simulations (Sec. IV) are performed to calculate π in realistic domain structures of (111)-oriented PbTiO₃ at room temperature. Given the structural similarity and close Curie temperature between PbTiO₃ and PbZr_{0.2}Ti_{0.8}O₃, the simulated pyroelectric effects (and trends) are expected to be comparable for these two ferroelectric materials [36,37]. The simulated domain structure [upper half, Fig. 4(d); Supplemental Material, Fig. S12(a)] is consistent with the experimental observations, featuring a domain band that includes all three degenerate polarization variants in the (111)-oriented heterostructures, marked in green, orange, and purple. The MD simulations are also performed at different temperatures ranging from 295 to 305 K, and within this range, the domain structure, specifically the volume density of domain walls separating differently polarized domains, is observed to remain unchanged (Supplemental Material, Fig. S13) [33]. Consequently, this approach rules out the potential contribution of thermally activated domain-wall movement to the pyroelectric response [i.e., $\pi_{\text{extrinsic}} = P_s (\partial \phi / \partial T)_{\sigma} = 0$]. Based on

statistical analysis of the electric dipole moment (*p*) within each unit cell (Sec. IV), the nanotwinned domain structure is divided into domain and domain-wall regions (Supplemental Material, Figs. S14 and S15) [33]. In turn, this approach enables the quantification of individual π contributions from the volume of material in the domains (π_D) and in the domain walls (π_{DW}) by simulating the temperature dependence of the local polarization. The overall pyroelectric coefficient (π_{total}) is then expressed as follows:

$$\pi_{\text{total}} = \pi_{\text{D}} + \pi_{\text{DW}} = \left(\frac{\partial P_{\text{D}}}{\partial T}\right)_{\sigma} + \left(\frac{\partial P_{\text{DW}}}{\partial T}\right)_{\sigma}.$$
 (2)

From the plot of polarization versus temperature [Supplemental Material, Figs. S14(d)], the rate of change (slope) of the polarization with respect to temperature gives different coefficients (i.e., $\pi_D = -389 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$, $\pi_{DW} =$ $-624 \ \mu C \ m^{-2} \ K^{-1}$, and $\pi_{total} = -460 \ \mu C \ m^{-2} \ K^{-1}$). This result suggests that the dipoles at domain walls are more susceptible to thermal stimuli. It should also be noted that the difference in the π values between the experimental data $(-358 \ \mu C \ m^{-2} \ K^{-1}$ for a 100-nm-thick heterostructure) and the simulation $(-460 \ \mu C \ m^{-2} \ K^{-1})$ is due to the difference in nanotwinned domain periodicity. The simulation, constrained by computational resources, assumes a four nanometer width for the periodicity and adopted periodic boundary conditions, whereas the 100-nm-thick heterostructure exhibits an approximate periodicity of 60 nm. Again, smaller periodicity leads to higher domainwall density, which results in a higher value of π for the simulations. Furthermore, in addition to extracting π by obtaining polarization values with respect to corresponding temperatures under static domain configurations, the MD simulations can be used to explore how the dipole moments change over time using ACF (Sec. IV). This approach provides insight into the temporal evolution and stability of a material system by investigating its dynamic, timedependent behavior under nonstatic conditions. The local susceptibility can be gauged by computing the ACF for each dipole, expressed as

$$C(t) = \frac{\langle p(t) \cdot p(0) \rangle}{\langle p(0)^2 \rangle},\tag{3}$$

where $\langle \cdots \rangle$ represents the ensemble average. As time progresses, the function C(t) assesses how well the current dipole moment remains correlated with its initial state. A rapid decay of C(t) to zero suggests that the dipole changes orientation quickly, indicating high flexibility and susceptibility. Conversely, a slow decay of C(t) indicates that the dipoles retain their initial orientation over longer periods, reflecting rigidity and reduced flexibility. A color map displaying the ACF values [lower half, Fig. 4(d); Supplemental Material, Fig. S12(b)] shows the spatially resolved values of C(t) at t = 25 ps. This map reveals that dipoles at the domain walls exhibit lower ACF values, indicated by the bright green regions in the color gradient, suggesting that they are significantly more flexible (susceptible) as compared to those in the bulk of the domains. It is important to note that no domain-wall motion occurs during the simulations. This lack of movement suggests stable domain structures within the material. The dipolar frustration present at the domain walls, however, can enhance the response of the dipoles in these regions, promoting the increased pyroelectric response.

To further elaborate on this relationship between the pyroelectric response and the structural properties of the domain walls, the polarization profile associated with 90° ferroelastic domain walls in the (111)-oriented films is extracted along the two in-plane directions, $[1\overline{1}0](P_x)$ and $[11\overline{2}](P_{Y})$ [Fig. 4(e)] and along the out-of-plane [111] (P_{Z}) [Fig. 4(f)]. In turn, the total magnitude of the polarization (P_{total} , the vector sum of the P_X , P_Y , and P_Z components) is calculated [Fig. 4(f), right axis]. The results indicate that the out-of-plane polarization (P_Z) along [111], which contributes to the pyroelectric response, actually increases at the domain wall [labeled as DW, and in the gray boxes, Figs. 4(e)–(g)], which occurs in conjunction with a reduction in the total polarization (P_{total}) at the domain walls. This reduction is a sort of "structural frustration" at the domain wall, a phenomenon reported before [19], and typically leads to a reduction in the total polarization. This reduction, in turn, increases the susceptibility to external stimuli, as confirmed by calculations of the ACF of the local dipoles. It can perhaps be thought of as moving the material within these domain walls to be closer to their critical temperature-wherein the susceptibility is enhanced. What is unique to the 90° domain walls in the (111)-oriented films is the enhancement of the P_{Z} component-an effect further visualized and understood by performing a coordinate transformation to express the polarization profile in conventional Cartesian axes. This transformation for P_X and P_Y [Fig. 4(g)] captures the evolution of a $[\bar{1}00]$ domain transforming to a [001] domain and then back to a [100] domain. These data show that both the $P_{[100]}$ and $P_{[001]}$ components in the domain-wall regions are *nonzero* and contribute to the P_Z component, which dictates the pyroelectric response. This interplay underpins the observed increase in P_Z .

The relationship between π and polarization (*P*) can be intuitively expressed as $\pi \propto P/\Delta U$, where ΔU represents the dipolar rotational barrier, which often scales inversely with the magnitude of polarization, $\Delta U \approx 1/P$. In weak (strong) ferroelectrics, both *P* and ΔU are small (large). This intrinsic competition makes optimizing the pyroelectric response particularly challenging. The observed enhancement of P_Z , coupled with a reduction in P_{total} , offers a microscopic explanation for the higher π in the walls. Because of the reduction in P_{total} , the dipoles remain responsive, resulting in a low ΔU . At the same time, the component of polarization that directly contributes to the pyroelectric response, P_Z , remains large. By leveraging both domain-wall and orientation engineering, we achieve dipoles at the domain walls that are not only responsive but also highly effective, enabling a significant enhancement in the pyroelectric response. In summary, the MD simulations show that the dipoles in the domain-wall regions have higher π values as compared to those in the domains; more generally, they identify new static domain-wall contributions to pyroelectricity.

III. CONCLUSIONS

Among (001)-, (101)-, and (111)-oriented PbZr_{0.2}Ti_{0.8}O₃ thin-film heterostructures, (111)-oriented heterostructures exhibit the most pronounced pyroelectric susceptibility. This enhanced response is attributed to their distinct structure, characterized by a high density of nanotwinned domain walls. By adjusting the thickness of the (111)-oriented heterostructures, the density of domain walls can be manipulated. Upon reducing the film thickness, a higher density of domain walls (consistent with Kittel's law) is obtained, and there is, in turn, a systematic enhancement of the pyroelectric response. MD simulations confirm that the enhanced response arises not from the motion of the domain walls but from the fact that the dipoles in the domain-wall regions exhibit a higher pyroelectric coefficient ($\pi_{\rm DW}$) as compared to those from the domains (π_D) . Thus, only in the (111)-oriented heterostructures, where there is a significantly higher fraction of domain walls, does one observe a marked increase in the overall pyroelectric coefficient (π_{total}). Overall, this study not only provides a deeper understanding of the microscopic origins of pyroelectric enhancements in (111)-oriented PbZr_{0.2}Ti_{0.8}O₃ thin-film heterostructures, but it also opens new pathways for enhancing pyroelectric susceptibility in materials by the manipulating domain-wall density.

IV. EXPERIMENTAL METHODS

A. Pulsed-laser deposition of thin-film heterostructures

Pulsed-laser deposition with a KrF excimer laser (248 nm, LPX 300, Coherent) was used to grow 150 nm PbZr_{0.2}Ti_{0.8}O₃/30 nm La_{0.67}Sr_{0.33}MnO₃ heterostructures on SrTiO₃ substrates (MTI Corp.) with (001), (110), and (111) orientations. The ceramic targets of chemistry Pb_{1.2}Zr_{0.2}Ti_{0.8}O₃ and La_{0.67}Sr_{0.33}MnO₃ were used for growth (Praxair Inc.). Both the PbZr_{0.2}Ti_{0.8}O₃ and La_{0.67}Sr_{0.33}MnO₃ and La_{0.67}Sr_{0.33}MnO₃ and La_{0.67}Sr_{0.33}MnO₃ and La_{0.67}Sr_{0.33}MnO₃ films were grown under the same conditions: a target-to-substrate distance of 60 mm, a heater temperature of 635 °C, a dynamic oxygen pressure of 200 mTorr, a laser fluence of 1.5 J cm⁻², and a laser repetition rate of 4 Hz. After growth, the samples were cooled at 10 °C min⁻¹ under an oxygen atmosphere maintained at a pressure of about 700 Torr.

B. Characterization of crystal and domain structure

To characterize the orientation-dependent $PbZr_{0.2}Ti_{0.8}O_3$ crystal structures, a high-resolution x-ray diffractometer (Panalytical, X'Pert Pro MRD) was used with copper K_{α} radiation (1.54 Å). A fixed receiving slit of 0.275 mm was used for the diffracted-beam optics with the PIXcel3D-Medipix3 detector. X-ray diffraction θ -2 θ line scans were performed using fixed-incident-optics slits of 1/2°, and RSM studies utilized slits of 1/16°. On-axis RSM measurements were conducted around the SrTiO₃ 002-, 110-, and 111-diffraction conditions for (001)-, (101)-, and (111)-oriented heterostructures, respectively. As for the characterization of the domain structure, the ferroelectric domain structures of PbZr_{0.2}Ti_{0.8}O₃ thin-film heterostructures were characterized by dual ac resonance tracking piezoresponse force microscopy (DART-PFM) using a commercial scanning probe microscope (MFP-3D, Asylum Research). PFM was performed using conductive Pt/Ircoated cantilevers (PPP-EFM, Nanosensors) and conductive Pt-coated cantilevers (HQ:NSC35/Pt, MikroMasch) with a first eigenmode resonant frequency (f_1) of around 75 kHz and a spring constant (k_1) of around ~2.8 N m⁻¹. The global and nanodomain structures were created by scanning areas of interest 3 times using a grounded tip while applying +8 V, -8 V, and +8 V to the bottom electrode.

C. Pyroelectric device fabrication

In accordance with previously defined processing methods [1,31], the development of electrothermal-test platforms used in this study is summarized here. The pyroelectric devices were defined via a photolithography process that involved four exposure steps. For each exposure and subsequent development process, standard I-line positive photoresist (Mir-701) was used via spin coating at a rate of 7000 rpm for 1 min to achieve a uniform photoresist thickness of about 500 nm. The process included prebaking at 90 °C for 90 sec before exposure and hard-baking at 100 °C for 60 sec before development. Exposures were carried out using a Heidelberg MLA150 Maskless Aligner at the Berkeley Marvell NanoLab, with an exposure wavelength of 370 nm and a dose of 250 mJ cm⁻². An ion-milling process was required to ion mill the trilayer heterostructures down to striplike trilayer active devices. This process was performed using the Intlvac Nanoquest system (beam voltage: 500 V; beam current: 38 mA; accelerator voltage: 100 V; angle of incidence: 45°) with an in situ secondary ion mass spectrometry system to monitor the etching process and corresponding etched layers. Next, a 200-nm-thick SiN_x layer was deposited using plasma-enhanced chemical vapor deposition (PECVD) at 350 °C with NH₃ and 10% SiH₄ in argon at a deposition rate of 7.5 nm min^{-1} , using an Oxford Plasmalab 80plus PECVD System. The SiN_x growth rate was optimized and verified with the Nanospec/AFT Model 3000 heterostructure thickness measurement system. Then, the SiN_x layer was further defined in the appropriate configuration by first covering it with another photoresist patterned layer and then subjecting it to a reactive-ionetching (RIE) process. This process was completed using oxygen (30 sccm) and CF₄ (90 sccm) gases under 100 W of rf power, with an etching rate of 37 nm min⁻¹ (SEMI RIE System). Lastly, the thermal resistive heating line on top of the devices was fabricated. A 5-nm-thick layer of titanium, serving as an adhesion layer, and an approximately 100-nm-thick layer of platinum was sputtered at room temperature with a base pressure of approximately 10^{-8} Torr. Titanium was sputtered at 20 W with an argon pressure of 3.3 mTorr, achieving a growth rate of $1.7 \text{ nm} \text{min}^{-1}$. Platinum was sputtered at 15 W with an argon pressure of 7.0 mTorr, achieving a growth rate of 8.7 nm min⁻¹.

D. Electrical and dielectric measurements

Each orientation and thickness-dependent heterostructure was measured to assess their ferroelectric and dielectric properties. To measure ferroelectric hysteresis loops, a Precision Multiferroic Tester was used (Radiant Technologies, Inc.). The hysteresis loop measurements were performed at 1 kHz with a double bipolar waveform. An E4990A Impedance Analyzer (Keysight Technologies) was used to measure dc bias-dependent dielectric permittivity, which ranged from -350 to 350 kV cm⁻¹ at 1 kHz, using an ac oscillation amplitude of 50 mV.

E. Pyroelectric measurements

Direct pyroelectric measurements were conducted using established measurement procedures [1,31]. To obtain the dc bias-dependent pyroelectric response loop, a dc bias was applied to the top electrode using a Keysight 33500B waveform function generator. The pyrocurrent was then measured at the bottom electrode with an SR830 lock-in amplifier, synchronized to the 2ω signal, in relation to the 1ω signal from the Keithley 6221 current source. A sinusoidal heating current described by $I(t) = I_0 \sin(\omega t)$ of 10-mA wave amplitude was applied via a Keithley 6221 current source across the metal heater line to introduce temperature oscillations in the ferroelectric thin-film heterostructure. The power input into the heater line is governed by the Joule heating principle

$$P(t) = I(t)^2 R(t) = \frac{I_0^2 R(t)}{2} (1 + \cos(2\omega t)).$$
(4)

Consequently, the time-varying temperature of the heater line can be expressed as

$$T(t) = T_0 + \Delta T_{2\omega} \cos(2\omega t + \psi), \qquad (5)$$

where $\Delta T_{2\omega}$ represents the amplitude of the temperature oscillation and ψ is the thermal phase lag. The time-varying resistance of the heater line varies with temperature, described by

$$R(t) = R_0 (1 + \alpha \Delta T_{2\omega} \cos(2\omega t + \psi))$$

= $R_0 + \Delta R \cos(2\omega t + \psi),$ (6)

where $\Delta R = \alpha R_0 \Delta T_{2\omega}$ and α refers to the temperature coefficient of resistance (TCR, $\alpha = (dR/dT)(1/R_0)$) of platinum. To measure the temperature oscillation $\Delta T_{2\omega}$, the voltage across the heater line is expressed using Ohm's law as $V(t) = I(t) \cdot R(t)$. Substituting the expressions for I(t)and R(t), we obtained

$$V(t) = I(t)^* R(t)$$

= $I_0 \cos(\omega t)^* [R_0 + \Delta R \cos(2\omega t + \psi)]$
= $R_0 I_0 \cos(\omega t) + \frac{\Delta R I_0}{2} [\cos(3\omega t + \psi) + \cos(\omega t + \psi)].$
(7)

The interaction between the applied heating current (1ω) and the resistance oscillation (2ω) results in a voltage drop along the heater line that appears at the third harmonic (3ω) . The 3ω term is directly related to ΔR , which is linked to the temperature oscillation $\Delta T_{2\omega}$, and can be measured by the 3ω method [38–40]. Because of the significant amplitude difference between the 1ω and 3ω signals (the 1ω signal being up to 3 orders of magnitude higher than the 3ω signal), a customized built-up Wheatstone bridge circuit was employed to nullify the 1ω signal, enabling the detection of a much smaller 3ω signal. The 3ω voltage is expressed as

$$V_{3\omega} = \frac{\Delta R I_0}{2} = \frac{\alpha R_0 \Delta T I_0}{2}.$$
 (8)

Utilizing a lock-in amplifier (SR830, Stanford Research lock-in amplifier), the 3ω voltage fluctuation ($V_{3\omega}$) was precisely detected for the determination of the average heater line temperature oscillation amplitude [Supplemental Material, Fig. S3(c)] [33], which is expressed as

$$\Delta T_{2\omega} = \frac{2V_{3\omega}}{\alpha R_0 I_0} = \frac{2V_{3\omega}}{\frac{dR}{dT} \frac{1}{R_0} R_0 I_0} = 2\frac{dT}{dR} \frac{R_0}{I_0} V_{3\omega} = 2\frac{dT}{dR} R_0 \frac{V_{3\omega}}{V_{1\omega}}.$$
(9)

Furthermore, to precisely quantify the temperature oscillation amplitude in the active ferroelectric layer, we utilized COMSOL MULTIPHYSICS, a numerical finite-element analysis (FEA) package, employing a one-dimensional heat transport model [1,12]. This approach allowed us to calculate a correction factor for precise predictions of the temperature oscillations perceived by the pyroelectric films [Supplemental Material, Fig. S5(d)] [33]. Given the known area of the capacitor ($A_{cap} = 6.0 \times 10^{-5} \text{ cm}^2$), the effective electrode area ($A_{electrode} = 2.7 \times 10^{-5} \text{ cm}^2$), the effective oscillations of the heater line ($\Delta T_{2\omega}$), and the heating frequency ($f, \omega = 2Pif$), π was extracted from the measured pyroelectric current (i_p), which is expressed as

$$i_p^{\rm rms} = \pi A_{\rm cap} \frac{dT}{dt} = \pi A_{\rm cap} (2\omega \Delta T_{2\omega} \cos(2\omega t + \psi)), \quad (10)$$

$$\pi = \frac{i_p^{\text{amp}}}{(A_{\text{electrode}} * \text{Correction Factor}) * (4Pi * f * \Delta T_{2\omega})}.$$
(11)

To ensure the reproducibility and consistency of π in each sample, at least three devices from each sample were measured (Supplemental Material, Fig. S6) [33]. The pyrocurrent and the temperature coefficient of resistance were independently measured for each device. This method ensured reliable and representative values of π , allowing for meaningful comparisons between samples.

F. Molecular-dynamics simulations

MD simulations were performed using the LAMMPS [41] package. A (111)-oriented $40\sqrt{2} \times 20\sqrt{6} \times 12\sqrt{3}$ supercell of PbTiO₃ (288,000 atoms) with periodic boundary conditions was simulated using a deep neural networkbased model potential, referred to as the deep potential (DP) [42], trained exclusively with density functional theory energies and atomic forces for 19,119 $Pb_xSr_{1-x}TiO_3$ configurations. This DP model can accurately reproduce various properties of PbTiO₃, including phonon spectra of tetragonal and cubic phases, the temperature-driven ferroelectric-to-paraelectric phase transition, and topological textures such as polar vortex lattices and electric dipole waves in PbTiO₃/SrTiO₃ superlattices [43]. The supercell has Cartesian axes aligned along the crystallographic axes $[11\overline{2}]$, $[1\overline{1}0]$, and [111], respectively. The supercell was first equilibrated by running DPMD simulations in the isobaric-isothermal (NPT) ensemble with in-plane lattice constants fixed at 300 K. Once equilibrium was reached, a stable configuration was used as a starting point for simulations at different temperatures ranging from 295 K to 305 K. All MD simulations were performed with a time step of 2 fs for integrating the equations of motion, temperature was controlled via the Nosé-Hoover thermostat, and pressure was maintained at 1.0 bar along the outof-plane direction using the Parrinello-Rahman barostat. At each temperature, the equilibrium run lasted 50 ps to obtain a converged, stable configuration. The dynamics of the dipole in each unit cell was analyzed by examining the ACF of the local dipole \vec{p}_i within the *i*th unit cell [44]:

$$C_i(t) = \vec{p}_i(t) \cdot \vec{p}_i(0) / \vec{p}_i(0)^2.$$

$$(12)$$

This ACF gives a measure of how fast the orientations of the local dipole change with time. By definition, C(t = 0) = 1, and it decays to zero once the direction of the dipole has become completely random. In ferroelectric systems, this function often converges to a nonzero value.

G. Domain color scheme for the MD simulations

The domains are colored based on the direction of the local polarization within each unit cell. The polarization of the unit cell was estimated using the following formula:

$$p^{m}(t) = \frac{1}{V_{uc}} \left[\frac{1}{8} Z_{Pb}^{*} \sum_{k=1}^{8} r_{Pb,k}^{m}(t) + Z_{Ti}^{*} r_{Ti}^{m}(t) + \frac{1}{2} Z_{o}^{*} \sum_{k=1}^{6} r_{o,k}^{m}(t) \right],$$
(13)

where $p^{m}(t)$ is the polarization of unit cell m at time t; V_{uc} is the volume of the unit cell; Z_{Pb}^* , Z_{Ti}^* , and Z_O^* are the Born effective charges of lead, titanium, and oxygen atoms; and $r_{\text{Pb},k}^{m}(t)$, $r_{\text{Ti}}^{m}(t)$, and $r_{O,k}^{m}(t)$ are the instantaneous atomic positions in unit cell m from MD simulations. Here, the local polarization p^m is defined as the local electric dipole divided by V_{uc} . The above equation is essentially the polarization resulting from the titanium-centered local dipole moment formed by the titanium and its nearest eight lead atoms and six oxygen atoms. For each local polarization vector, we then calculated the angle (θ) between its projection on (111) and $[11\overline{2}]$ and the in-plane polarization component. The local polarization was then colored based on the value of θ . The simulated domain pattern [viewed from the [111]; Fig. 4(d)] contains the three degenerate polarization variants and closely resembles the experimentally observed domain structures in (111)-oriented heterostructures.

H. Division of domains and domain-wall regions for the MD simulations

In certain ferroelectric systems, the dynamics of dipoles in proximity to domain walls exhibit heightened significance, and the positions of these domain walls are not static [45,46]. Although the system we investigated is characterized by negligible domain-wall motion, it is not entirely devoid of such phenomena. To obtain more accurate π values, we employed two distinct methods to distinguish between unit cells within the simulated domain configuration that belong to either domains or domain walls, based on their polarization range. *Method 1 (Narrow polarization component range).* When the given polarization component range was relatively narrow, domain walls and domains were differentiated based on specific ranges of polarization components and magnitudes. Domain walls and domains are identified when the polarization components and magnitude satisfy any of the following conditions:

$$\begin{split} & \mathsf{DW} \left\{ \begin{array}{l} p_x \in (-0.35, -0.1), \, p_y \in (-0.4, 0.1), \, |p| \in (0.55, 0.65) \\ p_x \in (0.1, 0.35), \, p_y \in (-0.4, 0.1), \, |p| \in (0.50, 0.70) \\ p_x \in (-0.05, 0.05), \, p_y \in (0.05, +\infty), \, |p| \in (0.55, 0.65) \\ & \mathsf{Domain} \left\{ \begin{array}{l} p_x \in (-0.5, -0.45), \, p_y \in (0.24, 0.3), \, |p| \in (0.68, 0.72) \\ p_x \in (0.45, 0.5), \, p_y \in (0.24, 0.3), \, |p| \in (0.68, 0.72) \\ p_x \in (-0.05, 0.05), \, p_y \in (-0.6, -0.5), \, |p| \in (0.68, 0.72) \end{array} \right. \end{split} \right. \end{split}$$

The selected domain regions [Supplemental Material, Fig. S14(a)] [33] exhibit more bulklike characteristics, indicating that the electric dipoles are concentrated in the central regions of the domain. Three distinct domain regions (marked in green, orange, and purple) correspond to three variants of polarization in the (111)-oriented PbZr_{0.2}Ti_{0.8}O₃ system. Domain walls and overall areas of analysis (domain + domain walls) are presented [Supplemental Material, Figs. S14(b) and 14(c), respectively] [33]. The calculated π values [Supplemental Material, Figs. S14(b) and 14(c), respectively] [33]. The calculated π values [Supplemental Material, Fig. S14(d)] [33] for the domain regions and the domain walls show significantly different values, as reported previously: $\pi_D = -389.06 \ \mu C \ m^{-2} \ K^{-1}$.

Method 2 (Broad polarization component range). Conversely, when the polarization component range is broadened to encompass as many polarization states as possible [Supplemental Material, Fig. S15(a)] [33], the π values [Supplemental Material, Fig. S15(d)] [33] are as follows: $\pi_D = -424.80 \ \mu C \ m^{-2} \ K^{-1}$, $\pi_{DW} = -577.30 \ \mu C \ m^{-2} \ K^{-1}$, and $\pi_{total} = -459.64 \ \mu C \ m^{-2} \ K^{-1}$. Since some portion of unit cells with higher tunability are considered domain regions, the π values obtained using this method are slightly higher than the previous one. Domain walls and domains are identified when the polarization components and magnitude satisfy any of the following conditions:

$$\mathsf{DW} \begin{cases} p_x \in (-0.35, -0.1), \, p_y \in (-0.4, 0.1), \, |p| \in (0.55, 0.65) \\ p_x \in (0.1, 0.35), \, p_y \in (-0.4, 0.1), \, |p| \in (0.50, 0.70) \\ p_x \in (-0.07, 0.07), \, p_y \in (-0.05, +\infty), \, |p| \in (0.4, 0.65) \\ \\ \mathsf{Domain} \begin{cases} p_x \in (-0.57, -0.38), \, p_y \in (0.17, 0.37), \, |p| \in (0.63, 0.77) \\ p_x \in (0.38, 0.57), \, p_y \in (0.17, 0.37), \, |p| \in (0.63, 0.77) \\ p_x \in (-0.12, 0.12), \, p_y \in (-0.67, -0.43), \, |p| \in (0.63, 0.77) \end{cases}$$

The first approach implements a more rigorous division of domains and domain walls, whereas the second approach aims to maximize the inclusion of the system's unit cells. The former yields more accurate π values within the domains but provides an upper bound estimate for the coefficients at the domain walls. Conversely, the latter approach offers a closer approximation to real systems but tends to overestimate domain π values while underestimating those at the domain walls. Despite the differences in values between these two approaches, the interrelation among the coefficients of the domain walls, the domain coefficients, and the overall coefficient remains unchanged, which shows $\pi_{DWs} > \pi_{All} > \pi_{Domain}$.

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C.-C.L. and L. W. M. conceived the project. C.-C.L. and P. K. synthesized the films and probed their structure using x-ray diffraction. C.-C.L. and D. L. fabricated the various device structures. J. K. performed the PFM studies. C.-C.L., A. B., and T. Y. K. performed the dielectric, pyroelectric, and other property studies. C.-C.L., Y. H., J. K., D. L., A. B., C. D., S. L., and L. W. M. graphed and analyzed the data. Y. H. and S. L. carried out the MD simulations. C.-C.L., L. W. M., Y. H., and S. L. wrote the paper with contributions from other authors. All authors read and reviewed the data and manuscript.

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The authors declare no competing interests.

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VIII. Dielectric response as a function of applied electric field, and IX. Molecular-dynamics simulations.

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