

**Phase-field simulation of domain size effect on dielectric and piezoelectric responses in
 $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ epitaxial thin films with superdomain structures**

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Abstract

Size effects of mesoscale ferroelectric domains on the macroscopic dielectric and piezoelectric responses in domain-engineered bulk piezocrystals have been extensively studied for more than two decades. However, less is known about the domain size effects in ferroelectric epitaxial thin films, especially for films consisting of low-symmetry ferroelectric phases and exhibits hierarchical superdomain structures. Herein, using phase-field simulations, we systemically evaluate the effective out-of-plane dielectric and piezoelectric coefficients, κ_{33}^* and d_{33}^* , as a function of the domain periods for two types of superdomain structures in ferroelectric $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ epitaxial thin films. In one type of the superdomain structures, we find that more than 70% increase of κ_{33}^* and nearly 20% increase of d_{33}^* can be achieved by tuning the domain period by a few tens of nanometers. Dissimilar behaviors are found when the domain period varies along different lateral directions, suggesting anisotropic domain size effects in thin films. By analyzing the local dielectric and piezoelectric responses from each domain variants and domain walls, we reveal that the domain size effect is governed by the variation of out-of-plane polarization inside the domains. Moreover, we also demonstrate enhanced domain size effects by modulating the misfit strains and temperature to approach the polymorphic phase boundaries, suggesting tunability of the size effect by doping and strain engineering. Our results reveal multimodal domain size dependence of dielectric and piezoelectric responses in low-symmetry ferroelectric epitaxial thin films, implying that domain size engineering can be used to tune macroscopic properties of thin-film ferroelectrics, similar to their bulk counterparts.

Keywords: ferroelectric thin film, domain structure, piezoelectric properties, dielectric properties, phase-field simulation, $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$

1. Introduction

Piezoelectricity refers to the capability of materials to convert between mechanical and electrical energies in terms of stress-induced electrical current and electric field-induced displacement. As a result, piezoelectric materials underpin a variety of electromechanical applications such as sensors, actuators, and ultrasound transducers[1]. The most widely used family of high-performance piezoelectric materials is the perovskite ferroelectric oxides, including lead zirconate titanate, barium titanate BaTiO_3 , and relaxor- PbTiO_3 -based solid solutions, in the form of ceramics, bulk single crystals and thin films[2]. Recent advances in the study of piezoelectric materials aim at developing more advanced materials with higher piezoelectric coefficients [3,4] as well as looking for nontoxic alternative materials with comparable performance as the prevailing lead-containing ones [5].

The progress made in the development of high-performance materials is benefited from the fundamental understanding of the origin of piezoelectric responses. Generally, the piezoelectric responses of materials originate from intrinsic and extrinsic contributions[6,7]. The intrinsic piezoelectric response refers to the field-induced lattice distortion associated with the change of the polarization, including polarization extension and rotation which depends on the field direction with respect to the electric dipole orientation[8]. Extrinsic contributions may come from many distinct mechanisms, such as domain walls displacement [7], breaking of centrosymmetry (i.e., flexoelectric effect [9] or compositional gradients [10]), field-induced phase transitions [11], presence of antiphase boundaries [12], domain wall-dislocation interactions [13,14] and migration of charged point defects[15]. The extrinsic contributions may dominate the intrinsic ones in some cases and give rise to giant piezoelectricity even in

centrosymmetric materials[15].

It has been known for long that the mesoscale microstructures of materials have a strong influence on its piezoelectric properties [16,17]. For example, the piezoelectric responses of polycrystalline BTO ceramics depend on the grain size [18], and higher piezoelectric responses are found in ceramics with finer grains, which was attributed to the increase of the density of mobile domain walls. The piezoelectric response of single crystals strongly depends on its orientation. For many perovskite ferroelectrics, the largest longitudinal piezoelectricity is found when the crystal is poled along a nonpolar direction wherein more than one symmetry-equivalent domain variants coexist and is known as the domain-engineered piezocrystals. It has also been found that the piezoelectric properties of the domain-engineered crystals vary with the average size of the domains. Although many earlier works reported that smaller domains lead to higher piezoelectricity [19–26], recent experimental and theoretical studies have revealed that the domain size effect on piezoelectricity can be more complex than expected. For example, opposite domain size effect wherein large domain yields higher piezoelectric properties has been revealed in relaxor-PbTiO₃ single crystals [3]. Moreover, it has been theoretically predicted that non-monotonous domain size dependence can appear in specific domain structures[27].

For piezoelectric effects in ferroelectric thin films, many studies have been focusing on the influences of film thickness and misfit strains on the piezoelectric responses [28,29]. It has been well-established that the clamping effect from the substrate can change the intrinsic piezoelectricity [30,31] by modifying the free energy landscape of the crystal and the extrinsic contribution by restricting the domain wall motion [32,33]. Therefore, the domain wall motion

in thin films is largely restricted comparing with their bulk counterparts. In contrast, much less is known about the domain size effect on piezoelectric properties in ferroelectric thin films. Is there any significant domain size dependence of piezoelectricity in thin films? If yes, do smaller or larger domains give rise to higher piezoelectricity? What is the mechanism of the domain size dependence in epitaxial thin films? Can the domain size effect be modulated? As piezoelectric thin films are key active components for applications such as nano-/micro-electromechanical systems[34], answers to these questions are of both fundamental scientific interest and technical relevance.

Here, we aim to address the above questions by theoretically evaluating the domain size effect on the out-of-plane piezoelectric response in ferroelectric epitaxial thin films using phase-field simulations. We choose the $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) epitaxial thin film as a model system which have aroused increasing research interests in recent years due to its lead-free nature, high piezoelectric activity[35–37], and capability of forming a rich variety of periodic and regular domain structures [38].

2. Phase-field modeling of superdomain structures and calculation of effective piezoelectric coefficient

We performed phase-field simulations using the ferroelectrics module of the phase-field package $\mu\text{-Pro}^{\text{®}}$. The total free energy F of the thin film system consists of contributions from bulk energy f_{bulk} , gradient energy f_{grad} , electric energy f_{elec} , elastic energy f_{elas} [39–41], i.e.,

$$F = \int_V [f_{\text{bulk}}(\mathbf{P}_i) + f_{\text{grad}}(\mathbf{P}_{i,j}) + f_{\text{elec}}(\mathbf{P}_i, \mathbf{E}_i) + f_{\text{elas}}(\mathbf{P}_i, \boldsymbol{\varepsilon}_{ij})] dV \quad (1)$$

where $\mathbf{P} = (P_1, P_2, P_3)$ is the spontaneous polarization, E_i is the electric field, ε_{ij} is the total

strain, and V is the system volume. The detailed formulations for f_{bulk} , f_{grad} , f_{elec} and f_{elas} are given below. For KNN thin film, an 8th-order polynomial is used for the bulk energy f_{bulk} , i.e.,

$$\begin{aligned} f_{\text{bulk}} = & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) + \alpha_{12}(P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) \\ & + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) + \alpha_{112}[(P_1^2 + P_2^2)P_3^2 + (P_1^2 + P_3^2)P_2^2 + (P_2^2 + P_3^2)P_1^2] \\ & + \alpha_{123}P_1^2 P_2^2 P_3^2 + \alpha_{1111}(P_1^8 + P_2^8 + P_3^8) + \alpha_{1122}(P_1^4 P_2^4 + P_1^4 P_3^4 + P_2^4 P_3^4) \\ & + \alpha_{1112}[(P_1^2 + P_2^2)P_3^6 + (P_1^2 + P_3^2)P_2^6 + (P_2^2 + P_3^2)P_1^6] \\ & + \alpha_{1123}(P_1^4 P_2^2 P_3^2 + P_1^2 P_2^4 P_3^2 + P_1^2 P_2^2 P_3^4) \end{aligned} \quad , \quad (2)$$

where the α 's are the Landau coefficients determined under the stress-free condition[31]. The gradient energy f_{grad} is written as

$$\begin{aligned} f_{\text{grad}} = & \frac{1}{2} g_{11}(P_{1,1}^2 + P_{2,2}^2 + P_{3,3}^2) + g_{12}(P_{1,1}P_{2,2} + P_{1,1}P_{3,3} + P_{2,2}P_{3,3}) + \\ & + \frac{1}{2} g_{44}((P_{1,2} + P_{2,1})^2 + (P_{1,3} + P_{3,1})^2 + (P_{2,3} + P_{3,2})^2) \end{aligned} \quad , \quad (3)$$

where the g_{11} , g_{12} and g_{44} represent the gradient energy coefficients, and $P_{i,j} = \frac{\partial P_i}{\partial x_j}$ ($i, j = 1, 2, 3$). The electric energy f_{elec} can be written as

$$f_{\text{elec}} = -\frac{1}{2} \kappa_0 \kappa_{ij}^b E_i E_j - E_i P_i, \quad (4)$$

where the κ_0 , κ_{ij}^b and E_i in Eq. (4) are the vacuum dielectric permittivity, the background relative dielectric permittivity tensor and electric field, respectively. The elastic energy f_{elas} can be written as

$$f_{\text{elas}} = \frac{1}{2} c_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^0) (\varepsilon_{kl} - \varepsilon_{kl}^0), \quad (5)$$

where the c_{ijkl} , ε_{ij} , ε_{ij}^0 represents the elastic stiffness tensor, total strain, and eigenstrain. The eigenstrain is related to the spontaneous polarization through the electrostrictive effect, $\varepsilon_{ij}^0 = Q_{ijkl} P_k P_l$, where Q_{ijkl} is the electrostrictive tensor. All the coefficients adopted in Eq.(2-5) for KNN can be found in literatures[31,38,42,43].

The evolution of $\mathbf{P}$ is governed by the time-dependent Ginzburg-Landau (TDGL)

equation,

$$\frac{\partial P_i(x,t)}{\partial t} = -L \frac{\delta F}{\delta P_i(x,t)}, \quad (i=1,2,3) \quad (6)$$

with L representing the kinetic coefficient. At each time step, the electrostatic and mechanical equilibrium equations are solved simultaneously with the short-circuit electric boundary conditions and mixed-typed mechanical boundary conditions, respectively[39,41]. The simulation system is discretized into $128\Delta x \times 128\Delta y \times 36\Delta z$ grid points with the grid size $\Delta x = \Delta y = \Delta z = 1$ nm. In all simulations of this work, the thickness of the KNN thin film is taken to be 20 nm, and the thickness of substrate layer is taken to be 13 nm. Notably, the substrate thickness in reality is usually much larger than the film. The value 13 nm is chosen here based on the assumption that the elastic deformation into the substrate can be ignored beyond this threshold. Detailed discussion on the choice of the substrate layer thickness can be found in Ref. [39].

To evaluate the domain size dependence of dielectric and piezoelectric responses, we first obtained the equilibrium domain structures of the a_1a_2/ac -type and a_1c/a_2c -type superdomains in KNN thin film by relaxing the preset domain structure with a prescribed domain period under zero macroscopic electric fields and stress. To obtain a superdomain structure with well-defined domain size, we preset the initial polarization configuration of the system by assigning local polarization vectors with corresponding directions (e.g., $P//[110]$ for $a_1^+a_2^+$ domain) and a uniform small magnitude ($|P| = 0.1$ C/m²). Then, these preset states were taken as the initial states to the simulations for relaxation. To avoid relaxing into different domain states and destroy the preset superdomain structure, we also turned off random noise during the relaxation

process. This method was used to obtain superdomain structures with regular morphology in our previous work [38]. In all cases studied here, there is no emergence of new domains or disappearance of preset domains during the relaxation, and hence the domain sizes of the preset structures are maintained.

Notably, in experiments, the piezoelectric coefficients are measured after poling the sample. To consider the poling process, only domain structures with net out-of-plane polarization are investigated in our work. Next, we applied a series of small electric fields E_3 (lower than 0.2 MV/m) along the out-of-plane direction of the film and monitor the changes of out-of-plane polarization ΔP_3 and strain component $\Delta \varepsilon_{33}$ of the films. The corresponding effective out-of-plane dielectric coefficient κ_{33}^* and converse piezoelectric coefficient d_{33}^* can be obtained by,

$$\kappa_{33}^* = \frac{1}{\kappa_0} \frac{\partial \Delta P_3}{\partial E_3}, \quad (7)$$

and

$$d_{33}^* = \frac{\partial \Delta \varepsilon_{33}}{\partial E_3}. \quad (8)$$

An example of calculating κ_{33}^* and d_{33}^* is given in Fig. S1. It can be seen that ΔP_3 and $\Delta \varepsilon_{33}$ are both linear with respect to the applied electric field E_3 . Therefore, κ_{33}^* and d_{33}^* can be obtained by the slopes of the ΔP_3 - E_3 and $\Delta \varepsilon_{33}$ - E_3 curves, respectively. Since the intrinsic dielectric and piezoelectric responses are considered in this work, the small magnitude of E_3 ensures negligible contributions from domain wall motion or field-induced phase transitions. Note that the asterisk is used in the superscripts of κ_{33}^* and d_{33}^* to distinguish the effective properties along the out-of-plane direction of the (001)_{pc}-oriented film from the crystallographic κ_{33} and

d_{33} along the polar axis of a polar single domain. The subscript pc stands for the pseudocubic coordinates, which will be omitted in the following discussion unless otherwise mentioned.

3. Results

3.1 The a_1a_2/ac -type and a_1c/a_2c -type superdomain structures

For a bulk KNN single crystal at room temperature and ambient pressure, the orthorhombic phase (space group $Amm2$) is the thermodynamically stable state, which has twelve ferroelectric domain variants with spontaneous polarization along the $\langle 110 \rangle$ directions. However, for (001)-oriented KNN epitaxial thin film, the anisotropic misfit strains imposed by the substrate break the degeneracy of the ferroelastic domain variants, giving rise to monoclinic domains (space group Pm) with only in-plane polarization component ($P_1 \neq 0, P_2 \neq 0, P_3 = 0$), denoted as a_1a_2 , and domains with both in-plane and out-of-plane polarization components, denoted as a_1c ($P_1 \neq 0, P_2 = 0, P_3 \neq 0$) and a_2c ($P_1 = 0, P_2 \neq 0, P_3 \neq 0$). The a_1a_2 -type domains include four variants depending on the sign of P_1 and P_2 denoted as $a_1^+a_2^+$, $a_1^-a_2^+$, $a_1^+a_2^-$, and $a_1^-a_2^-$. For example, $a_1^-a_2^+$ domains have $P_1 < 0, P_2 > 0, P_3 = 0$. Likewise, the a_1c -type domains include $a_1^+c^+$, $a_1^-c^+$, $a_1^+c^-$, $a_1^-c^-$ domain variants and the a_2c -type domains include $a_2^+c^+$, $a_2^-c^+$, $a_2^+c^-$, $a_2^-c^-$ domain variants.

The spatial configurations of these three types of ferroelastic domains give rise to a variety of intriguing domain morphology in epitaxial $K_xNa_{1-x}NbO_3$ thin films, some of which show hierarchical and regular patterns known as superdomains. For example, two typical superdomain structures have been reported in $K_xNa_{1-x}NbO_3$ epitaxial thin films, namely, the a_1a_2/ac -type and a_1c/a_2c -type superdomains. The former type consists of a pair of polydomains of a_1a_2 and ac (a_1c or a_2c) domains while the latter is constituted by a pair of polydomains of

a_1c and a_2c domains. The a_1a_2/ac -type superdomains form in films under highly anisotropic misfit strains while the a_1c/a_2c -type is stabilized in films under moderate biaxial compressive misfit strains. Notably, there are many different variants for both types of superdomains consisting of different a_1a_2 and ac domain variants [38]. However, only those superdomain structures with net out-of-plane polarization P_3 have nonzero piezoelectric response, and thus will be the focus in this study. Without losing generality, we choose the $a_1^+a_2^+/a_2^+c^+//a_1^-a_2^+/a_2^+c^+$ as an example for the a_1a_2/a_2c -type superdomain and the $a_1^-c^+/a_2^+c^+//a_1^+c^+/a_2^+c^+$ for the a_1c/a_2c -type superdomain, as shown in Fig. 1(a-b). Fig. 1(c-d) show the corresponding planar views of these two superdomain structures. Both types of superdomains show stripe-like morphology but the stripes extend along different directions. Specifically, the stripes of the a_1c/a_2c -type superdomains extend along $[110]$ and $[1\bar{1}0]$ while the stripes of the a_1a_2/a_2c -type superdomains are inclined by $\sim\pm 20^\circ$ with respect to $[010]$, which agree well with experimental measurements [44]. In addition, the a_1c/a_2c -type and a_1a_2/a_2c -type superdomains were termed as stripe-like and herringbone-like superdomains, respectively [45,46]. The definition of superdomain, superdomain wall, polydomain and domain walls are also illustrated in Fig.1 (e) for better understanding.

Following the procedure described in the Section 2, we evaluate the effective out-of-plane piezoelectric and dielectric coefficient, d_{33}^* and κ_{33}^* , as a function of the domain size for the two example superdomain structures. The domain size is defined by the lengths, L_x and L_y , representing the domain periods along the $[100]$ and $[010]$ directions, respectively, as labeled in Fig.1(c-d).

3.2 Domain size dependence of d_{33}^* and κ_{33}^* in a_1a_2/a_2c -type superdomains

We start from the domain size effect on piezoelectric and dielectric properties in a_1a_2/a_2c superdomain structures. We artificially construct a series of a_1a_2/a_2c superdomain structures with different L_x (from 16 to 48 nm) and L_y (from 40 to 216 nm) and then relax the systems to equilibrium states under the anisotropic in-plane misfit strain of $\varepsilon_{11}^{mis} = -0.4\%$ and $\varepsilon_{22}^{mis} = 1.0\%$. Fig. 2(a,c,e) show a few example superdomain structures obtained by this way with different L_x but fixed L_y (Fig. 2(a)), different L_y but fixed L_x (Fig. 2(c)), and varied L_y and L_x (Fig. 2(e)). The effective out-of-plane piezoelectric coefficient d_{33}^* and dielectric coefficient κ_{33}^* obtained by phase-field simulations as a function of L_x or L_y are shown in Fig. 2(b,d,f).

We find that when L_x is varied while keeping $L_y = 128$ nm, both κ_{33}^* and d_{33}^* increase linearly with the domain size L_x . Approximately, 15% enhancement of d_{33}^* and more than 41% enhancement of κ_{33}^* can be achieved when L_x increases from 16 nm to 48 nm. When L_y is varied from 40 to 216 nm while keeping $L_x = 32$ nm, both κ_{33}^* and d_{33}^* nonlinearly decrease with the increase of L_y with different extent (by 5% for d_{33}^* and 10% for κ_{33}^*). The opposite trends when changing L_x or L_y suggest that the domain size effect in ferroelectric thin films can be anisotropic, i.e., distinct domain size dependence can be found when the domain changes size along different directions. Notably, the maximal κ_{33}^* along [001] achieved by domain size engineering can reach 780 within the calculated range, which is drastically higher than 233[42] of a single-domain orthorhombic-phase bulk KNN crystal, while the maximal d_{33}^* is 123 pC/N along [001], which is relatively lower than that of the bulk value 221 pC/N [47].

We also computed d_{33}^* and κ_{33}^* by simultaneously varying L_x and L_y with a fixed ratio of $L_x/L_y = 1/4$. Comparing with the cases in Fig. 2(b) and (d), the domain size effects become more complex when L_x and L_y vary simultaneously. The trends of d_{33}^* and κ_{33}^* are no longer

coincident: despite that κ_{33}^* increases monotonously with the domain size, d_{33}^* show a non-monotonous behavior. A dip of d_{33}^* is found at $L_y = 80$ nm ($L_x = 20$ nm) along with some fluctuations in the range $60 < L_y < 100$ nm.

We further plotted all the calculated d_{33}^* and κ_{33}^* as a function of L_x and L_y in Fig. 3. It is found that d_{33}^* and κ_{33}^* show similar domain size dependence in general but with small deviations especially when L_y is small. Within the same range of domain sizes, κ_{33}^* show much higher tunability (from 511 to 874) than d_{33}^* (from 106 to 125 pC/N). Moreover, both materials responses depend more sensitively on L_x than L_y . Fig. 3 can be useful to guide the experimental optimization of dielectric and piezoelectric properties of KNN thin films by domain size engineering.

3.3 Domain size dependence of d_{33}^* and κ_{33}^* in a_1c/a_2c superdomains

We then turn to assess the domain size effect on d_{33}^* and κ_{33}^* for a_1c/a_2c -type superdomains in KNN thin film. A series of $a_1^+c^+/a_2^+c^+$ superdomains with different domain periods L_x and L_y under the in-plane misfit strain $\varepsilon_{11}^{mis} = \varepsilon_{22}^{mis} = 0.075\%$ at 400 K are obtained as shown in Fig.4(a,c). Fig. 4(a) illustrates the case with different L_x but fixed L_y while Fig. 4(c) shows the case with different L_y but fixed L_x . Both d_{33}^* and κ_{33}^* of the $a_1^+c^+/a_2^+c^+$ superdomains show a consistent, nonlinear L_x -dependence in Fig.4(b). Enhancement of up to 11% for d_{33}^* and 27% for κ_{33}^* is estimated when L_x increases from 19.2 nm to 31.2 nm at a fixed $L_y=128$ nm. When L_y varies while keeping L_x fixed, both d_{33}^* and κ_{33}^* show opposite domain size dependences as seen in Fig.4(d). Specifically, both d_{33}^* and κ_{33}^* drop nonlinearly by 22% and 51%, respectively, with L_y changing from 96 nm to 192 nm with L_x kept as 25.6 nm.

By comparing Fig. 2 and Fig. 4, we find that d_{33}^* and κ_{33}^* always show a consistent domain size dependence in both types of superdomain structures. Moreover, for both types of superdomain structures, d_{33}^* and κ_{33}^* increases when the polydomain size (i.e., L_x) increases but decreases when the superdomain size (i.e., L_y) increases.

4. Discussion

4.1 Local piezoresponses from domain variants and domain walls

To understand the domain size effects on the overall responses, we separately evaluated the local dielectric and piezoelectric contributions from each type of domain variants, domain walls, and superdomain walls. We find that the local polarization responses (ΔP_3) and strain responses ($\Delta \varepsilon_{33}$) are highly inhomogeneous and show strong spatial variations along the out-of-plane direction of the film. Taking the $a_1^+ a_2^+ / a_2^+ c^+ // a_1^- a_2^+ / a_2^+ c^+$ superdomains with $L_x = 32\text{nm}$, $L_y = 128\text{nm}$ as an example, we plotted the ferroelectric polarization under zero electric field (Fig. 5(a-c)), polarization responses ΔP_3 (Fig. 5(d-f)) and strain responses $\Delta \varepsilon_{33}$ (Fig. 5(g-i)) under the applied electric field of 0.1 MV/m in the x - y plane cross sections at the top ($z = 33$), middle ($z = 23$), and bottom ($z = 14$) of the film. In Fig. 5(a-c), the black arrows represent the in-plane polarization direction and the color corresponds the value of the out-of-plane polarization P_3 , from which the a_2c and a_1a_2 domains can be distinguished, as labeled in Fig. 5(a). We observe that the polarization distribution inside each domain is more uniform at the top layer than that at the bottom layer. From the film top to bottom, P_3 inside the a_2c domains reduces while P_3 inside the a_1a_2 domains increases. As a result, the polarization directions of the $a_1^+ a_2^+$ and $a_1^- a_2^+$ domains are no longer strictly in-plane, i.e., pointing toward $[110]$ and $[\bar{1}10]$ directions, but show a triclinic distortion, i.e., $P_1 \neq 0, P_2 \neq 0, P_3 \neq 0$. The distortion

becomes stronger approaching the film bottom. Moreover, the superdomain wall in the middle layer shows a zig-zag morphology, which is different from those at the top and bottom layers. This disruption at the superdomain walls have been discussed in our previous work[38].

As a result of the layer-dependent polarization distributions, ΔP_3 and $\Delta \epsilon_{33}$ inside each domain variants also become highly inhomogeneous, as shown in Fig.5 (d-f) and Fig.5 (g-i), respectively. The ΔP_3 inside the $a_1^+ a_2^+$ and $a_1^- a_2^+$ domain variants are higher than that of the $a_2^+ c^+$ domain variant at all layers, especially at the middle layer. Peak values of ΔP_3 can be found at the domain walls between an $a_1 a_2$ -type domain and an $a_2^+ c^+$ domain, especially near the superdomain wall. Interestingly, for each $a_1 a_2$ -type domain, the polarization responses are different at the adjacent domain walls, and these differences also depends on the layers. For example, the right-hand-side domain wall of the $a_1^- a_2^+$ domain (circled in red in Fig. 5(f)) is associated with a peak ΔP_3 while the left-hand-side domain wall has no enhancement in ΔP_3 . These inequivalent behaviors of the adjacent domain walls are likely due to the fact the $a_1 a_2 / a_1 c$ domain walls are inclined with respect to the in-plane direction. Similar asymmetry of local responses at a pair of domain walls have been reported in other inclined domain walls in ferroelectric thin films, such as the 90-degree a/c domain walls in PbTiO_3 [48] and 71-degree domain walls in BiFeO_3 [49].

The out-of-plane strain responses, $\Delta \epsilon_{33}$, also display strong spatial inhomogeneity and layer dependence, as shown in Fig.5 (g-i). In the top layer (Fig. 5g), the $a_2^+ c^+$ domains have positive $\Delta \epsilon_{33}$ while the $a_1 a_2$ -type domains show negative ones. The $\Delta \epsilon_{33}$ at domain walls is higher than those inside domain, and the peak values of $\Delta \epsilon_{33}$ occur near the superdomain wall. In the middle layer (Fig. 5h), the $\Delta \epsilon_{33}$ inside the domains become more uniform while the

domain wall contributions exhibit asymmetry with respect to the left- and right-hand-side of a domain. This asymmetry becomes more significant in the bottom layer (Fig. 5i) wherein one of the pair of domain walls has negligible $\Delta\epsilon_{33}$ whereas the other one has a strong positive $\Delta\epsilon_{33}$. The spatial dependence of $\Delta\epsilon_{33}$ is to some extent correlated with that of ΔP_3 but with slight deviations locally.

Fig. 5 indicates that the local polarization and strain responses to the applied field are highly layer dependent, making it less accurate to represent the domain and domain wall contributions merely by using the averaged local responses across the entire film thickness. Therefore, we performed a layer-resolved analysis for all simulation results in Fig. 2d (i.e., fixed $L_x = 32$ nm and different L_y) by averaging the total responses from each type of domains and domain walls within each layer, and plotted them against the layer number in Fig. 6. For the total response in each layer (Fig. 6(a)), there is a quasi-linear decrease of ΔP_3 from the film bottom to the top, along with drops at the two ends. Higher ΔP_3 is seen when L_y decreases, which agrees with the domain size dependence of κ_{33}^* and d_{33}^* shown in Fig. 2. The contribution from $a_1^+ a_2^+$ domains (Fig. 6 (b)) have consistent trends as the total responses in terms of the L_y and layer dependences. The other in-plane domain variant $a_1^- a_2^+$ show similar behavior and thus is omitted here. In contrast, the out-of-plane domain variants $a_2^+ c$ (Fig. 6(c)) shows an irregular layer dependence and relatively small magnitudes than that of the $a_1 a_2$ -type domain variants. The contributions from the domain walls, though exhibiting the largest magnitude, show opposite layer dependence to that of the total response and less definite size dependence. Comparing Fig. 6(b-d) with Fig. 6(a), we conclude that the domain size effects on

κ_{33}^* and d_{33}^* for the $a_1^+ a_2^+ / a_2^+ c^+ // a_1^- a_2^+ / a_2^+ c^+$ superdomain structures may be dominated by the local responses from the $a_1 a_2$ -type domains.

We further performed similar layer-resolved analyses to other measures of dielectric and piezoelectric responses induced by the applied field $E_3 = 0.1$ MV/m, including the variation of the out-of-plane strain $\Delta\epsilon_{33}$, the out-of-plane polarization ΔP_3 , the polarization modulus $\Delta|\mathbf{P}|$ and the rotation angle θ under an external electric field of. The choice of the latter two factors are inspired by the well-established model of polarization rotation and polarization elongation as the two major contributors to intrinsic piezoelectric responses in perovskite piezoelectric crystals [7]. To find the quantity most relevant to the overall piezoelectric response, we computed the layer-resolved correlation coefficient R between the L_y -dependence of d_{33}^* and the L_y -dependence of the four factors ($\Delta\epsilon_{33}$, ΔP_3 , $\Delta|\mathbf{P}|$ and θ). For each factor, it is averaged over the entire layer, the region of three domain variants ($a_1^+ a_2^+$, $a_1^- a_2^+$ and $a_2^+ c$ domain), and the domain wall region. Therefore, we define twenty factors in total and computed the correlations between their domain size (L_y) dependence and the L_y -dependence of d_{33}^* . We also computed the correlation coefficients for the twenty factors averaged over the entire film, as shown in the bottom of Fig. 7. The correlation coefficient R between the L_y -dependence of factor X (X can be $\Delta\epsilon_{33}$, ΔP_3 , $\Delta|\mathbf{P}|$ and θ of any type of the three domain variants or domain walls) at a given layer Z , denoted as $X(L_y, Z)$, and the L_y -dependence of d_{33}^* , denoted as $d_{33}^*(L_y)$, is calculated as

$$R = \frac{\text{cov}(d_{33}^*(L_y), X(L_y, Z))}{\sigma(d_{33}^*(L_y))\sigma(X(L_y, Z))},$$

where $\text{cov}(d_{33}^*(L_y), X(L_y, Z))$ is the covariance between $d_{33}^*(L_y)$ and $X(L_y, Z)$, and $\sigma(d_{33}^*(L_y))$ and $\sigma(X(L_y, Z))$ represent the standard deviation of $d_{33}^*(L_y)$ and $X(L_y, Z)$, respectively. The correlation coefficient R thus reflects the correlation between $d_{33}^*(L_y)$ and $X(L_y, Z)$. All R values are within -1 to 1, and a more positive (negative) R corresponds to a stronger positive (negative) correlation between $X(L_y, Z)$ and $d_{33}^*(L_y)$, suggesting that the factor X at layer Z contributes more to the overall domain size dependence of d_{33}^* .

Fig. 7 shows dominant positive correlation between the L_y -dependence of ΔP_3 with that of d_{33} , which can be attributed to the strong correlation between ΔP_3 and d_{33} of the two in-plane domain variants at all layers, i.e. $\Delta P_3^{a_1^+ a_2^+}$ and $\Delta P_3^{a_1^- a_2^+}$. In contrast, the correlations for the out-of-domain variant $\Delta P_3^{a_2^+ c^+}$ and domain wall ΔP_3^{DW} are weaker due to variations among different layers as also observed in Fig.6(c-d). The $\Delta \varepsilon_{33}^{layer}$ of the overall film show consistent domain size dependence as the d_{33}^* despite of fluctuations among layers. The $\Delta \varepsilon_{33}^{DW}$ of the overall film is the only one factor that exhibits strongly negative correlation, suggesting that the strain response at the DWs may not be a critical factor to determine the domain size dependence of the piezoelectricity. All the $\Delta|\mathbf{P}|$'s show positive correlations despite of moderate layer dependences, while all the $\Delta\theta$'s generally show weaker positive correlation than do the $\Delta|\mathbf{P}|$'s. By reorganizing the columns of the R matrix in terms of the types of domain variants and domain walls (Fig.S2), we can identify that the $a_1 a_2$ -type domains generally show consistent domain size dependence as that of the overall d_{33}^* , suggesting the dominant contributions to the overall responses from the $a_1 a_2$ -type domain variants.

In summary, despite of the complexity associated with the layer fluctuation of several factors, our statistical analysis reveals that the change in the out-of-plane polarization serves as

the primary microscopic mechanism to account for the domain size dependent of piezoelectricity for the a_1a_2/a_2c -type superdomain structures, and the a_1a_2 -type domains make the primary contributions.

4.2 Contribution of polydomains and superdomains to the domain size effects

We discuss the contribution of superdomains to the overall d_{33}^* as compared to a single bundle of polydomains. To this end, we consider two types of domain structures, namely, the a_1c/a_2c -type superdomains constituted by two alternating bundles of $a_1^-c^+/a_2^+c^+$ and $a_1^+c^+/a_2^+c^+$ polydomains (Fig. 8(a)) and the single-bundle $a_1^+c^+/a_2^+c^+$ polydomains (Fig. 8(b)). A series of domain structures with fixed $L_y = 156$ nm and varied L_x have been constructed and relaxed to the equilibrium under misfit strain $\varepsilon_{11}^{mis} = \varepsilon_{22}^{mis} = 0.075\%$ at 400K. The domain size (L_x) dependence of d_{33}^* are evaluated and plotted in Fig. 8(b) for L_x ranges from 18 to 32 nm. Instead of showing the absolute value of d_{33}^* , we present the relative difference, Δd_{33}^* , with respect to the minima of each case. We find that Δd_{33}^* of the single-bundle polydomain structure is generally smaller than that of the superdomain structure and fluctuates around 1.0 pC/N. In contrast, Δd_{33}^* of the superdomain structure continuously increases up to 11 pC/N. This result indicates that the presence of superdomains can remarkably increase the domain size effect, which is likely to due to the formation of superdomain walls associated with highly inhomogeneous polarization [38].

4.3 Tuning the domain size dependence of d_{33}^* by misfit strains and temperature

One question of immediate experimental interest is that whether the domain size effect in the thin films can be tuned. Here, we demonstrate the possibility to modulate the domain size effect by engineering the misfit strains and the polymorphic phase boundaries of KNN. Take the $a_1^+c^+/a_2^+c^+$ superdomain as an example, we evaluate the domain size effects of the same

structure at different misfit strains and temperatures, as shown in Fig. 9. The choice of the misfit strains and temperatures are guided by the temperature-misfit strain phase diagrams for (001)-oriented KNN thin films subject to equal-biaxial misfit strains (Fig. 9(a), replotted from Ref. [43]). In all cases with varied misfit strains shown in Fig. 9(a), we have examined that the preset domain sizes are maintained and not changed by the misfit strains. And the relative changes of d_{33}^* in each case, Δd_{33}^* , are plotted for better comparison. We find that, with ε_{11}^{mis} changing from -0.5% to 0.075% to approach the mix-phase region in the phase diagram, Δd_{33}^* increases from a negligible value to more than 20 pC/N (Fig. 9(b)). Moreover, when both the misfit strain and the temperature are changed to approach the phase boundary of the R_D phase region, Δd_{33}^* can also be enhanced remarkably (Fig. 9(c)). These two examples demonstrate that stronger domain size effect of piezoelectricity can be expected near a ferroelectric-ferroelectric phase transformation, which is consistent with the findings in ferroelectric bulk crystals [27]. Moreover, this finding suggests the possibility to achieve stronger domain size effect by engineering a ferroelectric polymorphic phase boundary to room temperature, e.g., by doping[50] or strain engineering[45].

We should point out that, in-principle, the equilibrium domain size in a ferroelectric thin film is correlated to the film thickness due to the competition between electrostatic, elastic energy and domain wall energies, following the Kittel's law[51–53]. In this work, we kept the film thickness as a constant when varying the domain size to isolate the effect of domain size change to the dielectric and piezoelectric responses and eliminate that from the change of film thickness. In reality, for a film with a given thickness, the same type of domain structure with different domain periods may correspond a series of metastable states associated with excessive electrostatic and/or elastic energies. In principles, these metastable states can be obtained by a careful control of local domains, e.g., via scanning probe techniques [54]. The covariation of film thicknesses and domain sizes and its effect on the domain size dependence of piezoelectric responses require more careful and in-depth consideration and will be examined in a future

publication. Notably, recent experiments have demonstrated continuous control of the domain size in one of the superdomain structures of $K_xNa_{1-x}NbO_3$ thin films [51], which provides possibility to validate our theoretical predictions.

4.4 The influence of flexoelectric effect on the piezoelectric response

As shown in Fig. 5, the polarization and strain distributions are highly inhomogeneous in the a_1c/a_1a_2 -type superdomain structure. It is expected that the flexoelectric effect, i.e., coupling between polarization and strain gradients, may be significant and contribute to the piezoelectric responses. To quantify the flexoelectric contribution, we performed additional phase-field simulations with considering the flexoelectric effect following Ref. [55]. The detailed description of the method and choice of the flexoelectric coefficients are given in Supporting Information Note 1.

Fig. S3(a-c) show the difference of the local out-of-plane strain responses in the middle layer of the KNN thin film under an applied field $E_3 = 0.1$ MV/m with and without considering the flexoelectric effect ($\Delta\epsilon_{33}^{\text{flexo}} - \Delta\epsilon_{33}^{\text{no-flexo}}$). It is found that all three independent components of the flexoelectric tensor, i.e., the longitudinal f_{11} , transverse f_{12} , and shear f_{44} components, can influence the local strain response and in different ways. Specifically, f_{11} mainly impacts the domain walls of the twin polydomains, i.e., between $a_1^+a_2^+$ and $a_2^+c^+$ or $a_1^-a_2^+$ and $a_2^+c^+$. In contrast, f_{12} mainly influences the superdomain walls between polydomains. For f_{44} , the variation is pronounced at both domain wall and superdomain wall regions. Notably, f_{12} and f_{44} generally have larger impacts on the local piezoelectric response than that from f_{11} , as indicated by the order of magnitude of $\Delta\epsilon_{33}^{\text{flexo}} - \Delta\epsilon_{33}^{\text{no-flexo}}$.

We also compared the overall out-of-plane effective piezoelectric coefficient, d_{33}^* , for the three cases with flexoelectricity and the case without flexoelectricity. We found that the variation of d_{33}^* is negligible (< 2 pC/N, $\sim 1\%$), as shown in Fig.R1(d). This may be explained by the fact that the local strain responses induced by flexoelectricity have positive and negative variations of comparable magnitude, which cancel out macroscopically. Therefore, the flexoelectric effect was neglected in all other simulations in this work.

In fact, the impact of flexoelectricity on the polarization and domain structures in

ferroelectrics at nanoscale will be more complex, such as widening of domain wall thickness, distortion of domain walls near surface, and vortex-like structures [56,57], which may also appear in the superdomain structures of KNN thin films and lead to unique piezoelectric responses. These interesting topics remain open questions to be explored systematically in future research.

5. Conclusion

In this work, we performed phase-field simulations to evaluate the domain size dependence of piezoelectric and dielectric response (d_{33}^* and κ_{33}^*) in KNN thin films with two representative superdomain structures. It shows that d_{33}^* and κ_{33}^* can either increase or decrease with reduced domain size, suggesting that the domain size effect is not universal in ferroelectric thin film, similar to that for the bulk piezoelectric crystals. The simulation results reveal highly inhomogeneous and layer-dependent behavior for the local piezoelectric and dielectric responses inside the domains. Layer-resolved statistical analyses on four key factors of the local responses ($\Delta\epsilon_{33}$, ΔP_3 , $\Delta|\mathbf{P}|$ and θ) suggest that the domain size effect in the a_1a_2/a_2c -type superdomains is dominated by the out-of-plane polarization variation ΔP_3 of the a_1a_2 -type domain variants. We also find that the domain size dependence is more pronounced near a polymorphic phase boundary, suggesting tunability of the domain size effect by chemical doping and misfit strain engineering. The domain size effect is shown to be enhanced with the presence of superdomain walls, indicating a new routine to enhance materials properties by the largely unexplored superdomain engineering.

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Figures and captions

Figure 1

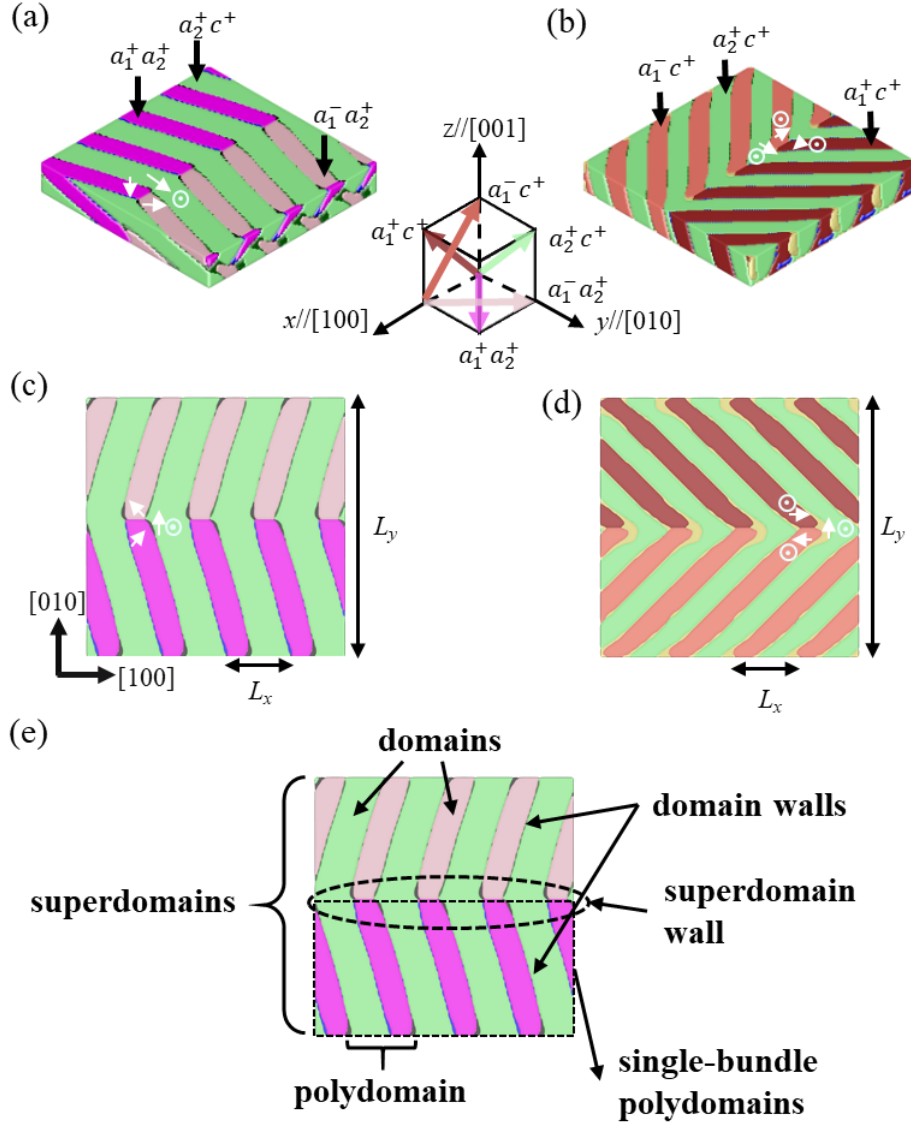


Fig.1 | Superdomain structures in (001)-oriented $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ thin films by phase-field simulations. (a,c) the a_1a_2/a_2c -type superdomain structures and (b,d) a_1c/a_2c -type the superdomain structures visualized from (a,b) a 3-D orthographic view and (c,d) a planar view. The arrows in the graphs indicate the polarization directions in each domain variant. The inset in the center indicates the coordinate system of the 3-D graphs and the polarization directions of each domain variants with corresponding colors. The period of one pair of twin domains along $[100]$ and $[010]$ directions are labeled by L_x and L_y , respectively. (e) A schematic to distinguish some key concepts (superdomain, polydomain, single-bundle polydomains,

domains, superdomain walls and domain walls) for describing the domain structures in this work.

Figure 2

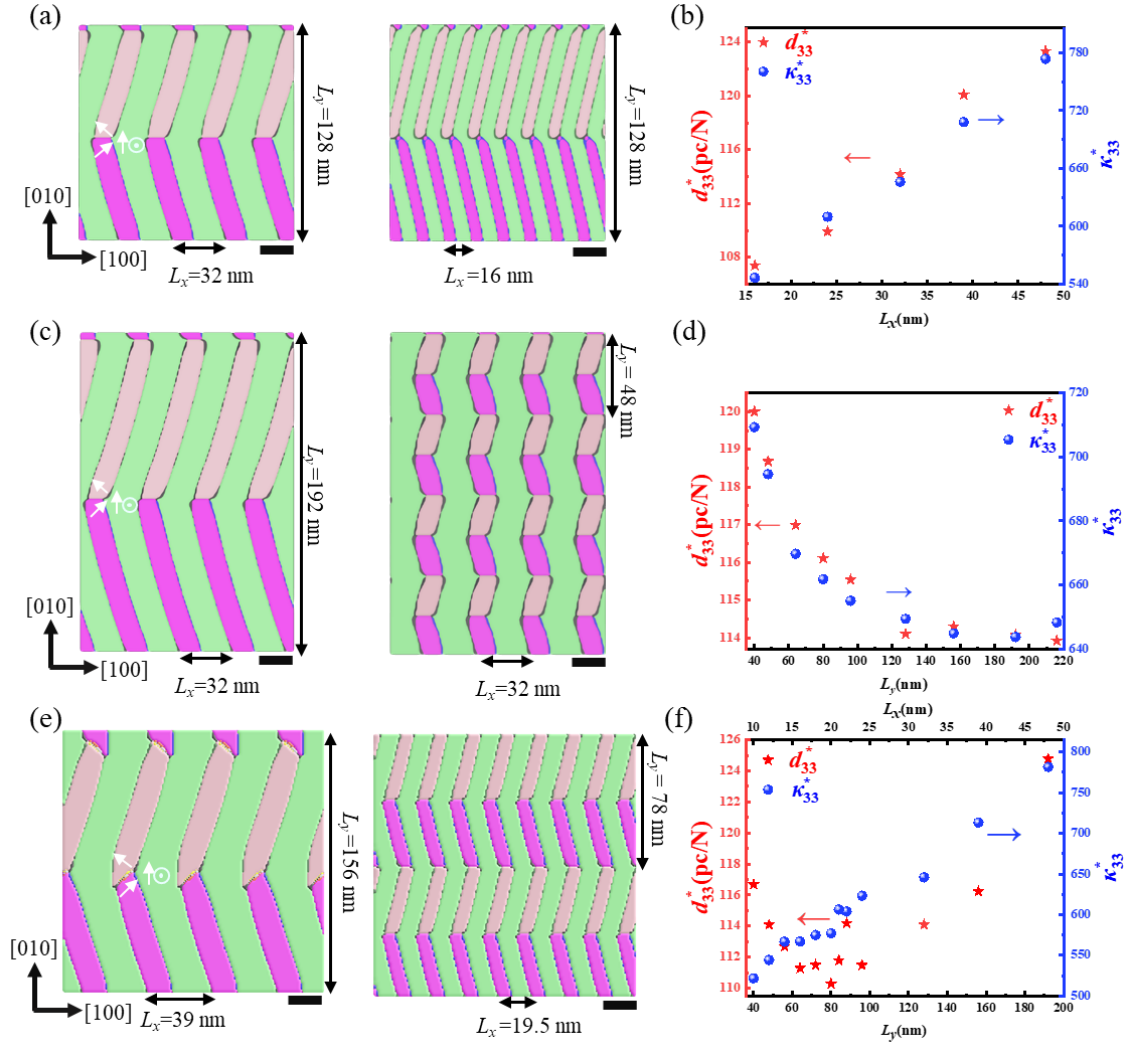


Fig.2 | Domain size effect on piezoelectric and dielectric properties of the a_1a_2/a_2c -type superdomains when the domain periods vary in one lateral direction. (a,c,e) Planar views of a_1a_2/a_2c -type superdomains with (a) different lateral period L_x but identical longitudinal period L_y , (c) different L_y but identical L_x and (e) varying L_x and L_y with a fix ratio of $L_x / L_y = 1/4$. The in-plane misfit strain is $\varepsilon_{11}^{mis} = -0.4\%$ and $\varepsilon_{22}^{mis} = 1.0\%$ and the temperature is 300 K. (b,d,f) The calculated out-of-plane piezoelectric coefficient d_{33}^* and dielectric constant κ_{33}^* as a function of (b) L_x , (d) L_y and (f) $L_y = 4 L_x$.

Figure 3

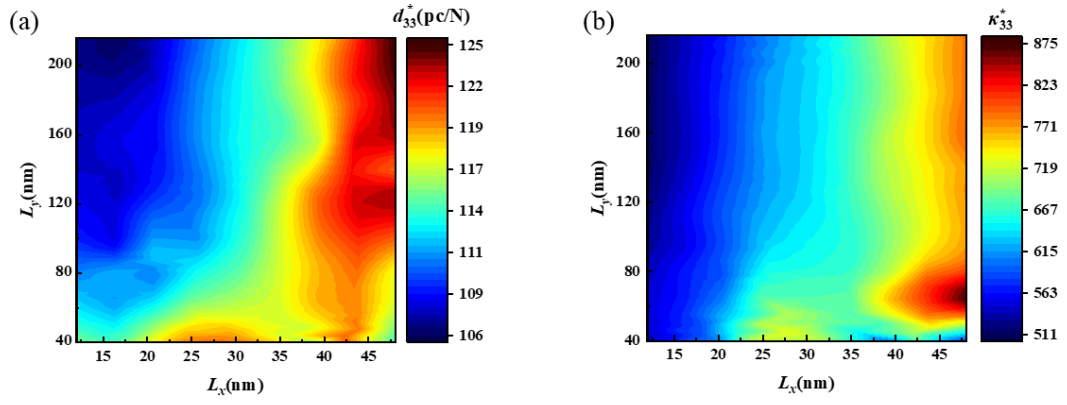


Fig.3 | The calculated mappings of piezoelectric and dielectric properties of the a_1a_2/a_2c -type superdomains at varying L_x and L_y . (a,b) The calculated out-of-plane (a) piezoelectric coefficient d_{33}^* and (b) dielectric constant κ_{33}^* as a function of L_x and L_y .

Figure 4

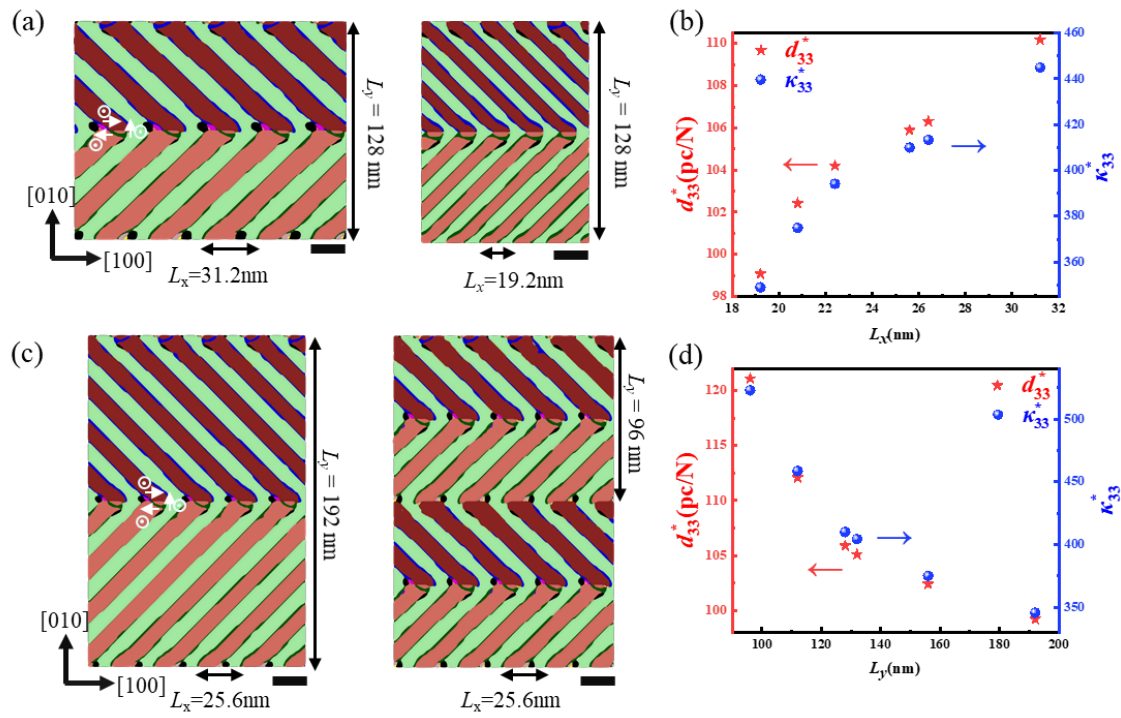


Fig.4 | Domain size effect on piezoelectric and dielectric properties of the a_1c/a_2c -type superdomains. (a,b) Planar views of stripe-like superdomains with (a) different lateral period L_x but identical longitudinal period L_y and (b) different L_y but identical L_x . The in-plane misfit strain is $\varepsilon_{11}^{mis} = \varepsilon_{22}^{mis} = 0.075\%$ and the temperature is 400 K. (c,d) The calculated out-of-plane piezoelectric coefficient d_{33}^* and dielectric constant κ_{33}^* as a function of (c) L_x and (d) L_y .

Figure 5

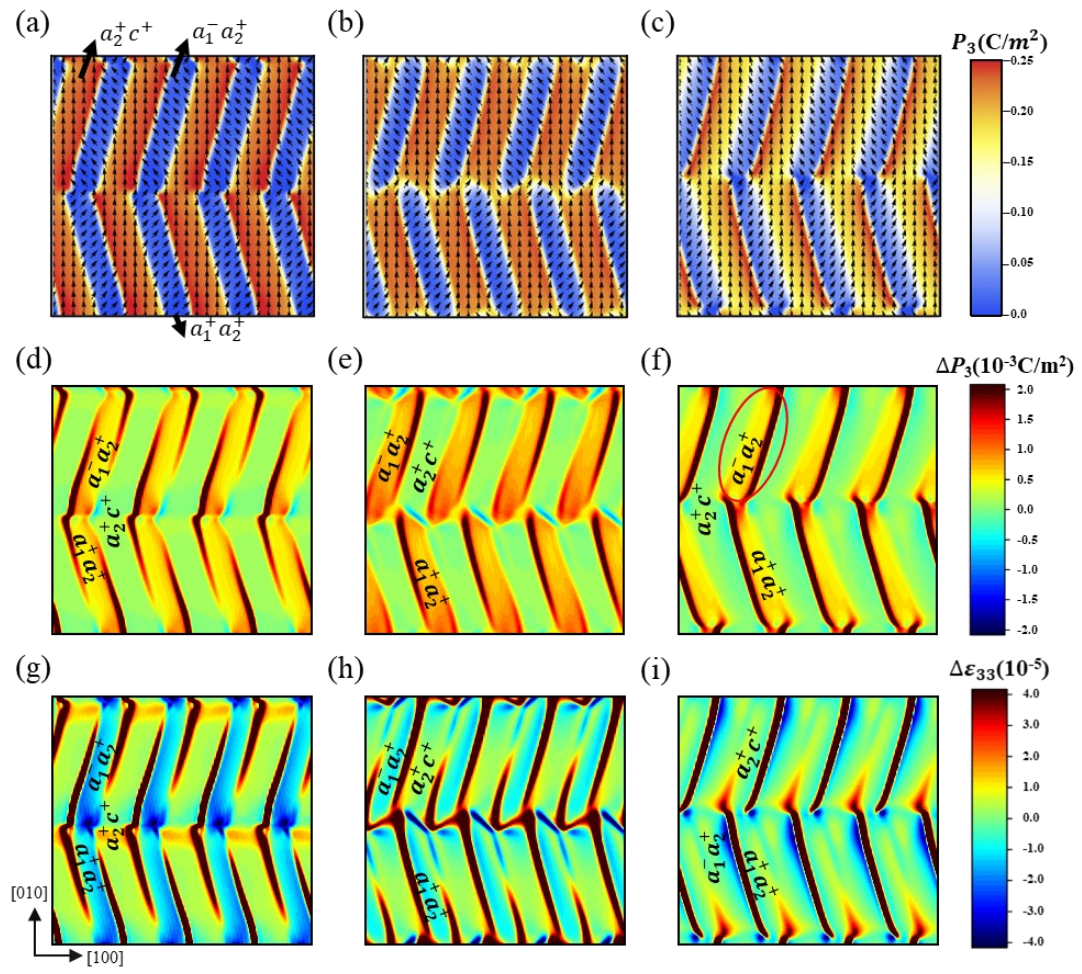


Fig.5 | The simulated (a – c) polarization distribution under zero electric field, (d – f) variation of out-of-plane polarization ΔP_3 , and (g – h) variation of out-of-plane strain $\Delta \epsilon_{33}$ at the (a,d,g) top, (b,e,h) middle and (c,f,i) bottom layers of the KNN thin film.

Figure 6

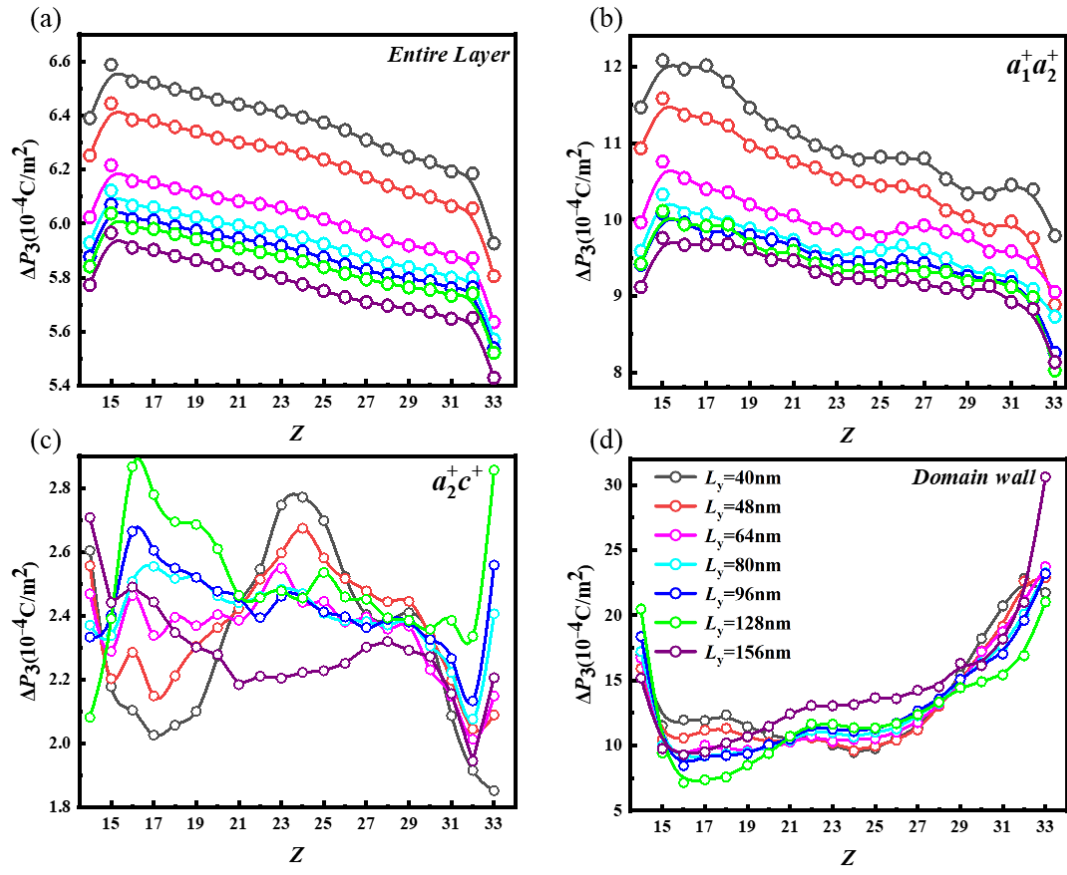


Fig.6 | The out-of-plane polarization ΔP_3 of the KNN thin film at different layers. The average variation of out-of-plane strain ΔP_3 of (a) entire layer and (b) $a_1^+ a_2^+$ domain variants (c) $a_2^+ c^+$ domain variants and (d) domain wall.

Figure 7

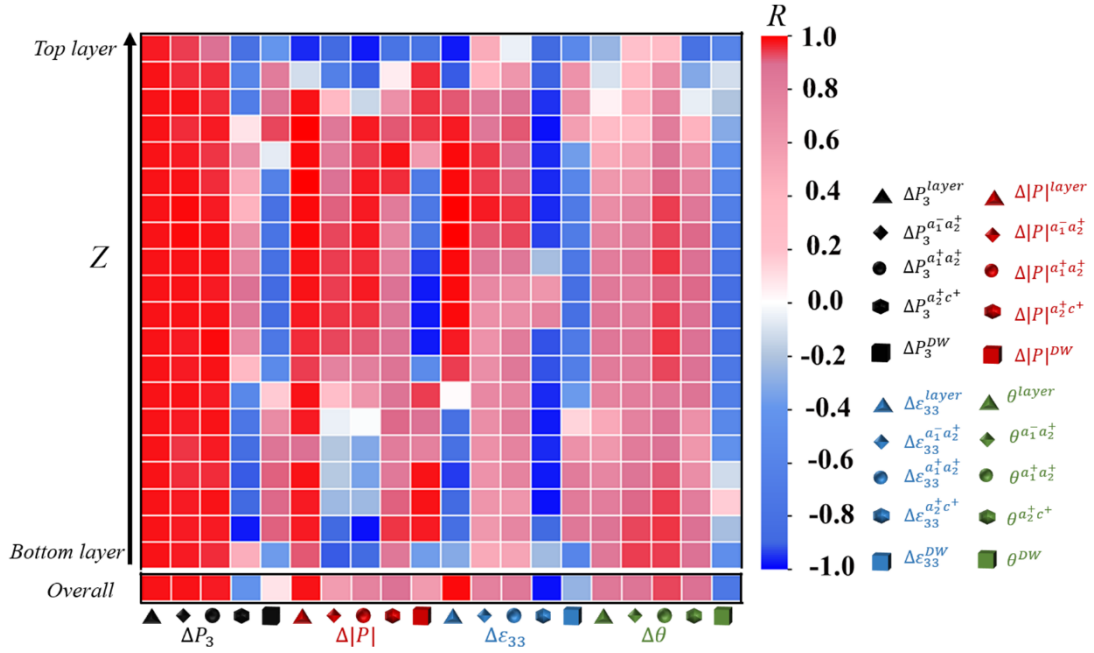


Fig.7 | The correlation between piezoelectric coefficient d_{33}^* and the variations of out-of-plane strain $\Delta \epsilon_{33}$, out-of-plane polarization ΔP_3 , the polarization modulus $|P|$ and rotation angle θ , with each annotated in black, red, blue and green colors. For the correlation of each factor, the average of entire layer, $a_1^- a_2^+$ domain, $a_1^+ a_2^+$ domain and $a_2^+ c^+$ domain and domain wall are represented by triangle, diamond, circle, hexagon and square symbols, respectively.

Figure 8

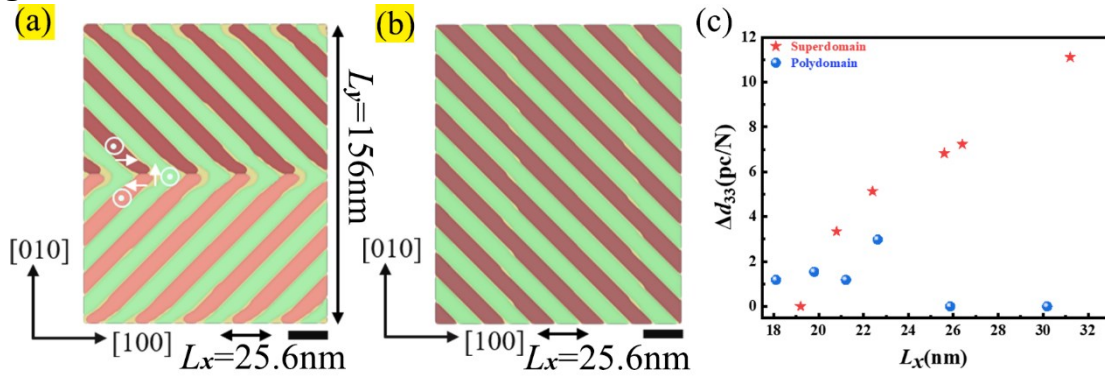


Fig.8 | Tuning the domain size effect on piezoelectricity of the a_1c/a_2c -type superdomains. (a) Schematic representation of the stripe-like superdomains and polydomain. The in-plane misfit strain is $\varepsilon_{11}^{mis} = \varepsilon_{22}^{mis} = 0.075\%$, and the temperature is 400 K. (b) The variation of the out-of-plane piezoelectric coefficient Δd_{33}^* as a function of L_x .

Figure 9

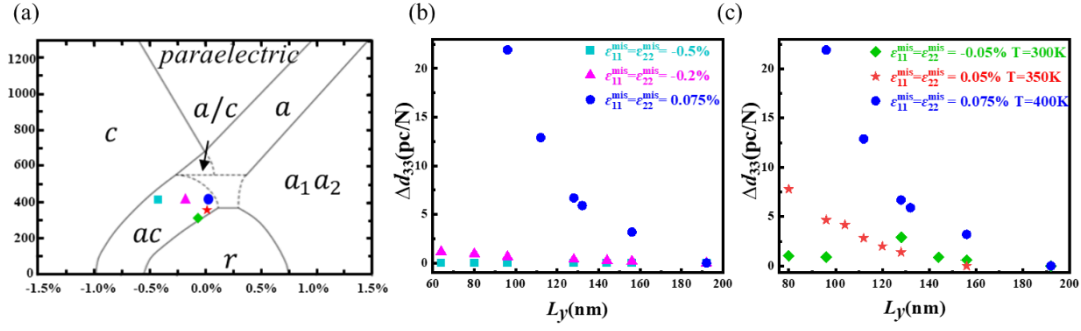


Fig.9 | Tuning the domain size effect on piezoelectricity of the a_1c/a_2c -type superdomains. (a) Temperature-misfit strain phase diagrams of $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$. The meaning of symbols for domain variants are: a ($P_1 \neq 0, P_2 = P_3 = 0$ or $P_2 \neq 0, P_1 = P_3 = 0$), c ($P_3 \neq 0, P_1 = P_2 = 0$), ac ($P_1 \neq 0, P_2 = 0, P_3 \neq 0$ or $P_1 = 0, P_2 \neq 0, P_3 \neq 0$), a_1a_2 ($P_1 \neq 0, P_2 \neq 0, P_3 = 0$), r ($P_1 \neq 0, P_2 \neq 0, P_3 \neq 0$). (b-c) The variation of the out-of-plane piezoelectric coefficient Δd_{33}^* as a function of L_x for stripe-like superdomains (b) under various in-plane misfit strains of $\varepsilon_{11}^{\text{mis}} = \varepsilon_{22}^{\text{mis}}$ at 400 K and (c) under varied misfit strains and temperatures. (a) is reprinted with adaption from Ref. [43]. With the permission of AIP Publishing.

Supporting Figure 1

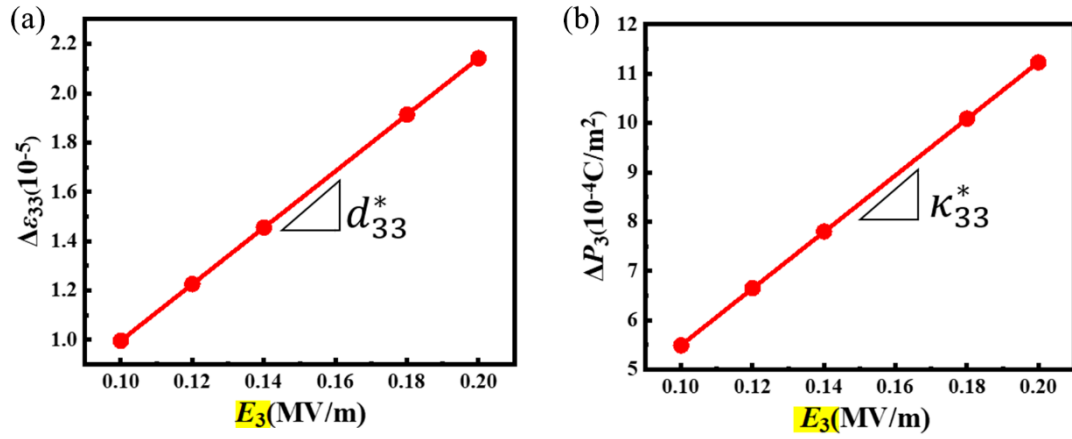


Fig.S1 | Example of the evaluation of the out-of-plane piezoelectric coefficient in the phase-field simulation. (a) The variation of out-of-plane strain $\Delta\epsilon_{33}$ as a function of the applied electric field E_3 . The slope of a linear fitting line gives the d_{33}^* . (a) The variation of the out-of-plane polarization ΔP_3 as a function of the applied electric field E_3 . The slope of a linear fitting line gives the κ_{33}^* .

Supporting Figure 2

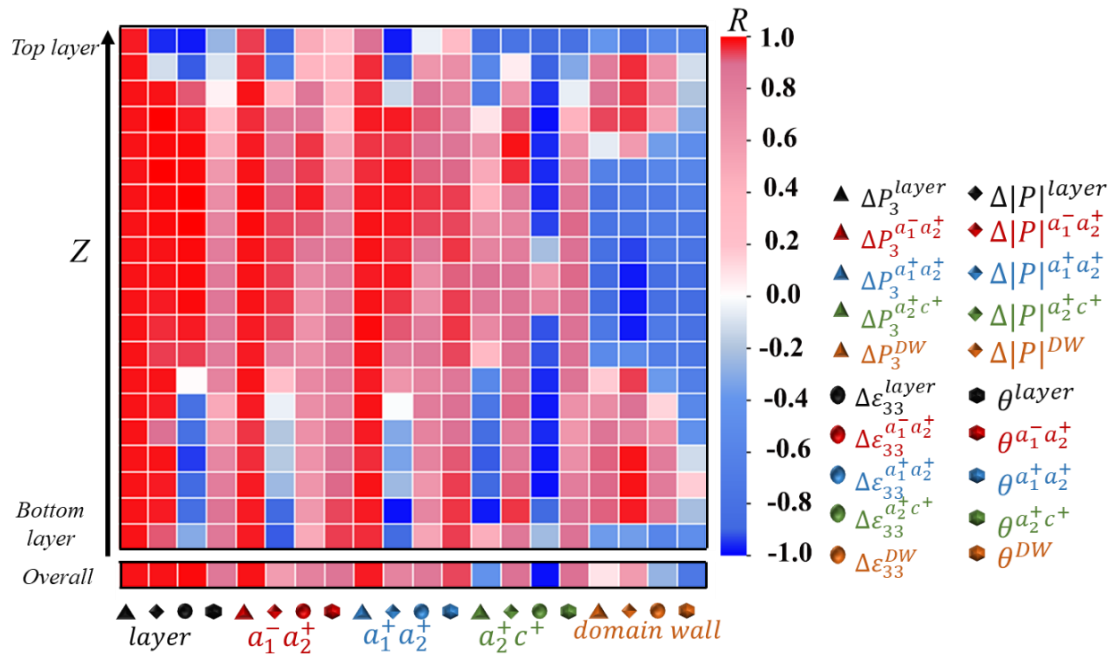


Fig. S2 | The replotting of Fig.7 by reorganizing the columns of the R matrix in terms of the types of domain variants and domain walls.

Supporting Figure 3

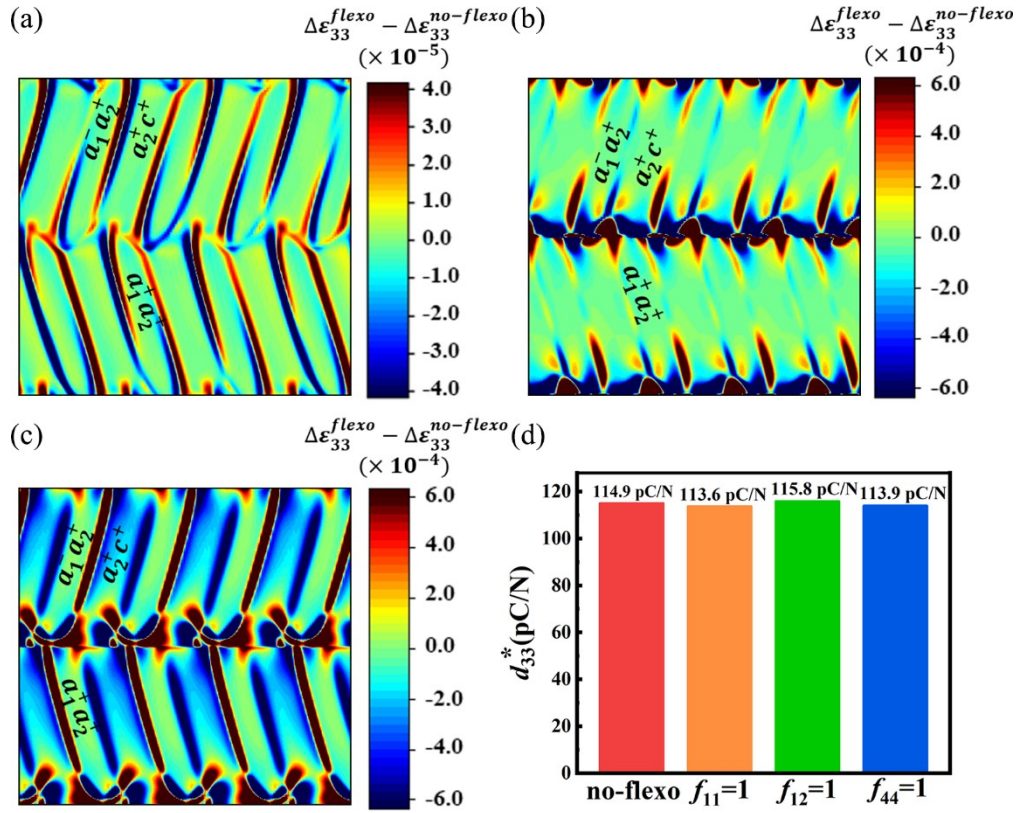


Fig.S3 | The influence of flexoelectric effect on piezoelectric response. (a-c) The mapping of $\Delta\epsilon_{33}^{flexo} - \Delta\epsilon_{33}^{no-flexo}$ for the middle layer of KNN thin film considering flexoelectric coefficients of (a) $f_{11}=1$ V, $f_{12}=0$, $f_{44}=0$, (b) $f_{11}=0$, $f_{12}=1$ V, $f_{44}=0$, and (c) $f_{11}=0$, $f_{12}=0$, $f_{44}=1$ V. (d) The calculated overall out-of-plane piezoelectric coefficient d_{33}^* with and without flexoelectric effect.