Highly mobile ferroelastic domain walls in compositionally graded ferroelectric thin films

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I) Heterostructure Design

When designing compositionally-graded heterostructures it is important to consider how both the local phase and lattice parameters evolve with composition. Inspection of the composition-temperature phase diagram (Fig. S1a) reveals a structural competition between tetragonal and rhombohedral symmetry on the Ti- and Zr-rich sides, respectively. Likewise, the room-temperature lattice parameter-composition evolution (Fig. S1b), reveals that the lattice parameters of the PbZr1-xTiO3 system do not vary linearly with composition, but instead change rapidly near the morphotropic phase boundary (MPB, x = 0.48), where rhombohedral and tetragonal phases can coexist. Based on this information, we focused on homogeneous-layer and compositionally-graded heterostructures of PbZr1-xTi0.5O3/30 nm SrRuO3/GdScO3 (110) (a = 5.45 Å, b = 5.75 Å, c

Figure S1. (a) PbZr1-xTiO3 phase diagram, adapted from B. Jaffe et al.11 (b) Bulk lattice parameter (shown in black) and calculated misfit strain (shown in blue) spanning across the PbZr1-xTi0.5O3 phase diagram. (c) Schematic illustrations of 100 nm homogeneous PbZr0.2Ti0.8O3 and compositionally graded PbZr0.8Ti0.2O3 ⇋ PbZr0.2Ti0.8O3 grown on /SrRuO3/GdScO3 (110)
2 Å, pseudocubic $a_{pc} = 3.973$ Å) grown using pulsed-laser deposition. Growth on GdScO$_3$ substrates provides lattice mismatches between -4.6% to 2% as one transitions from PbZrO$_3$ to PbTiO$_3$ (Fig. S1b, right axis). The composition of the bottom-most layer of the heterostructure was chosen to be the composition with the least lattice mismatch to the substrate (i.e., PbZr$_{0.2}$Ti$_{0.8}$O$_3$) and the compositional gradients were controlled to be compositionally-linear in nature throughout the thickness of the film. The selection of end-member compositions which minimize the lattice mismatch at the substrate-film interface provides an effective route to mitigate defects and relaxation in the heterostructures. Given these constraints, we focus in this work on 100 nm homogeneous PbZr$_{0.2}$Ti$_{0.8}$O$_3$ and compositionally-graded heterostructures which linearly vary from PbZr$_{0.2}$Ti$_{0.8}$O$_3$ at the substrate film interface (lattice mismatch 0.8% tensile) to PbZr$_{0.8}$Ti$_{0.2}$O$_3$ at the free surface (lattice mismatch -3.5% compressive) as schematically shown (Fig. S1c-d).

To measure the chemical gradients, compositionally-graded heterostructures were grown on bare SrTiO$_3$ (001) substrates using identical growth conditions. Rutherford backscattering spectrometry (RBS) was performed with incident ion energy of 3040 keV, incident angle $\alpha = 22.5^\circ$, exit angle $\beta = 25.35^\circ$, and scattering angle $\theta = 168^\circ$. Fits to the experimental data were completed using the RBS analysis software SIMNRA and were evaluated using an $R^2$ method with $R^2 = 1 - \frac{\sum(e_i-f_i)^2}{\sum(e_i)^2}$, where e-values and f-values correspond to experimental and simulated data, respectively. $R^2$ values were calculated about the Pb, Ti, and Zr film peaks to avoid artificially increasing the value of $R^2$ by the inclusion of substrate peaks. After fitting ($R^2 > 0.99$) it was found that the compositional gradient in the B-site varied smoothly from PbZr$_{0.2}$Ti$_{0.8}$O$_3$ to PbZr$_{0.2}$Ti$_{0.8}$O$_3$ (from substrate to film interface) matching well the desired compositional gradient (within experimental error). Furthermore, no Pb-loss or Pb gradients were observed in these films.

II) Additional X-ray Diffraction Studies

For both the homogeneous and compositionally-graded heterostructures studied herein, wide-angle $\theta$-2$\theta$ X-ray diffraction patterns were obtained (Fig. S3). All heterostructures studied were single-phase, fully-epitaxial, and (001)-oriented regardless of thickness or gradient design. In addition, RSM studies of the homogeneous and compositionally-graded heterostructures were completed about the 103- and 332-diffraction conditions of the films and substrate, respectively (Fig. S4a-b). The positions of the bulk and strained peaks for the parent phase(s) are provided for reference. Focusing on the 100 nm thick homogeneous heterostructures reveals that the heterostructures are nearly-coherently strained to the substrate. Moving to the compositionally-graded heterostructures, as expected the $Q_y$-values span continuously between the theoretical
strained peak positions of the parent phases. Taking a closer look at the diffraction pattern, there is a slight increase in spectral weight towards lower Qx-values and a slight decrease in spectral weight near the expected lattice parameter for strained PbZr0.8Ti0.2O3 indicating some degree of partial relaxation. To obtain a quantitative measure of the partial relaxation for the homogeneous and compositionally-graded heterostructures we applied an approach based on analyzing the breadth of the diffraction peak of the film relative to that of the substrate. Commonly-used approaches, for instance the Williamson-Hall approach which has been used in a number of recent publications, requires that the film of interest can be modeled as a single diffraction peak whose peak width is reflective of the degree of relaxation. In the case of the compositionally-graded heterostructures studied herein, however, the simultaneous change of composition, relaxation, and possibly phase makes the assumption of a single, clearly-defined diffraction peak untenable. In turn, no established approaches for inhomogeneous, compositionally-graded thin films are available to quantify strain relaxation and thus we developed a unique approach to provide a quantitative assessment of relaxation in compositionally-graded heterostructures.

To quantify the strain relaxation in the compositionally-graded heterostructures, we extracted the logarithmically-scaled, weighted-mean diffraction peak position from the reciprocal space maps about the 103-diffraction condition for the PbZr1-xTaxO3 (equation S1-2) as indicated (Fig. S4c, green marker).

\[ 2\theta_{ave} = \frac{\sum_{i=1}^{n} 2\theta \log I}{\sum_{i=1}^{n} \log I} \]  

\[ \omega_{ave} = \frac{\sum_{i=1}^{n} \omega \log I}{\sum_{i=1}^{n} \log I} \]  

Similarly, the average-relaxed (Fig. S4c, black marker) and average-strained (Fig. S4c, orange marker) peak positions were defined from the midpoint of the line between the relaxed and strained peaks of the end-member compositions as depicted graphically (Fig. S4c). The percentage of the film relaxed is then calculated by computing the relative distance of the projection of the weighted-mean peak position on the line defined by the average relaxed and strained peak position as described (Fig. S4d). Using this approach we found that the homogeneous PbZr0.2Ti0.8O3 heterostructures were coherently strained to the GdScO3 substrate within the experimental resolution limits, while the compositionally-graded heterostructures were ~10.6% relaxed. In spite of this partial relaxation, the compositionally-graded heterostructures retain a large majority of the

![Figure S3](image-url)
epitaxial strain imparted by the substrate. This stands in contrast to what is typically observed in heterogeneous films of the various parent materials (100 nm thick \(\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3\), \(\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3\), and \(\text{PbZr}_{0.8}\text{Ti}_{0.2}\text{O}_3\) heterostructures grown on \(\text{GdScO}_3\) substrates reveal 0% as previously mentioned, 84.0%, and 45.3% strain relaxation, respectively). Thus, consistent with what has been observed in group IV and III-V semiconductor systems, these results demonstrate that presence of the compositional-gradient (and in particular, those with minimal lattice mismatch at the film-substrate interface) provides a pathway to retain large residual strains and strain gradients not possible in homogeneous heterostructures.

Figure S4. Reciprocal space mapping about the 103-diffraction conditions for (a) homogeneous \(\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3\) and (b) compositionally-graded \(\text{PbZr}_{0.8}\text{Ti}_{0.2}\text{O}_3 \Rightarrow \text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3/\text{SrRuO}_3/\text{GdScO}_3\) (110) heterostructures. Dashed lines represent the coherently strain (vertical) and cubic (angled) lattice parameters and the expected peak positions for bulk (black) and strained (orange) versions of the parent phases are labeled in each graph. (c) Close-up of the 103-diffraction peak for \(\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3\) indicating the calculated weighted-mean peak position, average strain, and relaxed peak position. (d) Diagram showing the geometry used to calculate the residual strain.

III) Band-Excitation Piezoresponse Force Microscopy (BE-PFM)

Traditional approaches to scanning probe microscopy and in particular piezoresponse force microscopy (PFM) tend to rely on periodically exciting a cantilever using a single-frequency excitation at, or very near to, the cantilever resonance to perturb a sample, invoking a response in the cantilever amplified by its resonance. In single-frequency excitation approaches the response of the cantilever, and ultimately the signal of interest, is measured using a lock-in amplifier. While powerful for imaging highly-responsive materials with large domain features, the limitations of a single-frequency approach become obvious even when considering the simplest, idealized model of the cantilever resonance in the form of a simple harmonic oscillator (SHO). In this case, the response of the cantilever is primarily determined by the resonance frequency (defined by the tip-surface spring constant), amplitude (a measure of the response), and Q-factor (defined by the tip-surface dissipation) all of which are intimately linked to the tip-surface interaction, which in real measurements is constantly changing and therefore is unable to be deconvoluted. While more advanced approaches based on phase-locked loops (which use external circuitry to try to maintain the system at resonance) or dual-frequency resonance tracking (which excites, measures, and then tracks the resonance using two frequencies) provide a more accurate measure of piezoresponse, they still only provide minor improvements applicable under the strictest set of assumptions.
It is clear that to overcome these bandwidth limitations and accurately measure piezoresponse without artifacts imposed by changing cantilever dynamics it is crucial to measure the cantilever response over a large bandwidth near the cantilever resonance (as depicted in Fig. S5a). To do this, we applied band-excitation piezoresponse force microscopy (BE-PFM), which uses a computer generated waveform (Fig. S5b) which spans a band of frequencies near the measured cantilever resonance to electrically perturb the material (Fig. S5c). The response of the cantilever can then be measured with a high-speed data acquisition system and then Fourier transformed (Fig. S5d) into the frequency domain. Since, at each point along a scan, the measurement collects the amplitude ($A$) and phase ($\theta$), at each coordinate in space ($x, y$), and frequency ($\omega$), the data takes the form of two $\{A, \theta\}$, 3D matrixes ($x, y, \omega$). Following data collection, assuming that the tip-sample interaction is weak, the amplitude and phase can be fit to a SHO model as described in equation S3-4, where $A_0$ and $\omega_0$ is the amplitude and frequency at resonance.\(^7\)

$$A(\omega) = \frac{A_0 \omega_0^2}{\sqrt{(\omega^2 - \omega_0^2)^2 + (\omega \omega_0/Q)^2}}$$

$$\tan(\theta(\omega)) = \frac{\omega \omega_0/Q}{\omega^2 - \omega_0^2}$$

Following fitting (as shown in Fig. S5d), the error of the fits can be evaluated (i.e., the quality of the deconvolution), and if good, the data yields ($x, y$) maps of resonance amplitude ($A_0$), resonance frequency ($\omega_0$), and Q-factor or dissipation ($Q$) as well as the phase ($\theta$) of the response. Therefore, with the proper care, the application of BE-PFM enables the exclusion of cross-talk (associated with position dependent changes in the cantilever resonance) minimizing the contribution from the tip-surface interaction.

**IV) Domain Structure of Homogeneous PbZr\(_{0.8}\)Ti\(_{0.2}\)O\(_3\) Thin Film**

Here, for reference, we provide single-frequency piezoresponse force microscopy images of homogeneous, 100 nm thick PbZr\(_{0.8}\)Ti\(_{0.2}\)O\(_3\)/30 nm SrRuO\(_3\)/GdScO\(_3\) (110) heterostructures (Fig. S6a-b). These heterostructures exhibit mosaic domain structure common of rhombohedral ferroelectrics. This stands in contrast to the $c/a/c/a$-like domain structure we observe in the
compositionally-graded heterostructures even though, at the surface, these heterostructures have the same chemistries.

V) Nanobeam Diffraction and Partitioning

Elastic strain and local crystal rotation mapping around the domain structures was conducted using nanobeam electron diffraction (NBED) in an FEI Titan, operated at 300 kV. Strain mapping using NBED is a relatively new technique that calculates elastic strains and rigid-body crystal rotations directly from nanobeam diffraction patterns. In the TEM, a nanobeam probe is formed and diffraction patterns are collected in a grid pattern while the beam is rastered across the sample. Each diffraction pattern contains information on the crystal orientation and elastic strain. This information is directly related to the spacing and angles of the diffraction spots and can be extracted by calculating the position of the centroids of the diffractions spots and comparing them to the positions of the diffractions spots in an unstrained pattern (Fig. S7). Unlike other TEM-based strain mapping techniques such as geometric phase analysis (GPA), nanobeam diffraction has few restraints in terms of sample and scan geometry and mapping area. For example, NBED has been used to map out elastic strains in a GaAs/GaAsP multilayer device over a 1 x 1 µm region containing significant internal crystal rotations while still maintaining an elastic strain resolution of 0.1%, something that would not be possible using the more restrictive GPA approach.

In the present experiment, patterns were collected in a regular 160 x 160 nm grid pattern with a pattern collected every 2.5 nm. As the probe size was approximately 0.8 nm, the step size is the main spatial limitation of the analysis. A convolution mask was constructed in the shape of a NBED disk with the intensity near the edge of the disk weighted more heavily. This weighting helps avoid dynamic diffraction effects in the disk interiors. A sub-pixel resolution cross-correlation algorithm was applied to the convolution mask and the individual diffraction patterns to detect the centroids of the NBED disks. A reference spot was selected in the scan and designated as \( g_{\text{ref}} \). Subsequently, for each diffraction pattern the transformation matrix \( T \) was computed from the diffraction vectors \( g_i \) using \( g_i = T g_{\text{ref}} \). Polar decomposition was used to separate the transformation matrix \( T \) into a rotation matrix \( R \) and a symmetric strain matrix \( U \). In plane and out of plane strains were computed by \( \varepsilon_{xx} = 1-U_{00} \) and \( \varepsilon_{yy} = 1-U_{11} \) and the shear and rotation can be computed using \( \varepsilon_{xy} = 1-R_{01} \) and \( \theta = \cos^{-1}R_{00} \).

Following extraction of the local strain, thickness-dependent averaging was completed by averaging each line (in the out-of-plane direction) excluding those values associated with the \( a \) domains (those with in-plane polarized \( c \) axis). To isolate/partition the \( c \) domain regions from the \( a \) domains and substrate/bottom electrode, an arbitrary cutoff strain of -1.5% (in reference to the global mean strain) was used.

Figure S6. Single-frequency PFM (a) amplitude and (b) phase of homogeneous 100 nm PbZr\(_{0.8}\)Ti\(_{0.2}\)O\(_3\) / 30 nm SrRuO\(_3\)/GdScO\(_3\) (110) heterostructure.

Figure S7. Reference mask compared to location of diffraction spots in a measured pattern. Shifts of the diffraction spots between the reference and measured patterns are mapped onto each other using the transformation matrix \( T \).
The partitioned region (Fig. S8) shows that this cutoff is effective to partition the $c$ domains from the $a$ domains and substrate/bottom electrode.

Using the calculated average strain we are able to quantify the strain gradient in the material and compare this to the average theoretical maximum strain gradient of the heterostructure. To calculate the maximum theoretical strain gradient we determine the misfit strain between the PbZr$_{1-x}$Ti$_x$O$_3$ and the substrate at the bottom of and the top of the PbZr$_{1-x}$Ti$_x$O$_3$ film using equation S5, where $S_m$ is the misfit strain, $a_{film}$ is the lattice parameter of the film and $a_{bulk}$ is the bulk lattice parameter

$$S_m = \frac{a_{film} - a_{bulk}}{a_{bulk}} \quad (5)$$

In the case of the maximum theoretical strain gradient we are under the working assumption that the film is coherently strained to the substrate, and therefore, $a_{film} = a_{sub} = 3.973$ Å, while $a_{bulk}$ is 3.94 Å and 4.118 Å for PbZr$_{0.2}$Ti$_{0.8}$O$_3$ and PbZr$_{0.8}$Ti$_{0.2}$O$_3$, respectively. Using these values and assumptions the misfit strain for the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ and PbZr$_{0.8}$Ti$_{0.2}$O$_3$ is 0.83% (tensile) and -3.52% (compressive), respectively. Since this strain transitions over the film thickness (100 nm) the maximum theoretical strain gradient is $\sim 4.35 \times 10^5$ m$^{-1}$. To quantify the actual strain gradient based on the NBED studies, we calculate the average measured lattice parameter of the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ and PbZr$_{0.8}$Ti$_{0.2}$O$_3$ by multiplying the measured strain (in reference to the substrate lattice parameters) by the substrate pseudocubic lattice parameter. Using this approach, we find the lattice parameters to be 3.9704 Å and 4.0144 Å at the substrate-film interface (PbZr$_{0.2}$Ti$_{0.8}$O$_3$) and at the free surface (PbZr$_{0.8}$Ti$_{0.2}$O$_3$), respectively. By replacing $a_{film}$ with these measured values, we find the misfit strain to be, 0.77% tensile and -2.52% compressive for the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ and PbZr$_{0.8}$Ti$_{0.2}$O$_3$, respectively; giving rise to an actual strain gradient of $3.3 \times 10^5$ m$^{-1}$, slightly less than the maximum theoretical strain gradient, but still very large, demonstrating the efficacy of controlled compositional gradients in generating large strain gradients.

**VI) Band-Excitation Switching Spectroscopy (BE-SS)**

Building off the BE-based imaging technique used to image the samples studied herein, and described earlier, it is also possible to add additional dimensionality to such measurements, providing deeper insight into the response of the material. Specifically, here, instead of just measuring $\{A, \theta\}(x, y, \omega)$ we can add an additional dc-voltage dimensionality to the measurement [i.e., $\{A, \theta\}(x, y, \omega, V_{dc})$] enabling the measurement of local piezoelectric hysteresis loops while taking advantage of the enhanced measurement precision provided by band excitation. To do this, we superimposed a $n \times n$ grid ($n > 50$) on a previously scanned region of interest (Fig. S9a), with a horizontal fast scan and vertical slow scan direction. At each point, a full bipolar triangular switching waveform is applied to the cantilever (Fig. S9b-d) and readout is conducted in the off-state (i.e., remanent state) by superimposing a band-excitation waveform (sense pulse). This whole process happens rapidly (total elapsed time $< 5$ ms). Following data acquisitions the data is fit using SHO model as previously described (Fig. S9e), yielding data of the form $\{A_0, \omega_0, Q, \theta\}(x,$
By optimizing the rotation angle ($\phi$) to maximize the real component of the hysteresis loop mixed-signal ($A_0 \cos \phi$) it is possible to generate local piezoelectric hysteresis loops of the same general form as typical macroscopic ferroelectric hysteresis loops (Fig. S9f).

**VII) Piezoelectric Hysteresis Loops and Loop Fitting Process**

To extract average hysteresis loops reflective of the response within the $a$ and $c$ domains the spatial maps of the response were partitioned. To do this an arbitrary cutoff for the amplitude (offset) was chosen to partition the regions for the homogeneous and compositionally-graded heterostructures (Fig. S10a-b). From these figures it is clear that the partitioning method was effective at isolating the $c$ and $a$ domains. Once partitioned the mean piezoresponse along each voltage step can be calculated in both the $c$ and $a$ domain regions (as shown for the homogeneous and compositionally-graded heterostructures, Fig. S10c-d, respectively). Starting with the homogeneous heterostructures, we observe that the average hysteresis loop of the $c$ domains has a significantly large piezoresponse and slightly reduced coercivity as compared to the $a$ domains; an observation consistent with spatial maps included in the main text. In addition, the centroid of the hysteresis loop can be calculated (as shown by the hatched circles). The loop centroids for the homogeneous heterostructures show essentially no shift along the voltage axis between the $a$ and $c$ domains, again constant with the spatial maps of the offset. Moving on to the compositionally-graded heterostructures we notice that the $a$ and $c$ domains have nearly invariant remnant piezoresponse, this difference in response compared to the high-field piezoresponse is once again
an indication of the spring-like nature of these domains which rapidly back-switch, minimizing their observed piezoresponse in remanance. Changing our focus to the loop centroid we notice a significant shift (toward negative bias direction) at the $a$ domains compared to the $c$ domains. Again this observation is consistent with the spatial maps of the offset for the compositionally-graded heterostructures.

Once BE-SS is completed, it is useful to extract and fit the piezoelectric hysteresis loops to aid in the visualization process. To begin the fitting process, piezoelectric hysteresis loops need to be obtained from conventional piezoresponse butterfly loops (Fig. S11a) and phase loops (Fig. S11b). To do this, the optimum rotation angle is determined by shifting the phase ($\phi$) to maximize the real
component of the hysteresis loop \([\text{Acos}(\phi)]\) while minimizing the imaginary component \([\text{Asin}(\phi)]\). Once the piezoresponse hysteresis loops are obtained, the top and bottom branches of the hysteresis loop are isolated and fit using equation S6-9 (Fig. S11c-d).

\[
\sigma_1 = \left(\frac{b_1+b_2}{2}\right) + \left(\frac{b_2-b_1}{2}\right) \text{erf} \left(\frac{V-b_7}{b_5}\right) \quad (6)
\]

\[
\sigma_2 = \left(\frac{b_4+b_3}{2}\right) + \left(\frac{b_3-b_4}{2}\right) \text{erf} \left(\frac{V-b_8}{b_6}\right) \quad (7)
\]

\[
\Gamma_1 = \left(\frac{a_1+a_2}{2}\right) + \left(\frac{a_2-a_1}{2}\right) \text{erf} \left(\frac{V-E_c^-}{\sigma_1}\right) + a_3 V \quad (Upper \ Branch) \quad (8)
\]

\[
\Gamma_2 = \left(\frac{a_1+a_2}{2}\right) + \left(\frac{a_2-a_1}{2}\right) \text{erf} \left(\frac{V-E_c^+}{\sigma_2}\right) + a_3 V \quad (Lower \ Branch) \quad (9)
\]

where, \(V\) is the dc voltage, \(b_1-b_4\) control the sharpness of the loop corners (as \(b_x \to 0\) corner approaches 90°), \(b_5-6\) control the rate of transition from \(b_1\) to \(b_2\), and \(b_3\) to \(b_4\), respectively, \(b_6-7\) locate the midpoint of the transition from \(b_1\) to \(b_2\) and \(b_3\) to \(b_4\), respectively, \(a_1\) and \(a_2\) represent the bottom and top saturation amplitudes, \(a_3\) represents the linear contribution, \(E_c^-\) represents the negative and positive coercive fields, respectively. All these parameters are depicted schematically in (Fig. S11e). This set of empirical equations were derived because it represents the loop shape well and has empirical parameters which can be correlated to common loop shape features. To demonstrate the quality of the fit, we show an example piezoresponse hysteresis loop fit using this empirical equation (Fig. S11d, solid black line). From this fitting it is evident that this empirical equation fits the hysteresis loop well and accounts for all features of the ferroelectric hysteresis loop. Following fitting, a large set of spatial maps of loop shape parameters can be obtained.
References


