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Orientation-dependent structural phase diagrams and dielectric properties of PbZr$_{1-x}$Ti$_x$O$_3$ polydomain thin films

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The orientation-dependent equilibrium ferroelectric domain structures and dielectric properties of polydomain PbZr$_{1-x}$Ti$_x$O$_3$ thin films are investigated using a phenomenological Ginzburg-Landau-Devonshire thermodynamic model. We develop and describe three-dimensional, polydomain models for (001)-, (101)-, and (111)-oriented films and explore the evolution of the structure and dielectric permittivity of the system as a function of epitaxial strain across the composition range $0.5 \leq x \leq 1.0$. Our studies reveal that the film orientation, epitaxial strain, and composition can combine in unexpected ways to drive exotic phase stability and transformations which have intriguing implications for the properties. In particular, in (101)- and (111)-oriented films, the application of epitaxial strains along non-(001)-type crystallographic directions significantly reduces the stability range of the parent tetragonal phase (which is dominant in (001)-oriented films) and results in a variety of new symmetries. We also observe that the film orientation can be used to tune the relative fraction of intrinsic (i.e., within a domain) and extrinsic (i.e., from domain wall motion) contributions to the dielectric permittivity. Ultimately these studies reveal how composition, epitaxial strain, and film orientation provide for comprehensive control of the structure and properties of ferroelectric materials that go beyond traditional lattice mismatch effects.$^1,2$ Recent experimental work has demonstrated that the control of film orientation is one promising and effective approach to manipulate ferroelectric domain structure and properties.$^3,4$ In studies of thin-film materials, such as the model ferroelectrics PbZr$_{1-x}$Ti$_x$O$_3$ and BiFeO$_3$, it has been noted that the variation of film orientation could result in exotic crystal and domain structures and give rise to enhanced ferroelectric susceptibilities.$^5$–$^8$ In particular, recent work on (111)-oriented, tetragonal PbZr$_{0.2}$Ti$_{0.8}$O$_3$ films highlighted how domain-wall contributions to dielectric susceptibilities and ferroelectric switching characteristics can be dramatically tuned with film orientations.$^7$,$^8$ In fact, varying the relative orientation of applied electric fields relative to the direction of polarization in ferroelectrics has been shown to give rise to enhanced dielectric and piezoelectric response and it has even been suggested that it could potentially giving rise to frustrated poling.$^9$–$^{12}$

The ultimate control of domain structure and properties, however, requires not only empirical observation, but the insights and understandings gleaned from theoretical simulations. To date the majority of theoretical models including Ginzburg-Landau-Devonshire theories and phase-field modeling have been developed to study the evolution of ferroelectric thin-film structures and properties that are tunable with strain, composition, temperature, and thickness.$^{13}$–$^{20}$ Most of these studies, however, have focused on (001)-oriented heterostructures manifested in either monodomain or polydomain states. In fact, few studies have focused on systems of different orientations. For instance, thermodynamic calculations of (111)-oriented monodomain PbTiO$_3$ films, for instance, have predicted the presence of a dielectric anomaly in the paraelectric state that can be tailored from standard Curie-Weiss to diffuse-type by tuning the misfit strain.$^{21}$ Furthermore, recent first-principles calculations have suggested that a complex phase transition process, tuned by epitaxial strain, can occur in (111)-oriented PbTiO$_3$ and BaTiO$_3$ films$^{22}$ and that an unexpected triclinic phase and three distinct monoclinic phases may be possible in (110)-oriented BaTiO$_3$ films.$^{23}$ At the same time, for (101)-oriented PbZr$_{1-x}$Ti$_x$O$_3$ films with compositions near the morphotropic phase boundary, phase-field simulations suggest that mobile two-domain configurations can enhance piezoelectricity. Other phase-field simulations have also systematically studied the ferroelectric domain structures in (001)-, (101)-, and (111)-oriented BiFeO$_3$ films.$^{24}$ Despite these few examples, the vast majority of these studies focus on monodomain versions of materials which deviate from experimental (and practical) forms of these materials found in “thick” films (typically greater than just 25-50 nm) that exhibit a range of polydomain structures that result from a competition between elastic, electrostatic, domain wall, and other energies. In the prototypical ferroelectric PbZr$_{1-x}$Ti$_x$O$_3$ system, for instance, a comprehensive theoretical approach to understanding and systematically comparing the orientation-dependent domain structures, properties, and susceptibilities has not been undertaken.

In this work, we develop three-dimensional, polydomain phenomenological Ginzburg-Landau-Devonshire (GLD) thermodynamic models to produce orientation-,
composition- and strain-dependent phase diagrams that explore the evolution of structure and properties for thin films of the widely studied and technologically important tetragonal portion of the PbZr\(_{1-x}\)Ti\(_x\)O\(_3\) phase diagram. In particular, we study (001)-, (101)-, and (111)-oriented films and focus on the case of complex, polydomain phases in films above the critical thickness for domain formation. This work is accomplished by modifying the free-energy formalism for (001)-oriented heterostructures to allow for the construction of orientation-dependent, composition-strain phase diagrams for both (101)- and (111)-oriented films. We explore both phase and property \(i.e.\), dielectric permittivity \(i.e.\) evolution for each film orientation. Our studies reveal that the film orientation, epitaxial strain, and composition can combine in unexpected ways to drive exotic phase stability and transformations which have intriguing implications for the properties of materials. The models suggest that the variation of film orientation can dramatically impact the energetics of the system and the application of epitaxial strains along non-(001)-type crystallographic directions significantly reduces the stability range of the parent tetragonal phase \(i.e.\) dominant in (001)-oriented films) and results in a variety of new symmetries. We also observe that the film orientation can be used to tune the relative fraction of intrinsic \(i.e.\), within a domain) and extrinsic \(i.e.\), from domain wall motion) contributions to permittivity. This work has implications for the experimental design of ferroelectric heterostructures and could ultimately aid in the optimization of material response via a combination of film orientation, composition, and misfit strain control.

\[ F = \sum_{n=1}^{6} \sigma_n S_n \]  

\[ G = \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{111} (P_1^4 + P_2^4 + P_3^4) \]

\[ + \alpha_{12} (P_1^2 P_2^2 + P_2^2 P_3^2 + P_1^2 P_3^2) + \alpha_{111} (P_1^4 + P_2^4 + P_3^4) \]

\[ + \alpha_{112} [P_1^2 (P_2^2 + P_3^2) + P_2^2 (P_1^2 + P_3^2) + P_3^2 (P_1^2 + P_2^2)] \]

\[ + \alpha_{122} (P_1^2 P_2^2 P_3^2 - 1/2s_{111} (\sigma_1^2 + \sigma_2^2 + \sigma_3^2)) \]

\[ - s_{12} (\sigma_1 \sigma_2 + \sigma_2 \sigma_3 + \sigma_3 \sigma_1) - 1/2s_{44} (\sigma_1^2 + \sigma_2^2 + \sigma_3^2) \]

\[ - Q_{11} (\sigma_1 P_1^2 + \sigma_2 P_2^2 + \sigma_3 P_3^2) \]

\[ - Q_{12} [\sigma_1 (P_2^2 + P_3^2) + \sigma_2 (P_1^2 + P_3^2) + \sigma_2 (P_1^2 + P_2^2)] \]

\[ - Q_{44} (P_2 P_3 \sigma_4 + P_1 P_3 \sigma_5 + P_2 P_4 \sigma_6) \]

\[ (1) \]

\[ \dot{G} = \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{111} (P_1^4 + P_2^4 + P_3^4) \]

\[ + \alpha_{12} (P_1^2 P_2^2 + P_2^2 P_3^2 + P_1^2 P_3^2) + \alpha_{111} (P_1^4 + P_2^4 + P_3^4) \]

\[ + \alpha_{112} [P_1^2 (P_2^2 + P_3^2) + P_2^2 (P_1^2 + P_3^2) + P_3^2 (P_1^2 + P_2^2)] \]

\[ + \alpha_{122} (P_1^2 P_2^2 P_3^2 - 1/2 s_{111} (\sigma_1^2 + \sigma_2^2 + \sigma_3^2)) \]

\[ + s_{12} (\sigma_1 \sigma_2 + \sigma_2 \sigma_3 + \sigma_3 \sigma_1) - 1/2s_{44} (\sigma_1^2 + \sigma_2^2 + \sigma_3^2) \]

\[ - 1/2 \epsilon_0 (E_1^2 + E_2^2 + E_3^2) - E_1 P_1 - E_2 P_2 - E_3 P_3 \]

\[ (2) \]

where \(\alpha_1, \alpha_{ij}, \) and \(\alpha_{ijk}\) are the dielectric stiffnesses at constant stress, \(s_{mn}\) are the elastic compliances at constant polynomial, \(Q_{ij}\) are the electrostrictive constants of the paraelectric phase, and \(E_i\) are the components of external electric field in the film. The values of the above coefficients are provided in Table I.26

In order to apply the proper mechanical boundary conditions and to simplify the analyses for (101)- and (111)-orientations, we introduce new crystallographic reference frames for both cases. For (101)-oriented films, we use the crystallographic reference frame \(X' (x_1', x_2', x_3')\) where \(x_1', x_2',\) and \(x_3'\) correspond to the [001], [010], and [101] of reference frame \(X\). Likewise for (111)-oriented films we define reference frame \(X'' (x_1'', x_2'', x_3'')\) where \(x_1'', x_2'',\) and \(x_3''\) correspond to the [100], [110], and [111] of reference frame \(X\). In both the \(X'\) and \(X''\) reference frames \(x_3', \) and \(x_3''\),...
$x_i^o$ are defined to be perpendicular to the plane of the film and $x_i'$ ($x'_i$), $x_i''$ ($x''_i$) are aligned in the plane of the film. Thus the free energy ($G$ and $\tilde{F}$) can be rewritten as $G'$ and $\tilde{F}'$ or $G''$ and $\tilde{F}''$ in terms of $P'_i$, $\sigma'_n$ and $P''_i$, $\sigma''_n$ in the reference frame $X'$ and $X''$ using the following transformation matrices $t_{ij}$ and $t''_{ij}$, respectively:

$$
\begin{bmatrix}
-\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\
0 & -1 & 0 \\
\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}}
\end{bmatrix}
$$

(3)

$$
\begin{bmatrix}
\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\
\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\
\frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}}
\end{bmatrix}
$$

(4)

$P_i$ and $\sigma_n$ in the reference frame $X$ can be expressed in terms of $P'_i$, $\sigma'_n$ and $P''_i$, $\sigma''_n$ in the reference frames $X'$ and $X''$, respectively, via the relation $P = (t'_{ij}^{-1}) P', K = (t''_{ij}^{-1}) K' t'_{ij}$ and $P = (t''_{ij}^{-1}) P'', K = (t''_{ij}^{-1}) K'' t''_{ij}$, where $P$, $P'$, and $P''$ are polarization and $K$, $K'$, and $K''$ are stress tensor matrices in the reference frames $X$, $X'$, and $X''$, respectively. Thus the free energy $F$ can be transformed to free energy $\tilde{F}'$ and $\tilde{F}''$ in terms of $P'_i$, $\sigma'_n$ and $P''_i$, $\sigma''_n$ in the reference frames $X'$ and $X''$, where $P'_i$, $P'_2$, and $P'_3$ and $P''_i$, $P''_2$, and $P''_3$ are along $x_1'$, $x_2'$, and $x_3'$ and $x'_1$, $x'_2$, and $x'_3$ in reference frames $X'$ and $X''$, respectively. The explicit formalism of $\tilde{F}'$ and $\tilde{F}''$ are rather complex and thus for brevity we provide those in simplified form in equations (4) and (5) using $\tilde{P}'$, $\tilde{K}'$ and $\tilde{P}''$, $\tilde{K}''$ to represent the matrices $(t'_{ij})^{-1} P'$, $(t''_{ij})^{-1} P''$, $(t'_{ij})^{-1} K'$, and $(t''_{ij})^{-1} K''$, respectively.

$$
\tilde{F}' = \alpha_1 (P'_{11} + P'_{22} + P'_{33}) + \alpha_{11} (P'_{11}^q + P'_{22} + P'_{33}^q) \\
+ \alpha_{12} (P'_{11}^q P'_{22} + P'_{22}^q P'_{33} + P'_{33}^q P'_{11}) \\
+ \alpha_{111} (P'_{11}^q + P'_{22} + P'_{33}) + \alpha_{112} [P'_{11}^q (P'_{22} + P'_{33})] \\
+ \alpha_{1122} (P'_{11}^q P'_{22} + P'_{22}^q P'_{33} + P'_{33}^q P'_{11})
$$

(5)

$$
\tilde{F}'' = \alpha_1 (P''_{11} + P''_{22} + P''_{33}) + \alpha_{11} (P''_{11}^q + P''_{22} + P''_{33}^q) \\
+ \alpha_{12} (P''_{11}^q P''_{22} + P''_{22}^q P''_{33} + P''_{33}^q P''_{11}) \\
+ \alpha_{111} (P''_{11}^q + P''_{22} + P''_{33}) + \alpha_{112} [P''_{11}^q (P''_{22} + P''_{33})] \\
+ \alpha_{1122} (P''_{11}^q P''_{22} + P''_{22}^q P''_{33} + P''_{33}^q P''_{11})
$$

(6)

where $E'_1$ and $E''_1$ are components of external electric field in the reference frames $X'$ and $X''$. The complete, explicit formalisms for both $\tilde{F}'$ and $\tilde{F}''$ are provided in the Supplemental Materials. For polydomain structures, the thermodynamic equilibrium state can be described by the average free-energy density $\langle \tilde{F} \rangle$ which can be written as $\langle \tilde{F} \rangle = \sum_{k=1}^{n} \phi_k F_k$, $\langle \tilde{F}' \rangle = \sum_{k=1}^{n} \phi'_k F'_k$, and $\langle \tilde{F}'' \rangle = \sum_{k=1}^{n} \phi''_k F''_k$ for the (001)-, (101)-, and (111)-oriented films, respectively. In these equations, $\phi_k$ ($\phi'_k$ or $\phi''_k$) are the volume fraction of the $k$th domain type and $F_k$ ($F'_k$ or $F''_k$) are the energy density within the $k$th domain. It is possible to eliminate the stresses $\sigma$ ($\sigma'_n$ or $\sigma''_n$) from the $\langle \tilde{F} \rangle$ ($\langle \tilde{F}' \rangle$ or $\langle \tilde{F}'' \rangle$) using the following mechanical boundary conditions:

(001)-oriented films:

$$
\langle S_1 \rangle = \sum_{k=1}^{n} \phi_k S^k_1 = u_m, \langle S_2 \rangle = \sum_{k=1}^{n} \phi_k S^k_2 = u_m,
$$

(7)

$$
\langle S_6 \rangle = \sum_{k=1}^{n} \phi_k S^k_6 = 0,
$$

(8)

TABLE I: Values of thermodynamic coefficients for PbZr1-xTiO3 ($x = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0$) used in the Ginzburg-Landau-Devonshire modeling at $T = 300$ K.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1 (10^3 C^{-2}m^{-2}K^{-1})$</td>
<td>-0.49</td>
<td>-0.83</td>
<td>-1.24</td>
<td>-1.49</td>
<td>-1.64</td>
<td>-1.75</td>
</tr>
<tr>
<td>$\alpha_{11} (10^3 C^{-4}m^{-6}K^{-1})$</td>
<td>4.76</td>
<td>3.61</td>
<td>0.65</td>
<td>-3.05</td>
<td>-5.85</td>
<td>-7.25</td>
</tr>
<tr>
<td>$\alpha_{12} (10^3 C^{-4}m^{-6}K^{-1})$</td>
<td>1.74</td>
<td>3.23</td>
<td>5.11</td>
<td>6.32</td>
<td>7.06</td>
<td>7.50</td>
</tr>
<tr>
<td>$\alpha_{111} (10^3 C^{-6}m^{-10}K^{-1})$</td>
<td>1.34</td>
<td>2.86</td>
<td>3.25</td>
<td>2.48</td>
<td>2.52</td>
<td>2.60</td>
</tr>
<tr>
<td>$\alpha_{122} (10^3 C^{-6}m^{-10}K^{-1})$</td>
<td>6.13</td>
<td>8.50</td>
<td>10.25</td>
<td>9.68</td>
<td>8.10</td>
<td>6.10</td>
</tr>
<tr>
<td>$s_{11} (10^{-12} Nm^{-2})$</td>
<td>2.89</td>
<td>-4.06</td>
<td>-5.00</td>
<td>-4.90</td>
<td>-4.36</td>
<td>-3.66</td>
</tr>
<tr>
<td>$s_{12} (10^{-12} Nm^{-2})$</td>
<td>10.5</td>
<td>8.60</td>
<td>8.40</td>
<td>8.20</td>
<td>8.10</td>
<td>8.00</td>
</tr>
<tr>
<td>$s_{44} (10^{-12} Nm^{-2})$</td>
<td>-3.70</td>
<td>-2.80</td>
<td>-2.70</td>
<td>-2.60</td>
<td>-2.50</td>
<td>-2.50</td>
</tr>
<tr>
<td>$T^\infty (K)$</td>
<td>665.6</td>
<td>691.4</td>
<td>713.2</td>
<td>732.1</td>
<td>750.1</td>
<td>765.1</td>
</tr>
</tbody>
</table>
(101)-oriented films:

\[
\langle S'_1 \rangle = \sum_{k=1}^{n} \phi'_k S'_{1k} = u'_m, \quad \langle S'_2 \rangle = \sum_{k=1}^{n} \phi'_k S'_{2k} = u'_m,
\]

\[
\langle S''_1 \rangle = \sum_{k=1}^{n} \phi''_k S''_{1k} = 0, \quad \langle S''_2 \rangle = \sum_{k=1}^{n} \phi''_k S''_{2k} = u''_m,
\]

\[
\langle \sigma'_3 \rangle = \langle \sigma'_4 \rangle = \langle \sigma''_3 \rangle = 0, \quad \langle \sigma''_4 \rangle = 0,
\]

(111)-oriented films:

\[
\langle S''_1 \rangle = \sum_{k=1}^{n} \phi''_k S''_{1k} = u''_m, \quad \langle S''_2 \rangle = \sum_{k=1}^{n} \phi''_k S''_{2k} = u''_m,
\]

\[
\langle \sigma''_3 \rangle = \langle \sigma''_4 \rangle = 0, \quad \langle \sigma'_{3'} \rangle = \langle \sigma'_{4'} \rangle = 0,
\]

where \( S''_n \) (\( S'_{nk} \) and \( S''_{nk} \)) refers to the strain components in the \( k \)th domain which can be derived from \( S_n = -\partial G/\partial \sigma_n (S'_{nk} = -\partial G'/\partial \sigma'_{nk} \) and \( S''_n = -\partial G''/\partial \sigma''_n \) ) and \( u_m (u'_m \) or \( u''_m \) ) refers to the in-plane misfit strain with respect to the growth plane. In polycrystalline domains, these macroscopic conditions must be supplemented by the microscopic boundary conditions related to the presence of the domain walls. To achieve this, we can create a local reference frame \( Y (y_1, y_2, y_3) \) with \( y_3 \) perpendicular to the domain walls and thus the strain compatibility in the neighboring domains implies

\[
\sigma'_{n'} = \sigma''_{n'} (\sigma'_{n'} = \sigma''_{n'} \) or \( \sigma''_{n'} = \sigma''_{n'} \))(n = 1, 2, 3, 6)
\]

(12)

and the mechanical equilibrium of the domains implies that the stress components are related as

\[
\sigma'_{n'} = \sigma''_{n'} (\sigma'_{n'} = \sigma''_{n'} \) or \( \sigma''_{n'} = \sigma''_{n'} \))(n = 3, 4, 5, 6)
\]

In addition, we can set the average electric field \( \langle E_1 \rangle \) (\( \langle E''_1 \rangle \) or \( \langle E''_1 \rangle \)) to be zero in the case of the short-circuit boundary conditions and in the absence of a depolarization field. The microscopic electric field continuity equation thus yields the following boundary conditions:

\[
E_{3'} = E_{3'}^{k+1} (E_{3'}') = E_{3'}^{k+1} \) or \( E_{3'} = E_{3'}^{k+1} \),
\]

\[
E_{3''} = E_{3''}^{k+1} (E_{3''}') = E_{3''}^{k+1} \) or \( E_{3''} = E_{3''}^{k+1} \),
\]

\[
\varepsilon_0 E_{3'} + P_{3'} = \varepsilon_0 E_{3'}^{k+1} + P_{3'}
\]

\[
\varepsilon_0 E_{3''} + P_{3''} = \varepsilon_0 E_{3''}^{k+1} + P_{3''}
\]

\[
\varepsilon_0 E_{3'}^{k+1} + P_{3'}^{k+1} or \quad \varepsilon_0 E_{3''}^{k+1} + P_{3''}^{k+1}
\]

\[
(\varepsilon_0 E_{3'} + P_{3'}) = \varepsilon_0 E_{3'} + P_{3'}^{k+1}
\]

\[
(\varepsilon_0 E_{3''} + P_{3''}) = \varepsilon_0 E_{3''} + P_{3''}^{k+1}
\]

The above relations make it possible to derive the free-energy density for each film orientation in terms of polarization components \( P_{3'}^{k} (P_{3''}^{k} or P_{3''}^{k}) \) and domain volume fractions \( \phi_k (\phi'_k or \phi''_k) \). Performing the minimization of \( \langle F \rangle \) (\( \langle F' \rangle \) and \( \langle F'' \rangle \)), we can find the equilibrium polarizations and domain populations as a function of mismatch strain \( (u_m = (a_s - a_p)/a_s \) or \( a_p \) is the lattice parameter of the substrate and \( a_p \) is the lattice parameter of the cubic paraelectric phase of the film)\(^{27}\) for the respective film orientations.

Our thermodynamic theory also allows us to calculate the total out-of-plane dielectric permittivity \( (\varepsilon_\perp, \varepsilon'_\perp, \varepsilon''_\perp \) for \( (001)_-, (101)_-, \) and \( (111)-oriented films, respectively) as the sum of the intrinsic (the first term) and the motional extrinsic (the second term) contributions as

\[
\varepsilon_\perp = \sum_k \phi_k \frac{DP_{11}}{dE_{3}} + \sum_k \phi_k \frac{DP_{11}'}{dE_{3}}
\]

\[
\varepsilon'_\perp = \sum_k \phi_k \frac{DP_{11}'}{dE_{3}} + \sum_k \phi_k \frac{DP_{11}''}{dE_{3}}
\]

\[
\varepsilon''_\perp = \sum_k \phi_k \frac{DP_{11}''}{dE_{3}} + \sum_k \phi_k \frac{DP_{11}'''}{dE_{3}}
\]

Here the intrinsic dielectric susceptibility can be described as the reversible variation of polarization \( P_{11} (P_{11}' or P_{11}'') \) with varying electric field \( E_{11} (E_{11}' or E_{11}'') \)

\[
(\chi_{ij} = \frac{dP_{11}}{dE_{11}} or \chi''_{ij} = \frac{dP_{11}''}{dE_{11}'})
\]

With the relation \( E_{11} = \frac{dP_{11}}{dE_{11}} \) (\( E_{11}' = \frac{dP_{11}'}{dE_{11}} \) or \( E_{11}'' = \frac{dP_{11}''}{dE_{11}} \)), we can further use differentiation of free energy to derive the expression for the dielectric susceptibility. Using the inversion of the reciprocal dielectric susceptibility matrix \( (\Theta = [\eta_{ij}], \Theta' = [\eta_{ij}'], \Theta'' = [\eta_{ij}'']) \) for \( (001)_-, (101)_-, \) and \( (111)-oriented films, respectively, where \( \eta_{ij} = \frac{\partial^2 F}{\partial P_{ij} \partial P_{ij}} \) and \( \eta''_{ij} = \frac{\partial^2 F''}{\partial P_{ij} \partial P_{ij}} \) we find the dielectric susceptibility as \( \chi_{ij} = (\Theta_{ij}^{-1} \chi'_{ij} = (\Theta'_{ij}^{-1} or \chi''_{ij} = (\Theta''_{ij}^{-1} \) and thus the relative intrinsic dielectric permittivity as \( \varepsilon_{int} = \chi_{ij} + 1 \)

\[
(\chi'_{int} = \chi''_{ij} + 1 or \chi''_{int} = \chi''_{ij} + 1)
\]

For the film geometry considered in this work, we will only study the out-of-plane dielectric permittivity \( (\varepsilon_{int}, \varepsilon''_{int}, \varepsilon''_{int}) \) using the explicit expression for dielectric permittivity obtained by performing the inversion of the reciprocal dielectric susceptibility matrix \( (\chi'_{int} = \chi''_{ij} + 1, \varepsilon_{int} = \chi''_{ij} \)

\[
(\varepsilon_{int} = \chi''_{ij} + 1)+1, \varepsilon''_{int} = \chi''_{ij} \}
\]

(\(101\)-oriented films, the second term can be expanded as

\[
\sum_k P_{3} \frac{d\phi_k}{dE_{3}} = P_{3} \frac{d\phi_k}{dE_{3}} + P_{3} \frac{d\phi_k}{dE_{3}}
\]

where \( k = 1 \) represents the in-plane polarized a domains and \( k = 2 \) represents the out-of-plane polarized c domains. For c domains, the polarization along the \( (001) \) \( (P_{3}^1) \) is absent which can simply \( \sum_k P_{3} \frac{d\phi_k}{dE_{3}} \) to be \( P_{3}^2 \frac{d\phi_k}{dE_{3}} \). In addition, \( \phi_3 \) is known to

be \( 1 - \frac{(s_{11}-s_{12})(u_m-q_{22}P_{3}^2)}{s_{11}(Q_{11}-Q_{12}P_{3})+E_{3}(s_{11}-s_{12})} \)

by minimizing the total free energy, where \( P_{3} = P_{3}^2 \). Thus, \( P_{3} \frac{d\phi_k}{dE_{3}} \)

can be re-written as \( \frac{(s_{11}-s_{12})}{s_{11}(Q_{11}-Q_{12}P_{3})+E_{3}(s_{11}-s_{12})} \)

which is the analytic formula for the motional, extrinsic contribution in \( (011)-oriented films. For (101)-oriented films, however, the formula of \( \phi_3 \) is very cumbersome after performing the transformation matrix in the free energy of \( (011)-oriented system. Thus, we only obtained numerical solu-
tions for $\frac{d\phi}{dt}$. For (111)-oriented films, $\phi_k^e$ turns out to be independent on the electric field where $\frac{d\phi_k^e}{dt}$ is zero which indicates the absence of motional, extrinsic contributions in (111)-oriented films. Therefore, the intrinsic and the motional, extrinsic contributions to the dielectric permittivity can be calculated numerically in various strain regimes via such thermodynamic analyses. The details regarding the calculation and analysis for the phase diagrams and dielectric response will be discussed in Sec. III and Sec. IV, respectively.

III.PHASE DIAGRAMS OF MONODOMAIN and POLYDOMAIN PbZr$_{1-x}$Ti$_x$O$_3$ THIN FILMS

As noted above, few reports (either experimental or theoretical) have discussed any aspect of the strain- and composition-dependence of polydomain structures in (101)- and (111)-oriented PbZr$_{1-x}$Ti$_x$O$_3$ films. Thus, to aid the development of the polydomain phase diagrams from the limited resources, we first utilized a monodomain model to provide insights into various phases and structures that are potentially produced in this system. Details of this monodomain model used to extract the equilibrium monodomain phases for (001)-, (101)-, and (111)-oriented PbZr$_{1-x}$Ti$_x$O$_3$ films ($0.5 \leq x \leq 1.0$) are provided in the Supplemental Materials. Based on these equilibrium monodomain phases, the polydomain phases were hence evaluated numerically as the equilibrium states which possesses the minimum free energy at a given elastic strain condition and Ti content ($0.5 \leq x \leq 1.0$) using the polydomain model described above.

III.A (001)-Oriented Heterostructures

In (001)-oriented heterostructures, three monodomain phases were found to be present across the range of strain and composition values explored herein: 1) a tetragonal $c$ phase ($P_1 = P_2 = P_3 = 0$, $P_3 \neq 0$), 2) a monoclinic $r$ phase ($P_1 = P_2 \neq 0$, $P_3 = 0$), and 3) an orthorhombic $aa$ phase ($P_1 = P_2 = 0$, $P_3 = 0$) in the compressive, intermediate, and tensile strain regimes, respectively, where $P_1$, $P_2$, and $P_3$ are along the crystallographic directions $x_1$, $x_2$, and $x_3$ in reference frame $X$ ($x_1$, $x_2$, $x_3$) (Figure 1(a)). Note that the $c$ phase is energetically favored under large compressive strains since the strain stabilizes the out-of-plane $P_3$ component. Upon decreasing the compressive strain, the in-plane $P_1$ and $P_2$ components appear in the $r$ phase and finally, under the influence of large tensile strains, the structure evolves into the $aa$ phase with pure in-plane components.

Based on these monodomain results, we can further evaluate the polydomain structures. Performing the minimization of $F$ in terms of $P_i$ and $\phi_k$ for (001)-oriented PbZr$_{1-x}$Ti$_x$O$_3$ films at $T = 300$ K, we acquire results similar to the polydomain phase diagram predicted in prior work. To aid in the discussion, a table (Table II) is provided that indicates the notation which will be used to refer to each phase in the polydomain structures as well as the polarization components and symmetry of that phase. In the polydomain, (001)-oriented heterostructures, seven different, uniquely identifiable phase are observed (here noted in the notation to be used throughout the rest of this manuscript with the corresponding letter in parentheses demarcating the traditional nomenclature used in prior literature as a reference): $T_c$ ($c$), $T_a$ ($a$), $M_A$ ($r$), $M_B$ ($r$), $M_{C1}$ ($ca^*$), $M_{C2}$ ($ca$), $M_{C3}$ ($aa^*$). Again, specific definition of the polarization components of each phase is provided (Table II) and a schematic illustration of the various phases is provided (Figure 1(b), note that this illustration schematically shows the orientation of polarization within the unit cell in reference frame $X$).

The nomenclature used herein is different from the traditionally applied nomenclature for two reasons. First, in the subsequent analysis of (101)- and (111)-oriented heterostructures, no prior nomenclature has been established and thus we provide a unified naming pattern applicable to all systems. Second, the earlier nomenclature of the (001)-oriented heterostructures fails to accurately differentiate some of the subtle differences in structure that are observed. In this regard, we find two different tetragonal phases: one with the polarization along the out-of-plane $[001]$ which we refer to as $T_c$ ($c$) and one with the polarization in-the-plane along $[100]$ or $[010]$ which we refer to as $T_a$ ($a$). There are, additionally, a number of phases with monoclinic symmetry ($M_A$, $M_B$, and $M_{C1}$). The $M_A$ and $M_B$ phases possess polarizations only within (110) and the $M_{C1}$ phases possess polarizations only within (001). The $M_A$ and $M_B$ phases make up what has traditionally been referred to as the $r$ phase, as polydomain $r_1/r_2/r_1/r_2$ structures. Our studies reveal that it is possible for the polarization to rotate continuously within the (110) from 0.6 $< P_1/P_3 < 1.5$ across the strain range $-2.5% \leq \varepsilon \leq 2.5%$ thus leading to two sub-phases $M_A$ and $M_B$ in the so-called $r_1/r_2/r_1/r_2$ structure. For this work, the $M_A$ and $M_B$ phases are differentiated by the magnitude of the ratio $P_1/P_3$ which is $< 1.0$ in the $M_A$ phase but $> 1.0$ in $M_B$ phase. The $M_{C1}$ phases make up what has traditionally been referred to as the $aa^*$, $ca^*$, and $ca$ phases and in all cases two of the polarization components are non-zero and one is zero. Here the $i = 1, 2, 3$ and it refers to the polarization component that is zero to differentiate the phases.

Based on these calculated phases, we have constructed the composition-strain polydomain phase diagram for (001)-oriented films (Figure 1(c)). In the polydomain system, a single domain $T_c$ phase is present in the compressive strain regime. At intermediate strains, across most of the composition space explored here, a polydomain $T_c/T_a$ ($c/a/c/a$) domain structure is observed. Also at these intermediate strains, when the Ti content $x < 0.6$, a polydomain $M_A$ (or $M_B$) ($r_1/r_2/r_1/r_2$) domain structure is observed. Furthermore, due to a $P_2$ instability near the morphotrophic phase boundary, the polydomain $T_c/T_a$ ($c/a/c/a$) domain structure evolves into a polydomain $M_{C1}/M_{C3}$ ($ca^*/aa^*/ca^*/aa^*$) domain structure.
At larger tensile strains, a polydomain \( T_a \) \((a_1/a_2/a_1/a_2)\) domain structure is stabilized. Similar to what occurred at intermediate strain states, due to a \( P_3 \) instability near the morphotropic phase boundary, the polydomain \( T_a \) \((a_1/a_2/a_1/a_2)\) domain structure evolves into a polydomain \( M_{C2}/M_{C1} \) \((ca_1/ca_2/ca_1/ca_2)\). Overall, across much of the composition and strain space studied herein, with the exception of compositions near the morphotropic phase boundary, a tetragonal symmetry is maintained for the phases. The tetragonal phases can give rise to polydomain structures which are further complicated by the formation of monoclinic structures near the morphotropic phase boundary.

It is worth noting that although it may appear as if we only consider a two-domain configuration in this approach, because of the symmetry of the system and the resulting degeneracy of minority domain structures, extension to a three-domain configuration calculation is

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Notation</th>
<th>Polarization Components</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{1(c)} )</td>
<td>( P_1 = P_2 = 0, P_3 \neq 0 )</td>
<td>Tetragonal</td>
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<tr>
<td>( T_a(a) )</td>
<td>( P_2 = P_3 = 0, P_1 \neq 0 ) ((a_1)); ( P_1 = P_3 = 0, P_2 \neq 0 ) ((a_2))</td>
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<td>( M_A(r) )</td>
<td>( P_1 = P_2 \neq 0 &lt; P_3 \neq 0, 0.60 &lt; P_1/P_3 &lt; 1.0 )</td>
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<td></td>
</tr>
<tr>
<td>( M_B(r) )</td>
<td>( P_1 = P_2 \neq 0 &gt; P_3 \neq 0, 1.0 &lt; P_1/P_3 &lt; 1.5 )</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>( M_{C1}(ca^*) )</td>
<td>( P_1 = 0, P_2 \neq 0, P_3 \neq 0 )</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>( M_{C2}(ca) )</td>
<td>( P_1 \neq 0, P_2 = 0, P_3 \neq 0 )</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>( M_{C3}(aa^*) )</td>
<td>( P_1 \neq 0, P_2 = 0, P_3 = 0 )</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>( O )</td>
<td>( P_1 = P_2 \neq 0, P_3 = 0 )</td>
<td>Orthorhombic</td>
<td></td>
</tr>
<tr>
<td>( M_A )</td>
<td>( P_1 = P_2 \neq 0, P_3 \neq 0, 0.67 &lt; P_1/P_3 &lt; 0.95 )</td>
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<td></td>
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<tr>
<td>( M_{C2} )</td>
<td>( P_1 \neq 0, P_2 = 0, P_3 \neq 0, 0.27 &lt; P_1/P_3 &lt; 0.79 )</td>
<td>Monoclinic</td>
<td></td>
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<tr>
<td>( T)-like ( M_{C1} )</td>
<td>( P_1 \neq 0, P_2 \neq 0, P_3 = 0, 0.001 &lt; P_1/P_3 &lt; 0.19 )</td>
<td>Monoclinic</td>
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<tr>
<td>( T)-like ( M_{C2} )</td>
<td>( P_1 \neq 0, P_2 = 0, P_3 \neq 0, 0.001 &lt; P_1/P_3 &lt; 0.19 )</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>( R )</td>
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<td>Rhombohedral</td>
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<td>Monoclinic</td>
<td></td>
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<tr>
<td>( M_{A2} )</td>
<td>( P_1 = P_3 \neq 0, P_2 \neq 0, 0.67 &lt; P_1/P_3 &lt; 0.96 )</td>
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<td></td>
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<tr>
<td>( M_{A3} )</td>
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<tr>
<td>( T)-like ( M_{A1} )</td>
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<td>Monoclinic</td>
<td></td>
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<tr>
<td>( T)-like ( M_{A2} )</td>
<td>( P_1 = P_3 \neq 0, P_2 \neq 0, 0.001 &lt; P_1/P_3 &lt; 0.19 )</td>
<td>Monoclinic</td>
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<td>( T)-like ( M_{A3} )</td>
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<td>Monoclinic</td>
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redundant as it will provide the same overall fraction of minority domains as we obtain from the two-domain configuration. For instance, the $T_c/T_a$ (c/a/c/a) domain structure in (001)-oriented films in reality refers to both polydomain variants c/a1/c/a1 and c/a2/c/a2 wherein a1 and a2 point along P1 and P2, respectively. Since a1 and a2 are energetically degenerate under the biaxial strain conditions, if a three-domain configuration with a mixture of c/a1/c/a1 and c/a2/c/a2 domain structure variants is present, the volume fraction of each polydomain structure should be equal to each other. Thus the total volume fraction of a1 and a2 domains in the three-domain configuration is equal to the volume fraction of a1 or a2 domain in the case of a two-domain configuration.

### III.B (101)-Oriented Heterostructures

In (101)-oriented heterostructures, three monodomain phases were found to be present across the range of strain and composition values explored herein: 1) an orthorhombic O phase ($P_1 = P_2 \neq 0, P_3 = 0$), 2) a monoclinic $M_{C2}$ phase ($P_1 \neq 0, P_2 = 0, P_3 \neq 0$), and 3) a monoclinic $M_A$ phase ($P_1 = P_2 \neq 0, P_3 \neq 0$) in the compressive, intermediate, and tensile strain regimes, respectively, where $P_1$, $P_2$, and $P_3$ are along the crystallographic directions $x_1$, $x_2$, and $x_3$ in reference frame $X$ (Figure 2(a)). Note that the $O$ phase is energetically favored under large compressive strains since the strain stabilizes the out-of-plane polarization component. Upon decreasing the compressive strain, the in-plane polarization components appear in the $M_{C2}$ phase and finally the structure evolves into the $M_A$ phase with pure in-plane polarization components as a result of the application of tensile strain.

As we did before, we can leverage these monodomain results to further evaluate the polydomain structures. Performing the minimization of $\tilde{F}'$ in terms of $P_i'$ for (101)-oriented PbZr$_{1-x}$Ti$_x$O$_3$ films at 300 K, we can generate a composition-strain phase diagram. To aid in the discussion, a table (Table II) is provided that indicates the notation which will be used to refer to each phase in the polydomain structures as well as the polarization components and symmetry of that phase. In the polydomain, (101)-oriented heterostructures, five different, uniquely identifiable phases are observed: $O$, $M_A$, $M_{C2}$, $T$-like $M_{C1}$, and $T$-like $M_{C2}$. Again, specific definition of the polarization components of each phase is provided (Table II) and a schematic illustration of the various phases is provided (Figure 2(b), note that this illustration schematically shows the orientation of polarization within the unit cell in reference frame $X$).

In this case, the $O$ phase is found to have non-zero polarization in both the [100] and [010]. Additionally, we differentiate three monoclinic structures. The $M_A$ phase has $P_1 = P_2 \neq 0$, and $P_3 \neq 0$ where $0.67 < P_1/P_3 < 0.95$ and the polarization can only lie within the (110). The $M_{C2}$ phase has $P_1 \neq 0$, $P_2 = 0$, and $P_3 \neq 0$ where $0.27 < P_1/P_3 < 0.79$ and the polarization can only lie within the (100). Finally, there are two $T$-like $M_{C3}$ phases: $T$-like $M_{C1}$ ($P_1 \neq 0, P_2 \neq 0, P_3 = 0$) where $0.001 < P_1/P_2 < 0.19$ and $T$-like $M_{C2}$ ($P_1 \neq 0, P_2 = 0, P_3 \neq 0$) where $0.001 < P_1/P_3 < 0.19$. The $T$-like $M_{C2}$ phase is differentiated from the $M_{C2}$ phase in that it can only exist with $0.001 < P_1/P_3 < 0.19$ in the considered strain range ($-2.5\% < \varepsilon < 2.5\%$). In general, the $T$-like $M_{C1}$ phases can be considered as a monoclinically-distorted, but nearly-tetragonal structures with polarization slightly deviating from [010] and [001] for $i = 1$ and 2, respectively.

Based on these calculated structures, we have constructed the composition-strain polydomain phase diagram for (101)-oriented films (Figure 2(c)). In the polydomain system, a monodomain, $O$-phase region is stabilized under compressive strains and relatively Zr-rich portions of the composition range studied herein. Upon increasing the Ti-content, the structure morphs to the
$M_{C2}$ phase and a monodomain structure is still maintained. Note that this monodomain $M_{C2}$ phase persists all the way down to small strain regimes at $x < 0.7$. At small compressive and tensile strains, when the Ti content $x \geq 0.65$, the monodomain $M_{C2}$ phase is replaced by a polydomain T-like $M_{C1}$/T-like $M_{C2}$ domain structure. In the same strain regime, as the composition nears the morphotropic phase boundary, the $M_A$ phase is stabilized and a polydomain $M_A$ structure is formed. Overall, the composition-strain phase diagram of (101)-oriented heterostructures is found to exhibit a fewer number and less variation of stable phases as compared to the (001)-oriented heterostructures within the range of strain and composition considered herein. Additionally, the observed phases in the (101)-oriented films tend to take on monoclinic distortions due to the fact that in-plane misfit strain is akin to a shear strain on the tetragonal PbZr$_{1-x}$Ti$_x$O$_3$ unit cell. This is consistent with previously reported experimental observations, where a number of x-ray studies have confirmed the presence of dominant monoclinic symmetry in (101)-oriented PbZr$_{1-x}$Ti$_x$O$_3$ films with compositions near the morphotropic phase boundary.\textsuperscript{28,29}

### III.C (111)-Oriented Heterostructures

In the (111)-oriented heterostructures, three monodomain phases were found to be present across the range of strain and composition values explored herein: 1) a rhombohedral $R$ phase ($P_1 = P_2 = P_3 \neq 0$), 2) a monoclinic T-like $M_A$ phase ($P_1 = P_2 \neq 0, P_3 = 0$), and 3) a monoclinic $M_A$ phase ($P_1 = P_2 \neq 0, P_3 = 0$) in the compressive, intermediate, and tensile strain regimes, respectively, where $P_1$, $P_2$, and $P_3$ are along the crystallographic directions $x_1$, $x_2$, and $x_3$ in reference frame $X$ (Figure 3(a)). Note that the $R$ phase is energetically favored under large compressive strains (for all compositions studied herein) since the strain stabilizes the out-of-plane polarization component. Upon transitioning to tensile strain, in-plane polarization components appear in compositions with higher Ti-content, a T-like $M_A$ phase forms and in compositions with less Ti-content (or at large tensile strains and high Ti-content) a $M_A$ phase is observed.

Based on these monodomain results, we can further evaluate the polydomain structures. Performing minimization of $F''$ in terms of $P_i''$ at 300 K we can generate yet another composition-strain phase diagram to study the evolution of structure and phases in (111)-oriented films. To aid in the discussion, a table (Table II) is provided that indicates the notation which will be used to refer to each phase in the polydomain structures as well as the polarization components and symmetry of that phase. In the polydomain, (111)-oriented heterostructures, seven different, uniquely identifiable phases are observed: $R$, $M_{A1}$, $M_{A2}$, $M_{A3}$, T-like $M_{A1}$, T-like $M_{A2}$, and T-like $M_{A3}$. Again, specific definition of the polarization components of each phase is provided (Table II) and a schematic illustration of the various phases is provided (Figure 3(b), note that this illustration schematically shows the orientation of polarization within the unit cell in reference frame $X$).

In this case, the $R$ phase is found to have non-zero polarization along [100], [010], and [001]. Additionally, although all the monoclinic phases possess polarizations only within (110), we differentiate the monoclinic structures based on the different $P_1/P_3$ ratios that are possible. In particular, there are three $M_{Ai}$ phases ($M_{A1}$ ($P_1 = P_2 \neq 0$ and $P_3 \neq 0$) where $0.67 < P_1/P_3 < 0.96$, $M_{A2}$ ($P_1 = P_3 \neq 0$ and $P_2 \neq 0$) where $0.67 < P_1/P_2 <$...
0.96, and $M_{A_3}$ ($P_2 = P_3 \neq 0$ and $P_1 \neq 0$) where $0.67 < P_2/P_1 < 0.96$) and three T-like $M_{A_1}$ phases (T-like $M_{A_1}$ ($P_1 = P_3 \neq 0$ and $P_2 \neq 0$) where $0.001 < P_1/P_2 < 0.19$, T-like $M_{A_2}$ (where $P_3 \neq 0$ and $P_2 \neq 0$) where $0.001 < P_3/P_2 < 0.19$, and T-like $M_{A_3}$ ($P_2 = P_3 \neq 0$ and $P_1 \neq 0$) where $0.001 < P_2/P_1 < 0.19$) in the considered strain range ($-2.5% \leq \varepsilon \leq 2.5%$). In other words, the T-like $M_{A_i}$ phase is akin to a monoclinically-distorted, tetragonal structure with polarization slightly deviating from [001], [010], and [100] for $i = 1$, 2, and 3 while the $M_{A_i}$ phases possess a higher distortion and a polarization that can rotate smoothly all the way to the T phase.

Based on these calculated structures, we have constructed the composition-strain polydomain phase diagram for (111)-oriented films (Figure 3(c)). In the polydomain system, a monodomain, R-phase region is stabilized across all compositions under large compressive strains. At Ti-content $x \geq 0.6$ and in both the low compressive and high tensile strain regimes, the T-like $M_{A_i}$ phases are stabilized and a polydomain T-like $M_{A_1}$/T-like $M_{A_2}$/T-like $M_{A_3}$ domain structure is created. Under tensile strain and near the morphotropic phase boundary, the $M_{A_i}$ phase is stabilized and a polydomain $M_{A_1}$/M$_{A_2}$/M$_{A_3}$ domain structure is generated. In general, the phase diagram of (111)-oriented heterostructures exhibits the least number and variation of stable phases as compared to the (001)- and (101)-oriented heterostructures in the strain and composition range considered herein. Again, it is noted that although a two-domain configuration is directly derived based on the microscopic boundary conditions with equal volume fraction of $M_{A_i}$ (or T-like $M_{A_i}$) domains, in order to highlight the degenerate nature of all polarization variants, we represent this system as a thre-domain configuration with equal volume fraction, which has been experimentally observed in our previous work. 7,8 Additionally, the observed phases in the (111)-oriented heterostructures tend to take on rhombohedral (or monoclinically-distorted versions of rhombohedral) symmetry due to the fact that in-plane misfit strain is akin to a shear strain on the tetragonal PbZr$_{1-x}$Ti$_x$O$_3$ unit cell. Again, this is consistent with the previously reported experimental observations, where a number of x-ray studies have also confirmed the presence of dominant rhombohedral symmetry in (111)-oriented PbZr$_{1-x}$Ti$_x$O$_3$ films with compositions near the morphotropic phase boundary. 28,29

IV. DIELECTRIC PROPERTIES OF POLYDOMAIN PbZr$_{1-x}$Ti$_x$O$_3$ THIN FILMS

IV.A (001)-Oriented Heterostructures

Having studied the orientation-dependent, composition-strain phase diagrams in polydomain PbZr$_{1-x}$Ti$_x$O$_3$ heterostructures, we proceeded to explore the effects of strain, composition, and orientation on the dielectric response. First, we studied the composition-strain map for the intrinsic (Figure 4(a)) and total dielectric response (intrinsic plus extrinsic contributions) (Figure 4(b)) in (001)-oriented heterostructures and obtained similar results to those reported previously. 14,15,30 The maximum intrinsic response is found near the boundary between the polydomain $T_a$ and $M_{C_2}$/M$_{C_1}$ structures as a result of the effect of anisotropic dielectric permittivity, where the permittivity measured along the non-polar axis is higher than that measured along the polar axis and thus the $T_a$ structure, with pure in-plane polarization components, has the largest intrinsic response.

As compared to the intrinsic response, in the map of total dielectric response, enhanced effects can be observed in the $T_c/T_a$, polydomain $M_A$ (or $M_B$), $M_{C_1}$/M$_{C_3}$, and $M_{C_2}$/M$_{C_1}$ structures due to the contribution from extrinsic effects (i.e., domain wall motion). In particular, a large extrinsic contribution is observed in the polydomain $M_A$ (or $M_B$) structure which leads to the maximum total dielectric permittivity near the multicritical point at the boundary between the five polydomain phases and extending along the boundary between polydomain $M_A$ (or $M_B$) and $M_{C_1}$/M$_{C_3}$ structures due to the presence of opposite signs of out-of-plane polarization in the variants of the polydomain $M_A$ (or $M_B$) structure which, in
turn, leads to larger field-driven effects in these domain structures. The total dielectric response in the \( T_c \) and polydomain \( T_a \) domain structures remains the same since there are no domain walls in the \( T_c \) region and because of the degenerate nature of the \( T_a \) domain variants with respect to the electric field leads to no volume faction change under the electric field.

IV. B (101)-Oriented Heterostructures

We also studied the composition-strain map of the intrinsic (Figure 5(a)) and total dielectric response (intrinsic plus extrinsic contribution) (Figure 5(b)) for (101)-oriented heterostructures. Large intrinsic dielectric response is observed near the phase boundaries between the polydomain \( M_A \), \( T \)-like \( M_{C1} \)/\( T \)-like \( M_{C2} \), and \( M_{C2} \) structures, especially in films with lower Ti content and near zero strain, due to the structural instability near the morphotropic phase boundary. As compared to the intrinsic response map, the map of total dielectric response reveals enhanced response in the \( T \)-like \( M_{C1} \)/\( T \)-like \( M_{C2} \) structure due to the presence of additional extrinsic contributions from the domain walls. Such extrinsic contributions, however, are found to be less pronounced as the in the related \( T_c/T_a \) polydomain structure in the (001)-oriented heterostructures as a result of less preferential alignment of the electric field with a single polarization variant in the (101)-oriented heterostructures which provides less driving force for domain wall motion. The total dielectric response in the monodomain \( O \) and \( M_{C2} \) regimes remains the same as there are no domain walls present and in the polydomain \( M_A \) regime as the degenerate nature of variants in polydomain \( M_A \) with respect to the electric field which leads to no volume faction change under application of electric field.

IV. C (111)-Oriented Heterostructures

We also studied the composition-strain map for the total dielectric response (intrinsic plus extrinsic contribution) (Figure 6) in (111)-oriented films. Note that in the (111)-oriented heterostructures, the extrinsic contribution from domain wall motion is not present due to the single-domain nature of the \( R \)-phase regime and the degenerate nature of polarization variants in the polydomain \( T \)-like \( M_{A1} \)/\( T \)-like \( M_{A2} \)/\( T \)-like \( M_{A3} \) and \( M_{A1}/M_{A2}/M_{A3} \) structures where the structures are made up of equal volume fractions (i.e., \( 1/3 \)) of the different structural/polarization variants which results in the system having no electric field-driven domain fraction change. This noted, large intrinsic dielectric response can be obtained at the phase boundaries between the \( T \)-like \( M_{A1}/T \)-like \( M_{A2}/T \)-like \( M_{A3} \) and the \( M_{A1}/M_{A2}/M_{A3} \) phases due to the structural instability near the morphotropic phase boundary. It is also noted that the intrinsic response in the \( T \)-like \( M_{A1}/T \)-like \( M_{A2}/T \)-like \( M_{A3} \) regime in the (111)-oriented heterostructures is higher than the related structures in the other orientations (i.e., \( T_c/T_a \) polydomain structure in (001)-oriented heterostructures and the \( T \)-like \( M_{C1}/T \)-like \( M_{C2} \) polydomain structures in (101)-oriented heterostructures) due to the anisotropic dielectric response of \( \text{PbZr}_1-x\text{Ti}_x\text{O}_3 \) where the permittivity along the [100] is larger than that along the [001] and thus the intrinsic contribution to permittivity increases as the substrate normal is inclined more towards the [100]. Although the motional extrinsic response is not present in the (111)-oriented heterostructures, which leads to a lower overall response according to our calculation, recent experimental work indicates that (111)-oriented \( \text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3 \) films can exhibit greatly enhanced dielectric response among (001)-, (101)-, and (111)-oriented versions due to other possible enhancement mechanisms such as stationary domain wall contributions which have not been considered here. This added contribution arises from the fact that high domain wall densities can be achieved in the (111)-oriented heterostructures, thereby adding a new (and still underdeveloped) contribution from the volume domain wall phase in the material. Recent Ginzburg-Landau-Devonshire (GLD) models in \( \text{BaTiO}_3 \), for instance, suggest that such domain walls could give rise to an enhancement of susceptibilities between 1.1 to 1000-times that in the bulk and the experimental work suggests that the domain wall phase has a permittivity 6-70 times that of the bulk of the domain. Addition of such effects into these models will require additional insights into the

FIG. 5: The composition-strain map for (a) the intrinsic and (b) the total (intrinsic plus extrinsic contribution) dielectric response in (101)-oriented films.
nature of this effects and would require more advanced models that can provide realistic domain structures and densities to estimate the volume fraction of domain wall phase.

Overall, we have compared the predicted evolution of dielectric permittivity as a function of strain and composition for (001)-, (101)-, and (111)-oriented polydomain PbZr$_{1-x}$Ti$_x$O$_3$ films and here we will highlight some key similarities and differences. First, as is expected, the ferroelectric instability usually results in an enhanced dielectric response and thus irrespective of the film orientation enhanced dielectric permittivity is always present near the phase transition boundary. Second, varying the film orientation can tune the relative fraction of the intrinsic and extrinsic contribution to the dielectric permittivity. For instance, in PbZr$_{0.2}$Ti$_{0.8}$O$_3$ films, if we compare the dielectric response of polydomain $T_c/T_a$ structure in (001)-oriented films and its related counterparts, the T-like $M_{C1}/T$-like $M_{C2}$ structure in (101)-oriented films and the T-like $M_{A1}/T$-like $M_{A2}/T$-like $M_{A3}$ structure in (111)-oriented films, we can make a few observations. First at a given equivalent misfit strain, the highest intrinsic response is observed in (111)-oriented heterostructures (followed by (101)- and (001)-oriented heterostructures) as a result of the anisotropic dielectric response of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ where the permittivity along the [100] is larger than that along the [001] and thus the intrinsic contribution to permittivity increases as the substrate normal is inclined more towards the [100]. This is similar to the monodomain case where the permittivity exhibits higher values along non-polar directions (i.e., [111]) than polar directions (i.e., [001]) in tetragonal ferroelectrics. Second, the relative extrinsic contribution (from domain wall motion) to the permittivity decreases as we move from (001)- to (101)-oriented films (as a result of less preferential alignment of the electric field with a single polarization variant) and completely vanishes in (111)-oriented films due to the constant volume fraction of the three polarization variants which is independent of the electric field. Ultimately, the studies indicate that a judiciously chosen combination of elastic strain and film orientation can be used to access a wide variety of structural phase variants and correspondingly diverse dielectric response in ferroelectrics. This knowledge, in turn, can enable the response of a system like PbZr$_{1-x}$Ti$_x$O$_3$ to be optimized with relying simply on traditional chemical-routes (i.e., being near to the morphotropic phase boundary).

V. CONCLUSIONS

In this work, we have used a thermodynamic model to calculate the structural phase diagrams and dielectric response in polydomain (001)-, (101)-, and (111)-oriented PbZr$_{1-x}$Ti$_x$O$_3$ thin films. Our studies reveal that beyond simple chemistry and strain variations, the use of film orientation can enable dramatic changes in the energetics of the system and thus can be used to tune the structure of the equilibrium phases. In particular, we observe that in (101)- and (111)-oriented films, the stability of the parent $T$ phase is greatly reduced and it tends to evolve into a distorted version. We have observed monoclinic and rhombohedral phases present in the predicted phase diagram of (101)- and (111)-oriented films, respectively, which are consistent with previously reported experimental observations. Additionally, our work provides a theoretical platform by which to systematically optimize the dielectric response in thin films as a function of composition, strain, and orientation. Large dielectric susceptibilities can be found near phase transition boundaries where the ferroelectric instability is induced in these films. At the same time, we also observed that the film orientation can be used to tune the relative fraction of contributions from domain and domain wall motion to the dielectric permittivity. Ultimately, the use of additional orientations of films — beyond the predominantly studied (001)-oriented versions in the literature provide a rich and complex landscape in which we can potentially enhance and gain deterministic control over the properties of materials.

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