Phenomenological modeling of anisotropic dielectric properties in epitaxial (Pb, Sr)TiO$_3$ thin films

Cite as: AIP Advances 10, 015022 (2020); https://doi.org/10.1063/1.5126727
Submitted: 02 December 2019 . Accepted: 17 December 2019 . Published Online: 09 January 2020

Yecheng Ding $^{\circledast}$, and Wenhui Ma $^{\circledast}$
Phenomenological modeling of anisotropic dielectric properties in epitaxial (Pb, Sr)TiO$_3$ thin films

Cite as: AIP Advances 10, 015022 (2020); doi: 10.1063/1.5126727
Submitted: 2 December 2019 • Accepted: 17 December 2019 • Published Online: 9 January 2020

Yecheng Ding and Wenhui Ma

AFFILIATIONS
Department of Physics, Shantou University, Shantou, Guangdong 515063, People's Republic of China

Author to whom correspondence should be addressed: whma@stu.edu.cn

ABSTRACT
Strain tuning of polarization states and dielectric properties in (001) epitaxial (Pb, Sr)TiO$_3$ (PST) films is investigated using a thermodynamic phenomenological model. We find that our calculations of anisotropic dielectric properties and their electric field tunability at various in-plane strained states are in good agreement with relevant experimental data for epitaxial Pb$_{0.35}$Sr$_{0.65}$TiO$_3$ films when material constants are properly determined. Our modeling further suggests that dielectric tunability can be optimized by combined control of epitaxial strain and PST composition.

INTRODUCTION
Epitaxial strain can be used to manipulate structural transition and physical properties of ferroelectric thin films, such as enhancement of Curie temperature ($T_c$) and spontaneous polarization ($P_s$), occurrence of new phases, tuning of dielectric properties, strain-driven morphotropic phase boundary (MPB) and critical phenomena, and orientation control of phase stability and ferroelectricity. Epitaxial thin films of lead strontium titanate (Pb$_x$Sr$_{1-x}$TiO$_3$ or PST) have been prepared and characterized by a number of researchers mainly because of unique dielectric properties and high potential for tunable microwave device applications. Interestingly, recent theoretical studies revealed existence of the rhombohedral phase and low-temperature MPB in PST solid solution.

Experimentally, a number of methods can be used to change in-plane epitaxial strain, such as selection of substrates and control of cooling rate. Lin et al. have successfully grown high-quality anisotropically strained epitaxial Pb$_{0.35}$Sr$_{0.65}$TiO$_3$ (PST35/65) thin films on NdGaO$_3$ substrates by pulsed laser deposition and measured the lattice parameters and dc bias dependent dielectric properties. Lin et al. reported that fast and slow cooling led to c-axis and a-axis growth, respectively. A change in the cooling rate also gives rise to the difference in dislocation density for fast-cooled (FC) and slowly cooled (SC) samples. Clearly, such variation in strain relaxation leads to varied tunability of anisotropic dielectric properties. The previous theoretical findings in bulk PST and dielectric measurements of epitaxial PST films suggest this tunable dielectric solid solution is worth more thorough investigations.

Zembilgotov et al. pioneered modeling of the effect of anisotropic strain on epitaxial ferroelectric thin films. They constructed a misfit strain phase diagram for epitaxial PST35/65 and calculated zero-field in-plane dielectric anisotropy for the FC sample. It would be interesting if one can fully model the E-field tunability of anisotropic dielectric properties and study the effect of strain relaxation by comparing results on both the FC and SC samples.

In this paper, strain tuning of polarization states and dielectric properties in (001) epitaxial (Pb, Sr)TiO$_3$ (PST) films is investigated using a thermodynamic phenomenological model. Our present modeling of strain tuning of dielectric anisotropy and dielectric tunability in epitaxial PST films shows excellent agreement with relevant experimental data, thus providing a guide for strain engineering of the phase structure and physical properties of technologically important perovskite ferroelectrics. Besides delicate control of strain relaxation, our modeling suggests that dielectric tunability can be further
optimized by choosing a slightly higher Sr content.

**THEORY**

We consider a single-domain (001)-oriented epitaxial thin film grown on a dissimilar substrate, which is subjected to anisotropic in-plane strain. Our theoretical calculations are based on a free energy function given as

\[ F(T, u_i, P_1) = a_1^* P_1 + a_2^* P_2 + a_3^* P_3 + a_4^* (P_1^2 + P_2^2) + a_5^* P_1^2 \]

\[ + a_6^* (P_1 P_2 + P_2 P_3 + P_3 P_1) + a_{111} (P_1 + P_2 + P_3) + a_{12} (P_1^2 P_2 + P_2^2 P_3 + P_3^2 P_1) \]

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

\[ + a_{113} P_1^2 P_2^2 - E_1 P_1 - E_2 P_2 - E_3 P_3 + F_{\text{dir}}. \]

where \( T, u_i, P_1, \) and \( E_i \) are the temperature, in-plane strain, polarization, and electric field \((i, j = 1, 2,\) and \(3\) refer to pseudocubic \([100], [010],\) and \([001], \)directions, respectively). \( a_1^* \) and \( a_1^* \) are the renormalized dielectric stiffness coefficients, \( a_{ij} \) and \( a_{ij} \) are the high-order dielectric stiffness coefficients at constant stress. \( F_{\text{dir}} \) is a polarization-independent pure elastic energy term.

For bulk ferroelectrics under constant stress conditions, elastic Gibbs function \( G(T, \sigma, P) \) is the standard thermodynamic potential. For strained epitaxial films, Pertsev et al. derived in Ref. 3 a new potential \( F(T, u_i, P) \) via Legendre transformation \((F = G + u_i \sigma_1 + u_2 \sigma_2 + u_3 \sigma_3)\) and elimination of all the stress components \((\sigma_i).\) Since there is no traction on the film surface, \( \sigma_3 = \sigma_4 = \sigma_5 = 0.\) Here, strain is not considered here, so \( u_0 = 0.\) For coherent growth, \( u_i = u_{i0} \) on pseudocubic substrates, \( a_{ii} ^* \) and \( a_{ij} \) on anisotropic (e.g., orthorhombic) substrates. \( a_{ij} \) for strain-relaxed films, however, anisotropic in-plane strain might occur on both types of substrates. General equations for the in-plane strain components of epitaxial ferroelectrics (derived from \( u_i = -\partial \Delta G / \partial \sigma_1, u_2 = -\partial \Delta G / \partial \sigma_2 \) are given as

\[ u_1 = s_{12} \sigma_1 + s_{12} \sigma_2 + Q_{11} P_1 + Q_{12} (P_2^2 + P_3^2), \]

\[ u_2 = s_{12} \sigma_1 + s_{12} \sigma_2 + Q_{11} P_2 + Q_{12} (P_1^2 + P_3^2). \]

It can be seen that each of the strain \((u_i)\) and \(u_2\) is essentially composed of two parts: one is due to the substrate constraint or misfit stress and the other is due to occurrence of ferroelectricity. They are exactly the strain (either coherent or partially relaxed) of epitaxial ferroelectrics relative to the unconstrained paraelectric bulk-like state.

Our approach is fundamentally similar to those used before. For coherent growth, in-plane lattice parameters of the epitaxial films are the same as those of the substrates; therefore, \( u_1 \) and \( u_2 \) can be calculated as \((u_i - a_0)/b,\) where \( b \) and \( a_0 \) are lattice parameters of the substrate and the stress-free paraelectric films, respectively. In the case of strain-relaxed films, however, similar to Zembilgotov et al., \( a_{ii} ^* \) in the present work, in-plane strain \( u_i \) is deduced using \( u_i = (a_i - a_0)/a_0 \) \((i = 1, 2,\) where \( a_i \) is the measured in-plane lattice parameters of epitaxial films (e.g., those denoted by \( a \) and \( b \) shown in Refs. 11 and 12).

Except for dielectric stiffness \( a_1,\) all the relevant free energy coefficients and material constants used in the present calculations for PST were calculated as weighted averages of those known for pure PbTiO\(_3\) and SrTiO\(_3\) (see Table I and Refs. 16, 30, 34, and 35). A linearly averaged dielectric stiffness \((LA-\alpha)\) \( a_1 = 5.65 \times 10^3 \) \( (T = 716.5 \times 10^6 + 237.5) / (0.81 + 0.69x_{\text{Fe}}) \) was reported in the previous studies of bulk PST. In the present modeling, we mainly used this LA-\(a_1.\) However, as already realized before, \( LA-\alpha \) may somehow underestimate the transition temperature deduced from dielectric measurements, and certain adjustment might have to be tried for the Curie-Weiss temperature \( T_0 \) so as to better describe temperature dependent properties. Thus in our modeling of Pb\(_{0.55}\)Sr\(_{0.45}\)TiO\(_3\), besides LA-\(a_1,\) we also tried an alternative \( T_0 \)-adjusted dielectric stiffness \((TA-\alpha,\) as detailed in the section titled “Results and discussion”) in order to check whether one can actually realize better agreement with the measured anisotropic dielectric properties.

The expressions for the renormalized dielectric stiffness \( a_1^* \) under anisotropic in-plane strains \((i.e., u_i \neq u_2)\) are given as

\[ a_1^* = a_1 + u_2 (Q_{22} s_{12} - Q_{12} s_{11} + u_1 (Q_{12} s_{12} - Q_{22} s_{11}) / s_{12} - s_{11}), \]

\[ a_2^* = a_2 + u_1 (Q_{22} s_{12} - Q_{12} s_{11} + u_1 (Q_{12} s_{12} - Q_{22} s_{11}) / s_{12} - s_{11}). \]

Equilibrium polarization states are determined by minimizing the free energy function \( F \) shown by Eq. (1). Possible phases and polarization states that may occur are illustrated in Fig. 1 and listed as follows: (1) paraelectric state \( P_1 = P_2 = P_3 = 0;\) (2) three orthorhombic states, \( a_1 (P_1 = 0, P_2 = P_3 = 0), a_2 (P_1 = 0, P_2 = P_3 = 0), \) and \( c (P_1 = P_2 = P_3 = 0);\) (3) three monoclinic states, \( a_1 a_2 (P_1 = P_2 = P_3 = 0), a_1 c (P_2 = P_3 = 0), \) and \( a_2 c (P_1 = 0, P_2 = P_3 = 0);\) and (4) triclinic state, \( a^* (P_1 
eq P_2 
eq P_3).\) Relative dielectric constants \( \eta_i \) can be calculated from inversion of dielectric stiffness matrices \((\eta_0): \eta_0 = 1 / \varepsilon_0 \chi, \) in which \( \varepsilon_0 \) is the vacuum permittivity and \( \chi = \partial F / \partial P_1, \partial P_2, \partial P_3.\) Dielectric tunability \((\eta_0)\) is defined as \( \phi_0 = 1 - \eta_0 (E_i = 0) / \eta_0 (E_i = 0).\)

In order to properly model dielectric properties of epitaxial PST, it is of central importance to determine exact magnitude of the
in-plane strains $u_i$. However, single-crystal data of $a_0$ are not available. Therefore, we made a series of careful trials using relevant data from polycrystalline films and bulk ceramics reported in the literature, as will be described in detail in the section titled “Results and discussion.” Values of those $u_i$ are listed in Table II for both FC and SC films of Pb$_{0.35}$Sr$_{0.65}$TiO$_3$. Different cooling rates correspond to different epitaxial strain conditions. It turns out that our theoretical data of bias field dependent dielectric properties can fit experimental data well, suggesting that phenomenological modeling can make useful predictions of dielectric properties of PST epitaxial films if material constants are properly chosen.

### RESULTS AND DISCUSSION

A previous modeling of bulk PST pinpointed the potential influence of $E$-field induced symmetry-lowering and negative pressure on dielectric response and tunability. The present work is focused on modeling anisotropic dielectric properties measured in epitaxial PST35/65 subjected to anisotropic in-plane strain. Our aim is to understand the underlying mechanism and search for strain conditions and composition with optimized properties.

Determination of the initial phase (at zero field) is of foremost importance for accurate modeling of dielectric tunability under dc bias (see Table II). The room-temperature $u_1$-$u_2$ phase diagram of strained epitaxial PST35/65 is presented in Fig. 2. It can be seen that, at small strains, epitaxial PST is still in the paraelectric state (see the central triangle-shaped region), while with increasing strain levels, ferroelectric phases become stabilized. Based on the previous studies (e.g., Wang and Ma), it is tempting to expect that, in the $p$ phase field or at the boundary between $p$ and ferroelectric phases, dielectric response may be sensitive to an external stimulus, suggesting high tunability. As shown in Fig. 3, depending on the initial states depicted in Fig. 2 (also see Table II) and direction of the applied dc biasing field, phase changes occur with a variety of polarization rotations being induced.

Both the phase field of interest (i.e., high $\phi$ in principle) and the actual strain conditions (cf. Table II) involve the central part of the phase diagrams presented in Figs. 2 and 3. Our modeling is thus focused on this region. To have a glimpse of the relation between in-plane anisotropic strains and dc bias dependent dielectric response, we mapped the tunability factor $\phi_{11}$ (under the dc biasing field $E_1$) within the strain range of $-0.005 \leq u_i \leq 0.005$, as delineated in Fig. 4. It is clear that (1) as expected, high tunability is generally found in the $p$ phase field; (2) near the $p$-$a_2$ and $p$-$c$ phase boundaries, even higher tunability is available; and (3) $\phi_{11}$ is asymmetric for compressive and tensile strains, and more precisely, a tensile strain in the [100], or $a$ direction is advantageous for enhancing $\phi_{11}$. The present finding provides a clue on how to optimize the performance of thin film microwave dielectric devices.

In Fig. 4, each $\phi_{11}$ curve is plotted against $u_2$ (with $u_1$ fixed) and two $E_1$-field levels are applied to show field dependence of

![FIG. 1. Schematic diagram showing polarization directions of various phases considered in our calculations. At room temperature, the strain-free paraelectric state is cubic with a lattice parameter of $a_0$; while under anisotropic in-plane strain, the film is paraelectric orthorhombic above the Curie temperature $T_c$ and transforms to various ferroelectric states (orthorhombic, monoclinic, and triclinic) below $T_c$. The lattice parameters are $a$ (or $a_1$), $b$ (or $a_2$), and $c$, respectively.](image)

| TABLE II | Estimation of anisotropic in-plane strain ($u_1$ and $u_2$) and stable phases of pulsed laser deposition (PLD)-grown epitaxial PST. The listed strain values were calculated by assuming five sets of $a_0$ (in angstroms; I: 3.914; II: 3.919, extrapolated from Ref. 25; III: 3.920; IV: 3.923; V: 3.925) for paraelectric PST. $u_1$ and $u_2$ were derived from the lattice parameters 11,12 (in angstroms) measured at room temperature for fast cooled (FC) and slowly cooled (SC) samples. FC: $a = 3.9176$, $b = 3.9194$, and $c = 3.9214$; SC: $a = 3.9184$, $b = 3.9227$, and $c = 3.9172$. Phase$^1$ and phase$^2$ refer to the types of initial phases (at zero $E$-field) determined to be stable using linearly averaged (LA-$\alpha_1$) and $T_c$-adjusted (TA-$\alpha_1$) dielectric stiffness, respectively. See the section titled “Theory” for more details. |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | FC | | | | SC | | | |
| | | | Phase$^1$ | Phase$^2$ | | Phase$^1$ | Phase$^2$ | |
| $a_0$ (Å) | $u_1$ (%) | $u_2$ (%) | $a_1a_2$ | $a_1a_2$ | $a_1a_2$ | $a_1a_2$ | $a_1a_2$ | $a_1a_2$ |
| 3.914 | 0.0920 | 0.1380 |  |  | 0.1124 | 0.2223 |  |  |
| 3.919 | -0.0357 | 0.0102 | $p$ | $r^*$ | -0.0153 | 0.0944 |  |  |
| 3.920 | -0.0612 | -0.0153 | $p$ | $a_2c$ | -0.0408 | 0.0689 |  |  |
| 3.923 | -0.1376 | -0.0918 | $c$ | $c$ | -0.1172 | -0.0076 | $p$ | $a_2c$ |
| 3.925 | -0.1885 | -0.1427 | $c$ | $c$ | -0.1682 | -0.0586 |  |  |
FIG. 2. $u_1$-$u_2$ phase diagram ($E = 0$) of epitaxial Pb$_{0.35}$Sr$_{0.65}$TiO$_3$ films at 25 $^\circ$C.

FIG. 3. $u_1$-$u_2$ phase diagram of epitaxial Pb$_{0.35}$Sr$_{0.65}$TiO$_3$ films at 25 $^\circ$C under in-plane dc bias: (a) $E_1 = 30$ kV/cm; (b) $E_2 = 30$ kV/cm.

FIG. 4. Mapping of dielectric tunability for epitaxial Pb$_{0.35}$Sr$_{0.65}$TiO$_3$ films at 25 $^\circ$C under in-plane dc bias: (a) $E_1 = 10$ kV/cm; (b) $E_1 = 30$ kV/cm.

The variation of $\phi_{11}$ with $u_2$ is linked to polarization changes displayed in Fig. 5. Similar to the results for epitaxial PST shown in Figs. 4 and 5, in the previous studies of anisotropically strained PbTiO$_3$, a dielectric peak was found to appear at the $c$-$a_1$c transition (see Fig. 12 of Ref. 33), and dielectric anisotropy ($\eta_{11} > \eta_{22}$) under dc bias was found under tensile strain (i.e., $u_1 > 0$, see Fig. 14 of Ref. 33) as well.

During epitaxial growth at elevated temperatures, misfit stress in thin films can be relieved by formation of misfit dislocations over a critical thickness. Thus, in-plane epitaxial strain for a relaxed film is usually different from the coherent misfit strain ($b$-$a_0$)/$b$ defined in Ref. 3. Strain relaxation and its potential influence on the structure...
FIG. 5. In-plane strain ($u_2$) tuning of the polarization state calculated for epitaxial Pb_{0.35}Sr_{0.65}TiO_{3} under dc bias ($E_1 = 0$ and 30 kV/cm): (a) $u_1 = 0$; (b) $u_1 = 0.001$.

and properties are indeed a fairly interesting topic. In general, the extent of strain relaxation is dependent on thickness. In the experiments of Lin et al.,\textsuperscript{11,12} the thickness is fixed; therefore, variation in the epitaxial strain is due to the difference in the cooling rate during thin film processing. Evolution of threading dislocations during cooling determines the strain relaxation of epitaxial thin films.\textsuperscript{13} For slow cooling, there is sufficient time for dislocation evolution, resulting in efficient release of misfit stress at the interface, while for fast cooling, the films remain strained, especially near the interface. Neither thickness effect nor thin film processing is explicitly considered in this work. Instead, in the present modeling, disparity in the anisotropic dielectric properties for the FC and SC samples\textsuperscript{11,12} is treated as the influence of varied in-plane strain states (see Table II).

Our calculated curves of $\eta_{11}$ vs $E_1$ and $\eta_{22}$ vs $E_2$ and the measured data points for FC and SC samples are displayed in Figs. 6 and 7, respectively. As mentioned in the section titled “Theory,” trial calculations using a number of $a_0$ were made to find the most appropriate lattice constant for stress-free paraelectric cubic PST35/65. Again we stress that, in order to compare our theoretical results with experimental results on strain relaxed epitaxial films,\textsuperscript{11,12} rather than the misfit strain defined in Ref. 3 for coherently grown and fully strained films, in-plane strain deduced from deformation of the thin film lattice with respect to the strain-free paraelectric cubic reference

FIG. 6. Dielectric constant vs in-plane dc biasing field at 25 °C calculated for FC epitaxial Pb_{0.35}Sr_{0.65}TiO_{3} films assuming a series of in-plane strain that resulted from five sets of $a_0$ (see Table II). The solid diamonds are experimental data for the FC sample (Ref. 12). LA-α was used.

FIG. 7. Dielectric constant vs in-plane dc biasing field at 25 °C calculated for SC epitaxial Pb_{0.35}Sr_{0.65}TiO_{3} films assuming a series of in-plane strain that resulted from five sets of $a_0$ (see Table II). The solid diamonds are experimental data for the SC sample (Ref. 12). LA-α was used.
state was used. As for four of the five $a_0$, which come from experiments, the discrepancy may be ascribed to the difference in processing and residual strain of the powders and polycrystalline ceramics or thin films. Some small values of $a_0$ were suggested to be due to compressive strain or grain size effect.

Temperature dependent polarization and dielectric constants for PST35/65 with two different in-plane strain conditions (i.e., FC and SC samples, $a_0 = 3.925$ Å; see Table II for details on $u_1$ and $u_2$) are presented in Fig. 8. In sharp contrast to the case of the FC sample, for the SC sample due to pertinent $c$-a$_2$-c transition, $\eta_{22}$ is comparably greater than $\eta_{11}$ at room temperature (RT), although compressive in-plane strains lift $T_c$ and stabilize the initial tetragonal state for both samples. In the previous studies of bulk PST (see Fig. 7 of Ref. 30), where the initial phase is tetragonal ($P_3 \neq 0$) and $E_{001}$ is applied to tune the dielectric constants, a similar trend of dc biasing field dependence to those shown in Figs. 6 and 7 ($a_0 = 3.925$ Å) was obtained.

The present calculations indicate that combinations of LA-$\alpha_1$ and $a_0 = 3.923$–3.925 Å can give satisfactory agreement with the measured in-plane dielectric anisotropy and tunability. Such a stress-free paraelectric lattice cell size suggests slight volume contraction in strained epitaxial ferroelectric PST35/65 based on the reported lattice parameters, which appears somehow unusual if one compares this finding with the commonly known volume expansion below the Curie temperature in bulk perovskites. It is noted that some effects such as strain relaxation associated formation of dislocation and inhomogeneous strain are ignored in this work. Besides, such an unusual phenomenon cannot be attributed to a hydrostatic pressure effect. In contrast to the case of materials with a considerably higher $T_c$, for PST35/65, the ferroelectric-paraelectric

![FIG. 8. Polarization [panels (a) and (c)] and dielectric constants [\(\eta_{11}\) and \(\eta_{22}\); panels (b) and (d)] as a function of temperature calculated for FC and SC epitaxial Pb$_{0.35}$Sr$_{0.65}$TiO$_3$ films under dc bias. Panels (a) and (b): $E = 0$; panels (c) and (d): $E_1$ or $E_2 = 30$ kV/cm. LA-$\alpha_1$ was used, and $a_0 = 3.925$ Å was assumed. As indicated, the Curie temperature for bulk Pb$_{0.35}$Sr$_{0.65}$TiO$_3$ is $\sim 13^\circ$C.](image-url)
transition is close to RT. The present result can be understood if one assumes that the bulk state is indeed paraelectric at RT, while for the epitaxial film, $T_c$ is shifted up to a few degrees above RT due to strain enhancement of ferroelectricity. In perovskites close to $T_c$, the ferroelectric state generally has negligible thermal expansion. Consequently, ferroelectric lattice cell volume extrapolated to the high-temperature paraelectric region should be actually smaller than the paraelectric one, in contrast to the case of volume expansion in lattice cells when a high-temperature paraelectric state is extrapolated to a low-temperature ferroelectric region.

There is a discrepancy among the experimentally measured $T_c$ in powders, or polycrystalline ceramics and thin films, which may be due to the difference in processing and characterization methods that were used. Xing et al.\textsuperscript{37} found that $T_c$ for PST ($x_{Sr} = 0.5$) is well below RT, while Kang et al.\textsuperscript{38} and Jain et al.\textsuperscript{39} reported that PST becomes cubic at $x_{Sr} \sim 0.55$. $T_c$ for PST35/65 determined by structural characterization\textsuperscript{40} seems to differ from that indicated by dielectric measurements (i.e., dielectric maximum temperature $T_m$, which was found to be larger than 25 $^\circ$C\textsuperscript{41}). Detailed x-ray diffraction (XRD), Raman scattering, and differential scanning calorimetry (DSC) studies by Leal et al.\textsuperscript{42} suggested that tetragonal to cubic transition should occur at RT for $x_{Sr} \sim 0.65$, which agrees with the results of Kim et al.\textsuperscript{43}. Our modeling suggests the need for systematic temperature dependent measurement of lattice parameters of epitaxial thin films to corroborate the validity of $\alpha_0$ found in this work.

In this work, besides LA-$\alpha_1$,\textsuperscript{40} which gives rise to a $T_c$ of $\sim 13$ $^\circ$C (see Fig. 8(a)), an alternative dielectric stiffness (TA-$\alpha_1$) of 5.373 x 10\textsuperscript{-8} (T-43) ($T$ in $^\circ$C) was used, which leads to $T_c$ consistent with $T_m$ shown by dielectric measurements.\textsuperscript{41} To compare the validity of TA-$\alpha_1$ in modeling the field dependent anisotropic dielectric properties, we repeated the same calculations shown in Figs. 6 and 7, and the results are presented in Figs. 9 and 10. When TA-$\alpha_1$ is used, the initial phases are in general different (see Table II).

The triclinic phase ($r^*$) is found to exist adjacent to the central region of the $u_1$-$u_2$ phase diagram (not shown here). Similar modeling of the FC sample was reported by Zembilgotov et al.,\textsuperscript{44} in which a TA-$\alpha_1$ like dielectric stiffness was used and the calculated zero-bias dielectric anisotropy ($\eta_{22} > \eta_{11}$) agreed reasonably with the measured data. However, Zembilgotov et al. only considered the FC sample and did not model the field dependence of dielectric anisotropy. In this work, we have modeled the dielectric anisotropy under dc bias for both FC and SC samples. By comparing Figs. 9 and 10 with Figs. 6 and 7, one can immediately tell that the calculated curves using TA-$\alpha_1$ do not agree with the measured data points. Poor quantitative fit with experiments for both FC and SC samples makes the validity of TA-$\alpha_1$ questionable.

PST is a less studied material system, and due to lack of experimental data, the presently adopted free energy coefficients are essentially derived using the averaging method discussed in the section titled “Theory.” It is hoped that this work could stimulate more experimental studies on characterizations of the structure and properties. When careful measurements of phase boundaries and dielectric properties become available, a few sophisticated approaches reported in the literature can be utilized to construct thermodynamic potential of a solid solution system. In consideration of the topology and anisotropy of the energy surface, Heitmann and Rossetti\textsuperscript{45,46} showed how one can extract Landau-Devonshire coefficients from end components of solid solutions that display a morphotrophic phase boundary, such as (Ba, Sr)TiO\textsubscript{3}, Ba(Zr, Ti)O\textsubscript{3}, and (Ba, Ca)TiO\textsubscript{3}. Peng et al.\textsuperscript{47} showed how coefficients of thermodynamic potential can be determined by fitting to the experimentally observed phase transition temperatures, and dielectric constants and polarization data.

As shown above in Fig. 2, the triclinic $r^*$ phase does not appear in the $u_1$-$u_2$ phase diagram of PST35/65 computed using LA-$\alpha_1$. However, as shown in the computed $u_2$-$x_{Sr}$ phase diagram in Fig. 11,
the \( r^* \) phase is shown to occur in the PST composition with \( x_{3r} \) < -0.63, for which \( T_c \) is above RT. Figure 11 indicates that changing \( x_{3r} \) can modify phase stability and accordingly initial polarization states and dielectric properties under dc bias. As discussed above, when the initial phase is paraelectric (see Table II and Figs. 6 and 7), the dielectric tunability may be remarkably enhanced. To enunciate this point more vividly, we computed again the \( u_1-u_2 \) phase diagram using LA-\( \alpha \)-1 for PST30/70. It is clearly seen in Fig. 12 that as compared to PST35/65 (see Fig. 2), with the slightly increasing Sr content, bulk \( T_c \) is further reduced below RT, and now in the epitaxial thin films, the central \( p \) phase field becomes remarkably broadened. This result indicates that, unlike the case of PST35/65 (see Figs. 2 and 4) where the optimal window of strain tuning for better dielectric performance is fairly tight, now for PST30/70, a large \( \phi \) factor can be expected over a broader range of in-plane strain conditions.

CONCLUSIONS

Our theoretical data of bias field dependence of dielectric properties fit experimental data well when dielectric stiffness and stress-free paraelectric lattice constant are carefully determined, suggesting that phenomenological modeling can make useful predictions of polarization states and anisotropic dielectric properties of strained (Pb, Sr)TiO\(_3\) epitaxial films. Moreover, the present theoretical calculations show that dielectric tunability may be optimized by simultaneously manipulating the PST composition (i.e., Sr content) and anisotropic in-plane strain.

REFERENCES

1. K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L. Q. Chen, D. G. Schlom, and C. B. Eom, Science 306, 1005 (2004).
2. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A. K. Tagantsev, X. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy, and D. G. Schlom, Nature 430, 758 (2004).
3. N. A. Pertsiev, A. G. Zembligotov, and A. K. Tagantsev, Phys. Rev. Lett. 80, 1988 (1998).
4. Z. G. Ban and S. P. Alpay, J. Appl. Phys. 91, 9288 (2002).
5. H. Li, A. L. Roytburd, S. P. Alpay, T. D. Tran, L. Salamanca-Riba, and R. Ramesh, Appl. Phys. Lett. 78, 2354 (2001).
6. J. Zeches, M. D. Rossell, J. X. Zhang, A. J. Hatt, Q. He, C. H. Yang, A. Kumar, C. H. Wang, A. Melville, C. Adamo, G. Sheng, Y. H. Chu, J. F. Ihlefeld, R. Erni, C. Edereer, V. Gopalan, L. Q. Chen, D. G. Schlom, N. A. Spaldin, L. W. Martin, and R. Ramesh, Science 326, 977 (2009).
7. Y. Y. Liu and J. Y. Li, Phys. Rev. B 84, 132104 (2011).
8. Y. Y. Liu, L. Yang, and J. Y. Li, J. Appl. Phys. 113, 183524 (2013).
9. W. Ma, AIP Adv. 6, 045310 (2016).
10. W. Ma and F. Wang, AIP Adv. 7, 105120 (2017).
11. Y. Lin, X. Chen, S. W. Liu, C. L. Chen, J. Lee, Y. Li, Q. X. Jia, and A. Bhatta, Appl. Phys. Lett. 84, 577 (2004).
12. Y. Lin, X. Chen, S. W. Liu, C. L. Chen, J. Lee, Y. Li, Q. X. Jia, and A. Bhatta, Appl. Phys. Lett. 86, 142902 (2005).
13. Y. Lin, C. Dai, Y. R. Li, X. Chen, C. L. Chen, A. Bhatta, and Q. X. Jia, Appl. Phys. Lett. 96, 102901 (2010).
14. S. W. Liu, Y. Lin, J. Weaver, W. Donner, X. Chen, C. L. Chen, J. C. Jiang, E. I. Meletis, and A. Bhatta, Appl. Phys. Lett. 85, 3202 (2004).
15. S. W. Liu, J. Weaver, Z. Yuan, W. Donner, C. L. Chen, J. C. Jiang, E. I. Meletis, W. Chang, S. W. Kirchoefer, J. Horwitz, and A. Bhatta, Appl. Phys. Lett. 87, 142905 (2005).
16. G. Rispens, J. A. Heuer, and B. Noheda, Appl. Phys. Lett. 97, 262901 (2010).
17. M. Tyumin, M. Plekh, M. Antonov, and A. Kalvane, Phys. Rev. B 84, 224105 (2011).
18. S. Matzen, O. Nesterov, G. Rispens, J. A. Heuer, M. Biegalski, H. M. Christen, and B. Noheda, Nat. Commun. 5, 4415 (2014).
19. S. Fernandez-Pena, C. Lichtensteiger, P. Zubko, C. Weymann, S. Gariglio, and J. Triscone, APL Mater. 4, 086105 (2016).
20. S. Nomura and S. Sawada, J. Phys. Soc. Jpn. 10, 108 (1955).
21. V. V. Lemanov, E. P. Smirnova, and A. B. Nesterov, Ferroelectr. Lett. 22, 69 (1997).
22. Y. Somiya, A. S. Bhatta, and L. E. Cross, Int. J. Inorg. Mater. 3, 709 (2001).
23. K. T. Kim and C. I. Kim, Thin Solid Films 420, 544 (2002).
24. M. Jain, N. K. Karan, R. S. Katiyar, A. S. Bhatta, F. A. Miranda, and F. W. Van Keuls, Appl. Phys. Lett. 85, 275 (2004).
25. Y. Somiya, A. S. Bhatta, and L. E. Cross, Ferroelectr. Lett. 31, 119 (2004).
26. Z. Zhai, X. Yao, Z. Xu, and H. Chen, J. Appl. Phys. 100, 034108 (2006).
27. X. Lei, X. Dong, C. Mao, Y. Chen, F. Cao, and G. Wang, Appl. Phys. Lett. 101, 262901 (2012).
References

28 Z. Zheng, T. Hu, Y. Yao, W. Weng, G. Han, N. Ma, and P. Du, J. Alloys Compd. 576, 121 (2013).
29 Y. Somiya, A. S. Bhalla, and L. E. Cross, Ferroelectrics 507, 43 (2017).
30 W. Ma and X. Bu, Ferroelectrics 537, 90 (2018).
31 A. G. Zembilgotov, N. A. Pertsev, U. Böttger, and R. Waser, Appl. Phys. Lett. 86, 052903 (2005).
32 W. Ma and A. Hao, J. Appl. Phys. 116, 214110 (2014).
33 A. Hao and W. Ma, Ferroelectrics 494, 94 (2016).
34 M. J. Haun, E. Furman, S. J. Jang, H. A. McKinstry, and L. E. Cross, J. Appl. Phys. 62, 3331 (1987).
35 L. Q. Chen, Top. Appl. Phys. 105, 363 (2007).
36 F. Wang and W. Ma, J. Appl. Phys. 125, 082528 (2019).
37 X. Xing, J. Chen, J. Deng, and G. Liu, J. Alloys Compd. 360, 286 (2003).
38 D. H. Kang, J. H. Kim, J. H. Park, and K. H. Yoon, Mat. Res. Bull. 36, 265 (2001).
39 M. Jain, S. B. Majumder, R. Guo, A. S. Bhalla, and R. S. Katiyar, Mater. Lett. 56, 692 (2002).
40 S. Y. Kuo, C. T. Li, and W. F. Hsien, Appl. Phys. Lett. 81, 3019 (2002).
41 P. Ge, X. Jian, X. Lin, X. Tang, Z. Zhu, Q. Liu, Y. Jiang, T. Zhang, and S. Lu, J. Materiomics 5, 118 (2019).
42 S. H. Leal, M. T. Escote, F. M. Pontes, E. R. Leite, M. R. Joya, P. S. Pirani, E. Longo, and J. A. Varela, J. Alloys Compd. 475, 940 (2009).
43 A. A. Heitmann and G. A. Rossetti, Jr., J. Am. Ceram. Soc. 97, 1661 (2014).
44 M. Acosta, N. Novak, G. A. Rossetti, Jr., and J. Rödel, Appl. Phys. Lett. 107, 142906 (2015).
45 J. L. Peng, D. L. Shan, Y. Y. Liu, K. Pan, C. Lei, N. He, Z. Zhang, and Q. Yang, NPJ Comput. Mater. 4, 66 (2018).