Misfit-Strain Phase Diagram, Electromechanical and Electrocaloric Responses in Epitaxial PIN–PMN–PT Thin Films

Yun Ou 1,2,*, Yingying Wu 2 and Jinlin Peng 3,*

1 Hunan Provincial Key Laboratory of Health Maintenance for Mechanical Equipment, Hunan University of Science and Technology, Xiangtan 411201, China
2 School of Materials Science and Engineering, Hunan University of Science and Technology, Xiangtan 411201, China
3 All-Solid-State Energy Storage Materials and Devices Key Laboratory of Hunan Province, College of Information and Electronic Engineering, Hunan City University, Yiyang 413002, China
* Correspondence: ouyun101@hnust.edu.cn (Y.O.); pengjinlin@hnuc.edu.cn (J.P.)

Abstract: xPb(In1/2Nb1/2)O3-(1-x-y)Pb(Mg1/3Nb2/3)O3-yPbTiO3 (PIN–PMN–PT) bulks possess excellent electromechanical coupling and dielectric properties, but the corresponding epitaxial PIN–PMN–PT thin films have not yet been explored. This paper adopts a nonlinear thermodynamics analysis to investigate the influences of misfit strains on the phase structures, electromechanical properties, and electrocaloric responses in epitaxial PIN–PMN–PT thin films. The misfit strain–temperature phase diagram was constructed. The results reveal that the PIN–PMN–PT thin films may exist in tetragonal c-, orthorhombic aα-, monoclinic M-, and paraelectric PE phases. It is also found that the c-M and aα-PE phase boundaries exhibit a superior dielectric constant $\varepsilon_{11}$ which reached 1.979 × 10^6 with $u_m = -0.494\%$, as well as the c-M phase boundary showing a large piezoelectric response $d_{33}$ which reached 1.64 × 10^5 pm/V. In comparison, the c-PE and M-aα phase boundaries exhibit a superior dielectric constant $\varepsilon_{33}$ over 1 × 10^6 and $u_m = 0.316\%$ and the piezoelectric response $d_{33}$ reached 7235 pm/V. The large electrocaloric responses appear near the paraelectric–ferroelectric phase boundary. These insights offer a guidance for experiments in epitaxial PIN–PMN–PT thin films.

Keywords: misfit strain; PIN–PMN–PT; electrocaloric effect; ferroelectric thin films

1. Introduction

Ferroelectric materials, which exhibit a polarization with electromechanical coupling [1,2], have been employed in actuators, sensors, piezoelectric energy harvesters, storage devices, etc. [3,4]. Excellent performance is the key to the application of ferroelectric materials, which prompts people to continuously explore ferroelectric materials with an excellent performance [5–7]. Piezoelectric materials contain defects such as ferroelectric domains, oxygen vacancies, defect dipoles, and the strain [8–10]. PbMg1/3Nb2/3O3−PbTiO3 (PMN–PT) can reach an ultrahigh piezoelectric response ($d_{33} > 2000 \ pC/N$) and has electromechanical coupling factors ($k_{33} > 0.9$) [11], which have attracted much attention [12–15]. The novel ternary compound xPb(In1/2Nb1/2)O3-(1-x-y)Pb(Mg1/3Nb2/3)O3-yPbTiO3 (PIN–PMN–PT) has been proposed to increase the coercive field and phase transition temperature of these materials without a change in the piezoelectric properties [16–18]. Thus, compared with PMN–PT, PIN–PMN–PT remains a more ferroelectric state which is stable under high temperatures.

There are more studies on PIN–PMN–PT bulk. For instance, in the experimental aspect, Li et al. [11] investigated the ferroelectric, dielectric, elastic, piezoelectric, and electromechanical properties of tetragonal PIN–PMN–PT crystals. The electromechanical coupling exhibited a high dc bias electric field stability compared to its rhombohedral counterpart, and the single domain piezoelectric coefficients $d_{33}$ and $d_{15}$ were found to be
530 and 2350 pC/N, respectively. Lin et al. [18] studied the piezoelectric thermal stability of PIN–PMN–PT ternary ceramics near the morphotrophic phase boundary. The resulting temperature-dependent piezoelectric effects in the PIN–PMN–PT ceramics indicate that this ternary ceramics system within the MPB region shows a better temperature stability and increased usable temperature range compared with the PMN–32PT single crystals.

In the theoretical aspect, Lv et al. developed a Landau–Devonshire energy functional for PIN–PMN–PT to investigate the phase transformation, phase diagrams, and the electromechanical properties of the PIN–PMN–PT single crystal [19], which match well with the experiments. On the contrary, research on PIN–PMN–PT thin films has been rare. Compared to bulk films, thin films are grown on a substrate, which impose a strain constraint due to a substrate lattice mismatch [9,20–23]. It is known that the misfit strain can, in general, influence the phase structures and electromechanical properties in thin films [24]. The films have wider applications and a better adjustment than the bulks [8]. However, the influences of the misfit strain on the phase structures, electromechanical properties, and electrocaloric response in the epitaxial PIN–PMN–PT thin films have been lacking, which hinders the corresponding experimental studies. Notice that the misfit strain in the films is caused by the mismatch of lattice between the substrate and the film, which can be relaxed by a defect [25–29], such as a dislocation in the thicker films [30]. Thus, this article employs a nonlinear thermodynamic analysis to establish the misfit strain–temperature phase diagram for PIN–PMN–PT (26PIN–42PMN–32PT) thin films, which the stoichiometric composition are described by atomic%, from which the influences of the misfit strain on the phase structures, electromechanical properties, and electrocaloric responses are studied, offering a guidance for PIN–PMN–PT thin film experiments.

The structure of this article is as follows: the theory of nonlinear thermodynamics for ferroelectric thin films is outlined in Section 2, including the calculation methods for the electromechanical properties and electrocaloric response. The influences of the misfit strain on the phase structures, electromechanical properties, and electrocaloric responses of PIN–PMN–PT thin films are investigated in Section 3. The important discoveries and conclusions are summarized in Section 4.

2. Computational Model

2.1. Thermodynamic Potential of Thin Films and Electromechanical Properties

Lv et al. [19] developed a tenth-order Landau–Devonshire energy function for PIN–PMN–PT, which was restricted to the bulk structures. We consider the epitaxial PMN–PT–PIN thin films subjected to the in-plane biaxial misfit strain $\mu_m$, leading to the mixed boundary conditions as below [30,31]:

$$\varepsilon_1 = \varepsilon_2 = \mu_m, \varepsilon_6 = 0, \sigma_3 = \sigma_4 = \sigma_5 = 0$$

Thus, the thermodynamic potential of PMN–PT–PIN thin films can be obtained from the standard Gibbs function using the Legendre transform [30,31]:

$$G = a_1^\varepsilon (P_1 + P_2) + a_{11}^\varepsilon (P_1^4 + P_2^4) + a_{12}^\varepsilon (P_1 P_2)^2 + a_{13}^\varepsilon (P_1^2 + P_2^2) + a_3^\varepsilon P_3^2 + a_{33}^\varepsilon P_3^4 + a_{123}^\varepsilon (P_1 P_2 P_3)^2$$

$$+ a_{111}^\varepsilon (P_1 P_2 + P_1^2 + P_2^2) + a_{1111}^\varepsilon (P_1^6 + P_2^6 + P_3^6) + a_{1112}^\varepsilon (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2 + P_1^2 P_2 P_3^2)$$

$$+ a_{112}^\varepsilon (P_1^4 + P_2^4 + P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2)$$

$$+ a_{122}^\varepsilon [(P_1 P_2)^4 + (P_1 P_2)^2 (P_1 P_3)^2 + (P_1 P_3)^4 + (P_1^2 P_2^2 P_3^2)]$$

$$+ a_{11111}^\varepsilon (P_1^{10} + P_2^{10} + P_3^{10}) + a_{11112}^\varepsilon (P_1^6 P_2^4 + P_1^6 P_3^4 + P_2^6 P_3^4 + P_1^2 P_2 P_3^4)$$

$$+ a_{11122}^\varepsilon [(P_1 P_2 P_3)^2 + (P_1 P_2 P_3)^2 + (P_1 P_2 P_3)^2 + (P_1 P_2 P_3)^2]$$

$$+ a_{11111}^\varepsilon (P_1^4 P_2^4 + P_1^4 P_3^4 + P_2^4 P_3^4 + P_1^4 P_2 P_3^4 + P_1^4 P_2 P_3^4)$$

$$+ a_{11123}^\varepsilon [(P_1 P_2 P_3)^2 + (P_1 P_2 P_3)^2 + (P_1 P_2 P_3)^2] + \frac{\mu_m}{S_{11} + S_{12}} - E_1 P_1 - E_2 P_2 - E_3 P_3$$

(1)
With
\[ \alpha_1^* = \alpha_1 - \frac{\mu_m(Q_{11} + Q_{12})}{S_{11} + S_{12}}, \]  
(2)
\[ \alpha_3^* = \alpha_1 - \frac{2Q_{12}\mu_m}{S_{11} + S_{12}}, \]  
(3)
\[ \alpha_{11}^* = \alpha_{11} + \frac{S_{11}(Q_{11}^2 + Q_{12}^2) - 2Q_{11}Q_{12}S_{12}}{2(S_{11}^2 - S_{12}^2)}, \]  
(4)
\[ \alpha_{33}^* = \alpha_{11} + \frac{Q_{12}^2}{S_{11} + S_{12}}, \]  
(5)
\[ \alpha_{12}^* = \alpha_{12} - \frac{S_{12}(Q_{11}^2 + Q_{12}^2) - 2Q_{11}Q_{12}S_{11}}{2(S_{11}^2 - S_{12}^2)} + \frac{Q_{44}^2}{2S_{44}}, \]  
(6)
\[ \alpha_{13}^* = \alpha_{12} + \frac{Q_{12}(Q_{11} + Q_{12})}{S_{11} + S_{12}}, \]  
(7)
where \( P_i \) and \( E_i \) represent the components of polarization and external electric fields; \( \alpha_i, \alpha_{ij}, \alpha_{ijk}, \alpha_{ijkl}, \) and \( \alpha_{ijklm} \) are the dielectric constants under constant stress; \( \alpha_{ij}^* \) and \( \alpha_{ij}^* \) are the normalized dielectric constants; \( S_{ij} \) represents the elastic compliance coefficient; and \( Q_{ij} \) represents the electrostrictive coefficient. The material parameters used in the calculations are listed in Table 1.

According to the principle of the minimum energy, the polarization components of the thin films at stable configurations can be computed by solving the system of the equation:
\[ \frac{\partial G}{\partial P_1} = 0, \frac{\partial G}{\partial P_2} = 0, \frac{\partial G}{\partial P_3} = 0 \]

With the computed polarization components \( (P_1, P_2, P_3) \), the relative dielectric constant of the thin film can be calculated [32]:
\[ \varepsilon_{ij} = 1 + \frac{\eta_{ij}}{\varepsilon_0} \]  
(8)
where
\[ \eta = \chi^{-1} = \left[ \begin{array}{ccc} \frac{\partial^2 G}{\partial P_1^2} & \frac{\partial^2 G}{\partial P_1 \partial P_2} & \frac{\partial^2 G}{\partial P_1 \partial P_3} \\ \frac{\partial^2 G}{\partial P_2 \partial P_1} & \frac{\partial^2 G}{\partial P_2^2} & \frac{\partial^2 G}{\partial P_2 \partial P_3} \\ \frac{\partial^2 G}{\partial P_3 \partial P_1} & \frac{\partial^2 G}{\partial P_3 \partial P_2} & \frac{\partial^2 G}{\partial P_3^2} \end{array} \right] \]  
(9)

For (001)-oriented thin films, the piezoelectric coefficients \( d_{in} \) can be computed [22]:
\[ d_{in} = \frac{\partial s_{in}}{\partial P_1} \eta_{11} + \frac{\partial s_{in}}{\partial P_2} \eta_{12} + \frac{\partial s_{in}}{\partial P_3} \eta_{13}, \]  
(10)
where the strain \( S_i \) is obtained from the stress–strain relation [30]. The main focus has been placed on the significant piezoelectric coefficients \( d_{15} \) and \( d_{33} \). The strain components used for calculating the piezoelectric coefficients \( d_{15} \) and \( d_{33} \) are given as [32]:
\[ s_3 = \frac{2\mu_mQ_{12}}{S_{11} + S_{12}} + S_{12}(Q_{11} + Q_{12})(P_1^2 + P_2^2) + \left( Q_{11} - \frac{2S_{12}Q_{12}}{S_{11} + S_{12}} \right) P_3^2 \]  
(11)
where subscripts which is a function of polarization, depending on the working temperature

The material parameters used in the calculations [11,19,33].

Table 1. The material parameters used in the calculations [11,19,33].

| Coefficients | Values | Units |
|--------------|--------|-------|
| $a_1$        | $3.816 \times 10^4(T - 182)$ | C$^{-2}$m$^2$N, and T in °C |
| $a_{11}$     | $-1.212 \times 10^2$ | C$^{-4}$m$^2$N |
| $a_{12}$     | $-1.285 \times 10^2$ | C$^{-4}$m$^2$N |
| $a_{111}$    | $9.424 \times 10^2$ | C$^{-6}$m$^2$N |
| $a_{112}$    | $1.550 \times 10^8$ | C$^{-6}$m$^2$N |
| $a_{123}$    | $4.716 \times 10^9$ | C$^{-6}$m$^2$N |
| $a_{1111}$   | $3.190 \times 10^7$ | C$^{-8}$m$^2$N |
| $a_{1112}$   | $2.521 \times 10^0$ | C$^{-8}$m$^2$N |
| $a_{1122}$   | $-1.993 \times 10^3$ | C$^{-8}$m$^2$N |
| $a_{1233}$   | $-3.956 \times 10^0$ | C$^{-8}$m$^2$N |
| $a_{11112}$  | $-8.865 \times 10^0$ | C$^{-10}$m$^2$N |
| $a_{11122}$  | $1.717 \times 10^1$ | C$^{-10}$m$^2$N |
| $a_{11223}$  | $8.946 \times 10^3$ | C$^{-10}$m$^2$N |
| $a_{111122}$ | 0       | C$^{-10}$m$^2$N |
| $Q_{11}$     | 0.066   | m$^2$/C$^2$ |
| $Q_{12}$     | $-0.032$ | m$^2$/C$^2$ |
| $Q_{44}$     | 0.023   | m$^2$/C$^2$ |
| $S_{11}$     | $12.3 \times 10^{-12}$ | m$^2$/N |
| $S_{12}$     | $-7.1 \times 10^{-12}$ | m$^2$/N |
| $S_{44}$     | $15.1 \times 10^{-12}$ | m$^2$/N |
| $C_{latt}$   | $2.697 \times 10^6$ | J/m$^3$K |

2.2. Adiabatic Temperature Change in Electrocaloric Response

The electrocaloric (EC) effect is a phenomenon in a dielectric material that shows an adiabatic temperature change $\Delta T$ under an applied electric field change, or the entropy change induced by the isothermal conditions [34]. Following the method developed by Liu et al. in the previous work [35,36], we use an entropy-based analysis to calculate the EC adiabatic temperature change $\Delta T$ for the epitaxial PMN–PT–PIN thin films. In the literature [35–37], the total entropy $S_{total}$ of a ferroelectric thin film can be written as the sum of the dipolar entropy $S_{dip}$ and the lattice entropy $S_{latt}$,

$$S_{total}(E, T) = S_{dip}(E, T) + S_{latt}(T)$$  \hspace{1cm} (12)

In Equation (12), $S_{dip}(E, T)$ is the contribution from the dipolar degree of freedom, which is a function of polarization, depending on the working temperature $T$, the external electric field $E$, and the misfit strain. $S_{latt}(T)$ is assumed to be only correlated to the lattice contribution. Under the adiabatic condition, the total entropy change of the thin film is zero, leading to

$$S_{latt}(T_f) - S_{latt}(T_i) = -[S_{dip}(E_f, T_f) - S_{dip}(E_i, T_i)]$$  \hspace{1cm} (13)

where subscripts $i$ and $f$ correspond to the initial and final states, respectively. The change in $y$ $S_{latt}$ can be approximated by

$$S_{latt}(T_f) - S_{latt}(T_i) = \int_{T_i}^{T_f} C_{latt}(T) \frac{dT}{T} \approx C_{latt}(T_i) \ln \left( \frac{T_f}{T_i} \right)$$  \hspace{1cm} (14)

Note that $C_{latt}$ is the lattice heat capacity per unit volume. Combining Equations (13) and (14), the final state temperature $T_f$ can be calculated by

$$T_f = T_i \exp \left\{ -\frac{1}{C_{latt}} [S_{dip}(E_f, T_f) - S_{dip}(E_i, T_i)] \right\}$$  \hspace{1cm} (15)
Thus, the adiabatic temperature change in the electrocaloric response is given by

$$ \Delta T = T_f - T_i = T_i \exp \left\{ - \frac{1}{C_{\text{latt}}} \left[ S_{\text{dip}}(E_f, T_f) - S_{\text{dip}}(E_i, T_i) \right] \right\} - T_i $$

(16)

where the dipolar entropy $S_{\text{dip}}$ is associated with the dipolar free energy of the ferroelectric thin films and can be determined by [35–37].

$$ S_{\text{dip}}(E, T) = - \left( \frac{\partial G}{\partial T} \right)_E $$

(17)

3. Results and Discussion

The above nonlinear thermodynamics method is adopted to analyze the influences of the misfit strain on the phase structures, electromechanical properties, and electrocaloric response in PIN–PMN–PT thin films. The material parameters used in the calculations are listed in Table 1 [11,19,33], which accurately reproduce the phase diagrams and electromechanical properties in the PIN–PMN–PT bulk, indicating the reliability of the material parameters.

We first investigate the influence of the misfit strain on the phase structures of the PIN–PMN–PT thin films, as shown in Figure 1. Figure 1a,b show that under the in-plane biaxial misfit strain, PIN–PMN–PT thin films may exhibit the four phase structures, and their polarization characteristics are summarized in Table 2. It can be seen that the tetragonal c phase is easily formed under a compressive strain, and the orthorhombic aa phase is more easily formed under a tensile strain. The tetragonal phase c has a polarization along the [001]-direction. In contrast, the monoclinic M phase can exist under both a compressive strain and a tensile strain. At high temperatures, the paraelectric PE phase is formed. To more clearly observe the variation of polarization with the mismatch strain more clearly, the change in the polarization components with the misfit strain at room temperature is plotted in Figure 1c. It can be seen that with the misfit strain change from compressive to tensile, the PIN–PMN–PT films exhibit a tetragonal c phase, monoclinic M phase, and orthorhombic aa phase in turn. The out-of-plane component $P_3$ decreases within the monoclinic M phase. In contrast, the in-plane component $P_1$ exhibits the opposite trend. At room temperature, the c-M phase boundary is around $u_m = -0.49\%$, while the M-aa phase boundary is around $u_m = 0.315\%$.

| Phase          | Polarization                                      |
|----------------|--------------------------------------------------|
| Paraelectric PE| $P_1 = P_2 = P_3 = 0$                            |
| Tetragonal c   | $P_1 = P_2 = 0, P_3 \neq 0$                      |
| Orthorhombic aa| $P_3 = 0, |P_1| = |P_2| \neq 0$                                      |
| Monoclinic M   | $|P_1| = |P_2| \neq 0, P_3 \neq 0$                      |

Table 2. The polarization components of the epitaxial PIN–PMN–PT thin films in the absence of an external electric field.

Next, we investigate the influence of the misfit strain on the electromechanical properties of the PIN–PMN–PT thin films, including the dielectric and piezoelectric responses. Figure 2 presents the dielectric constants $\varepsilon_{11}$, $\varepsilon_{22}$, and $\varepsilon_{33}$ of the PIN–PMN–PT films at different temperatures and misfit strains. Due to the in-plane biaxial misfit strain on the thin films, it is expected that $\varepsilon_{11} = \varepsilon_{22}$. Figure 2a shows the excellent transverse permittivity in the vicinity of the c-M phase boundary and the aa-PE phase boundary. Figure 2b shows an excellent longitudinal permittivity in the vicinity of the c-PE phase boundary and the M-aa phase boundary. Figure 2c shows the trend of the dielectric constant at room temperature with respect to the misfit strain. Similarly, the dielectric response enhancement at the phase boundary is also observed in the BaTiO$_3$ [22] and BiFeO$_3$ [24,38] thin films due to the abrupt change in the polarization slope near the phase boundary. The sudden change in the polarization slope also causes the PIN–PMN–PT film to exhibit an excellent piezoelectric response near the phase boundary, as shown in Figure 3a,b, where the c-M phase boundary
has an excellent transverse piezoelectric response $d_{15}$, the c-PE phase boundary and $M$-aa phase boundary exhibit an excellent longitudinal piezoelectric response $d_{33}$. The piezoelectric response of the PIN–PMN–PT thin film at room temperature is shown in Figure 3c, which reaches a peak at the c-M phase boundary, and a peak at the $M$-aa phase boundary.

Finally, we investigate the influence of the misfit strain on the adiabatic temperature change $\Delta T$ in the electrocaloric response in PIN–PMN–PT thin films, as shown in Figure 4, where the electrical field is applied along the [001] direction with a variation ($\Delta E$) of 10 MV/m. The results show that large electrocaloric responses $\Delta T$ appear near the ferroelectric–paraelectric phase boundary at high working temperature because the dipoles in the paraelectric PE phase are easier to reorient when the external electrical field is changed. The corresponding $\Delta T$ at a fixed temperature and under a fixed misfit strain are shown in Figure 4b,c, where the peaks of the EC responses $\Delta T$ near the phase boundaries can be observed more clearly, suggesting that an appropriate misfit strain can enhance the EC response of the PIN–PMN–PT thin films.
Figure 3. The piezoelectric coefficients (a) $d_{15}$, and (b) $d_{33}$ as a function of misfit strain and temperature. (c) The corresponding piezoelectric coefficients as function of misfit strain $u_m$ at room temperature.

Figure 4. (a) The electrocaloric temperature change $\Delta T$ as a function of misfit strain and temperature under an electric field change $\Delta E = 10$ MV/m. (b) The corresponding $\Delta T$ at a fixed temperature. (c) The corresponding $\Delta T$ at fixed misfit strain.

4. Conclusions

In summary, we adopt a nonlinear thermodynamics analysis to study the influences of misfit strains on the phase structures, electromechanical properties, and electrocaloric responses of epitaxial PIN–PMN–PT thin films. It is found that the PIN–PMN–PT thin films may appear in tetragonal $c$-, orthorhombic $aa$-, monoclinic $M$-, and paraelectric PE phases. We also found that the $c$-$M$ and $aa$-PE phase boundaries show a superior dielectric constant, $\varepsilon_{33}$, as well as the $c$-$M$ phase boundary having a large piezoelectric response, $d_{15}$, while the $c$-PE and $M$-$aa$ phase boundaries show a superior dielectric constant, $\varepsilon_{33}$, and the piezoelectric response $d_{33}$. The adiabatic temperature change $\Delta T$ indicates that the paraelectric–ferroelectric phase boundary shows a large electrocaloric response. The findings offer guidance for PIN–PMN–PT thin film experiments.

Author Contributions: Y.O.: conceptualization, theoretical calculations, and writing the original draft. Y.W.: analysis of the data and review. J.P.: conceptualization, methodology, review, editing, and interpretation of the analyzed data. All authors have read and agreed to the published version of the manuscript.

Funding: This work was partially supported by the National Natural Science Foundation of China (11702092), and the project was supported by the Hunan Provincial Natural Science Foundation of China (2020JJ5182).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.
Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jiang, P.; Huang, B.; Wei, L.; Yan, F.; Huang, X.; Li, Y.; Xie, S.; Pan, K.; Liu, J.; Li, J. Resolving fine electromechanical structure of collagen fibrils via sequential excitation piezoresponse force microscopy. Nanotechnology 2019, 30, 205703. [CrossRef] [PubMed]

2. Zhu, Q.; Pan, K.; Xie, S.; Liu, Y.; Li, J. Nanomechanics of multiferroic composite nanofibers via local excitation piezoresponse force microscopy. J. Mech. Phys. Solids 2019, 126, 76–86. [CrossRef]

3. Liu, Y.; Seidel, J.; Li, J. Multiferroics under the tip: Probing magnetoelectric coupling at the nanoscale. Natl. Sci. Rev. 2019, 6, 626–628. [CrossRef]

4. Liu, Y.; Li, J. Seeing is believing: Negative capacitance captured at both nano-and macro-scales. Sci. Bull. 2019, 64, 361–363. [CrossRef]

5. Zhu, Q.; Pan, K.; Xie, S.; Liu, Y.; Li, J.; Shprintzen, R. Shear-driven morphotropic phase boundary in epitaxial ferroelectric thin films. Phys. Rev. B 2011, 84, 132104. [CrossRef]

6. Shprintzen, R. Shear-driven morphotropic phase boundary in epitaxial ferroelectric thin films. Phys. Rev. B 2011, 84, 132104. [CrossRef]
25. Kannan, V.; Trassin, M.; Kochmann, D.M. Kinetics of ferroelectric switching in poled barium titanate ceramics: Effects of electrical cycling rate. *Materialia* **2022**, *25*, 101553. [CrossRef]

26. Kathavate, V.S.; Kumar, B.P.; Singh, I.; Prasad, K.E. Analysis of indentation size effect (ISE) in nanoindentation hardness in polycrystalline PMN-PT piezoceramics with different domain configurations. *Ceram. Int.* **2021**, *47*, 11870–11877. [CrossRef]

27. Thong, H.; Li, Z.; Lu, J.; Li, C.; Liu, Y.; Sun, Q.; Fu, Z.; Wei, Y.; Wang, K. Domain Engineering in Bulk Ferroelectric Ceramics via Mesoscopic Chemical Inhomogeneity. *Adv. Sci.* **2022**, *9*, 2200998. [CrossRef]

28. Kathavate, V.S.; Sonagara, H.; Kumar, B.P.; Singh, I.; Prasad, K.E. Role of domain configurations on the mechanistic modelling of indentation size effects (ISE) in nanohardness of hard and soft PZT piezoceramics. *Int. J. Adv. Eng. Sci. Appl. Math.* **2021**, *13*, 63–78. [CrossRef]

29. Salem, M.N.; Ding, K.; Rödel, J.; Fang, X. Thermally enhanced dislocation density improves both hardness and fracture toughness in single-crystal SrTiO$_3$. *J. Am. Ceram. Soc.* **2022**, *1–12*. [CrossRef]

30. Liu, Y.; Zhu, Z.; Li, J.-F.; Li, J. Misfit strain modulated phase structures of epitaxial Pb(Zr$_{1-x}$Ti$_x$)O$_3$ thin films: The effect of substrate and film thickness. *Mech. Mater.* **2010**, *42*, 816–826. [CrossRef]

31. Pertsiev, N.; Zembilgotov, A.; Tagantsev, A. Effect of mechanical boundary conditions on phase diagrams of epitaxial ferroelectric thin films. *Phys. Rev. Lett.* **1998**, *80*, 1988. [CrossRef]

32. Liu, Y.; Yang, L.; Li, J. Strain-engineered orthorhombic-rhombohedral phase boundary in epitaxial bismuth ferrite films. *J. Appl. Phys.* **2013**, *113*, 183524. [CrossRef]

33. Zhou, Y.; Li, Q.; Zhuo, F.; Yan, Q.; Zhang, Y.; Chu, X. Anisotropic field induced phase transitions and negative electrocaloric effect in rhombohedral Mn doped Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ single crystals. *Ceram. Int.* **2018**, *44*, 9045–9052. [CrossRef]

34. Shan, D.; Pan, K.; Liu, Y.; Li, J. High fidelity direct measurement of local electrocaloric effect by scanning thermal microscopy. *Nano Energy* **2020**, *67*, 104203. [CrossRef]

35. Shan, D.; Lei, C.; Cai, Y.; Pan, K.; Liu, Y. Mechanical control of electrocaloric response in epitaxial ferroelectric thin films. *Int. J. Solids Struct.* **2021**, *216*, 59–67. [CrossRef]

36. Lei, C.H.; Liu, Y. Correlations between local electrocaloric effect and domains in ferroelectric crystals. *Appl. Phys. Lett.* **2022**, *121*, 102902. [CrossRef]

37. Pirc, R.; Kutnjak, Z.; Blinc, R.; Zhang, Q. Electrocaloric effect in relaxor ferroelectrics. *J. Appl. Phys.* **2011**, *110*, 074113. [CrossRef]

38. Peng, J.; Li, Q.; Shan, D.; Pan, K.; Yu, G.; Liu, Y. Phenomenological thermodynamic potentials for bulk and thin-film Ba(Zr$_{0.08}$Ti$_{0.92}$)O$_3$ single crystals. *J. Appl. Phys.* **2016**, *119*, 204103. [CrossRef]