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# Phase diagrams and physical properties of (111) oriented $Pb(Zr_{1-x}Ti_x)O_3$ thin films

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ABSTRACT

Based on the phenomenological Landau–Devonshire theory, the phase diagrams and physical properties of (111) oriented $Pb(Zr_{1-x}Ti_x)O_3$ thin films are investigated. The "misfit strain-temperature" phase diagrams of (111) oriented thin films are more complex than that of (001) oriented thin films due to the appearance of nonlinear coupling terms in the thermodynamic potential. The monoclinic $M_A$ phase, the triclinic $\gamma$ phase, the orthorhombic $O$ phase, and the cubic $C$ phase are stable. The compressive misfit strain induces the monoclinic $M_A$ phase, meanwhile the tensile misfit strain is beneficial to make the triclinic $\gamma$ phase and the orthorhombic $O$ phase stable. The ferroelectric and dielectric properties are calculated which are in great agreement with the experimental measurements. Moreover, the $Pb(Zr_{0.5}Ti_{0.5})O_3$ thin films with the Ti composition around the morphotropic phase boundary (MPB) have the large longitudinal dielectric and piezoelectric properties which are in accordance with the other theoretical results. Most importantly, the tensile misfit strain is prone to induce the larger dielectric and piezoelectric properties than that of compressive misfit strain, which may provide the guidance for experimental research.

## 1. Introduction

$Pb(Zr_{1-x}Ti_x)O_3$ thin films have been extensively investigated for applications in microelectromechanical system (MEMS) and non-volatile ferroelectric random access $Pb(Zr_{1-x}Ti_x)O_3$memories (FeRAMs) due to their large remnant polarization and piezoelectric property [1–3]. Physical properties of $Pb(Zr_{1-x}Ti_x)O_3$ thin films depend on many parameters, such as Zr/Ti ratio [4,5], orientation [6,7], film thickness [8], substrate [9], and so on. Among these factors, the research hotspots focused on the composition and orientation dependence of ferroelectric, dielectric and piezoelectric properties. During the past decades, the $Pb(Zr_{1-x}Ti_x)O_3$ thin films with (001) preferred orientation have been widely studied due to their attractive piezoelectric properties [10–12]. However (111) oriented $Pb(Zr_{1-x}Ti_x)O_3$ thin films have attracted great attention in recent years for use in FeRAMs because of owing large remnant polarization, low coercive field, and good reliability properties [13–19].

Experimentally, (111) oriented $Pb(Zr_{0.6}Ti_{0.4})O_3$ thin films deposited on $LaAlO_3/Pt(111)$ substrate by RF magnetron sputtering had the large remnant polarization [20]. The large value of remnant polarization may be attributed to the 180° domain configuration which is perpendicular to the film substrate plane, and an applied electric field a bit larger than $E_c$ can induce the 180° domain switching. The annealing processing is an important method to fabricate high-quality $Pb(Zr_{1-x}Ti_x)O_3$ thin films, and the crystalline orientation, grain size, electric properties can be improved [21,22]. The $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films with (111) preferred orientation were prepared on $Pt/Ti/SiO_2/Si$ substrates by a sol-gel method, and the effect of heating rates on the microstructure was researched [23]. A fast heating rate in annealing process can improve the microstructure and then the electric properties. In addition, the effect of substrate on the ferroelectric properties was studied in (111) orientation $Pb(Zr_{0.35}Ti_{0.65})O_3$ thin films [9]. (111) $CaF_2$ substrate and (111) $SrTiO_3$ substrate were chosen to induce the in-plane tensile and compressive misfit strain respectively which both produced the large remnant polarization of 50 μC/cm$^2$. For the moment, there is hardly any theoretical investigations on the physical properties of (111) oriented $Pb(Zr_{1-x}Ti_x)O_3$ thin films [24]. Therefore, the purpose of this paper is to investigate the physical properties of (111) oriented $Pb(Zr_{1-x}Ti_x)O_3$ thin films by

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utilizing the phenomenological Landau–Dovenshire theory.

In the present paper, the thermodynamic potential of (111) oriented $\mathrm{Pb(Zr_{1-x}Ti_x)O_3}$ thin films is constructed by applying the matrix transformation of the crystallographic reference frame and the film reference frame. The "misfit strain-temperature" phase diagrams and the physical properties of (111) oriented $\mathrm{Pb(Zr_{1-x}Ti_x)O_3}$ ($x$=0.4, 0.5, 0.6, 0.7) thin films are investigated. Then the theoretical results are compared with the experimental measurements.

## 2. Theory

For a cubic ferroelectric, the elastic Gibbs function $G$ is given as a function of polarization $\tilde{P}_i$, stress $\tilde{\sigma}_i$, and electric field $\tilde{E}_i$ [25,26].

$$\begin{aligned} G = {} & \alpha_1(\tilde{P}_1^2 + \tilde{P}_2^2 + \tilde{P}_3^2) + \alpha_{11}(\tilde{P}_1^4 + \tilde{P}_2^4 + \tilde{P}_3^4) \\ & + \alpha_{12}(\tilde{P}_1^2\tilde{P}_2^2 + \tilde{P}_1^2\tilde{P}_3^2 + \tilde{P}_2^2\tilde{P}_3^2) + \alpha_{111}(\tilde{P}_1^6 + \tilde{P}_2^6 + \tilde{P}_3^6) \\ & + \alpha_{112}[\tilde{P}_1^4(\tilde{P}_2^2 + \tilde{P}_3^2) + \tilde{P}_2^4(\tilde{P}_1^2 + \tilde{P}_3^2) + \tilde{P}_3^4(\tilde{P}_1^2 + \tilde{P}_2^2)] + \alpha_{123}\tilde{P}_1^2\tilde{P}_2^2\tilde{P}_3^2 \\ & - \tfrac{1}{2}s_{11}(\tilde{\sigma}_1^2 + \tilde{\sigma}_2^2 + \tilde{\sigma}_3^2) - s_{12}(\tilde{\sigma}_1\tilde{\sigma}_2 + \tilde{\sigma}_1\tilde{\sigma}_3 + \tilde{\sigma}_2\tilde{\sigma}_3) \\ & - \tfrac{1}{2}s_{44}(\tilde{\sigma}_4^2 + \tilde{\sigma}_5^2 + \tilde{\sigma}_6^2) - Q_{11}(\tilde{\sigma}_1\tilde{P}_1^2 + \tilde{\sigma}_2\tilde{P}_2^2 + \tilde{\sigma}_3\tilde{P}_3^2) \\ & - Q_{12}[\tilde{\sigma}_1(\tilde{P}_2^2 + \tilde{P}_3^2) + \tilde{\sigma}_2(\tilde{P}_1^2 + \tilde{P}_3^2) + \tilde{\sigma}_3(\tilde{P}_1^2 + \tilde{P}_2^2)] \\ & - Q_{44}(\tilde{P}_2\tilde{P}_3\tilde{\sigma}_4 + \tilde{P}_1\tilde{P}_3\tilde{\sigma}_5 + \tilde{P}_1\tilde{P}_2\tilde{\sigma}_6) - \tilde{E}_1\tilde{P}_1 - \tilde{E}_2\tilde{P}_2 - \tilde{E}_3\tilde{P}_3, \end{aligned} \tag{1}$$

where $\tilde{P}_i$, $\tilde{\sigma}_i$, and $\tilde{E}_i$ are defined in the crystallographic reference frame ($\tilde{X}_1, \tilde{X}_2, \tilde{X}_3$) aligned with the cube axes of the material. $\alpha_1$, $\alpha_{i,j}$, and $\alpha_{i,j,k}$ are the dielectric stiffness coefficients, $s_{ij}$ are the elastic compliances at constant polarization, and $Q_{ij}$ are the electrostrictive coefficients. All the above parameters used for calculations in $\mathrm{Pb(Zr_{1-x}Ti_x)O_3}$ thin films originate from Ref. [27]. Eq. (1) may be rewritten in the film reference frame ($X_1, X_2, X_3$) in order to obtain the thermodynamic potential of (111) oriented thin films [28,29]. Therefore, the polarization $\tilde{P}_i$, stress $\tilde{\sigma}_i$, and electric field $\tilde{E}_i$ are transformed into the film reference frame by using the frame transformation $\tilde{X}_i = A_{i,j}X_j$ with the frame transformation matrix $A_{i,j}$, such as $\tilde{P}_i = A_{i,j}P_j$.

For a (111) oriented thin film, the $X_3$ axis is parallel to [111] and perpendicular to the film substrate interface, the $X_1$ axis is along the [1 $\bar{1}$ 0]. Therefore, the frame transformation matrix $A_{i,j}$ is shown below [28,29]:

$$A_{i,j} = \begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 1/\sqrt{6} & 1/\sqrt{6} & -2/\sqrt{6} \\ 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \end{pmatrix}. \tag{2}$$

For a single domain ferroelectric thin film, the thermodynamic potential is obtained by the following Legendre transformation of $G$ [25]:

$$G_{film} = G + S_1\sigma_1 + S_2\sigma_2 + S_6\sigma_6, \tag{3}$$

where $S_1$, $S_2$, and $S_6$ are the misfit strains in the Voigt matrix notation. In this paper, we consider the case of a (111) oriented ferroelectric thin film epitaxially grown on a thick substrate. The in-plane misfit strains are given by $S_1 = S_2 = S_m$, and $S_6 = 0$. The stress $\sigma_i$ $(i = 1-6)$ in Eq. (3) can be eliminated by the mechanical boundary conditions: $\partial G/\partial\sigma_1 = \partial G/\partial\sigma_2 = -S_m$, $\partial G/\partial\sigma_6 = 0$, and $\sigma_3 = \sigma_4 = \sigma_5 = 0$. Consequently, the thermodynamic potential of (111) oriented ferroelectric thin film can be presented as follows:

$$\begin{aligned} G_{film} = {} & \alpha_1^*(P_1^2 + P_2^2) + \alpha_3^*P_3^2 + \beta_1P_1P_2 + \beta_3(P_1 + P_2)P_3 + \alpha_{11}^*(P_1^4 + P_2^4) \\ & + \alpha_{33}^*P_3^4 + \alpha_{12}^*P_1^2P_2^2 + \alpha_{13}^*(P_1^2 + P_2^2)P_3^2 + \beta_{12}(P_1^3P_2 + P_1P_2^3) \\ & + \beta_{13}(P_1 + P_2)P_3^3 + \beta_{23}(P_1^3 + P_2^3)P_3 + \beta_{123}(P_1^2P_2 + P_1P_2^2)P_3 \\ & + \alpha_{111}^*(P_1^6 + P_2^6) + \alpha_{333}^*P_3^6 + \alpha_{112}^*(P_1^4P_2^2 + P_1^2P_2^4) \\ & + \alpha_{113}^*(P_1^4 + P_2^4)P_3^2 + \alpha_{133}^*(P_1^2 + P_2^2)P_3^4 + \alpha_{123}^*P_1^2P_2^2P_3^2 \\ & + \beta_{122}(P_1P_2^5 + P_1^5P_2) + \beta_{113}(P_1^5 + P_2^5)P_3 + \beta_{133}(P_1 + P_2)P_3^5 \\ & + \beta_{112}P_1^3P_2^3 + \beta_{1123}(P_1^4P_2 + P_1P_2^4)P_3 + \beta_{1223}(P_1^3P_2^2 + P_1^2P_2^3)P_3 \\ & + \beta_{1233}P_1P_2P_3^4 + \beta_{1133}(P_1^2P_2 + P_1P_2^2 - P_1^3 - P_2^3)P_3^3 - E_1P_1 - E_2P_3 \\ & - E_3P_3, \end{aligned} \tag{4}$$

where $\alpha_i^*$, $\alpha_{ij}^*$, $\alpha_{ijk}^*$, $\beta_i$, $\beta_{ij}$, $\beta_{ijk}$, and $\beta_{ijkl}$ are the renormalized coefficients and calculated by the dielectric stiffness coefficients $\alpha_1$, $\alpha_{ij}$, and $\alpha_{ijk}$, elastic compliances $s_{ij}$, and electrostrictive coefficients $Q_{ij}$. The temperature dependence of ferroelectricity is mainly governed by the renormalized coefficient $\alpha_i^*$, and the misfit strain dependence is determined by the coefficients $\alpha_i^*$ and $\beta_i$. All the other renormalized coefficients are taken as temperature and misfit strain independent parameters.

The equilibrium thermodynamic states of (111) oriented thin film are determined by minimizing the potential $G_{film}$ with respect to polarization components under the fixed values of misfit strain and temperature. Here, we introduce the following notations for different equilibrium states that may occur in the film: (1) the cubic $C$ phase, where $P_1 = P_2 = P_3 = 0$, (2) the monoclinic $M_A$ phase, where $P_1 = P_2 < 0$, $P_3 > 0$, (3) the orthorhombic $O$ phase, where $P_1 = -P_2 \neq 0$, $P_3 = 0$, (4) the triclinic $\gamma_1$ phase, where $P_1 > 0$, $P_2 < 0$, $P_3 > 0$, $P_1^2 > P_2^2$, $P_1^2 > P_3^2$, (5) the triclinic $\gamma_2$ phase, where $P_1 > 0$, $P_2 > 0$, $P_3 > 0$, (6) the triclinic $\gamma_3$ phase, where $P_1 < 0$, $P_2 < 0$, $P_3 > 0$, $P_2^2 > P_1^2$, $P_2^2 > P_3^2$, (7) the triclinic $\gamma_4$ phase, where $P_1 > 0$, $P_2 < 0$, $P_3 > 0$, $P_3^2 > P_1^2$, $P_3^2 > P_2^2$, (8) the triclinic $\gamma_5$ phase, where $P_1 < 0$, $P_2 < 0$, $P_3 > 0$, $P_3^2 > P_1^2$, $P_3^2 > P_2^2$.

The equilibrium values of the polarization in the film frame are given by the equilibrium conditions $\partial G_{film}/\partial P_i = 0 (i = 1, 2, 3)$. By differentiating the thermodynamic potential $G_{film}$, we can derive an explicit expression for the reciprocal dielectric susceptibilities $\chi_{ij} = \partial^2 G_{film}/\partial P_i \partial P_j$. Thus, the matrix of reciprocal dielectric susceptibilities $\chi$ is obtained by

$$\chi = \begin{pmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{12} & \chi_{22} & \chi_{23} \\ \chi_{13} & \chi_{23} & \chi_{33} \end{pmatrix}. \tag{5}$$

The matrix inversion then enables us to find the dielectric susceptibility $\eta = \chi^{-1}$ and dielectric constant $\varepsilon_{ij} = \varepsilon_0 + \eta_{ij}$, here $\varepsilon_0$ is dielectric constant of free space. By substituting the equilibrium values $P_i$ of the polarization components into the expression derived for $\chi_{ij}$ via Eq. (4), the small-signal dielectric response $\varepsilon_{ij}$ is calculated. Generally speaking, the piezoelectric coefficient $d_{ln}$ is calculated as $d_{ln} = \partial S_n/\partial E_l = b_{kn}\eta_{kl}$, where $b_{kn} = \partial S_n/\partial P_k$ and $\eta_{kl}$ is the dielectric susceptibility. The strain $S_n = -\partial G/\partial\sigma_n$ can be obtained by differentiating the elastic Gibbs function $G$ [26].

## 3. Results and discussion

The "misfit strain-temperature" phase diagrams of (111) oriented $\mathrm{Pb(Zr_{1-x}Ti_x)O_3}$ ($x$=0.4, 0.5, 0.6, 0.7) thin films are shown in Fig. 1. The theoretical phase diagrams of (111) oriented thin films are more complex than that of (001) oriented thin films due to the appearance of nonlinear coupling terms in the thermodynamic potential. Generally, the cubic $C$ phase, the monoclinic $M_A$ phase, the triclinic $\gamma$ phase, and the orthorhombic $O$ phase are stable in