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Ferroelectric phase transition of $BaTiO_3$ single crystal based on a tenth order Landau-Devonshire potential

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ABSTRACT

In order to develop the Landau-Devonshire (LD) potential of the pervoskites $BaTiO_3$, the Gibbs free energy of $BaTiO_3$ single crystal has been expanded up to 10th-order polynomial. The coefficients of the LD formulation have been phenomenologically derived based on the proposed LD model. The dependences of the spontaneous polarization, the dielectric property, and the ferroelectric hysteresis loop on temperature have been investigated systematically by using our proposed 10th-order LD model. The phenomenological thermodynamic potential near the Curie point and the three dimensional non-convex free energy landscapes corresponding to the 4th, 6th, 8th, and the 10th-order model have been analyzed numerically. Based on the proposed LD potential and coefficients, the predicted results for $BaTiO_3$ crystal have also been compared with experimental results as well as theoretically results reported by other researchers.

1. Introduction

Ferroelectric ceramics, which are mainly used in high dielectric constant capacitors, sensors, transducers, memory devices, and various actuators, have attracted a great deal of attention of researchers and scientists in the past decades [1–7]. In the family of perovskite ABO_3 ferroelectric compounds, $BaTiO_3$ ceramics has been experimentally and theoretically investigated extensively for many years, including investigations of the grain size effect on the hysteresis properties of nanocrystalline $BaTiO_3$ polycrystals [8–12], the lattice dynamics and the electromechanical behavior of $BaTiO_3$ from first principles calculation, etc. [13,14]. Furthermore, Landau theory has been served as a conceptual bridge between microscopic models and observed macroscopic phenomena, which is particularly well suited to those systems with long range interactions such as ferroelectric materials. Therefore, the phase field approach based on Landau-Devonshire (LD) principles has also been employed to predict the phase transformation and the evolution of domain structures widely. For instance, Liu et al. [15] investigated on the hysteresis behaviors and domain patterns of nanocrystalline ferroelectric polycrystals by employing phase field model. Refs. [16,17] predicted the relationship between polarization and electric field for the ferroelectric single crystal by using phase field approach. As is known, this numerical approach has the advantage of simple energy representation although it may be difficult to correlate all parameters or coefficients of LD formulation to the materials' properties.

By using the phenomenological theory of LD, the Helmholtz free energy of the objective system has often been written as a truncated power series in term of the polarization with coefficients being chosen to ensure the predicted materials' properties. And the phase transition behavior of ferroelectric materials has been quantified by the retention of 4th or 6th order polarization terms of Helmholtz free energy in most published papers. For instance, Ball et al. [18] developed a stress dependent hysteresis model for ferroelectric materials in which the polarization component of the Helmholtz free energy is taken to be a 4th order polynomial. Devonshire wrote down a 6th-order classic LD potential to describe the thermodynamics of phase transitions in $BaTiO_3$ [19,20]. Bell and Cross [21] developed the thermodynamic description of the LD potential, and introduced a 6th order polarization terms into Helmholtz free energy for predicting the high electric field behavior of $BaTiO_3$ single crystal at low temperature. The developed thermodynamic potential can predict the properties of most of the perovskite ferroelectric ceramics quite well, including the various ferroelectric phase-transition temperatures. Li et al. [22] proposed an 8th-order LD potential for predicting the phase transitions, the evolution of domain structures and the other properties of $BaTiO_3$ for both thin films and bulk crystals. A similar formulation of LD potential for describing the Helmholtz free energy of $BaTiO_3$ was reported in Refs. [23–25]. Wang et al. [26] also suggested a different 8th-order LD potential and proposed a temperature dependent higher-order coefficients for describing the

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thermodynamic behavior of $BaTiO_3$, whereas a pressure-dependent higher-order coefficients and a corresponding 8th-order LD potential was suggested in Ref. [27]. To phenomenologically describe the phase transition at lower temperature, Salje et al. [28,29] considered and included the quantum mechanical effect into the classical LD potential. The results calculated by their proposed model shown that their model were in well agreement with experimental measurements. Vanderbilt and Cohen [30] argued that no monoclinic phase is possible in the 6th-order model, but an 8th-order theory can predict three kinds of equilibrium phases. They further confirmed that the monoclinic phase first arising in the phase diagram when the LD expansion is an 8th-order polynomial. In addition, topological analysis of the critical points of the free energy surface suggested that a new ferroelectric phase (triclinic) with the lowest symmetry will not emerge until the Devonshire theory has been carried out with a 12th-order polynomial. Sergienko et al. [31] also argued that an adequate LD description of the ferroelectric transitions could be achieved by use of a 12th-order expansion of the potential. Therefore, it seems necessary to investigate the 10th-order, even the 12th-order LD potential.

Based on these excellent works mentioned above, this paper will propose a 10th-order LD potential and the corresponding coefficients (15 parameters) for predicting the ferroelectric phase transitions phenomenologically. The effect of LD potential expressed with different order polarization terms taking on the ferroelectric phase transitions of $BaTiO_3$ has been analyzed systematically, including the dielectric temperature dependence, the temperature dependence of LD potentials with different expansion, and the temperature dependence of ferroelectric hysteresis loops. The predicted results based on our proposed potential and coefficients in this paper have also been compared with experimental results as well as theoretically results reported by other researchers. To the authors' knowledge, the proposed 10th-order LD potential and the corresponding coefficients for predicting the ferroelectric phase transitions of $BaTiO_3$ single crystal is first reported.

2. Tenth-order Landau-Devonshire (LD) model

Landau-Devonshire principle is an analysis of equilibrium behavior near a phase transition based on the consideration of crystal symmetry. Landau characterizes the transition in terms of an order parameter. In the case of paraelectric-ferroelectric transition, this order parameter is the polarization vector $\vec{P}$. And the free energy in the vicinity of the transition region can be expanded as a power series of the polarization $\vec{P}$, where only those symmetry-compatible terms are retained. A general form of the free energy density of a ferroelectric crystal, which is as a function of polarization and strain, can be written as formula (1) [15,19,20]:

$$\begin{aligned} f =& \frac{1}{2}a_{ijkl}P_{i,j}P_{k,l} + \left\{\frac{1}{2}\alpha_{ij}P_iP_j + \frac{1}{3}\beta_{ijk}P_iP_jP_k + \frac{1}{4}\gamma_{ijkl}P_iP_jP_kP_l \right. \\ &+ \frac{1}{5}\delta_{ijklm}P_iP_jP_kP_lP_m + \frac{1}{6}\omega_{ijklmn}P_iP_jP_kP_lP_mP_n \\ &+ \frac{1}{7}\pi_{ijklmno}P_iP_jP_kP_lP_mP_nP_o + \frac{1}{8}\xi_{ijklmnop}P_iP_jP_kP_lP_mP_nP_oP_p \\ &\left. + \frac{1}{9}\mu_{ijklmnopq}P_iP_jP_kP_lP_mP_nP_oP_pP_q + \frac{1}{10}\chi_{ijklmnopqr}P_iP_jP_kP_lP_mP_nP_oP_pP_qP_r \right\} \\ &+ \left\{ b_{ijkl}\varepsilon_{ij}P_kP_l + \frac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl} + f_{ijklmn}\varepsilon_{ij}\varepsilon_{kl}P_mP_n + g_{ijklmn}\varepsilon_{ij}P_kP_lP_mP_n \right\} \\ &+ \frac{1}{2k_0}(D_i - P_i)(D_i - P_i) \end{aligned} \tag{1}$$

where α_{ij}, β_{ijk}, γ_{ijkl}, δ_{ijklm}, ω_{ijklmn}, $\pi_{inklmno}$, $\xi_{ijklmnop}$, $\mu_{ijklmnopq}$, and $\chi_{ijklmnopqr}$ are the phenomenological LD coefficients. κ_0 is the permittivity of free space, D_i denotes the electric displacement. The other coefficients are the elastic, piezoelectric, and electrostrictive constant tensors. The first term of the free energy penalizes large gradients of polarization. The nine terms in the first brace is the LD potential. The four terms in the second brace are used to fit the spontaneous strain along with the non-linear dielectric, elastic, and piezoelectric properties. The final term is the energy stored within the physical entity. In this work, the 10th-order LD potential is applied for a stress-free ferroelectric $BaTiO_3$ single crystal. All the odd terms included in the formula (1) should be vanished due to the pervoskites $BaTiO_3$ parent phase is a centrosymmetric structure, whence, the free energy density can be rewritten as:

$$\begin{aligned} f =& \frac{1}{2}a_{ijkl}P_{i,j}P_{k,l} + \left\{\frac{1}{2}\alpha_{ij}P_iP_j + \frac{1}{4}\gamma_{ijkl}P_iP_jP_kP_l + \frac{1}{6}\omega_{ijklmn}P_iP_jP_kP_lP_mP_n \right. \\ &\left. + \frac{1}{8}\xi_{ijklmnop}P_iP_jP_kP_lP_mP_nP_oP_p + \frac{1}{10}\chi_{ijklmnopqr}P_iP_jP_kP_lP_mP_nP_oP_pP_qP_r \right\} \\ &+ \left\{ b_{ijkl}\varepsilon_{ij}P_kP_l + \frac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl} + f_{ijklmn}\varepsilon_{ij}\varepsilon_{kl}P_mP_n + g_{ijklmn}\varepsilon_{ij}P_kP_lP_mP_n \right\} \\ &+ \frac{1}{2\kappa_0}(D_i - P_i)(D_i - P_i) \end{aligned} \tag{2}$$

According to the Einstein summation convention, the 10th-order terms of LD potential in formula (2) can be written appropriately as an expansion in terms of three polarization component P_i (i = 1, 2, 3):

$$\begin{aligned} \Delta G =& a_1\left(P_1^2 + P_2^2 + P_3^2\right) + a_2\left(P_1^4 + P_2^4 + P_3^4\right) + a_3\left(P_1^6 + P_2^6 + P_3^6\right) \\ &+ a_4\left(P_1^8 + P_2^8 + P_3^8\right) + a_5\left(P_1^{10} + P_2^{10} + P_3^{10}\right) \\ &+ a_6\left(P_1^2P_2^2 + P_2^2P_3^2 + P_1^2P_3^2\right) \\ &+ a_7\left(P_1^4P_2^2 + P_1^4P_3^2 + P_1^2P_2^4 + P_1^2P_3^4 + P_2^4P_3^2 + P_2^2P_3^4\right) \\ &+ a_8\left(P_1^6P_2^2 + P_1^6P_3^2 + P_1^2P_2^6 + P_1^2P_3^6 + P_2^6P_3^2 + P_2^2P_3^6\right) \\ &+ a_9\left(P_1^4P_2^4 + P_2^4P_3^4 + P_1^4P_3^4\right) \\ &+ a_{10}\left(P_1^8P_2^2 + P_1^8P_3^2 + P_1^2P_2^8 + P_1^2P_3^8 + P_2^8P_3^2 + P_2^2P_3^8\right) \\ &+ a_{11}\left(P_1^6P_2^4 + P_1^6P_3^4 + P_1^4P_2^6 + P_1^4P_3^6 + P_2^6P_3^4 + P_2^4P_3^6\right) \\ &+ a_{12}\left(P_1^2P_2^2P_3^2\right) + a_{13}\left(P_1^4P_2^2P_3^2 + P_1^2P_2^4P_3^2 + P_1^2P_2^2P_3^4\right) \\ &+ a_{14}\left(P_1^6P_2^2P_3^2 + P_1^2P_2^6P_3^2 + P_1^2P_2^2P_3^6\right) \\ &+ a_{15}\left(P_1^2P_2^4P_3^4 + P_1^4P_2^2P_3^4 + P_1^4P_2^4P_3^2\right) \end{aligned} \tag{3}$$

where all of the coefficients are assumed to be temperature independent except $a_1 = \chi(T - T_0)$. The constant χ stands for the susceptibility, T_0 is the Curie temperature. Early theoretical investigations of ferroelectric phase transitions in perovskites indicated that ferroelectrics undergo a sequence of ferroelectric transition: from a cubic to a tetragonal, then to an orthorhombic and finally to a rhombohedral phase upon cooling [19,20]. In the framework of stress free conditions, the stable state of the paraelectric phase and the other three ferroelectric phases for the $BaTiO_3$ single crystal can be characterized by Eqs. (4)–(6) respectively [22]:

$$\textit{Paraelectric Cubic } (P_C) \quad P_1 = P_2 = P_3 = 0 \tag{4}$$

$$\textit{Ferroelectric Tetragonal } (F_T) \quad P_1 = P_2 = 0,\ P_3 \neq 0 \tag{5}$$

$$\textit{Ferroelectric orthorhombic } (F_O) \quad P_1 = 0,\ P_2 = P_3 \neq 0 \tag{6}$$

$$\textit{Ferroelectric rhombohedral } (F_R) \quad P_1 = P_2 = P_3 \neq 0 \tag{7}$$