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Effect of mechanical stress on phase stability and polarization states in ferroelectric barium titanate and lead titanate

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Abstract

The effect of normal and shear stress on phase transitions in $BaTiO_3$ and $PbTiO_3$ has been investigated using a modified Landau–Ginzburg–Devonshire phenomenological model based on assumption of constant stress boundary conditions. Stress–temperature phase diagrams have been developed, and the influence of stress on polarization stability has been analyzed. The results show monoclinic phases with various polarization states absent in stress-free $BaTiO_3$ may exist under uniaxial, biaxial, anisotropic three-dimensional, and shear stress conditions. For $PbTiO_3$, our calculations show that, under normal stress new phases cannot be generated and the only stable ferroelectric phase has tetragonal symmetry, but under shear stress orthorhombic, rhombohedral, and monoclinic phases can be stabilized.

Keywords: Ferroelectrics; Phase transition; Stress effect; Phenomenology; Polarization

1. Introduction

$BaTiO_3$ (BT) and $PbTiO_3$ (PT) are two typical members of ferroelectric perovskite oxides which can be used to produce high-frequency ceramic filters, surface acoustic wave devices, infrared sensors, and nonvolatile ferroelectric random access memories due to their excellent dielectric, piezoelectric, pyroelectric, and ferroelectric properties [1].

Over the past half century, stress effect has been one of the key issues in the study of phase transitions and physical properties of ferroelectrics [2–25]. Extensive experimental and theoretical studies of the impact of stress on dielectric properties of single crystals and ceramics have been carried out. The stress effect in ferroelectrics has been investigated by employing the Landau–Ginzburg–Devonshire (LGD) phenomenological theory [2–15,17,18,22,23].

The effect of uniaxial stress on phase stability and physical properties of BT and PT single crystals has been modeled in the framework of the LGD theory [2–4]. Budimir et al. [3] have shown that uniaxial tensile and compressive stress applied along spontaneous polarization of tetragonal BT and PT should reduce and enhance piezoelectric response, respectively. It has been suggested that flattening of the elastic Gibbs free energy profile and dielectric softening by uniaxial compressive stress is the reason for enhancement of piezoelectricity [3]. Recently, Schader et al. have investigated the dielectric behavior near the ferroelectric–paraelectric phase transition point of BT under uniaxial compressive stress, and explained the observed increase in the first-order nature of Curie transition by assuming stress dependence of the quadratic and quartic coefficients of the Landau series [4].

In the case of epitaxial thin films grown on lattice-mismatched single crystalline substrates, misfit stress and strain can have a substantial impact on thermodynamic equilibrium states, and dielectric and piezoelectric responses in perovskite oxide ferroelectrics [5–11]. Biaxial compressive stress was used to explain the upshift of Curie temperature in epitaxial PT films [12]. Because of two-dimensional (2D) clamping, in epitaxial thin films it is possible to stabilize several new phases not allowed in bulk crystals. The impact of biaxial misfit stress or strain on ferroelectric phase transitions and physical properties of BT and PT has been studied on the basis of phenomenological thermodynamic theory [5–12,20–24].

The effect of hydrostatic pressure on phase transitions, and physical properties of BT, PT, and $Pb(Zr, Ti)O_3$ (PZT) have

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been studied before [13–18]. Oh et al. [17] have reported that the Curie temperature increases while the transition temperature between two ferroelectric rhombohedral phases decreases with the increase of hydrostatic tensile stress. Recently Gao et al. [18] have analyzed hydrostatic pressure dependence of piezoelectricity in BT and PT crystals, and explained the increase of piezoelectric coefficients on the basis of the free energy profile.

Downshift of Curie temperature in BT and PT polycrystalline thin films and ceramics has been observed and attributed to the effect of stress that originates from grain boundary, domain boundary and other structural defects [19–21]. Based on Raman scattering and x-ray diffraction (XRD) results of single crystals, ceramics, and polycrystalline thin films, it has been suggested that clamping of neighboring grains may generate either hydrostatic pressure or anisotropic three-dimensional (3D) stress [19–21].

The effect of shear strain or stress on equilibrium phase states [2,10,26,28] has been theoretically calculated in recent years. The study of combined effect of shear strain and biaxial strain has indicated that shear strain irrespective of its sign suppresses the formation of ferroelectric tetragonal phase and raises the temperature of monoclinic phase formation [10]. Sun et al. [27] have investigated the combined effect of hydrostatic and shear stresses caused by surface bond contraction in nanocrystalline BT, showing that the grain size effect and the combined stress effect are not identical.

In this paper, we report the LGD phenomenological analyses of stress effect on phase stability and polarization states in BT and PT. We have investigated the effect of uniaxial, biaxial, hydrostatic, anisotropic 3D, and shear stress on phase transitions by using a modified elastic Gibbs free energy function. Accordingly, stress–temperature phase diagrams have been constructed, and the stress and temperature dependence of polarization states have been analyzed. Furthermore, we have made comparisons of phase stability and polarization states between BT and PT under stress.

2. Theory

The present theoretical calculations are based on a modified LGD phenomenological model that takes account of mechanical stress boundary conditions. When the sixth-order elastic Gibbs free energy is used to calculate the stress effect of BT, it has been found that there is no solution at large stress. Therefore, in this work we have employed the eighth-order LGD phenomenological thermodynamic potential [28] as shown below:

$$\begin{aligned}\Delta G = {} & \alpha_1(P_1^2+P_2^2+P_3^2)+\alpha_{11}(P_1^4+P_2^4+P_3^4)\\ & +\alpha_{12}(P_1^2P_2^2+P_2^2P_3^2+P_3^2P_1^2)+\alpha_{111}(P_1^6+P_2^6+P_3^6)\\ & +\alpha_{112}\left[P_1^2(P_2^4+P_3^4)+P_2^2(P_1^4+P_3^4)+P_3^2(P_1^4+P_2^4)\right]\\ & +\alpha_{123}P_1^2P_2^2P_3^2+\alpha_{1111}(P_1^8+P_2^8+P_3^8)\\ & +\alpha_{1112}\left[P_1^6(P_2^2+P_3^2)+P_2^6(P_1^2+P_3^2)+P_3^6(P_1^2+P_2^2)\right]\\ & +\alpha_{1122}(P_1^4P_2^4+P_2^4P_3^4+P_3^4P_1^4)\\ & +\alpha_{1123}(P_1^4P_2^2P_3^2+P_2^4P_3^2P_1^2+P_3^4P_1^2P_2^2)-\frac{1}{2}s_{11}(X_1^2+X_2^2+X_3^2)\\ & -s_{12}(X_1X_2+X_2X_3+X_3X_1)-\frac{1}{2}s_{44}(X_4^2+X_5^2+X_6^2)\\ & -Q_{11}(X_1P_1^2+X_2P_2^2+X_3P_3^2)\\ & -Q_{12}[X_1(P_2^2+P_3^2)+X_2(P_1^2+P_3^2)+X_3(P_1^2+P_2^2)]\\ & -Q_{44}(X_4P_1P_2+X_5P_3P_1+X_6P_1P_2) \qquad (1)\end{aligned}$$

where P_i and X_i are the polarization and stress along the direction i, in accordance with the crystallographic axes of the cubic state; α_i, α_{ij}, α_{ijk} and α_{ijkl} are dielectric stiffness and higher order stiffness coefficients at constant stress; s_{ij} the elastic compliances; and $Q_{ij}$the electrostrictive constants. The dielectric stiffness α_i is assumed to follow a linear temperature dependence based on the Curie–Weiss law. All other coefficients are assumed to be independent of temperature and stress. The equilibrium states of ferroelectric materials at various stress conditions have been determined by minimization of the elastic Gibbs free energy.

The free energy coefficients and materials parameters (in SI units, T in °C) taken from the literature are used in the present thermodynamic calculations. For BT [6,28] $a_1 = 4.124(T-115)\times 10^5$, $a_{11} = -2.097\times 10^8$, $a_{12} = 7.974\times 10^8$, $a_{111} = 1.294\times 10^9$, $a_{112} = -1.95\times 10^9$, $a_{123} = -2.5\times 10^9$, $a_{1111} = 3.863\times 10^{10}$, $a_{1112} = 2.529\times 10^{10}$, $a_{1122} = 1.637\times 10^{10}$, $a_{1123} = 1.367\times 10^{10}$, $Q_{11} = 0.11$, $Q_{12} = -0.043$, $Q_{44} = 0.059$, $s_{11} = 8.3\times 10^{-12}$, $s_{12} = -2.7\times 10^{-12}$, $s_{44} = 9.24\times 10^{-12}$. For PT [6,14,29]: $a_1 = 3.8(T-479)\times 10^5$, $a_{11} = -7.3\times 10^7$, $a_{12} = 7.5\times 10^8$, $a_{111} = 2.6\times 10^8$, $a_{112} = 6.1\times 10^8$, $a_{123} = -3.7\times 10^9$, $Q_{11} = 0.089$, $Q_{12} = -0.026$, $Q_{44} = 0.0675$, $s_{11} = 8.0\times 10^{-12}$, $s_{12} = -2.5\times 10^{-12}$, $s_{44} = 9.0\times 10^{-12}$.

Possible phases and polarization states that have been considered for the various stress conditions are summarized as follows:

(a) In the case of hydrostatic stress (X_1=X_2=$X_3 \neq 0$), similar to the stress-free crystals, the only possible ferroelectric phases are: tetragonal (T), orthorhombic (O), and rhombohedral (R), which have polarization components parallel to pseudo-cubic [100], [110], and [111] directions, respectively.

(b) Under uniaxial stress ($X_3 \neq 0$, X_1=X_2=0) and biaxial stress (X_1=$X_2 \neq 0$, X_3=0), the following phases may occur in BT and PT: (i) p phase (P_1=P_2=P_3=0); (ii) a phase (P_1 or $P_2 \neq 0$ and P_3=0); (iii) c phase ($P_3 \neq 0$ and P_1=P_2=0); (iv) aa phase (P_1=$P_2 \neq 0$ and P_3=0); (v) ac phase ($P_3 \neq 0$ and P_1 or $P_2 \neq 0$); and (vi) r phase (P_1=$P_2 \neq 0$ and $P_3 \neq 0$). The c and a phases have tetragonal symmetry. The aa phase has orthorhombic symmetry. The r and ac phases have monoclinic symmetry.

(c) In the case of anisotropic 3D stress ($X_1 \neq X_2 \neq X_3 \neq 0$), the following notation is used for possible phases in BT and PT: (i) p phase (P_1=P_2=P_3=0); (ii) a_1 phase ($P_1 \neq 0$ and P_2=P_3=0); (iii) a_2 phase ($P_2 \neq 0$ and P_1=P_3=0); (iv) c phase ($P_3 \neq 0$ and P_1=P_2=0); (v) a_1a_2 phase ($P_1 \neq 0$, $P_2 \neq 0$ and P_3=0); (vi) a_1c phase ($P_3 \neq 0$ and $P_1 \neq 0$); and (vii) a_2c phase ($P_3 \neq 0$ and $P_2 \neq 0$). The c, a_1, and a_2 phases have tetragonal symmetry. The a_1a_2, a_1c, and a_2c phases have monoclinic symmetry.