A phenomenological thermodynamic potential for BaTiO$_3$ single crystals

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A phenomenological thermodynamic potential was constructed based on the properties of bulk BaTiO$_3$ single crystals. An eighth-order polynomial of Landau-Devonshire expansion was employed. It reproduces bulk properties including the three possible ferroelectric transition temperatures and their dependence on electric fields, as well as the dielectric and piezoelectric constants. Different from the existing thermodynamic potential, it is applicable to predicting the ferroelectric phase transitions and properties of BaTiO$_3$ thin films under large compressive biaxial strains. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2042528]

I. INTRODUCTION

Ferroelectric BaTiO$_3$ ceramics and single crystals have been extensively studied for many decades, and their bulk ferroelectric phase transitions, crystal structures, and ferroelectric properties are well established. Based on the structures and properties of bulk ceramics and single crystals, a thermodynamic description of the Landau-Devonshire theory was developed by Bell and Cross.[1] It reproduces quite well most of the single-crystal structural and ferroelectric properties including the various ferroelectric phase-transition temperatures. It has been used to predict the effect of strain on the phase transitions and ferroelectric properties of BaTiO$_3$ thin films.[2–4] However, it is only applicable to BaTiO$_3$ films under relatively small compressive strains ($\leqslant 0.4\%$).[2–4] For a certain temperature range, there is no solution for equilibrium polarization under larger compressive strains, i.e., no ferroelectric phase transition. On the other hand, it has been shown that BaTiO$_3$ thin films may be subjected to much higher compressive strains, $>1\%$, due to substrate constraints. For example, it is recently discovered that BaTiO$_3$ films can be compressively strained as much as 1.6%, and the cubic to tetragonal ferroelectric transition temperature of BaTiO$_3$ thin films can be increased to over 600 °C,[5,6] a huge shift compared with bulk BaTiO$_3$ single crystals ($\sim$125 °C).[7–10]

In order to predict the phase transitions, domain structures, and ferroelectric properties of BaTiO$_3$ thin films under such large compressive constraints, a thermodynamic potential is required. The main objective of the paper is to construct such a thermodynamic potential.

II. PHENOMENOLOGICAL THERMODYNAMIC POTENTIAL

In a phenomenological description of the ferroelectric phase transitions in BaTiO$_3$, the spontaneous polarization $\boldsymbol{P} = (P_1, P_2, P_3)$ is chosen as the order parameter. The Landau-Devonshire potential is expanded as a polynomial of the polarization components $P_i (i=1,2,3)$.[11,12] In this work, we employed an eighth-order polynomial for the Landau-Devonshire potential. Under mechanical stress-free boundary condition, it is

$$
\begin{aligned}
f_0 =\ & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) \\
& + \alpha_{12}(P_1^2 P_2^2 + P_2^2 P_3^2 + P_1^2 P_3^2) + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) \\
& + \alpha_{112}[P_1^2(P_2^4 + P_3^4) + P_2^2(P_1^4 + P_3^4) + P_3^2(P_1^4 + P_2^4)] \\
& + \alpha_{123} P_1^2 P_2^2 P_3^2 + \alpha_{1111}(P_1^8 + P_2^8 + P_3^8) \\
& + \alpha_{1112}[P_1^6(P_2^2 + P_3^2) + P_2^6(P_1^2 + P_3^2) + P_3^6(P_1^2 + P_2^2)] \\
& + \alpha_{1122}(P_1^4 P_2^4 + P_2^4 P_3^4 + P_1^4 P_3^4) \\
& + \alpha_{1123}(P_1^4 P_2^2 P_3^2 + P_2^4 P_3^2 P_1^2 + P_3^4 P_1^2 P_2^2),
\end{aligned} \tag{1}
$$

where all of the coefficients are assumed to be temperature independent except α_1. α_1 is linearly dependent on temperature and obeys the Curie-Weiss law. The coefficients obtained in this work are listed in Table I. α_{11}, α_{111}, and α_{1111} were fitted to the ferroelectric transition temperature from paraelectric cubic phase to ferroelectric tetragonal phase and to the spontaneous polarization and dielectric constant of the tetragonal phase. α_{12}, α_{112}, α_{1112}, and α_{1122} were fitted to the properties of ferroelectric orthorhombic phase while the remaining two coefficients α_{123} and α_{1123} were determined from the ferroelectric rhombohedral phase. It should be noted that the existing thermodynamic potential[1] employed a sixth-order polynomial. In order to fit the three ferroelectric phase transitions as well as the ferroelectric properties as a

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TABLE I. Coefficients of Landau-Devonshire potential in Eq. (1) where T is temperature in °C.

Coefficients	This work	Bell and Cross[a]	Units
α_1	$4.124 \times 10^5 (T - 115)$	$3.34 \times 10^5 (T - 108)$	$C^{-2}\,m^2\,N$
α_{11}	-2.097×10^8	$4.69 \times 10^6 (T - 120) - 2.02 \times 10^8$	$C^{-4}\,m^6\,N$
α_{12}	7.974×10^8	3.23×10^8	$C^{-4}\,m^6\,N$
α_{111}	1.294×10^9	$-5.52 \times 10^7 (T - 120) + 2.76 \times 10^9$	$C^{-6}\,m^{10}\,N$
α_{112}	-1.950×10^9	4.47×10^9	$C^{-6}\,m^{10}\,N$
α_{123}	-2.500×10^9	4.91×10^9	$C^{-6}\,m^{10}\,N$
α_{1111}	3.863×10^{10}	0.0	$C^{-8}\,m^{14}\,N$
α_{1112}	2.529×10^{10}	0.0	$C^{-8}\,m^{14}\,N$
α_{1122}	1.637×10^{10}	0.0	$C^{-8}\,m^{14}\,N$
α_{1123}	1.367×10^{10}	0.0	$C^{-8}\,m^{14}\,N$

[a]Reference 1.

function of temperature, the coefficients α_1, α_{11}, and α_{111} were assumed to be dependent on temperature. It is the dependence of α_{11} and α_{111} on temperature that limits the application of the existing potential to small compressive strains. For comparison, the coefficients from Bell and Cross[1] are listed in the table as well.

With the new coefficients listed in Table I, the potential in Eq. (1) yields the transition temperatures: $T_{c(\text{Cubic}\leftrightarrow\text{Tetragonal})} = 125\,°C$, $T_{c(\text{Tetragonal}\leftrightarrow\text{Orthorhombic})} = 8\,°C$, and $T_{c(\text{Orthorhombic}\leftrightarrow\text{Rhombohedral})} = -71\,°C$ for BaTiO$_3$ single crystals under the stress-free condition. The ferroelectric properties calculated at room temperature are compared in Table II with available experimentally measured values[10,13–20] and those from the coefficients of Bell and Cross.[1,21] The polarizations and dielectric constants as a function of temperature obtained from the potential are shown in Figs. 1 and 2, respectively.

Since only the second-order coefficient is dependent on temperature linearly, the entropy change for a phase transition at the transition temperature T_c can be related to polarization as $\Delta S = [P^2_{\text{product}}(T_c) - P^2_{\text{parent}}(T_c)]/2\varepsilon_0 C$,[11] where ε_0 is the permittivity of vacuum and C is the Curie-Weiss constant. The entropy changes ΔS at the three transition points calculated from the thermodynamic potential are listed in Table III. The experimental data from Jona and Shirane[11] are included in the table for comparison. Although they were not used in the fitting of the potential, the calculated and experimentally measured values agree with each other very well.

III. PHASE TRANSITIONS UNDER ELECTRICAL FIELD

Under the presence of an external electric field $\boldsymbol{E} = (E_1, E_2, E_3)$, the Landau-Devonshire potential is rewritten as follows in order to take into account its effect:[1,21]

$$f = f_0 - E_1 P_1 - E_2 P_2 - E_3 P_3. \tag{2}$$

Based on Eq. (2), phase diagrams as a function of temperature and external applied electric field were constructed. Figures 3(a)–3(c) show the results for the cases where electric fields $\boldsymbol{E} = (0, 0, E_0)$, $\boldsymbol{E} = (E_0, 0, E_0)$, and $\boldsymbol{E} = (E_0, E_0, E_0)$ are applied, respectively. The stable ferroelectric phase corresponds to the minimum of f in Eq. (2) for a given temperature and electric field. For the applied electric field $\boldsymbol{E} = (0, 0, E_0)$ our results are in good agreement with the experimental results from Fesenko and Popov.[22]

There is a renewed interest in the piezoelectric properties of BaTiO$_3$ single crystals since it is believed that a significant enhancement could be achieved through domain engineering by applied electric fields.[19,20,23] We calculated the piezoelectric coefficient $d_{3i}(i=1,2,3)$ through the derivatives of strains with respect to the electric field for a BaTiO$_3$ single crystal polarized along the [001], [101], and [111] crystallographic axes, respectively. Under a stress-free condition, the strains in the single crystal are the spontaneous strains. For example, the spontaneous strain $e_{[l,m,n]}$ along any arbitrary direction $[l, m, n]$ with respect to the pseudocubic cell is calculated through

TABLE II. Properties of BaTiO$_3$ at room temperature $T = 25\,°C$.

Properties	This work	Others	Units
P_s	0.26	0.25,[b] 0.26,[c,d] 0.265[a]	$C\,m^{-2}$
ε_{33}	188	168,[e] 150,[b] 130±5,[f,g,h] 193[a]	
ε_{11}	3600	2920,[e] 3600,[b] 4400±400,[f,g,h] 3300[a]	
d_{33}	86.3	85.6,[e] 68.5,[f] 90±5,[g] 125,[i] 128,[j] 99.8[k]	$10^{-12}\,C\,N^{-1}$
d_{31}	−29.4	−34.5,[e] −33.4,[f] −32.5±2,[g] −40.8[k]	$10^{-12}\,C\,N^{-1}$

[a]Reference 1.
[b]Reference 10.
[c]Reference 13.
[d]Reference 14.
[e]Reference 15.
[f]Reference 16.
[g]Reference 17.
[h]Reference 18.
[i]Reference 19.
[j]Reference 20.
[k]Reference 21.

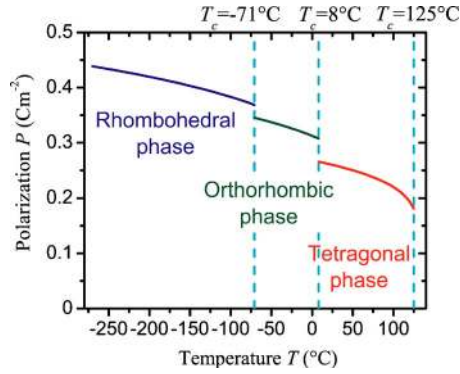FIG. 1. (Color online) Polarizations vs temperature in BaTiO$_3$ single crystal under stress-free condition, where $P=|\boldsymbol{P}|$, $\boldsymbol{P}=(0,0,P_t)$ in tetragonal phase, $\boldsymbol{P}=(P_o,0,P_o)$ in orthorhombic phase, and $\boldsymbol{P}=(P_r,P_r,P_r)$ in rhombohedral phase.

$$e_{[l,m,n]} = e_{11}^0 l^2 + e_{22}^0 m^2 + e_{33}^0 n^2 + 2e_{12}^0 lm + 2e_{13}^0 ln$$
$$+ 2e_{23}^0 mn, \tag{3}$$

where e_{ij}^0 is the spontaneous strain or transformation strain along pseudocubic axes,

$$e_{11}^0 = Q_{11}P_1^2 + Q_{12}P_2^2 + Q_{12}P_3^2,$$

$$e_{22}^0 = Q_{12}P_1^2 + Q_{11}P_2^2 + Q_{12}P_3^2,$$

$$e_{33}^0 = Q_{12}P_1^2 + Q_{12}P_2^2 + Q_{11}P_3^2 \tag{4}$$

$$e_{12}^0 = Q_{44}P_1P_2, \quad e_{13}^0 = Q_{44}P_1P_3, \quad e_{23}^0 = Q_{44}P_2P_3.$$

The electrostrictive coefficients $Q_{11}=0.10$, $Q_{12}=-0.034$, and $Q_{44}=0.029(\text{C}^{-1}\,\text{m}^2)$ from Yamada[24] were used for calculating the piezoelectric coefficients. Figures 4–6 show the predicted piezoelectric coefficients $d_{3i}(i=1,2,3)$ at room temperature as a function of applied electric field. Wada *et al.* investigated the enhancement of piezoelectric properties by applying an electric field along the [111] direction and found that $d_{33} \sim 203$ pC N^{-1} when $E_{[111]} < 0.6$ MV m^{-1}, $d_{33} \sim 145$ pC N^{-1} when 4.0 MV m$^{-1} < E_{[111]} < 5.0$ MV m^{-1}, and d_{33} had its maximum of 295 pC N^{-1} when 1.6 MV m$^{-1} < E_{[111]} < 2.6$ MV m^{-1}.[19] The experimental data agreed well
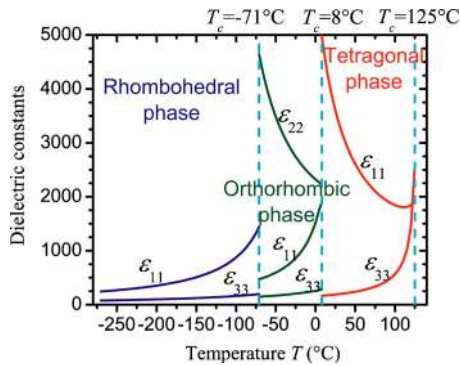

FIG. 2. (Color online) Dielectric constants in the corresponding ferroelectric phases where ε_{33} is along the polarization direction and ε_{11} and ε_{22} are along the two directions which are orthogonal to each other and to the polarization. For tetragonal and rhombohedral phases, $\varepsilon_{11}=\varepsilon_{22}$. For orthorhombic phase of $\boldsymbol{P}=(P_o,0,P_o)$, ε_{22} is along the [010] direction.

TABLE III. Entropy changes ΔS of BaTiO$_3$ for the three ferroelectric transitions.

Transition	This work		Others[a]
	[J m^{-3} K^{-1}]	[cal/(mole K)]	[cal/(mole K)]
Cubic to tetragonal	13535.1	0.124	0.12~0.125
Tetragonal to orthorhombic	9939.8	0.091	0.054~0.091
Orthorhombic to rhombohedral	6970.9	0.064	0.04~0.07

[a]Reference 11.

with our prediction (see Fig. 4). It may be noted that the piezoelectric coefficient d_{33} is the highest at phase-transition temperatures. A similar feature is found in Fig. 5 when the applied electric filed is along the [101] direction. There is no significant variation in the piezoelectric coefficients d_{33} and
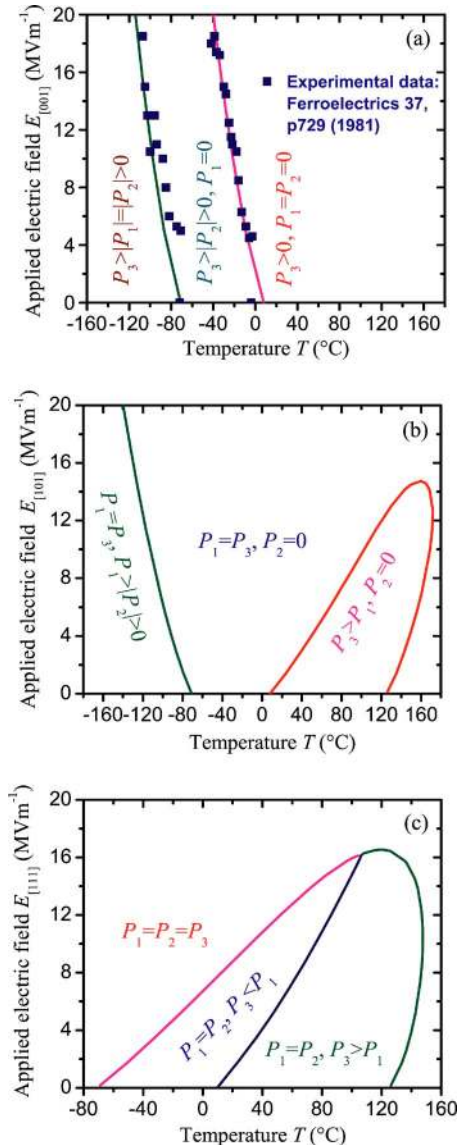

FIG. 3. (Color online) Phase diagram as a function of temperature and applied electric field (a) $\boldsymbol{E}=(0,0,E_0)$ so that $E_{[001]}=E_0$; (b) $\boldsymbol{E}=(E_0,0,E_0)$ so that $E_{[101]}=\sqrt{2}E_0$; (c) $\boldsymbol{E}=(E_0,E_0,E_0)$ so that $E_{[111]}=\sqrt{3}E_0$.
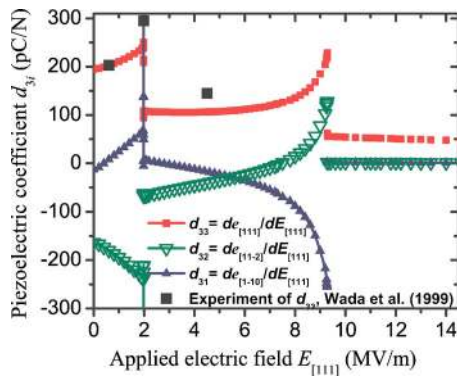
FIG. 4. (Color online) Piezoelectric coefficient d_{3i} vs applied electric field $E_{[111]}$ at room temperature.

d_{31}, however, with applied electric field $E_{[001]}$ (Fig. 6). This is consistent with the fact that there is no additional ferroelectric transition induced by the applied electric field $E_{[001]}$.

IV. SUMMARY

An eighth-order polynomial Landau-Devonshire potential was proposed for bulk $BaTiO_3$ single crystals. It reproduces the ferroelectric properties of $BaTiO_3$ single crystals as a function of temperature. The dependence of the ferroelectric transition temperatures and piezoelectric properties on applied electric field calculated from the potential agrees well with reported experimental data. It is found that the highest piezoelectric coefficient d_{33} always coincides with a ferroelectric transition.
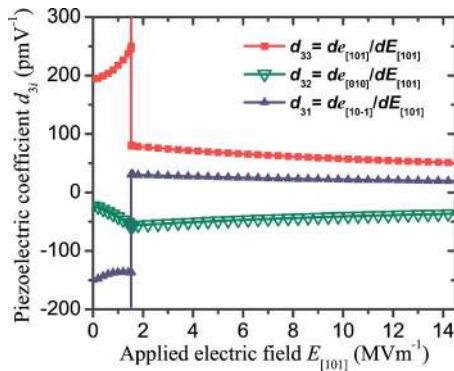

FIG. 5. (Color online) Piezoelectric coefficient d_{3i} vs applied electric field $E_{[101]}$ at room temperature.
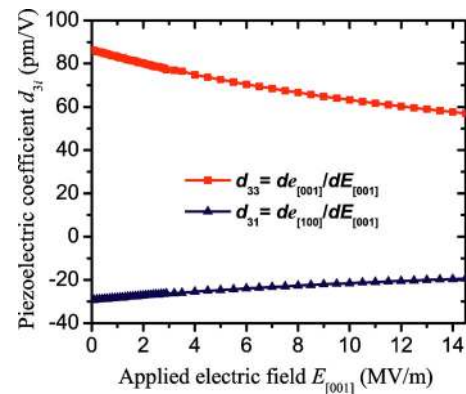

FIG. 6. (Color online) Piezoelectric coefficients d_{33} and d_{31} vs applied electric field $E_{[001]}$ direction at room temperature.

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