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A thermodynamic free energy function for potassium niobate

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A thermodynamic free energy function in the form of an eighth-order polynomial has been developed for bulk potassium niobate (KNbO₃), based on the Landau–Ginsburg–Devonshire phenomenological theory. The obtained free energy function successfully models the ferroelectric single domain (intrinsic) properties of KNbO₃, including the three sequential phase transition temperatures as well as polarizations, dielectric constants, and lattice constants along the whole ferroelectric temperature range. It is applicable to explaining and predicting the extrinsic contributions such as hydrostatic pressure on the bulks properties and substrate constraints on the thin films properties. © 2009 American Institute of Physics. [DOI: 10.1063/1.3081418]

As an important ferroelectric material in the large class of mixed oxide system with a perovskite-type structure, potassium niobate (KNbO₃) has been intensively investigated due to its large electro-optical coefficients, nonlinear optical coefficients, and electromechanical coupling factors for various electronic device applications.^{1–4} It is known that KNbO₃ is paraelectric with a cubic structure above its Curie point (or Curie temperature) of 435 °C. As temperature decreases from the Curie point, KNbO₃ undergoes a series of phase transitions (PTs) from cubic phase to three ferroelectric phases including tetragonal (435 °C), orthorhombic (225 °C), and rhombohedral (–50 °C) phases. All these PTs exhibit strong first-order PT characteristic and are related to a thermal hysteresis. The physical origin of these PTs is attributed to the dipole-dipole interactions resulted from a lattice deformation, and a shift in Nb ion due to the temperature variations.

The Landau–Ginsburg–Devonshire (LGD) phenomenological theory can provide insight into the nature of the PTs and ferroelectric properties.^{5–7} So far, however, the thermodynamic free energy function of the LGD phenomenological theory for KNbO₃ has not been completely determined yet. Several earlier studies focused on the thermodynamic free energy only for the cubic-tetragonal PT using a sixth-order polynomial with two unknown expansion coefficients.^{8–11} Few reports focused on the free energy for the orthorhombic and rhombohedral phases. Therefore, the objective of this work is to develop such a thermodynamic free energy function to reproduce the all known properties and predict any unknown properties of KNbO₃ bulks.

In a phenomenological theory of the ferroelectric PTs in KNbO₃, the spontaneous polarization \mathbf{P} with three components (P_1 , P_2 , P_3) in the system of rectangular coordinates whose axes (x_1 , x_2 , x_3) coincide with the KNbO₃ cubic primitive axes is chosen as an order parameter. Under stress-free condition, we expand the free energy into an eighth-order polynomial function of the polarization components as

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

where α with subscript index represents energy expansion coefficient. All of these expansion coefficients are assumed to be temperature independent except α_1 , which depends linearly on temperature and can be obtained by the Curie–Weiss law $\alpha_1 = (T - T_0) / (2\varepsilon_0 C_0)$, where T_0 is the Curie–Weiss temperature, ε_0 is the permittivity of free space, and C_0 is the Curie constant. The parameters have been fitted using the related experimental data. α_{11} , α_{111} , and α_{1111} were fitted based on the ferroelectric transition temperature from paraelectric cubic phase to ferroelectric tetragonal phase, the spontaneous polarization and dielectric constants of the tetragonal phase. α_{12} , α_{112} , α_{1112} , and α_{1122} were fitted based on the properties of ferroelectric orthorhombic phase. The remaining two coefficients α_{123} and α_{1123} were determined from the ferroelectric rhombohedral phase. The so-fitted coefficients are listed in Table I.

TABLE I. The fitted coefficients of Eq. (1) where T is temperature in °C.

Coefficient	This work	Unit
α_1	$4.273 \times 10^5 \times (T - 377)$	$\text{C}^{-2} \text{m}^2 \text{N}$
α_{11}	-6.36×10^8	$\text{C}^{-4} \text{m}^6 \text{N}$
α_{12}	9.66×10^8	$\text{C}^{-4} \text{m}^6 \text{N}$
α_{111}	2.81×10^9	$\text{C}^{-6} \text{m}^{10} \text{N}$
α_{112}	-1.99×10^9	$\text{C}^{-6} \text{m}^{10} \text{N}$
α_{123}	6.03×10^9	$\text{C}^{-6} \text{m}^{10} \text{N}$
α_{1111}	1.74×10^{10}	$\text{C}^{-8} \text{m}^{14} \text{N}$
α_{1112}	5.99×10^9	$\text{C}^{-8} \text{m}^{14} \text{N}$
α_{1122}	2.50×10^{10}	$\text{C}^{-8} \text{m}^{14} \text{N}$
α_{1123}	-1.17×10^{10}	$\text{C}^{-8} \text{m}^{14} \text{N}$

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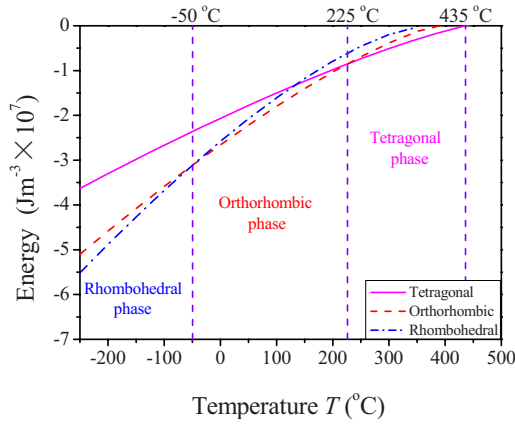


FIG. 1. (Color online) The LGD free energies of three ferroelectric phases as a function of temperature.

Using the fitted coefficients, we calculate the structural and ferroelectric properties of the KNbO₃ single domain from Eq. (1). Figure 1 shows the free energies of the three ferroelectric phases as functions of temperature, which are obtained by minimizing Eq. (1) with respect to the corresponding polarization of each phase. The polarization is assumed to be $\mathbf{P}=(0, 0, P_3)$ for the tetragonal phase, $\mathbf{P}=(P_3, 0, P_3)$ for the orthorhombic phase, and $\mathbf{P}=(P_3, P_3, P_3)$ for the rhombohedral phase. The actual stable state at given temperature is always corresponding to the minimum of the three free energies. Therefore, the tetragonal, orthorhombic, and rhombohedral phases are stable at the temperature ranges from 435 to 225 °C, 225 to -50 °C, and below -50 °C, respectively.

For any given temperature, the polarization of the corresponding stable phase can be obtained. Figure 2 gives the plot of polarization versus temperature. The magnitude of polarization decreases with increasing temperature and change abruptly at every transition temperature, exhibiting the characteristic of the first-order PT. The calculated value of polarization at the room temperature agrees well with the experimental data as given in Table II.

In addition, both entropy and latent heat changes for three ferroelectric PTs are in good agreement with the experiments.¹⁹

The dielectric constant (ϵ_{ij}) is one of the important properties of the ferroelectric KNbO₃ single crystal. Figure 3 shows the calculated dielectric constants in the three phases in comparison with experimental values. For the tetragonal

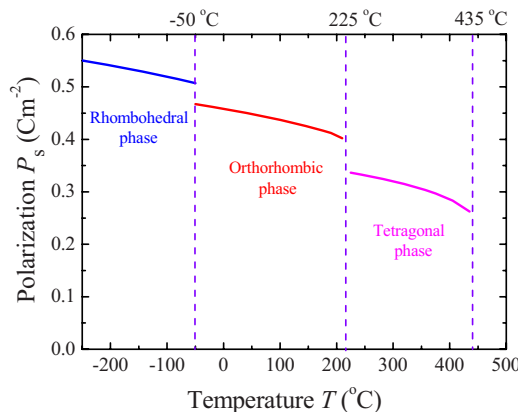


FIG. 2. (Color online) Polarization vs temperature in the KNbO₃ single domain, where $P_s=|\mathbf{P}|$.

TABLE II. Polarization (C/m²) and dielectric constant for KNbO₃ at room temperature $T=22$ °C from different sources.

Properties	This work	Experiment
P_s	0.45	0.3347, ^a 0.41, ^b 0.38, ^c
ϵ_{11}	171	0.38 ± 0.04, ^d 0.41 ± 0.02, ^e 0.42, ^f 0.43 ^g
ϵ_{22}	996	190, ^a 160 ± 10, ^b 140, ^c 150 ± 5, ^d 155.3 ^e
ϵ_{33}	57	1020, ^a 1000 ± 80, ^b 1200, ^c 985 ± 20, ^d 872.8 ^e

^aReference 12.

^bReference 13.

^cReference 14.

^dReference 15.

^eReference 16.

^fReference 17.

^gReference 18.

phase, ϵ_{11} agrees well with the only experimental value, while ϵ_{33} variation in the temperature is consistent with the experiment in spite of its underestimated absolute values.²⁰ Excellent agreement between the theory and experiment is obtained at the room temperature as listed in Table II.

Accompanying the PT, the spontaneous strain (e_{ij}^0) of ferroelectric crystal can be obtained by⁷

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

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

$$e_{33}^0 = Q_{11}P_3^2 + Q_{12}(P_1^2 + P_2^2),$$

$$e_{12}^0 = Q_{44}P_1P_2, \quad e_{13}^0 = Q_{44}P_1P_3, \quad e_{23}^0 = Q_{44}P_2P_3, \quad (2)$$

where Q_{11} , Q_{12} , and Q_{44} are the electrostrictive coefficients. The lattice constants, as one of important structural properties of KNbO₃, in different phases can be determined from the spontaneous strain as

$$a_T = a_0(1 + e_{11T}^0) = a_0(1 + e_{22T}^0), \quad c_T = a_0(1 + e_{33T}^0),$$

$$a_O = c_O = a_0(1 + e_{11O}^0) = a_0(1 + e_{33O}^0), \quad b_O = a_0(1 + e_{22O}^0),$$

$$a_R = a_0(1 + e_{11R}^0) = a_0(1 + e_{22R}^0) = a_0(1 + e_{33R}^0), \quad (3)$$

where the subscripts T , O , and R refer to the tetragonal, orthorhombic, and rhombohedral phases, respectively. a_0 is the pseudocubic lattice, $a_0=4.01529+1.92336 \times 10^{-5}T$,

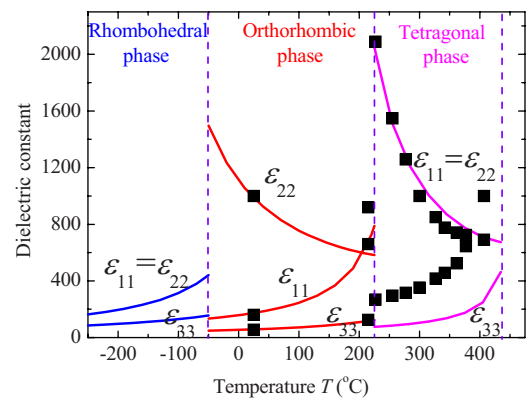


FIG. 3. (Color online) Dielectric constants vs temperature in the KNbO₃ single crystal. ϵ_{33} is along the polarization direction and ϵ_{11} and ϵ_{22} are along the two directions orthogonal to the polarization direction. For the tetragonal and rhombohedral phases, $\epsilon_{11}=\epsilon_{22}$. For the orthorhombic phase, ϵ_{22} is along the [010] direction. The scatter squares represent the experimental values and the solid lines represent the calculated values by the thermodynamic free energy.

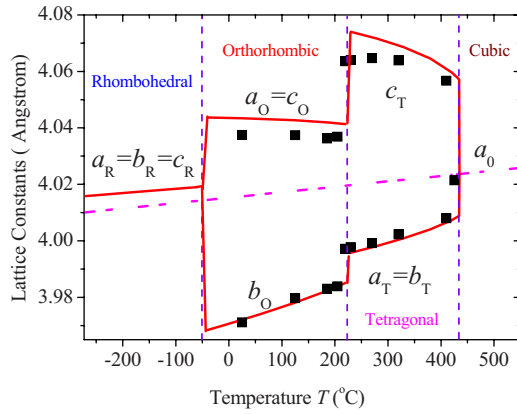


FIG. 4. (Color online) Lattice constant vs temperature in the KNbO₃ single crystal. The scatter solid squares represent experimental values from Ref. 21. The solid lines represent calculated values through the present free energy. The dashed line represents pseudocubic lattice a_0 .

which is fitted from the experimental data.²¹ Figure 4 shows the lattice constants of KNbO₃ as a function of temperature. The calculated lattice constants are in reasonable agreement with the experimental values. For the calculations, the electrostrictive coefficients of $Q_{11}=0.12 \text{ m}^4/\text{C}^2$, $Q_{12}=-0.053 \text{ m}^4/\text{C}^2$, and $Q_{44}=0.052 \text{ m}^4/\text{C}^2$ are used.⁸

The dynamic of the PT can be influenced by adjusting the external thermodynamic parameters, such as temperature, external field, and composition. Under the external stresses of $(\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6)$, the LGD potential can be rewritten by²²

$$f_\sigma = f_{\text{LGD}} - \frac{1}{2}s_{11}(\sigma_1^2 + \sigma_2^2 + \sigma_3^2) - s_{12}(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_3\sigma_2) - \frac{1}{2}s_{44}(\sigma_4^2 + \sigma_5^2 + \sigma_6^2) - Q_{11}(\sigma_1 P_1^2 + \sigma_2 P_2^2 + \sigma_3 P_3^2) - Q_{12}[\sigma_1(P_2^2 + P_3^2) + \sigma_2(P_1^2 + P_3^2) + \sigma_3(P_1^2 + P_2^2)] - Q_{44}(P_2 P_3 \sigma_4 + P_1 P_3 \sigma_5 + P_2 P_1 \sigma_6), \quad (4)$$

where s_{11} , s_{12} , and s_{44} are the elastic compliances. The PT temperature under an applied hydrostatic pressure of $\sigma_1 = \sigma_2 = \sigma_3 = -\sigma$ and $\sigma_4 = \sigma_5 = \sigma_6 = 0$ can be calculated by using Eq. (4) and the elastic constants in this calculation are $s_{11} = 4.6 \times 10^{-12} \text{ m}^2/\text{N}$, $s_{12} = -1.1 \times 10^{-12} \text{ m}^2/\text{N}$, and $s_{44} = 11.1 \times 10^{-12} \text{ m}^2/\text{N}$.⁸

The results of three ferroelectric phases under the various temperature and pressure are shown in Fig. 5. In the plot, the three oblique lines represent the transition point between the two phases. We can estimate the derivative of the pressure σ with respect to the PT temperature $\partial P/\partial T_c$, which is approximately -0.03 GPa/K for all the three PTs for KNbO₃. The PTs at room temperature occur at the pressure of 12.5 GPa and 6.1 GPa for the cubic-tetragonal and tetragonal-orthorhombic PTs, respectively. These calculated values are consistent with the experiments.²³⁻²⁵

In summary, a thermodynamic free energy function in the form of an eighth-order polynomial of the LGD theory has been constructed for bulk KNbO₃. Its correctness has been confirmed through comparing the calculated properties including the PT temperature, polarization, dielectric con-

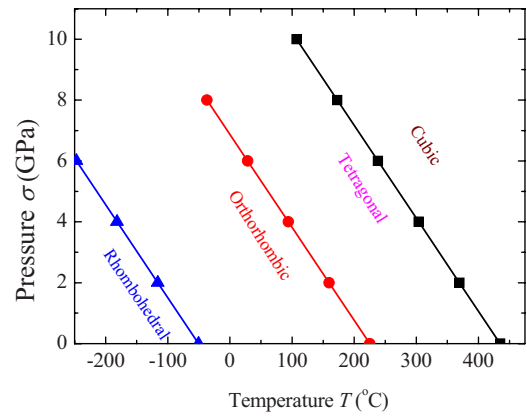


FIG. 5. (Color online) Phase diagram as a function of transition temperature and applied pressure for KNbO₃.

stant, and lattice constant with the corresponding experimental values. The dependence of ferroelectric transition temperatures on the applied pressure calculated from this energy also agrees with the reported experimental data. The quantitative depiction of the LGD energy using the fitted coefficients embedded in the phase-field model provides a way to predict the structural and ferroelectric properties of KNbO₃.

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