Note on the Piezoelectric Constant of $PbZrO_3$-$PbTiO_3$(PZT)

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SYNOPSIS

One of the best known solid solution of perovskites is the $PbTiO_3$-$PbZrO_3$ system which is usually abbreviated as PZT. In the phase diagram of this system, there is a drastic phase change from tetragonal to rhombohedral at the molar ratio around 50:50. The PZT crystals are widely used as a practical piezoelectric material because of its very strong piezoelectric effect near this morphotropic phase boundary. We try to explain this anomaly in piezoelectric constant by a phenomenological theory.

I. Introduction

Many oxides of the perovskite type undergo phase transitions from the paraelectric phase at high temperatures to the ferroelectric or antiferroelectric phase at low temperatures. These phase transitions of perovskite-type oxides can be classified into some groups. $BaTiO_3$ and $KNbO_3$ have successive phase transitions; they take the cubic structure at high temperatures, and on lowering the temperature, tetragonal, orthorhombic, and rhombohedral structures successively. On the contrary, $PbTiO_3$ has only one phase transition from the cubic phase at high temperatures to the tetragonal phase at low temperatures. There are also some perovskites which do not have any phase transitions down to very low temperatures.

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Our interest in this article is in the properties of mixed materials. We often have remarkable features in mixtures which are not expected at all from the properties of component materials. These features are usually difficult to explain theoretically.

When we make solid solutions from two perovskite-type oxides, we can observe various types of phase diagrams. Several works have been done to analyze and reproduce some of these phase diagrams. There are two different approaches to understand phase transitions of perovskite-type mixtures; the phenomenological theory and the electronic theory. The former is based on the Landau-Devonshire theory and works well when the mixed compound shows intermediate character of two starting materials; we can calculate physical parameters as averages weighted by concentrations[1),2)].

One has to resort to the electronic theory when the phase diagram can not be understood by the averaging method; recently we have successfully explained two examples in this category, $BaTiO_3$-$KNbO_3$ and $PbTiO_3$-$KNbO_3$ systems, in which the transition temperatures abruptly decrease on mixing[3)]. We can give physical interpretations to these phase diagrams by taking into account the effects of mixing on the electronic band structure.

In the phase diagram of $PbTiO_3$-$PbZrO_3$ system, there is a drastic phase change called morphotropic phase boundary from tetragonal to rhombohedral at the molar ratio around 50:50 (Fig.1)[4)]. It is known that a very intense piezoelectric effect appears near this boundary and hence PZT crystals are widely used as a practical piezoelectric material. The purpose of this article is to formulate a phenomenological theory for the explanation of this anomaly in piezoelectric constant.
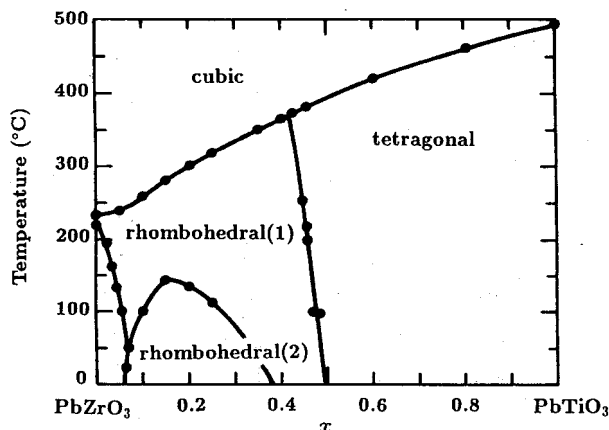

Fig.1 Phase diagram of $x \cdot PbTiO_3$-$(1 - x) \cdot PbZrO_3$.

II. Formulation

The most simple phenomenological theory for the ferroelectric phase transition is the one developed by Landau[5] and by Devonshire[6]. We here describe a simple example of formulation where the only one component of polarization is considered; in this case the crystal undergoes the phase transition from cubic to tetragonal.

The free energy can be written as

$$
\begin{aligned}
G(T, P, X) &= G(T, 0, 0) + \frac{1}{2}\chi P^2 + \frac{1}{4}\xi P^4 + \frac{1}{6}\zeta P^6 + \cdots \\
&+ \frac{1}{2}cX^2 + dXP^2 + \cdots.
\end{aligned}
\tag{1}
$$

Here, P is the spontaneous polarization and X, the strain. If we need three components of polarization, P and X in the following formulation should be replaced by $\boldsymbol{P} = (P_1, P_2, P_3)$ and $\boldsymbol{X} = (X_1, X_2, X_3, X_4, X_5, X_6)$, respectively. The parameter χ is expressed by

$$
\chi = \frac{4\pi}{C}(T - T_0)
\tag{2}
$$

and ξ, ζ, c, d, C, and T_0 are the parameters which identify the materials: We denote the temperature where the inverse dielectric constant vanishes by T_0 and the Curie constant by C.

The temperature is explicitly written as T and all other parameters are assumed to be independent of the temperature. We can obtain information on the behavior of the material at the vicinity of the transition temperature by relating theses parameters to experimental results through thermodynamic considerations.

The equilibrium conditions are

$$
\frac{\partial G}{\partial P} = 0 \;:\; \chi P + \xi P^3 + \zeta P^5 + 2dXP = 0,
\tag{3}
$$

and

$$
\frac{\partial G}{\partial X} = 0 \;:\; cX + dP^2 = 0.
\tag{4}
$$

From Eq.(4) we obtain

$$
X = -\frac{d}{c}P^2.
\tag{5}
$$

Substituting Eq.(4) into Eq.(3), we obtain the equilibrium values of P as the roots of equation

$$\chi P + \left(\xi - \frac{2d^2}{c}\right) P^3 + \zeta P^5 = 0, \tag{6}$$

or

$$P = 0 \quad \text{or} \quad \chi + \left(\xi - \frac{2d^2}{c}\right) P^2 + \zeta P^4 = 0. \tag{7}$$

When the parameter ξ is negative, the free energy given by two solutions of the above equation, the state $P = 0$ and $X = 0$ and the state $P \neq 0$ and $X \neq 0$ crosses at $T = T_C$ where the first order structural phase transition occurs. The system takes the cubic structure with $P = 0$ and $X = 0$ above T_C and the tetragonal structure with $P \neq 0$ and $X \neq 0$ below T_C.

To investigate the properties in the low temperature phase, we substitute

$$P = P_0 + p \quad \text{and} \quad X = X_0 + x \tag{8}$$

into Eq.(1) and calculate response functions. When we expand the new equation into a series in p and x, the terms with p^0 and x^0 give us the new value of the free energy at $P = P_0$ and $X = X_0$. The terms with p and x vanish because of the relations Eqs.(3) and (4). The coefficients of the terms with p^2, x^2, and px give the response functions closely related to the experimental results; for example,

$$p^2 \quad : \quad \frac{1}{2}\chi + \frac{3}{2}\xi P_0^2 + \frac{5}{2}\zeta P_0^4 + dX_0, \tag{9}$$

$$xp \quad : \quad 2dP_0, \tag{10}$$

$$x^2 \quad : \quad \frac{1}{2}c. \tag{11}$$

Equation (9) is the dielectric constant which shows discontinuous jump at T_C, Eq.(10) is the expression of the piezoelectric constant, and Eq.(11) is the elastic constant.

Based on the phenomenological theory, it is natural to propose the free energy of mixture written as

$$G(T, P, X) = x\, G_1(T, P, X) + (1 - x)\, G_2(T, P, X), \tag{12}$$

where $G_1(T, P, X)$ and $G_2(T, P, X)$ are the free energies of ferroelectrics I and ferroelectrics II, respectively, and x is the mixing rate. We apply the same idea as Eq.(12) to the parameters of the mixture and obtain

$$\xi = x\, \xi_1 + (1 - x)\, \xi_2,$$
$$T_0 = x\, T_0^1 + (1 - x)\, T_0^2,$$
$$\zeta = x\, \zeta_1 + (1 - x)\, \zeta_2, \quad \text{and so on.}$$

The piezoelectric constant of PZT system can thus be calculated for arbitrary concentrations.

III. Numerical Analysis on PZT

In the PZT system, we need three independent directions of the spontaneous polarization and six independent components of the strain tensor. The parameters in Eq.(1) will be expressed as follows:

$$
\begin{aligned}
G(T, P, x) = \ & G(T, 0, 0) + \frac{1}{2}\chi(P_1^2 + P_2^2 + P_3^2) + \frac{1}{4}\xi_{11}(P_1^4 + P_2^4 + P_3^4) \\
& + \frac{1}{2}\xi_{12}(P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2) + \frac{1}{6}\zeta_{111}P^6 \\
& + \frac{1}{2}\zeta_{112}(P_1^4 P_2^2 + P_2^4 P_3^2 + P_3^4 P_1^2) + \frac{1}{2}\zeta_{113}P_1^2 P_2^2 P_3^2.
\end{aligned} \tag{13}
$$

Here we only take the terms related to the polarization to determine the phase transition temperature. Thus there are seven phenomenological parameters for each material, C, T_0, ξ_{11}, ξ_{12}, ζ_{111}, ζ_{112}, and ζ_{113}. Some of these parameters are obtained from experimental results. Most reliable ones for $PbTiO_3$[1] are listed in Table 1. There are also another set of parameters for $PbTiO_3$. For $PbZrO_3$, however, only some of these parameters are known at least to our knowledge. In analyzing PZT, we therefore adjust the parameters of $PbZrO_3$ and some of these for $PbTiO_3$ so as to reproduce the experimental phase diagram of PZT.

Table 1. Phenomenological parameters for $PbTiO_3$

$C(°C)$	4.1×10^5
$T_0(°C)$	444.0
$T_C(°C)$	487.0
$\xi_{11}(cgs)$	-3.674×10^{-13}
$\xi_{12}(cgs)$	2.833×10^{-13}
$\zeta_{111}(cgs)$	1.92×10^{-23}

Expanding the free energy around the new stable state of PZT, we obtain the piezoelectric constant of this system by the same procedure as Eq.(10). Now the free energy which takes into account strain together with polarization has the form

$$
\begin{aligned}
G(T, P, x) = \ & G(T, 0, 0) + \frac{1}{2}\chi(P_1^2 + P_2^2 + P_3^2) + \frac{1}{4}\xi_{11}(P_1^4 + P_2^4 + P_3^4) \\
& + \frac{1}{2}\xi_{12}(P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2) + \frac{1}{6}\zeta_{111}P^6
\end{aligned}
$$

$$+\frac{1}{2}\zeta_{112}(P_1^4P_2^2 + P_2^4P_3^2 + P_3^4P_1^2) + \frac{1}{2}\zeta_{113}P_1^2P_2^2P_3^2$$
$$-g_{11}(X_1P_1^2 + X_2P_2^2 + X_3P_3^2)$$
$$-g_{12}\left[(X_1(P_2^2 + P_3^2) + X_2(P_3^2 + P_1^2) + X_3(P_1^2 + P_2^2)\right]$$
$$-g_{44}(X_4P_2P_3 + X_5P_3P_1 + X_6P_1P_2)$$
$$+\frac{1}{2}c_{11}(X_1^2 + X_2^2 + X_3^2) + c_{12}(X_1X_2 + X_2X_3 + X_3X_1)$$
$$+\frac{1}{2}c_{44}(X_4^2 + X_5^2 + X_6^2). \tag{14}$$

From this equation we obtain four solutions of stable phases, cubic, tetragonal, orthorhombic, and rhombohedral phases. In each stable state, we again substitute

$$P_1 = P + p_1, \quad P_2 = P + p_2, \quad P_3 = P + p_3, \quad \text{and} \quad \text{so} \quad \text{on}. \tag{15}$$

The piezoelectric constant is then evaluated using the coefficient g_{12} as

$$d_{31} = -2g_{12}P. \tag{16}$$

The numerical process is now in progress and the results will be reported elsewhere.

Acknowledgements

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