Morphotropic Phase Boundary in Solid Solution Systems of Perovskite-Type Oxide Ferroelectrics

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The origin of the appearance of the morphotropic phase boundary in the perovskite-type oxide solid solution systems and the increase in the dielectric susceptibilities in the vicinity of the boundary is theoretically clarified on the basis of a Landau-type free energy function. The dielectric susceptibilities are concretely expressed in terms of the model parameters, and found to diverge at the morphotropic phase boundary within the present model.

KEYWORDS: morphotropic phase boundary, dielectric susceptibility, free energy, Landau theory

1. Introduction

Oxide ferroelectrics belonging to the BaTiO₃ family often form complete solid solution systems. Some of them show several different phases according to the change in concentration of the end members. The solid solution system which will be discussed in the present paper is similar to the PbZrO₃–PbTiO₃ system,¹⁾ which has a morphotropic phase boundary in the temperature-composition phase diagram, that is, the boundary between rhombohedral and tetragonal ferroelectric phases. It is well known that the solid solution with a composition lying in the vicinity of the morphotropic phase boundary has large dielectric and piezoelectric constants.

The aim of the present paper is to show the origin of such large physical quantities based on a simple Landau-Devonshire theory. In §2 we present the free energy function, and in §3 we derive the expressions of dielectric susceptibilities. The discussion will be presented in the last section.

2. The Landau-Devonshire Free Energy^{2,3)}

Oxide ferroelectrics commonly exhibit a first order transition from the paraelectric cubic phase to the ferroelectric phases with lower symmetries. However, at temperatures much lower than the transition temperature whether the transition is of the first order or the second order is not important for a discussion of their physical properties. With this in mind, and to clarify the essence of the morphotropic phase transition in a simple way, we will write the free energy only in terms of the polarization components (the primary order parameters) truncated at the fourth order, as

$$f = \frac{\alpha}{2}(p_1^2 + p_2^2 + p_3^2) + \frac{\beta_1}{4}(p_1^4 + p_2^4 + p_3^4) + \frac{\beta_2}{2}(p_1^2 p_2^2 + p_2^2 p_3^2 + p_3^2 p_1^2), \qquad (1)$$

where α is temperature-dependent, given as $\alpha = a(T - T_0)$.

It has been clarified that for $\beta_1 > \beta_2$ and $\beta_1 + 2\beta_2 > 0$ the cubic-rhombohedral transition of the second order occurs, while for $\beta_2 > \beta_1 > 0$ the cubic-tetragonal transition of the second order also occurs.⁴⁾ The phase diagram in the $\alpha - \beta_2/\beta_1$ plane is shown in Fig. 1, where the vertical dotted line corresponds to the morphotropic phase boundary. The transition between the rhombohedral and the tetragonal phases must be of the first order due to symmetry reason.

Now, let us substitute in eq. (1) $\beta_1 = \beta_2 = \beta$, valid on the morphotropic phase boundary, and then the free energy



Fig. 1. The $\alpha - \beta_2/\beta_1$ phase diagram. C, T and R indicate the cubic, tetragonal and rhombohedral phases, respectively.

becomes

$$f = \frac{\alpha}{2}(p_1^2 + p_2^2 + p_3^2) + \frac{\beta}{4}(p_1^2 + p_2^2 + p_3^2)^2.$$
 (2)

It should be remarked that on the morphotropic phase boundary the free energy is isotropic, that is to say, the equal energy planes are the surfaces of spheres in a three-dimensional space. Physically this implies that no energy barrier exists between the rhombohedral and the tetragonal phases (the orthorhombic phase is now excluded from the consideration), or that both phases are "soft" enough for the transition to the other phase. As will be clarified in the next section, this feature is manifested as an increase in the dielectric constant.

3. Dielectric Constant

In this section let us derive the dielectric constants based on the free energy eq. (1). By adopting a golden rule, we obtain the Hessian, which in the present case is the 3×3 matrix composed of the second derivatives of the free energy by the order parameters:

$$\begin{pmatrix} f_{11} & f_{12} & f_{13} \\ f_{21} & f_{22} & f_{23} \\ f_{31} & f_{32} & f_{33} \end{pmatrix}_{0},$$
(3)

where $f_{ij} = \partial^2 f / \partial p_i \partial p_j$ and the symbol 0 shown outside of the matrix implies that the equilibrium values of the order parameters have to be substituted.

Solving a set of simultaneous linear equations with coefficients given by the above Hessian for given conditions, we can obtain the dielectric constants in the rhombohedral and the tetragonal phases. For the tetragonal phase, the ferroelectric axis is taken as the c-axis (indicated as 3), and the dielectric susceptibilities are obtained as

$$\chi_{11} = \chi_{22} = \frac{\beta_1}{(\beta_1 - \beta_2)\alpha},$$

$$\chi_{33} = \frac{-1}{2\alpha}.$$
 (4)

It is easily seen that on the morphotropic phase boundary specified with $\beta_1 = \beta_2$ the transversal dielectric susceptibilities χ_{11} and χ_{22} diverge at all temperatures.

On the other hand, for the rhombohedral phase the Hessian becomes

$$\left(\begin{array}{ccc}
A & B & B \\
B & A & B \\
B & B & A
\end{array}\right),$$
(5)

where

$$A = \alpha + (3\beta_1 + 2\beta_2)r^2,$$

$$B = 2\beta_2 r^2,$$
 (6)

with

$$r^2 = -\frac{\alpha}{\beta_1 + 2\beta_2} \,. \tag{7}$$

Then, we have to rotate the crystal axes to take the orthogonal crystal coordinate system conventional for the rhombohedral phase as

$$\begin{pmatrix} a'\\b'\\c' \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{2}} & 0\\ \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{-2}{\sqrt{6}}\\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} a\\b\\c \end{pmatrix}, \quad (8)$$

where the ferroelectric axis is taken as the new *c*-axis (c' above). For this new coordinate system, we obtain the dielectric susceptibilities as

$$\chi_{11} = \chi_{22} = -\frac{\beta_1 + 2\beta_2}{\alpha(\beta_1 - \beta_2)},$$

$$\chi_{33} = -\frac{1}{2\alpha}.$$
 (9)

It should be noted that in this case, too, the transversal dielectric susceptibilities diverge on the morphotropic phase boundary at all temperatures.

The dielectric susceptibilities in each phase are shown in Fig. 2 as the functions of β_2/β_1 .

In actual ceramics, an averaging process may be required to estimate the values of the dielectric susceptibilities of practical importance, because there are various grain orientations. There are several methods for obtaining the average, but here we only take the weighted mean, as

$$\chi = \frac{1}{3}(\chi_{33} + 2\chi_{11}). \tag{10}$$

This is also shown with dotted lines in Fig. 2. It is seen that χ diverges at all temperatures on the morphotropic phase boundary and obeys a rule similar to the Curie-Weiss law as the function of β_2/β_1 . This is the origin of an increase in the dielectric susceptibility in the vicinity of the morphotropic



Fig. 2. The β_2/β_1 -dependences of the dielectric susceptibilities. The ordinate shows $|a|\chi$ (but not χ itself).

phase boundary.

4. Discussions

In the present paper we have clarified the reason why the morphotropic phase boundary appears in the phase diagram of the oxide perovskite ferroelectric solid solution systems. It is seen that either the rhombohedral phase or the tetragonal phase is stabilized according to the relative dominance of the two fourth order terms in the free energy function. The divergence of the dielectric susceptibilities has the same origin as the appearance of the morphotropic phase boundary, i.e., the stability of one phase is lost at the boundary.

So far, however, we have only discussed the essence of the phenomena with a very simplified free energy. Therefore, to avoid misunderstandings due to the simplified explanations and also to indicate the plan of future research based on a more complete analysis, several comments are in order.

4.1 The composition dependence of β_1 and β_2

The parameters β_1 and β_2 may depend on composition, and therefore the morphotropic phase boundary must be the function of the composition. Huan *et al.* have reported on theoretical work regarding the morphotropic boundary.⁵⁾ However, they related the boundary directly with the composition and, as a result, it seems that they overlooked the relationship between model parameters, β_1 and β_2 , and the appearance of the boundary. Needless to say, it is important to correlate quantitatively the values of model parameters, β_1 and β_2 , with the composition.

4.2 The effect of the sixth-order terms in the polarization components

When the free energy function is isotropic (see eq. (2)), we cannot specify the phase of the system. For symmetry the tetragonal-rhombohedral phase transition must be of the first order, and therefore there must be some potential barrier between two phases. This barrier is due to higher order terms. In reality, an actual ferroelectric system is not free from the contribution of the sixth-order terms in polarization components, which is written as

$$\frac{\gamma_1}{6}(p_1^6 + p_2^6 + p_3^6) + \frac{\gamma_2}{2}[p_1^4(p_2^2 + p_3^2) + p_2^4(p_3^2 + p_4^2) + p_3^4(p_1^2 + p_2^2)] + \frac{\gamma_3}{2}p_1^2p_2^2p_3^2.$$
(11)

This is usually anisotropic, giving rise to the potential barrier mentioned above, unless the relation

$$\gamma_1 = \gamma_2 = \frac{\gamma_3}{2} \tag{12}$$

is satisfied. In general, the sixth-order terms make the morphotropic phase boundary deviate from the vertical (see Fig. 1), even if it is plotted as a function of β_2/β_1 .

The sixth-order terms have another effect. Namely, the divergence of the dielectric susceptibilities is suppressed, though they should become quite large at the morphotropic phase boundary as long as the boundary lies in the vicinity of the line $\beta_2/\beta_1 = 1$.

4.3 The cases of the first order transition from the paraelectric cubic phase

This is the case where β_1 and β_2 lie in the regions $\beta_1 < 0$ and/or $\beta_1 + 2\beta_2 < 0$. It should be noted that the isotropy of the free energy function is not directly related to the sign of β_1 and/or β_2 , because the isotropy is just due to $\beta_1 = \beta_2$. However, in this case the sixth-order terms are indispensable to stabilize the tetragonal and the orthorhobic phases, and therefore they may have a stronger effect on the suppression of the divergence of the dielectric susceptibilities.

4.4 Piezoelectric constants

To discuss the increase in the piezoelectric constant, we have to write the free energy function in terms of strain components as well as polarization components, as has been done earlier.⁶

As has been clarified so far, the appearance of the morphotropic phase boundary and the increase of the dielectric susceptibilities are the result of the relative balance of the contribution to the free energy from two fourth order terms. This can be used as one of the general guiding principles in the search for materials with large dielectric susceptibilities. Theoretical analyses along this line are now in progress.

- 1) B. Jaffe, W. R. Crook, Jr. and H. Jaffe: *Piezoelectric Ceramics* (Academic Press, London, 1971).
- 2) A. F. Devonshire: Philos. Mag. 40 (1949) 1040.
- 3) A. F. Devonshire: Philos. Mag. 42 (1950) 1065.
- 4) K. Fujita and Y. Ishibashi: Jpn. J. Appl. Phys. 36 (1997) 5214.
- M. J. Huan, E. Furman, S. J. Jang and L. E. Cross: Ferroelectrics 99 (1989) 63.
- 6) K. Fujita and Y. Ishibashi: Jpn. J. Appl. Phys. 36 (1997) 254.