Theoretical model for the morphotropic phase boundary in lead zirconate—lead titanate solid solution

Wenwu Cao and L. Eric Cross

Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

(Received 18 February 1992; revised manuscript received 14 September 1992)

A statistical model is proposed to address the problem of two-phase coexistence near the morphotropic phase boundary (MPB) in $Pb(Zr_{1-x}Ti_x)O_3$ solid-solution series. Functional forms for the molar fractions of tetragonal and rhombohedral phases inside the coexistence region are obtained, which may be used to replace the lever rule to describe the phase mixing in a complete binary solid-solution series without solubility gap. The model predicts that the width of this coexistence region is inversely proportional to the volume of each element in the statistical ensemble. In addition, the shift of the MPB composition from the composition of equal molar fraction of the two coexisting phases is found to be proportional to the width of the coexistence region. Several existing controversial experimental observations can be reconciled by this model.

I. INTRODUCTION

The most widely used piezoelectric ceramic today is lead zirconate titanate (PZT), a solid solution of $PbZrO_3$-$PbTiO_3$, with compositions near the morphotropic phase boundary (MPB). A MPB is defined as a compositional phase boundary at which the two adjacent phases in a phase diagram have equal Gibbs free energy. The phase diagram determined by Jaffe, Cook, and Jaffe[1] from x-ray-diffraction measurements is shown in Fig. 1. The MPB on this phase diagram was considered to be the composition at which the amount of tetragonal and rhombohedral phases is equal.[1] However, it was pointed out[2] that the molar ratio of the two low-temperature phases, i.e., rhombohedral:tetragonal, should be 3:2 instead of 1:1 at the MPB (defined by equating the free energies of the two phases), which provides an explanation for the discrepancy between the MPBs determined by using dielectric maximum and from x-ray-diffraction intensities.

Historically, the exact composition of MPB in PZT has never been precisely defined; it ranges from 45–50 mol % of $PbTiO_3$.[3-6] There is a coexistence region of the tetragonal and rhombohedral phases whose width is also not well defined,[5-9] ranging from 2–15 mol % of $PbTiO_3$ around the composition Ti/Zr = 48/52.

From many years of study on the PZT system, the following two facts are well accepted:

(1) The PZT system is a complete binary solid solution of $PbTiO_3$ and $PbZrO_3$ without solubility gaps.

(2) Below the paraelectric-ferroelectric transition temperature there exists a coexistence region of the tetragonal and rhombohedral phases near the MPB composition, although the width of this region is still a debatable issue. Adding small amounts of dopant can shift the MPB and increase the width of the coexistence region.

The lever rule, obtained from mass conservation, has been used to describe fact (2) above.[7,8] Although the data
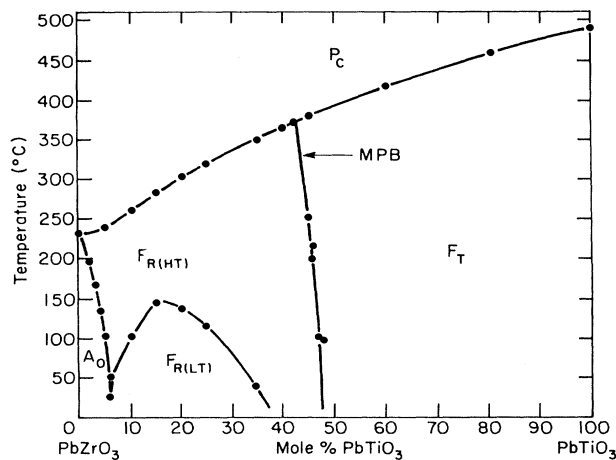

FIG. 1. Phase diagram of $PbZrO_3$-$PbTiO_3$ (PZT) solid-solution series by Jaffe, Cook, and Jaffe (Ref. 1).

fitting appears to be reasonable, the two edge compositions x_1 and x_2 in the lever rule actually specify a solubility gap, which is in contradiction with fact (1) above. An alternative explanation of the phase coexistence [fact (2) above] is to use the transition hysteresis argument within the context of a first-order phase transition by taking the composition as an independent variable.[10] This is also inadequate because the composition variable is already frozen in the temperature region ($T < 375\,°C$) where the two ferroelectric phases exist; the system only experiences a diffusionless structural phase transition at the Curie point. Solid-state reaction, which is needed to change the composition of PZT, cannot occur until above $800\,°C$. In other words, once a solid solution is formed at high temperature ($T > 800\,°C$), the chemical composition cannot be changed at low temperatures, but the system can have temperature-induced diffusionless structural phase transitions. Because the compositional degree of freedom has been frozen in the temperature region of interest, the transition hysteresis concept is not feasible. In addition, both explanations mentioned above lead to a definite width of the coexistence region which has not been observed experimentally.

Many physical properties of PZT reach their maximum or minimum at the MPB, which is also not well understood. From the definition of MPB, the two low-temperature structural phases are energetically degenerate at the MPB composition, and it is conceivable that the electric field or stress-driven phase transitions between the two ferroelectric structures are possible for the PZT of composition near the MPB. This field-induced phase transition could contribute substantially to the observed phenomena. In order to quantify this contribution, one must know the exact fraction of the two structural phases for a given composition in the low-temperature regime. Looking at classical thermodynamic and statistical theories, one finds that they cannot be directly applied to address our problem because the MPB is defined by equating the free energies of the tetragonal and rhombohedral phases, hence the energy difference (which is the only criterion in classical statistics) is zero. On the other hand, after a low-temperature structure is formed from the paraelectric-ferroelectric phase transition, the system may be "locked" into this structure because of the existence of a transition barrier between the two low-temperature phases (this is reflected in Fig. 1 as the nearly vertical line of the MPB). This "locked structure" is thermodynamically metastable below the transition temperature. Therefore, in reality we are not exactly dealing with the absolute thermodynamic equilibrium at temperatures well below T_c. It is our opinion that the coexistence of the two low-temperature phases in the PZT system is a result of quenched-in thermal fluctuations. Following this idea, the two observations in the PZT system mentioned above can be explained satisfactorily, and the fractions of the two coexisting phases can be quantified.

II. THE MODEL

As a starting point, we assume that the partitioning of the two phases does not change with temperature after being determined at the paraelectric-ferroelectric phase transition. We therefore only need to calculate the partitioning near T_c.

The question we are trying to address here is really the accessibility of all the low-temperature states during the phase transition. If we assume that all 14 states (8 in the rhombohedral phase and 6 in the tetragonal phase) are identical, then the molar ratio, rhombohedral:tetragonal, should be 4:3 at the MPB. But obviously these 14 states are not identical, the two low-temperature structures are geometrically *inequivalent*. In Ref. 2 we have applied this geometrical constraint in the statistical calculation of this ratio at the MPB, which is close to 3:2, and introduced the concept of probability polyhedron for systems with a vector order parameter. This concept may be used to calculate the distribution of energetically degenerate but geometrically inequivalent states resulting in a second-order phase transition (here the transition refers to the paraelectric-ferroelectric transition but not the one between the two low-temperature phases). In this paper we try to extend the model discussed in Ref. 2 to account for the coexistence of two energetically nondegenerate and geometrically inequivalent phases by incorporating the classical statistics.

In order to understand the underlying physics of the present problem, we first study the driving force for the phase transition. It has been shown using phenomenological theory that the paraelectric to ferroelectric phase transition in PZT for compositions in the vicinity of the MPB is of second order.[11] Therefore, thermal fluctuations are the driving force for this phase transition. Inevitably, these fluctuations will also play a key role in the probability distribution of the tetragonal and rhombohedral phases during cooling through the Curie point.

A. The probability polyhedron

The construction of probability polyhedron was described in Ref. 2. The only assumption made there was the orientational ergodicity of thermal fluctuations which is valid for either long-time observation of a single system or instant observation of a statistical ensemble.

In order to generalize the idea of probability polyhedron we give an equivalent definition below. Considering the fact that the number of surface planes in the polyhedron is equal to the number of allowed polarization directions, it is equivalent to say that in the fluctuating state each of the polarization states occupies an effective solid angle in the order parameter space, which is equal to the solid angle subtended by the polyhedron surface whose plane normal coincides with that polarization direction. The probability of attaining this polarization state on cooling through the phase transition is equal to its effective solid angle divided by 4π, the normalization constant.

Now we use this concept to describe the distribution of polarization states for the PZT of compositions sufficiently far from the MPB. In this case, the low-temperature phase is either tetragonal or rhombohedral. On the tetragonal side (Ti rich) of the MPB, the probability polyhedron is a cube with each of the six variants,

$(\pm p,0,0)$, $(0,\pm p,0)$, and $(0,0,\pm p)$, occupying an effective solid angle of $\Omega_i = 2\pi/3$ $(i = 1-6)$, where p is the magnitude of the polarization. Hence, the fraction being transformed into each of the polarization states in an ensemble (a ceramic can be treated as an ensemble of grains) is equal to $\Omega_i/(4\pi) = 1/6$, and the total polarization of the ensemble is zero in the order parameter space. Because of the one to one point mapping between the order parameter space and the real space, the total polarization in the real space is also zero for a statistical ensemble of particles. The same can also be said for the compositions on the rhombohedral side (Zr rich) of the MPB, for which the probability polyhedron is an octahedron. The effective solid angle for each variant is $\pi/2$ and the probability for each polarization state is $(\pi/2)/(4\pi) = 1/8$. Again, the net polarization of the ensemble of rhombohedral phase particles is zero. When the PZT composition is close to the MPB composition, the two low-temperature structural phases can coexist and the probability polyhedron will have 14 faces. In general, the tetragonal states and the rhombohedral states are not degenerate unless the composition is exactly on the MPB; therefore, we expect the effective solid angle representing the probability of each polarization state to change with composition.

There is an energy difference between the two structural phases when the composition is not exactly on the MPB; we introduce an anisotropy factor δ to describe this situation. As shown in Fig. 2, the distance of the surfaces (corresponding to different phases) from the center point of the polyhedron is represented by r_i $(= \overline{OT}$ or $\overline{OR})$, which controls the solid angle subtended by the surface. In other words, r_i determines the probability of attaining a specific polarization state using the concept we have introduced above; r_i must be a function of energy. At the MPB composition, the tetragonal and the rhombohedral phases are degenerate, and we have $r_T = r_R$. In this case, the actual magnitude of r_i does not matter since the solid angle partitioning is independent of r_i. But for the nondegenerate case, r_T and r_R are different and should depend on the energies of the two low-

temperature phases. We define the distribution anisotropy parameter δ as follows:

$$\delta = \frac{r_T - r_R}{r_T} , \tag{1}$$

which is a function of composition only when temperature and pressure are fixed.

$\delta = 0$ represents the MPB composition, at which the probability ratio of the rhombohedral and tetragonal phases is[2]

$$\frac{f_R}{f_T} = \frac{\pi - 6\arcsin[(3-\sqrt{3})/6]}{6\arcsin[(3-\sqrt{3})/6]} , \tag{2}$$

where f_R and f_T are the probabilities of the rhombohedral and tetragonal phases. This ratio is close to 3:2 instead of 1:1 given by Jaffe, Cook, and Jaffe.[1]

B. The distribution functions for the coexisting phases in PZT of composition near the MPB

There are upper and lower bounds for the value of δ. When δ decreases, the probability of transforming into the rhombohedral phase also decreases until $\delta = 1 - \sqrt{3}$; for δ less than this critical value, the low-temperature phase can only be tetragonal because the polyhedron becomes a cube. On the other hand, when δ increases, the probability of transforming into the tetragonal phase decreases, the upper limit for δ is $1 - 1/\sqrt{3}$, for $\delta \geq 1 - 1/\sqrt{3}$; the polyhedron becomes an octahedron, which means that the system can only be rhombohedral. There is another special value of δ, $\delta = 1 - 2/\sqrt{3}$, at which the representative surface of the rhombohedral phase on the probability polyhedron changes its shape from a six-sided polygon to a right triangle, and the representative surface for the tetragonal phase changes from a square to an eight-sided polygon. Therefore, in calculating the effective solid angle for each of the polarization states, one must use Figs. 2 and 3 for the cases of $\delta > 1 - 2/\sqrt{3}$ and $\delta < 1 - 2/\sqrt{3}$, respectively. It can be
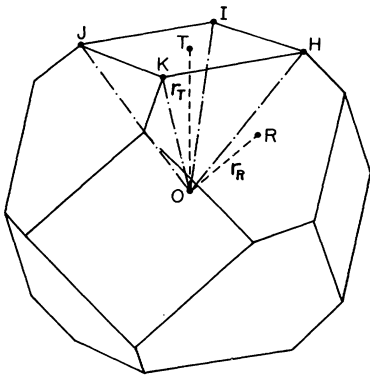

FIG. 2. Probability polyhedron for PZT system with the parameter δ in the range $1 - 1/\sqrt{3} > \delta > 1 - 2/\sqrt{3}$. At MPB, $\overline{OT} = \overline{OR}$ and $\delta = 0$.
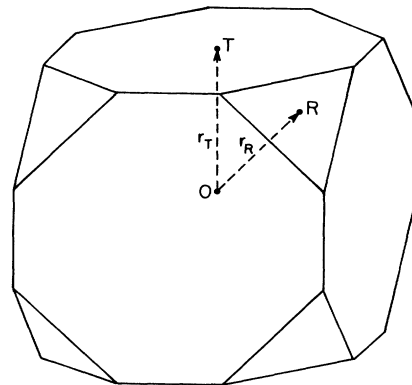

FIG. 3. Probability polyhedron for PZT system with the parameter δ in the range $1 - 2/\sqrt{3} > \delta > 1 - \sqrt{3}$, $r_T \neq r_R$.

shown that[12]

$$f_T = \begin{cases} \left| \dfrac{6}{\pi}\arcsin\left[\dfrac{\sqrt{3}[2(1-\delta)-\sqrt{3}]}{2(1-\delta)^2+[\sqrt{3}-(1-\delta)]^2} \right] \right|, & 1-\sqrt{3}<\delta<1-\dfrac{2}{\sqrt{3}}\ ; \\[4mm] \left| \dfrac{6}{\pi}\arcsin\left[\dfrac{[\sqrt{3}(1-\delta)-1]^2}{2+[\sqrt{3}(1-\delta)-1]^2} \right] \right|, & 1-\dfrac{2}{\sqrt{3}}<\delta<1-\dfrac{1}{\sqrt{3}}\ . \end{cases} \tag{3}$$

$$f_R = 1 - f_T\ . \tag{4}$$

C. The physical meaning of δ and the width of the coexistence region

In the PZT system, the free energies of the tetragonal and rhombohedral phases, G_T and G_R, depend monotonically on composition. The two free energies cross each other at the MPB.[13] From thermodynamics, at equilibrium only one of the two low-temperature phases is stable except at the MPB composition. However, in the vicinity of the MPB, one expects the energy difference of the two low-temperature phases to be very small; thermal energy can introduce some uncertainties in the distribution f_i, which obeys the canonical distribution. Since we have assigned the solid angle Ω_i to be proportional to the distribution function f_i, Ω_i may be written as follows:

$$\Omega_i \propto f_i \propto \exp\left[-\frac{G_i - G_c}{kT_c} \right]\ , \tag{5}$$

where k is Boltzmann's constant, G_i and G_c are the system free energies for the ith low-temperature structural phase and for the lowest energy phase ("ground state"), respectively. For a given surface area, the solid angle it subtends with respect to a given point in space is inversely proportional to the square of the distance between the surface and that point, i.e., $\Omega_i \propto 1/r_i^2$. Hence, from Eq. (5) the distance variable r_i can be written in terms of the free-energy difference:

$$r_i \propto \frac{1}{\sqrt{\Omega_i}} = \exp\left[\frac{G_i - G_c}{2kT_c} \right]\ . \tag{6}$$

By substituting Eq. (6) into Eq. (1) the parameter δ becomes

$$\delta = 1 - \exp\left[\frac{G_R - G_T}{2kT_c} \right]\ . \tag{7}$$

Using Eq. (7) and the limiting values of δ, one can calculate the required energy difference in order to obtain a single phase state:

$$|G_R - G_T| > kT_c \ln 3\ . \tag{8}$$

Therefore, the width of the coexistence region depends on how fast the energy difference $G_T - G_R$ changes with composition. An important conclusion can be drawn from Eq. (8); the width of the MPB depends on the volume of the element in the ensemble (for example, the particle size in a powder system). This is because the free-energy difference on the left-hand side of Eq. (8) is an

extensive variable while the product on the right-hand side is an intensive variable. This point can become more transparent if we recast Eq. (8) in the following form:

$$|g_R - g_T| = \frac{kT_c}{v}\ln 3\ , \tag{9}$$

where g_T and g_R are the free-energy densities of the two phases and v denotes the volume of each element in the statistical ensemble. Because the free-energy difference is small for PZT compositions sufficiently close to the MPB, we may write the free-energy density difference in terms of a series expansion around the MPB composition:

$$g_R - g_T = \sum_{n=1}^{\infty} \alpha_n (x - x_0)^n\ , \tag{10}$$

where x is the composition variable and x_0 is the MPB composition, and

$$\alpha_n = \frac{\partial^n}{\partial x^n}(g_R - g_T)\big|_{T,P}\ . \tag{11}$$

Note that Eq. (10) is a mathematical representation but not the Landau free energy, and there are no symmetry constraints for the expansion coefficients.

In a linear approximation, i.e., taking $\alpha_n = 0$ for $n \neq 1$, the width of MPB δx can be derived using Eqs. (9) and (10):

$$\Delta x = \frac{2kT_c}{\alpha_1 v}\ln 3\ . \tag{12}$$

Equation (12) indicates to us that the width of the coexistence region, Δx, is inversely proportional to the volume of the statistical element. Suppose Δx is 0.1 for a particle size of 0.1 μm, then it would be 0.0125 for a particle size of 0.2 μm. Therefore, it is not surprising that the values of Δx obtained by different processing techniques are quite different. It is also conceivable that for a well-sintered ceramic system or a single-crystal system, Δx will be too small to be detectable with the available experimental techniques, which gives an explanation as to why the coexistence could not be observed in some experiments, especially in a single-crystal system.

III. COMPARISON WITH EXPERIMENTS

Using the linear approximation, we can rewrite Eq. (7) in the following form:

$$\delta = 1 - \exp\left[\frac{(x - x_0)\ln 3}{\Delta x}\right] . \tag{13}$$

Here x_0 is the MPB composition and Δx is the width of the coexistence region as mentioned above. These two parameters can be obtained from fitting experimental data to the distribution functions given by Eqs. (3) and (4). In practice, the molar ratio of the two coexisting phases is measured from the integrated intensities of the x-ray-diffraction peaks of the rhombohedral and tetragonal phases. The value of x_0 may be obtained using Eq. (2), viz., at $x = x_0$ the intensity ratio of the rhombohedral phase to the tetragonal phase is roughly 3:2. Because the x-ray technique has a limited accuracy for a second phase of less than a few percent, especially when the diffraction peaks are not well separated, it is difficult to measure the coexistence width Δx. In order to overcome this difficulty, a useful relation is given below:

$$x_m - x_0 = \Delta x \left\{ \frac{1}{\ln 3} \ln \left[1 + \left[\frac{2\sin(\pi/12)}{1 - \sin(\pi/12)} \right]^{1/2} \right] - \frac{1}{2} \right\}$$

$$\approx 0.053 \Delta x , \tag{14}$$

where x_m is the equal fraction composition at which the molar ratio of the two phases is 1:1, which can be easily obtained from x-ray-diffraction measurements. Equation (14) was obtained by substituting Eq. (13) into Eq. (3) and letting $f_T = 1/2$.

For the pure PZT system, the coexistence region is not only very narrow but also very sensitive to the processing procedures; there are no reliable diffraction data in the literature. But when the system is slightly doped, the coexistence region becomes wider and the peaks become easily identifiable. As an example, we examine the experimental data of Hanh, Uchino, and Nomura,[8] which is for the solid-solution system

$$0.1Pb_{0.9}K_{0.1}(Zn_{1/3}Nb_{2/3})O_{2.95}$$

$$-(0.9 - x)PbZrO_3 - xPbTiO_3 .$$
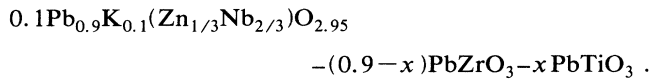
The squares and circles in Fig. 4 are the measured molar fractions of the rhombohedral and the tetragonal phases, respectively; the solid curves were obtained by Hanh, Uchino, and Nomura from fitting the experimental data to the lever rule, and the dotted curves are from the current model. Linear approximation [Eq. (13)] was used in the calculation and the two parameters $x_0 = 0.5027$ and $\Delta x = 0.2066$ were fitted to the experimental data using the nonlinear Levenberg-Marguardt method. The two special compositions x_0 (MPB) and x_m are also given in Fig. 4 as references.

Generally speaking, linear approximation is valid only when the two free-energy curves are relatively straight as a function of composition near the crossover point of the two free energies. It is expected that the calculated coexistence region could become slightly narrower when the full expansion in Eq. (10) is used.

From Fig. 4 one may find that the lever rule seems to give a good fit to the limited experimental data points, however, the derivatives of the distributions, df_R/dx and
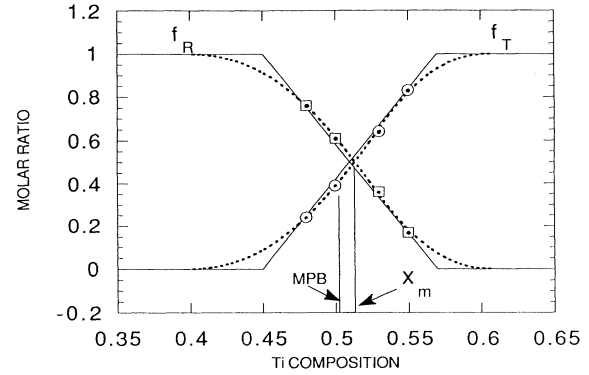

FIG. 4. The molar fractions of the rhombohedral and tetragonal phases inside the coexistence compositional region for $0.1Pb_{0.9}K_{0.1}(Zn_{1/3}Nb_{2/3})O_{2.95}-(0.9-x)PbZrO_3-xPbTiO_3$ solid solution. The squares and circles are the experimental data from Ref. 8, the solid curves were fitted from the lever rule, and the dotted curves were calculated using the proposed model under linear approximation.

df_T/dx are discontinuous at the compositions x_1 and x_2, which represent the existence of a solubility gap between x_1 and x_2. This is in contradiction with the complete solubility of the system. On the other hand, our model not only provides excellent fit to the experimental data, but also eliminates such derivative discontinuities, which makes it more suitable for describing the phase mixing in complete solid-solution systems.

In order to further illustrate the difference between the two theories, let us look at a binary system AC-BC and assume they form solid-solutions α and β for A-rich and B-rich compounds, respectively. Then, for any given composition x inside the coexistence region of α and β, we have the two theories describe the following situations:

(a) Lever rule

$$xAC + (1-x)BC = f_\alpha A_{x1}B_{1-x1}C(\alpha \text{ structure})$$

$$+ f_\beta A_{x2}B_{1-x2}C(\beta \text{ structure}) ; \tag{15}$$

(b) Present model

$$xAC + (1-x)BC = f_\alpha A_x B_{1-x}C(\alpha \text{ structure})$$

$$+ f_\beta A_x B_{1-x}C(\beta \text{ structure}) . \tag{16}$$

The lever rule specifies a solubility gap from x_1 to x_2, and the two coexisting phases have different chemical compositions as shown on the RHS of Eq. (15). On the other hand, our model was derived from the complete solubility of AC and BC, indicated on the RHS of Eq. (16), and the phase coexistence was considered as a frozen-in second metastable phase from thermal fluctuations.

IV. SUMMARY AND CONCLUSIONS

A theoretical treatment is proposed to calculate the molar fractions of the rhombohedral and tetragonal

phases near the MPB in a PZT system. Under the assumption that the partitioning of the two low-temperature phases is determined at the paraelectric-ferroelectric transition, the distribution functions are related to the effective solid angles associated with the low-temperature phases in the order parameter space. Analytic forms were obtained for the molar fractions of the two low-temperature phases inside the coexistence region. These molar fractions depend on a single parameter δ, which is a function of the free-energy difference of the two low-temperature phases. Besides the energy considerations, the geometrical constraints of a solid structure have been incorporated in the statistical calculations.

Using this model, the two contradictory facts of the PZT system mentioned in the introduction can be reconciled, as the current model allows for the phase coexistence in a complete solid-solution system without solubility gaps. In addition, the controversy about the undefined width of the coexistence region may also be explained using Eq. (9), which states that the width of the coexistence region is inversely proportional to the volume of the element in a statistical ensemble (such as the particle size in a powder system). Because the particle (or grain) size depends strongly on the processing technique,

a unique value for the width Δx cannot be well defined. The coexistence should not occur in a single-crystal system, which is consistent with the experimental observations.

The model was applied to the experimental data of Hanh, Uchino, and Nomura,[8] which is for the complete solid-solution system, $0.1Pb_{0.9}K_{0.1}(Zn_{1/3}Nb_{2/3})O_{2.95}-(0.9-x)PbZrO_3-xPbTiO_3$, and compared with the fitting using the lever rule. Although both theories provide good fit to the experimental data, the solubility gap specified by the lever rule makes it unsuitable to this problem, while the current proposed treatment can eliminate the two unphysical kinks in the distribution functions at x_1 and x_2 given by the lever rule. Therefore the proposed model is more consistent with the nature of complete solid-solution systems. Several predictions were made from the current model, including the relationship between the width Δx and the particle volume, which await further experimental verifications.

ACKNOWLEDGMENT

[1]B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics* (Academic, London, 1971), p. 136.

[2]W. Cao and L. E. Cross, Jpn. J. Appl. Phys. **31**, 1399 (1992).

[3]E. Sawguchi, J. Phys. Soc. Jpn. **8**, 615 (1953).

[4]B. Jaffe, R. S. Roth, and S. Margullo, J. Res. Nat. Bur. Stand. **55**, 239 (1955).

[5]A. V. Turik, M. F. Kupriyamov, E. N. Sidorenk, and S. M. Zaitsev, Zh. Tekh. Fiz. **50**, 2146 (1980) [Sov. Phys. Tech. Phys. **25**, 1251 (1980)].

[6]P. Gr Lucuta, F. L. Constantinesan, and D. Barb, J. Am. Ceram. Soc. **68**, 533 (1985).

[7]P. Ari-Gur and L. Benguigui, Solid State Commun. **15**, 1077 (1978).

[8]Lu Hanh, K. Uchino, and S. Nomura, Jpn. J. Appl. Phys. **17**, 637 (1978).

[9]M. L. A. Dass, U. Dahmen, G. Thomas, T. Yamamoto, and K. Okazaki, in *Proceedings of The Sixth IEEE International Symposium on Applications of Ferroelectrics, Bethlehem, PA*, edited by W. A. Smith (IEEE, New York, 1986), p. 146.

[10]V. A. Isupov, Fizika Tverd. Tela (Leningrad) **12**, 1380 (1970) [Sov. Phys. Solid State **12**, 1084 (1970)].

[11]M. J. Haun, E. Furman, H. A. McKinstry, and L. E. Cross, Ferroelectrics **99**, 27 (1989).

[12]W. Cao and L. E. Cross, J. Appl. Phys. (to be published).

[13]M. J. Haun, E. Furman, S. J. Jiang, and L. E. Cross, Ferroelectrics **99**, 63 (1989).