

The Ratio of Rhombohedral and Tetragonal Phases on the Morphotropic Phase Boundary in Lead Zirconate Titanate

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A method is introduced to determine the statistical distribution of energetically degenerate but geometrically inequivalent states in a temperature induced phase transition in solids. The method has been employed to calculate the ratio of the rhombohedral and tetragonal phases in the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ solid solution of the morphotropic phase boundary (MPB) composition. Our results indicate that the MPB determined by Jaffe, Cook and Jaffe [*Piezoelectric Ceramics* (Academic Press, London, 1971) p. 136] from structural measurements should be shifted to the rhombohedral side, which is more consistent with the MPB determined from dielectric measurements.

KEYWORDS: ferroelectric ceramic, PZT, lead zirconate titanate, morphotropic phase boundary

A phase diagram representing the subsolidus phase relations in the system $\text{PbZrO}_3\text{-PbTiO}_3$ taken from the book by Jaffe, Cook and Jaffe¹⁾ is given in Fig. 1. The system contains the well known solid solution series $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) which exhibits a variety of phase changes. In this system the most interesting compositions are for those on or near the so-called morphotropic phase boundary (MPB) (see the nearly vertical line on Fig. 1). PZTs in this compositional region have superior piezoelectric properties and are the primary materials currently used in most piezoelectric transducers and actuators. As shown in Fig. 1 the ferroelectric phase is rhombohedral on the left-hand side and tetragonal on the right-hand side of the MPB line, respectively (note: there should be a co-existence region of the two phases which is not shown in this phase diagram). The MPB in Fig. 1 as quoted from the book (Jaffe, Cook and Jaffe, p. 136) "is considered as that composition where the two phases are present in equal quantity".

The MPB drawn on a phase diagram is a composi-

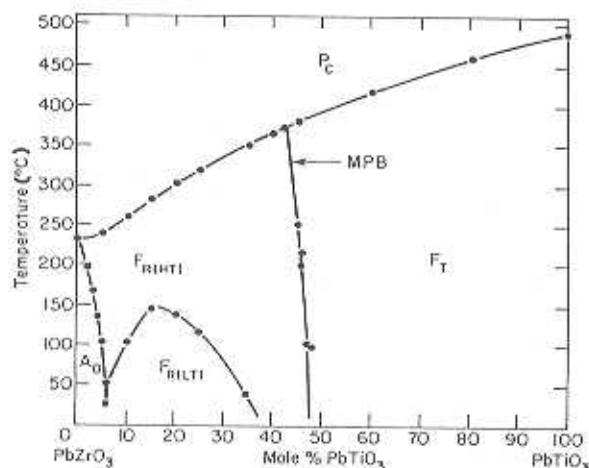


Fig. 1. Phase diagram of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ [after Jaffe, Cook and Jaffe, ref. 1].

tional boundary which is defined as the composition for which the free energies of two adjacent phases are equal. From thermodynamics, the free energy of a solid solution system depends on the following variables: temperature, pressure and composition. The compositional variable in the PZT case has a special property, it can only be directly accessed in certain temperature range. Out of that temperature range, the compositional variable can not be changed while keeping other variables fixed, as we know that a PZT solid solution can not be formed at room temperature. In order to change the composition at room temperature, one has to first heat up the system so that a single phase solid solution can be formed, then cool the system back down to room temperature after the new composition is formed. This special property of the compositional variable prevents direct thermodynamic analysis with this variable, and hence invalidates the transition hysteresis argument²⁾ in the explanation of the coexistence of two phases. Although the phase transition from the rhombohedral structure to the tetragonal structure must be of first order, it can not be realized while keeping the temperature unchanged, because the composition is not a directly accessible thermodynamic variable below a certain temperature limit. This is to say that we should address the temperature induced transition process in order to understand the effects of changing composition below a certain temperature limit.

There are two types of phase mixing: one is the mixing of phases of different chemical compositions and the other is the mixing of phases with different structures but identical chemical composition. At a first glance, it appears that the two problems seem to be similar, but they actually have quite different nature. The former reflects the law of mass conservation (obeying the lever rule), but the latter is actually a statistical distribution problem. It is the intention of this paper to provide a simple method dealing with the latter case.

From thermodynamic analyses, it is shown that the paraelectric-ferroelectric transition for compositions near the MPB is of second order within the experimental

error,⁹⁾ we therefore expect strong thermal fluctuations to occur near the transition temperature T_c . This thermal fluctuation is the sole driving force for the phase transition. For convenience we will work in the order parameter space. When the system is cooled down near T_c from the paraelectric phase, the magnitude of the thermal induced instant polarization $|P_{\text{inst}}|$ increases as the potential well around $P=0$ becomes flatter and flatter. Below T_c , the fluctuation is gradually frozen and the system acquires a new configurational state with a finite polarization. In a second order phase transition the transition process happens in a continuous fashion; but in a first order phase transition, a finite spontaneous polarization is obtained at the phase transition. The two cases are illustrated in Fig. 2 for a one-dimensional system, where the shaded area represents the level of thermal energy. In a one-dimensional system the number of allowed (two) orientations of the instant polarization is the same as that of the spontaneous polarization. But in two- and three-dimensional systems, there are no orientational constraints for thermal fluctuation (determined by the dimensionality of the problem only) although the magnitude of P_{inst} is regulated by the potential well around the origin. However, the allowed orientations for the spontaneous polarization P_0 are limited. The thick line and the solid dots in Fig. 3 illustrated this situation for a two-dimensional problem representing a square to rectangular ferroelectric phase transition. There are no orientational

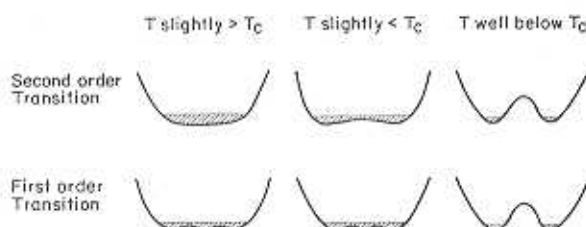


Fig. 2. Illustration of the potential wells and thermal fluctuations near the critical temperature T_c for both second and first order phase transitions in one dimension. The shaded areas represent thermal energy.

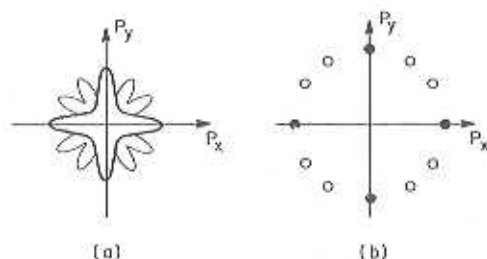


Fig. 3. Representation of fluctuating state and the ferroelectric states in order parameter space for a two-dimensional problem. (a) The thick and the thin lines are the profiles for the polarization fluctuations of the square-rectangular and square-oblique phase transitions, respectively, near T_c . (b) The solid dots are the degenerated rectangular ferroelectric states and the open circles are the degenerated oblique ferroelectric states, respectively, well below T_c .

constraints for P_{inst} in the fluctuating state [profile is represented by the thick line in Fig. 3(a)] but only four orientations for P_0 [solid dots in Fig. 3(b)] are allowed well below T_c .

The question we try to address in this paper is: what is the probability ρ_i for the system in Fig. 3(a) to become the i th low symmetry ferroelectric states in Fig. 3(b)? For the two-dimensional problem mentioned above, the answer $\rho_i=1/4$ may be obtained intuitively since the four low-temperature rectangle states are completely equivalent, i.e., these states are energetically degenerate and structurally identical. But in more general situations, intuition fails to provide an answer, for instance, the case shown in Fig. 3 where the energetically degenerated rectangle (solid dots) and the oblique (open circle) states are structurally different. In this case we need to follow a well-defined mathematical method to calculate these probabilities. Such a calculation is particularly useful for the study of PZT system, because at the MPB we have precisely such a situation, i.e., the tetragonal and rhombohedral phases are energetically degenerate.

It is obvious that the probability calculation is only meaningful in the fluctuating state. After the system being frozen into one of the low temperature states, thermal energy is no more effective to carry the system from one configuration to another. Our calculation is based on the following assumption:

The instant polarization P_{inst} is orientationally ergodic in the fluctuating state near T_c .

In other words, we assume that the thermal motion has no orientational preference, although as shown in Fig. 3, the magnitude $|P_{\text{inst}}|$ is regulated by the potential configuration and is a function of direction and temperature. An immediate inference from the assumption is that the average total polarization of the system is zero in the fluctuating state, or more concisely, $\langle P_{\text{inst}} \rangle = 0$ but $\langle P_{\text{inst}}^2 \rangle \neq 0$.

Now we try to correlate this thermal fluctuation with the transition probabilities to different structural phases. The assumption tells us that the trigger from the surrounding thermal bath is isotropic, but the actual structural change resulting from the trigger depends on the potential energy configuration. Because only a few isolated orientations for P_0 are allowed below T_c in the order parameter space, we expect that all P_{inst} oriented in the vicinity of an allowed polarization direction can potentially develop into that final polarization state. Hence we can assign each allowed polarization state an effective solid angle Ω_i in a three-dimensional order parameter space, the probability ρ_i of that state being formed under the trigger of thermal fluctuation is represented by $\Omega_i/(4\pi)$, where 4π is the normalization constant.

The next task is to define the boundaries of these solid angles. Imagine we apply a small dc field E to lift the degeneracy of the system. Under this field the system will be forced to develop into one of the allowed low temperature states whose polarization vector has the smallest possible angle with the applied electric field. If this field is applied to the system from another angle, it can either in-

duce the same polarization state or a different state depending on whether or not the field is still oriented inside the effective solid angle of that state. Considering at a temperature slightly below T_c , there are two adjacent energetically degenerate states represented by P_a and P_b , respectively, in the order parameter space (P_a and P_b form an angle ϕ), the boundary of the two effective solid angles for these polarization states may be defined by

$$E \cdot P_a = E \cdot P_b \quad (1)$$

Taking the coordinate systems as shown in Fig. 4 we can write eq. (1) in the following form,

$$P_2 \cos \phi = P_1 \cos (\phi - \phi). \quad (2)$$

Interestingly, the magnitude of the electric field has dropped out in eq. (2), hence if we take the limit $E \rightarrow 0$, the result in eq. (2) will still hold.

In reality, the problems of interest are those cases for which $P_a = P_b$, therefore, eq. (2) can be further simplified to

$$\phi = \phi/2. \quad (3)$$

Equation (3) states that the boundary of two effective solid angles is a plane in the order parameter space passing through the bisector of the angle ϕ and perpendicular to the plane containing P_a and P_b . If there exist more than two degenerate states, a boundary may be defined for each pair of adjacent effective solid angles using eqs. (2) or (3).

After the boundaries are defined, the remaining task becomes straightforward. We draw a polyhedron in the order parameter space surrounding the origin, whose edges are on the solid angle boundaries defined by eq. (3). For a PZT of MPB composition, the degenerated ferroelectric states include both rhombohedral and tetragonal phases. Assuming for the simplest case that $P_r = P_k = a$, then the corresponding polyhedron is shown in Fig. 5. The solid angle calculation can be written in terms of a surface integral on each of the corresponding surface which subtends that solid angle, for example

$$\Omega_{OHJK} = \iint_{\square OHJK} \frac{a \, ds}{(y^2 + a^2)^{3/2}} = 4 \int_0^b \int_0^{ab} \frac{a \, dx \, dy}{(x^2 + y^2 + a^2)^{3/2}}, \quad (5)$$

$$b = \frac{\sqrt{3}-1}{\sqrt{2}} a;$$

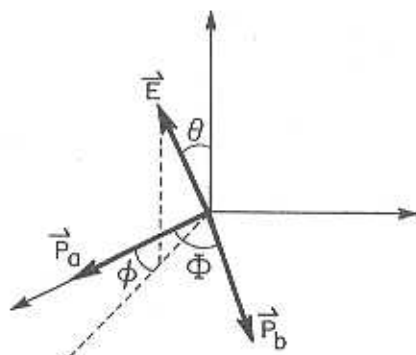


Fig. 4. Coordinate system used in the calculations of eqs. (2) and (3).

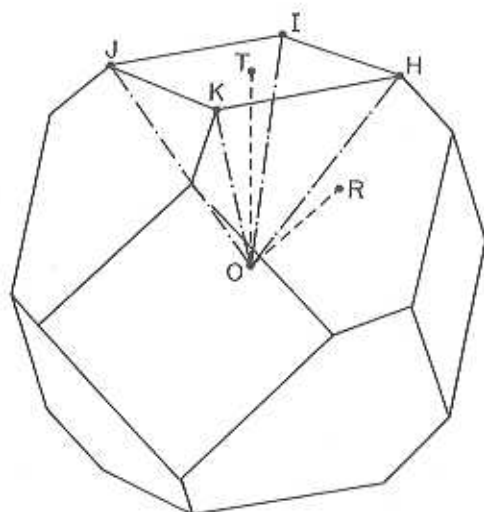


Fig. 5. The probability distribution polyhedron for PZT of the MPB composition, $OT=OR$. The solid angle subtended by the surface $OIHK$ with respect to the origin O divided by 4π represents the probability of the system being transformed into $(00P_r)$ state.

where ds is the area element on the surface $\square OHJK$ and r is the distance between ds and the center point T on that surface (Fig. 5). The integration of eq. (5) can be carried out to give an analytic solution

$$\Omega_{OHJK} = 4 \arcsin \left(\frac{3 - \sqrt{3}}{6} \right). \quad (6)$$

From this result and the arguments given above we conclude that for PZT of the MPB composition, the probability ratio for a system to be frozen into rhombohedral and tetragonal phases from the fluctuating state is given by

$$\frac{\text{Rhombohedral}}{\text{Tetragonal}} = \frac{1 - 6\Omega_{OHJK}/4\pi}{6\Omega_{OHJK}/4\pi} = \frac{\pi - 6 \arcsin \left(\frac{3 - \sqrt{3}}{6} \right)}{6 \arcsin \left(\frac{3 - \sqrt{3}}{6} \right)} \approx 1.459 \approx 3:2 \quad (7)$$

A ceramic system may be treated as an ensemble of domains, and each domain can be considered to be the system we have discussed above. Then, eq. (7) represents the molar ratio of the rhombohedral and tetragonal phases for a PZT ceramic of the MPB composition. This molar ratio can be calculated directly from X-ray diffraction intensities, therefore eq. (7) provides a criterion for the determination of the MPB.

Thermodynamics tells us that maximum values of many physical quantities should appear at the MPB composition due to the existence of maximum number of energetically degenerated states. However, several experimental results reveal that these maxima do not match with the MPB on Fig. 1 but often slightly deviate to the rhombohedral side.^{4,5} Our analysis above gives a reasonable explanation to this controversy. Naturally, if we use the ratio of 3:2 instead of 1:1 as the criterion for

the MPB, the MPB line on Fig. 1 would shift to the rhombohedral side.

The novel idea presented in this paper is to take into account the geometrical constraints in the calculation of the statistical distributions of those energetically degenerated states in solids. Through this paper we also intend to bring people's attention on treating solid systems, those thermodynamic theories developed for gas and liquid systems may not be valid and should be augmented to incorporate the characteristics of solids.

Finally, we like to point out that a special property pertaining to this problem has been used implicitly, i.e., the homotopy mapping between the real space and the order parameter space. Strictly speaking, thermal motion occurs in real space not in order parameter space. But because the order parameter is a vector in our problem, there is a one point to one point mapping between the

real space and the order parameter space, therefore we did not emphasize the difference between the two spaces in the text. However, if the order parameter is not a vector, one can not use the theory developed in this paper.

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