Symmetry of high-piezoelectric Pb based complex perovskites at the morphotropic phase boundary II. Theoretical treatment

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The structural characteristics of the perovskite-based ferroelectric Pb(Zn1/3Nb2/3)1−xTi xO3 at the morphotropic phase boundary (MPB) region (x≈0.09) have been analyzed. The analysis is based on the symmetry adapted free energy functions under the assumption that the total polarization and the unit cell volume are conserved during the transformations between various morphotropic phases. Overall features of the relationships between the observed lattice constants at various conditions have been consistently explained. The origin of the anomalous physical properties at MPB is discussed.

KEYWORDS: Piezoelectricity, morphotropic phase boundary, neutron diffraction, Pb(Zn1/3Nb2/3)O3/9%PbTiO3

§1. Introduction

The physical properties in solids at the phase boundaries between the two competitive stable phases tend to exhibit anomalous characteristics. A typical example is seen in the extraordinary transport phenomena such as high-Tc superconductivity and colossal magnetoresistance at metal-insulator phase boundary of the transition metal oxides. The high piezoelectric effect at the morphotropic phase boundary (MPB) observed in several perovskite-based ferroelectric materials may be considered to provide another interesting example of such phenomena at the structural phase boundary.

As is discussed in Part I1,2 of the present paper, the high piezoelectricity has been investigated from both experimental as well as theoretical aspects. Experimentally, Noheda et al.2–5) discovered a previously unknown monoclinic phase belonging to space group Cm (Ma-phase) in the boundary region between rhombohedral (R) and tetragonal phases in Pb1−xZrxO3 (abbreviated as PZTx). This is immediately followed by the theoretical work by Bellaiche et al.6) Based on the first principles calculations they showed that there should in fact exist Ma-phase within a narrow concentration range intervening between the high symmetry R- and T-phase in PZTx system in complete agreement with the experimental results. It is also pointed out that the high piezoelectricity is associated with the stabilization of the monoclinic phase.

Subsequently, X-ray measurements by Noheda et al.7) on another type of material Pb(Zn1/3Nb2/3)1−xTi xO3 (abbreviated as PZN-xPT) also revealed the existence of similar monoclinic phase at the MPB region, except that the space group in this case is Pm (Mc-phase) instead of Cm.

On the other hand, Ishibashi and Iwata8–10) developed a phenomenological theory on the physical properties at morphotropic phase boundary in perovskite solid solutions. He pointed out that depending on the coefficients of fourth order terms of the free energy expansion, the system stabilizes the orthorhombic phase intervening between the tetragonal and the rhombohedral phases. He
also discussed the dielectric\textsuperscript{8, 9} as well as elastic\textsuperscript{10} responses of the system at MPB and pointed out that the anomalous behavior in the susceptibility tensor components is in fact due to large electromechanical coupling constants of these materials. Fu and Cohen\textsuperscript{11} presented the key concept to understand the physics of high piezoelectricity: that is, the rotation of the spontaneous polarization during the structural transitions under electric field. Through first principles calculations they showed that there is a low energy path along the lines combining the symmetric directions of [111], [001] and [101] as shown in Fig.1. Upon application of the external field, the polarization would easily rotate along the particular path, which results in a large piezoelectric response. The stabilization of the monocrinic phase are considered to manifest this view point since monoclinicity is induced during the polarization vector continuously rotates along the specific path.

As is discussed by Noheda \textit{et al.}\textsuperscript{7} in the case of PZN-8PT, the M\textsubscript{c}-phase appears on the path between \( \mathbf{P} \parallel [001] \) and \( \mathbf{P} \parallel [101] \). This suggests that the high symmetry stable phase for composition around 8PT would be tetragonal and orthorhombic (O) rather than rhombohedral. In fact, depending on the prehistory of the sample preparation such as heat treatment, poling, etc., the orthorhombic phase is observed to become stabilized in PZN-9PT powder sample.\textsuperscript{12}

Recently, we carried out a neutron diffraction study using single crystals of PZN-9PT, with focus on the existence of M\textsubscript{c}-phase. The results are summarized in Part I of the present paper. In the present study, we develop a theoretical treatment based on a phenomenological arguments in order to analyze the experimental results presented in Part I. Since the treatment is phenomenological, unlike the treatment based on the first principles calculations, the conclusions depend on a few disposable parameters included in the free energy expression. Nevertheless, the results seem to provide some important insights into the specific physics at MPB regions.

\section*{2. Analysis of Experimental Data}

Using BaTiO\textsubscript{3} as a model system, Fu and Cohen\textsuperscript{11} developed a detailed theoretical treatment and discussed that the morphotropic phase transition scheme in BaTiO\textsubscript{3} is described by the rotation of the spontaneous polarization vector, \( \mathbf{P}_s \), within the \( (P_x, P_y, P_z) \) space moving along [111]→[001]→[101] directions as shown in Fig. 1. This process realizes the phases with rhombohedral, tetragonal and orthorhombic symmetry. Later, Vanderbilt and Cohen\textsuperscript{13} pointed out that when the energy terms up to the eighth order with respect to polarization are included in the free energy expansion, the monoclinic phases with the polarization along \( [\xi \xi \zeta] \) (M\textsubscript{c}-phase) and \( [\xi 0 \zeta] \) (M\textsubscript{c}-phase) directions can be stabilized.

Following these previous arguments, we also assume that the polarization moves on the surface of the sphere with \( |\mathbf{P}_s| \) conserved during the process of the polymorphic phase transitions in the present system. For later convenience, let us define the parameters to specify the orientation of polarization as it moves along the trajectory A and B in the \( \mathbf{P} \)-space (See Fig.1.) as follows:

\begin{equation}
\rho = \frac{P_x^2}{P_0^2}, \tag{2.1}
\end{equation}

\begin{equation}
\rho' = \frac{P_y^2}{P_0^2}, \tag{2.2}
\end{equation}

In the process A, \( \rho \) changes in the range of \( \frac{1}{3} \leq \rho \leq 1 \) as \( \mathbf{P} \) rotates from [111] \( (\rho = \frac{1}{3}) \) to [001] \( (\rho=1) \), while in the process B, \( \rho' \) changes in the range of \( 0 \leq \rho' \leq \frac{1}{2} \) as \( \mathbf{P} \) rotates from [001] \( (\rho'=0) \) to [101] \( (\rho' = \frac{1}{2}) \).

In addition, we further assume that the volume of the unit cell is also conserved throughout the sequential phase transitions. As is typically seen in the case of BaTiO\textsubscript{3}, this assumption seems to be satisfied well.

Since we are particularly interested in the lattice distortions, we give the expression of the ‘elastic’ free energy leaving the strain components as the independent variables rather than projecting on the polarization space. In order to make the treatment physically transparent, we construct the basis functions of the six dimensional direct product space of \((e_{xx}, e_{yy}, e_{zz}, e_{xy}, e_{xz}, e_{yz})\) associated with the irreducible representations of the point group m\textsuperscript{3}m as follows.

\begin{equation}
\psi_1 = \frac{1}{\sqrt{3}}(P_x^2 + P_y^2 + P_z^2) \in A_{1g},
\end{equation}

\begin{equation}
\psi_2 = \frac{1}{\sqrt{6}}(2P_x^2 - P_y^2 - P_z^2) \in E_g,
\end{equation}

\begin{equation}
\psi_3 = \frac{1}{\sqrt{2}}(P_x^2 - P_y^2) \in T_2g, \tag{2.3}
\end{equation}

\begin{equation}
\psi_4 = P_y P_z,
\end{equation}

\begin{equation}
\psi_5 = P_x P_y,
\end{equation}

\begin{equation}
\psi_6 = P_x P_z \in T_2g, \tag{2.4}
\end{equation}

and

\begin{equation}
e_1 = \frac{1}{\sqrt{3}}(e_{xx} + e_{yy} + e_{zz}) \in A_{1g},
\end{equation}

\begin{equation}
e_2 = \frac{1}{\sqrt{6}}(2e_{zz} - e_{xx} - e_{yy}) \in E_g,
\end{equation}

\begin{equation}
e_3 = \frac{1}{\sqrt{2}}(e_{xx} - e_{yy}) \in T_2g, \tag{2.4}
\end{equation}

\begin{equation}
e_4 = e_{yz},
\end{equation}

\begin{equation}
e_5 = e_{xz},
\end{equation}

\begin{equation}
e_6 = e_{xy} \in T_2g. \tag{2.4}
\end{equation}

Then, we can set up the simplest symmetry adapted elastic free energy including only the quadratic (or bilinear) terms as follows:

\begin{equation}
F_{el} = F_{el}^{(A_{1g})} + F_{el}^{(E_g)} + F_{el}^{(T_2g)}, \quad \tag{2.5}
\end{equation}

where

\begin{equation}
F_{el}^{(A_{1g})} = \frac{1}{2} c_1 e_1^2 - g_1 \psi_1, \tag{2.6}
\end{equation}

\begin{equation}
F_{el}^{(E_g)} = \frac{1}{2} c' (e_2^2 + e_3^2) - g' (e_2 \psi_2 + e_3 \psi_3), \tag{2.7}
\end{equation}

\begin{equation}
F_{el}^{(T_2g)}.
\end{equation}
The polarization which are explicitly given by
\[
\epsilon_{\text{irr}} = 2\epsilon_{\phi}(e_1^2 + e_5^2 + e_6^2)
\]
\[
- \sqrt{2}\epsilon_{\phi}(e_4\psi_4 + e_5\psi_5 + e_6\psi_6).
\] (2.8)
The second terms of these equations give the electrostrictive energies in the cubic perovskite system.

In these expressions, the independent thermodynamic variables are \(e_1^s\) (\(v = 1, \ldots, 6\)) while \(\psi_v^s\) are considered to be the parameters to define the orientation of the polarization which are explicitly given by \(\rho\) and \(\rho'\) in eqs. (2.1) and (2.2). Among the three terms in eq. (2.5), \(F_{\text{el}}^{(A_{1g})}\) is irrelevant to determine the stability of the system during the rotation of the polarization vector, since it is expressed in terms of \(e_1\) and \(\psi_1\) which are both assumed to be conserved.

Moreover, \(F_{\text{el}}^{(E_g)}\) is defined in the 2-dimensional space spanned by the basis of \(E_g\) representation (\(\epsilon_2\) and \(\epsilon_3\)), while \(F_{\text{el}}^{(T_{2g})}\) in the 3-dimensional space spanned by the basis of \(T_{2g}\) representation (\(\epsilon_4, \epsilon_5, \text{and} \epsilon_6\)). Therefore, in order to find the stable lattice distortions, we simply minimize \(F_{\text{el}}^{(E_g)}\) and \(F_{\text{el}}^{(T_{2g})}\) independently.

(i) \(E_g\)-space

By the standard minimization procedure, it is easily shown that the trajectory of the minimum energy \(\epsilon^0(\rho)\) is given by:

(a) Process A
\[
\begin{align*}
\epsilon_2^0(\rho) &= \frac{\sqrt{3}}{9\nu}(3\rho - 1), \\
\epsilon_3^0 &= 0.
\end{align*}
\] (2.9)

(b) Process B
\[
\begin{align*}
\epsilon_2^0(\rho) &= \frac{\sqrt{3}}{2\nu}(1 - 2\rho'), \\
\epsilon_3^0 &= \frac{\sqrt{3}}{2\nu}.
\end{align*}
\] (2.10)

where \(\epsilon_2\) and \(\epsilon_3\) are defined by 120° rotation of the \((\epsilon_2, \epsilon_3)\) coordinate system.

The trajectory followed by the representative point of the system in the \((\epsilon_2, \epsilon_3)\) space is given in Fig.2(a). In the figure, R, T and O represents the rhombohedral, tetragonal and orthorhombic phases respectively.

(ii) \(T_{2g}\)-space

Similarly, we have the trajectory of the energy minimum path:

(a) Process A
\[
\begin{align*}
\epsilon_2^0(\rho) &= \frac{\sqrt{3}}{9\nu}(3\rho - 1), \\
\epsilon_3^0 &= 0,
\end{align*}
\] (2.11)

(b) Process B
\[
\begin{align*}
\epsilon_4^0 = \epsilon_6^0 = 0, \\
\epsilon_3^0(\rho') &= \frac{\sqrt{3}}{2\nu}(1 - \rho').
\end{align*}
\] (2.12)

The trajectories followed by the representative point of the system in the \((\epsilon_4, \epsilon_5, \epsilon_6)\) space is given in Fig.2(b). Eqs. (2.9) to (2.12), together with the condition of the volume conservation \(e_{xx}^0 + e_{yy}^0 + e_{zz}^0 = 0\), give the set of lattice parameters of the stable state in terms of \(\rho\) or \(\rho'\) as shown in Table I. Notice among total of 30 lattice constants, there are only two disposable parameters, \(\Delta\) and \(\delta\), besides \(\rho\) and \(\rho'\). We utilized the values of \(e_1\) (the unique axis in T-phase) observed in 9PT5 and \(\beta\) (monoclinic angle in O-phase) in 9PT4 as tabulated in Part I.
(see Table I) to obtain the value of $\Delta$ and $\delta$ respectively.

Fig. 3 shows the sequence of the calculated lattice constants to be taken by the system as $\rho$ and $\rho'$ is varied to stabilize $(R) \rightarrow (M_a) \rightarrow T \rightarrow M_c \rightarrow O$, including the fictitious stable phases $R$ and $M_a$ which are not realized in the PZN-9PT system, but realized in the related materials. The observed values at lower temperatures given in Part I are indicated by the solid circles. We can not calculate the lattice parameters as a function of temperature for direct comparison with the experimental results, since the temperature dependences of $\rho(T)$ and $\rho'(T)$ are outside of the framework of the present treatment.

| | $\epsilon_{xx}$ | $\epsilon_{yy}$ | $\epsilon_{zz}$ | $\epsilon_{xy}$ | $\epsilon_{xz}$ | $\epsilon_{yz}$ |
|---|---|---|---|---|---|---|
| $R$ | $\rho$ | $\rho$ | $\Delta a$ | $\Delta b$ | $\Delta c$ | $\Delta \alpha$ | $\Delta \beta$ | $\Delta \gamma$ |
| $M_a$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $T$ | 1 | 0 | $-\frac{\Delta}{2}$ | $-\frac{\Delta}{2}$ | $\Delta$ | 0 | 0 | 0 |
| $M_c$ | $-\rho'$ | $-\frac{\Delta}{2}$ | $\frac{\Delta}{2}$ | $\frac{\Delta}{2}$ | $\frac{\Delta}{2}$ | 0 | $3\delta \sqrt{\rho'(1-\rho')}$ | 0 |
| $O$ | $-\frac{\rho'}{2}$ | $\frac{\Delta}{2}$ | $-\frac{\Delta}{2}$ | $-\frac{\Delta}{2}$ | $\frac{\Delta}{2}$ | 0 | $\frac{\Delta}{2}$ | $\frac{\Delta}{2}$ |

Fig. 3. The calculated variation of the lattice constants in PZN-9PT as the parameters $\rho$ and $\rho'$ is varied. The solid circles are the experimental values obtained by the present work (Part I). The figure includes the fictitious phases (R and $M_a$) which are not realized in 9PT, but realized in the closely related systems. The open squares indicate the data used for the numerical analysis. (See the Text.)

§3. Conclusions and Discussions

In conclusion, based on the symmetry adapted free energy function, we analyze the structural characteristics of PZN-9PT under the assumption that the total polarization and the unit cell volume are conserved during the transformations between various morphotropic phases. Overall features of the relationship between the observed lattice constants in various phases have been consistently explained.

So far, we have discussed the lattice distortions which are directly observed by the diffraction studies described in Part I. The energetic considerations concerning the stability of the phases seem to give more important insight into the physical properties of the system at MPB as discussed in the following.

Using eqs. (2.9) through (2.12), the free energy values of the rhombohedral ($F_{cl}(R)$), the tetragonal-($F_{cl}(T)$), and the orthorhombic-($F_{cl}(O)$) phases are given by

$$
\begin{align*}
F_{el}(R) &= -\frac{g'^2}{6c'}
F_{el}(T) &= -\frac{g'^2}{4c'}
F_{el}(O) &= -\frac{g'^2}{12c'} - \frac{g'^2}{6c'}
\end{align*}
$$

(3.1)

which means that $(F_{el}(O))$ is expressed by a fixed weighted mean of $(F_{el}(R))$ and $(F_{el}(T))$ as

$$
F_{el}(O) = \frac{1}{4} F_{el}(T) + \frac{3}{4} F_{el}(R),
$$

(3.2)

irrespective of the parameter values of $c'$s and $g'$s. Assuming, for simplicity, linear dependence of the parameters on the $x$-value (the concentration of PbTiO$_3$), the relative energies of the three phases change with respect to $x$ as schematically shown in Fig. 4. We see that the stable phases are generally given by either T- or R- phases while O-phase barely becomes one of the three degenerated ground states at the single critical concentration, $x_c$, where

$$
\frac{g'^2}{3c'} = \frac{g'^2}{6c'} \equiv A
$$

(3.3)

is satisfied. Notice the critical concentration $x = x_c$ is nothing but the MPB point. (See Fig.4.)

More generally, the free energy $F_{el}(\rho)$ and $F_{el}(\rho')$ with
an arbitrary polarization direction is given by,

\[ F_{el}(\rho) = -\frac{g'^2}{12c'}(3\rho - 1)^2 \]
\[ -\frac{g''^2}{8c''}(1 - \rho)(1 + 3\rho), \] (3.4)

\[ F_{el}(\rho') = -\frac{g'^2}{12c'} \frac{g'^2}{4c'} (1 - 2\rho')^2 \]
\[ -\frac{g''^2}{2c''}(1 - \rho'). \] (3.5)

It is easily seen that at MPB where eq. (3.3) is satisfied,

\[ F_{el}(\rho) = F_{el}(\rho') = A, \] (3.6)

irrespective of the values of \( \rho \) and \( \rho' \) which means that at MPB, the energy is completely degenerated throughout the postulated path of polarization rotation. Only by the introduction of higher order energy terms which are neglected in the present treatment, the degeneracy will be lifted so that either of O-, M\(_x\)- or M\(_L\)- phases may become stabilized in the MPB region as shown by Vanderbilt and Cohen.\(^{13}\) This situation may explain the experimental observations that depending on subtle differences of the prehistory of sample preparation, the symmetry of the stable state becomes different.

Furthermore, neglecting the higher order terms, we see that at \( x = x_c \) the system could move over between R\( \leftrightarrow \)M\(_x\)\( \leftrightarrow \)T\( \leftrightarrow \)M\(_L\)\( \leftrightarrow \)O under external forces such as electric field and stress without any cost of elastic energy. Therefore, at MPB some of the susceptibility tensor components of \( \chi_{ij} \) (dielectric constants), \( d_{ijk} \) (piezoelectric constants) and the inverse of \( c_{ijkl} \) (elastic constants) should critically blow up, although in the real system, the higher order effects would tend to prevent such a strong anomaly. Actually, Ishibishi and Iwata\(^{8-10}\) have given the explicit expressions for these susceptibility tensors, some of which tend to show the critical behavior. The above simple energy considerations seem to reveal the essential origin of the anomalous physical properties at MPB.

As a further application of this view point, we take notice on the elastic anomaly exhibited by hexagonal BaTiO\(_3\)\(^{14}\). It is known that hexagonal BaTiO\(_3\) (h-BT) undergoes two phase transitions successively as hexagonal \( \rightarrow \) orthorhombic (space group C22\(_2\)) \( \rightarrow \) monoclinic (space group P2\(_1\)).\(^{15,16}\) The relevant order parameter is the doubly degenerated phonon modes, \( Q_1 \) and \( Q_2 \). Ishibashi\(^{17,18}\) pointed out that the transition between O- and M- phases is caused by the rotation of the polarization vector of the mode in the 2-dimensional (\( Q_1, Q_2 \)) space, which is very similar to the feature presented in this paper if we replace \( P \) by \( Q \). However, it should be noticed that the anomaly at the O-M transition region in h-BT is manifested in the elastic compliances rather than piezoelectricity because the \( Q \)-modes are optically inactive. In this context, h-BT may be considered to provide another example belonging to the different category concerning MPB adventure.

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