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The giant piezoelectric effect: electric field induced monoclinic phase or piezoelectric distortion of the rhombohedral parent?

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Abstract

Lead zinc niobate–lead titanate (PZN–PT) single crystals show very large piezoelectric strains for electric fields applied along the unit cell edges e.g. $[001]_R$. It has been widely reported that this effect is caused by an electric field induced phase transition from rhombohedral ($R3m$) to monoclinic (Cm or Pm) symmetry in an essentially continuous manner. Group theoretical analysis using the computer program ISOTROPY indicates phase transitions between $R3m$ and Cm (or Pm) must be discontinuous under Landau theory. An analysis of the symmetry of a strained unit cell in $R3m$ and a simple expansion of the piezoelectric strain equation indicate that the piezoelectric distortion due to an electric field along a cell edge in rhombohedral perovskite-based ferroelectrics is intrinsically monoclinic (Cm), even for infinitesimal electric fields. PZN–PT crystals have up to nine times the elastic compliance of other piezoelectric perovskites and it might be expected that the piezoelectric strains are also very large. A field induced phase transition is therefore indistinguishable from the piezoelectric distortion and is neither sufficient nor necessary to understand the large piezoelectric response of PZN–PT.

1. Introduction

Piezoelectric single crystals with large maximum strains and electromechanical coupling factors have been known for some time in the relaxor ferroelectric perovskite $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_{3-x}\text{PbTiO}_3$ (PZN– x PT) [1, 2]. The current phase diagram (reproduced

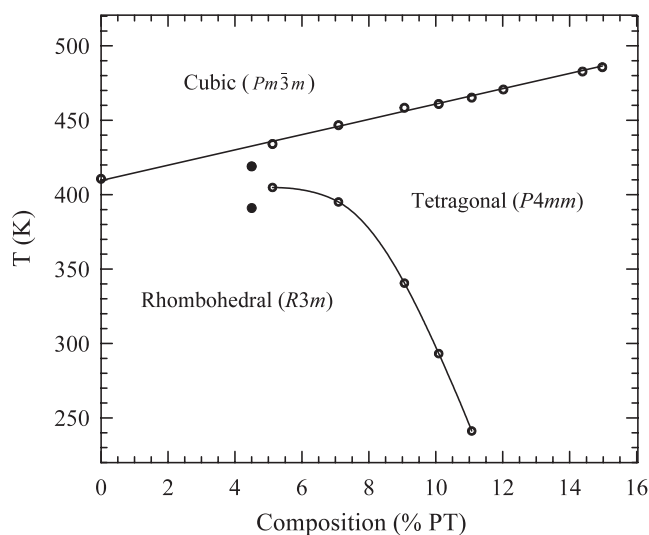


Figure 1. The PZN–PT temperature–composition phase diagram adapted from [1] (open symbols) with two additional points from [3] (filled symbols).

in figure 1) is similar to that of lead zirconate titanate (PZT) except that, in PZN–PT, the morphotropic phase boundary separating the rhombohedral and tetragonal phases is close to 9% PbTiO₃ (9% PT) at room temperature compared with ~48% PT in PZT. At $x < 9\%$ PT, the crystals are rhombohedral in the as-grown state with spontaneous polarization along $\langle 111 \rangle_R$. They exhibit maximum piezoelectric strains up to 1.7%, approximately ten times larger than conventional piezoelectric ceramics. This effect is sometimes referred to as the ‘giant piezoelectric effect’ [4]. Curiously, the maximum piezoelectric strains are obtained for electric fields along the rhombohedral unit cell edges $\langle 100 \rangle_R$ instead of parallel to the spontaneous polarization $\langle 111 \rangle_R$. These factors have recently caused a flurry of interest in both the materials engineering of technologically viable crystals and scientific understanding of the underlying mechanism.

Potential for technological application has been advanced by the growth of ever-larger crystals [5] and by stable and reproducible piezoelectric strain versus electric field behaviour achieved using a combination of field cooling and poling [6]. A domain structure engineered in this way is said to allow the crystals to survive the large strains without fracturing. The domain structure in PZN–PT is known to be complex and has yet to be fully characterized [7, 8].

Several mechanisms by which the large piezoelectric strains can be understood have been proposed. Kuwata *et al* [1] noted that the elastic constants are very soft and briefly suggested that the large piezoelectric coefficients are likely to derive from this. This idea has been recently revisited [9] where the elastic constants from single crystals grown by several groups were measured. This group inferred that PZN–9% PT single crystals are two-phase rhombohedral and tetragonal, with the mechanical softness of the rhombohedral phase the underlying cause for the giant piezoelectric effect. Some groups have noted that the saturation piezoelectric and dielectric coefficients are the same as those of the neighbouring tetragonal phase ($>9\%$ PT). As a result, a field induced rhombohedral to tetragonal phase transition was postulated as contributing to the very large strains [2]. First principles calculations on the model system BaTiO₃, have been used to suggest that the effect occurs by a continuous ‘polarization rotation’ between $[111]_R$ and $[001]_R$ [4]. A necessary condition for this to occur

in the simulations was ‘a flat energy surface (that is, soft force constants for ferroelectric displacements)’ [4] in agreement with Kuwata *et al* [1]. It has been shown that an expansion to 8th order is required to obtain this condition under the Devonshire theory [10].

Support for the polarization rotation model is elicited from a large body of experiments due to Noheda *et al* on crystals containing 4.5, 8 and 9% PT. Experiments were conducted using large $[001]_R$ poled single crystals and data recorded by a variety of diffraction techniques. Single crystal x-ray ($\lambda = 0.79$ and 0.38 \AA [11–13]) and neutron [14] diffraction data were recorded from crystals subjected to *in situ* electric fields up to 45 kV cm^{-1} in reflection geometry by reciprocal space scanning about the Bragg positions of a very small number⁵ of reflections. The neutron and short wavelength x-ray studies helped to distinguish between surface and bulk effects. Additional data were recorded using powder synchrotron x-ray diffraction at $\lambda = 0.79 \text{ \AA}$ from crushed poled single crystals in the size range $38\text{--}44 \text{ \mu m}$ [14–16].

These data have been interpreted jointly within the framework of the polarization rotation theory of Fu and Cohen [4] and the recently proposed monoclinic phase at the morphotropic phase boundary in PZT [17–19]. The experiments appear to indicate that the application of an electric field along $[001]_R$ induces a phase transformation from the as-grown rhombohedral state to a lower symmetry phase. By analogy with PZT, the lower symmetry form was postulated to be a similar though distinct monoclinic phase [11]. Adopting the notation of Vanderbilt and Cohen [10], the monoclinic phase in PZT is referred to as M_A (in space group Cm) and that in PZN–8% PT as M_C (in space group Pm). The subscripts refer to particular paths taken during Fu and Cohen’s polarization rotation mechanism. It was observed that the structural distortion remains upon removal of the electric field in some large crystals however the distortion is removed by crushing the crystals to below 38 \mu m . The subsequent synchrotron x-ray powder diffraction of the retained low symmetry phase in PZN–8% PT and PZN–9% PT indicated orthorhombic and not monoclinic symmetry as originally proposed [14, 15] and led to the drafting of a new phase diagram [12, 16]. During the work, considerable sample to sample variation was noted [13, 16] including variation in the apparent transition voltages between 11 and 30 kV cm^{-1} , and great variability in the phases present at zero field after poling (even the tetragonal phase was sometimes observed).

Considerable further analysis (including re-labelling of the zero field condition around 8% PT as monoclinic) has been used to refine the interpretation, culminating in the electric field–composition diagram shown in figure 2. Referring to figure 2, the mechanism for the giant piezoelectric effect is now proposed by Noheda *et al* to be a field induced rhombohedral to monoclinic phase transition (at arbitrarily small values of the electric field) followed by a monoclinic to tetragonal phase transition at high field (the latter being originally proposed by Park and Shrout [2]). In all, despite several revisions, a cogent model, widely published in the literature, has emerged from the work of Noheda *et al* [13].

We pause here to summarize what is unequivocally known about the piezoelectric response of PZN– x PT single crystals ($x < 9\%$).

- (i) The crystals exhibit very large piezoelectric strains for electric fields applied along the rhombohedral axes (e.g. $[001]_R$) and rather smaller strains for fields applied along the direction of spontaneous polarization $[111]_R$ [2].
- (ii) The as-grown crystals are rhombohedral in space group $R3m$ [3].
- (iii) The crystals have a complex domain structure [7, 8].
- (iv) Diffraction effects consistent with a monoclinic distortion occur under an applied electric field [11–14].

⁵ Often only one was reported.

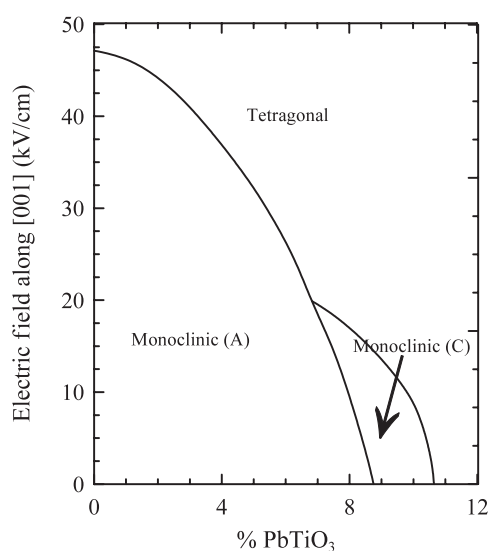


Figure 2. A schematic of the electric field–composition phase diagram, proposed by Noheda *et al* [13] for samples previously poled along $[001]_R$. At zero field, the symmetry is rhombohedral ($R3m$) in as-grown crystals and in poled crystals below 8% PT. Some crystals with $\geq 8\%$ PT have been reported to remain monoclinic unless ground or heated.

- (v) The monoclinic distortion is continuous (figure 2, [13]).
- (vi) The unit cell distortion is retained after removal of the field in some crystals at some compositions (e.g. 8% PT) though not at others (4.5% PT) [13].
- (vii) The distortion is lost if the crystals are ground to below $38 \mu\text{m}$ [12, 15].
- (viii) There is considerable sample-to-sample variability in regard to the physical appearance of crystals, domain coexistence within the same crystal [9, 20], crystal structures and phase changes [11, 16], and electrical and mechanical properties [21].

Notwithstanding the large amount of experimental data and analysis, there are still some deficiencies in our understanding of the giant piezoelectric materials. First, the inconsistent behaviour from crystal to crystal is suggestive of a greater microstructural influence than might be expected for a pure phase transition. Second, the polarization rotation mechanism has been developed without reference to the manner in which conventional piezoelectric crystals respond to electric fields applied in directions other than the direction of spontaneous polarization. What is the role of induced polarization? Third, the phase transition mechanism has been linked to the polarization rotation model. However, there is still no clear connection to the *magnitude* of the piezoelectric strains. There has been little or no recognition in the work of Noheda *et al* that the elastic constants of PZN–PT crystals are up to nine times smaller than conventional piezoelectric ceramics such as PZT and BaTiO_3 . In this paper, we investigate an alternative mechanism for the giant piezoelectric effect.

2. Group theoretical analysis of strains in rhombohedral crystals

The latest work from Noheda *et al* contains an electric field–composition phase diagram (figure 2) with a continuous transition from the zero field rhombohedral phase (R) to field induced monoclinic phases (M_A and M_C). This implies second order transitions from

Table 1. Macroscopic deformations of the space group $R3m$ (hexagonal setting). (The irreps here are referred to the zero field space group $R3m$, not the aristotype perovskite $Pm\bar{3}m$.)

Irrep	Mode	Order parameter	Deformation	Subgroup
Γ_1	1	(a)	$\varepsilon_{11} + \varepsilon_{22}$	$R3m$
	2	(a)	ε_{33}	$R3m$
Γ_3	1	($a, 0$)	$\varepsilon_{11} - \varepsilon_{22}$	Cm
	1	(a, b)	$\varepsilon_{11} - \varepsilon_{22}, -2\varepsilon_{12}$	$P1$
	2	($a, 0$)	ε_{13}	Cm
	2	(a, b)	$\varepsilon_{13}, \varepsilon_{23}$	$P1$

rhombohedral to monoclinic symmetry. Structural distortions may be represented by particular irreducible representations (irreps) of a parent space group. Taking as parent the space group of the aristotype cubic perovskite, $Pm\bar{3}m$, group theoretical analysis to find subgroups resulting from a ferroelectric displacement of the B-cation (irrep Γ_4^-) using the computer program ISOTROPY [22] has been conducted and reported previously [3]. It shows that the space group Cm (M_A phase) is a subgroup of $R3m$ (R phase)—however, the order parameter expansion contains a third order invariant so, under Landau theory, an $R3m \rightarrow Cm$ phase transition would be required to be first order. There is no group–subgroup relationship between $R3m$ and Pm (M_C phase). Extension of the group theoretical analysis to allow in-phase (irrep M_3^+) and out of phase (irrep R_4^+) octahedral rotations coupled with the B-cation displacements does not alter these conclusions [23]. Thus, according to group theory, there can be no continuous $R \rightarrow M$ transition such as appears on the phase diagram in figure 2 [13].

On the other hand, the symmetry of a crystal may be lowered without a phase transition by an externally driven deformation such as elastic strain or piezoelectric strain. In the absence of a phase transition, such a process is necessarily continuous. We propose below that the monoclinic distortions reported up until now are simply the piezoelectric response to the applied electric field.

ISOTROPY can display the macroscopic deformations associated with different kinds of irreps. This allows the symmetry of a crystal structure subjected to various kinds of external stimuli to be evaluated. Macroscopic deformations that transform as bases for irreps of the parent space group $R3m$ are given in table 1.

Deformations such as a basal plane dilation or c -axis dilation transform like the irrep Γ_1 and preserve the parent symmetry $R3m$. Shear deformations or volume-conserving deformations of the basal plane transform like the two-dimensional irrep Γ_3 and lead to monoclinic (Cm) or triclinic ($P1$) symmetry. Specifically, a non-zero value of $\varepsilon_{11} - \varepsilon_{22}$ or ε_{13} (the other shear strains being zero) imposes monoclinic symmetry in space group Cm , the same space group proposed for the M_A phase. Deformations with $\varepsilon_{12} \neq 0$ and/or $\varepsilon_{23} \neq 0$ lower the symmetry to triclinic, in space group $P1$.

3. Application to the piezoelectric distortion in rhombohedral PZN–PT

The converse piezoelectric effect is defined by:

$$\varepsilon_{jk} = d_{ijk} E_i \quad (1)$$

where ε_{jk} are the elements of the strain tensor, d_{ijk} are the piezoelectric moduli and E_i are the components of the electric field vector \mathbf{E} . There is an implied summation over i . Rhombohedral structures may be set in a primitive rhombohedral unit cell or a tripled hexagonal unit cell [24]. The extraordinary piezoelectric strains in PZN–PT are along one

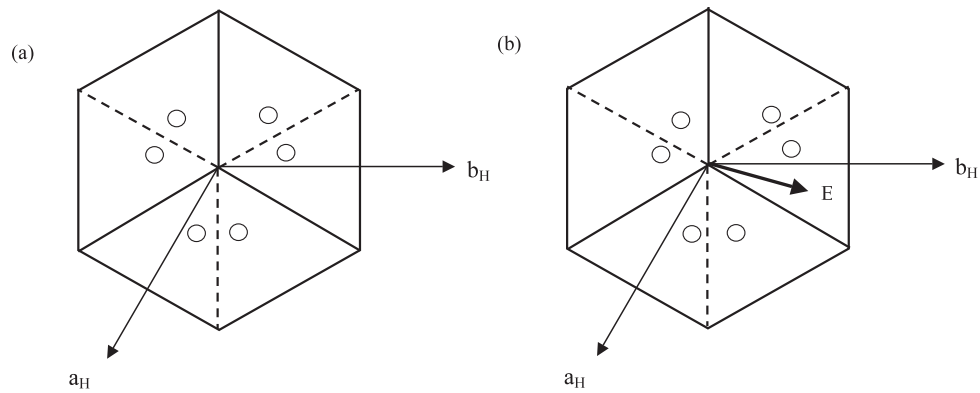


Figure 3. Simplified symmetry diagram of the rhombohedral space group $R3m$ viewed along $[111]_R$ ($[001]_H$) adapted from [24]. (a) shows the symmetry of the undistorted cell and (b) illustrates that the effect of a general electric field is to destroy the 3 mirror planes. In the special case of a field vector contained within one of the mirror planes (e.g. a field along one of the $(100)_R$ directions), that mirror plane is retained.

of the $(100)_R$ directions of the rhombohedral unit cell, depending on the poling direction chosen. However, the irreps of space groups are defined with respect to orthogonal axes, as are the tensor quantities ε_{jk} and d_{ijk} . In operating on rhombohedral space groups, the program ISOTROPY uses the hexagonal unit cell and then orthogonal axes defined by $a'_o = \frac{1}{2}[210]_{aH}$, $b'_o = b_H$ and $c'_o = c_H$. Within this setting, $[100]_R$ becomes $\frac{1}{3}[201]_o$.

To determine the effect of an electric field E along $[100]_R$ we first resolve this field into its components along the principal axes of the orthogonal cell. On substituting for the unit cell dimensions of PZN–PT we obtain $(0.816, 0, 0.577)E$, where E is the magnitude of E . Substituting into (1) and expanding gives the strain tensor:

$$\varepsilon = \begin{pmatrix} 0.577d_{311} + 0.816d_{111} & 0 & 0.816d_{113} \\ 0 & 0.577d_{311} - 0.816d_{111} & 0 \\ 0.816d_{113} & 0 & 0.577d_{333} \end{pmatrix} E. \quad (2)$$

Combining the entries as indicated in table 1, we note that the only non-zero deformations are:

$$\begin{aligned} \varepsilon_{11} - \varepsilon_{22} &= 1.632d_{111}E && \text{(imposes monoclinic symmetry in } Cm) \\ \varepsilon_{13} &= 0.816d_{113}E && \text{(imposes monoclinic symmetry in } Cm) \\ \varepsilon_{11} + \varepsilon_{22} &= 1.154d_{311}E && \text{(no effect on symmetry)} \\ \varepsilon_{33} &= 0.577d_{333}E && \text{(no effect on symmetry)}. \end{aligned}$$

The implication is that, in a truly single crystal of rhombohedral PZN–PT, an infinitesimal electric field along *any* of the rhombohedral unit cell edges ($[100]_R$, $[010]_R$ or $[001]_R$) causes a monoclinic deformation of the unit cell, and the result can be described in space group Cm .

The argument may be visualized by considering the rhombohedral structure set in the standard hexagonal unit cell (figure 3(a)). The symmetry elements of $R3m$ are a 3-fold rotation (about $[001]_H$ or $[111]_R$) and mirror planes perpendicular to b_H , a_H and $-(a_H + b_H)$. The mirror planes in fact contain the rhombohedral axes ($[100]_R$, $[010]_R$ and $[001]_R$). It may be seen that a general distorting field (E_1, E_2, E_3) destroys all the mirror symmetry. If however the electric field lies along a rhombohedral axis that is within one of the mirror planes, that mirror plane is preserved by the deformation. Reference to the *International Tables for Crystallography*, Volume A [24], confirms that the only maximal *translationengleiche* (type I) subgroup of $R3m$ preserving a mirror plane is indeed Cm .

It is impossible to distinguish this purely piezoelectric distortion from a phase transition by diffraction or other crystallographic means, because the symmetry has genuinely been reduced to monoclinic in the presence of the electric field. The question of whether PZN–PT undergoes a field induced $R \rightarrow M$ phase transition or not becomes far more subtle and is reserved for section 4. Some inferences may be made from diffraction-derived structural information as a function of electric field strength, however this information is strongly influenced by the complex domain structure of the crystals.

4. Discussion

In sections 2 and 3, we demonstrated that an $R \rightarrow M$ phase transition is not required for monoclinic diffraction patterns to be observed. The piezoelectric distortion of any rhombohedral ($R3m$) ferroelectric perovskite by a field along one of the rhombohedral axes produces a monoclinic unit cell conforming to the space group Cm . In this section we will consider whether the observed behaviour in PZN–PT is best described by a genuine phase transition or not.

Phase transitions are defined (and observed) as discontinuities in a physical characteristic or its derivative(s) in response to a change in a state variable such as temperature or electric field. Conversely, without a phase transition all physical characteristics, and all their derivatives, vary with respect to state variables in a continuous manner. Phase transitions in crystalline materials often result in a change in crystal symmetry, but the converse, that a change in crystal symmetry implies a phase transition, is not strictly correct. For example, a tetragonal structure will necessarily become orthorhombic if a mechanical stress is applied along a non-unique axis. However, if no phase transition occurs, all characteristics, and the *apparent symmetry* of these characteristics, will vary smoothly with respect to the applied stress. The induced distortions are generally small and, depending on the measurement probe and the purpose for which the measurement is made, the material is often regarded as if the symmetry was unaltered.

A distinction can be made between our piezoelectric strain hypothesis and a true $R \rightarrow M$ phase transition if the spontaneous polarization can be determined. We have shown that in both cases an electric field along $[100]_R$ will lower the symmetry from $R3m$ to Cm . This will allow the polarization to rotate from $\langle 111 \rangle_R$ to a direction $\langle 1 + \delta, 1 - \delta, 1 - \delta \rangle_R$. In our piezoelectric strain hypothesis the value of δ must vary continuously with respect to the order parameter and hence the external electric field. In particular, for zero external field, δ must be zero and the polarization must be equal to that expected in the rhombohedral case. This would not be expected for the $R \rightarrow M$ phase transition hypothesis, as the transition must be first order implying some hysteresis. There is some experimental support for our case from the measured remanent polarization, P_R , for PZN [2] and PZN–8% PT [25]. In both cases the P_R for samples poled along $\langle 111 \rangle$ and $\langle 001 \rangle$ obey the rule $P_R \langle 001 \rangle = 1/\sqrt{3} P_R \langle 111 \rangle$, consistent with the individual domains of the $\langle 001 \rangle$ poled samples being rhombohedral with spontaneous polarizations along $\langle 111 \rangle_R$ [2].

Proponents of the $R \rightarrow M$ phase transition report that the monoclinic symmetry sometimes persists after removal of the electric field. According to the latest work [16], this only occurs over a relatively small composition range close to the morphotropic phase boundary. Furthermore, it has been reported that the retained monoclinic distortion is destroyed by grinding the crystals to below $38 \mu\text{m}$ [12, 15]. This suggests that the retained zero field distortion is due to residual strains trapped in the crystals by the domain structure or incipient nuclei of the tetragonal phase. Evidence for the latter is found in optical microscopy [7, 26] and neutron diffraction [14]. It appears that grinding allows the residual strains to be relaxed and in addition may cause some ferroelastic reorientation of the domains.

Table 2. Elastic compliances of PZN–PT and some other ferroelectric perovskites.

Material	s_{ij}^E (10^{-12} Pa $^{-1}$)					
	s_{11}	s_{12}	s_{13}	s_{33}	s_{44}	s_{66}
BaTiO ₃ single crystal (see [28])	8.05	−2.35	−5.24	15.7	18.4	8.84
PZT poled poly-crystal (see [29])	15.5	−4.0	−8.3	21.2	45.0	38.9
PZN–8% PT multi-domain single crystal poled along [001] (see [30])	87	−13.1	−70.0	141	15.8	15.4

Irrespective of whether the monoclinic distortion is a phase transition or not, it is not itself sufficient to explain the magnitude of the strains. The magnitude of piezoelectric strains is not fundamentally linked to symmetry, but to the piezoelectric moduli and ultimately to the elastic constants⁶. The elastic constants of PZN–PT are known to be up to nine times softer than in comparable ferroelectric perovskites. Some reported values are compared in table 2. It has been suggested previously by Kuwata *et al* that the elastic compliance may be the source of the large piezoelectric coefficients [1] and this was recently extended to the large piezoelectric strains in two-phase 9% PT samples [9]. Examination of the maximum piezoelectric strain across the temperature–composition phase diagram shows a steady increase as the morphotropic (R–T) phase boundary is approached. There is a parallel increase in the elastic compliances. Since composition is a state variable it is possible to consider, at a constant temperature, an R → T phase transition as a function of composition. We propose that as the % PT in rhombohedral PZN–PT increases, the approaching transition leads to significant softening of some elastic constants and this is ultimately responsible for the giant piezoelectric response. For a pseudo-cubic phase (R), the elastic softening required lies along the pseudo-cubic unit cell edges (i.e. along $\langle 001 \rangle_R$) because this is the direction of the order-parameter driven transition to the tetragonal phase at approximately 9–10% PT. The R → T transition is required to be first order. However, given the narrowness of the two-phase region it may well be only weakly first order (i.e. close to tri-critical).

The acid test of our hypothesis is whether it can explain the unequivocal observations in the introduction, particularly (i), (iv) and (v). It explains the monoclinic distortion in the data of Noheda *et al* very well. It explains why the monoclinic distortion is continuous whereas an R → M phase transition is required to be first order. It gives a rationale for why the elastic constants are soft and how this leads naturally to large piezoelectric strains along $\langle 001 \rangle_R$. Observations (vi) and (vii) relating to retention of the monoclinic distortion are consistent with residual stress mediated by the micro-domain structure and possibly two-phase nature of some crystals. A quantitative connection is beyond the scope of this work. It is important to note here that the mechanism proposed does not in any way preclude a genuine electric field induced first order R → T transition at high field.

We close with a few comments on the polarization rotation model. In the literature on PZN–PT, the monoclinic phases and the rotation of the polarization vector appear to be intricately linked. This linkage may be due to the belief that in a rhombohedral phase the polarization is restricted in direction to $\langle 111 \rangle_R$ and so only its magnitude can change. But this is only strictly true when the external field is zero or lies along the polar axis. Our hypothesis does not preclude polarization rotations, but it does imply that the rotation is continuous with respect to the electric field and equal to zero for zero electric field. Some polarization rotation under an

⁶ The piezoelectric moduli are related to the elastic compliances via $d_{ijk} = e_{ilm}s_{lmjk}^E$ [27]. The electromechanical coupling constants e_{ilm} are dependent on crystal structure and are expected to be relatively constant over the range of perovskites considered here. Hence, the d_{ijk} are approximately linear in the s_{lmjk} .

electric field will necessarily occur as it is a factor in the total energy and is allowed because the induced distortion has removed the symmetry constraint. This is what was observed for BaTiO₃ by Fu and Cohen [4] whose density functional theory calculations were performed on what are essentially distorted rhombohedral cells. It should be noted though that no direct observations of polarization rotation in PZN–PT exist. In fact the only relevant polarization measurements, that of the remanent polarization of [001] poled PZN–PT, suggest that the polarization rotation is zero for zero applied field which is more in keeping with our piezoelectric strain hypothesis than that of an R → M transition.

5. Conclusions

In this paper, we have argued that an R → M phase transition is unnecessary to explain the experimental observations as long as we take into account the unusually soft elastic constants of PZN–PT. Confirmation of the origin of this softness is beyond the scope of this paper however we have speculated that it may be associated with the approach to the composition driven R → T phase transition. What should be stressed is that there is no compelling evidence that the softness is due to an R → M phase transition. The observation of very large piezoelectric strains and monoclinic distortions in the PZN–PT system are equally well understood in terms of a simple piezoelectric distortion of the parent rhombohedral phase mediated by the soft elastic constants. When the distortion becomes very large, there may be a genuine first order transition to the tetragonal phase.

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References

- [1] Kuwata J, Uchino K and Nomura S 1981 *Ferroelectrics* **37** 579–82
- [2] Park S-E and Shrout T R 1997 *J. Appl. Phys.* **82** 1804–11
- [3] Forrester J S, Piltz R O, Kisi E H and McIntyre G J 2001 *J. Phys.: Condens. Matter* **13** L825–33
- [4] Fu H and Cohen R E 2000 *Nature* **403** 281–3
- [5] Kobayashi T, Shimanuki S, Saitoh S and Yamashita Y 1997 *Japan. J. Appl. Phys.* **36** 6035–8
- [6] Paik D-S, Park S-E, Wada S, Liu S-F and Shrout T R 1999 *J. Appl. Phys.* **85** 1080–3
- [7] Ye Z-G, Dong M and Zhang 1999 *Ferroelectrics* **229** 223–32
- [8] Fujishiro K, Vlokh R, Uesu Y, Yamada Y, Kiat J-M, Dkhil B and Yamashita Y 1998 *Japan. J. Appl. Phys.* **37** 5246–8
- [9] Ogawa T, Yamauchi Y, Numamoto Y, Matsushita M and Tachi Y 2002 *Japan. J. Appl. Phys.* **41** (1AB) L55–7
- [10] Vanderbilt D and Cohen M H 2001 *Phys. Rev. B* **63** 094108
- [11] Noheda B, Cox D E, Shirane G, Park S-E, Cross L E and Zhong Z 2001 *Phys. Rev. Lett.* **86** 3891–4
- [12] Cox D E, Noheda B, Shirane G, Uesu Y, Fujishiro K and Yamada Y 2001 *Appl. Phys. Lett.* **79** 400–2
- [13] Noheda B, Zhong Z, Cox D E, Shirane G, Park S-E and Rehring P 2002 *Phys. Rev. B* **65** 224101
- [14] Ohwada K, Hirota K, Rehrig P W, Gehring P M, Noheda B, Fujii Y, Park S-E and Shirane G 2001 *J. Phys. Soc. Japan* **70** 2778–83
- [15] Noheda B, Cox D E and Shirane G 2001 IMF-10 (*Madrid, Sept. 2001*)
- [16] La-Orauttapong D, Noheda B, Ye Z-G, Gehring P M, Toulouse J, Cox D E and Shirane G 2002 *Phys. Rev. B* **65** 144101
- [17] Noheda B, Cox D E, Shirane G, Gonzalo J A, Cross L E and Park S-E 1999 *Appl. Phys. Lett.* **74** 2059–61
- [18] Noheda B, Gonzalo J A, Cross L E, Guo R, Park S-E, Cox D E and Shirane G 1999 *Phys. Rev. B* **61** 8687–95

-
- [19] Noheda B, Cox D E, Shirane G, Guo R, Jones B and Cross L E 2000 *Phys. Rev. B* **63** 14103
- [20] Nomura S, Takahashi T and Yokmizo Y 1969 *J. Phys. Soc. Japan* **27** 262
- [21] Shimanuki S, Saito S and Yamashita Y 1998 *Japan. J. Appl. Phys.* **37** 3382–5
- [22] Stokes H T and Hatch D M 'ISOTROPY'—www.physics.byu.edu/~stokesh/isotropywww.html
- [23] Stokes H T, Kisi E H, Hatch D M and Howard C J 2002 *Acta Crystallogr. B* **58** 934–8
- [24] 1989 *International Tables for Crystallography, Volume A: Space Group Symmetry* (Dordrecht: Kluwer–Academic) pp 19–20 and p 520 IUCr
- [25] Viehland D 2000 *J. Appl. Phys.* **88** 4794–806
- [26] Belegundu U, Du X H, Cross L E and Uchino K 1999 *Ferroelectrics* **221** 67–71
- [27] Nye J F 1957 *Physical Properties of Crystals* (Oxford: Oxford University Press) p 183
- [28] Jaffe B, Cook W R and Jaffe H 1971 *Piezoelectric Ceramics* (London: Academic) p 74
- [29] TRS Ceramics www.trsceramics.com/property.html
- [30] Zhang R, Jiang B, Jiang W and Cao W 2003 *Mater. Lett.* **57** 1305–8