



Morphotropic Phase Boundary Perovskites, High Strain Piezoelectrics, and Dielectric Ceramics

Edited by
Ruyan Guo
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Proceedings of the Dielectric Materials and Multilayer Electronic Devices Symposium and the Morphotropic Phase Boundary Phenomena and Perovskite Materials Symposium held at the 104th Annual Meeting of The American Ceramic Society, April 28–May 1, 2002 in St. Louis, Missouri and the High Strain Piezoelectrics Symposium held at the 103rd Annual Meeting of The American Ceramic Society, April 22–25 2001 in Indianapolis, Indiana.

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Cover photo: Microstructure of the fracture surface of a green barium titanate compact after binder burn-out is courtesy of T. Sugawara, M. Shimizu, T. Kimura, K. Takatori, and T. Tani, and appears as figure 12 in their paper "Fabrication of Grain Oriented Barium Titanate," which begins on page 389.

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Preface

The content of this Ceramic Transactions volume comprises the proceedings of the symposium on dielectric materials and multilayer electronic devices and the symposium on morphotropic phase boundary phenomena and perovskite materials, held April 28–May 1, 2002, during the 104th Annual Meeting of The American Ceramic Society (ACerS) in St. Louis, Missouri and the focused session on high strain piezoelectrics, held April 22–25, 2001, during the 103rd Annual Meeting of ACerS in Indianapolis, Indiana.

The Electronics Division of ACerS led the organization of the three symposia featured in this volume. The symposium on dielectric materials and multilayer electronic devices focused on the latest scientific and technological developments in multilayer electronics, with papers covering a range of topics—from assessment to the state-of-the-art in materials development and device fabrications. The focused session on high strain piezoelectrics addressed the recent progress on the development of high strain ferroelectric perovskite materials, particularly their crystal growth and textured ceramic synthesis for commercial and defense applications. The symposium on morphotropic phase boundary phenomena and perovskite materials was a consecutive effort following the focused session on high strain piezoelectrics to explore further the structure-property relationships connected with the morphotropic phase boundary, particularly of perovskite ferroelectric materials.

Forty-eight papers are featured in this volume. They are organized into four parts: morphotropic phase boundary material systems and their structure-property-chemistry relations; synthesis of high strain piezoelectric crystals and textured ceramics; dielectric materials development and device fabrications; and materials and design issues for piezoelectric materials.

The organizers of these symposia acknowledge the contributions of the invited speakers, oral and poster presenters, symposium session chairs, and the ACerS program coordinators for making these symposia successful.

The editors of this volume express their sincere appreciation to all authors and manuscript reviewers for their efforts in making this volume possible. The Basic Science Division of ACerS and the Ceramic Society of Japan is acknowledged for their co-sponsorship for the symposium on dielectric materials and multilayer electronic devices.

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Morphotropic Phase Boundary Material Systems and Their Structure-Property-Chemistry Relations

LOCAL ATOMIC STRUCTURE AND MORPHOTROPIC PHASE BOUNDARY

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ABSTRACT

While the crystallographic structure shows a sharp change at the morphotropic phase boundary (MPB), the local atomic structure, determined by the pulsed neutron atomic pair-density function (PDF), varies continuously across the boundary. This implies that local properties change smoothly across the boundary, and the nature of the transition is of the order/disorder type. It poses a serious question on placing undue emphasis on symmetry, and suggests that we should take a local view in trying to understand the phenomena related to the MPB, such as piezoelectricity in PZT.

INTRODUCTION

The energy of atomic bond in most ceramic materials is of the order of 1 eV, far larger than thermal energy, kT . Thus ceramics are "hard" materials, which do not respond well to external forces. Near the phase transition, however, the free energies of two phases are close to each other, and therefore small forces can affect the balance between the phases, and consequently hard materials can exhibit "soft" materials behavior. For this reason the needs of functional materials often drive the researchers to look into materials in the vicinity of phase transition. A morphotropic phase boundary (MPB) is one of these phase boundaries, and has been used in producing highly responsive materials, such as $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) [1]. It should be noted, however, that even when the free energies of the two phases are close to each other, there usually is an energy barrier for the system to overcome in going through the transition, except for the case of a perfect second order transition with a soft-mode. Thus the sensitivity of the material depends upon the nature of the phase transition and the phase boundary.

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The MPB of PZT divides the tetragonal phase in the Ti-rich side and the orthorhombic phase on the Zr-rich side of the phase diagram. The two structures are related by mechanical shear, and indeed at low temperatures an intermediate monoclinic structure was found at low temperatures, which smoothly bridge the two phases [2]. Crystallographically the phase changes are well defined with definite changes in symmetry. The lattice constants continuously but strongly change through the MPB, and thus one may expect the properties to change rather drastically at the boundary. However, many properties change rather smoothly across the MPB. In this paper we show that the local structure changes little across the boundaries, and this is the reason why properties evolve smoothly across the boundaries.

METHOD OF PDF ANALYSIS

The atomic structure of crystalline solids is usually described by a crystallographic structure. The crystal structure, however, assumes perfect periodicity in the atomic arrangement, while the real structure could be deviated from it. Strictly speaking the atomic structure is never periodic because of lattice thermal or quantum vibration. It is well known, however, in the case of harmonic oscillation this effect can be described quite well by the Debye-Waller factor. The trouble is that even though real deviations are rarely harmonic, people tend to use the Debye-Waller approximations indiscriminately. While local disorder is often described in terms of the excess Debye-Waller factor, it is dangerous to take the values of the Debye-Waller factor too seriously [3].

On the other hand the method of atomic pair-density function (PDF) describes local deviations without an approximation. The PDF, $\rho_0 g(r)$, is given by

$$\rho_0 g(r) = \frac{1}{2\pi^2} \int_0^\infty [S(Q) - 1] \sin(Qr) Q dQ \quad , \quad (1)$$

where ρ_0 is the atomic density, $S(Q)$ is the structure function, and $Q (= 4\pi \sin \theta / \lambda)$ is the scattering vector, where θ is the diffraction angle [3,4]. The structure function $S(Q)$ is obtained from the diffraction intensity as a function of Q after corrections for absorption, normalization, background, incoherent scattering and multiple-scattering. It is important that $S(Q)$ includes not only the Bragg peaks but also the diffuse scattering, which often is dismissed as a part of background in the crystallographic analysis. Because it includes diffuse scattering the PDF can describe both the periodic and aperiodic components of the structure. This method has long been used in the study of liquids and glasses, but its use for crystals with disorder became feasible because of the advent of synchrotron based sources such

as pulsed neutron sources or synchrotron radiation sources [5]. This is because theoretically the integration in eq. (1) has to be carried out to infinity in Q , while the upper limit of Q is set by the wavelength of the probe, since $Q < 4\pi/\lambda$. Terminating the integration at Q_{max} produces error called termination error. The value of Q_{max} has to be sufficiently large to reduce the termination error to a negligible amount. With the regular x-ray sources in the laboratory Q_{max} is only about $17 \text{ \AA}^{-1}$ with a Mo tube, and with thermal neutron sources Q_{max} is even lower, around $12 \text{ \AA}^{-1}$. With pulsed neutron sources it is now extended to $35 - 40 \text{ \AA}^{-1}$, which produces termination error small enough to be comparable to statistical noise [6].

PDF OF PZT

The pulsed neutron diffraction data of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.4, 0.48, 0.6$) were obtained at $T = 10 \text{ K}$ with the GPPD spectrometer of the IPNS at Argonne National Laboratory. The data were first processed by the Rietveld analysis to determine the average crystallographic structure. The results confirmed the earlier report [2] on the symmetry of the crystals, namely, 60%-Ti (tetragonal phase, $P4mm$), 48%-Ti (monoclinic phase, Cm) and 40%-Ti (rhombohedral phase, $R3c$, the so called "low temperature rhombohedral" phase) [7]. The PDF's calculated from the Rietveld results (lattice constants, atomic positions and the thermal fac-

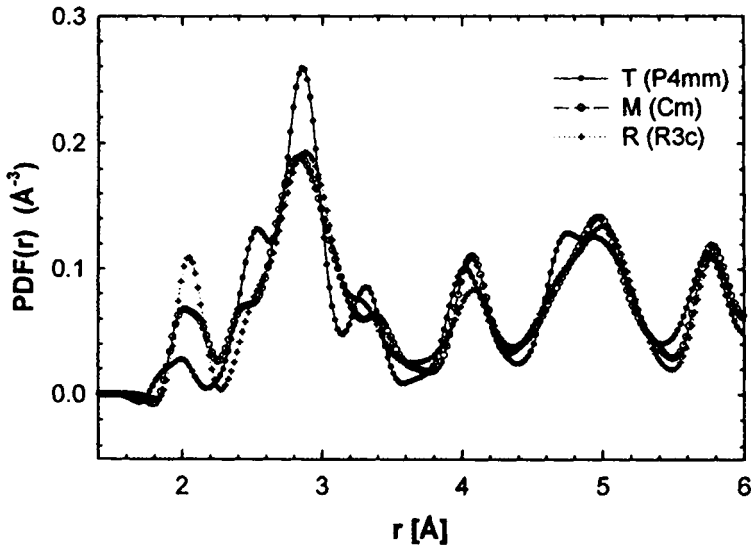


Fig. 1 The PDF of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.4, 0.48, 0.6$) calculated using the results of the Rietveld analysis of the pulsed neutron diffraction data.

tors) are shown in Fig. 1. Reflecting the change in the symmetry the PDF's of the three phases differ considerably. In contrast the actual PDF obtained from the same data, shown in Fig. 2, show much less differences among the three. Note that the Rietveld analysis is based only upon the Bragg peak position and intensity, while the PDF contains the information on local disorder by including the diffuse scattering as well. It is clear that it is dangerous to rely upon the crystal structure when we consider the changes in the properties with composition over this portion of the phase diagram.

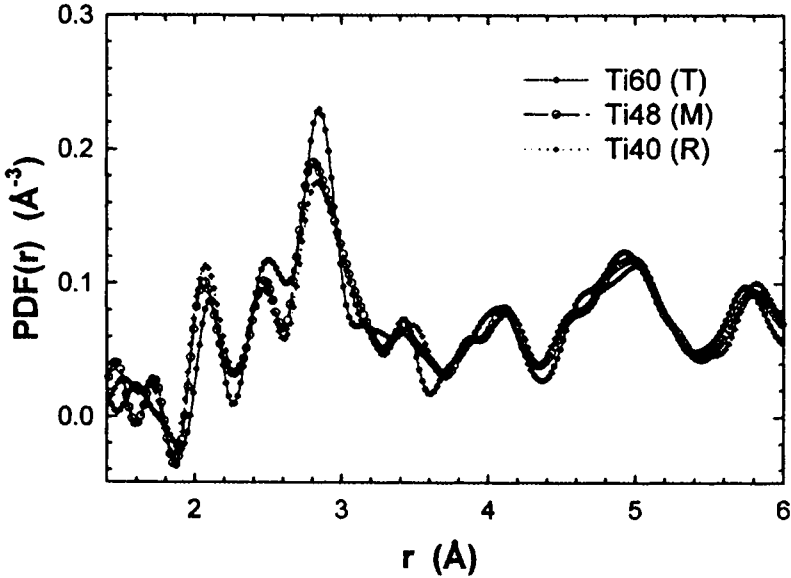


Fig. 2. The PDF of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.4, 0.48, 0.6$) obtained from the same data set used for the Rietveld analysis, but by direct Fourier-transformation (eq. (1)) including the diffuse scattering intensity. Note that the differences among the three PDF's are much less than in Fig. 1.

COMPARISON WITH THE AVERAGE STRUCTURE

We will now compare more carefully the measured PDF with the PDF calculated for the average structure using the parameters obtained by the Rietveld analysis (model PDF) for each composition. Figs. 3 - 5 compare the PDF's up to 3.5 Å. The most pronounced differences are the following:

1. In the $x = 0.4$ sample the peak at $2.45 \text{ \AA}$ is clearly seen in the measured PDF, while it is smeared in the calculated PDF.
2. In the $x = 0.48$ sample the shape and height of the $2.0 \text{ \AA}$ peak are different. Again the peak at $2.45 \text{ \AA}$ is more clearly seen in the measured PDF than in the calculated PDF.
3. In the $x = 0.6$ sample the first peak is very different between the two.

Comparison of the PDF's from $4 \text{ \AA}$ to $10 \text{ \AA}$ shows that the agreement is best for the $x = 0.6$ sample, then the $x = 0.4$ sample, and the $x = 0.48$ sample shows the worst agreement.

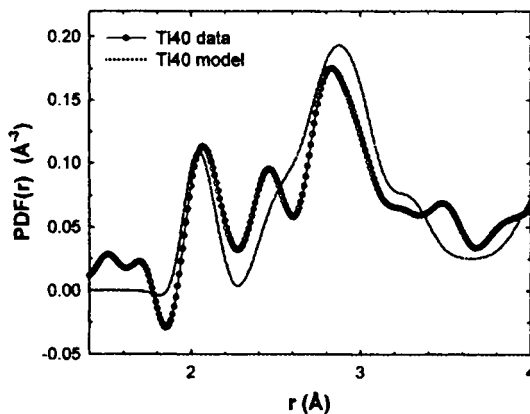


Fig. 3 Model and measured PDF's for the $x = 0.4$ (R) sample.

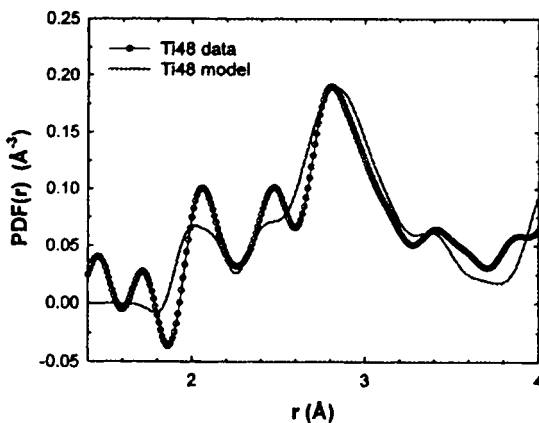


Fig. 4 Model and measured PDF's for the $x = 0.48$ (M) sample.

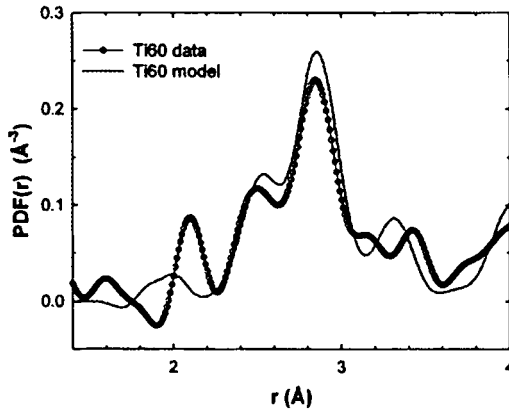


Fig. 5 Model and measured PDF's for the $x = 0.6$ (T) sample.

(Ti,Zr)-O Peak

The partial PDF's for the Ti-O and Zr-O peaks calculated for the crystal structure are shown in Figs. 6 and 7. The Ti-O peak is negative because of the negative neutron scattering length of Ti. In the T phase Ti is off-centered on the TiO_6 octahedron in the [100] direction. In the R phase Ti is displaced along the cubic [111] axis toward the face-center of the TiO_6 octahedron. In the crystal structure Ti and Zr occupy equivalent sites and have the same environment, since it assumes perfect periodicity and random mixing of Ti and Zr. The measured first peak includes both the Ti-O correlation and the Zr-O correlation, and is shown in Fig. 8 for three phases. Since negative Ti-O peaks and positive Zr-O peaks cancel each other it is a little difficult to sort out each contribution. For instance in the average structure both the Ti-O and the Zr-O correlations have a peak at 2.0 Å, and thus they almost completely cancel each other in the T phase as shown in Fig. 1. However, the measured PDF peak differs considerably except for the R phase.

The main reason for this discrepancy is that in the average structure Ti and Zr occupy equivalent sites and have the same environment, so that the Ti-O bonds and the Zr-O bonds are assumed to have the same lengths and always cancel each other in the PDF, and the composition dependence only changes the degree of cancellation. However, in reality Ti-O bonds are not equal to Zr-O bonds in length. Because Ti^{4+} is smaller than Zr^{4+} , the negative Ti-O peaks tend to appear in the left of the Zr-O peaks, allowing us to study them separately.

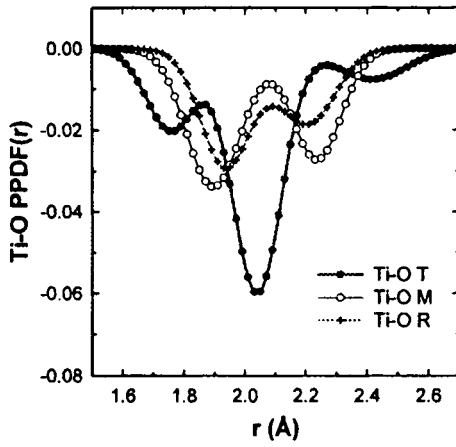


Fig. 6 The Ti-O peak calculated with the parameters determined by the Rietveld analysis for each phase.

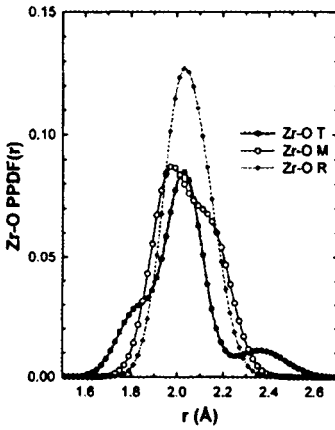


Fig. 7 The Zr-O peak calculated with the parameters determined by the Rietveld analysis for each phase.

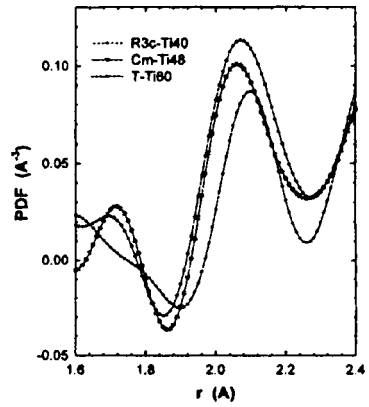


Fig. 8 Measured PDF's for the three phases in the region of (Ti,Zr)-O peak.

The shape of the first peak of the measured PDF is similar for all three phases, with a negative sub-peak around 1.85 – 1.9 Å and a positive sub-peak around 2.05 Å. Obviously the first negative sub-peak is due to Ti-O correlation, while the second positive sub-peak describes the Zr-O bonds. While there may be partial cancellation of the Ti-O and Zr-O peaks due to overlap, cancellation is far from complete as in the model structure. The measured PDF proves that the TiO_6 octahedra are smaller than the ZrO_6 octahedra, as expected from crystal chemistry. This point was confirmed by the recent LDF calculation [8].

It is clear that the Zr-O peak is not strongly split in any of these phases, suggesting that Zr-O bond is little bifurcated, as is in the T phase. This result is in strong disagreement with the implication of the average structure, which assumes that Zr is equally polarized as Ti. However, this is reasonable since a Zr^{4+} ion is a large ion that barely fit in the ZrO_6 octahedron and does not leave a space for reduction in the bondlength. The tetragonal structure of PbTiO_3 exists because Ti-O bond can be strongly compressed through the off-centering of Ti ion. Since Zr-O bond cannot be much compressed, Zr is incompatible with the tetragonal structure. ZrO_6 octahedra may still be polarized through bending of the O-Zr-O bond, which distorts the O_6 cage (transverse polarization), but it is not polarized in the longitudinal manner with the modification of the Zr-O bondlength as in TiO_6 . Since the tolerance factor of PbZrO_3 is appreciably less than one (0.973), ZrO_6 octahedra become rotated with the increased Zr content, resulting in a rhombohedral or orthorhombic structure.

On the other hand the Ti-O peak appears to be always split, suggesting strong polarization of Ti ions. Upon closer examination the negative peak in the R and M phases is consistent with the Ti polarization along [111], while that in the T phase suggests polarization along [100], both in agreement with the average structure, except that the bondlengths are overestimated in the average structure.

Pb-O Peak

The partial PDF for Pb-O correlation calculated for the average structure is shown in Fig. 9. The measured second peak of the PDF shown in Fig. 10 includes both the Pb-O peak and the O-O peak at 2.8 Å. The peak at 2.45 Å is prominently seen in the measured PDF for all three phases, while in the calculated partial PDF that peak is prominent only in the T phase, and not resolved in the M and R phases. On the other hand the peak at 3.3 Å in the model PDF of the T phase is absent in the measured PDF.

It is interesting to note that the 2.45 Å Pb-O peak is strong also in PbZrO_3 (orthorhombic), and is seen almost always in the Pb containing perovskite crystals [9]. This peak is due to the strong Pb-O covalent bonds that always off-center Pb in the O_{12} cage. Therefore we conclude that Pb ion is always off-centered even in the R and M phases, either along [100] as in PbTiO_3 or along [110] as in PbZrO_3 .

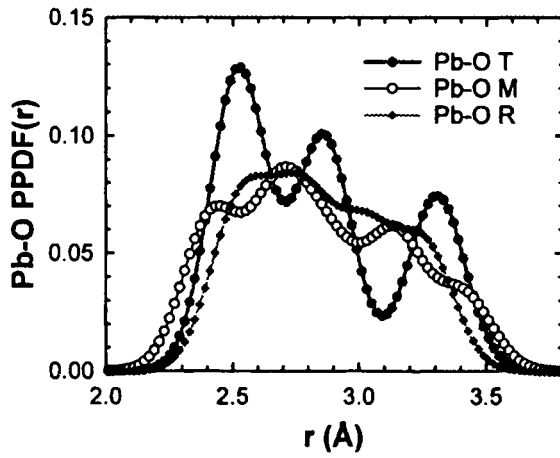


Fig. 9 Calculated Pb-O peak of the PDF for three samples.

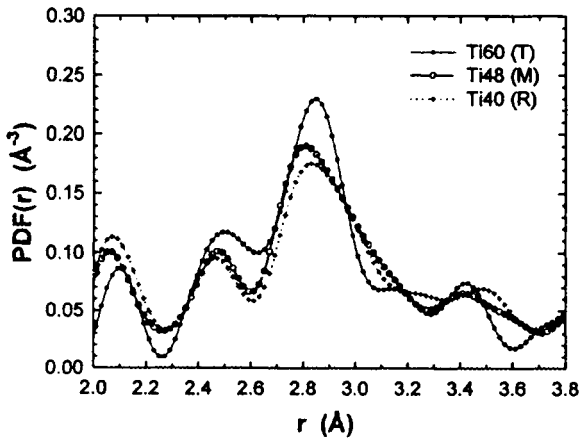


Fig. 10 Measured PDF's in the region of the second peak (Pb-O and O-O peaks) for three phases. The peaks at 2.05 - 2.1 Å are part of the first peak (Zr-O).

Pb polarization is non-collinear, varying from site to site, and in the R phase it is along the [111] direction only in average. This conclusion is in agreement with our earlier study of the R phase [10]. At the same time the Pb environment is disordered also in the T phase. The long Pb-O distances in the model T phase that produce the peak at 3.3 Å are due to non-bonding Pb-O correlation, and can easily be disturbed by disorder. Thus it is not surprising that the peak at 3.3 Å is not seen in the measured PDF of the T phase.

THE REAL LOCAL STRUCTURE

Through the comparisons above it is clear that the local structure of PZT is significantly deviated from the average structure. The local structure of each element often resembles that of a different phase; for instance the environment of Pb ion is always similar to that in the T or O (orthorhombic) phase, and the local distortions of the Zr-O bonds is similar to those in the T phase, even in the M and R phases. The results are summarized in Table 1. While the local structure of the T phase is in agreement with the average structure, those in the M and R phases are different from the average structure, suggesting that these phases are locally strongly disordered. Also, only Ti follows the average structure, while the local environments of Zr and Pb are nearly invariant.

Element\Phase	T	M	R
Ti	T	M	R
Zr	T	T	T
Pb	T	T-O	T-O

Table 1 Types of the local environment of each element in three phases of PZT.

MODEL OF PZT

Deviations of the local structure from the average structure as described above lead us to a rather different picture of the real structure of PZT than the one the crystal structure may lead us to believe. Firstly, only the T phase is a relatively homogeneous, "real" phase, while the M and R phases are "composite"

phases in which the dominant symmetries of the local components are different from the average. The crystal symmetry reflects merely a result of statistical averaging of the local distortion that varies from site to site.

To simplify the picture we note firstly that the PDF shows that the Zr-O bonds are ferroelectrically not very active. Therefore Zr could be eliminated from our consideration of the mechanism of high dielectric response, except that the transverse polarization must contribute to the total polarizability. Secondly the PbO_{12} cage is always polarized by nearly the same amount, but the direction of polarization is random in the M and R phases.

These observations lead us to a simple but clear picture of the dielectric interactions in PZT. In this model PZT is a collection of locally polarized PbO_{12} cages (local Pb polarizations), on the simple cubic (sc) lattice, connected by Ti. The change in the average crystal symmetry affects the polarization of Ti, and thus that of Pb. Since Zr is ferroelectrically inactive, replacing Ti by Zr dilutes the interaction among Pb. Zr, however, plays an important role in changing the overall symmetry because of its size, disfavoring tetragonal symmetry, and changing the dielectric constant through its transverse polarizability.

If we start from PbTiO_3 and gradually replace Ti with Zr (decrease x), tetragonal distortion of the structure decreases due to dilution of interaction by Zr. It is interesting to note that the tetragonality linearly extrapolates to zero at around 30% Ti, close to the bond percolation concentration for the sc lattice. This justifies the picture of Zr diluting the Ti interaction. T_C , however, decreases less rapidly because of the transverse polarizability of Zr maintains overall ferroelectric interaction.

At nearly 50% Ti the structure changes into M and R phases, because Zr ion is not compatible with the tetragonal structure as we discussed above. However, PbO_{12} remains polarized along [100] or [110] as in T or O phases, thus this local incompatibility or frustration leads to a disordered non-collinear structure of Pb polarization.

Note that the tetragonal distortion of PZT in the T phase linearly extrapolates to about 1/3 of that in PbTiO_3 even at $x = 0.5$. Thus it is likely that the M phase or the R phase close to MPB has local tetragonal distortion of this amount, but its direction is distributed equally in x , y and z directions, resulting in no tetragonal distortion in the average structure. Therefore the phase transition at the MPB has to be the order/disorder type with the local units with tetragonal distortion. The local structure evolves continuously, even though the average structure changes rapidly from a tetragonal structure to a nearly cubic M or R structure.

The results presented here are consistent with the findings by Raman scattering measurements. A soft-mode behavior is known to be associated with the MPB in PZT [11-13], but the soft-mode appears only on the R phase side, and

not in the T phase side. Also the modes are highly damped by disorder, on both sides of the MPB. As we have shown here the transition from the R phase to the T phase is an order/disorder transition, where the coherence of the local tetragonal units becomes infinite at the MPB. Thus a soft-mode behavior is expected. However, the transition from the T phase to the R phase is a percolative transition due to dilution by Zr, so that only the central peak is expected, rather than the soft-mode.

CONCLUSIONS

The comparison of the local structure of PZT with the average structure across the MPB illustrates the danger of discussing the properties of the solid based only on the crystal structure and changes in the symmetry. The PDF results show that locally the structure changes only gradually and continuously, and the transition from the tetragonal to rhombohedral structure occurs because the tetragonal distortion in the T phase is disrupted in the R phase, and becomes only short-range with its direction equally distributed in x , y and z directions, and thus resulting in no tetragonal distortion in the average. Thus the M and R phases are locally strongly disordered, not only because of chemical disorder, but also because the preferred environment of each element is mutually incompatible with each other. This problem is less acute in the T phase, so that the T phase suffers mainly from chemical disorder alone. In order to understand the nature of phase transition correctly, it is therefore crucial to obtain the local information, not only the information on the long-range structure.

ACKNOWLEDGMENT

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STRUCTURE AND DYNAMICS OF THE FERROELECTRIC RELAXORS $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ AND $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$

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ABSTRACT

We review some of the current research on two of the ultra-high piezoelectric relaxors $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN). The discovery of a monoclinic phase in $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) in 1999 by Noheda *et al.* forced a reassessment of the structural symmetries found near the morphotropic phase boundary in PZT, as well as in the PbTiO_3 (PT) doped systems PZN-PT, and PMN-PT. All three systems are now known to have nearly identical phase diagrams that exhibit a rhombohedral-monoclinic-tetragonal structural sequence with increasing PbTiO_3 concentration. The dynamical properties of these relaxors are controlled by the unique nature of the so-called polar nanoregions (PNR), which first appear at the Burns temperature T_d as evidenced by the onset of diffuse scattering. That this diffuse scattering persists to temperatures below the Curie temperatures of PMN (220 K) and PZN (410 K) indicates that the phase transitions in these relaxors are very different from those observed in ordinary ferroelectrics. They also differ in this regard from what would be expected in the often-quoted model based on analogy with the random field effect.

INTRODUCTION

Current relaxor research spans a wide range of technical and scientific areas, from industrial applications, to basic experimental measurements, to first-principles theoretical calculations. The relaxor systems PZN-PT and PMN-PT, which have shown the most promise in the area of device applications, were discovered during the early 1980's [1]. However impressive advances in our understanding of the origin of their exceptional piezoelectric properties have only been achieved during the last several years. These advances are summarized in a series of up-to-date review articles [2-5]. These reviews reference a large number

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of recent publications. Consequently we have targeted the focus of this review on a few recent developments that we believe are changing the direction of research on relaxors.

With respect to structural studies, the monoclinic phase first discovered in PZT [6-8] has now been documented in the two key relaxor systems PZN-PT and PMN-PT, as shown in Fig. 1. Some details of these structural aspects will be in the next section.

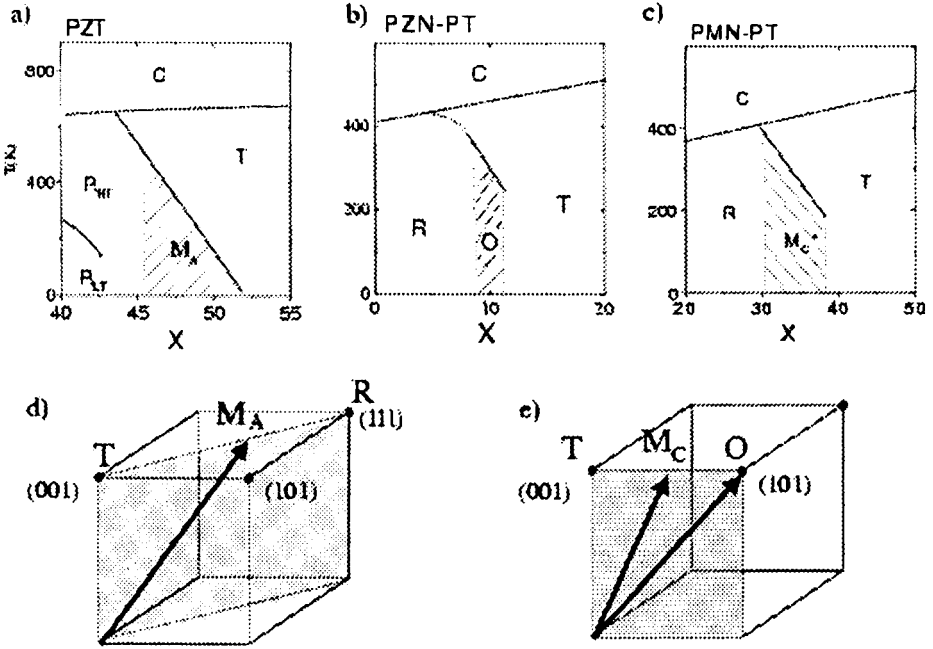


Fig. 1 Phase diagrams are shown for a) PZT, b) PZN-PT, and c) PMN-PT. The hatched regions indicate the M_A and M_C phases located near the MPB. From Noheda [3].

Gehring *et al.* have summarized the dynamical aspects of relaxor phase transitions in a recent review [2]. The existence of a true ferroelectric soft mode in these relaxor systems is now conclusively established after a series of neutron scattering experiments on PZN-PT, PZN, and PMN [9-12]. The centerpiece here is the existence of the so-called polar nanoregions, or PNR. Burns and Dacol first proposed the existence of these unique entities, which are intrinsic to relaxors, in a seminal paper [13]. The onset of the diffuse scattering at the Burns temperature T_d , and thus its connection to the PNR, was first reported in the pioneering paper

by Naberezhnov *et al.* [14]. Hirota *et al.* later related the static atomic arrangements within the PNR to the ionic vibrations of associated with the soft TO mode through an analysis of the diffuse scattering [15]. A detailed discussion of this is given in a later section. It appears now that all of the important characteristics of relaxors are attributable to the persistence of the PNR both above and below the Curie temperature T_c .

MONOCLINIC PHASES NEAR THE MPB

The existence of a narrow region of monoclinic phase located between the rhombohedral and tetragonal phases was first discovered in ceramic samples of PZT [8]. Later detailed structural studies were carried out for the PZN-PT system, where Park and Shrout [16] reported ultrahigh piezoelectric behavior. As shown in panel (b) of Fig. 1, the monoclinic phase was subsequently discovered in this system as well [17-19]. This phase is actually orthorhombic, but the M_C phase is extremely close in energy, and a very small electric field $E//[001]$ is sufficient to induce the monoclinic phase where the polarization can rotate between the O and T phases shown in panel (e) [3]. Very recently, a similar phase diagram was reported for PMN-PT [20-21].

Vanderbilt and Cohen [22] highlighted the key features of these phase diagrams in lucid fashion using a phenomenological theory. They demonstrated that only tetragonal, orthorhombic, and rhombohedral structural distortions appear when the free energy expansion is limited to 6th order. Indeed, only when one includes the 8th order term do the monoclinic phases M_A and M_C , shown in the lower part of Fig. 1, appear in the phase diagram. Both of these new monoclinic phases have already been established as one can see in the top figures. The orthorhombic phase in PZN-PT can be regarded as the end member of the M_C phase. Actually one crystal of M_C symmetry was found in PZN-9%PT [18]. The M_A phase in PZT was also derived by Bellaiche *et al.* [23] using the first-principles theoretical approach.

As emphasized by these theoretical papers, these new monoclinic phases appear only in extremely anharmonic crystals; thus they rarely exist in nature. Because of the nearly flat free-energy surfaces, these monoclinic phases can easily be transformed into other nearby phases either by electric field or mechanical stress. This is probably closely related to the great potential of these materials in industrial applications.

This phase degeneracy is manifested in many different ways in experimental observations. One example of this degeneracy is shown in the x-ray diffraction data of Fig. 2 obtained from a powder sample of PMN-35%PT [24]:

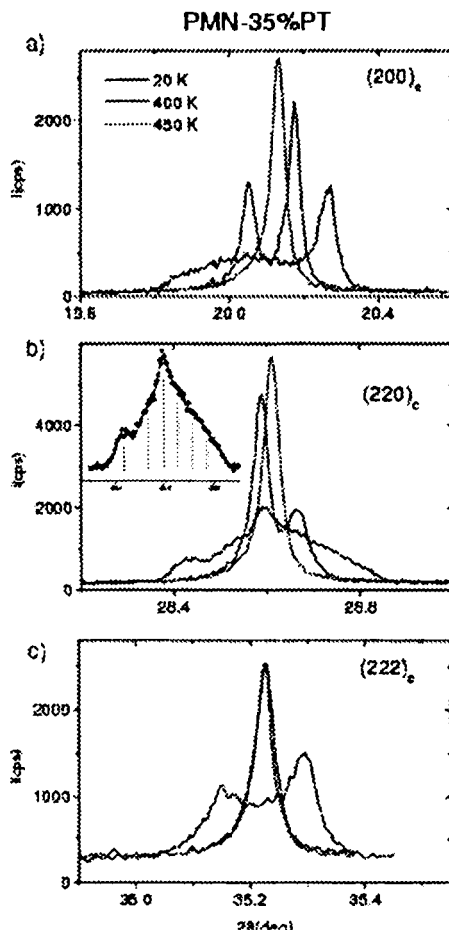


Fig. 2 X-ray profiles of powdered PMN-35%PT. From Noheda *et al.* [24].

This particular composition goes through a cubic-tetragonal-monoclinic phase sequence on cooling. As one can see clearly in Fig. 2, the x-ray profiles in the cubic (450 K) and tetragonal (400 K) phases are very sharp. Only in the monoclinic phase do the profiles become very broad. This is not due to a co-existence of two phases in the usual sense. Rather it is the flatness of the free-energy surface that permits two monoclinic structures, with slightly different lattice parameters, to coexist. In a similar fashion, an optical study of a crystal with a similar PbTiO_3 concentration reported finding different polarization directions in different parts of the crystal [25].

STRUCTURAL CHANGES UNDER ELECTRIC FIELD

The structural modifications induced by an applied electric field are, of course, one of the most intensively studied topics on high piezoelectric oxides. One of the more interesting x-ray experiments in this area was reported by Guo *et al.* [26] on ceramic PZT $x=42\%$, which is the rhombohedral phase. The standard concept of a poled ceramic at some elevated temperature involves the reorientation of preferred domains under an electric field as shown in Fig.3:

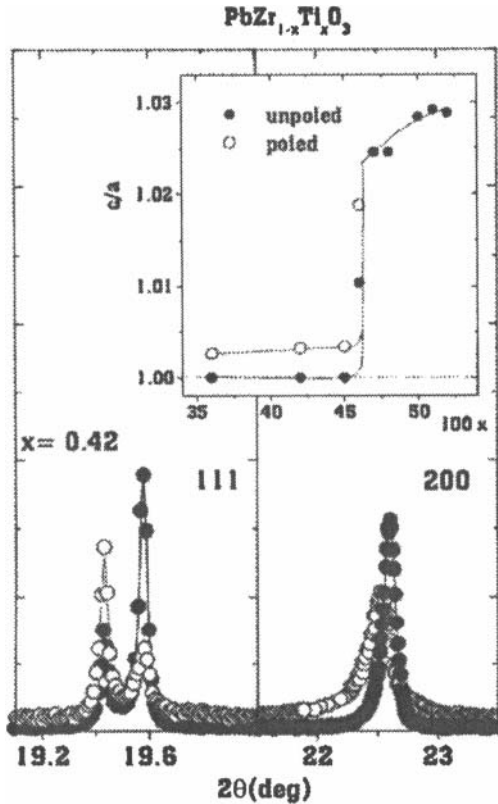


Fig. 3. Poling-induced changes in the x-ray profiles of PZT containing 42% Ti. The positions of the (200) peaks are shifted by poling, and are an indication of the induced, and retained, monoclinic phases. The inset shows unpublished data of Noheda and Guo [27]: this induced monoclinic phase is observed over a wide range of Ti concentration. From Guo *et al.* [26].

The flood of research activity on PZN-PT was sparked by the report of Park and Shrout [16] of giant strains reaching 1.6% by poling the rhombohedral concentration of PZN-8%PT along [001]. An extensive series of x-ray studies have been carried out on this crystal [17,19,21,24,28]. In contrast to the PZT system, for which only ceramic samples are available, high-quality single crystals of the relaxor PZN-PT can be grown. Noheda *et al.* [21,28] demonstrated the existence of a skin effect in this system in which the near-surface structure, of order a few microns deep, is strongly modified by the unusually strong piezoelectric coupling. In other words, the true structure of the crystal bulk can be revealed only by the use of sufficiently high-energy x-rays (~60 keV), or by use of neutrons, which by their nature are more highly penetrating than x-rays.

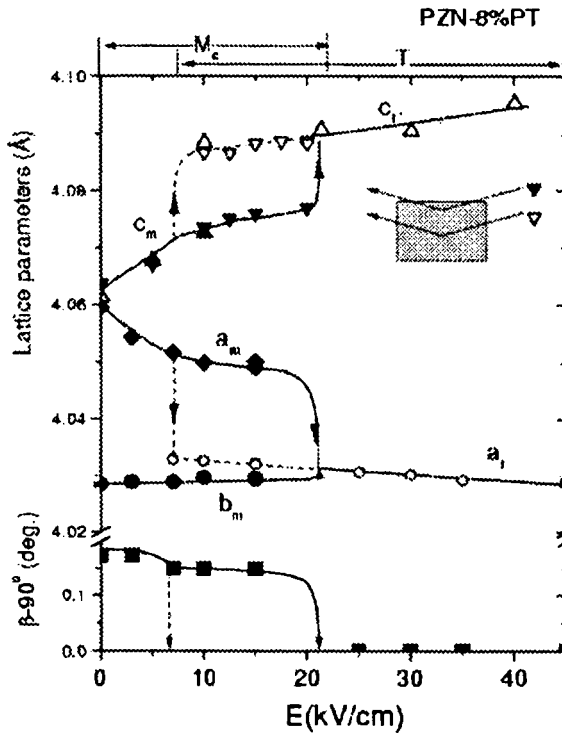


Fig. 4 Structural changes in PZN-8%PT as a function of electric field applied along [001] [24]. The crystal transforms from a high-field tetragonal phase to a low-field monoclinic M_C phase around $E = 22$ kV/cm. From Noheda *et al.* [24].

As shown in Fig. 4, the polarization sequence for PZN-8%PT involves the monoclinic phase, not the rhombohedral phase. Starting originally from the rhombohedral-to- M_A path, the system jumps over to the M_C path and stays there. This delicate polarization path was studied theoretically by Fu and Cohen [29] and Bellaiche *et al.* [30].

Very recently, Ohwada *et al.* [31] systematically studied the polarization path as a function of temperature and field-cooling history, and mapped out the phase diagram shown in Fig. 5. Their astonishing finding is the creation of the M_C phase with an electric field as low as 500 V/cm applied in the tetragonal phase. They found that the expected rhombohedral phase is never realized in the field ($E \parallel [001]$) vs. temperature phase diagram. They discovered a new phase X, which is nearly cubic, that is only established under zero-field cooling. Further discussion regarding this phase X will be given at the end of this review.

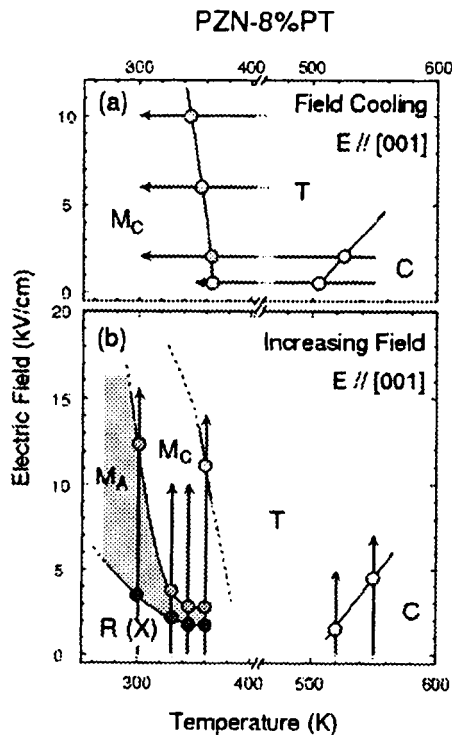


Fig. 5 Field versus temperature phase diagram of PZN-8%PT with $E \parallel [001]$. The M_A - M_C phase boundary was explicitly identified in this study. Once induced, the M_C phase remains after removal of the field. From Ohwada *et al.* [31].

PHONON DISPERSION AND WATERFALL

Different groups have measured the lattice dynamics of PMN at high temperatures using neutron scattering techniques [11,14]. Above the Burns temperature $T_d = 620$ K the dynamics of PMN are similar to those observed in cubic PbTiO_3 . A well-defined, low-frequency, transverse optic (TO) phonon is observed throughout the Brillouin zone in PMN at 1100 K, which follows the dispersion curve shown in Fig. 6 [11]. The reduced momentum transfer (wave vector) q is measured in reciprocal lattice units ($1 \text{ r.l.u.} = 1.55 \text{ \AA}^{-1}$) relative to the zone center along the $[010]$ symmetry direction.

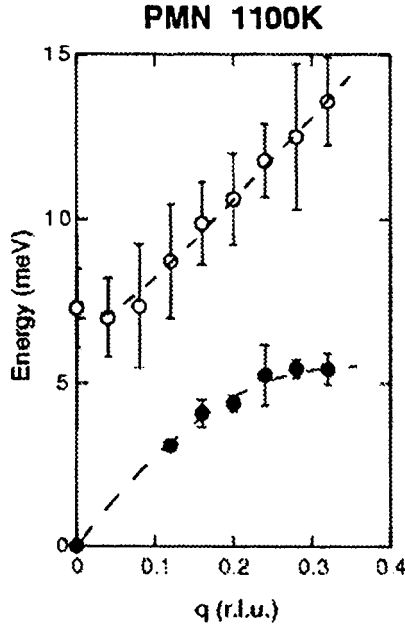


Fig. 6. Transverse optic (TO) (open circles) and transverse acoustic (TA) (solid circles) phonon dispersions in PMN measured at 1100 K along the $[010]$ direction. Vertical bars indicate the phonon linewidths. From Gehring *et al.* [11].

This situation changes with the appearance of the polar nanoregions below T_d . The polar nanostructure intrinsic to the relaxors PMN and PZN that forms below the Burns temperature effectively impedes the propagation of long-wavelength TO phonons, and gives rise to a strong wave vector dependent damping. As the phonon lifetimes decrease in response to the growing number of PNR, the corresponding phonon linewidths (which vary inversely with lifetime) increase. This is the explanation for the now well-known “waterfall” feature observed

below T_d in PZN, shown in Fig. 7, as well as in PMN, PZN-PT and PMN-PT [9,11].

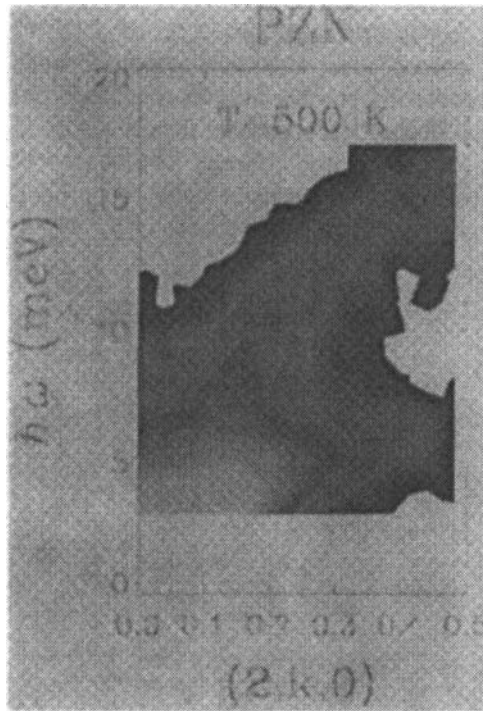


Fig. 7. Logarithmic color contour plot of the neutron inelastic scattering intensity measured in PZN at 500 K in the (200) Brillouin zone. Yellow represents the highest intensity. The vertical red region around $k = 0.14$ r.l.u. corresponds to the waterfall anomaly in which the TO phonon branch *appears* to plummet into the TA branch. From Gehring *et al.* [10].

Below T_d the long-wavelength (low- q) TO phonons become overdamped over a range of q starting from the zone center ($q=0$). In other words, no phonon peak appears in the neutron scattering spectra at non-zero frequency over this range of q . Instead, the spectral weight of the total scattering function $S(q,\omega)$ is pushed towards the elastic ($\omega=0$) channel, and a simultaneous increase in diffuse scattering is observed [14-15]. For wave vectors larger than a temperature-dependent critical wave vector q_{wf} , i.e. for sufficiently small wavelengths, a normal propagating TO phonon mode is observed. Thus q_{wf} is clearly related to the size and density of the PNR. In Fig. 7, q_{wf} is of order 0.14 r.l.u., or $0.20 \text{ \AA}^{-1}$.

However, the intrinsic value of q_{wf} is difficult to ascertain from measurements of the waterfall because the dynamical structure factor varies from one Brillouin zone to another. For this reason the vertical waterfall anomaly appears centered at different q -values for measurements made in the (200) zone compared to those made in the (300) zone. In the absence of a theoretical description of the phonon scattering cross section that provides an explicit dependence of the phonon linewidth Γ on the PNR, it is impossible to make more than a rough estimate of the intrinsic q_{wf} , and thus the intrinsic size/density of the PNR. A more quantitative, albeit phenomenological, model is provided by a mode-coupling description that is discussed in a later section.

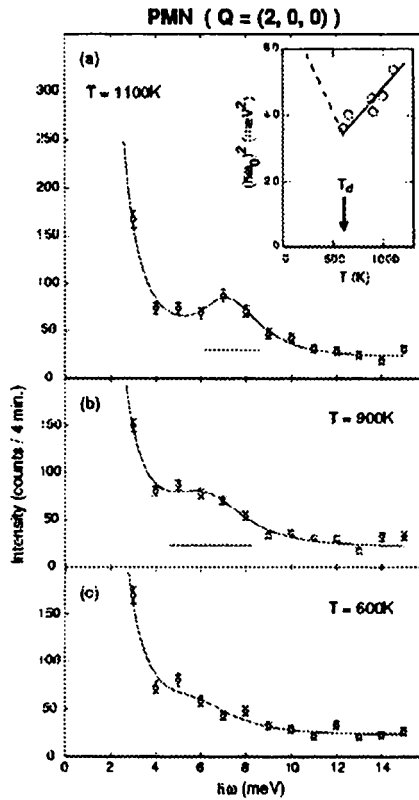


Fig. 8. Zone center TO phonon peak profiles measured at $Q = (200)$ at a) 1100 K, b) 900 K, and c) 600 K ($< T_d$). The horizontal bars indicate the intrinsic phonon linewidths. From Gehring *et al.* [11].

DISPLACED POLAR NANOREGIONS

The concept of the polar nanoregion is central to an understanding of the lattice dynamics of the relaxors PMN and PZN. The key questions concern the origin and structure of the PNR. A clue to the origin of the PNR was provided by the neutron scattering measurements by Gehring *et al.* on PMN between 1100 K and $T_d \sim 620$ K, which yielded the first unambiguous evidence of a soft TO mode in this system [11]. The data in Fig. 8 document the evolution of the zone center TO mode upon cooling from 1100 K to just below the Burns temperature. In addition to softening to lower energy with decreasing temperature, one sees that the soft mode broadens rapidly in energy (i.e. the phonon lifetime decreases). Intriguingly, the soft mode becomes so broad near T_d that it is effectively overdamped. This is interesting because the overdamping of the soft mode would then seem to coincide with the formation of the PNR, thereby suggesting that the two phenomena are related. In other words, the PNR may originate from the condensation of the soft mode.

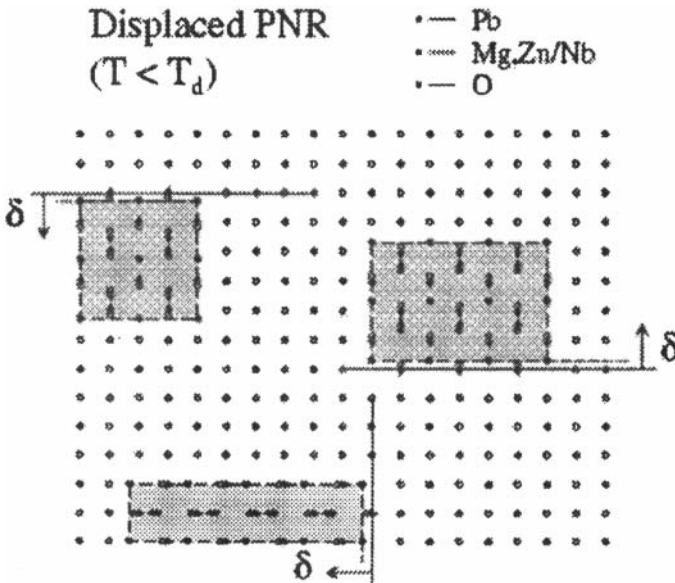


Fig. 9. A schematic representation, suggested by the model of Hirota *et al.*, of how the PNR (shaded regions) are displaced relative to the underlying cubic lattice. Arrows indicate (for simplicity) a Slater-type of tetragonal distortion.

To test this idea, Hirota *et al.* performed a careful analysis of the diffuse scattering in PMN [15]. As mentioned in the introduction, the onset of diffuse scattering in PMN was found to coincide with T_d , and thus connected to the PNR [14]. The room temperature ionic displacements in PMN had already been determined in 1995 by Vakhrushev *et al.* from careful neutron diffuse scattering measurements made near 16 different reciprocal lattice positions [32]. Surprisingly, the ionic displacements did not preserve the unit cell center of mass, as is required of any distortion that originates from the condensation of a transverse optic vibration. However Hirota *et al.* noticed that by adding a constant δ to the displacements of each atom in the unit cell, the remaining shifts could be made to satisfy the necessary center of mass condition. This idea gave birth to the concept of a “phase-shifted condensed soft mode,” or equivalently “displaced polar nanoregions,” which are depicted schematically in Fig. 9.

One possible method to test the concept of the displaced PNR experimentally would be to measure the diffuse scattering in PMN or PZN above and below T_c both with and without an electric field applied along the [001] direction. If the diffuse scattering measured along the field direction should decrease, while that along the perpendicular direction stays constant, then such an observation would lend further credence to this novel picture. Preliminary data from Ohwada, as yet unpublished, suggest that this may be the case [33].

SOFT MODES BELOW T_c

Neutron inelastic experiments by Wakimoto *et al.* on a larger single crystal of PMN significantly extend the previous soft mode measurements to much lower temperatures [12]. The major results from this study are summarized in Fig. 10. A striking finding is that, some 400 K below the Burns temperature, the soft TO mode reappears, i.e. it is no longer overdamped. Further, the square of the soft mode energy varies linearly with temperature, which is the hallmark of a ferroelectric soft mode. The solid black lines shown in the bottom panel of Fig. 10 indicate the range of temperatures over which this ferroelectric behavior was observed. These results represent a dynamical signature of a ferroelectric phase transition, thereby implying that the crystal symmetry is no longer cubic. As such they challenge the accepted view that PMN remains cubic at low temperatures. In this regard it is particularly interesting to note that the soft mode reappears very close to the temperature $T_c = 213$ K because this is the temperature at which the electric-field-induced ferroelectric state in PMN is lost upon zero-field heating [34]. It is tempting to speculate that the low-temperature phase of PMN is the same phase X as that found in PZN by Ohwada *et al.* [31].

The top panel of Fig. 10 shows the temperature dependence of the TA phonon linewidth Γ . Naberezhnov *et al.* were the first to observe an increase in the TA

linewidth near the Burns temperature [14]. The results of Wakimoto *et al.* reveal the remarkable finding that Γ actually peaks, and then decreases below 400 K, before finally recovering essentially the same value at T_c as observed at T_d . While these data were taken at a specific value of $q = 0.20$ r.l.u. in the (200) Brillouin zone, similar results were obtained for wave vectors $q = 0.12$ and 0.16 r.l.u. Thus the overdamping of the soft mode, and its subsequent recovery, appear to coincide with the anomalous broadening, and then narrowing, of the TA phonon, respectively. The broadening of the TA mode at T_d suggests that the PNR create a non-uniform distortion of the lattice that affects the acoustic phonon lifetimes. However the diffuse scattering in PMN continues to increase below 300 K [14]. Therefore the PNR persist to low temperature. It was speculated that the “shifted” or displaced nature of the PNR shown in Fig. 9 provides a barrier to the formation of a long-range ordered ferroelectric state in PMN at T_c .

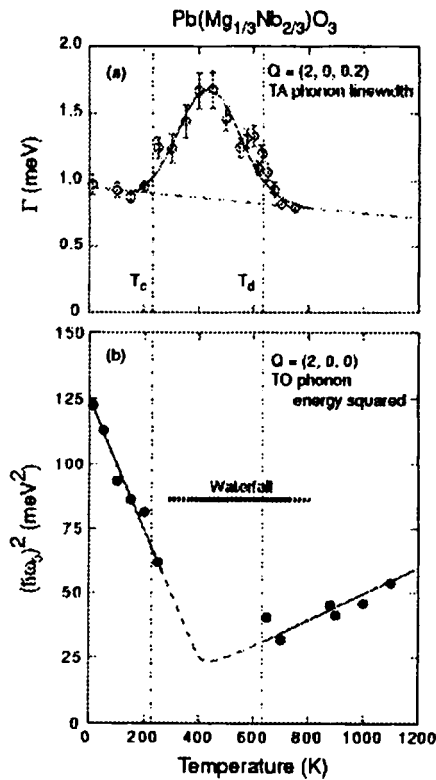


Fig. 10. Temperature dependence of the soft mode energy squared (lower panel) and the linewidth Γ of the TA mode (top panel). From Wakimoto *et al.* [12].

MODE COUPLING MODEL

Wakimoto *et al.* have very recently performed a quantitative analysis of the phonon lineshapes measured using neutron scattering techniques above the Burns temperature at 690 K in PMN [35]. Their findings indicate that the differences in the profiles and apparent energies of both the TA and TO phonons measured in the (200) and (300) Brillouin zones are well described by a simple model that couples the TA and soft TO modes. The primary parameter in this model is the q and T -dependent TO phonon linewidth $\Gamma(q,T)$. An example of how the TA phonon energy can appear to vary in different zones is shown in Fig. 11. The inset shows a systematic difference in the TA energies measured at $(2,0,q)$ and $(3,0,q)$, while the top and bottom panels highlight large differences in the intensities of both the TA and TO modes. The solid lines represent fits to the mode-coupling scattering cross section convolved with the instrumental resolution function. The data are clearly well described by the model in both the (200) and (300) zones.

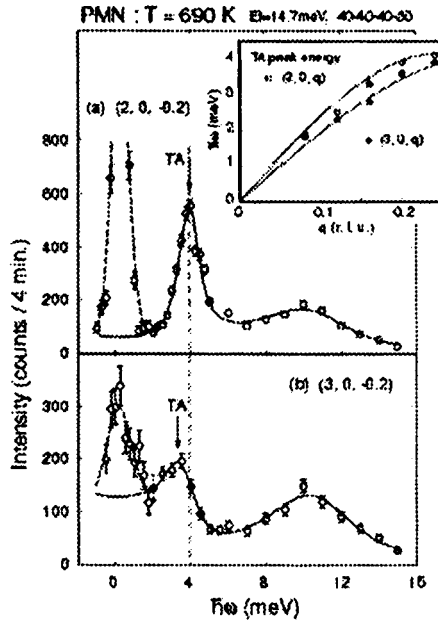


Fig. 11. Comparison of the TO and TA phonon profiles measured at $(2,-0.2,0)$ and $(3,-0.2,0)$. Notice the apparent shift of the TA phonon energy indicated by the vertical dashed line. From Wakimoto *et al.* [35].

This use of mode-coupling to describe phonon lineshapes in perovskite systems is not new. Harada *et al.* used a mode-coupling model to describe the asymmetric phonon lineshapes in BaTiO₃ in 1971 [36], while Naberezhnov recognized the importance of mode-coupling in PMN in their seminal paper in 1999 [14]. However in the context of Hirota *et al.*'s model of the displaced PNR, the mode-coupling approach brings a beautiful and unifying element to the ever-evolving picture of relaxor lattice dynamics. Namely, given that the soft TO mode is coupled to the TA mode, then it contains an acoustic component that, in turn, provides a natural origin for the uniform phase shift δ of the PNR when the soft mode condenses at the Burns temperature T_d . This idea is due to Y. Yamada [37].

FUTURE TOPICS

Two important topics on the basic research of relaxors have yet to be fully explored. The first one concerns a more definitive characterization of the polar nanoregions. The relationship between the atomic shifts below T_d with the ionic vibrations of the soft TO mode was resolved by a proper analysis of the diffuse scattering [15]. However, we still have no unique picture of how these shifts are created. The mode-coupling approach of Wakimoto *et al.* [35] seems promising, yet it lacks the final connecting piece. Yamada has proposed an alternative model that assumes the softening of the T1 acoustic mode along the [110] direction [38]. However experimental support for this assumption is lacking.

Another related question concerns the ratio of the volume of the PNR to that of the unshifted ferroelectric regions below T_c . There is a huge diffuse scattering below T_c , as pointed out long ago by Vakhrushev *et al.* [39]. In principle, the integrated diffuse scattering cross section expressed in units of the total scattering cross section of the crystal may give an estimate of this ratio. We would also like to know the change in size of the PNR between T_d and T_c . This question is complicated by the fact that the diffuse scattering intensity depends not only on the volume of the PNR, but also on the magnitude of the PNR displacements.

Closely related to the questions about the PNR is the discovery of the new phase X in PZN by the neutron measurements of Ohwada *et al.* [31]. Very recently, a high-energy x-ray study by Xu *et al.* confirmed the presence of phase X in PZN after zero-field cooling [40]. The skin of this crystal does indeed transform into the expected rhombohedral phase. But the bulk of the crystal, a few microns below the surface, transforms into a new phase that is nearly cubic and only slightly tetragonally distorted. It is speculated that this phase X is caused by the persistence of the PNR to temperatures below T_c , and which therefore coexist with the regular ferroelectric state. Somehow, the PNR are unable to deform coherently into the rhombohedral phase without the help of an applied field oriented along the [111] direction. In this respect, it is interesting to

note that PZN-8%PT between 510 K and 380 K manages to form a tetragonal distortion on cooling in zero field [31]. Further study of the diffuse scattering under different field-cooled conditions may provide the key to this problem.

ACKNOWLEDGMENTS

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MORPHOTROPIC PHASE BOUNDARY AND RELATED PROPERTIES IN RELAXOR-BASED PIEZOELECTRIC PEROVSKITE SOLID SOLUTIONS

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ABSTRACT

The solid solutions between relaxor ferroelectrics and normal ferroelectric PbTiO_3 show extraordinary piezoelectric properties if the composition is close to the morphotropic phase boundary (MPB). Recent experimental results on the crystal structure of the MPB phases of these materials are reviewed in relation to their electromechanical properties and discussed based on the phenomenological approach.

INTRODUCTION

For many years lead zirconate-titanate $(1-x)\text{PbZrO}_3 - x\text{PbTiO}_3$ [PZT] was the recognized number one high-performance piezoelectric perovskite material. For this solid solution system, the term "morphotropic phase boundary" (MPB) was used to designate an almost temperature independent border at $x \approx 0.5$, which separates a rhombohedral Zr-rich phase from a tetragonal Ti-rich phase in the temperature (T) – composition (x) phase diagram. Very strong piezoelectric activity of PZT with the composition close to the MPB was discovered about fifty years ago by Jaffe *et al.*¹ Since then, considerable improvement of the technologically important properties of PZT has been achieved, first of all by means of the substitution of some other metal ions for Pb and/or (Zr, Ti). For example, d_{33} piezoelectric constant has been increased from ~ 400 pC/N to ~ 800 pC/N.²

Great opportunities for the development of new piezoelectric materials emerged from the investigation of other perovskite systems with the existence of MPB. Excellent piezoelectric properties were recently found in the solid solutions of PbTiO_3 [PT] with the so-called relaxor ferroelectrics, such as $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3$ [PZN-PT] and $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3$

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[PMN-PT]. These two systems exhibit an MPB at $x \approx 0.09$ and $x \approx 0.35$, respectively, and similar to the case of PZT, the symmetry of the phase with small Ti content is rhombohedral, and a tetragonal phase is observed at large x . The important point is that good quality crystals of relaxor-PT solid solutions have successfully been grown, as opposed to PZT that can only be prepared in the form of ceramics so far. The superior properties of single crystals over ceramics are generally expected in particular because of the anisotropy of crystals as compared with the averaging properties over randomly oriented grains in ceramics. In the case of relaxor-based crystals, however, the anisotropy is so huge that more substantial theoretical efforts appear to be necessary in order to provide a satisfactory explanation on it.³ Piezoelectric coefficients d_{33} larger than 2000 pC/N and electromechanically coupling coefficients k_{33} higher than 90 % have been found along the pseudocubic [001] direction¹ in the rhombohedral compositions of PMN-PT and PZN-PT close to the MPB.² Promising results were recently reported for PMN-PT textured ceramics, in which $d_{33} \sim 1200$ pC/N was achieved.⁴ The structure of the relaxor-based piezoelectric materials, the crystal chemistry and the applications have recently been reviewed in a series of papers.^{2,5,6,7,8} To successfully develop the relaxor-PT piezoelectric materials, the mechanisms of their extraordinary properties, especially the role of the MPB in the occurrence of these properties should be understood. In the present paper we review and discuss some of the latest developments in this field.

FINE STRUCTURE OF THE MPB

One of the most striking achievements in the recent research on high-performance piezoelectric materials was the discovery of an intermediate low-symmetry phase in the range of MPB. This phase was found in PZT at first,⁹ and then in the PZN-PT and PMN-PT solid solutions. The finding became possible thanks to the availability of advanced research techniques such as high-resolution synchrotron x-ray and neutron diffraction. In fact, the phase diagrams of all the three systems look quite similar, as schematically shown in Fig. 1. The high-temperature cubic (space group $Pm\bar{3}m$) phase transforms at the Curie point into the rhombohedral $R\bar{3}m$ (at low x) or tetragonal $P4mm$ (at high x) phase. With further decrease of temperature, the rhombohedral phase remains unchanged, but the tetragonal one can transform, in a certain compositional interval, into the rhombohedral phase or the low-symmetry phase, which is orthorhombic (space group $Bmm2$), monoclinic M_C (Pm) or monoclinic M_A (Cm) in PZN-PT, PMN-PT and PZT, respectively. Thus, in contrast to what was believed before, the MPB in these materials is not merely the border between rhombohedral and tetragonal

* Since in all MPB phases the angles between the crystallographic axes deviate from 90° very slightly, we refer to the axis of the cubic phase in all cases.

phases, but a more complex region, containing a slim of low-symmetry intermediate phase. Strictly speaking, there are two morphotropic phase boundaries in these systems, the first one between the rhombohedral and the low-symmetry phases, and the second one between the low-symmetry and the tetragonal phases. Nevertheless, it is convenient to use the term MPB for the concentration range between and including the two boundaries.

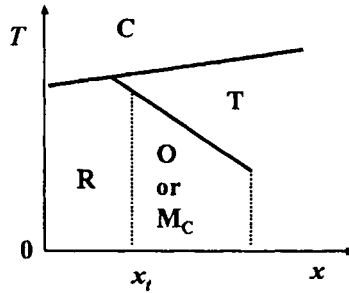


FIG. 1. Schematic phase diagram of PMN-PT and PZN-PT solid solutions in the vicinity of MPB. C, R, M_C, O, and T refer to the stability regions of the cubic, rhombohedral, monoclinic, orthorhombic, and tetragonal phases, respectively (Adapted from Ref. 6).

Table I. Crystallographic phases observed at room temperature by x-ray and/or neutron diffraction in the composition range of MPB in the relaxor-PT piezoelectric solid solutions.

Material	Composition range (%)	Stable phase	Metastable phases, induced by an electric field, $E \langle 001 \rangle$	References
PMN-PT	$x \leq 30$	R	(M _A)	10,11
	$30 < x < 35$	M _C		10,12,13,
	$x \geq 35$	T		10
PZN-PT	$x \leq 8$	R	M _A , (M _C), (O), T	14,15,16,17,18,19
	$8 < x < 11$	O or		20
		M _C		13,21
	$x \geq 11$	T		20

In the tetragonal (T), rhombohedral (R) and orthorhombic (O) phases, the possible directions of the spontaneous polarization vector P_s are restricted by

symmetry, so that it has to be parallel to $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$, respectively. In the monoclinic phase the restriction imposed by symmetry is softer. Any P_S directions within the $\{100\}$ planes (for the Pm phase) or within the $\{110\}$ planes (for the Cm phase) are permitted.

As can be seen from the phase diagram in Fig. 1 and the data in Table I, a comparatively small change of Ti concentration, x , near MPB can lead to the transition of the low-symmetry phase into the tetragonal or rhombohedral phase. This implies that the energies of all these non-cubic phases are close and the presence of other constraints, such as an electric field or a stress, may also trigger phase transitions. These induced transitions were indeed observed. Table I summarizes the results of the structural investigations, in which the new induced phases were detected by means of x-ray and/or neutron diffraction under application of an external electric field. Interestingly, some of these new phases (put into brackets in Table I) subsist after the field is removed.

PHENOMENOLOGICAL DESCRIPTION OF THE MPB

The phase transitions and properties of the perovskite ferroelectrics can be successfully described in the frame of Landau phenomenological theory adapted to the case of ferroelectric transitions by Devonshire and then by many other authors. In this theory the dependence of the free energy density F is represented as the expansion in powers of the polarization P (and maybe some other parameters). If the expansion coefficients and their temperature and composition dependences are known, the equilibrium magnitude and direction of the polarization (i.e. the spontaneous polarization P_s) at any temperature and composition can be found analytically by minimizing the $F(P)$ function. The properties of the crystal, which are related to the specific expansion coefficients, can also be calculated. To determine the expansion coefficients one needs to fit them to experimental data by an appropriate way. This procedure in principle makes it possible to describe any phases and phase transitions, but difficulties encountered in practice may be considerable. The cubic, tetragonal, rhombohedral and orthorhombic phases, which were initially known to exist in the perovskite materials, can be successfully described by the expansion of F up to sixth order of P (see for example Ref. 22). To account for all the phases observed in relaxor-PT materials and the transitions between them, a twelfth-order expansion appears to be necessary.^{23,24} The problem becomes extremely complicated. More substantial and accurate experimental results than those available so far are needed to determine the expansion coefficients and to describe the properties quantitatively.

In view of that, we try to use another approach here. We will describe the $F(P)$ dependences graphically, but not analytically. The experimentally established details concerning the sequence of phases observed at different compositions, temperatures and applied electric fields will be used to achieve this

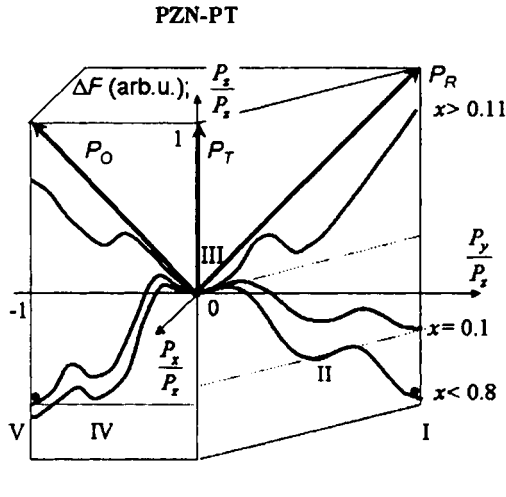
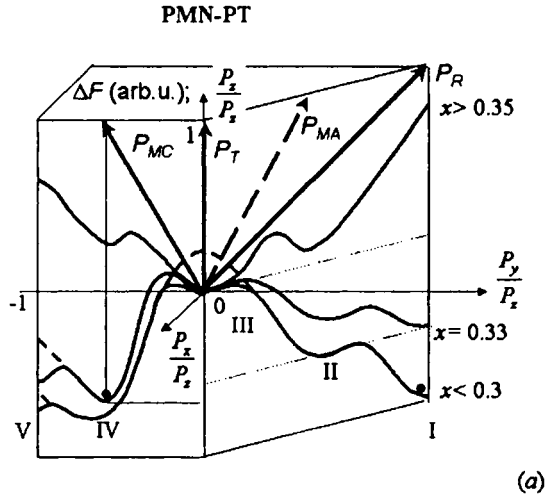


FIG. 2. Cross-section of the free energy surface on the (100) and (110) planes and the directions of spontaneous polarization for (a) $(1-x)\text{PMN}-x\text{PT}$ and (b) $(1-x)\text{PZN}-x\text{PT}$ crystals of different compositions around the MPB at room temperature. Arrows show the spontaneous polarization vectors for the tetragonal (P_T), rhombohedral (P_R), monoclinic M_C (P_{MC}), monoclinic M_A (P_{MA}) and orthorhombic (P_O) phases. The stable states of each system are marked by the filled circles.

goal. Although such an approach does not allow the calculations of the physical quantities, it systematizes and clarifies the known data and facts, thereby providing an illustrative basis for future more elaborate phenomenological theory.

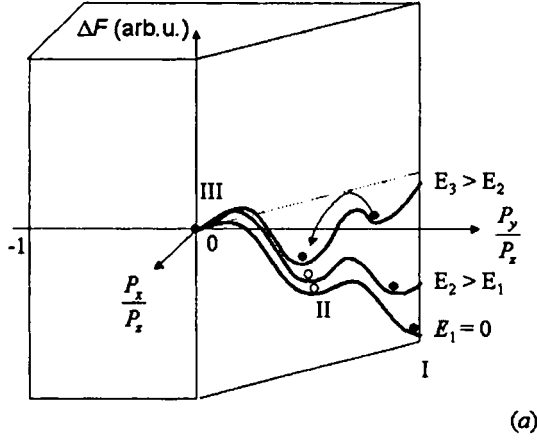
To show $F(P_x, P_y, P_z)$ in three dimensions, we plot this function on the $F-(P_x/P_z)-(P_y/P_z)$ coordinates. Fig. 2 shows the assumed diagrams related to PMN-PT and PZN-PT crystals at zero field. The free energy in these diagrams is defined relative to the energy of the tetragonal phase. Every local minimum is related to a certain crystallographic phase (stable or metastable). In particular, the minimum at $P_x = P_y = 0$ corresponds to the tetragonal phase, and the minima at $|P_x/P_z| = |P_y/P_z| = 1$, $0 < |P_x/P_z| = |P_y/P_z| < 1$, $|P_y/P_z| = 1$ and $P_x = 0$, and $0 < |P_y/P_z| < 1$ and $P_x = 0$, correspond to the rhombohedral, monoclinic Cm (M_A), orthorhombic and monoclinic Pm (M_C) phases, respectively.* The spontaneous polarization vectors of these phases are shown on the $(P_x/P_z)-(P_y/P_z)-(P_z/P_z)$ coordinates. The energy profile depends on temperature, composition of solid solution, etc.. The deepest (global) minimum position defines the symmetry of the stable phase, but the system can be transformed into some other (metastable) phases with higher energy by external forces, e.g. by an electric field applied along a suitable direction. Below we will discuss each of the solid solutions separately.

PMN-PT at Room Temperature

The PMN-PT crystal with a composition within the rhombohedral range of the phase diagram ($x < 0.3$) can be described by the energy diagram presented in Fig. 2 (a) (the minimum designated as I is the global minimum). Experiments¹¹ show that the symmetry of a rhombohedral crystal with composition close to MPB does not change after poling by a weak [001] directed electric field ($E < 5$ kV/cm) and after removal of the field. However, when the poling field is higher (e.g. $E = 43$ kV/cm), the crystal transforms into the metastable phase of M_A symmetry. This behavior can be understood with the help of Fig. 3 (a), which depicts the evolution of the energy curves under an external [001]-oriented electric field. It is clear that the field gives rise to the rotation of the spontaneous polarization vector from the initial [111] direction toward the direction of the field, i.e. [001]. Such a rotation means that both P_x/P_z and P_y/P_z become smaller than unity, i.e. the corresponding energy minimum (Minimum I) moves to the left with increasing field. As it follows from the first-principle calculations,²⁵ in the course of rotation the equality $P_x/P_z = P_y/P_z$ holds, i. e. the polarization vector remains within the (110) plane. This also means that the symmetry of crystal decreases and becomes monoclinic, as long as the field is applied. If the field is not very high (like E_2 in Fig. 3), the system stays in the Minimum I, and after the field is switched off, it returns to the initial (rhombohedral) state so does the

* The monoclinic M_B (Cm) phase would correspond to the minimum at $|P_x/P_z| = |P_y/P_z| > 1$, but this phase has not been observed in perovskite high-performance piezoelectrics so far.

PMN-PT



PZN-4.5%PT

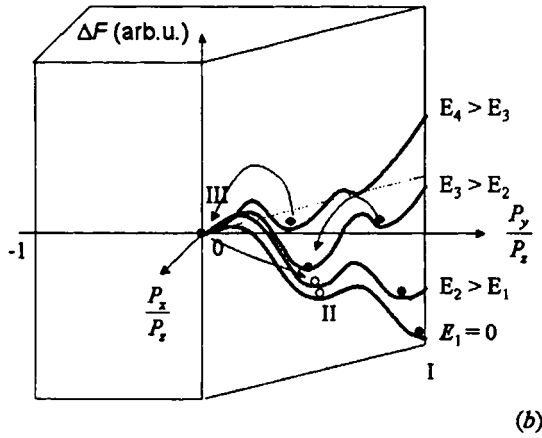


FIG. 3. Cross-section of free energy surface by (100) and (110) planes, illustrating the field induced ($E||[001]$) phase transitions in the rhombohedral PMN-PT (a), PZN-4.5%PT (b) and PZN-8%PT (c) crystals. Arrows show the switching of the system from one phase to another. The states of the system are marked by the filled circles (upon increasing field) and by the open circles (upon decreasing field).

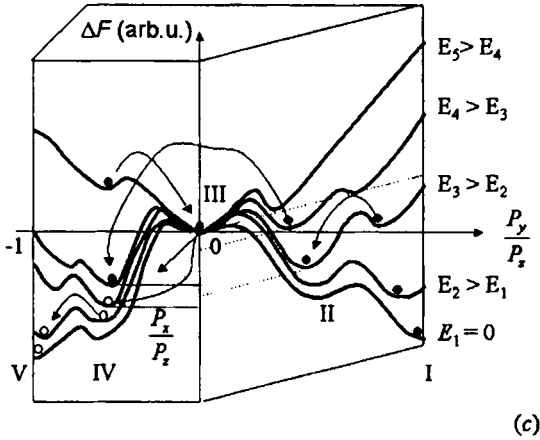


FIG. 3 (Cont.)

minimum. But under a strong field (like E_3 or stronger) the Minimum II becomes lower than the Minimum I, and the system can "jump" into the "true" monoclinic M_A phase (Minimum II), overcoming the potential barrier. After the field is decreased to zero, the system can move back to state I, or, if the barrier between I and II is high enough, it remains in the (metastable) monoclinic state II. As mentioned above, in PMN-PT the latter scenario is realized.

Of course, the field along any $\langle 100 \rangle$ (or close) directions should produce the same effect on the crystal. On the other hand we can predict that the field in any $\langle 111 \rangle$ direction should not lead to the transition into other phases because it should not rotate the polarization (and change P_x/P_z and P_y/P_z).

It follows from the above that the experiments under application of an electric field can help reveal the possible metastable phases. In particular, we demonstrate that the metastable M_A phase exists alongside with the stable R phase in PMNT-PT. Another metastable phase, the monoclinic M_C , should also exist here (at least in the close proximity to the MPB). Indeed, the R phase in PMN-PT transforms into M_C phase with increasing x (see Table I), and it should be a first-order transition,²⁴ but at any first-order transition, the metastable states of the adjacent phases should persist on both sides of the transition.

Thus, based on the phenomenological analysis of the experimental data, we can conclude that in the rhombohedral phase of PMN-PT adjacent to MPB, the energy surface contains at least three local minima, I, II and IV. No experimental

data are available which would allow us to conclude whether or not the other local minima exist. Under these circumstances, the dashed curves in Fig. 2 (a) are valid.

With increasing x , the tetragonal phase appears after R and M_C (see Table I). As the transition between R and M_C is of first order, the metastable R phase is expected to exist for the monoclinic compositions close to MPB. The order of $M_C \rightarrow T$ transition cannot be determined *a priori*,²⁴ but the experiment shows that it is also the first-order transition.¹⁰ Thus, the metastable T and M_C phases (with the corresponding local minima as shown in the diagrams of Fig.2a) can be expected in the M_C and T compositions, respectively.

The experimental structural data concerning field-induced phase transitions in the tetragonal and monoclinic phases of PMN-PT have not been published, but a strong enough electric field, when applied in the $\langle 100 \rangle$ directions, is expected to transform M_C into T phase (by switching from Minimum IV to III) or into R phase (IV $\rightarrow$ I switching) when applied along $\langle 111 \rangle$. The tetragonal phase may be transformed into M_C by a field applied in the $\langle 110 \rangle$ (or close) directions.

PZN-PT at Room Temperature

In order to provide a description in agreement with the experimental data of Table I, one should assume the sequence of $F(P)$ configurations with increasing x shown in Fig.2(b). The influence of electric field was studied for two rhombohedral compositions, PZN-4.5%PT and PZN-8%PT.¹⁹ A field along the $[111]$ direction, as expected, did not change the rhombohedral symmetry. The influence of a $[001]$ -directed field will be discussed below. In a comparatively weak field, PZN-4.5%PT behaves in the same way as the rhombohedral phase of PMN-PT, i.e. a monoclinic distortion of M_A type appears, and after removing the field, the rhombohedral phase recovers (in Ref.19, R phase was observed in crystals previously poled by a field of 10 kV/cm). But in stronger fields, the crystal further transforms to the tetragonal phase via a first-order transition (i.e. with abrupt changes of lattice parameters), and after removal of the field, it remains in the monoclinic phase,¹⁹ which means that Minimum II (corresponding to the "true" phase M_A , metastable at $E=0$) really exists between Minima I and III. This process is shown schematically in Fig. 3 (b) by arrows, connecting the local Minima I, II and III. With decreasing field, the crystal jumps back from T to M_A phase with a significant hysteresis,¹⁹ suggesting that the energy barrier between II and III states (characteristic of the first-order transitions) is not high enough to keep the crystal in the tetragonal phase at zero field.

In PZN-8%PT, a weak field also induces the M_A symmetry, but with increasing the field strength, the crystal undergoes a transition into the monoclinic M_C phase and then, only afterward, into the T phase.^{14,16-19} It is not clear if a transition into the "true" monoclinic M_A phase (i.e. the phase having the local energy Minimum II) takes place, or the system remains in the field-disturbed state

I until the transition into M_C . We assume by analogy with PZN-4.5%PT that local Minimum II exists, but the assumption should be verified, e.g. by the experiments in which the (metastable) M_A phase would be observed at zero field.

The sequence of the states for PZN-8%PT is illustrated in Fig. 3 (c). In a small field ($E=E_2$), the system remains in Minimum I, while at a higher field ($E=E_3$) it moves into Minimum II (the "true" M_A phase). Further increase of the field strength gives rise to the transition into the M_C phase at $E=E_4$. During this transition, the polarization leaves the (110) plane to lie in the (100) plane, i.e. the system temporarily adopts a reduced (triclinic) symmetry. It is not clear if the intermediate triclinic phase (so far missed in the experiments) really exists in the narrow field strength interval, or the system merely moves over the energy barrier separating Minima II and IV, which is reduced by the field. It seems that the latter case is most probable to occur, because the experimental field dependences of lattice parameters¹⁹ show a quite abrupt (and single) anomaly. A higher field induces the tetragonal phase. After removing the field, the crystal was shown to appear in the orthorhombic phase,¹⁹ i.e. the $III \rightarrow IV \rightarrow V$ sequence is proven to be valid.

Experiments also showed^{19,26} that once the crystal enters the O phase, the [001]-directed field cannot transform it back to the R phase. The rhombohedral phase can only be recovered by annealing above the Curie temperature, or by crushing the crystal. But the monoclinic M_C or the tetragonal phase can be readily induced by the field. This can be understood with the help of Fig. 5. In a small field (such as E_2) the energy barrier between Minima V and II [located somewhere outside the (100) and (110) planes] is very high. In a strong field (E_4 or higher) the barrier decreases, but the energy of state I becomes larger than that of state V. Thus there is no driving force for the $O \rightarrow R$ transition to occur. Only the transitions to the M_C or T phase are possible, but the O phase recovers when the field is removed, and therefore the crystal appears to be "locked" in the metastable O phase.

The Influence of Temperature

We can now explain why in the relaxor-PT solid solutions, no phase transitions between the R and low-symmetry phases have been observed with the change of temperature, i.e. a strictly vertical line at $x = x_c$ forms the boundary between the R and M_C (or O) phases in the experimentally determined $T - x$ phase diagram (Fig. 1).

Fig. 4 shows the temperature evolution of the energy curves (using the PZN-PT curves as an example) for the composition $x = x_c$ in the vicinity of the transition temperature T_i from the tetragonal into the R phase. At $T > T_i$ the tetragonal phase is stable (because the energy minimum III is global). At $T = T_i$ the energies of the three phases, T, O and R, are the same (by the definition of