Modern Piezoelectrics

Structural and Microstructural Aspects

Rajeev Ranjan

Rajeev Ranjan is Associate Professor in the Department of Materials Engineering, Indian Institute of Science Bangalore. His research interests are in the field of structure-property correlations in ferroelectrics and multiferroic materials.

The presence or absence of piezoelectricity has a direct relationship with the point group of the crystal structure. In this article, starting from a general background, a brief account of the phenomena associated with anomalous piezoelectric response in advanced piezoelectric materials is presented. Some of the landmark discoveries that shaped the field, both in terms of new materials as well as the scientific understanding of the mechanisms are highlighted. Towards the end, there is a brief discussion of the viewpoints with regard to factors such as domain wall motion, low symmetry monoclinic phase, phase transition, polarization rotation theory and adaptive phase theory which contribute to the piezoelectric response in advanced piezoelectrics.

1. Introduction

Piezoelectricity is a phenomenon involving the generation of voltage on application of mechanical stress (direct piezoelectric effect). Piezoelectric materials also change shape on application of an electric field (converse piezoelectric effect). The phenomenon was discovered in 1880 by the French physicists Pierre Curie and Jacques Curie in single crystals of quartz, tourmaline, Rochelle salt, cane sugar. Biological materials such as bone and proteins also exhibit piezoelectricity. During World War I, in 1917, single crystalline quartz piezoelectric-based transducers were used by Paul Lengevin, a French physicist, to make SONAR (**SO**und **N**avigation **A**nd **R**anging), a device for underwater communication and navigation and for detection of submarines. This success led to

intense research in the field of piezoelectric materials. A paradigm shift in piezoelectric research happened after the discovery of ferroelectricity in a synthetic oxide material $BaTiO_3$. This material was discovered in 1941 during World War II when attempts were being made to find substitutes for mica, a natural mineral used extensively in the capacitor industry during that time, and whose supply from South America to the US was severely affected during the war. $BaTiO_3$ ceramic became a wonder material in the capacitor industry as its dielectric constant was ~ 1000, i.e., about ten times the values which other ceramics known at that time possessed (for example, dielectric constant of TiO_2 is ~ 110). This also meant that the size of the capacitor could be miniaturized without compromising on the capacitance[1]. This paved the way for miniaturization of electronic circuits. That, this material also exhibited ferroelectricity, a phenomenon involving switching of the spontaneous polarization on reversal of the applied electric field, was demonstrated in 1945 by von Hippel. After application of a strong electric field, (traditionally known as poling), the ceramic $BaTiO_3$ disc exhibits polarization, and such a disc can be used as a piezoelectric material.

With this discovery, a new era in piezoelectrics began. Oxide ceramics are easy to make and fabricate on a mass scale as compared to single crystal quartz and their piezoelectric properties are far superior. The subsequent years saw the discovery of several new synthetic ferroelectric perovskites materials and the landmark discovery of an anomalous piezoelectric response in the solid solution of $PbTiO_3 - PbZrO_3$, famously known as PZT[2] [1]. Suitably modified PZT have piezoelectric constants as high as 600×10^{-12} C/N (a considerable advancement as compared to quartz which exhibits a piezoelectric constant of $\sim 2 \times 10^{-12}$ C/N). Currently, perovskite ferroelectrics are used in a variety of devices

> The discovery of the very large dielectric constant in $BaTiO_3$ ceramics was a landmark discovery that revolutionized the capacitor industry.

[1] Capacitance (C) for a parallel plate capacitor is defined as $C = e_0 e_r A/d$, where A is the area, d is the distance between the plates separated by an insulating material with relative dielectric constant e_r. e_0 is permittivity of free space (8.854×10^{-12} Farads/meter). Large capacitances can be achieved by use of very large e_r insulating material and keeping the area small.

[2] PZT is a common abbreviation of lead-zirconate-titanate, $Pb(Zr_x Ti_{1-x})O_3$.

The discovery of anomalous piezoelectric properties in PZT laid the foundation for the development of advanced piezoelectric materials.

such as pyroelectric night surveillance devices, memory devices in computers, electro-optic light valves, as ignitors in spark plugs, medical diagnostic transducers, ultrasonic motors, high precision displacements on the scale of nanometers, stereo twitters, buzzers, etc. [2]. The discovery of ferroelectricity in oxide perovskites also led to a paradigm shift in the scientific understanding of the mechanism(s) associated with ferroelectricity in crystals. Before the discovery of ferroelectricity in $BaTiO_3$, the scientific community tacitly assumed that ferroelectricity existed only in H-bonded crystals such as Rochelle salt [3].

2. Mathematical Formalism of the Piezoelectric Phenomenon

As pointed earlier, the application of external stress on piezoelectric materials induces not only strain (Hooke's law) but also charge on the crystal surface (direct piezoelectric effect), and the application of an electric field not only induces polarization but also strain (converse piezoelectric effect). Within the framework of a linear response, both the effects can be represented mathematically in terms of coupled tensor equations; The repeated indices are summed over 1-3 as is usual in tensor analysis:

$$S_{ij} = s_{ijkl}T_{kl} + d_{kij}E_k \, ,$$

$$D_i = d_{ijk}T_{jk} + \varepsilon_{ij}E_k \, ,$$

where S is strain, s is elastic compliance, T is stress, d is piezoelectric coefficient, D is dielectric displacement, E is electric field, and ε is permittivity.

3. Crystallographic Requirement

In general, the physical properties of crystals are anisotropic, i.e., the values of the properties measured along crystallographically inequivalent directions of a single

crystal are different. Apart from the translational symmetry, crystals also exhibit one of the 32 crystallographic point group symmetries, also known as crystal classes. For example, the point group of cubic ABO_3 perovskite structure is m$\bar{3}$m. Neumann's principle suggests that the symmetry of the physical properties of a crystal must include the point group symmetry of the crystal. When this principle is applied to crystals with center of inversion symmetry, $\bar{1}$, all the piezoelectric tensor coefficients turn out to be zero. This implies that centrosymmetric crystals cannot exhibit piezoelectricity. Of the 32 crystal classes, only 20 (1, 2, m, 222, mm2, 4, $\bar{4}$, 422, 4mm, 42m, 3, 32, 3m, 6, $\bar{6}$, 622, 6mm, 62m, 23, 43m) can exhibit the phenomenon of piezoelectricity. Among these, the crystal classes 1, 2, m, mm2, 4, 4mm, 3, 3m, 6, 6mm can exhibit spontaneous polarization, i.e., polarization without application of external electric field or stress. These are known as polar crystal classes and materials exhibiting these point groups are known as pyroelectrics. Pyroelectric materials generate a temporary voltage when heated or cooled.

> Piezoelectricity is intimately related to the point group of the crystal.

4. Ferroelectric Perovskites

Among the inorganic oxides, ferroelectricity is exhibited by several compounds in the Tungsten–Bronze, Aurillius family of structures, perovskites, etc. [3]. From the view point of piezoelectric properties, the focus of research is more on the oxide perovskites since several alloy systems in this family have shown exceptionally large piezoelectric response. Apart from $BaTiO_3$, which was the first discovered ferroelectric in the oxide community, $KNbO_3$, $LiNbO_3$, $PbTiO_3$, $PbZrO_3$, $SrTiO_3$, $BiFeO_3$, $Na_{1/2}Bi_{1/2}TiO_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$ also exhibit ferroelectric properties, either at room temperature or away from it. The hallmark of a ferroelectric material is that it shows a polarization–electric field (P–E) hysteresis (*Figure* 1), analogous to the magnetization-magnetic field (M–H) in ferromagnets.
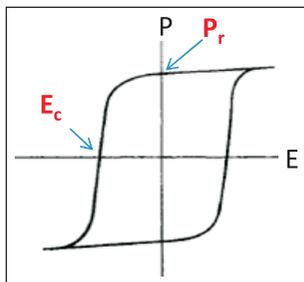
Figure 1. Schematic of a electric field – polarization hysteresis, characteristic of a ferroelectric material. P_r and E_c are remanent polarization and coercive field respectively.

The analogy of the hysteresis was taken to such extremes that in spite of the fact that no iron (ferro-) element was present in materials exhibiting polarization–electric field hysteresis, they were labeled as ferroelectrics! Apart from the similarity of the shape of the M–H and P–E curves, there is nothing common with regard to the very origin of ferromagnetism and ferroelectricity. Ferromagnetism originates due to quantum mechanical spin exchange interaction between electrons and there may not be any crystal structure change across a ferromagnetic–paramagnetic transition. For example, Fe remains in body-centered cubic structure across the ferromagnetic–paramagnetic transformation (~ 770 °C). Ferroelectric–paraelectric transition, on the other hand, involves change of crystal structure. For example, $BaTiO_3$ exhibits cubic structure (space group Pm3m) above 130 °C, i.e., in the paraelectric state and tetragonal (space group P4mm) structure in the ferroelectric state below 130 °C (*Figure* 2). The same structural change is exhibited by $PbTiO_3$ at ~ 490 °C and $KNbO_3$ at 410 °C [3]. In the tetragonal phase, the Ti-ion is displaced from the body-center position along the [001] direction (see *Figure* 2). The oxygen ions are also displaced along the same axis by a different amount. The onset of spontaneous polarization below the Curie point is also accompanied by the onset of a spontaneous lattice strain. For example, just above the Curie, point the cubic lattice parameters ($a = b = c$) of the non-polar (P m$\bar{3}$m) paraelectric phase of $BaTiO_3$
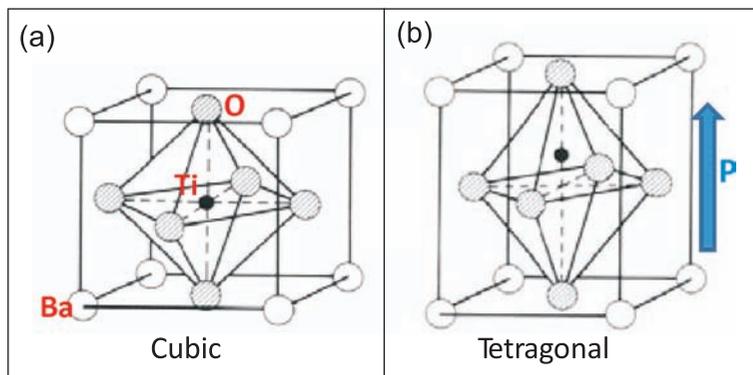
Figure 2. Crystal structure of $BaTiO_3$ in the cubic para-electric phase (a) and tetragonal ferroelectric phase (b). The vertical arrow represents spontaneous polarization along [001] in the tetragonal phase.


(a) Cubic (b) Tetragonal

is 4.009 Å. Just below the Curie point, the polar tetragonal P4mm phase exhibits $a = 4.003$ Å and $c = 4.022$ Å. The spontaneous tetragonal strain $(c/a - 1)$ is therefore ~0.005 in the ferroelectric phase. The strain (x) and polarization (P) in ferroelectrics are strongly coupled (strain is proportional to square of polarization) and is responsible for the large piezoelectric response [4].

5. Ferroelectrics Domains

When a structure transforms from a high symmetry state to a low symmetry state, the higher symmetry of the parent phase is preserved by formation of oriented domains. Domain formation is therefore a common feature in crystalline materials undergoing structural phase transformation. In ferroelectrics, the overall domain configuration also takes into consideration the minimization of the electrostatic depolarization energy resulting from the uncompensated charges on the crystal surface due to the onset of the spontaneous polarization, and the elastic energy associated with the creation of the domain walls [3, 4]. The domain formation makes the total polarization of a ferroelectric single crystal, zero. A ferroelectric domain wall separates two regions inside the crystal with different orientations of polarization. If $\mathbf{P}_1$ and $\mathbf{P}_2$ are the polarizations across a domain wall whose normal is $\mathbf{n}$, then, the domain wall will be charged with surface charge density $\sigma = (\mathbf{P}_1 - \mathbf{P}_2) \cdot \mathbf{n}$. Hence, unless this quantity is zero at a domain wall, the domain wall will be charged. For the tetragonal ferroelectric phase which has originated by cooling from the cubic paraelectric state as in $BaTiO_3$, $KNbO_3$ or $PbTiO_3$, the ferroelectric regions domain walls can either be separating with polarization 180° or $\sim 90^o$ rotated with respect to each other, as shown in the schematic in *Figure* 3. For the rhombohedral phase, the polarizations would be along the eight <111> pseudocubic directions and the non-180 ^{o} ferroelectric domain walls would be 109° and 71°. Evidently, as the crystal symmetry be-

Figure 3. Schematic of a 180° domain wall (left) and a 90° domain wall (right) in a tetragonal ferroelectric crystal. The direction of polarization in a given region is determined by the shifting of the central cation (represented by filled circles) away from its geometrical center [5].
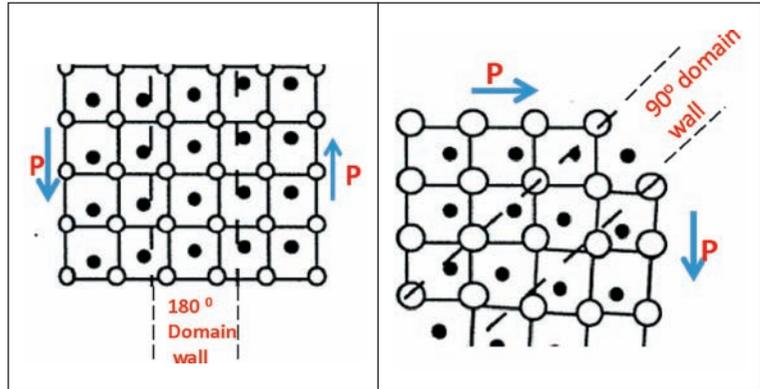
comes lower, such as in monoclinic structures, the domain walls will be more complex. The domain patterns can be changed on application of an external electric field or mechanical stress. On application of the electric field, the unfavorably oriented domains shrink in size by motion of the domain walls. The motion of domain walls can not be reversed by increasing the electric field, as the walls are pinned by defect centers which are present randomly across the specimen. This is the reason for the non-linear and hysteretic polarization–electric field curve commonly observed in ferroelectric materials [6]. One important consequence of this is that even after the field is switched off after subjecting the specimen beyond its coercive field, the specimen develops a remanent polarization.

Thus, even if a ferroelectric specimen is a ceramic body made up of several randomly-oriented small polycrystals (grains) bonded to each other, the application of a strong electric field can make the entire ceramic disc behave like a polar specimen having net polarization. This is schematically shown in *Figure* 4. The process of application of a strong electric field on a ferroelectric ceramic disc is conventionally known as poling. A poled ferroelectric ceramic exhibits piezoelectricity. This procedure is analogous to the making of permanent magnets using ferromagnetic materials by placing them in a high

The ability to induce permanent polarization after the application of strong electric field led ferroelectric ceramics to be used as piezoelectric elements.
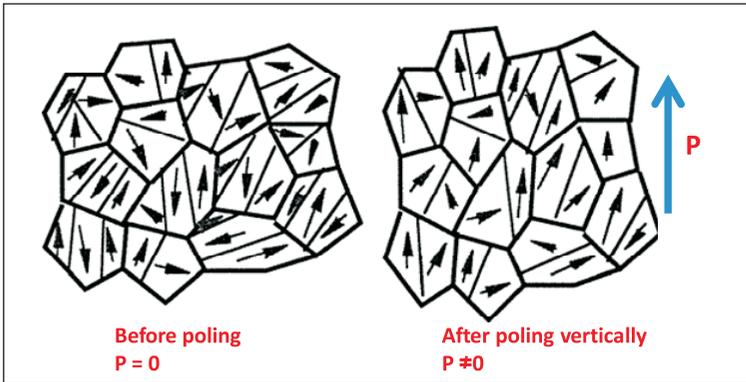
Figure 4. Schematic of domains in a polycrystalline ceramics. The net polarization of the specimen is zero before electric poling (left). Poling induces a net polarization in the ceramic.

magnetic field and is considered as a landmark historical development in the field of ferroelectricity since it allowed the oxide ferroelectric ceramics, which are much cheaper and could be readily manufactured as compared to single crystals, to be used as piezoelectrics elements in devices.

6. Domain Wall Motion – Rayleigh Law

The piezoelectric response in ferroelectric materials has contributions from the motion of the domain walls (extrinsic contribution) and also due to the strain induced in the lattice (intrinsic contribution) by the external electric field. In the recent past, efforts have been made to understand how domain wall motion contributes to the piezoelectric response in ferroelectrics. In this context, it may be pointed out that only the non-180º ferroelectric–ferroelastic domain wall movement contributes to the piezo-response as their movement changes the shape of the crystal. The size of the ferroelectric domains, their density and mobility are a function of grain size, impurities and crystal structure, chemical heterogeneity, etc. [6]. This provides opportunities to tailor dielectric and piezoelectric properties in ferroelectric ceramics by controlling the average grain size and chemical compositions. The dielectric constant of $BaTiO_3$, for example, shoots up to ~ 5000 for grain size ~ 1 micron as compared to ~ 1000 for grain size ~ 10 microns [7]. Very recently, using electric field- dependent X-ray diffraction

Rayleigh law offers a way to estimate the contribution of domain wall motion in determining the piezoelectric response in ferroelectric specimens.

technique, the enhanced permittivity and piezoelectric response have been related to an increased mobility of the 90° domains [8].

The hysteretic behaviour resulting from irreversible domain wall displacements at moderate electric fields (near the coercive limit) is a major drawback for applications requiring high precision displacements. The past decade and a half witnessed extensive research to quantify the role of irreversible domain wall motions in the hysteretic and non-linear dielectric and piezoelectric response in ferroelectric systems. Damjanovic and Demartin [9] have suggested a way to quantify the linear and non-linear contributions by measuring the property coefficients as a function of electric field/mechanical stress amplitude and frequency. This methodology is based on the application of the Rayleigh law which was riginally developed for characterizing the movement of domain walls in ferromagnets. In this formalism, a ferroelectric/ferromagnetic domain wall moves in a medium in which the potential energy of the wall is an irregular function of the wall position. The irregularity of the potential energy is due to random pinning defects of different strengths. For direct piezoelectric effect (stress as stimulus) and low stress level, the Rayleigh law can be expressed as:

$$Q_0 = d_{\mathrm{int}} X_0 + \alpha X_0^2 \,,$$
$$d_{33} = d_{\mathrm{int}} + \alpha X_0 \,, \quad \text{or}$$
$$d_{33}/d_{\mathrm{int}} = 1 + (\alpha/d_{\mathrm{int}}) X_0 \,,$$

where Q_0 is amplitude of the measured charge on application of a sinusoidal stress, $X = X_0 \sin(\omega t)$, X_0 being amplitude and ω being the frequency of this stress. Also, d_{33} is the longitudinal piezoelectric coefficient of the ceramic specimen (i.e., polarization measured along the same axis as the applied stress) $= Q_0/X_0$, d_{int} is the intrinsic (linear) piezoelectric coefficient due to lattice strain and reversible motion of domain wall and α is the Rayleigh parameter quantifying non-linearity and irre-

versible domain wall motions [9]. α/d_{int} gives the relative increase in d_{33} per unit stress due to the irreversible motion of the domain walls. Hard and soft piezoelectrics are characterized by how large or small the value of α/d_{int} is. For $BaTiO_3$ and $SrBi_4Ti_4O_{15}$ ceramics, this quantity has been reported to be 0.26×10^{-6} Pa^{-1} and 0.0006×10^{-6} Pa^{-1}, respectively, thereby suggesting significant irreversible domain wall motion contribution to the piezoelectric response in $BaTiO_3$ as compared to the other [10].

An analogous equation exists for polarization (P), permittivity (ε) and electric field (E):

$$P_3 = \varepsilon_{\mathrm{int}}E_0 + \alpha E_0^2; \;\; E = E_0\sin(\omega t); \;\; \varepsilon_{33} = \varepsilon_{\mathrm{int}} + \alpha E_0$$

By fitting the measured ε_{33} versus E_0 data, the parameters $\varepsilon_{\mathrm{int}}$ and α can be determined. The contribution due to irreversible domain wall motion is obtained from the ratio $\alpha E_0/\varepsilon_{33}$. The P–E hysteresis in the low (sub-coercive) field regime is given by

$$P_3 = (\varepsilon_{\mathrm{int}} + \alpha E_0)E \pm \alpha/2(E_0^2 - E^2),$$

where '+' corresponds to decreasing field and '−' to increasing field [11].

7. Domain Switching Measured by Diffraction

More recently, there is increasing interest in diffraction-based techniques to measure the contribution of non-180º domain wall motion with regard to piezoelectric response in ferroelectric ceramics. When an electric field is applied to bulk ceramic specimen, two things will happen: (i) straining of the lattice and (ii) switching of the domains. X-ray diffraction can give information about both in one go. The lattice strain can be measured using the shift in the Bragg peak positions, while the switching of domains can manifest as alteration in the intensity ratio of the symmetry-related peaks. For example, the X-ray powder diffraction of the tetragonal phase of $BaTiO_3$

Electric field dependent X-ray diffraction study can give a quantitative estimation of non-180° domain switching on application of electric field.

will show (002) and (200) pair of Bragg reflections in the intensity ratio of approximately 1:2. If the pellet is not textured, this ratio is expected by diffraction from pellets as well. Since polarization in the tetragonal phase is parallel to the c-axis of the tetragonal unit cell, domains whose c-axis is not parallel to the electric field will tend to align themselves in the field direction. This will disturb the randomness associated with the orientation of the planes in the zero field state and induced preferred orientation. Relative to the unpoled state, the fraction of the $200 \rightarrow 002$ domain switching is given by [12],

$$\eta_{002} = -\frac{1}{3} + \frac{I_{002}/I_{002}^{\text{unpoled}}}{I_{002}/I_{002}^{\text{unpoled}} + 2(I_{200}/I_{200}^{\text{unpoled}})}.$$

Here, I_{002} and I_{200} are the intensities of the 002 and 200 Bragg peaks measured after application of the poling field. Calculations show that approximately 35% of the piezoelectric contribution can come from non-180° domain switching in ferroelectric ceramics [12]. The anomalous dielectric and piezoelectric properties at grain size of ~ 1 micron in $BaTiO_3$ have also recently been shown to be related to enhanced switching of the non-180° ferroelectric domains [8].

8. Monoclinic Phase and Anomalous Piezo-response in Perovskites

So far, we have discussed the electric field-induced lattice strain and domain wall motions as the contributing factors in determining the piezoelectric response in ferroelectric materials. The absolute values of the piezoelectric response can however be significantly enhanced by inducing inter-ferroelectric criticality by chemical substitution, temperature and pressure. This was first realized in the solid solution of $PbTiO_3$ and $PbZrO_3$, $Pb(Zr_xTi_{1-x})O_3$ for $x = 0.52$. This alloy is famously known as PZT in the ferroelectric community [1]. The composition–temperature phase diagram of this pseudo-binary system exhibits a nearly vertical boundary at
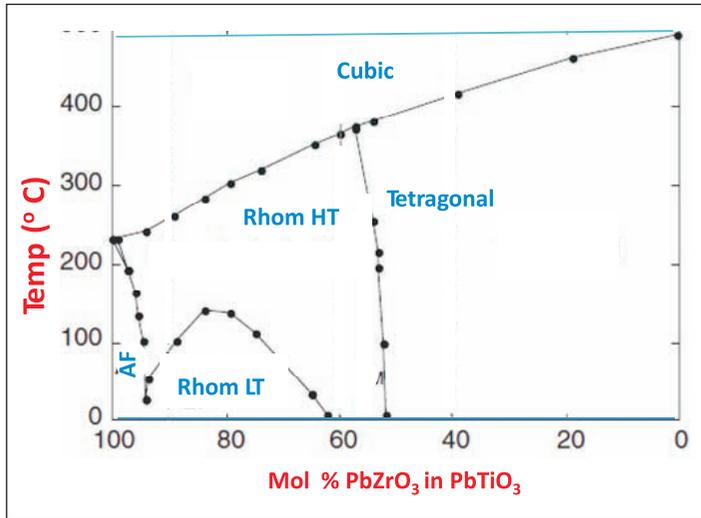
Figure 5. Phase diagram of the $PbZrO_3$–$PbTiO_3$ ferroelectric system. Rhom HT represents high temperature rhombohedral phase, Rhom LT is low temperature rhombohedral phase, AF is antiferroelectric phase. The morphotropic phase boundary (MPB) separating rhombohedral (Rhom HT) is shown by nearly vertical line at 52 mole percent of $PbZrO_3$ [11].

$x = 0.52$, now commonly known as the morphotropic phase boundary (MPB), which separates a tetragonal phase field from a rhombohedral phase field (*Figure* 5) by nearly a vertical line. Ever since its discovery, PZT has been the material of choice in the field for piezoelectric applications. By alloying with suitable dopants, piezoelectric coefficient as high as 600 pC/N has been achieved in PZT ceramics. The mechanism associated with the anomalous piezoelectric response has been extensively debated in literature for over a decade. An interesting development happened in 1997 when Park and Shrout [13] showed that the solid solution of $0.92Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.08PbTiO_3$ (PZN–PT) with rhombohedral crystal structure and spontaneous polarization oriented along the pseudocubic $<111>_c$[3] axis exhibits longitudinal piezoelectric coefficient[4] of about 2000 pm/V along its non-polar $<001>_c$ axis (this value is 1000 times that for quartz!). The authors attributed this anomalously large piezoelectric response to the rotational action of the polarization from $<111>_c$ towards the $<001>_c$ axis. These results found theoretical support by Du *et al* whose phenomenological free energy calculations predicted that for rhombohedral PZT compositions, the piezoelectric response would be more along the [001] and not along

[3] Subscript c represents direction with respect to the cubic unit cell.

[4] Piezoelectric coefficients as measured by direct piezoelectric effect experiment is often represented in a unit of pico-Coulomb per Newton (pC/N). Piezoelectric coefficients as measured by converse piezoelectric experiment is generally represented in unit of pico-meter per Volt (pm/V). Both the units are however equivalent

the [111] rhombohedral direction [14]. Noheda *et al* [15] reported the existence of monoclinic (M_A)[5] phase for compositions exhibiting morphotropic phase boundary and suggested that this structure provides the structural bridge between the rhombohedral and tetragonal structures across the MPB. Based on atomistic first principles calculations, Fu and Cohen [16] proposed a polarization rotation model to explain the anomalous piezoelectric property in ferroelectrics. The authors showed that a flat energy surface near the rhombohedral phase will cause the polarization to rotate away from the $<111>_c$ direction with ease on application of electric field and is responsible for the large piezoelectric response [16]. The monoclinic phase (M_A) discovered by Noheda et al was immediately used in justification of the polarization rotation theory as this phase provides a mirror plane $(1\bar{1}0)_c$ containing the $[001]_c$ and $[111]_c$ directions in which the polarization can continuously rotate. The schematic of the polarization rotation pathways is shown in *Figure* 6. Subsequently, another type of monoclinic phase (M_C) was discovered for the MPB compositions of the $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN–PT) [17]. The M_C phase provides continuous rotation of polarization from [001] (spontaneous polarization in the tetragonal phase) to [101] (spontaneous polarization in the orthorhombic phase) (*Figure* 6.). First principles calculations and phenomenological free energy based approaches have also predicted these low symmetry phases

Figure 6. Schematic of polarization pathways in ferroelectric perovskites. The polarization directions are shown with arrows. For the tetragonal, rhombohedral and orthorhombic phases, the polarizations are fixed along $[001]_c$, $[111]_c$ and $[101]_c$ directions respectively.
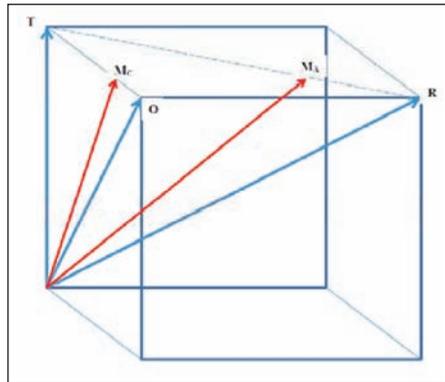
in PZT and PZN–PT and PMN–PT ferroelectric alloys [5]. Sometimes, the emphasis on the monoclinic phase has been mistakenly understood to be that the presence of this phase is sufficient to increase the piezoelectric response. This is not quite so. The very presence of monoclinic symmetry does not by itself guarantee an anomalous piezoelectric response. For high piezoelectric response, it is absolutely necessary that the system is in the proximity of an inter-ferroelectric instability. In PZT, PMN–PT and PZN–PT, the monoclinic phases are sandwiched in a narrow composition interval on one side by wide tetragonal phase field and on the other side by a wide rhombohedral phase field. It is this nearness to the thermodynamic criticality which makes for the anomalous piezoelectric response in MPB compositions (also) exhibiting monoclinic as one of the coexisting phase. In this context, it may be mentioned that a monoclinic phase has recently been reported in a ferroelectric compound $Na_{1/2}Bi_{1/2}TiO_3$. However its piezoelectric coefficient is not anomalous ($\sim$70 pC/N). Another instance is that of a non-perovskite ferroelectric – bismuth titanate $Bi_4Ti_3O_{12}$ – which possesses monoclinic symmetry (point group m, space group B1a1) but has unremarkable properties [18].

9. Adaptive Versus Genuine Monoclinic Phase

Interestingly, there is another alternative theory – generally known as the adaptive phase theory – according to which, the low symmetry monoclinic phase often suggested in ferroelectric perovskites near MPB composition by X-ray/neutron diffraction studies, is not a genuine crystallographic phase [19]. As discussed above, when point group symmetry changes across a phase transition, domains appear in the low symmetry phase. Creation of domain walls separating two domains costs energy to the system which is compensated by other mechanisms such as reduction in the depolarization energy [3, 4]. If the domain wall energy for a given system de-

High piezoelectric response is obtained in ferroelectric materials near an interferroelectric instability.

Debate continues on whether the mechanism associated with the anomalous piezoelectric response is primarily due to a genuine monoclinic phase or due to nano-sized domains of tetragonal/ rhombohedral phases.

creases drastically, a system can afford to have a large number of domains. The high piezoelectric response in the framework of this theory is therefore associated with the ease of motion of the domain walls on application of electric field or stress. This is in contrast to the polarization rotation theory proposed by Fu and Cohen [16] which attributes the anomalous response to the ease of rotation of the polarization within the unit cell (intrinsic contribution) on application of an electric field.

Under certain conditions, such nano-domains can give rise to coherent scattering resulting in additional peaks in the diffraction patterns, which may be interpreted as being due to symmetry lowering distortion of the structure [20]. This is called the 'adaptive monoclinic' phase in the literature. Wang [20] has derived relationships between the lattice parameters of the adaptive monoclinic phases and the lattice parameters of the high symmetry phase whose nano-domains are responsible for the adaptive phase. For example, the monoclinic M_A phase, as per this theory, can appear as a result of coherent diffraction from twinned nano-domains of true rhombohedral structure (R3m). The relationship between the lattice parameters of the adaptive M_A phase (a_m, b_m, c_m) and the rhombohedral lattice parameters (a_r, α_r) are given by

$$a_m \approx \sqrt{2}a_r \left(1 + \tfrac{1}{2}\cos\alpha_r\right);$$
$$b_m = \sqrt{2}a_r\sqrt{1 - cos\alpha_r};$$
$$c_m \approx a_r.$$

A similar relationship exists between the tetragonal (P 4mm) lattice parameter and the adaptive M_C monoclinic phase [20]. Recently, it was shown that the monoclinic distortion in the ferroelectric $Na_{1/2}Bi_{1/2}TiO_3$ can be interpreted in terms of the adaptive phase [10]. Debate continues in literature with regard to these two different viewpoints. One strong support for the genuinity of the monoclinic phases in ferroelectric perovskites comes

from the results of first principles [5] and phenomeno-
logical free energy [21] based studies which indeed pre-
dict the stability of such low symmetry phases in mono-
domain crystals.

10. Conclusions

A brief overview of the important structural and mi-
crostructural aspects that influence the piezoelectric re-
sponse in advanced piezoelectric materials has been pre-
sented. The extrinsic (domain) and intrinsic (lattice)
contributions to the overall piezoelectric response in fer-
roelectric materials have been discussed along with the
techniques used to quantify them. In the end, various
mechanisms associated with anomalous piezoelectric re-
sponse in perovskite ferroelectrics have been highlighted
with the emphasis on the role of low symmetry mon-
oclinic phases near inter-ferroelectric transition in en-
abling the high piezo-response.

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Address for Correspondence
Rajeev Ranjan
Department of Materials
Engineering
Indian Institute of Science
Bangalore 560 012, India.
Email:
rajeev@materials.iisc.ernet.in

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