

## CHAPTER 2

### LITERATURE REVIEW

It is the intent of this chapter to provide a brief description of necessary concepts including the characteristics of normal and relaxor ferroelectric materials. In addition, the reviews of prior studies on hysteresis properties of PMN-PZT ceramics are presented.

#### **21. Basic Definitions and Characteristics of Ferroelectric Materials**

##### **21.1. Piezoelectricity**

Piezoelectricity is a phenomenon which was discovered in 1880 by Jacques and Pierre Curie.<sup>11</sup> The name “piezo” is derived from the Greek, meaning “to press” hence, piezoelectricity is the ability of certain crystalline materials to develop an electrical charge proportional to an applied mechanical stress.<sup>6</sup> This is also called the direct piezoelectric effect. Piezoelectric materials also show a converse effect, where a geometric strain (deformation) is produced on the application of a voltage. The piezoelectric effect in a crystal results from the creation of electric dipole moments (polarization) and the establishment of electric field across the specimen by application of external force.

All crystals can be divided into 32 different classes or point groups utilizing elements, as shown in figure 2.1. Within the 32 point groups, 21 classes are noncentrosymmetric, a necessary condition for piezoelectricity to exist, and only 20 are piezoelectric. Among these 20 point groups, only 10 can display a spontaneous polarization, which is designated as pyroelectric. A subgroup of the spontaneous polarized pyroelectric is a very special category of materials known as ferroelectrics. Materials in this group possess spontaneous polarization that is reversible by an electric field of some magnitude less than the dielectric breakdown of the material itself.

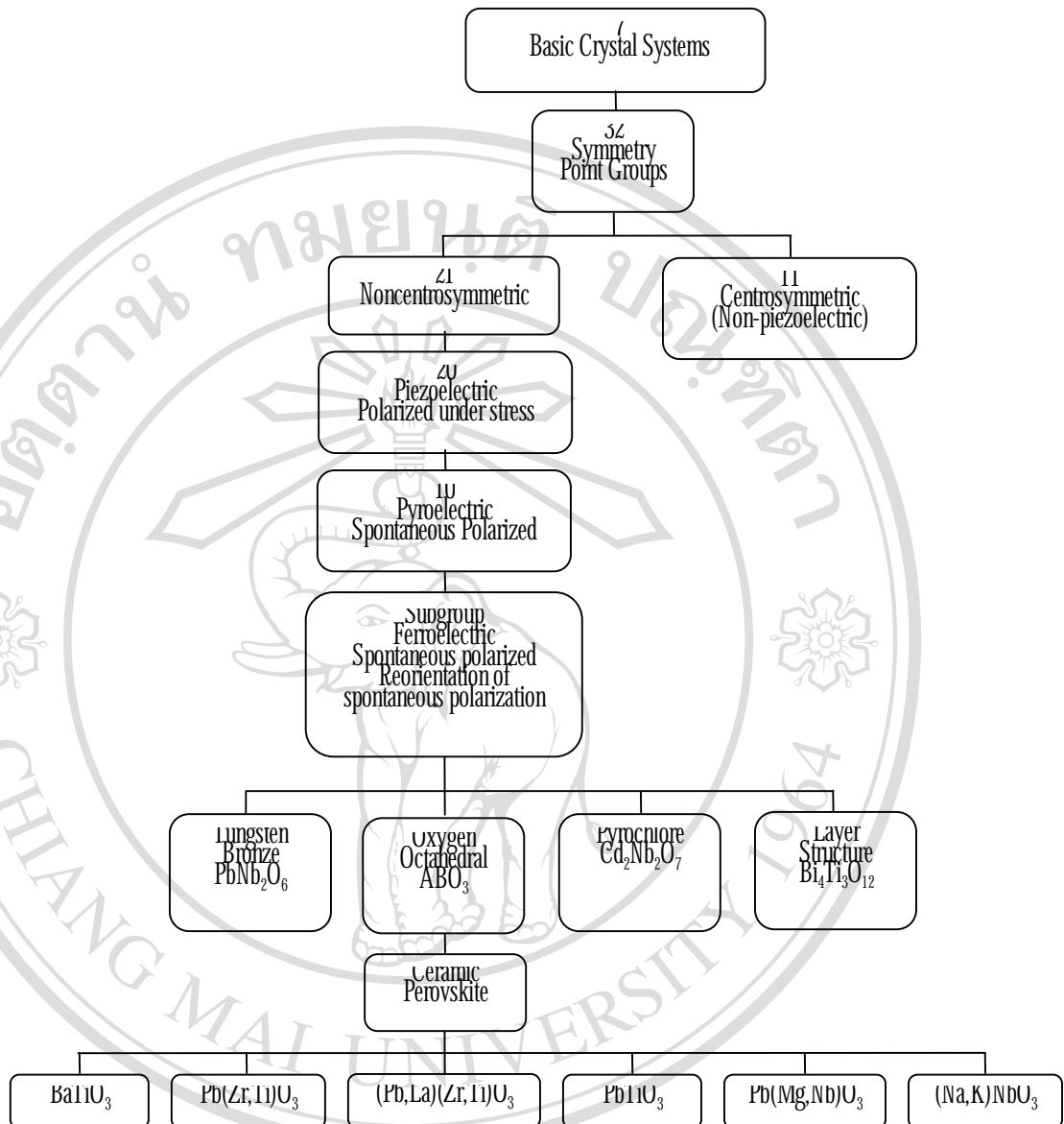


Figure 2.1 Interrelationship of piezoelectric and subgroups on the basis of symmetry<sup>11</sup>

## 21.2 Pyroelectricity

Out of the 20 point groups which show the piezoelectric effect, 10 point groups have only a unique polar axis. In absence of any load, they develop a polarization spontaneously and form a permanent dipole within the unit cell. Such kinds of crystals are called polar crystals. The spontaneous polarization is defined as the value of dipole moment per unit volume or the value of charge per unit area on the surface perpendicular to the axis of spontaneous polarization. The

value of spontaneous polarization depends on the temperature, this phenomenon is called pyroelectric effect and the crystals with this effect are called pyroelectric.<sup>13</sup>

### 21.3 Ferroelectricity

Ferroelectricity is a phenomenon which was discovered by Valasek in 1921.<sup>14</sup> The name refers to magnetic analogies, though it is somewhat misleading as it has no connection with iron at all. Rochelle Salt was the first material found to show ferroelectric properties such as a spontaneous polarization on cooling below the Curie temperature, ferroelectric domains and a ferroelectric hysteresis loop. As described above, pyroelectric shows a spontaneous polarization in a certain temperature range. If the magnitude and direction of spontaneous polarization can be reversed by an external electric field, it can be said to show ferroelectric behavior. Hence, all crystals and successfully poled ceramics which show ferroelectric behavior are pyroelectric, but not vice versa. For example tourmaline shows pyroelectricity but is not ferroelectric. Therefore, ferroelectrics are polar materials that possess at least two equilibrium orientations of the spontaneous polarization vector in the absence of an external electric field, and in which the spontaneous polarization vector may be switched between those orientations by an electric field.

#### 21.3.1. Ferroelectric Phase and Domains

Ferroelectrics may exhibit one or more ferroelectric (polar) phases (example of ferroelectric phase as shown in figure 2.2) that show a domain structure in which the individual domain states can be oriented by an applied field. Within a ferroelectric crystal, the homogenous areas with the same spontaneous polarization orientation are referred to as domains, and domains are separated by interfaces called domain wall.<sup>17</sup> A ferroelectric single crystal, when grown, has multiple ferroelectric domains. A single domain can be obtained by domain wall motion made possible by the application of an appropriate electric field. A very strong field could lead to the reversal of the polarization in the domain, known as domain switching.<sup>18</sup> Structure of a ferroelectric domain depends on the structure of the crystal. In a ferroelectric crystal, the variety of domain patterns and the number of types of domain wall depend on the number of orientations of the dipole moment when the spontaneous polarization occurs from the prototype phase.

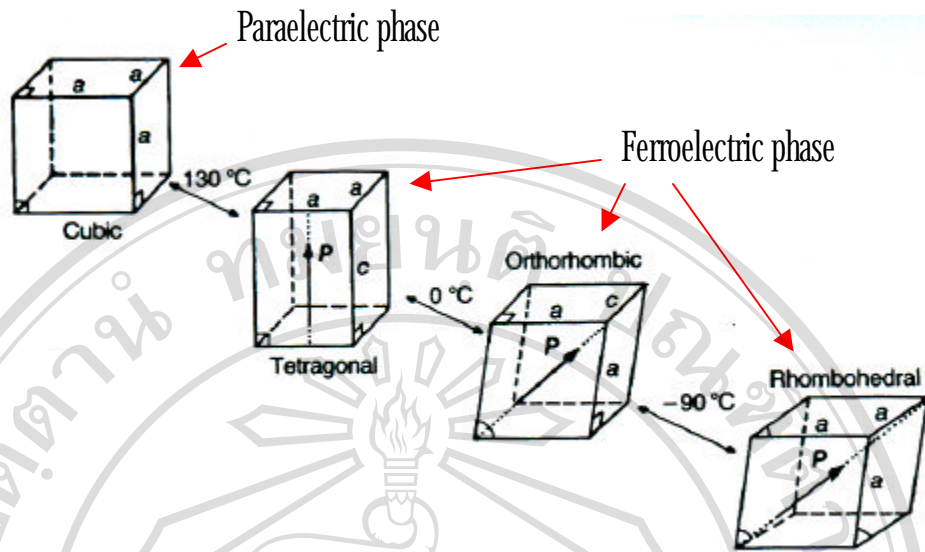


Figure 2.2 Unit cells of the ferroelectric phases of BaTiO<sub>3</sub><sup>6</sup>

For example, the tetragonal structure has a polar axis along the  $c$  axis, with an applied field in the opposite direction to the polarization, the neighboring domains are reduced and the entire region affected by the field will eventually switch into the new direction. Switching through  $90^\circ$  can be induced through the ferroelastic effect by applying a compressive stress along the polar axis without an accompanying electric field. The presence of mechanical stress in a crystal results in the development of domain wall configuration to minimize the strain. An example is presented in figure 2.3.<sup>19</sup> Switching through  $180^\circ$  is unaffected by mechanical stress. Figure 2.4 depicts  $180^\circ$  domain formation which minimizes the electrostatic energy of the system.<sup>19</sup>

The reason of domain walls formation is still not exactly clear. The generally acknowledged explanation is both  $180^\circ$  and  $90^\circ$  domain walls are formed to minimize the electrostatic energy of depolarizing fields arising from spontaneous polarization and the formation of  $90^\circ$  domain walls may also nucleate associated with spontaneous strain of the unit cell.<sup>13</sup>

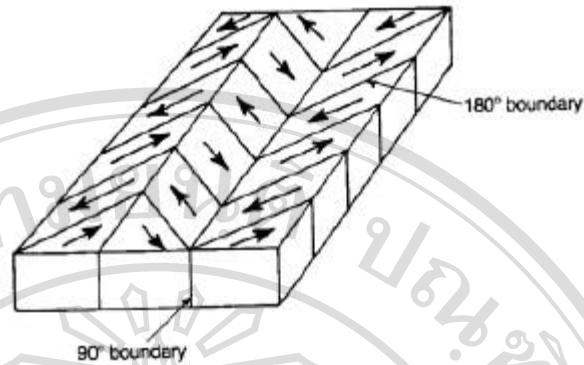


Figure 2.3 Schematic illustration of 180° and 90° domain walls<sup>19</sup>

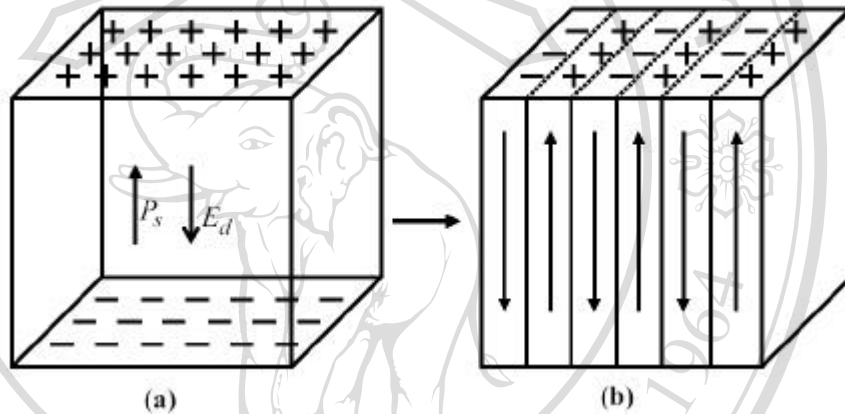


Figure 2.4 (a) Surface charge associated with spontaneous polarization  
(b) formation of 180° domains to minimize electrostatic energy<sup>19</sup>

Domain structures are strongly dependent on the symmetry of the ferroelectric phase. As the charges occur in symmetry resulting in different domain configurations, the other material properties will also be influenced.

### 21.3.2 Curie Temperature and Phase Transition in Ferroelectrics

Ferroelectrics undergo a phase transition corresponding to change in the crystal structure. This phase transition occurs at a particular temperature and is followed by same electric polarization amplitude and orientation modifications. Ferroelectrics have a transition temperature called the Curie temperature ( $T_c$ ). At temperature  $T > T_c$  the crystal does not exhibit ferroelectricity, while for  $T < T_c$  it is ferroelectric. Therefore, the Curie temperature is the temperature from which the ferroelectric crystal undergoes a structural phase transition, from a

paraelectric phase at  $T > T_c$  (the spontaneous polarization is vanished) to a ferroelectric one at  $T < T_c$  (with a spontaneous polarization).

Below  $T_c$ , the crystal exhibits ferroelectricity. The ferroelectric structure is created by a distortion of the paraelectric structure. As a result, the ferroelectric phase always has a lower symmetry than the paraelectric one. At  $T < T_c$ , the ions move from their equilibrium position (in the paraelectric phase) to create a spontaneous polarization. When a crystal is cooled down below  $T_c$ , the paraelectric-ferroelectric phase transition may be of two types: displacive or order-disorder. Ferroelectrics with a perovskite type structure exhibit a phase transition of the first type, i.e. displacive. Sequential structural phase transitions may occur in addition to the paraelectric to ferroelectric one. For instance,  $\text{BaTiO}_3$  has three ferroelectric phases below  $130^\circ\text{C}$  ( $T_c$ ) their phase transition temperatures are  $0^\circ\text{C}$  and  $90^\circ\text{C}$ .<sup>6</sup> Figure 2.2 represents the unit cell distortion occurring at  $T_c$ , when the paraelectric-ferroelectric phase transition happens.

### 21.3.3 Polarization Switching Process in Ferroelectrics

As mentioned before, the domains in ferroelectric polycrystal ceramics can be reoriented by an electric field or by a mechanical stress loading of sufficient magnitude. When an external electric field is applied to a ferroelectric ceramic, the domains more closely align to the external field direction grow to the detriment of the others. A very strong field could lead to the reversal of the polarization in the domain, known as polarization (or domain) switching.<sup>13</sup> As seen in figure 2.5, both  $180^\circ$  and  $90^\circ$  domain switching can occur in this case. This dynamic characteristic of a ferroelectric domain is anisotropy and depends on temperature and on the applied electric field.<sup>19</sup>

When an external field is applied opposite to the direction of polarization of a domain, a new domain may occur in the old domain by means of nucleation and growth.<sup>13</sup>

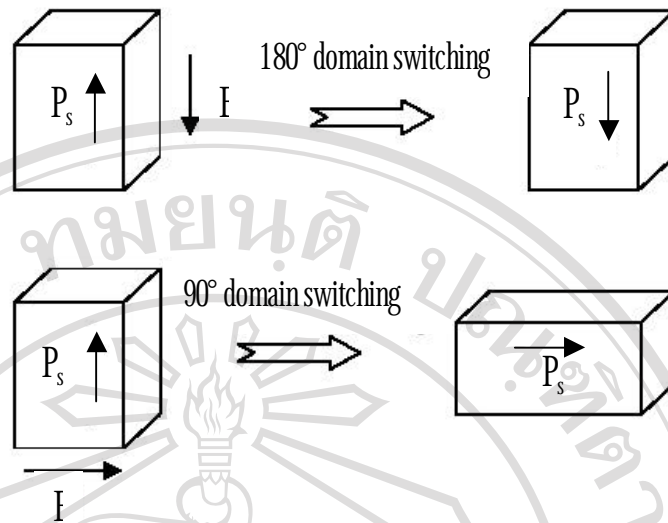


Figure 2.5 Schematic of 90° and 180° domain switching induced by an electric field above the coercive strength ( $E \geq E_c$ )<sup>20</sup>

The polarization process occurs in a ferroelectric ceramic when an electric field is applied. Starting with 90° and 180° domain patterns, the remanent dipole moments begin to rotate towards the direction of an externally applied electric field. When the electric field is removed, some dipole moment rotates back but not completely, resulting in a remanent polarization.

#### 21.34 The Hysteresis Loop of Ferroelectric

Another important characteristic of ferroelectrics is the ferroelectric hysteresis loop. Polarization reversal (switching) is a characteristic of ferroelectricity which can be observed by measuring the hysteretic polarization versus electric field (P-E) relationship below  $T_c$ .<sup>13</sup> A ferroelectric hysteresis loop can be observed by means of a Sawyer-Tower circuit (as seen in figure 2.6).<sup>17, 21</sup> As alternating voltage (V) is applied across the electrodes on the ferroelectric material  $C_x$  placed on the horizontal plates of an oscilloscope; hence the quantity plotted on the horizontal axis is proportional to the field across the ferroelectric material.  $C_0$  is a linear capacitor (with large capacitance) that is connected in series with the ferroelectric material  $C_x$ . The voltage across the linear capacitor  $C_0$  is therefore proportional to the polarization of the ferroelectric material.

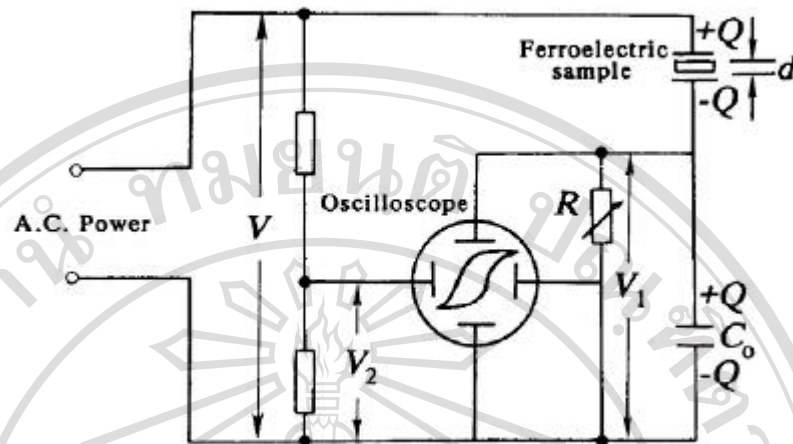


Figure 2.6 Schematic circuit of Sawyer-Tower for the observation of P-E characteristics of ferroelectric<sup>17</sup>

A typical loop is shown in figure 2.7. Application of a low electric field generates a linear relationship between P and E, because the field is not large enough to switch any domain and the crystal will behave as a normal dielectric material (paraelectric). The behavior corresponds to the segment OA of P-E loop in figure 2.7. As the electric field strength increases, a number of the domains with opposite polarization direction will switch towards the field direction, producing a rapid increase in polarization (segment AB). When all the domains are aligned as well as possible in the field direction a saturation state is reached (BC). At this saturation state, appropriately oriented crystals will be composed of a single domain.

As the field strength decreases, the polarization will decrease (BD) but does not go back to zero. When the field is reduced to zero, some of the domains will remain aligned and the crystal will exhibit a *remanent polarization* ( $P_r$ ). The extrapolation of the linear segment BC of the hysteresis loop back to the polarization axis (CBE) represents the value of the *spontaneous polarization* ( $P_s$ ), in the case of an appropriately oriented, of fully poled crystal.

The remanent polarization in a crystal cannot be removed until the applied field in the opposite direction reaches a certain value (at the point F in the Figure 2.7). The strength of the field required to reduce the polarization back to zero is called the *coercive field strength* ( $E_c$ ). Further, increase of the field in the negative direction will cause an alignment of the dipoles in



this direction and the cycle can be completed by reversing the field direction once again. Thus the relation between  $P$  and  $E$  is represented by a hysteresis loop (CDFGHC) as shown in Figure 2.7.<sup>13</sup>

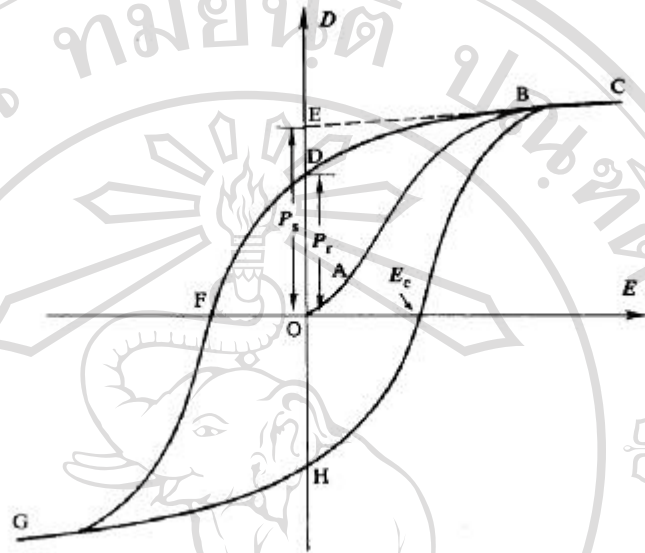


Figure 2.7 A typical P-E hysteresis loop in ferroelectric<sup>13</sup>

### 21.3.5 Poling of Ferroelectrics

After sintering, the ferroelectric ceramics are polycrystalline, and consist of grains and grain boundaries. Each grain can be considered as a ferroelectric single crystal, which is split in to many domains below the Curie temperature (see figure 2.8, left). Every domain has a certain spontaneous polarization and strain. Since the spontaneous polarization is randomly distributed the piezoelectricity and ferroelectricity from the domain cancel each other out in the macroscopic mean. For this reason, there is no residual macroscopic polarization. No discernable piezoelectricity is present in this “virgin” state of the material.



Figure 2.8 Schematic illustration of the domain structure and poling process<sup>22</sup>

The polycrystalline ferroelectric ceramics may be brought to a polar state by applying a strong electric field with a magnitude above the coercive field ( $E_c$ ). This process, called poling, cannot orient grains, but can reorient domains within individual grains in the direction of the field (see figure 2.8, middle). During poling, the material elongates along the field and contracts in the directions perpendicular to the field. The polarization after removal of the field is called remanent polarization ( $P_r$ ) (see figure 2.8, right). The actual remanent polarization of a ferroelectric ceramic material is always lower than the spontaneous polarization within a single domain. This is due to the fact that domains can only be oriented to some certain crystalline axes and because some domains will switch back to their initial states after the poling field is removed (driven by internal stresses).<sup>13</sup>

The poling process produces a ceramic material that acts very similar to a single domain crystal possessing both ferroelectric and piezoelectric properties. In 1945, Gray discovered this method, which was considered as one of the most starting discoveries during the research history of piezoelectricity, since the “poling” process is a key to turn an inert ceramic material into an electromechanically active material with a multitude of industrial and commercial uses.<sup>11</sup>

#### 21.4 Perovskite Structure

Most of the useful ferroelectrics, such as barium titanate ( $\text{BaTiO}_3$ ), lead titanate ( $\text{PbTiO}_3$ ), lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT) and potassium niobate ( $\text{KbO}_3$ ) have the perovskite structure. Perovskite is a family name of a group of materials and the mineral name of calcium titanate ( $\text{CaTiO}_3$ ) having a structure of the type  $\text{ABO}_3$ . The perovskite

structure can be also regarded as a cubic close-packed arrangement, the structure can be considered as FCC-derivative structure in which the larger A cation and oxygen together form an FCC lattice. The smaller B cation occupies the octahedral site in this FCC array and has only oxygen as its nearest neighbors.<sup>22</sup> As shown in figure 2.9, A-site cations (A: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, etc.) occupy the corners of a cube, while B-site cations (B: Ti<sup>4+</sup>, Zr<sup>4+</sup>, Sn<sup>4+</sup>, Nb<sup>5+</sup>, Ta<sup>5+</sup>, etc.) sit in the body center. Three oxygen atoms per unit cell rest on the faces. A perovskite structure can also be thought as a BO<sub>6</sub> octahedron network. The structure is also very tolerant to cation substitution to both A and B sites of lattice, and hence may lead to more complex compounds, such as Pb(Fe<sub>1/2</sub>Ta<sub>1/2</sub>)O<sub>3</sub>, Pb(Co<sub>1/4</sub>Mn<sub>1/4</sub>W<sub>1/2</sub>)O<sub>3</sub>, Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> and Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>.<sup>17,23</sup>

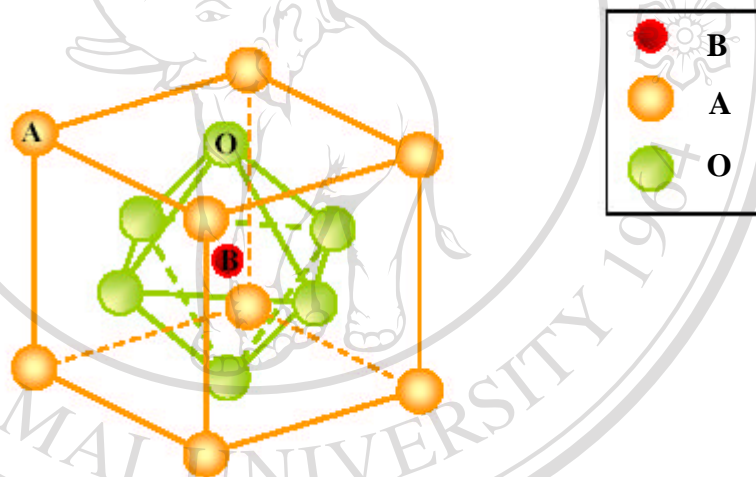


Figure 2.9 A cubic ABO<sub>3</sub> perovskite-type unit cell<sup>23</sup>

## 2.2 Normal and Relaxor Ferroelectrics

Normal ferroelectrics, such as PZT and BaTiO<sub>3</sub>, undergo a first or second order transition between ferroelectric and paraelectric phases at a well defined temperature usually called the Curie temperature. Upon increasing temperature, at T<sub>c</sub> the spontaneous polarization vanishes abruptly for the first order transition and slowly for the second order transition. A representation of the polarization versus temperature behavior is shown in figure 2.10 for the first and second order transitions.

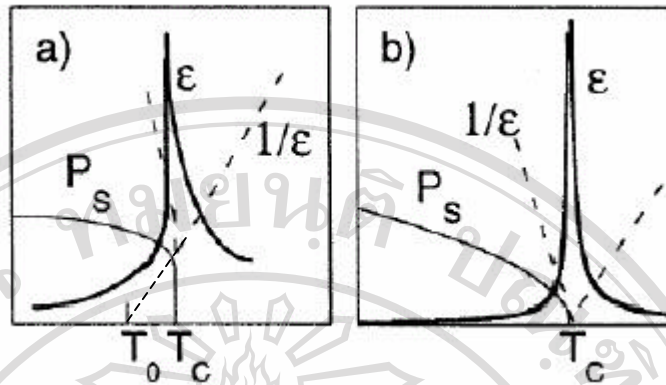


Figure 2.10 Schematic temperature dependence of the dielectric permittivity ( $\epsilon$ ) and spontaneous polarization ( $P_s$ ) for (a) a first-order and (b) a second-order ferroelectric<sup>24</sup>

At the transition, material exhibits a discontinuity in dielectric properties. The dielectric permittivity versus temperature shows sharp maxima at the transition temperature. The dielectric permittivity is a function of temperature. At temperature above  $T_c$ , the temperature dependence of the dielectric susceptibility ( $1/\epsilon$ ) is linear for a normal first or second order transition. Similar discontinuities are observed in the polarization versus temperature behavior. For normal ferroelectric materials, the depolarization temperature and temperature of dielectric maxima occur at the same temperature.

Relaxor ferroelectric are members of a group of materials, commonly called “diffuse phase transition” ferroelectrics, that do not exhibit distinct first or second order characteristics during the transformation between the paraelectric and ferroelectric phases. Several investigators have attempted to explain the phenomena underlying behavior in the relaxor ferroelectric, refining the compositional heterogeneity model proposed by Smolenskii in 1954 for complex perovskites.<sup>25</sup> Micro-inhomogeneities produce a by a non-random B-site cation distribution, as composed normal disordered complex perovskites such as PZT, results in the statistical distribution of chemically distinct micro-regions with broad range of Curie temperature.

The general characteristics distinguishing “relaxor” ferroelectric from normal ferroelectrics identified by Cross in 1987<sup>26</sup> and summarized in Table 2.1. The dielectric response in the paraelectric-ferroelectric transition region is significantly more “diffuse” than normal ferroelectrics, with maximum relative dielectric permittivities greater than 20,000. A typical plot

of dielectric permittivity versus temperature data is shown in figure 2.11. The temperature corresponding to the maximum dielectric permittivity ( $\epsilon_{\max}$ ) is referred to as the temperature of the maximum dielectric permittivity ( $T_{\max}$ ). The dielectric permittivity and loss exhibit dispersion near the transition, with  $\epsilon_{\max}$  decreasing and shifting to higher temperatures with increasing measuring frequency. The temperature of the maximum dielectric loss does not coincide with  $T_{\max}$  in relaxors. The loss increases with measurement frequency. Above  $T_{\max}$ , instead of a linear temperature dependence of the dielectric susceptibility, relaxors follow a square-law dependence.

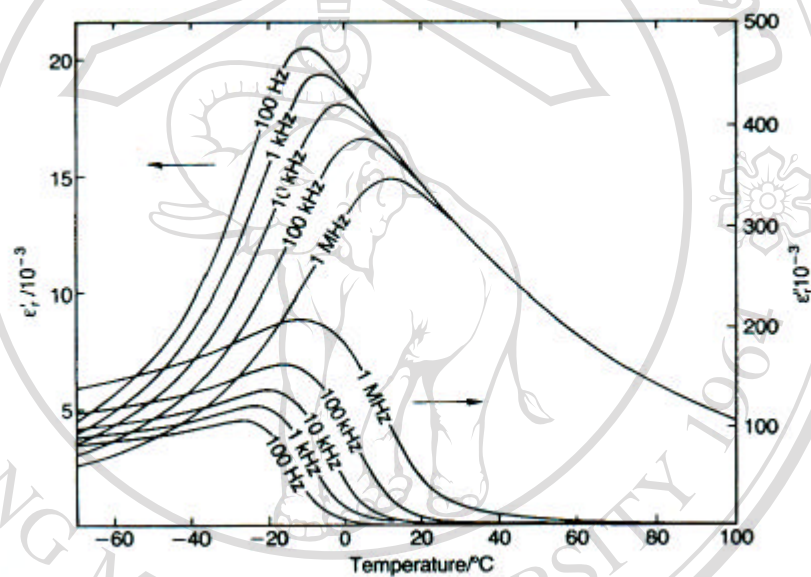


Figure 2.11 Temperature dependence of dielectric permittivity and loss factor for relaxor ferroelectric of PMN ceramic<sup>19</sup>

Table 2.1 Differences between normal and relaxor ferroelectric<sup>27</sup>

Property	Normal ferroelectric	Relaxor ferroelectric
Dielectric temperature dependence	Sharp 1 <sup>st</sup> or 2 <sup>nd</sup> order transition at Curie temperature ( $T_c$ )	Broad diffused phase transition at Curie maxima ( $T_{max}$ )
Dielectric frequency dependence	Weak frequency dependence	Strong frequency dependence
Dielectric behavior in paraelectric range ( $T > T_c$ )	Follow Curie-Weiss law	Follow Curie-Weiss square law
Remanent polarization ( $P_r$ )	Strong $P_r$	Weak $P_r$
Scattering of light	Strong anisotropy	Very weak anisotropy to light
Diffraction of X-Rays	Line splitting due to deformation from paraelectric to ferroelectric phase	No X-Ray line splitting

### 2.21. PZT Ceramics

PZT is the abbreviation for solid solution of  $x\text{PbZrO}_3$ -(1-x) $\text{PbTiO}_3$  ( $0 < x < 1$ ) binary system. Its chemical formula is  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ . PZT was first reported as ferroelectric material in 1952, and Shirane established the phase diagram. In 1954, PZT was reported as a useful piezoelectric material by Jaffe *et al.* Since then, PZT and its modified families become the most economically important category for civil and military piezoelectric applications.<sup>11</sup>

Both  $\text{PbTiO}_3$  and  $\text{PbZrO}_3$  are perovskite type crystals. Below their respective  $T_c$ ,  $\text{PbTiO}_3$  is in a tetragonal ferroelectric phase, where the dipole moment in neighboring unit cells are aligned parallel, whereas  $\text{PbZrO}_3$  is in an orthorhombic antiferroelectric phase, where the dipole moments in neighboring cells are aligned antiparallel. The  $\text{Ti}^{4+}$  ions in  $\text{PbTiO}_3$  can be partially substituted by  $\text{Zr}^{4+}$  with a molar ratio  $x$  to form a binary system (solid solution) with the following chemical formula  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ . This solid solution is called lead zirconate titanate (PZT). It also belongs to the perovskite-type ferroelectrics. In this solution,  $\text{Zr}^{4+}$  and  $\text{Ti}^{4+}$  occupancy on the B-site cation positions is random as seen in figure 2.12.

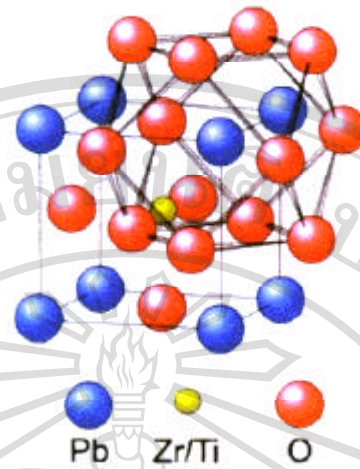


Figure 2.12 Cubic perovskite-type structure of PZT

The phase diagram of the PZT solid solution is shown in figure 2.13, where the  $T_c$ -line is the boundary between the cubic paraelectric phase and the ferroelectric phases. A morphotropic phase boundary (MPB) divides the regions of ferroelectric phase into two parts: a tetragonal phase region on the Ti-rich side and a rhombohedral phase region on the Zr-rich side. At room temperature, this boundary is at the point of Zr/Ti  $\sim$  52/48. In the region where Zr/Ti lies between 100/0 and 94/6, the solid solution is an antiferroelectric orthorhombic phase exhibiting no observable piezoelectric effect.

Most PZT materials of technological importance have compositions near the morphotropic phase boundary, and PZT ceramics usually exhibit their maximum values of relative dielectric permittivity and electromechanical coupling coefficient close to this MPB (see figure 2.14).

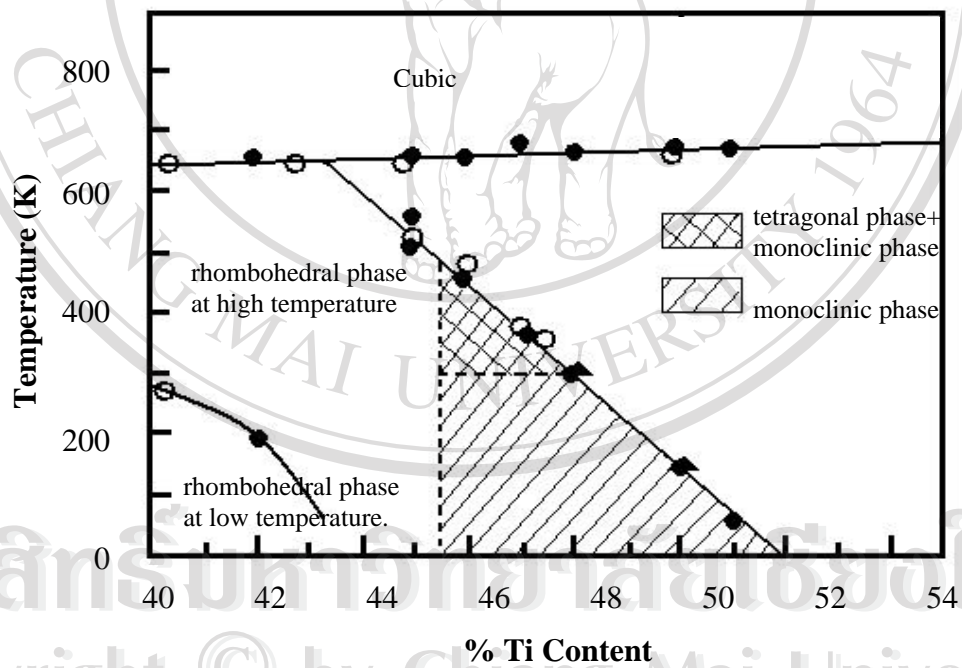
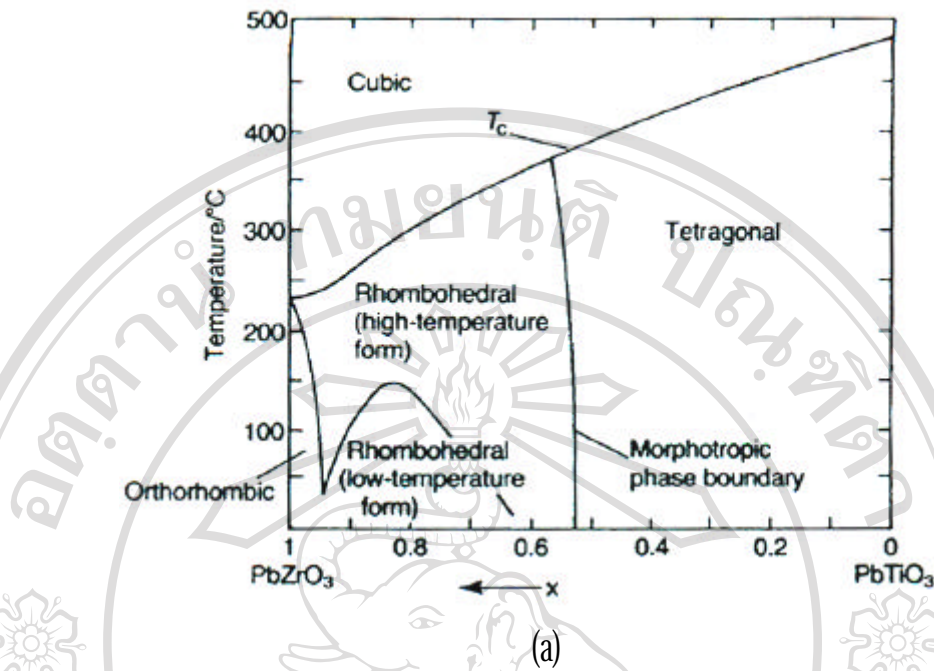


Figure 2.13 Phase diagram of the  $\text{PbTiO}_3$ - $\text{PbZrO}_3$  solid solution (a) by Jaffe *et al.*,<sup>6</sup> (b) by Noheda *et al.*<sup>7</sup>



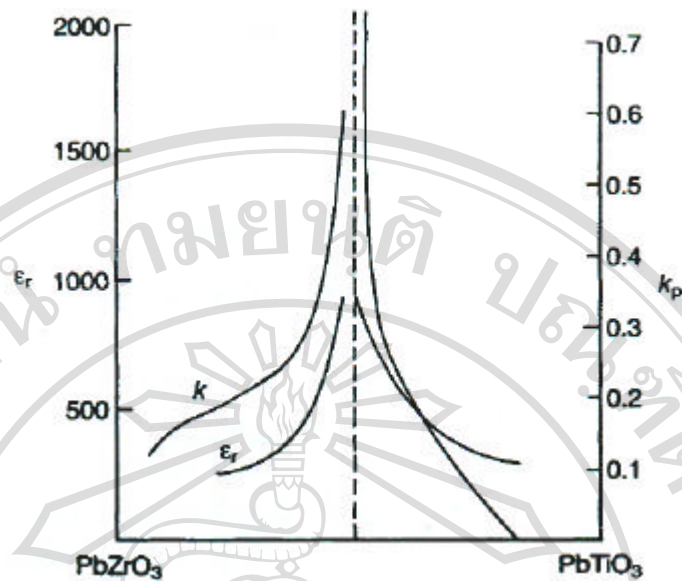


Figure 2.14 Dielectric and piezoelectric properties of the  $\text{PbTiO}_3$ - $\text{PbZrO}_3$  solid solution<sup>6</sup>

The maximum piezoelectric properties of PZT near MPB are due to more domain switching possibilities than in a single ferroelectric phase material.<sup>28</sup> Investigations have demonstrated that there can be a co-existence of the tetragonal and rhombohedral phases over a certain composition interval around the MPB. The tetragonal phase possesses 6 domain states along the equivalent [100] direction, and the rhombohedral phase possesses 8 domain states along the equivalent [111] direction. There are totally 14 possible poling directions near the MPB over a very wide temperature range, which may in part explain the extremely pronounced piezoelectric effects of PZT ceramics with composition near this boundary.

## 2.2.2 PMN Ceramics

Lead magnesium niobate, PMN or  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  was first synthesized by Smolenskii and Agranovskaya in 1958.<sup>29</sup> PMN is the prototypical relaxor ferroelectric and consists of a mixed B-site: Pb occupies the corner A-site and the B-site can be either magnesium and niobium ions. A small region of 1:1 chemical ordering of the B-site Mg and Nb ions is shown in figure 2.15. The 1:1 ordering found in PMN is somewhat unexpected given the Mg:Nb stoichiometry of 1:2, but it was suggested that this non-stoichiometric ordering may actually help stabilize the perovskite over the pyrochlore structure in PMN.<sup>13</sup> On the other hand, the Nb-rich matrix phase

appear to decrease the non-stoichiometric order regions of Mg:Nb. Its dielectric behavior is shown in figure 2.11. Its very large maximum in permittivity exhibits a broad transition and is also measurement frequency dependent which is the characteristics of relaxors. As the measurement frequency is increased, the maximum of the permittivity decreases while the temperature of that maximum increases. In normal ferroelectrics, the sharp transition in permittivity also indicates a phase transition as the symmetry of the crystal changes. For relaxors, however, the broad peak in dielectric permittivity does not always correspond to a structural phase transition, so the temperature of the maximum permittivity is designated  $T_m$  instead of  $T_c$ . In the case of PMN, there are local polar regions that exist well above  $T_m$ , and flipping of polar domains continues below it.

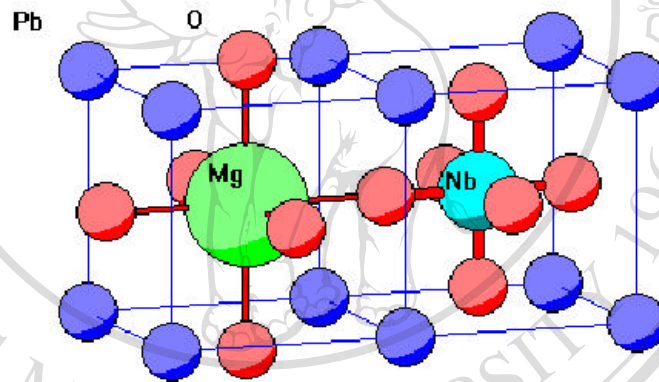


Figure 2.15 Two unit cells of the perovskite structure of PMN showing the chemical-ordering model. The B-site marked Mg is referred to as the B' site while Nb ions are on the B'' sites<sup>30</sup>

There has been a growing interest in understanding the ordering that occurs at the B-sites. The compositional fluctuations within nanodomain were believed to create different regions having varying Curie temperature<sup>14</sup>, thus giving PMN its broad relaxor response. Smolenskii proposed that local inhomogeneities in chemistry and/or structure result in microdomains having a distribution of Curie temperatures, leading to a diffuse peak in dielectric constant.<sup>11</sup>

Theoretical interpretations of relaxors have been offered using various models. Specifically, the compositional fluctuations on the B-site are believed to be responsible for the

relaxor behavior. A clearer understanding of the charge heterogeneity within PMN and its relation to the ferroelectric domains should help to understand the behavior of this relaxor. Yet PMN has found applications in a variety of devices where its unique properties have been exploited, even if they are not perfectly understood.

### 2.3 Prior Studies of Hysteresis Properties on PMN-PZT ceramics

$\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.67})\text{O}_3\text{-Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  solid-solution system in ceramic near the morphotropic phase boundary (MPB) have a high dielectric permittivity and a high electromechanical coupling coefficient and are useful as application devices.<sup>28</sup> Previously, there have been several investigations on PMN-PZT system.<sup>8,9,15,16,32-39</sup> However, these previous works have only focused on the influence of temperature and frequency on dielectric properties and effects of uniaxial stress on ferroelectric properties of PMN-PZT ceramics. Thus far, there has been no systematic study on effect of poling conditions and composition on ferroelectric properties of the ceramics.

The initial work of Ramana *et al*<sup>85</sup> considered the hysteresis properties of the ternary 0.5PMN-0.5PZT ceramics with Ag substitution, and concluded that the ceramics shown good square hysteresis loops. Moreover, the hysteresis parameters which are spontaneous polarization ( $P_s$ ) and remanent polarization ( $P_r$ ) increase with increasing Ag content. There is a slight increase in the coercive field ( $E_c$ ). The composition with 3 mole% Ag exhibits a maximum  $P_r$  and  $P_s$  with minimum dielectric loss. This indicates that the orientation of domains increases with increasing Ag content.

Shil'nikov *et al*<sup>86,37</sup> studied effect of temperature to hysteresis parameters on 0.89PMN-0.11PZT ceramic. They studied the temperature dependence of both the remanent polarization ( $P_r$ ) and found the greatest rate of the change of  $P_r$  with temperature happen at the temperature of transition from the macrodomain state to the microdomain state. They also found that in low temperature region (-185 to -50 °C) the PMN-PZT ceramics may have the regular polar “domain-like” structure. Asymmetric ferroelectric loop was also observed, and thought to be a result of the existence in a sample of the “internal bias” field. The fields can arise due to the structure defects of dipole defects in materials.

In 2003, Koval *et al*<sup>8</sup> have undertaken study on structure and electrical properties of (x)PMN-(1-x)PZT (when x=0.125, 0.25 and 0.5) ceramics as function of the PMN content. They

found that the shapes of hysteresis loop differ between the MPB compositions, a characteristic of the suppressed ferroelectric interaction. Moreover, they studied the effect of temperature to hysteresis loop of PMN. They found that the slim loop can be seen at 25°C, and when decreasing temperature to -43°C, an enchantment saturated polarization is observed further lower temperature to -120°C, ferroelectric type hysteresis loop becomes apparent in polarization behavior. It was concluded that the PMN content in ternary (x)PMN-(1-x)PZT solid solution substantially suppresses long-range co-operation between ferroelectrically active dipoles. While the room temperature state of 0.125PMN-0.875PZT with a composition near the MPB was confirmed to be long-range ordered ferroelectric, that of 0.5PMN-0.5PZT demonstrated a typical relaxor ferroelectric. The presence of a pseudocubic phase in the system also significantly reduced a piezoelectricity.

Yimnirun *et al*<sup>88</sup> studied the ferroelectric properties of various compositions of (x)PMN-(1-x)PZT. They found that the hysteresis loop of PZT ceramic is a typical “square” form, while the hysteresis is more of “slim” loop when more PMN content is added to the system. It was then concluded that an addition of PMN induces the relaxor behaviors of PMN into the PMN-PZT ceramic system. Hence, the ferroelectric properties of the ceramics in PMN-PZT system move gradually from normal ferroelectric state in PZT to the relaxor ferroelectric state in PMN.

Finally, Shaw *et al*<sup>89</sup> investigated the doping effect on ferroelectric properties of 0.18PMN-0.82PZT materials. They found that the hysteresis loops are significantly modified by addition of Nb<sup>5+</sup>, and change only moderately when being doped with Mg<sup>2+</sup>. Moreover, the polarizations (P<sub>r</sub> and P<sub>s</sub>) were first increased with a small addition of Nb<sup>5+</sup> ions. Polarizations decrease only slightly with addition of Mg<sup>2+</sup> ions. The coercive field (E<sub>c</sub>) varies with the dopant content in significantly different manner. It increases markedly with the concentration of niobium. However, it decreases only slightly with the addition of magnesium. The investigators then concluded that the properties become hard when Nb<sup>5+</sup> is added and soften when Mg<sup>2+</sup> is added to 0.18PMN-0.82PZT material.