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1.1 Ferroelectrics

Ferroelectric oxides have very important applications in electronics. As the field of nanoelectronics has become more and more important, the effort to build smaller and faster devices has pushed ferroelectrics to an even more prominent position. The potential of ferroelectrics to serve as memory devices has been known since the mid-1950s. Ferroelectric oxides represented by the general structural formula ABO$_3$ are the most commonly and widely used among the perovskite family of materials. Among ferroelectrics, lead zirconate titanate, Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZT) is receiving intensive scientific and technical attentions due to its outstanding properties such as high Curie temperature, high dielectric permittivity and high electromechanical characteristics. Modifications of the PZT materials and the effects of dopants had been researched extensively to improve its properties for various applications in sensors, actuators, ferroelectric random access memory (FERAM), infrared (IR) detectors, electro-optic light valves, medical ultrasound imaging etc. Therefore, PZT is one of the most widely used material for device applications [1-5]. One significant merit for PZT is that its properties can easily be tailored for specific applications by appropriate chemical substitution. Hence it becomes important to understand the various mechanisms by which different substituents influence the properties of PZT.

1.1.1 General properties of Ferroelectrics

Ferroelectricity is characterized by a spontaneous polarization that can be switched through the application of an electric field. Ferroelectric materials are a subset of piezoelectric materials. Piezoelectric materials become electrically polarized when they are mechanically strained. This property arises from the symmetry of certain crystal classes as shown in Figure1.1 [5].
For the piezoelectric phenomenon to occur in a material, the crystal lattice should have no centre of symmetry. Of the 32 crystal classes or point groups, 11 of the crystal classes have a centre of symmetry and are not therefore polar. The remaining 21 classes have no centre of symmetry and with one exception (class 432), have polar properties making them piezoelectric. The absence of symmetry in piezoelectric materials results in microscopic dipoles caused by the displacement between the positive and negative charges in the unit cell. 10 of the 20 piezoelectric crystal classes have no net polarization, as the microscopic dipoles sum to zero except when the crystal is strained. The remaining 10 piezoelectric classes contain a unique polar axis even in the unstrained condition, along which they are spontaneously polarized—these are called pyroelectric materials. If the temperature of the crystal is changed, a change in polarization is induced. This leads to the term pyroelectricity i.e., electricity released by heat. The ferroelectrics are a sub group of pyroelectrics. They have a spontaneous polarization, as do the pyroelectrics, but they have the additional property that the direction of spontaneous polarization can be reversed by an applied external electric field. Four types of ceramic ferroelectrics are shown in Figure 1.1 with typical examples representing the type based on its unit cell structure.
Fig. 1.1 Classification of piezoelectrics on the basis of symmetry.

[Source: Ferroelectric Ceramics: History and Technology, G.H. Haertling, J.Am.Ceram.Soc. 82(4)797-818(1999)]
1.1.2 Piezoelectricity

Piezoelectricity was detected in crystals, such as quartz, zinc blende and tourmaline by Jacques and Pierre Curie, in 1880. They found that if certain crystals were subjected to mechanical stress, they would become electrically polarized and the degree of polarization would be proportional to the applied stress. The name “piezo” is derived from the Greek, meaning, “to press”; hence, piezoelectricity is the generation of electricity as a result of a mechanical pressure. In the year 1881 Lippmann predicted that if an electric field is applied to a piezoelectric crystal it deforms and in the same year Curie brothers demonstrated the effect experimentally. This means that electrical energy can be transduced into mechanical energy and is referred to as the reverse piezoelectric effect [1, 6].

In any piezoelectric crystal, each unit cell has a dipole. A dipole results from a difference between the centre of positive charges and centre of the negative charges in a unit cell. The external charge due to the net internal dipole in the crystal is the polarization, measured as charge per unit area. Thus for a crystal to exhibit the piezoelectric effect, its structure should have no centre of symmetry. A stress (tensile or compressive) applied to such a crystal will alter the separation between the positive and negative charge sites in each elementary cell leading to a net polarization at the crystal surface. The effect is practically linear, i.e. the polarization varies directly with the applied stress and is direction dependent so that compressive and tensile stresses will generate electric fields and hence voltages of opposite polarity.
The relationship between the electric variables, field and displacement, and elastic variables, stress and strain, can be written in the general form as shown in equations (1.1 and 1.2).

\[
D = e^T E + dT 
\]

\[
S = s^E T + dE 
\]

where \(D\), \(S\) and \(T\) represents dielectric displacement, strain and stress respectively. The first equation describes the direct and second the converse piezoelectric effect.

1.1.3 Ferroelectric domains and Hysteresis loop

Ferroelectric crystals possess regions with uniform polarization called ferroelectric domains (Figure 1.2). Within a domain, all the electric dipoles are aligned in the same direction. There may be many domains in a crystal separated by interfaces called domain walls.

A ceramic is an agglomeration of small crystals, fitted together in a random way and therefore when a ferroelectric single crystal is grown, ferroelectric domains are formed [1, 7]. They usually have domain structure, as the twinned configuration has lower free energy than the single domain configuration. Due to the random orientation of domains, a ceramic of an ordinary piezoelectric material appears to be non-piezoelectric. To make the ceramic piezoelectric, an electric field must be applied to switch the polar axes of the crystallites in the ceramic ferroelectric to those directions allowed by symmetry which are nearest to that of the electric field.
Fig. 1.2 Schematic representation of the regions with uniform alignment of spontaneous polarization (ferroelectric domains).

### Table 1.1 Allowed polar directions in a crystal

<table>
<thead>
<tr>
<th>Crystal symmetry</th>
<th>Polar axis</th>
<th>Number of equivalent directions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal</td>
<td>[001]</td>
<td>6</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>[111]</td>
<td>8</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>[110]</td>
<td>12</td>
</tr>
</tbody>
</table>

All the domains in a ceramic can never get fully aligned along the poling axis because the allowed orientations of the polarization are restricted by the symmetry as shown in Table 1.1. For example, if the material has a rhombohedral perovskite structure then the polarization gets oriented along one of the eight [111] directions. After this process called “poling” the ceramic resembles a piezoelectric single crystal in that it has a net dipole moment and will respond linearly to the applied electric field. A single domain can thus be obtained by
domain wall motion which was made possible by the application of an electric field. A very strong field could lead to the reversal of the polarization in the domain, known as domain switching. The polarization reversal can be observed by measuring the ferroelectric hysteresis as shown in Figure 1.3. As the electric field strength is increased, the domains start to align in the positive direction giving rise to a rapid increase in the polarization. At very high field levels, the polarization reaches a saturation value ($P_s$). The polarization does not fall back to zero when the external field ($E$) is removed. When $E=0$ some of the domains remain aligned in the positive direction, hence the crystal will show a remanant polarization ($P_r$). The crystal cannot be completely depolarized until a field of magnitude $E_c$ is applied in the negative direction. The external field needed to reduce the polarization to zero is called the coercive field strength ($E_c$). If the field is further increased in the opposite direction, the direction of polarization flips. Similar to the response during positive fields, saturation ($-P_s$) and remanance ($-P_r$) are exhibited in the negative field also and hence a hysteresis loop is obtained.

A considerable amount of information can be obtained from a hysteresis loop. (i) high remanent polarization ($P_r$) relates to high internal polarizability, strain and electromechanical coupling.(ii) For a given material, the switching field ($E_c$) is an indication of the grain size(lower $E_c$ means larger grain size and higher $E_c$ means smaller grain size).(iii) a high degree of loop squareness usually indicates better homogeneity and uniformity of grain size.(iv) an off-centered loop from the zero voltage point indicates some degree of internal electrical bias that may be caused by internal space charge and or/ aging.

Polycrystalline piezoelectrics are also characterized by their field-induced strain as shown in Figure 1.4. In the converse piezoelectric effect, the dipole
moment per unit volume changes in response to an electric field and this change is accompanied by the movement of ions, thereby causing strain.

**Fig.1.3** P-E Hysteresis loop for a typical ferroelectric crystal

**Fig.1.4** A typical Strain- Electric field response curve
The shape resembles that of a butterfly, and it is often referred to as the “butterfly loop”. When an electric field is applied in the direction of spontaneous polarization, the domains start to align in the direction of polarization and a strain results. A polarization switch of 90° causes considerable switching strain than the 180° switch. If the electric field is decreased to zero, the strain decreases, but significant permanent strain still remains. When the electric field is increased in the opposite direction the strain further decreases until all the polarization induced strain is cancelled and the overall strain is zero. Further increase of the reverse field beyond this point (coercive field) produces the phenomenon of domain switching and a strain results. Finally a symmetric ‘butterfly’ shaped curve is obtained when the electric field is brought back to zero. In the ferroelectric case, the switching strain accompanying the polarization reversal process results in the loop, with the remanent strain state in the centre of the loop.

1.1.4 Curie point and phase transitions

All ferroelectric materials have a transition temperature called the Curie point ($T_c$). On decreasing the temperature through the Curie point, a ferroelectric crystal undergoes a phase transition from a paraelectric phase to a ferroelectric phase. At a temperature $T > T_c$ the crystal does not exhibit ferroelectricity, while for $T < T_c$ it is ferroelectric. Near the Curie point or transition temperatures, thermodynamic properties including dielectric, elastic, optical and thermal constants show an anomalous behaviour. This is due to the distortion of the crystal as the structure changes.

1.1.5 Dielectric properties

For good insulators, dielectric constant ($K$) does not vary much with frequency. In ferroelectrics, and especially in poled piezoelectric samples, there
is a strong dependence of $K$ on frequency. At low frequencies, non-uniform conductivity gives rise to interfacial polarization which contributes to the effective dielectric constant and loss. This effect is strongly frequency dependent. Dipole relaxation connected with impurities and domain wall motion also may contribute to frequency dependence. The conventional measurement at 1 kHz gives a free dielectric constant $K_T$ which includes a piezoelectric component. Above all elastic resonance frequencies and their major harmonics, one observes a clamped constant $K_S$. Here inertia blocks the piezoelectric effect. In the resonance regions, the electric capacitance is overshadowed by the admittance of the mechanical branch of the equivalent circuit. In the vicinity of each resonance or harmonic, the measured capacitance undergoes violent changes with frequencies and bears little relation to the free or clamped dielectric constant. The ratio between the free and clamped dielectric constant is related to the piezoelectric coupling constant by equation 1.3

$$K_S = K_T (1-k^2)$$ ......................................................... (1.3)

where $k$ is called the electromechanical coupling factor. At frequencies far below resonance, piezoelectric ceramics are fundamentally capacitors.

1.2 Types of ferroelectric materials

The ferroelectric materials have been grouped according to their structure. The perovskite ferroelectrics, the focus of this thesis, belong to the corner sharing oxygen octahedral structure.

1.2.1 The Perovskite structure

Some of the most important ferroelectric oxides crystallize in the perovskite structure. This structure may be described as a simple cubic unit
cell with a large cation ($A^{2+}$) on the corners, a smaller cation ($B^{4+}$) in the body centre and oxygen ($O^{2-}$) in the centers of the faces. The structure is a network of corner-linked oxygen octahedra, with the smaller cations, $B^{4+}$, filling the octahedral sites ($B$ sites) and the larger $A^{2+}$ cations filling the dodecahedral sites ($A$ sites) created by the linked octahedra. A typical $ABO_3$ unit cell structure is given in Figure 1.5 (a).

In prototypic forms, the geometric centers of the $A^{2+}$, $B^{4+}$ and $O^{2-}$ ions coincide giving rise to a non-polar lattice. When polarized, the $A$ and $B$ ions are displaced from their geometric centers with respect to the $O^{2-}$ ions, to give a net polarity to the lattice. On cooling below the Curie point $T_c$, a tetragonal structure develops where the centre of $A^{2+}$ and $B^{4+}$ ions are displaced relative to the $O^{2-}$ ions, leading to the formation of electric dipoles. Spontaneous polarization developed is the net dipole moment produced per unit volume for the dipoles pointing in a given direction. Figure 1.5(b) shows the polarization of a $ABO_3$ unit cell.
Fig. 1.5 (a) ABO$_3$ perovskite type unit cell (b) unit cells illustrating the polarization reversal. ▶️ $A^{2+}$ ▶️ $B^{4+}$ ▶️ $O^{2-}$
A wide variety of cations can be substituted in the perovskite structure. The relationship given by the equation 1.4

\[
    t = \frac{(r_A^{2+} + r_O^{-})}{\sqrt{2}(r_B^{4+} + r_O^{-})} \tag{1.4}
\]

describes the basic criterion for adopting the ideal cubic perovskite structure where \( t \) is the tolerance factor and \( r_A^{2+} \), \( r_B^{4+} \) and \( r_O^{-} \) indicate the ionic radii of large cation, small cation and anion respectively[8]. Structures whose tolerance factor \( t \) is about 0.95-1.0 are cubic, those with lower values are slightly distorted but non-ferroelectric, and those slightly over 1.0 are ferroelectric. Besides the ionic radii, other factors such as polarizability and nature of bonds must also be taken into account. In the compositions which satisfy the above mentioned requirements, the valency of the A cation may range from 1 to 3 (\( \text{Pb}^{2+}, \text{Ca}^{2+}, \text{Na}^{+} \) etc) and that of the B cations from 3 to 5 (\( \text{Ti}^{4+}, \text{Zr}^{4+}, \text{Nb}^{5+} \) etc). The simultaneous substitution into both A and B sites with different ions can be used to tailor the properties of these materials.

Piezoelectric applications have been reported from a number of compositions and solid solutions including \( \text{BaTiO}_3 \), \( \text{Pb(ZrTi)}_3 \), \( \text{PbLa(ZrTi)}_3 \), \( \text{PbNb}_2\text{O}_6 \), \( \text{NaNbO}_3 \) and \( \text{PbTiO}_3 \). Foremost of these has been \( \text{BaTiO}_3 \), which dates from the early 1940s. In the past several decades, \( \text{BaTiO}_3 \) has been largely replaced by the PZT and PLZT for piezoelectric applications. This is because PZT and PLZT compositions have the following advantages:

(i) higher electromechanical coupling coefficients than \( \text{BaTiO}_3 \).
(ii) higher $T_c$ values, which permit higher temperatures of operation.

(iii) compositions at or near MPB can be well poled.

(iv) possess a wide range of dielectric constants.

(v) form solid-solution compositions with many different constituents, thus allowing a wide range of achievable properties.

1.3 Lead Zirconate Titanate (PZT) System

Lead Zirconate Titanate is a binary solid solution of PbZrO$_3$ an antiferroelectric (orthorhombic structure) and PbTiO$_3$ a ferroelectric (tetragonal structure). Substitution of Zr$^{4+}$ for Ti$^{4+}$ in PbTiO$_3$ reduces the tetragonal distortion and ultimately causes the appearance of another ferroelectric phase of rhombohedral symmetry. Still more Zr$^{4+}$ causes the appearance of the orthorhombic antiferroelectric (A$_o$) PbZrO$_3$ phase with a small field of stability and a tetragonal antiferroelectric phase (A$_T$) near the Curie point. Lead Zirconate Titanate [Pb(Zr$_x$Ti$_{1-x}$)O$_3$, PZT] has a perovskite type structure with the Ti$^{4+}$ and Zr$^{4+}$ ions occupying the B site. The PZT phase diagram is shown in Figure 1.6. At high temperatures PZT has the cubic perovskite structure which is paraelectric ($P_c$). On cooling below the Curie point, the structure undergoes a phase transition to form a ferroelectric tetragonal ($F_T$) or rhombohedral ($F_R$) phase. In the tetragonal phase, the spontaneous polarization is along the $<100>$ set of directions while in the rhombohedral phase the polarization is along the $<111>$ set of directions.
The boundary between the tetragonal and rhombohedral phases is nearly independent of temperature and is called morphotropic phase boundary (MPB). The morphotropic tetragonal-rhombohedral phase boundary is considered as a specific composition. It is required that this be a two-phase zone and this has been experimentally confirmed. The MPB separating the two ferroelectric tetragonal and rhombohedral phases has a room temperature composition with a Zr/Ti ratio of ~52/48. Most physical properties such as dielectric and piezoelectric constants show an anomalous behaviour at the morphotropic phase boundary. PZT ceramics with the MPB composition show excellent piezoelectric properties as shown in Figure 1.7.

This may be summarized as being due to (i) the existence of a mixture of phases at the boundary, (ii) a concurrent maximum in dielectric constant at the
MPB, (iii) a larger number of reorientable polarization directions existing in the MPB region, and (iv) a maximum in mechanical compliance in the boundary region, permitting maximum domain reorientation without physically cracking. The poling of the PZT ceramic is also made easy at this composition because the spontaneous polarization within each grain can be switched to one of the 14 possible orientations (eight [111] directions for the rhombohedral phase and six [100] directions for the tetragonal phase). Below the Zr/ Ti ratio of 95/5 the solid solution is antiferroelectric with an orthorhombic phase. The rhombohedral ferroelectric phase has two phases; a high temperature phase and a low temperature phase. Although both appear to be simple cell rhombohedral by X-ray diffraction, neutron diffraction studies indicate a multiple rhombohedral cell for the low temperature phase.

Fig.1.7 Effect of composition on the dielectric constant $\varepsilon_r$ and electromechanical coupling factor $k_p$ in PZT
1.4 La-Doped Lead Zirconate Titanate (PLZT) System

PLZT is a transparent ferroelectric ceramic formed by doping La\(^{3+}\) ions on the A sites of lead zirconate titanate (PZT). The PLZT ceramics have the same perovskite structure as PZT. Figure 1.8 shows the PLZT system with the parent PZT phase diagram [5] and it indicates that the effect of adding lanthanum to the PZT system is (i) maintaining extensive solid solution throughout the system (ii) giving rise to broad areas of different phases with different applications (iii) reduction of the T\(_{c}\) with increasing lanthanum. The room temperature phase diagram of the PLZT system [9] is given in Figure 1.9. The phase diagram is shown only up to 30 at.% La, since higher La contents produce a cubic nonferroelectric phase at room temperature for all (Zr/Ti) ratios. Some important features of the phase diagram are (i) small variations in La content produce large changes in areas of phase stability, (ii) increasing La content extends the antiferroelectric (AFE) phase over the ferroelectric (FE) phase, (iii) increasing La content favors the tetragonal ferroelectric phase over the rhombohedral. A moderately broad transition region (cross-hatched area) exists between the ferroelectric-antiferroelectric compositions in this region. The hysteresis loops for various compositions are also shown in Figure 1.9.
**Fig. 1.8** Phase diagram of the PZT and PLZT solid – solution systems

[Source: Ferroelectric Ceramics: History and Technology, G.H. Haertling, J.Am.Ceram.Soc. 82(4)797-818(1999)]
Fig. 1.9  Room Temperature Phase Diagram of PLZT with representative hysteresis loops at various compositions

PLZT ceramic compositions in the tetragonal ferroelectric region show hysteresis loops with a very high coercive field ($E_c$). Materials with this composition exhibit linear electro-optic behavior for $E<E_c$. PLZT ceramic compositions in the rhombohedral ferroelectric region of the PLZT phase diagram have loops with a low coercive field. These PLZT ceramics are useful for optical memory applications. PLZT ceramics compositions with the relaxor ferroelectric behavior are characterized by a slim hysteresis loop. They show large quadratic electro-optic effects which are used for making flash protection goggles to shield them from intense radiation. This is one of the biggest applications of the electro-optic effect shown by transparent PLZT ceramics. The PLZT ceramics in the antiferroelectric region show a hysteresis loop expected from an antiferroelectric material. These components are used for memory applications.

In order to suit some specific requirements for certain applications, piezoelectric ceramics can be modified by doping them with ions which have a valence different from those in the lattice. Piezoelectric PZT ceramics having the composition at or near the MPB can be doped with ions to form “hard” and “soft” PZT. Hard PZT are doped with acceptor ions such as $K^+$, $Na^+$ (at the A site) and $Fe^{3+}$, $Al^{3+}$, $Mn^{3+}$ (at the B site), creating oxygen vacancies in the lattice. Hard PZT usually have lower permittivity, small dielectric loss and lower piezoelectric coefficients. These are more difficult to pole and depole, thus making them ideal for hard-drive applications. On the other hand, soft PZT are doped with donor ions such as $La^{3+}$ (at A site) and $Nb^{5+}$, $Sb^{5+}$ (at B site) leading to the creation of A site vacancies in the lattice. Soft PZT are characterized by higher values of dielectric permittivity, dielectric losses,
piezoelectric coefficients and are easy to pole and depole. They can be used for applications requiring very high piezoelectric properties, such as actuators.

1.5 Defect Chemistry of PZT

In semiconductors, doping is widely employed. Aliovalent dopants are used to realize $n$- and $p$- type conduction and to form junctions for specific device applications. Similar doping principles can be used in oxides to alter the electrical properties. Undoped PZT exhibits $p$-type conductivity. This is due to the presence of holes caused by the A-site vacancies due to higher volatility of Pb$^{2+}$ as shown below:

$$V_{pb} \rightarrow V_{pb}^* + 2h^*$$ ......................................................... (1.5)

1.5.1 Donor-doping

A positive ion replacing another of lower vacancy, for eg: - La$^{3+}$ for Pb$^{2+}$ acts as a ‘donor’ (D) contributing extra electrons. Donors on the A-site are more common due to the lower volatility of many trivalent cations, M$^{3+}$. Considering only the lead oxide sublattice, a trivalent donor (D) on the A-site would lead to the formation of electrons as shown in equation 1.6,

$$D_{2}O_{3} \xrightarrow{2PbO} 2D_{pb}^* + 2O_a + \frac{1}{2}O_2 + 2e^' \text{.............. (1.6)}$$

or could be compensated by the formation of an A-site vacancy as shown in equation 1.7

$$D_{2}O_{3} \xrightarrow{3PbO} 2D_{pb}^* + 3O_a + V_{pb}'' \text{......................... (1.7)}$$
For PZT, a typical B-site donor is Nb$^{5+}$ whereas La$^{3+}$ is the most common A-site donor.

### 1.5.2 Acceptor-doping

A positive ion replacing a higher valency ion, for eg: - K$^+$ for Pb$^{2+}$ acts as an ‘acceptor’ (A) creating holes. In PZT, acceptors on the B-site are more common. Considering only the TiO$_2$ sublattice, a trivalent acceptor (A) in the B-site would lead to the formation of holes as shown in equation 1.8

\[
A_2O_3 + \frac{1}{2} O_2 \rightarrow 2A'_{Ti} + 4O_o + 2h^* \quad \text{......... (1.8)}
\]

or could be compensated by the formation of oxygen vacancy as shown in equation 1.9

\[
A_2O_3 \rightarrow 2A'_{Ti} + 3O_o + V_o^{**} \quad \text{......................... (1.9)}
\]

where $D_{Pb}^*$, $V_{Pb}^{**}$, $O_o$, $V_o^{**}$ represent a negatively charged A-site, doubly negatively charged A-site vacancy, lattice oxygen and doubly positively charged oxygen vacancy respectively.

### References


Technische Physik 8, 251 (1927).