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Doctorate of Philosophy

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Field-Induced Antiferroelectric-Ferroelectric Phase Switching Behavior in Lead Strontium Zirconate Titanate Ceramics

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ABSTRACT

Lead zirconate titanate (PZT) materials are used widely as transducers and actuators in a variety of applications. The phase diagram of PbZrO$_3$-PbTiO$_3$-SrTiO$_3$-SrZrO$_3$ system (called PSZT) shows a long AFE-FE phase boundary suitable for field-induced phase transition study.

Initially, the phase transitions in PSZT ceramics are studied to assist in understanding the effects of compositional modification on the relative stabilities of the AFE and FE phases. This yielded modified AFE-FE phase boundary for the PSZT family based on the polarization and structural information. The stabilization of the AFE phase by increasing Sr$^{2+}$ and Zr$^{4+}$ content produced increased AFE-FE transition field and decreased polarization.

Phase transitions with respect to temperature are investigated by means of polarization hysteresis and dielectric properties measurements. These observations are discussed in terms of Goldschmidt’s tolerance factor and soft-mode theory.

The entropy difference ($\Delta S$) during AFE-FE phase switching is calculated using a modified Clausius-Clapeyron approach. The dependence of the switching field on temperature (dE/dT) is found to be greater for the reverse switching than for forward phase transition. An explanation is provided in terms of the relative coupling strength of the domains.

The longitudinal field-induced strain in the PSZT systems is in the range of 0.2%-0.5% indicating possibilities for creating large strain actuators using selected
compositions. However, PSZT ceramics displayed degradation in polarization and field-induced strain with increasing number of the switching cycles.

In order to increase the field-induced strain and reduce the remnant strain, composition PSZT 15/80/20 is doped with various amounts of La$^{3+}$ or Nd$^{3+}$ (1-3 atom%). The stabilization of the AFE structure by La$^{3+}$ or Nd$^{3+}$ doping resulted in increased AFE-FE phase transition field and decreased temperature of the maximum dielectric constant. The induced strain is maximized at 2 atom% La$^{3+}$ or Nd$^{3+}$ doping with negligible remnant strain.

Using innovative in situ x-ray diffraction technique, direct observations of the unit cell parameters of the AFE phase and subsequent electric field-induced FE phase of selected PSZT ceramics are preformed. This volume increase accounts for most of the large field-induced longitudinal strain during AFE-FE phase transition.
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1. INTRODUCTION

As the demand for sensors, memory chips, and actuators has grown over the past decades, the technology for controlling the dielectric and piezoelectric properties of materials have become very important for the development of devices. An electric actuator is a device that is capable of transducing an input energy into a mechanical output energy. Conventional devices that are driven by motors or coils have serious problems in precise positioning. The use of magnetic field-induced strains in solid-state piezomagnetic and magetostrictive transducers require the added complexity of magnetic coils and gears, and the induced strains are relatively small ($10^{-5}$) for practical application. Consequently, the development of ceramic actuators through use of electric field-induced strains in ferroelectric materials [1, 2] has been of great interest.

Piezoelectric actuator materials are based primarily on lead zirconate titanate (PZT) and further modified form. These soft ferroelectrics exhibit an almost linear relation between strain and applied field below 1 kV/cm [3], but for high fields there is a nonnegligible hysteresis as a result of the domain switching. Traditional ceramic actuators suffer from imprecision in the displacements rising from domain reorientation effects and hysteresis. Strain verses electric field hysteresis can be minimized with the use of hard PZT. However, the reduction in hysteresis and loss comes at the expense of $d_{33}$ (~200-300 pC/N) and subsequent low strain level [4]. Another category of commercial actuator is electrostrictor. Hysteresis in the strain-field dependence is minimal or negligible in a selected temperature range. High precision positioning may be controlled by electrostrictive strain that is proportional to the square of the polarization. But, the electrostrictive strain level is especially small at low fields and normally it does
not exceed 0.15%. This limitation originates from the electrostrictive material’s breakdown strength and polarization saturation.

Electrostrictiction-like effects are also evident in nonpolar antiferroelectric materials that undergo a phase change from antiferroelectric to ferroelectric phase when a sufficiently high electric field is applied. Lead zirconate titanate (PZT) ceramics are extensively used as piezoelectric sensors, transducers, and actuators in a variety of applications because of their excellent electromechanical response. A ferroelectric crystal (FE) is one which shows a spontaneous electric polarization and whose direction of the spontaneous polarization can be reversed by an electric field. On the other hand, an antiferroelectric crystal (AFE) is one whose structure can be considered as being composed of two alternating sublattices polarized spontaneously in antiparallel directions. In general, the different antiferroelectric (AFE) and ferroelectric (FE) phases are distinguished by small (~0.02 nm) displacement of ions from a common high-temperature cubic prototypical form [5]. Switching between forms can be accomplished without breaking any energetic bonds. The free energy difference in PZT ceramics may be modified compositionally to such an extent that a stable antiferroelectric phase can be switched to a ferroelectric form by an electric field at room temperature. Since the atomic arrangement of AFE is more compact than that of the FE counterpart [5], one may expect a large strain in this field-induced AFE-FE phase transition process.

The conventional PZT materials generally have compositions close to the ferroelectric rhombohedral-tetragonal (F_R-F_T) morphotropic phase boundary (MPB) due to the existence of a very high electromechanical coupling factor (coupling factor in planar mode, \(K_p \approx 0.6\) and coupling factor in thickness mode, \(K_t \approx 0.55\)) [6]. The
anomalously high dielectric and piezoelectric properties are due to the coupling between two equivalent energy states, allowing optimum domain reorientation during the poling process. The compositions near AFE-FE boundary (A-o-Fi), at around Zr/Ti = 95/5, also shows very high electromechanical coupling factor (K_t as high as 0.55 and K_p as high as 0.4) [7]. Conventional PZT materials produce a typical strain of 0.1% [8], whereas electric field-induced AFE-FE transition can yield a strain of 0.3% in Sn and Nb-doped PZT, and even as high as 0.8% in Sn and La-doped PZT systems [5,9].

Thus, there has been a new interest in the Zr-rich end of the PZT phase diagram, close to the antiferroelectric-ferroelectric phase boundary (Zr/Ti = 95/5), where the switching between AFE-FE phase can be accomplished by the application of a suitable electric field, temperature, or pressure [10]. In La-, and Sn-modified PLZST ceramics [11,12], with a decrease in temperature, the field-induced FE phase becomes a thermodynamically stable phase and the field required for AFE-FE transition diminishes. The phase switching is also fast (1-2 μs) [13] to make these materials useful for many potential applications. Uchino et. al [14,15] have worked extensively on Nb- and Sn-doped PZT system and have found that the AFE-FE phase transition-induced strain shows other interesting properties like shape-memory effect and digital on/off type strain, which are very promising properties for designing novel devices like latching relays, digital displacement transducers, mechanical clamps, and surface acoustic wave filters.

Similar to La and Sn, Sr is also an antiferroelectric phase stabilizer. When Sr^{2+} is added to the PZT system, it replaces Pb^{2+} site in the perovskite structure. The phase diagram of the PbTiO_3-PbZrO_3-SrTiO_3-SrZrO_3 system (Figure 1.1) shows a long AFE-FE phase boundary suitable for the field-induced phase transition study [16]. Sr addition
can retain the orthorhombic antiferroelectric phase, $A_o$, up to Pb/Sr ratio of 72/28 and a new tetragonal antiferroelectric phase, $A_T$, emerges which is stable up to Pb/Sr ratio of 65/35. The composition in the $A_o$ region is not suitable for field-induced $A_o/F_R$ phase transition study because it does not have a long common boundary with the $F_R$ phase and so the field required for AFE/FE switching may be too high to be used experimentally in the laboratory. However, in the $A_T$ region, the compositions are energetically so close to those of the $F_R$ form that the switching between the $A_T/F_R$ form may be easily accomplished by an applied electric field. But, such a systematic study has not been reported in the literature until a recent study from our group [17]. Therefore, this work was focused on Sr-containing PZT ceramics and placed especially emphasis on the electric field induced AFE-FE phase transition. In order to understand the relative phase stability of AFE and FE phases with variation of compositions, two groups of specimens with either fixed Sr$^{2+}$ or Ti$^{4+}$ content were selected with the nominal composition $(\text{Pb}_{1-x}\text{Sr}_x)(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3$ ($0.1 \leq x \leq 0.3$) and $(\text{Pb}_{0.9}\text{Sr}_{0.1})(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ ($0.1 \leq y \leq 0.2$). A modified AFE/FE phase boundary is proposed according to the structure analysis and polarization characterization.

The influences of temperature on dielectric and piezoelectric properties were also systematically studied. The characteristics of field-induced strains were investigated for compositions situated at the AFE, FE phase regions and AFE/FE phase boundary. High field-induced strain was observed for composition close to AFE/FE phase boundary associated with undesirable remnant strain.

In order to reduce the remnant strain and increase the magnitude of strain value, different amounts of La$^{3+}$ and Nd$^{3+}$ were doped in PSZT ceramics. Attempts have been
made to study the maximum strain attainable and their influence of dielectric properties and microstructures. A novel method to directly analyze the crystal structure change during AFE-FE phase transition, *i.e.* *in situ* XRD, was developed in this study. AFE and FE phase stability was monitored as a function of the electric field. The unit cell jump was proven to be responsible for the large field-induced strain.

Fig. 1.1 PbTiO$_3$-PbZrO$_3$-SrTiO$_3$-SrZrO$_3$ phase diagram (after Ikeda [16]).
2. LITERATURE REVIEW

2.1 Advantage of Piezoelectric Type Materials for Actuator Applications

Actuator materials are an important class of smart materials which can convert an electric or magnetic signal into a mechanical displacement, or vice versa. The demand for new actuators has increased remarkably due to the sub-micrometer fabrication in electronic chip elements. The desired common features for an actuator include: large displacement, good positioning reproducibility, quick response, low driving energy and degradation, stable temperature characteristics, and small size and weight. The most widely used actuator materials are piezoelectric Pb(Zr,Ti)O$_3$, electrostrictive Pb(Mg,Nb)O$_3$, magnetostrictive (Tb,Dy)Fe$_2$. The comparison among these three different types of actuators is summarized in Table 1.1 [1].

Table 1.1 Comparison among magnetostriction, piezostriction, and electrostriction actuators

<table>
<thead>
<tr>
<th>Properties</th>
<th>Magnetostriction</th>
<th>Piezostriction</th>
<th>Electrostriction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain ($\Delta l/l$)</td>
<td>$10^5 \sim 10^3$</td>
<td>$10^4 \sim 10^2$</td>
<td>$10^9 \sim 10^3$</td>
</tr>
<tr>
<td>Hysteresis</td>
<td>Large</td>
<td>Large</td>
<td>Small</td>
</tr>
<tr>
<td>Aging</td>
<td>Small</td>
<td>Large</td>
<td>Small</td>
</tr>
<tr>
<td>Response</td>
<td>nsec $\sim$ µsec</td>
<td>msec</td>
<td>µsec</td>
</tr>
<tr>
<td>Drive power</td>
<td>Magnetic coil</td>
<td>Electric field</td>
<td>Electric field</td>
</tr>
</tbody>
</table>

In addition to the small magnetic field-induced strains, the use of magnetostrictive actuators requires complex magnetic coils. The leakage of magnetic field prohibits its application near integrated circuit. Consequently, the development of ceramic actuators through use of the electric field-induced strains in ferroelectric and electrostrictive
materials has been of great interest. For ferroelectric type materials, particularly in the perovskite structure oxides, a substantial level of polarization and strain can be induced under realizable electric field in various materials. The hysteresis for the strain-field dependence can be minimized with the use of hard PZT. However, the high precision positioning may be obtained by electrostrictive effect. The thermal expansion is on the order of $10^{-6}$, in most case, less than the field-induced strain. The recovery of the zero field dimension is excellent. From the viewpoint of reliability, electrostrictive materials are comparable to the best piezoelectric ceramics.

2.2 Basis for Piezoelectricity in Ceramics

Piezoelectricity is an electromechanical property possessed by a select group of materials. It was discovered in 1880 by Pierre and Jacques Curie during their systematic study of the effect of pressure on the generation of electrical charge by some crystals. Two effects are manifest in Piezoelectricity: the direct effect and the converse or inverse effect. The direct effect is identified with the phenomenon whereby electrical charge is generated from a mechanical stress, whereas the converse effect is associated with the mechanical movement generated by the application of an electrical field. The basic equations that describe these two effects in regard to the electric and elastic properties are

\[
D = dX + \varepsilon^X E \quad \text{(direct effect)} \quad (2.1)
\]

\[
S = s^X X + dE \quad \text{(converse effect)} \quad (2.2)
\]

where \(D\) is the dielectric displacement, \(X\) is the stress, \(E\) is the electric field, \(S\) is the strain, \(d\) is the piezoelectric coefficient, which is numerically equal in both equations, \(\varepsilon^X\) is the dielectric constant at constant stress, which means the piezoelectric element is
mechanically unconstrained, and \( s^E \) is the material compliance (inverse of modulus of elasticity) at constant electric field, which means the electrodes on the elements are shorted together. High \( d \) coefficients are desirable for those ceramics that are used in vibrational device, such as ultrasonic echo sounders, and underwater microphones.

For the piezoelectric phenomenon to occur in a material, the crystal lattice should have no center of symmetry. Of the 32 crystal classes or point groups, 20 are piezoelectric, as shown in Fig. 2.1 [18]. Out of these 20 piezoelectric crystal classes, a further subdivision may be made consisting of 10 crystal classes which contain a unique polar axis (an electric dipole moment) even in the unstrained condition, along which they are spontaneously polarized - these are called pyroelectric. 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 subgroup of pyroelectrics. They have a spontaneous polarization, as do the pyroelectrics, but they have the added property that the direction of the spontaneous polarization can be reversed by an applied external electric field. Four types of ceramic ferroelectrics are shown in Fig. 2.1 with typical examples representing the type based on its unit cell structure. Of these different types of ferroelectrics, perovskite type \( \text{ABO}_3 \) is by far the most important category. \( \text{BaTiO}_3 \), PZT (lead zirconate titanate), PLZT (La-modified PZT), PT (lead titanate), \( \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 \) (PMN), \( (\text{Na,K})\text{NbO}_3 \) represent the commercial bulk ferroelectric ceramics manufactured in the industry today. Present applications of piezoelectric ceramics include ultrasonic vibrators, ultrasonic transducers, ignition devices, ceramic filters, pressure sensors, piezoelectric transformers, etc. Many of these applications have already been practically realized.
Fig. 2.1. Interrelationship of piezoelectric and subgroups on the basis of symmetry [18].
2.3 Basis for Ferroelectricity and Antiferroelectricity in Ceramics

2.3.1 The Perovskite Structure

Most of the ferroelectric materials can be described by the general formula ABO$_3$ which corresponds to perovskite type of structure. A typical PZT structure is shown in Fig. 2.2. Here a B cation (Zr$^{4+}$ or Ti$^{4+}$) of smaller size is surrounded by 6 anions in an octahedral configuration and an A cation (Pb$^{2+}$) of larger size has 12 fold co-ordination with the anions. When an electric field is applied to this unit cell, the Ti$^{4+}$ or Zr$^{4+}$ ions shifts to a new position along certain crystallographic directions of the unit cell. The individual ions approximately align with the direction of the electric field. When this ionic movement occurs, it leads to a macroscopic change in the dimensions of the unit cell and the ceramic. The strain can be as high as a few tenths of a percent elongation in the direction of the applied and about one-half that amount in the other two orthogonal directions [19]. Because of a ceramic is composed of a large number of randomly oriented crystallites, a poling process, the application of a static electric field under appropriate conditions of temperature and time, can align the polar axis in the crystallites of a ferroelectric ceramic as near to the field direction as the local environment and crystal structure allows [20]. The homogeneous areas with the same polarization orientation in the materials are regard as domains, with domain walls existing between areas of unlike polarization direction. The domain reorientation requires small ionic movement in the specific crystallographic directions. It follows that the greater is the number of possible directions the more closely the polar axis of the crystallite in a ceramic can be brought into the direction of the poling direction. For example, the tetragonal structure (4mm) allows six $\{100\}$ directions, while the rhombohedral (3m)
allows eight directions. In the PZT morphotropic phase boundary, both tetragonal and rhombohedral crystallite are present, the number of alternative crystallographic directions rises to 14 and the extra alignment is attained.

Fig. 2.2. (a) A typical perovskite ABO$_3$ unit cell structure and (b) three-dimensional network of BO$_6$ octahedra (after Xu [20]).
A useful approach to the influence of the ionic radii on the crystal structure is the concept of tolerance factor for the perovskite structure, ABX$_3$. According to Goldschmidt [19], the tolerance factor is defined by the formula as:

$$t = \frac{R_A + R_X}{\sqrt{2(R_B + R_X)}}$$  \hspace{1cm} (2.3)

where $R_A$, $R_B$ and $R_X$ are the ionic radii of the A and B cations and the anion (X), respectively. This tolerance factor is an empirical equation that can be used as a rough guideline. When $t = 1.0$, ideal cubic perovskite is obtained. In practice, those structures with $t = 0.95-1.0$ are cubic, those with still lower $t$ values are slightly distorted but non-ferroelectric, and those slightly over 1.0 tend to be ferroelectric [20]. Besides the ionic radii, other factors such as polarizability and character 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.), while that of the X anions may be 1 to 2 ($\text{O}^{2-}$, $\text{F}^{-}$, $\text{Cl}^{-}$ etc.).

### 2.3.2 Origin of Spontaneous Polarization

In a polar structure, each dipole is influenced by its neighbors. For simplicity, assuming the dipole moments results from the equal displacement of one kind of ion A relative to the crystal lattice, there exist a local field ($E_{\text{loc}}$) from the surrounding polarization P to any individual ion A.

$$E_{\text{loc}} = \left(\frac{\gamma}{3\varepsilon_0}\right) P$$  \hspace{1cm} (2.4)

where $\gamma$ is the Lorentz factor, $\varepsilon_0$ is the permittivity of vacuum.
This local field is the driving force of the ion shift. Thus, the Lorentz factor is sometimes seen as a measure of the strength of dipole interactions. If the ionic polarizability of ion is $\alpha$, then the dipole moment of the unit cell is:

$$\mu = (\alpha \gamma / 3 \varepsilon_0) P$$  \hspace{1cm} (2.5)

Considering $N$ number of atoms per unit volume, the energy of the dipole moment is:

$$W_{\text{dip}} = N(-\mu E_{\text{loc}}) = -(N\alpha \gamma^2/9\varepsilon_0^2)P^2$$  \hspace{1cm} (2.6)

When the ions are displaced from their nonpolar equilibrium positions, the increase of the elastic energy per unit volume is:

$$W_{\text{elas}} = N[(k/2)u^2 + (K/4)u^4]$$  \hspace{1cm} (2.7)

where $u$ is the ions displacement from their equilibrium positions ($u = P/Nq$, where $q$ is the electric charge), $k$ and $K$ are force constants.

The total energy can be expressed as (Fig. 2.3 [1]):

$$W_{\text{tot}} = W_{\text{dip}} + W_{\text{elas}}$$

$$= [k/(2Nq^2) - N\alpha \gamma^2/(9\varepsilon_0^2)]P^2 + [K/(4N^3q^4)]P^4$$  \hspace{1cm} (2.8)

The first order derivative of the total energy $W_{\text{tot}}$ related to polarization $P$ shows:

$$\frac{\partial W_{\text{tot}}}{\partial P} = P[-k/Nq^2 - 2r^2N\alpha q^2/\varepsilon_0] + K/N^3q^4P^3 = 0$$  \hspace{1cm} (2.9)

Hence,

$$P^2 = [(2N\alpha \gamma^2/9\varepsilon_0^2) - (k/Nq^2)]/[K/N^3q^4]$$  \hspace{1cm} (2.10)

From Eq.(2.10), one can see that there are two solutions for $P$ where the total energy will be minimum. This has been represented in Fig. 2.3(c).
Fig. 2.3. Energy explanation of the origin of spontaneous polarization (after K. Uchino [1]).
2.3.3 Characteristics of Ferroelectric and Electrostrictive materials

It is evident that all the piezoelectric materials need not be ferroelectric, but most of the commercially used piezoelectric materials have ferroelectric property. The general ferroelectric properties may be listed as follows:

(1) They are in the polar class of crystals, i.e., crystal structures lacking a center of symmetry and thus containing electric dipoles in the lattice.

(2) They undergo a displacive transformation to lower crystal symmetry when cooled below a critical temperature, called Curie temperature.

(3) They have a high dielectric constant rising to a peak at the Curie temperature. Above that temperature, the dielectric constant decreases according to Curie-Weiss law

\[ \varepsilon = \frac{C}{T-T_o} \quad (2.11) \]

where \( \varepsilon \) is the relative permittivity, \( C \) is Curie-Weiss Constant and \( T_o \) is the Curie-Weiss Temperature. \( T_o \) is slightly lower than the exact transition temperature \( T_c \).

Also, above the Curie temperature, the material loses its ferroelectricity.

(4) When cooled below the Curie temperature, spontaneous polarization occurs, and the cubic to low symmetry crystal structure transformation causes an increase in the volume of the crystal and thus strains the system. In order to counteract this strain, the system breaks into a domain structure, which can be visualized under polarized light.

The effective piezoelectric coupling factor is a direct measurement of overall strength of the electromechanical effect, which is defined as follows:

\[ k^2 = \frac{\text{mechanical energy converted to electrical energy}}{\text{input mechanical energy}} \quad (2.12) \]

or
\[ k^2 = \frac{\text{electrical energy converted to mechanical energy}}{\text{input electrical energy}} \]  \hspace{1cm} (2.13)

Since the conversion from one form of energy to another is incomplete, \( k \) is always less than one. For ceramics, \( k_p \) is a typical measurement used in comparing different materials, it varies from 0.35 for BaTiO\(_3\) to as high as 0.72 for PLZT.

Electrostriction is another electromechanical effect that exists in ferroelectrics. Although electrostriction is a general property of all dielectric materials, it can be very large in ferroelectric materials just above Curie temperature. In electrostriction, the sign of the strain under an electric field is independent of the polarity of the field and is proportional to the even powers of the field or polarization. The corresponding equation is

\[ S = QP^2 \]  \hspace{1cm} (2.14)

where \( S \) is the strain, \( P \) is the polarization, and \( Q \) is the electrostrictive coefficients.

The electrostrictive material usually has a Curie temperature lower than room temperature with a very small coercive field of less than 0.1 kV/mm. The characteristics for electrostrictive materials are

1. Hysteresis in the strain-field dependence is minimal or negligible in a selected temperature.
2. No poling is required. While piezoelectric materials require poling process, which leads to a significant aging effect due to the depoling.
3. A limited usable temperature range due to the strong temperature dependence of the electrostrictive effect.
4. Especially small deformation at low fields, and higher operating voltage is required to achieve moderate deflection.
2.3.4 Phenomenological Theory of AFE-FE Phase Transition

Analogous to the magnetic materials, there exists another class of materials called antiferroelectrics. An antiferroelectric crystal is defined as a crystal whose structure can be considered as being composed of two sublattices polarized spontaneously in antiparallel direction and whose ferroelectric phase can be induced by applying an electric field. Experimentally, the reversal of spontaneous polarization in ferroelectric is observed as a single hysteresis loop and the induced phase transition in antiferroelectrics as a double hysteresis loop, when a low frequency ac field of suitable strength is applied.

Figure 2.4 shows the P-E relationship in paraelectric, ferroelectric, and antiferroelectric materials. Transition between the antiferroelectric and ferroelectric phase is known to occur as a function of temperature, stress, and electric field. Because the transition is accompanied substantial changes in mechanical strain and polarization, these phase-change materials are very attractive for charge-storage capacitors, shape-memory effects, transducers and actuators applications.

The possibility of the existence of antiferroelectrics was predicted by Kittel [21] before these materials were discovered. Cross [22] considered the induced FE state from AFE state, the total Gibbs free energy at high field and polarization can be expressed as

\[
G = \frac{1}{2} (f-\frac{g}{2})P_A^2 + \frac{1}{2} (f+\frac{g}{2})P_F^2 + \frac{h}{8} (P_A^4 + P_F^4 + 6P_A^2P_F^2) - P_F E \tag{2.15}
\]

where \(P_F = P_a + P_b\), \(P_A = P_a - P_b\), \(f\), \(g\), and \(h\) are temperature dependent coefficients, \(E\) is the electric field strength, \(P_a\) and \(P_b\) are the sublattice polarization.

The possible values for \(P_A\) corresponding to minima in the free energy at an applied field can be obtained from the Eq. 2.16.
Fig. 2.4. Typical hysteresis loops in paraelectric, ferroelectric and antiferroelectric materials (after K. Uchino [1]).
\[
\frac{\partial G}{\partial P_A} = (f - \frac{g}{2})P_A + \frac{12h}{8} P_A P_F^2 + \frac{h}{2} P_A^3 = 0
\] (2.16)

From Eq. (2.16), two possible solutions are

\[P_A = 0 \] (2.17)

or

\[P_A^2 = -3P_F^2 - \frac{2(f - g/2)}{h} \] (2.18)

Solutions \(P_A = 0\) (Eq. 2.17) and \(P_A \neq 0\) (Eq. 2.18) correspond to the electric field-induced polarization of the AFE phase before and after switching to the FE phase, respectively.

The phenomenology for the AFE-FE transition as a theoretical predication was proposed by Kittel assuming zero stress condition [21]. However, this description was unable to explain the pressure-dependence of the antiferroelectric Neel temperature in antiferroelectric ceramics such as PbTiO\(_3\). By considering the effects of stress, field and temperature, the full Gibbs free energy expression of AFE state can be defined by Wang et al. as [23]:

\[
G = G_0 + \frac{1}{4} f_2 (P_a^2 + P_b^2) + \frac{1}{8} f_4 (P_a^4 + P_b^4) + \frac{1}{12} f_6 (P_a^6 + P_b^6) + \frac{1}{2} n(P_a P_b) + \frac{1}{2} g_4 \delta^2 + \\
\frac{1}{2} g_4 \delta^4 + \frac{1}{4} d \delta^2 (P_a^2 + P_b^2) + \frac{1}{2} c \delta^2 + \frac{1}{2} Qh(P_a^2 + P_b^2 + 2RP_a P_b) p - \frac{1}{2} E(P_a + P_b) 
\] (2.19)

where \(E\) is the electric field, \(p\) is the pressure, \(c\) is the compressibility, \(Q\) is the electrostrictive coefficient, \(R\) is the structure factor, \(n\) is the coupling between \(P_a\) and \(P_b\), \(f_2\) is the function temperature, \(d\), \(f_4\), \(g_4\) and \(f_6\) are constants, and \(\theta\) is the angle of octahedral tilt.

The equilibrium condition of the Gibbs free energy is shown from Eq. (2.20) to (2.22):
\[
\frac{\partial G}{\partial P_a} = 0 \quad (2.20)
\]
\[
\frac{\partial G}{\partial P_b} = 0 \quad (2.21)
\]
\[
\frac{\partial G}{\partial \varepsilon} = 0 \quad (2.22)
\]

The requirement of stable condition of the Gibbs free energy for the antiferroelectric phase is:

\[
\frac{\partial^2 G}{\partial P_a^2} > 0 \quad (2.23)
\]
\[
\frac{\partial^2 G}{\partial P_b^2} > 0 \quad (2.24)
\]
\[
\left( \frac{\partial^2 G}{\partial P_a^2} \right) \left( \frac{\partial^2 G}{\partial P_b^2} \right) - \left( \frac{\partial^2 G}{\partial P_a \partial P_b} \right) > 0 \quad (2.25)
\]

From equilibrium and stability requirement, the AFE-FE phase transition fields were obtained [23]:

\[
|E_A| = \frac{2}{3} (2n - f_2)^{3/2} \sqrt{3f_4} \quad (2.26)
\]
\[
|E_F| = (f_2 + 2n)^{1/2} \frac{\sqrt{3(n - f_2)}/27f_4}. \quad (2.27)
\]

where \(|E_A|\) is the upper limit of the antiferroelectric state. \(|E_F|\) is the lower limit of the metastable ferroelectric state. The AFE-FE phase transition could occur within the \(E_F-E_A\) range.
2.3.5 Soft Mode Theory

Soft mode theory was first proposed by Raman and Nedungadi [24] to describe the displacive transition between $\alpha$ and $\beta$ quartz. Cochran [25,26] applied soft mode to many other displacive phase transition in the late 1950’s. They suggested that the phase transitions in certain ferroelectrics might result from an instability in one of the normal vibrational modes of the lattice. It proved to be a very useful description of this type phase transition.

At temperature above the Curie temperature, the materials can be seen to comprise many acoustic and optic phonons, at wide range frequencies. These phonons are of wavelengths on the order of one unit cell in length to lengths in macro scale. The optical vibration shows the relative motion between atoms in the unit cell. The optical wave is also called the polarization wave, because only this wave can cause the polarization within the crystal. As the temperature is reduced, certain optical phonon modes begin to slow down. At a critical temperature, the frequency of one or more of these modes becomes zero and this is termed soft mode. The frequency of any normal mode, comprised of a strictly harmonic contribution and a temperature dependent anharmonic contribution, can be expressed by

$$\omega_T^2 = \omega_o^2 + \gamma T$$ \hspace{1cm} (2.28)

where $\omega_T$ is the frequency of any normal mode, $\omega_o$ is the strictly harmonic frequency for the normal mode, $\gamma$ is a constant, and $T$ is the temperature.

The soft mode frequency ($\omega_s = \omega_T$) at a ferroelectric phase transformation can be determined by

$$\omega_s^2 = \omega_o^2 + \gamma T = k ([SRT] - [LRF] + BT)$$ \hspace{1cm} (2.29)
where B= γ/k, k is the reciprocal of the reduced mass of mode i, LRF is the long-range force, SRF is the short-range force, and ([SRT] − [LRF] + BT) is the effective force constant. Therefore, the frequency of the soft mode is determined by the effective force constant which depends on the balance of competing forces in the crystal. When the long-range force compensates the short-range force, the mode softens which results in a phase transformation.

According to the extensive hydrostatic pressure investigations on the ferroelectric and antiferroelectric phase transformation, Samara [27] proposed a reversal in the roles of the long-range and short-range ordering forces for the lattice stability of antiferroelectric materials. Hence, the soft mode frequency at an antiferroelectric phase transition can be simplified as:

$$\omega_s^2 = \omega_0^2 + \gamma T = k ( [LRF] - [SRT] + BT) \quad (2.30)$$

The FE state is characterized by a long-range order domain structure with a macroscopic spontaneous polarization. The soft mode must be both polar and of long-range wavelength [28] (Brillioun Zone Center Mode). The FE phase transition is driven by a distorting force (DF) from long-range columbic interaction. The restoring force (RF) which prevent the phase transition to FE is short-range interaction. The AFE phase, on the other hand, is characterized by the opposite sublattice polarizations in adjacent cell, the soft mode has a finite wavelength (Brillioun Zone Boundary Mode). The antiferroelectric ordering is driven by a distorting force (DF) from short-range interaction, while the restoring force is the long-range interaction. Yang [29] further suggested a general relationship for the soft-mode frequency which can be expressed as:

$$\omega_s^2 = k ( [RF] - [DF] + BT) \quad (2.31)$$
Both FE and AFE transformations are driven by a distorting force either a long-range or short-range interactions in a crystal. If the applied field enhances the distorting force, it decreases the soft-mode frequency and transforms to a new phase. Conversely, if the external field reinforces the restoring force, it stiffens the soft phonon mode and stabilizes the parent phase [29]. These theoretical arguments provided the principles in understanding the ferroelectric and antiferroelectric phase transition based on the balance of competing forces at the macroscopic level. Additional information about soft modes in ferroelectrics and antiferroelectrics are referred [28, 30-31].

2.4 PZT System

Pb(Ti, Zr)O\textsubscript{3} (PZT) materials which have the perovskite structures are known for their unique combination of dielectric, piezoelectric, pyroelectric, and electro-optical properties. The PZT system is currently the most important ferroelectric material, being used in a variety of applications such as non-volatile memories, optical devices, piezoelectric transducers and actuators [32]. Since the 1960’s, a lot of work including theoretical studies of phase transition [33, 34] analysis of ceramic properties during phase transitions [35, 36] and studies of phase transition applications [37] have been conducted.

2.4.1 Additives in PZT System

PZT ceramics are mostly used with some modifiers or additives to enhance and optimize the properties for different applications. According to the valences of the dopants used, they are classified as:
(1) Off-valent donor additives such as Nb\(^{5+}\) replacing Zr\(^{4+}\) or La\(^{3+}\) replacing Pb\(^{2+}\), etc. The donors are usually compensated by A-site vacancies. These additives and vacancies enhance the domain reorientation, and strain magnitude. Materials produced by these additives are characterized by relatively square hysteresis loop, low coercive field, high dielectric constant and high coupling factor.

(2) Off-valent acceptor additives such as Fe\(^{3+}\) replacing Zr\(^{4+}\). The acceptors are compensated by oxygen vacancies and usually have limited solubility in the lattice. Domain reorientation is limited, and hence ceramics with acceptor additives are characterized by poorly developed hysteresis loops, lower dielectric constant, lower dielectric loss, and higher aging rates.

(3) Isovalent additives such as Ba\(^{2+}\) or Sr\(^{2+}\) replacing Pb\(^{2+}\) or Sn\(^{4+}\) replacing Zr\(^{4+}\), in which the substituting ion is of the same valence and approximately same size as the replaced ion. Solid solution ranges with these additives are quite high. Other properties may include lower dielectric loss and high aging rates.

2.4.2 The AFE-FE phase boundary in PZT system

The PZT phase diagram is illustrated in Fig. 2.5, where it can be seen that the morphotropic phase boundary (MPB) is a significant feature. An MPB denotes an abrupt structure change with composition at constant temperature in a solid solution. In the PZT system, it is close to the composition Zr/Ti \(\approx 52/48\) at room temperature. An abrupt change in the lattice parameters of PZT occurs near MPB, where some physical properties, such as dielectric constant and piezoelectric coupling factors show anomalous
behaviors (Fig. 2.6) [6]. Similar results have been reported in other binary piezoelectric ceramic system, such as the PbTiO$_3$-PbHfO$_3$ and PbTiO$_3$-PbSnO$_3$ systems.

Recently there has been a great deal of interest especially in the antiferroelectric-ferroelectric (AFE/FE) phase boundary (Zr/Ti ≈ 95/5) [23]. This interest stems from the fact that there are regions in the PZT phase diagram where AFE and FE phases coexist and thus, for these compositions, free energy difference may be very small. As the ferroelectric domains carry a large spontaneous electric polarization and the AFE phase is centric, it is not surprising that the AFE form close to boundary composition can be switched into ferroelectric form under high electrical field.

The AFE/FE phase boundary was influenced by compositional modifications. Addition of Sn$^{4+}$ in PZT system can extend the AFE phase field, influence the phase transition characteristics, and can alter the shape and slope of the AFE-FE phase boundary. By proper manipulation of the Sn$^{4+}$, Ti$^{4+}$ and Zr$^{4+}$ ratio, Wang et al. [38] obtained a vertical AFE-FE phase boundary in the high zirconium area near Zr/Ti = 95/5 of PZT phase diagram, where no temperature induced phase transformation takes place up to around 150°C. The compositions in the vicinity of the phase boundary showed the existence of FE and AFE phases in a single grain by TEM [39, 40]. So, there was no distinct AFE-FE phase boundary.

The PE$\rightarrow$FE phase transition leads to a volume increase, whereas the PE$\rightarrow$AFE transformation causes the crystal to contract; i.e., the atomic arrangement of AFE is more compact than that of the FE counterpart (the unit cell volume is in this order FE > PE > AFE). Thus, one may also expect FE compositions close to the boundary to invert to AFE under suitable hydrostatic or uniaxial stress. As the volume decreases in the FE$\rightarrow$AFE
transformation, compression favors AFE phase, whereas tension favors FE phase [41]. More specifically, a phase transition from a stable AFE form to a FE form can be accomplished by an electric field, while a phase change from a stable FE state to an AFE state can be forced by a stress. The fact that the AFE-FE switching is feasible by the application of electrical, mechanical, and thermal excitation has especially made PZT ceramic system a very attractive candidate for potential device applications.

Fig. 2.5. PbZrO₃-PbTiO₃ phase diagram (after Jaffe et al. [6]).
2.4.3 Field-Induced Strain Mechanism and Domain Configurations in Ferroelectric Ceramics

For ferroelectric ceramics, the electric field induced strain includes a piezoelectric strain, an electrostrictive strain and a strain associated with a ferroelectric domain reorientation. Both piezoelectric and electrostrictive strains result from ionic shifts from their equilibrium positions by an electric field application.

The magnitude of electrically-induced strains in ferroelectric and antiferroelectric materials is well-known to be dependent on the polarization switching mechanism. For example, polarization switching by the creation and subsequent motion of 90° domains results in significantly larger shape changes, than switching by 180° domains. Large strain accommodations at twin boundaries are required for switching by 90° domains, resulting in relatively large macroscopic shape changes on polarization reversal. However, only
small accommodations at the boundaries are required for switching by 180° domains, resulting a significantly smaller macroscopic shape changes [42].

A strain associated with a ferroelectric domain reorientation is shown in Fig. 2.7 [43]. State 1 exhibits the initial poled two-dimensional domain configuration for a polycrystal ferroelectric ceramic. When an external electric field applied opposite to the poling direction, the sample should shrink at first and the deformation reaches a minimum at the coercive field, as shown in state 2. Above coercive field, the sample begins to expand. Near the maximum field, all the reversible polarizations have been reversed. The induced strain is caused by the 90° type domain wall motion. If applied electric field goes back to zero, the strain is decreased. This is caused by the 90° type domain partially back to its initial state. The domain configuration becomes state 5 through state 4 by an inverse application of electric field. The polarization direction in state 5 is opposite to state 1. However the strain is the same as that for state 1.

For ferroelectric materials, domain formation associated with the phase transition partially release the strain energy and reduce the electrostatic energy rising from the spontaneous polarization change. So, domain structures develop until the energy released through the reduction in electrostatic and strain energy balance the energy gained in the formation of domain walls.

The variation of crystal size influences the domain size. From the balance of the depolarization energy and domain wall energy [44], one can show that the relationship between the domain size and the grain size is

$$D = \left[ \left( \frac{\delta}{dP^2} \right) t \right]^{1/2}$$  \hspace{1cm} (2.32)
where $\sigma$ is the energy density of the domain wall, $P$ is the spontaneous polarization, and $\varepsilon$ is the effective dielectric constant.

In the grain size range of 3-10 $\mu$m, the strain energy could not be completely released and the grain size and domain size relationship obeyed the expected parabolic relationship. However, the departure to smaller domain widths than expected by the parabolic relationship was observed for the sub-micrometer grain sizes. This deviation may be due to the changes in the boundary conditions. Clamping of domain walls at the grain boundaries from its neighbors will cause the relative increase in the domain density at smaller grain size [33].

Fig. 2.7. Schematic explanation of the strain change in a ferroelectric ceramic associated with the domain reorientation [43].
2.4.4 Field-Induced Strain Mechanism in Antiferroelectric Ceramics

(1) Theoretical Derivation

Actuators made by PZT ceramics are ideal for many applications since they can be operated by electric fields, are compact, can produce precise deformations and high strains. Furthermore, certain classes of material, due to metastability of induced ferroelectric phases, are capable of maintaining a residual strain even after the electric field has been switched off.

Cross and Uchino theoretically derived the unit cell volume change associated with the field-induced antiferroelectric-ferroelectric phase transition [11,45]. To simplify the matter, spontaneous polarization occurring only along axis 3 under the presence of hydrostatic pressure was considered. They proposed the general free energy function form as:

\[
\Delta G = \frac{1}{2} \alpha(T)(P_{a3}^2 + P_{b3}^2) + \frac{1}{4}\beta(P_{a3}^4 + P_{b3}^4) + \frac{1}{6}\gamma(P_{a3}^6 + P_{b3}^6) + \eta P_{a3} P_{b3}
\]

\[-(1/2)S_h \sigma^2 + Q_h \sigma (P_{a3}^2 + P_{b3}^2 + 2\Omega P_{a3} P_{b3})\]  

(2.33)

where \( P_{a3} \) and \( P_{b3} \) denote the two-sublattice polarizations, \( \eta \) is the dielectric stiffness constant, \( S_h \) is the hydrostatic compressibility, \( \sigma \) is the hydrostatic pressure, and \( Q_h \) and \( \Omega \) are electrostrictive constants (they are related to the intra- and inter-sublattice coupling respectively).

Introducing the transformation \( P_F = (P_{a3} + P_{b3})/\sqrt{2} \) and \( P_A = (P_{a3} - P_{b3})/\sqrt{2} \) leads to the following expression:

\[
\Delta G = \frac{1}{2} \alpha(T)(P_F^2 + P_A^2) + \frac{1}{8}\beta(P_F^4 + P_A^4 + 6P_F^2P_A^2) + \frac{1}{12}\gamma(P_F^6 + P_A^6 + 15P_F^4P_A^2 + 15P_F^2P_A^4) + \frac{1}{2}\eta(P_F^2 - P_A^2) - (1/2)S_h \sigma^2 + Q_h \sigma (P_F^2 + P_A^2) + \Omega (P_F^2 - P_A^2)
\]  

(2.34)
The elastic equation of the state follows as:

\[
\frac{\partial \Delta G}{\partial \sigma} = \frac{\Delta V}{V} = S_h \sigma + Q_h (1 + \Omega) P_F^2 + Q_h (1 - \Omega) P_F^2
\]  

(2.35)

If the sample is unclamped, then the stress \( \sigma = 0 \). Under antipolar state, \( P_e = 0 \), then we have

\[
(\Delta V/V)_A = Q_h (1 - \Omega) P_A^2
\]  

(2.36)

In perovskite antiferroelectrics, when the coupling between the two sublattices lowers the free energy of the system, \( \Omega \) is positive and larger than 1. The total volume change is negative which means the antiferroelectric state is more compact than the paraelectric prototype state it is derived from.

Under polar state, \( P_A = 0 \), then we have

\[
(\Delta V/V)_F = Q_h (1 + \Omega) P_F^2 = Q_h P_F^2 + Q_h \Omega P_F^2
\]  

(2.37)

The first term \( Q_h P_F^2 \) is the volume expansion caused by the normal electrostriction, the second term \( Q_h \Omega P_F^2 \) is the volume expansion caused by the breaking up of the two antiparallel sublattice. If the piezoelectric strain is neglected, the volume change associated with the field-induced antiferroelectric-ferroelectric phase transition can be estimated to be

\[
(\Delta V/V)_F - (\Delta V/V)_A = Q_h (1 + \Omega) P_F^2 - Q_h (1 - \Omega) P_A^2
\]

\[
= 2Q_h \Omega P_F^2
\]  

(2.38)

So, the volume change is proportional to the \( \Omega \) coefficient. The stronger the coupling between the two sublattices, the larger the volume change.
(2) AFE-FE Phase Switching Sequences

The AFE-FE phase transition involves complicated phenomenological interactions, including not only structural phase transition but also the coupling among domains. A two-stage model for AFE-FE phase transitions was suggested by Uchino [15]. First, there is an isotropic volume expansion due to the AFE-FE phase transition. Second, there is an anisotropic strain associated with the FE domain reorientation. A more detailed study considering both longitudinal and transverse strain was conducted and multiple switching steps for AFE-FE phase transition was proposed by Park et al. [46]. Figure 2.8 shows the possible AFE-FE switching sequences in lead lanthanum zirconate titanate stannate (PLSZT) ceramics. A step-by-step sequence is presented as follows:

1. Random AFE to oriented AFE after field exposure: A virgin sample (Fig.2.8a) with randomly oriented AFE domains becomes preferentially oriented AFE (Fig.2.8b) after electric field exposure.

2. Orientated AFE to orientated FE at the switching field: AFE unit cells become FE with their polarization directions trying to align along the external applied field in order to minimize free energy. When an AFE tetragonal primitive cell switches to rhombohedral FE with c-axis expansion, it is associated with a slight decrease in the a axis. There is a slight decrease in the longitudinal dimension and a large increase in the transverse direction in comparison to an electric field exposed sample.

3. Orientated FE to poled FE at an applied field larger than the switching field: With further application of the electric field, some FE domains will try to align more
closely to the field direction through the $109^\circ$ domain reorientation. The ceramic exhibits an increase in the longitudinal strain [Fig. 2.8d].

(4) Piezoelectric region: If an even higher field is applied, the longitudinal strain continues to increase as a result of the piezoelectric effect [Fig. 2.8e].

(5) When the field is removed, the FE phase returns to an orientated AFE state [Fig. 2.8f]. If the ceramic is heated to temperatures significantly above AFE-PE transition temperature, it recovers the random AFE state corresponding to the virgin sample.

Fig. 2.8. Schematic diagram of AFE-FE switching procedure in lead lanthanum zirconate titanate stannate ceramics (afte Park et al. [46]).
(3) Experimental Observations

W. Y. Pan et al. [5,11] studied the AFE-FE transition associated strain as a function of the composition in the tetragonal \((\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr, Ti, Sn})\text{O}_3\) ceramics for field-induced ultra-high-strain actuator applications. They used the ternary phase diagrams developed by Berlincourt [47] (Fig. 2.9) to find specific compositions close to the AFE-FE phase boundary. A maximum field-induced longitudinal strain of 0.85% and volume expansion of 0.95% were observed in the composition \((\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.66}\text{Ti}_{0.09}\text{Sn}_{0.25})\text{O}_3\) at room temperature (Fig. 2.10). Switching from the AFE form to the FE form is controlled by the nucleation of the FE phase from the AFE phase. Under continuous ac field driving, the hysteretic heating effect introduces a temperature rise, changing the original room temperature switching behavior.

Electric fatigue is a major obstacle for piezoelectric ceramics based on reversals of spontaneous polarization. Cross et al. [5,11] studied fatigue effect under a.c. field excitation in PLZSnT family. The field-induced degradation was evaluated by measuring the polarization and strain response as a function of switching cycles. The induced polarization and strain decreased when the antiferroelectric ceramics were driven electrically through the phase change repeatedly. The average life cycle is in the range of \(10^6-10^7\). Since different surface finishing conditions result in different amount of flaws on the surface and might affect the degradation differently, fatigue life can be improved by carefully polishing the sample surfaces. A new cleaning procedure, using ultrasonic cleaning followed by heating at 500-600°C to burn off the organic solvent, was proposed by Jiang et al. [48]. Fatigue did not occur even after more than \(10^8\) switching cycles.
Fig. 2.9. Ternary phase diagram for the system Pb$_{0.99}$La$_{0.02}$(Zr,Sn,Ti)O$_3$ at 25°C [47].

Fig. 2.10. Polarization and longitudinal strain hysteresis loops for composition (Pb$_{0.97}$La$_{0.02}$)(Zr$_{0.66}$Ti$_{0.09}$Sn$_{0.25}$)O$_3$ [5].
(4) Kinetics of Field-Induced AFE-FE Phase Transition

Lead lanthanum zirconate titanate stannate antiferroelectric ceramics have been investigated for potential application in energy conversion and actuators since mid 50s. More recently, the kinetics of the field-induced antiferroelectric to ferroelectric phase transition was studied [5, 13].

For the polarization reversal in ferroelectric crystals, the switching time under a low field level is controlled by the nucleation of new domains. The maximum switching current ($I_{max}$) and switching time ($t_s$) under the low applied electric field ($E$) can be expressed as:

$$I_{max} \sim e^{-\alpha/E} \quad (2.39)$$
$$t_s \sim e^{\alpha/E} \quad (2.40)$$

where $\alpha$ is the so-called activation field.

Under a high electric field, the switching is controlled by domain wall motion. The switching current and time can be expressed as:

$$I_{max} \sim KE \quad (2.41)$$
$$1/t_s \sim KE \quad (2.42)$$

where $k$ is a constant which is a measure of the ease with which the domain walls move [49]. The field-induced AFE-FE switching associated with phase boundary movement is different from the polarization reversal in ferroelectric crystals. The activation field is in the range of 15 to 20 kV/mm in PLZST ceramics. The activation field which is about 10 kV/cm in Nb-doped PZT system for the polarization reversal has been reported by Li et al. [50]. The higher activation field in field-induced AFE-FE phase transition compared to
those observed in ferroelectric ceramics indicates that the nucleation of a new phase is more difficult than that the nucleation of new domains.

Since the forward electric field favors the ferroelectric phase, an over applied electric field should not improve the backward switching speed. The forward switching time can be improved dramatically by applying a large electric field. However, there are controversies in the literature regarding the switching time from antiferroelectric to ferroelectric forms. A very long time up to 0.1 sec. was reported [51]. In contrast, a very short switching time of 1 µsec. was observed under the applied field above 30 kV/cm in PLSnZT system.

2.4.5 Effects of Composition and Temperature on Phase Transition

For the application of AFE ceramics, it is desirable to have low switching field coupled with high strain. Large hysteresis is undesirable since the generated is difficult to dissipate. Effect has been made to search for compositions with both low switching fields and hysteresis [52]. Influences of PbO content, A- and B-site ions modifications have been investigated to tailor the AFE-FE phase transition behavior and associated properties.

(1) Effect of PbO Content

The effect of PbO content on AFE-FE phase transition characteristics and dielectric properties has been investigated in Y-modified lead zirconate titanate stannate ceramics [53]. XRD pattern suggests that additional excess PbO up to 5 mol% could be tolerated in the orthorhombic perovskite structure. The forward transition field (AFE-FE)
increased with the increase of excess PbO. This indicated that antiferroelectric phase stabilized with increasing excess PbO addition and more electric energy was needed for the domain wall motion to induced AFE-FE phase transition. This phenomenon can be explained by the following defect equations.

The Pb vacancies were formed when the \( \text{Y}^{3+} \) ions substituted the Pb\(^{2+}\) ions as shown by

\[
Pb(B^+,B^-)O_3 + xY_2O_3 \rightarrow [Pb_{1-3x}Y_{2x}V_{Pbx}] (B^+,B^-)O_3 + 3x \text{ PbO} \uparrow \tag{2.43}
\]

However, Pb vacancies decreased when excess PbO was added as follows:

\[
[Pb_{1-3x}Y_{2x}V_{Pbx}] (B^+,B^-)O_3 + y \text{ PbO} \rightarrow [Pb_{1-3x+y}Y_{2x}V_{Pb(x+y)}] (B^+,B^-)O_3 + 0.5yO_2 \uparrow \tag{2.44}
\]

Therefore, excess PbO filled the vacancies formed by donor doping or PbO evaporation. The resultant decrease of vacancies inhibited the rotation of antiferroelectric domain and also disturbed the motion of the ferroelectric domain wall [54]. The maximum strain in Y-doped PLZSnT system with no excess PbO was about 0.4%, and it decreased to about 0.2% with the addition of 5 mol% excess PbO.

\(2\) A-Site Ions Modifications

Effect of \(\text{Sr}^{2+}\) and \(\text{Ba}^{2+}\) Modifications

A-site modifications based on tolerance factor consideration and phase stability can be used to tailor lead lanthanum zirconate stannate titanate (PLZSnT) ceramics properties. Both Ba and Sr were demonstrated as effective dopants for reducing hysteresis and controlling the switching field in different regions of the PLSnZT phase diagram. Cross et al. [55] investigated the effect of electric properties of strontium and barium additions in the PLZSnT system. Addition of \(\text{Sr}^{2+}\) produced higher AFE-FE switching
field with less hysteresis. Composition Pb_{0.98}Sr_{0.05}La_{0.02}(Zr_{0.55}Sn_{0.3}Ti_{0.15})_{0.995}O_3 which had 5% Sr^{2+} addition showed AFE-FE phase transition at room temperature even though compositionally located in the FE region. This indicated that Sr^{2+} was an AFE stabilizer. A longitudinal strain of 0.25% and polarization of 34 µC/cm² were obtained at 7.9 kV/mm switching field. With respect to tolerance factor considerations Ba^{2+} is larger than Pb^{2+} (1.48 and 1.32 Å, respectively), therefore stabilizing the FE phase, increasing the space that the B-site cation can “rattle”. Ba^{2+} modification decreases the temperature of maximum dielectric constant and increases the FE-AFE phase transition temperature. However, these changes also make the AFE temperature range rather small.

**Effect of La^{3+} and Nd^{3+} doping**

La^{3+} cation is a well known higher valency substitution on the Pb^{2+} site which creates A-site vacancies to preserve charge neutrality [56]. At moderate concentrations, higher valency impurities lead to an enhanced ease of polarization switching under ac field. At higher concentrations, a disordering of the ferroelectricity occurs, which results in relaxor ferroelectric behavior and polar nanodomains [57].

The PbZrO$_3$-PbTiO$_3$ phase diagram shows that the AFE$_0$ phase is stable up to about 6% PbTiO$_3$. Above this amount the FE$_R$ is stabilized. As the lanthanum content is increased, the range of the antiferroelectric orthorhombic phase is extended. Depending on the Zr/Ti ratio, Dai et al. [58] have observed a critical lanthanum content above which long-range ordering is broken. Above the critical limit the paraelectric phase transforms into either a ferroelectric or antiferroelectric relaxor phase.
Defect complexes in La\textsuperscript{3+} modified materials are relatively immobile below the phase transformation temperature. The spatial distribution of defect complexes is frozen in at temperatures greater than that of the dielectric maximum. Consequently, defects randomly distribute in the domains and cannot diffuse to domain boundaries. The domain structures of La\textsuperscript{3+} modified PZT ceramics have been recently investigated by transmission electron microscopy. Different domain structures were developed with increasing La\textsuperscript{3+} concentration [59,60]. Micrometer-sized domains are characterized by normal ferroelectric phase transformation characteristics. Tweed-like structures are characterized by a strong broadening of the temperature-dependent dielectric response, while polar nanodomains are characterized by relaxor ferroelectric characteristics.

The addition of Nd\textsuperscript{3+} in PZT ceramics caused significant changes on piezoelectric parameters. A substantial enhancement of piezoelectric coefficient and grain refinement by Nd\textsuperscript{3+} addition has been observed [61]. The field-induced strain in ferroelectric (Pb,Ba)(Zr,Ti)O\textsubscript{3} ceramic increased by Nd\textsuperscript{3+} doping [62]. It was also observed Nd\textsuperscript{3+} modification results in enhancement of fracture toughness $K_{IC}$ and hardness of PZT ceramics. A $K_{IC}$ of 2.05 Mpa m$^{1/2}$, dielectric constant of 680 and $d_{33}$ of 240 pC/N was obtained for Nd\textsuperscript{3+} modified PZT (Zr/Ti = 40/60) ceramics.

(3) B-Site Ions Modifications

Ti\textsuperscript{4+} and Zr\textsuperscript{4+} ions, having ionic radii of 0.69 Å and 0.79 Å in PZT, respectively, can be replaced by Sn\textsuperscript{4+} (with an ionic radius of 0.74 Å). Jaffe [63] found that if Sn\textsuperscript{4+} is substituted in PZT system, it goes to B-site and replaces Zr\textsuperscript{4+} and stabilizes the AFE phase. He showed that in PZT systems containing Sn\textsuperscript{4+}, the temperature interval in which
the FE and the AFE phases are of nearly equal energy is markedly wider than in composition not containing Sn$^{4+}$. The effect of varying Zr:Sn and Ti:Sn ratios near the AFE-FE morphotropic phase boundary (MPB) was evaluated in PLZSnT system [52]. It was found that on decreasing the Ti:Sn ratio, the switching field increased and the hysteresis remained constant. On the other hand, increasing the Zr:Sn ratio caused the switching field to decrease and the hysteresis to increase. To produce the desired decrease in both switching field and hysteresis through B-site variation is still not successful. These variations can only produce compositions with lowered switching field and constant hysteresis.

Another very important observation with variation of B-site ions is in the nature of the transverse strain. In conventional piezoelectric systems, the transverse strain is of the opposite sign of the longitudinal strain. But, the field-induced AFE-FE phase transition produces longitudinal and transverse strains of the same sign. This signifies isotropic volume expansion, i.e., both a and c dimensions of the unit cell increase simultaneously in the phase transition process [9]. Uchino et al. [64] have created a multilayer shape memory actuator with an Nb-, and Sn-doped PZT ceramics by tape casting. The induced strain reaches up to 0.3%, which is much larger than that expected in normal piezoelectrics or electrostrictors. In this case, an antiferroelectric to ferroelectric phase change is responsible for the shape change. Figure 2.11 shows the field-induced strain characteristics of two different compositions Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.6}$Sn$_{0.4}$)$_{1-y}$Ti$_y$O$_{3}$ (y=0.060 and y=0.063) in PNZSnT family. In the type I (y=0.060), the strain increases abrupt with increasing the electric field. The strain is due to the AFE-FE phase transition and it decreases and returns to the initial state with decreasing the field. This is referred to as a
digital displacement transducer because of the two on/off strain states. On the contrary, in
the type II (y=0.063), the field-induced strain will not diminish despite of the decreasing
field. Once the FE state has been induced, the materials will memorize its FE state even
under zero field condition, although it can be erased with a small reverse bias field. This
shape memory ceramic does not require a continuous electric field application, but a pulse
drive, thereby saving considerable energy.

\[ y = 0.060 \quad \text{and} \quad y = 0.063 \]

Fig. 2.11. Field-induced strain characteristics of two different compositions (y=0.060,
and y=0.063) in Pb\(_{0.99}\)Nb\(_{0.02}\)[(Zr\(_{0.6}\)Sn\(_{0.4}\))\(_{1-y}\)Ti\(_y\)]\(_{0.98}\)O\(_3\) family [1].

### 2.4.6 Pressure Dependence of Field-Induced Phase Transitions

In addition to temperature, the application of pressure can also greatly affect the
phase transition. A transition from either paraelectric or ferroelectric to antiferroelectric in
perovskites involves a decrease in specific volume. The unit cell volume of the
paraelectric phase is intermediate between that of ferroelectric and the antiferroelectric
states. In the ferroelectric state the unit cell is elongated parallel to the polar axis, while in
the antiferroelectric state one of the axes perpendicular to the anti-parallel displacements is shorter than the cubic phase [41]. These size relationships are consistent with the phenomena observed, with hydrostatic compression favoring antiferroelectricity while planar tension favoring ferroelectricity.

When a crystal undergoes a structural change, the crystal structure and symmetry can be distorted. A hydrostatic pressure increases the short-range interactions between adjacent cations and anions ($\propto r^{-10}$, where $r$ is the interionic distance) more rapidly than it does the long-range Coulomb force ($\propto r^{-3}$) [31]. It has also been found that both the symmetry and magnitude of hydrostatic pressure has a profound effect on the phase transition temperature. The shift in transition temperature with hydrostatic pressure can be described by Clausius-Clapeyron equation, as shown in Eq. (2.45).

$$\frac{dT_c}{dP} = \frac{\Delta V T_c}{\Delta H}$$

(2.45)

where $P$ is the external pressure, $T_c$ is the transition temperature, $\Delta H$ and $\Delta V$ are the enthalpy and volume change at the phase transition, respectively. The linear dependence of the transition temperature on pressure has been observed in many PZT ceramics.

Figure 2.12 shows the shift in transformation temperatures with heating ($T_A$) and cooling ($T_F$) cycles under hydrostatic pressure in lead stannate zirconate titanate system [29]. The material transforms into AFE state when temperature is higher than $T_A$, and reverts back to the FE state as temperature when temperature is below $T_F$. The negative slope indicates hydrostatic pressure tends to lower the AFE-FE transformation temperature and extend the stability of the AFE phase. Since hydrostatic pressure enhances the short-range coupling of AFE sublattices. Hence, a smaller volume AFE phase is able to stabilize at lower temperatures.
Fig. 2.12. Pressure dependence of transformation temperature ($T_A$ and $T_F$) in accordance with the Clausius-Clapeyron relationship [29].

Pan et al. [5] also investigated the field-induced phase transition from antiferroelectric to ferroelectric under hydrostatic pressure in various PZT systems. It was observed that the transition field increased but the polarization decreased with increasing hydrostatic pressure in PLZSnT system. Hydrostatic pressure also increases the AFE-FE switching time. If the applied field level is kept constant, the hydrostatic pressure will eventually suppress the field-induced phase transition. At a low hydrostatic pressure level, the induced polarization is almost maintained at a constant level. At about 100 MPa, the induced polarization begins to decrease because the transition field approaches the applied field. This evidence further confirms that the antiferroelectric form is more
compact than the ferroelectric counterpart. Hydrostatic pressure favors the smaller volume antiferroelectric form and therefore increases the transition field.

2.4.7 AFE-FE phase transition in high Zr-content thin and thick films

PZT thin films (PbTiO$_3$, PLZT, PZT) have been extensively investigated for more than two decades in the field of electrical and optical applications. Since bulk ceramics usually have less dielectric breakdown strength than films, most of the field-induced phase transition study in bulk ceramics is focused on the compositions in the AFE tetragonal system close to the $A_T$-$F_R$ phase boundary. Remnant polarization and strain, which are undesirable, are often associated with the decreasing the electric field strength. This problem can be solved in thin and thick films by selecting compositions in the AFE orthorhombic region with high Zr content. Zero remnant polarization and strain can be obtained in Nb- and La-doped AFE films. In addition to the high dielectric strength on the order of 1 MV/cm of thin films, low operating voltage, integration into microtype devices, and large geometrical flexibility are other advantages of thin films over bulk ceramics. The synthesis of antiferroelectric thin films (film thickness < 1 µm) has been motivated by the large strain values reported in the bulk ceramic materials.

In general, there are two major categories of deposition technique for thin films: physical vapor deposition and chemical processes. Physical vapor depositions involve sputtering, laser ablation, and evaporation, while chemical processes involve chemical vapor deposition and chemical solution deposition such as sol-gel and metalloorganic deposition (MOD). Due to the advantages of good stoichiometry control, high deposition
rates, and low equipment costs, sol-gel and MOD have been extensively used in producing thin films of PZT and other materials.

In most of the thin film deposition techniques, the as-deposited PZT films have amorphous structure. Post-annealing is necessary to convert the amorphous phases into the desired perovskite structure. One of the main problems in preparing lead-containing ferroelectric and antiferroelectric films is lead oxide evaporation. The lead deficiency causes the presence of pyrochlore phase within the film which is detrimental to film performance. It is widely accepted that pyrochlore has a cubic structure, with a formation of $A_2B_2O_{7-x}$, richer in Zr and deficient in Pb than the perovskite structure. Since most antiferroelectric materials have more complex compositions compared to ferroelectric materials, this makes the preparation of antiferroelectric films more challenging than ferroelectric films.

Tani and Payne [65] have successful fabricated PLZT ferroelectric and PNSnZT antiferroelectric thin films using PbO overcoat technique. Based on a 2-methoxyethanol-based sol-gel method, the deposition of a single layer of an unhydrolyzed PbO precursor solution after all the required solution deposition was used. The excess PbO enhance the formation of perovskite structure and limit the development of second phase.

The AFE-FE phase transition behavior of thin films in the PLSnZT system has been investigated by Brooks et al. [66,67]. Different compositions in varying proximity to the AFE-FE phase boundaries were prepared by a sol-gel spin coating method. The transition fields for the thin film were found to be larger than the bulk ceramics, while the maximum polarizations and strains measured in the films were lower. Possible
explanations for the observed behaviors were given as residual stresses due to substrate clamping and a metastable coexistence of the AFE and FE phases.

Sol-gel derived thin films of antiferroelectric to ferroelectric phase transition in Nb-doped PSnZT have been studied utilizing the hydrolysis-resistant precursor by Gaskey et al. [68]. Electric field-induced strains up to 0.33% have been optically determined for an AFE orthorhombic composition, with tunable electromechanical coefficients. Film properties showed only slight variation with electrode size over a range of diameters from 0.8 mm to 6.35 mm. With a capacitance density of 30-35 µF/cm², Nb-doped PSnZT films are promising as high-energy storage capacitors.

While the strains resulting from the field-forced AFE-FE transition making La-, Nb-doped PSnZT films useful for microactuator application, the highest strain value reported in thin films due to AFE-FE phase switching was observed in lead zirconate family [69]. Textured PZ thin film were formed by a sol-gel method and crystallized with a pseudocubic (111) and (100) preferred orientation. Strain as high as 0.7% was observed by interferometry. The high dielectric strength (100 MV/m) made the AFE-FE switching observable with full saturation at room temperature. Phase cycling of the relative large strain is believed to lead eventually dielectric breakdown via mechanical failure.

As many microelectromechanical devices require larger displacements than can be obtained in thin films, the preparation and characterization of antiferroelectric thick films (film thickness>1 µm) through sol-gel processing have been reported since 1990s [70,71]. There is a new interest in the preparation and characterization of antiferroelectric thick film based on the processing technique of ferroelectric thick films.
Adding excess lead precursor in the starting solution and using rapid thermal annealing are the most common method to control thick film lead loss during high temperature pyrolysis and annealing. High quality Nb- and La-doped PSnZT antiferroelectric thick films were developed through multi-step annealing and suitable lead oxide overcoat layers [72]. The 5 µm thick Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.85}$Sn$_{0.13}$Ti$_{0.02}$)$_{0.98}$O$_3$ films show square hysteresis loops with no remnant polarization, and a strain level up to 0.48% (Fig. 2.13). The sharp increase of strain level makes it suitable for high strain digital actuation application. The 5 µm thick Pb$_{0.97}$La$_{0.02}$(Zr$_{0.65}$Sn$_{0.31}$Ti$_{0.04}$)$_{0.98}$O$_3$ shows slanted hysteresis loops with very small hysteresis, zero remnant polarization, and a strain level up to 0.38% (Fig. 2.14). The gradual increase of strain with applied field makes it suitable for high strain analogy actuation applications with fast response speed.

Fig. 2.13 Electric field-induced polarizations and strains of Nb$^{5+}$-doped PZSnT films [72].
Fig. 2.14 Electric field-induced polarizations and strains of La$^{3+}$-doped PZSnT films [72].
3. OBJECTIVES

The field-induced AFE-FE phase transition in Sr-modified PZT system is very interesting because although this phase diagram was developed by Ikeda around 40 years ago, very few field-induced phase transition studies have been performed. In the light of the work previously discussed for Sn-, Nb-, and La-doped PZT systems, the fabrication and study of the field-induced phase transition characteristics in Sr-modified PZT system is investigated in this study to evaluate the potentials of PSZT system for novel device applications. The purpose of this work is to evaluate the effect of compositional modifications on the electrical properties of lead strontium zirconate titanate ceramics, as well as to examine their electrically induced AFE-FE phase transition behavior. The main project objectives are

(1) selecting compositions in FE, AFE regions and close to the FE-AFE phase boundary

(2) developing processing methods for synthesizing Sr-modified PZT and doped PSZT ceramics using tape casting technique

(3) characterizing the ferroelectric and dielectric properties of selected compositions

(4) observing temperature and fatigue responses of polarization behavior

(5) evaluating their electromechanical response with respect to the dopant concentration in order to improve field-induced strain characteristics

(6) using in situ x-ray diffraction to study the unit cell change during field-induced AFE-FE phase transition.
4. EXPERIMENTAL PROCEDURES

4.1 Sample Preparation

The processing flow chart for fabrication of the Sr-modified PZT is shown in Fig. 4.1. The raw powders were obtained from Aldrich Chemical Company: PbO (99.9+% <10 µm), TiO$_2$, ZrO$_2$ (99+% <5 µm), and Sr(NO$_3$)$_2$ (ACS reagent grade crystals 99+%). These highly pure raw oxide powders: PbO, TiO$_2$, ZrO$_2$, and Sr(NO$_3$)$_2$ were wet-mixed with distilled water and ball-milled in polyethylene bottle containing ZrO$_2$ milling media for 2 hours. The milling conditions used were a ZrO$_2$ media/powder ratio of 4/1, and a liquid/powder ratio of 3/1. An amount of 1 vol % Darvan C (ammonium polymethacrylate, R. C. Vanderbilt Company) was added as a dispersant. It counteracted the agglomerating tendency of the powders and made the dried cake soft enough for milling. Darvan C is expected to decompose calcination temperature because of its low boiling point (100°C).

After drying the slurry, the dried cake was crushed and ball milled for 20 hours. Then, the powders were calcined at 850°C for 1.5 hours. The calcined powders were ball-milled with ZrO$_2$ for additional 15 hours before preparation of the tape casting slurry. The tape casting slurry was prepared from PSZT powder, solvent (a mixture of toluene and methyl isobutyl ketone, Fisher Chemical), binder (polyvinyl butyral, Monsanto Company), dispersant (diisodecyl glutarate, The C. P. Hall Company) and plasticizer (Dipentaerythritol Pentaacrylate Esters, Sartomer Company). Table 4.1 shows a tape casting slip composition used for PSZT ceramics. After ball milling for 6 hours, the dissolved air in the slurry was removed by subjecting the slip to a vacuum container for 5 minutes. Then, the slurry was cast on a fixed bed tape-casting machine at a casting speed
of 0.5 m/min and Doctor blade height of 0.20 mm. After the tapes were dried, they had sufficient strength and flexibility to survive cutting into 25 mm x 25 mm sheets for lamination. The dried tapes were stacked and pressed under a laminating machine (Tetrahedron Associates Inc., CA). The green tapes can adhere to themselves without binder spray on both surfaces. The lamination was done at 115°C using the two-stage loading: 3.8 MPa for 15 minutes, and then 8.2 MPa for another 15 minutes. Subsequently, the preform was placed into a furnace, heated to 350°C in air with a heating rate of 1°C/min, held there for 3 hours, and then heated at the same heating rate to 600°C and kept there for 2 hours. The organic ingredients such as binder, plasticizer, and dispersant were removed during this binder removal step. Sintering was done over a temperature range 1300°C-1350°C in a PbO rich atmosphere provided by the PbZrO₃ powder in two closed Al₂O₃ crucibles. After sintering the samples experienced about 2% weight loss.

Fig. 4.1. Flow chart for processing Sr-modified PZT by tape casting and sintering route
Table 4.1 Tape casting slip composition used for PSZT ceramics

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Function</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSZT Powder</td>
<td>Ceramic</td>
<td>100</td>
</tr>
<tr>
<td>PVB (Butvar B-76)</td>
<td>Binder</td>
<td>3.2</td>
</tr>
<tr>
<td>Tolune</td>
<td>Solvent</td>
<td>20.4</td>
</tr>
<tr>
<td>Methyl Isobutyl Ketone</td>
<td>Solvent</td>
<td>10.2</td>
</tr>
<tr>
<td>Dipentaerythritol Pentaacrylate</td>
<td>Plasticizer</td>
<td>3.8</td>
</tr>
<tr>
<td>Diisodecyl Glutarate</td>
<td>Dispersant</td>
<td>0.36</td>
</tr>
</tbody>
</table>

**4.2 Electroding**

The sintered samples were mechanically thinned with 240 and 400 grit SiC papers in order to obtain parallel surfaces. Then, they were polished using 600 and 1200 grit SiC papers for coarse polishing to a thickness of 0.5 mm. Residual surface stresses created by grinding and polishing were minimized by a heat-treatment at 550°C for one hour in air.

For polarization and dielectric properties measurements, “Dopont 7095” silver paste was used to for painting the electrodes on the sample. The electrode layer should be thin and uniform. If the paste thickens in the bottle, then the thinner “Depont 8250” can be used to thin the paste down to a proper viscosity level. After painting, it was dried in an oven at around 100°C for an hour. After this initial drying, the sample was baked in the oven at 500°C for 0.5 hour. This high temperature baking was necessary to remove the organic substances used in the silver paste. After this heat treatment, the resistance value of electrode layer was less than 1 ohm.

For field-induced longitudinal strain measurements, silver electrodes of ~3 mm diameter were used for good electrical connection to copper wires. On bottom surface,
this electrode was in the center and on the top surface, this was in the corner. In order to 
obtain very uniform electrode layer, Au was sputtered to the rest area of sample surfaces. 
Due to the machine quality and sputter technique, resistance values of electrode layer 
were about 1-2 ohm.

4.3 Microscopy

After coarse polishing, the samples were followed by a polish using 15, 6, 3, 1 
and 0.1 µm diamond paste on a “Texmet 1000” cloth. Etching solution that was used: 5% 
HNO₃ + 5% HCl + 8 drops HF + 90% DI water. The samples were etched for 10 seconds 
with an immediate washing under running water. Then, the microstructures were checked 
under an optical microscope. The grain sizes were analyzed using Image-plus software. 
The microstructures of fatigued samples were investigated by scanning electron 
microscopy (SEM) at 25 kV.

4.4 Powder Surface Area and Slurry Viscosity Measurement

Gemini 2360 surface area analyzer (Micromeritics Instrument Corporation) was 
used to measure the powder surface area after ball milling. PSZT slurry viscosity was 
measurement by a Brookfield Digital Viscometer.

4.5 Polarization Hysteresis Loop Measurement

The polarization (P) versus electric field (E) was measured using a modified 
Sawyer and Tower circuit (Fig. 4.2) at different temperatures. The hysteresis loop was 
displayed by an oscilloscope in which the X channel measured the voltage across the R₂
and the Y channel measured the voltage induced across the capacitor $C_x$. The quantity plotted on the horizontal axis is proportional to the field across the sample. Field was obtained by dividing the X channel reading by the thickness of the sample. A linear capacitor $C_x$ is connected in series with the sample $C_o$. As the charge accumulated = Capacitance x Voltage induced, if the capacitance of the capacitor $C_x$ was known then the charge accumulated across the sample can be obtained by multiplying the measured voltage with the known capacitance of the capacitor $C_x$. Once the charge accumulated was known, then the polarization was calculated by dividing the charge by the surface area of the electrode printed on the sample. The conduction loss was minimized by adjusting the variable resistors. The small resistance in $R_2$ makes sure the voltage across the oscilloscope is small and falls in the acceptable range. A TL062CP operational amplifier with a resistance of over $10^9$ was used to protect the oscilloscope in case the sample breaks down.

Fig. 4.2. Sawyer-Tower circuit used for polarization measurement
During testing, the samples were submerged into silicone oil (Aldrich Chemical Company, Inc.) to assure a homogeneous temperature and to prevent arcing. The A. C. power was supplied using a high-voltage amplifier (Model 601C, Trek Incorporated). For high temperature measurements, a hot plate was used to heat the insulating oil and a thermometer was used to measure the oil temperature near the sample. For low temperature measurements, ice and liquid nitrogen was used as the coolant. All P-E curves were measured using an amplified sine waveform at 0.1Hz, created by a function generator (Model 3011B, BK Precision) after the oil bath temperature maintained constant for 3 minutes. The remnant polarization (Pr) and coercive field were evaluated by measuring the electrical polarization values at zero electric field and electric field values at zero polarization.

4.6 Field-Induced Strain Measurement

MTI-2000 fotonic sensor was used to measure the field-induced strain. Figure 4.3 depicts the interaction of adjacent transmit and receive fiber as the light is reflected from a target. It can be seen that at zero gap, the light in the transmit fiber will be reflected directly into itself and little or no light would be transferred to the receive fiber. As the gap increases, some of the reflected light is captured by the receive fiber and carried to the photo-sensitive detector. As the gap increases further, a distance will be reached at which a maximum of the reflected light is transferred to the receive fiber. Further increases in the gap will result in a decrease in the light at the receive fiber face and a corresponding drop in the output signal from the photo sensor.
Typical fiber optic sensor calibration curve is shown in Fig. 4.4. The front slope (range 1) of the calibration curve is very steep and exhibits linear behavior. This means that very small changes in displacement appear as large linear change in received light. In Fig. 4.4, the front slope has a value of $54.10 \text{ Å/mV}$.

The schematic setup of longitudinal strain measurement was shown in Fig. 4.5. A fine polished copper plate was used as a mirror. The incident light from optic fiber was reflected off by the mirror attached at one end of the insulating rod of which another end was in contact with the sample. The optic fiber tip was fixed to a positioner which provided the distance adjustment against the samples during calibration. When the sample vibrated under an a.c. driving field, the reflected light was detected and converted to corresponding voltage signal. The sample and optical fiber section were placed on a special table to isolate the setup from extraneous vibration. All these signals were
recorded by a computer-based data acquisition system. The voltage output of the probe’s photocell can be monitored with an oscilloscope by using the MTI-2000 analogy output. The change in voltage caused by sample displacement can be captured, viewed, and measured directly on oscilloscope’s screen.

Fig. 4.4. Typical fiber optic sensor calibration curve

Fig. 4.5. Schematic showing arrangement for longitudinal strain measurement
4.7 Dielectric Properties and Resistivity Measurement

RLC Digibridge (QuadTech, Inc.) was used to measure dielectric properties as a function of temperature at different frequencies. A digital multimeter via a platinum resistance thermometer was mounted close to the electrode of the sample fixture. The ceramic samples were heated in air at a rate of about 3°C/min to about 200°C. Capacitance and loss tangent were recorded manually every 1-2°C. Capacitance was converted to dielectric constant using the sample geometry and permittivity of air. The relative dielectric constant $\varepsilon_r$ was determined from the relationship

$$\varepsilon_r = \frac{C h}{\varepsilon_0 A}$$

(4.1)

where $C$, $h$ and $A$ are capacitance, the sample thickness and the electroded area respectively.

1865 Megaohmometer/IR tester (QuadTech, Inc.) was used to measure high resistance at room temperature. Test voltage was determined by sample resistance range. 100 VDC was applied when the sample resistance range was in the range of $10^5$-$10^{13}$ ohms.

4.8 X-ray Diffraction Measurement

Phase analysis of sintered samples was done by an X-ray diffractometer (Siemens Model D-500) with Cu-K$_\alpha$ radiation. Lattice constants were calculated from d-spacing obtained by x-ray diffraction.

_In situ_ x-ray diffraction spectra were taken at room temperature with Philips X’ert diffractometer. The x-ray diffraction study was operated under the following conditions: an accelerating voltage of 55 kV and a current of 45 mA. The diffractometer is equipped
with a sample holder attachment which allows to apply high d. c. voltage to the ceramics. X-ray diffraction scan parameters include a step size of 0.01° and a counting time per step of 1 s. The samples were approximately 0.2 mm in thickness. Silver paste was used as base electrode and thin layer of Au was deposited on the top surface of the sample. To prevent flashover, unsputtered area of about 1 mm width was left around the periphery of the electrodes. The thin Au electrode helped to minimize the attenuation of x rays during in situ x-ray diffraction measurements.
5. RESULTS AND DISCUSSION

Since the field-induced phase transition behavior is strongly affected by the temperature and sample compositions, the \( A_T-F_R \) phase boundary position is very important for this investigation. Although the \( \text{PbTiO}_3-\text{PbZrO}_3-\text{SrTiO}_3-\text{SrZrO}_3 \) phase diagram was developed about 40 years ago, the deviation of \( A_T-F_R \) phase boundary from published phase diagram was recently found by our previous work [17]. Furthermore, from thermodynamic point of view, it is expected that the \( A_T-F_R \) phase boundary in the \( \text{PbTiO}_3-\text{PbZrO}_3-\text{SrTiO}_3-\text{SrZrO}_3 \) system is not a line but a region where two phases coexist.

In order to identify the practical composition regions suitable for the field-induced \( A_T-F_R \) transition investigation, compositions with either fixed \( \text{Ti}^{4+} \) or \( \text{Sr}^{2+} \) content were selected with the nominal composition \((\text{Pb}_{1-x}\text{Sr}_x)(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3\) \((0.1\leq x\leq0.3)\) and \((\text{Pb}_{0.9}\text{Sr}_{0.1})(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3\) \((0.1\leq y\leq0.2)\). The compositions represented by the formula \( \text{Pb}_{1-x}\text{Sr}_x(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3 \) is simplified as \( 100x/100(1-y)/100y \) in the following discussion.

5.1 Processing of Sr-Modified PZT Ceramics

Processing of Sr-modified PZT ceramics were done through mixed oxides and sintering route. As Sr was the key component, it was essential to have a homogeneous distribution of Sr in the solid solution. \( \text{Sr(NO}_3)_2 \) was used because it is soluble in water during wet mixing. Thus, \( \text{Sr(NO}_3)_2 \) is distributed uniformly in the solution. In the calcination stage, \( \text{Sr(NO}_3)_2 \) decomposes to \( \text{SrO} \) upon heating to moderately low temperatures and react with other oxides to form the PSZT solid solution. Thermal
analysis, TGA and DTA, show that Sr(NO$_3$)$_2$ melts at 570°C and decomposes to SrO at around 700°C [17]. So, Sr(NO$_3$)$_2$ met our processing-related requirements.

The inherent problem with high temperature processing of lead-containing ceramics is the high volatility of PbO due to its low boiling point (880°C). XRD studies of the calcined Sr-modified PZT powders at different temperatures have shown that well-crystallized PSZT phase is achieved after calcining at 850°C for 1.5 hr [17]. This relatively low calcination temperature can also decrease the fluctuations in chemical composition of PZT ceramics due to PbO loss [73]. On the other hand, 850°C is high enough for the decomposition of Sr(NO$_3$)$_2$ to SrO. Hence, calcination was done at 850°C in a covered crucible. During calcination, some initial sintering also occurred between the particles. It was essential to expose new particle surfaces for the sake of high reactivity during sintering. Since finer particles homogenize the composition and sinter faster, another ball-milling was necessary after calcination. The average multi-points BET surface area of powder was about 1.5 m$^2$/g after ball milling.

The solvents used in ceramic processing must dissolve the organic additives incorporated into the slurry, that is, the dispersants, binders, and plasticizers. The mixture of two organic liquids (toluene and methyl isobutyl ketone) was used to make up the solvent, because the solubility of a polymer was generally greater in an optimized mixed-solvent system than in any individual pure solvent [74]. Excellent uniformity and fairly strong and flexible PZT tapes were prepared using PVB based slip. In contrast, PZT tapes prepared by acrylic base may be more brittle, depending on the amount of plasticizer [75,76]. Although Dipentaerythritol Pentaacrylate Esters (plasticizer) can easily be dissolved in Toluene, the Polyvinyl butyral can only be partially dissolved in Toluene.
Table 5.1 summarizes the solubility data on the PVB in different solvents at room temperature over a time period of 30 minutes. Even with the addition of 0.8 g dispersant, PVB still caused bridging flocculation and large agglomeration existed in the pure toluene solvent.

Table 5.1 Solubility of PVB in different solutions at room temperature

<table>
<thead>
<tr>
<th>PVB (g)</th>
<th>Solvent (g)</th>
<th>Dispersant (g)</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>Toluene (15)</td>
<td>0.8</td>
<td>65% Dissolved</td>
</tr>
<tr>
<td>0.2</td>
<td>MIBK (15)</td>
<td>0</td>
<td>100% Dissolved</td>
</tr>
<tr>
<td>0.2</td>
<td>Toluene (10), MIBK (5)</td>
<td>0</td>
<td>100% Dissolved</td>
</tr>
</tbody>
</table>

PVB is prepared by condensation reaction of an acid-catalyzed butyraldehyde with PVA. Since the conversion is not complete, the resulting product is a copolymer of both PVB and PVA. The chemical structure of PVB which is shown in Fig. 5.1(a) can be regarded to be composed of three parts. The left part which contain two ether groups is non polar, while both the middle and right parts are polar. It is not surprising that PVB can only partially dissolved in non-polar Toluene. Methyl Isobutyl Ketone (abbreviated as MIBK), which is a weak polar solvent, can greatly improve the solubility of the PVB. The chemical structures of Toluene and MIBK are shown in Fig. 5.1(b) and (c), respectively. Even without any dispersant, PVB can completely dissolve both in pure MIBK and mixture of Toluene and MIBK after 10 minutes.
Fig. 5.1. Chemical structure of (a) PVB (binder), (b) Tolune (solvent) and (c) MIBK (solvent)
Diisodecyl Glutarate was used as dispersant for deagglomeration and stabilization of PSZT particles in the slurry. Because the competition for adsorption of additives can reduce the state of dispersion, Diisodecyl Glutarate should be added before PVB binder. Otherwise, the PVB has a tendency to be absorbed onto the particle surface and hence can interfere with the adsorption of the dispersant [77]. The average slurry viscosity was 1700 mPas at room temperature. After casting and drying, all the tapes were flexible and easily released from the polyester carrier film except for the composition \( \text{Pb}_{0.7}\text{Sr}_{0.3}\text{Zr}_{0.8}\text{Ti}_{0.2} \) tapes. This high Sr-content tapes showed a greater adherence to the film surface and were brittle compared to other PSZT tapes. Small adjustments were made to slip formulations as following: the amount of plasticizer was increased from 2.8% to 5.0%, in the meantime, solvent was also increased from 22% to 27% to decrease the viscosity of the slip. Flexible and easily released tapes were produced by these modifications. Dipentaerythritol Pentaacrylate Esters increased the flexibility of the tape and were beneficial for easily removing of tapes from the polyester film. Karas et al. [78] have also observed that polyethylene glycol (used as a plasticizer) is primarily responsible for smooth stripping of the \( \text{BaTiO}_3 \) tape from a glass surface.

Figure 5.2 (a) and (b) show the SEM micrographs of PSZT samples before and after binder burn out, respectively. The uniformity of the powder size is seen before binder removal step. After organic ingredients burn out, the porous and agglomerated structure is observed.
Fig. 5.2. SEM micrographs of PSZT pellets (a) before binder burn out, (b) after binder burn out.
5.2 Microstructures and Physical Properties of Sr-modified PZT Ceramics

Table 5.2 shows the compositions selected in PSZT system, their simplified form and some physical properties. The densities of compositions PSZT 10/80/20 at various sintering temperatures for a fixed sintering time of 3.5 hr are shown in Fig. 5.3. PZT ceramics typically sinter in the temperature of 1200-1350°C. In general, the density increases with increasing sintering temperature. However, the density of PSZT ceramic is affected by the sintering condition in a complex way. In this investigation, the density maximizes at 1320°C. Further increase in the sintering temperature, results in the reduction of density because of excess PbO evaporation.

Table 5.2 Summary of PSZT compositions, simplified forms and their physical properties

<table>
<thead>
<tr>
<th>Composition</th>
<th>Simplified Form</th>
<th>Density (g/cm³)</th>
<th>Mean Grain Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{Pb}<em>{0.9}\text{Sr}</em>{0.1})(\text{Zr}<em>{0.8}\text{Ti}</em>{0.2})\text{O}_3)</td>
<td>PSZT 10/80/20</td>
<td>7.59</td>
<td>4.9 ± 2.1</td>
</tr>
<tr>
<td>((\text{Pb}<em>{0.85}\text{Sr}</em>{0.15})(\text{Zr}<em>{0.8}\text{Ti}</em>{0.2})\text{O}_3)</td>
<td>PSZT 15/80/20</td>
<td>7.48</td>
<td>3.6 ± 1.2</td>
</tr>
<tr>
<td>((\text{Pb}<em>{0.825}\text{Sr}</em>{0.175})(\text{Zr}<em>{0.8}\text{Ti}</em>{0.2})\text{O}_3)</td>
<td>PSZT 17.5/80/20</td>
<td>7.44</td>
<td>3.1 ± 1.8</td>
</tr>
<tr>
<td>((\text{Pb}<em>{0.8}\text{Sr}</em>{0.2})(\text{Zr}<em>{0.8}\text{Ti}</em>{0.2})\text{O}_3)</td>
<td>PSZT 20/80/20</td>
<td>7.42</td>
<td>2.4 ± 0.9</td>
</tr>
<tr>
<td>((\text{Pb}<em>{0.7}\text{Sr}</em>{0.3})(\text{Zr}<em>{0.8}\text{Ti}</em>{0.2})\text{O}_3)</td>
<td>PSZT 30/80/20</td>
<td>7.25</td>
<td>2.1 ± 0.8</td>
</tr>
<tr>
<td>((\text{Pb}<em>{0.9}\text{Sr}</em>{0.1})(\text{Zr}<em>{0.825}\text{Ti}</em>{0.175})\text{O}_3)</td>
<td>PSZT 10/82.5/17.5</td>
<td>7.61</td>
<td>4.0 ± 1.5</td>
</tr>
<tr>
<td>((\text{Pb}<em>{0.9}\text{Sr}</em>{0.1})(\text{Zr}<em>{0.86}\text{Ti}</em>{0.14})\text{O}_3)</td>
<td>PSZT 10/86/14</td>
<td>7.63</td>
<td>3.2 ± 1.3</td>
</tr>
<tr>
<td>((\text{Pb}<em>{0.9}\text{Sr}</em>{0.1})(\text{Zr}<em>{0.87}\text{Ti}</em>{0.13})\text{O}_3)</td>
<td>PSZT 10/87/13</td>
<td>7.64</td>
<td>2.5 ± 1.2</td>
</tr>
<tr>
<td>((\text{Pb}<em>{0.9}\text{Sr}</em>{0.1})(\text{Zr}<em>{0.9}\text{Ti}</em>{0.1})\text{O}_3)</td>
<td>PSZT 10/90/10</td>
<td>7.65</td>
<td>1.8 ± 0.9</td>
</tr>
</tbody>
</table>
Figure 5.4 shows the microstructures of polished and acid-etched surfaces of the PSZT ceramics. The densities and grain sizes were measured after the samples were sintered at 1320°C for 3.5 hrs. Compared to the density of PSZT 10/80/20, 7.59 g/cm$^3$, densities for specimens with partial $\text{Sr}^{2+}$ substitution for $\text{Pb}^{2+}$ decreased depending on the degree of substitution, while densities for specimens partial $\text{Zr}^{4+}$ substitution for $\text{Ti}^{4+}$ increased with increasing $\text{Zr}/\text{Ti}$ ratio. The mean grain size was in the range of 2-5 µm, and it decreased with increasing $\text{Sr}^{2+}$ content. The standard deviation of grain size was in the range of 0.9-1.8 µm irrespective of the kind of substitution atom and the degree of substitution. Lange and Kellett [79] demonstrated that grain growth in a densifying powder compact is primarily due to interparticle mass transport and is associated with grain boundary motion. The formation of PZT through a solid-phase reaction can mainly be attributed to the diffusion of $\text{Pb}^{2+}$ ions [20]. Since PbO has high vapor pressure and
increases the mass transport in multi-ion piezoelectric ceramics, compositions with high Pb\(^{2+}\) contents show large grain size.

The domain configuration in PSZT 10/80/20 ceramic was revealed by chemical etching under polarized light (Fig. 5.4). The domain patterns are normally within one grain. A series of domain boundaries running parallel to each other are walls between domains where the polarization vectors are at 71° or 109° to each other, while the 180° domain walls are usually hard to observe due to the extremely small wall width. For compositions located in AFE region and away from the AFE-FF phase boundary, AFE domain patterns was not observed in this investigation.

Fig. 5.4 (a) Typical microstructures of PSZT ceramics with different Sr\(^{2+}\) content
5.3 Structure Characterizations and Field-Induced Phase Transition at Room Temperature

Figure 5.5 shows room temperature X-ray diffraction patterns of the PSZT ceramics as a function of the strontium concentration. The diffraction data indicate a complete solid solubility with no other detectable phases present in PSZT system. PSZT 10/80/20 is located in the Fr region of the PSZT phase diagram, and all diffraction peaks could be fitted to a single rhombohedral phase with the cell parameter of $a = 4.117 \text{ Å}$ and $\alpha_{Rh} = 89.9^\circ$. 
Fig. 5.5. Comparison of XRD spectrum of PSZT 100x/80/20 ceramics with different Sr\(^{2+}\) content

PSZT 15/80/20 which is located in the A\(_T\) region but close to the A\(_T\)-F\(_R\) phase boundary, the (200) and (211) peaks start to split as shown in Fig. 5.5. With increasing Sr\(^{2+}\) content, the splitting of the diffraction peaks from rhombohedral to tetragonal system is more obvious. For PSZT 17.5/80/20 and 20/80/20, near 2\(\theta \approx 43.5^\circ\), the split peaks are 200 (lower angle side) and 002 (higher angle side) of the tetragonal system. In addition, the (211) peak also splits into 211 (lower angle side) and 112 (higher angle side) peaks. The coexistence of tetragonal and rhombohedral phases around morphotropic phase boundary in PZT (MPB) had been previously demonstrated by X-ray diffraction by splitting of the (200) diffraction peak only into triplets of type (002)\(_T\), (200)\(_R\), (200)\(_T\) [80] or splitting of the (h00) and (h01) type reflections in triplets at the same time [81]. No triplet was detected in the diffraction spectra in PSZT 17.5/80/20 ceramic even when the scan rate was decreased from 3.0\(^\circ\) to 0.6\(^\circ\) per minute for better accuracy.
The variation of tetragonality as a function of Sr\(^{2+}\) content is shown in Fig. 5.6. With increasing Sr\(^{2+}\) concentration, the (200)\(_T\) and (002)\(_T\) peaks for PSZT 20/80/20 move closer to each other. The width between (211)\(_T\) and (112)\(_T\) peaks is also decreased due to the increased tetragonal c/a ratio with increasing Sr\(^{2+}\) content, as shown in Table 5.3. For PSZT 30/80/20, it is hard to distinguish (200)\(_T\) (002)\(_T\) and (211)\(_T\) (112)\(_T\) peaks due to its tetragonal c/a ratio close to 1.

![Graph showing variation of tetragonality with Sr\(^{2+}\) content in PSZT 100x/80/20 ceramics](image)

Fig. 5.6. Variation of tetragonality with Sr\(^{2+}\) content in PSZT 100x/80/20 ceramics

<table>
<thead>
<tr>
<th>Composition</th>
<th>(c_{\text{Tet.}}) (Å)</th>
<th>(a_{\text{Tet.}}) (Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSZT 15/80/20</td>
<td>4.116</td>
<td>4.145</td>
<td>0.993</td>
</tr>
<tr>
<td>PSZT 17.5/80/20</td>
<td>4.096</td>
<td>4.120</td>
<td>0.994</td>
</tr>
<tr>
<td>PSZT 20/80/20</td>
<td>4.093</td>
<td>4.108</td>
<td>0.996</td>
</tr>
<tr>
<td>PSZT 30/80/20</td>
<td>4.071</td>
<td>4.081</td>
<td>0.998</td>
</tr>
<tr>
<td>PSZT 10/82.5/17.5</td>
<td>4.092</td>
<td>4.122</td>
<td>0.993</td>
</tr>
<tr>
<td>PSZT 10/86/14</td>
<td>4.105</td>
<td>4.137</td>
<td>0.992</td>
</tr>
<tr>
<td>PSZT 10/87/13</td>
<td>4.110</td>
<td>4.147</td>
<td>0.991</td>
</tr>
<tr>
<td>PSZT 10/90/10</td>
<td>4.111</td>
<td>4.151</td>
<td>0.990</td>
</tr>
</tbody>
</table>
Fig. 5.7. Comparison of polarization behavior of PSZT 100x/80/20 ceramics with different Sr$^{2+}$ content
A comparison of the polarization behavior of PSZT ceramics with different Sr\(^{2+}\) content is shown in Fig. 5.7. The hysteresis loop of PSZT 15/80/20 shows field-induced AFE-FE phase transition and presence of remnant polarization reflects the metastability of the induced ferroelectric phase. The field-induced AFE-FE phase transition behavior is much clear in PSZT 17.5/80/20 and 20/80/20 ceramics that the induced ferroelectric phases can be completely recovered to the AFE phase with decreasing field strength. For PSZT 30/80/20, the P-E behavior is linear up to field strength close to 6 kV/mm with no evidence of field-induced AFE-FE phase transition. This is consistent with its location in the antiferroelectric phase region and far away from the A\(_T\)-F\(_R\) phase boundary.

![Graph showing changes of forward switching field and polarization as a function of Sr\(^{2+}\) content in PSZT 100x/80/20 ceramics](image)

Fig. 5.8. Changes of forward switching field and polarization as a function of Sr\(^{2+}\) content in PSZT 100x/80/20 ceramics
The forward switching field is increased while the polarization is decreased with increasing \( \text{Sr}^{2+} \) content, as shown in Fig. 5.8. This demonstrates that \( \text{Sr}^{2+} \) addition stabilizes the antiferroelectric phase, and a higher switching field is required for AFE-FE phase transition. The amount of hysteresis, which represents the difference in the AFE-FE forward transition field and FE-AFE backward transition field, decreases as \( \text{Sr}^{2+} \) content is increased, as shown in Table 5.4. It means less energy is dissipated during the phase switching and it has the potential of “on-off” type actuator application.

Table 5.4 Field-induced properties of PSZT 100x/80/20 ceramics

<table>
<thead>
<tr>
<th>PSZT Composition</th>
<th>( E_C ) or ( E_{AF} ) (kV/mm)</th>
<th>( E_{AF} ) (kV/mm)</th>
<th>( \Delta E ) (kV/mm)</th>
<th>( P_r ) (( \mu \text{C/cm}^2 ))</th>
<th>( P_{max} ) (( \mu \text{C/cm}^2 ))</th>
<th>( S_l ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/80/20</td>
<td>1.2</td>
<td>-</td>
<td>FE</td>
<td>32</td>
<td>40</td>
<td>0.20</td>
</tr>
<tr>
<td>15/80/20</td>
<td>2.4</td>
<td>0.3</td>
<td>2.1</td>
<td>6</td>
<td>38</td>
<td>0.27</td>
</tr>
<tr>
<td>17.5/80/20</td>
<td>3.8</td>
<td>2.0</td>
<td>1.8</td>
<td>4</td>
<td>34</td>
<td>0.32</td>
</tr>
<tr>
<td>20/80/20</td>
<td>4.0</td>
<td>2.5</td>
<td>1.5</td>
<td>0</td>
<td>31</td>
<td>-</td>
</tr>
<tr>
<td>30/80/20</td>
<td>AFE</td>
<td>-</td>
<td>AFE</td>
<td>0</td>
<td>6</td>
<td>-</td>
</tr>
</tbody>
</table>

\( E_C \) is the coercive field for ferroelectric composition; \( E_{AF} \) is the electric field at which AFE-FE switching occurs; \( E_{FA} \) is the electric field at which FE-AFE switching occurs; \( \Delta E \) is the hysteresis, \( E_{AF}-E_{FA} \); \( P_r \) is the remnant polarization; \( P_{max} \) is the maximum polarization; The \( E_{AF} \) and \( E_{FA} \) values were determined from the P-E data by two-line intercept method. \( S_l \) is the field-induced longitudinal strain.

The comparison of XRD spectrum of PSZT ceramics with different Zr/Ti ratio but same \( \text{Sr}^{2+} \) content is illustrated in Fig. 5.9. As the Zr/Ti ratio increases, that is, as the composition is varied horizontally from left to right in the PSZT phase diagram, splitting occurs on some peaks. For PSZT 10/82.5/17.5, the splitting of (200) (211) peaks demonstrate that this composition belongs to the tetragonal system, and the separation
between these splitting peaks are increased due to the corresponding smaller tetragonal c/a ratio with higher Zr/Ti ratio, as shown in Fig. 5.10. For PSZT 10/90/10, this composition is further away from the $A_T$-$F_R$ phase boundary, splitting even starts to occur for (100) peak. The crystal structures determined by XRD are consistent with the corresponding dielectric hysteresis behaviors that are shown in Fig. 5.11, except for PSZT 10/82.5/17.5. Although this composition is located in the $A_T$ region of the original phase diagram [16], the squareness of P-E loop displays apparent ferroelectric hysteresis. This discrepancy may be due to the small free energy difference between the $A_T$ and induced $F_R$ phase. When the electric field is removed, there is not enough driving force to make the electrically induced $F_R$ go back to the $A_T$ phase. So, the $F_R$ phase is retained even when the field strength is decreased to zero. This explanation is supported by the comparison of the XRD patterns before and after dielectric hysteresis loop measurement, which is illustrated in Fig. 5.12. Compared with the virgin sample, ferroelectric rhombohedral peaks were detected for electric field exposed PSZT 10/82.5/17.5 sample.
Fig. 5.9. Comparison of XRD spectrum of PSZT 10/100(1-y)/100y ceramics with different Zr/Ti ratio

Fig. 5.10. Variation of the tetragonality with Zr\(^{4+}\) content in PSZT 10/100(1-y)/100y ceramics
Fig. 5.11. Comparison of polarization behavior of PSZT 10/100(1-y)/100y ceramics with different Zr/Ti ratio
Fig. 5.12. X-ray diffraction patterns of PSZT 10/82.5/17.5 samples (1) before and (2) after being exposed to an electric field

Fig. 5.13. Changes of forward switching field and polarization as a function of Zr$^{4+}$ in PSZT 10/100(1-y)/100y ceramics
With increasing ferroelectrically inactive Zr\textsuperscript{4+} content, the compositions are placed further away from the A\textsubscript{T}-F\textsubscript{R} phase boundary into the antiferroelectric phase region. The phase switching field is increased and the induced polarization is decreased due to the more stable antiferroelectric phase, as shown in Fig. 5.13. For PSZT 10/90/10, the ferroelectric phase cannot be induced even at the field strength of 6 kV/mm. Unlike PSZT ceramics modified with different amount of Sr\textsuperscript{2+}, the hysteresis increases when Zr\textsuperscript{4+} content is increased (Table 5.5).

Table 5.5 Field-induced properties of PSZT 10/100(1-y)/100y ceramics

<table>
<thead>
<tr>
<th>PSZT Composition</th>
<th>E\textsubscript{C} or E\textsubscript{AF} (kV/mm)</th>
<th>E\textsubscript{FA} (kV/mm)</th>
<th>∆E (kV/mm)</th>
<th>(P_r) (µC/cm\textsuperscript{2})</th>
<th>(P_{\text{max}}) (µC/cm\textsuperscript{2})</th>
<th>(S_l) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/82.5/17.5</td>
<td>1.4</td>
<td>-</td>
<td>FE</td>
<td>30</td>
<td>39</td>
<td>0.22</td>
</tr>
<tr>
<td>10/86/14</td>
<td>3.7</td>
<td>0.4</td>
<td>3.3</td>
<td>4.5</td>
<td>34</td>
<td>0.50</td>
</tr>
<tr>
<td>10/87/13</td>
<td>5.3</td>
<td>1.4</td>
<td>3.9</td>
<td>3.0</td>
<td>26</td>
<td>0.29</td>
</tr>
<tr>
<td>10/90/10</td>
<td>AFE</td>
<td>-</td>
<td>AFE</td>
<td>0</td>
<td>5</td>
<td>-</td>
</tr>
</tbody>
</table>

\(E_C\) is the coercive field for ferroelectric composition; \(E_{AF}\) is the electric field at which AFE-FE switching occurs; \(E_{FA}\) is the electric field at which FE-AFE switching occurs; \(\Delta E\) is the hysteresis, \(E_{AF}-E_{FA}\); \(P_r\) is the remnant polarization; \(P_{\text{max}}\) is the maximum polarization; The \(E_{AF}\) and \(E_{FA}\) values were determined from the P-E data by two-line intercept method. \(S_l\) is the field-induced longitudinal strain.

As outlined in section 2.3.1, the tolerance factor (Eq. 2.3) suggested by Goldschmidt, can be used to explain stability of the AFE/FE phase with varying Sr\textsuperscript{2+} or Zr\textsuperscript{4+} content. For Pb\(_{1-x}\)Sr\(_x\)(Zr\(_{1-y}\)Ti\(_y\))O\(_3\) ceramics, the tolerance factor can be calculated as [10]:

\[
t = \frac{\hat{R}_A + R_o}{\sqrt{2} (\hat{R}_B + R_o)}
\]

(5.1)
\[
R_A' = [(1-x)R_{\text{Pb}}^3 + xR_{\text{Sr}}^3]^{1/3} \quad (5.2)
\]
\[
R_B' = [(1-y)R_{\text{Zr}}^3 + yR_{\text{Ti}}^3]^{1/3} \quad (5.3)
\]

where \(R_A'\) and \(R_B'\) denote the mean radii of the groups of ions occupying A and B sites, respectively, and where \(R_0\) denotes the radius of the oxygen ion. The tolerance calculation results are shown in Table 5.6.

Table 5.6 Variation of tolerance factor of PSZT ceramics

<table>
<thead>
<tr>
<th>PSZT Composition</th>
<th>(R_A') (Å)</th>
<th>(R_B') (Å)</th>
<th>t</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/80/20</td>
<td>1.3152</td>
<td>0.7704</td>
<td>0.8846</td>
</tr>
<tr>
<td>15/80/20</td>
<td>1.3126</td>
<td>0.7704</td>
<td>0.8837</td>
</tr>
<tr>
<td>17.5/80/20</td>
<td>1.3115</td>
<td>0.7704</td>
<td>0.8834</td>
</tr>
<tr>
<td>20/80/20</td>
<td>1.3103</td>
<td>0.7704</td>
<td>0.8830</td>
</tr>
<tr>
<td>30/80/20</td>
<td>1.2640</td>
<td>0.7704</td>
<td>0.8679</td>
</tr>
<tr>
<td>10/82.5/17.5</td>
<td>1.3152</td>
<td>0.7731</td>
<td>0.8838</td>
</tr>
<tr>
<td>10/86/14</td>
<td>1.3152</td>
<td>0.7764</td>
<td>0.8823</td>
</tr>
<tr>
<td>10/87/13</td>
<td>1.3152</td>
<td>0.7773</td>
<td>0.8819</td>
</tr>
<tr>
<td>10/90/10</td>
<td>1.3152</td>
<td>0.7803</td>
<td>0.8807</td>
</tr>
</tbody>
</table>

\(R_A'\) and \(R_B'\) are the mean cubic radii of the groups of ions occupying A and B sites, respectively; t is the tolerance factor.

Sr\(^{2+}\) has smaller ionic radius (1.27 Å) than Pb\(^{2+}\) (1.32 Å). Thus, the addition of strontium decreases the tolerance factor and stabilizes the AFE phase. According to the lattice parameters for PSZT system determined by XRD investigation (Table 5.3) [82], the tetragonal unit cell shrinks with increasing amount of Sr\(^{2+}\), so decreases the space
where B-site cation is allowed to rattle [54]. Hence, polarizability decreases and this increases stability of the AFE phase with increasing Sr$^{2+}$ content.

On the other hand, PSZT ceramics in the horizontal group have different Zr/Ti ratio but same Sr$^{2+}$ content. Since Zr$^{4+}$ has larger ionic size (0.79 Å) than Ti$^{4+}$ (0.68 Å), the increase of Zr$^{4+}$ decreases the tolerance factor. The variation of the tolerance value $t$ with respect to the value $t_o$ corresponding to the composition close to AFE/FE phase boundary, can be used to establish the stable phase of the material. For example, PSZT 10/82.5/17.5 is a composition close to the $A_T$-$F_R$ phase boundary and has a tolerance value of $t = 0.8838$. If $t$ is larger than $t_o$, the material is ferroelectric; If $t$ is smaller than $t_o$, the material is antiferroelectric (Table 5.6).

Unlike the criteria of Ikeda for determining the $A_T$-$F_R$ boundary position mainly by crystal form, electrical response of PSZT is more attractive for field-induced phase transition application, so the $A_T$-$F_R$ boundary position is determined according to the polarization response in this investigation. Based on above observations, a dotted line is drawn in Fig. 5.14 near PSZT 17.5/80/20 and PSZT 10/87/13, and it approximately shows the shift of $A_T$-$F_R$ phase boundary. Compositions near the dotted line show double hysteresis response and have the potential for high field-induced strains. In contrast, compositions with higher Sr$^{2+}$ or lower Ti$^{4+}$ than the dotted line are in the AFE field. Much higher electric field is required for inducing AFE-FE phase transition.

5.4 Conclusions

In this section, PSZT ceramics were developed by tape-casting and sintering route. The characterization data from X-ray diffraction and field-induced phase transition
were reported. Attention was paid to the effect of composition variations on AFE-FE phase transitions at room temperature. X-ray diffraction and polarization hysteresis results indicated that most selected compositions conform to published phase diagram. However, the $A_T$-$F_R$ phase boundary shifted down to lower $Ti^{4+}$ and higher $Sr^{2+}$ side based on polarization response in this investigation. Thus, a modified AFE-FE phase boundary is generated.

Fig. 5.14. Compositions (▲) close to the dotted line show field-induced AFE-FE phase transition, and those (△, ▽) away from the dotted line are either FE or AFE.
Compositional modifications, with respect to varying Sr$^{2+}$ and Ti$^{4+}$ content, produced a change in phase stability. Increasing the Sr$^{2+}$ content increased the tetragonal c/a ratio, decreased the hysteresis and polarization, but increased the switching field. Increasing Zr$^{4+}$ content, which is ferroelectrically inactive, decreased the polarization and tetragonal c/a ratio, but increased the switching field and hysteresis.

5.5 Phase Transitions with Respect to Temperature and Electric Field

5.5.1 Temperature Dependence of Field-Induced Phase Transition and Dielectric Properties of PSZT with different Sr$^{2+}$ content

The phase transition in PSZT family depends not only on the location of the composition in the phase diagram but also on the operating temperature. A series of experiments were performed to characterize the behavior of PSZT ceramics at different temperatures. The transition fields for each composition are determined by two lines intercept method [12,83]. Figure 5.15 systematically shows the determination of forward transition field ($E_{AF}$) and reverse transition field ($E_{FA}$). The point of initiation of AFE-FE was chosen as the forward transition field and the point of finalization of FE-AFE was chosen as reverse transition field. So, $E_{AF}$ controls the onset of AFE to FE transition under external electric field while the $E_{FA}$ indicates where a complete coupling of the AFE sublattice that occurs when the field induced FE phase reverts back to the AFE state [84]. Since the phase transition is not so abrupt in real ceramics, Cross et al. [11] used another way to determine the phase transition field. Similar to a coercive field in a ferroelectric loop, they took 50:50 points on the way up and back to define the forward and reverse phase transition fields. Strictly neither of these approximations in the
literature is correct, and these transition fields also depend on the internal stress and grain sizes [85]. Since the “coercive field” in the induced butterfly loop lacks any physical meaning to phase transition, it seems more logical to choose the first method to simplify the true situation.

![Fig. 5.15. Schematic diagram illustrating the determination of forward phase transition field $E_{AF}$ and reverse phase transition field $E_{FA}$](image)

Figure 5.16 shows the dielectric constant and loss factor for PSZT 10/80/20 ceramic as a function of temperature. A phase transition at 190°C is obvious by the sharp decrease in the dielectric constant which is explained by the Curie-Weiss relationship. Figure 5.17 shows the P-E behavior for PSZT 10/80/20 ceramic at different temperatures. At 0°C, a field of 4.8 kV/mm induced a remnant polarization $P_r$ of ~ 32 µC/cm² and a hysteresis loop with a coercive field $E_c$ of ~1.2 kV/mm. At 55°C, $P_r$ and $E_c$ had values of
~34 µC/cm² and ~1.0 kV/mm, respectively. The lower coercive field Ec with higher temperature suggests an ease of domain switching. On further heating to 110°C, Pr increased to ~36 µC/cm² and Ec decreased to ~0.7 kV/mm. The shape of the hysteresis loops confirms the ferroelectric nature of the phase in the intermediate temperature range (0°C-110°C). At 130°C, leakage loss became obvious as shown by the roundness of the hysteresis loop at the high field strength, which corresponds to an increase in the dielectric loss as shown in Fig. 5.16. The conduction loss, which is only partially minimized by the compensation resistor, leads to the additional charge accumulation on the reference capacitor in the Sawyer and Tower circuit. Thus, the actual charge density or polarization on sample surface at 130°C is lower than the values shown in Fig. 5.17. Field-induced antiferroelectric-ferroelectric phase transformation response is not observed below 190°C. Above 190°C, the paraelectric phase (PE) is stable.

Fig. 5.16. Dielectric constant (open circles) and loss factor (solid circles) for PSZT 10/80/20 ceramic as a function of temperature
The dielectric response for PSZT 15/80/20 ceramic is shown in Fig. 5.18. The temperature for the dielectric maxima ($T_{max}$), decreased to 183°C. The maximum dielectric constant ($K_{max}$) also decreased with increasing strontium addition. The temperature-dependent polarization behavior of PSZT 15/80/20 is shown in Fig. 5.19. At -15°C, this composition shows a ferroelectric hysteresis loop. However, above 0°C, the AFE-FE phase transition as well as the decrease in hysteresis with increasing temperature are seen. The observed maximum polarization is ~37 µC/cm$^2$. On further increase of the temperature, the double hysteresis loop characteristics of the AFE-FE transition becomes
more pronounced. At 80°C, the antiferroelectric phase is reversibly recovered upon lowering the field. The maximum polarization is decreased to ~34 μC/cm² and the degree of hysteresis (E_AF-E_FA) is significantly reduced. The antiferroelectric phase is known to have significantly lower dielectric loss than the ferroelectric phase in Nb- and Sn-modified PZT system [86]. This behavior may also be true in Sr-modified PZT system. For PSZT 15/80/20, both AFE and FE phases may coexist at room temperature. The metastable FE phase easily transformed to the AFE state with increasing temperature at low field which is responsible for lower tanδ with increasing temperature (25°C-50°C). The dielectric loss factor in the intermediate temperature range (50-140°C) is lower than that below 50°C, indicating the absence of a ferroelectric state. These results indicate that the stability of phases upon heating for PSZT 15/80/20 follows the sequence, rhombohedral ferroelectric, tetragonal antiferroelectric, and paraelectric cubic.

![Fig. 5.18. Dielectric constant (open circles) and loss factor (solid circles) for PSZT 15/80/20 ceramic as a function of temperature](image)

Fig. 5.18. Dielectric constant (open circles) and loss factor (solid circles) for PSZT 15/80/20 ceramic as a function of temperature
The dielectric response and temperature-dependent polarization behaviors for PSZT 17.5/80/20 ceramics are shown in Figs. 5.20 and 5.21, respectively. $T_{\text{max}}$ decreased to 165°C for composition PSZT 17.5/80/20 with higher Sr$^{2+}$ content indicating further stabilization of the antiferroelectric and paraelectric phases with strontium addition. In comparison with composition PSZT 15/80/20 which shows FE response at -15°C, the composition PSZT 17.5/80/20 shows mixed AFE/FE P-E loop even at -20°C. These observations on composition PSZT 17.5/80/20 indicate that the AFE-FE phase transition shifts to lower temperature with increasing Sr$^{2+}$ content. Similar to PSZT 15/80/20
ceramic, PSZT 17.5/80/20 shows decreased polarization and hysteresis with increasing temperature. At 60°C, the P-E behavior is linear up to 2 kV/mm with no evidence of remnance. Double hysteresis loop is observed with increasing field strength. The dielectric loss decreased with increasing temperature which is consistent with narrow P-E loops. These slim loops indicate low energy loss on switching. The appearance of a “pseudoremanent” polarization in the P-E loop at 100°C is not a true lattice polarization effect and may be attributed to the increase of conductivity with temperature.

Fig. 5.20. Dielectric constant (open circles) and loss factor (solid circles) for PSZT 17.5/80/20 ceramic as a function of temperature

Figure 5.22 displays the Curie temperature and maximum dielectric constant $\varepsilon_{\text{max}}$ for PSZT ceramics as a function of Sr$^{2+}$ content. Sr$^{2+}$ is a common dopant that shifts the Curie peak to a lower value in BaTiO$_3$ and PZT [20]. Sr$^{2+}$ addition decreases not only the Curie temperature but also the maximum dielectric constant in this investigation.
Fig. 5.21. Temperature-dependent polarization behavior for PSZT 17.5/80/20 ceramic

Fig. 5.22. $\varepsilon_{\text{max}}$ and $T_{\text{max}}$ for PSZT 100x/80/20 ceramics as a function of Sr$^{2+}$ content
Since phase transition temperature is a structure sensitive parameter, the changes in phase transition temperature may be explained through crystal structure considerations. Ions substitutions distort the unit cell and induce strain in the lattice. Compressive stress usually decreases the Curie temperature. Yamamoto et al. [87] have shown a linear relation between the crystal tetragonality factor (c/a) and the Curie temperature in PLZT ceramics. The ceramic with less deviation from c/a =1 results in lower Curie temperature. Previous x-ray investigation showed that Sr$^{2+}$ substitution decreased the unit cell size and increased the tetragonal c/a ratio close to 1 (Table 5.3). So, the materials were subjected to compressive stress with increasing Sr$^{2+}$ content. Thus, Sr modification in PZT decreases the temperature for maximum dielectric constant ($T_{max}$) from 190°C to 183°C for PSZT 10/80/20 and to 165°C for PSZT 15/80/20 and PSZT 17.5/80/20, respectively.

5.5.2 Temperature Dependence of Field-Induced Phase Transition and Dielectric Properties of PSZT with different Zr$^{4+}$ content

The dielectric response of PSZT 10/82.5/17.5 is shown in Fig. 5.23. The temperature of the dielectric maximum $T_{max}$ increases slightly to 195°C with increasing Zr$^{4+}$ content compared with $T_{max}$ for PSZT 10/80/20. Although PSZT 10/82.5/17.5 was in the antiferroelectric phase region where only $A_T$ phase was assumed to exist between 0°C and $T_{max}$ [16], in practice ferroelectric responses were observed between 0°C and 110°C as shown in Fig. 5.24. This is consistent with our modified $A_T$/F$_R$ phase boundary where PSZT 10/82.5/17.5 is located in F$_R$ region. Similar to PSZT 10/80/20 composition, the coercive field decreases and leakage loss increases at higher temperature for PSZT 10/17.5/82.5 ceramic.
Fig. 5.23. Dielectric constant (open circles) and loss factor (solid circles) for PSZT 10/82.5/17.5 ceramic as a function of temperature

Fig. 5.24. Temperature-dependent polarization behavior for PSZT 10/82.5/17.5 ceramic
The PSZT 10/86/14 composition, with higher Zr\(^{4+}\) content, displayed higher \(T_{\text{max}}\) value of 204°C as shown in Fig. 5.25. Lossy ferroelectric like hysteresis loop is observed at -10°C (Fig. 5.26). Field-induced AFE-FE phase transition is evident at temperature of 0°C and above. With increasing temperature, more induced FE phase returns back to its original AFE state at zero field strength. When the temperature is increased to 65°C, the antiferroelectric state is fully recovered with decreasing field. It indicates that stability of the FE phase is decreased with increasing temperature.

The dielectric response of composition PSZT 10/87/13 (Fig. 5.27) is found to be similar to that for PSZT 10/86/14. Although loss factor increased rapidly at high temperatures for compositions PSZT 10/87/13 and 10/86/14, the tan\(\delta\) is still low below 150°C. The temperature of the dielectric maximum \(T_{\text{max}}\) representing the AFE-PE transition increased to 207°C and became more diffused with increasing Zr\(^{4+}\) content. The increase of \(T_{\text{max}}\) may be related to the decreased tetragonal c/a ratio (Table 5.3) for composition PSZT 10/86/14. Composition PSZT 10/86/14 shows ferroelectric response at -10°C, whereas composition PSZT 10/87/13 exhibits mixed AFE/FE phase at this temperature and shows ferroelectric hysteresis behavior at -15°C. (Fig.5.28). This suggests the decrease of \(T_{\text{AFE-FE}}\) with increasing Zr\(^{4+}\) content or the antiferroelectric phase is stabilized at lower temperature.
Fig. 5.25. Dielectric constant (open circles) and loss factor (solid circles) for PSZT 10/86/14 ceramic as a function of temperature

Fig. 5.26. Temperature-dependent polarization behavior for PSZT 10/86/14 ceramic
Fig. 5.27. Dielectric constant (open circles) and loss factor (solid circles) for PSZT 10/87/13 ceramic as a function of temperature

Fig. 5.28. Temperature-dependent polarization behavior for PSZT 10/87/13 ceramic
The maximum dielectric constant ($\varepsilon_{\text{max}}$) for compositions with different Zr$^{4+}$ is illustrated in Fig. 5.29. The Curie temperature increases with increasing Zr$^{4+}$ substitution as a result of more deviation of tetragonal c/a ratio from c/a = 1. The decreased $\varepsilon_{\text{max}}$ due to higher Sr$^{2+}$ and Zr$^{4+}$ additions (Figs. 5.22, 5.29) may be explained using the soft-mode model [25]. The soft mode frequency in ferroelectric is given by the following equation [88]:

$$\hat{u}^2(q = 0, j_i) = \hat{u}_T^2 = K(T - T_n)$$  \hspace{1cm} (5.4)

where q is the wave vector, $j_i$ designates the pertinent transverse optical branch, and K is a constant. The static dielectric constant [$\hat{\varepsilon}(q=0)$] is given by the generalized Lydane-Sachs-Teller (LST) relationship:

$$\hat{\varepsilon}/\hat{\varepsilon}_\infty = \prod_i [(\hat{u}_L)^2/(\hat{u}_T)^2]$$  \hspace{1cm} (5.5)

where $\hat{\varepsilon}_\infty$ is the optical dielectric constant, and $\hat{u}_L$ and $\hat{u}_T$ are the longitudinal and transverse optical phonon frequencies. LST relationship shows that a large static dielectric constant is related to a low frequency ferroelectric (q=0) transverse optical mode. The competition between antiferroelectric and ferroelectric modes may exist in PSZT ceramics. The ferroelectric zone center mode may control the magnitude of the static dielectric constant. Samara [89] suggested that only two soft modes really influence the AFE-FE transition. The first was $\Gamma_{25}$, a long-range FE mode which was responsible for high $\varepsilon_{\text{max}}$. The other was $\Sigma_3$, which resulted in the stabilization of the AFE phase. The depression of $\varepsilon_{\text{max}}$ is likely a reflection of the reduced influence of the FE soft-modes. Since ferroelectric phase is manifested by large volumes of uninterrupted, oriented dipoles, the increasing of Sr$^{2+}$ or Zr$^{4+}$ content may interrupt the long range dipolar
coupling and dampen the zone center polar phonon mode. The contribution of the zone boundary mode to the dielectric response is significantly less than that of the zone center and this leads to lower dielectric constant.

Following the internal field model of dielectrics [25], the Curie-Weiss temperature \( T_0 \) can be related to the Curie constant \( C \) by the Lorentz factor as

\[
T_0 = \gamma C
\]  

(5.6)

where \( \gamma \) is the Lorentz factor and reflects the strength of dipole coupling in the lattice.

Fig. 5.29. \( \varepsilon_{\text{max}} \) and \( T_{\text{max}} \) for PSZT 10/100(1-\( y \))/100y ceramics as a function of \( \text{Zr}^{4+} \) content
Equation 5.6 relates the microscopic parameter $\gamma$ to the experimentally accessible parameters $C$ and $T_o$. Figures 5.30(a) and 5.30(b) show plots of the inverse dielectric constant as a function of temperature for various compositions. The dashed lines are extrapolations using the Curie-Weiss relationship. The intersections of the dashed lines with the temperature axis give the Curie-Weiss temperature ($T_o$). The Curie constant ($C$) is calculated according to Curie-Weiss law (Eq. 2.11). The calculated values of Curie constant $C$ and the Lorentz factor are listed in Table 5.7. A decrease in $\gamma$ occurred as the Sr$^{2+}$ or Zr$^{4+}$ content increased in PSZT ceramics. The decrease of $\gamma$ reflects a weakening of the long-range coupling between dipoles. Addition of Sr$^{2+}$ or Zr$^{4+}$ tends to decrease $\varepsilon_{max}$ which has been attributed to the stabilization of the AFE phase. Lorentz factor calculations support this observation as well.

Table 5.7 Dielectric data for PSZT family

<table>
<thead>
<tr>
<th>Composition</th>
<th>10/80/20</th>
<th>15/80/20</th>
<th>17.5/80/20</th>
<th>10/82.5/17.5</th>
<th>10/86/14</th>
<th>10/87/13</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_o$ ($^\circ$C)</td>
<td>160</td>
<td>104</td>
<td>90</td>
<td>145</td>
<td>110</td>
<td>95</td>
</tr>
<tr>
<td>$C$ ($10^5$ $^\circ$C)</td>
<td>3.18</td>
<td>2.07</td>
<td>1.96</td>
<td>3.29</td>
<td>4.25</td>
<td>4.42</td>
</tr>
<tr>
<td>$\gamma$ ($10^{-4}$)</td>
<td>5.28</td>
<td>5.02</td>
<td>4.59</td>
<td>4.41</td>
<td>2.59</td>
<td>2.15</td>
</tr>
</tbody>
</table>

$T_o$ is the Curie-Weiss temperature, $C$ is the Curie constant, and $\gamma$ is the Lorentz factor.
Fig. 5.30. Inverse dielectric constant as a function of temperature for (a) PSZT 100x/80/20 and (b) PSZT 10/100(1-y)/100y ceramics
5.5.3 Thermodynamic Analysis of Field-Induced Phase Transition

For field-induced AFE-FE phase transition to occur, electric work done to AFE state must be greater than the FE nucleation barrier. On examining the energetic balance encountered in an AFE material subjected to an applied external field, two sources of resistance to nucleation of the FE phase are considered [90]. One of the energetic impediments to switching is the depolarization field that is set up in the crystal to counter the spontaneous polarization. The other barrier to the AFE-FE switching is hydrostatic pressure, as the surrounding materials resist the volume change (expansion) that accompanies the AFE-FE transition. The Gibbs free energy associated with the AFE-FE transition can be described as follows:

\[
\Delta G_{\text{AFE-FE}} = \Delta G_{\text{c,AFE-FE}} + E_d + E_{str} \quad (5.7)
\]

where \(\Delta G_{\text{c,AFE-FE}}\) is the change of chemical free energy accompanying the AFE-FE phase transition, \(E_d\) and \(E_{str}\) are related to the change of depolarization energy and strain energy during AFE-FE phase transition.

Because the atomic arrangement of the AFE phase is more compact than that of the FE counterpart, compressive stress will be generated during AFE-FE phase transition. Zero \(\Delta G_{\text{c,AFE-FE}}\) is not enough to induce the AFE-FE switching. The transition will occur only when external energy is applied to overcome these energy barriers. Excess field will aid in the growth of the FE phase and domain switching. However, the reverting from FE to AFE involves a volume shrinkage to a net zero polarization. Therefore, reverse switching is an easier procedure.

The stability of FE and AFE states can be considered from the full Gibbs function

\[
dG = -SdT - PdE - \varepsilon d\sigma \quad (5.8)
\]
where \( S, \sigma, E, \) and \( P \) are the entropy, exterior stress, electric field strength, and spontaneous polarization, respectively. At equilibrium state,

\[
dG^{\text{AFE}} = dG^{\text{FE}} \tag{5.9}
\]

Under normal experimental conditions, there is no exterior stress or constant stress, that is \( d\sigma = 0 \). A modified Clausius-Clapeyron approach gives

\[
\frac{dE}{dT} = -\frac{\Delta S}{\Delta P} = -\frac{\Delta H}{T \Delta P} \tag{5.10}
\]

where \( \Delta H \) and \( \Delta P \) are the enthalpy and polarization changes at the AFE-FE transition. From Eq. 5.10, a martensitic-type approach [12] was suggested and the transition field from AFE-FE was given by

\[
E = -\frac{\Delta H}{\Delta P} \ln \frac{T}{T_F} \tag{5.11}
\]

where \( T_F \) is the undercooling temperature which is associated with the transition barrier. From Eq. 5.11, the transition field from AFE-FE increases linearly with increasing temperature and this dependence is consistent with experimental data in Nb- and Sn-modified PZT system. However, the temperature dependence with transition field does not hold in Sr-modified PZT system. The forward and reverse transition fields of PSZT ceramics as a function of temperature are illustrated in Figs. 31 (a) and (b), respectively. For all these selected compositions, the forward field strength (\( E_{\text{AF}} \)) to induce the ferroelectric state slightly decreases with increasing temperature, while the reverse switching field (\( E_{\text{FA}} \)) which is related to the AFE sublattice coupling increases linearly with increasing temperature. Similar temperature dependence of forward transition field was also observed in other antiferroelectric thin films or bulk ceramics [83,90]. The slope forward transition field with temperature (\( dE_{\text{AF}}/dT \)) was -0.63 kV/cm K in PZT 97/3
films [83]. Sawaguchi [91] quoted a temperature dependence of switching field as -1.65 kV/cm K in PbZrO$_3$ ceramic. These disagreements between the experimental observation and thermodynamic model may be due to the assumption in the model that enthalpy change at phase transition is independent of temperature. It can be seen from Eq. 5.10 that $\Delta H$ is a function of temperature, and can be reasonably assumed as

$$\Delta H = a + bT$$

(5.12)

where $a$ and $b$ are coefficient.

Using Clausius-Clapeyron equation, the enthalpy change from temperature $T_0$ to $T$ will be

$$\Delta E = \frac{T - T_0}{\Delta P} \left[ a + \frac{b}{2(T + T_0)} \right]$$

(5.13)

So, the temperature dependence of the transition field is determined by the sign and magnitude of coefficient $a$ and $b$.

The lowered stability of the FE phase with increasing temperature is believed to result in higher reverse switching field. However, as only short-range coupling prevails in AFE state, it is less affected by thermal disturbances than long-range order of the FE structure. By this reasoning, forward switching field is less impacted by the temperature than the reverse switching field. This is consistent with the slope ($dE/dT$) which was determined from the temperature-dependence of transition field, as shown in Tables 5.8 and 5.9, respectively. The slope ($dE/dT$) of reverse phase transition is larger than the slope of forward phase transition in PSZT system, which is consistent with the extent of ordering for the AFE and FE phases.
Fig. 5.31. Temperature-dependence of (a) forward and (b) reverse transition field of PSZT ceramics.
The entropy and enthalpy difference due to AFE-FE forward and reverse phase transition for selected PSZT compositions can be calculated from Clausius-Clapeyron equation 5.10. These results are listed in Table 5.8 and 5.9, respectively. The entropy change value during AFE-FE phase transition in PSZT ceramics is in the same order of that in La- and Sn- modified PZT system [46]. The small value of $\Delta S$ at the AFE-FE phase transition indicates that ordering of the AFE states of PSZT is close to the FE ordering.

Table 5.8 Data obtained from Clausius-Clapeyron equation on forward (AFE-FE) phase transition

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\frac{\text{d}E}{\text{d}T}$ (kV/cm K)</th>
<th>$\Delta S$ at 298 K ($10^{-3}$ J/Kcm$^3$)</th>
<th>$\Delta H$ at 298 K (J/Kcm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15/80/20</td>
<td>-0.06</td>
<td>1.83</td>
<td>0.55</td>
</tr>
<tr>
<td>17.5/80/20</td>
<td>-0.109</td>
<td>3.32</td>
<td>0.99</td>
</tr>
<tr>
<td>10/86/14</td>
<td>-0.073</td>
<td>2.19</td>
<td>0.65</td>
</tr>
<tr>
<td>10/87/13</td>
<td>-0.158</td>
<td>3.63</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Table 5.9 Data obtained from Clausius-Clapeyron equation on reverse (FE-AFE) phase transition

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\frac{\text{d}E}{\text{d}T}$ (kV/cm K)</th>
<th>$\Delta S$ at 298 K ($10^{-3}$ J/Kcm$^3$)</th>
<th>$\Delta H$ at 298 K (J/Kcm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15/80/20</td>
<td>0.187</td>
<td>5.70</td>
<td>1.69</td>
</tr>
<tr>
<td>17.5/80/20</td>
<td>0.139</td>
<td>4.24</td>
<td>1.26</td>
</tr>
<tr>
<td>10/86/14</td>
<td>0.146</td>
<td>4.39</td>
<td>1.31</td>
</tr>
<tr>
<td>10/87/13</td>
<td>0.218</td>
<td>5.01</td>
<td>1.49</td>
</tr>
</tbody>
</table>
5.5.4 Conclusions

In this study, the temperature dependent polarization behavior and dielectric response were investigated. It was shown that the stability of FE and AFE phases were influenced by temperature. For ferroelectric compositions, the coercive field decreased with increasing temperature. For compositions located in the antiferroelectric region and away from the AFE/FE phase boundary, AFE-FE phase transition was evident from the double hysteresis loop at room temperature, while ferroelectric hysteresis loop was observed with decreasing temperature. These results indicated that the stable phase changed from the ferroelectric to antiferroelectric to paraelectric form with increasing temperature.

The temperature for maximum dielectric constant ($T_{\text{max}}$) decreased with increasing Sr$^{2+}$ content, while $T_{\text{max}}$ increased with increasing Zr$^{4+}$ content. The magnitude of the dielectric constant at $T_{\text{max}}$ decreased with Sr$^{2+}$ or Zr$^{4+}$ content due to the decreased contribution of zone boundary mode to the dielectric constant.

Both the forward transition field ($E_{\text{AFE-FE}}$) and reverse transition field ($E_{\text{FE-AFE}}$) increased with increasing Sr$^{2+}$ or Zr$^{4+}$ content. For PSZT ceramics, the reverse transition field ($E_{\text{FE-AFE}}$) increased with increasing temperature, while the forward transition field ($E_{\text{AFE-FE}}$) decreased with increasing temperature. Since the dependence of the reverse switching field on temperature (dE/dT) was larger than that for forward phase transition, the short-range nature of the AFE sublattice coupling was less affected by thermal disturbances than the long-range order of the FE structure.
5.6 Field-Induced Strain and *In Situ* X-ray Diffraction Study in PSZT ceramics

The transition between the antiferroelectric and ferroelectric phases can be driven by temperature change, mechanical stress, or electric field. Lead zirconate titanate stannate and other modified PZT compositions have been studied extensively for potential actuator applications. Large strain and low switching field is preferred for AFE-FE phase transition application. The large field-induced strain is believed to be due to the increase of the unit cell volume upon phase transition. Most of past studies of the crystal structure observations are based on free energy calculations and transmission electron microscopy, in which the FE phase has been induced by means other than the electric field, such as temperature change [92]. In order to clarify the composition-dependent field-induced strain behavior, it is necessary to directly analyze the structure changes because of an applied electric field. However, *in situ* XRD study on the field-induced phase transition is challenging and very limited investigation has been done, except for the work done by Blue et al. [93]. In this section, electric field-induced strain, *in situ* x-ray diffraction study and related crystal structures changes are reported for selected compositions.

The electrically-induced strain behaviors for PSZT ceramics at room temperature are shown in Fig. 5.32. The strain vs. electric field curves exhibit typical butterfly shapes for PSZT 10/80/20 and 10/82.5/17.5. Above the coercive field, the 71° and 109° domains start to align in the direction of the applied field with 180° domains remain nonstrain producing. Consequently, the polarization is increased rapidly with further increase in the field and accompanied by an expansion in the longitudinal direction. The typical
longitudinal strain at ~5.5 kV/mm is 0.2% for PSZT 10/80/20 and 0.22% for PSZT 10/82.5/17.5, respectively.

Fig. 5.32. Field-induced strain behaviors of PSZT ceramics
For PSZT 15/80/20 ceramic, which is located in the antiferroelectric region of the PSZT phase diagram, the antiferroelectric phase recovers with decreasing field, but some metastable FE phase is still present at the zero field strength. So, the field-induced strain does not return back to zero when the applied electric field is decreased to zero. For PSZT 17.5/80/20, which is away from the $\Delta_T/F_R$ phase boundary, the antiferroelectric state is more stable at low field in comparison to the ferroelectric phase. Both, the remnant polarization and strain, are close to zero when the field strength is reduced to zero. Above a switching field, of about 3.8 kV/mm, the AFE-FE phase transition starts. With further increase in field, FE domains continue to align along the applied field. This process leads to increased polarization and induced strain. Further increase in the field (>5.5kV/mm for PSZT 17.5/80/20) leads to saturation. A total longitudinal strain of 0.32% is believed to be as a result of the structural transformation and domain reorientation.

An unusually high field-induced strain of 0.86% at 5.5 kV/mm is observed for composition PSZT 10/86/14 at room temperature. However, reproducibility of such a high strain in different batches was difficult because of the small changes in composition during processing and the fact that the loss of PbO was hard to control. About 0.5% longitudinal strain is consistently observed close to 6 kV/mm field strength for PSZT 10/86/14. For PSZT 10/87/13 with higher Zr$^{4+}$ content, the switching field ($E_{AF}$) from antiferroelectric phase to ferroelectric phase increased greatly to 5.3 kV/mm. The low induced polarization value of PSZT 10/87/13 may result in small volume change, decreasing its strain level to 0.29% at 6 kV/mm.
The comparisons of PSZT 15/80/20 {200} type x-ray diffraction patterns under different applied electric fields are shown in Fig. 5.33. This range of 2θ was chosen since the tetragonal (T) and rhombohedral (R) phases are distinguishable on the XRD. The (200) reflections form a doublet in the tetragonal phase while (200) is a singlet in the rhombohedral phase. A low scan rate of 0.3°/min is selected for better accuracy. As is seen from the results of the diffraction patterns, (200)\textsubscript{T} (200)\textsubscript{R} and (002)\textsubscript{T} were observed under zero bias field. This demonstrates the coexistence of tetragonal and rhombohedral phases in PSZT 15/80/20. Since this composition is near the A\textsubscript{T}/F\textsubscript{R} phase boundary, the small energy difference between tetragonal and rhombohedral phases results in phase coexistence. At the forward phase transition field \(E_{AF}\) of 2.4 kV/mm, the intensity of rhombohedral peak is increased while the intensity of tetragonal peak is decreased. At the maximum bias field, which is 6 kV/mm, only rhombohedral peak is detected. Since the relative amount of one phase is proportional to its integrated intensity, this indicates that the relative amount of rhombohedral phase increases with increasing bias field and the phase transition from tetragonal to rhombohedral phase is completed at 6 kV/mm.

The \textit{in situ} XRD patterns for PSZT 17.5/80/20 ceramics are illustrated in Fig. 5.34. At zero applied field, only tetragonal phase Bragg reflections are obtained, which is consistent with the fact that this composition is away from the A\textsubscript{T}/F\textsubscript{R} phase boundary. At forward phase transition field \(E_{AF}\) of 3.8 kV/mm, the intensities of tetragonal (200) and (002) peaks are reduced. A new peak at 2θ = 43.95° due to induced ferroelectric phase was found, and it developed into a high intensity peak at 6 kV/mm. Since PSZT 17.5/80/20 shows pure AFE structure at zero bias field, this may be the reason it displays
higher field-induced strain than PSZT 15/80/20 which is a mixture of the FE and AFE phases.

Fig. 5.33. Variation of \{200\} XRD line profile of PSZT 15/80/20 ceramic at (a) E = 0 (b) \(E_{AF} = 2.4\) and (c) \(E_{max} = 6.0\) kV/mm applied fields

Fig. 5.34. Variation of \{200\} XRD line profile of PSZT 17.5/80/20 ceramic at (a) E = 0 (b) \(E_{AF} = 3.8\) and (c) \(E_{max} = 6.0\) kV/mm applied fields
The XRD patterns as a function of bias field of PSZT 10/86/14 and PSZT 10/87/13 ceramics are shown in Fig. 5.35 and 5.36, respectively. For PSZT 10/86/14, the induced ferroelectric (200) peak was detected at $\theta = 43.77^\circ$ at $E_{AF} = 3.7$ kV/mm, as shown in Fig. 5.35(a). Both the tetragonal and induced rhombohedral (111) peaks were coexisting at the phase transition field, as shown in Fig. 5.35(b). At an applied field of 6 kV/mm, the tetragonal peak was not detected and corresponding diffraction spectrum could be fit by a rhombohedral phase with $a_R = 4.134\,\text{Å}$, $\alpha_R = 89.86^\circ$ and $V_R = 70.63\,\text{Å}^3$. In comparison to its tetragonal unit cell volume of $70.25\,\text{Å}^3$, 0.54% volume jump is caused by the forced AFE-FE phase transition. It is in good agreement with the result of field-induced strain measured by fotonic sensor.

![Fig. 5.35(a). Variation of {200} XRD line profile of PSZT 10/86/14 ceramic at (a) $E = 0$ (b) $E_{AF} = 3.7$ and (c) $E_{max} = 6.0$ kV/mm applied fields](image-url)
Fig. 5.35(b). Variation of \{111\} XRD line profile of PSZT 10/86/14 ceramic at (a) \( E = 0 \) (b) \( E_{AF} = 3.7 \) and (c) \( E_{max} = 6.0 \) kV/mm applied fields

Fig. 5.36. Variation of \{200\} XRD line profile of PSZT 10/87/13 ceramic at (a) \( E = 0 \) (b) \( E_{AF} = 5.3 \) and (c) \( E_{max} = 6.0 \) kV/mm applied fields
PSZT 10/87/13 shows similar XRD patterns under external bias field. However, the diffraction peaks are best fit with a combination of a tetragonal and rhombohedral phases at 6.0 kV/mm, indicating the filed forced phase transition is not complete. Since PSZT 10/87/13 is away from the \(A_T/F_R\) phase boundary, partial AFE-FE phase transition results in its lower strain.

5.6.1 Conclusions

Field-induced strain accompanying AFE-FE phase transition is related to the change in the primitive perovskite cell and induced FE domain reorientation. The longitudinal field-induced strain in the Sr-modified PZT systems was in the range 0.2%-0.5%.

In situ x-ray diffraction as a function of applied fields was used as a new approach to determine the unit cell volume change. Compositions near the modified AFE-FE phase boundary, which have moderate switching field and large induced polarization, produced high field-induced strains.

The coexistence of AFE and FE phases were found for composition close to the modified \(A_T/F_R\) phase boundary and located in FE region. The AFE-FE phase transition was not completed for composition away from the boundary. So, the field-induced strain was reduced in above two cases.
5.7 Fatigue Behavior of PSZT ceramics

Electric fatigue is another important property that needs to be understood for actuator application. The degradation of elastic strain under high a.c. field with increased switching cycles severely limits the application of ferroelectric and piezoelectric materials.

The a.c. field induced degradation was evaluated by measuring the a.c. field-induced polarization and strain as a function of switching cycles. Ferroelectric PSZT 10/80/20 and antiferroelectric PSZT 10/86/14 ceramics were chosen as two representative compositions for the fatigue study. To study the change of remnant polarization ($P_r$) and coercive field ($E_c$), the normalized remnant polarization and coercive field as functions of the switching cycles of PSZT 10/80/20 ceramics are shown in Fig. 5.37. The changes of $P_r$ and $E_c$ were very small until $10^4$ switching cycles. However, $P_r$ decreased after $10^4$ switching cycles and only 81% of the original polarization value remained at $10^6$ switching cycles. Similar behavior was seen for coercive field; $E_c$ dropped to 85% of the original value at $10^6$ switching cycles.

The polarization hysteresis loops and field-induced strains of PSZT 10/86/14 as a function of switching cycles are shown in Fig. 5.38. The polarization decreased after $10^3$ switching cycles and about 95% polarization was remaining at $10^5$ switching cycles. At $10^6$ switching cycles, 88% of the initial polarization remained. Since internal stresses are introduced during the AFE-FE phase switching, some local regions are subjected to compressive stresses. AFE phase may not be able to switch to FE phase in these high compressive regions. This results in decreased polarization with increasing switching cycles. It was observed that the induced strain maintained the initial magnitude (0.5%) up
to about $10^3$ cycles and then the value decreased with switching cycles. At $10^5$ cycles, the induced strain dropped to about 80% of the original value.

Fig. 5.37. Normalized remnant polarization (open circle) and normalized coercive field (close circle) as a function of switching cycles for PSZT 10/80/20 ceramics
Fig. 5.38. Polarization and field-induced strain behaviors as a function of switching cycles for PSZT 10/86/14 ceramics
Fatigue in ferroelectric ceramics have been explained by the stabilization of domain walls and these stabilized domain walls can be recovered by heating the fatigued sample to above Curie temperature [94]. The space charges can react with domain walls and defects, and reorient the domain into a more stable state. When the fatigued sample was subjected to high temperature annealing, pinned domains and internal stresses could be relieved. When the temperature was lowered to room temperature, unpinned domains were formed again with redistribution of the defects and space charges. In our experiments, for PSZT 10/80/20, a sample that was subjected to $10^6$ switching cycles, was heated to 500°C for 2 h. It was observed that the remnant polarization recovered to 92% of original value (Fig. 5.39(a)). Total recovery did not occur at even 310°C higher than the Curie point. Also, coercive field decreased with the number of switching cycles during fatigue test. PSZT 10/86/14 ceramic was also subjected to high temperature annealing at 500°C for 2 h, but the induced polarization did not fully recover (Fig. 5.39(b)).

These results indicated that the domain wall pinning did not appear to be the only contributor to the fatigue behavior in PSZT ceramics. The most possible other mechanism of fatigue in the PSZT ceramics is microcracking. Because of the electromechanical anisotropy in the individual grains and large internal stresses during the switching cycles, microcracks could be initiated from pores or weak grain boundaries. These microcracks could not be healed by annealing at high temperature. Jiang et al. [95] attributed the fatigue of PLZT ceramics to contaminated surface instead of intrinsic structure deterioration or changes in domain distribution. They observed that a part of the electrode was peeled off from the sample surface during the switching process. The
ceramic-electrode interface of composition PSZT 10/86/14 before and after 10⁶ switching cycles is shown in Figs. 5.40 (a) and (b), respectively. Partial failure of the electrode was directly observed under SEM on the electroded surface of fatigued samples. The surface deterioration could be the result of electrochemical reaction, such as the field-induced chemical decomposition near the sample surface [59,60] or the migration and entrapment of defects (mainly oxygen vacancies, cations) at the electrode-ceramic interface [96]. On repeated electric loading, the electrode layers get delaminated from the sample surface. So, it decreases the effective area on which the electric field is applied. The regions under good electrode contact are under a higher electric field, while the regions under deteriorated interface experience a lower electric field. Hence, these two regions cannot switch simultaneously under a constant electric field. This generates stress concentrations at the boundaries between switched and nonswitched regions. This indicates that the sample surface may be another source of degradation and crack initiation. The dependence of degradation rate on the surface finishing condition in antiferroelectric ceramics was reported by Pan et al. [11]. We believe that the cracks initiate from pores and ceramic-electrode interface and propagate into the bulk sample, thereby leading to their degradation.

5.7.1 Conclusions

PSZT ceramics displayed degradation in polarization and field-induced strain with increasing number of switching cycles. By high temperature annealing, field-induced polarization was only partially recovered in Sr-modified PZT ceramic.
The comparison of the interfaces between electrode and ceramic revealed the partial failure of the electrode after fatigue test. Interface failure was suggested as one of the degradation mechanism leading to the reduced properties.

Fig. 5.39(a) Comparison of polarization behavior of fatigued PSZT 10/80/20 ceramic before (close cycle) and after 500°C annealing (open cycle)

Fig. 5.39(b) Comparison of polarization behavior of fatigued PSZT 10/86/14 ceramic before (close cycle) and after 500°C annealing (open cycle)
Fig. 5.40. Comparison of ceramic-electrode interface of composition PSZT 10/86/14 (a) before and (b) after fatigue test
5.8 Modification of PSZT Ceramics by Donar (La-, Nd-) Doping

The electromechanical properties of PSZT can be optimized by controlled doping for a particular application. From PLZT phase diagram [18], adding La$^{3+}$ to PZT system decreases stability of the FE phase and increases stabilities of the AFE and PE phases. This indicates that La$^{3+}$-doping increases coupling of the two AFE sublattices and electrostrictive coefficient. Uchino et al. [62] studied the doping effect of various rare earth metals on the field-induced strain in (Pb,Ba)(Zr,Ti)O$_3$ ceramics. At an applied field of 1.0 kV/mm, Nd$^{3+}$ doped ceramics showed maximum strain of 0.13%. Nd$^{3+}$ modification substantially enhanced the piezoelectric strain coefficient d$_{33}$ of PbZr$_{0.4}$Ti$_{0.6}$O$_3$. Both the mechanical and electrical properties peaked at 2 atom% Nd$^{3+}$ addition [97], which makes Nd$^{3+}$-doped PZT attractive for actuators and other high power ultrasonic transducers applications. Hence, PSZT 10/86/14 and 15/80/20 ceramics, which are close to AFE/FE phase boundary, were doped with different amounts of La$^{3+}$ or Nd$^{3+}$. The effects of doping on the electromechanical behavior of these samples were studied.

Because of the high packing density in perovskite structure, the presence of interstitial ions is unlikely. Hence, doping of PSZT with La$^{3+}$ or Nd$^{3+}$ is by aliovalent substitution of Pb$^{2+}$ by dopants. This results in substantial concentrations of vacancies. Thus, the La$^{3+}$ doped PSZT compositions can be prepared by assuming either A-site or B-site vacancies. The A-site vacancy formula is

$$(\text{Pb}_{1-x} \text{Sr}_x)_{1-3x/2} \text{La}_x (\text{Zr}_{1-y} \text{Ti}_y) \text{O}_3$$

and the B-site vacancies formula is

$$\text{Pb}_{1-2x} \text{Sr}_2 \text{La}_x (\text{Zr}_y \text{Ti}_{1-y})_{1-x/4} \text{O}_3$$
The actual location of these vacancies in either A-site or B-site of the unit cell has not yet been completely resolved. It is most probable that both A-site and B-site vacancies exist [98,99]. The La\(^{3+}\) doped specimens studied in this investigation were fabricated according to A-site formula. Consequently, the charge imbalance due to La\(^{3+}\) was compensated by creating A-site vacancies.

As Nd\(^{3+}\) has an ionic radius of 1.15 Å, which is relatively close to that of Pb\(^{2+}\) (1.32 Å), it seems that Nd\(^{3+}\) goes mostly to A-site in the perovskite structure. The Nd\(^{3+}\) doped samples were made according to formula \((\text{Pb}_{1-x}\text{Sr}_x)_{1-3z/2}\text{Nd}_6(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3\). Figure 5.41(a) and (b) show the polarization hysteresis loops for PLSZT 1/10/86/14 and PNSZT 1/10/86/14, respectively. The addition of 1 atom% La\(^{3+}\) or Nd\(^{3+}\) to PSZT 10/86/14 produced a highly stable AFE phase, which could not be switched even at a high applied field of 6 kV/mm at room temperature. Hence, the following discussion is confined to 1-3 atom% La\(^{3+}\) or Nd\(^{3+}\) doping in PSZT 15/80/20. Table 5.10 shows the compositions selected in doped-PSZT system, their simplified form, and some physical properties. The average grain size of PLSZT and PNSZT decreased with increasing La\(^{3+}\) or Nd\(^{3+}\) doping amount.
Fig. 5.41. Polarization hysteresis loops of (a) PLSZT 1/10/86/14 and (b) PNSZT 1/10/86/14 ceramics
Table 5.10 Summary of doped-PSZT compositions, simplified forms and their physical properties

<table>
<thead>
<tr>
<th>Composition</th>
<th>Simplified Form</th>
<th>Density (g/cm$^3$)</th>
<th>Mean Grain Size ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pb$<em>{0.85}$Sr$</em>{0.15}$)$<em>{0.985}$ La$</em>{0.01}$ (Zr$<em>{0.8}$ Ti$</em>{0.2}$) O$_3$</td>
<td>PLSZT 1/158020</td>
<td>7.52</td>
<td>12.1 ± 3.8</td>
</tr>
<tr>
<td>(Pb$<em>{0.85}$Sr$</em>{0.15}$)$<em>{0.97}$ La$</em>{0.02}$ (Zr$<em>{0.8}$ Ti$</em>{0.2}$) O$_3$</td>
<td>PLSZT 2/158020</td>
<td>7.49</td>
<td>8.1 ± 2.8</td>
</tr>
<tr>
<td>(Pb$<em>{0.85}$Sr$</em>{0.15}$)$<em>{0.955}$ La$</em>{0.03}$ (Zr$<em>{0.8}$ Ti$</em>{0.2}$) O$_3$</td>
<td>PLSZT 3/158020</td>
<td>7.47</td>
<td>6.6 ± 1.7</td>
</tr>
<tr>
<td>(Pb$<em>{0.85}$Sr$</em>{0.15}$)$<em>{0.985}$ Nd$</em>{0.01}$ (Zr$<em>{0.8}$ Ti$</em>{0.2}$) O$_3$</td>
<td>PNSZT 1/158020</td>
<td>7.59</td>
<td>8.2 ± 2.4</td>
</tr>
<tr>
<td>(Pb$<em>{0.85}$Sr$</em>{0.15}$)$<em>{0.97}$ Nd$</em>{0.02}$ (Zr$<em>{0.8}$ Ti$</em>{0.2}$) O$_3$</td>
<td>PNSZT 2/158020</td>
<td>7.58</td>
<td>7.2 ± 1.8</td>
</tr>
<tr>
<td>(Pb$<em>{0.85}$Sr$</em>{0.15}$)$<em>{0.955}$ Nd$</em>{0.03}$ (Zr$<em>{0.8}$ Ti$</em>{0.2}$) O$_3$</td>
<td>PNSZT 3/158020</td>
<td>7.53</td>
<td>6.2 ± 1.5</td>
</tr>
</tbody>
</table>
5.8.1 Structure Characterizations and Dielectric Properties of Doped-PSZT Ceramics

Figures 5.42 and 5.43 display room temperature x-ray diffraction spectra for La- and Nd-doped PSZT ceramics, respectively. The splitting of the tetragonal (200) and (211) peaks are clearly seen in PLSZT and PNSZT ceramics. The values of crystal tetragonality factor of compositions with different dopant concentrations are shown in Table 5.11. The results indicate that the value of crystal tetragonality factor increases with increasing either La$^{3+}$- or Nd$^{3+}$- dopant amount. Further, for the same amount of dopant concentration, the lattice parameters of PNSZT compositions are lower than those of PLSZT samples. The primitive unit cell also shrinks with La$^{3+}$ and Nd$^{3+}$ substitution for Pb$^{2+}$ site. Since the ionic size of Nd$^{3+}$ (1.15 Å) is smaller than that of La$^{3+}$ (1.22 Å), it is understandable that the unit size of Nd-doped sample is smaller than that of La-doped specimen.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$c_{\text{Tet.}}$(Å)</th>
<th>$a_{\text{Tet.}}$(Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLSZT 1/15/80/20</td>
<td>4.093</td>
<td>4.121</td>
<td>0.993</td>
</tr>
<tr>
<td>PLSZT 2/15/80/20</td>
<td>4.086</td>
<td>4.112</td>
<td>0.994</td>
</tr>
<tr>
<td>PLSZT 3/15/80/20</td>
<td>4.081</td>
<td>4.102</td>
<td>0.995</td>
</tr>
<tr>
<td>PNSZT 1/15/80/20</td>
<td>4.087</td>
<td>4.111</td>
<td>0.994</td>
</tr>
<tr>
<td>PNSZT 2/15/80/20</td>
<td>4.082</td>
<td>4.104</td>
<td>0.995</td>
</tr>
<tr>
<td>PNSZT 3/15/80/20</td>
<td>4.079</td>
<td>4.093</td>
<td>0.997</td>
</tr>
</tbody>
</table>
Fig. 5.42. Comparison of XRD spectrum of PLSZT 100x/15/80/20 with varying La$^{3+}$ contents

Fig. 5.43. Comparison of XRD spectrum of PNSZT 100x/15/80/20 with varying Nd$^{3+}$ contents
The dielectric responses at 1 KHz for PLSZT and PNSZT with 0-3% La\(^{3+}\) or Nd\(^{3+}\) doping are plotted in Figs. 5.44 and 5.45, respectively. Similar dielectric behavior was displayed by these two donor-doped samples. The value of maximum dielectric constant \(\varepsilon_{\text{max}}\) continuously dropped and the dielectric constant maxima shifted towards lower temperature with increasing amount of La\(^{3+}\) or Nd\(^{3+}\) doping. At maximum dielectric constant temperature \(T_{\text{max}}\), peak broadening increased with increasing La\(^{3+}\) or Nd\(^{3+}\) content. Up to 20 KHz, the position of diffused dielectric peaks was not dependent on the applied frequency. Since the ABO\(_3\) perovskite structure can be viewed as a network of BO\(_6\) octahedron, following the model proposed by Thomas [100], the BO\(_6\) octahedron is coupled to each other via the A-site cations. The net effect of La\(^{3+}\) or Nd\(^{3+}\) doping is the partial substitution of Pb\(^{2+}\) ions and occurrence of A-site vacancies. As a consequence, the coupling between the BO\(_6\) octahedron decreases with introduced vacancies. Hence, it results in the disruption of the FE coupling. This favors the establishment of weakly coupled local dipole moments and suppresses the maximum dielectric constant \(\varepsilon_{\text{max}}\) and transition temperature \(T_{\text{max}}\). As short-range coupling is present in PSZT 15/80/20, the antiferroelectric contribution to \(\varepsilon_{\text{max}}\) is less impacted by the chemical substitutions. The maximum reduction of \(\varepsilon_{\text{max}}\) is only about 1000 in all these La\(^{3+}\) or Nd\(^{3+}\) doped compositions. At higher dopant content, the increase in diffuseness of the transformation at \(T_{\text{max}}\) suggested an increased break-up of the lattice periodicity. From the microscopic view, the compositional and polarization fluctuations are responsible for broadened AFE-PE phase transitions. The La\(^{3+}\) and Nd\(^{3+}\) dopants and vacancies may not be uniformly distributed in the lattice. Some clustered BO\(_6\) octahedron containing no dopant or A-site
vacancies is proposed in PLZT materials [58]. These nonuniform structures would account for diffused dielectric response.

Fig. 5.44. Dielectric constant as a function of temperature for PLSZT 100x/15/80/20 compositions.

Fig. 5.45. Dielectric constant as a function of temperature for PNSZT 100x/15/80/20 compositions.
Because of the high volatility of lead and oxygen, PZT ceramics usually exhibit nonstoichiometry, especially when sintered in air. The creation of lead and oxygen vacancies is caused by PbO volatility:

$$\text{Pb}_x^+ + \text{O}_x^+ \rightarrow \text{V}_{\text{Pb}}^- + \text{V}_o^+ + \text{PbO}_g$$ \quad (5.14)

Although the lead vacancies $\text{V}_{\text{Pb}}$ and oxygen vacancies $\text{V}_o$ are widely recognized as the predominant point defects, experiments have shown that conductivity is P-type. This is presumably due to “superoxidation”, that is excess of cation vacancies over oxygen vacancies [6]. Since $\text{Pb}^{2+}$ occupies the center of the oxygen octahedron, ionic conduction by lead vacancy is not significant at room temperature. Thus, it is clear that due to superoxidation, the system is rich in holes, as can be seen from Eq. 5.15.

$$x \text{Pb}_x^+ \rightarrow x \text{V}_{\text{Pb}}^- + 2x h^+$$ \quad (5.15)

where $x$ is the amount of Pb vacancy.

Substitution of trivalent ions for $\text{Pb}^{2+}$ contributes electrons results in charge imbalance in the system. This charge imbalance can be compensated by two different mechanisms.

Case 1: electron-hole compensation

$$(1-x) \text{Pb}_x^+ + y \text{M}_2\text{O}_3 \rightarrow 2y\text{M}_{\text{Pb}}^- + 2ye^- + (1-x-2y) \text{Pb}_x^+ + 3y \text{O}_o^x$$ \quad (5.16)

where $y$ is the amount of doping, and M represents either La or Nd.

The electrons created due to doping, as shown in Eq. 5.16, combine with holes existing in the system (Eq. 5.15). Thus, electron-hole compensation takes place and this results in the decrease of hole concentration. An overall defect reaction may be represented as shown in Eq. 5.17.
\[
Pb_{p_b}^x + yM_2O_3 \rightarrow 2yM_{Pb}^\cdot + 2(x-y)h^\cdot + xV_{Pb}^\cdot + (1-x-2y)Pb_{p_b}^x + 3yO_o^x \quad (5.17)
\]

This is consistent with our experimental observations. The increasing of resistivity as a function of La\(^{3+}\) and Nd\(^{3+}\) concentration is shown in Fig. 5.46 and 5.47, respectively. Both La\(^{3+}\)- and Nd\(^{3+}\)-doped compositions possess high resistivity which increases with the addition of dopant amount and attains a maximum value at 2 mol %. This is also an added evidence that the modified PSZT ceramics is p-type conduction whose conductivity is reduced through compensation by donor substituents.

Case 2: Ti polaron formation, as shown in Eq. 5.18

\[
(1-x)Pb_{p_b}^x + yM_2O_3 \rightarrow 2yM_{Pb}^\cdot + 2yTi_{Ti}^\cdot + (1-x-2y)Pb_{p_b}^x + 3yO_o^x \quad (5.18)
\]

This compensation mechanism is supported by sample’s color change due to La\(^{3+}\) and Nd\(^{3+}\) doping. Undoped PSZT ceramics are yellow, while doped compositions are pale blue or green. Since the bluish color indicates the presence of Ti\(^{3+}\) [101], this proves the possible charge compensation mechanism in doped PSZT by reduction of Ti\(^{4+}\) to Ti\(^{3+}\). From observed results for La\(^{3+}\) and Nd\(^{3+}\) doped PSZT systems, it appears that both electron-hole compensation and Ti polaron formation mechanisms play roles in charge balance.

As the doping concentration increases, the electrons introduced by trivalent substitutions may no longer be fully compensated by above two mechanisms. These electrons increase the conductivity. As seen from Fig. 5.46 and 5.47, higher La\(^{3+}\) and Nd\(^{3+}\) concentration results in decreased resistivity. The defect reaction at higher doping concentration may be represented as in Eq. 5.19.

\[
Pb_{p_b}^x + yM_2O_3 \rightarrow 2yM_{Pb}^\cdot + 2(y-x)e^\cdot + xV_{Pb}^\cdot + (1-x-2y)Pb_{p_b}^x + 3yO_o \quad (5.19)
\]
Fig. 5.46. Dependence of resistivity on La$^{3+}$ concentration

Fig. 5.47. Dependence of resistivity on Nd$^{3+}$ concentration
5.8.2 AFE-FE Phase Transitions and In Situ XRD Study in Doped-PSZT Ceramics

Electrically induced polarization and strain for different amounts of La\(^{3+}\) and Nd\(^{3+}\) doped compositions are shown in Figs. 5.48 and 5.49, respectively, and some transition data are summarized in Table 5.12. Although induced polarization increases with decreasing La\(^{3+}\) and Nd\(^{3+}\) content for these doped compositions, the induced strain, however, is maximized at 2 atom\% La\(^{3+}\) or Nd\(^{3+}\) doping (2/15/80/20). Comparing La\(^{3+}\) - and Nd\(^{3+}\)-doped PSZT, it is interesting to note that Nd\(^{3+}\)-doped PSZT compositions not only exhibit a larger strain levels but also smaller transition field (E_{AFE-FE}) value. As discussed previously, the strain caused by phase switching is primarily based on two parameters, the change in the primitive perovskite cell and domain reorientation. Undoped PZT material is P-type semi-conductive due to Pb evaporation during sintering, so the donor doping to a little amount should cause the charge neutralization and smooth movement of domain wall [40]. From the AFE-FE switching model proposed by Park et al. in section 2.4.4, the ease with which domain walls move can be correlated to large field-induced strain. Thus, field-induced strain in appropriate donor doped PSZT composition will have larger value than undoped composition.

For 1 atom\% La\(^{3+}\) or Nd\(^{3+}\) doped composition, the remnant polarization in the P-E loop indicated the existence of mixed AFE/FE phases in the doped sample. With increasing amount of the dopant (La\(^{3+}\) or Nd\(^{3+}\)) to 2 atom\%, the remnant polarization decreased to zero. This suggested that 2 atom\% doped composition was devoid of FE phase at zero applied field. The field-induced strain caused by the AFE-FE phase transition is larger than that caused by FE domain switching. Thus, the mixture AFE/FE phases in 1% doped composition resulted in less field-induced strain than the strain of 2%
doped composition. Since La$^{3+}$ and Nd$^{3+}$ stabilize the antiferroelectric phase, the AFE-FE transition field is increased with increasing dopant level. For 3% (La$^{3+}$ or Nd$^{3+}$) doped composition, the AFE-FE phase transition may not be completed at an applied field of 6 kV/mm. The unswitched AFE phase in 3% (La$^{3+}$ or Nd$^{3+}$) doped composition produced less strain than the 2% doped composition.

Table 5.12 Dielectric and field-induced properties of La- and Nd- doped PSZT ceramics

<table>
<thead>
<tr>
<th>Composition</th>
<th>$K_{RT}$</th>
<th>$\tan\delta$ (%)</th>
<th>$K_{max}$</th>
<th>$E_{AF}$ (kV/mm)</th>
<th>$P_{max}$ (µC/cm$^2$)</th>
<th>$S_1$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLSZT 1/15/80/20</td>
<td>1055</td>
<td>1.26</td>
<td>1905</td>
<td>3.40</td>
<td>33</td>
<td>0.29</td>
</tr>
<tr>
<td>PLSZT 2/15/80/20</td>
<td>1065</td>
<td>1.02</td>
<td>1680</td>
<td>3.75</td>
<td>30</td>
<td>0.40</td>
</tr>
<tr>
<td>PLSZT 3/15/80/20</td>
<td>1070</td>
<td>0.85</td>
<td>1525</td>
<td>4.05</td>
<td>22</td>
<td>0.19</td>
</tr>
<tr>
<td>PNSZT 1/15/80/20</td>
<td>1090</td>
<td>1.30</td>
<td>2030</td>
<td>2.70</td>
<td>35</td>
<td>0.31</td>
</tr>
<tr>
<td>PNSZT 2/15/80/20</td>
<td>1080</td>
<td>1.05</td>
<td>1690</td>
<td>3.25</td>
<td>32</td>
<td>0.45</td>
</tr>
<tr>
<td>PNSZT 3/15/80/20</td>
<td>1070</td>
<td>0.92</td>
<td>1530</td>
<td>3.60</td>
<td>27</td>
<td>0.26</td>
</tr>
</tbody>
</table>
Fig. 5.48. Field-induced polarization and strain behaviors of PLSZT ceramics
Fig. 5.49. Field-induced polarization and strain behaviors of PNSZT ceramics
Among all the doped compositions investigated, PNSZT 2/15/80/20 ceramic shows the highest field-induced strain. Hence, this composition was selected for temperature dependent polarization behavior and in situ XRD study.

The temperature dependent polarization behavior for PNSZT 2/15/80/20 is shown in Fig. 5.50. In comparison with undoped PSZT 15/80/20 which shows FE response at –15°C, composition PNSZT 2/15/80/20 shows AFE-FE phase transition at the same temperature. This may be due to increased stability of AFE state by Nd³⁺ doping. As discussed in section 5.8.1, Nd³⁺ doping disrupts the FE coupling with introduced A-site vacancies. This favors the stabilization of short range ordered AFE structure as a result of delicate competition between FE and AFE phase. With increasing temperature, slim P-E loop was observed up to 150°C. Figure 5.50 shows polarization behavior recorded at 125°C. The lack of “pseudoremanent” polarization in the P-E loop at high temperature may be attributed to the increase of resistivity by 2 atom% Nd³⁺ doping.

As shown in Table 5.11, PNSZT 2/15/80/20 x-ray diffraction spectrum could be fit by a tetragonal phase with a=4.104 Å and c=4.082 Å. The changes in the {111} XRD line profile under different applied fields are shown in Fig. 5.51. Upon application of a forward switching field \( E_{AF} = 3.3 \) kV/mm, the tetragonal (111) peak still remained, but a new peak near 37.9° emerged. AFE phase has the tetragonal symmetry and it does not cause the {111} peak to split. So, this new peak that is observed could be the peak of induced ferroelectric phase. At an applied field of 6 kV/mm, the tetragonal (111) peak was not detected and resultant profile could be fit to the {111} peaks of a rhombohedral structure.
Fig. 5.50. Temperature dependent polarization behavior for PNSZT 2/15/80/20 ceramic
Fig. 5.51. Changes of \{111\} x-ray diffraction line profile of PNSZT 2/15/80/20 ceramic at (a) $E = 0$ (b) $E_{AF} = 3.3$ and (c) $E_{max} = 6.0$ kV/mm bias fields

![Graph showing changes in x-ray diffraction profile](image)

Fig. 5.52. Changes of \{200\} x-ray diffraction line profile of PNSZT 2/15/80/20 ceramic at (a) $E = 0$ (b) $E_{AF} = 3.3$ and (c) $E_{max} = 6.0$ kV/mm applied fields

![Graph showing changes in x-ray diffraction profile](image)
The comparisons of (200) and (002) x-ray diffraction patterns under different applied electric fields are shown in Fig. 5.52. The intensity of the diffraction peak due to the Kα₂ line is approximately 50% of the intensity of the diffraction peak due to the Kα₁ line. At the phase transition field $E_{AF}$ of 3.3 kV/mm, XRD line profile showed a shoulder near $2\theta \approx 44.1^\circ$. This shoulder corresponds to ferroelectric phase. At a field of 6.0 kV/mm only the rhombohedral (200) peak is seen with little or no evidence of the tetragonal (200) diffraction peak.

Based on the in situ XRD study, unit cell parameters of rhombohedral structure are $a_R = 4.103 \text{ Å}$, $\alpha_R = 89.83^\circ$ and $V_R = 69.07 \text{ Å}^3$. Figure 5.53 schematically shows the change of the unit cell size because of the field-induced AFE-FE phase transition. Thus, the transition from antipolar to polar dipole ordering results in a large increase of 0.47% in the unit cell volume. Thus, the 0.45% macroscopic longitudinal strain measured is mainly due to this unit cell expansion.
Fig. 5.53. Schematic showing the change of the unit cell for PNSZT 2/15/80/20 ceramic by field-induced AFE-FE phase transition

5.8.3 Conclusions

The microstructures, dielectric and electromechanical properties of PSZT ceramics were investigated as a function of donor doping content. Maximum dielectric constant was depressed and dielectric peak was broadened with increasing La$^{3+}$ or Nd$^{3+}$ content.

The resistivity was strongly affected by donor doping. Substitution of trivalent ions for Pb$^{2+}$ contributed electrons, and reduced the hole conductivity as a result of electron-hole compensation.

The occurrence of A-site vacancies introduced by La$^{3+}$ or Nd$^{3+}$ doping disrupted the long range FE coupling, and stabilized AFE phase.

From *in situ* XRD study, complete AFE-FE phase transition is observed for PNSZT 2/15/80/20 at an applied field of 6 kV/mm. A large increase in unit cell volume was responsible for the high strain behavior.
6. SUMMARY

A systematic study comprising of processing, measurements of electromechanical and dielectric properties, and in situ x-ray diffraction was conducted in lead strontium zirconate titanate ceramics. This study concentrated on the analysis of electric field-induced antiferroelectric-ferroelectric phase transition as a function of composition and temperature.

Based on structure characterizations and polarization responses, a modified $A_T-F_R$ phase boundary was generated. Increasing ferroelectrically inactive $\text{Sr}^{2+}$ and $\text{Zr}^{4+}$ contents stabilized the antiferroelectric phase, and this resulted in lower polarization and higher switching field.

Temperature dependent polarization and field-induced longitudinal strain were experimentally studied. The dependence of switching field on temperature was theoretically analyzed using modified Clausius-Clapeyron approach. The short range order of the AFE sublattice was found to be less affected by thermal disturbances than the long range order of the FE sublattice.

The longitudinal field-induced strain produced in lead strontium zirconate titanate ceramics was in the range of 0.2-0.5%. Composition close to $A_T-F_R$ phase boundary displayed high strain. The partial phase transition for composition away from the phase boundary reduced the strain value.

The field-induced electromechanical behavior was also investigated as a function of doping level. Donor doping ($\text{La}^{3+}$, $\text{Nd}^{3+}$) increased the stability of AFE phase and diffused the dielectric response. The resistivity and field-induced strain was maximized at 2 atom% doping.
A novel in situ x-ray diffraction technique was developed for direct observation of the unit cell change upon phase transition. The unit cell volume increase was found to be responsible for large field-induced strain associated with the AFE-FE phase transition.
7. RECOMMENDATION FOR FUTURE RESEARCH

Future work is aimed at a deeper understanding of the following issues.

1. Microstructure observation (domain structure, grain size) and their effect on the field-induced AFE-FE phase transition.

2. The characterization of fatigue behavior in La- or Nd- doped AFE ceramics would be beneficial for development of reproducible ceramic actuators.

3. B-site doping has resulted in “ON/OFF” type strain behavior in PZT systems. Hence, the effect of B-site doping on PSZT ceramics should be investigated for potential actuator applications.

Acknowledgments

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