University of Puerto Rico Rio Piedras Campus College of Natural Science Doctoral Program in Chemical Physics

Investigations on rare earth doped lead zirconate titanate for energy storage applications

By

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We hereby recommend that the research work presented by Mohan K. Bhattarai in this thesis entitle "Investigations on rare earth doped lead zirconate titanate for energy storage applications" is accepted for the partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Physics Program.

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ABSTRACT

The thesis presents the studies of pure lead zirconate titanate $PbZr_{0.53}Ti_{0.47}O_3$ (PZT) and lanthanum and scandium co-doped PZT ceramics synthesized by solid-state reaction method and thin films fabricated via pulse laser deposition technique. We synthesized PZT and $(PbZr_{0.53}Ti_{0.47})_{0.90}(La_xSc_{1-x})_{0.10}O_3$ (PL10x) where $0.0 \le x \le 0.8$.

The XRD patterns analyzed by Rietveld refinement indicate that PZT and PL10x ceramics are polycrystalline and exhibit well-defined diffraction peaks of the perovskite phase suggesting tetragonal phase symmetry (P4mm) of crystal structure. These results corroborate the deconvoluted Raman spectra using the phonon function. The presence of E(TO) and A(TO) Raman bands in low-frequency modes and mid-frequency modes confirm the vibration of A-site (Pb/La) cations, and displacement of B-site (Zr/Ti/Sc) cations and O atoms along with c -axis suggest the existence of ferroelectric ordering in compounds. The recorded EDX spectrums of ceramics confirm the presence of constituent elements (Pb, Zr, Ti, La, Sc, and O), along with their respective characteristic x-ray emission lines, and SEM images exhibit a well-defined granular structure with an average grain size ~ 2 μm .

We designed metal ferroelectric metal capacitors of ceramics as Ag/PL10x/Ag for dielectric and ferroelectric measurements. Temperature-dependent dielectric permittivity (ϵ') exhibits the diffuse phase transition (DPT) behavior enhanced on increasing lanthanum contents, which also decreases the ferroelectric phase transition temperature. Analyzing DPT for the highest content of lanthanum

(PL8) by modified Curie-Weiss results $1 \le \gamma \le 2$ supports the peak broadening of material composition and confirms the existence of relaxor properties.

Room temperature polarization-electric field (P-E) loops of Ag/PL10x/Ag ceramic capacitors confirm ferroelectricity. The P-E loops, suggest the normal ferroelectric behavior with enhanced polarization for lower contents of lanthanum. However, the higher content of lanthanum provides the slim loop hysteresis, which is the typical property of relaxor ferroelectric material. These results support the dielectric behavior of capacitors. We calculated the energy storage performance of the PL8 capacitor. It provides higher recoverable energy density (U_{re}) ~ 1162 mJ/cm^3 with an efficiency (η) of ~ 79 %. These obtained results provide that lanthanum and scandium co-doped ceramic capacitors are potential candidates for ferroelectric memory and energy storage applications.

PZT and PL10x thin films were fabricated on top of a buffer layer of LSMO $(La_{0.67}Sr_{0.33}MnO_3)$ on MgO (100) substrate using the PLD technique. The X-ray diffraction peaks show a single-phase perovskite structure of thin films with a preferred (100) orientation that coincides with the MgO and tetragonal phase symmetry (P4mm) corroborating the ceramics sample. Further, we analyzed the peak broadening of XRD peaks by Williamson and Hall's (W–H) method. It suggests that peak broadening occurs on the doping samples, which increases on increasing lanthanum compared to scandium might be due to higher atomic radii of lanthanum compared to scandium. AFM images exhibit surface roughness increases for a higher content of lanthanum thin films due to an increase in peak broadening supporting the crystal size analysis by the W-H method. The analysis of Raman spectra further confirms the structural stability and ferroelectric ordering of thin-film capacitors.

We deposited Pt at the top of grown thin films to design metal ferroelectric metal capacitors as Pt/PZT/LSMO and Pt/PL10x/LSMO for dielectric and ferroelectric measurements. The temperature-dependent ϵ' shows the strong frequency dependency for the PL0, PL6, and PL10x thin film capacitors. The analysis of ferroelectric behavior by Curie-Weiss's law exhibits the degree of deviation from the Curie-Weiss law i.e; ΔT_m on doped thin films. It provides the value of $\Delta T_m \sim 15$ K, 90K, 50K, and 70K for PZT, PL0, PL6, and PL8 respectively due to compositional induced diffuse phase transition behavior. The DPT of PL0, PL6, and PL8 capacitors were further analyzed by a modified Curie-Weiss law. It yields ($1 \leq \gamma \leq 2$) indicating that these thin-film capacitors exhibit incomplete diffuse phase transition (DPT) on those material compositions. The reasonably well-fitted non-linear curve using the Vogel-Fulcher relation further confirms the relaxor behavior of materials.

The polarization-electric field (P-E) loops of thin-film capacitors support ferroelectricity. It shows typical ferroelectric loops with enhanced polarization and reduced coercive field for PL2, and PL4 thin films. However, PL0, PL6, and PL8 capacitors attribute slim loop hysteresis suggesting a relaxor ferroelectric nature. The PL0 and PL6 thin films show a better spontaneous polarization (P_s). We examined the energy storage capacity and efficiency of these thin films using unipolar P-E loops. The superior energy stored performance were achieved on PL0 and PL8 thin film capacitors which yielded $U_{re} = 54.63 J/cm^3$ and $26.4 J/cm^3$ with $\eta \sim 70.22$ % and 66 % respectively.

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ABBREVIATIONS & SYMBOLS

Absolute permittivity = ϵ Atomic force microscopy = AFM Charge-coupled device = CCD Coercive field = E_C Crystalline size = D Curie point = T_C Depolarizing field (E_d) Energy stored density = U_{st} Energy recovered density = U_{re} Efficiency = η Energy dispersive X-ray = EDX Ferroelectrics = FEs Relaxor Ferroelectrics = RFEs Anti Ferroelectrics = AFEs Linear dielectrics = LDs Lattice strain = L_s Lead zirconate titanates = $Pb[Zr_xTi_{1-x}]O_3(0 \le x \le 1)$ or PZTs Lead zirconate titanate = $PbZr_{0.53}Ti_{0.47}O_3$ or PZT $(PbZr_{0.53}Ti_{0.47})_{0.90}(La_xSc_{1-x})_{0.10}O_3 = PL10x$ $La_{0.67}Sr_{0.33}MnO_3 = LSMO$ Loss tangent = $\tan \delta$ Morphotropic phase boundary = MPB

Maximum electric field = E_{max} Maximum polarization = P_m Remnant polarization = P_r Saturated polarization = P_s Perovskite = ABO_3 Polar nano regions = PNRs Polarization-electric field = P-E Potassium dihydrogen phosphate = KDP Pulse laser deposition = PLD Relative permittivity = ϵ' Scanning electron microscopy = SEM Transmission electron microscopy = TEM Vacuum permitivity = ($\epsilon_0 = 8.8542 \times 10^{-12} C^2/Nm^2$) X-Ray Diffraction = XRD

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- 1. M. K. Bhattarai, S. P. Pavunny, and R. S. Katiyar, "Effect of La and Sc co-doping on dielectric and ferroelectric properties of PZT for energy storage capacitors," *J. Appl. Phys.*, vol. 130, no. 3, p. 34103, 2021, doi: 10.1063/5.0053176.
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CHAPTER 1

Introduction

1.1 FERROELECTRICS

Generally, materials that possess nonzero switchable electric polarization without an electric field are known as ferroelectric materials. Ferroelectric polarization can be switched from one state to another state by applying an electric field higher than a threshold value, known as the coercive field (E_C). The term "ferroelectric" was derived from its magnetic analog "ferromagnetic", a phenomenon discovered in magnetic materials that have a spontaneous magnetization in materials such as iron.[1] The nonzero switchable polarization in ferroelectrics only exists below a certain fixed temperature, above which these materials transform into a paraelectric state and cease to have such nonlinear remnant polar behavior. This transformation temperature is commonly known as Curie temperature or Curie point (T_C). This phenomenon was first observed by the well-known theoretical physicist Peter Debye in 1912 during his well-known work on dielectrics, where he hypothesized "a permanent electric dipole moment in a certain class of molecules, even in the absence of an electric field".[2]

About a decade later in 1921, while studying Rochelle salt (sodium potassium tartrate), a white crystalline material with orthorhombic symmetry, experimental observation of ferroelectricity and its analogy with ferromagnetism was done by Joseph Valasek, and later he published the first ferroelectric loop on Rochelle salt.[3] In another decade, in 1932, potassium dihydrogen phosphate (KDP) was the second material found exhibiting ferroelectricity.[4]

In the year 1941, strategic advancement and doping barium into TiO_2 ,

resulted in the discovery of $BaTiO_3$, possessing a dielectric constant above 1000, a value at least 10 times higher than any known dielectric material at that time. Later in 1945, this new material, was also tested ferroelectric which gave the path to a new journey towards the application of ferroelectric materials, ever-expanding perovskite family of isostructural materials, which showed excellent performance for a variety of applications, such as ferroelectricity and other related phenomena.[5]

Thus, ferroelectric materials possess switchable spontaneous polarization below T_C . The spontaneous polarization and its switching phenomena make the ferroelectric material exhibit polarization–electric field (P–E) hysteresis loop as shown in Figure 1.3. Where P_r is called remnant polarization, P_s is the saturated polarization, and E_C is the coercive field, at which the polarization direction can be switched. A most important feature of ferroelectric materials is the presence of domain structure and polarization direction exist in each of the domains, which aligns dipoles in different directions to minimize electrostatic and elastic energy, and domain wall movement and switching produce hysteresis and saturation nonlinearities.[6] As shown in Figure 1.3, in general, the polarization is head to tail, and switching is accompanied by domain wall movement and new domain. Hence, there are basically, two fundamental requirements for a material to exhibit ferroelectric behavior; (i) it should have a spontaneous dipole moment in the absence of an external electric field, and (ii) the permanent dipole moment should be switchable between multiple symmetry equivalent states by the application of the electric field.[7]



Figure 1.1: Classification of piezoelectric materials and their point group

The necessity of having a non-zero spontaneous dipole moment is closely associated with the crystallographic nature of materials which can be possible only if there exists an absence of a center of symmetry. Figure 1.1 illustrates, out of 32 points groups, only 10 can exhibit ferroelectricity.[8] The Venn diagram in Figure 1.2 shows the relationship between various types of ferroelectric, pyroelectric, piezoelectric, and dielectric materials. All crystal structures can be divided into 32 crystal classes where the center of symmetry plays a significant role in their properties. Crystal structures with a center of symmetry have such an arrangement of atoms around a point or center that by the inversion, we can get the same arrangement of atoms in the crystal. Out of 32 crystallographic point groups, 11 exhibit center symmetry, and 21 are non-centrosymmetric. However, one of the 21 groups, has an inversion center, causing it to lose its non-centrosymmetric nature. Thus, 20 non-centrosymmetric point groups have asymmetric properties. All the crystals in these 20 classes are piezoelectric. The application of mechanical stress, in non-centrosymmetric crystal, creates a

displacement of a positive and negative charge, hence creating a local dipole which leads to the possibility of long-range polarization. However, the mechanical stress causes small movement of charge in centrosymmetric that can compensate by the symmetric distribution of charges.[9] Thus the ferroelectric materials are the subclass of piezoelectric materials with a non-centrosymmetric crystal structure.



Figure 1.2: The Venn diagram showing the relationship between various types of dielectric materials

1.2 POLARISATION HYSTERESIS LOOP

Figure 1.3 shows the typical electric polarisation hysteresis (P-E) loop of ferroelectric materials.*P*-*E* loop is a great sign of ferroelectric materials and is worth using the term D-E loop rather than the P-E loop because polarisation is obtained through electric displacement (D) measurement. But approximately electric polarization (P) is nearly equal to D, so either term would be fine to call it, and throughout this, we use P-E for our convenience. For a dielectric material, the presence of the electric field, E make the electron cloud slightly shifted inducing a

local electric dipole moment that is called electric displacement (D) while for ferroelectric material P will dominate D that can be written as

$$D = \epsilon_0 E + P \tag{1.1}$$

Where ϵ_o is the free space permittivity and P depend linearly on E and isotropic material, viz.

$$P = \epsilon_0 \chi_e E \tag{1.2}$$

Where, χ_0 is electric susceptibility of the material. Using Equation 2 in 1, we get

$$D = \epsilon_0 (1 + \chi_e) E = \epsilon E \tag{1.3}$$

Where, the permitivity

$$\epsilon = \epsilon_0 \epsilon' \tag{1.4}$$

and relative permitivity

$$\epsilon' = 1 + \chi_e \tag{1.5}$$



Figure 1.3: Typical electric polarisation hysteresis (P-E) loop for ferroelectric

1.2.1 Ferroelectric Domain Wall

In a ferroelectric material, the spontaneous polarization P_S will produce a surface charge on the top and bottom that causes a depolarizing field (E_d) whose direction is opposite to P_S . It leads to an increase in free energy, therefore the system minimizes the energy by annihilating the E_d , which is due to the formation of domains. Domains are regions with the same polarization directions. The spontaneous polarization in different domains possesses different directions resulting in net domain zero and E_d . Neighboring domains are separated by boundaries called domain walls. Depending on the angles between polarizations in neighboring domains, there exist 90⁰- 180⁰ domain walls.[10] Figure 1.4 (a & b) gives a schematic illustration of the 90⁰ and 180⁰ domain walls.



Figure 1.4: Schematic illustration of the 90^0 and 180^0 domain walls

1.3 DIELECTRIC POLARISATION

When an electric field is applied to a capacitor, the dielectric material (or electric insulator) becomes polarized, such that the negative charges in the material move toward the positive electrode and the positive charges shift toward the negative electrode. Since charges can not freely move in an insulator, the polarization effect that opposes the applied field draws charges onto the electrodes, resulting in storing energy in the capacitor.[11] The ability to store energy in an applied electric field is called dielectric constant or relative permittivity (ϵ'). The degree of polarization P is related to ϵ' and the electric field strength (E) as follows:

$$P = \epsilon_0 (\epsilon' - 1)E \tag{1.6}$$

Where; $\epsilon_0 (= 8.8542 \times 10^{-12} C^2 / Nm^2)$ is a physical constant known as the permitivity of vacuum or free space. ϵ' can be expressed as $\epsilon' = \epsilon / \epsilon_0$. Higher polarization ability can store more energy, as the energy stored density (U_{st}) of the capacitor is related as[12]

$$U_{st} = \int E dp \tag{1.7}$$

The total polarization of dielectric material (P_t) is the sum of four sources of charge displacement or polarization i.e; electronic polarization (Pe), ionic polarization (Pi), orientation polarization (Pd), and space charge polarization (Ps).

$$P_t = P_e + P_i + P_d + P_s \tag{1.8}$$

The Figure 1.5 shows the schematic diagram of dielectric polarization in the material. Different polarization mechanism occurs within the material which results in the frequency dependence of the ϵ' and dielectric loss.[13] The figure 1.6 exhibits the dielectric polarization and frequency response of various polarization.

1.3.1 Electronic polarization

Electronic polarization takes place due to the displacement of positive charge and negative charge in the dielectric material by the application of an external electric field. Figure- demonstrates the charge distribution of an atom in absence of an electric field and the presence of an external electrical field. This process occurred throughout the material and as a whole material is polarised. The nucleus of the atom and the center of its electron cloud shift away from each other, creating a tiny dipole with a very small polarization effect, contributing a small dielectric constant compared with other polarization. It responds to higher frequencies $>10^{13}$ Hz

1.3.2 Atomic or Ionic polarization

Ionic polarization occurred only in those dielectric materials in which atoms contain ionic bonds.[14] It results in the shifting of positive and negative ions and forms a dipole moment. It usually occurs in solid materials, example; NaCl. It responds to frequencies range $(10^{10} - 10^{13})$ Hz and contributes higher permittivity than electronic polarization.

1.3.3 Orientational polarization

Dipole or orientation polarization occurs due to re-alignment of the permanent dipole moments within the materials.[13] This type of polarization exhibits even in the absence of an electric field but due to random orientation, the net effect of polarization becomes zero. When an electric field is applied externally, the molecules with permanent dipole moment orient themselves according to the direction of the applied electric field resulting in net polarization.[14] Such type of polarization responds in the frequencies ranges ($10^6 - 10^{10}$)Hz and contributes a larger dielectric constant compared to electronic and ionic polarization.

1.3.4 Interface or Space charge polarization

Interface polarization occurs from the limited displacement of free charges and their accumulation at the interfacial area. It occurs in heterogeneous materials and low frequencies range ($< 10^{6}$ Hz). When the electric field is applied grain boundary generally traps charges moving under the applied electric field leading to a dipole



in the interface producing a massive contribution of the dielectric constant.[15]

Figure 1.5: Dielectric polarization in ferroelectric materials



Figure 1.6: Frequency response of various polarization

1.4 FERROELECTRIC MATERIALS

1.4.1 Ferroelectric perovskite

For several decades, the search for the novel smart material is an extremely active field of research, and to this purpose, ferroelectric is an extensively studied field of research. Consequently, many materials showing different properties can be found within one structural family (perovskite, spinel, etc.). The Perovskite materials with ABO_3 structure have been extensively studied considered for a wide range of piezoelectric and ferroelectric device applications such as transducers, actuators, sensors, hydrophones, electro-optical modulators due to superior performance and greater flexibility of design.[16] The term "perovskite" has been derived from the name of the naturally occurring mineral $CaTiO_3$, the first known isostructural compound named after the noted Russian mineralogist L. A. Pervoski.[17] The term "perovskite" was originally used for ABO_3 type compounds with the cubic crystal structure (space group Pm3m), which are not ferroelectric. However, a small distortion from cubic symmetry may result in ferroelectricity in those materials known as ferroelectric perovskite. The ferroelectric perovskites are represented by ABO₃, where both A and B positions are occupied by metal cations, with A having a larger ionic size than B.[18] A typical perovskite structure is illustrated in Figure 1.7. The A-site cations occupy the eight corners of the cell, whereas the B-site ones are positioned at the center of the cell. The two cations have 12-fold and 6-fold coordination respectively. The oxygen anions occupy the six "face-centered" positions, forming an octahedron around the B-site cation.[3] Some of the commonly studied perovskite materials are barium titanate $(BaTiO_3)$, lead titanate $(PbTiO_3)$, strontium titanate

 $(SrTiO_3)$, lead zirconate titanate $(PbZrTiO_3)$, barium zirconate titanate $(BaZrTiO_3)$, strontium barium titanate $(SrBaTiO_3)$, potassium niobate $(KNbO_3)$, etc.



Figure 1.7: A typical perovskite *ABO*₃ structure

1.4.2 Lead Zirconate Titanate

Lead zirconate titanate $Pb[Zr_xTi_{1-x}]O_3(0 \le x \le 1)$ or PZTs, which is a solid solution of lead zirconate $(PbZrO_3)$ and lead titanate $(PbTiO_3)$, is one of the most important members in the ferroelectric perovskite family due to its exceptional ferroelectric and piezoelectric properties.[18] PZT has general formula is ABO_3 ; where A is a divalent cation (Pb^{2+}) occupies at corners of the cube, B is a tetravalent cation $(Zr^{4+}orTi^{4+})$ occupies at a body-centered position and O is divalent anions at the face-centered position of cubic structure. The ionic radii
Pb^{2+} (1.29 Å) and O^{2-} (1.42 Å) make a face-centered cubic array having lattice parameter ~ 4 Å.[18] When an external electric field is applied to PZT, the Zr^{4+} or/and Ti^{4+} ions shifts toward up or down along the direction of field associated.[19] A wide variety of cations can be substituted in the PZT satisfying the Goldschmidt tolerance factor (t).[20]

$$t = (R_A + R_0) / \sqrt{2(R_B + R_0)}$$
(1.9)

Where; R_A = Radius of larger cation A (Pb²⁺)

 R_B = Radius of smaller cation A (Zr⁴⁺ or Ti⁴⁺)

 R_0 = Radius of anion (O²⁻)

Depending upon the value of t, the structure can be listed as follows.

t = 0.95 to 1 for cubic perovskite structure

t < 0.95 for non ferroelectric

t > 1 for ferroelectric

To satisfy Equation 1.9, dopant ions occupy a specific site. Thus as a thumb rule cations having larger ionic radii replace the A-site, whereas cations having smaller ions occupy the B site. Some dopants with intermediate ionic radii can be incorporated on either site, called atmospheric dopants.[21]

1.4.3 Doping Effect in PZTs

The crystal structure, dielectric, and other related physical properties, such as Curie temperature, electrical conductivity, and ferroelectric behavior of PZT can be tuned by doping different dopants in A or/and B sites.[22] Doping is an effective way to improve the material performance to use in different applications. Basically, there are three types of dopants; (i) donor dopants (ii) acceptor dopants (iii) isovalent dopants.[18] Donar dopants which are higher valance cations such as A-site or B-site donor (substitute with chemical valences higher than the original A/B site cations) such as La^{3+} , Nd^{3+} , Sb^{3+} , etc. for A-site and Nb^{5+} , Ta^{5+} etc. for B-site induce cation vacancy and facilitate easy domain wall motion during polling resulting soft PZT. Donor doping does not completely suppress the formation of oxygen vacancies; rather, it concentrates them in the grain boundary region.[18] Higher permittivity, high remnant polarization, are expected by donor doping in PZT. The donar doped Nb results in a significant increase in dielectric constant (ϵ') and piezoelectric charge coefficient (d_{33}) of the PZT ceramics at morphotropic phase boundary (MPB).[23]

A-site or B-site acceptor (substitute with chemical valences lower than the original A/B site cations) such as Na^+ , K^+ , etc. for A-site and Mg^{2+} , Fe^{3+} , Sc^{3+} etc. for B-site enhances oxygen vacancy and make domain wall motion difficult resulting hard PZT. Lower dielectric loss, increase in mechanical quality factors, enhanced endurance, high coercivity are expected by acceptor doping in PZT. The fatigue behavior of PZT thin films was improved by acceptor dopants (Na, Mg, Fe).[24] Isovalent dopants are of similar valance and ionic radii of the replaced cations such as Ba^{2+} , Sr^{2+} replace Pb^{2+} and Sr^{4+} replace Zr^{4+}/Ti^{4+} .

1.4.4 PZT Phase diagram and concept of morphotropic phase boundary

The Figure 1.8 exhibits the phase diagram of PZTs, the increase in substitution of Ti by Zr reduces the tetragonality of a compound. When the composition of Zr/Ti ration \sim 1, PZTs are considered as morphotropic phase boundary (MPB) as shown in Figure 1.8. This composition has special interest due to its remarkable dielectric, piezoelectric, electrochemical, and ferroelectric properties which make

them verv attractive for numerous electronic applications.[25],[26] $PbZr_{0.53}Ti_{0.47}O_3$ (PZT), and $PbZr_{0.52}Ti_{0.48}O_3$ are the most extensively studied MPB composition and enhanced performance has reported. Recently Hemeda et.al have reported an enhanced mass attenuation coefficient of nanocrystalline $PbZr_{0.52}Ti_{0.48}O_3$ can be suitable for gamma-ray shielding.[27] The lattice parameter of $PbZr_{0.52}Ti_{0.48}O_3$ by Riedvelt method was calculated a = 4.044 Å and c = 4.138 Å.[28] However co-existence of tetragonal, rhombohedral, and monoclinic phases was also reported by Ragini et.al.[29][28] Several studies suggested the dominance of tetragonal structure for La^{3+} doped[23] and Sr^{2+} [30] in PZT towards the MPB region. It could be due to the smaller ionic radius of La^{3+} than that of Pb^{2+} which induces lattice distortion and shrinkage in volume accompanied by a reduction in the a-axis and c-axis.[31],[32],[33]



Figure 1.8: Morphotropic Phase Boundary in lead zirconate titanate

1.5 RELAXOR FERROELECTRIC AND DIFFUSE PHASE TRANSITION

1.5.1 Definition

Relaxor ferroelectric (RFEs) are the ferroelectric with diffuse phase transition (DPT).[34] The meaning of relaxor is delay dielectric response at high frequency. RFEs have received the attention of the scientific community due to their unique dielectric, piezoelectric and ferroelectric properties. Some of the distinguishing features are as follows:

(i) A phase transition occurs in a wide temperature range with its diffused dielectric constant maximum at temperature (T_m) is known as a diffuse phase transition.

(ii) The temperature T_m corresponds to maximum dielectric permittivity exhibits a strong frequency-dependence such that its magnitude decreases with increasing frequency.

(iii) Remnant polarization, P_r decreases gradually as temperature increases. Even when the temperature is higher than Tm, there is still ferroelectricity because of the existence of the so-called nano-polar region (PNR).

(iv) The Curie-Weiss law doesn't follow the temperature-dependent dielectric permittivity near Tm. However, it obeys the Curie-Weiss law above Tc for normal ferroelectric. Here T_C is Curie temperature for normal ferroelectrics.

(v) There exist polar nano regions (PNRs) above T_m , which is absent in normal ferroelectrics.

(vi) It exhibits a slim ferroelectric hysteresis loop due to the presence of PNRs. This contrasting behavior of relaxor ferroelectric with normal ferroelectrics is shown in Figure.

1.5.2 Polar Nano Region

The concept of PNRs in REFs is quite interesting to understand its peculiar physical properties. In ferroelectric, the large-size domains with specific dipole moments are randomly distributed throughout the material. When the electric field is applied the domains are aligned in the direction of an associated field, which leads to the formation of macroscopic polarization.[35] The polarization is further enhanced with the electric field and reached the maximum polarization (P_m) . Usually, the normal ferroelectric exhibits large values of characteristic parameters (P_s , P_r , E_c , and hysteresis loss). However, it is interestingly observed that the ions (cations) in parent compounds replaced by the small number of foreign ions (in terms of different ionic charge and radius) lead to break the long-range ferroelectric polar order domains and, converted into a large number of polar islands which are known as polar PNRs.[36] In the present context, the fundamental factor related to the formation of PNRs have been related to the appearance of intrinsic inhomogeneity in the material due to the compositional fluctuation at the crystallographic sites and structural modification of the unit cell.[34] It is observed that the ferroelectric hysteresis loop becomes slim (having low hysteresis loss) in nature with the increase of the percentage of nanodomains. It occurs due to the reduction of correlation length between order parameters (dipole moments).[37]

The formation of PNRs is associated with the compositional fluctuation at the lattice sites of the crystal structure. The randomness in A-site and B-site of ABO_3 perovskite depends upon the ionic sizes, the charge of cations, and distribution of cations in the sublattice, etc. Thus, the short-range order (SRO) and long-range order (LRO) of domain distribution are created.[37] SRO can be represented by the

continuous order distribution of cations on the neighboring sites where, the size of the domain order range from 20 to 800 Å in diameter, whereas LRO is extended above 1000 Å.[38] Hence, the diffuse phase transition behavior is the characteristic feature of a disordered system in which the random lattice disorder-induced the dipole impurities and defects at the crystal sites. In normal FEs, correlation length (r_c) is considered up to the length in which dipole entities are correlated with each other.[34] However, r_c in RFEs significantly reduced, which forms the polar nano regions by frustrating the long-range ordering in FEs similar to the dipolar glasslike behavior.

1.6 POWER AND ENERGY DENSITY

The capacitors that promptly store and release electrical energy are primary concerns in modern electronics and power devices systems. However, the most available capacitors possess low energy densities compared to commonly used storage devices such as batteries or fuel cells. Capacitors are commonly used in electronic devices to maintain power supply while a battery is being charged. The "Ragone plot" is used for the performance comparison of various energy storing devices, where specific energy density (Wh/kg) vs specific power (W/kg) in logarithmic scale is plotted as shown in Figure 1.9.[39]



Figure 1.9: Ragone plot for various electrical energy storage devices

It provides the available energy of an energy storage device for a constant active power request. Here, we see that battery systems offer advantages where high energy density is essential, but they have relatively low power output. Instead, supercapacitors (capacitors) can deliver very high power so that delivery time is fast but energy storage capacity is very limited. Thus Optimization of high power capacitors with the ability to store high energy is challenging and an enormous field of future technology could provide the way to save energy and address the issue of energy crisis.

1.7 ENERGY DENSITY OF DILECTRIC CAPACITORS

The maximum amount of electrical energy stored per unit volume (U_{st}) in a dielectric capacitor configured in a metal-insulator-metal (MIM) structure is

determined by the relation.

$$U_{st} = CV^2/2 = \epsilon_0 \epsilon' E_{BD}^2/2$$
 (1.10)

Where C is the capacitance, V is applied voltage, and E_{BD} is breakdown electric field strength. ϵ_0 is vacuum permittivity and ϵ' is the relative permittivity of the capacitor. The equation shows that the energy stored performance of the capacitor is directly proportional to the ϵ' and E_{BD} . Theoretically, U_{st} of a capacitor is estimated using the relation;[40]

$$U_{st} = \int_{P_0}^{P_m} EdP : 0 \le E \le E_{max}$$
(1.11)

Where P_m is maximum polarization at the maximum electric field (E_{max}). Similarly, the recoverable energy capacity (U_{re}) per unit volume of the capacitor is released when it discharges from the applied electric field E_{max} to zero.

$$U_{re} = \int_{P_m}^{P_r} EdP : 0 \le E \le E_{max}$$
(1.12)

Where, P_r is the remnant polarization. The higher efficiency of the capacitor is essential for the practical applications of the capacitor, which can be obtained as

$$\eta = \frac{U_{re}}{U_{st}} \times 100\% \tag{1.13}$$

For dielectric materials, the U_{re} and U_{st} can be determined by measuring the green shaded area of the P-E loop as shown in Figure 1.10. The Figure 1.10 shows the schematic diagram of the P-E behavior of linear dielectrics (LDs), ferroelectrics

(FEs), relaxor ferroelectric (RFEs), and antiferroelectrics (AFEs).



Figure 1.10: Schematic diagram of the P-E behavior of linear dielectrics (LDs), ferroelectrics (FEs), relaxor ferroelectric (RFEs), and antiferroelectrics (AFEs)

From the hysteresis of relaxor ferroelectric, we observe that RFEs have a combination of linear and non-linear PE regions. This feature in the first quadrant of the PE loop provides enhanced storage capacity with a rapid discharge rate.

1.8 OBJECTIVES AND MATERIAL SELECTION

Lead-zirconate titanates $Pb(Zr_xTi_{1-x})O_3$ (PZTs) materials have been extensively studied ABO_3 perovskite for many years due to their potential applications in numerous fields such as memory devices[41] high energy storage[42],

piezoelectric devices[43], sensors and actuators[44], and ultrasonic Promising features of PZTs, such as high dielectric transducers[45], etc. permittivity (ϵ') , high spontaneous polarization (P_s) , ultra-high strain (d_{33}) , and high piezoelectric response make its extensive ranges of utilization.[44],[46] The crystal structure, dielectric, and other related physical properties, such as Curie temperature, electrical conductivity, and ferroelectric behavior of PZT can be tuned by doping different dopants in A or/and B sites. A suitable amount of doping is an effective way to improve the material performance to use in different applications.

In PZTs, the Morphotropic phase boundary (MPB) composition has special interest due to its remarkable dielectric, piezoelectric, electrochemical, and ferroelectric properties.[25],[26] We have chosen $PbZr_{0.53}Ti_{0.47}O_3$ (PZT) which is one of the most extensively studied MPB compositions and reported remarkable dielectric and ferroelectric performance.The present work aimed to synthesize lanthanum and scandium co-doped PZT ceramics by solid-state method and thin films by using pulsed laser deposited technique and analyze their structural, dielectric, electrical, and ferroelectric properties.

The cation substitution in favorable sites, either A-site/B-site or both of PZTs, improves domain wall mobility and electronic properties. Several investigations have been reported in La^{3+} doped PZTs system as a very good relaxor material suitable for high-energy storage applications.[47],[48] Hao et. al investigated thin films of $Pb_{0.91}La_{0.09}(Zr_{0.35}Ti_{0.65})O_3$ and reported $U_{re} \sim 28.7 \ J/cm^3$ with $\eta \sim$ 57%.[49] Enhanced $U_{re} \sim 58.4 \ J/cm^3$ and a $\eta \sim 81.2\%$ at high applied field of ~ 3.4 MV/cm in $Pb_{0.90}La_{0.1}(Zr_{0.52}Ti_{0.48})O_3$ thin films were achieved.[50] Role of Sc^{3+} doping on B-site is reported to improve the relaxor behavior in $Pb_{0.78}Ba_{0.22}Sc_{0.5}Ta_{0.5}O_3$ [51], and $PbSc_{0.5}Nb_{(1-x)/2}Ta_{x/2}O_3$ with $0 \le x \le 1$ [52]. In addition, the complex doping in the PZTs system plays a significant role in the charge balance between the A-site, B-site, and oxygen vacancies.[53]

In this project, we investigated the effect of lanthanum and scandium doping on the dielectric and ferroelectric properties of PZT for non-volatile memory and energy storage applications. The La^{3+} and Sc^{3+} co-doping on PZT considering the significant role of mixed doped cations, in the charge balance between A- and B-sites and oxygen vacancy. We analyzed the microstructure, dielectric and ferroelectric properties, of bulk and thin-film capacitors. The dielectric and ferroelectric results presented in the thesis will hopefully contribute to the progress in electronic applications, such as memory, power, and high energy storage devices.

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CHAPTER 2

Synthesis & Characterization Techniques

In this chapter, we focus on the detailed description of sample preparation and characterization of the sample. At first, we show bulk material synthesis and thin-film fabrication. Finally, the sample characterization techniques used in this research are reviewed.

2.1 SYNTHESIS TECHNIQUE

2.1.1 Solid State Reaction Method

Synthesis of high-quality material is essential for device applications, thus several factors are needed to be considered such as purity of raw materials, degree of mixing, the temperature of calcination and/or sintering to achieve the best possible materials. The solid-state reaction route is the most widely used technique for bulk synthesis from the mixture of solid materials. Some of the advantages of this method include easy availability of precursors, low cost, and industrial production. This method is generally followed by diffusion, reaction, nucleation, and growth. A higher nucleation rate than the nucleus's growth formation of nano crystallite is expected. In contrast, a lower nucleation rate than the nucleus's growth results in a lump crystal formation.[1] In the solid-state reaction method, the homogeneous mixture of the stoichiometric weighted compound is taken and processed through major steps such as mixing, calcination, grinding, pressing, and sintering.[2]

The required stoichiometry of chemical oxides powdered is weighed out and placed in a low-energy ball mill or high energy ball mill for an optimized period, with stabilized zirconia balls in methanol media for mixing, subsequently dried and finely crushed using mortar and pestle. The finely crushed mixture was put in a closed alumina crucible and kept for calcination in a high-temperature furnace such as Carbolite HTF1700 for a specific period. Calcination refers to the process of heating materials to a high temperature in a controlled environment.[3]

The calcined materials were again crushed then phase composition, particle size, and aggregation of ceramics powdered is examined. The principal objective of this step is; to remove volatile substances and moisture, optimize particle size, the surface area, and create a new phase of the particles. The fine crushed calcined powder mixed with a binding agent such as polyvinyl alcohol is pressed in the form of thick pellets and target at high uniaxial pressure. These pellets and targets were sintered at high temperatures. During the sintering process powder material transform into a dense material via thermal treatment. Mostly this process is performed at slightly higher than calcination temperature. The purpose of this step is to enhance crystal quality and minimize crystal defects.

2.1.2 Pulse Laser Deposition

Pulse laser deposition (PLD) is one of the versatile physical vapor deposition (PVD) techniques to deposit crystalline thin films/nanofilms. It is a commonly used technique for thin-film growth because it allows the fabrication of crystalline film with high epitaxy, smooth, polycrystalline, and complex heterostructures such as superlattice and multilayers, etc. This technique involves mainly three major steps:

(i) Ablation of target materials, (ii) formation of high energy plume, and (iii) growth of thin film on the substrate. During this process, the laser energy is used

to excite the surface of a target which results in electronic excitation, heating, and physical ablation of surface atoms/molecules. Hence the ablated materials are deposited into a suitably placed substrate in the vacuum chamber, consequently growing the thin film of desired thickness. Although the plume retains the stoichiometry of the target, the ablation process is done in the presence of background gas such as oxygen, argon, etc. to avoid material loss. High purity oxygen gas is used while growing oxide thin films. There are several parameters to optimize to get high-quality thin films. Some of the parameters include; laser energy, the distance between target and substrate, growth temperature, base vacuum, oxygen partial pressure, annealing temperature, etc. should be optimized. The schematic diagram of PLD is shown in Figure 2.1.

Advantages of PLD

i) A single chamber of PLD may include many target holders which facilitate for multilayer growth of different materials.

ii) One laser can serve in many vacuum systems.

iii)The energy source is well confined at the target which contributes to the efficiency, flexibility, and control of the processes.

The energy source is outside the chamber which helps to adjust in energy and wavelength of experimental demand

Disadvantages of PLD

i) It is not suitable for large scale production.

ii) Difficult to optimize uniformly grown thin films.

iii) High roughness in films.



Figure 2.1: Schematic showing the basic elements of pulsed laser deposition

2.1.3 Magnetron Sputtering

Sputtering technology has been applied and developed as a method of coating since the 1940s. The sputtering methods can be roughly classified as DC magnetron sputtering, RF magnetron sputtering, and multistation planar magnetron sputtering. DC or direct current magnetron sputtering requires a negative voltage on the sputtering target, so only conductor materials can be sputtered.[4] In this research, we used the sputtering technique to make top electrodes in thin films. Since the metal target has good thermal conductivity, this gives DC magnetron sputtering the advantage of a high deposition rate.

The DC sputtering is a Physical Vapor Deposition (PVD) Coating technique where a target material to be used as the coating is bombarded with ionized gas molecules causing atoms to be "Sputtered" off into the plasma. These vaporized atoms are then deposited when they condense as a thin film on the substrate to be coated. This system is a versatile technique used to grow thin films as well as an electrode in thin films. It is the most basic and inexpensive type of sputtering for PVD metal deposition and electrically conductive target coating materials. Two major advantages of DC as a power source for this process are that it is easy to control and is a low-cost option if you are doing metal deposition for coating.

Figure 2.2 shows the basic configuration of a DC Sputtering coating system as the target material to be used as a coating is placed in a vacuum chamber parallel to the substrate to be coated. The vacuum chamber is evacuated to a base pressure $\sim 10^{-6}$ Torr and then backfilled with a high purity inert process gas usually Argon due to its relative mass and ability to convey kinetic energy upon impact during high energy molecular collisions in the plasma that creates the gas ions that are the primary driving force of sputter thin film deposition. Generally, sputter pressure ranging from 0.5mTorr to 100mTorr is used in associated with the DC power of suitable voltage.



Figure 2.2: DC magnetron sputtering

In this work, we used a Platinum (Pt) target to make the upper electrode in a grown thin film. We used a shadow mask of an area of 100 microns. We created a base vacuum $\sim 10^{-6}$ Torr and Pt was coated at 100 mTorr pressure using high purity Argon gas. We have used optimized applied voltage in the ranges of 10 to 30 V for 5-15 minutes.

2.2 CHARACTERISATION TECHNIQUES

2.2.1 X-Ray Diffraction

X-Ray Diffraction (XRD) is a non-contact and non-destructive powerful technology to identify the phases of materials. It provides structural properties such as crystal size, epitaxy, phase composition, preferred orientation, defect in crystal, etc. In addition, this technique is used to measure the thickness of thin films, and atomic arrangements in amorphous materials and at interfaces. The X-ray intensities can provide quantitative and qualitative information about the atomic arrangements at interfaces. X-rays are a form of electromagnetic radiation of very short wavelength (λ) ranging from 0.10 to 10 nm and photon energies 100 eV to 100 keV.

X-rays are produced within the X-ray machine, also known as an X-ray tube. Common targets used in an X-ray tube are Cu, Mo, and Co which possess $\lambda = 1.54$ Å, 0.8 Å, and 1.79 Å emits energy of 8 keV, 14 keV, and 14.5 keV respectively. X-rays are generated via interactions of the accelerated electrons with electrons of tungsten nuclei within the tube anode.[5] The law explaining the relationship between an x-ray light shooting into and its reflection off from a crystal surface is called Bragg's law.[6] In 1913 Physicist W.H. Bragg and his son W. L. Bragg introduced this principle. It states that when the x-ray beam of λ is incident into a crystal surface, constructive interference will occur when

$$2dsin\theta = n\lambda \tag{2.1}$$

Where θ is the angle of incidence, n is a whole number, and d is the path difference. The schematic diagram of Bragg's law is shown in Fig 2.3.



Figure 2.3: Schamatic diagram of Bragg's law

In this research, we used a Rigaku D/Max Ultima III X-ray diffractometer in Bragg-Brentano (BB) geometry using Cu-K α 1 radiation of λ = 1.5404 Å. XRD patterns of materials (ceramics and thin films) were collected in the range of 2θ = 20^{0} to 80^{0} .

2.2.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM), is a versatile technique widely used in various fields such as nanotechnology, material science, biology, and the life sciences for imaging micro and nanostructure morphology and characterizations of the chemical composition of various materials. It uses the incident beam of electrons scans across the sample surface and interacts with the sample to generate backscattered secondary electrons that are used to create an image of the sample.[7]

This technique is commonly used in material science to illustrate the

microscopic structure and several phases from each other due to its high resolution, and a great facility for microanalysis.[8] It produces signals such as characteristics X-rays, secondary electrons, backscattered electrons (BSE), specimen current, cathodoluminescence, and transmitted electrons. The signal result from the interaction of the electron beam with an atom at the surface of the sample is as shown in the schematic Figure 2.4. It yields a three-dimensional appearance due to a very narrow electron beam. The characteristic X-rays and BSE are used in analytical SEM. When the intensity of the BSE signal strongly coincides with the atomic number of the specimen, BSE provides the distribution of different elements in a sample. Characteristic X-rays are emitted when the electron beam removes an inner shell and releases energy.[9] Those are used to identify the presence of elements in the sample.



Figure 2.4: Illustration of Scanning Electron Microscopy

In this work, microstructure grain growth, and the surface topography of the bulk samples were analyzed using an SEM (JEOL JSM-6480LV) at a magnification of 5000x and 10000x with an applied voltage of 20V

2.2.3 Energy Dispersive X-ray

Energy Dispersive X-ray (EDX) analysis is a standard method for identifying and quantifying elemental compositions. EDX system is generally attached to an electron microscopy instrument such as scanning electron microscopy (SEM) or transmission electron microscopy (TEM).



Figure 2.5: Schamatic diagram of Energy Dispersive X-ray

In the SEM system equipped with EDX, the atoms on the surface are excited by the electron beam, emitting certain wavelengths of X-rays that are characteristic of the atomic structure of the elements. These X-ray emissions are analyzed by an energy-dispersive detector (a solid-state device that discriminates among X-ray energies).[10] Then relevant elements are assigned, yielding the composition of the atoms on the specimen surface. A schematic describing the EDX spectroscopy method is shown in Figure 2.5.[11]

In this research, the EDX system was attached with SEM.

2.2.4 Atomic Force Microscopy

Atomic force microscopy (AFM) is a type of scanning probe microscope, which uses a fine probe to record over a surface rather than the use of a beam of light or electron. AFM is a powerful technique that enables the imaging of thin films and several nanostructures. Since, its invention in 1986, provides great achievements in the development of surface science and opened the field of nanoscience and nanotechnology.[12] AFM is used to measure and localize many different forces, including adhesion strength, magnetic forces, and mechanical properties. An AFM operates in contact mode and tapping mode. In the contact mode, the AFM tip is in continuous contact with the surface. On contrary, in the tapping mode, the AFM cantilever vibrates above the surface of a sample such that the tip is only in intermittent contact with the surface which helps to reduce shear forces due to tip movement. The tapping mode is commonly recommended for AFM imaging. The contact mode is only used for specific applications, such as force curve measurements. In addition to capturing an image, the AFM technique can also be used to manipulate atoms and structures on a variety of surfaces. [13]

AFM consists of a sharp tip that is approximately 10 to 20 nm in diameter, which is attached to a cantilever. AFM tips and cantilevers are micro-fabricated from Si or Si3N4. The tip moves in response to tip–surface interactions, and this movement is measured by focusing a laser beam with a photodiode. During the image acquisition, the interaction between the tip and the surface depends on the

distance between them. The attractive force between tip and surface is weak if their interatomic distance is large. When the tip approaches the surface, the attraction increases until the atoms are so close together that electron clouds start electrostatic repulsion. It signifies that the interaction force becomes zero in a few angstroms.[12]

The images of thin films sample were captured using an AFM (Digital Instruments, Veeco Metrology Group) using Nanoscope V controller.

2.2.5 Raman Spectroscopy

Raman Spectroscopy is a non-destructive optical technique used for studying the chemical structure, phase, crystallinity, and molecular vibration of a material. Raman is a light scattering technique where the incident beam of high-intensity source laser light scatters by a molecule.

Most of the scattered light possesses the same frequency (or color), $f_s = f_0$ as the incident laser light is called "Rayleigh Scatter". Even though Relay scattering has much importance in real life, it does not provide useful information about the material. Where f_0 is the incident frequency and f_s is the frequency of scattered light. However, a small portion of light (typically 0.0000001%) scatter at a different frequency (or colors), $f_s \neq f_0$ depending upon the chemical structure of the material, is called "Raman Scatter". Thus, when the sample is irradiated by an intense laser beam in UV visible region, the strong relay scattering occurs which is elastic scattering has the same frequency (f_0). In this case, the energy of the scattered photon (hf_s) = energy of incident photon (hf_0).

On the other hand, Raman scattering is inelastic scattering where incident photons interact with the molecule in such a way that the scattered photon shifts the frequency to either $f_0 - f_m$ or $f_0 + f_m$ by gaining or losing the energy. Where f_m is a vibrational frequency. Here $(hf_s) \neq ((hf_0))$. Very weak inelastic scattering phenomena "Raman effect" were observed in a remarkable experiment performed by C. V. Raman together with K. S. Krishnan (1928).[14] Raman spectroscopy is based on the Raman effect.

The Raman scattered light having frequency $f_0 - f_m$ is called a stoke and $f_0 + f_m$ is called an anti-stoke line. These two lines are equally displayed from the Raleigh line. The figure 2.6 shows a schematic of the Raleigh scattering, Raman scattering, stoke, and anti-stoke line. According to classical theory, Raman scattering is explained as follows; The electric field strength (E) of the electromagnetic wave changes with time (t) as given by

$$E = E_0 \cos(2\pi f_0 t) \tag{2.2}$$

Where E_0 is vibrational amplitude energy. If a diatomic molecule is irradiated by this light the electrical induced electric moment is given by

$$P = \alpha E \tag{2.3}$$

Here, alpha is the polarizability of the molecules. Thus

$$P = \alpha E_0 \cos(2\pi f_0 t) \tag{2.4}$$

If the molecule is vibrating with the frequency f_m , the nuclear displacement q is given as

$$q = q_0 \cos(2\pi f_m t) \tag{2.5}$$

Where q_o is vibrational amplitude. For a small amplitude of vibration, α is a linear function of q which can be written as

$$\alpha = \alpha_0 + \beta q_0 + \dots + \dots \tag{2.6}$$

Where α_0 is the polarizability at the equilibrium position, and $\beta = (d\alpha/dq)_0$ is the rate of change in α to q evaluated at an equilibrium position. Thus using the above Equations we obtain the following result.

$$\alpha = \alpha_0 E_0 \cos(2\pi f_0 t) + \frac{1}{2} \times \beta q_0 E_0 [\cos(2\pi (f_0 + fm)) + \cos(2\pi (f_0 - fm))] \dots + \dots$$
(2.7)

Where the first term represents an oscillating dipole that radiates light of frequency f_0 (Raleigh scattering) while the second term corresponds to the Raman scattering of frequency $f_0 + fm$ (anti-stoke) and $f_0 - fm$ (stoke). If β is zero, the vibration is not Raman active. Thus the vibration is Raman active if the rate of change of polarizability (α) with vibration is not zero.[14],[15]



Figure 2.6: Showing Rayleigh and Raman scattering process

In this research, the Raman measurements were performed in the

backscattered geometry using a Horiba-JY T64000 spectrometer equipped with a triple grating monochromator and a Coherent Innova 90 Argon ion laser operating at 514.5 nm. The charge-coupled device (CCD), collects and processes the Raman scattered signal through the 50X objective. In this system, we used liquid nitrogen for CCD cooling which is required to make it suitable for high-grade spectroscopy. The temperature-dependent Raman spectra of the sample were recorded by using a Linkam module in a vacuum.

2.2.6 Dielectric Spectroscopy

$$\epsilon' = \frac{\epsilon}{\epsilon_0} \tag{2.8}$$

Where ϵ is an absolute permittivity $\left(\frac{C^2}{N/m^2}\right)$ and ϵ_0 is the permittivity of vacuum $(8.8542 \times 10^{-12} \frac{C^2}{N/m^2})$

In this investigation, we studied planar capacitors with a metal ferroelectric metal (MFM) configuration as shown in Figure 2.7. The parallel surface (top and bottom electrodes) for the pellet were made of the silver paint coat. Thin-film capacitors were made with LSMO (bottom electrode) and platinum (Pt; top electrode). The $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) buffer layer was grown on MgO substrate and Pt was deposited by direct current (dc) magnetron sputtering using a shadow mask. Thus the ferroelectric capacitors engineered in this research act as parallel plate capacitors. The capacitance of parallel plate capacitor is given by equation;

$$C_P = \frac{\epsilon' \epsilon_0 A}{d} \text{ implies that } \epsilon' = \frac{C_P d}{\epsilon_0 A}$$
(2.9)

Where A is an area of a capacitor, d is the distance between two electrodes. The principal interest of characterization in this research includes ϵ' and dielectric loss

factor. The dielectric loss factor or loss tangent $(\tan \delta)$ is defined as the ratio of the imaginary part to a real part of permittivity.

$$\tan \delta = \frac{\epsilon^{"}}{\epsilon'} = \frac{1}{2\pi C_P R_P}$$
(2.10)



Figure 2.7: Schematic illustration of typical ferroelectric capacitors with conducting top and bottom electrodes

In this study, the real part and imaginary part of capacitors were recorded in an HP4294A Impedance Analyzer. These parameters were measured in the frequency ranges of 100 Hz to 1 MHz. The temperature-dependent dielectric measurements were carried out using a programmable temperature control system (MMR Technology Inc. Model K20).

2.2.7 Ferroelectric Measurement

The polarization (P) reversal or switching under an applied electric field (E) is one of the prominent features of the ferroelectric materials, consequently forming a hysteresis loop between P and E. The polarization is related to strain and the polarization charge can be used in a feedback loop to drive the piezoelectric with a nonlinear electric field producing a linear displacement.[16] In this study, the polarization hysteresis loop of ferroelectric capacitors was examined by using a modified Sawyer-tower circuit. Room temperature hysteresis of ceramics capacitors was recorded at 50 Hz frequency under an applied voltage of 5000 V (max, instrumental limitation).

In addition, hysteresis loops of thin-film capacitors were recorded at various voltages up to 100V (instrumental limitation) in frequency ranges of 100 Hz to 1 MHz. Temperature-dependent hysteresis loops of thin-film capacitors were measured using the MMR Technology Inc. Model K20.
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CHAPTER 3

Studies on Rare Earth Doped Lead Zirconate Titanate Ceramics

3.1 INTRODUCTION

Ferroelectrics are polar materials that possess at least two orientations of spontaneous polarization in the absence of an external electric field. The switching of polarization occurs by the application of an external electric field which results in a hysteresis loop; the "sign of ferroelectricity". The magnitude or direction of the spontaneous polarization can be tailored as a function of pressure, temperature, frequency, or applied fields due to the pyroelectric nature of the materials.[1]

The unique features of ferroelectric materials make them suitable for a wide range of applications, many of which are related to electronics or biomedical applications. [2] The ferroelectric materials are commonly used for nonvolatile memories. [3] On the other hand, relaxor ferroelectric materials [4] and antiferroelectric materials [5] are more widely applied in power and energy storage devices. With the rapid progress of electronic devices and power systems, the demand for high power energy storage has grown significantly.[6] The dielectric capacitors with high energy-storage densities have drawn much attention due to multiple uses of electronics applications in wind power generators, lasers, medical defibrillators, etc..[7],[8] Relaxor ferroelectrics are studied materials among the intensively for energy most storage applications.[9],[10] The relaxor ferroelectrics with its slim polarization electric field hysteresis (P-E) loop yields superior charge/discharge energy densities.[11] Relaxor behavior in ferroelectrics can be achieved due to either frustration or

compositionally induced disorder.

Lead zirconate titanate $(PbZr_xTi_{1-x}O_3, PZTs)$ is one of the most important and promising members of the ferroelectric perovskite family ABO_3 due to its exceptional ferroelectric and piezoelectric properties.[12] In recent years PZTs have been investigated broadly.[13]

In PZTs ceramic system, morphotropic phase boundary (MPB) compositions have been extensively studied due to their remarkable dielectric, piezoelectric, electrochemical, and ferroelectric properties which make them very attractive for numerous electronic applications, and novelty could be expected.[14]It is referred to as MPB, when $x \sim 0.5$ and the phase transition occurs from the tetragonal to the rhombohedral ferroelectric phase. [15] However, some dielectric anomaly was also reported in the vicinity of the phase boundary for PZTs. [16] The PZTs with compositions (Zr/Ti : 53/47) and (Zr/Ti : 52/48) exhibits extraordinary high piezoelectric, pyroelectric and ferroelectric response with a ferroelectric (tetragonal) to paraelectric (cubic) phase transition at ~ 660K. [17],[18]

PZTs are well studied ferroelectric materials and systematic substitution of the ions either on A-site (Pb) or B-site (Zr/Ti) or both to innovate new materials and achieve higher performance. It is a promising research path to follow. Theoretical study shows that higher ionic radii dopants, such as La^{3+} , Nd^{3+} , Ta^{5+} , Sm^{3+} (donor dopants) and lower ionic radii such as Sc^{3+} , Yb^{3+} , Fe^{3+} (acceptor dopants) ions can enter A-site and/or B-site, respectively, and can strengthen domain wall mobility which in turn may enhance the electronic properties of PZT.[19],[20] The studies on La^{3+} doped $Pb_{1y}La_y(Zr_xTi_{1-x})O_3$ (PLZTs) compositions are reported as relaxor or antiferroelectric materials that can be promising materials for potential power and energy storage devices application.[21],[22],[7] The La^{3+} substitution in PZTs results in lattice distortion and enhanced tetragonality of the PLZTs unit cell and consequently, enhances spontaneous polarization and endurance (~ 10^8 cycles). [23][24] In addition, report shows that Sc doping improves the relaxor behaviors in several perovskites such as $Pb_{0.78}Ba_{0.22}Sc_{0.5}Ta_{0.5}O_3$ [25] and $PbSc_{0.5}Nb_{(1-x)/2}Ta_{x/2}O_3$ with $0 \le x \le 1$.[26]

However, an insight into the energy storage behaviors, such as the recovered energy density (U_{re}) and the storage energy efficiency (η) of these capacitors is yet to be explored. It is expected that La^{3+} and Sc^{3+} co-doping on lead zirconate titanate, could result in a slim *P*-*E* loop consequently providing superior energy stored capacity with enhanced η . This co-doping may enhance the site disorder thereby possibility of charge frustration is expected to maintain charge neutrality leading to affecting the existing PNRs and governing relaxor behavior.

In this investigation, we present detailed studies on the structural, dielectric, and ferroelectric properties of ceramics compounds $(PbZr_{0.53}Ti_{0.47})_{0.90}(La_xSc_{1-x})_{0.10}O_3$ (PL10x; where x = 0.2, 0.4, 0.6 and 0.8, viz. PL2, PL4, PL6, and PL8 respectively). We studied the effect due to La^{3+} and Sc^{3+} co-doping on PZT in various concentrations for possible ferroelectric memory and energy storage applications.

3.2 EXPERIMENTAL DETAILS

Here we synthesized ceramic powders of $(PbZr_{0.53}Ti_{0.47})_{0.90}(La_xSc_{1-x})_{0.10}O_3$, [viz; PL10x] where x = 0.2, 0.4, 0.6 and 0.8 via a conventional solid-state reaction method.

Powders of high purity oxide materials namely lead (II) oxide (99.9%), zirconium (IV) oxide (99.5%), titanium (IV) oxide (99.8%), lanthanum oxide

(99.9%), and scandium oxide (99.99%) from Alpha Aesar products were used as precursors. An excess of 10 weight % PbO was added to recover the loss of lead during calcination and sintering at high temperatures.[27],[28] The required stoichiometry of chemical oxides powdered was weighed out then placed in a low-energy ball mill for 24 hrs, with stabilized zirconia balls in methanol media for mixing, subsequently dried then put in a closed alumina crucible and kept for calcination in a Carbolite HTF1700 furnace at 1100 °C for 10 hrs.

The calcined powder was again crushed and mixed with binding agent 5 wt% polyvinyl alcohol, and pressed in the form of thick pellets (13 mm diameter) and target (It was prepared to fabricate thin films by PLD) at a uniaxial pressure of $\sim 5 \times 10^4$ Pa and $\sim 8 \times 10^4$ Pa respectively. These pellets and targets were heat-treated at 400 °C for 2 hours to remove organic binders followed by sintering at 1200 °C for 5 hours. During the sintering process powder materials transform into a dense material via thermal treatment. Mostly this process is performed at a slightly higher than calcination temperature. The purpose of this step is to enhance crystal quality and minimize crystal defects. The flow chart of calcination and sintering of the sample is shown in Figure 3.1.



Figure 3.1: Flow chart of calcination (top) and sintering (bottom) of PL10x ceramics

We checked the phase purity and orientation of the powder and pellets at room temperature by a Rigaku Ultima III X-ray diffractometer (XRD) equipped with $CuK\alpha$ radiation ($\lambda = 1.5405$ Å) source configured in Bragg-Brentano ($\theta - 2\theta$) geometry under operating at 40 kV and 44 mA. The surface topography and stoichiometry of the bulk ceramics were analyzed by using scanning electron microscopy (SEM) and energy dispersive X-ray (EDS) excited by an electron beam of energy 20 kV. We spread a high purity silver paste, homogeneously at the top and bottom faces of the pellets, and then dried them at 150°C for 2 hours to make the electrodes. Thus the prepared capacitors Ag/PL10x/Ag were used for dielectric and ferroelectric measurements. The schematic illustration of Ag/PL10x/Ag ferroelectric capacitors is shown in the inset of Figure 3.2. The temperature-dependent dielectric constant (ϵ') and loss tangent ($tan\delta$) were recorded in a wide range of temperatures (100 to 650 K) at various frequencies (100 Hz to 1 MHz) by using a programmable temperature controller (MMR K-20) and an impedance analyzer (HP 4294A). The room temperature polarization versus electric field (P-E hysteresis loop) plot was obtained using a radiant hysteresis tester at 50 Hz.



Figure 3.2: Schematic illustration of typical ferroelectric capacitor with conducting top and bottom silver (Ag) electrodes

3.3 RESULTS AND DISCUSSION

3.3.1 X-Ray Diffraction

The XRD patterns with the Rietveld analysis shown in Figure 3.3 (a-d) indicate that all PL10x ceramics are polycrystalline and exhibit well-defined diffraction peaks of the perovskite phase. Rietveld refinements were executed after examining XRD peaks with the JCPDS file. The corresponding peaks were well matched per JCPDS # 33-0784, which suggested tetragonal symmetry (P4mm) of crystal structure. Various investigations have suggested the dominance of tetragonal structure for La^{3+} doped[29] and Sr^{2+} [30] in PZT towards the MPB

region. It could be due to the smaller ionic radius of La^{3+} than that of Pb^{2+} which induces lattice distortion and shrinkage in volume accompanied by a reduction in the a-axis and c-axis.[30][31][32]We used crystallographic database COD: 1521265 CIF file [33] for a matching phase of the sample, and the Pseudo-Voigt function for profile simulation in FullProf suite software.[34]

The Rietveld refinement data reinforces the tetragonal symmetry (P4mm) of a However, at MPB some investigations for such composition have sample. demonstrated tetragonal, monoclinic, and rhombohedral structures co-exist as well.[35][36] The data of the refinement process such as lattice parameters (a & c), unit cell volume (v), Full width-half maxima (FWHM) parameters (viz. U, V, W), R_{wp} , R_{exp} , and χ^2 are summarized in Table 1. We achieved satisfactory results of R_{wp} , and χ^2 . Although χ^2 for the sample is slightly higher, the well-correlated parameters $R_{wp} > R_{exp}$, the positive and negative value of u, v, w, and the output plot imply the acceptance of our refinement process. Noheda *et.al* have reported tetragonal phase symmetry for $Pb(Zr_{0.52}Ti_{0.48})O_3$ with Rwp ~ 4 % and χ^2 value ~ 11.[17] The detailed satisfactory parameters for Rietveld refinements are well explained by Brian.[37] We obtained a slight variation of lattice parameters in different compositions. The higher lattice parameters and volume of the PL4 sample suggest that beyond a certain amount of lanthanum doped in PZT leads to shrinkage of the volume of an atom.



Figure 3.3: (a-d) Room temperature XRD and Rietveld refinement of various composition

Table 3.1: Refinement structural parameters and agreement factors for PL10x at room temperature with space group P4mm

Sample	PL2	PL4	PL6	PL8
Parameters				
a (Å)	4.0811	4.1098	4.0819	4.0628
c (Å)	4.0917	4.1226	4.0929	4.0727
v (Å ³)	68.1488	69.6326	68.1955	67.2254
U	0.6766	2.5206	0.1662	0.3137
V	-0.0679	-0.6034	-0.2537	-0.1511
W	0.0769	0.1103	0.0446	0.0645
R_{wp}	6.7	7.2	5.6	4.38
R_{exp}	2.9	3.5	2.9	2.4
$\chi^{2}(\%)$	7.1	6.5	3.5	2.3



Figure 3.4: Williamson and Hall (W–H) plot for various composition

The peaks broadening of XRD data were analyzed in terms of the crystalline size and lattice strain because of dislocation. The instrumental broadening (β) was corrected, corresponding to each diffraction peak of the ceramic powder using the relation.[38]

$$\beta^2 = \sqrt{\beta^2(measured) + \beta^2(instrumental)}$$
(3.1)

The average nanocrystalline size (D) of the sample was calculated using the Debye-Scherrer equation

$$D = \frac{K\lambda}{\beta cos\theta} \tag{3.2}$$

Where D is the crystalline size (nm), K is Scherrer constant (= 0.9), λ is the wavelength of the $CuK\alpha$ radiation (=1.5406 Å), and β is the FWHM. The strain-induced (Ls) in the sample due to crystal imperfection and distortion was calculated using the formula;

$$L_S = \frac{\beta}{tan\theta} \tag{3.3}$$

It can be noticed from Equations 3.2 and 3.3, the peak width from crystallite size varies as $1/\cos\theta$, whereas the strain varies as $tan\theta$. We calculated the crystalline size of the polycrystalline sample by applying the modified Scherrer equation as proposed by Williamson and Hall (W–H). This method proposed a method of deconvolution size and strain broadening by looking at the peak width as a function of the diffracting angle 2θ and obtaining the mathematical equation.[38]

$$\beta cos\theta = L_S 4 sin\theta + \frac{K\lambda}{D} \tag{3.4}$$

The plot of $\beta cos\theta$ (radian) along the y-axis and $sin\theta$ (radian) along the x-axis is shown in Figure 3.4 (a-d). We calculated the D from the intercept and obtained 33.98 nm for PL2 which decreases with higher incorporation of La^{3+} concentration suggesting high peak broadening, which could be due to higher atomic radii of lanthanum compared to scandium. The average crystalline size of $PbZr_xTi_{1-x}O_3$ nanoparticles by sol-gel synthesis is 14nm [39], which is slightly smaller than our sample synthesized by the solid-state method. The details of D and Ls are summarized in Table 3.2.

Sample	PL2	PL4	PL6	PL8
Parameters				
$L_S(\%)$	1.63	0.99	0.52	0.41
D (nm)	33.98	32.24	32.62	28.52

Table 3.2: The strain (Ls) and crystalline size (D) for all studied composition

3.3.2 SEM and EDS Measurements

The recorded EDX spectrums of PL10x ceramics are plotted in Figure 3.5 (a-d). It confirms the presence of constituent elements (Pb, Zr, Ti, La, Sc, and O), along with their respective characteristic x-ray emission lines (O: $K\alpha$ 0.525 keV, Zr: $L\alpha$ 2.042 keV, La: $L\alpha$ 4.683 keV, Ti: $K\alpha$ 4.508 keV, Pb: $M\beta$ 5.076 keV, Pb: $L\alpha$ 10.552 keV & Sc: $K\alpha$ 4.089 keV). We compared the average Pb:La:Zr:Ti:Sc atomic ratio from the respective characteristics lines and their stoichiometry observing good agreement. We observed an average grain size ~ 2 µm and a well-defined granular structure with some pores in SEM images of PL10x pellets shown in the Inset of Figure 3.5 (a-d).



Figure 3.5: EDX spectrum of PL10x polycrystalline sample measured at room temperature [Inset: SEM micrograph]

3.3.3 Raman Spectroscopy

In the MPB, the PZT has the coexistence of Rhombohedral, tetragonal, and/ or monoclinic phases.[17],[40] Raman active modes at room temperature for various symmetries across the MPB of PZT are summarized by Deluca et.al. [40] In the rare-earth-doped ceramic specimens of $Pb_{0.92}La_{0.08}(Zr_{0.60}Ti_{0.40})_{0.98}O_3$ and $Pb_{0.92}Pr_{0.08}(Zr_{0.60}Ti_{0.40})_{0.98}O_3$, the prominent bands of Raman spectra were

observed from tetragonal features. [41] We fitted the experimental data with the Voigt function and obtained well-defined deconvolution peaks for all PL10x samples.



Figure 3.6: Room temperature Raman spectra

The Figure depicts the room temperature experimental Raman spectra (black hole) and fitted data (solid red line) (Rayleigh scattering is not shown). The deconvolution peaks obtained suggest that dominance features of mode result from tetragonal. These results corroborate the analysis of X-ray diffraction peaks. In addition, Filho *et.al* suggested the existence of tetragonal symmetry at MPB.[42] At room temperature PZT has a tetragonal crystal structure with a space group or C_{4v}^1 .[43] In the tetragonal symmetry, the optical vibrational modes are given as 3T1u + T2u irreducible representation. Each T1u mode transforms as the A1 +E irreducible representation whereas the T2u mode transforms as an E+B1 mode. The A1 and the E modes are both Raman and infrared active, whereas the B1 mode is Raman active. The long-range electrostatic force lifts the double degeneracy of a transverse mode (TO) and a longitudinal mode (LO). [41]

Thus we have assigned the deconvoluted peaks according to C_{4v}^1 which are closely related to earlier research carried out is shown in Figure 3.6.[42],[44] The distinct features of A1(TO1) mode ~ 140 cm^{-1} for PL10x sample suggest tetragonal symmetry of sample. The peaks slightly shifted towards lower wavenumber on higher lanthanum doping, which could be the strain/stress lattice disorder or bond length distortion.[43] The lowest wave number E1(TO1) and A1(TO1), phonons in the spectral line originate from Pb represents the vibration of Pb mode against Zr/Ti and O. [41] Further, we observed E(TO2), E(TO3), A(TO2), A1(TO3) bands consists of modes displacement of Zr/Ti and O atoms along with c -axis.[45] The presence of those peaks suggests the existence of ferroelectric ordering in doped compounds. We observed E(LO3) and A1(LO3) modes with a possible contribution of the nonpolar oxygen breathing mode above ~ $700cm^{-1}$.[46] It is reported that the A1(TO2) ~ 275 cm^{-1} mode can be used as a sign of the tetragonal phase.[42]

Raman spectra of PL10x polycrystalline sample recorded in the temperature range of 80 to 550 K are presented in Figure 3.7. On the increasing temperature, we observed overlap in spectra and large line widths, making the identification of

individual modes clumsy. It can be caused by the static atomic displacement from their ideal positions because of lattice strain due to the material's thermal history as well as due to compositional substitution by atoms with mismatched cationic radii and valencies.[47] The significant shift in Raman modes for most of the modes was observed with an increase in temperature towards the lower wavenumber, which is either due to the softening of the lattice with the rise of temperature or the introduction of thermal disorder in PL10x due to cations substitutions. All of the identified modes were found to be encountering consistent softening with the temperature rise.

Above 450 K, most of the modes undergo significant damping, and A1 (1TO) and A1 (2TO) soft modes lose their prominence and disappear which can be considered as the smooth order-disorder displacive phase transition wherein the ferroelectric tetragonal to paraelectric cubic symmetry distortion commences before the disappearance of ferroelectric ordering. The presence of prominent A1 (1TO) and A1(2TO) modes in the 80 to 450 K temperature window shows that the tetragonal phase is intact in this range. [42] So the La and Sc substitution results in the significant lowering of Curie temperature T_c of pure PZT which is reported to be ~ 653 K.[48]



Figure 3.7: Raman spectra of PL10x measured at 80-550 K

3.3.4 Dielectric Spectroscopy

The variation in the real part of dielectric permittivity (ϵ') and the loss tangent ($tan\delta$) as a function of frequency ($10^2 - 10^6$)Hz and temperature (100 - 650 K) of various studied ceramics capacitors are shown in Figures 3.8 and 3.9.



Figure 3.8: Frequency-dependent dielectric constant (ϵ') of PL10x ceramic capacitors at different temperatures [Inset: variation of dissipation factor ($tan\delta$) of PL10x with frequency at various temperatures]



Figure 3.9: Reciprocal of temperature-dependent dielectric constant (ϵ') of different compositions at various frequencies

We observed room-temperature dielectric constant (ϵ') ~ 270, 476, 1620 and 992 for x = 0.2, 0.4, 0.6, and 0.8 respectively at a frequency of 10 kHz. It was found that, for compositions with higher amounts of lanthanum concentration, reduced loss tangent ($tan\delta \leq 0.05$) and enhanced ϵ' than that of pure and Nb-doped PZT as reported.[28] This observed enhancement of ϵ' on increasing the concentration of La^{3+} is in fairly good agreement with the report by Laishram *et.al.*[30] The increase in tan δ at higher frequencies is associated with the disordered ferroelectric materials.[49] Similar behavior were observed in $(1 - x)(Na_{0.5}Bi_{0.5})_{0.7}Sr_{0.3}TiO_3 xBi(Mg_{2/3}Nb_{1/3})O_3$ which could be due to the ion jump relaxation at a higher frequency.[50] Prabu *et.al* reported $\epsilon' \sim 150$ at 100 kHz for 5% La^{3+} doped $PbZr_{0.52}Ti_{0.48}O_3$ electroceramics synthesized by sol-gel method in room temperature.[51] Figure 3.9 depicts the reciprocal of temperature-dependent dielectric constant ϵ' of four different compositions studied at various frequencies. We observed a transition from ferroelectric to relaxor ferroelectric phase around 380 K for the PL8, which is slightly lower than a thin-film capacitor of the same composition (~ 450K).[52] While decreasing Lanthanum content, it is shifting towards higher temperature. One can notice that for PL6 the phase transition appears around ~ 625 K at 100 kHz [Figure 3.10] and it appears that for PL2 and PL4 the transition temperature is well above 650 K. Relaxor behavior was not observed at room temperature for PL2, PL4, and PL6 capacitors as evident from their P-E hysteresis loops [Figure 3.12(a)].



Figure 3.10: Dielectric constant of various composition capacitors

3.3.5 Curie-Weiss law

Furthermore, we examined the relaxor properties of the PL8 ceramic capacitor. Figure 3.11 (a) exhibits the temperature-dependent relative permittivity (T vs $1000/\epsilon'$ graph) at 100 kHz frequency for PL8 where the broadening in the ϵ' over the wide range of temperature could be a diffuse phase transition (DPT) in materials.[49] The broadness in such a plot is one of the significant behavior of the disordered ferroelectric materials with diffuse phase transition[53] which can be better explained by the well-known Curie- Weiss Law above T_m . The reciprocal of dielectric permittivity $(1/\epsilon')$ is given by Equation 3.5.[54],[55]

$$\frac{1}{\epsilon'} = \frac{T - T_0}{C}; (T > T_C)$$

$$(3.5)$$

Where T_m represents the corresponding temperature of ϵ' maxima and C is the Curie-Weiss constant. T_0 is the Curie-Weiss temperature (T_C) for second-order phase transition and less than T_m for first-order phase transition. Figure. 3.11(a) illustrates the degree of deviation from the Curie-Weiss law i.e.

$$\Delta T_m = T_{cw} - T_m \tag{3.6}$$

Where T_{CW} represents the temperature from which the ϵ' starts to deviate. $1/\epsilon'$ begins to deviate from the Curie-Weiss law at Burns temperature which is quite higher than the curie temperature.[56]



Figure 3.11: (a) Temperature-dependent reciprocal of dielectric constant $(1000/\epsilon')$ of PL8 ceramics showing T_m and T_{cw} (b) $ln(T-T_m)$ versus $ln(1/\epsilon' - 1/\epsilon_m)$ of PL8 above T_m

We estimated $C = (2.07 \pm 0.06)x10^5$ K from Figure 3.11(a) using a linear fit of Equation 3.5 above T_{CW} , which is in good agreement with $PbZr_{0.53}Ti0.47O_3$.[57] This calculated value is in proper order agreement for other relaxor ferroelectric materials.[58],[59] We obtained the values of T_m and ΔT_m as 380 K, and ~ 160, respectively. The higher value of ΔT_m shows evidence of a composition-induced DPT behavior.[8] Moreover, the DPT can be described by a modified Curie-Weiss law given in Equation 3.7.[60]

$$\frac{1}{\epsilon'} - \frac{1}{\epsilon'_m} = \frac{(T - T_m)^{\gamma}}{C'}; (1 \le \gamma \le 2)$$
(3.7)

Where C' is a Curie-Weiss-like constant and the parameter γ gives DPT character. When $\gamma = 1$, a normal Curie- Weiss law is obtained, and $\gamma = 2$ describes a DPT behavior. The γ value between 1 and 2 represents the incomplete DPT.[61] Figure 3.11(b) shows the plot of $ln(T - T_m)$ versus $ln(1/\epsilon' - 1/\epsilon_m)$ at a frequency of 100 kHz and their theoretical fitting for PL8 capacitor. The black dot lines

represent the experimental value and the red solid line represents linear fitting and obtained $\gamma \sim 1.94 \pm 0.05$ $(1 \le \gamma \le 2)$ indicating a diffuse phase transition behavior in this material composition. This value is in good agreement with our studies on relaxor thin film capacitor $0.90[PbZr_{0.53}Ti_{0.47}]0.10(La_{0.8}Sc_{0.2})O_{3-\delta}$ that had shown $\gamma \sim 1.96.$ [62]

3.3.6 Ferroelectric Measurements

3.3.6.1 Electric field polarization (P-E) loop



Figure 3.12: (a) P-E hysteresis loops of ceramics under $\sim 60 \text{ kV/cm}$ at 50 Hz electrodes (b) corresponding value of Ec, Pr, and Pm

Figure 12(a) exhibits the observed room temperature polarization-electric field (P-E) loops of PL10x at 50 Hz under an applied electric field of ~ 60 kV/cm. The coercive field (E_C) was found to decrease on increasing La^{3+} concentration. The highest (E_C was observed for lower content of La^{3+} ; PL2 & PL4. This is following the report on Sc^{3+} doped $PbZr_{0.53}Ti_{0.47}O_3$ wherein no substantial reduction in E_C was observed.[63] In addition we noticed that on increasing the lanthanum

content the spontaneous polarization (P_S) first increases and maximum for PL6 ($P_S \sim 35\mu C/cm^2$) and again decreases in PL8. Figure 12(b) shows a clear picture of the observed polarization and coercive field of the PL10x capacitors, and their numerical values are given in Table 3.3. We perceived a slim hysteresis loop and higher differences in ($P_s - P_r$) value for PL8 suggesting that, this composition is relaxor in nature, which is in good agreement with the DPT character discussed in the previous section. The charge differences and imbalances disorder the long-range polar region and generate short-range nano polar regions (PNRs) are accountable for the slim hysteresis loop.[64],[65] Theoretical approach to ABO_3 perovskites, such as PZT attributes the relaxor properties to the compositional disorder of dopants into their host lattice.[10]

Table 3.3: The Coercive field (Ec), remnant polarization (Pr) and maximum polarization (Pm) for all studied composition under applied electric field 60 kV/cm

Sample	PL2	PL4	PL6	PL8
Parameters				
$E_c(kV/cm)$	17.12	16.90	10.79	1.16
$P_r(\mu C/cm^2)$	1.87	5.8	20.10	1.07
$P_m(\mu C/cm^2)$	6.04	17.42	34.48	25.98

3.3.6.2 Energy density calculation

The recoverable energy density (U_{re}) of dielectric material is released when it discharges from the associated electric field E_{max} to zero.[50]

$$U_{re} = \int_{P_m}^{P_r} EdP : 0 \le E \le E_{max}$$
(3.8)

Where E is the applied electric field, P is displacement charge density for

ferroelectric materials, P_r is the remnant polarization, and P_m is the maximum polarization under the applied field respectively. Similarly, when an applied electric field increases from zero to E_{max} , the polarization reaches P_m . Thus the electrical energy stored per unit volume (U_{st}) of a capacitor is estimated as;

$$U_{st} = \int_{P_0}^{P_m} EdP : 0 \le E \le E_{max}$$
(3.9)

Since; the larger value of U_{re} the greater energy-storage efficiency (η) can be expected by using Equation 3.10.

$$\eta = \frac{U_{re}}{U_{st}} \times 100\% \tag{3.10}$$

$$Where; U_{st} = U_{re} + U_{Loss} \tag{3.11}$$



Figure 3.13: Schematic diagram of unipolar P-E loop

Figure 3.13 represents the typical unipolar hysteresis (P-E) loop and the energy storage properties of the relaxor ferroelectric capacitors that can be quantified by the numerical integration over this loop. The total area (green + orange) area represents U_{st} while charging, the green area is U_{re} of the capacitor while discharging the capacitor, and the orange area represents the energy lost (U_{loss}).

Figure 3.15 (a) shows the comparative graph of U_{re} , U_{st} , and η under an applied electric field of ~ 60 kV/cm at 50 Hz. We obtained the highest U_{re} for Ag/PL6/Ag capacitor, but it has a low efficiency may not be suitable for practical applications of energy storage capacitors. We achieved a higher efficiency of \sim 79 % with a U_{re} of ~ 1162 mJ/cm^3 under an applied electric field of ~ 97 kV/cm for Ag/PL8/Ag capacitor from the P-E hysteresis loop shown in Figure 3.14. However, Lin *et.al* reported superior energy density $U_{re} = 2510 \ mJ/cm^3$ with $\eta =$ 86.89 % 327 kV/cm under high applied electric field for $(1 - x)BaTiO_3x(K_{0.73}Bi_{0.09}NbO_3)$ ceramics.[66] Figure 3.15 (b) to demonstrate the results of energy storage parameters calculated for PL8. Our results are comparable with reports of Li *et.al* in $(Pb_{0.97}La_{0.02})(Zr_{0.95}Ti_{0.05})O_3$ ceramics.[67] Report on $(Pb_{1x}La_x)Ti_{1x/4}O_3$ with x = 0.28 has estimated U_{re} of ~ 310 mJ/cm^3 with a high η of ~ 91% at 60 kV/cm.[68] In $Pb(Mg_{1/3}Nb_{2/3})O_3$ relaxor ferroelectric ceramic capacitor U_{re} value calculated was ~ 470 mJ/cm^3 with an η of ~ 78 % in an associated electric field of 70 kV/ cm.[69] In a multilayer ceramics capacitor $(SrTiO_3 + Li_2CO_3)/(0.94Bi_{0.54}Na_{0.46}TiO_30.06BaTiO_3)$ (STL/BNBT) the U_{re} ~ 241 mJ/cm³ was achieved under a high applied electric field of 237 kV/cm.[70] Hence, the results of $(PbZr_{0.53}Ti_{0.47})_{0.90}(La_xSc_{1-x})_{0.10}O_3$ have better energy storage performance at lower operating voltage.



Figure 3.14: P-E hysteresis loops of Ag/PL8/Ag ceramics capacitor under various applied electric fields at 50 Hz



Figure 3.15: (a) Comparison of recoverable energy density (Ure) & stored energy density (Ust) under an applied electric field ~ 60 kV/cm for the Ag/PL10x/Ag. [Inset: efficiency] (b) The U_{re} , U_{st} , and (η) as a function of the electric applied field for the Ag/PL8/Ag various electric fields

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CHAPTER 4

Studies on Rare Earth Doped Lead Zirconate Titanate Thin Films

4.1 INTRODUCTION

In recent years, the study of ferroelectric oxides has been revolutionized by the application of thin-film-based studies leading to many advances in the understanding of ferroelectric physics and the realization of novel polar structures and functionalities. It has driven the development of advanced synthesis, characterization, and simulations of epitaxial thin films/nanofilms, and in turn, provided new insights for various potential electronic applications. Today, scientists are actively working to apply these ferroelectric films capacitors in many applications, including novel non-volatile memory, logic architectures, high power, and energy conversion devices.[1] The Dielectrics materials for high energy densities have been mainly focused on linear dielectrics (LDs), ferroelectrics (FEs), Relaxor ferroelectrics (RFEs), and antiferroelectrics (AFs). Among these, FEs with higher remnant polarization are more suitable for non-volatile memories. [2] Instead, RFs and AFs with superior energy storage capacity are more commonly used in high power and energy stored device applications. [3],[4],[5] The slim polarization-electric field (P-E) hysteresis loop of relaxor ferroelectrics yields a more substantial area to store the energy and exhibits high discharge capacity.[6] Relaxors behaviors in a FEs are governed by the evolution of polar nanoregions (PNRs), which originated from the chemical frustration that occurs in a compositionally induced disordered system to maintain charge neutrality.[7]

Lead-zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ (PZTs) thin-film capacitors have been

extensively studied ABO₃ perovskite for many years due to its potential applications in numerous fields such as memory devices [8] high energy storage[9], piezoelectric devices[10], sensors and actuators [11] and ultrasonic transducers [12], etc. Promising features of PZTs, such as high dielectric permittivity (ϵ') , high spontaneous polarization (P_s) , ultra-high strain (d_{33}) , and high piezoelectric response make its extensive ranges of utilization.[11],[13] Moreover, it has compositional specialty (Zr/Ti) and its properties can be tuned with the desired substitution of cations on either A site (Pb) or/and B-site (Zr/Ti). One can tailor these properties of PZT as a FEs thin film capacitor with a higher concentration of Ti [14] however, the AFEs phase was observed for the lower value of Ti \leq 5 [15]. The cation substitution in favorable sites either A-site/B-site or both of PZTs improves domain wall mobility and electronic properties. Several investigations have reported La^{3+} doped PZTs system is a very good relaxor material suitable for high-energy storage applications. [16],[17] Role of Sc^{3+} doping on B-site is reported to improve the relaxor behaviors in $Pb_{0.78}Ba_{0.22}Sc_{0.5}Ta_{0.5}O_3$ [18], and $PbSc_{0.5}Nb_{(1-x)/2}Ta_{x/2}O_3$ with $0 \le x \le 1$ [19]. In addition, the complex doping in the PZTs system plays a significant role in the charge balance between the A-site, B-site, and oxygen vacancies.[20]

In this research, we report a systematic study of La^{3+} and Sc^{3+} co-substituted thin films on PZT considering the significant role of mixed doped cations, in the charge balance between A- and B-sites and oxygen vacancy. Here, we expect to improve the understanding of ferroelectric behavior, consequently enhancing the energy storage capacity of thin-film capacitors. We analyzed the microstructure, dielectric and ferroelectric properties of thin films and their suitability in electronic applications such as memory, power, and high energy storage devices.

4.2 EXPERIMENTAL DETAILS

Highly oriented thin films of stoichiometric formula $PbZr_{0.53}Ti_{0.47}O_3$ (PZT) and $(PbZr_{0.53}Ti_{0.47})_{0.90}(La_xSc_{1-x})_{0.10}O_3$ where; x= 0, 0.2, 0.4, 0.6 and 0.8 denoted as [abbr. PL10x] PL0, PL2, PL4, PL6, and PL8 respectively were fabricated by using the pulsed laser deposition (PLD) technique. The KrF excimer laser with λ = 248 nm, f = 10 Hz was used in PLD. First, a buffer layer of $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) thickness ~ 30 nm was deposited on a highly cleaned MgO (100) substrate, and subsequently, PZT or PL10x thin films of thickness ~ 300 nm were grown by the PLD method.[21] For all deposition, ultrahigh pure oxygen was used as a carrier gas. The thickness of the grown thin films was controlled by the total number of shots applied and later verified by using an Ambios Tech XP-200 profilometer. The optimized deposition parameters are summarized in Table 4.1.

Sample	Energy	Shot	Growth	O ₂ growth	Annl.	O_2 Annl.
	of laser	frequency	temp.	pressure	temp	pressure
	(mJ)	(Hz)	(cm)	(mTorr)	(^{0}C)	$\overline{(Torr)}$
LSMO	200	5	600	150	650	300 for 30
						minutes.
PL10x	250	10	650	150	700	300 for 30
						minutes.

Table 4.1: Optimized thin films deposition parameters

Before depositing thin films, the MgO substrate was cleaned with acetone by sonication for 15 minutes followed by sonication with distilled water for 10 minutes and dried up with high-pressure nitrogen gas.

We examined the orientation and phase purity of thin films by x-ray diffraction (XRD; CuK α radiation with wavelength λ = 1.5405Å) at room temperature. The atomic force microscopy (AFM) micrograph of PZT and PL10x

thin films were recorded in contact mode over an area of 3 μm x 3 μm and 25 nm z-scale. For dielectric and ferroelectric measurements, we deposited Pt at the top of thin films (top electrode) by DC sputtering technique (Power = 20 W, helium pressure = 100 mTorr, deposition time = 8 minutes, and base vacuum of $\sim 10^{-6}$ Torr using a metal shadow mask of an area $\sim 10^{-8}m^2$, whereas LSMO acts as a bottom electrode. Then we used a profilometer to find out the exact area of Pt electrodes and obtained an average area $\sim 1.5 \times 10^{-8} m^2$ which was used for all the calculations of dielectric and ferroelectric parameters. Thus, PZT and PL10x are considered as LSMO/(PZT)PL10x/Pt capacitors throughout this thesis in dielectric and ferroelectric chapters. The impedance analyzer (Model: HP4294A) and MMR Technologies K-20 programmable temperature controller (K-20) were used to record frequency-dependent capacitance (Cp) and loss tangent (dissipation factor) in a wide range of temperatures 100-650 K at frequencies ranges 100 Hz - 1 MHz. The room temperature ferroelectric hysteresis curves (P-E loops) were obtained using a Sawyer Tower test configuration of the Radiant technology (Model: RT 6000 HVA-4000 V) and MMR K-20 instrument.

4.3 RESULTS AND DISCUSSION

4.3.1 X-Ray diffraction

Figure 4.1 exhibits the room temperature XRD patterns of highly oriented PZT and PL10x thin films grown on MgO (100) substrates by using the PLD technique. We observed a single-phase perovskite structure of thin films with preferred (100) coincide with MgO (100) orientation. We noticed diffraction peaks for PZT film at $2\theta \sim 21.76$, 44.36, and 68.82 correspond to (100), (200), and (300) planes respectively. It seems a slight distortion in doped (lanthanum and scandium)

films i.e; PL10x. As per the XRD patterns, these films are highly oriented along the (100) plane with a large amount of tetragonality (JCPDS files 33-0784). Various studies have demonstrated the dominance of tetragonal structure for such PZTs systems with La^{3+} doping.[22], [23]



Figure 4.1: Room temperature XRD of PZT and PL10x thin films

The Reitveld refinement of XRD data of bulk materials $(PbZr_{0.53}Ti_{0.47})_{0.90}(La_xSc_{1-x})_{0.10}O_3$ [24] were obtained tetragonal symmetry which followed by a report of Noheda *et.al* for $Pb(Zr_{0.52}Ti_{0.48})O_3$ [25]. However, Kumar

et.al reported in PZTs over the morphotropic phase boundary (MPB) region the tetragonal and rhombohedral phases with space group P4mm and R3c coexist at room temperature.[26]

The XRD data were further analyzed to observe the peak broadening in terms of the crystalline size and lattice strain due to dislocation. The instrumental broadening (β) was corrected, corresponding to each diffraction peak of thin films using the relation. [27]

$$\beta^2 = \sqrt{\beta^2(measured) + \beta^2(instrumental)}$$
(4.1)

The average nanocrystalline size of the PZT and PL10x thin films was calculated using the Debye-Scherrer equation

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{4.2}$$

where D = crystalline size (nm), K = Scherrer constant (0.9), and λ = wavelength of the Cu K α radiation (1.5406 Å), and β is the peak width at half-maximum intensity. The strain-induced (Ls) in thin films due to crystal imperfection and distortion was calculated using the formula:

$$L_S = \frac{\beta}{tan\theta} \tag{4.3}$$

From these Equations 4.2 and 4.3, it is clear that the peak width from crystallite size varies as $1/\cos\theta$, whereas the strain varies as $tan\theta$. Williamson and Hall (W–H) proposed a method of deconvoluting size and strain broadening by considering the peak width as a function of the diffracting angle 2θ and obtaining

the mathematical equation.[28]

$$\beta = L_S 4 tan\theta + \frac{K\lambda}{D} \tag{4.4}$$

which is rearranged as,

$$\beta cos\theta = L_S 4 sin\theta + \frac{K\lambda}{D} \tag{4.5}$$

The lattice planes corresponding to peaks (1 0 0), (2 0 0), (3 0 0) for the respective thin films were deconvoluted with the Gaussian model to calculate $\beta \& \theta$. The linear fitting of $\beta cos\theta$ (radian) along the y-axis and $sin\theta$ (radian) along the x-axis is shown in Figure 4.2. We calculated the D from the y-intercept and obtained 35.28 nm for the PZT sample consequently decreasing on doped ($La^{3+}\&Sc^{3+}$) PZT thin films. In addition, the highest incorporation of lanthanum (PL8) exhibits the lowest crystal size (22.39 nm). It suggests that peak broadening occurs on the doping samples and the highest peak broadening observed for PL8, might be due to higher atomic radii of lanthanum compared to scandium. It is reported that D ~ 30 nm for ~ 300 nm thin films of $(Pb_{0.91}La_{0.09})(Zr_{0.65}Ti_{0.35})_{0.977}O_3$ compound.[29] The calculated parameters D and L_S for all studied compositions are presented in Table 2.



Figure 4.2: Williamson and Hall (W-H) plot

Table 4.2: Linear fit of Equation	n 4.5 and	d parameters	D, Ls and	R^2 for
PZT and PL10x thin films comp	position			

Parameters	y = mx + C	R^2	D	L_S
			(nm)	(%)
PZT	$0.0164 \pm 0.0048 + 0.0039 \pm 0.0019$	0.8364	35.28	1.64
PL0	$0.0126 \pm 0.0016 + 0.0043 \pm 0.0065$	0.9683	32.24	1.63
PL2	$0.0140 \pm 0.0031 + 0.0050 \pm 0.0012$	0.9064	27.73	1.40
PL4	$0.0124 \pm 0.0006 + 0.0051 \pm 0.0002$	0.9935	27.18	1.24
PL6	$0.0087 \pm 0.0020 + 0.0051 \pm 0.0008$	0.8982	27.18	0.87
PL8	$0.0062 \pm 0.0029 + 0.0060 \pm 0.0011$	0.6328	22.39	0.62

4.3.2 AFM Measurements

Figure 4.3 shows AFM micrographs of PZT and PL10x thin films. We observed smooth surface topography with an average roughness (R_a) of ~ 2.10, 2.13, 2.04, 4.53, 4.66, and 9.03 nm for PZT, PL0, PL2, PL4, PL6, and PL8 respectively. We noticed thin film without doping i.e., PZT and low doping lanthanum acquire low (R_a) that increased on higher lanthanum doping yielding roughness of 9.03 nm for PL8 thin film, and it might be due to the higher ionic radius of lanthanum (1.061 Å) than scandium (0.745 Å). These results are corroborated with observed XRD peak broadening due to La^{3+} and Sc^{3+} in PZT thin films. Additionally, higher incorporation of La^{3+} concentration resulted in higher roughness as evident from AFM images. A decrease in crystal size causes higher peak broadening which consequently increases the surface roughness of thin films.[30][29] The insets in Figure 4.3 shows 3D images of respective thin films.



Figure 4.3: AFM micrograph of PZT and PL10x thin films [inset: 3D image of respective thin films]

4.3.3 Raman Spectroscopy

In the various study, the researchers have reported, the coexistence of Rhombohedral, tetragonal, and/ or monoclinic phases in the MPB.[25],[31] Emerson *et.al* reported tetragonal symmetry in $PbZr_{0.50}Ti_{0.50})O_3$. In addition, the prominent bands of Raman spectra observed from tetragonal phase in $Pb_{0.92}La_{0.08}(Zr_{0.60}Ti_{0.40})_{0.98}O_3$ and $Pb_{0.92}Pr_{0.08}(Zr_{0.60}Ti_{0.40})_{0.98}O_3$.[32] We fitted the experimental data with the Voigt function and obtained well-defined deconvolution peaks for all PZT and PL10x thin films. The Figure 4.4 depicts the

room temperature experimental Raman spectra (black hole) and fitted line (solid red line) (Rayleigh scattering is not shown). The deconvoluted peaks suggested that dominance features of mode result from tetragonal. In our investigation of PL10x bulk materials, as discussed in chapter 3, the deconvolutions of Raman spectra have shown the dominance of tetragonal features. Raman mode of PZT and PL10x thin films corroborate the Rietveld analysis of X-ray diffraction peaks and Raman spectra of bulk compositions.

At room temperature, PZT has a tetragonal crystal structure with a space group or C_{4v}^1 .[33] In the tetragonal symmetry, the optical vibrational modes are given as 3T1u + T2u irreducible representation. Each T1u mode transforms as the A1 + E irreducible representation whereas the T2u mode transforms as an E+B1 mode. The A1 and the E modes are both Raman and infrared active, whereas the B1 mode is Raman active. The long-range electrostatic force lifts the double degeneracy of a transverse mode (TO) and a longitudinal mode (LO).[32] Thus we have assigned the deconvoluted peaks according to C_{4v}^1 which are closely related to earlier research carried out as shown in Figure 4.4.[34],[35]

By analyzing the spectrum using a damped harmonic oscillator model six modes were obtained in the wavenumber range 100-800 cm^{-1} . The observed A1(TO2) and E(TO3) bands suggest the existence of ferroelectric ordering in PZT and PL10x thin films.[36] The presence of prominent A1(TO2) mode is the feature of the tetragonal phase. [34] The broadening of bands could be due to substitutional disorder due to the occupancy of cation sites A by La and B by Zr/Ti/Sc cations. This is expected due to the fluctuation in the bond strength of BO6 octahedra and Pb/La-O bond and hence the observed spectrum is the statistical sum of all those expected possible frequencies.



Figure 4.4: Room teperature Raman spectra of PZT and PL10x thin films

Raman spectra of PZT and PL10x thin films recorded in the temperature range of 80 to 550 K are presented in Figure 4.5. Upon increasing temperature, the spectra exhibit gradual change; softening the bands further, and their intensity reduces. One can notice that above 350 K, the prominent symmetric E(LO2) band disappears completely as shown in Figure 4.5 (a-f). As expected, on increasing temperature, the tetragonal distortion reduces, and the PZT and PL10x systems are expected to transform to the cubic phase. A similar phase transition to the cubic phase has been reported.[31] We observed E(LO3) and A1(LO3) modes with

a possible contribution of the nonpolar oxygen breathing mode above $\sim 700 cm^{-1}$.[37]



Figure 4.5: Teperature dependent Raman spectra of PZT and PL10x thin films

4.3.4 Dielectric Spectroscopy

The frequency dependence of the real component of relative dielectric permittivity (ϵ') at various temperatures from 100 – 650 K for PZT and PL10x thin films are shown in Figure 4.6 (a-f) and their respective dielectric loss tangent ($tan\delta$) in the right y-axis. A strong frequency dispersion with a significant decay in dielectric constant above 10⁵Hz is found, while ϵ' was observed to be stable below the 10⁵ Hz frequency. The present dielectric behavior is similar to that of

ferroelectric thin films such as $PbZr_{0.52}Ti_{0.48}O_3$.[38] and $Pb(Zr_{0.2}Ti_{0.8})_{0.70}Ni_{0.30}O_{3-\delta}$ [39]. The loss tangent in the frequency range 10^2 to 10^4 Hz is almost constant at ≤ 0.10 followed by a drastic increment in its trend was seen above 10^5 Hz. The low dielectric constant and larger loss at a higher frequency is argued to be due to the semiconducting nature of the bottom electrode and its response to the probe frequency. [40] We calculated the value of $\epsilon' \sim 1064$, 4631, 567, 820, 2016, and 556 for PZT, PL0, PL2, PL4, PL6, and PL8 respectively recorded at 1 kHz frequency. Thus, a suitable proportion of La^{3+} and Sc^{3+} can tailor the dielectric properties of the materials.



Figure 4.6: Frequency dependencies of dielectric constant (ϵ') of PZT and PL10x thin films in the temperature ranges (100 – 650 K) and respective loss tangent ($tan\delta$) on right y-axis

A comparison of temperature-dependence of the relative permittivity (*temperature* vs ϵ') measured at a frequency of 1 kHz is shown in Figure 4.7. One can notice that PZT, PL0, PL6, and PL8 have dielectric maxima at $\epsilon_m^i \sim 575$ K, 450

K, 525 K, and 450 K respectively denoted as T_m . It is expected that such a peak for PL2 and PL4 may exist above 650 K, which is out of limiting temperature for measurements. Furthermore, we observed ϵ° as diffused over a wide range of temperatures on PL0, PL6, and PL8. In ferroelectric materials, such type of behavior is pronounced as diffused phase transition (DPT), known as disordered ferroelectric materials. [41],[42]



Figure 4.7: Comparision of temperature-dependent relative permittivity of PZT and PL10x thin films at a frequency of 1 kHz

4.3.4.1 Curie-Weiss law

The ferroelectric behavior with the DPT phenomenon of the dielectric materials can be explained by the Curie-Weiss law above T_m .[43] The relationship for ϵ' with the temperature above T_m is given by Equation 4.6.

$$\frac{1}{\epsilon'} = \frac{T - T_0}{C}; (T > T_C)$$
 (4.6)

Where; C is the Curie-Weiss constant and T_0 is Curie-Weiss temperature T_C for the second-order phase transition and less than T_m for the first-order phase transition. [44]

Figure 4.8 (a-c) shows the reciprocal of ϵ' with temperature for PL0, PL6, and

PL8 thin films. As we fitted using Equation 4.6, we observed T_0 is above T_m for all thin films. We noticed the value of T_0 is reduced for the higher doping on lanthanum. We noticed the degree of deviation from the Curie-Weiss law i.e; ΔT_m on doped thin films.

$$\Delta T_m = T_{cw} - T_m \tag{4.7}$$

The observed value of $\Delta T_m \sim 15$ K, 90K 50K, and 70K for PZT, PL0, PL6, and PL8 respectively due to compositional induced diffuse phase transition behavior.[45] Where T_{cw} represents the temperature from which ϵ' begins to deviate. The higher value of ΔT_m shows evidence of a composition-induced DPT behavior.[46] Some of the parameters calculated are shown in Table 4.3.

Parameters	ϵ_m	$T_m(K)$	C(K)	$T_{CW}(K)$	$\Delta T_m(K)$	γ
Sample						
PZT	1064	575	$(71.25 \pm 0.02) imes 10^5$	590	15	1.19 ± 0.05
PL0	4408	450	$(31.02 \pm 0.08) imes 10^5$	570	120	1.54 ± 0.15
PL6	2016	525	$(34.13 \pm 0.09) \times 10^5$	575	50	1.69 ± 0.05
PL8	556	450	$(2.96 \pm 0.04) \times 10^5$	520	70	1.95 ± 0.16

Table 4.3: Summary of calculated dielectric parameters of PZT, PL0, PL6, and PL8 thin films at 1 kHz

Moreover, the DPT can be described by a modified Curie-Weiss law given in Equation 4.8[47] Where γ provides DPT behavior and C' is Curie-Weiss like constant.

$$\frac{1}{\epsilon'} - \frac{1}{\epsilon'_m} = \frac{(T - T_m)^{\gamma}}{C'}; (1 \le \lambda \le 2)$$
(4.8)

For $\gamma = 1$, a normal Curie-Weiss law is obtained, and $\gamma = 2$ describes a complete diffuse phase transition. The value of γ lies between 1 and 2 representing an

incomplete diffuse phase transition of the materials.[48] The fitting with an Equation 4.5 is shown in Figure 4.7(a-d) inset, at 1 kHz frequency for PZT, PL0, PL6, and PL8 thin films. The black dot lines represent the experimental value and the red solid line represents linear fitting.



Figure 4.8: Curie-Weiss behavior at 1 kHz in thin films(a)PZT (b) PL0 (c) PL6 (d) PL8 [Inset: $ln(T - T_m)$ vs $ln(\frac{1}{\epsilon'} - \frac{1}{\epsilon'_m})$ of respective films]

We achieved $\gamma \sim 1.19 \pm 0.05, 1.54 \pm 0.15, 1.69 \pm 0.05$, and 1.95 ± 0.16 $(1 \leq \gamma \leq 2)$ for PZT, PL0, PL6, and PL8 respectively indicating that PL0, PL6, and PL8 thin films exhibit incomplete diffuse phase transition behavior on those material compositions. Thus, on increasing Lanthanum concentration such behavior is more dominant than undoped or lower doped lanthanum. It also indicates that dopants with $La^{3+} > Sc^{3+}$ increase the DPT of the materials. However, only scandium doped film also shows the dominant relaxor properties.

4.3.4.2 Vogel-Fulcher relation

We observed the DPT of PL0, PL6, and PL8 thin films, one can notice that ϵ'_m decreases and T_m shifts towards higher temperature with increasing frequency. Thus, we analyzed the frequency dependency of T_m by using the Vogel-Fulcher relation given in Equation 4.9.[49]

$$f = f_0 exp[\frac{-Ea}{(T_m - T_{VF})}]$$
(4.9)

Where; f_0 is the pre-exponential factor, K_B is Boltzmann's constant, E_a is the activation energy, and T_{VF} is the characteristic Vogel-Fulcher freezing temperature.[50],[51]

The reasonably well-fitted non-linear curve yielded physically acceptable & values is agreement reports in good with the earlier on $Pb(Zr_{0.53}Ti_{0.47})_{0.60}(Fe_{0.5}Ta_{0.5})_{0.40}O_3$. [52] The fitting parameters are summarized in Table 4.4. Hence, the analysis of the Vogel-Fulcher relation provides further evidence that PL0, PL6, and PL8 thin films are relaxor ferroelectric materials. In addition, we obtained a comparatively slim polarization electric field (P-E) hysteresis loop of those thin films which suggests a suitable proportion of lanthanum and scandium on PZT enhances the spontaneous polarization.

Table 4.4: Fitted parameters of PL0, PL6, and PL8 thin films using Vogel-Fulcher Equation

Parameters	$E_a(eV)$	$T_{VF}(K)$	f_0	R^2
Sample				
PL0	0.037	397	1.538×10^{6}	0.9890
PL6	0.031	477	1.125×10^{6}	0.9735
PL8	0.054	411	1.503×10^{6}	0.9612



Figure 4.9: Vogel-Fulcher relation in the frequency range of 0.1 - 100 kHz of (a) PL0 (b) PL6 and (c) PL8 thin films

4.3.4.3 Cole-Cole Plot

Figure 4.10(a-f) shows the Cole-Cole plots of the temperature-dependent dielectric permittivity of the real (ϵ') and imaginary (ϵ ") part of PZT and PL10x thin films at a frequency range $10^2 - 10^6$ Hz. Some characteristics of ϵ' versus ϵ " response for PZT and PL10x thin films in the wide ranges of temperature (100 – 650) K are the following:

(i) High-temperature variation of the ϵ' radius of the semicircular arc,

(ii) With increasing temperature the permittivity contribution (ϵ' radius, when $\epsilon^{"} = 0$) in the Cole-Cole plot increases, since the intercept of the semicircular arc gives an estimation of sample resistance. This indicates that the resistance increases from PL0 to PL6 and again decreases for PL8. The lanthanum and

scandium ions incorporation could be responsible for the change in its conduction properties.[38],[53] In addition, the decrease in the resistance for PL8 is due to higher doping of Lanthanum compared to scandium may facilitate the domain wall motion.[54]

(iii) the films exhibit multi-dispersive relaxation time on increasing the temperature. Two intercepts between the real axis ϵ' and the circular arc, assign for the static dielectric constant, ϵ_S (largest value ϵ' radius, when $\epsilon'' = 0$) and the optical dielectric constant, ϵ_{∞} (smallest value ϵ' radius when $\epsilon'' = 0$) were observed in all samples which increased on doping compounds, this large increase is due to the variation of the domain wall motion that affects the resistance of the compound. These observed changes in the shape of Cole-Cole plots of dopant films might be due to different strains produced by doping ions that result in a variation in the dielectric and conductivity properties of the materials.[55],[56]



Figure 4.10: Cole-Cole plots of the temperature-dependent dielectric permittivity real part (ϵ') vs imaginary part (ϵ ") for PZT & PL10x thin films

4.3.5 Ferroelectric Measurements

4.3.5.1 Electric field polarization (P-E) loop

Figure 4.11 exhibits a room temperature comparative polarization-electric field (P-E) loops of PZT and PL10x thin films at 2 kHz under the same applied electric field of ~ 0.67 MV/cm. From this comparative graph of PZT and PL10x thin films, we observed typical ferroelectric loops with enhanced polarization and reduced coercive field for PL2, and PL4 thin films. We observed maximum $(P_S \sim 95\mu C/cm^2)$ for PL0 thin film capacitor. Furthermore, PL0, PL6, and PL8 show slim hysteresis loop with high $\Delta P (P_m - P_r)$. These changes in parameters of the hysteresis loop were due to the substitution of scandium and lanthanum in $PbZr_{0.53}Ti_{0.47}O_3$ (PZT). The slim loop hysteresis of PL0, PL6, and PL8 thin films

suggests that these compositions are relaxors in nature, which is in good agreement with the DPT character discussed in the dielectric spectroscopy. The charge differences and imbalances disorder the long-range polar region and generate short-range nano polar regions (PNRs) are accountable for the slim hysteresis loop.[57] The lead zirconate titanate attributes the relaxor properties to the compositional disorder of dopants into their host lattice.[7] We observed slight asymmetries at positive and negative branches in the hysteresis loop of thin films that could be due to different work functions of the top (Pt) and bottom (LSMO) electrodes.[58],[59] In addition to the layer interface effect which acts as pinning centered, defect-related oxygen vacancy and impurities might be also responsible for the observed asymmetry hysteresis loop.[60],[61]



Figure 4.11: Room temperature P-E hysteresis loops of LSMO/PZT/Pt and LSMO/PL10x/Pt thin film capacitors measured under same applied electric field (0.67 MV/cm) at frequency 2 kHz

4.3.5.2 Energy density calculation

The energy storage capacity of relaxor ferroelectric materials is one of the essential parameters for evaluating materials engineering applications. It can be estimated using unipolar P-E loops under the external applied electric field. When an applied electric field increases from zero to E_{max} , the polarization reaches P_m . Thus the electrical energy stored per unit volume (U_{st}) of a relaxor ferroelectric capacitor is estimated as; [62], [63]

$$U_{st} = \int_{P_0}^{P_m} EdP : 0 \le E \le E_{max}$$
(4.10)

Where E is the applied electric field, P is displacement charge density for ferroelectric materials, and P_m is the maximum polarization under the applied field respectively. Similarly the recoverable energy density (U_{re}) of relaxor ferroelectric capacitor is released when it discharges from the associated electric field E_{max} to zero.

$$U_{re} = \int_{P_m}^{P_r} EdP : 0 \le E \le E_{max}$$

$$(4.11)$$

Where, P_r is the remnant polarization. To estimate these values, we analyzed the positive branch of the P-E curve. Based on Equations 4.10 and 4.11, the value of U_{st} and U_{re} can be easily obtained by numerical integration of the area between the polarization axis and the curves of the P-E loops. For the practical application, higher efficiency of the capacitor is required which can be calculated as

$$\eta = \frac{U_{re}}{U_{st}} \times 100\% \tag{4.12}$$

We estimated the energy storage capacity at 300 K for the same applied electric field (0.67 MV/cm) for PZT and PL10x thin films, achieving enhanced $U_{re} U_{st}$, and η in PL10x thin films. The estimated U_{re} value was the greatest ~14 J/cm^3 with η = 62.75 % for PL0. However we obtained better η = 66.67 % with U_{re} = 4.82 J/cm^3 for PL8. The ferroelectric and energy storage parameters of PZT and PL10x thin film capacitors are summarized in Table 4.5. Considering energy storage capacity and efficiency (>50%), we further, analyzed the positive branch of the P-E loop for possible high energy storage applications. Figure 4.12 (a-c) shows the unipolar P-E hysteresis loops of PL0, PL6, and PL8 thin films at 300 K measured under various applied electric fields at 2 kHz of frequency.

Table 4.5: Summary of ferroelectric and energy storage parameters of PZT and PL10x thin films under 20V (0.67 MV/cm) at 2 kHz frequency

Parameters	P_r	P_m	E_C	U_{re}	U_{st}	η (%)
Sample	$(\mu C/cm^2)$	$(\mu C/cm^2)$	(kV/cm)	(J/cm^3)	(J/cm^3)	
PZT	24.4	35.3	187	1.26	14.37	8.76
PL0	20.7	95.3	11	14.10	22.47	62.75
PL2	35.3	65.1	103	6.27	19.39	32.01
PL4	26.4	61.1	50	6.38	15.99	39.89
PL6	9.6	71.9	152	12.24	22.92	53.4
PL8	3.6	19.2	50	3.82	5.73	66.67

We calculated U_{re} , U_{st} , and η for PL0, PL6, and PL8 films from their respective P-E loops. We achieved the highest $U_{re} = 54.63 \ J/cm^3$ with $\eta = 70.22\%$ at applied electric field of 1.82 MV/cm (close to its breakdown electric field (E_{BDS})) and frequency of 2 kHz for PL0 thin films. The obtained values of PL0 are superior than the reports in $Pb_{0.91}La_{0.09}(Zr_{0.35}Ti_{0.65})O_3$ thin films, $U_{re} \sim 28.7 \ J/cm^3$ with $\eta \sim 57\%$.[64] However, they have achieved better $\eta = 83.51\%$ with less $U_{re} = 21.28$ J/cm^3 in $BaZr_{0.20}Ti_{0.80}O_3$ (BZT) thin films. [65] On the other hand, Nguyen et al. had reported $U_{re} \sim 13.7 \ J/cm^3$ and a $\eta \sim 88.2\%$ at 1 MV/cm in $Pb_{0.90}La_{0.1}(Zr_{0.52}Ti_{0.48})O_3$ thin films grown on SRO/STO/Si substrates using pulsed laser deposition.[66]

Material	U_{re}	η (%)	Electric Field	Worked by
Composition	(J/cm^3)		(MV/cm)	
BT/BST	12.24	67	1.65	Ortega et.al
				[6]
Sm-BFBT	152	90	3.5	Pan <i>et.al</i> [67]
PLZT	13.7	88	1	Nguyen et.al
				[66]
PLZT/LNO	22	77	1.96	Tong <i>et.al</i>
				[68]
PLZT	30	78	2.18	Hu et.al [69]
PLZT	28.7	57	2.17	Hao <i>et.al</i> [64]
PLZT	58.4	81.2	3.4	Nguyen
				<i>et.al</i> [70]
BZT	30.4	82	3	Sun <i>et.al</i> [71]
BZT	21.28	83.51	2	Gu et.al[65]
BCZT	8.23		3.8	Pan et.al[72]
PZT/PZO	21.1	63.3	1.7	Zhang
				<i>et.al</i> [73]
PZT/BZT/PZT	39.27	78.71	2	Gu et.al [65]
PL0	54.22	70	1.82	Present work
PL6	51.55	47.38	2.67	Present work
PL8	26.54	65.88	2.67	Present work

 Table 4.6:
 Energy density and efficiency of various thin films composition



Figure 4.12: Room temperature positive branch of P-E hysteresis loops of LSMO/PL0/Pt, LSMO/PL6/Pt, and LSMO/PL8/Pt thin film capacitors in various electric field at frequency 2 kHz



Figure 4.13: U_{re} , U_{st} , & η of PL0, PL6, and PL8 thin film capacitors at 2 kHz under various electric fields

Similarly we achieved $U_{re} = 51.15 \ J/cm^3$ with $\eta = 47.38\%$ and $U_{re} = 26.54$ J/cm^3 with $\eta = 65.88\%$ for PL6 and PL8 thin films respectively under an applied electric field 2.67 MV/cm (Near E_{BDS}) and frequency of 2 kHz. Thus, we achieved enhanced energy storage capacity than the studies on oriented $PbZr_{0.52}Ti_{0.48}O_3$ thin films, that reported $U_{re} \sim 8 J/cm^3$ and $\eta \sim 79.6\%$ under an electric MV/cm. applied field of 0.8 [74] Furthermore, $Pb(Zr_{0.4}Ti_{0.6})O_3/BaZr_{0.2}Ti_{0.8}O_3/Pb(Zr_{0.4}Ti_{0.6})O_3 (PZT/BZT/PZT)$ multilayer thin films have shown better energy storage performance than single-layer thin films.[65] Thus these materials might be useful for making sandwich structures to achieve superior energy density performance. Recently, Zhang *et.al* reported energy stored capacity and breakdown strength can be enhanced using sandwich structure design in thin films.[73] The estimated values of PL0, PL6, and PL8 are shown in Figure 4.13 and summarized in Table 4.7. We observed U_{re} and U_{st} of PL0, PL6, and PL8 thin films are directly proportional to the applied electric field. However, η is slightly decreased with an increase in an electric field for PL6, and PL8 as reported by $0.942(Na_{0.535}K_{0.48}NbO_3)0.058LiNbO_3$ (KNNLN) films.[75] The comparison of our present results with other reported values on several thin films; U_{re} and η values are presented in Table 4.6.

Table 4.7: Summary of calculated values of energy storage parameters of PL0, PL6, and PL8 thin films measured under higher electric fields at 2 kHz frequency

Sample	E(MV/cm)	0.67	1	1.33	1.67	2	2.33	2.67
	$U_{re}(J/cm^3)$	14.1	22.72	32.45	43.13	54.63		
PL0	$U_{st}(J/cm^3)$	22.47	34.73	47.94	62.33	77.8	-	-
	η (%)	62.75	65.42	67.69	69.19	70.22		
	$U_{re}(J/cm^3)$	12.24	17.64	23.1	29.15	36.02	43.21	51.15
PL6	$U_{st}(J/cm^3)$	22.92	34.27	46.73	60.73	75.22	92.12	107.95
	η (%)	53.4	51.48	49.43	47.99	47.88	47.38	47.38
	$U_{re}(J/cm^3)$	3.82	6.67	9.94	13.67	17.84	22.22	26.54
PL8	$U_{st}(J/cm^3)$	5.73	9.98	14.79	20.59	26.52	33.48	40.28
	η (%)	66.67	66.83	67.21	66.73	67.26	66.36	65.88

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CHAPTER 5

Conclusions & Future Works

5.1 CONCLUSIONS

We studied the effects of La^{3+} and Sc^{3+} content on the structural, dielectric, and ferroelectric, properties of $PbZr_{0.53}Ti_{0.47}O_3$ (PZT) and $(PbZr_{0.53}Ti_{0.47})_{0.90}(La_xSc_{1-x})_{0.10}O_3$ (PL10x) where $0 \le x \le 0.8$.

The summary of the results rare earth doped PZT ceramics:

Rietveld's refinement of XRD data indicated that PZT and PL10x ceramics stabilized as tetragonal symmetry (P4mm) of crystal structure which was further supported by the analysis of the vibrational mode of Raman spectra. We applied a modified Scherrer equation to determine the crystal size and peak broadening. The crystal sizes obtained in this study validated the previous studies of PZT compounds. The incorporation of $La^{3+} > Sc^{3+}$ resulted in higher peak broadening, due to higher atomic radii of lanthanum compared to scandium. We obtained the highest dielectric constant ($\epsilon' \sim 1620$) for the PL6 ceramics capacitor with a low coercive field and high remnant polarization that suggested a promising candidate for ferroelectric memory application. The ferroelectric to relaxor ferroelectric phase transition temperature of the material compositions decreased on increasing La^{3+} concentration. The PL8 ceramics capacitor revealed relaxor behavior with diffuse phase transition parameter (γ) ~ 1.94 implying a higher proportion of lanthanum doping in PZT enhanced the relaxor properties.

The relaxor behavior was further confirmed by the slim loop P-E loop of the capacitor. However, other compositions (PL2, PL4, and PL6) showed typical ferroelectrics P-E loops. We achieved $U_{re} \sim 1162 \ J/cm^3$ with η of \sim 79% under an

applied electric field of \sim 97 kV/cm. Thus our results demonstrated that the PL8 ceramic capacitor is a promising candidate for power and energy storage applications.

The summary of the results of the PZT and rare earth doped thin films:

The XRD patterns of PZT and PL10x thin films revealed highly oriented (100) films with the perovskite phase of tetragonal symmetry. We achieved higher (ϵ') for PL0 and PL6 thin films. We noticed that the role of increasing lanthanum contents (decreasing scandium) resulted in the broadening of dielectric permittivity with temperature and ferroelectric phase transition lowered to 450 K. However only scandium doping thin film (PL0) couldn't lower the ferroelectric phase transition. We analyzed the temperature-dependent ϵ' using the modified Curie-Weiss law. The PL0, PL6, and PL8 thin film capacitors exhibited relaxor ferroelectric properties further supported by the Vogel-Fulcher relation. Cole-Cole plot analysis showed the samples exhibited multi-dispersive relaxation time on increasing the temperature. In addition, we observed a large increase in the resistance of the samples, when the amount of the lanthanum dopant was increased because the lanthanum modifies the domain wall motion in the samples.

The P-E hysteresis loops exhibited the role of lanthanum and scandium causing compositional changes in coercive fields. The P-E loops of PZT, PL2, and PL4 exhibited typical ferroelectric features. Instead, PL0, PL6, and PL8 showed a relaxor ferroelectric behavior which corroborated the analysis of dielectric data.

We achieved superior energy storage performance $U_{re} = 54.63 \ J/cm^3$ with $\eta \sim$ 70% for PL0 under 1.82 MV/cm and $U_{re} = 26.54 \ J/cm^3$ with $\eta \sim 66$ % for PL8 thin film capacitors. The study demonstrated the idea that by tuning $La^{3+}\&Sc^{3+}$, the dielectric and ferroelectric functional properties of PZT thin films can be controlled for suitable electronic applications. The higher dielectric constant, breakdown strength, superior performance of U_{re} , and η of PL0 and PL8 thin film capacitors could be better for the potential use of high power and high energy device applications.

5.2 FUTURE WORKS

Thin films prepared in this investigation, have shown that some of the compositions are potential candidates for energy storage application. As a continuity of this project study of heterostructure multilayer thin films is recommended. As reported in several recent investigations, the enhanced discharged energy density (U_{re}) and efficiency (η) of thin-film capacitors could be achieved by designing the multilayered structures of suitable compounds. The multilayer sandwich structure can be engineered and optimized by selecting the compositions which have shown excellent energy stored performance. The designing of multilayer heterostructure thin films of PL0, PL6, and PL8 with PZT could be a suitable choice to achieve superior energy storage performance.

Additionally, I have a plan to study perovskite ferroelectric oxide materials as an anode for Li-ion rechargeable batteries. As one of the two electrodes in a lithium battery, the anode is loaded up with lithium ions during charging and releases them during discharge. Graphite is the material of choice for lithium battery anodes today, and serves them well, remaining stable across thousands of charging cycles. Specifically, I am interested to explore $PbTiO_3$ and $BiFeO_3$ and their composites for Li-ion rechargeable batteries. Lead-acid batteries are a well-known, system there are well-established supply chains for lead, as well as systems in place to recycle the material at the end of its life.

Although, for the lithium-ion battery graphite is the choice of anode material we would like to see improvements in their storage capacity, and these lead base compounds, and composite could be a possible alternative for anode material. Some of the research carried out on lead titanate and bismuth titanate has proven that those materials could be promising for an anode system. Along with the selection of the materials, modifying synthesis techniques, and optimizing suitable electrolytes and binders could further help to achieve the enhanced stored capacity and stability of the battery.