Energy density and storage capacity of La\(^{3+}\) and Sc\(^{3+}\) co-substituted Pb(Zr\(_{0.53}\)Ti\(_{0.47}\))O\(_3\) thin films

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Abstract
We studied the energy density and storage capacity properties of rare-earth modified lead zirconate titanate thin films. Highly oriented thin films of (PbZr\(_{0.53}\)Ti\(_{0.47}\))(1−y)(La\(_x\)Sc\(_{1−y}\))\(_3\)O\(_3\) wherein; [for y = 0 and x=0 viz PL0] and, [for y = 0.1 and x = 0.2, 0.4, 0.6 and 0.8 viz PL2, PL4, PL6 and PL8 respectively] abbreviated as PL10x have been synthesized on MgO (100) substrate by the pulsed laser deposition technique. The higher proportion of lanthanum increased the broadening of dielectric permittivity and dielectric maxima that shifted to higher temperatures with increasing frequency, signifying the relaxor-type behavior of these films. The value of the relaxation parameter varies from γ = 1.69 for PL6 and 1.95 for PL8 that was estimated from the linear fit of the modified Curie-Weiss law indicating the relaxor nature satisfying Vogel-Fulcher relation. Furthermore, we achieved enhanced spontaneous polarization of the fabricated thin films. Slim loop hysteresis was observed on tuning lanthanum and scandium and the estimated recovered energy density (U\(_r\)) is 51.15 J cm\(^{-3}\) and 26.54 J cm\(^{-3}\) with efficiency (η) of 47.38% and 65.88% respectively for PL6 and PL8 thin films. The high dielectric permittivity, high breakdown strength, and enhanced energy storage density of thin films could make it promising materials for memory, power electronics, and energy storage applications.

1. Introduction

Lead–zirconate titanate Pb(Zr\(_y\)Ti\(_{1−y}\))O\(_3\) (PZT) thin film capacitors have been extensively studied ABO\(_3\) perovskite for many years due to its potential applications in numerous fields such as memory devices [1, 2], high energy storage [3], piezoelectric devices [4], sensors and actuators [5] and ultrasonic transducers [6], etc. Promising features of PZT, such as high dielectric permittivity (\(\varepsilon\)), high spontaneous polarization (P\(_s\)), ultrahigh strain (d\(_{33}\)), high piezoelectric response make its extensive ranges of utilization [5, 7]. 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 ferroelectric thin film capacitor with the higher concentration of Ti [8, 9], however, the antiferroelectric (AFE) phase was observed for the lower value of Ti \(\leq 5\) [10, 11]. The cation substitution in PZT improves a domain wall mobility depending upon the size of ions, the larger ions such as La\(^{3+}\), Nd\(^{3+}\), Sr\(^{2+}\) and Ta\(^{5+}\) favor A-site, while lower ionic radii such as Sc\(^{3+}\), Yb\(^{3+}\), and Fe\(^{3+}\) occupy B-site [9, 11, 12].

La\(^{3+}\) doped Pb\(_{0.92}\)Zr\(_{0.52}\)Ti\(_{0.48}\)O\(_3\) (PLZT) on A-site increases thermal stability of thin films which could be suitable for energy storage applications [13], and attributes easy orientation and mobility of domain walls [14] increases spontaneous polarization (P\(_s\)) of PbZr\(_{0.52}\)Ti\(_{0.48}\)O\(_3\) [15], consequently storing higher energy. Our earlier studies of Sc\(^{3+}\) doped on B-site, PbZr\(_{0.53}\)Ti\(_{0.47}\)O\(_3\) (PZTS) showed an increase of P\(_s\) and exhibited improved energy density of the thin-film capacitor [16]. Role of Sc\(^{3+}\) doping is reported to improve the relaxor behavior in several perovskites such as Pb\(_{0.75}\)Ba\(_{0.25}\)Sc\(_{0.5}\)Ta\(_{0.5}\)O\(_3\) [17] and PbSc\(_{0.5}\)Nd\(_{0.5}\)Ta\(_{0.5}\)(PSNT) with 0 \(\leq x \leq 1\).
Also, mixed doped in PZT system plays a significant role in charge balance between the A-site, B-site, and oxygen vacancies [19]. Dalakoti et al have studied the substitution of $\text{Sr}^{2+}$ and $\text{Zn}^{2+}$ together in PZT and reported a significant increase in polarization [9].

In this study, we report a systematic study of $\text{La}^{3+}$ and $\text{Sc}^{3+}$ substituted thin films on PZT considering the significant role of mixed doped cations, for the charge balance between A- and B-sites and oxygen vacancy. Thin films were grown on MgO (100) substrate applying pulse laser deposition (PLD) technique on a thin buffer layer of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) of various compositions. The respective targets of different compositions were made by a solid-state reaction method [20]. We measured the microstructure, ferroelectric properties, dielectric properties of thin films, and analyzed their suitability in electronic applications such as memory and energy storage devices.

### 2. Experimental

Highly oriented thin films of stoichiometric formula $(\text{PbZr}_{0.53}\text{Ti}_{0.47})_{1−y}(\text{La}_y\text{Sc}_{1−y})_3\text{O}_3$ wherein; $[y = 0$ and $x = 0]$ denoted as PL0 and $[y = 0.1$ with $x = 0.2, 0.4, 0.6$ and 0.8] denoted as PL2, PL4, PL6 and PL8 respectively abbreviated as PL10x $(x = 0, 0.2, 0.4, 0.6$ and 0.8) were synthesized by pulsed laser deposition (PLD) technique using a KrF excimer laser $(\lambda = 248 \text{ nm}, f = 10 \text{ Hz})$. First, we grew thin buffer layers of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) on MgO (100) substrate, and subsequently, PL10x films were grown. We followed the detailed procedure to grow thin films by PLD [21–23]. The thickness $(\sim 300 \text{ nm})$ of the grown thin films was controlled by the total number of shots applied and later we verified it by using an XP-200 profilometer. The optimized deposition parameters are summarized in table 1.

We measured the orientation and phase purity of thin films by x-ray diffraction (XRD; CuK$_\alpha$ radiation with wavelength $\lambda = 1.5405 \text{ Å}$) at room temperature. The atomic force microscopy (AFM) micrograph of PL10x thin films was recorded in contact mode over an area of $3 \mu\text{m} \times 3 \mu\text{m}$ and 20 nm z-scale. For electrical and dielectric measurements, we deposited Pt at the top of thin films (top electrode) by DC sputtering technique (Power 20 W, helium pressure 100 mTorr and time 8 min with a base vacuum of $10^{-6} \text{ Torr}$) using a metal shadow mask of an area $\sim 10^{-8} \text{ m}^2$. Then we used a profilometer to find out the exact area of Pt electrodes and obtained an average area $\sim 1.5 \times 10^{-8} \text{ m}^2$ which was used for all the calculations of dielectric and ferroelectric parameters. The dielectric and ferroelectric properties of thin films (PL10x) with the bottom electrode (LSMO) and top electrode (Pt) were studied. Thus, PL10x is considered as LSMO/PL10x/Pt capacitors throughout this manuscript 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 (C) and loss tangent (dissipation factor) in the wide range of temperature 100–650 K at frequencies ranges 100 Hz–1 MHz. Then relative dielectric permittivity ($\varepsilon''$) was calculated using equation (1) [24].

$$
\varepsilon'' = \frac{Cd}{\varepsilon_0 A}
$$

Where, $C$, $d$, and $A$ and are the capacitance (F), thickness (m), electrode surface area of a capacitor ($\text{m}^2$) of the thin films respectively, and $\varepsilon_0 (=8.85 \times 10^{-12} \text{ F m}^{-1})$ is the free space dielectric constant. The temperature-dependent ferroelectric hysteresis curves ($P$–$E$ loops) were obtained using a Sawyer Tower test configuration of the Radiant technology (Model: RT 6000 HVA-4000 V).
3. Result and discussion

3.1. Structural and microstructural results

The room temperature XRD patterns of highly oriented PL10x thin films were grown on MgO (100) substrates by employing PLD technique and are shown in figure 1(a). We observed a single-phase perovskite structure of thin films with preferred (100) coincide with MgO (100) orientation. We observed diffraction peaks for PL0 film at $2\theta \sim 21.76$, 44.36 and 68.82 correspond to (100), (200), and (300) planes and a slight distortion in doped films (lanthanum and scandium) films. 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 PZT composition with $La^{3+}$ doping [25, 26]. Reitveld refinement of XRD data carried out by Noheda et al reported as tetragonal symmetry for Pb($Zr_{0.52}Ti_{0.48}$)O$_3$ system [27]. In addition, the PZT system at MPB revealed a higher tetragonal symmetry over rhombohedral phase [28]. This is due to smaller ionic radius of $La^{3+}$ than that of Pb$^{2+}$ which induces lattice distortion and shrinkage in volume accompanied with reduction in $a$-axis and $c$-axis [25, 29]. However, it has also been reported that PZT over morphotropic phase boundary (MPB) region the tetragonal and rhombohedral phases with space group P4mm and R3c coexists at the room temperature for [30].

![Figure 1. Room temperature (a) XRD Bragg peaks of thin films (b) Williamson and Hall (W–H) plot.](image-url)
We used XRD data to analyze the peak broadening in terms of the crystalline size and lattice strain due to dislocation. The instrumental broadening ($\beta$) was corrected, corresponding to each diffraction peak of thin films using the relation [31]:

$$\beta = \sqrt{(\beta^2_{\text{measured}} + (\beta^2_{\text{instrumental}})} \tag{2}$$

The average nanocrystalline size was calculated using Debye–Scherrer formula: The average nanocrystalline size of thin films sample is calculated using Debye–Scherrer equation

$$D = \frac{K\lambda}{\beta \cos \theta} \tag{3}$$

where $D = \text{crystalline size in nanometer}$, $K = \text{Scherrer constant (0.9)}$, and $\lambda = \text{wavelength of the Cu K\alpha radiation (1.5406 Å)}$ and $\beta = \text{the peak width at half-maximum intensity}$. The strain-induced ($L_s$) in thin films due to crystal imperfection and distortion was calculated using the formula:

$$L_s = \frac{\beta}{\tan \theta} \tag{4}$$

From this equation and the Scherrer equation, 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 looking at the peak width as a function of the diffracting angle $2\theta$ and obtained the mathematical equation [32, 33].

$$\beta = L_s \tan \theta + \frac{K\lambda}{D} \tag{5}$$

It can be rearranged as,

$$\beta \cos \theta = L_s \sin \theta + \frac{K\lambda}{D} \tag{6}$$

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 $\beta$ and $\theta$. The linear fitting of $\beta \cos \theta$ (radian) along y-axis and $\sin \theta$ (radian) along x-axis is shown in figure 1(b) and the fitted parameters are shown in table 2. We calculated the D from the y-intercept and obtained 35.28 nm for PL0 (viz; PZT) sample consequently decreases 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. Melo et al reported D $\sim$ 30 nm for $\sim$300 nm in (Pb0.9La0.09)(Zr0.65Ti0.35)O3 thin films [34]. The calculated parameters D and $L_s$ for all compositions are provided in table 2.

Figures 2(a)–(e) shows AFM micrographs of thin films which exhibited smooth surface topography with an average roughness ($R_s$) of $\sim$1.81, 2.21, 3.47, 4.49, 8.69 nm for PL0, PL2, PL4, PL6, and PL8 respectively. Thin films without doping i.e., PL0 has low $R_s$ that increased on lanthanum doping contents yielding roughness of $\sim$8.69 nm for PL8 thin film, and it may be due to higher ionic radius of lanthanum (1.061 Å) to scandium (ionic radii 0.745 Å). We observed XRD peak broadening due to La$^{3+}$ and Sc$^{3+}$ in PZT thin films, and 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 [34, 35]. One can notice distinct surface roughness of respective films in 3D images as shown in the inset of figures 2(a)–(e).

### 3.2. Dielectrics behavior

The frequency ($\omega$) dependence of the real component of relative dielectric permittivity ($\varepsilon'$) at various temperatures from 100–650 K for all compositions of thin films are shown in figures 3(a)–(e) and their respective dielectric loss tangent (tan$\theta$) in right y-axis. We observed stable $\varepsilon'$ with high value and low tan$\theta$ in a wide range of frequencies in good agreement as reported in ferroelectric thin films of PbZr0.52Ti0.48O3 [36]. We obtained room
temperature (300 K) the value of $\varepsilon' = 1064, 567, 820, 2016$ and $556$ for PL0, PL2, PL4, PL6, and PL8 respectively recorded at 1 kHz frequency. Thus, a suitable proportion of $\text{La}^{3+}$ and $\text{Sc}^{3+}$ can tailor dielectric properties.

A comparison of temperature-dependence of the relative permittivity ($\varepsilon'$ versus temperature) measured at frequency 1 kHz is shown in figures 4(a), (b). One can notice that PL0, PL6, and PL8 have dielectric maxima at $\varepsilon'_m \sim 575 \text{ K}, 525 \text{ K},$ and $450 \text{ K}$ respectively denoted as $T_m$. It is expected that such a peak for PL2 and PL4 existed
above 650 K, out limiting temperature for measurements. Furthermore, we observed \( \varepsilon' \) as diffused over a wide range of temperatures on PL6 and PL8 which is in agreement with the earlier research on Lanthanum doped lead zirconate titanate thin films [37]. In ferroelectric materials, such type of behavior is pronounced as diffused phase transition (DPT) [38], known as disordered ferroelectric materials [39].

The ferroelectric behavior with the DPT phenomenon of the dielectric materials can be explained by Curie-Weiss law above \( T_m \) [40]. The relationship for \( \varepsilon' \) with the temperature above \( T_m \) is given by equation (7).

\[
\frac{1}{\varepsilon'} = \frac{T - T_0}{C} \quad (T > T_c)
\]

Where; \( C \) is Curie-Weiss constant and \( T_0 \) is Curie-Weiss temperature (\( T_c \)) for second-order phase transition and less than \( T_m \) for the first-order phase transition [41].

Figures 5(a)–(c) show the reciprocal of \( \varepsilon' \) with temperature for PL0, PL6 and PL8 thin films. As we fitted using equation (2), 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 observed a degree of deviation, \( \Delta_{\text{cw}} = T_{\text{cw}} - T_m = 15, 50, \) and 70 for PL0, PL6 and PL8 respectively due to compositional induced diffuse phase transition behavior [21]. Where \( T_{\text{cw}} \) represents the temperature from which \( \varepsilon' \) begins to deviate. Some of the parameters calculated are shown in table 3.

In addition, the modified Curie-Weiss law can also explain the DPT behavior of the relaxor materials related by equation (8) [42]. Where, \( \gamma \) provides DPT behavior and \( C' \) is Curie-Weiss like constant.

\[
\frac{1}{\varepsilon'} - \frac{1}{\varepsilon_{m}} = \frac{(T - T_m)^\gamma}{C'} \quad (1 \leq \gamma \leq 2)
\]

For \( \gamma = 1 \), a normal Curie-Weiss law is obtained, and \( \gamma = 2 \) describes a complete diffuse phase transition. The value of \( \gamma \) lies between 1 and 2 representing incomplete diffuse phase transition of the materials [41]. \( \gamma = 1 \)
denotes normal ferroelectric material whereas 2 represents complete phase transition behavior of relaxor materials.

The fitting with an equation (8) is shown in figures 5(a)–(c) inset, at 1 kHz frequency for PL0, PL6 and PL8 thin films. We obtained γ as 1.19 ± 0.05, 1.69 ± 0.05 and 1.95 ± 0.16 indicating that PL6 and PL8 thin films exhibit incomplete diffuse phase transition. Thus, on increasing Lanthanum concentration such behavior is dominant than undoped or lower doped of lanthanum. It also indicates that dopants with La$^{3+}$ > Sc$^{3+}$ increase the DPT of the materials.

As we observed the DPT of PL6 and PL8 thin films, where $\varepsilon'_m$ decreases and $T_m$ shifts towards higher temperature with increasing frequency. Furthermore, we analyzed the frequency dependency of $T_m$ by using the Vogel–Fulcher relation given in equation (9) [43].

$$f = f_0 \exp \left( \frac{-E_a}{k_B(T_m - T_{VF})} \right)$$

Where; $f_0$ is the pre-exponential factor, $T_{VF}$ is the characteristic Vogel–Fulcher freezing temperature, $E_a$ is the activation energy and $k_B$ is Boltzmann’s constant [44, 45].

The reasonably well fitted non-linear curve shown in figure 6, yielded $f_0 \sim 10^6$ Hz, $T_{VF} = 477$ K and 411 K and factor, $E_a = 0.031$ eV and 0.054 eV respectively and are physically acceptable values [46]. These are in good agreement with the earlier reports on Pb(Zr$_{0.53}$Ti$_{0.47}$)$_{0.60}$Fe$_{0.3}$Ta$_{0.5}$O$_{3}$ [47]. The earlier report on Pb(Zr$_{0.5}$Ti$_{0.4}$)$_{0.9}$Sc$_{0.1}$O$_{3}$ had shown $E_a = 0.037$ eV and $f_0 = 1.538 \times 10^6$ Hz [16]. Thus, analysis of Vogel–Fulcher relation, further supports PL6 and PL8 thin films behave disorder ferroelectric, typically called relaxor ferroelectric materials. In addition, one can notice a comparatively slim polarization electric field ($P-E$) hysteresis loop of those thin films which suggest higher content of lanthanum on PZT strengthen the spontaneous polarization.

Figures 7(a)–(c) show the Cole–Cole plots of the temperature-dependent dielectric permittivity of the real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of PL10x thin films at frequency range $10^2$–$10^6$ Hz. We observed some characteristics of $\varepsilon'$ versus $\varepsilon''$ response for PL10x thin films in the temperature ranges 100–650 K. (i) The $\varepsilon'$ radius of the semicircular arc shows high variation with temperature, (ii) With increasing temperature the bulk permittivity contribution ($\varepsilon'$ radius, when $\varepsilon'' = 0$) 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 incorporation of the La$^{3+}$ and Sc$^{3+}$ ions could be responsible for change in its conduction properties [36, 48]. These dopants are mainly of two types: La$^{3+}$ is a donor dopant that produces a soft PZT and Sc$^{3+}$ is an acceptor dopant that produces a hard PZT. 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 [49, 50]. (iii) the samples exhibit multi-dispersive relaxation time on increasing the temperature. Two intercepts...
between the real axis $\varepsilon'$ and the circular arc, assign for the static dielectric constant, $\varepsilon_s$ (largest value $\varepsilon'$ radius, when $\varepsilon'' = 0$) and the optical dielectric constant, $\varepsilon_\infty$ (smallest value $\varepsilon'$ radius, when $\varepsilon'' = 0$) 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 could be due to different strains, that are produced by the different sizes of the doping ions that produce a variation of the dielectric and conductivity properties of the materials [51, 52].

3.3. Ferroelectric properties

The energy storage performance of ferroelectric materials is one of the key indicators for evaluating materials engineering applications. It can be estimated using unipolar $P-E$ loops under the external applied electric field. According to the definition of energy-storage density using $P-E$ hysteresis loops, the stored energy per unit volume ($U_{st}$) and the recovered energy per unit volume ($U_{re}$) are given by [53]

$$U_{st} = \int_{P_{re}}^{P_{m}} E dP$$

$$U_{re} = \int_{P_{re}}^{P_{m}} E dP$$

Where; $E$ is the applied electric field, $P$ is the displacement charge density for ferroelectric materials, and $P_r$ is the remnant polarization, $P_m$ is the maximum polarization. Evidently, based on equations (10) and (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. To estimate these values, we analyzed the positive branch of $P-E$ curve and calculated the energy storage efficiency ($\eta$) as

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

Figures 8(a)–(e) shows temperature-dependent (100–500 K) $P-E$ hysteresis loops of PL10x thin film measured under an applied electric field of 0.67 MV cm$^{-1}$ electric field at 1 kHz frequency. Reproducible and stable ferroelectric loops with slight changes in polarization and coercive field were observed for all thin films. From the comparative graph of PL10x thin films as shown in figure 8(f), we observed typical ferroelectric loops with enhanced polarization and reduced coercive field for PL2 and PL4 thin films. Furthermore, PL6 and PL8 show slim loop hysteresis 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 PbZr0.53Ti0.47 (PZT). We estimated the energy storage capacity at 300 K for the same applied electric field (0.67 MV cm$^{-1}$) for PL10x thin films, achieving enhanced $U_{re}$, $U_{st}$ and $\eta$ due to doping elements. The estimated $U_{re}$ value estimated was the greatest $\sim 12.24$ with $\eta = 53.4\%$ for PL6. But we had better $\eta = 66.67\%$ with $U_{re} = 4.82$ J cm$^{-3}$ for PL8 thin films. All the calculated parameters are

Figure 7. (a)–(e) Show Cole-Cole plots of the temperature-dependent dielectric permittivity real part ($\varepsilon'$) versus imaginary part ($\varepsilon''$) for PL10x thin films.
summarized in Table 4. Considering energy storage capacity and efficiency, we further analyzed the positive branch of P-E loop for possible energy storage applications. Figures 9(a), (b) show the room temperature unipolar P-E hysteresis loops of PL6 and PL8 thin films measured under various applied electric fields at 2 kHz of frequency. The slim loop of these thin-film capacitors revealed relaxor ferroelectric behavior in PL6 and PL8 in line with dielectric results. We observed slight asymmetries at positive and negative branches in the hysteresis loop of PL6 and PL8 films that could be due to different work functions of top (Pt) and bottom (LSMO) electrodes [54, 55]. 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 [56, 57].

Near the breakdown electric field (~2.67 MV cm⁻¹) at 2 kHz frequency, the enhanced polarization \(P_r \sim 46.6 \mu C \cdot cm^{-2}\) and \(P_m = 125.4 \mu C \cdot cm^{-2}\), consequently yielded \(\Delta P_m = \frac{P_m}{P_r} = 2.69\), and reduced \(E_C \sim 205 \text{ kV cm}^{-1}\) were obtained for PL6 films. In the similar applied electric field, for PL8 films \(E_C\) was further reduced to 12 kV cm⁻¹ and \(P_r \sim 8.4 \mu C \cdot cm^{-2}\) and \(P_m \sim 39.2 \mu C \cdot cm^{-2}\), achieved \(\Delta P_m = 4.66, \) which resulted in slimmer P-E loop strengthening \(\eta\). Thinner P-E loops were achieved in our films than undoped PbZr_{0.53}Ti_{0.47}O₃ (PZT) [58], PbZr_{0.40}Ti_{0.60}O₃ [59] films which were expected. It is obvious that higher \(\Delta P_m\) would better to achieve enhanced \(\eta\).

We estimated \(U_{re}, U_{st}\) and \(\eta\) for PL6 and PL8 films from their respective P-E loops. It turns out to be \(U_{re} = 51.15 \text{ J cm}^{-3}\), \(U_{st} = 107.95\) and \(\eta = 47.38\%\) at an applied electric field of 2.67 MV cm⁻¹ and frequency 2 kH for PL6 thin films which is in good agreement with \(U_{st} = \varepsilon_0 e' E_{BD}^2 / 2\), where \(E_{BD}\) is electric breakdown strength.
PL6 possesses higher $\varepsilon'$ and high breakdown strength. The obtained values of PL6 are comparable with slightly less $\eta$ as reported 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 $\eta \sim 57\%$ [60]. We thus achieved enhanced energy values than the studies on oriented Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ thin films, $U_{re} \sim 8$ J cm$^{-3}$ and $\eta \sim 83.51\%$ at 1 kV cm$^{-1}$, synthesized by chemical solution method [63]. On the other hand, Nguyen et al had reported $\eta \sim 13.7$ J cm$^{-3}$ and a $\eta \sim 88.2\%$ under an applied electric field of 0.8 MV cm$^{-1}$ in 10% La-doped epitaxial PLZT thin films grown on SRO/STO/Si substrates using pulsed laser deposition. By comparing with this result, we have achieved higher $U_{re} = 26.54$ J cm$^{-3}$ but with slightly less $\eta = 65.88\%$ for PL8 thin films under an applied electric field 2.67 MV cm$^{-1}$ and frequency of 2 kHz. The energy storage performance of our thin films showed higher breakdown strength and better $U_{re}$ as compared to BaZr$_{0.20}$Ti$_{0.80}$O$_3$ (BZT) thin films showing $U_{re} = 21.28$ J cm$^{-3}$ and $\eta = 83.51\%$ [63], however, these films have shown enhanced and better energy storage capacity for multilayer 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), thus these materials might be useful for making sandwich structure to achieve high energy density capacitors. We observed $U_{re}$ and $U_{st}$ of PL6 and PL8 thin films are directly proportional to the applied electric field. However, $\eta$ is slightly decreased with an increase in an electric field is expected as reported by 0.942[Na$_{0.535}$K$_{0.48}$NbO$_3$]$-$0.058LiNbO$_3$ (KNNLN) films [64].

The summary of the estimated value of ferroelectric functionalized parameters of PL6 and PL8 thin films is given in table 5.

4. Conclusion

The XRD patterns of (PbZr$_{0.53}$Ti$_{0.47}$)$_{1-y}$La$_{y}$Sc$_{1-y}$O$_3$ thin films revealed highly oriented (100) films with the perovskite phase. The dielectric data revealed an increase of dielectric permittivity when lanthanum content increased by 6%, however, a further increase of lanthanum (8%) resulted in the reduction of dielectric constant. We further noticed the role of increasing lanthanum contents (decreasing scandium) resulting in broadening of dielectric permittivity with temperature and ferroelectric phase transition from 575 K to 450 K. It clearly indicated that analysis of modified Curie-Weiss law for the thin films PL6 and PL8 behave relaxor-ferroelectric which further supported by Vogel-Fulcher relation. Cole-Cole plot analysis showed the samples exhibit multi-dispersive relaxation time on increasing the temperature. In addition, a large increase in the resistance of the samples was observed when the amount of the lanthanum dopant was increased because the lanthanum modifies the domain wall motion in the samples.
Table 5. Summary of calculated values of energy storage parameters of PL6 and PL8 thin films measured under various electric fields at 2 kHz frequency.

| Sample | E (MV cm\(^{-1}\)) | 0.67 | 1 | 1.33 | 1.67 | 2 | 2.33 | 2.67 |
|--------|---------------------|------|---|------|------|---|------|------|
| PL6    | \(u_{re} (J \text{ cm}^{-3})\) | 12.24 | 17.64 | 23.1 | 29.15 | 36.02 | 43.21 | 51.15 |
|        | \(u_{a} (J \text{ cm}^{-3})\)  | 22.92 | 34.27 | 46.73 | 60.73 | 75.22 | 92.12 | 107.95 |
|        | \(\eta\)              | 53.4 | 51.48 | 49.43 | 47.99 | 47.88 | 47.38 | 47.38 |
| PL8    | \(u_{re} (J \text{ cm}^{-3})\) | 3.82 | 6.67 | 9.94 | 13.67 | 17.84 | 22.22 | 26.54 |
|        | \(u_{a} (J \text{ cm}^{-3})\)  | 5.73 | 9.98 | 14.79 | 20.59 | 26.52 | 33.48 | 40.28 |
|        | \(\eta\)              | 66.67 | 66.83 | 67.21 | 67.73 | 67.26 | 66.36 | 65.88 |

The polarization electric field (P-E) plot exhibits the role of lanthanum and scandium causes a substantial reduction in coercive fields. Furthermore, enhanced polarization was achieved on PL2, PL4 and PL6 thin films. In addition, PL6 and PL8 thin films show the slim loop P-E curve, which indicates a relaxor-ferroelectric nature. We achieved \(u_{re} = 51.15 \text{ J cm}^{-3}\) with \(\eta = 47.38\%\) for PL6 under 2.67 MV cm\(^{-1}\) at 2 kHz frequency and \(\eta = 65.88\%\) with \(u_{re} = 26.54 \text{ J cm}^{-3}\) for PL8 thin films. The study confirms the idea that, by tuning La\(^{3+}\) and Sc\(^{3+}\), the dielectric and ferroelectric functional properties of thin films can be controlled for better memory, power electronics, and energy storage devices.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] He B and Wang Z 2016 Enhancement of the electrical properties in Ba\(_3\)TiO\(_3\)/PbZr\(_{0.52}\)Ti\(_{0.48}\)O\(_3\) ferroelectric superlattices ACS Appl. Mater. Interfaces 8 6736–42
[2] Li D H, Lee E S, Chung H W and Lee S Y 2006 Comparison of the effect of PLT and PZT buffer layers on PZT thin films for ferroelectric materials applications Appl. Surf. Sci. 252 4351–4
[3] Wang J, Su Y J, Wang B, Ouyang J, Ren Y H and Chen L Q 2020 Strain engineering of dischargeable energy density of ferroelectric thin-film capacitors Nano Energy 72 104665–73
[4] Wolf R A and Trolier-McKinstry S 2004 Temperature dependence of the piezoelectric response in lead zirconate titanate films J. Appl. Phys. 95 1397–406
[5] Izumskaya N, Alivov Y I, Cho S I, Morkoč H, Lee H and Kang Y S 2007 Processing, structure, properties, and applications of PZT thin films Crit. Rev. Solid State Mater. Sci. 32 111–202
[6] Zhu R, Fang B, Zhao X, Zhang S, Chen Z, Ding J and Luo H 2018 Enhancing piezoelectric properties of high-Curie temperature PMN-PT piezoelectric ceramics by citrate method J. Alloys Compd. 735 496–509
[7] Pandey S K, James A R, Prakash C, Goel T C and Zimik K 2006 Dielectric and ferroelectric properties of pulsed laser deposited lead zirconate titanate (65/35) thin film Thin Solid Films 513 95–8
[8] Pandey S K, James A R, Prakash C, Goel T C and Zimik K 2004 Electrical properties of PZT thin films grown by sol-gel and PLD using a seed layer Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 112 96–100
[9] Dalakoti A, Bandypadhyay A and Bose S 2006 Effect of Zn, Sr, and Y addition on electrical properties of PZT thin films J. Am. Ceram. Soc. 89 1140–3
[10] Wang X, Yang T, Peláiz-Barranco A, Mendez-González Y and Guerra J D S 2016 Switching and energy-storage characteristics in PLZT 2/5/3 antiferroelectric ceramic system J. Adv. Dielectr. 06 1620003–7
[11] Gonnard P and Troccaz M 1978 Dopant distribution between A and B sites in the PZT ceramics of type ABO\(_3\) J. Solid State Chem. 23 321–6
[12] Haccart T, Remiens D and Cattan E 2003 Substitution of Nb doping on the structural, microstructural and electrical properties in PZT films Thin Solid Films 423 235–42
[13] Hu G, Ma C, Wei W, Sun Z, Lu L, Mi S-B, Liu M, Ma B, Wu J and Jia C 2016 Enhanced energy density with a wide thermal stability in epitaxial Pb0.53Bi0.47Zr0.52Ti0.48O3 thin films Appl. Phys. Lett. 109 193904

[14] Rath M, Mityal M, Murakami M and Ramachandra Rao M S 2019 Controlled piezotronic properties on recoverable energy storage density in rare-earth ions doped epitaxial PZT thin films J. Phys. D: Appl. Phys. 52 304001–7

[15] Mukherjee D, Hordogoda M, Pesquisa D, Ghosh D, Jones J L, Mukherjee P and Wittanachchi S 2017 Enhanced ferroelectric polarization in epitaxial (Pb1−xLa0.5)Zr0.52Ti0.48O3 thin films due to low la doping Phys. Rev. B 95 1–11

[16] Bhattarai M K, Mishra K K, Instan A A, Bastakoti B P and Katiyar R S 2019 Enhanced energy storage density in Sc3+ substituted Pb(Zr0.53Ti0.47)O3 nanoscale films by pulse laser deposition technique Appl. Surf. Sci. 490 451–9

[17] Marovina V et al 2006 Structural, optical and dielectric properties of relaxor-ferroelectric Pb0.5Ba0.25Sr0.25TiO3 thin films J. Phys. Condens. Matter 18 385–93

[18] Correa M, Kumar A and Katiyar R S 2012 Microstructure-Relaxor Property Relationship of Microstructure-Relaxor Property Relationship 426 112–21

[19] Ramam K and Chandramouli K 2009 Dielectric and piezoelectric properties of combinatorial effect of A-site isovalent and B-site acceptor doped zirconia ceramics Silikaty 53 189–94

[20] Bhattarai M K, Pavunny S P, Instan A A, Scott J F and Katiyar R S 2017 Effect of off-center ion substitution in morphotropic lead zirconate titanate composition J. Appl. Phys. 121 194102–9

[21] Instan A A, Pavunny S P, Bhattarai M K and Katiyar R S 2017 Ultrahigh Capacitive Energy Storage in Highly Oriented Ba(Zr0.9Ti0.1)O3 Thin Films Prepared by Pulsed Laser Deposition J. Non-Cryst. Solids 414 142903–7

[22] Zhu T J, Lu L and Lai M O 2005 Pulsed laser deposition of lead-zirconium titanate thin films and multilayered heterostructures Appl. Phys. A Mater. Sci. Process. 81 147–51

[23] Dugu S, Bhattarai M K, Kumari S, Instan A A, Pradhan D K, Holcomb M, Scott J F and Katiyar R S 2020 Observation of relaxor-ferroelectric behavior in gallium ferrite thin films Appl. Surf. Sci. 523 14645–69

[24] Tang H, Lin Y, Andrews C and Sodano H A 2011 Nanocomposites with increased energy density through high aspect ratio PZT nanowires Nanotechnology 22 015702–10

[25] Laishram R, Thakur O P, Bhattacharya D K and Harsh 2010 Dielectric and piezoelectric properties of la doped lead zinc niobate-lead zirconium titanate ceramics prepared from mechano-chemically activated powders Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 172 172–6

[26] Kalem V, Am B and Timuin M 2011 Dielectric and piezoelectric properties of PZT ceramics doped with strontium and lanthanum Ceram. Int. 37 1265–75

[27] Noheeda B, Gonzalo J, Cross L and Guo R 2000 Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite: the structure of PbZr0.52Ti0.48O3 J. Phys. Rev. B 61 8687–95

[28] Hammer M and Hoffmann M J 1998 Detailed x-ray diffraction analyses and correlation of microstructural and electromechanical properties of La-doped PZT ceramics J. Electroceramics 2 75–84

[29] Deng G, Yin Q, Dong A, Zheng W, Cheng W and Qiu P 2005 High piezoelectric and dielectric properties of la-doped 0.3PbZn0.7Ta0.3O3-0.7PbTi1−xZrxO3 ceramics near morphotropic phase boundary J. Am. Ceram. Soc. 88 2310–4

[30] Kumar A, Mishra S K and Verma V K 2015 Detailed dielectric and rietveld analysis of Sr2+ substituted PZT–PMN ceramics J. Mater. Sci. Mater. Electron. 26 2769–74

[31] Jayasankar K, Pandey A, Mishra B K and Das S 2016 Evaluation of microstructural parameters of nanocrystalline Y2O3 by x-ray diffraction peak broadening analysis Mater. Chem. Phys. 171 195–200

[32] Khorsand Zak A and Abadi M J 2010 Characterization and x-ray peak broadening analysis in PZT nanomaterials prepared by modified sol-gel method Ceram. Int. 36 1905–10

[33] Dongol M, El-Denglawey A, Abdel El Sakka M and Yahia I S 2015 Thermal annealing effect on the structural and the optical properties of Nano CdTe films Optik (Stuttg). 126 1532–7

[34] Meo M, Araujo E B, Shvartsman V V, Shur V Y and Khoklin A L 2016 Thickness effect on the structure, grain size, and local piezoresponse of self-polarized lead lanthanum zirconate titanate thin films J. Appl. Phys. 120 054101–5

[35] Amorin L H C, Da Silva Martins L and Urbano A 2018 Commitment between roughness and crystallite size in the vanadium oxide thin film electro-optical properties Mater. Res. 22 1–6

[36] Barrionuevo D, Ortega N, Kumar A, Chatterjee R, Scott J F and Katiyar R S 2013 Thickness dependent functional properties of PbZr0.53Ti0.47O3/La0.5Sr0.5TiO3 heterostructures Thickness dependent functional properties of PbZr0.53Ti0.47O3 heterostructures J. Appl. Phys. 114 234103–10

[37] Bhattarai M K, Mishra K K, Dugu S, Instan A A and Katiyar R S 2019 Ferroelectric ordering and energy storage density of thin films capacitor by doping La3+ and Sc3+ on Pb(Zr0.53Ti0.47)O3 using pulse laser deposition technique Appl. Phys. Lett. 114 0–5

[38] Baijai P K, Pastor M and Singh K N 2014 Diffuse phase transition and electrical conductivity of Pb(Ca1/3Nb2/3)O3 J. Electroceramics 43 1403–10

[39] Vuong L D, Gio P D, Tho N T and van Cuong T 2013 Relaxor ferroelectric properties of PZT–PZN–Pmnm ceramics Indian J. Eng. Mater. Sci. 20 555–60 (http://mosp.nus.ac.res.in/handle/123456789/255657)

[40] Menash H, Necira Z and Bouafar A 2013 Structural and Relaxor Behavior of Pb0.95La0.05(Zr0.9Ti0.1)O3: Mn2+ (Mn1/3Sr2/3)O3 J. Mater. Sci. Eng. A 635 160–20 [https://scholar.google.fr/citations/user=KauMrHCAAJAAJ?hl=fr]

[41] M’Peko J, Peixoto A G, Ilmen M and Gago-Mo-Sage L M 2005 Electrical properties of Nb-doped PZT 65/35 ceramics: influence of Nb and excess PbO J. Electroceramics 15 167–76

[42] Zhang T F, Huang X X, Tang X G, Jiang Y P, Liu Q X, Lu B and Lu S G 2018 Enhanced electrocaloric analysis and energy-storage performance of lanthanum modified lead titanate ceramics for potential solid-state refrigeration applications Sci. Rep. 8 396–408

[43] Delgado M, Colia E V, Griffin P, Weissman M B and Viehland D 2009 Field dependence of glassy freezing in a relaxor ferroelectric Phys. Rev. B - Condens. Matter Mater. Phys. 79 10–3

[44] Stringer C J, Shirout T R and Randall C A 2007 High-temperature ferroelectric relaxor ceramics: a comparative study J. Appl. Phys. 101 054107–13

[45] Maiti T, Guo R and Bhalia A S 2008 Structure-property-dielectric property phase diagram of BaZr0.9Ti0.1O3 system J. Am. Ceram. Soc. 91 1769–80

[46] Janhua B, Bongkarn T, Kolodianothy T and Vittayakorn N 2017 High piezoelectric response and polymeric phase region in the lead-free piezoelectric BaTiO3–CaTiO3–BaSnO3 ternary system RSC Adv. 7 30166–76

[47] Sanchez D A, Kumar A, Ortega N, Katiyar R S and Scott J F 2010 Near-room temperature relaxor multiferroic Appl. Phys. Lett. 97 21–5

[48] Chawla M, Shekhawat N, Agarwal S, Sharma A and Nair K G M 2014 Cole–cole analysis and electrical conduction mechanism of N+ implanted polycarbonate J. Appl. Phys. 115 1–7
[49] Sahoo B and Kumar Panda P 2013 Effect of lanthanum, neodymium on piezoelectric, dielectric and ferroelectric properties of PZT J. Adv. Ceram. 2 37–41

[50] Kour P, Pradhan S K, Kumar P, Sinha S K and Kar M 2016 Enhanced ferroelectric and piezoelectric properties in La-modified PZT ceramics Appl. Phys. A Mater. Sci. Process. 122 1–7

[51] Coşkun M, Polat A O, Coşkun F M, Durmuş Z, Caglar C M and Türüt A 2018 The electrical modulus and other dielectric properties by the impedance spectroscopy of LaCrO₃ and LaCr₀.9₀Ir₀.1₀O₃ perovskites RSC Adv. 8 4634–48

[52] Newnham R E 2005 Properties of Materials : Anisotropy, Symmetry, Structure (New York: Oxford University Press)

[53] Lim K W, Peddigari M, Annapureddy V, Hwang G T, Choi J J, Kim G Y, Yi S N and Ryu J 2018 Energy storage characteristics of {001} oriented Pb(Zr₀.₂₅Ti₀.₇₅)O₃ thin film grown by chemical solution deposition Thin Solid Films 660 434–8

[54] Gu J, Sun Q, Chen X, Song Y, Tang Y, Wang D and Qu P 2019 Energy storage performance of sandwich structured Pb(Zr₀.₅₅Ti₀.₄₅)O₃/BaZr₀.₃Tb₀.₇O₃/Pb(Zr₀.₅₅Ti₀.₄₅)O₃ films Crystals 9 575–84

[55] Peddigari M, Palnedi H, Hwang G T, Lim K W, Kim G Y, Jeong D Y and Ryu J 2018 Boosting the recoverable energy density of lead-free ferroelectric ceramic thick films through artificially induced quasi-relaxor behavior ACS Appl. Mater. Interfaces 10 20720–7