DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF COMBINATORY EFFECT OF A-SITE ISOVALENT AND B-SITE ACCEPTOR DOPED PLZT CERAMICS

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This investigation highlights the influence of isovalent Sr and acceptor Mn modified PLZT near morphotrophic phase boundary for phase formation, microstructure, density, dielectric and piezoelectric properties. $[Pb_{0.9896-y}La_{0.0104}Sr_y][Zr_{0.529}Ti_{0.471}]_{0.9949}$ $Mn_{0.005}O_3$ (PLSZMT) where y = 0, 0.2, 0.4, 0.6, 0.8 and 1 mol.%, polycrystalline solid solutions were synthesized by solid state reaction method. X-ray diffraction patterns indicated that undoped composition had shown coexistence of both rhombohedral and tetragonal phases while increasing Sr content resulted in phase shift to tetragonal phase. Grain size and apparent density enhanced with the increasing Sr content up to y = 1 mol.%. The optimum ε_{RT}, d_{33} and kp were observed at y = 1 mol.%, respectively which could be suitable for piezoelectric applications.

INTRODUCTION

Lead zirconate titanate (PZT) ceramics can be classified into two groups: "hard" and "soft". Hard PZT ceramics can withstand high levels of electrical excitation which are well suited for high voltage or high power generators and transducers, while the important feature of soft PZT is the high sensitivity and permittivity which are well suited for various sensors and actuators, transducers etc. The soft (donor) and hard (acceptor) doping in PZT and their combinatory effects near the morphotrophic phase boundary (MPB) had been reported [1]. Using element substitution, one can tailor the properties as desired. PLZT crystallizes with the ABO_3 perovskite structure in which Pb^{2+} and La^{3+} ions occupy the A-site and Zr^{4+}/Ti^{4+} ions occupy B-site. The lanthanum-modified PZT known as PLZT $[(Pb^{2+}, La^{3+})(Zr^{4+}, Ti^{4+})O_3]$ near morphotrophic phase boundary (MPB with (Zr/Ti ratio ≈ 53/47) had been studied and tailored for specific properties, since these compositions contribute best ferroelectric and piezoelectric properties. The higher orders in dielectric and piezoelectric response of $Pb(Zr_xT_{1-x})O_3$ system is found near morphotrophic phase boundary (designated as MPB) at x ≈ 0.53.

The influence of soft doping (isovalent Sr [2] or Ba [3, 4]) and the hard doping ions like (acceptors Ag^+ [5] at A-site and Mn^{2+}/Mn^{3+} [6-8] which occupy the B-site in the perovskite structure had been extensively investigated for various specific properties required in either thin films or bulk ceramics. The distribution of A-site and B-site vacancies in PLZT [9] ceramics had been extensively investigated. PZT had been studied with varied dopants. It is known that donor doping cause lead vacancies and hard doping cause oxygen vacancies. Manganese-doped PZT thin films prepared through sol-gel technique was studied by Zhang et al [10]. Lead may be substituted by isovalent cations including Ca^{2+}, Ba^{2+}, Sr^{2+} and Cd^{2+} as well as off-valent substitutions such as rare-earth ions Sm^{3+} and Y^{3+} while maintaining the perovskite crystal structure responsible for the strong ferroelectric behaviour [11]. Dielectric properties of ferroelectric ceramics substituting alkaline-earth elements such as Ca, Sr, and Ba for La in PLZT were investigated for MLCs applications with thin dielectric layers [12]. The MPB shifts from 53/47 (Zr/Ti) to 56/44 (Zr/Ti) with isovalent substitutions had been found to have optimum ferroelectric and piezoelectric nature.

However, the combinatory effect of hard (acceptor, Mn) and soft doping (isovalent, Sr and donor, La) doped PZT studies on dielectric and piezoelectric properties are very limited and have not been addressed. The aim of this study is to investigate the combinatory effects of both soft and hard doping and it is therefore of great interest to study the phase formation, microstructure, density, dielectric and piezoelectric properties of isovalent Sr on acceptor Mn modified PLZT system is reported. The stoichiometric compositions have been represented in Table 1.

General formula				[Pb$_{1-x-y}$La$_x$Sr$_y$][Zr$_z$Ti$_{1-z}$]$_{1-(x/4)-(m/2)}$Mn$_m$O$_3$		
1-x-y	PbO		Pb^{2+}	R$_{Pb}$ = 1.49Å	Pb^{2+} is substituted by La^{3+} and Sr^{2+} at A-site of PZT = 1-x-y	
x	Donor	La$_2$O$_3$	La^{3+}	R$_{La}$ = 1.36Å	R$_{Pb}$ = 1.49Å	La^{3+} substitutes Pb^{2+} at A-site of PZT
y	Isovalent	SrCO$_3$	Sr^{2+}	R$_{Sr}$ = 1.44Å	R$_{Pb}$ = 1.49Å	Sr^{2+} substitutes Pb^{2+} at A-site of PZT
z and 1-z	ZrO$_2$ and TiO$_2$		Zr^{4+} Ti^{4+}	R$_{Zr}$ = 0.72Å R$_{Ti}$ = 0.605Å		Ti^{4+} balances Zr^{4+} at B-site of PZT
m	Acceptor	MnCO$_3$	Mn^{2+}	R$_{Mn}$ = 0.67Å		Mn^{2+} replaces Zr^{4+}/ Ti^{4+} at B-site of PZT
V$_B$	B-site vacancies		Combination of isovalent and acceptor cations at A-site and B-site of PLZT, respectively.		1-(x/4)-(m/2)	
Compositions			Formulae			
Stoichiometric formula			[Pb$_{0.9896-y}$La$_{0.0104}$Sr$_y$][Zr$_{0.529}$Ti$_{0.471}$]$_{0.9949}$Mn$_{0.005}$O$_3$			

Sr = 0 mol.%
0.9896PbO + 0.0052La$_2$O$_3$ + 0.5263021ZrO$_2$ + 0.4685979TiO$_2$ + 0.005MnCO$_3$ → [Pb$_{0.9896}$La$_{0.0104}$][Zr$_{0.529}$Ti$_{0.471}$]$_{0.9949}$Mn$_{0.005}$O$_3$ + 0.005CO$_2$↑

Sr = 0.2 mol.%
0.9876PbO + 0.0052La$_2$O$_3$ + 0.002SrCO$_3$ + 0.5263021ZrO$_2$ + 0.4685979TiO$_2$ + 0.005MnCO$_3$ → [Pb$_{0.9876}$La$_{0.0104}$Sr$_{0.002}$][Zr$_{0.529}$Ti$_{0.471}$]$_{0.9949}$Mn$_{0.005}$O$_3$+ 0.007CO$_2$↑

Sr = 0.4 mol.%
0.9856PbO + 0.0052La$_2$O$_3$ + 0.004SrCO$_3$ + 0.5263021ZrO$_2$ + 0.4685979TiO$_2$ + 0.005MnCO$_3$ → [Pb$_{0.9856}$La$_{0.0104}$Sr$_{0.004}$][Zr$_{0.529}$Ti$_{0.471}$]$_{0.9949}$Mn$_{0.005}$O$_3$ + 0.009CO$_2$↑

Sr = 0.6 mol.%
0.9836PbO + 0.0052La$_2$O$_3$ + 0.006SrCO$_3$ + 0.5263021ZrO$_2$ + 0.4685979TiO$_2$ + 0.005MnCO$_3$ → [Pb$_{0.9836}$La$_{0.0104}$Sr$_{0.006}$][Zr$_{0.529}$Ti$_{0.471}$]$_{0.9949}$Mn$_{0.005}$O$_3$ + 0.011CO$_2$↑

Sr = 0.8 mol.%
0.9816PbO + 0.0052La$_2$O$_3$ + 0.008SrCO$_3$ + 0.5263021ZrO$_2$ + 0.4685979TiO$_2$ + 0.005MnCO$_3$ → [Pb$_{0.9816}$La$_{0.0104}$Sr$_{0.008}$][Zr$_{0.529}$Ti$_{0.471}$]$_{0.9949}$Mn$_{0.005}$O$_3$ + 0.013CO$_2$↑

Sr = 1.0 mol.%
0.9796PbO + 0.0052La$_2$O$_3$ + 0.01SrCO$_3$ + 0.5263021ZrO$_2$ + 0.4685979TiO$_2$ + 0.005MnCO$_3$ → [Pb$_{0.9796}$La$_{0.0104}$Sr$_{0.01}$][Zr$_{0.529}$Ti$_{0.471}$]$_{0.9949}$Mn$_{0.005}$O$_3$ + 0.015CO$_2$↑

x = La = 1.04, m = Mn = 0.5, y = 0, 0.2, 0.4, 0.6, 0.8 and 1 mol.% respectively. Zr:Ti ratio = 52.9:47.1

EXPERIMENTAL

Ceramic Processing

PLSZMT ceramics were prepared by solid state reaction method from raw powders of analytical grade (99.99% purity) PbO, La$_2$O$_3$, SrCO$_3$, ZrO$_2$, TiO$_2$ and MnCO$_3$. An excess 5wt.% PbO was added to all compositions. The detailed fabrication of ceramics and characterization are stated elsewhere [13]. The batch powders were ball milled using zirconia balls and ethanol as media for 24 h. The dried powders were calcined at 915°C for 3 h in a high purity alumina crucible by maintaining air atmosphere. Calcined powders were ball milled using zirconia balls and ethanol as media for 24 h to crush agglomerates and to minimize the particle size. The calcined fine powders were mixed with 5 wt.% polyvinyl alcohol (PVA, as binder) and were pressed into pellets of 12 mm diameter and 2-3 mm thickness using steel die and hydraulic press with uniaxial pressure of 700-900 kg/cm^2. Binder was burned off at 500°C for 3 h and the green bodies were sintered at 1225°C for 3 h. The sintering process was conducted in a lead-rich environment and fired in closed alumina crucibles to minimize lead oxide volatilization. After sintering process, the samples were cooled to the room temperature in furnace.

Structural Characterization

Phase analysis was carried out by Philips X-ray diffractometer for sintered specimens (PW-1710, CuKα radiation, Ni filter, 1°/min). Microstructure analysis was carried out for polished and fractured ceramic surfaces by JEOL JSM 840A scanning electron microscopy. The particle size of the calcined powder was studied by using a transmission electron microscope JEOL JEM 1200. Apparent densities of sintered ceramics were measured using the Archimedes method.

Dielectric and Piezoelectric Characterization

Electroded specimens were characterized for temperature dependent dielectric response (ε_{RT}, ε_{Tc}, T_c and tanδ) by using HP-4192A Impedance Analyzer at 1 kHz. Electroded specimens were poled in silicon oil bath at 100°C by applying a dc field 20 kV/cm. The piezoelectric planar coupling coefficients (k_p) of the poled samples were characterized using a HP-4192A impedance analyzer through the resonance and anti-resonance technique. The piezoelectric charge coefficients (d_{33}) were characterized using a Berlincourt piezo-d-meter.

RESULTS AND DISCUSSION

XRD analysis and tolerance factor

The XRD patterns of Sr modified PLZMT system can be observed in Figure 1. We have studied the effect of isovalent Sr addition on the phase transformation in PLZMT ceramic system. Basically, all samples present a pure perovskite structure. X-ray diffraction patterns indicated that undoped composition had shown coexistence of both ferroelectric rhombohedral and ferroelectric tetragonal perovskite phases which is consistent with the fact that the compositions are near the
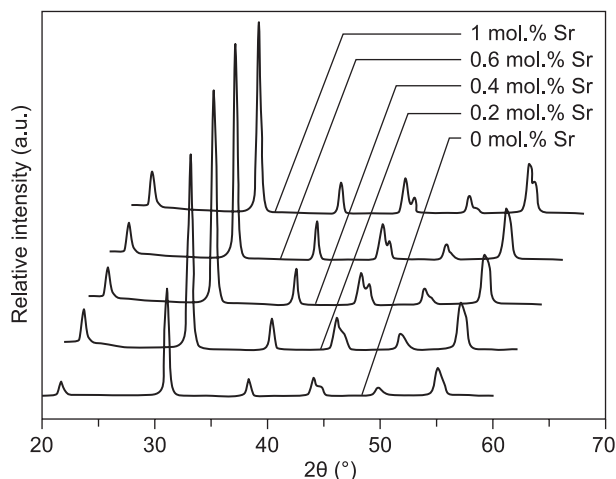

Figure 1. XRD patterns of Sr modified PLZMT system.

MPB. Whereas, increasing Sr content resulted in phase shift to ferroelectric tetragonal phase with peak splitting at (200) and (002), and (211) and (112), respectively, and at 1 mol.% Sr the phase attained intensified tetra-gonality. The tolerance factor and averaged electronegative difference have been represented in Table 2. Figure 1 clearly shows the influence of addition of Sr on the structure of the samples prepared. Indeed, increasing Sr content tends to transform the average symmetry to tetragonal one near MPB. Besides, no secondary phases have been detected. This has been verified through the tolerance factor.

In the perovskite structure, A-cations occupy the corner positions of the perovskite, the B-cations occupy the body-center position, and oxygen anions are situated at the face-centered positions. There are many types of phases, viz. ferroelectric, anti-ferroelectric, pseudocubic etc. The packing situation of the perovskite structure may be characterized by a tolerance factor t which can be calculated as given below:

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

where R_A is ionic radii of A-site cations, R_B is ionic radii of B-site cations and R_X is ionic radii of anion

If t is equal to 1, the packing is said to be ideal. If t is larger than 1, there is too large a space available for B ion, and therefore, this ion can move inside its octahedron. In general, t should be $0.9 < t < 1.1$ to form 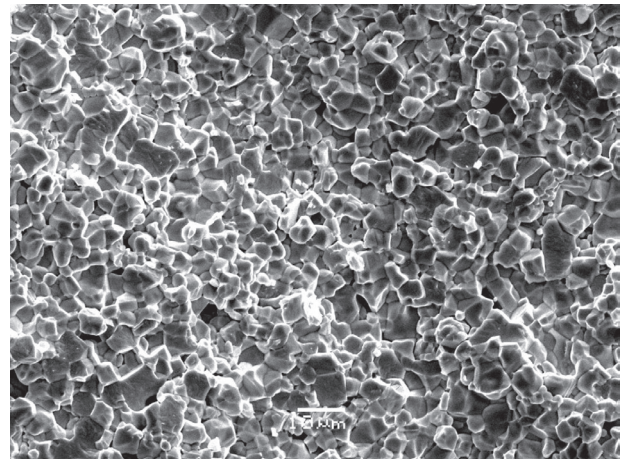a stable perovskite structure. In addition to using the tolerance factor (t) to categorize ferroic behaviour in perovskites, Halliyal and Shrout [14] found the (t) = tolerance factor and (e) = electronegativity for a range of perovskites showing the stability of the perovskites.

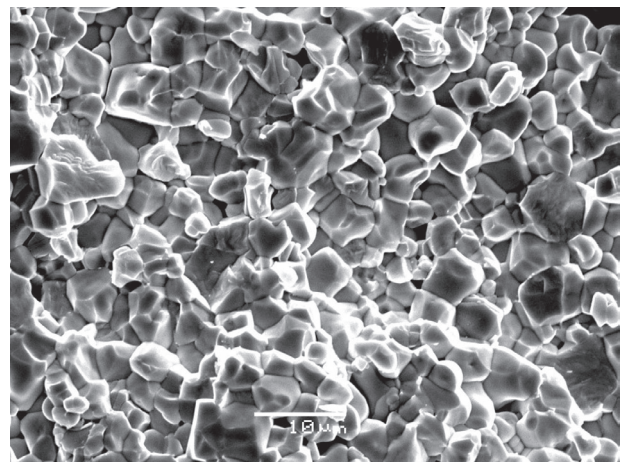$$e = (\chi_{AO} + \chi_{BO})/2 \qquad (2)$$

where χ_{AO} = electronegativity difference between A cation and oxygen and χ_{BO} = electronegativity difference between B cation and oxygen.

$$e = \frac{\{0.9896 - y\chi_{Pb-O} + 0.0104\chi_{La-O} + y\chi_{Sr-O} + [(0.9949)(0.529\chi_{Zr-O} + 0.471\chi_{Ti-O})] + 0.005\chi_{Mn-O}\}}{1.9999}$$

It can be determined that Mn^{2+} ($R_{Mn} = 0.67$Å) could occupy the B-site of PLZT lattice as acceptor owing to the similar ionic radius of Zr^{4+} ($R_{Zr} = 0.72$Å) and Ti^{4+} ($R_{Ti} = 0.605$Å) while the isovalent Sr^{2+} occupies the A-site of PLZT partially substituting Pb^{2+}. The ionic radius of isovalent Sr^{2+} ($R_{Sr} = 1.44$Å) is similar to Pb^{2+} ($R_{Pb} = 1.49$Å). Therefore, Sr^{2+} ions partially substitutes Pb^{2+} ions and La^{3+} ions enter the A-site occupied by Pb^{2+} while the vacancies are caused at B-site. The ionic radii

Table 2. Tolerance factor (t) and Averaged electronegative difference (e) of Sr modified PLZMT compositions.

Sr (mol.%)	t	e
0	0.98878	1.56649
0.2	0.98874	1.56770
0.4	0.98871	1.56891
0.6	0.98867	1.57012
0.8	0.98864	1.57133
1	0.98860	1.57254

a)

b)

Figure 3. SEM micrographs (fractured surfaces) of: a) 0.2 and b) 1 mol.% Sr modified PLZMT.

Figure 2. Apparent density of Sr modified PLZMT system.

of La^{3+} (R_{La} = 1.36Å) is less than Pb^{2+}, so the excess charge of the isovalent ions (Sr^{2+}) must be compensated by vacancies in the perovskite lattice. In PZT ceramics, at MPB, both tetragonal and rhombohedral phases coexist and it is known that dopant nature, type and concentrations can alter the phase stability. It is observed that increase in Sr content resulted in tetragonality. Incorporation of La^{3+} and Sr^{2+} into A-site sub-lattice of perovskite structure stabilizes tetragonal phase against co-existence of phases, as a consequence, the location of the MPB composition range is displaced towards PT-rich end enhancing the tetragonality in the lattice.

Microstructure and density

Figure 2 depicts apparent density of Sr modified PLZMT system. Figure 3 shows scanning electron micrographs (fractured surfaces) of 0.2 and 1 mol.% Sr modified PLZMT, respectively. Figure 4 represents transmission electron micrograph of 1 mol.% Sr modified PLZMT system. As can be observed from Figure 2 the high densification achieved is confirmed by its non-porous, fine grain boundary with homogeneous microstructure. It can be observed that the grain size increased with Sr addition and Mn content present in the system. Generally, Mn ions exist in Mn^{2+} and Mn^{3+} states in the perovskite structure [15] and prefer entering into the oxygenic octahedral center of the perovskite system substituting the B-site. The Mn ions will enter into the perovskite lattice to substitute Zr^{4+}/Ti^{4+} ions at B-site which causes oxygen vacancies and donor La^{3+} at A-site causes vacancies at B-site. The oxygen vacancies and lead vacancies are compensated by donor La^{3+} and isovalent Sr^{2+} at PT-rich end which enhances the transfer of mass and energy between reactants, thus improving the sintering behaviour and inducing an increase in grain size resulting in enhanced density. Addition of Sr content up to 1 mol.% resulted in significantly increased
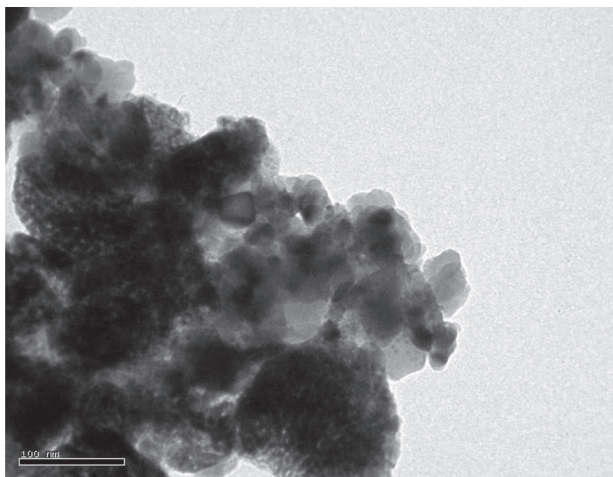
grain size. The transmission electron microscopy (TEM) studies for calcined powders revealed that fine and semi-agglomerated ceramic powders. The scanning electron micrographs indicated the increasing grain growth and densification of the ceramics.

Dielectric properties

Figure 5 shows the dielectric properties of Sr modified PLZMT system. It is observed that isovalent Sr^{2+} addition at A-site and acceptor Mn^{2+} substituting Zr^{4+}/Ti^{4+} at B-site resulted in increasing dielectric constant at room temperature while decreasing the Curie temperature. It is well known that at PT rich end the best electrical properties can be achieved. Manganese is believed to be an effective additive for the electrical properties based on the researches on lead titanate-based ceramics [16-18]. Most of the researchers ascribed the variation of electrical properties to the hard doping effect [17] and/or the sintering–assisting effect. In our study we observed that as Sr content increased, the Sr^{2+} ions partially substituting Pb^{2+} ions, diminishes the Curie temperature. The degree of the Curie temperature continuously decreased from undoped (298°C) to 196°C of 1 mol.% Sr, respectively. The dielectric maximum (ε_{Tc}) was maximum at y = 1 (ε_{Tc} = 10974). It is observed for y = 1 mol.%, the dielectric constant is maximum (ε_{RT} = 1497). The Ti-rich compositions tend to react with the PbO-rich atmosphere during sintering resulting in high density in turn influencing the dielectric constant. The higher the density (pore-free ceramics), the higher the dielectric constant and lower the dielectric loss. The dielectric loss (tanδ_{RT}) gradually decreased from undoped to 1 mol.% Sr in the series. It is reported that for isovalent doping, the substituting ions had same valency and nearly same ionic size as the replaced ions [19]. Since, Mn^{2+} substitute (Zr,Ti)$^{4+}$, and Sr^{2+} substitute Pb^{2+} in PLZT system which could have enhanced the dielectric properties. The isovalent Sr and lead vacancies along with the sintering temperature aided the domain wall orientation enhanced

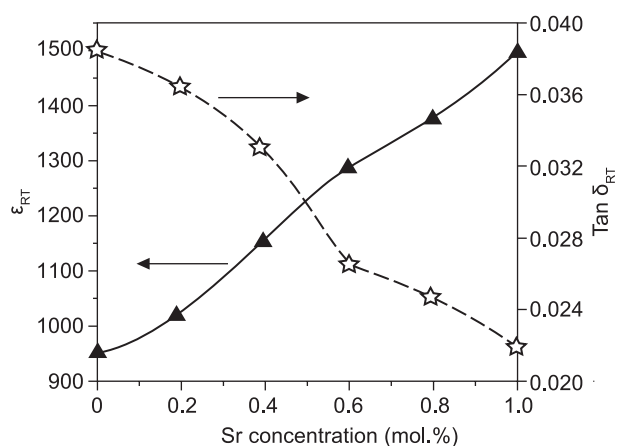Figure 4. TEM micrograph of 1 mol.% Sr modified PLZMT system.

Figure 5. Dielectric properties of Sr modified PLZMT system.

the polarization thereby increased the dielectric constant. It is observed that domain size and domain wall orientation in the PT-rich end (ferroelectric tetragonal structure) remarkably contributes to the dielectric and piezoelectric properties [20]. Thus, the charge balancing between the lead, cation (dopants) and oxygen vacancies due to the mixed influence of donor (La), isovalent (Sr) and acceptor (Mn) additives in the system enhanced the dielectric properties.

Piezoelectric properties

Figure 6 depicts piezoelectric properties of Sr modified PLZMT system. The grain size has strong effect on the magnitude of the dielectric and piezoelectric pro-perties. As the grains become finer under the same electric field the absolute values of the polarization increases in the system. One special significant merit for PZT ceramics is that doping foreign ions substituting part for the host atoms could modify their piezoelectric characterizations. This depends on the site occupied by the dopant in the ABO_3 perovskite structure. With increasing Sr content the piezoelectric properties of PLSZMT improved. The piezoelectric charge coefficient ($d_{33} = 534$ pC/N) and piezoelectric planar coupling coefficient ($k_p = 0.523$) exhibited optimum values with the increasing Sr content up to 1 mol.%. The increase of lead vacancies with the addition of donor dopants could generate electrons by ionization; most of the holes from lead vacancies are compensated by electrons from the donor level to enhance electrical properties of PZT, as a result, higher electromechanical properties could be achieved. Sr modified PLZMT piezoceramics were easily poled to facilitate the domain motion reorientation, thereby causing high dielectric and piezoelectric properties. The combined effect of donor and acceptor dopants resulted in higher piezoelectric coefficients. Therefore, these materials are promising for piezoelectric applications.
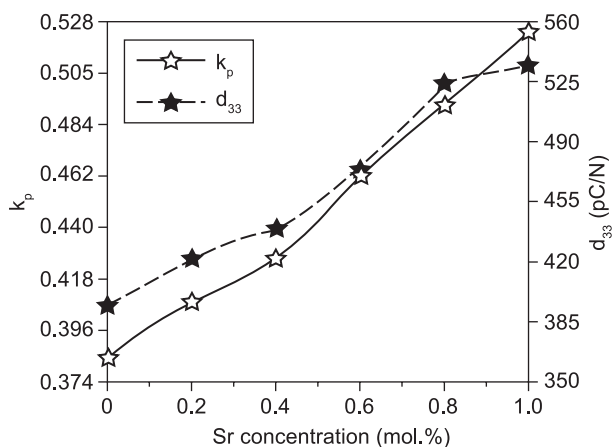
CONCLUSIONS

Soft and hard additives or donor and acceptor dopants causing or balancing lead, cation (dopants) and oxygen vacancies in the perovskite structure play a vital role in determining the electrical and electromechanical properties. The combinatory influence of donor (La), isovalent (Sr) and acceptor (Mn) modified perovskite system is reported. Increasing Sr content resulted in phase shift from coexistence of phases to ferroelectric tetragonal phase with peak splitting at (200) and (002), and (211) and (112), respectively, and at 1 mol.% Sr the phase attained intensified tetragonality. The oxygen vacancies and lead vacancies are compensated by donor La^{3+} and isovalent Sr^{2+} at PT-rich end which enhances the transfer of mass and energy between reactants, thus improving the sintering behaviour and inducing an increase in grain size and density. The charge balancing between the lead, cation and oxygen vacancies due to the mixed influence of donor, isovalent and acceptor additives in the system enhanced the dielectric properties. This study highlights the combined influence of donor and acceptor dopants and remarkable influence on dielectric and piezoelectric properties. Among the series, 1 mol.% Sr modified PLZMT resulted in higher ε_{Rt}, ε_{Tc}, low $\tan\delta_{Rt}$ and high piezoelectric coefficients which could be promising for piezoelectric applications.

Figure 6. Piezoelectric properties of Sr modified PLZMT system.

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