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Structural and dielectric properties of Sb-doped PLZT ceramics

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Abstract

Lead Zirconate Titanate (PZT), a member of ABO_3 (A = mono or divalent, B = tri to pentavalent ions) family is a solid solution of lead titanate and lead zirconate ceramics. PZT ceramics with compositions near Morphotropic Phase Boundary (MPB) offer good ferroelectric, piezoelectric and electrical properties. It is well established that the substitution of La^{3+} at the Pb site of PZT (PLZT) gives improved optoelectronic and piezoelectric properties of the materials. In most of the complex PLZT compounds (by increasing the La content in Zr or Ti rich compounds) broadened dielectric peaks or diffuse phase transitions with relaxation character in the transition temperature have been observed. For better understanding of the diffuse phase transition on double doping at the Pb site of PLZT near the MPB and the changes in physical or device parameters, we have carried out systematic studies on structural and dielectric properties of the compounds. In this paper, we report the study of the effect of paired dopants (La and Si) in PZT ceramics. Samples of Sb-doped PLZT were synthesized by high-temperature solid-state solution reaction technique. Preliminary crystal structure and microstructure of the compounds were studied by X-ray diffraction technique. Detailed dielectric studies of the samples suggest that they undergo ferroelectric paraelectric diffuse phase transition. Temperature dependence of dc resistivity of the compounds exhibits Negative Temperature Coefficient Resistance behavior.

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Keywords: C. Electrical conductivity; Dielectric permittivity; Diffuse phase transition; dc resistivity

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1. Introduction

Ferroelectric oxides of a general formula ABO_3 (A = mono or divalent ions, B = tri to pentavalent ions) are very important because of their potential applications, such as dynamical and volatile memory component, transducers, sensors and many other active and passive devices [1–3]. The device parameters of the system can be modified with suitable substitution at the A and B sites [4–7]. Lead zirconate titanate $Pb(ZrTiO_3)$ (PZT) is a solid-solution of ferroelectric $PbTiO_3$ and antiferroelectric $PbZrO_3$ in different Zr/Ti ratio. It is well established that in the range of morphotropic phase boundary, the electromechnical properties of lead zirconate titanate ceramics are more pronounced and exhibit a two-phase system. In case of exactly identical ceramic processing parameters, the dielectric and electromechnical properties of these ceramics depend strongly on the additives as well as on Zr/Ti ratio. It has been observed that Lead Lanthanum Zirconium Titanate (PLZT) undergoes a diffuse phase transition in which the transition is smeared out over a certain temperature interval, due to gradual change in physical properties in this temperature interval, mainly due to compositional fluctuation [8–10]. Several investigators [11,12] have studied the properties of PZT or modified PZT ceramics fabricated from high-temperature solid-state reaction technique. In order to tailor the physical properties of the PZT ceramics to suit for device fabrication, we have examined the effects of trivalent dopants at Pb site with certain Zr/Ti ratio [13–15]. Since not much attention has been paid to study the effect of pair dopants of PZT ceramics, we investigate the structural, electrical and other related properties of double doped PZT, i.e. $Pb_{0.9}(La_{1-z}Sb_z)_{0.1}(Zr_{0.55}Ti_{0.45})_{0.975}O_3$ (PLSZT) for z = 0.0, 0.3, 0.5, 0.7.

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2. Experimental

Polycrystalline samples of PLSZT with different Sb concentration mentioned above were synthesized by a high temperature solid-state reaction technique using high purity oxides; PbO (99.9% M/S Aldrich Chemical, USA), TiO_2 (99.9% M/S Sdfine-Chem Ltd.), La_2O_3 (99.99% M/S Indian Rare-Earth Ltd.), Sb_2O_3 (99.99% M/S Aldrich Chemical) and ZrO_2 (99.99% M/S Aldrich Chemical) in air atmosphere. The above compounds in a suitable stoichiometry were thoroughly mixed in an agate mortar for 4 h. The mixed materials were then calcined in a platinum crucible at 900 °C for 4 h. The process of grinding and calcination was repeated till homogeneous fine powder of desired PZT compound was obtained. Finally the pellets were sintered at 1230 °C for 2 h. A PbO rich atmosphere was maintained with $PbZrO_3$ powder to minimize lead loss during sintering. The formation and quality of PLSZT compound was checked with X-ray diffraction technique. The dielectric permittivity (ε) and loss tangent ($\tan\delta$) of the compounds were measured using a HP4623B LCR meter as a function of frequency at room temperature (RT) and temperature (RT to 650 K) at 10 kHz. The dc resistivity of the compounds was measured using a Keithley-617 programmable electrometer with a laboratory-fabricated experimental setup.

3. Results and discussion

The sharp and single diffraction peaks (Fig. 1) of the polycrystalline PLSZT compounds indicate homogeneity and better crystallization of the samples. The X-ray analysis indicates that the compounds were of single phase with tetragonal structure. All the reflection peaks were indexed using observed interplanar spacing d, and lattice parameters of PLSZT (Table 1)were determined using a least-squares refinement method. All the calculations were done using a computer program package Powdin [16]. A good agreement between calculated and observed d values of all diffraction lines (reflections) of PLSZT of different composition suggests that there is no change in the basic crystal structure of PLZT on substitution of Sb. However, some changes in the intensity of a few reflections have been observed which may be due to (a) variation in particle size, and (b) the presence of Sb with different *z* values.

Fig. 2 shows the variation of ε of PLSZT with temperature at a frequency of 10 kHz. Here, the dielectric permittivity increases gradually with an increase in temperature up to transition temperature (T_c, K) and then decreases. The region around the dielectric peak is broadened. The broadening or diffuseness of peak occurs mainly due to compositional fluctuation and/or substitution disordering

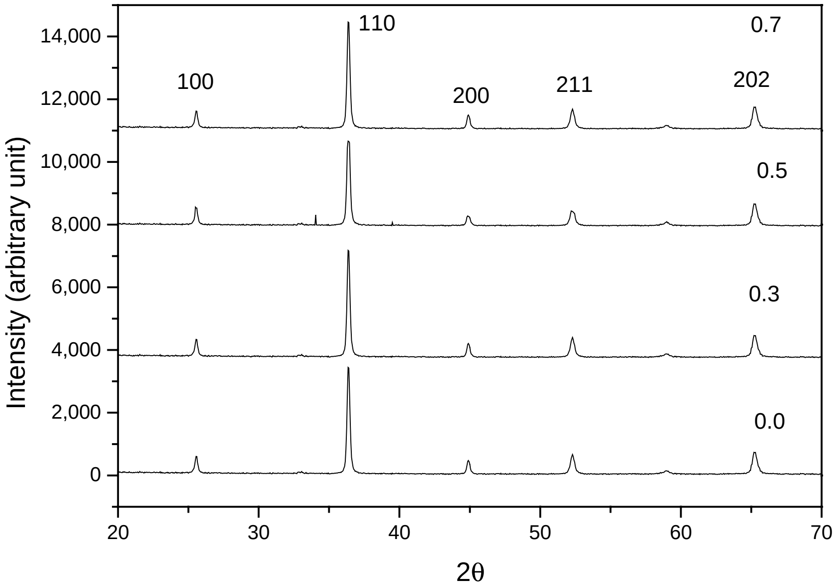

Fig. 1. XRD diffractogram of PLSZT ceramics.

Table 1
Lattice parameters (Å) of PLSZT with standard deviation of $\Delta d = 10^{-4}$ Å

Sample	*z*	Structure	*a*	*c*	*c*/*a*	Unit cell volume (Å^3)	Distortion	Measured density (g/cm^3)
PLZT	0.0	Tetragonal	4.0275	4.2717	1.06	69.2	0.04	7.45
PLSZT	0.3	Tetragonal	4.0533	4.8001	1.13	78.8	0.01	7.67
	0.5	Tetragonal	4.1322	4.7194	1.13	80.5	0.12	7.76
	0.7	Tetragonal	4.0610	4.6234	1.17	76.4	0.09	7.88

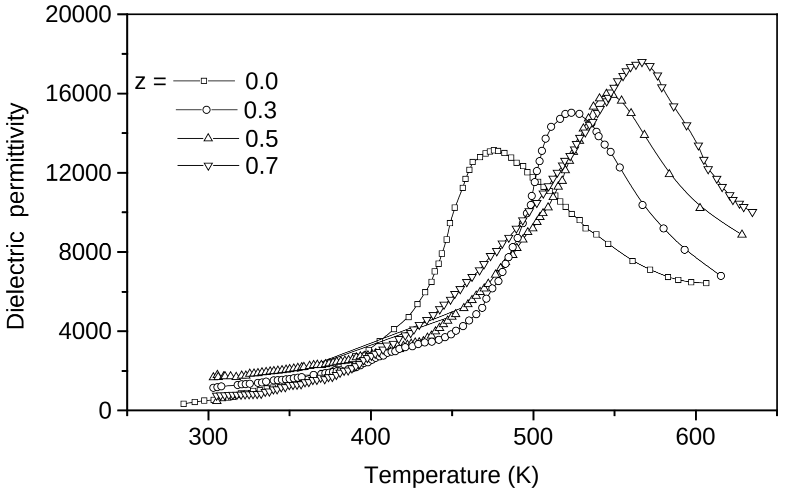

Fig. 2. Variation of (ε) of PLSZT as a function of temperature at 10 kHz.

in the arrangement of cations in one or more crystallographic sites of the PLSZT structure. The value of peak dielectric permittivity ($\varepsilon_{\max}$) increases with the increase of concentration of Sb up to $z = 0.7$.

The quantitative assessment of the diffusivity (γ) of the broadened peaks in the paraelectric phase was evaluated using the expression $(1/\varepsilon - 1/\varepsilon_{\max})$ versus $(T - T_c)^{\gamma}$ [17]. The value of γ for all compositions was extracted from the plot of $\ln(1/\varepsilon - 1/\varepsilon_{\max})$ versus $\ln(T - T_c)$ (Fig. 3) by fitting a straight line equation. The value of γ was found to be between 1 (normal Curie Weiss behavior) and 2 (completely disordered), which further confirmed the diffuse phase transition in the materials.

The ac electrical conductivity for all the samples was calculated from the conductivity relation $\sigma = \omega\varepsilon\varepsilon_0 \tan\delta$, where ε_0 is the vacuum dielectric permittivity and ω is the angular frequency. The activation energy E_a was evaluated from the $\ln\sigma$ versus T^{-1} graph (Fig. 4) and using the conductivity relation $\sigma = \sigma_0 \exp(-E_a/k_B T)$ where k_B is the Boltzmann constant [18,19]. An anomaly (a change in slope) was observed near the transition temperature T_c for all the compositions of PLSZT. The activation energy E_a of the compounds was calculated from the slope of $\ln\sigma_{ac}$ versus $1/T$ and is tabulated in Table 2. The value of activation energy in the paraelectric phase is found to be very low. A low value of activation energy has been observed in many Pb based ferroelectric complex compounds [20]. This may be due to ionic solids having a limited number of mobile ions being trapped in relatively stable potential wells during their motion through the solid. Due to a rise in temperature the donor cations are taking a major part in the conduction process. The donors have created a level (i.e. band-donor level), which is much nearer to the conduction band. Therefore, only a small amount of energy is required to activate the donors. In addition to this, a slight change in stoichiometry (i.e. the metal to oxygen ratio) in multi-metal complex oxides causes the creation of

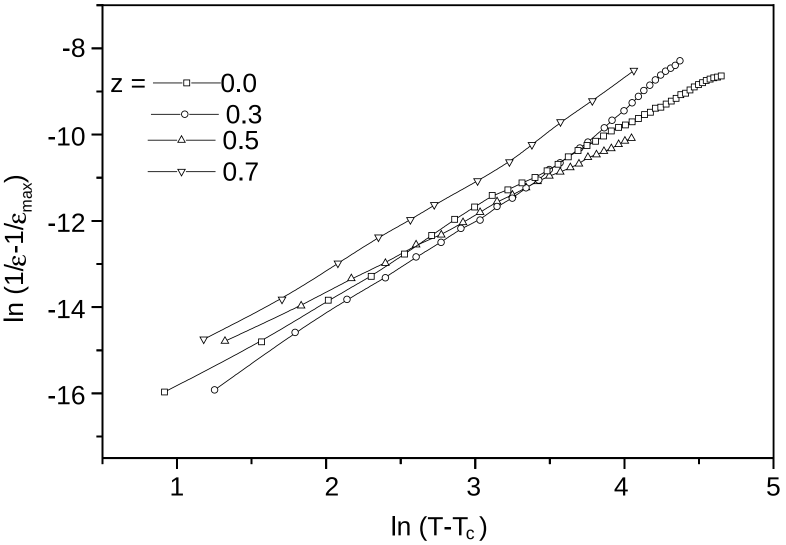

Fig. 3. Variation of $\ln(1/\varepsilon - 1/\varepsilon_{\max})$ with $\ln(T - T_c)$ at 10 kHz.

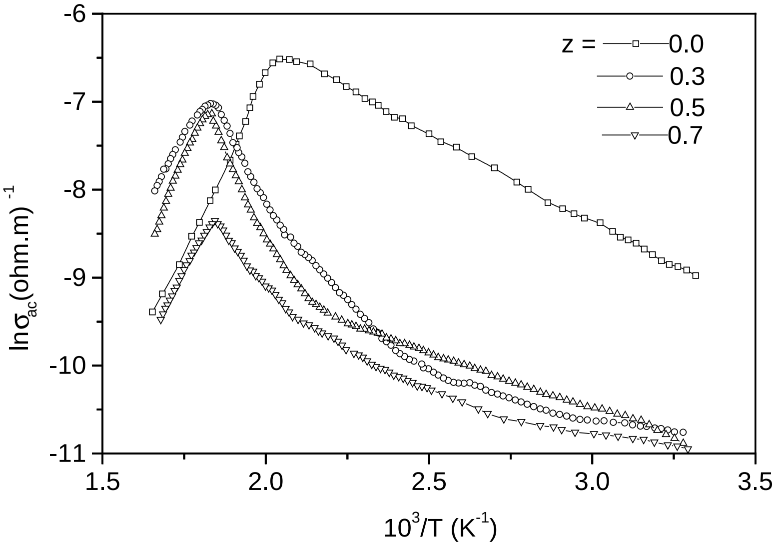

Fig. 4. Variation of $\ln \sigma_{ac}$ as a function of inverse of absolute temperature ($1/T$) of PLSZT at 10 kHz.

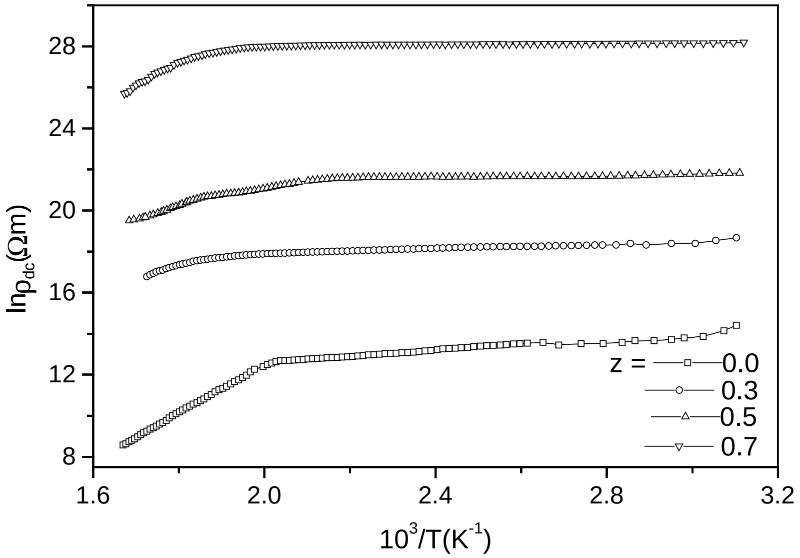

Fig. 5. Variation of dc resistivity ($\ln \rho$) with inverse of absolute temperature ($10^3/T$) of PLSZT.

large number of donors or acceptors, which creates donor or acceptor-like states in the vicinity of conduction or valence bands. These donors or acceptors may also be activated with small energy [21].

Table 2
Dielectric parameters of PLSZT ceramics at 10 kHz

Physical parameters	Compositions			
	$z = 0.0$	$z = 0.3$	$z = 0.5$	$z = 0.7$
ε_{max}	13133	15023	15978	17589
ε_{RT}	756	1670	1146	1165
$\tan \delta_{RT}$	0.03	0.04	0.05	0.03
T_c (K)	475	523	545	566
E_a (eV)	0.25	0.26	0.55	0.52
γ	1.83	1.86	1.89	1.91

Fig. 5 shows the temperature variation of dc resistivity ($\ln \rho$) for all PLSZT samples at constant biased electric field 0.1 kV/cm. The resistivity was found to increase with the increase in Sb concentration. This is an important feature for a ferroelectric material to be used for device applications. It is also seen that dc resistivity decreases with increase in temperature because of the addition of thermal energy. This variation also shows that the compound has a Negative Temperature Coefficient of Resistance (NTCR).

4. Conclusion

PLSZT ceramics have tetragonal crystal structure at room temperature exhibiting better homogeneity and formation of perovskite phase compounds. La and Sb pair doping in PZT exhibits many interesting feature, such as shift in transition temperature, diffuse phase transition and increase of dielectric constant. The compound also has the NTCR characteristic and can be used in many devices and system applications.

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