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Softening transitions in ferroelectric Pb (Zr, Ti) o_3 ceramics doped with neodymium oxide and lanthanum oxide

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Abstract: *The effect of La^{3+} and Nd^{3+} on dielectric and ferroelectric properties of $Pb(Zr_{0.52}Ti_{0.48})O_3$ was studied. The powders were prepared by "mixed oxide" route followed by calcinations at 800^0c for 4 h. XRD analysis of the calcined powders confirms the tetragonal phase in the undoped PZT, PLZT and PNZT ceramics were identified. SEM study of sintered pellets reveals the decrease in grain size with the change in dopant as 1at% Nd^{3+} and 1at% La^{3+} respectively. The dielectric properties were maximum for 1at% Nd^{3+} and 1at% La^{3+} respectively. Based on the above study, it is concluded that PZT doped with La^{3+} and Nd^{3+} produce softening transitions in PZT.*
Keywords: *lead zirconate titanate; mixed oxide; dielectric; softening transitions.*

I. Introduction

Lead zirconate titanate (PZT) is considered as one of the most widely studied piezoelectric materials for various applications. Currently, these materials are in the fore front for the application in aerospace vibration control, precision flow control as a replacement of solenoid-based flow control, fuel injection system in automobile industry, energy harvesting from different vibration sources, and so on [1–5]. These applications of PZT materials require the development of materials with very good properties. In the case of PZT, the properties are enhanced or tailor made by the addition of different dopants in "A" or "B" sites [6–11]. These dopants are mainly of two types: "donor" dopants, such as La^{3+}, Nb^{5+}, Ce^{3+} and Ta^{5+}, which produce "soft" PZT; "acceptor" dopants, such as K^+, Na^+, Sc^{3+} and Fe^{3+}, which produce "hard" PZT. The soft dopants facilitate the domain wall motion; thereby, the electronic properties are much better compared to undoped PZT. La is one of the most widely studied dopants in PZT system [12–15]. Haertling [12] reported that La^{3+} increases the squareness of the hysteresis loop and decreases the coercive field (E_c), improves the dielectric constant, electromechanical coupling coefficient, mechanical compliance (S) and enhances the optical transparency. Xiang *et al*. [13] reported that lanthanum substitution increases the level of diffuseness of the phase transition and 7.6 mol% lanthanum-modified PZT exhibits relaxor behavior. They also reported the tetragonality of PZT decreases with the increase in La^{3+} concentration. Mohidden *et al*. [16] studied the effect of Nd -doped PZT and reported that the grain size decreases with the increase of Nd concentration and the phase transition is of diffused nature without relaxor behavior. They also reported that the dielectric constant and dissipation factor have shown strong lower frequency dispersion. Thamjaree *et al*. [17] studied the development of phase formation of Nd on PZT. However, there is hardly any study about the effect of combination of both La and Nd on properties of PZT. Therefore, in this study, an attempt had been made to study the effect of both the dopants on microstructure and dielectric properties of PZT. The lead zirconate titanate [Pb(Zr, Ti)O_3] ceramics, to which oxides such as La_2O_3, Nb_2O_5, Fe_2O_3, NiO, MnO_2,IrO_2, ThO_2, WO_3, Cr_2O_3 and U_3O_8 have been added and studied by several workers (Jaffe *et al* 1971; Thomann 1972; Troccaz *et al* 1978; Wu *et al* 1982; Heywang and Thomann 1984; Moulson and Herbert 1990; Katiyar *et al* 1994, 1997) due to their wide application in various piezoelectric,ultrasonics and underwater devices along with various actuators and sensors in different fields of science and technology. The effect of addition of rare earth oxides in Pb(Zr, Ti)O_3 ceramics have mostly been related with the incorporation of La^{+3} ions into Pb(Zr,Ti)O_3 ceramics which increases their dielectric constant, electromechanical parameters and dielectric loss and decreases mechanical quality factor. It has been reported that the effect of doping of Sm^{+3} and Nd^{+3} are similar to La^{+3} doped lead zirconate titanate ceramics (Wu *et al* 1982). Some of the dielectric and electromechanical parameters have been reported for few compositions of Nd_2O_3 added to Pb(Zr, Ti)O_3 near to morphotropic phase boundary (Thomann 1972; Tandon *et al* 1992), $Pb_{0.98}$ $Sr_{0.02}$ ($Li_{0.008}$ $W_{0.012}$ $Ti_{0.46}$ $Zr_{0.52}$)O3 (Wu *et al* 1982) and Pb($Zr_{0.95}$ $Ti_{0.5)}$$O_3$ ceramics (Xue *et al* 1990). Inspite of these studies relatively meager information is available regarding the various dielectric and electromechanical parameters at different levels of Nd_2O_3 addition near to morphotropic phase boundary. It is well known that the electromechanical properties of PZT depend strongly on additives as well as the morphotropic phase boundary. The present investigation was undertaken to study the effect of Nd_2O_3 addition to lead zirconate titanate ceramic at 52/48 Zr/Ti ratio near the morphotropic phase boundary on the various dielectric Properties.

II. Experiment

PZT powders corresponding to compositions Pb (La or Nd)($Zr_{0.52}Ti_{0.48}$)O_3, were prepared using the standard solid state reaction route. The additives used are La and Nd. Weighed mounts of PbO, ZrO_2 and TiO_2 (Aldrich Chemical Company Inc, USA) powders were mixed and wet ball-milled in isopropanal using zirconium balls in a polypropylene jar for 5 h. The dried powder was crushed and calcined in a closed platinum crucible at a temperature of 850^0C for 2 h. The ball-milled powder was mixed with 2wt% PVA as binder. The powder was then pelletized in a steel die into pellets. The pellets were subsequently sintered at 1200^0C for 2 h in a closed crucible using PZ+10% PbO atmosphere powder which has a PbO partial pressure nearly the same as that of PZT [18,19]. Sintered pellets were leveled, polished and electrode with silver paste. The samples were then poled in a DC field of 2 kV/mm in a silicone oil bath for 30 min, and the piezoelectric, dielectric and ferroelectric properties were measured. The pellets were carefully weighed before sintering and also after sintering. For comparison, one batch of PZT without any modification was also sintered. The density of sintered pellets was greater than 95% of the theoretical density.

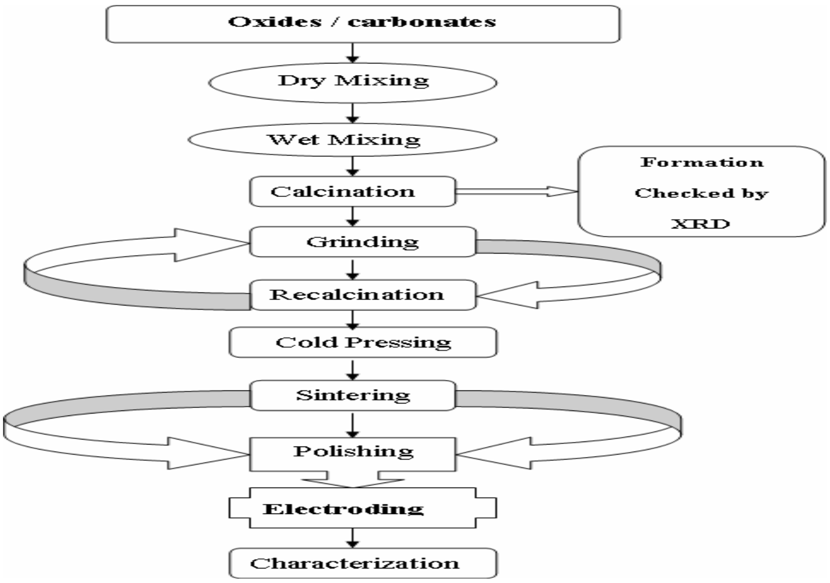

Fig. 2 Flow chart of the mixed oxide route for making PZT ceramics.

III. Characterizations

PZT phase formation was confirmed by X-ray diffraction (XRD) technique (M/s. Phillips, Holand).The morphology of the PZT sintered pellets was ascertained by scanning electron microscope (LEO440i). The dielectric measurements of the sample were done by HIOKI3532-50LCR HiTester instrument.

IV. Results and discussions

4.1. X-ray diffraction studies

Room temperature (30^0C) XRD patterns of the samples on calcined powders have been shown in "Fig. 3-5" .The sharp and single diffraction peaks indicate a better homogeneity and crystallization of the samples. All the diffraction peaks were indexed in different crystal systems (tetragonal, rhombohedra and monoclinic) using observed interplanar spacing 'd' in a computer program package ''PowdMult''[20].These d-values are compared with the single crystal data available in ASTM index card, lattice parameter measurements were done using the standard extrapolation method[21].The results are tabulated in "table 1".

XRD patterns of undoped, La $^{3+}$ -and Nd^{3+}-doped PZT samples are presented in "Fig.4 and 5". Pure tetragonal phase (characterized by tetragonal splitting) was found in undoped PZT and pure rhombohedra phase in higher dopant concentration (1at%). the XRD patterns of the La-doped and Nd-doped system confirming the presence of only the perovskite phase. In comparison with the undoped composition, c/a ratio increased for the La-doped and Nd-doped composition "Table.1" along with a increase in Tc "Table.2".

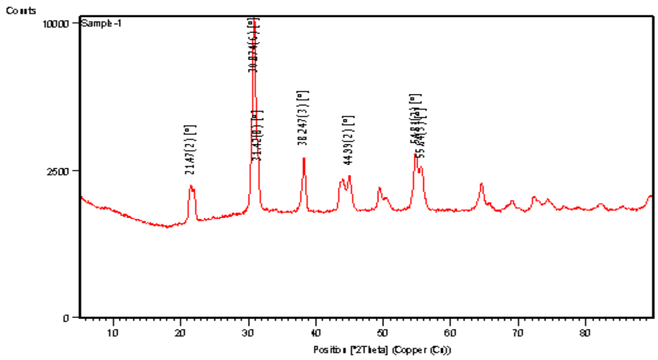

Fig.3. X-ray powder diffraction pattern for the system Pb $(Zr_{0.52}Ti_{0.48})$ O3.

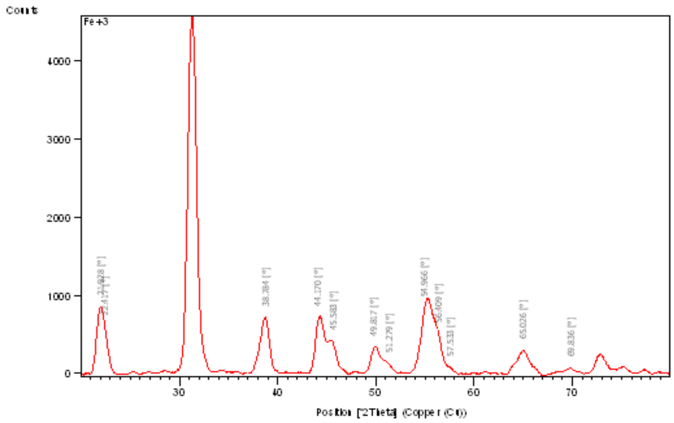

Fig.4. X-ray powder diffraction pattern for the system PbNd $(Zr_{0.52}Ti_{0.48})$ O3.

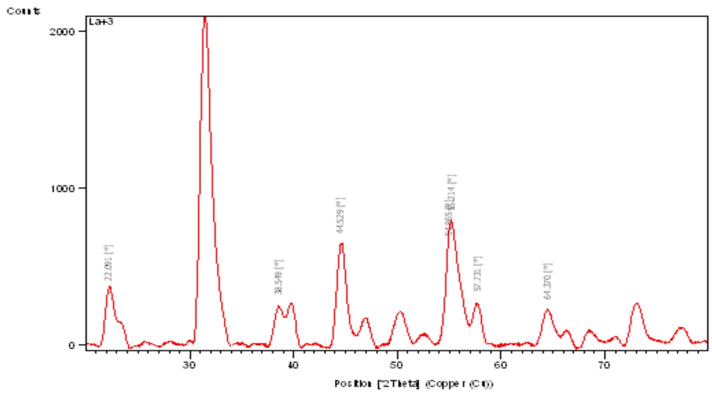

Fig.5. X-ray powder diffraction pattern for the system PbLa $(Zr_{0.52}Ti_{0.48})$ O3.

Table 1.

Element	Cell Parameters		c/a ratio
	c	A	
Undoped PZT	4.02638	4.03855	0.996
PLZT	4.0662	4.02058	1.0113
PNdZT	4.09750	4.05020	1.0116

Table 2.

Material	PZT	La^{3+}	Nd^{3+}
$Є_{RT}$	2300	3413	3500
$Є_{Tc}$	7250	18924	19000
Tc	360	156	182

4.2. Micro structural analysis

From the SEM micrographs, the micro structural characteristics of samples can be obtained in order to confirm the fabrication conditions. The microstructures of pure PZT without dopants and with dopants (La, Nd) are shown in “Fig: 6”.It obvious that the grain size is strongly influenced by the additive content. The undoped PZT has an average grain size of ~5 micro meters. however, it is noted that the impurity addition of both La^{+3} and Nd^{+3} ions results in an increased grain size. From these figures it is clear that the shape of the grains changes and size also increases with incorporation of La^{+3} and Nd^{+3} ions. When they substituted for Pb^{2+} reduction in oxygen vacancies occur due to the addition of La^{+3} and Nd^{+3} ions which enhances the grain size. [22] Typical SEM pictures of chemically etched sintered pellets are presented in Fig.6. The grain size increases with the doped Nd^{3+} and La^{3+} respectively.

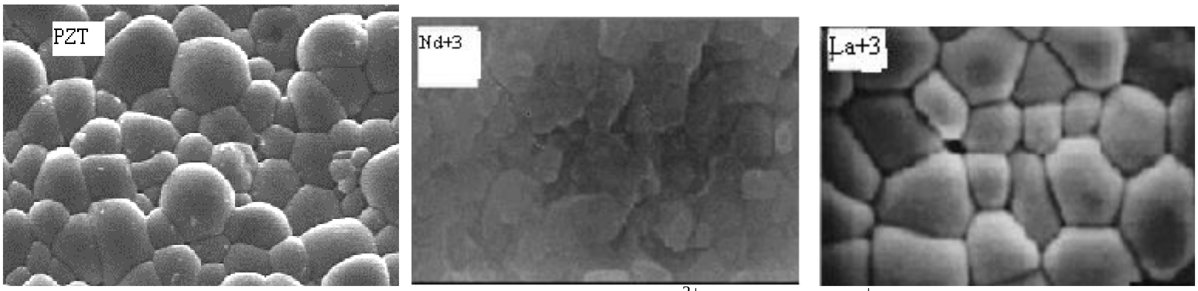

Fig.6. SEM pictures of chemically etched (a) undoped, (b) Nd^{3+} doped, (c) $La3^{+}$ doped PZT calcined pellets.

4.3 Dielectric properties

The dielectric constant of PZT samples are presented in “Fig.7”. The dielectric constant was maximum for samples with 1at% Nd^{3+} and also for samples with 1at% La^{3+}. As per micro structural study, the grain size was maximum at these compositions. i.e., the increase in grain size decreases the volume fractions of grain boundaries. Therefore, increasing the domain wall mobility thus increases the dielectric constant. As expected, the loss factor trend was opposite to that of dielectric constant.

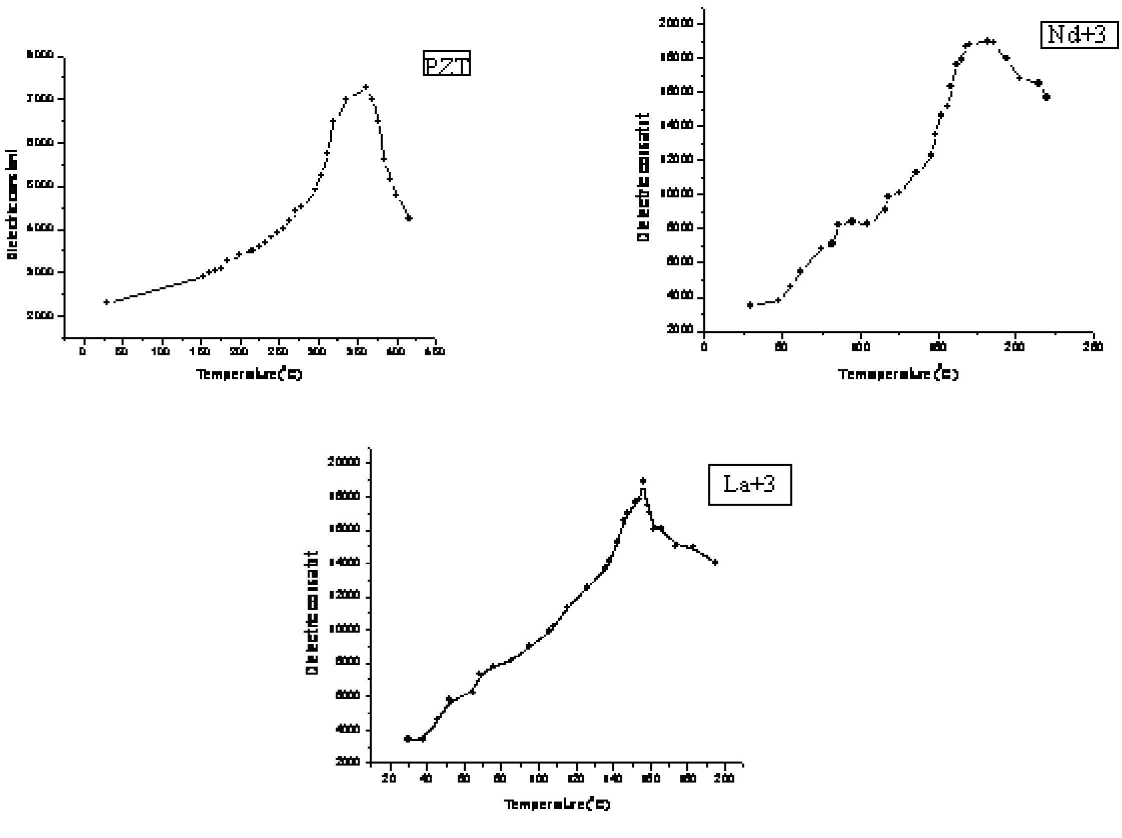

Fig.7. Temperature dependence of dielectric constant (ε) of the PZT ceramics at 1kHz.

V. Conclusions

In this dissertation, the structure and properties of Pb (Zr_xTi_{1-x}) O3-based piezoelectric ceramics added with Lanthanum, Niodium, Sodium and Potassium were investigated using mixed-oxide ceramics synthesis method. Structural analysis was done using Riveted refinement with Fullprof software. The fabrication ferroelectric ceramics starts with powder preparation. The powder is then pressed to the required shapes and sizes, and the green shapes are in turn processed to mechanically strong and dense ceramics. The more important processes that influence the product characteristics and properties are powder preparation, powder calcining and sintering. The next steps are machining, electroding and poling: application of a DC field to orient the dipoles and induce piezoelectricity. Pb ($Zr_{0\cdot52}Ti_{0\cdot48}$) O3 ceramics modified with monovalent and trivalent additives are prepared using the standard solid state reaction route. The additives used are La and Nd.

XRD is an analytical and most common technique for the study of crystal structure and atomic spacing. It is also used for the identification of phase of a crystalline material and also provides information on unit cell dimensions. The sharp and single diffraction peaks indicate a better homogeneity and crystallization of the samples.

Scanning electron microscopy is used to study the microstructure and topographies of the sample. From the SEM micrographs of PZT, PLZT, PNdZT. It can be seen that the grain distributions on the individual dense single-phase compositions are almost uniform at the surface, which are mostly spherical. The average grain sizes of PZT, PLZT, and PNdZT do not follow any correlation among them. it is noted that the impurity addition of both La^{+3} and Nd^{+3} ions results in an increased grain size. Ceramics with acceptor additives are characterized by lower dielectric constants, low dielectric losses. This is analogous to the behavior of soft PZT doped with donor ions(La^{+3} or Nd^{+3}). It was observed that the conductivity in all the cases was on the rise up to the Tc and afterwards the conductivity reduces with the increase of temperature. When the higher valence ions; such as La^{3+}, Nd^{3+}, they increase the resistivity of ceramics. Based on the study of microstructure and dielectric properties. It is concluded that Nd^{3+} and La^{3+} exhibit same properties. They enhance the electrical properties and resulting soft PZT.

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