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Effect of rare earth (La, Nd, Sm, Eu, Gd, Dy, Er and Yb) ion substitutions on the microstructural and electrical properties of sol-gel grown PZT ceramics

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Abstract

Polycrystalline samples of $(Pb_{0.92}R_{0.08})(Zr_{0.6}Ti_{0.4})_{0.98}O_3$ (R = La, Nd, Sm, Eu, Gd, Dy, Er and Yb) (PRZT) were sol-gel grown. The structural and microstructural properties of the compounds were examined through XRD, SEM, and TEM techniques. Detail analyses of the dielectric constant at different temperatures (30–430 °C) at 10^4 Hz suggest that the compounds (except Yb doped PZT) undergo diffuse phase transition of the second order. Piezoelectric and polarization studies provided some interesting physical parameters useful for device applications.

Keywords: Dielectric properties; Phase transitions; PZT; Sol-gel process; X-ray methods

1. Introduction

There has been considerable interest in the solid solutions of lead zirconate–titanate, $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) with a perovskite ABO_3 type (A = mono or divalent, B = tri-hexavalent ion) structure due to its possible forefront applications in the areas of research as well as in industrial applications.[1–6] A considerable amount of works have been done on modified PZT ceramics prepared from high-temperature solid-state reaction technique.[7–10] It is found that the properties of PZT are very much sensitive to its compositional fluctuations near the morphotropical phase boundary (MPB), particle size, doping, calcination and sintering temperature.[1,3,7,11] In recent years, sol-gel processing of ceramics has attracted greater interest because of its inherent advantages as compared to other conventional processing techniques.[12–14] The sol-gel process confers low calcination and sintering temperature, a high degree of molecular mixing, chemical homogeneity and good control of stoichiometry. In addition, smaller particle size offers a higher rate of densification both due to an increase in the driving forces for sintering and due to a smaller distance of mass transport needed to fill the pores permitting the lowering of sintering temperature and the achievement of the fine grain ceramics.[12–16]

Although a large amount of work has been carried out on the modified PZT with its various Zr/Ti ratio, no report has been made on the systematic effect of rare-earth ions substitution at Pb-site with Zr/Ti = 60/40. This particular composition has been selected due to its proximity to MPB. The objective of this work is to report the systematic comparative study on the crystal structures, microstructures, electric (dielectric, polarization), and piezoelectric properties for better understanding the nature of phase transition in sol-gel grown $(Pb_{0.92}R_{0.08})(Zr_{0.60}Ti_{0.40})_{0.98}O_3$ (R = La, Nd, Sm, Eu, Gd, Dy, Er and Yb) (here after denoted as PRZT) ceramics and finding their suitability towards device application on which not much have been reported.

2. Experimental

The precursors used to prepare the polycrystalline PRZT samples were high purity (99.99%)

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$Pb(CH_3COO)_2{\cdot}3H_2O$, $(CH_3COO)_3R{\cdot}H_2O$, $Zr(C_3H_7O)_4$, and $Ti[(CH_3)_2CHO]_4$. Glacial acetic acid and deionized water were used as solvents while ethylene glycol was used as an additive in order to get a monolithic gel. The individual sols were prepared following the procedures outlined in Refs. 15 and 16. The oven-dried powdered gels were calcined at 550 °C for 15 h to get fine and homogeneous powders. The powders were cold-pressed into pellets at 6×10^7 kg m^{-2} pressure using a hydraulic press. The pellets were then sintered conventionally at four different temperatures, 1000, 1100, 1200 and 1300 °C for 2 h.[11,17,18] During sintering, $PbZrO_3$ powder was used as a lead source in the crucible to minimize volatilization of lead. The sintered ceramic samples of about 1 cm diameter were ground to give parallel plates of 1 mm thickness, and polished with 1 μm diamond paste to a smooth surface finish. The density of the sintered pellets was measured by the Archimedes' method and was found to be 97–98% of the theoretical density.

The formation and quality of the desired compounds were checked by X-ray diffraction (XRD) technique with powder diffractometer (Philips PW 1877) using CuK$_\alpha$ radiation (λ = 1.5418 Å) in a wide range of Bragg angle ($20° \leqslant 2\theta \leqslant 70°$) at room temperature with the scanning rate 3° min^{-1} on powders as well as on sintered pellets.

The microstructures of the samples were analysed by scanning electron microscopy (SEM) (CAMSCAN 180) and transmission electron microscopy (TEM) (JEM 200 CX).

Silver electrodes were applied to both surfaces of the annealed ceramic samples and then fired-on in an oven at 150 °C for 1 h for a complete removal of moisture before electrical measurements. The dielectric constant (ε) and tangent loss ($\tan\delta$) of the samples were obtained using a GR 1620 AP capacitance measuring assembly, as a function of frequency (400–10^4 Hz) at room temperature and as a function of temperature (30–430 °C) at frequency of 10^4 Hz.

The temperature variation of saturation polarization (P_s) and coercive field (E_c) of the samples were recorded at 50 Hz using a dual-trace oscilloscope attached to a modified Sawyer-Tower circuit.

The electrical poling of the samples was carried out under a dc field of 15 kV/cm for 1 h in silicone oil bath below their transition temperature. The poled samples were then kept, after which, piezoelectric coefficient (d_{33}) measurements were carried by Berlincourt d_{33} piezometer at 25 Hz.

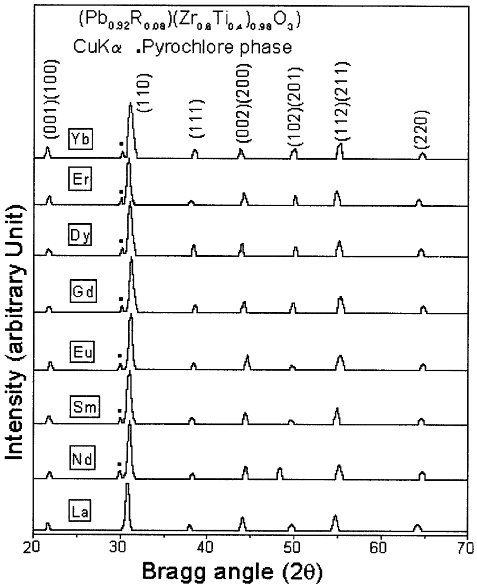

Fig. 1. Comparison of XRD of PRZT compounds.

3. Results and discussion

Room temperature (30 °C) XRD patterns of the PRZT samples on calcined powders have been compared in Fig. 1. 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, rhombohedral and monoclinic) using observed interplanar spacing '*d*' in a computer program package "PowdMult".[19] A tetragonal unit cell was finally selected on the basis of the best agreement between calculated and observed interplanar spacing '*d*' of all the diffraction lines of individual PRZT, and minimum $\Sigma\Delta d = \Sigma(d_{obs}-d_{cal})$. Hence the studied PRZT(8/60/40) belongs to tetragonal phase near MPB.[20,21] The tetragonal cell parameters refined by a least-squares method of the PowdMult software are given in Table 1. A small amount of pyrochlore phase is observed in all the compounds except PLZT, whose relative amount to the perovskite phase was estimated using the following peak area ratio

$$\%\text{Pyrochlore} = \frac{A_{\text{pyrochlore}}}{A_{\text{pyrochlore}} + A_{(110)}}$$

Table 1

Comparison of crystal system (CS), lattice parameters (*a* and *c*), density (*D*), average grain size (*s*) from SEM of PRZT compounds

R	CS	Cell parameters		*c*/*a*	*D* (g/cc)	*s* (μm)
		a	*c*			
La	T	4.0049	4.0102	1.0013	8.31	2.80
Nd	T	4.0585	4.3838	1.0802	7.41	2.27
Sm	T	4.0896	4.0953	1.0014	7.83	2.21
Eu	T	3.9606	4.0658	1.0266	8.41	2.50
Gd	T	3.9768	4.1908	1.0538	8.10	2.48
Dy	T	4.0042	4.0524	1.0120	8.28	2.43
Er	T	4.0142	4.0953	1.0202	8.16	2.25
Yb	T	4.0953	4.1154	1.0049	7.81	2.36

T = tetragonal.

where $A_{\text{pyrochlore}}$ and $A_{(110)}$ are the areas under the 100% (100) pyrochlore peak and (110) perovskite peak, respectively.[22] The relative amount of pyrochlore phase is estimated to be in the range of 2–3% in the samples (except PLZT). Moreover, no remarkable variation of the pyrochlore phase amount has been observed for the studied PRZTs sintered at other temperatures. The pyrochlore phase amount is negligibly small, and hence the materials still can be considered as single-phase. The works of Govindan et al.[23] and Sharma et al.[24] also suggested the possibilities of pyrochlore phase presence. Finally from the XRD study of different PRZTs a small change in lattice parameters is observed but a particular trend in their variation with different dopants could not be found out.

From the SEM micrographs of PRZT (Fig. 2) 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 and their average size is given in Table 1. The average grain sizes of different PRZTs do not follow any correlation among them.

Fig. 3 shows some of the representative TEM micrographs of PRZT calcined powders. When the powders were washed in alcohol under ultrasonic agitation, very uniform particles appear. It can be seen that the particles are well dispersed particularly for La-doped PZT and the average particle size is ~120 Å. However, the larger particles ⩽150 Å, showed some agglomeration.[25]

Fig. 4 shows the variation of dielectric constant (ε) and tangent loss (tanδ) as a function of frequency (400–10^4 Hz) at room temperature (30 °C). The dielectric constant was found to be almost independent of frequency. The tanδ initially decreases and then becomes constant for all the compositions studied here. This nature of variation of tanδ and ε with frequency was observed for other Zr/Ti ratio also.[26]

Fig. 5 shows the variation of ε of PRZT with temperature (0–430 °C) at 10^4 Hz. It has been observed that all the compounds (except Yb-doped PZT) undergo diffuse ferro-paraelectric phase transition at their respective phase transition temperatures, the corresponding Curie temperature (T_c) with dielectric maximum ($\varepsilon_{\max}$) have been given in Table 2. Interestingly we found that the $\varepsilon_{\max}$ attained the highest value for the PRZTs sintered at 1300 °C and became diminished for sintering at lower temperatures. However, the corresponding T_cs remain the same for the PRZTs sintered at various temperatures. This is probably due to the better densification in the samples. The detail effect of sintering temperature on PRZT ceramics along with the variation in grain size will be reported in a separate paper. Hence, through out this paper we only report the best results of PRZTs sintered at 1300 °C.

The observed broadening or diffuseness in the dielectric variation with temperature occurs mainly due to compositional fluctuations and/or substitutional disordering in the arrangement of cations in one or more crystallographic sites of the structure. This leads to the microscopic or nanoscopic heterogeneity in the compounds, with different local Curie points.[1] The degree of diffuseness in the dielectric peaks of the compounds was estimated using the relationship

$$\left(\frac{1}{\varepsilon}-\frac{1}{\varepsilon_{\max}}\right) \propto (T-T_c)^{\gamma} \qquad (1)$$

where ε is the dielectric constant at temperature T, $\varepsilon_{\max}$ is its maximum value at T_c, and γ is a measure of diffuseness. The plots of $\ln(1/\varepsilon - 1/\varepsilon_{\max})$ versus $\ln(T-T_c)$ for PRZT are shown in Fig. 6. It is observed that the variation is almost linear. The mean value of the exponent γ (diffusivity) for different system was extracted from these plots by fitting a straight-line equation. The value of γ was found (Table 2) to be nearly 2 (i.e. $1.4 \leqslant\ \leqslant 1.9$), which confirms that diffuse phase transitions occur in the materials with a high degree of disorder. The deviation of the phase transition behaviour from the Curie–Weiss type can be assumed to be due to disordering in the system. It is also observed that the reciprocal dielectric constant is a linear function of temperature on both sides of T_c except within the range of ±20 °C around it (Fig. 7). The ratio of the temperature gradients of the reciprocal dielectric constant for the ferroelectric and paraelectric phases is about 2:1 in the present study, which conclude the nature of the phase transition as second order.[27]

The ac conductivity was calculated using the relation $\sigma = \varpi\ \varepsilon\ \varepsilon_0\ \tan\delta$ where, ε_o is the vacuum dielectric constant, ϖ is the angular frequency. This relationship is

Table 2
Comparison of ε, tanδ, γ, T_c and E_a of PRZT compounds

R	ε_{RT}	tanδ_{RT}	$\varepsilon_{\max}$	tan$\delta_{\max}$	T_c (°C)	γ	E_a (eV)	P_r (μC/cm^2)	E_c (kV/CM)	d_{33} (pC/N)
La	3413	0.072	18924	0.016	156	1.56	0.53	21.90	6.65	569
Nd	2148	0.005	6577	0.007	182	1.68	0.25	8.84	6.61	269
Sm	737	0.071	5594	0.051	284	1.70	0.18	7.58	5.51	151
Eu	404	0.080	7588	0.070	349	1.92	0.26	5.41	5.28	53
Gd	187	0.098	12864	0.064	337	1.91	0.63	8.31	3.11	–
Dy	528	0.085	12673	0.014	368	1.48	0.33	6.75	3.97	84
Er	422	0.046	11123	0.031	354	1.40	0.86	10.78	7.22	75
Yb	194	0.029	–	0.086	–	–	–	–	–	–

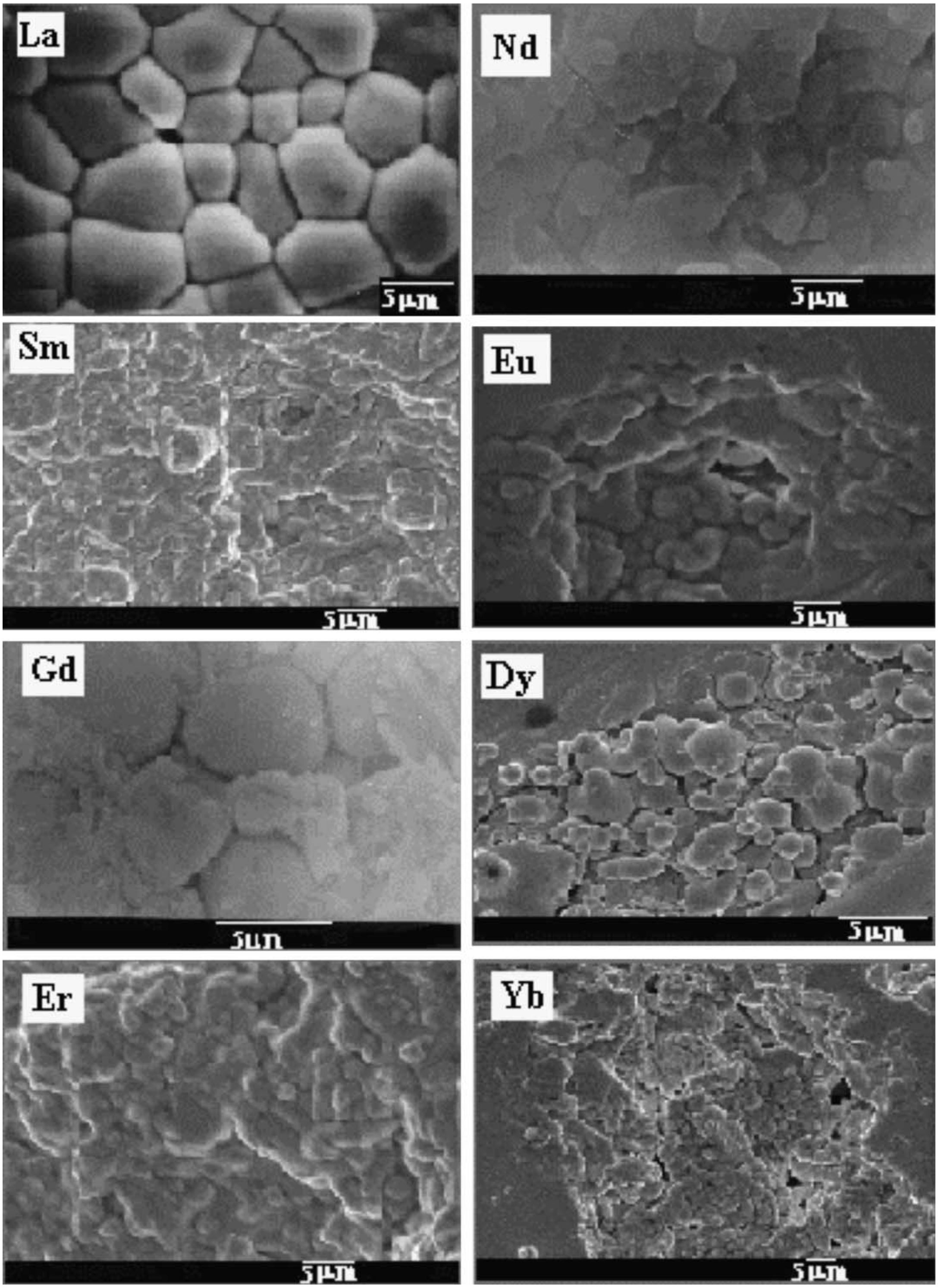

Fig. 2. SEM micrographs of PRZT compounds.

more meaningful as the pure charge transport is the major contributor to the loss mechanisms. Again, this is not always true in the case of polycrystalline materials. The peaks in the loss tangent plots (Fig. 8) suggest that for certain temperature interval from RT, generally the dissipation factors are relatively high indicating the participation of different kinds of loss mechanisms: for instance, one such mechanism may be due to porosity leading to a parallel conduction. It is, therefore, difficult to separate out the effects of the loss contributions from different loss mechanisms in order to isolate the pure charge transport mechanism, which in turn could be used

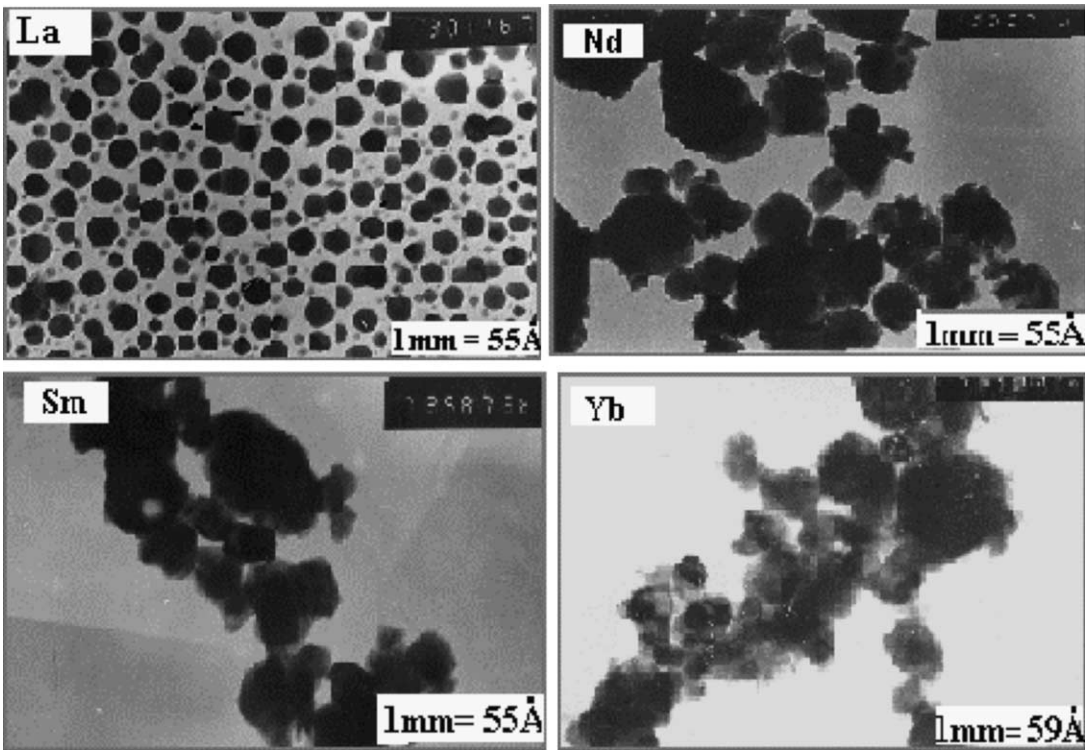

Fig. 3. Transmission electron micrographs of PRZT compounds.

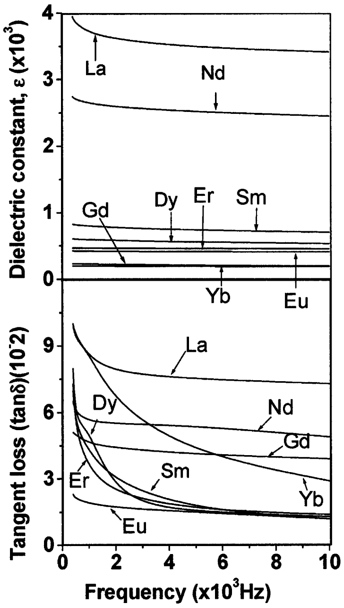

Fig. 4. Variation of dielectric constant (ε) and tangent loss (tanδ) of PRZT as a function of frequency at room temperature.

in the estimation of conductivity by using the equation. Hence the use of the conductivity relation given above is to some extent approximate at regions where the loss tangents are quite high and is more realistic at temperatures where the loss tangents are appreciably low. The conductivity of the samples was estimated using the above mentioned conductivity relation. It was observed

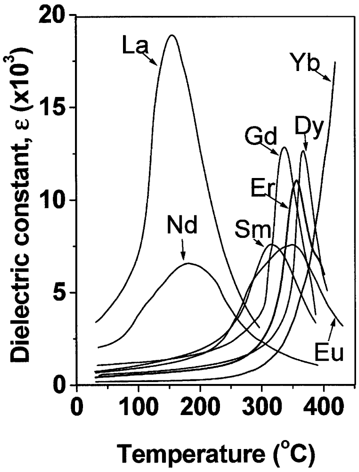

Fig. 5. Variation of relative dielectric constant (ε) of PRZT as a function of temperature at 10^4 Hz.

that the conductivity in all the cases was on the rise up to the T_c and afterwards the conductivity reduces with the increase of temperature (Fig. 8).

The activation energy (E_a) of all the compounds was estimated using the relation $\sigma = \sigma_0 \exp(-E_a/K_B T)$ in which, K_B is the Boltzmann constant. The activation energy of all the as estimated in the ferroelectric region near T_c (Fig. 8), where the charge carrier transport mechanism is all-important and significant. The values E_a are tabulated in Table 2. A low value of activation energy has been observed in many Pb-based ferroelectric complex compounds.

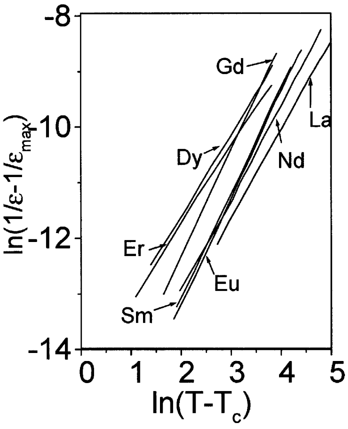

Fig. 6. Log–log plots of Eq. (1) for measurements on PRZT at 10^4 Hz.

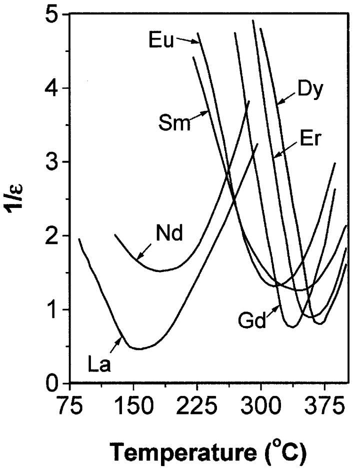

Fig. 7. Temperature variation of $1/\varepsilon$ of PRZT at 10^4 Hz.

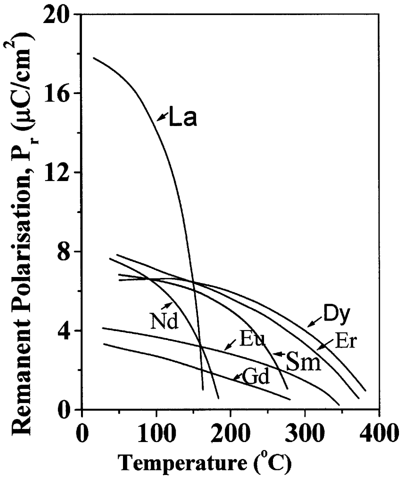

Fig. 9. Temperature dependence of spontaneous polarization (P_s) of PRZT at 50 Hz.

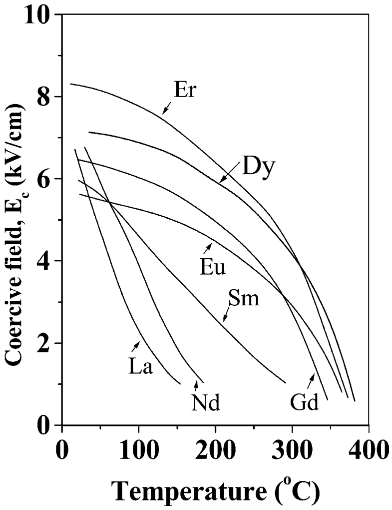

Fig. 10. Temperature dependence of coercive field (E_c) of PRZT at 50 Hz.

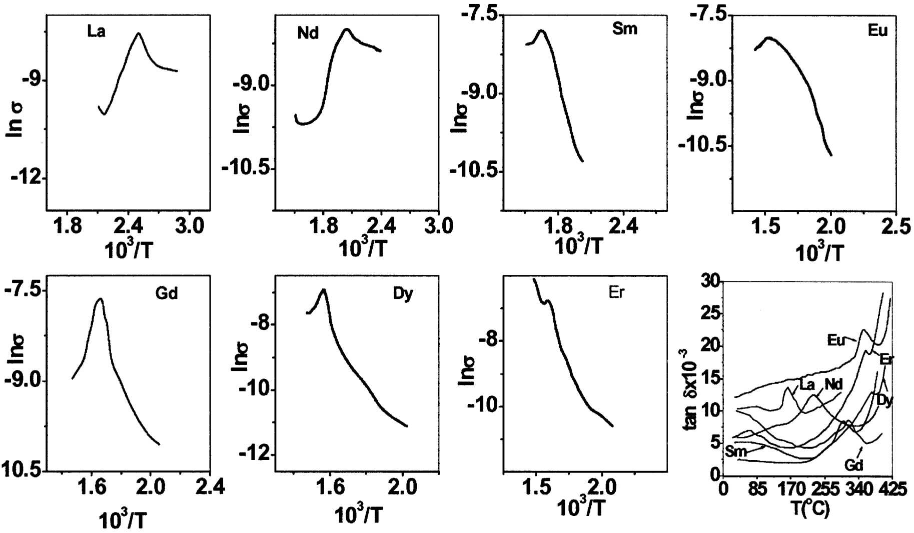

Fig. 8. $\ln\sigma$ (mho m^{-1}) vs. $10^3/T$ (K^{-1}) plots of PRZT at 10^4 Hz.

A high electric field (~20 to 25 kV cm^{-1}) was required to obtain saturation polarization. The remanent polarization (P_r) and coercive field (E_c) were determined from the hysteresis loop. It is observed that the hysteresis loops at 30 °C for all the compounds are memory type. This may be the cause of higher tetragonality in the compound.[28] Temperature dependence of P_r and E_c of the materials are shown in Figs. 9 and 10, respectively. It has been observed that the coercive field and polarization gradually decrease with temperature, which probably results due to the diffuse phase transition in the studied PRZTs. The slow and continuous changes in both the parameters indicate a second order phase transition in these compounds.[28]

4. Conclusion

In the present work we have reported the unique effects of adding a fixed amount (8 mol%) of certain rare-earth additives on the structural, dielectric, polarization, and piezoelectric properties of near MPB composition of PRZT. The main conclusions can be summarized as follows: X-ray diffraction studies confirmed tetragonal symmetry for all the studied samples. A very good agreement is observed between the experimental and calculated *d*-values in XRD. Though a poor pyrochlore phase exists in these materials, fabricating a pure single phase materials may not be necessarily give a high dielectric constant. From SEM micrographs no systematic variation in the grain size with different dopants is observed. From our dielectric study, we can prescribe the above materials as good dielectric materials due to their high dielectric constant and low tangent loss. Studies of the electrical properties of the PRZT compounds lead to a stable ferroelectric state over a wide range and the phase transition in these materials is diffuse-type and of second order. Moreover, the results obtained from the piezoelectric measurements show that the PRZT compounds are of the soft type and hence suitable for phonographic pick-up and similar devices. The observed differences in the electrical parameters are caused by the distortion in the perovskite structure. This may be due to the different size of the additives.

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References

1. Lines, M. E. and Glass, A. M., *Principles and Applications of Ferroelectrics and Related Materials*. Oxford University Press, Oxford, 1977.
2. Buchanan, R. C., *Ceramic Materials for Electronics*. Marcel Decker, New York, 1986.
3. Smyth, A. P., *Dielectric Behaviour and Structure*. McGraw Hill Publishers, New York, 1955.
4. Herbert, J. M., *Ceramic Dielectrics and Capacitors*. Gordon and Breach Science Publishers, New York, 1985.
5. Cross, L. E., Ferroelectric materials for electromechanical transducer applications. *Jpn. J. Appl. Phys.*, 1995, **34**, 2525–2532.
6. Pilgrim, S. M., Sutherland, A. E. and Winzer, S. R., Diffuseness as a useful parameter for relaxor ceramics. *J. Am. Ceram. Soc.*, 1990, **73**, 3122–3125.
7. Haertling, G. H., PLZT electrooptic materials and applications—a review. *Ferroelectrics*, 1987, **75**, 25–55.
8. Haertling, G. H., Ferroelectric ceramics: history and technology. *J. Am. Ceram. Soc.*, 1999, **82**, 797–818.
9. Takahashi, M., Electrical resistivity of lead zirconate titanate ceramics containing impurities. *Jap. J. Appl. Phy.*, 1971, **10**, 643–651.
10. Wei Hng, Q. and Hoon, H., Effects of dopants on the microstructure and properties of PZT ceramics. *Mater. Chem. and Phys.*, 2002, **75**, 151–156.
11. Snow, G. S., Fabrication of transparent electrooptic PLZT ceramics by atmosphere sintering. *J. Am. Ceram. Soc.*, 1973, **56**, 91–96.
12. Noheda, B., Gonzalo, J. A., Cross, L. E., Guo, R., Park, S.-E., Cox, D. E. and Shirane, G., Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite: The structure of $PbZr_{0.52}Ti_{0.48}O_3$. *Physical Review B (Condensed Matter)*, 2000, **61**, 8687–8695.
13. Setter, N. and Waser, R., Electroceramic materials. *Acta Mater.*, 2000, **48**, 151–178.
14. Brinker, C. J. and Scherer, G. W., *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*. Academic Press Publishers, New York, 1990.
15. Yi, G., Wu, Z. and Sayer, M., Preparation of $Pb(Zr,Ti)O_3$ thin films by sol gel processing: Electrical, optical, and electro-optic properties. *J. Appl. Phys.*, 1988, **64**, 2717–2724.
16. Shannigrahi, S. R., Choudhary, R. N. P., Acharya, H. N. and Sinha, T. P., Characterizations of sol-gel grown (PbLa-Li)(Zr0.60Ti0.40)O_3. *J. Appl. Phys.*, 1999, **85**, 1713–1721.
17. Rukmini, H. R., Choudhary, R. N. P. and Prabhakara, D. L., Effect of sintering temperature on Na-modified PLZT ceramics. *Mater. Chem. and Phys.*, 2000, **64**, 171–178.
18. Rukmini, H. R., Choudhary, R. N. P. and Prabhakara, D. L., Sintering temperature dependent ferroelectric phase transition of $Pb_{0.91}(La_{1-z/3}Li_z)_{0.09}(Zr_{0.65}Ti_{0.35})_{0.9775}O_3$. *J. Phys. and Chem. Of Solids*, 2000, **61**, 1735–1743.
19. Wu, E., POWD, an interactive powder diffraction data interpretation and indexing program, ver. 2.1, , School of Physical Science, Flinders University of South Australia Bedford Park, S.A. 5042, Australia.
20. Shannigrahi, S. R., Choudhary, R. N. P. and Acharya, H. N., Structural and dielectric properties of Nd modified Pb(Zr0.60Ti0.40)O_3 ceramics. *Mat Sci Eng B- Solid*, 1990, **60**, 31–39.
21. Shannigrahi, S. R. and Choudhary, R. N. P., Structural and dielectric properties of sol-gel derived PLZT(x/60/40). *J. Electroceram*, 2000, **5**, 201–209.
22. Garg, A. and Agrawal, D. C., Effect of rare earth (Er, Gd, Eu, Nd, and La) and bismuth additives on the mechanical and piezoelectric properties of lead zirconate titanate ceramics. *Mater. Sci. and Eng. B*, 2001, **86**, 134–143.
23. Govindan, A., Sharma, H. D., Tripathi, A. K., Pillai, P. K. C. and Goel, T. C., Studies on the dielectric, piezoelectric, pyroelectric and structural properties of $(Pb_{1-x}Gd_x)(Zr_{0.6}Ti_{0.4})O_3$. *Ferroelectrics*, 1992, **134**, 217–222.
24. Sharma, H. D., Tripathi, A. K., Vijayraghwan, C., Goel, T. C.,

Pillai, P. K. C. and Govindan, A., Dielectric and pyroelectric characteristics of PZT doped with gadolinium. *Mater. Sci. Eng. B*, 1994, **25**, 29–33.

25. Akbas, M. A. and Lee, W. E., Characterisation and densification of PLZT powder co-precipitated from chloride–nitrate solutions. *British Ceramic Transactions*, 1996, **95**, 49–52.
26. Choudhary, R. N. P. and Mal, J., Diffuse phase transition in Cs-modified PLZT ferroelectrics. *Mat. Sci. and Eng. B*, 2002, **90**, 1–6.
27. Dekker, A. J., *Solid State Physics*. Macmillan, New York, 1991.
28. Moulson, A. J. and Herbet, J. M., *Electroceramics*. Chapman and Hall Publishers, New York, 1990.