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DIELECTRIC, FERROELECTRIC AND PIEZOELECTRIC PROPERTIES OF La $^{3+}$SUBSTIUTED PZT CERAMICS

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Lanthanum substituted lead zirconate titanate (PLZT) nanocrystallite with stichometry formula $Pb_{0.90}La_{0.10}$ $(Zr_{0.52}Ti_{0.48})$ O_3 have been synthesized by sol gel process. The effect of nanocrystallite on dielectric, ferroelectric and piezoelectric properties of La^{3+} substituted PZT was studied. The average crystallite size of the PLZT powder was 21nm.Variation of dielectric constant with temperature at 100 kHz frequency was studied. Dielectric constant (ε) of PLZT (10/52/48) pellet at Curie temperature (~288^{0}c) was found to be 10437. The ferroelectric hysteresis (P-E) loop of PLZT ceramic was studied as a function of applied electric voltage. Study of variation of piezoelectric coefficient (d_{33}) of PLZT pellet with varying polling field shows maximum d_{33} value was124pC/N at 40kv/cm.

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1. Introduction

The search for novel smart material is an extremely active field of research and to this purpose ferroelectric material has been under focus for last seven decades. Consequently a large number of materials showing different physical effects can be found within one structural family (perovskite, spinel, etc.). Lead zirconate titanate (PZT) with different physical property belongs to the noncentro symmetric ABO_3 perovskite type structure .Basically it is the solid solutions phase of the $xPbZrO_3$-(1-x) $PbTiO_3$ (0<x<1) binary system. It has optimum piezoelectric and electrostrictive properties for composition near the morph tropic phase boundary (MPB) ~52/48 [1-3]. The MPB is almost temperature indep endent phase boundary that separates the two ferroelectric phases the rhombohedral phases (F_RR3c) and the tetragonal phase (F_TP4mm) [4]. Lead based ferroelectric lead zirconate titanate has been considered for a wide range of piezoelectric and ferroelectric device applications such as transducers, actuators, sensors, hydrophones, electro-optical modulators [5-9].

The physical properties or device parameters of PZT can be tailored by synthesizing the material with improved processing techniques and making suitable substitutions at A or B-sites. To enhance its property, a wide variety of substitutions have been made at different atomic sites of PZT in its single crystal structure. The effects of substitution have been investigated extensively to improve its properties for various applications [10-12]. According to the rules of Goldschmidt, the substituted cation enters into the site (A o r B) in the ABO_3 perovskite structure if the ion and the substituted ion radii do not differ by more than 15%.

A wide variety of cations can be substituted in the perovskite structure .Generally, the do pants can be classified as isovalent substitute, acceptor and donor. The rare-earth ions

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(substituted at A-sites) have a marked influence on the physical properties of PZT. PZT substitute with La generally known as PLZT have been most widely known for their optical transparency, broad categories of composition and various electro-optic coefficients [9-11].

The size effects in piezoelectric has become vital because of their potential applications in under water sensor system and non volatile memory devices. The miniaturization of the component is accompanied by the need of reducing the grain size. So nano crystalline material is of great interest both from technology and application point of view [13-14].

According to the literature survey the nano PZT material have been prepared by several methods like hydrothermal [15], mechanical activation route [16], polymer precursor [17] and wet chemical co precipitation [18].

The so gel is one of the excessively used routes for the preparation of nano powders. This technique is particularly important for preparation of ceramics, since the mixing of reagents occurs on an atomic rather than a particular scale. This allows control over stichometry and is thus advantageous for synthesis of multi component oxide. The low processing temperature has been facilitating integration with semiconductor [19-21].

The study of nano crystallite structure shows enhance dielectric properties and dwindle in ferroelectric and piezoelectric properties of PZT [22-23].

In the present work PLZT nano ceramic is prepared by the metal alkoxide based sol-gel method. The dielectric, ferroelectric and piezoelectric property of the sample has been studied.

2. Experimental details

To prepare lanthanum substituted PLZT by sol-gel process, 2- methoxy ethanol (99.8%, Aldrich) has been used as the starting precursor and acetyl acetone (99.99%, Aldrich) has been used as the chelating agent. lead(II) acetate trihydrate(99.99%purity, Aldrich), Zirconium (IV)isopropoxide (70wt.% solution in 1-propanol,Ald rich) and titanium(IV) isopropoxide (97%purity, Aldrich) were used as the starting reagents and lanthanum (III)acetate trihydrate(99%purity, Aldrich) was used as the additive to prepare the PLZT precursor sol with Stoichiometry of $Pb_{0.9}La_{0.1}(Zr_{0.52}Ti_{0.48})O_3$.

Thermal behavior of the green gel was examined by thermo gravimetric (TG) and differential thermal analysis (DTA) with a heating rate of 10°C / min in the temperature range of 100°C -1000°C. The phase purity and homogeneity of the obtained sample was determined by powder X-ray diffractometry .X-ray diffraction (XRD) measurement was performed at 2θ values ranging from $15^0$and 70^0 using Philips X-ray diffractometer with Ni-filter CuKα radiation. The nanocrystalline PLZT calcined powder was granulating and mixed with Polyvinylalchol (PVA, 5% aqueous solution) in a mortar and pestle. The mixed powder was compacted to circular discs of 12 mm in diameter and ~1.5 mm in thickness by uniaxial pressing machine at 200Mpa. The binder was removed by heating the pellet at 550°C. Then binder burnout components were sintered at 1100^0C for 3 hours in a hermetically sealed alumina crucible in a muffle furnace. The surface morphology of the sintered samples was analyzed using scanning electron microscope (SEM, JEOL Model-T330).The electro ding of the sintered pellet was done by the silver paste. The dielectric constant of the sample was measured with the variation of temperature. The sample was poled at varying polling field at an elevated temperature (~120°C) for 30 minute in silicon oil. The polarization-voltage (P-V) hysteresis measurement of poled PLZT pellet was done by Radiant technology made Hysteresis analyzer Version: 4.4.0 model at room temperature. The piezoelectric co-efficient (d_{33}) of the polled pellet was measured by the SINOCERA YE2730Ad_{33} meter with the variation of polling field.

3. Result and discussion

Fig. 1 shows the differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) of the dried powder. The weight loss was occurred in four steps as indicated by TGA curves. The DTA graph shows four endothermic with four exothermic peaks. In first stage loss was observed around 90°C with an endothermic peak due to the removal of water molecule. In second stage a small exothermic peak was observed around at 270° due to simultaneous decomposition of organic molecule. Third weight loss with two endothermic peaks was attributed to multi decomposition. The weight loss in TGA curve associated with endothermic peak in DTA curve may be due to transformations in to metastable phase which formed prior to crystallization. A broad exothermic peak in DTA range of 500-980°C associate with no weight loss in TGA curve corresponds to the crystallization of perovskite PLZT phase. So the powder had been calcined at 880°C.

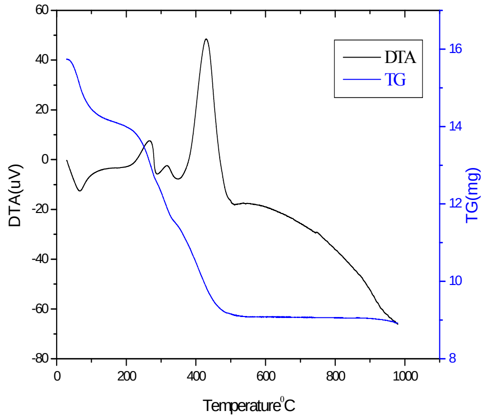

Fig. 1. DTA/TGA of PLZT (10/52/48).

Fig. 2 shows the powder XRD pattern of PZT doped with lanthanum, PLZT (10/52/48) calcined at 880°C. Pattern shows a Pure Crystalline perovskite phase with no pyrochlore phase was detected. Average crystallite size has been calculated using Scherer's formulae. Scherer's formula is defined as $D = \frac{K\lambda}{\beta \cos\theta}$. Where the constant K depends upon the shape of the crystallite size (=0.89, assuming the circular grain), β is the Full Width at Half Maximum (FWHM) of intensity (a.u.) vs.2θ (degree) profile, λ is the wavelength of the CuK_α radiation (=0.1542 nm), θ is Braggs' diffraction angle and D is the average crystallite size [24-25]. In Scherer's formula average crystallite size has been calculated using Gaussian fit to the peaks in XRD pattern. D has been taken as average to all the peaks. The value of average crystallite size is 21 nm.

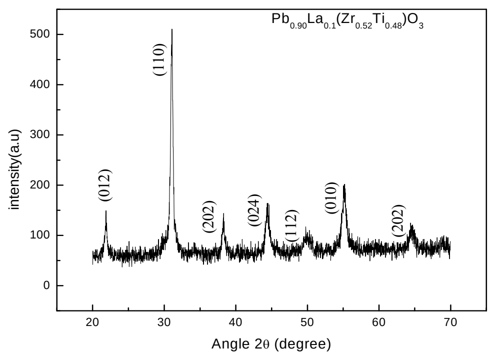

Fig. 2. XRD pattern of PLZT (10/52/48) Powder calcined at 880 ^{0}C.

The scanning electron micrograph of PLZT (10/52/48) nanoceramics sintered at 1100°C for 30 min shown in the Fig. 4. Qualitatively it has been observed from figures that the grains were uniformly distributed. The average grain size is around 1μm. This leads to enhancing the rate of sinterablity leading to low sintering temperature.

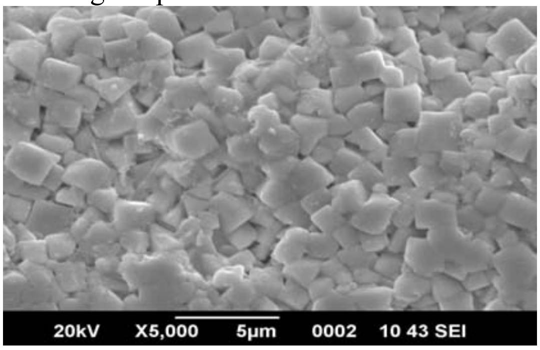

Fig. 3. Scanning electron micrograph (SEM) of PLZT (10/52/48) sample sintered at 1100°C.

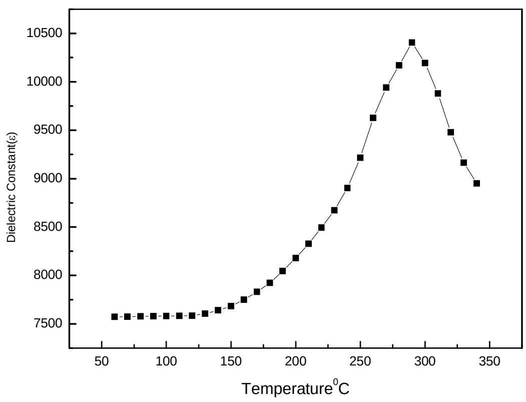

Fig. 4. Variation in dielectric constant with temperature of PLZT (10/52/48) sintered pellet at 1100°C.

Fig. 4 shows the variation of dielectric constant (ε) of PLZT (10/52/48) sample with temperature at 100 kHz frequency. It was observed that the dielectric constant (ε) increases with the increase in temperature and reaches a maximum value at T_C (~288°c). Then the dielectric constant (ε) was decreases with further increase in temperature as is usual with any dielectric material. The dielectric peak is broad, which is generally a feature of ferroelectric materials. The dielectric constant of PLZT at T_c (~288°c) was found to be 10437 at 100 kHz.

The large value of dielectric constant with respect to reduce grain size is due to increase in the number of defects and electric dipoles. The dipole-dipole interaction depends on the location of the dipoles (grain core or grain boundary).when the grain size of the confined system is reduced, the fraction of dipole at the interface increases significantly and dielectric constant is increased.

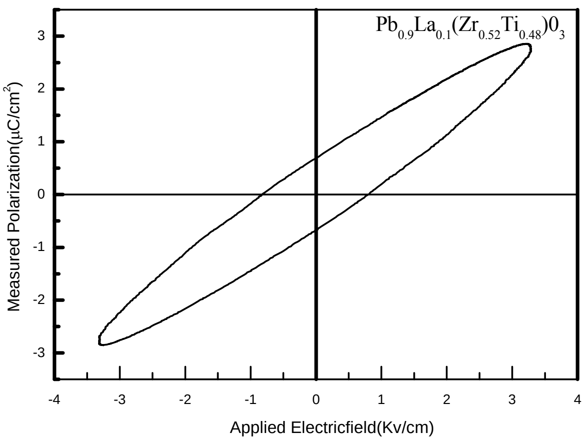

Fig. 5. P-E loop of PLZT (10 /52/48) sample.

The Measured polarization verses applied electric field curve of PLZT (10/52/48) pellet polled at 40 kv/cm for 0.5 hours was shown in Fig. 5. The remanent polarization (P_r) was 0.6924 µC/cm^2 and the saturation polarization (P_{max}) was 2.854 µC/cm^2. The coercive field (E_C) was found to be 0.810Kv/cm. The lower value of electric field (E_c) has an advantage in device application since the power losses are minimized and the switching voltage reduced.

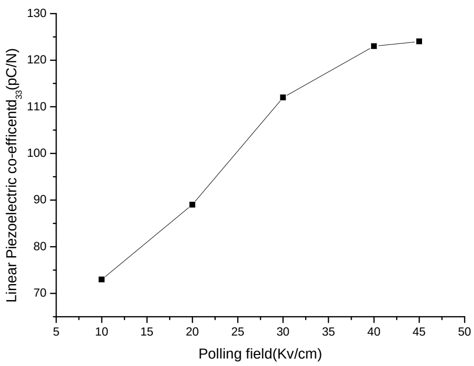

Fig. 8. Variation of longitudinal piezoelectric co-efficient (d_{33}) with polling field.

Fig. 8 shows the variation of longitudinal piezoelectric co-efficient (d_{33}) of PLZT (10/52/48) nano ceramics with varying polling field. It has been observed that with increasing the polling field the piezoelectric co-efficient (d_{33}) increases. Maximum value of linear piezoelectric co-efficient (d_{33}) was 124 pC/N at 40Kv/cm polling field. With further increase in the polling field it remains almost same. It indicate the orientation of the domain reach its final alignment here. The piezoelectric coefficient also decreases due to decrease in crystallite size related with the decrease in domain size.

4. Conclusion

Nanocrystalline lanthanum substituted lead zirconate titanate $Pb_{0.9}La0.1$ ($Zr_{0.52}Ti_{0.48}$) O3 has been synthesized successfully by sol gel method. The nanocrystalline PLZT sample shows high dielectric constant and small ferroelectric and piezoelectric behavior. The dielectric constant increase with the decrease in crystallite size due to the fraction of dipoles at interfaces increase significantly [22-23].

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References

[1] V. A. Isupov, Ferroelectrics, **46**, 217 (1983).
[2] B. Jafe, H. Jafe, W. R. Cook, Piezoelectric Ceramics Academic Press, London, 1971.
[3] P. Ari-Gur, L. Benguigui, Solid State Commun. **15**, 1077 (1974).
[4] B. Noheda, J. A. Gonzalo, L. E. Cross, R. Guo, S. E. Park, D. E. Coxand G. Shirane, Phys. Rev. B. **63**, 014130 (2000).
[5] E. M. Lines, A. M. Glass, Principles and Applications of Ferroelectrics and Related Materials. Claredon, Oxford, 1977.
[6] G. H. Haertling, J. Am. Ceram. Soc. **82**, 797 (1999).
[7] L. C. Lynnnworth, IEEE Trans. Sonics and ultrasonic SU-22, 71 (1975).
[8] W. P. Mason, J. Acoust. Soc. Amer. **70**, 1561 (1981).
[9] Y. Yamashita, H. Yokoyama, H. Honda, T. Takahashi, Jap. J. Appl. Phys. **20**, 183 (1981).
[10] J. Bernard, Piezoelectric Ceramics. Academic, London, (1971).
[11] F. Kulcsar, J. Am. Ceram. Soc., **42**, 49 (1959).
[12] G. H. Heartling, J. Am. Ceram. Soc, **82**, 797, (1999).
[13] D. Handen, NATO Sci. High Techn. **76**, 335 (2000).
[14] G. H. Heartling, J Am Ceram Soc. **82**(4), 797 (1999).
[15] S. F. Wang, Y. R. Wang, T. Mahalingam, J. P. Chu, K. U. Lin, Mater. Chem. Phys. **87**, 53 (2004).
[16] J. S. Benjamin, Mechanicalalloying, Sci, Amer, **234**, 40 (197 6).
[17] V. Vinothini, P. Singh, M. Balasubramanian, ceram. Int, **32**, 99 (2006).
[18] R. N. Das, A. Pathak, P. Pramanik, J. Am. Ceram. Soc. **81**, 3357 (1998).
[19] Y. I. Park, M. Nagai, M. Miyayam, T. Kudo, J. Matter. Sci., **36**, 1995 (2001).
[20] M. L. Calzada, R. Sirerea, F. Carmonaand, B. Jimenze: J Am. Ceram. Soc. **78**, 1802 (1995).
[21] T. M. Susan, J. Chen, K. Vedam, R. E. Newnham: J. Am. Ceram. Soc.**78**, 1907 (1995).
[22] S. K. S. Parashar, R. N. P. Choudhary, B. S. Murty, J. Appl. Phys **94**, 6091 (2003).
[23] A. Q. Jiang, G.. H. Li, L. D. Zhang, J Appl. Phys **83**, 4878 (1998).
[24] B. D. Culity, Elements of X-ray Diffraction, second ed., Addison-Wesley Series, 1978.
[25] C. Suryanarayana, M. Grant Nortan, X-ray Diffraction: A Practical Approach, Plenum Publishing Corporation, New York, 1998.