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Structural and Dielectric Characterization of La Modified PZT (52/48) Nano Ceramic Material for Electronic Applications

K. Roy, T. Mukherjee
Department of Electronics and Communication Engineering
Haldia Institute of Technology ICARE Complex, PO HIT
Haldia-721657W.B India
kushalroy1979@gmail.com

Dr. S. Chatterjee
Department of Biotechnology
Haldia Institute of Technology ICARE Complex, PO HIT
Haldia-721657W.B India
shambac@gmail.com

Ella Karunakar
Department of CSE, NRI Institute of Technology,
Agiripalli, Andhra Pradesh

Dr. T. Satyanarayana
Department of EIE, LBR College of Engineering, Andhra Pradesh

Abstract: The objective of the presented work is to investigate the effects of varying concentration of La as hard dopant on structural, morphological and dielectric properties of lead zirconium titanate (PZT). The base material PZT was prepared by sol-gel technique on lab scale to reduce the injection of sintering defects. After addition of varying weight percentage of La, the different composite materials were analyzed under scanning electron microscope to study the structural modifications taking place. X-Ray diffraction patterns were studied in combination with variation of dielectric constant with temperature and frequency. it is observed that a single phase perovskite structure with tetragonal phase is formed for all compositions of PLZT. The dielectric constant of undoped PZT is found to be 11,300 at a temperature of $500^{O}C$ and frequency of 100Hz. The results further indicate that the dielectric properties of the pure-phase PZT are better than La doped PZT at higher temperature.

Keywords: *Sol-Gel technique, PZT nano ceramic system, Dielectric constant*

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I. INTRODUCTION

The applicability of ferroelectric nano ceramic material in wide range of applications is attributed to its modifiable properties. For the past few decades the solid solution $PbZrO_3$-$PbTiO_3$, commonly known as Lead zirconate titanate (PZT), has dominated commercially because of its superior dielectric and piezoelectric properties. In particular, its large piezoelectric response has made PZT one of the most widely used materials for electromechanical applications. It shows large remnant polarization (P_r) at small coercive electric fields (E_c). Near the morphotrophic phase boundary (MPB) between the rhombohedral and tetragonal phases in the binary $PbZrO_3$-$PbTiO_3$ system (at 50-55 % of $PbZrO_3$), the dielectric constant and piezoelectric coefficients show maximum values [1-3]. A lot of research was carried out on PZT to explore the possibility of its various applications. To mention a few: Tahar et al. [4] prepared the PZT a powder by modified sol-gel process and diethanolamine (DEA) was used as a complex agent to keep the metal ions in homogeneous solutions without undergoing precipitation. Also, they investigated the structural properties of the prepared sample with various heat treatments. Ghasemifard et al. [5] synthesized the lead zirconate titanate (PZT) nanopowders by the metal organic and salt precursor's sol-gel combustion technique. They discussed the effects of calcination temperature on lattice parameter and tetragonality of PZT powders. Smitha et al. [7] obtained the monophase perovskite PZT ceramics using self-sustaining polyol auto-combustion method and they studied the structural and dielectric properties with temperature variation. Raju et al. [8] prepared the PZT (52/48) ceramic materials by citrate sol-gel method and they investigated the dielectric constant and loss tangent for various temperatures by applying frequency of 1 kHz to 1 MHz. They obtained the relative dielectric constant at Curie temperature (T_c) as 4862 for applied frequency of 1 kHz. Vijendra et al. [9] prepared the $PbZr_xTi_{1-x}O_3$ ($0.0 \leq x \leq 1.0$) ceramics by solid-state reaction technique.

To our observation, the electrical properties of PZT having Zr/Ti ratio of 52/48 has been studied very rarely [10-13]. In this work, PZT (52/48)

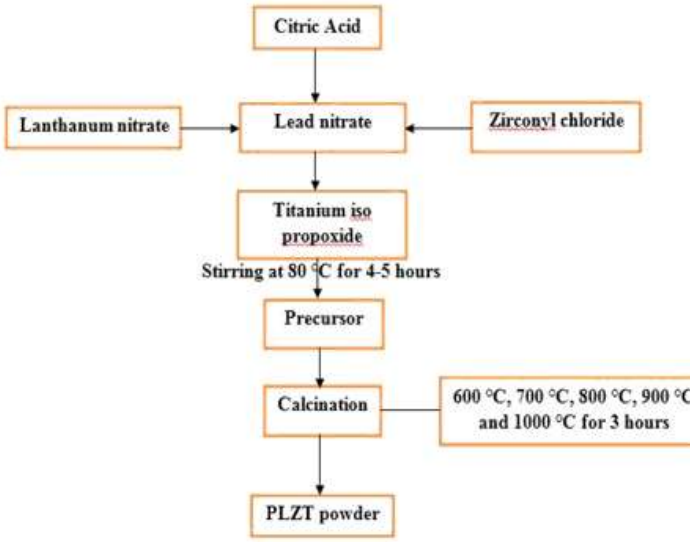
 ISSN: 2454-4248
12 – 16

powder was synthesized by sol-gel technique. The temperature dependence of dielectric constant (range from 25 °C to 500 °C) was carried out at different frequencies in the range 100 Hz - 1MHz. The results were analyzed and discussed in detail.

II. SAMPLE PREPARATION

Citric acid monohydrate (Merck, 99.5%), lead (ll) nitrate (Merk, 99.0%), titanium tetra-isopropoxide (Merk, 98%), nitric acid (Merck, min. 69.0% GR) and zirconium oxychloride (Thomas Baker, 98.0%), lanthanum (III) nitrate hexahydrate (Alfa Acer, 99.9%) and poly vinyl alcohol (PVA, Fischer, Molecular Weight: 125,000) were purchased and used as such for synthesis without any further purification. Water used was distilled and deionized (DI) using a „Milli-Q" water purification system (Millipore Milli Q185 Plus System, Millipore, USA). These materials were used for the preparation undoped and lanthanum doped PZT (52/48) ceramics

Polycrystalline samples of PZT were prepared by the sol-gel technique. As a first step, citric acid was dissolved in 100 ml distilled water and the solution was stirred for 10 min continuously at room temperature. After getting a homogeneous solution, zirconium oxychloride and titanium isopropoxide were added followed by lead nitrate for undoped PZT. For the preparation of lanthanum doped PZT, lanthanum nitrate was also added to the solution. Finally 5 ml nitric acid (HNO_3) was added to improve the process. The complexed solution was stirred well for 1 hr at room temperature to give a clear and homogeneous solution. Finally the gel formed and it was dried at 80 °C. After the auto-combustion of the gels, the resultant powders were precalcined at 600 °C for 3 hrs. Further, the precalcined sample were then calcined at different temperatures such 700 °C, 800 °C, 850 °C, 900 °C and 1000 °C for 3 hrs to obtain the desired single-phase powders.



III. RESULTS and DISCUSSIONS

1. Structural and morphological studies

The TGA and DTA of PZT (52/48) and PLZT (10/52/48) powder was carried out in He atmosphere with a heating rate of 20^{O}C per min. The TG graph of PZT exhibit three major losses; one located between 180^{O}C-246^{O}C 9about 9%), second occurring between 290^{O}C-392^{O}C (about 22%) and third one located between 430^{O}C-656^{O}C. On the contrary TGA of PLZT (10/52/48) exhibits two major losses; first one located between 180^{O}C-246^{O}C (about 8%) and other occurring between 290^{O}C-380^{O}C (about 18%). This is due to major decomposition reaction of citric acid and other organic compounds. The DTA curves are in confirmation with these observations. There are three exothermic peaks in DTA curve at 156°C, 346 °C and 475 °C. The first one may be corresponding to the combustion of most of the organic species entrapped in PLZT polymerized gel such as citric acid and titanium (lV) isopropoxide. The second one with a temperature range of 290°C – 380°C is due to the decomposition of organic compounds and the combustion of residual carbon contents. The third broad peak centered at 475°C indicates the beginning of crystallization of the perovskite phase.

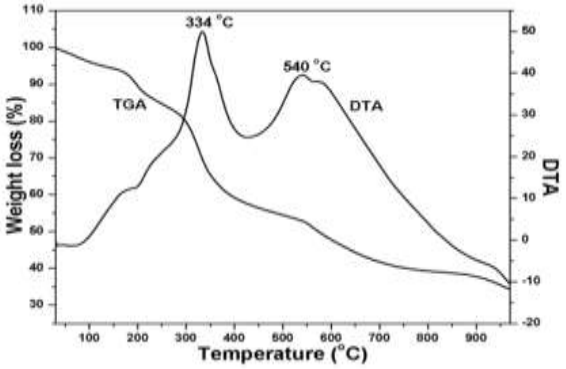


Figure 1: TGA/DTA curve for the PZT powders synthesized by sol-gel route

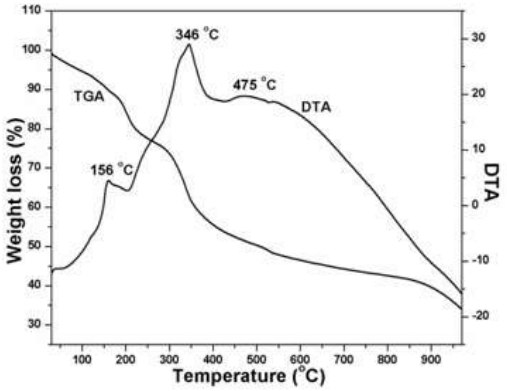


Figure 2: The thermogravimetry (TG) and differential thermal analysis (DTA) of dried gel in helium environment.

 ISSN: 2454-4248
12 – 16

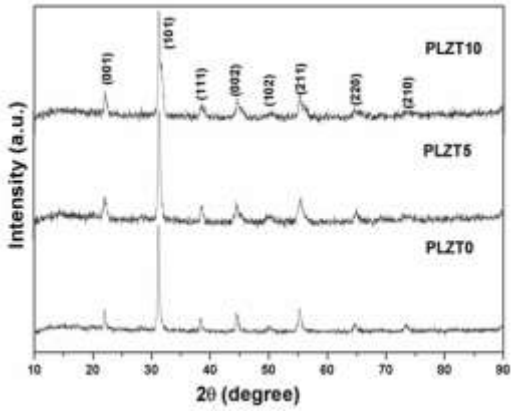


Figure 3 Room temperature XRD patterns of PZT ceramics with various % of La content.

The formation of desired compound and its structural parameters were determined using X-ray diffraction data. Figure 3 shows the X-ray diffraction pattern of the calcined powder recorded at room temperature. The single and sharp intensity peaks indicate the formation of perovskite phase and all compositions are free from pyrochlore ($A_3B_4O_{13}$) phase, which is considered to be unwanted in the PZT system. All the peaks were indexed using observed interplanar spacing (d) and compared with "JCPDS" data to identify the phases. Furthermore, a small shift in the peak intensity positions suggest that there is a slight variation of lattice constant and the basic crystal structure of PZT has not been affected with doping of La-ion at A-site.

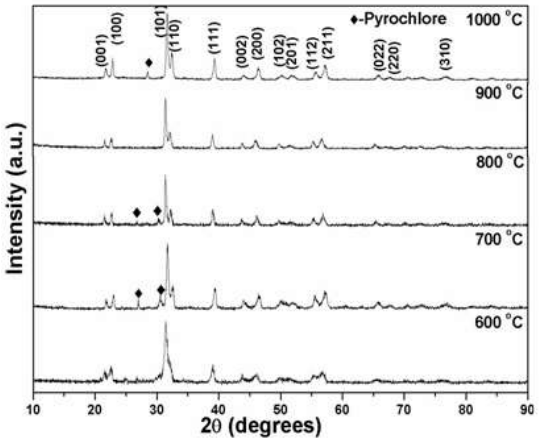


Figure 4 XRD patterns of PZT powders calcined at different temperatures.

The powder XRD patterns were obtained for the powders calcined at 600 °C, 700 °C, 800 °C, 850 °C, 900 °C and 1000 °C using PANalytical Xpert diffractometer in the range of Bragg"s angle (2θ) 10°- 90° with the Cu Kα line (λ=1.54 Å) and these patterns are shown in Figure 4. It is clear from the figure that, in the case of the sample calcined at 600 °C, crystallization is almost complete and the perovskite PZT phase along with a small impurity phase is formed. The impurity phase was identified as pyrochlore phase. The XRD patterns for the samples calcined at temperatures 700 °C and 800 °C also show that the perovskite phase is observed along with the pyrochlore phase. However, this impurity phase is found to gradually decrease from 700 °C to that calcined at 800 °C. For the sample calcined at a temperature of 900 °C, pyrochlore phase disappears and the peaks of the perovskite phase are observed clearly confirming the formation of PZT. Thus, it is observed that the pyrochlore phase gradually decreases with the increase of calcination temperature from 600 °C and it disappears at 900 °C. A sharp intensity peak (2θ = 31.20°) indicates the formation of perovskite PZT phase which can be matched with the JCPDS file no. 33-0784. The XRD pattern clearly shows no unwanted phase formation like pyrochlore, indicating that the sol-gel process used in the present study is a suitable technique. The XRD pattern at 1000 °C shows the presence of pyrochlore phase and this may be due to the melting of PbO at high temperature. The broad XRD peaks clearly indicate the presence of nano crystalline particles.

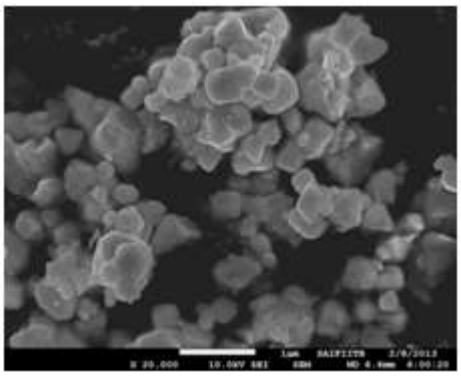


Figure 5: SEM micrograph of PLZT (10/52/48) powder calcined at 850 °C for 3 hrs.

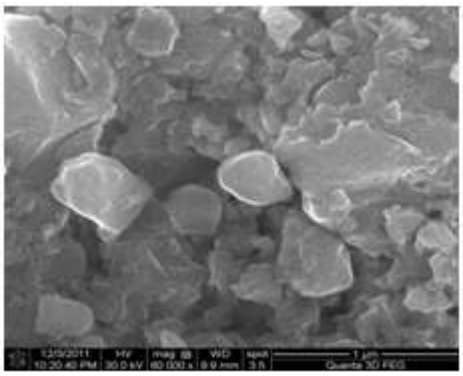


Figure 6: pellet after sintering at 875 °C for 4 hrs

 ISSN: 2454-4248
12 – 16

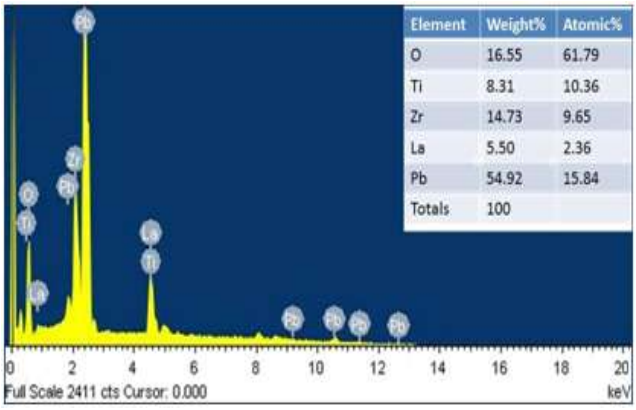


Figure 7: EDAX measurements for PLZT (10/52/48) powder.

The surface of the PLZT (10/52/48) pellet was imaged using scanning electron microscope. The SEM images (Figure 5 and 6) show the average particle size around 0.3 µm for powder sample and 0.5 µm for pellet. The increase in particle size of the pellet as compared to powder data could be due to agglomeration of particle that resulted from pelletization (with addition of PVA and sintered at 875 °C for 4 hrs). The presence of lanthanum was also confirmed from the EDX measurement (Figure 7) and the EDX shows a clear lanthanum peak.

2. Dielectric studies

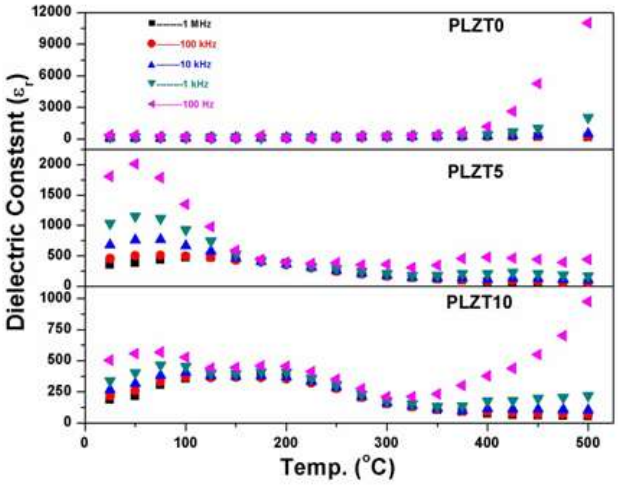


Figure 8 Dielectric permittivity vs temperature for compositions 0/52/48, 5/52/48 and 10/52/48 at various frequencies.

The temperature dependent variation of relative dielectric permittivity of La modified PZT (52/48) ceramics as a function of both temperature (ranging from 25 °C to 500 °C) and frequency (ranging from 100 Hz to 1 MHz) are shown in Figure. 5.5. For pure PZT, the dielectric constant shows small variation with rise in temperature for all frequencies till 350 °C and from 350 °C the dielectric constant increases slightly for 1 kHz and a rapid rise for 100 Hz (low frequency) with the temperature. For the frequency 10 kHz, 100 kHz and 1 MHz, the dielectric constant is very low for the entire temperature range. For PLZT (5/52/48), from 25 °C to 100 °C, for all frequencies, the dielectric constant increases initially with rise in temperature. After dielectric constant reaching a maximum at a temperature 50 °C, dielectric constant decreases with increase in temperature. In this temperature range, from 25 °C to 100 °C, the ε_r is observed to fall with the rise in frequency and it is true for all values of max. ε_r. The increase in ε_r is appreciably large for the low frequency in this temperature range. Between 150 °C to 300 °C, the variation of ε_r with frequency is not much appreciable and also ε_r shows low values. From 300 °C to 500 °C, ε_r increases slightly for low frequency (100 Hz) whereas for other frequencies there is no much change.

For PLZT (10/52/48) from 25 °C to 100 °C, the variation of ε_r with frequency shows a trend similar to that for PLZT (5/52/48) except that the fall in ε_r to the minimum value occurs around 150 °C for 5 at.% and around 300 °C for 10 at.%. The dielectric response of 5 at.% is significantly larger at all frequencies in this temperature range than for 10 at.%. The maximum ε_r value for 5 at.% at 100 Hz is almost 4 times that of 10 at.% in this temperature range. This is due to large doping concentration (10 at.%) which significantly diffuses the dielectric response. From 400 °C to 500° C, an exponential increase is observed in the dielectric response for 100 Hz similar to that for pure PZT whereas for other frequencies, the behavior is almost similar to that for 5 at.%.

IV. CONCLUSION

The dielectric and ferroelectric properties of perovskite $Pb_{1-x}La_x(Zr_{0.52}Ti_{0.48})O_3$ (x=0, 0.05, 0.10) ceramics prepared via sol-gel route were reported. The prepared PLZT ceramic was identified by X-ray diffraction method as a single phase material with a perovskite structure having tetragonal phase for all compositions. TGA/DTA analysis shows that the single phase compound formation takes place above 380 °C. The dielectric measurement was carried out as a function of both temperature (range 25 °C to 500 °C) and frequency (100 Hz and 1 MHz). At the temperature of 500 °C and the frequency of 100 Hz, the dielectric study of the undoped PZT gives dielectric constant $\varepsilon_r \approx 11{,}300$. The results indicate that the dielectric properties of the pure-phase PZT are better than La doped PZT at higher temperature. It was also noted that in the vicinity of room temperature, the dielectric constant is less for undoped PZT and 10 at.% than for 5 at.% La content for all frequencies. From the above discussion, it is inferred that the 5 at.% doping concentration shows better dielectric properties than that of 10 at.% at low temperature while undoped PZT is better at higher temperature than 5 at.% and 10 at.%.

 ISSN: 2454-4248
12 – 16

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