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PLZT COMPOSITE SYNTHESIS TO STUDY THE MATERIAL CHARACTERSTIC

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Abstract: The PZT composites are almost used with a dopant, a modifier or other chemical constituent or constituents like La, Mn, etc. to improve and optimize their basic properties for specific applications. Lead lanthanum zirconium titanium oxide (PLZT) was initially developed by Haertling et.al., as a promising novel electro-optic material. Since that time, studies have focused on various applications, ranging from capacitors, transducers, actuators and electro-optic switches to pyro-electric detectors etc, as it has high dielectric constant, high piezo-electric, ferro-electric, pyro-electric properties. The Lead Lanthanum Zirconium Titanium Oxide (PLZT) composite $[(Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{0.35})O_3]$ is synthesized by simple Sol-Gel process using constituent nitrates and a solvent. The resulting powder is characterized using XRD, Particle Size Analyzer, SEM, TG-DTA, UV- Visible spectroscopy and HR-TEM. The structural parameters such as the lattice constants (a, c), X-ray density (ρ_x), Porosity %, average crystallite size (D) have been determined using X-ray diffraction (XRD). Particle size is determined by Particle size Analyzer (PSA), Average grain size and surface morphological studies were carried out using Scanning Electron Microscopy (SEM) and d- spacing value of the material is determined using HR-TEM techniques.

Keywords: PLZT, Sol-gel, High Di-electricity, Peroviskite, Stoichiometric Ratio, Polyvinylpyrrolidone

I. INTRODUCTION

Lead zirconium titanium oxide (PZT) was developed by Haertling, as a promising novel electro-optic material it is the most important member in the lead based peroviskite ferroelectric family [1]. ABO_3 group materials are mainly used as an engineering material in electro-ceramic industry [2]. The PLZT unit cell consist of a corner-linked network of oxygen rhombohedral with Zr^{+4} and Ti^{+4} ions occupying B site within the rhombohedral cage and Pb^{+2} and La^{+3} ions occupies A site created by linked rhombohedral. Here yellow color atoms represent A group elements, black color atoms represent B group elements and white atoms represent oxygen (O) elements. As a result of the different values between Pb^{+2} and La^{+3} some of the A site and B site are vacant to maintain electrical neutrality in the structure. The nitrates of Pb, La, Zr, and oxide of Ti are taken in required amounts of stoichiometric ratio for the synthesis of [(Pb La)(Zr Ti)O_3] composite. There have been several reports on PZT modified with some lanthanide ions. Haertling, Land reported that Pb^{+2} ions could be substituted by the La^{+3} ions of its comparable ionic size. The PZT composite are almost used with a dopant, a modifier or other chemical constituent or constituents like La, Mn, Ba etc. to improve and optimize their basic properties for specific applications. Examples of these additives include off-valent donors, such as Nb^{5+} replacing Zr^{4+}or La^{3+} replacing Pb^{+2}[3,4]. The donors are usually compensated by A-site vacancies. These additives (and vacancies) enhance domain reorientation ceramics produced with these additives are characterized by square hysteresis loops, low coercive field, high remnant polarization, high dielectric constants, maximum coupling factors, higher dielectric loss, high mechanical compliance and reduced aging [5]. Dopants are usually added in concentrations of ≤ 3%. Modifiers are substituted into the original PZT composition as solid solution constituents in concentrations of ≥5%.One system that embraces all compositional aspects of the dielectric, piezo-electric, pyro-

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electric, ferroelectric and electro-optic ceramics is the PLZT system[6,7]. The formation of PLZT composite depends on physiochemical characteristics [8].A number of preparation techniques for PLZT have been reported, such as Ball-Milling, Chemical method, Mechano chemical process, Hydrothermal reaction, High Energy Ball-Milling.

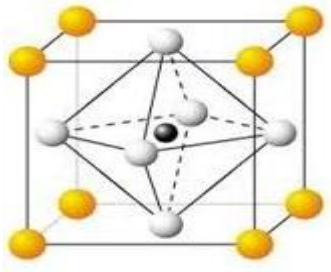

Figure 1 Schematic structure of ABO3 group

Among these methods, Sol-Gel is well accepted to be a simple and promising method in the preparation of PLZT composite. This method is a wet chemical technique for the fabrication of ceramic materials. In this process, the sol (or solution) evolves gradually towards the formation of a gel-like network containing both a liquid phase and a solid phase. Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and poly-condensation reactions to form a colloid. The basic structure or morphology of the solid phase can range anywhere from discrete colloidal particles to continuous chain-like polymer networks. The advantages of Sol-Gel method includes (a) Higher deposition rates, (b) Good stoichiometric control, (c) Lower initial facility costs and lower processing temperature.

II. EXPERMENTAL PROCEDURE

Lead Lanthanum zirconium titanium oxide composite was prepared using Sol-Gel Process. The Starting precursors were Lead Nitrate [$Pb(NO_3)_2$], Lanthanum Nitrate [$La(NO_3)_3.6H_2O$], Zirconyl Nitrate [$ZrO(NO_3)_2.2H_2O$] and Titanium Isopropoxide [$C_{12}H_{28}O_4Ti$][9]. The powder composition [$Pb_{0.92}La_{0.08}(Zr_{0.65}\ Ti_{0.35})O_3$] was prepared by dissolving Lead, Lanthanum and Zirconyl nitrates in double distilled water in the desired ratio. Titanium Isopropoxide was then added directly to the nitrate solution drop-by-drop while stirring. The Ammonia solution was added to the aqueous nitrate solution to maintain pH-value of the solution 7. Polyvinylpyrrolidone (PVP) was taken in the ratio of 1:2 to the solvent to form a gel. The solution was heated at 80^{o}C with constant stirring till zero-gel is formed. The dried cake was crushed thoroughly in a mortar and was calcined at 650^{o}C for 2 hours in muffle furnace. The preparation of PLZT composite is diagrammatical represented in the Fig.1. The powder was crushed and X-ray diffraction patterns of samples were recorded using X-ray diffracto-meter (model: Bruker d8 Advance) with Cu-ka (λ=1.5418Å) radiation source. The SEM studies were carried using Scanning Electron Microscope (Model: JEOL JSM-6360A). The average grain size (grain diameter) of the samples was determined from SEM images. The HR-TEM studies were carried out using JEOL (Germany) GmbH - JEOL JEM-2100.

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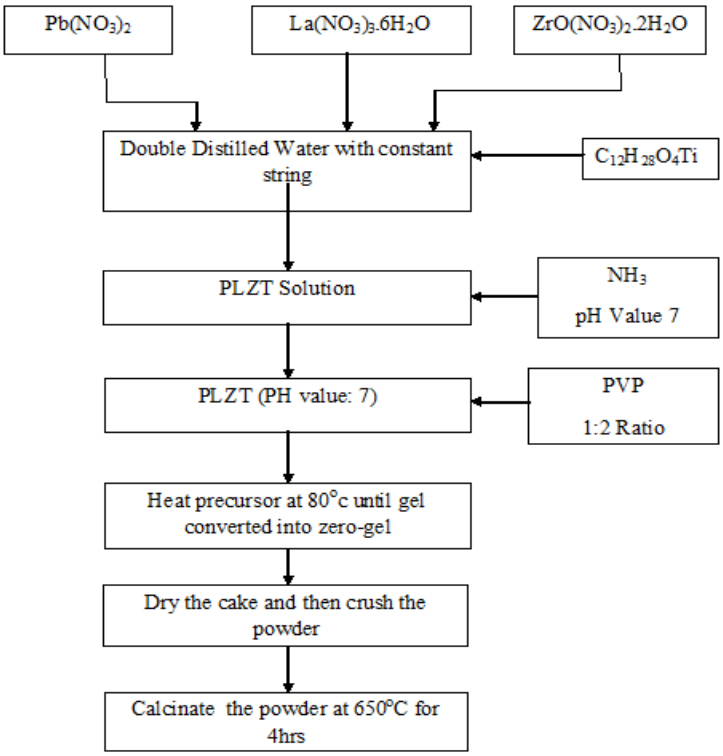

Figure 2 Schematic representation of PLZT composite using simple sol-gel synthesis procedure

III. RESULTS AND DISCUSSION

The X-ray diffraction pattern for PLZT composite is shown in Fig.3. The X-ray diffraction patterns sample clearly indicates formation of crystallite phase. The XRD patterns showed the absence of non-reacted products or intermediate crystalline phases. The positions of all the Bragg lines were used to obtain the inter-planer spacing. The peaks were indexed by comparing the inter-planar distance with the JCPDS data for PLZT (Card No: 53-0785).

The lattice parameters were calculated by the relation [10].

$$\frac{1}{d^2} = \frac{(h^2+k^2)}{a^2} + \frac{l^2}{c^2} \qquad (1)$$

where, d is inter-planer distance, a and c are lattice parameters, (h, k , l) are Millar indices.

The X-ray density (ρ_x) was calculated using the expression [11].

$$\rho_x = \frac{M}{N_A\, a^2 c} \qquad (2)$$

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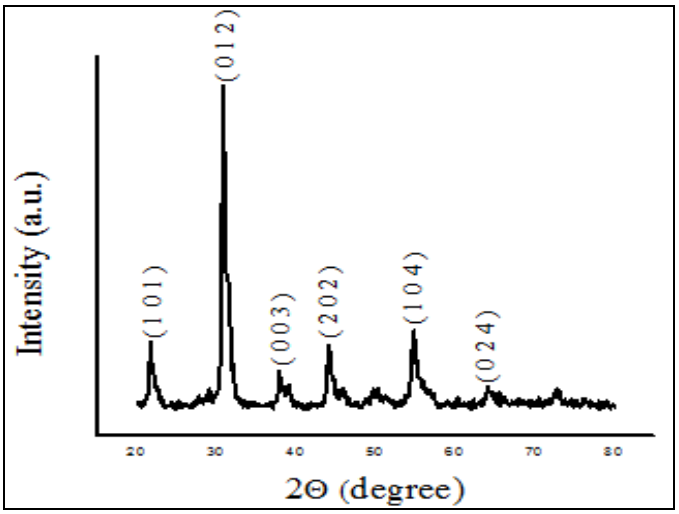

Figure 3 X-Ray Diffractogram (model Bruker d8 Advance) of PLZT composite

where N_A indicates the Avogadro's number, M indicates the molecular weight, a and c are lattice constants.

The actual density (ρ_a) was determined by [12].

$$\rho_a = \frac{M}{V} \qquad (3)$$

The porosity of the samples was calculated using the relation [13].

$$\text{Porosity \%} = \left\{\frac{100(\rho_x - \rho_a)}{\rho_a}\right\} \% \qquad (4)$$

The average crystallite size (D_p) obtained for sample was 16.8 nm respectively, as estimated by Scherrer's equation as follows [14].

$$D_p = \frac{k\lambda}{\beta \cos\theta} \qquad (5)$$

Where k = 0.9 (assuming the particles are spherical in shape), λ is x-ray wavelength, B is full width at half maximum (FWHM) of the diffraction peak and θ is Bragg diffraction angle. Considering the above equations, Lattice constants a = 4.07845 A^o, c = 4.0346 A^o, volume $(A^o)^3$ = 63.985. X-ray density(ρ_x) = 5.68 gm/mol. $(A^o)^3$, Porosity % = 16.05 and average crystallite size(nm) = 17.5.

Fig.4. Illustrates the Particle size of synthesized PLZT composite, The obtained particle size using Particle size analyzer (HORIBA SZ-100) is 30.4nm.

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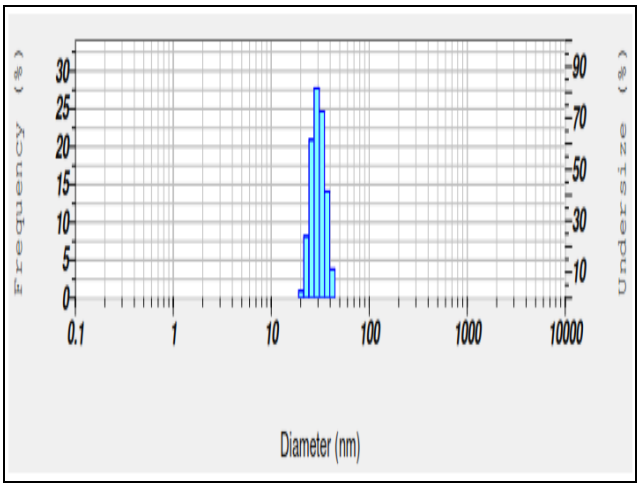

Figure 4 Particle size analyses (HORIBA SZ-100) of PLZT composite.

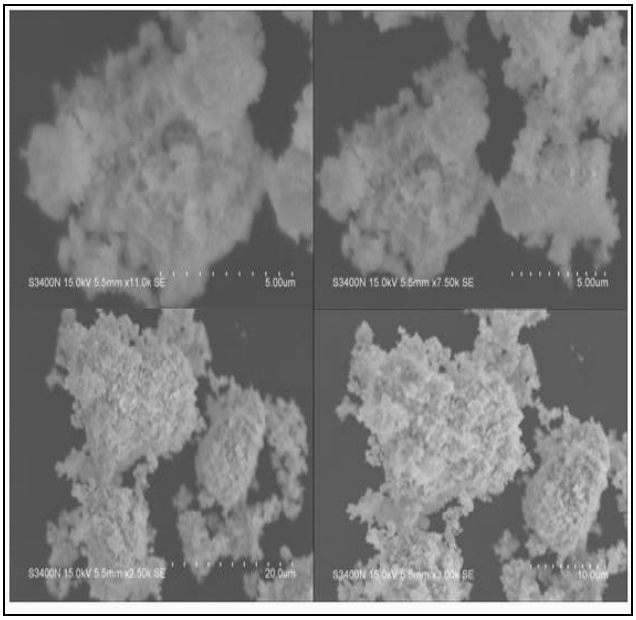

Figure 5 SEM Analysis of PLZT composite

Fig.5. Illustrates the SEM micrographs for PLZT samples. Maximum densification and spherical shape grains are observed in the PLZT sample using SEM analysis. The average grain size was estimated as ~ 0.36 µm. The small grain size observed in PLZT sample leads to small domain spacing and the reduction of distance through which the walls move, resulting in the increase of piezoelectric coefficient.

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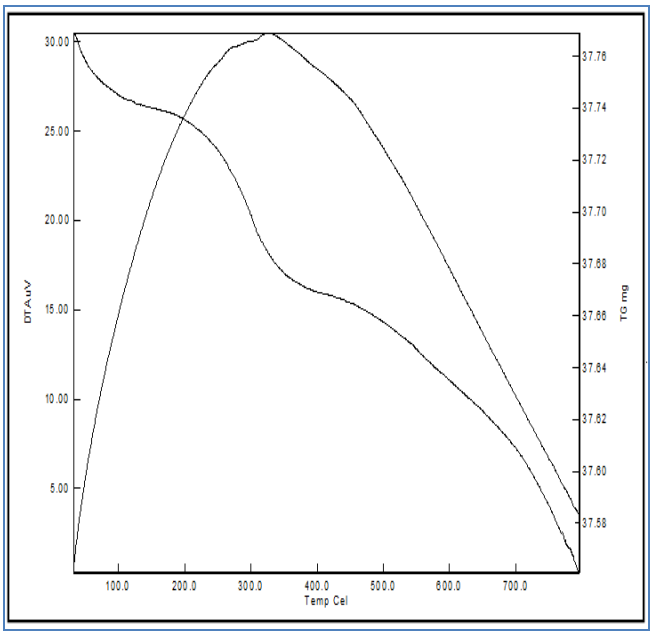

Figure 6 TG/DTA cure Analysis of PLZT material

From the Fig.6. TG/DTA curve we analyzed the weight loss of the material with respect to temperature variation. where the total weight loss of the PLZT composite is of 0.5 mg.

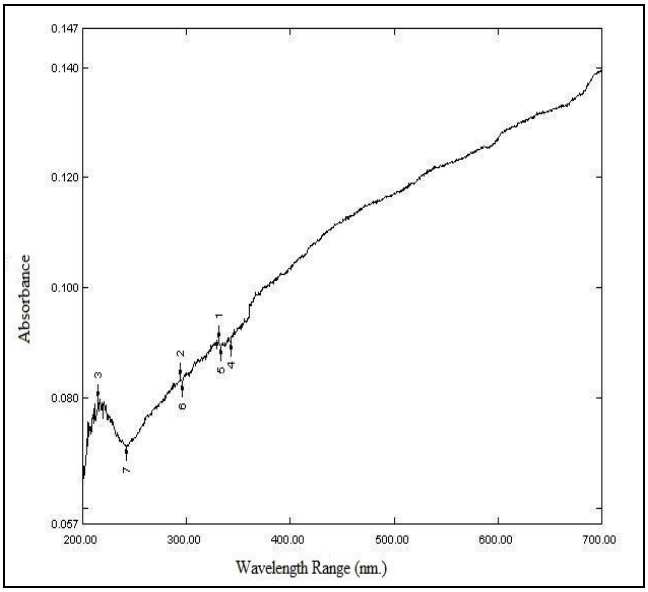

Figure 7 UV-Visible spectroscopy for PLZT composite

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From Fig.7. UV-Visible spectroscopy (UV-2400PC Series) we observed that the maximum absorption wavelength of PLZT material is 331.50nm .

TEM images in Fig.8. Determines the d spacing value between the parallel planes as 0.22nm which was similar to the d spacing value determined from the XRD data.

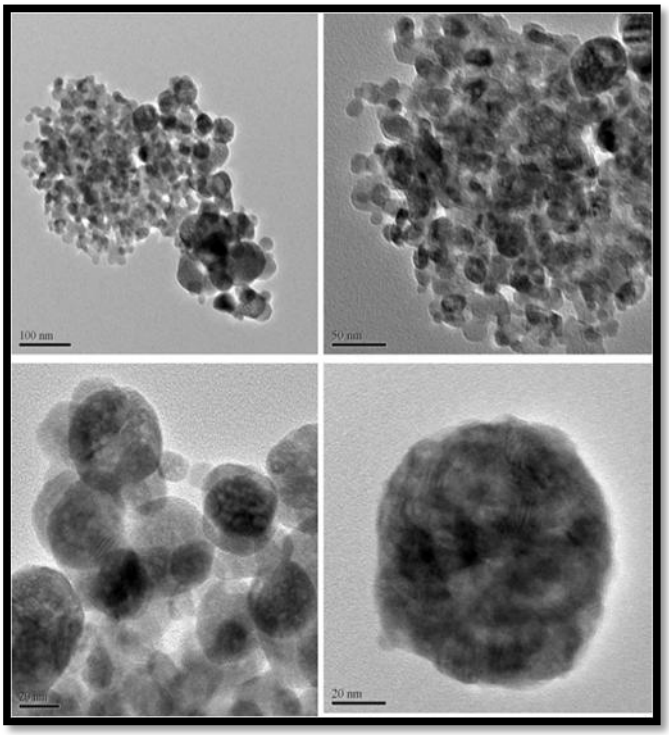

Figure 8 HR-TEM images for the as synthesized PLZT nano particles

IV. CONCLUSIONS

In this paper PLZT composite was prepared using simple sol-gel method and the material characteristic were studied. The obtained average crystallite size as 17.5nm, particle size 30.4nm, average grain size ~ 0.36 µm, total weight loss 0.5mg, maximum absorption 331.50nm and d-spacing 0.22nm.

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REFERENCES

[1] G.H. Heartling, *PLZT electroopic materials and applications – a review, Ferroelectrics*, Vol. 75, 25-55, 1987.
[2] J. Handerek, et al., *Zjawiska kinetyczne w ferroelektrycznych I antyferroelektrycznych krysztalach o strukturze perowskitu, Prace naukowe U.S. nr 310,* Katowice 1979.
[3] Abdul Samee Fawzi, A. D. Sheikh, V. L. Mathe, *Effect of synthesis method on structural, dielectric and ferroelectric properties of* $Pb_{0.93}La_{0.07}(Zr_{0.60}Ti_{0.40})O_3$ *system*, ISSN 0975-508X CODEN (USA) AASRC9 Archives of Applied Science Research, 3 (5):631-644, 2011.

ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

(ISO 3297: 2007 Certified Organization)

Vol. 2, Issue 8, August 2013

[4] Soma Dutta and R. N. P. Choudhary, P. K. Sinha, Awalendra K. Thakur, *Microstructural studies of (PbLa)(ZrTi)O_3 ceramics using complex impedance spectroscopy*, Journal of Applied Physics, Volume 96, Number 31, August 2004.
[5] E.G. Fesenko, R. Skulski, Z. Surowial, *Niektóre problemy fizyki strukturalnych przemian fazowych w ferreoelktrykach tlenowo-oktaedrycznych*, Prace Wydzialu Techniki 30, Wydawnictwo Uniwersytetu Slaskiego, Katowice 1997.
[6] B. Jaffe, et al., *Piezoelectric ceramics*, Academic press London and New York 1971.
[7] G.H. Heartling: *Ferroelectric ceramics, history and technology*, J.Am. Ceram. Soc. 82(4) , 797-818, 1999.
[8] *Haertling Gene H* , J. Am. Ceram. Soc. 82 797–818, 1999.
[9] Puja Goel, Subhash Sharma, Ajit Ram James, Kanhaiya Lal Yadav, Structural and dielectric properties of phosphorous-doped PLZT ceramics, Pramana journal of physics, Vol. 65, No. 6 December2005.
[10] Dombale P D, M. Phil. Dissertation, Shivaji University, Kolhapur 2000.
[11] Mahajan R P, Ph. D. Thesis, Shivaji University, Kolhapur 2000.
[12] Mahmud S T, A. K. M. Akther Hossain A K M, A. K. M. Abdul Hakim, M. Seki, *J. Mag. Mag. Mater*., 305 269, 2006.
[13] Shalaka C, Navale V. Ravi, I. S. Mulla, *Sensors and Actuators* B 139 466, 2009.
[14] Williamson, W. H. Hall, *Acta Matllurgica*, 1 22, 1953.

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