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Structural and dielectric properties of $Pb_xZr_{1-x}TiO_4$ (x=0.1- 0.4) ceramics by solid state reaction method

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Abstract

A series of lead doped zirconium ceramics $Pb_xZr_{1-x}TiO_4$ (x=0.1-0.4), have been synthesized via conventional solid state reaction method, to understand the effect of Zr substitution at Pb site on the structural and dielectric properties. X-ray diffraction for confirm that orthorhombic structure thereby finding the lattice parameters. The scanning electron microscopy (SEM) images was showed that there is less roughens, no agglomeration, good distribution and matrix of $Pb_xZr_{1-x}TiO_4$ (x=0.1-0.4) Dielectric studies were carried out for the all prepared samples using LCR controller, here the temperature is effects on structure and dielectric properties of the prepared samples of $Pb_xZr_{1-x}TiO_4$, has been studied systematically. The good and best dielectric properties were observed. The observed results of this composition makes promising for antenna and dielectric resonator applications.

Key words: Solid state reaction, Structural analysis (XRD, SEM) and dielectric properties (LCR controller).

1. INTRODUCTION:

Lead and lead zirconium based ceramic materials represent the main class of ferroelectric materials used commercially in the form of multilayer capacitors, piezoelectric transducers, pyroelectric detectors and optical sensors [1-5]. These ceramics properties are strongly influenced by the synthesis method, dopant, cation distribution etc., [3]. There are several reports on the effect of chemical substitutions on the properties of the zirconium titanates but limited to structural or technological studies on these materials. The lead doped zirconium titanate with chemical formula $Pb_xZr_{1-x}TiO_4$ (x=0.1-0.4) (PZT) is a ceramic perovskite material that shows a noticeable piezoelectric effect, which finds practical applications in the area of electro ceramics. The present study is aimed at synthesizing new ceramics via simple solid state reaction, and to study their structural, morphological and dielectric studies in order to assess their industrial potentialities. Being piezoelectric material, it works as sensor and actuator. The dielectric constant of PZT can range from 300 to 3850 depending upon orientation and doping [5]. In addition, due to its pyro electric nature, it can be used as a heat sensor. Moreover, it is a ferroelectric material which can reveal ferroelectric memory applications due to its spontaneous polarization behavior. $Pb_xZr_{1-x}TiO_4$ is being used as a candidate material and exhibit excellent antenna and optoelectronic devices applications [11].

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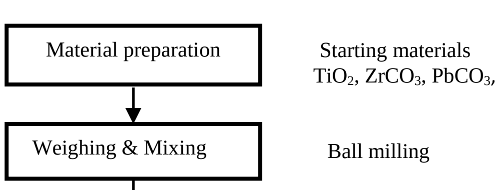
2. EXPERIMENTAL PROCEDURE

The present work is carried out using conventional solid state diffusion technique for the preparation of titanates. In the present synthesis technique the raw materials with high purity chemicals of $ZrCO_3$ (99.5% purity), TiO_2 (99.54% purity), PbO (99.9% purity) (all from Sigma-Aldrich of 99.9%) were used. The flowchart of preparation of titanates is shown in Figure 1.



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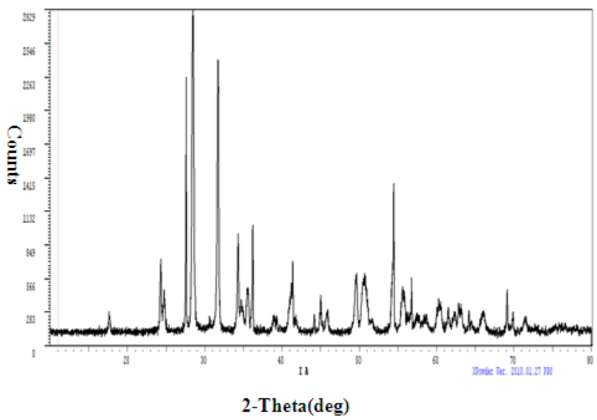
The raw materials of reagent grade as mentioned in above were weighed in an electronic single pan balance as per the stoichiometric planed. Then the weighed materials were transferred into agate mortar of ball miller and ground the mixture for over two hours, the powders were uniaxially pressed initially into a cylindrical disc of 1.2 cm in diameter and about 2 mm of thickness using die-set at a pressure of 10 Tons. This mixed powder pellets was calcined in the temperature range of 1050-1250°C for 10-14 hours. The purpose of the sintering is to increase the mechanical strength of the pellet. These pellets were then annealed at ~300°C for about 2 hours under vacuum (10^{-2} torr) to remove the strain introduced due to mechanical stress. X-ray diffraction profile was recorded at room temperature with Seifert X-ray diffractometer using Ni-filtered Cu-K_{α} radiation (λ = 1.54056Å) at a rate of 2°/min. in the range of 10°-90° for the confirmation of the sample. And also the prepared sample involves the detailed study of dielectric properties of mixed titanate dioxide compounds.

3. RESULTS AND DISCUSSIONS

There are many experimental techniques available for the characterization of a material. Owing to the importance of the materials and available techniques, X-Ray diffraction (XRD), Scanning electron microscopy (SEM) were carried for the structural, surface properties. For the understanding of the conduction mechanism dc electrical conductivity and thermoelectric power measurements were carried. Because of the insulating behavior of the compounds dielectric constant and dielectric loss measurements were carried. The details of methods of measurements were reported below.

X-Ray diffraction profiles were used for the determination of the crystal structure of the prepared compounds. The X– ray diffraction profiles are of the prepared samples $Pb_xZr_{1-x}TiO_4$ (x=0.1 to 0.4) (Fig. 2-5). In these figures the intensity of the scattered X-rays diffraction was plotted against the scattering angle (2θ). The X-ray characteristic peaks are at 2θ equal to 21.403, 21.640, 30.431, 30.3621, 37.650, 43.602, 44.103, 54.194, 63.754, with miller indices (120), (002), (040), (122), (042), (240), (004), (162), (244), indicating that orthorhombic form resemble, those recorded at the international Center for Diffraction Data (JCPDS) number 89-8012, 34.0415. The sharp peaks in these figures confirm the formation of the compound. These profiles have been used for the interpretation of the crystal structure. From these peaks the crystalline size has been calculated using the Scherer formula [6]: $D_P=K\lambda/\beta \cos\theta$, where β is the angular width at half-maximum intensity, θ is the scattering angle, λ is the wavelength of x-rays and K is the Boltzmann constant. Here K=0.9 has been used in the calculation of the crystallite size. These results are shown in the table 1. It is observed that the particle sizes in all the compounds are around 138-347 nm. The highest particle size was observed in $Pb_xZr_{1-x}TiO_4$ (0.3). It may be due to the high temperature calcination will enhance the particle size and reduce the defect density. The phase of compounds was identified using Crystal Impact's Match software program. X-ray profiles were indexed using Material Studio software program and then accurate cell parameters were obtained with an accuracy of >0.1%. Thus obtained cell parameters were used to construct 3D crystal structure. These values were compared with values reported in the literature and found that they were in good agreement. The detailed structure parameters for the prepared samples $Pb_xZr_{1-x}TiO_4$ (x=0.1 to 0.4) like cell parameters, and crystal system are presented. Crystal system and lattice parameters for all the samples were reported.



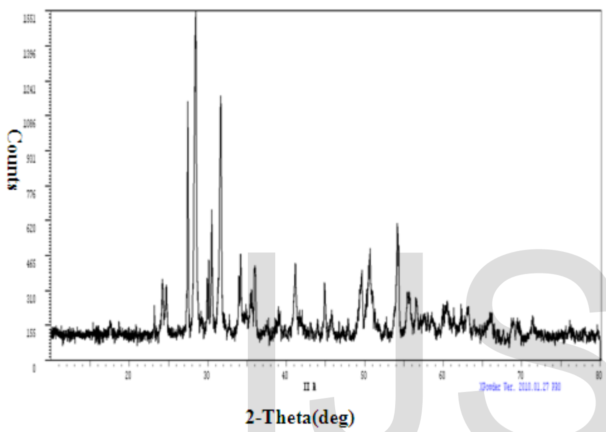
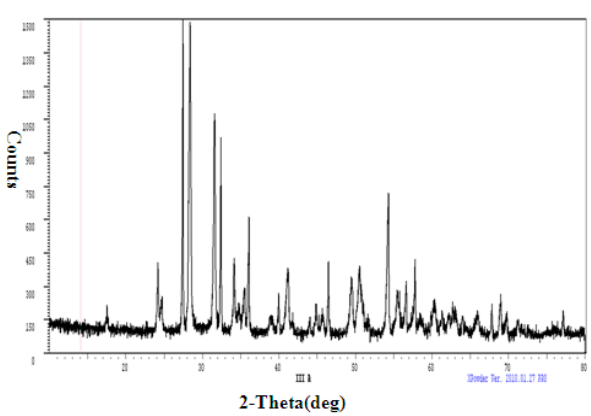


Fig.2. Shows the XRD of $Pb_{0.1}Zr_{0.9}TiO_4$ ceramics

Fig.3. Shows the XRD of $Pb_{0.2}Zr_{0.8}TiO_4$ ceramics



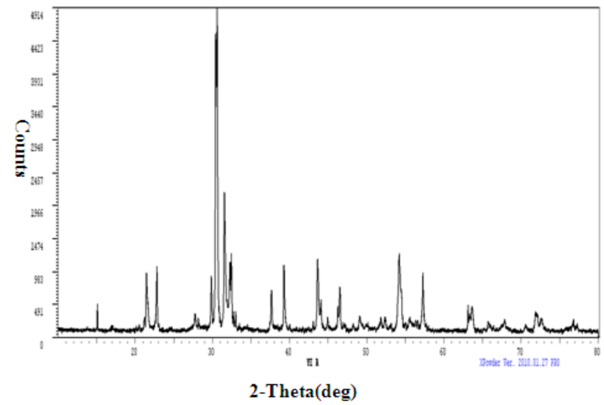


Fig.4. Shows the XRD of $Pb_{0.3}Zr_{0.7}TiO_4$ ceramics

Fig.5. Shows the XRD of $Pb_{0.4}Zr_{0.6}TiO_4$ ceramics

Table 1. Parameters obtained from X-ray profile and SEM images

Ceramics	a	b	c	α	β	γ	D(nm)	G_a (μm)
$ZrTiO_4$	23.238	15.62	4.006	90.00	100.23	90.00	138	4.83
$Pb_{0.1}Zr_{0.9}TiO_4$	23.639	15.83	4.012	90.00	100.23	90.00	140	4.97
$Pb_{0.2}Zr_{0.8}TiO_4$	23.472	15.41	4.022	90.00	100.23	90.00	334	5.3
$Pb_{0.3}Zr_{0.7}TiO_4$	23.719	15.99	4.024	90.00	100.23	90.00	347	6.19
$Pb_{0.4}Zr_{0.6}TiO_4$	23.361	15.68	4.003	90.00	100.23	90.00	238	6.49

3.2. SCANNING ELECTRON MICROSCOPY (SEM)

Scanning Electron Microscopy is a powerful tool to investigate surface morphology of solids by shown in figure 6-10. The microstructure of the lead doped zirconium titanate was studied in the present investigation employing JEOL J. SM-35 scanning electron microscope. The samples used in the present investigation were of $Pb_xZr_{1-x}TiO_4$ (x = 0.1 to 0.4*)*. The average grain size (G_a) was calculated as 4.83-6.81μm, using the following formula and noticed that it is increasing with increasing concentration of lead dopant. Average grain size $\mathbf{G_a = \frac{1.5\,L}{MN}}$, Where L = the total test line length, M = the magnification, N = the total number of intercepts which the grain boundary makes with the line [7-8].

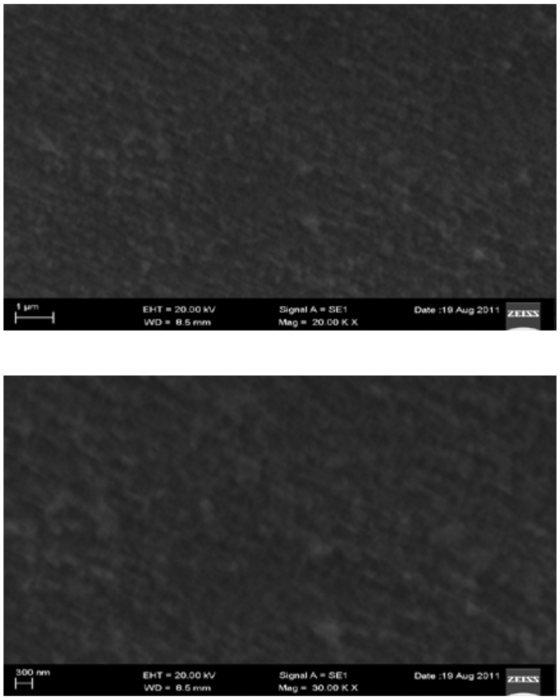


Fig.6. Shows the SEM images of $ZrTiO_4$ ceramics

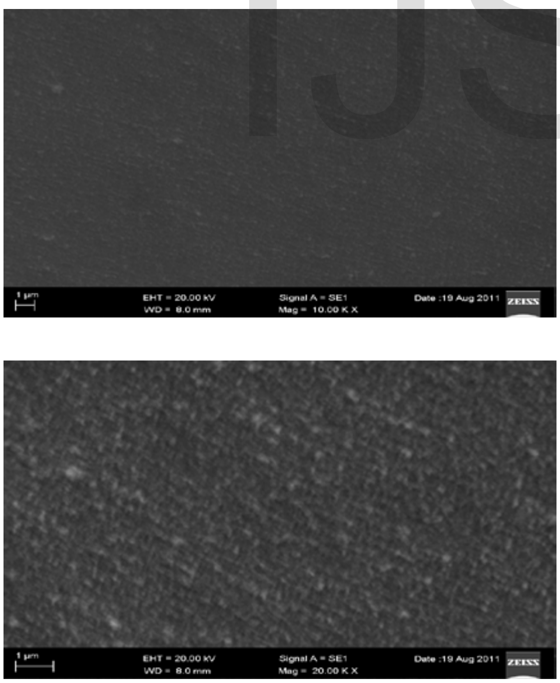


Fig.7. Shows the SEM images of $Pb_{0.1}Zr_{0.9}TiO_4$ ceramics

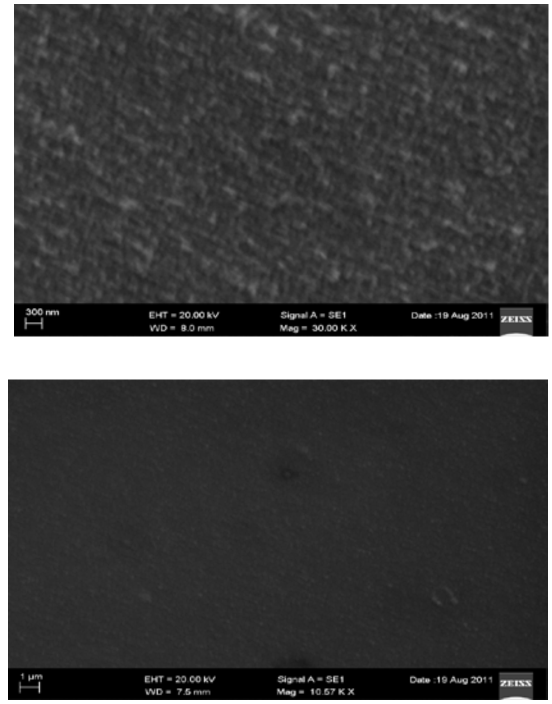


Fig.8. Shows the SEM images of $Pb_{0.2}Zr_{0.8}TiO_4$ ceramics

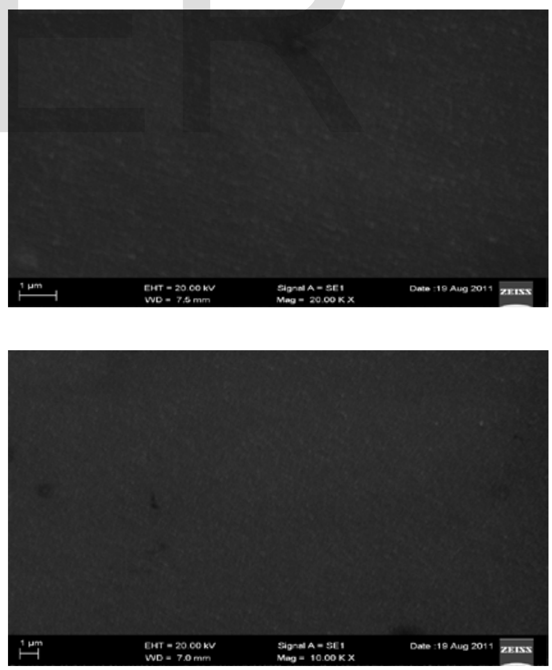
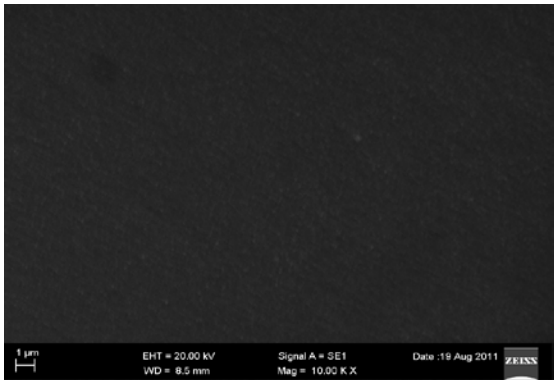


Fig.9. Shows the SEM images of $Pb_{0.3}Zr_{0.7}TiO_4$ ceramics



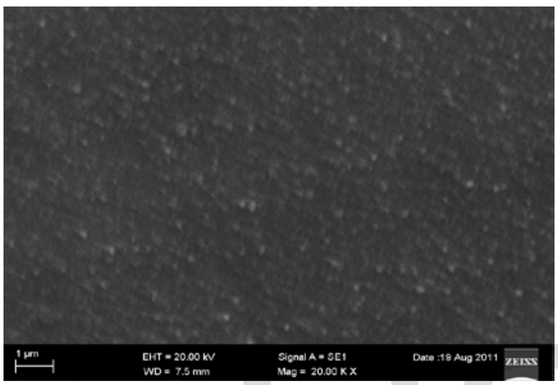
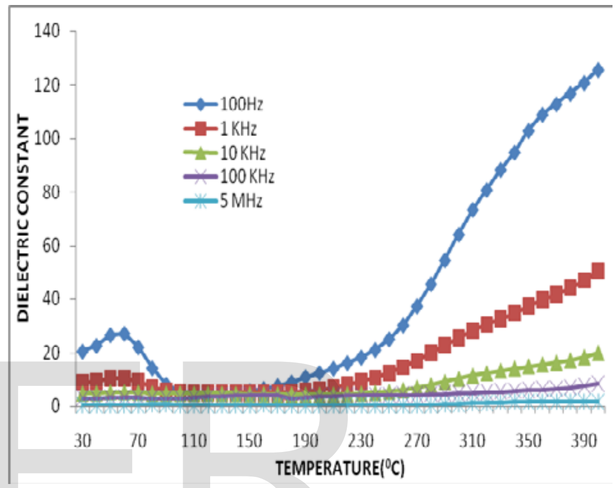


Fig.10. Shows the SEM images of $Pb_{0.4}Zr_{0.6}TiO_4$ ceramics

A study of the experimental variations of the dielectric constant and dielectric loss (tan δ) has been carried out by the two terminal capacitance methods. The test sample was taken in the form pellet of approximately 1cm diameter and 0.2-0.3 cm thickness and is fixed between the two nickel plated brass circular discs which serve as electrodes the two sides of the specimen disc were coated with a thin layer of conducting silver paint for providing good electrical contacts. One of the metal discs which serve as the electrodes was spring loaded to take care of the effect of thermal expansion of the specimen, while making measurements of high temperatures. In the present study of ceramics, the dielectric parameters such as dielectric permittivity and dielectric loss tangent (tan δ) of the samples were measured using a HIOKI 3532-50 LCR meter in the frequency range of 100 Hz to 5 MHz at different temperatures shown in plots. We made a comparison between the dielectric properties of undoped and lead doped ZT. The results expressed that permittivity of ε_r=22 was obtained and it is in close agreement with the literature value of ZT. Owing to the addition of lead into the site of ZT high dielectric constant and low loss was obtained. Therefore, these stoichiometric materials have got applications in variety of fields such as phase shifters, oscillators, antennas, microwave devices, low noise needed devices, and capacitors needed circuitry systems [9, 10]. In few cases the relaxations have been observed for plots of dielectric loss. For x=0.3 concentration high dielectric constant of ε_r=236 was obtained. The plots concerning the dielectric constant and dielectric loss were depicted in the following figures 11-30.



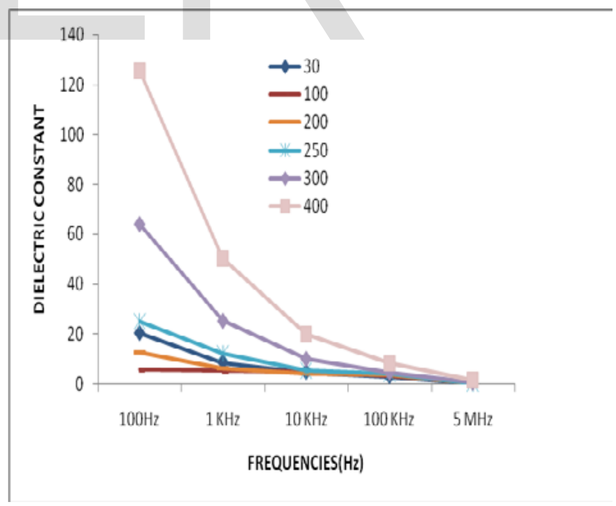
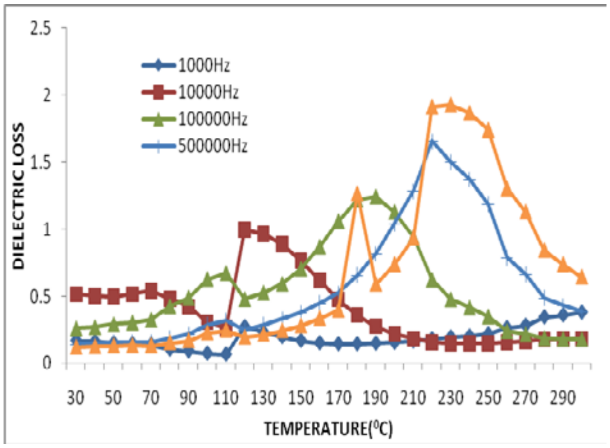


Fig.11. Shows the temperature Vs dielectric constant plot of undoped $ZrTiO_4$

Fig.12. Shows the frequency Vs dielectric constant plot of undoped $ZrTiO_4$



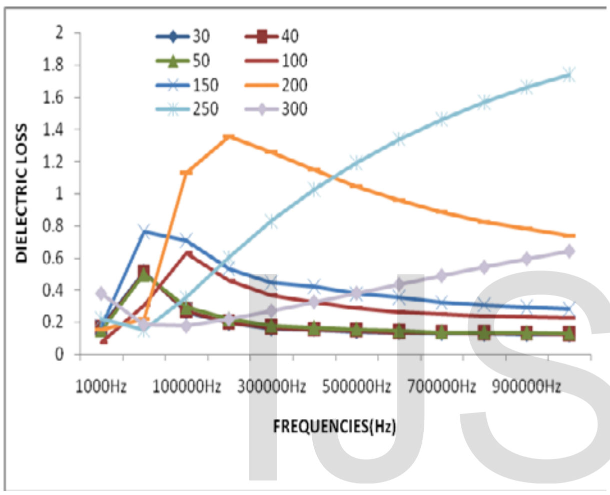
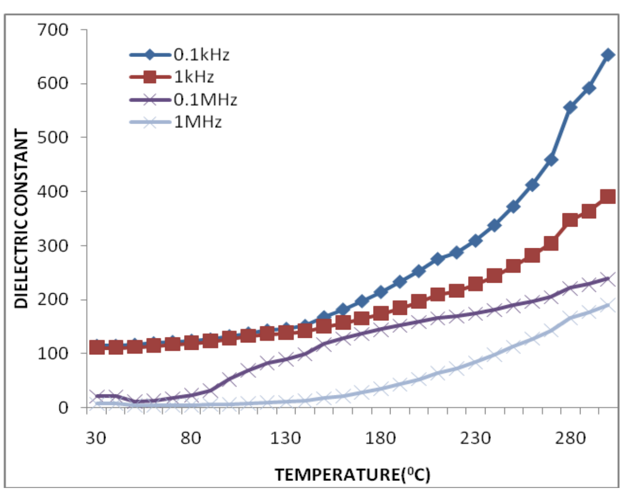


Fig. 13. Shows the temperature Vs dielectric loss plot of undoped $ZrTiO_4$

Fig. 14. Shows the frequency Vs dielectric loss plot of undoped $ZrTiO_4$



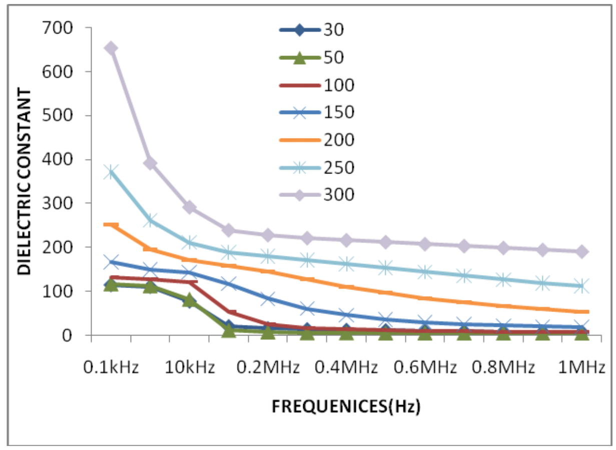
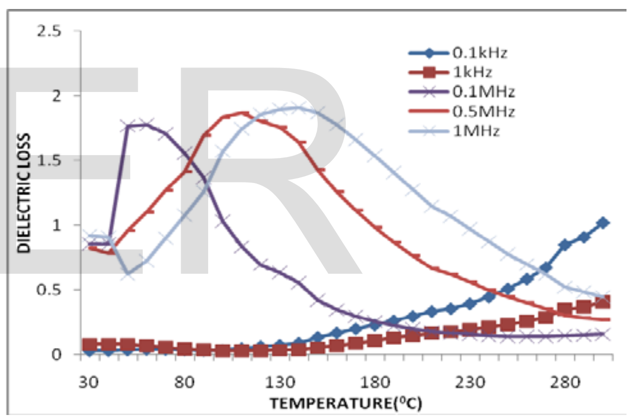


Fig. 15. Shows the temperature Vs dielectric constant plot of $Pb_{0.1}Zr_{0.9}TiO_4$

Fig. 16. Shows the frequency Vs dielectric constant plot of $Pb_{0.1}Zr_{0.9}TiO_4$



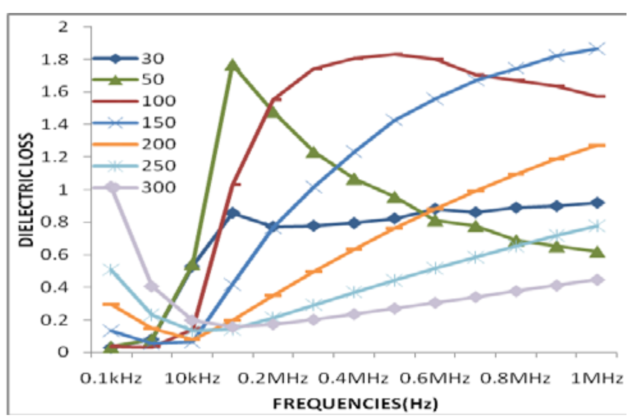
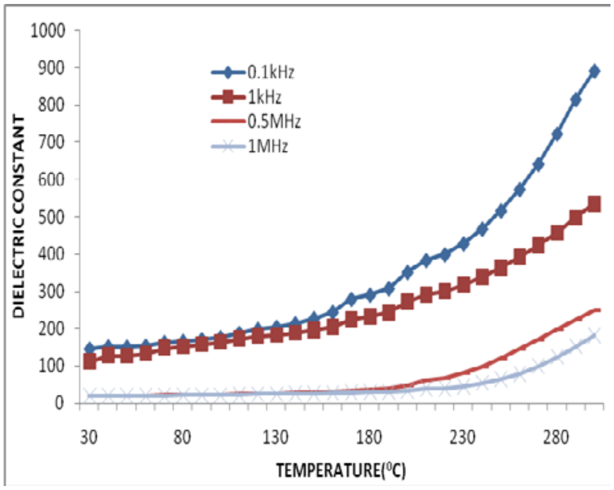


Fig. 17. Shows the temperature Vs dielectric loss plot of $Pb_{0.1}Zr_{0.9}TiO_4$

Fig. 18. Shows the frequency Vs dielectric loss plot of $Pb_{0.1}Zr_{0.9}TiO_4$



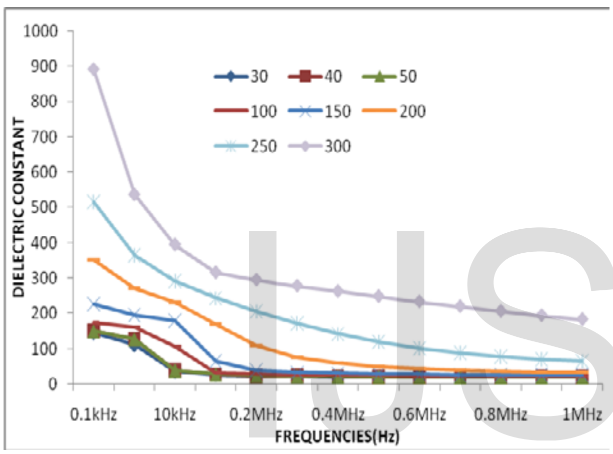
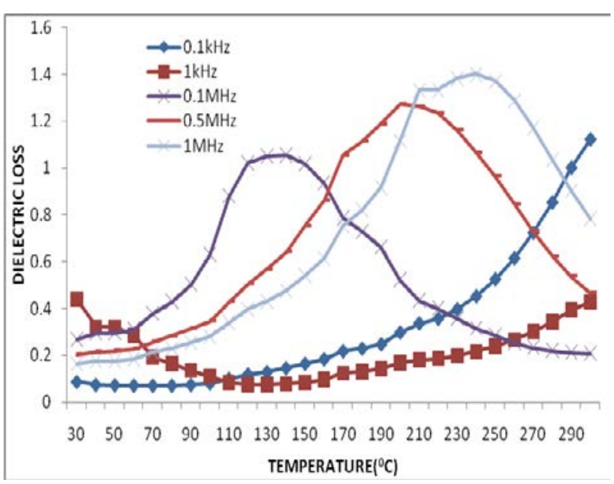


Fig. 19. Shows the temperature Vs dielectric constant plot of $Pb_{0.2}Zr_{0.8}TiO_4$

Fig. 20. Shows the frequency Vs dielectric constant plot of $Pb_{0.2}Zr_{0.8}TiO_4$



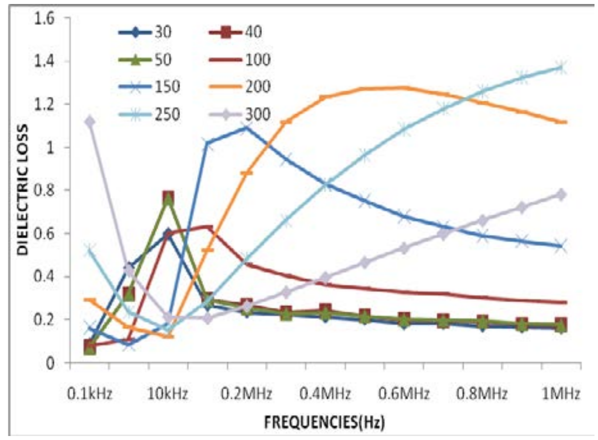
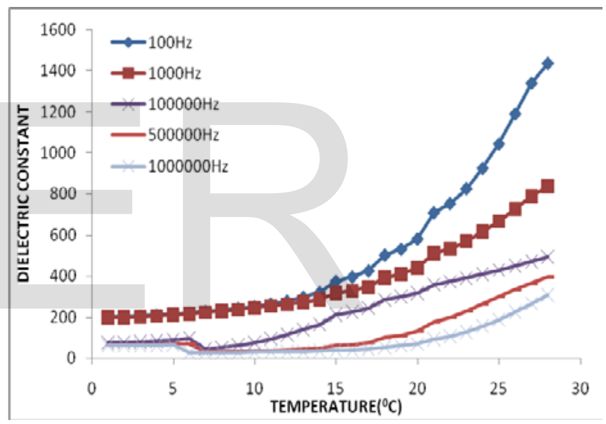


Fig.21. Shows the temperature Vs dielectric loss plot of $Pb_{0.2}Zr_{0.8}TiO_4$

Fig.22. Shows the frequency Vs dielectric loss plot of $Pb_{0.2}Zr_{0.8}TiO_4$



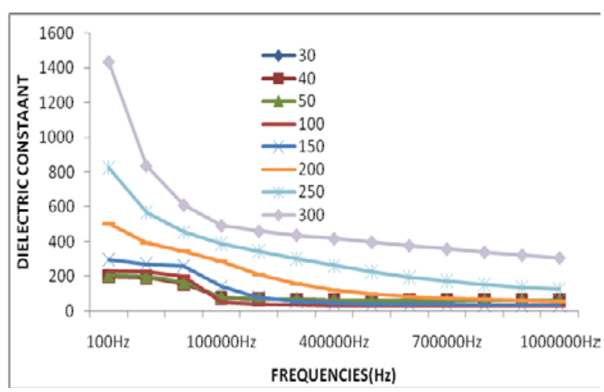


Fig.23. Shows the temperature Vs dielectric constant plot of $Pb_{0.3}Zr_{0.7}TiO_4$

Fig.24. Shows the frequency Vs dielectric constant plot of $Pb_{0.3}Zr_{0.7}TiO_4$

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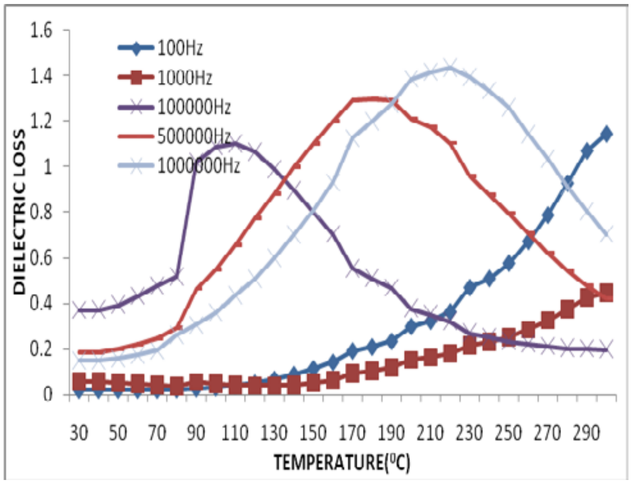


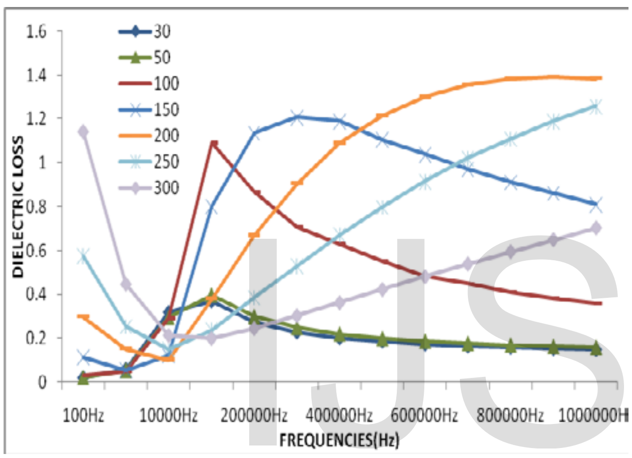
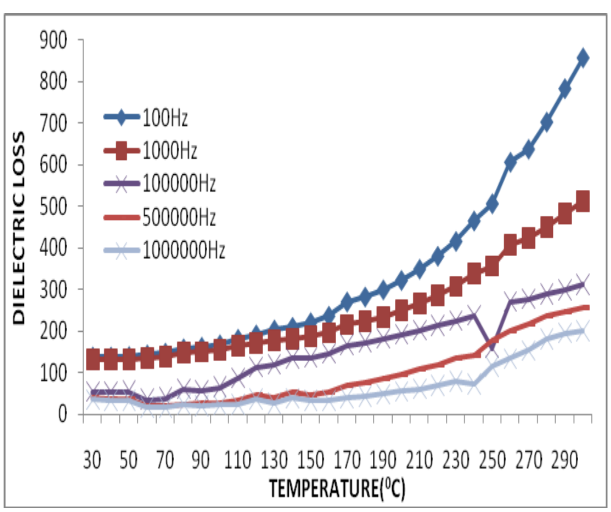


Fig.25. Shows the temperature Vs dielectric loss plot of $Pb_{0.3}Zr_{0.7}TiO_4$

Fig.26. Shows the frequency Vs dielectric loss plot of $Pb_{0.3}Zr_{0.7}TiO_4$



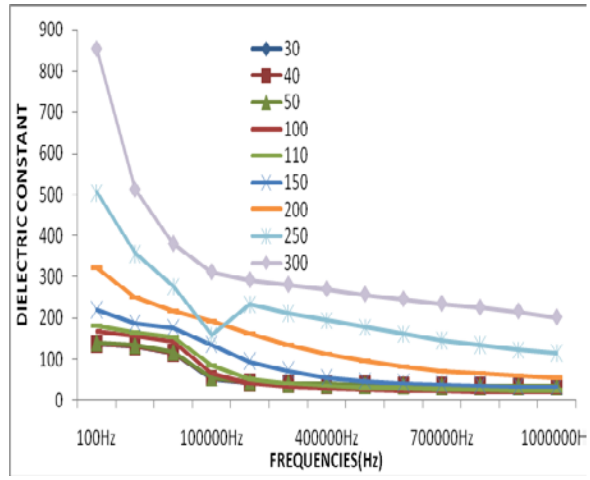
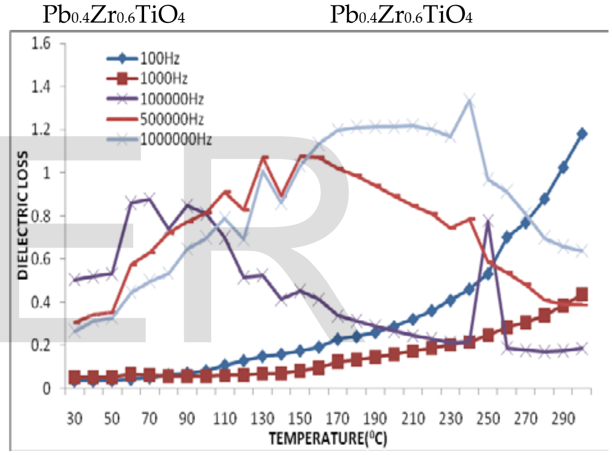


Fig.27. Shows the temperature Vs dielectric loss plot of $Pb_{0.4}Zr_{0.6}TiO_4$

Fig.28. Shows the frequency Vs dielectric constant plot of $Pb_{0.4}Zr_{0.6}TiO_4$



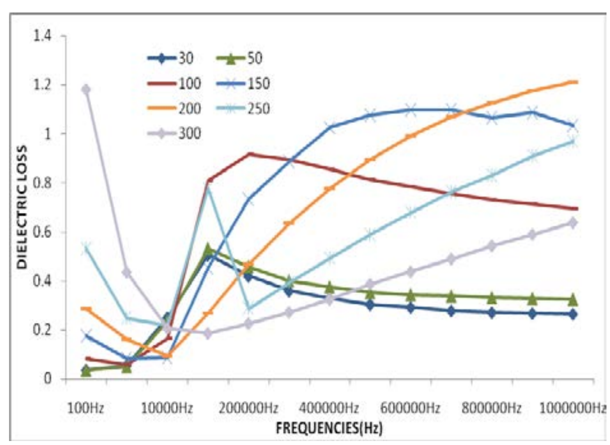


Fig.29. Shows the temperature Vs dielectric loss plot of $Pb_{0.4}Zr_{0.6}TiO_4$

Fig.30. Shows the frequency Vs dielectric loss plot of $Pb_{0.4}Zr_{0.6}TiO_4$

4. CONCLUSION

In this study lead doped zirconiuam titanate prepared through the synthesis of solid state reaction and then characterized using XRD, SEM, to study the structral and morphological properties. The orthorombic structure was indexed from the diffraction pattern. Moreover, the avarage crystallite size was found in the range of 150-300 nm and the grain size was calculated from the SEM micrographs. Dielectric behavior was studied for the synthesized samples and further dielectric loss and dielctric constants were reported. These reports are sutable for dielectric resonator, antenna and optoelectronic device applications.

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