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Structural and Dielectric Properties of PZT Ceramics Prepared by Solid-State Reaction Route

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Abstract− Polycrystalline Pb $(Zr_{1-x}Ti_x)O_3$ with x = 0.50 abbreviated as PZT has been prepared by high energy solid-state reaction technique. Analysis of XRD patterns of this composition suggests the formation of PZT phase with tetragonal structure. SEM studies were used for microstructural characterization. The dielectric properties of PZT ceramics have been characterized. The measurements have been made in frequency ranging from 100 Hz to 1 MHz and between room temperature (RT) and 550ºC for low and high frequencies. At RT, the value of dielectric constant (ε_r) is 515.492 at 1 KHz whereas the loss tangent is 0.005. From ε_r (T) measurements, the Curie temperature of our sample has been determined at 380ºC. The increase of ε_r observed at high temperatures and low frequencies in the paraelectric state are explained, this abnormal behavior is due to the migration of oxygen ions towards the electrodes.

Keywords− Dielectric properties, PZT, Phase transition, SEM, Solid-state reaction technique, XRD etc.

1 INTRODUCTION

Lead zirconate titanate Pb $(Zr_{1-x}Ti_x)O_3$ or PZT, is one of the best known ferroelectric materials due to its remarkable ferroelectric and piezoelectric properties in polycrystalline form [1-3]. It is most widely used piezoelectric ceramic materials in devices like actuators, ultrasonic transducers, sensors, resonators, ferroelectric memory, optoelectronic, piezoelectric transformers [4-6].

Lead zirconate titanate, $Pb(Zr_{1-x}Ti_x)O_3$ or PZT, is solid solution of two simple perovskite, lead titanate ($PbTiO_3$) and lead zirconate ($PbZrO_3$) with broad range of curie temperature. These compounds crystallize in ABO_3 type structure, where the A and B-sites are occupied by Pb^{2+} and (Zr^{4+}, Ti^{4+}) ions respectively. At room temperature PZT, presents two ferroelectric phases, a tetragonal phase in the titanium rich and a rhombohedral phase one in the zirconium rich side [7-8]. A wide range of compositions of PZT ceramics have been investigated with an emphasis on dielectric, piezoelectric and pyroelectric properties. Near the morphotropic phase boundary (MPB), PZT has maximum value of the dielectric and the electromechanical coupling coefficients. Lead zirconate titanate (PZT) material continues to be well-studied system because of its technologically important applications.

The main objective of this work is to prepare and characterize the perovskite type compounds capable enough to continue in pyroelectric and electronic applications.

2 EXPERIMENTAL PROCEDURE

PZT ceramics were prepared by the conventional solid state reaction. The raw materials, PbO, ZrO_2, and TiO_2 were weighted according to the stiochiometric formula Pb $(Zr_{1-x}Ti_x)O_3$ with x = 0.50. An excess of 5 wt% PbO is added to starting materials to compensate for the evaporation of lead during sintering at high temperature. The raw materials were mixed first in air medium then in ethanol medium with the help of agate mortar and pestle. The mixed material was calcined in alumina crucible at temperature 875ºC for 2hr at heating and cooling rate 5ºC /minute. The calcined powders were further mixed and 5 wt% poly vinyl alcohol (PVA) were added to the mixture as a binding agent. After this powders was converted into cylindrical pellets in steel die punch by applying pressure with the help of hydraulic press. Pellets were sintered at 1200ºC for 2hr with the heating and cooling rate 5ºC /minute. During sintering, $PbZrO_3$ was used as lead source in the crucible to minimize volatilization of lead.

The XRD spectra were observed on sintered pellets with an X-ray diffractometer (Brucker D8) at room temperature, using CuK_α radiation over a wide range of Bragg angles (20º ≤ θ ≤ 80º). The morphology, exact size, shape and distribution of the lead zirconate titanate (PZT) particles were determined by scanning electron microscope (SEM, Carl Evo 40). For dielectric measurement, pellets were electrode with platinum by RF sputtering. Dielectric studies were done by measuring capacitance of the sample with Agilent 4284A precision LCR meter as a function of frequency and temperature.

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3 RESULTS AND DISCUSSION

3.1 STRUCTURAL AND MICROSTRUCTURAL STUDY

Fig.1 shows the XRD patterns of PZT ceramic with stiochiometric composition of Pb $(Zr_{1-x}Ti_x)O_3$ (x = 0), collected at room temperature. According to literature, the XRD pattern of PZT ceramic at room temperature corresponds to a single phase tetragonal perovskite structure, with its a-axis value is 4.027 and c/a ratio is 1.023, which is in consistent with the

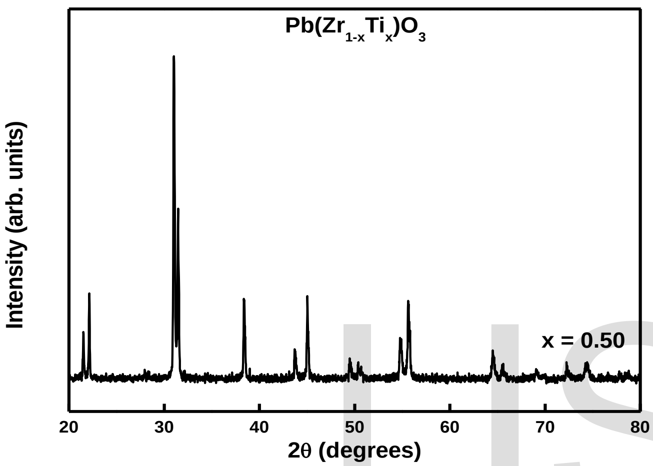

Fig.1 Room temperature XRD pattern of PZT ceramic

reported value in the literature [9-10]. The sharpness of the diffraction peaks in the XRD pattern suggests better homogeneity and crystallinity of the PZT ceramic.

Fig.2 Shows the scanning electron micrograph of PZT

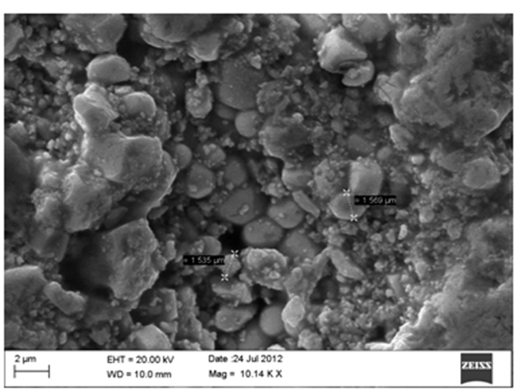

Fig. 2: SEM micrograph of Pb $(Zr_{1-x}T_{ix})O_3$ (x = 0.50) ceramic at room temperature.

ceramic with the composition $Pb(Zr_{1-x}Ti_x)O_3$ with x = 0.50. From the nature of micrograph that the grains are nearly spherical in shape, low porosity and no grain growth was observed in the sample. The value of average grain size is consistent with the value of nearly equal to 1.55μm reported in the literature [11].

3.2 DIELECTRIC PROPERTIES

Fig.3 shows the variation of dielectric constant (ε_r) with frequency at room temperature. It is observed from dielectric constant (ε_r) vs frequency curve (fig.3) that the dielectric

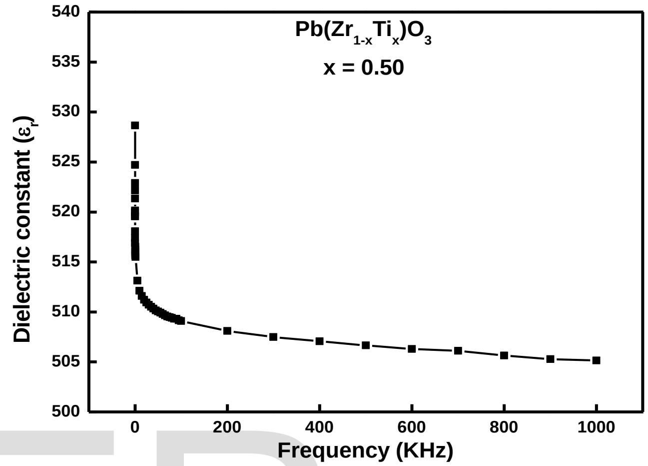

Fig.3 Frequency dependent dielectric constant (ε_r) of PZT ceramic at room temperature (RT)

constant demonstrate sharp decline up to 95KHz thereafter it shows a gradually decline in its value up to higher frequency. The value of dielectric constant (ε_r) at 1 KHz is 515.492 and value of dielectric loss (tanδ) is found to be 0.005 at same frequency.

Dielectric measurements have been carried out from

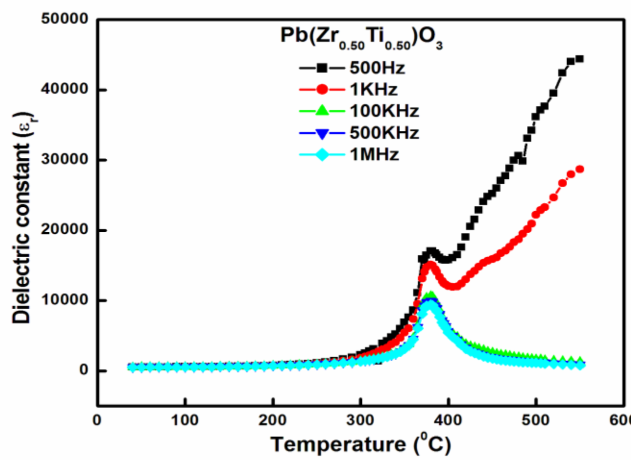

Fig.4 Temperature dependent dielectric constant (ε_r) of PZT ceramic at different frequency

RT to 550ºC in the frequency 500Hz to 1MHz. This enables the examination of the transition from tetragonal ferroelectric

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state to cubic paraelectric state. Fig.4 shows the curves for PZT ceramic at various frequencies between 500Hz and 1MHz. A maximum is observed at T_C = 380ºC. It is independent of frequency which is characteristics of classical ferroelectric. The anomalies in the dielectric constant (ε_r) after its maximum values are observed at lower frequencies (500 Hz & 1 KHz). In the paraelectric region at frequencies lower than 100 KHz the increase of dielectric constant (ε_r) at higher temperatures are due to the migration of oxygen ions [12].

The maximum value of ε_r are 17042.223, 15131.287, 10639.699, 9961.424 and 9406.022 at frequencies 500 Hz, 1 KHz, 100 KHz, 500 KHz and 1MHz respectively.

4 CONCLUSIONS

$Pb(Zr_{1-x}Ti_x)O_3$ (x = 0.50) ceramics have been successfully prepared by a solid-state reaction technique. The XRD pattern of the PZT ceramic confirmed their single phase perovskite with tetragonal structure. SEM studies reveals that the average grain size of the PZT ceramic is found to 1.55µm. At room temperature and frequency at 1 KHz, the dielectric study of the PZT ceramic gives a dielectric constant ε_r = 515.492 and a loss tangent tanδ = 0.005. Measurement at high temperatures permit to determine, from the maximum of ε_r (T), the Curie temperature T_C = 380ºC of the ferroelectric-paraelectric phase transition of PZT ceramic.

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