Study of structural and electrical properties of transitional metal doped Lead Zirconate Titanate piezoelectric compounds

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***Abstract*: The polycrystalline compounds of $Pb_{1-x}M_x\ Zr_{0.52}Ti_{0.48}O_3$ (M= Ni or Mn; x = 0, 0.1) were synthesized using standard ceramic technique. Powder X-ray diffraction (XRD) studies of these compounds suggest that they can be formed in single-phase perovskite structure. Scanning electron microscopy (SEM) analysis shows that the grains are distributed uniformly in the compounds. Detailed studies of dielectric properties (ϵ, tanδ, and Z) of the compounds as a function of temperature have been done for these three samples.**

***Keywords*: X-ray diffraction, piezoelectric, dielectric constant**

I. Introduction:

Lead Zirconate titanate ceramics are widely used as piezoelectric sensors, for ultrasonic wave production etc [1,2] . Properties of these ceramics depend strongly on composition and synthesis methods. At morphotropic phase boundary (MPB) condition the piezoelectric activity is optimum [3] . The MPB is an almost-temperature-independent phase boundary that separates two ferroelectric phases: a tetragonal crystal structure (P4mm) and a rhombohedral structure (R3c) and at this condition anomalously high piezoelectric properties are achieved. Further improvements are made to the electromechanical properties through compositional modifications.

In this work we attempted to improve dielectric properties by doping Nickel and manganese in place of lead in $PbZr_{0.52}Ti_{0.48}O_3$. we also tried to improve the curie temperature with dopants. Since increase in curie temperature will be useful for using the material at higher temperatures.

II. Experimental:

Synthesis:

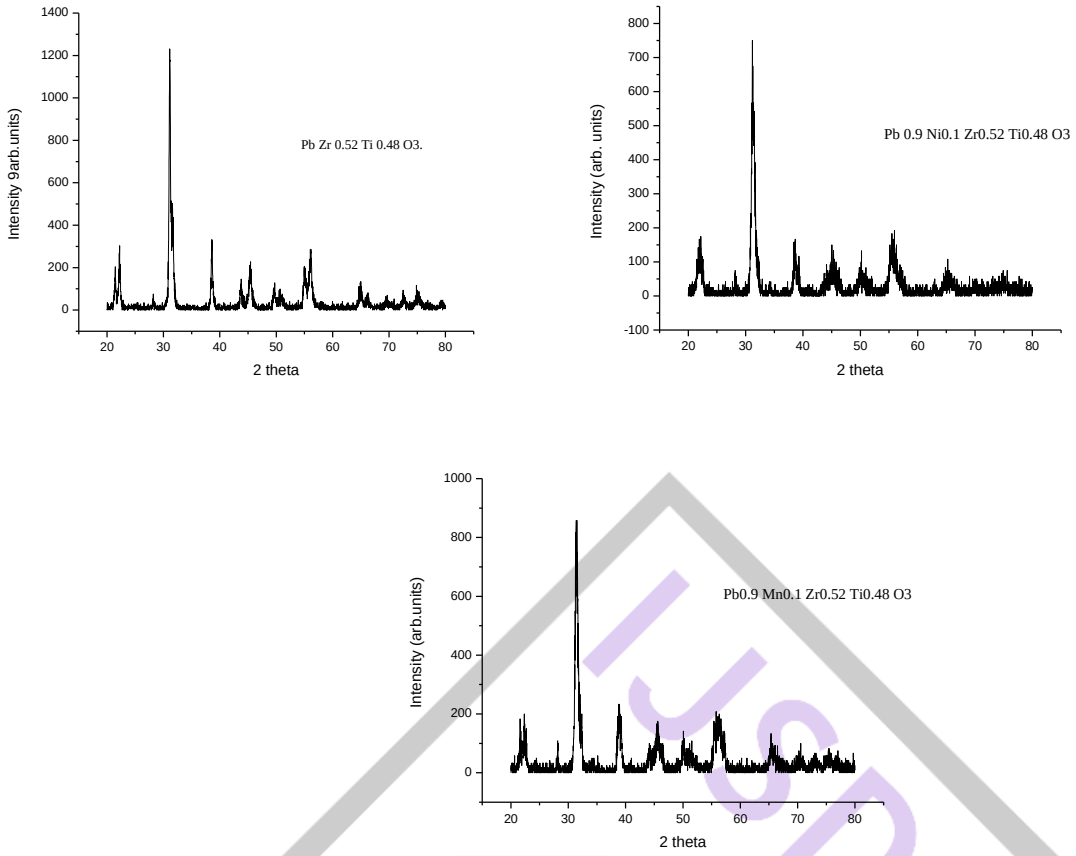
PZT ceramics of composition $Pb_{1-x}M_xZr_{0.52}Ti_{0.48}O_3$ (M= Ni or Mn; x = 0, 0.1) were prepared by standard ceramic method. PbO, ZrO2, TiO2 and nickel oxide or manganese dioxide were taken in stiochiometric amounts. They are grounded in agate mortar for 10 hours and then calcined at 900 ^oC for four hours. This calcined powder was again grounded into fine powder and then made into pellets of 10mm diameter. These pellets were sintered at 1150^oC for two hours. The heating rate was maintained at 5^oC per minute and was cooled to room temperature naturally.

These samples were then subjected to XRD, SEM and impedance measurements. Impedance measurements were done on unpoled samples to check the intrinsic properties of prepared samples.

III. Results and Discussion:

X ray diffraction:

XRD pattern as shown in the figure shows the doing variation for nickel and manganese in the Figure 1.

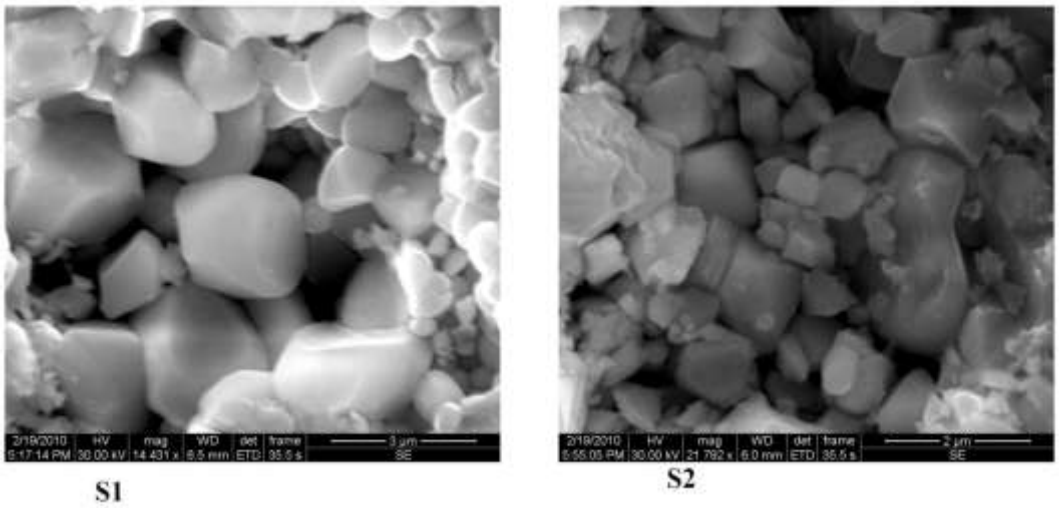


Figures 1 a, b and c: XRD patterns PZT, Nickel doped PZT and Manganese doped PZT.

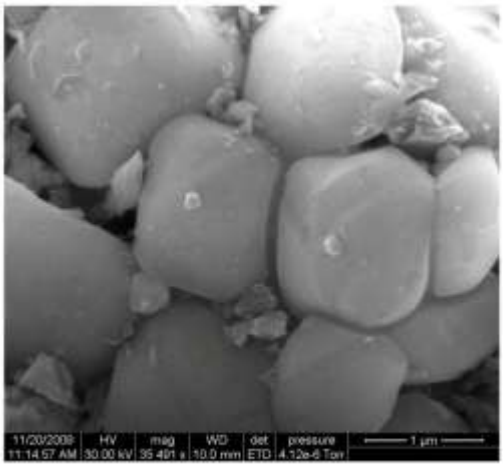
The obtained peaks are indexed and no extra impurities have been found. The nature of the XRD peak suggests the temperature used for sintering is sufficient for phase formation with good crystalline nature in the sample. Comparing the standard data base, the values of lattice parameter have been indexed. The lattice parameter for S1 samples (a= 3.99224, c= 4.14908), S2 sample (a= 4.0101, c=4.10373) and S3 (a=3.96985, c=4.139115) show clear variation and affect of higher atomic number of nickel.

Scanning Electron Microscope:

SEM pattern observed from Figure 2 shows the sudden drop in the grain size for doping of nickel and higher grain size for manganese.



S1 S2



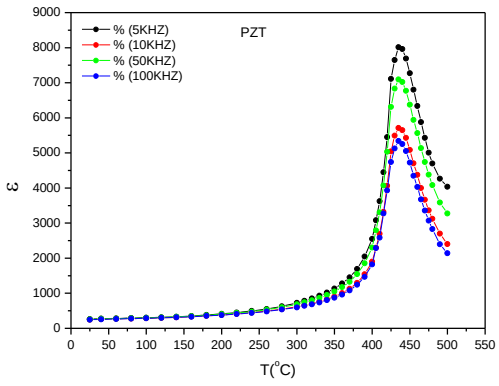
S3

Figures 2: SEM pictures of $PbZr_{0.52}Ti_{0.48}O_3$, $Pb_{0.9}Ni_{0.1}Zr_{0.52}Ti_{0.48}O_3$ and $Pb_{0.9}Mn_{0.1}Zr_{0.52}Ti_{0.48}O_3$

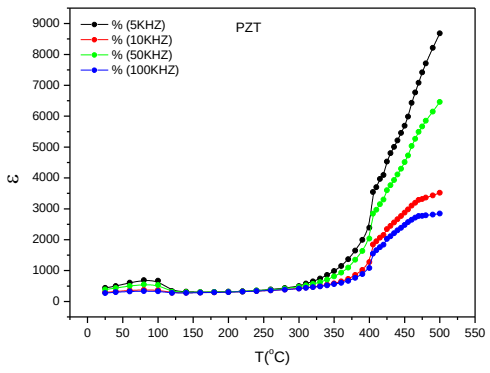
The grain size observed from the picture could be estimated as 3 μm for S1 samples, 0.4 μm for S2 sample and 1μm for S3 sample. This could be variation could be understood on the basis of atomic radius or size of the nickel and manganese. The Nickel which has higher valency could migrate in to different structures leading to lower grain size when compared to Manganese. The lower density values of manganese could also lead to higher porous nature could affect the dielectric properties of the samples.

Dielectric properties

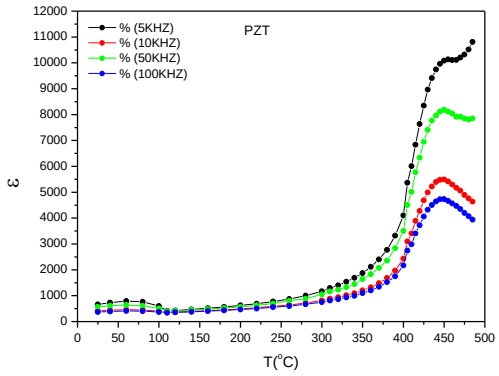
The Variation of dielectric constant and loss (tan δ) with temperature at selected frequency (5 kHz,10 KHz, 50 kHz and 100 kHz) was measured for the samples and shown in Figure 3 and Figure 4.



S1

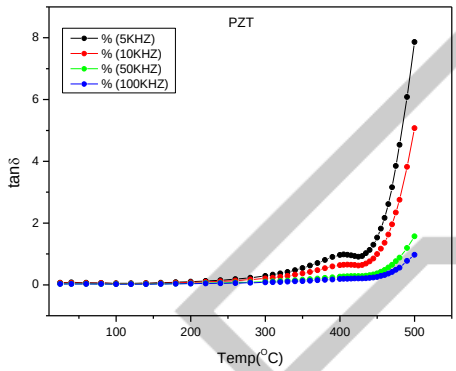


S2

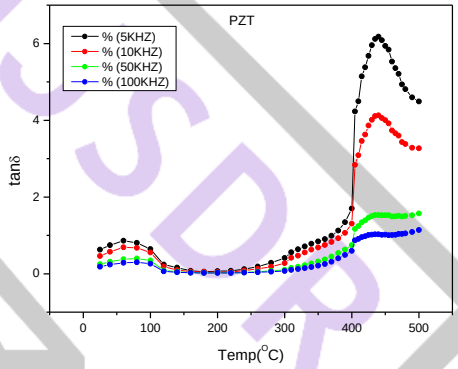


S3

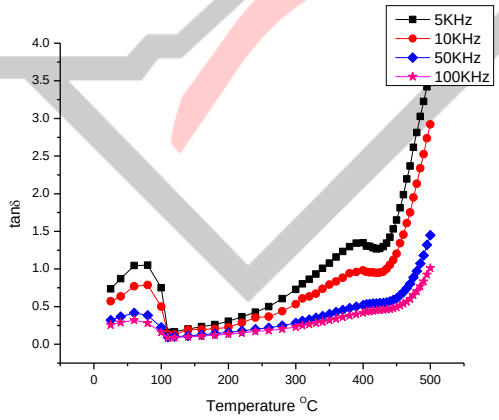
Figure 3: variation of dielectric constant with temperature of $PbZr_{0.52}Ti_{0.48}O_3$, $Pb_{0.9}Ni_{0.1}Zr_0$ and $Pb_{0.9}Mn_{0.1}Zr_{0.52}Ti_{0.48}O_3$



S1



S2



S3

Figure 4: variation of tanδ with temperature of $PbZr_{0.52}Ti_{0.48}O_3$, $Pb_{0.9}Ni_{0.1}Zr_{0.52}Ti_{0.48}O_3$ and $Pb_{0.9}Mn_{0.1}Zr_{0.52}Ti_{0.48}O_3$

The figures shows the normal dielectric behavior of the samples associated under investigation due to polarization as suggested by Maxwell Wagner [4]. It can be observed that dielectric constant is result of frequency driven phenomenon decreasing with increase in frequency as shown in figure 3. The dielectric constant decrease for higher frequency could be understood on the absence of polarization at higher frequency. With rise in temperature, the dielectric constant increases and resonance peak is observed. It is evident from that the dielectric constant increases with increase in temperature reaching out high value for sample S1 & S3 then showing transition temperature (T_d). T_d is transition temperature is not observed for the samples S2 and S3

suggesting that the doping of Nickel (Ni^{2+}/N^{i3+}) suggesting the presence of resonance peak at higher temperature range. Applied field along with temperature is not sufficient for the samples S2 to excite the dipoles which could show polarization. The behavior of dielectric constant at different temperature could be understood on the basis of inability of charge carriers which cannot orient themselves at lower temperature [same two references above]. With rise in temperature, charge carriers which are trapped will acquire energy to liberate them and able to obey the polarization laws easily under the influence of field. The simplest expression which can express the dependence of dielectric constant, conductivity and tanδ with frequency is given by [5]:

$$\varepsilon' = \frac{4\pi\sigma}{\omega \tan\delta} \qquad (1)$$

The dielectric constant contributed from the charges which are trapped in the volume or dipoles which are frozen or displaced in the domain structure. These plays a significant contribution in the relaxation and conduction process associated. The force exerted by the applied field on the charges or ions creating angle subtended between the dipole and field generating loss associated measured by tanδ. The variation of tanδ for the samples for different temperature range measured under different applied field condition as shown in the Figure 4. Tanδ showed lower values for higher frequency which is similar behavior as seen for dielectric. The figure suggests the rise in angle subtended with rise in the thermal energy among the dipoles under the applied field. This rise will continue up to a point then fall causing relaxation as shown in the sample S2. The transition observed in the figure 2 could be due to high losses associated with magnesium. The sample S1 and S3 no transition indicating the continuation rise of angle with change in the temperature which could be due to dielectric nature in the samples rises through charge carriers. The above changes could be understood on the basis of frequency dependence on activation energy given the relation [6]:

$$f = f_{\circ} \exp\left(\frac{-E_d}{k \cdot T}\right) \qquad (2)$$

For ‘k ‘ is the Boltzmann constant and ‘Ed’ is the activation energy. The replacement of concentration with manganese could lead to higher porosity which further contributes to higher tanδ causing lower transition temperature.

IV. Conclusions:

The lattice parameter for S1 samples (a= 3.99224, c= 4.14908), S2 sample (a= 4.0101, c=4.10373) and S3 (a=3.96985, c=4.139115) show clear variation and effect of higher atomic number of nickel. From the figure2 it has been observed that the Nickel which has higher valency could migrate in to different structures leading to lower grain size when compared to Manganese. From figure 3 it is evident thatdielectric constant is result of frequency driven phenomenon decreasing with increase in frequency and the dielectric constant increases with rise in temperature and resonance peak is observed. From figure 4 it is observed that tanδincreases with temperature and also tanδ decreases with increase in frequency.

References:

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