

A Comparative Study of Structural and Dielectric Properties of Fe and Ni doped PZT ceramics

Nitu Kumari, Jagdhar Mandal, P. L. Meena

Abstract—Ceramic samples of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PZT), $\text{Pb}_{0.95}\text{Ni}_{0.05}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PNZT) and $\text{Pb}_{0.95}\text{Fe}_{0.05}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PFZT) were prepared by conventional solid state reaction method to study the effect of Fe^{3+} and Ni^{2+} substitution at A site on the crystal structures and dielectric properties. Single phase formation along-with no significant change in the structural symmetry was observed with Ni^{2+} and Fe^{3+} . The effect of Ni^{2+} and Fe^{3+} substitution on the dielectric constant, $\epsilon'(\omega)$, and loss tangent, $\tan\delta$, was studied over a wide range of frequency and temperature. The values of $\epsilon'(\omega)$ decreases with Ni^{2+} and Fe^{3+} content in PZT ceramic. The transition temperature of PZT decreases from 683 K to 298 K with substitution of Ni^{2+} and Fe^{3+} ion.

Index Terms— Ceramic, $\text{Pb}_{1-x}\text{A}_x(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, XRD

I. INTRODUCTION

Lead zirconate titanate (PZT) ceramics are the well-known class of ferroelectric materials of choice in a wide range of applications in several fields like high energy capacitors, nonvolatile memories (FERAM), ultrasonic sensors, infrared detectors and electro-optic devices [1] - [3]. They are expressed by the general formula ABO_3 of the perovskite structure in which the site A is occupied by Pb^{2+} (Ionic radii = 1.18Å) and the site B is occupied both by Zr^{4+} (0.72Å) and Ti^{4+} (0.61 Å). The properties of the material can be enhanced by doping of different transition metal ions at A and B sites in perovskites [4]. Only on the sizes of the sites determine the doping at A and B sites and doping is found to be independent of the donor and acceptor properties of the foreign ions.

In present study single-phase compositions of PZT, PNZT and PFZT ceramic composition have been prepared by solid-state reaction method, and the structural and dielectric properties has been investigated systematically.

II. EXPERIMENTAL DETAILED

$\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PZT), $\text{Pb}_{0.95}\text{Ni}_{0.05}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PNZT) and $\text{Pb}_{0.95}\text{Fe}_{0.05}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PFZT) ceramic compositions were prepared by conventional solid state reaction method using high purity (> 99.9%) starting materials consisting of PbO, ZrO_2 , TiO_2 , Fe_2O_3 , and NiO. Excess amount of PbO was added to compensate the lead evaporation during high sintering process. The reactant

oxides (PbO , ZrO_2 , TiO_2 , NiO and Fe_2O_3) were mixed thoroughly with the help of mortar and pestle for 4 hrs and calcined at 800 °C for 5 hrs. Calcined powders were pressed at a pressure of 6 tons to obtain ~ 2 mm thick circular discs of 12 mm diameter. The discs were finally sintered at 1250 °C for 2 hrs in a programmable muffle furnace. The steps were taken for representation of ceramic samples is shown in Fig. 1.

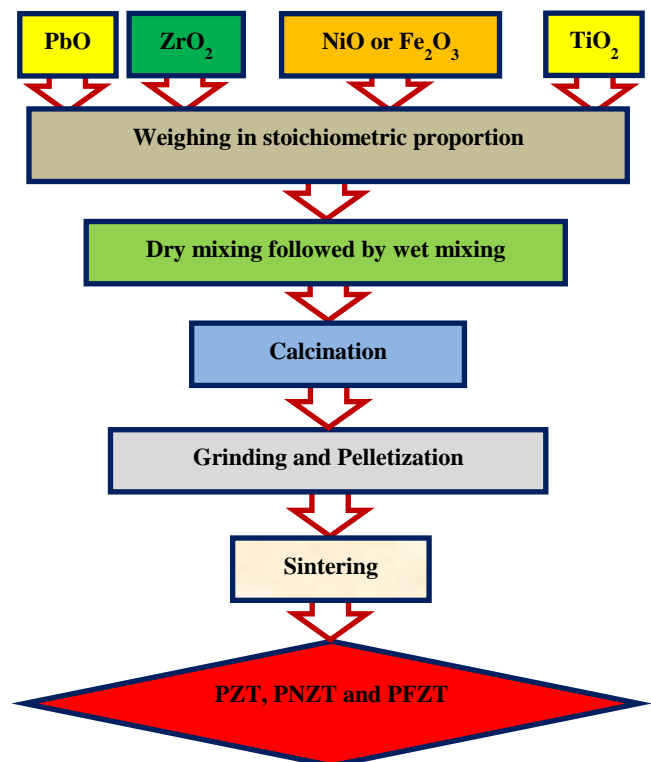


Fig. 1: Steps for preparation of PZT, PNZT and PFZT ceramic samples.

Room temperature X-ray powder diffraction (XRD) patterns were recorded using a Bruker D8 X-ray diffractometer with copper $\text{K}\alpha$ radiation in the step scanning mode with a 0.01° step size in the range $20^\circ \leq 2\theta \leq 60^\circ$. XRD data was analyzed using PowderX software. The dielectric measurements of the prepared ceramic samples were carried out using Agilent 4284A precision LCR meter in the metal-insulator-metal (MIM) configuration. For MIM configuration both faces of cylindrical discs were highly polished and coated with fine silver paste to serve as electrodes.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the powder XRD pattern for PZT, PFZT and PNZT ceramic compositions at room temperature. The XRD

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patterns show the formation of a single phase, and all the observable reflection planes could be indexed as shown in Fig. 1. PZT, PNZT and PFZT ceramic were crystallized in the tetragonal structure with space group P4mm [5] - [6]. The estimated value of the lattice parameters, *a*, *c* and *c/a* ratios are presented in Table 1, and in agreement with the earlier reported results [7]. No structural change was observed in the basic crystal symmetry of PZT except that the systematic small shift in the peak positions toward higher diffraction angle with substitution of Fe³⁺ and Ni²⁺ ions at A-site (Fig.1), which compensate Pb²⁺ ions or A-site vacancies. From the diffraction data it is evident that there is the formation of single phase perovskite structure for all compositions.

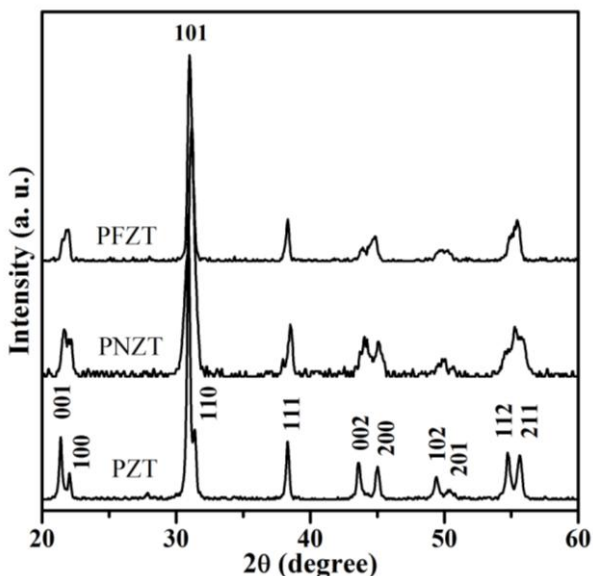


Fig. 2: XRD patterns for PZT, PNZT and PFZT.

Fig. 3 shows the scanning electron micrograph (SEM) of sintered PZT, PNZT and PFZT ceramics. Micrographs indicate non homogeneous distribution of polycrystalline grains throughout the surface of material. The average grain size calculated from the micrograph of PZT, PNZT and PFZT is presented in table 1.

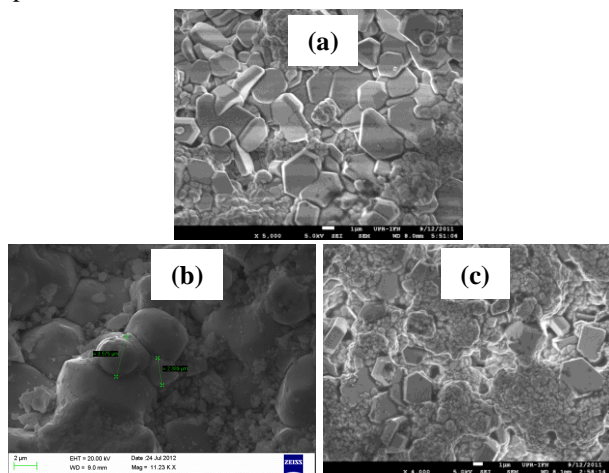


Fig. 3: SEM micrograph for (a) PZT, (b) PNZT and (c) PFZT ceramic samples.

Figs. 4 (a) and (b) show the room temperature dielectric constant, $\epsilon'(\omega)$, and loss tangent, $\tan\delta$, as a function of frequency range from 100 Hz to 1.0 MHz for PZT, PNZT and

PFZT ceramic samples. The $\epsilon'(\omega)$ exhibits a dispersion at low frequencies and a linear variation at higher frequencies for PZT, PFZT. The dispersion in $\epsilon'(\omega)$ at low frequencies may be the contribution of different type of polarization (interfacial, dipolar, atomic/ionic and electronic), however, the dispersion is negligible in the case of PNZT ceramic. PZT doped with Fe³⁺, $\epsilon'(\omega)$ increase, however Ni²⁺ doped instead of Fe³⁺ dielectric constant decrease at room temperature [8]. This may be attributed to Fe³⁺ was larger grain size than Ni²⁺. As the grain size increased, the maximum dielectric constant increased and the transition temperature decreased (table 1), respectively.

Table 1. Lattice parameters (*a* and *c*), ratio (*c/a*), grain size (*D*) and transition temperature (*T_c*)

Ceramics	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>	<i>D</i> (μm)	<i>T_c</i> (K)
PZT	4.008	4.123	1.029	0.25	683
PNZT	4.005	4.136	1.033	0.21	650
PFZT	4.010	3.970	1.028	0.41	298

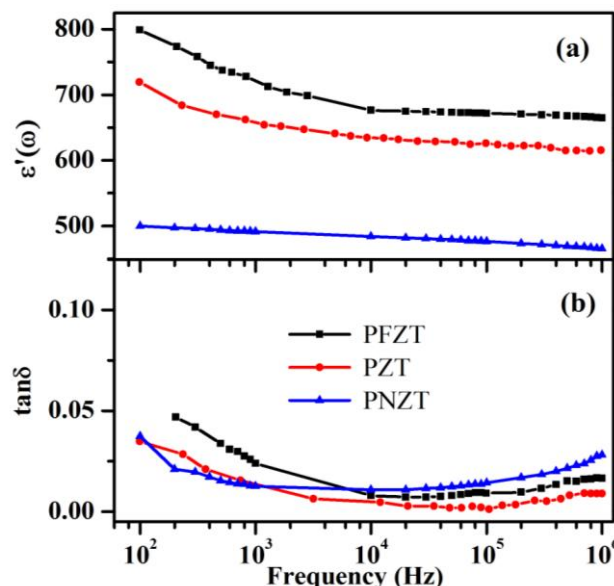


Fig. 4: Room temperature variation of $\epsilon'(\omega)$ and $\tan\delta$ as a function of frequency for PZT, PNZT and PFZT ceramics.

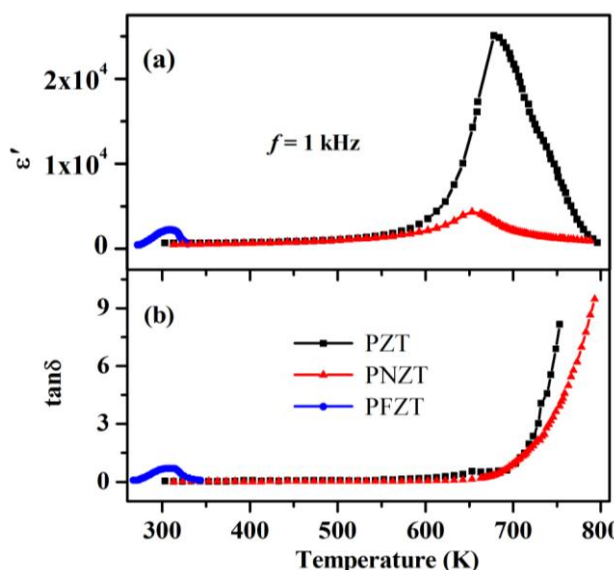


Fig. 5: Variation of ϵ' and $\tan\delta$ as a function of temperature at 1 kHz for PZT, PNZT and PFZT ceramics sample.

A low anomaly has been observed in the $\tan\delta$ for PZT, PNZT and PFZT sample at low frequencies while for higher frequencies it shows linear behavior with very low values.

Fig. 5(a) and (b) show the temperature variation of $\epsilon'(\omega)$ and $\tan\delta$ for PZT, PNZT and PFZT ceramics at 1.0 kHz, respectively. The transition temperature (T_C) of $\epsilon'(\omega)$ shifted towards the room temperature with Fe^{3+} doped in PZT while in the case of Ni^{2+} slightly less observed [Fig. 5(a) and Table 1]. It is also clear from Fig. 5(a) that the values of maximum $\epsilon'(\omega)$ at T_C for Fe^{3+} and Ni^{2+} doped PZT are lower than the pure PZT. The values of $\tan\delta$ for PZT and PNZT are small and nearly independent of temperature below T_C and increases as temperature increases [Fig. 5(b)]. However, a prominent peak in $\tan\delta$ for PFZT observed. The presence of peak and higher values of $\tan\delta$ is indicating a relaxation process. This type of behavior in $\epsilon'(\omega)$ and $\tan\delta$ indicate preeminent dc conductivity contributions as a consequence of higher grain boundary area which favors inter-grain conductivity. Additionally, peaks of $\tan\delta$ near the transition temperature region at high frequency are representative of strong absorption [9].

IV. CONCLUSION

In this study, PZT, PNZT and PFZT ceramic samples were synthesized successfully by solid state sintering method. These ceramics sample exhibit good homogeneity and formation of a single-phase compound with tetragonal structure. SEM indicates homogeneous distribution of polycrystalline grain throughout the surface of material. Fe^{3+} and Ni^{2+} doping in PZT provide many interesting features of the materials, such as the shift in transition temperature and modification of dielectric properties.

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