Lead Zirconate Titanate Piezoelectric Ceramics with Nickel Oxide Additions

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Abstract:- This paper presents research results on the electro–mechanical behavior of piezoelectric ceramics for use in actuator applications. The material being investigated is a lead zirconate titanate piezoelectric ceramic with the composition $Pb_{1-x}Ni_x (Zr_{0.52}Ti_{0.48})O_3$. The X-ray diffraction study shows the formation of homogeneous polycrystalline tetragonal structure. Grain size decreases with increasing Ni^{2+} concentration. Dielectric behaviors of the x = 0.00, 0.05, 0.10 ceramics are more of normal ferroelectrics. With increase in Ni^{2+} concentration ε'_{max} decreases whereas no trends are observed in transition temperatures (T_c) with increase in Ni^{2+} concentration. Piezoelectric property measurements reveal that the pure PZT ceramic exhibits higher piezoelectric coefficient which is found to be 185 pC/N and further piezoelectricity exists in all Ni doped PZT ceramics in decreasing order.

Keywords:- Dielectric, Ferroelectric, PNZT, Piezoelectric, solid solutions.

I. INTRODUCTION

Lead-based perovskite-type solid solutions consisting of the ferroelectric materials have attracted a growing fundamental and practical interest because of their excellent dielectric, piezoelectric and electrostrictive properties which are useful in actuating and sensing applications [1]. Lead zirconate titanate ceramics ($Pb(Zr_{1-x}Ti_x)O_3$ or PZT) with compositions near x = 0.48 have been known the morphotropic phase boundary (MPB) for many year. The piezoelectric constant, dielectric constant and electromechanical coupling coefficient all exhibit a pronounced maximum value for the composition corresponding to this phase boundary. The component closest to the MPB then becomes the main research focus for PZT ceramics. However, PZT ceramics are fairly lossy as a result of their highly hysteretic behavior. In the corresponding to the composition near x = 0.48, which separates the region of the stable tetragonal ferroelectric phase (the T phase) from the region of the stable rhombohedral ferroelectric phase (the T phase). In this situation, the morphotropic phase boundary corresponds not to the conventional phase transition observed under variation in temperature but to the phase transition induce by change in the concentration of components. However, it is also shown earlier researcher [2].

We have been interested in piezoelectric material PZT because it has unique characteristics. Piezoelectricity is the charge that accumulates in certain solid materials (crystals, certain ceramics) in response to applied mechanical stress. The word piezoelectricity means electricity resulting from pressure. PZT ceramics have been of great interest and technological importance in ultrasonic applications such as hydrophones, actuators and underwater transducers, sensor [3-5]. This results from their ability to accomplish coupling between mechanical and electric signals as well as their possibility of obtaining very high values for some piezoelectric coefficients. Previous studies into the electro–thermomechanical response of piezoelectric materials in the low electric field regime have been conducted by a number of researchers. Jona and Shirane [6] reported that the crystal's dimensions are functionally dependent upon temperature. Later, Jaffe and Berlincourt [7] noted that the piezoelectric strain coefficients depend upon temperature. Haun [8] suggested that the polarization-related electrostrictive coefficients, Q_{ij} are independent of both composition and temperature variations. However, these coefficients do not permit closed form solutions of combined electro–thermoelastic problems due to nonlinearities involved. Zhang et al. [9] attributed the temperature dependence of the piezoelectric strain coefficients to the mobility of extrinsic domains, most likely the non-180° domains. Other papers [10] provide details on how to include the temperature-dependent behavior of the piezoelectric coefficients in constitutive relations using thermodynamic approaches. While all of these studies provide valuable information on the electro–thermomechanical behavior of PZT, most are focused on sensor-related issues ~i.e., high frequency and low electric field are inappropriate for actuators ~i.e., low frequency and high electric field.

II. EXPERIMENTAL PROCEDURE

The different ceramics composition of $Pb_{1-x}Ni_x (Zr_{0.52}Ti_{0.48})O_3$ (x = 0.00 to 0.10) are prepared and synthesized by conventional solid state reaction method. The precalcined mixture of PbO, ZrO_2, TiO_2, NiO of

Alfa Aesar with purities of > 99.9% are used as starting material. These powders are mixed thoroughly first in air atmosphere and then in alcohol medium with the help of agate mortar and pestle for 4hrs and later calcined at 800°C for 5 hrs. The mixed powders are pressed hydraulically to form disc shaped pellets 12 mm diameter and 1.5 mm thick, with 5wt% polyvinyl alcohol (PVA) as a binder. The pellets are stacked in a covered alumina crucible filled with PZ powders to prevent lead loss. Finally, the sintering is carried out a sintering temperature at 1250°C for 2hrs with 5 min/°C heating and cooling rates. X-ray diffraction (XRD) studies of these ceramic samples are performed using a Bruker D8 X-ray diffractometer with Cu k_α radiation at room temperature. The piezoelectric constant (d_{33}) of PNZT ceramics are measured by piezometer (model PM 35) as a function of Ni^{2+} concentration. The surface morphology of the pellets of PFZT is studied using a scanning electron microscopy (Carl Zeiss Evo) 40 to understand the size and quality and grains distribution. The dielectric measurement of the $Pb_{1-x}Fe_x(Zr_{0.52}Ti_{0.48})O_3$ ceramics are carried out using Agilent 4284A precision LCR meter as a function of frequency (20 Hz -1 MHz) in metal-insulator-metal configuration. To investigate the electronic transport mechanism of the PFZT solid solution both faces of pallets are highly lapped, polished and thinly coated with platinum on TiO_2 tamplet layered PFZT pellets by RF-sputtering to serve as electrodes. TiO_2 tamplet layers are used to improve adhesion of the conducting layer. The polarization hysteresis loop of $Pb(Zr_{0.52}Ti_{0.48})O_3$ are measured using a automatic PE loop pressure system at room temperature.

III.   CHARACTERITION

"3.1 XRD"

Room temperature XRD patterns of the sintered pellets of PNZT are shown in Fig.1. The X-ray diffraction (XRD) spectra of the sintered samples are recorded in the 2θ range of 20° - 80° with step of 0.02° and scanning rate of 1°/min. These have sharp and single diffraction peaks, indicating better homogeneity and crystallization of the samples. All the reflection peaks were indexed and lattice parameters of the compounds were calculated using a powder diffraction refinement computer program (PowderX) [C. Dong, 1999] and the crystal structure is found to be tetragonal with space group p4mm [11]. The diffraction peaks of PNZT were indexed according to previously reported results [12]. There is no change in their basic structure of PZT with substitution of Ni^{2+} ions at A site or Pb^{2+} site up to x = 0.2, which compensate Pb^{2+} site vacancies. The values of lattice parameters 'c' of PNZT ceramic composition is found to increase with increasing Ni^{2+} concentration while "a = b" slightly decreases (4 table). The estimated value of lattice strain c/a ratio is increases linearly with increasing substitution of Ni^{2+} in polycrystalline solid solution of PZT. The diffraction peak shifting toward a higher 2θ value with increasing the Ni^{2+} concentration also indicates that the lattice parameter 'a' of PFZT ceramic is reduced. Figure 2 shows the scanning electron micrograph (SEM) of sintered PNZT ceramics. Micrographs indicate non homogeneous distribution of polycrystalline grain throughout the surface of material. The average grain size calculated from the micrograph of PZT is 0.25 μm. As increase the Ni^{2+} concentration decreases the grain size. Grain size for x = 0.00 (0.36 μm) and for x = 0.10 (0.26 μm).
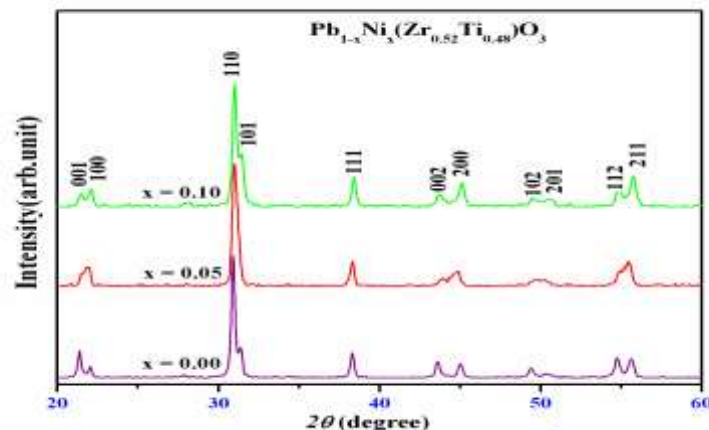

Fig.1. X-Ray patterns of $Pb_{1-x}Ni_x(Zr_{0.52}Ti_{0.48})O_3$ with different Ni^{2+} concentration x= 0.00 to 0.10.

"4.Table"

Comparison of lattice parameter, grain size, and dielectric parameters of PNZT samples

Physical parameters		Composition $Pb_{1-x}Ni_x(Zr_{0.52}Ti_{0.48})O_3$		
		X = 0.0	X = 0.05	X = 0.10
Lattice parameters in (Å)	a	4.067	4.042	4.012

	c	4.134	4.146	4.167
c/a		1.016	1.025	1.038
Grain size (μcm)		0.36	0. 28	0.26
ε'_{max} (100KHz)		22912	1412	1339
T_c (K)		643	691	693
d_{33} (pC/N)		185	130	121
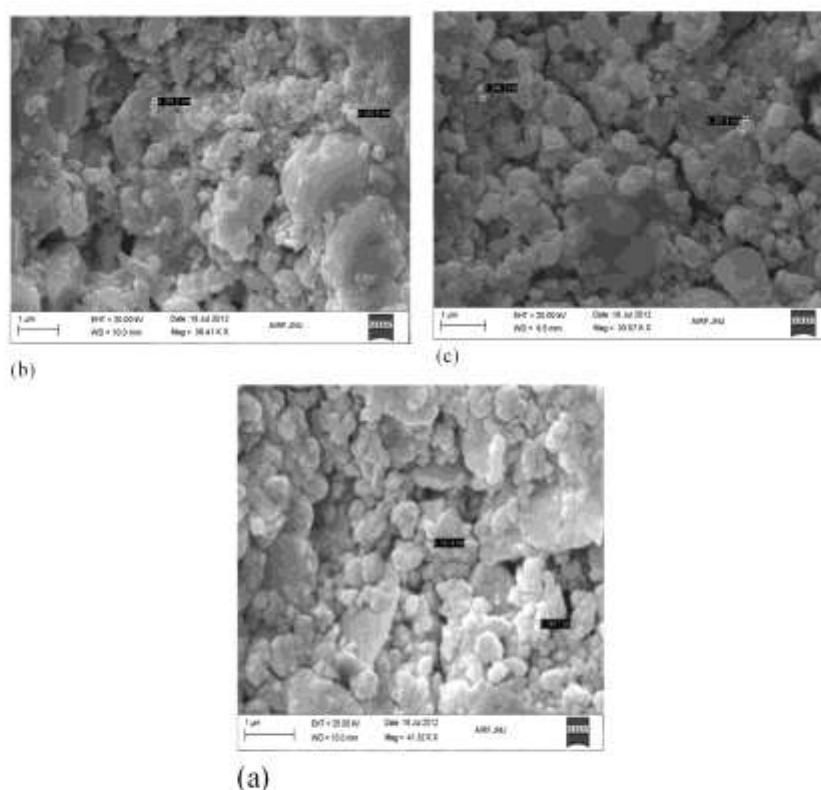
(b)

(c)

(a)

Fig.2. SEM micrograph of $Pb_{1-x}Ni_x(Zr_{0.52}Ti_{0.48})O_3$ with different Ni^{2+} concentration

(a) x = 0.00, (b) x = 0.05, (c) x= 0.10.

IV. DIELECTRIC AND PIEZOELECTRIC PROPERTIES

In PZT ceramics near the MPB, where the tetragonal and rhombohedral phases coexist, temperature-induced phase transition between the two phases should be a first order phase transition. Fig.3 Show the temperature dependence of dielectric constant and loss at 100 kHz, 500 KHz and 1 MHz. The variation of Curie temperatures (T_c) and dielectric properties with composition are listed in Table 1. The behavior of ε' identifies our samples as nonrelaxor. Maximum dielectric constant at T_c (ε'_{max} = 22912) could be achieved in pure PZT ceramic. Increasing Ni^{2+} concentration generally dielectric constant is decreases and T_c is slightly increases. The ε' shows weak temperature dependence in the temperature range 300 -600 K for all PNZT ceramic samples however strong temperature dependence of permittivity is observed at higher temperature ranges (>600 K). The presence of ferroelectric to paraelectric phase transition peaks of ε' in the temperature range of 650−700K are clearly seen in Fig. 3 for all PNZT ceramic samples, where ε' is maximum which is an evidence of existence of ferroelectricity in all fabricated solid solutions. It may be recognized to the fact that with decrease in grain sizes the dielectric constant decrease [13].The temperature verses dielectric loss curve for all the compositions of PNZT ceramics are examined and presented in Fig.3. The dielectric losses for all PNZT ceramics are observed with low value at lower
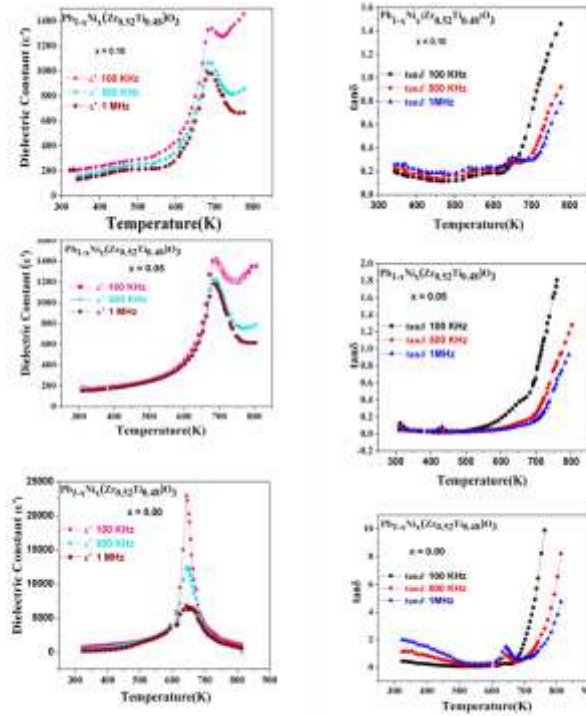
Fig. 3. The temperature dependent of dielectric constant and loss of PNZT ceramics sample at different frequency with different Ni^{2+} concentration $x = 0.00$ to 0.10.

Temperatures until it reaches to the phase transition temperature regions whereas above the phase transition temperatures it increases rapidly.

Fig.4 shows the piezoelectric constant (d_{33}) of PNZT ceramics as a function of Ni^{2+} concentration measured by piezometer (model PM 35). The value of piezoelectric constant (d_{33}) decreases with increase in Ni^{2+} concentrations (table1). Piezoelectric property measurements reveal that the pure PZT ceramic exhibits higher piezoelectric coefficient which is found to be 185 pC/N and further piezoelectricity exists in all Ni^{2+} doped PZT ceramics in decreasing order. From fig.4 it can be observed that the decreases the grain size, d_{33} have been also decreasing. These experiential results are opposite to those observed by Okazaki and Nagata [13]. According to Okazaki and Nagata, there are certain space-charge sites within grain boundaries and domain walls such as impurity atoms and lattice vacancies which create a space-charge field to control the movement of domain walls. The grain size increased, the surface area of the space-charge field which restrict the movement of domain walls decreased and thus piezoelectric coefficient improve. Similarly, previous research has also confirmed that piezoelectric coefficients have always shown an increase with increasing grain size [14] because the domain walls are expected to be quite free in larger grains considering that grain boundaries will give additional pinning points to the moving walls.
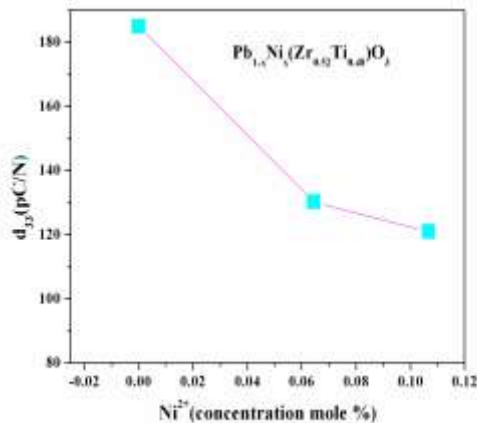

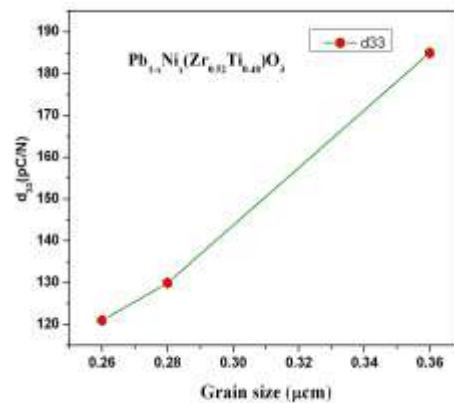Fig. 4(a). Piezoelectric constant (d_{33}) as a function of Ni^{2+} concentration.

Fig. 4(b). Piezoelectric constant (d_{33}) as a function of grain size.

V.   CONCLUSION

In this work, the synthesis of Ni^{2+} modified PZT ceramics in the region of the morphotropic Phase Boundary (MPB) has been investigated. The ceramics exhibited a complete tetragonal phase for this samples PNZT ceramics prepared by a high-temperature, solid-state reaction technique reveal good homogeneity and formation of a single-phase compound with tetragonal structure. The values of lattice parameters '*c*' of PNZT ceramic composition is found to increase with increasing Ni^{2+} concentration while "$a = b$" slightly decreases. Grain size decreases with increasing Ni^{2+} concentration. The behavior of ε' identifies our samples as nonrelaxor. With increase in Ni^{2+} concentration ε'_{max} decreases whereas transition temperatures (T_c) increase. The grain size played dominant roles in determining the magnitudes of dielectric constant (ε') and piezoelectric constant d_{33}, respectively.

FIG captions

Fig.1. X-Ray patterns of $Pb_{1-x} Ni_x (Zr_{0.52} Ti0.48)O_3$ with different Ni^{2+} concentration x= 0.00 to 0.10.

Fig.2. SEM micrograph of $Pb_{1-x} Ni_x (Zr0_{.52}Ti_{0.48})O_3$ with different Ni^{2+} concentration a x = 0.00, (b) x = 0.05, (c) x= 0.10.

Fig.3. The temperature dependent of dielectric constant and loss of PNZT ceramics sample at different frequency with different Ni^{2+} concentration x = 0.00 to 0.10.

Fig. 4(a). Piezoelectric constant (d_{33}) as a function of Ni^{2+} concentration.

Fig. 4(b). Piezoelectric constant (d_{33}) as a function of grain size.

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