

Structural and dielectric properties of Nb and Fe co-doped PZT ceramic prepared by a semi-wet route

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ABSTRACT

In the present work, detailed investigation of dielectric, piezoelectric and ferroelectric properties of Nb and Fe co-doped PZT ceramic near the MPB composition has been carried out. $\text{Pb}_{1-3x/2} \text{Fe}_x (\text{Zr}_{0.52} \text{Ti}_{0.48})_{1-5y/4} \text{Nb}_y \text{O}_3$ (PFZTN) ceramics for $x = 1-6$ mol% and $y = 5.50$ mol% have been prepared by a semi-wet route. X-ray diffraction studies confirm the formation of single phase perovskite structure. It is shown that Fe doping in PZNT improves the dielectric, ferroelectric and piezoelectric properties of ceramics. It has been found that at room temperature, dielectric constant and d_{33} start to increase up to the composition $x = 0.05$ and thereafter decrease. The maximum value of dielectric constant and d_{33} has been found for the composition $x = 0.05$. It has been shown that doping of Fe does not affect over the transition temperature upto $x = 0.04$. The value of remnant polarization is of the order of $11.62 \mu\text{C}/\text{cm}^2$ at $x = 0.04$. The investigated material seems to be promising candidate for multilayer capacitor applications. Copyright © 2014 VBRI press.

Keywords: X-ray diffraction; dielectric properties; phase transition; ferroelectric loop.



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Introduction

In the last few decades, it is extensively reported in the literature that lead zirconate titanate, $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x\text{O}_3)$, (PZT) ceramics are potential materials for electromechanical device applications. Above the Curie temperature, the unit cell of PZT is cubic in nature, however, below the Curie temperature, it is distorted in nature either in tetragonal or rhombohedral phase [1]. The boundary between the tetragonal (T) and rhombohedral (R) phases at room temperature is known as Morphotropic Phase Boundary (MPB) [2], which entirely depends on the Zr/Ti ratio, nature of dopants and method of preparation of material [3, 4]. The structural modification influences the properties of PZT. It has been observed that the properties of PZT ceramics are extensively sensitive near the MPB. Composition corresponding with MPB exhibits maximum values for the permittivity and electromechanical coupling factor [5, 6]. However, PZT are often modified by doping agents into the A or B site of perovskite ABO_3 structure. The doping agent is generally responsible for enhancing the properties of these materials for specific applications. The enhanced properties are usually due to the addition of one or more cations which can replace Pb^{2+} in site A and /or couple ($\text{Zr}^{4+} / \text{Ti}^{4+}$) in site B of perovskite structure (ABO_3) [7].

Several reports have been published on the effect of dopants on the structure, dielectric and electromechanical response of PZT ceramics. Solanki et al. have reported that PZT with 6% Sr^{2+} shows Cc space group [8]. In more recent work, these authors have also reported that PZT having the composition $x = 0.525$ does not correspond with Cc space group [9]. Wathore et al. [10] have reported the effect of temperature on dielectric constant and electromechanical coupling factors of Sr^{2+} modified PZT, (PSZT) ceramics. These authors have shown that with increasing temperature, dielectric constant and electromechanical coupling factor (k_p) initially decrease and then again start to increase. Du et al. [11] have reported the effect of Fe_2O_3 doping on the microstructure and piezoelectric properties of PNN-PZT ceramics. Luo et al. [12] have reported the behavior of PFN modified PMN-PZT ceramics having chemical formula $(0.90-x)\text{PMN}-0.10\text{PFN}-x\text{PZT}$ ($x = 0.10$ to 0.90). These workers found that the dielectric constant shows maximum response for the composition at $x = 0.10$. Cordero et al. [13] have reported that $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ with $0.455 \leq x \leq 0.53$ near the MPB (tetragonal (T) and rhombohedral (R) phase) composition, a monoclinic phase (M) exist. Singh et al. [14] have reported the effect of La modified PZFNT ceramics. These workers have shown that addition of La in PZFNT, significantly enhances the remnant polarization. Bammannavar et al. [15] have reported the magnetic properties and magnetoelectric effect of $x\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4(1-x)\text{PZT}$ composites. These authors claim that maximum ME voltage coefficient of 0.84 mV/cm Oe could be observed for 15% of ferrite phase and 85% of ferroelectric phase in the composites. Kahoul et al. [16] have reported the structural and electrical properties of $\text{Pb}_{0.98}\text{Sm}_{0.02}[(\text{Zr}_y\text{Ti}_{1-y})_{0.98}(\text{Fe}^{3+}_{1/2}\text{Nb}^{5+}_{1/2})_{0.02}]\text{O}_3$ ceramics. It has been shown that the composition containing Zr/Ti ratio of 55/45 exhibits good piezoelectric properties which makes this material a promising candidate for high-power multilayer piezoelectric transformer applications. Fang et al. [17] have reported the phase transition, structural and dielectric properties of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -doped $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 ceramics. It has shown that with increasing PT content, coexistence of rhombohedral and tetragonal phases takes place and ceramic exhibits maximum response of piezoelectricity. In the $1-x(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3-x\text{PbTiO}_3$ ($0.05 \leq x \leq 0.08$) ceramic system have tetragonal and monoclinic phases with space group $P4mm$ and Cm near the Morphotropic phase boundary [18].

It is thus evident from the earlier work that the modified PZT material can be explored for valued technological applications. Ions having higher valence such as Nb^{5+} cause vacancies in the A site called lead vacancies whereas the lower valence ions such as Fe^{3+} result in oxygen vacancies [19]. Thus doping of Nb^{5+} in PZT, reduces the coercive field, aging kinetic, elasticity modulus and increases the piezoelectric and dielectric constant. The addition of Nb^{5+} atoms also decreases the mechanical quality factor (Q_m) [20-22]. On the other hand, PZT doped with iron exhibits lower value of dielectric constant and increases the value of mechanical quality factor [20, 23-24]. Therefore, according to Takahashi [25], oxygen vacancies generated by the addition of iron are suppressed for equimolar compositions of Nb^{5+} and Fe^{3+} .

From literature, it is found that the properties of PZT ceramics can be modified by doping either at A-site or B-site. However, there is no report in the literature about the dielectric and piezoelectric properties for Nb_2O_5 and Fe_2O_3 co-doped PZT ceramics. In the present work, we report the effect of doping elements Nb_2O_5 and Fe_2O_3 in PZT and study their effect on dielectric and piezoelectric properties. The aim of this study is attributed to achieve better understanding of structure, dielectric, piezoelectric and ferroelectric behavior of the Nb and Fe doped PZT synthesized ceramics.

Experimental

Materials

High purity AR grade materials e.g. PbCO_3 (99.9%), Fe_2O_3 (98.0%), TiO_2 (99.0%), ZrO_2 (99.0%) and Nb_2O_5 (99.0%) (Merck KGaA, Darmstadt, Germany) were mixed in an agate mortar and pestle to prepare $\text{Pb}_{1-3x/2}\text{Fe}_x(\text{Zr}_{0.52}\text{Ti}_{0.48})_{1-5y/4}\text{Nb}_y\text{O}_3$ abbreviated as (PFZTN) ceramic for $x = 1-6$ mol% and $y = 5.5$ mol%.

Synthesis method

The ceramic having chemical formula $\text{Pb}_{1-3x/2}\text{Fe}_x(\text{Zr}_{0.52}\text{Ti}_{0.48})_{1-5y/4}\text{Nb}_y\text{O}_3$ abbreviated as (PFZTN) for $x = 1-6$ mol% and $y = 5.5$ mol% were prepared by a semi-wet route [26]. The composition $(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_2$ has been prepared by a chemical co-precipitation technique followed by subsequent decomposition at 900°C for 3 hours. The powders of desired stoichiometric ratio of PbCO_3 , Fe_2O_3 , Nb_2O_5 and $(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_2$ were accurately weighed and thoroughly mixed in a ball mill for 10 hours. Acetone was used as a mixing media. The powders were then dried at 100°C for 1 hour to remove the moisture. The calcination was carried out at 850°C for 4 hours. The powders were then compacted at 5.0 KN load in a steel die of diameter 13mm to obtain circular discs using 2% PVA solution as binding agent. The edges of circular pellets were cleaned with 8/0 class of emery paper to remove the iron contents. The green circular pellets were heated at 500°C for 1 hour to burn the PVA binder. The pellets were then sintered at 1000°C for 5 hours in the presence of PbZrO_3 powder to prevent the PbO loss during the high temperature sintering. The sintered pellets were cooled to room temperature in the furnace.

Characterizations

X-ray diffraction

Powder X-ray diffraction (XRD) patterns were recorded at room temperature using Rigaku X-ray diffractometer having $\text{Cu-K}\alpha$ radiations. The diffraction patterns were recorded at a scan rate of 1 degree per minute for 2θ varying from $20-70^\circ$.

Microstructure

The microstructure analysis was carried out using SEM (JEOL PSM 800) at room temperature. The average grain size of samples was calculated with the help of line intercept method.

Dielectric measurements

The relative dielectric constant (ϵ_r) and $\tan\delta$ of Fe_2O_3 and Nb_2O_5 co-doped PZT ceramics were obtained as a function of temperature at different frequencies using HIOKI – LCR (3522-50) meter in a PID controlled heating chamber. For dielectric measurements, sintered pellets were polished and coated with high purity silver paste on adjacent faces as electrode and then dried for 1 hour at 500°C to make parallel plate capacitor geometry.

Piezoelectric and ferroelectric measurement

Piezoelectric charge coefficients (d_{33}) of PFZTN ceramics were measured using a Berlincourt piezometer. Coated samples were poled in silicon oil both at 120°C for 1 hour under a static DC electrical field of 3.5 kV/mm. P-E loop tracer (Marine India), based on modified Sawyer-Tower circuit was used to trace polarization versus electric field loops at 50Hz.

Results and discussion

Structural analysis

Fig. 1 depicts the XRD patterns of Nb_2O_5 and Fe_2O_3 co-doped PZT powder ceramics at room temperature. The XRD profiles collected at different 2θ clearly indicate that calcined powders of modified PZT with Nb_2O_5 and Fe_2O_3 for various x values are single phase in nature. The patterning of XRD profiles using JCPDS file confirms that for composition up to $x = 0.04$, samples are highly pure in nature. For $x = 0.05$ and 0.06 , a secondary phase appears as discernible in the XRD profile. However, some minor peaks appear at $2\theta = 28^\circ$ and 33° which could be due to the growth of the tetragonal phase of PZT as the parent composition is very close to the MPB region. It is known that for a rhombohedral structure, (111) is a doublet and (200) is a single, whereas for tetragonal structure, the (111) is a singlet and (200) is doublet.

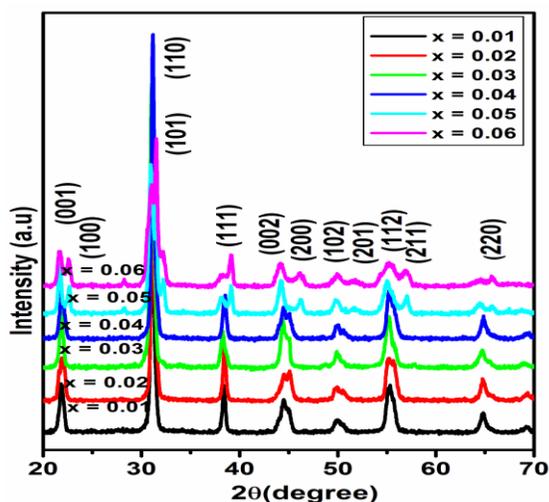


Fig. 1. XRD patterns of PFZTN ceramics with addition of Fe_2O_3 of 1 mol%, 2 mol%, 3 mol%, 4 mol%, 5 mol% and 6 mol%.

The observed XRD patterns as shown in **Fig. 1** clearly indicate that for $x = 0.01$, the structure is tetragonal. With increasing amount of x , the structure remains tetragonal upto $x = 0.04$, and then tends to switch into a mixed phase.

For $x = 0.05$, (111) and (200) evolutions split as evident from the diffractogram. The splitting of (111) and (200) peaks clearly indicates that for $x = 0.05$, PZT doped with Fe_2O_3 and Nb_2O_5 is a mixture of two phases. It is also noted that for $x = 0.05$, PZT doped with Fe and Nb has a phase boundary independent of temperature which shows the existence of the MPB. For the composition $x = 0.06$, the structure is again two phase in nature. It is thus evident that addition of Nb_2O_5 and Fe_2O_3 in PZT initiates structural changes along with modifications in the properties. It is thus investigated from the present finding that both T and R phases coexist at $x = 0.05$. It may be noted that the ionic radii of Fe^{3+} slightly smaller than Pb^{2+} and Nb^{5+} is approximately similar to the B site ($\text{Zr}^{4+}/\text{Ti}^{4+}$) resulting into an intensified tetragonal phase in the ceramic.

Micro structural analysis

SEM images at 50kX magnification for all the compositions are shown in **Fig. 2**. From the figure, it is inferred that all samples have uniform microstructure. There is no evidence of pores in the samples. Using the line intercept method, the average grain size of the samples was determined. The densities of the doped PZT ceramics increase with the doping level. Maximum density is attained at $x = 0.05$. The Fe^{3+} doping in PZT will create Pb^{2+} vacancies in order to maintain electro-neutrality. As a result, the densification is enhanced in the material. The decrease of density in material may be due to decrease of diffusivity of Pb^{2+} . The relative density is more than 96% and the average grain size is approximately in the order of 1.0- 2.0 μm . Following earlier work [27], grain growth takes place with increase in Fe^{3+} content in the matrix.

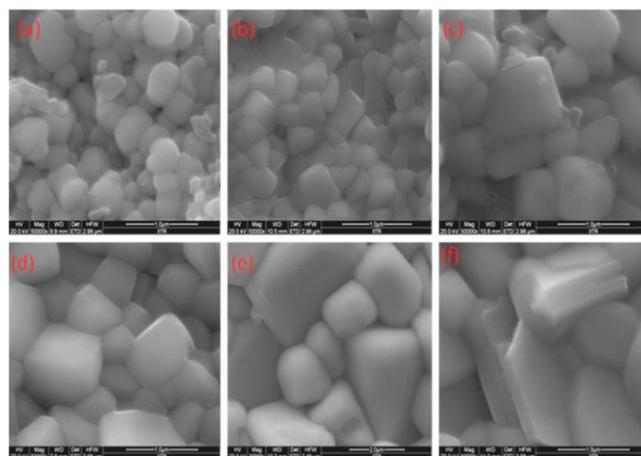


Fig. 2. SEM micrographs PFZTN ceramics with addition of Fe_2O_3 of (a) 1 mol% (b) 2 mol% (c) 3 mol% (d) 4 mol% (e) 5 mol% and (f) 6 mol%.

In our work, the grain growth is directly related to the dopant content and it is thus in close agreement with earlier findings for Nb^{5+} and Fe^{3+} doped PZT ceramics [27]. The doping on A-site with Fe^{3+} and B-site with Nb^{5+} influences the microstructure and the grain growth takes place.

Dielectric and piezoelectric analysis

Fig. 3 shows the temperature dependent behavior of dielectric constant for Fe_2O_3 modified PZNT at 1 kHz. It can be seen from the figure that Fe_2O_3 plays significant

role in governing the phase transition behavior and dielectric properties of PZNT. It is also evident from the figure that with increasing concentration of Fe_2O_3 , the transition temperature for co-doped PZT remains almost constant up to $x = 0.04$. However, for $x \geq 0.04$, T_c increases significantly as can be seen from the Fig. 3.

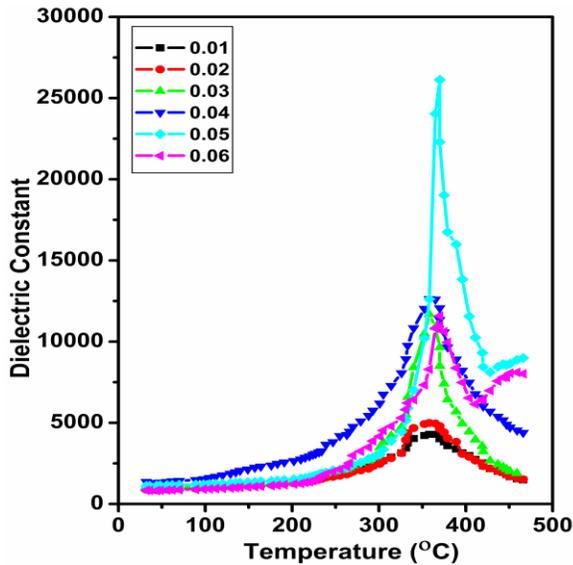


Fig. 3. Temperature dependent dielectric response of PFZTN ceramics at 1 kHz.

Frequency dependent studies of dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) have been carried out at 1 kHz, 10 kHz and 100 kHz. Fig. 4 depicts the variation of ϵ_r and $\tan(\delta)$ at different frequencies. It can be seen from figure that both dielectric constant and dielectric loss decrease with increasing frequency and follow strong temperature and frequency dependent relation. Dielectric constant and dielectric loss increase with increasing temperature for all the samples and attain maxima at T_c and then start to decrease due to the appearance of a paraelectric cubic phase. This study confirms that at transition temperature, tetragonal phase converts into cubic phase. It can be seen from the figure that the T_c is 358°C for the compositions $x = 0.01, 0.02, 0.03$ and 0.04 . However, for $x = 0.05$ and 0.06 , the value of T_c shows an increment of the order of 12°C ($T_c = 370^\circ\text{C}$). It is therefore investigated that the addition of Fe_2O_3 ($x = 0.05, 0.06$) into Nb_2O_5 substituted PZT increases the transition temperature to the higher side. It is also evident from ϵ_r Vs temperature studies that there is a broad dielectric maxima up to the composition $x = 0.03$. However, the broadening decreases after $x > 0.03$. This finding also suggests the existence of a diffuse phase transition. The wide and diffuse nature of profile may be attributed to the presence of micro-heterogeneity in the materials. Micro-heterogeneity arise due to random occupation of A and B sites by different ions having different ionic radii of the elements. Such a heterogeneous distribution of cations leads to different state of polarization and hence different relaxation time in different regions appears [28]. It is also evident from the Fig. 4(e) that above 200°C , there is a hump in the dielectric plot for $x = 0.05$ which may be attributed to the appearance of two phase region (T and R) as shown earlier by Mishra and Pandey

[29] for pure PZT. We also think that such characteristic may be significant in poled specimens of Fe modified PZNT. A further study over high temperature XRD is in progress to examine the nature of phase transition in each composition.

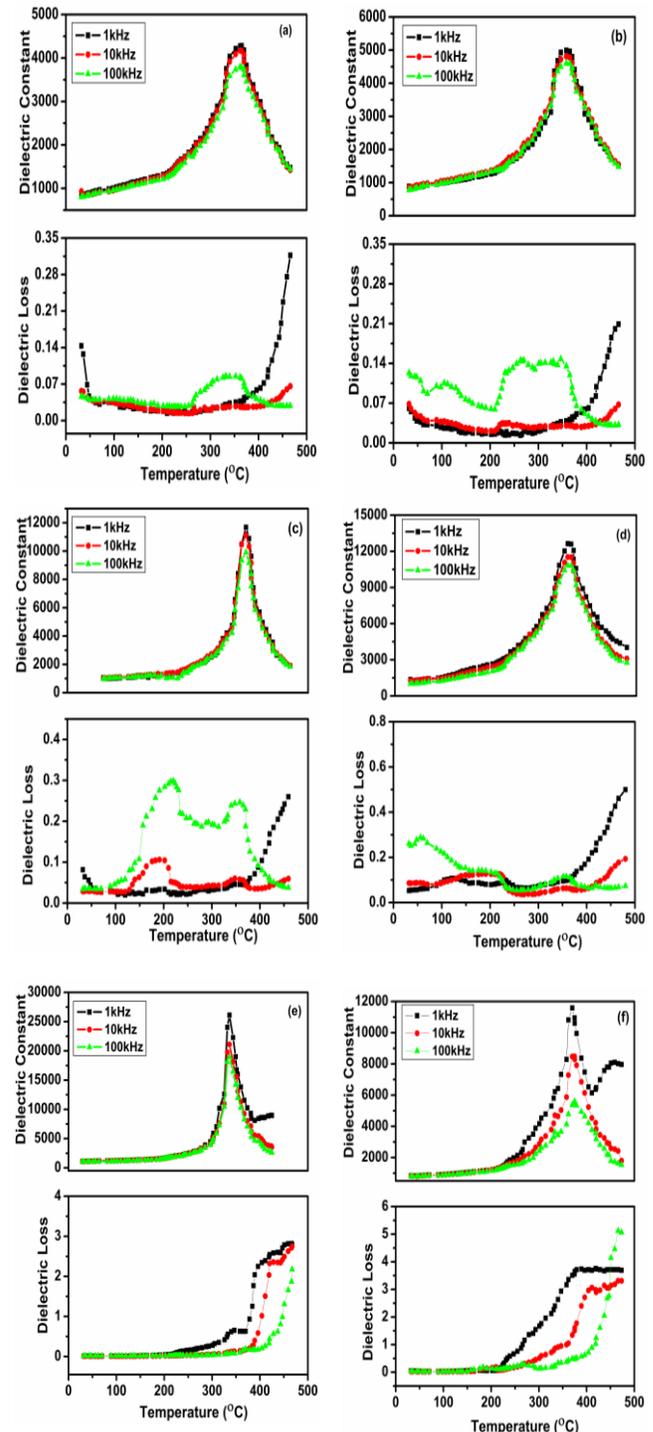


Fig. 4. Temperature dependent nature of dielectric constant and dielectric loss for PFZTN ceramics with addition of Fe_2O_3 (a) $x = 0.01$, (b) $x = 0.02$, (c) $x = 0.03$, (d) $x = 0.04$, (e) $x = 0.05$ and (f) $x = 0.06$.

Table 1 shows the room temperature ϵ_r and d_{33} values for various composition ($x = 0.01, 0.02, 0.03, 0.04, 0.05$ and 0.06) for Fe_2O_3 modified PZNT. It is discernible from the table that both ϵ_r and d_{33} have larger value for the

composition $x = 0.05$. For other compositions ($x = 0.01, 0.02, 0.03, 0.04$ and 0.06), the values for ϵ_r and d_{33} are lower. The increase in dielectric constant and d_{33} for 5mol% of Fe^{3+} doped PZNT may be attributed to the trivalent nature of Fe^{3+} and pentavalent Nb^{5+} which promotes the motion of domain walls resulting into highly intensified tetragonality and high permittivity in the ceramic [30, 31]. Further increment in Fe^{3+} ions in the system lattice brings reorientation and thus dielectric constant decreases [32] as evident from **Table 1** ($x = 0.06$).

Table 1. Electrical properties of Fe modified PZTN at room temperature.

	Amount of Fe_2O_3 (mol)	ensity (g/cm^3)	Relative Density (%)	T_c	ϵ_r at RT	d_{33}
PFZTN	0.01	7.32	89	358°C	852	220
	0.02	7.47	92	358°C	883	247
	0.03	7.66	94	358°C	1063	314
	0.04	7.66	94	358°C	1117	353
	0.05	7.81	96	370°C	1364	374
	0.06	7.59	90	370°C	843	300

In the present finding, it is shown that with increasing Fe^{3+} content, the value of d_{33} of the PFZTN ceramics initially increases and then decrease. PFZTN exhibits larger value of d_{33} for $x = 0.05$ since the rhombohedral and the tetragonal phases coexist for composition $x = 0.05$ and the reason may be attributed to the appearance of MPB phase for $x = 0.05$, which contributes additional response to external forces [17].

Table 2. Comparison of coercive field (E_c) and remnant polarization (P_r) at room temperatures for Nb and Fe Co-doped PZT.

S.No	Amount of Fe_2O_3 (mol)	(E_c) (kV/cm)	(P_r) ($\mu\text{C}/\text{cm}^2$)	(P_{max}) ($\mu\text{C}/\text{cm}^2$)
1	0.01	8.08	7.19	10.94
2	0.02	11.19	7.02	9.83
3	0.03	6.78	9.61	15.03
4	0.04	11.45	11.62	15.52
5	0.05	9.5	7.72	13.19
6	0.06	9.98	5.83	9.26

Ferroelectric analysis

Fig. 5 shows the response of polarization versus electric field of the PFZTN ceramics with $x = 0, 0.01, 0.02, 0.03, 0.04, 0.05$ and 0.06 measured at room temperature. The variations of coercive field (E_c), remnant polarization (P_r) and maximum polarization (P_{max}) for all the samples are listed in **Table 2**. All compositions show open and well saturated hysteresis loop, confirming ferroelectricity in samples measured at room temperature.

It is observed that $x = 0.05$ modified PFZTN at MPB composition gives maximum remnant polarization (P_r) of $11.62 \mu\text{C}/\text{cm}^2$ and this value gradually decreases with increase of dopant concentration in the material. This may be related to the remnant polarization which reflects the internal polarizability of the material. Therefore, lower is the remnant polarization; lower is the polarizability of the material.

The composition $x = 0.05$ close to the MPB region may have tetragonal and rhombohedral phases which coexist

together to give fourteen possible polarization directions [33]. Due to the presence of coexistence of multiple phases, enhancement in ferroelectric and piezoelectric properties occurs [34].

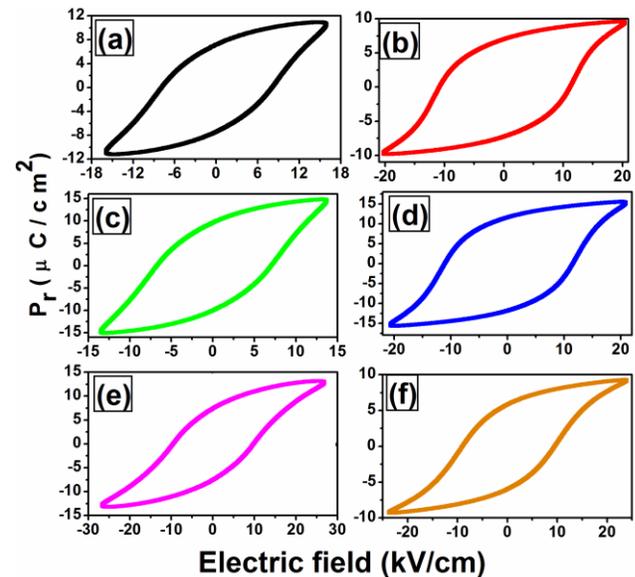


Fig. 5. Hysteresis loop for of Fe modified PZNT ceramics for (a) $x = 0.01$, (b) $x = 0.02$, (c) $x = 0.03$, (d) $x = 0.04$, (e) $x = 0.05$ and (f) $x = 0.06$.

Conclusion

We have shown in the present work that the dielectric, piezoelectric and ferroelectric properties improves to significant extent for Fe_2O_3 and Nb_2O_5 modified PZT. The dielectric and piezoelectric as well as ferroelectric properties of Fe modified PZNT ceramics have improved characteristics near the MPB. Microstructures of all the samples revealed that average grain size starts to reduce with Fe doping in PZNT ceramic. Addition of Fe_2O_3 in PZNT system influences the transition temperature to higher end and brings structural changes in the material. The values of dielectric constant, piezoelectric charge coefficient (d_{33}), remnant polarization (P_r) and coercive field (E_c) are found 1364, 374pC/N, $11.62 \mu\text{C}/\text{cm}^2$ and 11.48 kV/cm, respectively. Fe modified PZNT ceramics near MPB show improved hysteresis loop compared to pure PZT, which may be exploited for random access memory applications.

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