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INFLUENCE OF Fe$^{3+}$ AND Mn$^{3+}$ (B-SITE ACCEPTOR DOPANTS ON PZT (53/47)

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Some of the contents presented in this chapter have appeared in the following research publications:

1. K.P.Rema and V.Kumar “Structure– Property Relationship in Mn- doped (Pb$_{0.94}$Sr$_{0.06}$)(Zr$_{0.53}$Ti$_{0.47}$)O$_3$”, J. Am.Ceram.Soc. 91 (1), 164-168 (2008).


5.1 Introduction

In PZT, the optimum piezoelectric properties can be obtained near the morphotropic phase boundary (MPB) where the Zr/Ti ratio is ~53/47[1,2]. The piezoelectric properties of PZT with compositions near MPB have been modified with several isovalent and nonisovalent substituents at the A and/or B sites, giving rise to the classifications “soft” and “hard.” Donor dopants such as Nb$^{5+}$ ions at the B site impart soft characteristics to PZT, which include higher values of dielectric constant, dielectric loss, piezoelectric constants ($k_p$, $d_{33}$), and low aging rates. Lower-valent substituents at the B-site of ABO$_3$ render the PZT “hard” [3-7]. Typical B-site lower-valent substituents are Mn$^{3+}$, Fe$^{3+}$ and Al$^{3+}$. ‘Hard’ PZT is characterized by lower values of dielectric constant, dielectric loss, higher mechanical quality factor ($Q_m$), and a high aging rate. A-site doping with cations of the same valence enables the Curie temperature, $T_c$, to be modified. A-site isovalent Sr$^{2+}$-substituted PZT with an MPB composition, (Pb$_{0.94}$Sr$_{0.06}$)(Zr$_{0.53}$Ti$_{0.47}$)O$_3$ [PSZT], which is ferroelectrically harder[1], have been studied intensively for high-power applications that requires a low dielectric loss, tan δ, high electromechanical coupling factor($k_p$), and high $Q_m$. Although several studies have been reported[3-17] on the B-site aliovalent ion (such as Fe$^{3+}$, Mn$^{3+}$, Al$^{3+}$, Cr$^{3+}$, etc.)-substituted PZT, most of them have correlated the properties on the basis of oxygen vacancies in the lattice. While such charge compensation mechanisms and the influence of the resulting defect structure on the electrical properties have been widely studied, structural perturbations brought about by some of the dopants and their influence on the electrical properties have not been studied in detail, especially with respect to PZT of an MPB composition. Although Kamiya et al. [8] have ascribed the “soft” nature of Mn-doped PZT
to structural changes, detailed investigations on the factors responsible for such structural changes have not been reported. Also, there is considerable scatter in the data in the literature with regard to the site substitution and doping mechanism. Therefore, the influence of Mn$^{3+}$ dopant on the structure and their relation with the electrical properties of PSZT has been investigated in detail. The results were compared with the influence of another typical B-site dopant, Fe$^{3+}$.

5.2 Experimental Procedure

A PSZT solid solution with an MPB composition was chosen as the basis for doping with different amounts ($0.001 \leq y \leq 0.02$) of M (M= Mn$^{3+}$ or Fe$^{3+}$) to yield the compositions with the general formula $(\text{Pb}_{0.94}\text{Sr}_{0.06})(\text{Zr}_{0.53}\text{Ti}_{0.47})_z M^{3+}_y\text{O}_3$ where $z=1-3/4y$. The materials were synthesized by the sol–gel method as per the procedure adapted from our earlier work [18]. For the preparation of the precursor solution, stoichiometric amounts of basic lead acetate, $(\text{CH}_3\text{COO})_2\text{Pb.Pb(OH)}_2$ (ACS reagent grade, Merck, Mumbai, India), strontium acetate, Sr$(\text{CH}_3\text{COO})_2$ (99.9% purity, Aldrich, Steinheim, Germany), zirconium acetylacetonate, Zr$(\text{CH}_3\text{COCH=CHC(O)CH}_3)_4$, (>98% purity, Merck, Hohenbrunn, Germany), and manganese (III) acetylacetonate, Mn $(\text{CH}_3\text{COCH=CHC(O)CH}_3)_3$ (tech.grade, Aldrich), or iron (III)acetylacetonate, Fe$(\text{CH}_3\text{COCH=CHC(O)CH}_3)_3$ (tech.-grade, Aldrich), were dissolved in acetic acid, [CH$_3$COOH]/[Zr+Ti+Mn (or Fe)]=25, and were mixed with titanium tetraisopropoxide, Ti$(\text{OC}_3\text{H}_7)_4$ (97% purity, Aldrich)in isopropyl alcohol under constant stirring. To induce hydrolysis, water, [H$_2$O]/[Ti]=2, was added dropwise to this solution and stirring was continued for another hour. The clear homogeneous precursor solution was then transferred to a glass Petri dish and allowed to gel at room temperature. The gel-derived powders,
obtained after calcination at 600°C for 2 h, were isostatically pressed at 200 MPa into pellets of diameter 10 mm and thickness 1.0 mm.

![Diagram of process flow chart for sol-gel processing of PSZTM (M=Mn III / Fe III)](image)

**Fig. 5.1** Process flow chart for sol-gel processing of PSZTM (M=MnIII/FeIII)
The PSZTM specimens were sintered, in static air, at a temperature of 1200°C for 3 h under constant PbO atmospheres maintained using a mixture, PbZrO$_3$+10%ZrO$_2$, as reported [15,19]. All X-ray diffraction (XRD) measurements were performed on sintered and powdered samples on an X-ray diffractometer (Model-D5005, Bruker, Karlsruhe, Germany) with CuK$_\alpha$ radiation using a step size of 0.021 and accounting time of 3 s per step. The sintered PZT specimens were polished and electroded with a silver paste and subsequently cured at 700°C for 30 min and poled at temperatures around 95°C for 60 min by applying a DC electric field of 2.5 kV/mm in a silicone oil bath. The piezoelectric characteristics were measured 24 h after poling. The electromechanical characteristics were determined from the resonance measurements [20]. The $d_{33}$ constant was measured by applying a known force to the electroded surfaces of the piezoelectric specimen and measuring the electrical charges generated in the same direction using a $d_{33}$ meter (Model Pennebaker 8000, APC Inc., Mackeyville, PA). The dielectric properties of the sintered compacts were determined at 1 kHz using an impedance analyzer (Model 4192A, Agilent Technologies, Palo Alto, CA). The microstructures of the sintered pellets were recorded using an SEM (Model JSM-840A, JEOL, Tokyo, Japan). The diffuse reflectance spectra were measured on sintered and powdered samples using a UV-Vis spectrophotometer (Model UV 2400, Shimadzu, Tokyo, Japan). The Curie temperature, $T_c$, was determined on sintered and powdered samples using a differential scanning calorimeter (Model DSC 822E, Mettler Toledo, Schwerzenbach, Switzerland) in a nitrogen atmosphere, at a constant heating rate of 10°C/min. Ferroelectric hysteresis (P-E) of the sintered compacts were measured using a TF Analyser (Model 200D, aix ACT, Germany).
5.3 Results and Discussion

5.3.1 B-site Mn doped PSZT

The XRD patterns as a function of B-site aliovalent dopant concentration are shown in Figure 5.2. The composition without the B-site dopant is tetragonal (Figure 5.2(a)). In comparison with the undoped composition, the c/a ratio increases for the 1 atom % Mn doped composition (Figure 5.2(b), Table 5.1), along with an increase in $T_c$ (Figure 5.3). On further increasing the Mn content, the perovskite structure changes from tetragonal to rhombohedral (Figure 5.2) along with a reduction in $T_c$ (Figure 5.3).

This can be explained on the basis of the coordination effect of Mn$^{2+}$ cation. In PSZT, for low Mn-dopant concentrations ($y \leq 0.001$), Mn$^{2+}$ is incorporated into the A site of the perovskite as reported [6] earlier. Mn$^{2+}[r_{\text{Mn}^{2+}}(\text{CN-8}) = 1.10 \text{ Å}]$ is too small to have a symmetric dodecahedral coordination of O$^{2-}$ ions and is therefore displaced off-center to have eight near neighbors and four distant anions, thus causing a dipolar moment whose effect leads to an increase in $T_c$. 
Fig. 5.2 X-ray diffraction patterns of (Pb_{0.94} Sr_{0.06})(Zr_{0.53} Ti_{0.47})_xMn_yO_3; y (at.%) = (a) 0; (b) 0.001; (c) 0.002; (d) 0.003; (e) 0.004; (f) 0.005; (g) 0.01; (h) 0.015; and (i) 0.02.
Table 5.1 c/a ratio of \((\text{Pb}_{0.94}\text{Sr}_{0.06})(\text{Zr}_{0.53}\text{Ti}_{0.47})_{\text{z}}\text{Mn}_{\text{y}}\text{O}_{3}\)

<table>
<thead>
<tr>
<th>(PS)(ZT)\text{Mn}<em>{\text{y}}\text{O}</em>{3}\text{y(atom%)}</th>
<th>c/a ratio</th>
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<td>1.0067</td>
</tr>
<tr>
<td>0.02</td>
<td>1.002</td>
</tr>
</tbody>
</table>

Fig. 5.3 Effect of Mn\(^{3+}\) content(y) on \(T_{c}\) of \((\text{Pb}_{0.94}\text{Sr}_{0.06})(\text{Zr}_{0.53}\text{Ti}_{0.47})_{\text{z}}\text{Mn}_{\text{y}}\text{O}_{3}\).
For higher concentrations ($y > 0.001$), the dopant ion Mn$^{3+}$ substitutes for the B-site ions (Ti$^{4+}$, Zr$^{4+}$) because of similar ionic radii. In the MnO$_6$ octahedra, Mn$^{3+}$($d^4$) adopts the high-spin state. Because high-spin $d^4$ systems, in octahedral symmetry, contain a degenerate ground state, Jahn–Teller (J–T) distortion occurs, in which the $t_{2g}$ level splits into $B_2(d_{xy})$ and $E(d_{xz},d_{yz})$, while $e_g$ splits into $B_1(d_{x^2-y^2})$ and $A_1(d_{z^2})$ as shown in Figure 5.4.

![Diagram](image)

Fig.5.4 Alteration of orbital energies of Mn$^{3+}$($d^4$) in octahedral symmetry due to "z–in" type J–T distortion; $\Delta_0 \gg \delta_1 \gg \delta_2$. J–T, Jahn–Teller.
Because the $e_g$ orbitals are directly involved in $\sigma$ B–O bonding (B=Mn$^{3+}$), the J–T distortion is quite significant and, as a consequence, elongation of the four equatorial Mn–O bonds and the contraction of the two axial Mn–O bonds result in the decrease of the c/a ratio and $T_c$.

J–T distortion is confirmed from the diffuse reflectance spectra (Figure 5.5). The two broad absorption features at ~14 200 cm$^{-1}$ ($\nu_1$) and ~24 000cm$^{-1}$ ($\nu_2$) are due to the spin-allowed d–d transitions, $^5A_1 \leftrightarrow ^5B_1$ ($\nu_1$); $^5A_1 \leftrightarrow ^5B_2$ ($\nu_2$) (Figure 5.4). On the basis of the assignments of the observed spin-allowed d–d bands, a crystal field splitting ($\Delta_o$) of 11,625 cm$^{-1}$ and a CFSE of 139 kJ/mol are determined, which are comparable, to those reported[21,22] for Mn$^{3+}$ in relatively symmetric cubic environments.

Fig. 5.5  Diffuse reflectance spectra of(Pb$_{0.94}$Sr$_{0.06}$)(Zr$_{0.53}$Ti$_{0.47}$)$_2$Mn$_y$O$_3$. 

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Figures 5.6-5.8 show the changes in the dielectric and piezoelectric characteristics of Mn-doped systems. The dielectric characteristics $\varepsilon_r$, tan $\delta$ (Figure 5.6), increase with increasing Mn content. The slight decrease in $\varepsilon_r$ for the 1.5 at. % Mn-doped system is due to the smaller grain size.

![Graph showing the effect of Mn content on dielectric constant ($\varepsilon_r$) and loss factor (tan $\delta$)](image)

**Fig. 5.6** Effect of Mn$^{3+}$ content (y) on $\varepsilon_r$ and tan $\delta$ of (Pb$_{0.94}$Sr$_{0.06}$)$_2$(Zr$_{0.53}$Ti$_{0.47}$)$_2$Mn$_y$O$_3$
Fig. 5.7 Effect of Mn\(^{3+}\) content (y) on $d_{33}$ and $k_p$ of (Pb\(_{0.94}\)Sr\(_{0.06}\))(Zr\(_{0.53}\)Ti\(_{0.47}\))\(_2\)Mn\(_y\)O\(_3\).
Fig. 5.8 Effect of Mn$^{3+}$ content (y) on $g_{33}$ and $Q_m$ of (Pb$_{0.94}$Sr$_{0.06}$)(Zr$_{0.53}$Ti$_{0.47}$)$_2$Mn$_y$O$_3$. 
It is seen that the electromechanical coupling factor ($k_p$), piezoelectric constant ($d_{33}$), piezoelectric voltage coefficient ($g_{33}$), and mechanical quality factor ($Q_m$) show a similar variation with increasing Mn$^{3+}$ concentration. When $y$ (at.%) $=$ 0.001, all the characteristics decreased owing to the increase in the tetragonality. When $0.001 < y \leq 0.004$, $k_p$, $d_{33}$, and $g_{33}$ increase. The highest values of $k_p = 0.55$, $d_{33} = 451$ pC/N, and $g_{33} = 46.3 \times 10^{-3}$ V/mN are obtained for the composition with $y = 0.004$, which corresponds well with the MPB composition (Figure 5.9(e)) and a more uniform microstructure (Figure 5.10(d)). The mechanical quality factor, $Q_m$, is also the highest for the 0.4 at.% Mn-doped system, indicating the pinning of domain walls by the oxygen vacancies. Further addition of Mn$^{3+}$ above 0.4 at.% led to a decrease in the dielectric and piezoelectric characteristics, indicating the solubility limit of Mn$^{3+}$ in the perovskite lattice. This is also supported by the reduction in grain size beyond 0.4 at.% Mn-doped composition (Figures 5.10(e) and (f)).

The various mechanisms by which the aliovalent dopant ion Mn$^{3+}$ influence the electrical and mechanical characteristics of PSZT are (i) to bring about a change in the crystal structure from tetragonal to rhombohedral through J–T distortion, which increases the dielectric and electromechanical characteristics through enhanced domain wall mobility, and (ii) to create oxygen vacancies that pin the domain walls, which increases the mechanical characteristics. Therefore, Mn-doped systems exhibit certain "soft" characteristics as a result of structural change from tetragonal to rhombohedral due to J–T distortion of the BO$_6$ octahedra.
Fig. 5.9 Diffraction from (111), (002), and (200) planes of (Pb$_{0.94}$Sr$_{0.06}$)(Zr$_{0.53}$Ti$_{0.47}$)$_2$Mn$_y$O$_{3+y}$; y (at.%)= (a) 0; (b) 0.001; (c) 0.002; (d) 0.003; (e) 0.004; (f) 0.005; and (g) 0.01.
Fig. 5.10 Scanning electron micrographs of sintered specimens of 
\((\text{Pb}_{0.94}\text{Sr}_{0.06})(\text{Zr}_{0.53}\text{Ti}_{0.47})_2\text{Mn}_y\text{O}_3;\ y\ (\text{at.}%)=\ (a)\ 0;\ (b)\ 0.001;\ (c)\ 0.003;\ (d)\ 0.004;\ (e)\ 0.01;\ and\ (f)\ 0.02.
5.3.2 B-site Fe-doped PSZT

Figure 5.11 shows the XRD patterns of the Fe-doped system confirming the presence of only the perovskite phase. In comparison with the undoped composition, c/a ratio decreases for the Fe-doped composition (Table 5.2) along with a decrease in $T_c$ (Figure 5.12).

![XRD patterns of Fe-doped PSZT](image)

**Fig. 5.11** XRD patterns of $(\text{Pb}_{0.94} \text{Sr}_{0.06})(\text{Zr}_{0.53} \text{Ti}_{0.47})_2 \text{Fe}^{3+}_y \text{O}_3 ; z=1-3/4y$ (a) $y=0$ (b) .001 (c) .002 (d) .003 (e) .004 (f) .005 and (g) .01
These are due to the decrease in B-O-B coupling as a result of incorporation of Fe$^{3+}$-cations at the B-site. Incorporation of Fe$^{3+}$ at the B-site is also confirmed by the continuous decrease in the Curie temperature, $T_c$ as shown in Figure 5.12. Figure 5.13 A shows the P-E characteristics of the PSZTFe virgin specimens at room temperature revealing double-loop nature. The P-E characteristics are similar to those reported for ferroelectrics containing randomly oriented polarisable defects [23,24]. The degree of double-loop characteristics is quite pronounced. The magnitude of the remanent polarization ($P_r$) decreases as the double-loop characteristic increases and the switchable polarization is considerably less than that of the undoped system. The mechanism by which the B-site dopant influences the polarization switching characteristics of PSZT can be explained as follows.

Table 5.2  c/a ratio of (Pb$_{0.94}$ Sr$_{0.06}$)(Zr$_{0.53}$Ti$_{0.47}$)$_2$Fe$_y$O$_3$

<table>
<thead>
<tr>
<th>$y$ (atom%)</th>
<th>c/a ratio</th>
<th>Structure</th>
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<tbody>
<tr>
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<td>Tetragonal</td>
</tr>
<tr>
<td>0.001</td>
<td>1.021</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>0.002</td>
<td>1.021</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>0.003</td>
<td>1.021</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>0.010</td>
<td>1.016</td>
<td>Tetragonal</td>
</tr>
</tbody>
</table>
Influence of $\text{Fe}^{3+}$ and $\text{Mn}^{3+}$ (B-site acceptor dopants on PZT (53/47)

Fig. 5.12 $T_c$ of PSZTFe as a function of Fe-content
Fig. 5.13 A. P-E hysteresis characteristics of Fe-doped virgin PSZTF$_y$ specimens at room temperature. (a) $y = 0$ (b) 0.001 (c) 0.002 (d) 0.003 and (e) 0.005
Fig. 5.13 B. P-E hysteresis characteristics of Fe-doped poled PSZTFe_y specimens at room temperature. (b) 0.001 (c) 0.002 (d) 0.003 and (e) 0.005
For the trivalent acceptor dopant M at the B-site of the perovskite, charge compensation is achieved by creating oxygen vacancy as represented in equation 5.1;

\[
M_xO_3 \xrightarrow{2BO^-} 2M_y^+ + 3O_O + V_O^{2+} \quad \text{.......................... (5.1)}
\]

where \( M_y^+ \) indicates a singly negatively charged acceptor at the B-site and \( V_O^{2+} \) a doubly positively charged oxygen vacancy with respect to the neutral lattice according to Kröger and Vink.

![EPR spectrum](image)

**Fig. 5.14** EPR spectra of \((Fe'_{Ti} - V_o^-)\) defect –dipole in PSZTFe

The negatively charged trivalent dopant at the B-site forms a defect-dipole with the positively charged \( V_o^- \), \([M_y^+ - V_o^-]\). In the EPR spectrum (Figure 5.14) the signals at \( g \approx 5.7 \) and \( g \approx 4.3 \) are characteristic of \((Fe'_{Ti} - V_o^-)\) defect-dipole in
PZT of MPB composition [25]. Such defect-dipoles, if they are mobile, have been reported to pin domain walls suppressing nucleation and growth of domains in the direction of the applied electric field [4, 26, 27]. In the case of the poled samples, the P-E curves (Figure 5.13B) reveal strong asymmetry with only a single loop. The polarization is switchable only to the reverse-biased state. Also the magnitude of this switchable polarization decreases with increasing Fe-content. For \([\text{Fe}^{3+}] \geq 0.005\), the P-E curve is considerably constricted (Figure 5.13B(e)). The P-E curves are similar to those reported for A-site K+-substituted PZT (65/35) [23]. In poled specimens, as a result of the applied electric field, the defect-dipoles undergo a preferred alignment leading to the development of an internal electric field (\(E_i\)). This internal electric field (\(E_i\)) was estimated from the current curves as shown in Figure 5.15 and are plotted in Figure 5.16.

![Fig. 5.15 Estimation of \(E_i\) from the current curve](image-url)
Since the current is given by the equation 5.2, the current curves (Figure 5.15) were obtained by differentiating the polarization curves as described previously [27].

\[
i(E) = \frac{dP}{dt} \left[ E(t) \right] = \frac{dP}{dE} \cdot \frac{dE}{dt}
\]

\[\text{.................................... (5.2)}\]

With increasing Fe\(^{3+}\) concentration, \(E_i\) increases up to a maximum value of -10kV/cm. for an Fe concentration as low as 0.4 at.%. This shows that very high internal electric fields are developed with Fe-doping as a result of the preferred alignment of the \((Fe^{3+}_{Ti} - V_o^-)\) defect-dipole. These results also correlate well with their piezoelectric and dielectric characteristics (Figures 5.17A and B).

![Graph](image)

**Fig. 5.16** Internal electric field \((E_i)\) as a function of the dopant concentration in poled specimens of PSZTFe
Fig. 5.17 Effect of dopant concentration on (A) piezoelectric and (B) dielectric characteristics of PZT Fe

Fig. 5.18  SEM micrographs of sintered specimens of PSZTFeyO₃; $y(\text{at.\%}) = (\text{a}) \ 0; \ (\text{b}) \ 0.001; \ (\text{c}) \ 0.002; \ (\text{d}) \ 0.005; \ \text{and} \ (\text{e}) \ 0.01$
The micrographs shown in Figures 5.18(a)-(e) reveal well defined microstructures with crystal-like faces up to a Fe-dopant concentration, $y \leq 0.005$. It is seen that the grain size is strongly influenced by the Fe content. The undoped composition (Fig. 5.18a) has an average grain size of 8.0 µm. As the Fe content increases, the grain size decreases to 3.0 µm for the composition with a Fe-dopant concentration, $y=0.01$ (Fig. 5.18e). This reduction in grain size is due to the inhibition of grain growth by the oxygen vacancies as a result of Fe doping. There is good correlation between the microstructures and the electrical characteristics.

5.3.3 Degree of acceptor – nature of B-site Fe, Mn – doped PSZT

Thus in PZT, there exist differences in the acceptor-nature of various substituents at the B-site. Acceptor impurities are known to exhibit significant polarization pinning effects [14-17]. The differences in the acceptor-nature of different dopants are therefore expected to manifest in their polarization switching characteristics. However no detailed studies have been reported investigating the differences in the acceptor-nature of different dopants. Therefore an important constituent of the present investigation is to determine the degree of acceptor-nature of two typical B-site acceptors in PZT viz. Mn$^{3+}$ and Fe$^{3+}$ by studying their polarization switching effects.

Figure 5.19 shows the P-E characteristics of the Mn-doped PSZT virgin specimens at room temperature revealing double-loop nature. The degree of double-loop characteristics is less in the case of Mn-doped systems (Figure 5.19), whereas it is pronounced in Fe-doped systems (Figure 5.13A). In the virgin specimens, where the defects are randomly-oriented and mobile, the difference in the polarization characteristics is attributed to the enhanced mobility and therefore
decreased domain-pinning effects of the \( Mn'_\text{Ti} - V_\text{o}^- \) defect-dipole when compared to that of the \( Fe'_\text{Ti} - V_\text{o}^- \) defect-dipole.

**Fig. 5.19** P-E hysteresis characteristics of Mn-doped PSZT\(_x\) specimens at room temperature. (a) \( y=0 \) (b) 001 (c) 002 (d) 003 (e) 004 (f) 005
In the case of the poled samples, the P-E curves of the Fe$^{3+}$-doped systems reveal strong asymmetry with only a single loop (Figure 5.13B) whereas in the case of Mn$^{3+}$-systems the effect is considerably less (Figure 5.20). In poled specimens, as a result of the applied electric field, the defect-dipoles undergo a preferred alignment leading to the development of an internal electric field ($E_i$). This internal electric field ($E_i$) was estimated from the current curves as described previously and are plotted in Figure 5.21.

**Fig. 5.20** P-E hysteresis characteristics of Mn-doped compositions after poling (b) $y=0.001$ (c) $0.003$ (d) $0.005$ and (e) $y=0.01$
With increasing dopant concentration, $E_i$ increases up to a maximum value of -3kV/cm for 1.0 at% Mn$^{3+}$-doped system. With Fe-doping, $E_i$ is comparatively very high, with a value of -10kV/cm, for a dopant concentration of only 0.5 atom%. This shows that very high internal electric fields are developed with Fe-doping as a result of a stronger preferred alignment of the $(Fe'_n - V_o)$ defect dipole. The relatively harder nature of the Fe$^{3+}$-doped systems is also well correlated with their lower values of dielectric loss ($\tan \delta$) and higher values of mechanical quality factor ($Q_m$) as shown in Figure 5.22.

**Fig. 5.21** Internal field ($E_i$) as a function of the dopant concentration in PSZTM[M=Fe/Mn]
5.4 Conclusion

Aliovalent dopant ions of suitable size, although limited in solubility, can cause profound changes in the dielectric and piezoelectric properties of PZT. In Mn\(^{3+}\)-doped PSZT, as a result of the transformation of the crystal structure from tetragonal to rhombohedral, owing to J–T distortion, they
exhibited both “soft” and “hard” characteristics. A good correlation has been obtained between the structure and electrical properties of Mn$^{3+}$-doped PSZT. Fe$^{3+}$-doped systems exhibit typical characteristics of “hard” ferroelectrics.

A detailed investigation of the Polarization Switching characteristics of Mn$^{3+}$ and Fe$^{3+}$-doped PSZT has revealed the influence of the defect dipoles viz. $(Fe^{3+}_n - V^-_o)$ and $(Mn^{3+}_n - V^-_o)$ on the polarization switching characteristics. These dipoles are found to have high mobilities in virgin specimens whereas they are preferentially oriented in poled specimens leading to the development of significant internal electric fields and therefore in their acceptor characteristics. Fe$^{3+}$-doped PZT are found to be ferroelectrically harder when compared to Mn$^{3+}$-doped systems. These results are also found to correlate well with their observed dielectric and piezoelectric characteristics. This study provides a useful basis for the selection of appropriate acceptor dopant in PZT-based piezoelectric systems.

References


Influence of Fe³⁺ and Mn³⁺ (B-site acceptor dopants on PZT (53/47)


