Piezoelectric and pyroelectric properties of Sr-doped PZT (PSZT) with minor manganese additions

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Abstract. A systematic study was performed to see the effect of Manganese addition and temperature gradient on the electrical properties of PSZT. Pb$_{0.96}$Sr$_{0.04}$(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PSZT) containing 0.3%, 0.5%, and 1% Mn was prepared by the sol gel method in order to ensure good stoichiometry and enhanced purity. The powders were calcined at 550 °C and sintered at 1200 °C to achieve 98% of the theoretical density. High field ac study was performed by (P-E) hysteresis measurements at different temperatures (RT, 60, 90, 120 and 150 °C) using an electric field up to 3 kV/mm. It was observed that for a lower Mn concentration P-E loops are pinched at the center while this constriction is found to decrease for greater concentrations. The optimized results were obtained for the 1 mol% of Mn content with 4 mol% of Sr. The values of $Q_m$, $k$, $d_{33}$ and tanδ were measured as 756, 0.38, 257 and 0.002 respectively. Higher temperatures coupled with a gradual increase of the electric field resulted in a shift of the hysteresis loops along electric field axis, indicating the presence of an internal bias field. Dependence of pyroelectric properties on applied electric field was also investigated. The value of pyroelectric coefficient was found maximum 6.25 × 10$^{-4}$ (C/m$^2$K) at 3 kV/mm.

1. Introduction
Lead Zirconate Titanate (PZT) ceramics are famous for their enormous applications in ultrasonic transducers, actuators, vibration sensors, IR (pyroelectric) sensors, dynamic RAM’s, electro-caloric coolers for computers and capacitor array [1-3]. Main peculiarity of PZT materials is hysteresis dependence of permittivity, polarization, and pyroelectric behavior on doping and applied electric field [4]. Electrical properties of PZT can be tailored by incorporating appropriate dopants to meet technical demands of user based applications. Donor dopants (La$^{3+}$, Bi$^{3+}$ (for A-site) and Sb$^{5+}$ and Nb$^{5+}$ (for B-site)) impart soft characteristics to the host material, while, acceptor( K$^+$, Na$^+$ (for site A) and Fe$^{3+}$, Al$^{3+}$, Mn$^{3+}$ (for site B)) dopants are responsible for hardening effect [5,6,7]. The deficiency of positive charge occurred as a result of acceptor doping is compensated by oxygen vacancies and excess positive charge is responsible of lead vacancies [8].

Along with doping electrical after effects are also responsible for change in properties. Volume effect, domain effect, and domain boundary effect are three famous mechanisms used to explain the effect of added impurities and ageing related phenomena [9]. Z. Cao [10] observed improved pyroelectric property...
along with double hysteresis loop for Mn-doped PLZT system. The possibility of presence of antiferroelectric phase was rejected on the basis of high piezoelectric and pyroelectric coefficients. For practical purpose it is normally preferred to use more than one dopant to maneuver a broad range of properties. Strontium (Sr$^{2+}$) is a famous isovalent dopant and it is found to have profound effect on dielectric constant but has relatively little effect on other parameters i.e. $Q_m$, $k$ (piezoelectric coupling), resistivity and temperature dependence. However on the other hand, acceptor dopants are reputed for raising the $Q_m$, amplitude and lower resistivity [7].

In this study, Sr and Mn were co-doped at A and B sites in PZT (52/48), respectively to improve its electrical properties. Effect of complex doping on piezoelectric, pyroelectric and hysteresis properties was studied. The impact of electric field and temperature was also investigated to understand the resultant effect.

2. Experimental

\[ \text{Pb}_{0.96}\text{Sr}_{0.04}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{1-x}\text{Mn}_x\text{O}_3 \] for $x = 0.03$, $0.05$ and $0.1$ was prepared using sol-gel method. For this purpose; Lead acetate was dissolved in appropriate quantity of Isopropanol with small additions of acetic acid at $80^\circ C$. The solution was distilled to remove water and extra solvent. Strontium acetate and manganese acetate were added to this solution. Separately, titanium isopropoxide and zirconium-n-propoxide were refluxed in isopropanol at $100^\circ C$ and stabilized the solution with acetyl acetone. The two solutions were mixed together drop wise and stirred for an hour. Hydrolysis was carried out by adding water in 1:2 to the metal mixture. The sol was then converted to a viscous gel in a rotary evaporator and was further dried in vacuum oven at $120^\circ C$. The dried gel was then calcined at $550^\circ C$ for 4 hours. Calcined powder was milled in high energy ball mill with Zirconia balls in water for six hours. Phase confirmation was made by XRD [11] PVA was added as binder in resulting slurry and dried at $50^\circ C$. The powder was pressed in the form of small pallets in a die. Binder was then removed at $270^\circ C$ for an hour and sintered at $1150^\circ C$ for two hours. Sintered pallets were electroded with silver paste and fired at $550^\circ C$ for 30 min. Density greater than 99% of the theoretical density was achieved for all compositions.

Polarization electric field (P-E) hysteresis measurements were carried out using a computer-controlled function generator (Agilent 33220A) in conjunction with a high-voltage ($\times 1000$) amplifier (Trek 10/10B). A two probe sample holder was immersed in a silicone oil bath placed at a heating stage. The temperature was controlled by the temperature controller (Eurotherm 818P) with accuracy of $\pm 0.5^\circ C$. AC pulses of varying magnitude with frequency 2 Hz were applied to the sample and the induced current was integrated to calculate the polarization in order to obtain the P-E characteristics of material. Schematic diagram of the measurement setup is shown in Figure 1. After P-E measurements, samples were heated at $450^\circ C$ for 30 min to nullify the ageing effects. Poling was carried out at $120^\circ C$ with a dc field of 2-3KV/mm in silicone oil bath. Piezoelectric charge coefficient $d_{33}$ was measured using Piezometer (piezometer Systems, UK). Dielectric constant, resistance and loss factors were measured using a precision LCR meter (7600 Quad Tech, USA). Admittance-susceptance loop was taken using (Transducer analyzer TA-2000, Lecore systems, UK) to obtain $Q_m$, $k$ and $G$. Pyroelectric coefficient was derived from temperature dependence of remnant polarization ($P_r$).
3. Results and discussion

Figure 2 shows P-E hysteresis loops of (Sr, Mn) doped PZT for varying Mn content at room temperature, 90 °C and 150 °C. At room temperature; variation in Mn content doesn’t seem to have considerable effect on polarization, but this effect is pronounced at higher temperatures. At 90 °C the values of remnant polarization (P_r) are 0.022, 0.0295 and 0.048 C/m^2 for 0.3, 0.5 and 1.0 mol% of Mn respectively, which shows an increasing trend with concentration. These values almost doubled for 150 °C as 0.029, 0.041 and 0.093 C/m^2 respectively, following the same trend. It is evident from Figure 2 that the hysteresis loops are thin and constricted/pinched at the center which confers to the hard nature of material. Unease of switching at such high field of 3 kV/mm can also be regarded as the side of the constriction. It is observed that the switching is improved with rise in temperature for 1.0 mol% Mn only while for lower concentrations of Mn constriction is still present.

As strontium ion (Sr^{2+}) replaces lead ion (Pb^{2+}) at A-site as an isovalent dopant; it doesn’t disturb the electro neutrality of the crystal. It also improves the dielectric constant and ease of switching in result [7,10, 12]. However, Manganese as an acceptor dopant at B-site creates positive charge deficiency which is compensated by oxygen vacancies. These oxygen vacancies form defect dipoles and result in the pinning of domain rotation. The field which opposes the change in domain orientation resulting in the resistance to domain switching is called internal bias field [7, 10, 13, 14]. Internal bias can also be regarded as a strong reason for constriction of hysteresis loops. Internal bias; if present in a material causes a shift of P-E hysteresis loop from its centre along the electric field axis [15]. The dependence of internal bias field on temperature and applied electric field is shown in figure 3 for different manganese concentrations.

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**Figure 1.** Schematic Diagram of P-E system.
It can be seen that at low field strength the bias field is approximately negligible but it is significant at higher fields especially for the values where switching starts to appear: 1.6 kV and above. It is apparent that with the ease of hysteresis switching the opposing force is also rising to keep the system in low free energy state. Same like hysteresis saturation trend, the bias field is again higher, 0.15 kV/mm for 1.0 mol% and decreasing gradually for 0.5 and 0.3 mol% Mn as 0.005 and 0.0025 (kV/mm) at room temperature. From figure 2 we deduce that the temperature also plays a significant role in the rise of internal bias which can be explained in terms of the relationship of temperature and broadening of hysteresis loop resulting in an increase in bias field too.
Figure 3. Dependence of internal bias field on temperature and applied field for different mol% of manganese (a) 0.3, (b) 0.5 and (c) 1.0.

Figure 4 shows plots of remnant polarization versus temperature of 1.0 mol% Mn-doped PZT for different applied electric fields. The overall trend of remnant polarization is increasing with increasing temperature. For fields up to 1 kV/mm this dependence is linear however beyond this field non-linearity subjected to hysteresis switching increases, resulting a sharp increase in remnant polarization with temperature, which is maximum for 3 kV/mm.
The temperature dependent polarization of PZT makes it important for pyroelectric applications. The pyroelectric coefficient \( p \) can be determined from the temperature dependence of remnant polarization using the following relation [16].

\[
p = \frac{dP_r}{dT}
\]  

(1)

There are two modes of operation of pyroelectric IR detectors. The first one operates without external electric field at temperatures considerably lower than Curie point while in second mode an optimal dc field is applied at temperatures near phase transition to exploit the peaking of polarization near curie point. The later mode permits higher sensitivities and lower [17]. Pyroelectric coefficient was determined from the slope of \( P_r \) versus temperature plots at different bias fields from figure 4. The field dependent values of pyroelectric coefficients are \( 5.17 \times 10^{-5}, 1.31 \times 10^{-4}, 3.22 \times 10^{-4}, 4.13 \times 10^{-4}, 5.05 \times 10^{-4} \) and \( 6.25 \times 10^{-4} \) C/m\(^2\)K for 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 kV/mm, respectively.

\[ \text{Figure 4. Variation of remnant polarization with temperature at different applied fields.} \]

Piezoelectric properties of the poled samples are shown in Table 1. It is evident that the relative dielectric constant is decreasing with increasing Mn content. There is a little effect on piezoelectric coefficient \( d_{33} \) and coupling coefficient \( k \), however the former shows a decreasing and later presents an increasing trend. Manganese addition has lifted the mechanical quality factor \( Q_m \) to an appreciable. Because the Ionic radii of Mn\(^{3+}\) and Mn\(^{4+}\) are 0.62 Å and 0.52 Å respectively, as compared to the host ions Zr\(^{4+}\) (0.79) and Ti\(^{4+}\) (0.68), substitution of Mn at B-site leads to the shrinkage of crystal cell [10] which may be the cause of improvement in quality factor.
Table 1. Electrical properties of manganese doped PSZT

| Composition | $\varepsilon_r$ | $d_{33}$ (pC/N) | Q | R (kΩ) | G (mS) | K | tan$\delta$ |
|-------------|----------------|-----------------|---|--------|--------|---|-----------|
| MPSZT 0.3   | 1137           | 273             | 342| 1.80   | 20.8   | 0.3| 0.003     |
| MPSZT 0.5   | 1044           | 270             | 506| 2.60   | 35.6   | 0.32| 0.008     |
| MPSZT 1.0   | 974            | 257             | 756| 1.26   | 64.5   | 0.38| 0.002     |

4. Conclusions

PZT system was co doped with Mn (acceptor dopant) and Sr (isovalent dopant) to enhance the electrical properties of the material. Sr was added to facilitate the switching process and Mn was impregnated for the improvement of mechanical quality factor. The pyroelectric property was also investigated from the temperature dependent behavior of remnant polarization. The optimized results were obtained for the 1 mol% of Mn content with 4 mol% of Sr. The values of $Q_m$, $k$, $d_{33}$ and tan$\delta$ were measured as 756, 0.38, 257 and 0.002. Higher values of $Q_m$ with low loss factor makes this material more suitable for application purposes. Maximum value of pyroelectric coefficient $6.25 \times 10^{-4}$ was obtained at 3 kV/mm.

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