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Short communication

Structural and electrical properties of double doped (Fe^{3+} and Ba^{2+}) PZT electroceramics

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Abstract

Fe and Fe–Ba doped lead zirconate titanate (PZT) ceramics near the morphotrophic phase boundary (MPB) were prepared by the solid-state oxide route. X-ray diffraction studies were carried out for PZT samples to confirm the phase formation. Dielectric and piezoelectric measurements were carried out by varying frequency and sintering temperature. The electromechanical coupling factor (K_p) for Fe and Fe–Ba doped PZT ceramics was found to be 0.49 and 0.53. Scanning electron microscopy (SEM) studies were carried out to measure the grain size and its effect on dielectric and piezoelectric properties. Hysteresis (P–E) loops were traced for both compositions by varying the electric field, to the polarization behavior and its effect on the properties. Both higher mechanical quality factor, Q_m (880) and coupling factor, K_p (0.53) were obtained for Fe–Ba doped PZT ceramics.

Keywords: Dielectrics; Hysteresis loop; Mechanical quality factor; Piezoelectric materials

1. Introduction

PZT [$Pb(Zr,Ti)O_3$], based ceramics a solid solution of ferroelectric $PbTiO_3$ and anti-ferroelectric $PbZrO_3$, are forefronts both in the area of research and technology point of view. PZT based materials because of its superior properties [1–3] had been widely used in high power ultrasonics, SONAR transducers and structural health monitoring applications. The effects of dopants had been investigated extensively to tailor the functional properties of the material for prospective applications. A lot of work had been done in the past to study the effects of changes of PZT by substitution of single isovalent, supervalent or subvalent dopants with varying concentrations in the A or B site [4–6]. Further few researchers had reported the effect of double doping on both A and B site to adhere the advantages of both donor and acceptor doping [7–9]. But the effect of Fe and Ba (acceptor and isovalent) double doped PZT ceramics are not studied exclusively by any researchers for obtaining both high piezoelectric coefficient and mechanical quality factor. Our goal in the present work is to investigate the effect of Fe and Fe–Ba doped PZT ceramic for obtaining high mechanical quality factor, coupling coefficient and dielectric properties for high power generators and SONAR systems. The work is highlighted more on the effect of subvalent and isovalent doping and its influence on pinching of hysteresis loop.

2. Material and methods

PZT material with the following compositions, [$Pb(Zr_{0.53}Ti_{0.47})O_3+Fe_2O_3$ (1 wt%) and $Pb(Zr_{0.53}Ti_{0.47})O_3+$(1 wt%) Fe_2O_3+(1 wt%) $BaCO_3$] were prepared by mixed oxide route using high purity raw materials. The compositions were designated as PZTF and PBZTF respectively. The powders were mixed and ball milled in water medium for 24 h. The milled powder was calcined at 1000 °C in a closed alumina crucibles for 2 h.

The prepared samples were confirmed for phase formation by using an X-ray diffractometer (Model PW-3020, Philips) with Cu Kα radiation. The binder polyvinyl alcohol (PVA) was added to powder and disks of diameter 20 mm and thickness 2 mm were

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compacted and sintered over the temperature range of 1200 to 1300 °C. Micro-structural studies of the sintered compacts were carried out using Scanning Electron Microscope (SEM) (Model No.JSM-6360, JEOL). The sintered discs were electroded using silver paste and then poled at 3 kV/mm in silicone oil bath at 100 °C for 30 min. The dielectric and piezoelectric properties of poled samples were measured after 24 h of poling. The capacitance was measured by LCR Bridge (Model 4262 A, Hewlett Packard) at varying frequency from 100 Hz to 1 MHz. Dielectric constant (ε), mechanical quality factor (Q_m) and coupling coefficient (K_p) were calculated by standard formulae using measured values of capacitance, resonance and anti-resonance frequencies. The P–E loop was traced by hysteresis tracer (TF Analyzer, 2000, FE module).

3. Results and discussion

The XRD patterns of PZT, PZTF (Fe doped) and PBZTF (Fe and Ba doped) samples sintered at 1250 °C for 30 min are shown in Fig. 1. The patterns show sharp diffraction peaks, which indicate single perovskite phase, better homogeneity and crystallization of the samples. The tetragonal, splitting of peaks has been observed at 45° for double doped PZT samples (PBZTF). Whereas in both undoped and Fe doped PZT, no such tetragonal splitting has been witnessed. The phenomenon indicated that introduction of dopants Ba^{2+} and Fe^{3+} induce the formation of tetragonal phase. It may be explained by the fact that acceptor substitution of Zr^{4+} or Ti^{4+} by Fe^{3+} ions create oxygen vacancies, on the contrary, isovalent substitutions of Pb^{2+} ions by Ba^{2+} do not create oxygen vacancies. The addition of Ba^{2+} ions decrease the unit cell volume that results in the formation of tetragonal phase [10–12].

The SEM of the fracture surfaces of PZTF and PBZTF sintered samples, are shown in Fig. 2(a) and (b), respectively. The samples are sintered at optimum sintering condition at 1250 °C and grain size is measured by linear intercept method. The micro-structure reveals the grain size of 2.0 μm for PZTF and 1.2 μm for PBZTF samples. It also indicates the uniform grain growth and tightly bonded grains with homogeneous micro-structure. The addition of Fe^{3+} and Ba^{2+} results in reduction of grain size. Ba ions accumulate near the grain boundary region and inhibit the grain growth. The phase changes from rhombohedral to tetragonal are evidenced by sharp decrease in grain size for PBZTF samples.

The variation of K_p as a function of sintering temperature is shown in Fig. 3. It is observed that PBZTF have higher K_p than the PZTF samples. This may be because of higher tetragonal splitting and poling efficiency. The increase in poling efficiency is due to the increase in resistivity of Ba doped PZT. In

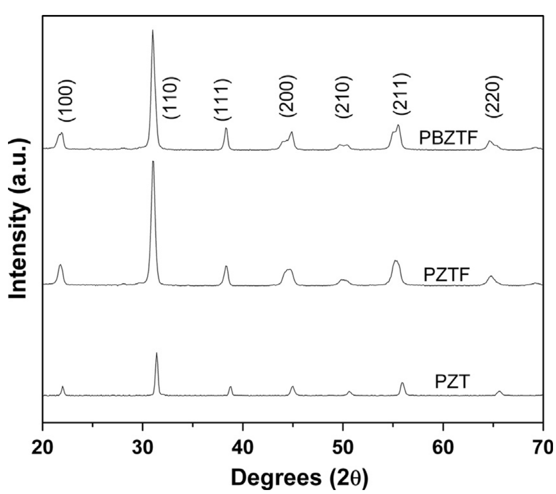

Fig. 1. XRD patterns of PZT, PZTF and PBZTF sintered specimens.

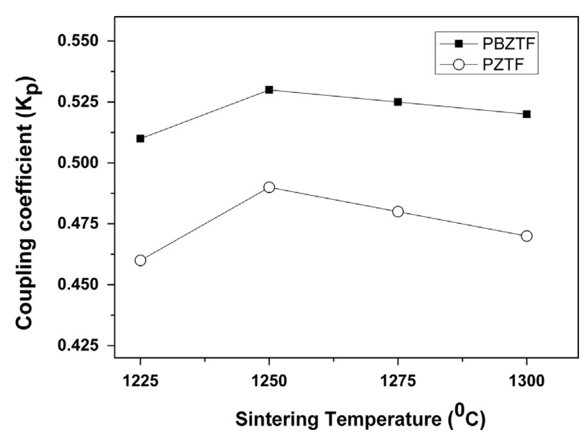

Fig. 3. Variation of coupling coefficient with sintering temperature for PZTF and PBZTF samples.

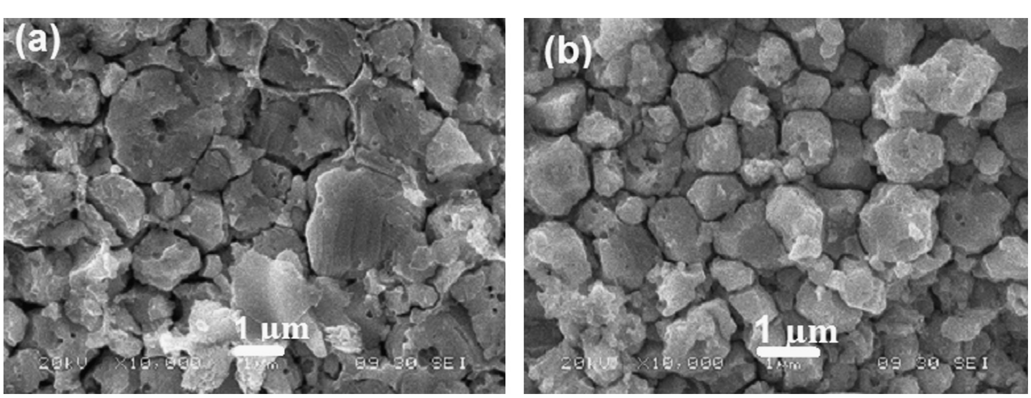

Fig. 2. SEM of (a) PZTF and (b) PBZTF sintered samples.

PZTF samples, doping with Fe^{3+} results in oxygen vacancies and that hinder the domain wall motion. It was also observed that K_p increases with sintering temperature until it reaches the optimum conditions (1250 °C) and then decreases for both PZTF and PBZTF sample. The mechanical quality factor (Q_m) at optimum sintering temperature (1250 °C) is found to be 980 for PZTF and 880 for PBZTF samples. This may be due to increase in domain wall friction with decrease in grain size. It is vital to note that Q_m of 880 is achieved along with K_p of 0.54 for PBZTF samples. The mechanical quality factor of piezoceramic materials reported in the literature and their progress are compared in Table 1.

The variation of dielectric constant with frequency for PZTF and PBZTF ceramics are shown in Fig. 4. As the frequency increases, the dielectric constant decreases for both samples. Decreasing trend of dielectric constant is justified because of the contribution of all the polarization mechanisms at lower frequencies (~100 Hz) [25]. Space charge, ionic and electronic polarizations become inoperative in that order with increase in frequency. But for a particular frequency, higher dielectric constant is observed for PBZTF samples. It may be due to increase in domain wall motion, higher poling efficiency and finer grain size. Generally in fine grained ferroelectrics, the fraction of dipoles at the interface increases significantly and results in higher dielectric constant. The variation of dielectric constant with temperature at 1 kHz for both the compositions is shown in Fig. 5. Dielectric constant increases gradually with increasing temperature up to the transition point and subsequently it decreases. Dielectric properties of PZT materials are dependent on both intrinsic and extrinsic mechanisms. The reduction in dielectric constant at lower temperature (below 273 K), are due to drop in dipole orientation and domain wall motion. The extrinsic mechanisms are thermally activated process that can be easily hampered at lower temperatures [26,27]. Few researcher are also reported the presence of ferroelectric correlations at lower temperatures in transition metal oxides due to rattling of Ti^{4+} cation within TiO_6 octahedra. It is also observed that PZTF samples have higher Curie temperature than PBZTF samples.

The hysteresis loop of the PZTF and PBZTF sintered samples are depicted in Fig. 6. Based on the obtained dielectric and piezoelectric properties, dielectric spectroscopy measurements, positive up and negative down (PUND) results and Maxwell–Wagner type relation, it is confirmed the loop as ferroelectric loop and not to be confused with banana loops at low frequency [28,29]. The similar type of loop is also reported for Fe-doped PZT materials [30]. The marginal appearance of dumb bell shaped double hysteresis is observed

Table 1
Mechanical quality of various piezoelectric materials.

Material	Q_m	Refs.
PZT (52/48)	100	[13]
Nb-PZT	97, 50	[14,15]
La-Nb-PZT	122	[16]
Sr doped PZT	400	[17]
0.5PSN–0.43PT	38	[18]
PST-PT	30	[19]
BNT-BT	800	[20]
PZT-PMN	800	[21]
PYN-PMN-PZT	1000	[22]
PYN-ZT	1200	[23]
PMS-PZT	1300	[24]
Fe-PZT	980	Present paper
Fe-Ba-PZT	880	

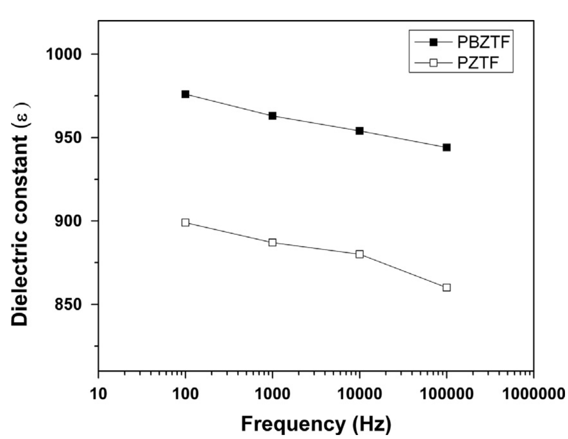

Fig. 4. Variation of dielectric constant with frequency for PZTF and PBZTF samples.

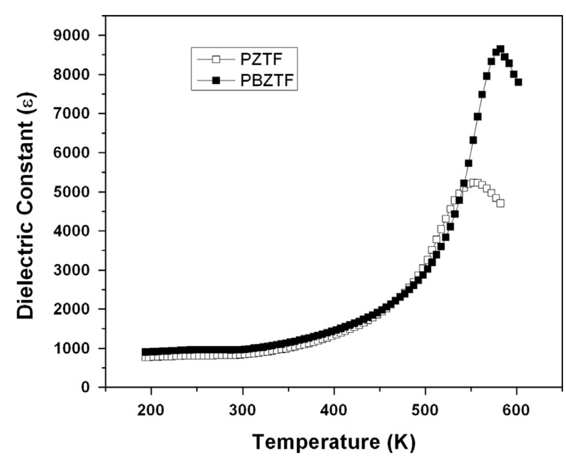

Fig. 5. Variation of dielectric constant with temperature for PZTF and PBZTF samples.

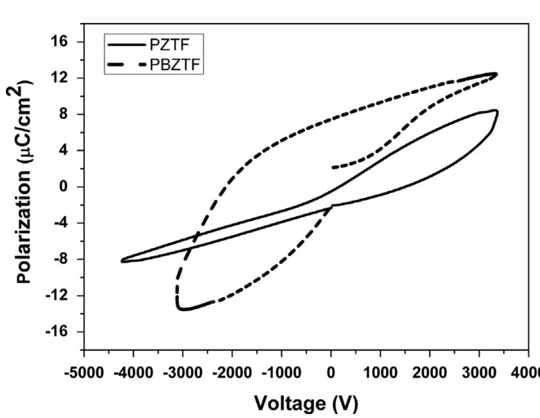

Fig. 6. Hysteresis loop of PZTF and PBZTF samples.

for PZTF samples. Strong loop pinching is observed in Fe^{3+} doped samples whereas the pinching is reduced with Ba^{2+} doping of PZT ceramics. The loop, pinching may be due to oxygen vacancy–acceptor defect dipoles, which generate a resorting force for domain walls and reduce their displacements to limit the properties [30]. The reduction in loop pinching of PBZTF ceramics may be due to Ba^{2+} doping do not create oxygen vacancies and that decreases the conductivity and increases the domain wall movement. The value of polarization is found to be more for PBZTF samples because of the reduction in grain size.

4. Conclusions

In this work we have reported the effect of Fe and Fe–Ba doping on structural and electrical properties of PZT ceramics near the morphotropic phase boundary with fixed Zr/Ti (53/47) ratio prepared by mixed oxide route. XRD studies confirm perovskite phase with better homogeneity and crystallization of the samples. Decrease in grain size and mechanical quality factor; increase in dielectric constant and spontaneous polarization are observed in PBZTF samples. The pinching of hysteresis loop and its reduction in pinching are observed in PZTF and PBZTF samples respectively.

References

[1] T. Yamamoto, Optimum preparation methods for piezoelectric ceramics and their evaluation, American Ceramic Society Bulletin 71 (1992) 978–984.

[2] F. Kulsar, Electromechanical properties of lead titanate zirconate ceramics with lead partially replaced by calcium or strontium, Journal of the American Ceramic Society 42 (1959) 343–349.

[3] K. Okazaki, K. Nagata, Effects of grain size and porosity on electrical and optical properties of PLZT ceramics, Journal of the American Ceramic Society 56 (1973) 82–86.

[4] T.B. Weston, A.H. Webster, V.M. McNamara, Lead zirconate titanate piezoelectric ceramics with iron oxide additions, Journal of the American Ceramic Society 52 (1969) 253–257.

[5] C. Cheon, J.S. Park, Temperature stability of the resonant frequency in Cr_2O_3-doped Pb(Zr, Ti)O_3 ceramics, Journal of Materials Science Letters 16 (1979) 2043–2046.

[6] S. Sharma, R. Singh, T.C. Goel, S. Chandra, Synthesis, structural and electrical properties of La modified PZT system, Computational Materials Science 37 (2006) 86–89.

[7] R. Rai, S. Sharma, N.C. Soni, R.N.P. Choudhary, Investigation of structural and dielectric properties of (La, Fe) doped PZT ceramics, Physica B 382 (2006) 252–256.

[8] P. Goel, K.L. Yadav, A.R. James, Double doping effect on the structural and dielectric properties of PZT ceramics, Journal of Physics D: Applied Physics 37 (2004) 3174–3179.

[9] C. Miclea, C. Tanasoiu, C.F. Miclea, L. Amarande, A. Gheorghiu, F.N. Sima, Effect of iron and nickel substitution on piezoelectric properties of PZT type ceramics, Journal of the European Ceramic Society 25 (2005) 2397–2400.

[10] K. Ramam, M. Lopez, Ferroelectric and piezoelectric properties of Ba modified Lead zirconate titanate ceramics, Journal of Physics D: Applied Physics 39 (2006) 4466–4471.

[11] R.S. Nasar, M. Cerqueira, E. Longo, E.R. Leite, J.A. Varela, A. Beltran, J. Andres, Experimental and theoretical study on the piezoelectric behavior of barium doped PZT, Journal of Materials Science 34 (1999) 3659–3667.

[12] R. Koduri, L.S. Hermosilla, Effect of Ba in ferroelectric and piezoelectric properties of the PLZT(1,2/55/45), Physica Status Solidi A 203 (2006) 2119–2127.

[13] S. Cheng, S. Fu, C. Wei, Low-temperature sintering of PZT ceramics, Ceramics International 13 (1987) 223–231.

[14] M. Masaki, H. Hashimoto, W. Masahiko, I. Suzuk, Measurements of complex materials constants of piezoelectric ceramics: Radial vibration mode of a ceramic disk, Journal of the European Ceramic Society 28 (2008) 133–138.

[15] B. Chen, C. Huang, L. Wu, Promotion of piezoelectric properties of lead zirconate titanate ceramics with (Zr, Ti) partially replaced by Nb_2O_5, Solid-State Electronics 48 (2004) 2293–2297.

[16] V. Singh, H.H. Kumar, D.K. Kharat, S. Hait, M.P. Kulkarni, Effect of lanthanum substitution on ferroelectric properties of niobium doped PZT ceramics, Materials Letters 60 (2006) 2964–2968.

[17] N.N. Wathore, C.M. Lonkar, D.K. Kharat, Effect of temperature on polarization reversal of strontium-doped lead zirconate titanate (PSZT) ceramics, Bulletin of Materials Science 34 (2011) 129–132.

[18] H. Ursic, J. Tellier, J. Holc, S. Dmovsek, M. Kosec, Structural and electrical properties of 0.57PSN–0.43PT ceramics prepared by mechanochemical synthesis and sintered at low temperature, Journal of the European Ceramic Society 32 (2012) 449–456.

[19] J.F. Wang, J.R. Giniewicz, A.S. Bhalla, Piezoelectric properties of modified lead scandium tantalite ceramics, Materials Letters 30 (1997) 47–52.

[20] H.J. Lee, S. Ural, L. Chen, K. Uchino, S. Zhang, High power characteristic of lead-free piezoelectric ceramics, Journal of the American Ceramic Society 95 (2012) 3383–3386.

[21] S. Priva, H. Kim, K. Uchino, Low temperature coefficient of resonance frequency composition in the system Pb(Zr, Ti)O_2-Pb($Mn_{1/3}Nb_{2/3}$)O_3, Journal of the American Ceramic Society 87 (2004) 1907–1911.

[22] H. Chen, C. Fan, Fabrication and properties of PYN-PMN-PZT quaternary piezoelectric ceramics for high power, high temperature application, Materials Letters 64 (2010) 654–656.

[23] Y. Zhang, H. Chen, D. Mao, Processing, structure and electrical properties of MnO_2- doped $Pb(Yb_{1/2}Nb_{1/2})_{0.10}(Zr_{0.47}Ti_{0.53})_{0.90}O_3$ ceramics, Ceramics International 39 (2013) 159–163.

[24] H. Du, Z. Pe, Z. Li, Effect of sintering temperature and composition on microstructure properties of PMS-PZT ceramics, Transactions of Nonferrous Metals Society of China 16 (2006) 165–169.

[25] P. Lunkenheimer, S. Krohns, S. Riegg, S.G. Ebbinghaus, A. Reller, A. Loidl, Colossal dielectric constants in transition-metal oxides, European Physical Journal 180 (2010) 61–89.

[26] M. Li, A. Feteira, D.C. Sinclair, A.R. West, Incipient Ferroelectricity and microwave dielectric resonance properties of $CaCu_{2.85}Mn_{0.15}Ti_4O_{12}$ ceramics, Applied Physics Letters 91 (2007) 132911.

[27] A. Loidl, S. krohns, J. Hemberger, P. Lunkenheimer, Bananas go paraelectric, Journal of Physics: Condensed Matter 20 (2008) 191001–191003.

[28] J.F. Scott, Ferroelectrics go bananas, Journal of Physics: Condensed Matter 20 (2008) 21001–21002.

[29] N.K. Singh, A. Panigrahi, R.N.P. Choudhary, Structural and dielectric properties of $Ba_5EuTi_{3-x}Zr_xNb_7O_{30}$ relaxor ferroelectrics, Materials Letters 50 (2001) 1–5.

[30] L. Jin, Z. He, D. Damjanovic, Nanodomains in Fe^{3+} -doped lead zirconate titanate ceramics at the morphotrophic phase boundary, Applied Physics Letters 95 (2009) 012905–012908.