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Effect of Samarium substitution on dielectric properties of (Pb)(Zr, Ti, Fe, Nb)O_3 type ceramic system

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Abstract

The influence of Samarium substitution on the dielectric properties of modified PZT composition with representative formula [$Pb_{1-x}Sm_xZr_{0.588}Ti_{0.392}Fe_{0.01}Nb_{0.01}O_3$] system is reported. Samarium (Sm) was varied from 0 to 0.01/FU in the present system in a step of 0.0025. The samples were prepared by the traditional solid state reaction process. XRD analysis showed all the samples to be single phase with tetragonal structure. Dielectric properties were studied in detail as a function of frequency and temperature (from room temperature (RT) 30 to 400 °C). All compositions show phase transition and the transition temperature (T_C) is found to decrease with increase in Sm substitution. Room temperature dielectric constant shows an increasing trend while loss improves with Sm doping.

Keywords: D. PZT; PZTFN; Samarium; Dielectric; XRD

1. Introduction

Lead zirconate titanate ($PbZr_{1-x}Ti_xO_3$, $0 \leq x \leq 1$, PZT), which is a solid solution of lead zirconate (PZ) and lead titanate (PT), is an important ferroelectric material for a variety of applications such as high energy capacitors, nonvolatile memories, infrared detectors, smart sensors and actuators and electro-optic devices [1–3]. The highest piezoelectric coupling coefficient and high permittivity of PZT are obtained for compositions close to morphotropic

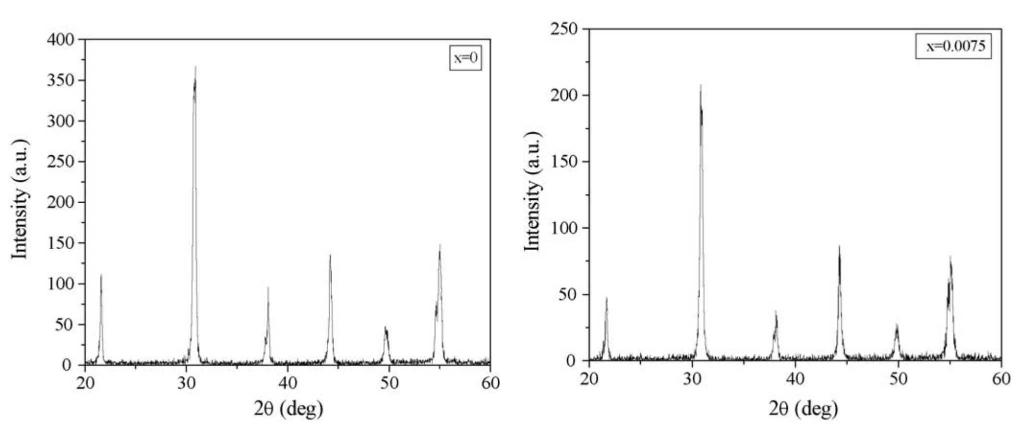

Fig. 1. XRD patterns of the samples with $x = 0$ and $x = 0.0075$.

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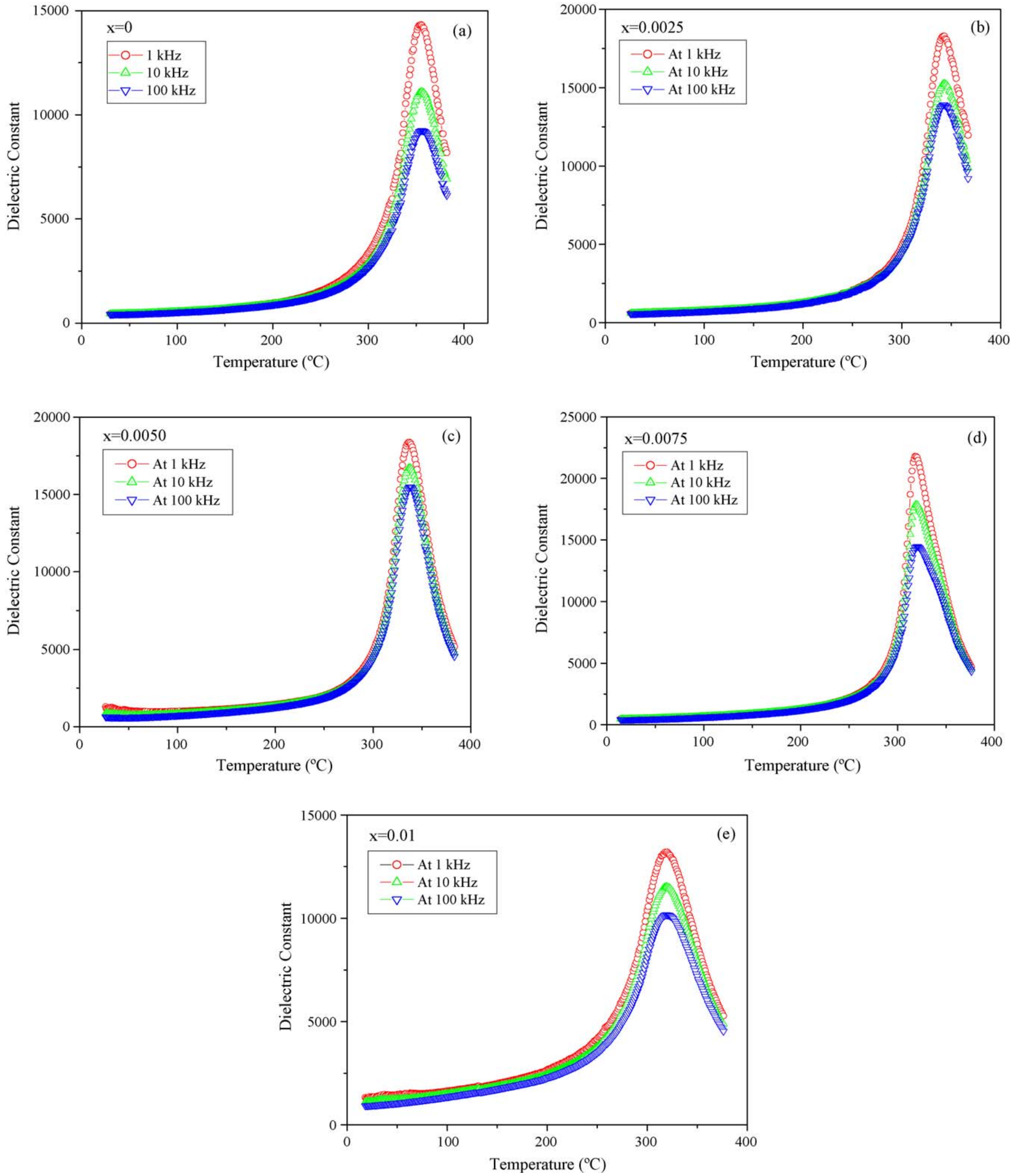

Fig. 2. Temperature dependence of dielectric constant (ε) at different frequencies for $Pb_{1-x}Sm_xZr_{0.588}Ti_{0.392}Fe_{0.01}Nb_{0.01}O_3$ system (a) $x = 0$, (b) $x = 0.0025$, (c) $x = 0.0050$, (d) $x = 0.0075$ and (e) $x = 0.01$.

phase boundary (MPB) between tetragonal and rhombohedral phases [4]. The PZT system undergoes a morphotropic phase transition in which ferroelectric tetragonal structure transforms to a ferroelectric rhombohedral structure. The elastic, piezoelectric and dielectric properties of PZT show anomalies near MPB. These anomalies are responsible for strong electromechanical behavior and make these materials highly suitable for practical applications [5–9]. Adding oxide group additives such as ''Softners'' and ''Hardners'' into PZT can modify its properties further. Softners reduce the elastic modulus, coercive field strength and aging effects; and increase permittivity and dielectric and mechanical losses. Doping of hardeners reduces dielectric constant and increases frequency constant, mechanical quality factor and aging effects. Hard PZTs are doped with acceptor ions such as K^+, Na^+ (at A site) and Al^{3+}, Fe^{3+}, Mn^{3+} (at B site) creating oxygen vacancies in the lattice [10,11]. Soft PZTs are doped with donor ions such as La^{3+}, Sm^{3+}(at A site) and Nb^{5+}, Sb^{3+} (at B site) leading to creation of A site vacancies in the lattice [12–15]. In the present work, we have synthesized Sm^{3+} substituted PZTFN ceramics with general formula $[Pb_{1-x}Sm_xZr_{0.588}Ti_{0.392}Fe_{0.01}Nb_{0.01}O_3]$ for different Sm concentration ($x = 0$, 0.0025, 0.0050, 0.0075, 0.01). Here dielectric properties of the materials prepared via solid state route are reported.

2. Experimental details

2.1. Ceramic processing

A conventional dry ceramic method was adopted to prepare polycrystalline samples with compositional formula $Pb_{1-x}Sm_xZr_{0.588}Ti_{0.392}Fe_{0.01}Nb_{0.01}O_3$. The substitution parameter x was varied from 0 to 0.01 in steps of 0.0025. Stoichiometric amounts of AR grade PbO, Sm_2O_3, ZrO_2, TiO_2, Fe_2O_3 and Nb_2O_5 were mixed to get the powder mixture. About 2 wt.% of excess PbO was added to counteract the volatilization of PbO during firing. The powder mixture was ball milled for 12 h in distilled water using zirconia balls and dried in oven. The dried powder was calcined at 800 °C for 4 h in a conventional furnace. The calcined powder was ball milled again and recalcined at 850 °C for 4 h. Recalcined powder was ball milled and then dried powders were mixed with small amount of diluted polyvinyl alcohol (PVA) binder and uniaxially pressed in form of circular discs of 15 mm diameter and 1 mm thickness at a pressure of 10 tonnes. The discs were sintered at 1250 °C for 4 h in closed alumina crucible in lead rich atmosphere to minimize lead loss during sintering.

2.2. Structural characterization

The formation and quality of the compound were checked by an X-ray diffraction technique. The XRD patterns were recorded at room temperature using D8 Advance X-ray diffractometer (Bruker AXS) in a range of bragg angles 2θ ($20^\circ \leq 2\theta \leq 60^\circ$) with a scanning rate of $2^\circ\ min^{-1}$.

2.3. Dielectric behavior

The sintered discs were lapped using microgrit powder on a flat glass surface. The samples were ultrasonically cleaned and flat surfaces were electroded with silver paste applied on both faces of pellets to form electrodes and fired at 400 °C for 1 h. Dielectric properties (dielectric constant (ε) and loss tangent ($\tan\delta$)) were measured using an automated setup as a function of temperature and frequency with heating rate of $1\ ^\circ C\ min^{-1}$. The setup consists of LCR meter Agilent 4263B and a programmable temperature chamber interfaced to PC. From the plots of dielectric constant versus temperature, phase transition temperature, T_C, was determined.

3. Results and discussions

XRD analysis showed all samples to be single phase with tetragonal structure. Typical XRD patterns for samples with $x = 0$ and 0.0075 are shown in Fig. 1.

Fig. 2 represents the variation of ε as a function of temperature at different frequencies for all the samples. It is observed in all the compositions that as temperature increases, the value of dielectric constant increases and passes through a maximum (at T_C) and then decreases. T_C is found to decrease with increasing Sm content that is due to weakening of ferroelectric strength by Sm substitution. The position of dielectric maxima does not change with frequency. This indicates characteristics of normal ferroelectrics [16]. The value of dielectric constant and loss decreases with increase in frequency. The higher value of dielectric constant at low frequency is due to the various types of polarization mechanisms. The increase in loss at elevated temperatures is caused by a corresponding conductivity increase [17].

Transition temperature (T_C), room temperature (30 °C) values of dielectric constant (ε_{RT}), ε_{max}, loss factor at room

Table 1
Variation of T_C, ε_{RT}, ε at T_C, $\tan\delta_{RT}$ and $\tan\delta$ at T_C with varying concentration of Samarium in $Pb_{1-x}Sm_xZr_{0.588}Ti_{0.392}Fe_{0.01}Nb_{0.01}O_3$ PZTFN samples at 10 kHz.

x	T_C(°C)	ε_{RT}	ε at T_C	$\tan\delta_{RT}$	$\tan\delta$ at T_C
0	355	440	11,095	0.017	0.18
0.0025	343	610	15,260	0.023	0.14
0.0050	336	840	16,680	0.108	0.71
0.0075	330	990	17,865	0.033	0.14
0.01	319	1170	11,520	0.051	0.12

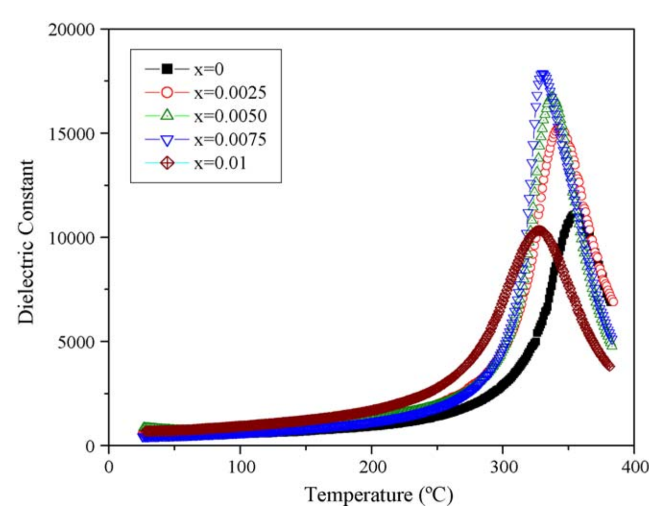

Fig. 3. Dielectric constant (ε) versus temperature plot of different compositions of $Pb_{1-x}Sm_xZr_{0.588}Ti_{0.392}Fe_{0.01}Nb_{0.01}O_3$ system at 10 kHz.

temperature, tan δ_{RT}, tan δ at T_C at 10 kHz for all the samples are listed in Table 1. There is a significant increase in dielectric constant at T_C with increase in x from 0 to 0.0075 and afterwards decreases upto 0.01 which has been shown in Fig. 3.

4. Conclusions

Samarium modified PZTFN ceramics were prepared by conventional dry ceramic method with dense single phase perovskite structure. Structural and dielectric properties of the materials have been studied. Single phase with tetragonal structure was confirmed by XRD analysis for all the samples. Dielectric constant was found to increase with increase in Sm concentration. Improvement in dielectric loss is observed with increase in doping of Samarium.

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