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Study of structural, Dielectric and Ac conductivity of PZT ceramics modified by substitution of Sm ion

Kanay Barik*, Rajiv Kumar, Sanjay Kumar Sinha
Research Scholar, Kolhan University, (INDIA)
Associate Professor, Jamshedpur Workers College, Jamshedpur 831012, (INDIA)
Associate Professor, BIT Mesra, Patna, (INDIA)
E-mail- kanaybarik2010@gmail.com; drrajiv96@gmail.com; sksinha@bitmesra.ac.in

ABSTRACT

The influence of Sm substitution on the structural and dielectric properties of $Pb_{1-x}Sm_x(Zr_{0.6}Ti_{0.4})_{1-x/4}O_3$ (PSZT) (x = 0.00, 0.04, 0.08 and 0.12) composition prepared from mixed oxide method at high temperature were synthesized. The formation of single – phase compounds were confirmed by X- ray diffraction studies which were found to be in tetragonal phase at room temperature. The variation of dielectric constant and tangent loss with temperature at selected frequencies exhibit their phase transition above room temperature. The Conduction process was found to be mixed type.

KEYWORDS

Perovskite;
Diffraction;
Conductivity;
Dielectric;
Tetragonal phase.

INTRODUCTION

Lead zirconate titanate or PZT with general chemical composition Pb (Zr, Ti) O_3 is a well known ferroelectric ceramic. A considerable amount of works have been done on modified PZT ceramics prepared from high-temperature solid-state reaction technique[1]. The properties of PZT are very much sensitive to its compositional fluctuations near the morphotropic phase boundary (MPB), particle size, doping, calcinations and sintering temperature. PZT is used in a wide range of piezoelectric, pyroelectric and ferroelectric device application. It is well established that the electrical and electrochemical properties of the PZT strongly depends on the substitution of rare earth element lanthanum and exhibits tremendous applications in electronics and electro – optics. The physical properties and device parameters of PZT – based compounds are greatly influenced by chemical substitutions, synthesis process, and some other factors[2]. The literature survey on pure and modified PZT materials reveals that no systematic studies have been reported on physical properties and device parameters of Sm-substituted PZT (i.e., PSZT) with Zr/Ti ratio 60/40. In view of the above, we have studied the effect of samarium substitution on structural, dielectric, and ac conductivity properties of PZT (Zr/Ti: 60/40) ceramics, which is reported here.

EXPERIMENTAL DETAILS

The samples of Sm – modified PZT $Pb_{1-x}Sm_x(Zr_{0.6}Ti_{0.4})_{1-x/4}O_3$ (where x = 0.00, 0.04,

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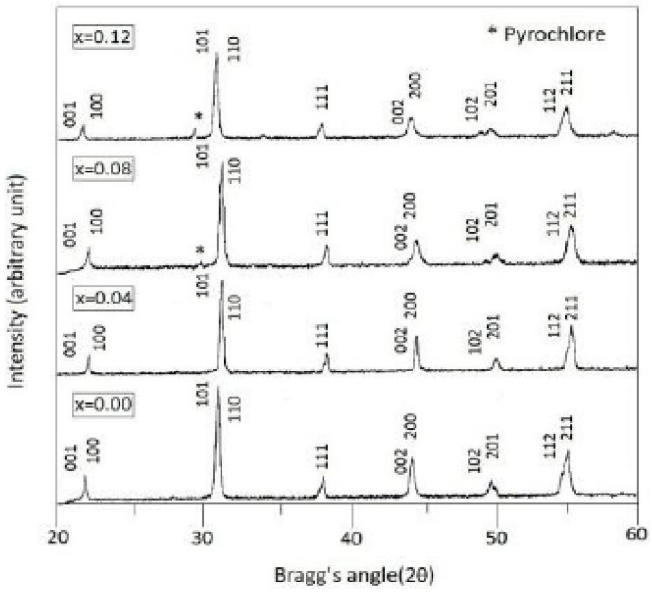

Figure 1 : The comparison of XRD patterns of $Pb_{1-x}Sm_x(Zr_{0.6}Ti_{0.4})_{1-x/4}O_3$ (for x = 0.00, 0.04, 0.08, and 0.12)

0.08, and 0.12) were prepared by a high- temperature solid-state reaction technique. 3% more PbO has been taken to compensate lead loss at high temperatures. These oxides were mixed thoroughly in a dry condition for 2h in air, and then, in methanol medium for 2h using agate mortar and pestle to get homogeneous mixture of the materials. Now, the well mixed oxides were calcined, first at 950 °C, then at 1000°C for 10h[3]. Finally, the formation of desired compounds was confirmed by XRD patterns of calcined powders at 1100°C/10h. The homogeneous powder of the compounds were pressed into cylindrical pellets of 10 m diameter and 2-3 mm thickness under a uniaxial pressure of 4×10^6 N/m^2 using hydraulic press. Polyvinyl alcohol was used as a binder to reduce brittleness of the pellets. These pellets were sintered at an optimized temperature of 1200°C for about 10h in alumina crucibles in order to get maximum density. The X-ray diffraction data of the calcined powders were recorded using X-ray diffractometer (Rigaku Miniflex, Japan) with λ = 1.5405 °A in a wide range of Bragg's angles 2θ(20° ≤ 2θ ≤ 80°) at a scanning rate of 3°/minute[4]. Using phase sensitive multimeter (PSM; Model 1735) the dielectric data of the materials were obtained in a wide range of frequency (10^2–10^6 Hz) and temperature (room temperature - 500°C) at a potential difference of 1V.

RESULTS AND DISCUSSION

Structural analysis

The room temperature XRD patterns of polycrystalline $Pb_{1-x}Sm_x(Zr_{0.6}Ti_{0.4})_{1-x/4}O_3$ with x = 0.00, 0.04, 0.08, and 0.12 exhibit sharp and single peaks along with few peak splits. The sharpness of the peaks split gradually decreases with the higher concentration of Sm. The XRD patterns as compared to the reported ones confirm the formation of single phase with tetragonal crystal structure. All the reflection peaks were indexed in tetragonal crystal system using computer software POWDMULT. On the basis of best agreement between the observed (obs) and the calculated (cal) d - spacing (i.e.,$\sum \Delta d = d_{obs} - d_{cal}$ = minimum), all the PSZT compounds were found to be in tetragonal crystal system with their refined lattice parameters given in TABLE 1. There is a pyrochlore phase in each of the XRD patterns of PSZT having Sm content x = 0.08 and 0.12 near the PSZT peak – 101. Though these peaks are undesirable, it is some time essential for formation of the perovskites. The percentage of pyrochlore phase in PSZT for x = 0.08 and 0.12 was estimated as 6.1% and 7.8%, respectively.

Dielectric study

Dielectric property is the most important property of ceramic materials. The dielectric constant and dielectric loss were calculated in a wide range of temperature (room temperature to 500 °C) and frequencies (10^3– 10^6 Hz) from the data obtained by using the experimental systems containing 'Phase sensitive multimeter'. The variation of relative dielectric constant of PSZT (having Sm contents x = 0.00, 0.04, 0.08, and 0.12) with temperature at selected frequencies (10^3– 10^6 Hz) is shown in Figure 2. From the graphical variations we get that ε_r decreases on increasing frequency which indicates a normal behavior of the ferroelectric and/or dielectric materials. The higher values of ε_r at lower frequency are due to the simultaneous presence of all types of polarizations (space charge, dipolar, ionic, electronic, etc.) which is found to decrease with the increase in frequency. At high frequencies (>10^{12} Hz) electronic polarization only exists in the materials. When temperature of PSZT samples is increased, ε_r

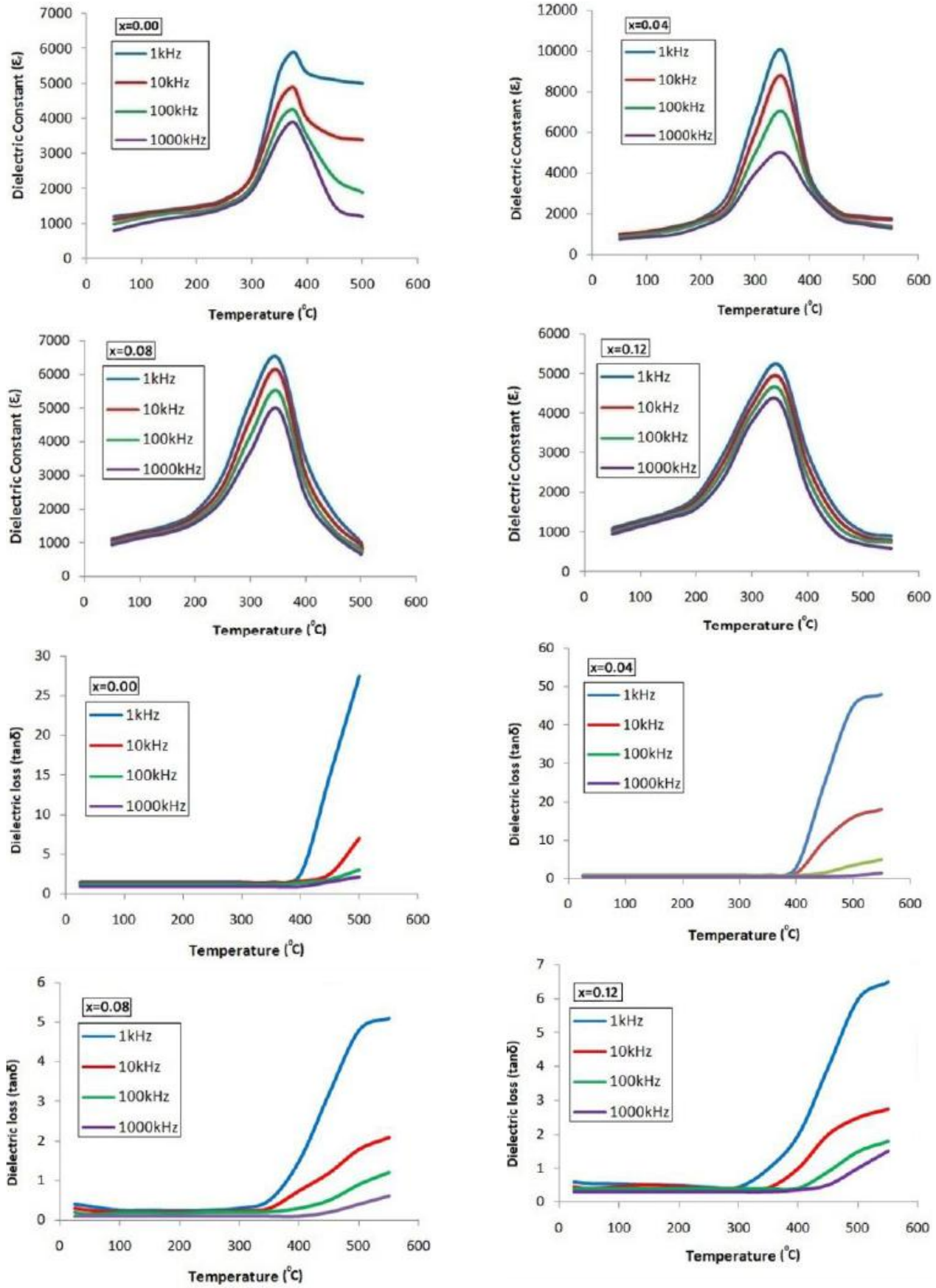

Figure 2 : Temperature-frequency dependence of relative dielectric constant (δ_r) and tangent loss (tan δ) for *x* = 0.00, 0.04, 0.08, and 0.12

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first increases slowly and then rapidly up to a maximum value[5]. As at this Tc, phase transition takes place between ferroelectric-pyroelectric phases. At the higher temperature (≥Tc), the space charge polarization originates due to mobility of ions and imperfections in materials and thus contributes to a sharp increase in ε_r. When the temperature of PSZT samples is increased above transition temperature, dielectric constant begins to decrease obeying Curie – Weiss law. The ε_{max} is found to increase with increase in Sm^{3+} content through x = 0.00 to 0.04 and then shows a sharp decrease. The temperature corresponding to ε_{max} is found to decrease with the increase in samarium concentration in PSZT.

The temperature – frequency dependence of dielectric loss (tanδ) of PSZT ceramic samples is shown in Figure 2. It has been observed that the value of tanδ is very low and nearly remains unchanged until a certain high temperature. If the temperature of the materials is further increased above this temperature, tanδ exhibits a sharp increase. If the frequency of the PSZT materials is increased, the value of tanδ decreases as expected.

Ac conductivity

The dielectric materials are normally non – conducting in nature possessing no free charge carriers. When a solid polycrystalline dielectric material is kept under the action of an external electric field, electrical conduction takes place due to ordered motion of weakly bound charged particles[6]. In the complex impedance spectroscopy technique, the ac conductivity of dielectric material is calculated from the conducting relation $\sigma_{ac} = \omega\varepsilon_o\varepsilon_r \tan\delta$, where $\grave{u}$ is the angular frequency and $\mathring{a}_o$ the permittivity of free space[7]. The temperature – frequency dependence

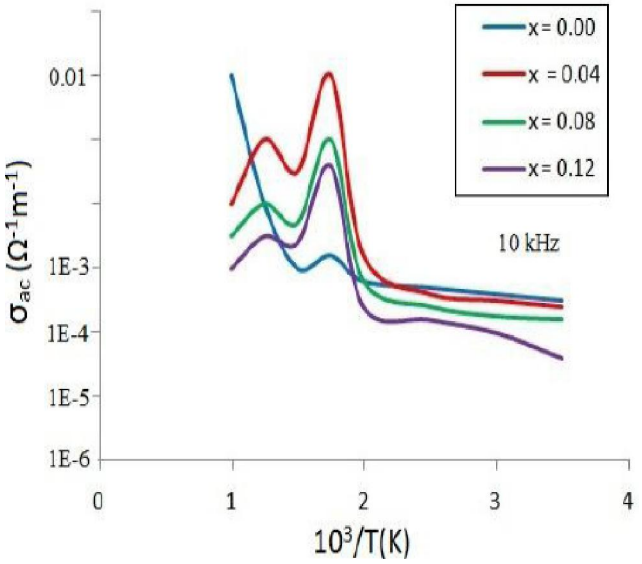

Figure 3 : Temperature-frequency dependence of ac conductivity $Pb_{1-x}Sm_x(Zr_{0.6}Ti_{0.4})_{1-x/4}O_3$ for x = 0.00, 0.04, 0.08 and 0.12

of ac conductivity of with *x* = 0.00, 0.04, 0.08, and 0.12 is shown in Figure 4. The value of ac conductivity is almost found to increase with increase in temperature. A sharp maximum in σ_{ac} at T_c (observed by dielectric analysis) indicates a marked dispersion which may be due to the increase in polarizability. If the temperature is further increased above T_c, the conductivity data appears to fall on a straight line exhibiting a typical behavior of the dc component of the conductivity[8]. The linear variation of σ_{ac} over a wide range of temperature supports the existence of thermally activated transport properties in the materials following the Arrhenius equation:

$\sigma_{ac} = \sigma_0 \exp(-\frac{E_a}{K_B T})$,

where σ_o is the pre-exponential factor, K_B the Boltzmann constant and E_a the activation energy.

TABLE 1 : Comparison of the lattice parameters, ε_{max} and T_c of $Pb_{1-x}Sm_x(Zr_{0.6}Ti_{0.4})_{1-x/4}O_3$ for x = 0.00, 0.04, 0.08 and 0.12

	Sm composition			
Parameters	**x = 0.00**	**x = 0.04**	**x = 0.08**	**x = 0.12**
a	4.0561(16)	4.0074 (55)	4.0165(53)	4.0743(36)
c	4.0731(16)	4.0600(55)	4.0602(53)	4.0917(36)
c/a	1.0041(16)	1.01312(50)	1.0108(50)	1.0042(50)
ε_{max}	5789	9978	6544	5387
T (C)	375 ± 0.25	351 ± 0.25	342 ± 0.25	334 ± 0.25

CONCLUSIONS

X - ray diffraction data obtained from the calcined powders of polycrystalline samples of Sm-modified PZT (i.e.,) has confirmed their tetragonal phase with the presence of a small amount of pyrochlore phase during higher concentration of Sm for x = 0.08 and 0.12 was estimated as 6.1% and 7.8%, respectively.

The dielectric constant, tangent loss, and transition temperature of PSZT as a function of temperature at selected frequencies has exhibited that maximum or peak are strongly dependent on Sm content. The value of electrical conductivity (ac) of PSZT depends not only on singly ionized ion in low temperature (ferroelectric phase) region but also due to doubly ionized ion in the high-temperature region.

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