STUDY OF STRUCTURAL AND DIELECTRIC PROPERTIES OF PZT CERAMICS MODIFIED BY SM ION SUBSTITUTION

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Abstract

The Effect of Sm substitution on the structural and dielectric properties of $Pb_{1-x}Sm_x(Zr_{0.4}Ti_{0.6})_{1-x/4}\ O_3$ (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 XRD studies which were found to be in tetragonal phase at room temperature 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. When the temperature of PSZT samples is increased above transition temperature, dielectric constant begins to decrease obeying Curie – Weiss law. The Conduction process was found to be mixed type. The variation of dielectric constant and tangent loss with temperature at selected frequencies exhibit their phase transition above room temperature.

Keywords: *Ferro electricity, Perovskite, Diffraction, Transducer, Doping.*

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1. INTRODUCTION

There has been considerable interest in the solid solutions of lead zirconate–titanate, due to its possible forefront applications in the areas of research as well as in industrial applications [1- 3]. 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 A considerable amount of works have been done on modified PZT ceramics prepared from high-temperature solid-state reaction technique. Now days, with suitable modification in the compound, it is widely used for actuators, pyroelectric detectors, transducers, electro – optic, ferroelectric random access memory, sensors, etc. The physical properties and device parameters of PZT – based compounds are greatly influenced by chemical substitutions, synthesis process, and some other factors. It is well observed that the La-modified PZT has tremendous applications in electronics and electro-optics [4]. 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 40/60 [5-7]. In view of the above, we have studied the effect of samarium substitution on structural, dielectric, properties ceramics, which is reported here.

2. Experimental Details

The samples of PSZT i.e. $Pb_{1-x}Sm_x(Zr_{0.4}Ti_{0.6})_{1-x/4}O_3$ (where x = 0.00, 0.04, 0.08, and 0.12) were prepared by a high- temperature solid-state reaction technique. In an alumina crucible, the homogeneous mixed ingredients were calcined at an optimized temperature of 1100◦C for 10 hours. Using hydraulic press, the calcined powders, with small amount of polyvinyl alcohol as binder, were converted into pellets at a pressure of 4×10^6 N/m^2. These pellets were sintered in an alumina crucible at an optimized temperature of 1200◦C for 10 hours aiming to get nearly 97% of theoretical density. The X-ray diffraction (XRD) data on 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. The dielectric data of the materials were obtained on silver electroded samples using phase sensitive multimeter in a wide range of frequency (10^2–10^6 Hz) and temperature (room temperature - 500◦C) at a potential difference of 1V with the stabilized temperature at an interval of 2.5◦C.

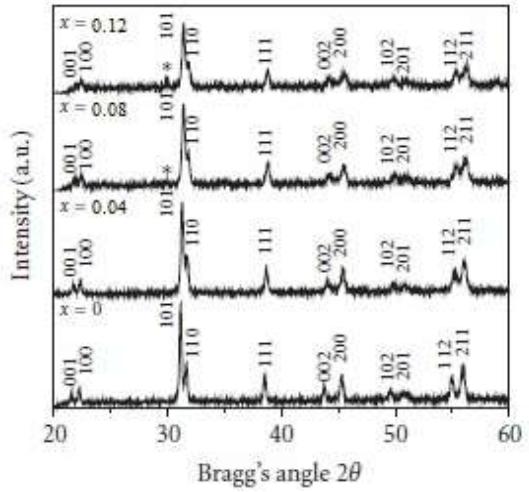


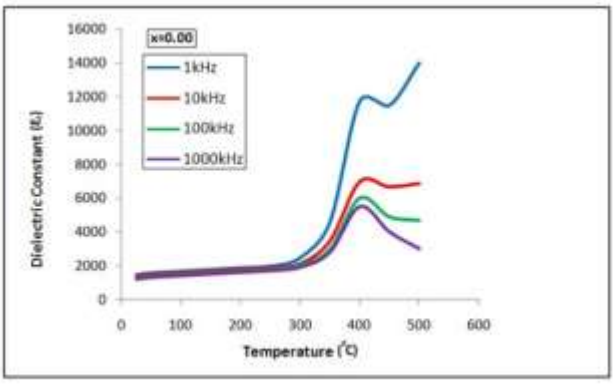
Figure 1: The comparison of XRD patterns of $Pb_{1-x}Sm_x(Zr_{0.4}Ti_{0.6})_{1-x/4}O_3$ (for x = 0.00, 0.04, 0.08, and 0.12).

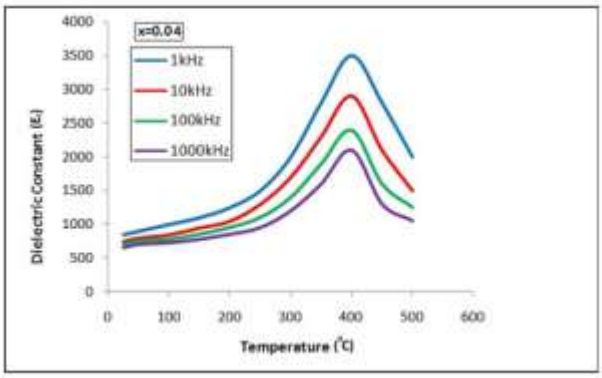
3. Results and Discussion

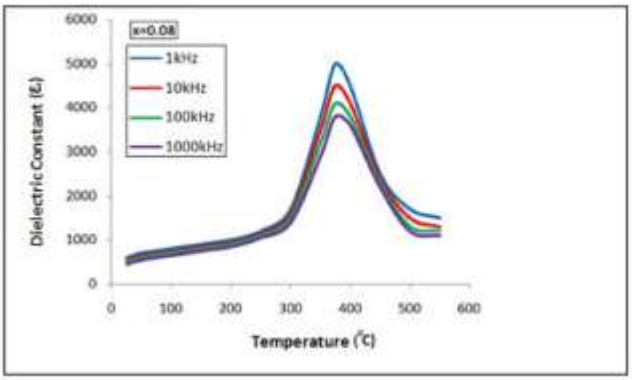
3.1 Structural Analysis - The nature of XRD patterns of $Pb_{1-x}Sm_x(Zr_{0.4}Ti_{0.6})_{1-x/4}O_3$ (PSZT) with x = 0.00, 0.04, 0.08, and 0.12 (Figure 1) confirms the formation of single phase with tetragonal crystal structure [8]. Using computer software POWDMULT all the reflection peaks were indexed in tetragonal crystal system. 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. In the XRD patterns, there is an additional peak (for $x \geq 0.08$) usually referred as secondary or pyrochlore phase [9, 10]. Though these peaks are undesirable, it is some time essential for formation of the perovskites [11]. The percentage of pyrochlore phase in PSZT for x = 0.08 and 0.12 was estimated as 6% and 8.5%, respectively.

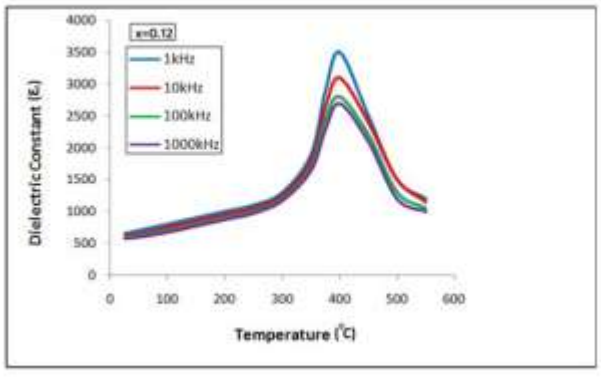
3.2 Dielectric Study - The variation of relative dielectric constant (ε_r) of PSZT having Sm contents x = 0.00, 0.04, 0.08, and 0.12 with temperature at selected frequencies (10^3– 10^6 Hz) is shown in Figure 2 below. It is found that ε_r decreases on increasing frequency which indicates a normal behavior of the 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 first increases slowly and then rapidly up to a maximum value. Temperature of the material corresponding to ε_{max} is called Curie or critical temperature (T_c). As at this T_c, phase transition takes place between ferroelectric-pyroelectric phases so it is also called transition temperature. At the higher temperature ($\geq T_c$), the space charge polarization originates due to mobility of ions and imperfections in materials and thus contributes to a sharp increase in ε_r [12]. The value of ε_{max} is found to be highest for PZT. As Sm content in PSZT increases, the value of εmax exhibits a sharp decrease for x = 0.04, then an increase for x = 0.08, and again decrease for x = 0.12. The value of T_c is found to be highest for PZT which decreases gradually on increasing Sm content in PSZT. However, for each PSZT samples Tc is found to be unaffected with the change in frequency supporting the nonrelaxor behavior of Sm-modified PZT. The values of ε_{max} and T_c of PSZT are compared in Table 1.

The frequency-temperature dependence of tangent loss (tan δ) of PSZT is shown in Figure 2. With the increase in temperature, tan δ is found to be very low and almost remains constant up to T_c beyond which it indicates a significant increase. The nature of variation of tan δ at higher frequency and temperature can be explained by space-charge polarization. This tan δ decreases with the increase in frequency as expected [13 - 15].









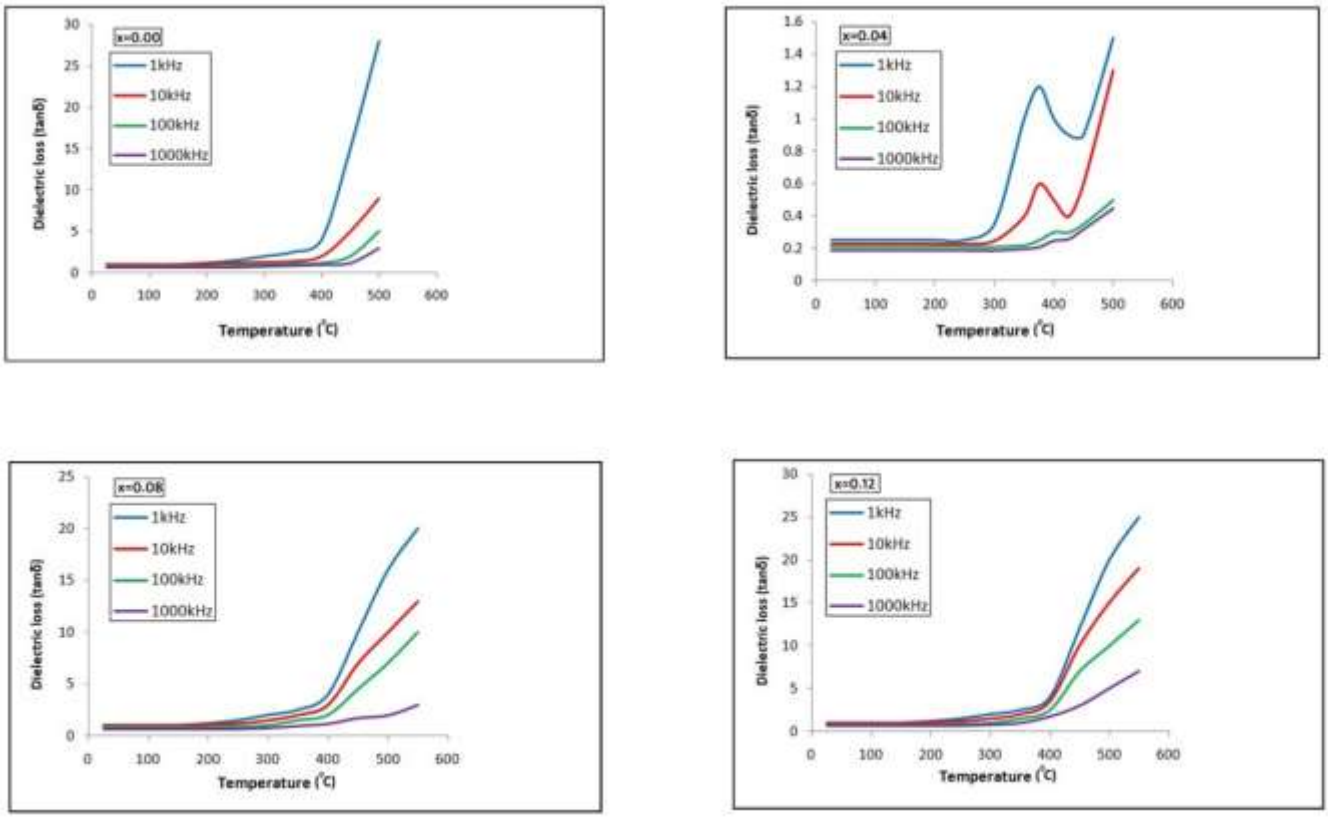


Figure 2: Temperature-frequency dependence of relative dielectric constant (ε_r) and tangent loss (tan δ) $Pb_{1-x}Sm_x(Zr_{0.4}Ti_{0.6})_{1-x/4}O_3$ for x = 0.00, 0.04, 0.08, and 0.12

Table 1: Comparison of the lattice parameters, ε_{max} and T_c of $Pb_{1-x}Sm_x(Zr_{0.4}Ti_{0.6})_{1-x/4}O_3$ 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	4.0042(21)	3.9966(50)	3.9725(50)	3.9785(50)
c	4.1348(21)	4.1146(50)	4.0844(50)	4.1081(50)
c/a	1.0326(21)	1.02952(50)	1.02816(50)	1.0325(50)
ε_{max}	11850	3501	5155	3610
T (C)	404 $\pm$ 0.25	383 $\pm$ 0.25	371 $\pm$ 0.25	364 $\pm$ 0.25

4. CONCLUSIONS

Structural analysis using room temperature X - ray diffraction data obtained from the calcined powders of polycrystalline samples of Sm-modified PZT (i.e., $Pb_{1-x}Sm_x(Zr_{0.4}Ti_{0.6})_{1-x/4}O_3$) has confirmed their tetragonal phase with the presence of a small amount of pyrochlore phase during higher concentration of Sm (6% for x = 0.08 and 8.5% for 0.12). 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 electrical conductivity (ac) of PSZT may not only due to singly ionized in low temperature (ferroelectric phase) region but also due to doubly ionized in the high-temperature region.

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