Hindawi Publishing Corporation
Research Letters in Physics
Volume 2009, Article ID 382578, 4 pages
doi:10.1155/2009/382578

Research Letter

Effect of Sm Substitution on Structural, Dielectric, and Transport Properties of PZT Ceramics

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Received 24 November 2008; Accepted 1 January 2009

Recommended by Lian Gao

The polycrystalline samples of $Pb_{1-x}Sm_x\,(Zr_{0.45}Ti_{0.55})_{1-x/4}O_3$ (PSZT) (where x = 0.00, 0.03, 0.06, and 0.09) were prepared by a high-temperature solid-state reaction technique. Preliminary X-ray structural analysis of the materials at room temperature has confirmed their formation in single-phase with tetragonal crystal structure. The temperature dependence of dielectric response of the samples at selected frequencies has exhibited their phase transition well above the room temperature. The variation of ac conductivity with temperature and the value of activation energy reveal that their conduction process is of mixed type (i.e., singly ionized in ferroelectric region and doubly ionized in paraelectric phase).

1. Introduction

Lead zirconate titanate (PZT) is a well-known ferroelectric material with a perovskite ABO_3 structure (A = mono or divalent and B = tri-hexavalent ions) [1–3]. It is widely used for many applications such as actuators, transducers, and pyroelectric detectors. It is a solid-state solution of ferroelectric $PbTiO_3$ and antiferroelectric $PbZrO_3$ exhibiting two ferroelectric phases: a tetragonal phase in titanium rich and a rhombohedra phase in zirconium-rich compositions [4, 5]. The separation line between these two phases is called morphotropic phase boundary (MPB) where the electrical properties of the materials rise to a great extent [6]. However above and below MPB, it has many interesting properties useful for devices.

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 [7, 8].

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 45/55 [9–13]. In view of the above, we have studied the effect of samarium substitution on structural, dielectric, and ac conductivity properties of PZT (Zr/Ti: 45/55) ceramics, which is reported here.

2. Experimental Details

The polycrystalline samples of Sm-modified PZT (i.e., PSZT) $Pb_{1-x}Sm_x\,(Zr_{0.45}Ti_{0.55})_{1-x/4}O_3$ (where x = 0.00, 0.03, 0.06, and 0.09) were prepared by a high-temperature solid-state reaction technique using high-purity (99.9%) oxides (i.e., PbO, ZrO_2, TiO_2, and Sm_2O_3) in a suitable stoichiometry with 3% more PbO (to compensate lead loss at high temperatures). The homogeneous mixed ingredients were calcined at an optimized temperature and time (1100°C, 10 hours) in an alumina crucible. The calcined powders, with small amount of polyvinyl alcohol (PVA) as binder, were converted into pellets at a pressure of 4×10^6 N/m^2 using hydraulic press. These pellets were sintered in an alumina crucible at an optimized temperature and time (1200°C, 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 Å in a wide range of Bragg's

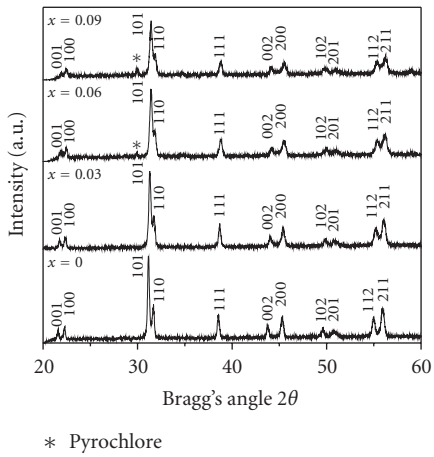

Figure 1: The comparison of XRD patterns of $Pb_{1-x}Sm_x(Zr_{0.45}Ti_{0.55})_{1-x/4}O_3$ for $x = 0.00$, 0.03, 0.06, and 0.09.

angles 2θ ($20^\circ \leq 2\theta \leq 80^\circ$) at a scanning rate of 3°/minute. The dielectric data of the materials were obtained on silver-electroded samples using phase sensitive multimeter (PSM; Model 1735) in a wide range of frequency (10^2–10^6 Hz) and temperature (room temperature -500°C) at a potential difference of 1 V with the stabilized temperature at an interval of 2.5°C.

3. Results and Discussion

3.1. Structural Analysis. The nature of room temperature XRD patterns of $Pb_{1-x}Sm_x(Zr_{0.45}Ti_{0.55})_{1-x/4}O_3$ (PSZT) with $x = 0.00$, 0.03, 0.06, and 0.09 (Figure 1) as compared to the reported ones [14, 15] confirms the formation of single phase with tetragonal crystal structure. All the reflection peaks were indexed in tetragonal crystal system using computer software POWDMULT [16]. On the basis of best agreement between the observed (obs) and the calculated (cal) d-spacing (i.e., $\sum \Delta d = d_{\text{obs}} - d_{\text{cal}} =$ 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 $x \geq 0.06$) usually referred as secondary or pyrochlore phase [17, 18]. Though these peaks are undesirable, it is some time essential for formation of the perovskites [19]. The percentage of pyrochlore phase in PSZT for $x = 0.06$ and 0.09 was estimated [20] as 3% and 7%, respectively.

3.2. Dielectric Study. The variation of relative dielectric constant (ε_r) of PSZT (having Sm contents $x = 0.00$, 0.03, 0.06, and 0.09) with temperature at selected frequencies (10^3–10^6 Hz) is shown in Figure 2. It is found 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 first increases slowly and then rapidly up to a maximum value ($\varepsilon_{\max}$). Temperature of the material corresponding to $\varepsilon_{\max}$ is called Curie or critical temperature (T_c). As at this T_c, phase transition takes place between ferroelectric-paraelectric 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 [21, 22]. The value of $\varepsilon_{\max}$ is found to be highest for PZT. As Sm content in PSZT increases, the value of $\varepsilon_{\max}$ exhibits a sharp decrease for $x = 0.03$, then an increase for $x = 0.06$, and again decrease for $x = 0.09$. 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 T_c is found to be unaffected with the change in frequency supporting the nonrelaxor behavior of Sm-modified PZT [23]. The values of $\varepsilon_{\max}$ and T_c of PSZT are compared in Table 1.

The frequency-temperature dependence of tangent loss ($\tan\delta$) of PSZT is shown in Figure 2. With the increase in temperature, $\tan\delta$ 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 $\tan\delta$ at higher frequency and temperature can be explained by space-charge polarization [23]. This $\tan\delta$ decreases with the increase in frequency as expected [24].

3.3. ac Conductivity. The ac conductivity (σ_{ac}) of PSZT for $x = 0.00$, 0.03, 0.06, and 0.09 at frequency 10 kHz was calculated using dielectric relation

$$\sigma_{\text{ac}} = \omega\varepsilon_o\varepsilon_r \tan\delta, \tag{1}$$

where ω is the angular frequency and ε_o the permittivity of free space. Figure 3 shows an increasing trend of ac conductivity around T_c. 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. Above T_c, the conductivity data appears to fall on a straight line exhibiting a typical behavior of the dc component of the conductivity [23]. 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:

$$\sigma_{\text{ac}} = \sigma_o \exp\left(-\frac{E_a}{K_B T}\right), \tag{2}$$

where σ_o is the pre-exponential factor, K_B the Boltzmann constant and E_a the activation energy. The value of activation energy (E_a) of PSZT was found to be 0.93, 0.57, 1.45, and 0.79 for $x = 0.00$, 0.03, 0.06, and 0.09, respectively, in the high-temperature paraelectric phase which suggests its dependence on ionization level of oxygen vacancy [25–27].

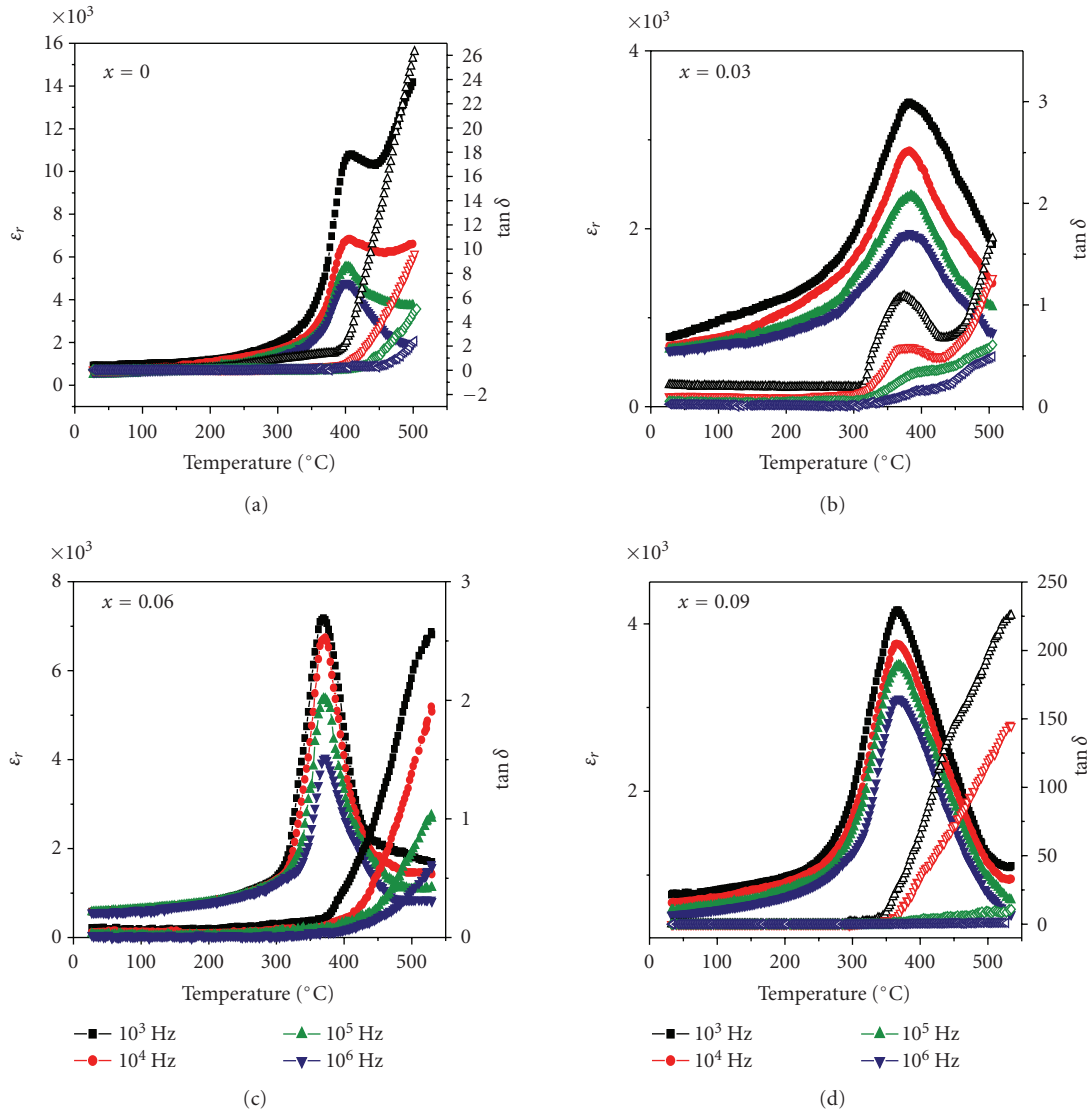

Figure 2: Temperature-frequency dependence of relative dielectric constant (ε_r) and tangent loss ($\tan\delta$) of $Pb_{1-x}Sm_x$ $(Zr_{0.45}Ti_{0.55})_{1-x/4}O_3$ for $x = 0.00$, 0.03, 0.06, and 0.09.

Table 1: Comparison of the lattice parameters, ε_{max} and T_c of $Pb_{1-x}Sm_x$ $(Zr_{0.45}Ti_{0.55})_{1-x/4}O_3$ for $x = 0.00$, 0.03, 0.06, and 0.09.

Parameters	Sm composition			
	$x = 0.00$	$x = 0.03$	$x = 0.06$	$x = 0.09$
a	4.0040(21)	3.9933(50)	3.9727(50)	3.9773(50)
c	4.1324(21)	4.1120(50)	4.0888(50)	4.1018(50)
c/a	1.0321(21)	1.0297(50)	1.0292(50)	1.0313(50)
ε_{max} (1 kHz)	10850	3420	7188	4163
T (°C)	405 ± 0.25	382 ± 0.25	370 ± 0.25	365 ± 0.25

4. Conclusions

Preliminary structural analysis using room temperature X-ray diffraction data obtained from the calcined powders of polycrystalline samples of Sm-modified PZT (i.e., $Pb_{1-x}Sm_x$ $(Zr_{0.45}Ti_{0.55})_{1-x/4}O_3$) has confirmed their tetragonal phase with the presence of a small amount of pyrochlore phase during higher concentration of Sm (3% for $x = 0.06$ and 7% for 0.09). Detailed study of dielectric properties of PSZT as a function of temperature at selected frequencies has exhibited that maximum or peak dielectric constant, tangent loss, and transition temperature are strongly dependent on

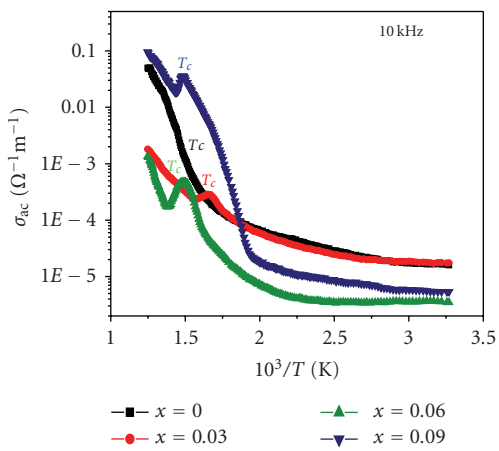

Figure 3: Temperature-Frequency dependence of ac conductivity of $Pb_{1-x}Sm_x$ $(Zr_{0.45}Ti_{0.55})_{1-x/4}O_3$ for $x = 0.00$, 0.03, 0.06, and 0.09 at 10 kHz.

Sm content in PSZT. 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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