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Structural, dielectric and electrical properties of Sm-modified $Pb(SnTi)O_3$ ferroelectric system

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Abstract. We have synthesized $(Pb_{1-x}Sm_x)(Sn_yTi_{1-y})_{1-x/4}O_3$ (PSmST) polycrystalline ferroelectric ceramics with $x = 0{\cdot}05$, $0{\cdot}07$, $0{\cdot}1$ and $y = 0{\cdot}45$ by a solid-state reaction technique and performed preliminary X-ray diffraction (XRD) analysis, detailed temperature and frequency dependence dielectric measurements on them. The a.c. conductivity has been investigated over a wide range of temperature and the activation energy ($E_{a.c.}$) has also been calculated. It is observed that (i) the dielectric permittivity (e) and loss tangent (tan d) are dependent on frequency, (ii) the temperature of dielectric permittivity maximum shifts toward lower temperature side with the increase of samarium ion (Sm^{+3}) concentration at the Pb sites, and (iii) observed and calculated d-values of XRD patterns show that the compounds have been formed in orthorhombic single phase.

Keywords. XRD; dielectric permittivity; loss tangent; a.c. conductivity.

1. Introduction

It is found that a wide variety of complex compounds/solid solutions based on $PbTiO_3$ (PT) can be prepared by single or multi-elemental substitutions/doping at the Pb or Ti sites for different industrial applications. Selection of dopants or substitutions to tailor some physical properties of PT is based on many factors including (a) charge neutrality, (b) tolerance factor, (c) ionic radius and (d) solubility/miscibility. Substitution of lanthanides and/or group ΠA at the Pb sites and zirconium at the Ti sites with different Zr/Ti ratio (i.e. PZT, PLZT) have provided many solid solutions with interesting properties for wide industrial applications. In view of this we have planned to study the effect of rare-earth on structural, ferroelectric and electrical properties of rare earth ions doped Pb(SnTi)O_3(PST). In this communication we would like to report structural, ferroelectric and electrical properties of PSmST with different Sm/Pb ratio (i.e. $(Pb_{1-x}Sm_x)(Sn_yTi_{1-y})_{1-x/4}O_3$).

2. Experimental

Polycrystalline samples of $(Pb_{1-x}Sm_x)(Sn_yTi_{1-y})_{1-x/4}O_3$ ($x = 0{\cdot}05$, $0{\cdot}07$, $0{\cdot}1$) were prepared by a high-temperature solid-state reaction technique using high purity oxides PbO, SnO_2, TiO_2 and Sm_2O_3. These anhydrous oxides were weighed accordingly to the required stoichiometric and mixed them thoroughly in wet atmosphere (ethanol) and dried and calcined at 1000°C for 5 h. The homogenous powders of PSmST were pressed into cylindrical pellets of diameter 9·8 mm and thickness 1·19 mm under an isostatic pressure of about 7×10^7 kg/m^2 using a hydraulic press. During sintering (1040°C), a compensating $PbZrO_3$ atmosphere was used. An X-ray diffractogram on calcined powder in a wide range of Bragg angles ($20° \le 2q \le 80°$) was recorded at room temperature using a Philips X-ray diffractometer with CuK_a radiation ($l = 1{\cdot}542$ Å) at a scanning rate of 2°/min.

The dielectric permittivity (e), loss tangent (tan d) and a.c. conductivity were obtained as a function of frequency (100 Hz to 2 MHz) at room temperature (31°C) and temperature (304 K to 623 K) at frequency (10 kHz) using a HIOKI 3235 LCR Hi-tester meter (Japan) with a laboratory-made sample holder.

3. Results and discussion

Figure 1 shows the room temperature X-ray diffraction (XRD) patterns of calcined powder of each member of the PSmST family ($x = 0{\cdot}05$, $0{\cdot}07$, $0{\cdot}1$ and $y = 0{\cdot}45$). The refined cell parameters for the different compositions of PSmST are compared in table 1. The frequency dependence of dielectric permittivity (e) and loss tangent (tan d) of all the Sm-doped $Pb(SnTi)O_3$ compounds at room temperature are shown in figures 2 and 3, respectively. It has been found that with increase of frequency, the dielectric permittivity decreases, and hence show a typical characteristics of a normal dielectrics. Figure 4 shows the temperature variation of dielectric permittivity of all the Sm doped PSmST samples. It is clear from table 2 that the materials have undergone a phase transition from ferroelectric to paraelectric at 592 K, 574 K and 565 K for Sm content from $x = 0{\cdot}05$, $0{\cdot}07$, $0{\cdot}1$, respectively. It is

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Table 1. Cell parameters (Å) and crystalline structure of $(Pb_{1-x}Sm_x)(Sn_{0.45}Ti_{0.55})_{1-x/4}O_3$.

x	*a*	*b*	*c*	Volume	Structure
0·05	8·5197(40)	9·2358(40)	10·9022(40)	857·86	Orthorhombic
0·07	8·5380(20)	9·2464(20)	10·9153(20)	861·72	Orthorhombic
0·1	8·5228(20)	9·2365(20)	10·8740(20)	8556·01	Orthorhombic

Table 2. Dielectric and electric parameters for $(Pb_{1-x}Sm_x)(Sn_{0.45}Ti_{0.55})_{1-x/4}O_3$ (PSmST).

Parameters	$x = 0{\cdot}05$	$x = 0{\cdot}07$	$x = 0{\cdot}1$
Density (D) (g/cm^3)	6·699	6·651	6·645
e_{max} at T_c (10 kHz)	2600	2058	1905
tan d at T_c (10 kHz)	0·096	0·075	0·054
T_c (K)	592	574	565
$E_{a.c.}$ (eV)	0·73	0·59	0·54

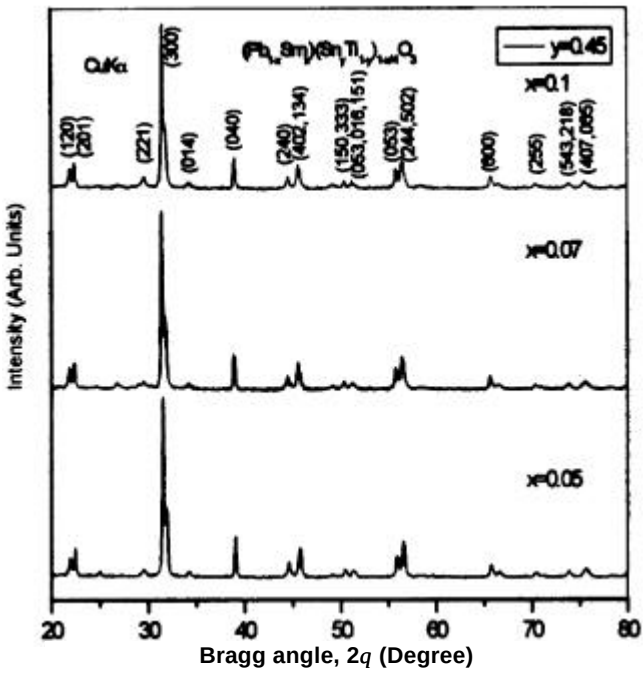

Figure 1. Comparison of XRD patterns of the compounds at room temperature.

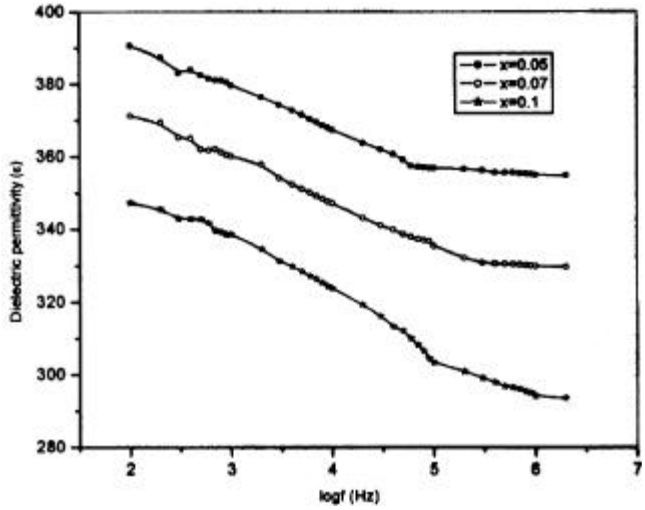

Figure 2. The frequency variations of dielectric permittivity (e) at room temperature (31°C).

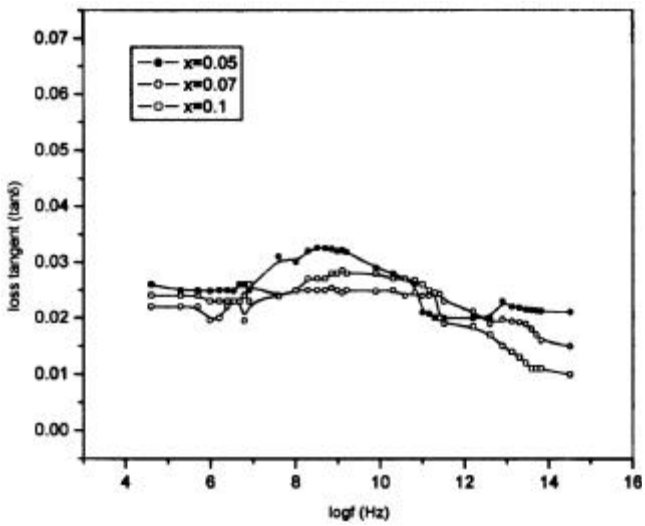

Figure 3. The frequency variations of loss tangent (tan d) at room temperature (31°C).

found that for higher Sm contents the permittivity peak gets broadened and hence diffuse phase transition (DPT) occurs in PST. Figure 5 shows that loss tangent (tan d) is varying slowly with temperature with very low value between 304 K and 500 K for all doped samples, beyond 500 K this parameter loss tangent (tan d) increases very fast with increasing temperature and hence reaches its maximum value. The activation energy, $E_{a.c.}$ in the high temperature phase (paraelectric region), for all the doped compounds has been calculated from the slope of ln $s_{a.c.}$ vs (10^3/T) plot (figure 6) using the conductivity relation

$$s = s_o e^{(-E_{a.c.}/K_B T)},$$

where K_B is Boltzmann constant.

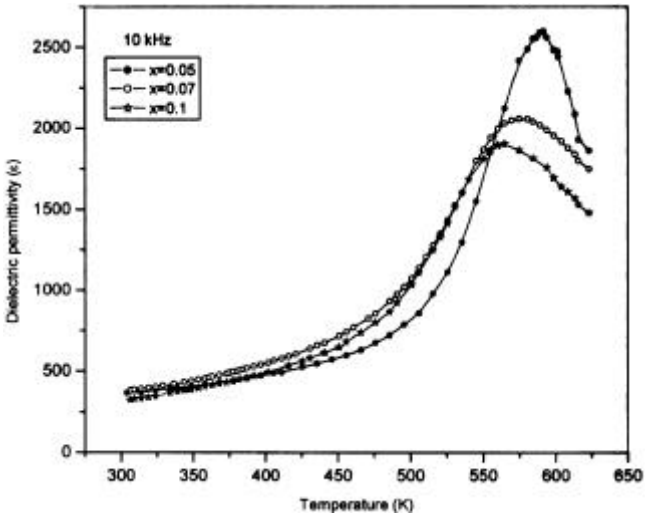

Figure 4. Temperature variation of dielectric permittivity (*e*) of the compounds at 10 kHz.

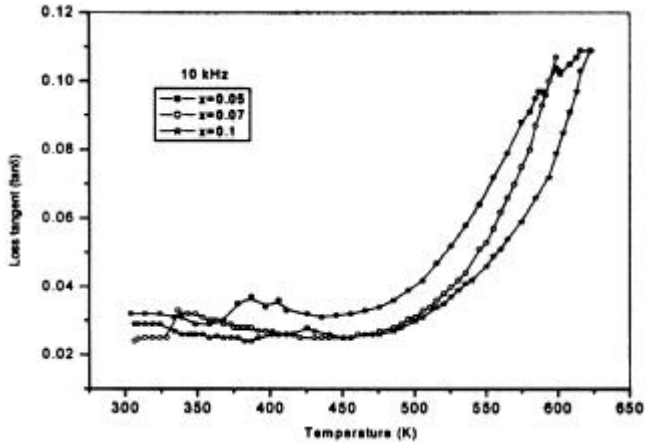

Figure 5. Temperature variation of loss tangent (tan *d*) of the compounds at 10 kHz.

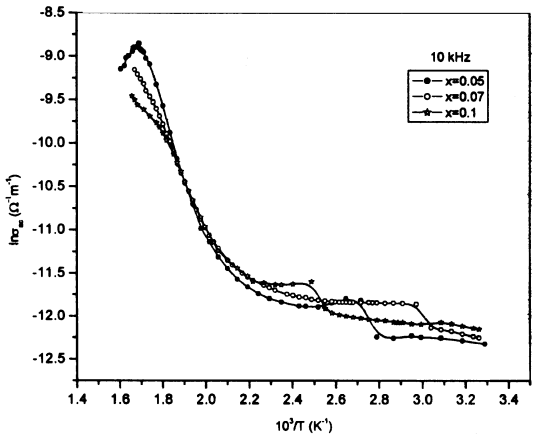

Figure 6. Temperature dependence of a.c. conductivity of the compounds at 10 kHz.

4. Conclusions

The temperature of the dielectric permittivity maximum have been shifted toward lower temperature side and the permittivity maximum decreased with the increase of Sm concentration in the PSmST compounds. Preliminary analysis of XRD patterns shows that compounds have orthorhombic structure.