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Structural, dielectric and electrical properties of Ca modified $BaSn_{0.15}Ti_{0.85}O_3$ Ceramics

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Polycrystalline samples of $(Ba_{1-x}Ca_x)(Sn_{0.15}Ti_{0.85})O_3$ ($x = 0$, 0.03, 0.06 and 0.09) of perovskite structural family have been prepared by a high-temperature solid-state reaction technique. Preliminary room temperature X-ray study confirmed the formation of single-phase compound with tetragonal structure. The Scanning electron microscope shows the uniform distribution of the grains throughout the surface of the samples. Dielectric studies as a function of frequency at different temperature suggests that the compounds undergo diffuse phase transition (DPT). The d.c. and a.c. conductivities have been investigated over a wide range of temperature and the activation energy was calculated. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Since the discovery of ferroelectricity in $BaTiO_3$ [1] having high relative permittivity and transition temperature much above room temperature, a large number of simple and complex oxides with perovskite structure having a general formula ABO_3 (A = mono or divalent, B = tri-hexavalent ions), have been been examined for search of ferroelectric properties which has wide range of applications. The selection of dopants or substitutions at different atomic sites is based on many factors including (a) charge neutrality (b) tolerance factor $t = (r_A + r_o)/\sqrt{2}(r_B + r_o)$ where r_A and r_B are the radius of the A and B site ions and r_o is the ionic radius of oxygen (c) ionic radius (d) solubility/miscibility. Ceramics based on Barium titanate ($BaTiO_3$) are frequently used to manufacture multiplayer capacitors [2]. Though a lot of works on different substitutions on $BaTiO_3$ have been done in the past, no work has been reported on effect of any cation on the ferroelectric properties of $BaSn_{0.15}Ti_{0.85}O_3$ ceramics. It has already been reported earlier that on substitution of different concentration of Sn at the A-site of $BaTiO_3$, the dielectric constant was maximum when $x = 0.15$ [3]. The distribution of cations at different sites has a dramatic effect on the physical properties of the parent compound. In view of this we have synthesized and studied various properties of a group of new compounds having a general formula $Ba_{1-x}Ca_xSn_{0.15}Ti_{0.85}O_3$ where $x = 0$, 0.03, 0.06 and 0.09. Here we report the preliminary structural and detailed dielectric and electrical properties of the compounds.

2. Experimental procedure

Polycrystalline samples of $Ba_{1-x}Ca_xSn_{0.15}Ti_{0.85}O_3$ ($x = 0$, 0.03, 0.06 and 0.09) were prepared by a high-temperature solid- state reaction technique using high purity oxides and carbonates: $BaCO_3$ (99% M/s Glaxo Laboratories, India), $CaCO_3$ (98.5% M/s Loba Chemical India), SnO_2 (99% M/s Loba Chemical India) and TiO_2 (99.9% M/s s.d.fine Chemical, India). These anhydrous oxides and carbonates were weighed accordingly to the required stoichometric and mixed in wet atmosphere (methanol) in an agate mortar for 2 h, and then dried by slow evaporation. The air-dried powder of the compounds was calcined at 1250°C for 12 h. The process of mixing and calcinations was repeated until homogeneous fine powder of the compounds was obtained. The calcined powder was used to make cylindrical pellets of diameter 10 mm and thickness 1–2 mm using a hydraulic press at a pressure of 6×10^7 N/m^2. Polyvinyl alcohol (PVA) was used as a binder to reduce the brittleness of the pellets. The pellets were sintered at 1275°C for 15 h in an air atmosphere. The formation of single-phase compound was checked by an X-ray diffraction (XRD) technique using an X-ray powder diffractometer with CuK_α radiation ($\lambda = 1.542$ Å) in a wide range of Bragg angles 2θ ($20^\circ \leq 2\theta \leq 100^\circ$) at the scanning rate of 2°/min. To study surface morphology and grain distribution on the flat surfaces of the sintered pellet, scanning electron micrographs of the sample were taken with JEOL JSM −580 scanning electron microscope (SEM). In order to study the electrical properties, both the flat surfaces of the samples were polished and electroded with highly pure silver paint. All the silver painted/electroded samples were dried at 180°C for 4 h to remove the moisture, if any. Measurements of dielectric constant (ε) and tangent loss (tan δ) were carried out a function of frequency at different temperature with the help of a HIOKI 3532 LCR HITESTER. The d.c. resistivity was obtained as a function of tem-

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perature at a constant electric field of 10 V with the help of Keithley (model 617) programmable electrometer.

3. Results and discussion

The XRD patterns of the samples have been compared in Fig. 1. The room temperature XRD peaks were found to be sharp and single indicating good homogeneity and formation of single-phase compound. All the reflection peaks were indexed and the lattice parameters were determined in various crystal systems and unit cell configuration using a computer program package "powdmult" [4]. On the basis of the best agreement between d_{obs} and d_{cal} (Table II), a suitable unit cell of the compounds was selected in the tetragonal system. The refined unit cells parameter is given in Table I. The change in intensity of the reflection peaks was observed, this may be due to the variation of the crystallite size or due to the change in concentration. The crystallite size of the compounds was calculated from the broadening of the strong and medium reflection peaks scattered in wide 2θ range using Scherrer's equation, $P = 0.89\lambda/\beta_{1/2}\cos\theta$ [5] where $\beta_{1/2}$ = half peak width. As the powder sample was used in recording XRD patterns, the peak broadening due to the mechanical strain, instrumental error, beam divergence etc have been ignored in the calculation of the crystallite size. With this limited number of reflections it was not possible to determine the space group of the compounds with the limited number of reflections.

Fig. 2 shows SEM micrographs of the sintered pellets. The grains are uniformly distributed throughout the surface which suggests the compactness and homogeneity of the samples.

TABLE I Comparison of cell parameters (a and c in Å), volume V (in Å) and crystallite size P (in Å) of $Ba_{1-x}Ca_xSn_{0.15}Ti_{0.85}O_3$ (x = 0, 0.03, 0.06 and 0.09) compounds

x	a	c	V	P
0	4.0049 [03]	4.0308 [03]	64.65	314
0.03	4.0053 [01]	4.0215[01]	64.52	322
0.06	4.0054[01]	3.9915[01]	64.06	328
0.09	4.0057[01]	3.9921[01]	64.04	332

TABLE II Comparison of d_{obs} [o] and d_{cal}[c] (in Å) of $Ba_{1-x}Ca_xSn_{0.15}Ti_{0.85}O_3$ (x = 0, 0.03,0.06 and0.09) compounds (x = 0, 0.03, 0.06 and 0.09) with the relative intensity in parenthesis

hkl	$x = 0$	$x = 0.03$	$x = 0.06$	$x = 0.09$
001	4.0042[o]	4.0042[o]	4.0042[o]	4.04042[o]
	(16)	(20)	(17)	(18)
	4.0049[c]	4.0053[c]	3.9915[c]	4.0053[c]
110	2.8356[o]	2.8313[o]	2.8259[o]	2.8313[o]
	(100)	(100)	(100)	(100)
	2.8319[c]	2.8322[c]	2.8273[c]	2.8322[c]
111	2.3151[o]	2.3151[o]	2.3094[o]	2.3151[o]
	(25)	(31)	(30)	(32)
	2.3172[c]	2.3156[c]	2.3098[c]	2.3156[c]
200	2.0081[o]	2.0060[o]	1.9956[o]	2.0060[o]
	(20)	(25)	(24)	(26)
	2.0024[c]	2.0026[c]	1.9958[c]	2.0026[c]
201	1.7956[o]	1.7923[o]	1.7890[o]	1.7923[o]
	(06)	(07)	(06)	(05)
	1.7933[c]	1.7927[c]	1.7900[c]	1.7927[c]
211	1.6407[o]	1.6354[o]	1.6327[o]	1.6354[o]
	(25)	(26)	(27)	(24)
	1.6420[c]	1.6563[c]	1.6314[c]	1.6363[c]
202	1.4212[o]	1.4162[o]	1.4135[o]	1.4192[o]
	(11)	(13)	(12)	(14)
	1.4205[c]	1.4190[c]	1.4137[c]	1.4190[c]
301	1.2707[o]	1.2663[o]	1.2663[o]	1.2663[o]
	(06)	(05)	(04)	(07)
	1.2738[c]	1.2666[c]	1.2662[c]	1.2666[c]

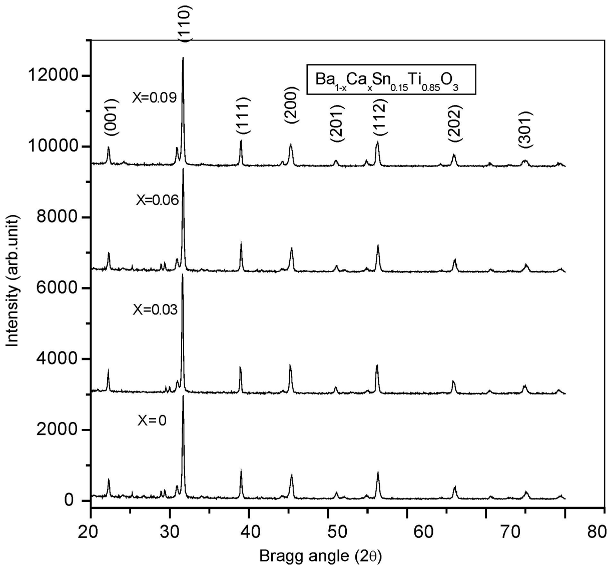

Figure 1 XRD patterns of $Ba_{1-x}Ca_xSn_{0.15}Ti_{0.85}O_3$ (x = 0, 0.03, 0.06 and 0.09) compounds.

Fig. 3 shows the variation of dielectric constant and tangent loss as a function of frequency (100 Hz-1 MHz) of all the compounds at room temperature. Both dielectric constant and tangent loss decreases sharply for low frequency but beyond 200 kHz they are almost frequency independent. The higher value of dielectric constant at lower frequency suggests the presence of all kinds of polarization (i.e. interfacial, atomic, ionic, dipolar, electronic, etc.) in this low range frequency. At higher frequencies (>10 kHz) the main contribution to the dielectric constant comes from the atomic and electronic polarization only [6].

Fig. 4 shows the variation of the dielectric constant of the compounds with temperature at different concentration of Ca. It follows a general trend of the ferroelectrics i.e. the dielectric constant increases with the rise in temperature upto its maximum value (ε_{max}) at the Curie temperature (T_c) where it undergoes a phase transition from ferroelectric to paraelectric phase. The transition temperature of the parent compound is well above room temperature but with the increase in doping concentration for $x = 0.03$ the transition temperature shifts to higher temperature and for further increase in concentration ($x = 0.06$ and 0.09) it shifts to below room temperature Table III. The shifting of transition temperature for $x = 0.03$ may be due to some structural disorder. Though the value of the dielectric constant is maximum when $x = 0.15$ but when Ca is substituted in the A-site the value of the dielectric constant

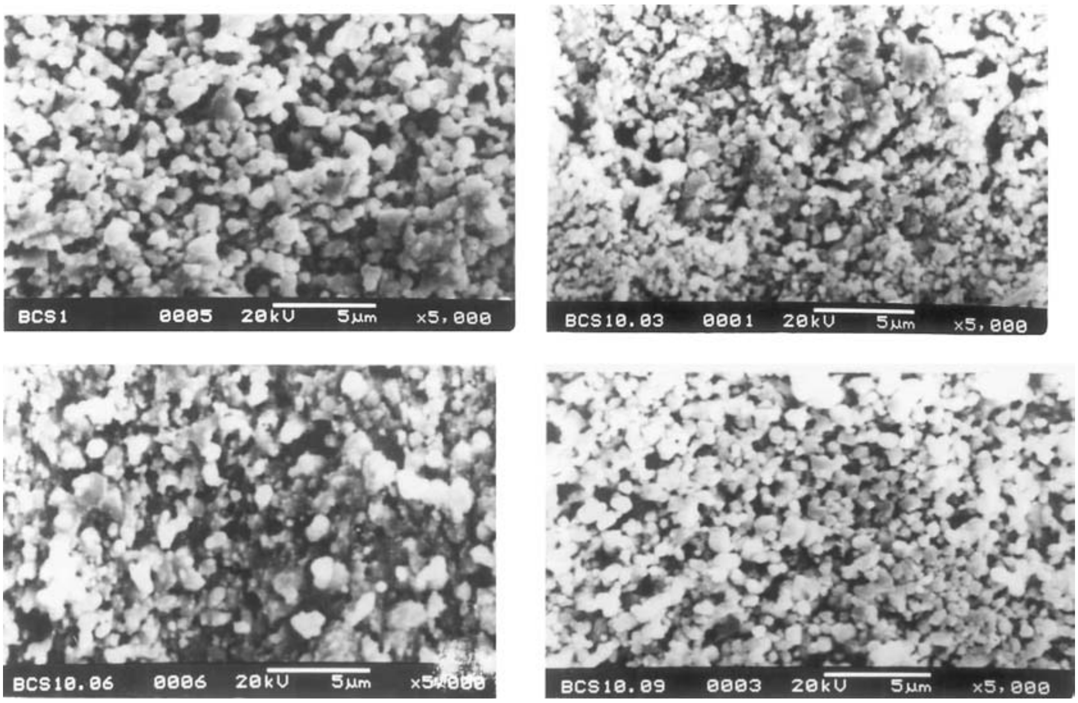

Figure 2 SEM photographs of $Ba_{1-x}Ca_xSn_{0.15}Ti_{0.85}O_3$ ($x = 0$, 0.03, 0.06 and 0.09) compounds.

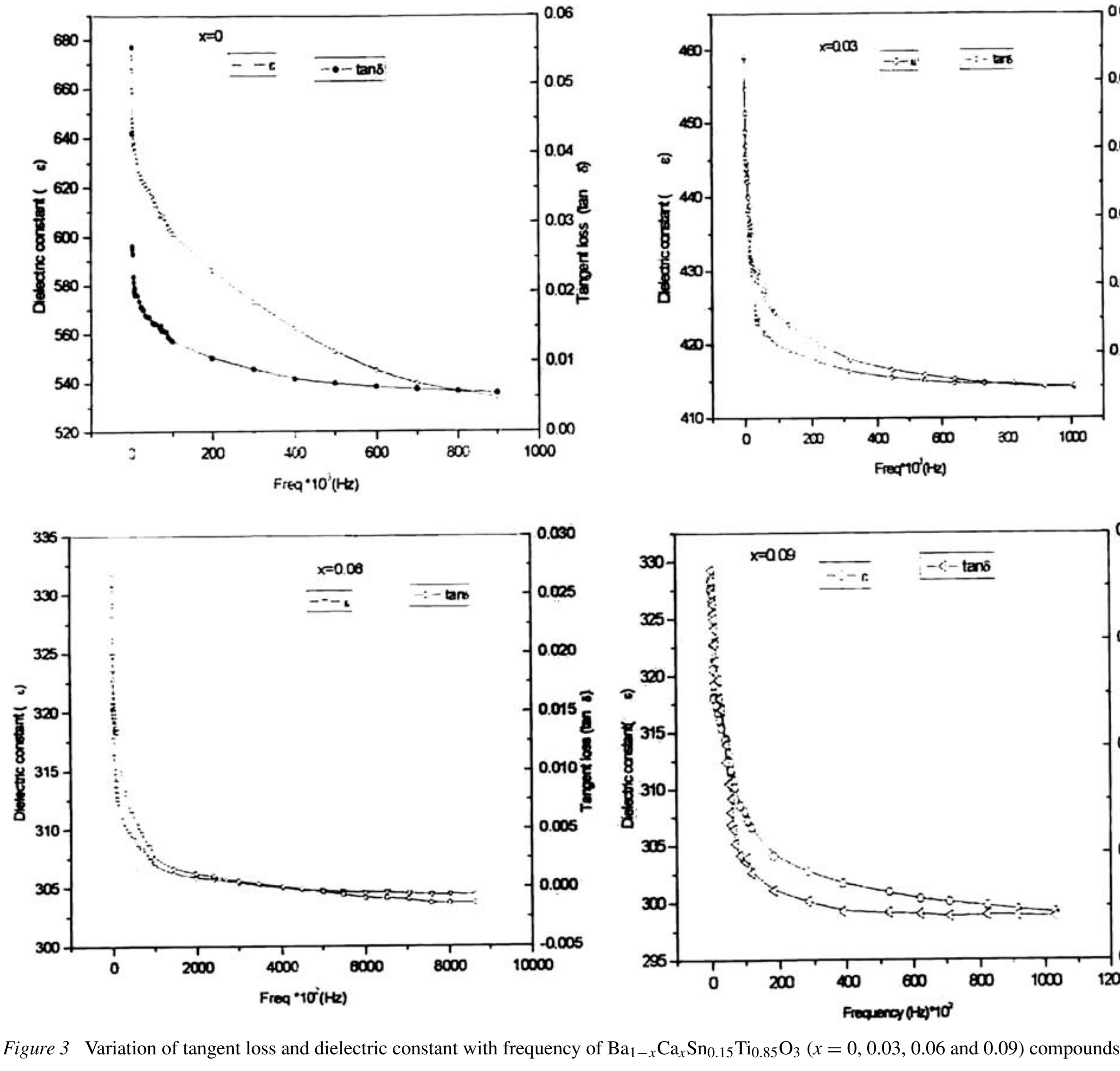

Figure 3 Variation of tangent loss and dielectric constant with frequency of $Ba_{1-x}Ca_xSn_{0.15}Ti_{0.85}O_3$ ($x = 0$, 0.03, 0.06 and 0.09) compounds.

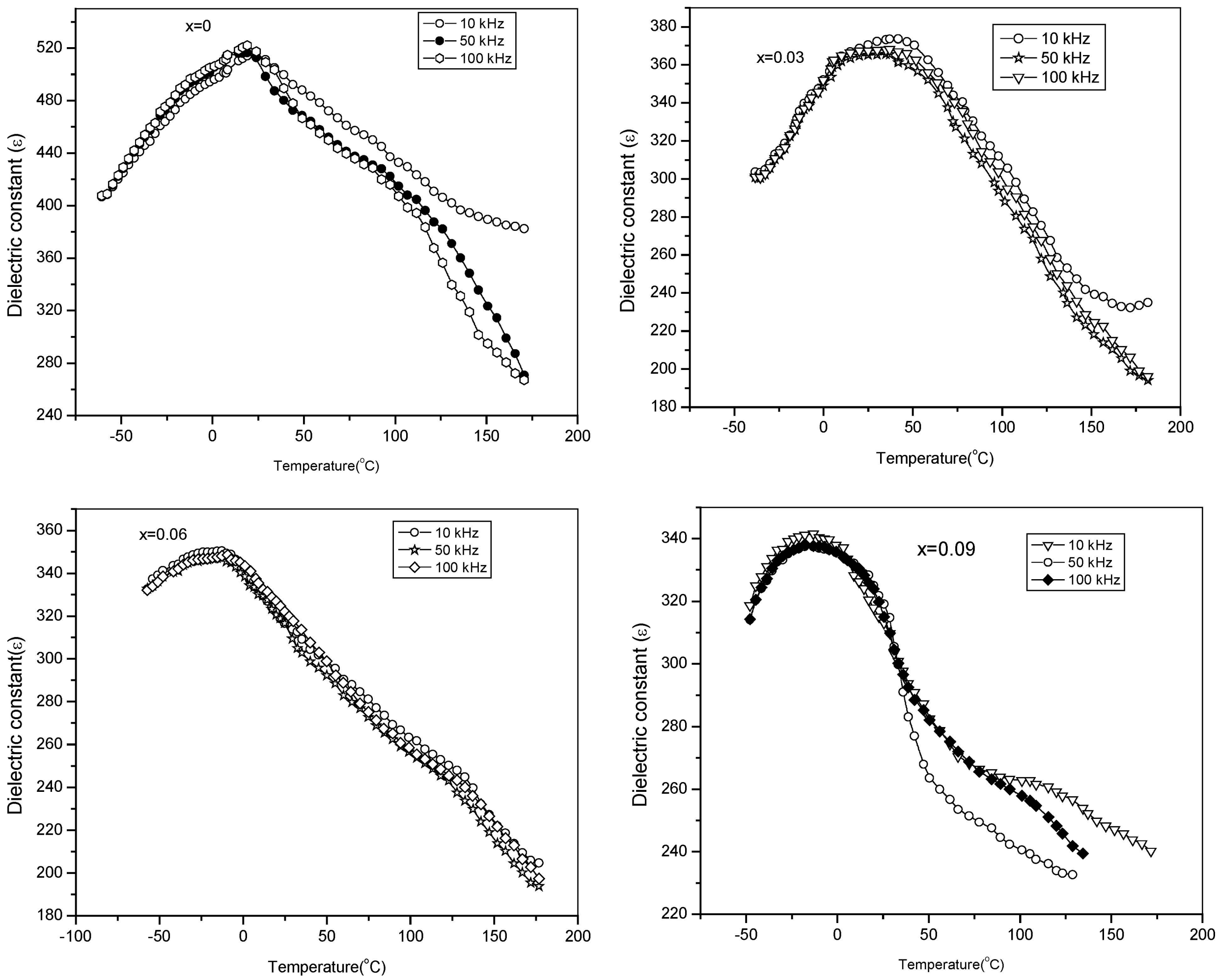

Figure 4 Variation of dielectric constant at three frequencies (10, 50 and 100 kHz) of $Ba_{1-x}Ca_xSn_{0.15}Ti_{0.85}O_3$ ($x = 0, 0.03, 0.06$ and 0.09) compounds.

decreases to a much smaller value. The value of the dielectric constant decreases with the increase in concentration Table III. This shows that doping has produced an effect on the parent compound. It is observed that the compounds have the maximum value of the dielectric constant at a particular temperature for all three frequencies (10, 50 and 100 kHz), hence they do not exhibit relaxor property. The dielectric peak was found to be broadened over a certain temperature interval which indicates the existence of diffuse phase transition (DPT) and the broadness increases with the increase in doping when 3% Ca was doped in the A-site and then decreased with the increase in Ca concentration. DPT occurs mainly due to the compositional fluctuation or substitutional disordering in the arrangement of cations in one or more crystallographic sites of the structure [7, 8]. This leads to the microscopic inhomogenity in the compound and causes a distribution of local Curie points. The degree of diffuseness of diffusivity (γ) is estimated by the empirical relation $\ln\,(1/\varepsilon - 1/\varepsilon_{\max}) = \gamma \ln (T - T_c) + C$ [9] where ε is the dielectric constant at temperature T, $\varepsilon_{\max}$ is the maximum value of ε at T_c and C is the proportionality constant. Fig. 6 shows the variation of $\ln\,(1/\varepsilon - 1/\varepsilon_{\max})$ wit $\ln\,(T{-}T_c)$. The value of γ was calculated from the slope of the graph and was found to be 1 (for normal fer-

TABLE III Comparison of some dielectric parameters of $Ba_{1-x}Ca_xSn_{0.15}Ti_{0.95}O_3$ ceramics ($x = 0, 0.03, 0.06$ and $x = 0.09$)

x	T_c	$\varepsilon_{\max}$ at 10 kHz	γ	E_a (a.c.)	E_a (d.c.)
0.0	19	514	0.99	0.063	0.114
0.03	37	373	1.53	0.067	0.095
0.06	−12	350	1.43	0.029	0.051
0.09	−13.5	341	1.5	0.024	0.096

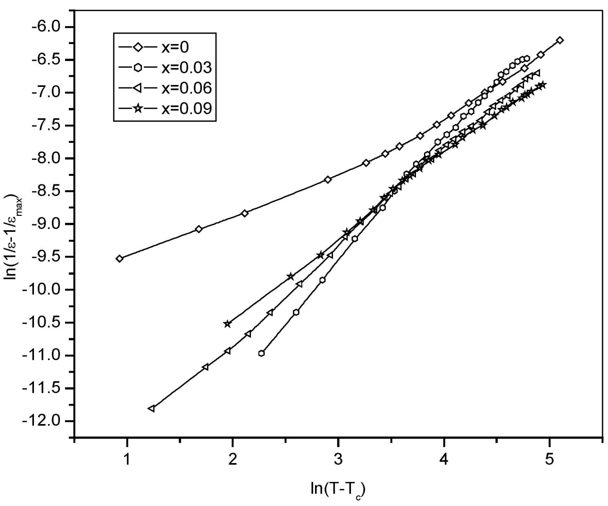

Figure 5 Variation of $\ln(1/\varepsilon - 1/\varepsilon_{\max})$ with $\ln(T - T_c)$.

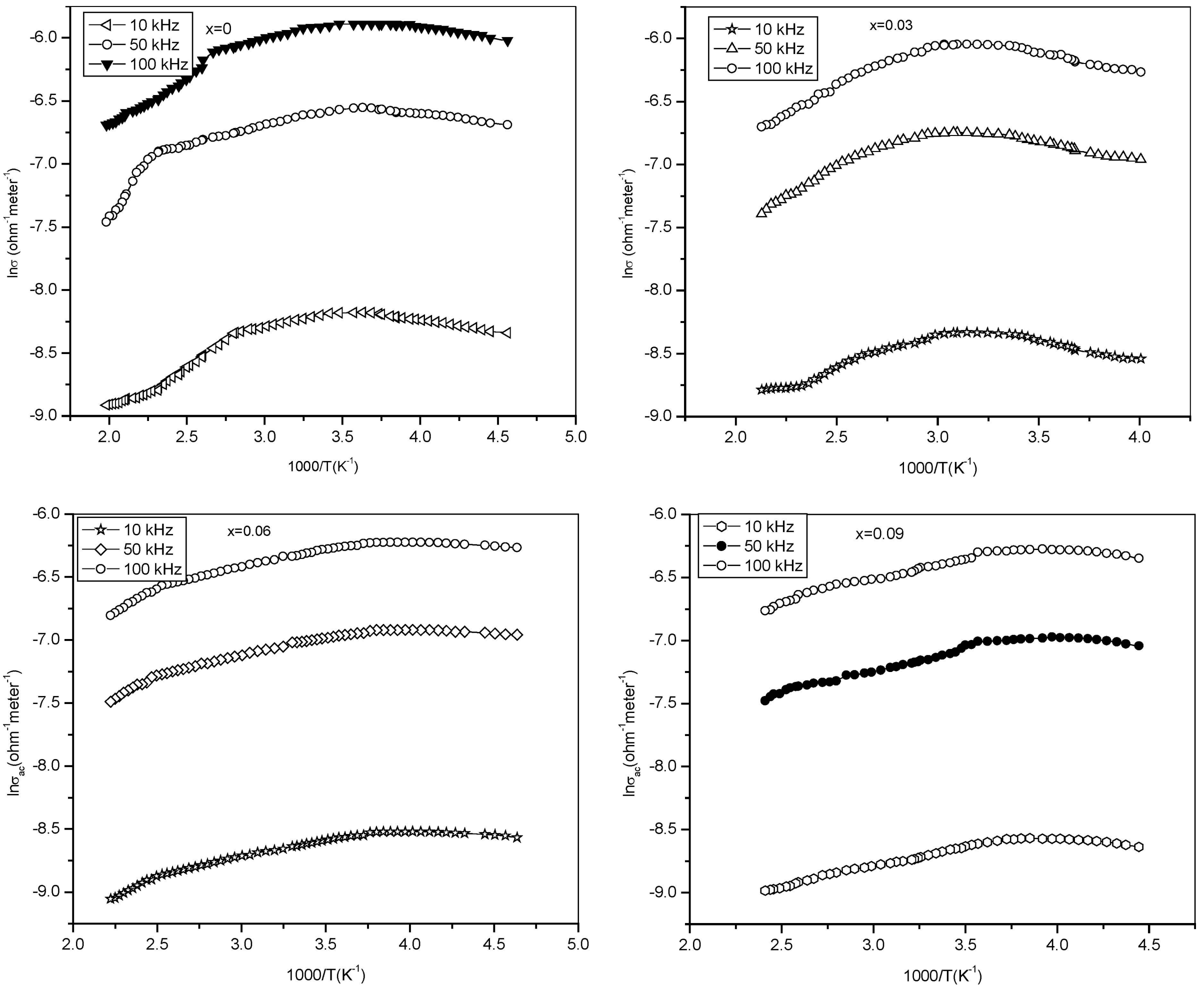

Figure 6. Variation of ln $\sigma_{\text{a.c.}}$ with the inverse of temperature at 10 kHz of $\text{Ba}_{1-x}\text{Ca}_x\text{Sn}_{0.15}\text{Ti}_{0.85}\text{O}_3$ ($x = 0$, 0.03, 0.06 and 0.09) compounds.

roelectrics) and 2 (completely disordered compounds) (Table III).

Fig. 5 shows the plot of a.c. conductivity with $10^3/T$ at three different frequencies (10, 50 and 100 kHz) for all the compounds. It shows a change in slope at the temperatures observed at dielectric anomaly (T_c) of the materials. The peaks in a.c. conductivity for all the frequencies is due to the high value of the dielectric constant (ε) at T_c and because the a.c. conductivity $\sigma_{\text{a.c.}} = \omega\omega_o \tan\delta$ strongly depends on dielectric constant (ε) as well as frequency of the applied electric field and $\tan\delta$. This type of anomaly is due to the difference in activation energy of the Para electric and ferroelectric region [10].

The activation energy $E_{\text{a.c.}}$ at 10 kHz in the Para electric region for all the compounds have been calculated from the slope of ln $\sigma_{\text{a.c.}}$ with $10^3/T$ using the conductivity relation $\sigma_{\text{a.c.}} = \sigma_o \exp(-E_{\text{a.c.}}/K_BT)$ where K_B is the Boltzmann constant. It is considered that the a.c. conductivity is contributed by hopping of localized and free charges. The values of the activation energy of the different compounds are given in Table III. The ionic conduction plays a major role at higher temperature for both a.c. and d.c. conductivity.

Fig. 6 shows the variation of $\sigma_{\text{d.c.}}$ with $10^3/T$ at a constant voltage of 10 V, the higher value of conductivity at higher temperature may be possible due to the supply of more and more energy as the temperature increases and due to addition of thermal energy the electrons are set free from the O^{2-} ions. When an electron is introduced in the sample it might be associated with cations and hence result in an unstable state [11]. The d.c. activation energy is calculated using the conductivity relation $\sigma_{\text{d.c.}} = \sigma_o \exp(-E_{\text{a.c.}}/K_BT)$

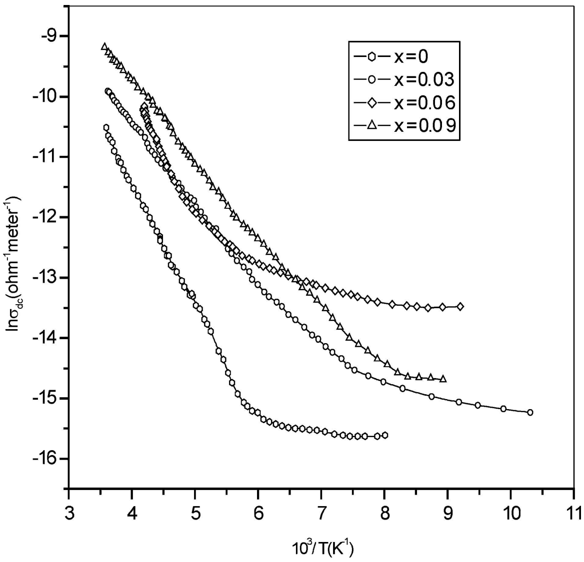

Figure 7 Variation of ln $\sigma_{\text{d.c.}}$ with the inverse of temperature for $\text{Ba}_{1-x}\text{Ca}_x\text{Sn}_{0.15}\text{Ti}_{0.85}\text{O}_3$ ($x = 0$, 0.03, 0.06 and 0.09) compounds.

in the higher temperature region and is given in Table III.

4. Conclusion

$Ba_{1-x}Ca_xSn_{0.15}Ti_{0.85}O_3$ compounds with $x = 0$, 0.03, 0.06 and 0.09 have tetragonal structure. The compounds do not show any frequency dispersion of the dielectric constant, hence they have non-relaxor property. The transition temperature shifts to below room temperature side as the concentration is increased. The d.c. resistivity decreases with increase in temperature hence exhibiting its semiconducting behavior at higher temperature.

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