Structural, Dielectric and Electrical Studies of 
$\text{Ba}_{5-x}\text{Ca}_x\text{SmTi}_3\text{Nb}_7\text{O}_{30}$ ($x = 0,1$) Ferroelectric Ceramics

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In the present work, samples of compositions $\text{Ba}_{5-x}\text{Ca}_x\text{SmTi}_3\text{Nb}_7\text{O}_{30}$ ($x = 0, 1$) were prepared by solid state reaction method. X-ray diffractographs (XRD) show the formation of single phase samples. Microstructural studies of the specimen have been performed by scanning electron microscopy (SEM). Detailed dielectric properties of the compounds as a function of frequency and temperature show that the compounds undergo non-relaxor kind of ferroelectric-paraelectric phase transition of diffuse nature with the increase in Curie temperature ($T_c$) on the substitution of calcium. The temperature dependence of dc conductivity shows that the conductivity increases with increase in temperature suggesting that the compounds have a negative temperature coefficient of resistance (NTCR) behaviour.

Key Words: Tungsten-bronze structure, Microstructure, Dielectric properties, Electrical properties.

INTRODUCTION

Since the discovery of ferroelectric properties in $\text{BaTiO}_3^1$, a large number of oxides of different structural families, such as perovskite (ABO$_3$), tungsten bronze (TB), etc. have been studied in search of new materials for device applications, such as actuators$^2$, pyroelectric detectors$^3-4$, transducers$^5$, electro-optic$^6-8$, ferroelectric random access memory$^9$, etc. Among them some of the members of TB structural family, such as lead barium niobates, barium sodium niobates, barium strontium niobates, potassium lanthanum niobates, etc. have been found to be promising and useful for many devices$^{10-13}$. The tungsten bronze structure has a general chemical formula $[(A_1)_2(A_2)_d(C)_4][(B_1)_2(B_2)_s]O_{30}^{14}$, where the A sites are usually filled by divalent or trivalent cations, and the B sites by tetravalent or pentavalent cations. This structure consists of a complex array of distorted BO$_6$ octahedra sharing corners in such a way that three different types of interstices (A$_1$, A$_2$, B$_1$, B$_2$ and C) are available for cations substitution that can tailor the physical properties of the materials for device applications. Generally, the smallest interstice C site is empty, so the general formula can be written as $A_8B_{10}O_{30}$ for tungsten bronze structure. Recent studies suggest that TB structured $\text{Ba}_3\text{RTi}_3\text{Nb}_7\text{O}_{30}$ and $\text{Sr}_3\text{RTi}_3\text{Nb}_7\text{O}_{30}$ ($R = \text{rare earth}$) compounds are more interesting because of their diffuse type of phase transition with transition
temperature well above room temperature\textsuperscript{15-17}. However, the unavailability of sufficient literature on the effects of the substitution of calcium for barium in $\text{Ba}_5\text{SmTi}_3\text{Nb}_7\text{O}_{30}$ has led us to carry out the present work. In this paper, we report the structural, dielectric and electrical properties of $\text{Ba}_{5-x}\text{Ca}_x\text{SmTi}_3\text{Nb}_7\text{O}_{30}$ ($x = 0, 1$) ferroelectric ceramics.

**EXPERIMENTAL**

Samples of compositions $\text{Ba}_{5-x}\text{Ca}_x\text{SmTi}_3\text{Nb}_7\text{O}_{30}$ with $x = 0, 1$ were synthesized by solid-state reaction method taking high purity $\text{CaCO}_3$, $\text{BaCO}_3$, $\text{TiO}_2$, $\text{Nb}_2\text{O}_5$ (all from M/s Aldrich, USA) and $\text{Sm}_2\text{O}_3$ (M/s Alfa Aesar, USA) in their stoichiometric proportions. The materials were thoroughly ground in an agate mortar and passed through sieve of appropriate size. This powder mixture was then calcined at 1100 °C for 20 h in an alumina crucible. The calcined mixture was ground and admixed with 5 wt.% polyvinyl alcohol (M/s Aldrich, USA) as a binder and then pressed at ~ 300 MPa into disk shaped pellets. These pellets were then sintered at 1300 °C for 10 h. This is the optimized sintering condition found from the extensive studies reported elsewhere\textsuperscript{18}.

X-ray diffractogram of the sintered pellet was recorded using Bruker diffractometer (model D8 Advance) in the range $10^\circ < \theta < 70^\circ$ with CuK\textsubscript{α} radiation ($\lambda = 1.5405$ Å). The granular morphology of the sample was investigated using Scanning Electron Microscope (Jeol, JSM – 840), operated at 20 kV. The sintered pellets were polished and coated with silver paste on both sides to act as electrodes and cured at 325 °C for 1 h. The dielectric measurements were carried out using HP 4284A LCR meter operating at oscillation amplitude of 1 V. The dc electrical resistivity of the samples was measured as a function of temperature at a constant voltage of 10 V using a Keithley 6517A programmable electrometer.

**RESULTS AND DISCUSSION**

Fig. 1 shows the XRD patterns of the studied samples. It is observed that single phase tungsten-bronze structure is obtained in both the samples. Lattice parameters of the samples, deduced from the X-ray diffractograms and refined using least square refinement method by a computer program package – PowderX\textsuperscript{19}, are listed in Table 1. It is observed that tetragonal strain (c/a) increases on the substitution of calcium.

The effects of calcium substitution on the microstructure have been examined by SEM and the obtained micrographs are shown in Fig. 2. It shows that the average grain size increases on addition of calcium. Also, there is presence of both spherical and cylindrical grains in calcium substituted compound as compared to only spherical grains in calcium free specimen.
The dielectric constant ($\varepsilon^\prime$) and dielectric loss (tan $\delta$) of all the samples were measured from room temperature to 300 °C at different frequency, namely, 1 kHz, 10 kHz, 100 kHz and the variation is shown in Fig. 3. It is found that both the compounds show dielectric anomaly at the Curie temperature ($T_c$) indicating the occurrence of ferroelectric-paraelectric phase transition. It is also observed that the compounds have the same $T_c$ at all the above mentioned frequencies, suggesting that the compounds do not show any relaxor behaviour. The broad dielectric peaks at all the frequencies indicate diffuse nature of the phase transition. Further, it is observed that the dielectric constant decreases on substitution of calcium (Table 1). This is possibly due to the decrease in the net polarization in the calcium contained compound as the ionic polarizability; $\alpha_D$ of Ca is 3.16 Å$^3$ compared to that of Ba 6.40 Å$^3$. However, $T_c$ increases from 170 °C (in x = 0 specimen) to 198 °C (in x = 1 specimen). Larger value of tetragonal strain (c/a) on adding calcium (Table 1) indicates that a larger amount of thermal energy is required for the phase transition resulting in an increase in $T_c$. 

![X-ray diffraction patterns of Ba$_{5-x}$Ca$_x$SmTi$_3$Nb$_7$O$_{30}$ (x = 0, 1)](image)

![SEM micrographs of Ba$_{5-x}$Ca$_x$SmTi$_3$Nb$_7$O$_{30}$ samples with (a) x = 0 and (b)x =1](image)
For both the compounds, at the above mentioned frequencies, the variation of dielectric loss with temperature shows that the loss is almost constant at lower temperatures but at higher temperatures it increases sharply, particularly at low frequency.

Fig. 3. Variation of dielectric constant ($\varepsilon'_r$) and dielectric loss (tan $\delta$) with temperature at 1 kHz, 10 kHz and 100 kHz frequencies of Ba$_{5-x}$Ca$_x$SmTi$_3$Nb$_7$O$_{30}$ compounds

Fig. 4 shows the variation of dc conductivity ($\sigma_{dc} = 1/\rho$) with absolute temperature for both the compositions. It is seen from the figure that at low temperatures the conductivity is constant. But at higher temperatures, it increases with temperature confirming that both the compounds have negative temperature coefficient of resistance (NTCR) behaviour, a typical characteristic of dielectric materials$^{22}$. The activation energy have been calculated using the Arrhenius equation $\sigma_{dc} = \sigma_o \exp (-E_a / k_B T)$ in the higher temperature region and is given in Table 1.

Fig. 4. Variation of dc conductivity with the inverse of absolute temperature
**TABLE 1**

<table>
<thead>
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<th>x</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>(\varepsilon'<em>r) (</em>{\text{max}}) at 100 kHz</th>
<th>(E_a) (eV)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>6.4106</td>
<td>5.5595</td>
<td>6.8112</td>
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<td>303</td>
<td>0.32</td>
</tr>
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<td>5.5914</td>
<td>6.8250</td>
<td>1.0820</td>
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<td>0.37</td>
</tr>
</tbody>
</table>

**Conclusion**

X-ray diffraction analysis confirm the formation of \(\text{Ba}_{5-x}\text{Ca}_x\text{SmTi}_3\text{Nb}_7\text{O}_{30}\) (\(x = 0, 1\)) compounds, having single phase and orthorhombic structure. Microstructural studies reveal that there is an increase in average grain size on substitution of calcium. The dielectric studies show that the value of dielectric constant decreases and Curie temperature increases on addition of calcium. Both the compounds have a diffuse type of ferroelectric – paraelectric phase transition exhibiting non-relaxor behaviour. Negative temperature coefficient of resistance (NTCR) behaviour is observed in the compounds.

**ACKNOWLEDGEMENTS**

One of the authors (PG) is grateful to Council of Scientific and Industrial Research (CSIR), New Delhi, India for the award of Senior Research Fellowship. The authors thank All India Council for Technical Education (AICTE), New Delhi, India for the grant of a research project.

**REFERENCES**