

Pyroelectricity in calcium substituted sodium bismuth titanate layer structured ferroelectric ceramics

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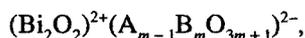
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Abstract. Pyroelectric properties of bismuth layer structured calcium substituted sodium bismuth titanate $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ca}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ with $x=0$ (NBT) and $x=0.1$ (0.1 NCBT) were studied by measuring the current under short circuit condition. Spontaneous polarization and figures of merit were evaluated from the measured values of pyroelectric coefficients, dielectric constant and loss tangent. The pyroelectric properties were studied in poled and short circuit condition from 30°C to 700°C. The results obtained were discussed in the light of dielectric and conductivity properties of the samples.

Keywords. Pyroelectricity; ferroelectricity; dielectric constant; loss tangent; conductivity.

1. Introduction

Ferroelectric oxide ceramics are used in a very broad range of functional ceramics and form the materials base for majority of applications. These applications account for more than 60% of the total high technology ceramics market world wide (High technology ceramic news 1990). Devices using dielectric, piezoelectric and pyroelectric properties of ferroelectrics received continued attention particularly the pyroelectric effect for infrared detection and infrared imaging. Pyroelectric systems rely upon the strong temperature sensitivity of electric polarization (Whatmore *et al* 1980; Porter 1981). Bismuth layer structured ferroelectrics (BLSF) which belong to Aurivillius family of compounds were reported to be pyroelectric materials and have a generalized formula (Aurivillius 1949):



where A is a mono or di or trivalent ion or a mixture of them, B represents Fe^{3+} , Ti^{4+} , Nb^{5+} , Ta^{5+} , W^{6+} etc and the integer 'm' takes any of the values from 3 to 8 and denotes number of perovskite layers. These compounds are built up by regular intergrowth of $(\text{Bi}_2\text{O}_2)^{2+}$ layers and perovskite layers $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$. Many compounds belonging to this family were synthesized by Smolenskii *et al* (1961) and Subba Rao (1962a, b).

In this family of compounds bismuth oxide layer is very strong as substitution of bismuth ions in Bi_2O_2 layer is considered to be difficult (Newnham 1968). On the other hand, the bismuth atoms in the perovskite layer

can be readily replaced by large number of univalent, divalent and trivalent cations. The size requirements were no more stringent than those of perovskite structure itself. In all these compounds 'a' and 'b' values do not show much change. However, there is an observed change in 'c' value (Chen Daren and Guo Yanyi 1982). Calcium modified sodium bismuth titanate i.e. $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ca}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ ceramics were reported to display excellent piezoelectric and pyroelectric properties (Takenaka and Sakata 1988, 1991). These ferroelectrics were characterized by low dielectric constants (ϵ) and high Curie temperatures (T_c), hence larger anisotropy in electromechanical coupling factors, K (K_{33} and K_{31}) as compared with those of the widely used lead zirconate titanate (PZT) ceramics (Takenaka and Sakata 1980). Therefore, BLSF materials are considered to be ideal candidates for piezoelectric applications at high temperatures and frequencies or pyroelectric materials with large figure of merit. These ceramics, however, have two disadvantages in a poling process—one is due to their crystal structure in which the rotation of spontaneous polarization is two-dimensionally restricted and the other having large coercive field or high Curie temperatures. It is observed that the pyroelectric properties of these ceramics depend strongly on poling conditions like poling temperature, poling field and poling time etc. So there is an intense activity to improve strategy for poling and also to control the Curie temperatures of basic compounds by substitution of suitable aliovalent ions (Takenaka and Sakata 1988). With this view a study was undertaken on calcium substituted sodium bismuth titanate to probe their pyroelectric behaviour. The pyroelectric properties of ordinary fired and hot forged samples of NBT were reported by Takenaka and Sakata (1991) by using dynamic method

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with 0.1% Mn doping. In the present paper we report the results of our pyroelectric measurements of NBT and 0.1 NCBT in the light of dielectric, conductivity and microstructure studies.

2. Sample preparation

Polycrystalline samples of NBT mixed system with the general formula $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ca}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ with $x = 0$ and 0.1 were prepared by conventional double sintering technique by using (99.9% pure) AR grade constituent oxides and carbonates. The constituents were mixed thoroughly in an agate mortar to make homogeneous mixture and pre-calcined at a temperature of 800°C for 2 h. After calcination, the material was finely ground by mixing with 1% polyvinyl alcohol. The ground powders were pressed into circular discs of diameter 1 cm and 1–2 mm thickness at a pressure of 30 MPa and were finally sintered at 1000°C for 2 h in an air atmosphere and cooled to 400°C at 60°C per h and then furnace cooled.

3. X-ray diffraction

The X-ray powder diffractogram (XRD) of the samples was taken with CuK_α radiation ($\lambda = 1.548 \text{ \AA}$). The XRD patterns of NBT and 0.1 NCBT are shown in figures 1a and b. X-ray diffraction patterns of this system indicate a single phase with pseudo orthorhombic symmetry. The average densities of the samples, determined by the Archimedes principle, is shown in table 1. The X-ray density in NBT is around 86% and that of 0.1 NCBT is 90% of the experimental density. The experimental

densities of NBT obtained in the present study are higher than those reported earlier (Subba Rao 1962a, b).

4. Scanning electron microscopy

SEM photographs of the present samples were obtained using JEOL SEM 5410 in low vacuum. The SEM photos of NBT and 0.1 NCBT samples are shown in figures 2a and b.

5. Poling procedure

The samples were poled electrically prior to the dielectric and pyroelectric measurements. The samples were poled at 150°C under DC field of 100 kV/cm using a stabilized power supply and cooled to room temperature in the presence of the field.

6. Conductivity measurements

The large areas of the samples were painted with ultra fine and high quality grade silver paste for good electrical contact prior to the measurements. AC conductivity

Table 1. Summary of the pertinent data of NBT–0.1 NCBT samples.

Compound	NBT	0.1 NCBT
Lattice parameters (Å)	a = 5.423 b = 5.450 c = 40.65	a = 5.456 b = 5.448 c = 40.63
a/c	0.1334	0.1342
$\rho_{\text{X-ray}}$ (g/cc)	7.63	7.60
ρ_{expt} (g/cc)	6.58	6.69
ρ_{expt} (reported) (g/cc)	6.3	–
Particle size (Å)	258	249
Resistivity ($\Omega\text{-cm}$)		
at RT	2.9×10^9	1.7×10^8
at 150°C	2.0×10^9	5.0×10^6
at 300°C	1.0×10^7	1.0×10^5
at 600°C	4.5×10^2	5.6×10^2
ϵ (100 kHz)	213.6	143.5
Tan δ (100 kHz)	0.7027	0.0015
Activation energy of conduction at 400°C (eV)	1.07	0.58
Activation energy of dipoles at 400°C (eV)	0.59	1.06
Relaxation time (μs) at 30°C ($\text{C}/\text{cm}^2\text{-}^\circ\text{C}$)	23	150
Pyroelectric coefficient at 30°C ($\text{C}/\text{cm}^2\text{-}^\circ\text{C}$)	1.6×10^{-12}	90×10^{-12}
P_s ($\mu\text{C}/\text{cm}^2$)	4.08×10^{-7}	8.8×10^{-4}
F_D ($\text{C-cm}/\text{J}$)	0.046×10^{-11}	64.8×10^{-11}
F_V ($\text{C-cm}/\text{J}$)	0.00265×10^{-11}	0.22×10^{-11}

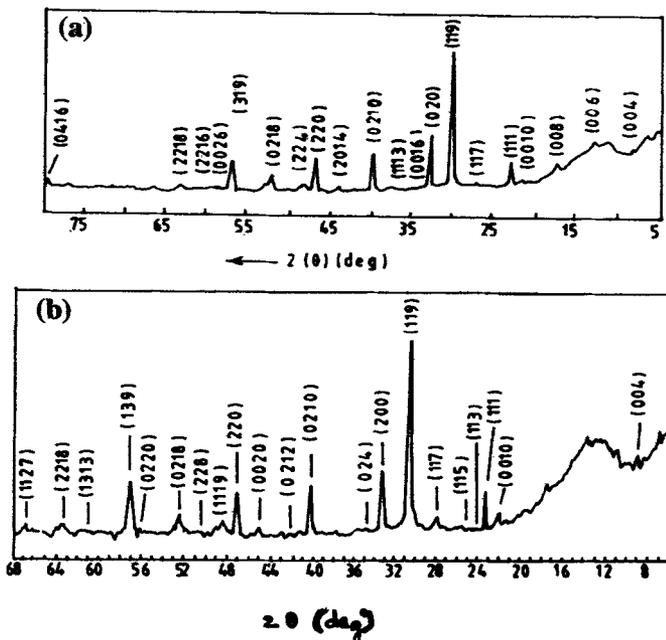


Figure 1. X-ray diffractogram of a. NBT and b. 0.1 NCBT.

measurements were performed using HP 4192 A impedance analyzer which is interfaced to an IBM PC for acquisition and analysis of the data. DC conductivity measurements were also done with a conventional two-probe setup by measuring resistance with 610C electrometer at different temperatures.

7. Pyroelectric measurements

Pyroelectric measurements were made by keeping the sample in between two electrodes of the sample holder which is inserted in a tubular furnace whose temperature was varied with a constant heating rate of 5°C/min. The current generated by the sample was measured using 610C Keithley electrometer. The pyroelectric coefficient is defined as

$$S = \frac{dP_s}{dT} = \frac{dP_s}{dt} \frac{dt}{dT}$$

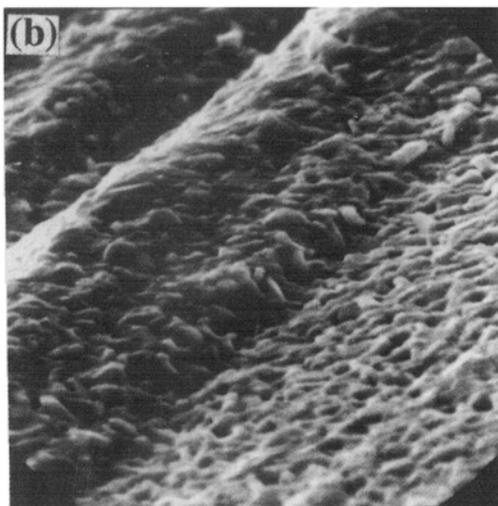
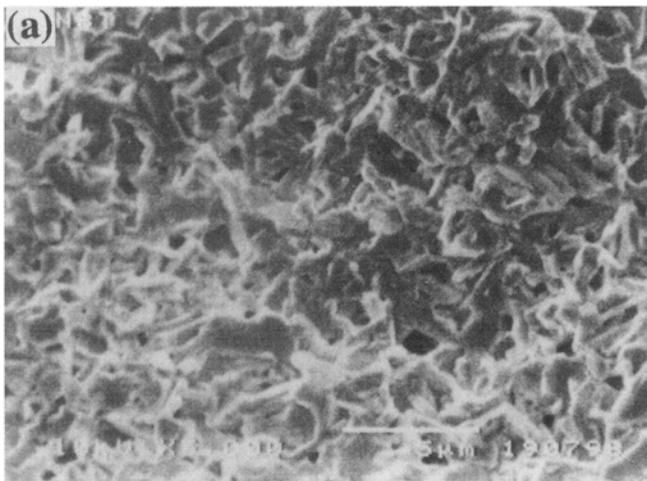


Figure 2. SEM micrographs of a. NBT at 10 kV and ×5000 and b. 0.1 NCBT at 25 kV and ×3600.

where dP_s/dt is current density (I/A) which appears due to temperature change of spontaneous polarization (P_s) and A the surface area of the electrodes. Hence $P_s = \int_{T_c}^T SdT$. Therefore, P_s can be evaluated from the area under the S vs T curve.

8. Results

The variation of pyroelectric coefficient as function of temperature is shown in figure 3. The variation of dielectric constant as a function of frequency is shown in figure 4. These samples show a decrease in dielectric constant with the increase of frequency attaining a constant value beyond 100 kHz. Pure NBT samples show high dielectric constant at low frequencies in general. The samples show small variation of dielectric constant with temperature till 300°C. Beyond this temperature there is an increasing trend in the value of dielectric constant showing a peak at 585°C and 595°C for NBT and 0.1 NCBT samples, respectively. The peak in the dielectric constant versus temperature shifts towards higher temperature with the addition of calcium content.

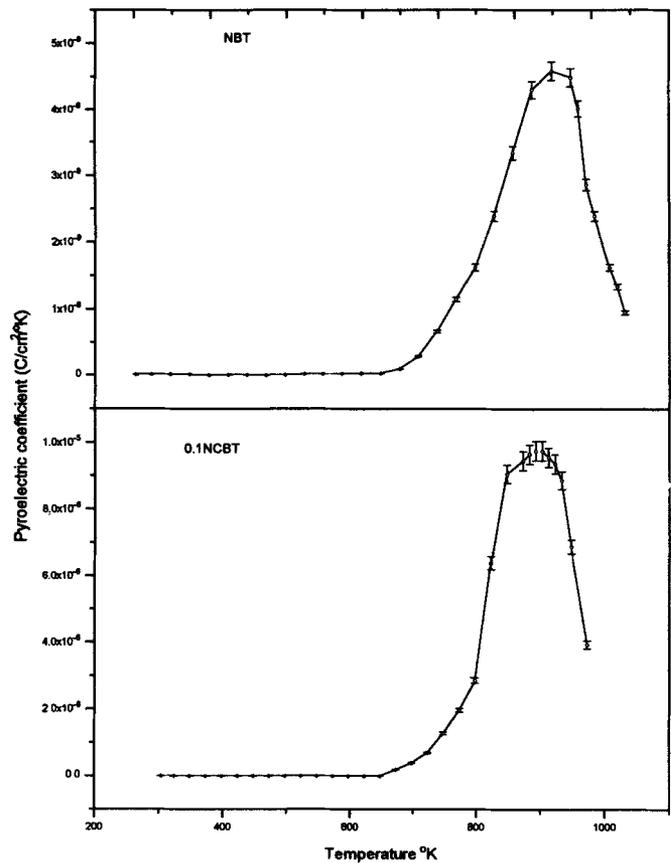


Figure 3. Pyroelectric coefficient vs temperature of NBT and 0.1 NCBT.

Calcium bismuth titanate ($\text{CaBi}_4\text{Ti}_4\text{O}_{15}$) was reported to have a transition temperature of 785°C (Takenaka and Sakata 1991). The observed pyroelectric current under short-circuit condition when heated linearly with time and dielectric peaks confirms the ferroelectric nature of the present system of samples. Using dielectric constant and loss tangent data, AC conductivity of these samples has been calculated and plotted as function of temperature for NBT and 0.1NCBT samples in figure 5. These graphs show two slopes. From $\log \sigma_{AC}$ versus $10^3/T$ plots activation energy for conduction before the onset of ferroelectric phase transition (at 400°C) is calculated and shown in table 1. DC conductivity plots of the samples are shown in figure 6.

9. Discussion

The room temperature pyroelectric coefficients of NBT and 0.1NCBT samples are $1.5287 \times 10^{-7} \text{ C/m}^2\text{-}^\circ\text{C}$ and $8.8525 \times 10^{-6} \text{ C/m}^2\text{-}^\circ\text{C}$. The pyroelectric current and coefficient are almost constant up to 400°C , beyond which the pyroelectric current increases up to ferroelectric Curie temperature and then shows a decrease. Calcium substituted NBT samples show large values of pyroelectric coefficient compared to NBT. A good pyroelectric material should have high pyroelectric coefficient, low dielectric constant, loss and low specific heat (Srinivasan and Narayanan 1980). The value of pyroelectric coefficient in these materials is possibly a function of Na-Ca/Bi ratio (Takenaka and Sakata 1991). This is very useful from the device point of view, since instead of varying material temperature to obtain optimum device characteristics it is possible to vary crystal composition and operate the device at lower temperature. Another important feature in these materials is their ability to manipulate the conduction.

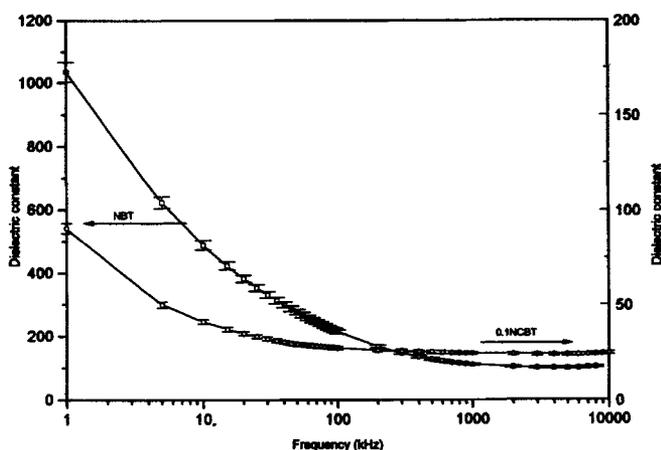


Figure 4. Variation of dielectric constant with frequency.

The higher Curie temperatures have the advantage of resistance to depoling and to be electrically biased for long term of operation. The temperature variation of spontaneous polarization for these materials is very little over a large range of temperatures. Mixed pyroelectric materials like the one used in the present study offer the possibility to alter the Curie temperature and pyroelectric coefficient, dielectric constant and loss by varying the composition leading to the improvement of pyroelectric detector efficiency. The mixed system generally shows decreased thermal hysteresis thereby increasing the stability of the materials. The increase in transition temperature with increase of Ca content suggests that the T_C is related to change of lattice distortion. The smaller values of $\tan \delta$ are preferable for a good pyroelectric material with high signal to noise ratio. The figures of merit F_V and F_D which are calculated using material constants judge the infrared sensing capability of the material. The structure of the present compounds consists of $(\text{Bi}_2\text{O}_2)^{2+}$ layers, interleaved with perovskite like $[(\text{Na}_{0.5}\text{Bi}_{0.5})\text{Ca}_{1-x}\text{Bi}_4\text{Ti}_4\text{O}_{13}]^{2-}$ layers. The bismuth oxide layer is almost inviolate.

$(\text{Bi}_2\text{O}_2)^{2+}$ layers are made up of square pyramidal, BiO_4 groups shearing their basal edges. Present compounds

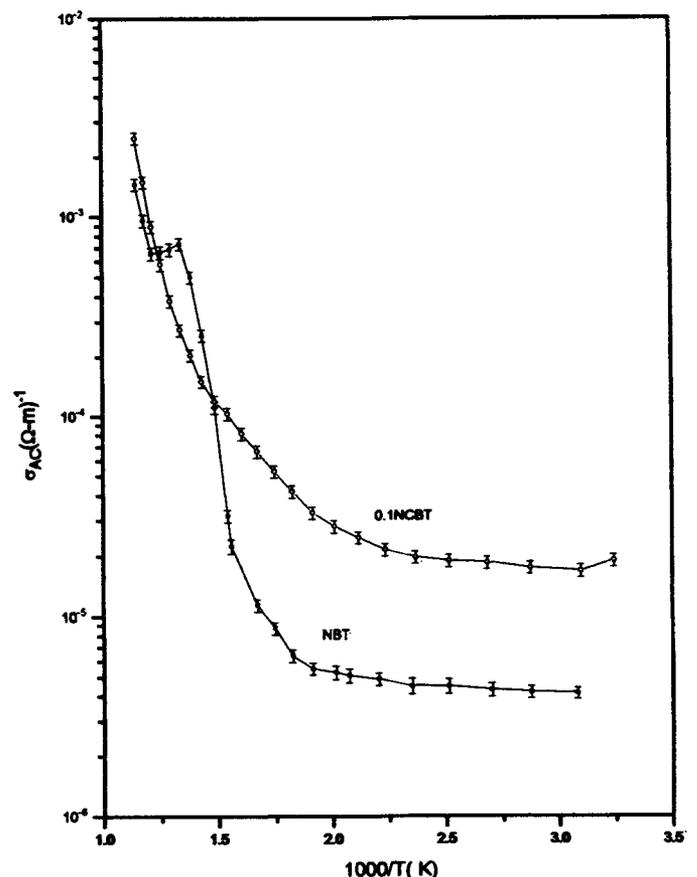
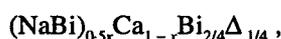


Figure 5. $\log \sigma_{AC}$ vs $10^3/T$ for NBT and 0.1NCBT.

consist of four perovskite like layers with TiO_6 octahedra and spontaneous polarization takes place in these layers (Rama Sastry *et al* 1988). While in the perovskite layers, the ionic polarization would involve the displacement of the highly charged B site cations away from the centres of their coordination octahedra. The structural consequence of this polarization is to distort the environment of the B cations from the regular octahedra to distorted octahedra configuration thereby lowering the crystal symmetry.

The molecular formula for $(\text{NaBi})_{0.5x}\text{Ca}_{1-x}\text{Bi}_4\text{Ti}_4\text{O}_{15}$ system, can also be written in the form of $\text{Bi}_2\text{O}_2 4[(\text{NaBi})_{0.5x}\text{Ca}_{1-x} 1/4\text{Bi}_{2/4} 1/\Delta_{1/4}\text{TiO}_3]$. The latter shown in the square bracket obviously belongs to ABO_3 type. The ion in 'A' position is



where Δ indicates cation unoccupancy. This introduces strain into the lattice. Larger number of bismuth ions in 'A' position and their larger polarizability may contribute to the ferroelectricity (Chen Daren 1986). Oxygen octahedra within the compounds with bismuth layer structure consisting of even number of perovskite layers,

will exhibit a zig-zag like pattern along c-axis with mirror symmetry (Newnham *et al* 1971). As the cation Ca^{2+} with small ionic radius was used to replace $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}^{2+}$ in 'A' position, the angle of zig-zag would be small as evidenced from a/c ratio. It is seen from our data that the replacement of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}^{2+}$ with calcium ion increases Curie constant and decreases density.

Calcium has low polarizability compared to the bismuth ion. Hence it is expected that 0.1 NCBT should show low dielectric constant, high T_C as observed in the present measurements. The sample 0.1 NCBT has more experimental density and low particle size and hence low dielectric constant and loss tangent. The fitting of Curie-Weiss law gives a value of Curie constant of the order of 10^5 °C and Curie temperature around 600°C (Rama Sastry *et al* 1998).

The present samples have been fired in air at 1000°C. At this temperature oxygen is expected to escape from the sample creating oxygen vacancies. During subsequent cooling the oxygen enters the lattice again but cannot totally compensate for the loss. This is the case with all titanates like BaTiO_3 , SrTiO_3 etc (Newnham *et al* 1971). The observed conductivity in the present samples may be due to the mobility of oxygen vacancies as in the case of other perovskite oxides. The oxygen movement takes place within the octahedra and also from one octahedra to another within perovskite layers. The conductivity curves show two slopes and the activation energies in the high temperature region is given in table 1. The activation energy for conduction is calculated at 400°C before the onset of transition.

Low temperature conductivity is basically because of the defects and reflects space charge. This is also indicated by dielectric constant-frequency and $\tan \delta$ -frequency graphs. In the low temperature region, since there are large concentration of defects and vacancies and their agglomerations with few free charges, it is expected that the conductivity and activation energy for conduction would be less because of multiple and complex variety of relaxations present in the sample. The vacancies present in the sample (both at A and B positions of ABO_3 structure) and lattice defects could be responsible for the observed conductivity. The sample 0.1 NCBT shows low activation energy.

In these compounds Ca^{2+} ion was substituted for $(\text{Na}_{0.5}\text{Bi}_{0.5})^{2+}$ ion. Therefore Ca^{2+} ion may effectively act as an acceptor dopant leading to more oxygen vacancies. These vacancies may be locked-up forming charge complexes leading to higher relaxation times in comparison to NBT (Rama Sastry 1998). At higher temperatures possibly these complexes disassociate giving rise to more oxygen vacancies leading to higher conductivity in the materials (Warren *et al* 1996). This explains observed pyroelectric currents. Takenaka and Sakata (1980)

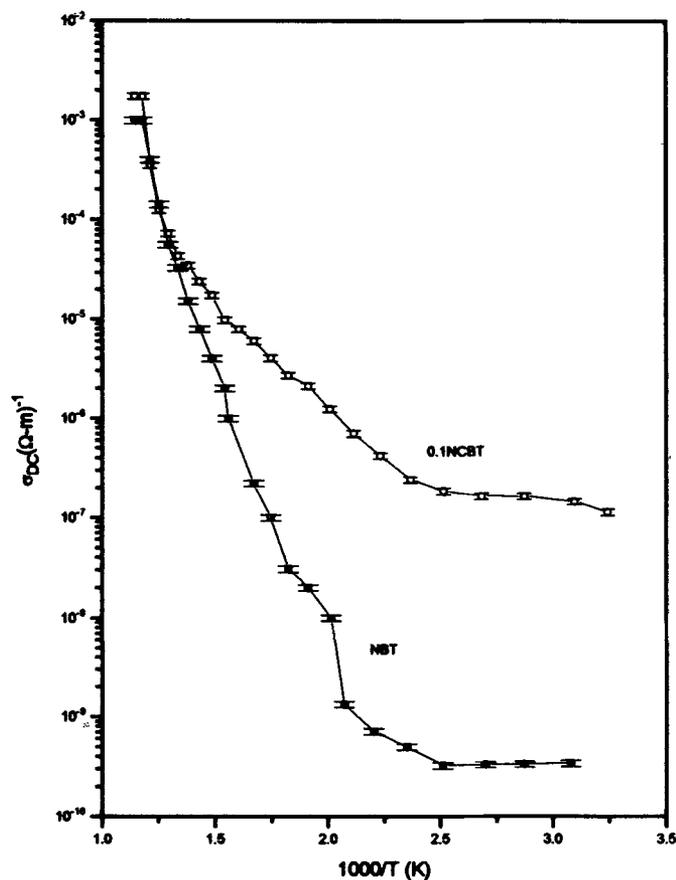


Figure 6. $\text{Log } \sigma_{\text{DC}}$ vs $10^3/T$ for NBT and 0.1 NCBT.

reported the dynamic pyroelectric studies of NBT-CBT system and have shown that the hot forged samples have much higher values of pyroelectric parameters like p , F_D and F_V . The hot forged samples with Mn doping show an increase in the values of these parameters by about two fold (Takenaka and Sakata 1991). Mn doping perhaps has a role in locking up charge complexes over entire temperature range of observation, thereby restricting the increase in pyroelectric properties.

Larger increase in the pyroelectric current, pyroelectric coefficient and figures of merit was observed in the present study with the substitution of calcium in NBT. This increase, in view of the observed larger conductivity, lower activation energy for conduction, larger activation energy for dipoles, higher relaxation times (table 1) in 0.1 NCBT suggest that substitution of calcium in 0.1 NCBT leads to the formation of locked-up charge complexes (Rama Sastry 1998). These charge complexes are inactive at lower temperatures, but as the temperature is raised, they are set free and made available for contributing to the pyroelectric properties.

10. Conclusions

NBT samples doped with 0.1 mole% of calcium exhibit high Curie temperatures, low dielectric constants and low loss. Pyroelectric parameters were found to be high in calcium substituted compound. The lattice distortion due to calcium substitution may be related to observed increase in pyroelectric properties. 0.1 NCBT sample shows the presence of locked-up charges at low

temperatures and with increase of temperatures, probably these charges are set free leading to observed effects in the electrical and pyroelectric properties of the material.

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