

Electrical Transport Properties in Zr Substituted NBT Electronic System

P. S. Sahoo, L. K. Mishra and S. Behera

Department of physics
North Orissa Unuversity, Baripada, Mayurbhanj, Odisha, India

B. B. Mohanty

Department of Physics
Betnoti College Betnoti, Mayurbhanj, Odisha, India
Email address: banabihari4u@gmail.com

D. Panda

PXE, DRDO, Chandipur, Balasore Odisha, India

R. N. P. Choudhary

Department of Physics, I T E R, Bhubaneswar. Odisha, India

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Abstract: $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.95}\text{Zr}_{0.05}\text{O}_3$ is a Polycrystalline perovskite electro ceramic synthesised by mixed oxide process. The dielectric characterisation of the compound is analysed here carefully and presented. Room temperature XRD profile of the compound establishes the formation of a single-phase orthorhombic crystal structure. From SEM micrograph, inhomogeneously distributed grains are observed all over the surface of the compound. The dielectric characterisation of the sample is studied as a function of temperature. The relative dielectric constant (ϵ_r) of the sample reduces with rise in frequency exhibiting a typical characteristic of ferroelectrics. Dielectric anomaly is observed at $\sim 400^\circ\text{C}$ showing ferro to para electric phase transition in the compound. The ac electrical conductivity is observed to be varying with inverse absolute temperature and frequency, explaining separate conduction mechanism in the material.

Keywords: Ceramics, dielectric, XRD analysis.

1. Introduction

Researchers in the present era paid much emphasis to develop eco-friendly research materials. In this regard, lead-free multiferroic systems have drawn much more attraction over the last few decades in the growth of upcoming generation electronic materials for devices application. Detailed literature survey reveals that some work in this direction has been done on lead free perovskite ferroelectric compounds having vast applications in sensors, actuators, magnetically modulated transducers, energy harvesting devices, etc.¹⁻⁷. In this paper emphasis has been given on the dielectric characteristic and conductivity property of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.95}\text{Zr}_{0.05}\text{O}_3$ eco-friendly perovskite ferroelectric ceramic.

2. Theoretical background

The electrical characterization of the ferroelectric ceramics depends upon their dielectric properties. The dielectric phenomena is a consequence of short-range motion of charge carriers in presence of an applied electric field. The dielectric properties in ferroelectric materials are controlled by the field strength, frequency as well as temperature. The frequency dependent dielectric phenomena is represented in forms of the complex relative permittivity

$$\varepsilon r = \varepsilon r'(\omega) - i\varepsilon r''(\omega),$$

here, $\omega = 2\pi f$ is the angular frequency, f is the frequency of applied ac field^{8,9}

$\varepsilon r''$: imaginary part of the complex dielectric constant, $\varepsilon r'$: real part of the complex dielectric constant.

The loss tangent ($\tan \delta$) or the dissipation factor is the ratio of the imaginary (out of phase components) to that of the real part (in phase components) of the complex dielectric constant which is^{10,11}

$$\tan \delta = \frac{\varepsilon r''}{\varepsilon r'}.$$

The temperature dependent dielectric constant is explained by Curie-Weiss law as follows. These materials exhibit an increase in dielectric constant (εr) till phase transition is reached and then it decreases and satisfies the Curie-Weiss law⁸

$$\varepsilon r = \frac{C}{T - T_c}.$$

3. Experimental Details

2.1. Material preparation: The polycrystalline ceramic sample $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.95}\text{Zr}_{0.05}\text{O}_3$ is synthesized with appropriate stoichiometric ratio of required ingredients; Na_2CO_3 , BiO_2 , TiO_2 , ZrO_2 of highest quality (>99.9% pure). The precursors are weighed, thoroughly mixed in air atmosphere in an agate mortar for 3 h and then in wet methanol for another 3 h. Calcination of the mixed powders are done at an optimized temperature and time (900 °C for 24 h) in air. The calcined powder is then hard pressed into pellets with a uniaxial hydrostatic press under a pressure of 4×10^6 N/m². The required ceramic sample is obtained by sintering the pellets in air atmosphere at 950°C for 12 h. Finally, the pellets are silver coated, and then dried at 1500C for 2h before carrying out electrical measurements.

The formation of compound is investigated by XRD spectra done at environmental temperature using Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) over a broad range of Bragg angles ($20^\circ \leq 2\theta \leq 80^\circ$) at a scanning speed 2° min^{-1} . The surface texture of the compound is analyzed by the data obtained from a scanning electron microscope (SEM) (Hitachi S3400N). All the electrical measurements are carried out by using a computer-controlled LCR Hi-Tester (HIOKI 3532-50, Japan) in a wide range of frequencies (0.1 kHz–1 MHz) and temperatures (30–500°C).

4. Results and Discussion

3.1 Structural and microstructural analysis: The analysis of XRD-profile (Figure 1, left) of the polycrystalline compound is completed using a standard computer program Powd Mult)¹². The XRD analysis of the compound establishes the creation of a single-phase orthorhombic crystal structure. The lattice parameters are estimated to be: $a = 8.5584$ (39) Å, $b = 9.8449$ (39) Å and $c = 10.7439$ (39) Å. As a consequence of the finest resemblance between observed (d_{obs}) and calculated (d_{cal}) inter planar spacing d (i.e., $\sum (d_{\text{obs}} - d_{\text{cal}}) = \text{minimum}$), a single-phase orthorhombic structure is selected. The SEM (Figure 1, middle) profile describes the surface texture of the sample where, grains of irregular in shape are observed to be inhomogeneously distributed in every part of the surface of

the material with existence of some porosity. From histogram (Figure 1, right) the mean grain size is measured as $6.7\mu\text{m}$.

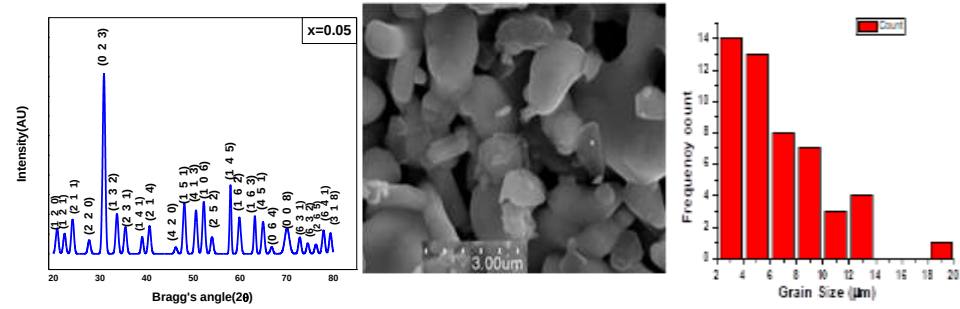


Figure 1. XRD patterns (left), SEM micrograph (middle) and histogram (right) of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.95}\text{Zr}_{0.05}\text{O}_3$ compound.

3.2 Dielectric properties: The temperature and frequency dependent relative dielectric constant (ϵ_r) is as in Figure 2. The figure shows dielectric phase transition at a temperature $\sim 400^\circ\text{C}$. The dielectric constant (ϵ_r) is an increasing function of temperature in ferroelectric phase below transition temperature (T_c) and then decreases in para electric state. The maximum value of ϵ_r are measured to be $\sim 555, 406, 357, 277$ and 258 for $10, 50, 100, 500, 1000$ kHz frequencies respectively. The high value of dielectric constant of this sample indicates that it may be very much useful in devices applications. From the loss tangent ($\tan \delta \sim T$) plot (Figure 2, right), $\tan \delta$ is observed to be very small nearing zero up to $\sim 250^\circ\text{C}$ and then increases with temperature. This is because of the improvement of conduction process and trimming in the ferroelectric domain wall contribution etc.¹³.

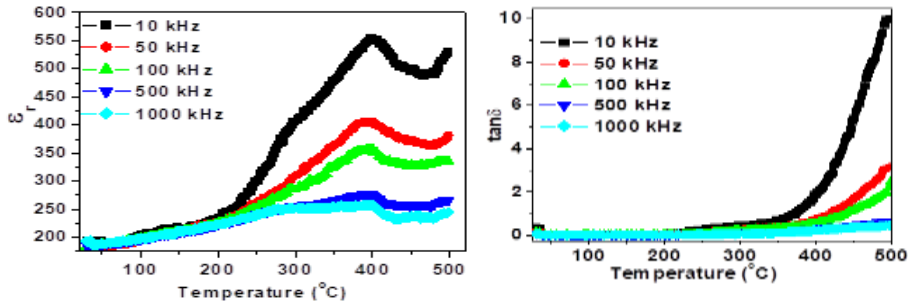


Figure 2. Variation of ϵ_r (left) and loss tangent ($\tan \delta$) (right) with temperature of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.95}\text{Zr}_{0.05}\text{O}_3$ at selected frequencies.

3.3 ac conductivity study: The $\sigma_{ac} \sim (103/T)$ graph at different frequencies is drawn in Figure 4(left). The plot is divided into three distinct frequency independent regions with different slopes having separate activation energy. The activation energy in different zones are given in Table 1. The compound exhibits negative temperature coefficient of resistance (NTCR) behaviour that is confirmed from the rise in σ_{ac} with rise in temperature. Low temperature dispersion is clearly observed but when temperature rises dispersion in conductivity narrows and the two curves intermingles into a single curve. This is because of reunion of released space charges and electrode polarization¹⁴. Oxygen vacancies play key role for conduction mechanism in ferroelectrics¹⁵.

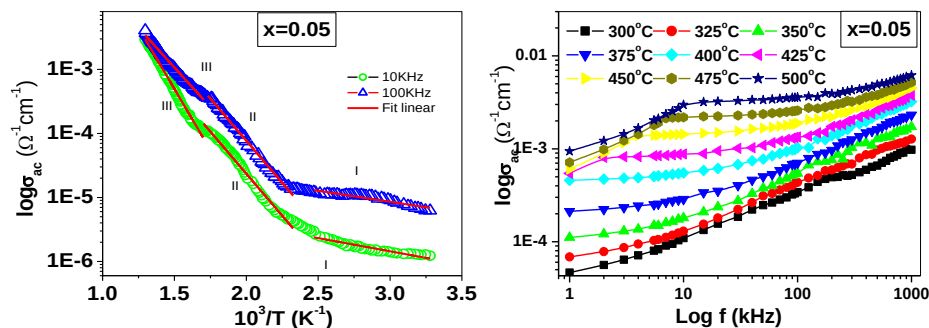


Figure 4. $\log \sigma_{ac} \sim 10^3/T$ (left) at selected frequencies and $\log \sigma_{ac} \sim \log f$ (right) of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.95}\text{Zr}_{0.05}\text{O}_3$.

The frequency variation of σ_{ac} at some temperatures is shown in Figure 4 (right).The figure shows increase in the value of σ_{ac} with increasing frequency and renounce of frequency after a certain value for this compound and at high frequency side the compound shows dc conductivity. The compound displays dispersion phenomena obeying Jonscher's power law at all frequencies. The rise in conductivity with a rise in temperature and frequency, confirms the negative temperature coefficient of resistance (NTCR) behaviour as seen in semiconductors. Similar trend has been observed in other compounds of this family¹⁶.

Table 1. Comparison of activation energy E_a (eV) at various zones of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.95}\text{Zr}_{0.05}\text{O}_3$ at two different frequencies from σ_{ac} vs. $1/T$ graphs

Compound	Frequency (KHz)	E_a (ev)		
		I	II	III
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.95}\text{Zr}_{0.05}\text{O}_3$	10	0.8170	0.5211	0.7579
	100	0.0680	0.5221	0.4921

5. Conclusions

The compound is synthesized using solid state reaction route. The formation of single phase orthorhombic compound is confirmed from room temperature X-ray diffraction studies. Dielectric anomaly is observed at a temperature $\sim 400^{\circ}\text{C}$. The dielectric constant (ϵ_r) increases with temperature in ferroelectric phase below transition temperature (T_c) and then decreases in para electric state. Small value of $\tan \delta$ indicates good dielectric material. NTCR behaviour is confirmed from the increase in σ_{ac} with rise in temperature. In σ_{ac} vs. $1/T$ graph, low temperature dispersion is clearly observed and for higher temperature conductivity dispersion narrows and the two curves merge into a single curve due to reunion of released space charges and electrode polarization. σ_{ac} is an increasing function of frequency and becomes independent of frequency after a certain value and towards higher frequency side the compound shows dc conductivity. The compound displays dispersion phenomena obeying Jonscher's power law at all frequencies.

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