

Low-Frequency Dielectric Dispersion and Impedance Spectroscopy of Lead-Free $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) based Ferroelectric Ceramic

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Abstract

$(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.89}\text{Ba}_{0.11}\text{Zr}_{0.04}\text{Ti}_{0.96}\text{O}_3$ (0.11BNBZT) ceramic were prepared by using solid-state reaction method. A single phase perovskite (ABO_3) structure with tetragonal symmetry was confirmed by X-ray diffraction. The dielectric behavior, impedance relaxation were investigated in a wide range of temperature (30°C - 600°C) and frequencies (45Hz-5MHz). The grain morphologies were analyzed by using a Scanning Electron Microscopy (SEM) analysis. The temperature dependence of dielectric behavior and the frequency dependence of impedance relaxation were investigated. A broadened dielectric constant peak were observed over a wide temperature range and also indicate a relaxor behavior. The complex impedance plot exhibited semicircle plot, which is explained by the grain effect of the bulk. The center of the impedance semicircles lie below the real axis, which indicates that the impedance response is a Cole-Cole type relaxation.

Keywords: Perovskite structure; Ferroelectric; Dielectric; Relaxor; Impedance

Introduction

Lead-containing ferroelectric materials such as $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) and PZT-based [1,2] multi component ceramics have been widely used as sensors, actuators and ultrasonic transducers in various electronic devices because of their excellent piezoelectric properties. However, PbO vaporization problems during the sintering process and treatment of Pb containing products cause crucial environment pollution. Recently, much more attention has been paid to the investigation of lead free piezoelectric materials for the replacement of the lead containing ferroelectrics [3].

As such, lead free ceramics have attracted considerable attention. The $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) and NBT based system with ABO_3 perovskite structure is one of important lead-free based materials [4-7]. NBT has a high Curie temperature ($T_c=320^\circ\text{C}$) and possesses strong ferroelectricity, exhibiting a relatively large polarization ($P_r=38 \mu\text{C}/\text{cm}^2$) and high coercive field ($E_c=73 \text{ kV}/\text{cm}$) at room temperature. Although, NBT exhibits a large coercive field and relatively large conductivity, it is hard to be poled for practical applications. NBT had two phase transitions; it has anti ferroelectric phase below 200°C and paraelectric phase at 320°C . Recently, the effect of doping in NBT [5-7] and several solid solutions to improve the properties of NBT have been investigated. It has been reported that NBT-based ceramics with their compositions modified with the addition of BaTiO_3 [8], BiFeO_3 [9], NaNbO_3 [10], CeO_2 [11], MnO_2 [12]. Among them ($\text{Bi}_{0.5}\text{Na}_{0.5-1-x}\text{Ba}_x\text{TiO}_3$ (BNBT) ceramics are more interesting because of the existence of rhombohedral, tetragonal structure, Morphotropic Phase Boundary (MPB), MPB for the BNBT composition lies between 6% and 7% BaTiO_3 .

A necessary condition for fabrication of high performing materials is knowledge of their physical properties, but the dielectric dispersions and the impedance relaxation of the NBT based systems are not fully studied. The contribution of the grains and the grain boundaries are evaluated by using complex impedance. Complex impedance spectroscopy is a good technique to investigate the microstructure and the electrical properties.

In the present work, ZrO_2 has been added to $(\text{Bi}_{0.5}\text{Na}_{0.5-1-x}\text{Ba}_x\text{TiO}_3$ (BNBT) i.e., $(\text{Na}_{0.5}\text{Bi}_{0.5-0.89})_{0.11}\text{Zr}_{0.04}\text{Ti}_{0.96}\text{O}_3$ ceramic has been prepared

and investigated in the dielectric and impedance properties over a wide frequency range from 45 Hz to 5 MHz and temperature range from 30°C - 600°C .

Experimental

The conventional mixed oxide technique was used to prepare $(\text{Na}_{0.5}\text{Bi}_{0.5-0.89})_{0.11}\text{Zr}_{0.04}\text{Ti}_{0.96}\text{O}_3$ (0.11BNBZT) ceramic. The commercially available chemicals of Bi_2O_3 , Na_2O_3 , BaCO_3 , ZrO_2 and TiO_2 with purity higher than 99.9% were used as starting materials. These oxides and carbonates were mixed according to the desired chemical formula and were grounded for 10 h and calcined at $850^\circ\text{C}/2\text{h}$. After calcination, the ground powder was pressed into disks with 12 mm diameter and about 2 mm in thickness. The disk was sintered at $1180^\circ\text{C}/3\text{hrs}$ in air. The density of the sintered sample was measured using the Archimedes principle. The phase structure was examined using x-ray powder diffraction analysis using a $\text{Cu K}\alpha$ radiation. For the observation of the microstructure samples were polished and thermally etched. Finally, the microstructures were observed by scanning electron microscopy (SEM: JEOL_JY: Model 5800F).

For electrical measurements, silver paste was applied on both surfaces of the disk and thermally etched at 650°C . The capacitance of the ceramic used for calculating dielectric constant was measured as a function of temperature, complex impedance by using computer interfaced LCR Hi-Tester (HIOKI 3532-50, Japan).

Results and Discussion

Figure 1 shows an x-ray diffraction pattern of 0.11BNBZT ceramic, exhibits pure perovskite structure with tetragonal symmetry feature with (111) peak around 40° of 2θ . As crystal structure transformed

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from rhombohedral into a tetragonal symmetry there is splitting of (200) and (002) peak around 46.5° of 2θ , which has been observed in XRD pattern (Figure 1). Lattice parameters have been calculated by using POWD software. Lattice parameters, cell volume, experimental and theoretical density, porosity has been tabulated in Table 1.

The scanning electron micrograph of the sintered ceramic (011BNBZT) is shown in Figure 2, indicating that the ceramic is highly dense with less porosity. Based on the measurement of Archimedes principle, the experimental density of ceramic is 95% of theoretical density. The average grain size has been calculated by using line intercept method. The average grain size of the studied ceramic is $1.21\ \mu\text{m}$.

Figure 3; depict the temperature dependence of real part of dielectric constant of 0.11BNBZT at various frequencies, indicating a relaxor like behavior [13]. At low frequencies, a phase transition from ferroelectric to anti ferroelectric is observed at around 100°C which is referred as depolarization temperature. Such type of transition was also reported in BNT-NNT-BT [14], BNT- PbTiO_3 [15] and BNT-BKT-BLT [16] ceramics. But, with an increase of frequency, the ceramics show pure ferroelectric behaviors up to their transition temperatures. Such as, phenomenon might be probably due to cation disorder by random distribution of Na^+ , Bi^+ and Ba^{2+} at the A-sites of the lattice [17-19]. There is an existence of three phases of ferroelectric, anti ferroelectric and paraelectric in different temperature ranges.

The dielectric constant has frequency dependence especially, at the low frequencies, which is called the low frequency dielectric dispersion. A strong low-frequency dielectric dispersion has also been observed in NBT which was previously reported [20]. At temperature above T_m and at low frequencies, the dispersion is increased, which is caused by an increase in the electrical conductivity. The dielectric peak appears to broaden with respect to increase in frequency which may be attributed to the structural disorder in the system. The real part of the dielectric constant, describes the “elastic” loss-free reaction of the material to an externally applied ac electric field.

Impedance spectroscopy

The electrical properties of the materials have been investigated using Complex Impedance Spectroscopy (CIS). It is an important tool to analyze the electrical properties of a polycrystalline material in view of its capability of correlating the sample electrical behavior to its microstructure [21].

Figure 4 represents the real part of impedance (Z') as function of frequency. Z' has higher values at lower frequency and decreases up to 100 kHz and attains a constant value beyond that. The pattern shows the sigmoidal variation as a function of frequency in the low frequency region followed by a saturation region in the frequency region. This suggests the presence of mixed nature of polarization behavior in the material.

Figure 5 presents the variation of imaginary part of impedance (Z'') as a function of frequency at different set of temperatures. With the increase of frequency, the real part of impedance (Z') and imaginary part of impedance (Z'') decreases with increase in frequency. At higher frequency side all the curves merge. As the temperature increases the peak has been observed in (Z'') vs frequency curve [22]. The peak shifts towards higher frequency side with increasing temperature showing that the resistance of the bulk material is decreasing. Also, the magnitude of Z'' decreases with increasing frequency. This would imply that dielectric relaxation is temperature dependent and

there is apparently not a single relaxation time. It is evident that with increasing temperature, there is broadening of the peaks and at higher temperatures, the curves appear almost flat [23].

The diffusiveness of Z'' peaks indicate the distribution of relaxation times and the increase in full width at half of the Z'' maxima with the increase of temperature indicate the increase in distribution of relaxation frequency. This distribution of relaxation frequency is attributed to the cationic disorder due to the random occupations of A and B-sites of cations with different ionic radius and valence states. The random distribution causes multiple relaxations that are shown by broadening of Z'' peaks. The appearance of peak in Z'' vs frequency plots indicate some sort of relaxation related to oxygen vacancies present in the studied sample. It has been known that the oxygen vacancies are the main cause of domain wall clamping. This clamping

Composition	Lattice parameters (Å)		c/a	V(Å ³)	Density(gm/Cm ³)		Porosity %
	a	c			ρ_{Exp}	ρ_{cal}	
0.11BNBZT	3.832	3.930	1.025	57.72	5.96	6.21	95

Table 1:

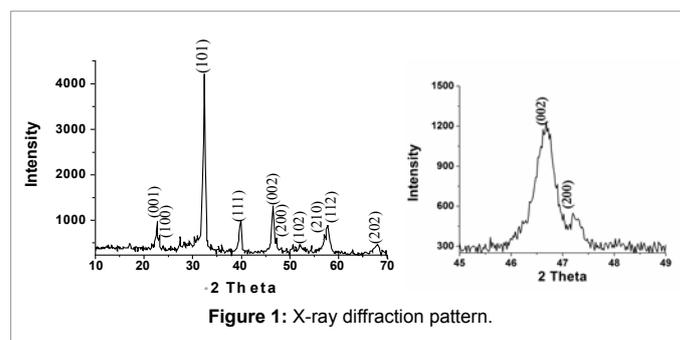


Figure 1: X-ray diffraction pattern.

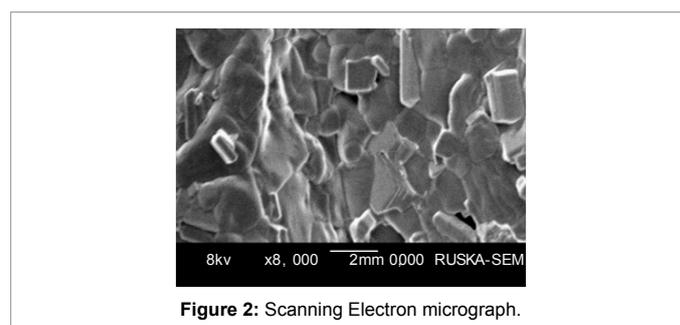


Figure 2: Scanning Electron micrograph.

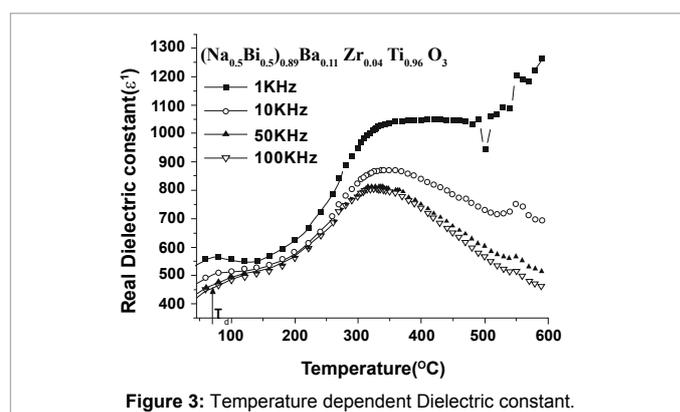


Figure 3: Temperature dependent Dielectric constant.

will restrain the macro-micro domain switching in some degree, which in turn will affect the polarization in the material. Increase in oxygen vacancies will increase the domain wall clamping and decreases the polarization state.

Figure 6 shows the frequency dependences of the real part (Z') and the imaginary part (Z'') of the complex impedance at a temperature 530°C. With increasing frequency, the real part Z' decreases while the imaginary parts Z'' shows a peak. Then, the complex impedance plot of studied material exhibits one impedance semicircle arc. Thus, one impedance arc of the studied material is representative of the bulk properties of the grains (dc resistivity). The center of the impedance semicircular arcs lie below the real axis. Thus, the impedance relaxation can be explained by using Cole-Cole response [24, 25]. The electrical contribution of the grains was introduced by using equivalent circuit as shown in Figure7 and Figure 8 shows the temperature dependent spectra (Nyquist plot) of 0.11BNBZT material. The impedance spectrum is featured by semicircle arcs. The nature of variation of the arcs with temperature and frequency provides various clues of the materials. The impedance spectra are characterized by the appearance of a two semicircle arcs. The presence of single semi circular arc indicated that the electrical process contribution as form a bulk materials (grain interior), which can be modeled as an equivalent circuit comprising of a parallel combination of bulk resistance (R_b) bulk capacitance (C_b) and leaky capacitance (Q_b). Appearance of another semicircular arc near above 450°C indicates the beginning of the intergranular activities (grain boundary effect) within the sample with definite contribution from both bulk and grain boundary effects (Figure 8). The intercept of

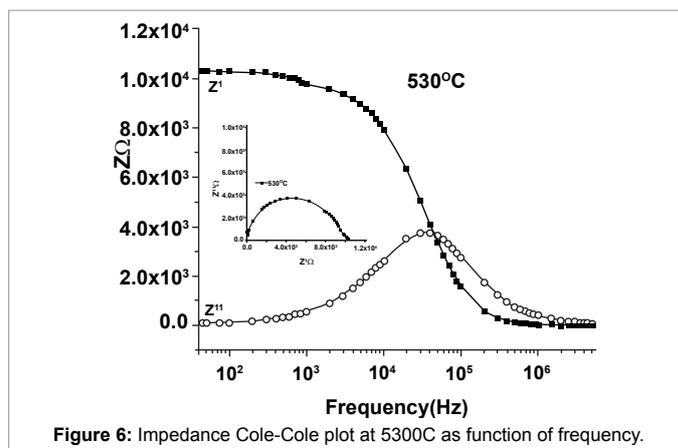


Figure 6: Impedance Cole-Cole plot at 530°C as function of frequency.

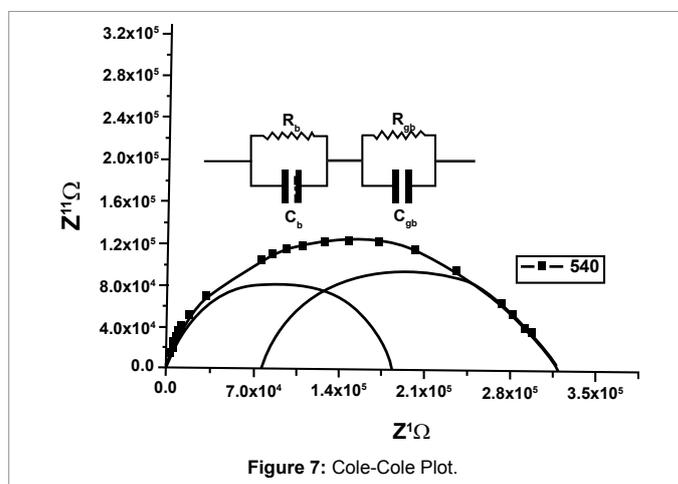


Figure 7: Cole-Cole Plot.

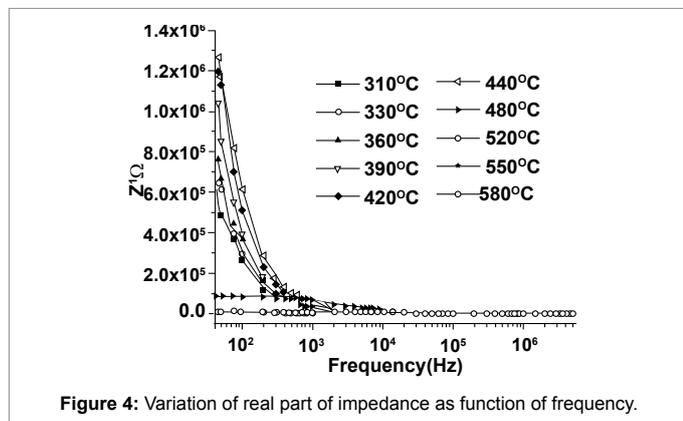


Figure 4: Variation of real part of impedance as function of frequency.

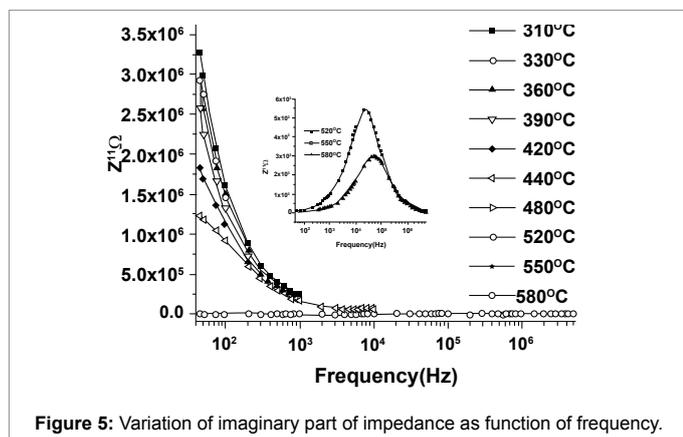


Figure 5: Variation of imaginary part of impedance as function of frequency.

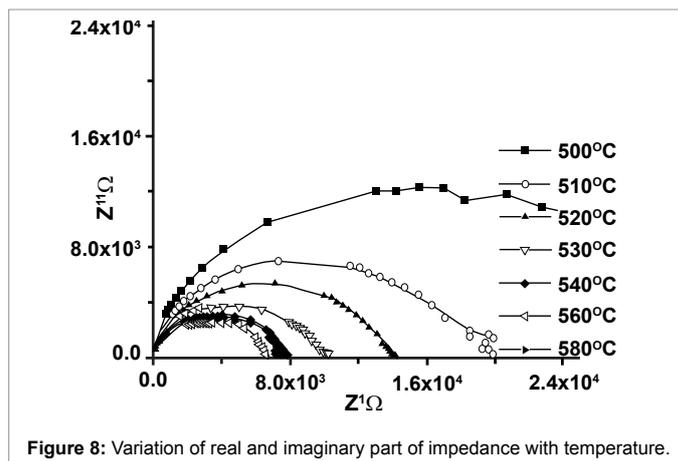


Figure 8: Variation of real and imaginary part of impedance with temperature.

the semicircular arc with real axis (Z') gives us an estimate of the bulk resistance (R_b) and grain boundary resistance (R_{gb}) of the material. It has been observed that the bulk resistance of the materials decreases with increase in temperature showing a typical semiconducting property, i.e., Negative Temperature Coefficient of Resistance (NTCR) behavior [26]. It can be noticed that the center of the semicircle arc lies below the real axis suggesting the relaxation to be of poly dispersive Non-Debye type in sample. This may be due to the presence of distributed elements in the material electrode system.

Conclusion

The solid solution of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.89}\text{Ba}_{0.11}\text{Zr}_{0.04}\text{Ti}_{0.96}\text{O}_3$ (0.11BNBZT) was prepared using high temperature solid state reaction technique. X-ray diffraction studies reveal perovskite structure with tetragonal symmetry. SEM analysis explained the grain morphology on the surface of the material. The temperature dependence of dielectric constant shows relaxor behavior, leading to conclusions that three phases of ferroelectric, anti ferroelectric, and paraelectric states exist in different temperature ranges. The grain and grain boundary contribution have been separated using impedance spectroscopy analysis equivalent circuit to explain electrical phenomena occurring inside the material which revealed the Non-Debye type relaxation present in the material.

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