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Effect of Space Charge Polarization and Dielectric Relaxation in Lead-Free Relaxor Ferroelectric

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Abstract

High permittivity dielectrics ceramics are often used for commercial multilayer ceramic capacitors, actuators applications, and are highly promising materials for dynamic random access memory (DRAM) and microelectromechanical systems (MEMS) applications due to its very stable, high insulating characteristic against voltage. Many studies have been conducted to enhance the above mentioned properties and most of the improvements have been achieved by doping with a small quantity of additives with some ferroelectric perovskite lead and lead free compounds. Especially, $Na_{0.5}$ $Bi_{0.5}$ TiO_3 (NBT) is one of the promising materials for environmental friendly application in compare to lead based composition. Extensive studies have been made on NBT based relaxor ferroelectric ceramic with a simultaneous substitution of $Ba^{2+}$and Zr^{4+} at A-site and B-site having led to the establishment and acceptance of the space charge polarization on the basis of explaining their structure and dielectric properties. A Polycrystalline $0.92(Bi_{0.5}Na_{0.5})Ba_{0.08}Z_{0.04}T_{0.96}O_3$ (0.08BNBZT) material has been prepared by conventional solid state reaction method. X-ray diffraction pattern reveals a tetragonal structure having lattice parameters. The diffuseness parameter γ =1.59 has been established the relaxor nature. The dielectric relaxation obeyed the Vogel-Fulcher relation. Impedance spectroscopy is a convenient tool to evaluate the contribution of electrical components such as grain (g) (bulk), grain–boundary (g_b) or polarization phenomena, which influences the device properties of a material. Conductivity studies in the materials obey the Jonscher's power Law in frequency (45Hz -5MHz), temperature (35^0C-600^0C) range.

Keywords: X-ray Diffraction, relaxor ferroelectrics, Space charge, Impedance, conductivity.

Introduction

Since 1970s, there has been a growing interest for mixed composition of normal and relaxor ferroelectrics, because they exhibit very high dielectric permittivities, high coupling coefficients and high piezoelectric coefficients. Relaxor ferroelectrics are crystalline materials and have been widely studied in the recent years due to their remarkable properties and wide prospects of practical applications. One among them is PMN. Lead-based perovskite relaxors such as PMN have been emerged as one of the most widely studied and technologically important classes of ferroelectric oxides [1-4]. One characteristic feature that is shared by all relaxor ferroelectrics, which exhibit a diffuse and frequency dependent maximum in their relative permittivity, is the occurrence of some type of localized disorder in their crystal structures. In lead free materials Sodium Bismuth Titanate $Na_{0.5}$ $Bi_{0.5}$ TiO_3 (NBT) is currently considered as potential ferroelectric material [5]. The NBT system is known to be a typical relaxor ferroelectric with A-site complex [6]. The material BNBZT has been investigated in terms of variation in their dielectric and piezoelectric properties due to various dopants and the formation of solid solution with other compounds, the studies on grain growth, impedance and conductivity studies has not studied much. NBT modified at A- and B-sites with barium at A-site and Zirconium at B-site, i.e., $(Bi_{0.5}Na_{0.5})_{0.92}Ba_{0.08}Zr_{0.04}Ti_{0.96}O_3$ (0.08BNBZT), which is just above the MPB region and it is one of the promising candidates for dynamic random access memory, decoupling capacitors, and dielectric field tunable elements for high frequency device applications. In view of the important properties exhibited by the material and also conductivity impedance spectroscopy studies has not been reported in the literature survey, an attempt has been made to study on structural and electrical properties of $(Bi_{0.5}Na_{0.5})_{0.92}Ba_{0.08}Zr_{0.04}Ti_{0.96}O_3$ (0.08BNBZT).

Experimental

Polycrystalline $(Bi_{0.5}Na_{0.5})_{0.92}Ba_{0.08}Zr_{0.04}Ti_{0.96}O_3$ (0.08BNBZT) material has been synthesized by solid state reaction method. Initially, mixture containing raw materials has been calcined at 850^0C for 3 hrs. A homogenous, single phase of the calcined powder has been confirmed via x-ray powder diffraction (XRD) technique and sintered at 1180^0C/3hrs. The average grain size of sintered ceramic has been measured through scanning electron microscopy (SEM). Silver electrodes were printed on opposite disc faces and were cured at 600^0C for 15min. Electrical measurements has been carried out over a frequency (45Hz -5MHz) and temperature (35^0C-600^0C) range by using Hioki LCR meter.

Results and discussion

X-ray Diffraction

Fig. 1 shows the XRD pattern of 0.08BNBZT ceramic and insert figure show microstructure. The pattern shows that the composition is a single phase with tetragonal perovskite structure without the evidence of additional phases. Where as XRD patterns with high Ba^{2+} concentration show strong (200) peak splitting which is

indicative of the tetragonal phase and at low concentration of Ba^{2+} show (200) peak transformed to a single peak which suggests rhombohedral symmetry. The reflection at 47^0, which is assigned as (002), (200), confirmed to be a tetragonal phase [7]. The bulk density of sintered material has been measured by the Archimedes method; the experimental density achieved is 95% to that of theoretical density. The values of lattice parameters are a=b=3.79 Å, c=3.88 Å The grain size of the sample has been calculated from linear intercept method. The observed average grain size from micrograph is 2.91 μm.

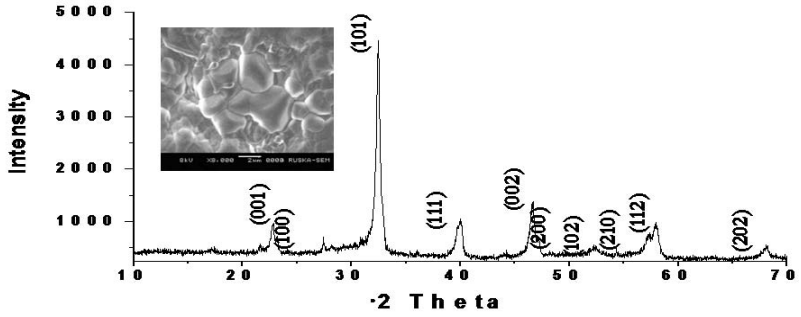

Figure 1: XRD pattern of 0.08BNBZT (insert fig Microstructure).

Dielectric Studies

Fig.2 shows a broad maximum (diffuse phase transition, denoted as DPT) and strong frequency dispersion indicating the relaxor behviour of 0.08BNBZT. It is observed that the temperature T_m at which the permittivity is maximum shifted to higher temperature side, while ε_{max} decreased as frequency increases

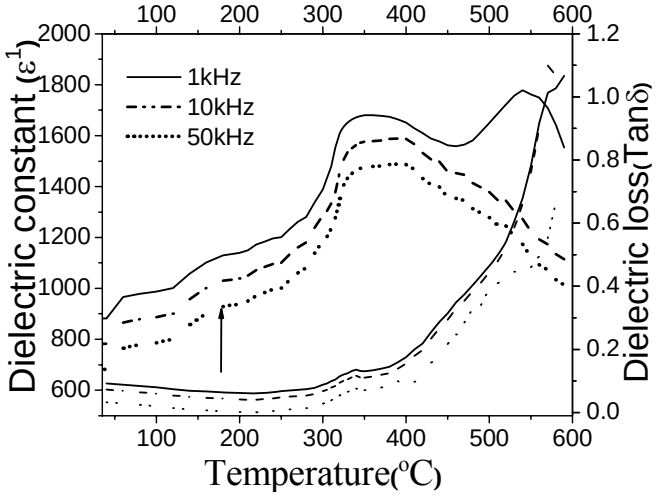

Figure 2: Temperature Dependence of electrical permittivity of 0.08BNBZT at various frequencies.

A shoulder type curve has been observed in the low temperature region at about 200^0C, ascribed to ferro-anti ferroelectric transition. The curve becomes much pronounced with increase in barium and zirconium content. Broad peak near 350^0C depends on the barium concentration. The broad response of the peak indicates the diffused nature of phase transition in the material. The broadening of the dielectric peaks has been attributed to the disorder in the arrangements of barium and zirconium ions, leading to a microscopic heterogeneity in the composition and thus a distribution of different local curie points [8]. These results indicate that substitution of barium and zirconium brings interesting changes in dielectric and ferroelectric properties of the material.

Defect induced dielectric relaxation would be directly related to the concentration of defects. In the present material, the defects could be related to oxygen vacancies. Which is defined by Kroger –Vink notation [9]. Generally, the dielectric properties of ceramics are arised due to intra-grain, inter-grain electrode process. The motion of charges could occur in a variety of fashions Viz.., charge displacement, dipole reorientation, space charge formation etc... Contribution to the dielectric constant from the oxygen vacancy induced dielectric relaxation is significantly larger at high temperatures rather than that at lower temperatures. At high temperature, there is an insufficient energy and the contribution of the oxygen vacancy induced dielectric relaxation becomes significant.

In order to examine the diffuse phase transition and relaxor behaviour in the material more closely, the relation between ε and T above T_m can be expressed by modified Curie –Weiss law proposed by Martirena and Burfoot[10].

$$\frac{1}{\varepsilon_r(\omega,T)} = \frac{1}{\varepsilon_m(\omega)}1 + \left[\frac{[T - T_m(\omega)]^\gamma}{2\delta_\gamma^2}\right]$$

where, ω is the angular frequency, T_m is the temperature at maximum dielectric permittivity ε_m, δ_γ, γ are the diffuseness parameter and critical exponent respectively. The parameter γ ($1 \le \gamma \le 2$) represents the degree of dielectric relaxation of a relaxor. Linear regression analysis gives γ=1.59 at 1kHz (insert Fig.3), which clearly indicates the diffuse phase transition in the material and is found to increase with increase in frequency. The non-equality of phase transition temperature obtained from ε-T and tanδ-T measurement also confirms the diffuse phase transition.

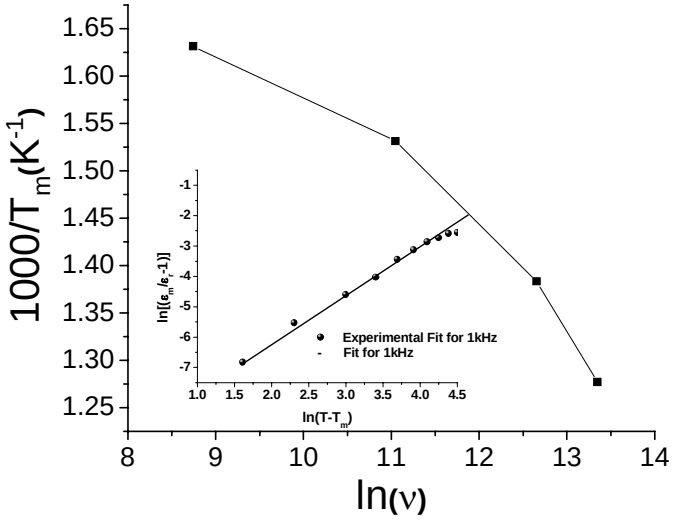

Figure 3: Vogel-Fulcher relation.

Fig 3 shows the temperature dependence ($1/T_m$) of relaxation frequency ln(ν). A linear least square fit of dielectric data as in equation

$$\nu = \nu_0 \exp\left[\frac{-E_a}{K_B(T_m - T_f}\right]$$

Where ν, ν_o, K_B and E_a are respectively the operating frequency, pre-exponential factor, Boltzmann constant and the activation energy. T_f is the freezing frequency. T_f is regarded as the temperature where the dynamic reorientation of the dipolar cluster polarization can no longer be thermally activated.

Calculated values are $T_f = 158^0$C, E_a=0.1120eV and $\nu_o = 1.26 \times 10^8$ Hz. These values are well matched with reported values [11, 12]. The value of ν_o is found to lie in the optical frequency range of lattice vibration. An excellent fit of the Vogel-Fulcher law with the experimental data constitutes strong evidence for a static freezing temperature of thermally activated polarization fluctuations in 0.08BNBZT. Therefore the dielectric relaxation in the present material may be considered as analogous to that of dipolar glass with polarization fluctuations above a static freezing temperature [13].

Impedance studies

In Fig. 4, the insert fig shows the variation real and imaginary parts of Z^1 and Z^{11} respectively of impedance at various frequencies corresponding to the temperatures, 520^0C, 550^0C, 580^0C.The magnitude of Z^1 decreases as a function of frequency with increasing temperature and merges above10kHz for all temperatures which is attributed to the release of space charges. These curves also display a single relaxation process, indicating an increase in ac conductivity upon increasing temperature and frequency.

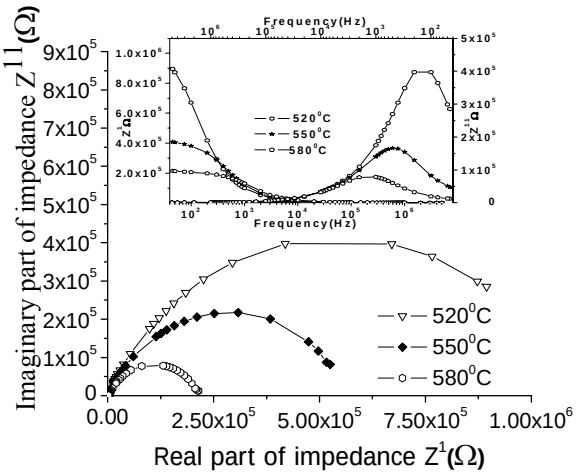

Figure 4: Cole –Cole Plots.

From the complex impedance plot at various temperatures it is observed that as temperature increases two semicircles obtained with different values of resistance of grain (Rg) and grain boundary (Rgb) indicating the increase in conductivity of the material. Hence the grain and grain boundary effects could be separated at these temperatures. Further more, it can be seen that the cole-cole plots represents a non-debye type relaxation. This may be due to the presence of distributed elements in the material–electrode system. It is evident from Fig.5 that there is a decrease in the value of R_g, which is associated with increase in conductivity with increase in temperature. Also, a decrease in the R_{gb} values with increment of temperature suggests the lowering of the barrier towards the mobility of charge carriers aiding electrical conduction at higher temperature [14].

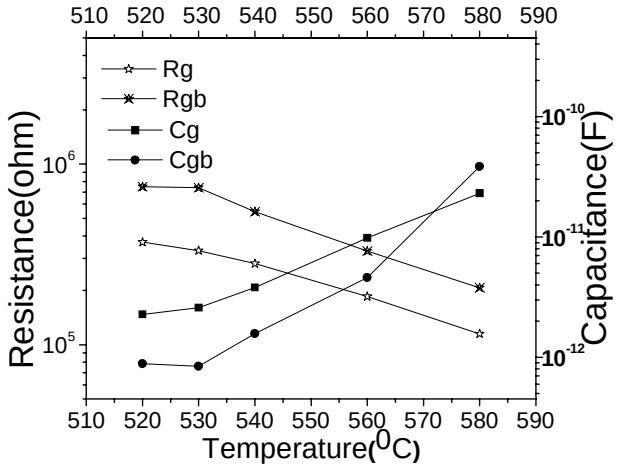

Figure 5: Temperature dependence of Rg, Rgb, Cg and Cgb.

Conductivity studies

In the present material (Fig.6), the ac conductivity is found to increase with increase in frequency suggesting the bound carriers trapped in the sample. The slowly varying conductivity at lower frequencies corresponds to space charge polarization [15]. Also, a change in slope has been observed at a particular frequency is related to ion hopping frequency [16-18]. This trend representing that conductivity in the ceramic obey the Jonscher law [19], $\sigma(\omega) = \sigma_{dc} + A\omega^n$, where σ_{dc} is frequency independent conductivity, the coefficient A and the frequency exponent n are thermally activated material dependent quantities. The term $A\omega^n$ contains ac dependence and characterizes all dispersion phenomenona.

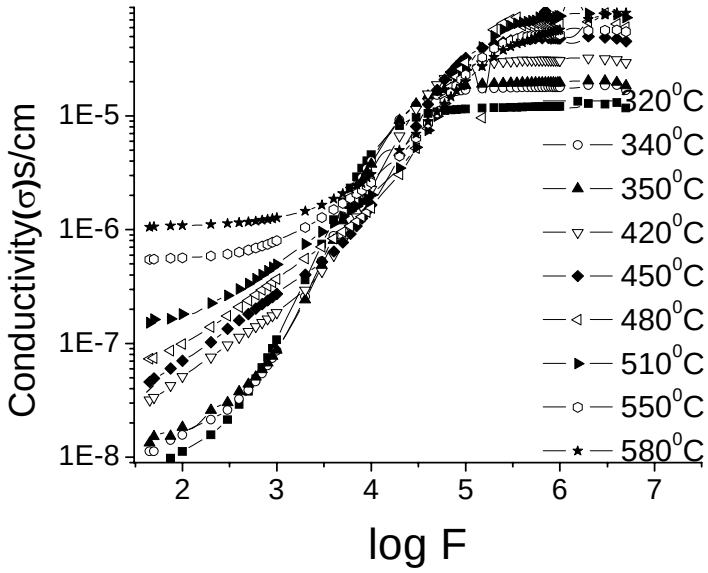

Figure 6: Dependence of ac conductivity on frequency at various temperatures.

In low temperature region (298^0C -398^0C), the conductivity showed dispersion (Fig.7), where as, curves are found to merge at higher temperature region, revealing predominance of an onset of intrinsic conductivity mechanism. The conductivity is found to obey the arrhenius behaviour. The activation energies of ac and dc conductivity in the material have been evaluated and are given in table.1.

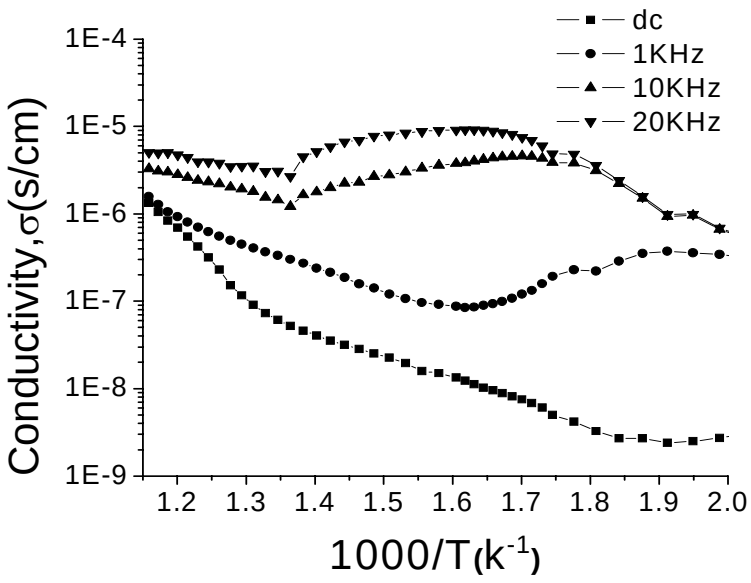

Figure 7: Dependence of ac conductivity with inverse of temperature at various frequencies.

Table 1

Temperature Range (^{O}C)	Conductivity Activation Energy (eV) ac dc 1kHz 10kHz 20kHz
330-350	0.25 0.11 0.20 0.18
380-470	0.22 0.23 0.14 0.13
510-570	0.69 0.27 0.16 0.09

From the calculated values, the activation energy of dc conductivity is found to be more than that of ac conductivity. The observed low values of activation energies may be due to the carrier transport through hopping between localized states in disordered manner.

Conclusions

Polycrystalline material 0.08BNBZT, has been prepared by a high temperature solid state reaction technique, and found to be single phase with perovskite type tetragonal structure which is just above MPB. Effect of barium and zirconium lead to a broad response of the peak indicates the diffused nature of phase transition and a change in dielectric and ferroelectric properties of the material. Impedance analyses indicated the presence of grain and grain boundary effects. The dielectric relaxation in this system has been found to be of non-debye type. The ac conductivity studies have been found to obey the universal power law.

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