



## Structural, Microstructural, Dielectric and Transport Properties of Barium Bismuth Niobate

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### ABSTRACT

Bismuth layer-structured ferroelectric (BLSF) compound barium bismuth niobate (BBN) with a chemical formula  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  has been prepared using a solid-state reaction technique. Preliminary structural and microstructural properties of the compound were investigated through X-ray diffraction technique and SEM-microphotographs respectively. Its dielectric properties have been analyzed within a wide range of temperature and frequency. Relative dielectric constant ( $\epsilon_r$ ) of the material is found to be higher at a lower frequency suggesting a normal behavior of ferroelectrics. Studies of temperature-frequency dependence of dielectric studies show broadened anomaly (with shift in peak) suggesting the occurrence of diffused-relaxor type of ferroelectric phase transition well above the room temperature. Temperature dependence of the ac-conductivity at selected frequencies and the values of activation energies in the different regions suggest that the conduction process in the material is mainly due to singly ionized oxygen vacancies in the ferroelectric region.

**Key words:** Bismuth layer-structured ferroelectric (BLSF), BBN, XRD, SEM, dielectric properties, relaxor

### INTRODUCTION

As lead-free piezoelectric and ferroelectric materials, bismuth layer-structured ferroelectric (BLSF) compounds have attained considerable importance due to their potential applications in research and industries in the form of multilayer capacitors, high temperature sensor, non-volatile random access memory (NVRAM), etc [1-6]. These are the oxides of Aurivillius family with a general formula  $(\text{Bi}_2\text{O}_2)(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})$ , where the A-site is occupied by lower valence larger size cations (such as,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  or  $\text{Pb}^{2+}$ ), the B-site by higher valence smaller size cations (such as,  $\text{Ta}^{5+}$ ,  $\text{Nb}^{5+}$  or  $\text{W}^{6+}$ ) and 'n' the number of perovskite  $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$  unit cells intergrowth between  $(\text{Bi}_2\text{O}_2)^{2+}$  layers [7-9]. The perovskite blocks offer large possibilities in terms of compositional flexibility that allows various combinations of cations A and B. Selective dopants may be added to the Aurivillius phases to enhance or decrease certain material properties. From the literature survey we found that most of the works reported on the ferroelectric materials are confined to barium titanate ( $\text{BaTiO}_3$ ) and lead zirconate titanate (PZT) based compounds [10-11]. But very little attention has been made on ferroelectric materials of Aurivillius family. This paper reports on the structural, microstructural, dielectric and transport properties of the lead-free ferroelectric compound barium bismuth niobate (BBN).

### EXPERIMENT

The polycrystalline sample of barium bismuth niobate  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  of bismuth layer-structured ferroelectric (BLSF) family was prepared by a solid-state reaction technique using high purity (99.9%) ingredients;  $\text{BaCO}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  (all from M/S Loba Chemie, Inc. Bombay, India) in suitable stoichiometry. To compensate bismuth-loss at high calcination and sintering temperatures, extra 3% wt of  $\text{Bi}_2\text{O}_3$  was added to the mixture. The ingredients were, first, mixed in dry air and then, in alcohol medium and finally, calcined at an optimized (repeated heating) temperature of  $950^\circ\text{C}$  for 10h. Using polyvinyl alcohol (PVA) as binder, the calcined powder was converted into pellets at  $4 \times 10^6 \text{ N/m}^2$  pressure. These pellets were sintered at temperature of  $1050^\circ\text{C}$  for 10 h so as to get maximum density (95% of theoretical density).

The preliminary structural analysis of calcined powders was performed at room temperature using data obtained from X-ray diffractometer (Rigaku Miniflex, Japan) with  $\text{CuK}_\alpha$  radiation ( $\lambda=1.5405 \text{ \AA}$ ) in a wide range of Bragg's angles  $2\theta$  ( $20^\circ \leq 2\theta \leq 80^\circ$ ) at the scanning rate of  $3^\circ/\text{min}$ . Surface morphology of the surfaces of BBN-sample was carried out using microphotographs obtained through scanning electron microscope (SEM, JEOL JSM-5800).

For analysis of electrical properties of the material, smooth flat surfaces of the pellet were painted with high-purity air-drying silver paint, and then dried at  $150^\circ\text{C}$  for 4 h. Now, using phase sensitive multimeter (PSM; Model 1735) along with its accessories, different electrical data were recorded within a wide range of temperatures and frequencies, and then various electrical parameters were analyzed.

## RESULTS AND DISCUSSION

### Structural and Microstructural Analysis

Fig.1 shows the XRD-diffraction pattern and SEM-microphotographs of barium bismuth niobate (BBN) at room temperature. Most of the XRD-reflection peaks were indexed in different crystal system and unit cell configurations using a computer program 'POWDMULT' [12]. With the best agreement between observed (obs.) and calculated (cal.) d-spacing (i.e.,  $\sum \Delta d = d_{\text{obs}} - d_{\text{cal}} = \text{minimum}$ ), the material is found to be a single phase in tetragonal crystal system with the lattice parameters:  $a = 5.6017$  (24) and  $c = 26.1442$  (24). The crystallite size of the sample was roughly estimated through broadening of few XRD peaks in a wide  $2\theta$  range using Scherrer's equation [13];  $D = K\lambda / (\beta_{1/2} \cos \theta_{\text{hkl}})$ , where  $K = 0.89$ ,  $\lambda = 1.5405 \text{ \AA}$  and  $\beta_{1/2}$  = peak width of the reflection at half intensity. Its crystallite size was found to be in nanometer range (<50nm). SEM-microphotograph of the surfaces of sintered BBN sample exhibits almost uniform densely packed and uniformly distributed grains separated by grain boundaries. The average grain size estimated through linear intercept method is found to be 39 nm.

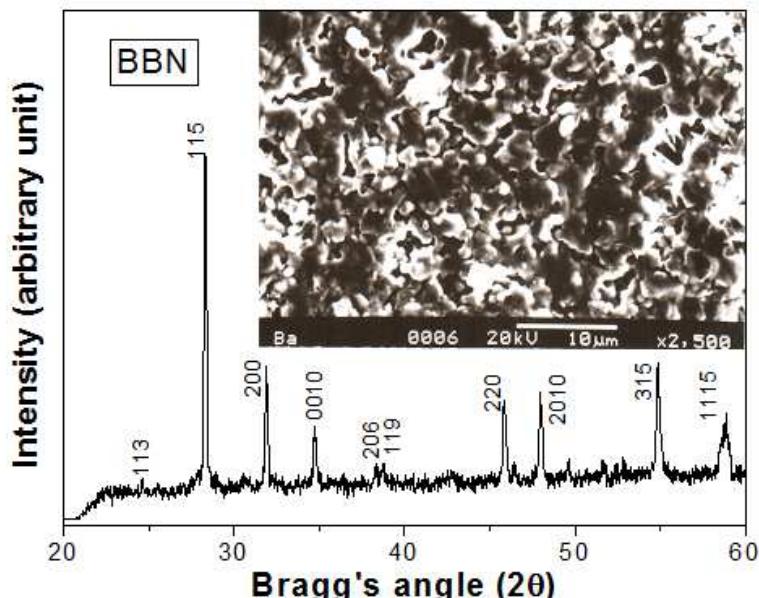


Fig.1 XRD-diffraction pattern and SEM-microphotograph of  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  at room temperature

### Dielectric Analysis

Temperature dependence of relative dielectric constant ( $\epsilon_r$ ) and tangent loss ( $\tan\delta$ ) of  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  sample at  $10^3$ ,  $10^4$ ,  $10^5$  and  $10^6$  Hz are shown in Fig.2. The value of  $\epsilon_r$  is found to decrease with the increase in frequency which indicates about the typical ferroelectric behavior of the material. The higher value of  $\epsilon_r$  at lower frequencies exhibits the simultaneous presence of all the types of polarizations, (i.e., space charge, orientation, ionic and electronic polarization) that decreases with the increase in frequency [14-15]. However, due to experimental limitations we could not proceed above 1 MHz. With the increase in temperature,  $\epsilon_r$  gradually increases up to a maximum value  $\epsilon_{\text{max}}$  at a temperature (called transition temperature ( $T_c$ )) where transition takes place between ferroelectric to paraelectric phase. Also, the value of  $T_c$  is found to increase with the increase in frequency which suggests occurrence of the relaxor behavior of the material [16-17].

The variation of tangent loss ( $\tan\delta$ ) with temperature at selected frequencies exhibits a very low value of  $\tan\delta$  at room temperature. It remains low up to a high temperature beyond which it shows a significant increase mainly due to oxygen vacancies. At higher temperatures, oxygen vacancy increases, gets activated and becomes more mobile which increases the polarization. It is also observed that  $\tan\delta$  decreases with the increase in frequency which suggests about the decrease in polarization with the increase in frequency [18].

Diffuseness of the dielectric peaks has been analyzed through empirical formula [19]:  $1/\epsilon_r - 1/\epsilon_{\max} = C (T - T_c)^\gamma$ , where exponent  $\gamma$  gives the value of degree of diffuseness. Fig.3 shows the variation of  $(1/\epsilon_r - 1/\epsilon_{\max})$  with  $(T - T_c)$  and using linear fit method, the value of  $\gamma$  is estimated to be 1.18 at  $10^5$  Hz and 1.73 at  $10^6$  Hz. It suggests about the diffuse type phase transition suggesting the existence of relaxation process in the material.

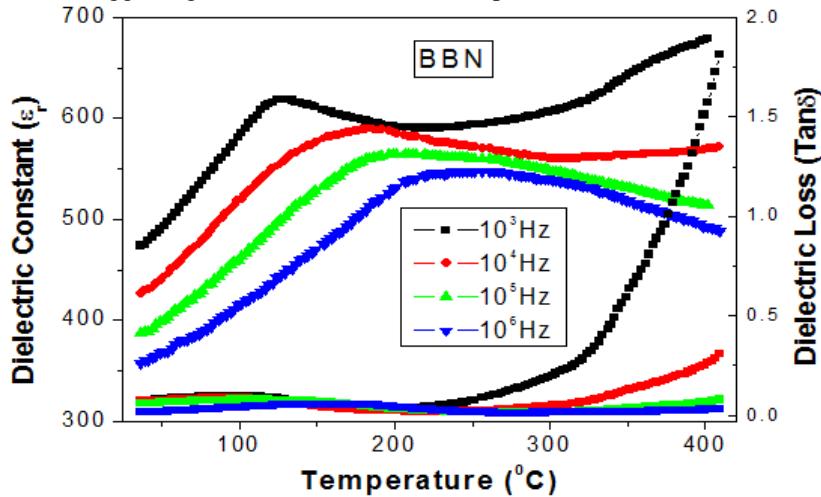


Fig.2 Temperature dependence of dielectric constant ( $\epsilon_r$ ) and tangent loss ( $\tan\delta$ ) of  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  at  $10^3$ ,  $10^4$ ,  $10^5$  and  $10^6$  Hz

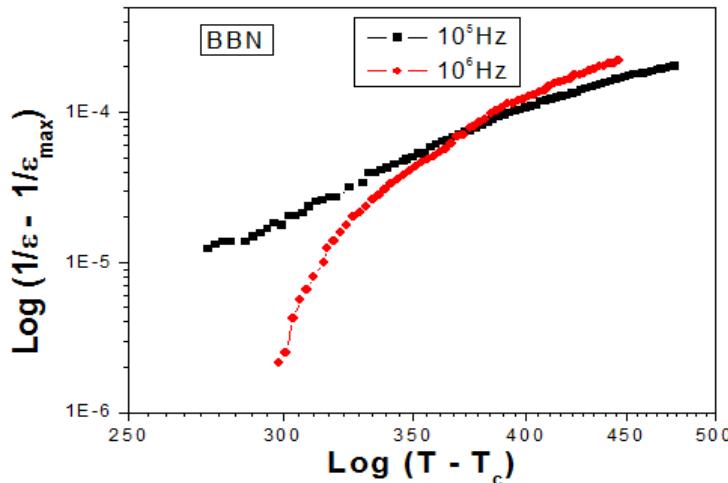


Fig.3 Variation of  $\log (1/\epsilon_r - 1/\epsilon_{\max})$  with  $\log (T - T_c)$  of  $\text{BaBi}_2\text{Nb}_2\text{O}_9$

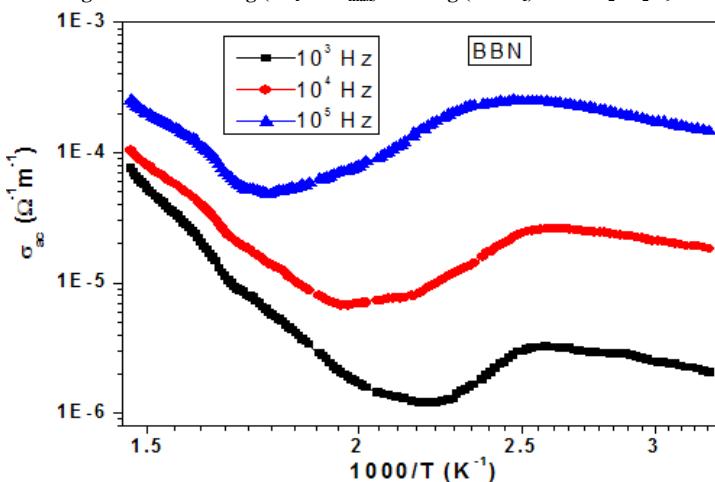


Fig.4 Temperature dependence of ac-conductivity ( $\sigma_{ac}$ ) of  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  at  $10^3$ ,  $10^4$ ,  $10^5$  Hz

#### AC Conductivity Analysis

The AC conductivity ( $\sigma_{ac}$ ) of barium bismuth niobate has been estimated at different temperatures using formula;  $\sigma_{ac} = \omega\epsilon_0\epsilon_r \tan\delta$ , where  $\omega$  is the angular frequency and  $\epsilon_0$  is the permittivity of free space. Fig.4 shows the temperature dependence of  $\sigma_{ac}$  at selected frequencies where different slope changes appear in different regions indicating multiple activation process with different energies.

With the increase in temperature, it exhibits a linear variation in the low-temperature region supporting the existence of thermally activated transport properties in the materials. But at higher temperatures,  $\sigma_{ac}$  shows an increasing behavior mainly due to the increase in polarizability. At very high temperatures, its values almost fall on a straight line along with the merging tendency of curves at all the frequencies which suggests about the typical behavior of dc component. The ac-conductivity is very much related to activation energy ( $E_a$ ) through the Arrhenius equation;  $\sigma_{ac} = \sigma_0 \exp(-E_a/K_B T)$ ; where  $\sigma_0$  is the pre-exponential term and  $K_B$  the Boltzmann's constant. The value of activation energy of the BBN sample is found to be less than 1 eV. It suggests about the ferroelectric behavior of the material which may be due to the presence of singly ionized oxygen vacancies in the conduction process [20-22].

## CONCLUSION

Barium bismuth niobate ( $\text{BaBi}_2\text{Nb}_2\text{O}_9$ ) was prepared through a high-temperature solid-state reaction technique. XRD analysis confirms its formation in single phase tetragonal crystal system. Crystallite size of the compound is found to be in nanometer range. Microstructural analysis through SEM-microphotographs indicates the formation of almost uniform and densely packed grains separated by grain boundaries. Dielectric constant ( $\epsilon_r$ ) of the sample is found to be high with the ferro-para phase transition well above the room temperature. The transition temperature ( $T_c$ ) is found to increase with the increase in frequency which suggests about its relaxor behavior. The value of degree of diffuseness  $\gamma$  indicates diffuse type phase transition in the material. The tangent loss ( $\tan\delta$ ) of the sample is found to be low at lower temperature but exhibits a significant rise at high temperatures. Both the dielectric constant ( $\epsilon_r$ ) and tangent loss ( $\tan\delta$ ) of the sample exhibit decreasing trends with the increase in frequency. AC-conductivity of the compound is found to increase with the increase in temperature. The value of activation energy shows that the conduction process in the material is due to singly ionized oxygen vacancies in the ferroelectric region.

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