Investigation of Impedance and Electric Modulus Properties of Bismuth Layer-Structured Compound Barium Bismuth Niobate

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Abstract: - **Barium bismuth niobate ($BaBi_2Nb_2O_9$: BBN), the ferroelectric compound of Aurivillius family, has been prepared through high-temperature mixed-oxide method. Using complex impedance spectroscopy (CIS) technique, real and imaginary parts of impedance (Z) and electric modulus (M) of the material were investigated within wide range of temperatures and frequencies. Impedance analysis indicates the presence of mostly bulk resistive (grain) contributions in the material which exhibits a decreasing tendency with the increase in temperature. It indicates negative temperature coefficient of resistance (NTCR) type behaviour of the material. Complex modulus plots indicate the presence of grain (bulk) along with grain boundary contributions in the material. It also supports the NTCR type behaviour of the material. Both the complex impedance and complex modulus plots indicate the presence of non-Debye type of relaxation in the material.**

Keywords: Aurivillius family; BBN; CIS; Electric impedance: Electric modulus

I. INTRODUCTION

Lead-free oxides of Aurivillius family with general formula $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})$, have come into prominence as an excellent piezoelectric and ferroelectric materials with their potential applications in research and industries [1-3]. A-site is occupied by lower valence larger size cations (K^+, Na^+, Ba^{2+}, Ca^{2+}, Sr^{2+} or Pb^{2+}), B-site by higher valence smaller size cations (Ta^{5+}, Nb^{5+} or W^{6+}) and integer 'n' is the number of perovskite $(A_{n-1}B_nO_{3n+1})^{2-}$ unit cells intergrowth between $(Bi_2O_2)^{2+}$ layers [4-6]. The behaviour of Aurivillius phases may be modified with compositional flexibility of perovskite blocks that allows various combinations of cations A and B aiming to enhance or decrease certain material properties as per the requirement.

The literature survey of ferroelectric materials reveals that most of the works reported in this field are confined to the electrical and electromechanical properties of barium titanate ($BaTiO_3$) and lead zirconate titanate (PZT) [7] based compounds. Very little attention has been made on the other ferroelectric families. Particularly, no systematic work has been reported on complex impedance behaviour of barium bismuth niobate. This paper reports on the temperature-frequency dependence of impedance and electric modulus properties of barium bismuth niobate (BBN) using complex impedance spectroscopy (CIS) technique.

II. BACKGROUND OF CIS

Complex impedance spectroscopy (CIS) [8] is a useful experimental technique to investigate micro-structural and electrical properties of polycrystalline electro-ceramics. This CIS-technique is very useful in analyzing real and imaginary parts of complex electrical parameters so as to get the true picture of material properties. It enables us to resolve the relaxation contributions, like, bulk effects, grain boundaries and electrode interface effects in the frequency domain of materials.

In complex impedance spectroscopy, frequency dependent behaviour of the materials may be expressed in terms of complex impedance (Z^*), complex electric modulus (M^*), complex dielectric constant (ε^*) and tangent loss ($\tan\delta$), which are related to each other through the relations: $Z^* = Z' - jZ''$, $M^* = 1/\varepsilon^*(\omega) = M' + jM''$, $\varepsilon^* = \varepsilon' - j\varepsilon''$ and $\tan\delta = \varepsilon''/\varepsilon'$. Where ($Z'$, M', ε') and (Z'', M'', ε'') are the real and imaginary components of impedance, modulus and permittivity respectively, $j = \sqrt{-1}$ the imaginary factor, C_0 = vacuum capacitance.

III. EXPERIMENTAL DETAILS

Bismuth layer-structured ferroelectric (BLSF) compound Barium bismuth niobate ($BaBi_2Nb_2O_9$) has been prepared through high-temperature mixed-oxide method using ingredients: $BaCO_3$, Bi_2O_3 and Nb_2O_5 (99.9% purity, M/S Loba Chemie, Inc. Bombay, India) in suitable stoichiometry. To compensate bismuth-loss at high calcination and sintering temperatures, extra 5% wt of Bi_2O_3 was added to the mixture. The ingredients were mixed in an

alcohol medium and then calcined at an optimized temperature of 950°C for 10 hour. Using polyvinyl alcohol (PVA) as binder, the calcined powder was converted into pellets at 4×10^6 N/m^2 pressure. These pellets were sintered at an optimized temperature of 1050°C for 10 hour so as to get maximum density (97% of theoretical density).
For analysis of electrical properties of the material, smooth flat surfaces of the pellets were painted with high purity air-drying silver paint and then dried at 150°C for 4 hr. Using Phase Sensitive Multimeter (PSM; Model 1735) along with its accessories, different electrical data were recorded within wide range of temperatures and frequencies and then various electrical parameters were analyzed.

IV. RESULTS AND DISCUSSION

4.1. Complex impedance analysis

The variation of real part of impedance (Z') of barium bismuth niobate (BBN) with frequency at different temperatures is shown in Fig-1. At higher temperatures, Z' is found to decrease with the increase in temperature and achieves a very low value at higher temperatures. It exhibits low frequency dispersion mainly due to polarization and then monotonous decrease with the increase in frequency. This shows increase in ac-conductivity of the material with the increase in temperature as well as frequency. At higher frequencies, Z' achieves nearly a very low constant value and becomes almost independent of frequency as well as temperature. At lower frequencies, Z' decreases with the increase in frequency supporting a slow dynamic relaxation process in the materials probably due to space charge that gets released at higher frequencies [9-11].

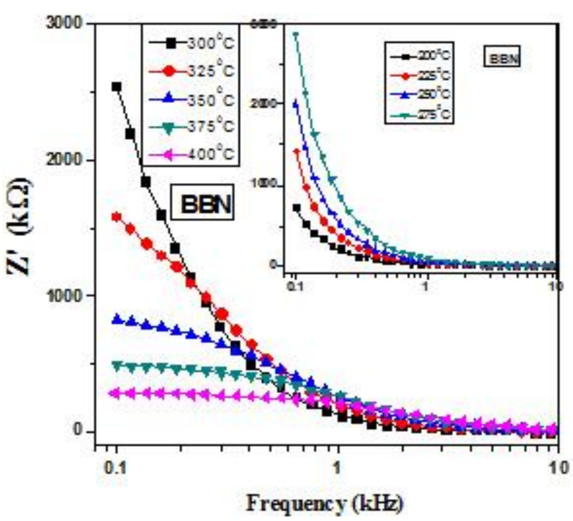

Fig-1: Variation of Z' of $BaBi_2Nb_2O_9$ with frequency at different temperatures

Fig-2 shows the variation of imaginary part of impedance (Z") of the BBN-sample with frequency at different temperatures. The value of Z" is found to decrease with increase in temperature as well as frequency and achieves a very low constant value at higher frequencies where it becomes independent of both frequency and temperature. At lower frequencies some peaks are observed exhibiting a shifting tendency towards higher frequencies with the increase in temperature. The peak height gradually decreases with the increase in temperature and they finally merge in the high frequency region. It suggests about thermally activated relaxation process in the materials and indicates reduction in bulk resistance with the increase in temperature. It may be due to presence of space charge polarization at lower frequencies and its elimination at higher frequencies. The observed asymmetric broadening of peaks indicates about the presence of some electrical processes in the materials with spread of relaxation time. This may be due to the presence of immobile species at low temperature and defects at higher temperatures [12].

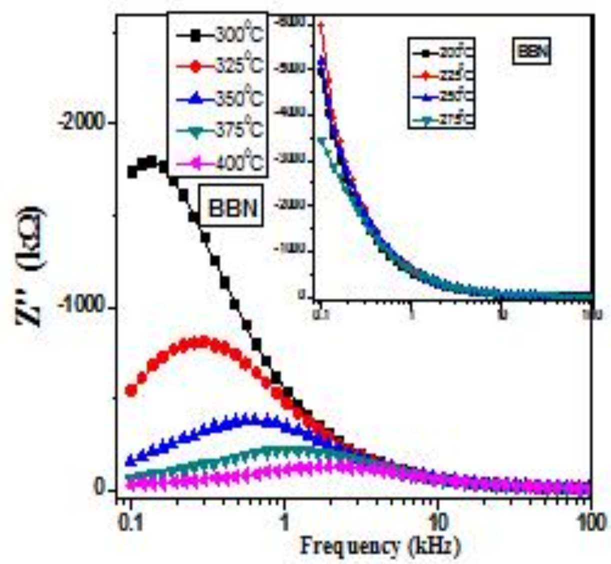

Fig-2: Variation of Z" of $BaBi_2Nb_2O_9$ with frequency at different temperatures

Fig-3 shows the complex impedance spectrum (Z'~Z"; Nyquist plot) of $BaBi_2Nb_2O_9$ compound at different temperatures. Appearance of semicircular arc at different temperature shows that electrical properties in the material arise mainly due to the contribution of bulk effect. At lower temperatures only single arcs are obtained which are transformed into semicircles at higher temperatures. The formation of full, partial or no semicircles depends on the strength of relaxation and also experimentally available frequency range [13]. Electrical process taking place within

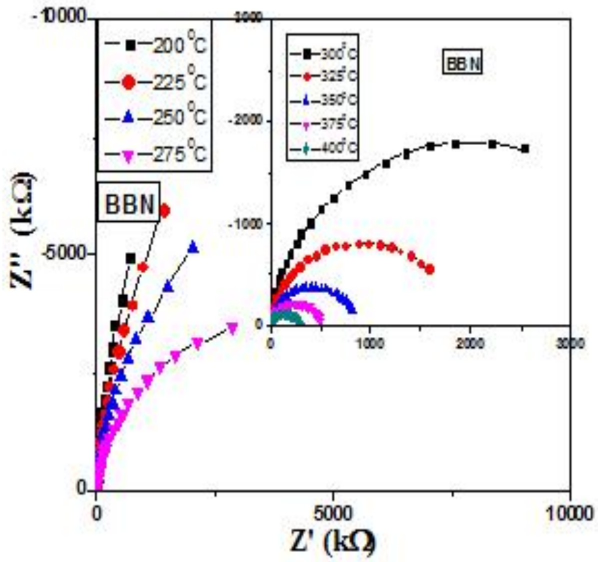

Fig-3: Complex impedance plots (Z'~Z'') of $BaBi_2Nb_2O_9$

the materials may be modelled (as an RC circuit) on the basis of the brick-layer model [8]. In Nyquist plots, intercept of semi-circular arcs on real Z'-axis gives the value of bulk resistance (R_b) which is found to decrease with increase in temperature. It suggests about the negative temperature coefficient of resistance (NTCR) type behaviour of the BBN-compound. These plots exhibit depressed semicircles with centres lying below the real Z'-axis which confirms the presence of non-Debye type of relaxation in the material [14-15].

4.2. Complex modulus analysis

The variation of real part of electric modulus (M') of $BaBi_2Nb_2O_9$ with frequency at different temperatures is shown in Fig-4. M' is found to be very low at lower frequencies and exhibits an increasing trend with the increase in frequency. It shows continuous dispersion on increasing frequency which may be due to short range mobility of charge carriers under the action of an induced electric field. But at higher temperatures, M' increases rapidly with the increase in frequency as well as temperature which attributes temperature dependent relaxation process in the materials. Also it is observed that the dispersion region shifts towards higher frequencies with increase in temperature suggesting long-range mobility of charge carriers [16]. The observed plateau region or its tendency indicates about frequency invariant dc behaviour of the material.

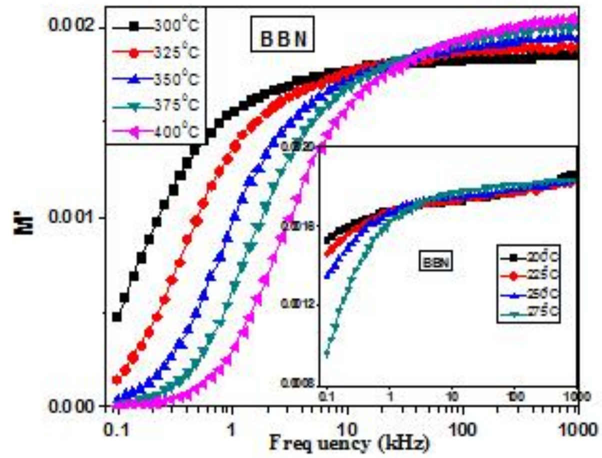

Fig-4: Variation of M' of $BaBi_2Nb_2O_9$ frequency at different temperatures

Fig-5 shows the variation of imaginary part of electric modulus (M'') of the BBN compound with frequency at different temperatures. It exhibits modulus peaks at higher temperatures such that the relaxation frequencies shift towards higher frequencies with increase in peak height as temperature increases. It indicates thermally activated behaviour of relaxation time [17]. The observed asymmetry in peak broadening indicates the spread of relaxation time with different time constant which supports the non-Debye type of relaxation in the materials. The low value of M'' observed at lower frequencies may occur due to the absence of electrode polarization phenomena.

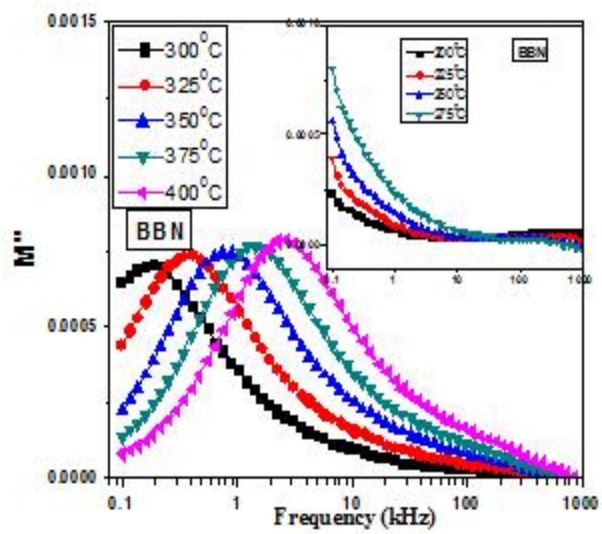

Fig-5: Variation of M'' of $BaBi_2Nb_2O_9$ frequency at different temperatures

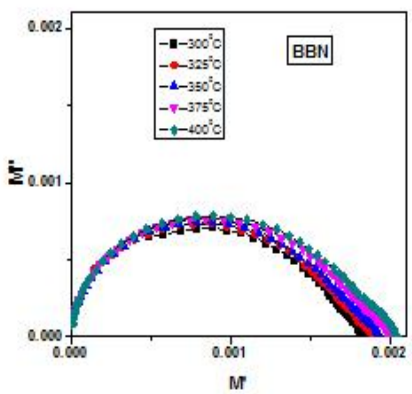

Fig-6: Complex modulus plots (M'~M'') of $BaBi_2Nb_2O_9$

The temperature dependence of complex modulus spectrum (i.e. M' vs. M'' spectrum) of barium bismuth niobate is shown in Fig-6. At higher temperatures, semi-circular arcs are observed tending to form two semicircular arcs indicating the presence of both grain and grain boundary contributions in the material. Their centres appear to lie below the real M'-axis which indicates spread of relaxation with different time constant and thus supports the phenomenon of non-Debye type of relaxation in the materials. Intercepts of these semicircles on real M'-axis appear to shift towards higher values of M' as temperature increases. It indicates increase in capacitance with the increase in temperature and supports NTCR type behaviour of the material since the bulk capacitance (C_b) is inversely proportional to the bulk resistance (R_b).

CONCLUSION

Polycrystalline samples of barium bismuth niobate ($BaBi_2Nb_2O_9$) were prepared by mixed oxide method at 1050°C temperature. Real and imaginary parts of complex impedance and modulus properties of the material were investigated by using complex impedance spectroscopy (CIS) technique. At a particular temperature, the observed single arc in the form of single/double semicircles (or tendency) in both the complex impedance and modulus plots confirms about the formation of sample in single phase. Impedance analysis indicates the presence of mostly bulk (grain) resistive contributions in the material whereas complex modulus plots shows the presence of grains as well as grain boundary contributions in the material. It is due to the fact that impedance plot highlights the phenomenon with largest resistance whereas electric modulus plot highlights the phenomenon with smallest capacitance. Due to the large difference between resistive values of grains and grain boundaries, it is not possible to get two semicircles on the same impedance plot [18]. Both impedance and modulus analysis support the typical behaviour of negative temperature coefficient of resistance (NTCR) of the material. They also confirm the presence of non-Debye type of relaxation phenomenon in the material.

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