

Preparation and characterization of Barium iron niobate (BFN)

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Abstract- The ferroelectric ceramic barium iron niobate $Ba(Fe_{1/2}Nb_{1/2})O_3$ (BFN) is synthesized by a solid state reaction technique. The X-Ray diffraction of the sample at room temperature shows a monoclinic phase. The field dependence of the dielectric response and the conductivity are measured in a frequency range from 10Hz to 1MHz and in temperature range from 50 to 400°C. The sample sintered at 1100-1300°C for 4hr, have higher dielectric constant in room temperature than PMN, PFN and earlier reported BFN.

Keywords- DPT; Solid state route; Relaxor; Cole-Cole; Dielectric

I. INTRODUCTION

The relaxor ferroelectric barium iron niobate: $BaFe_{0.5}Nb_{0.5}O_3$ (BFN) was first synthesized via solid state reaction, by Saha and Sinha [1] in 2002. In recent years there has been a considerable amount of interest in the investigation of high dielectric constant materials for capacitor and other electronic devices. The materials having a diffuse phase transition (DPT) or have received the most attention due to their broad maximum in the temperature dependence of dielectric constant [2]. The high values of dielectric constant of BFN in a very wide temperature interval are due to disorder in the distribution of B-site ions in the perovskite unit cell. This may lead to the appearance of composition fluctuations and, as a consequence, to different local Curie temperatures in the different regions of ceramics [3]. They reported that the material exhibited very high values of dielectric constant in a very wide temperature range. However, the sintering temperature in their preparation was 1250°C, exhibiting the dielectric constant (ϵ_r) of 30,000. Therefore, in order to find the optimum conditions of sintering process for obtaining higher values of dielectric constant (ϵ_r), we synthesized $BaFe_{0.5}Nb_{0.5}O_3$ (BFN) via the solid state reaction technique. Various temperatures of calcining and sintering were carried out, phase evolution and the physical properties of the ceramics were studied.

II. EXPERIMENTAL

The initial ingredients Fe_2O_3 (98% Sigma-Aldrich), Nb_2O_5 (99.9% Sigma-Aldrich), $BaCO_3$ (99.9% Sigma-Aldrich) were used. Initially, $FeNbO_4$ (wolframite) was prepared by mixing Fe_2O_3 and Nb_2O_5 , calcined at 1000°C/4hr. Thereafter $FeNbO_4$ and $BaCO_3$ mixed in molar ratio. The mixture was calcined at 900°C/4hr with heating rate 250°C/hr to obtain the BFN perovskite. The obtained product were crushed and pelletised of 9mm diameter and 2mm thickness. The pellets were sintered for 1100°C and 1300°C for 4hr. The density of the

sintered pellets were determined using Archimedes principle [4], relative density was calculated. Table.1 lists the nomenclature used in the present work to represent BFN samples and their sintering conditions.

Sr. No.	Sample Code	Bulk Density (gm/cm^3)	Porosity (%)	Percentage loss of barium oxide
1	BF11	6.1	6.81	0%
2	BF13	6.3085	3.66	0.1666%

TABLE I. NOMENCLATURE OF BFN CERAMIC SAMPLE

Number The crystal structure of BFN was confirmed by X-ray powder diffraction (XRD) using $CuK\alpha_1$ radiation, with the help of PANalytical X-ray powder diffractometer at 40 kV and 30 mA. The relative percentage of perovskite and pyrochlore phase present was determined using equation,

$$\text{Perovskite phase (\%)} = \frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{pyro}}} \quad (1)$$

here I_{perov} and I_{pyro} refer to the intensities of the (110) perovskite and (222) pyrochlore peaks, respectively. These are the most intense reflections in XRD patterns corresponding to both the phases. The relative permittivity (ϵ_r) and dissipation factor ($\tan\delta$) were measured at different frequencies 1, 10 and 100 kHz in between 50 to 400°C temperature range and conductivity also measured using computer controlled HP-4192A LF impedance analyzer. The temperature was controlled with an accuracy of $\pm 1^\circ C$ using Eurotherm temperature controller.

III. RESULT AND DISCUSSION

A. Analysis Phase Formed

The X-ray powder diffraction (XRD) patterns of BFN are shown in Fig.1. XRD patterns of PFN is well matches with the JCPDS data (file no. No.00-017-0187) confirm the formation of single phase with the monoclinic structure. The obtained result matched with the previous reported data [1, 5]. The relative percentage of perovskite phase increases with sintering temperature. The particle size estimate from the full width half maximum (FWHM) of (011) diffraction peak. Practically, the Scherrer formula (Eq.2), which assumes that the small crystalite size to be the only case of line brodening [6].

$$d_{XRD} = \frac{ky}{\beta(\theta) \cos \theta} \quad (2)$$

where λ , $\beta(\theta)$, θ $k \sim 1$ are wavelength of x-ray, FWHM of the diffraction line, angle of diffraction and the constant, respectively. The comparison of maximum intensity of BFN, pyrochlore phase percentage of perovskite phase and particle size after sinter as shown in Table.1.

It is reported, dielectric properties of BFN depends on porosity. Therefore it was worthwhile to determine percentage porosity of the synthesized barium iron niobate. To get dense barium iron niobate, sintering temperature required $>1200^{\circ}\text{C}$, thereafter for calculation of bulk density, theoretical density and porosity are necessary [7]. Bulk density (d_b) of the material is given by total weight of the pellet divided by total volume of the pellet. True density or theoretical density (d_{th}) is given as molecular weight of the sample divided by volume of its unit cell. The % porosity of the barium titanate was calculated using formula, % Porosity = $[(d_{th}-d_b)/(d_{th})] \times 100$, Bulk density (d_b) of all the samples of BFN were calculated as mentioned above and given in Table.1. Theoretical density (d_{th}) of BFN has been calculated from molecular weight of the barium titanate divided by volume of its unit cell. The percentage of porosity was calculated using equation.1 and found to be approximately 3-6.

B. Dielectric Characterization

Fig.2 and 3 shows the variation of relative permittivity (ϵ_r) and dielectric loss ($\tan \delta$) with temperature at different frequencies 1 kHz, 10 kHz and 100 kHz temperature range $50-400^{\circ}\text{C}$ for BF11 and BF13 sample respectively. It is evident that the diffuse phase transition (DPT) temperature with relative permittivity of all samples is high. A significant improvement in the value of dielectric permittivity is observed with increasing sintering temperature. No systematic trend is observed for dielectric loss. The variation of dielectric permittivity drops to rather very low values for frequency greater than 10 kHz, such a drastic decrease can be explained in terms of the interfacial polarization. The transition temperature is shifted toward the lower temperature (for BF11 is 240°C and for BF13 is 295°C) observed for 1kHz. The maximum density of BFN ceramic (sintered at 1300°C) was 6.3 g/cm^3 . At high temperature Fe^{2+} changes to Fe^{3+} causing the defect of the crystal growth where the second phase may start to grow. However, from XRD patterns no second phase was detected in these high sintering temperature samples. The

dielectric constant of BFN ceramics increased with increasing temperature and became broad curve from 200°C onward for BF13 and 300°C onward for BF11. As is widely known, the co-existence of Fe^{2+} and Fe^{3+} ions on equivalent crystallographic sites can frequently give rise to an electron hopping type of conduction mechanism, which, owing to finite hopping probabilities, tends to come into effect at lower frequencies.

C. Electrical characterization:

Complex impedance spectroscopy is a experimental technique to analyze dynamics of the ionic movement in solids. Contribution of various microscopic elements such as grain, grain boundary and interfaces to total dielectric response in polycrystalline solids can be identified by the reference to an equivalent circuit, which contains a series of array of parallel RC elements [8]. To study the contribution due to different effects, Cole-Cole analyses have been made at different temperatures. It is observed that the impedance data at low temperatures i.e. up to 200°C , do not take the shape of a semicircle in the Cole-Cole plot rather presents a straight line with large slope, suggesting the insulating behavior of the compound at low temperatures. It can further be seen that with the increase in temperature the slope of the lines decreases and they curve towards real (Z') axis and at temperature above 300°C , a semicircle could be traced, indicating the increase in conductivity of the sample. The Cole-Cole plot also provides the information about the nature of dielectric relaxation in the system. For pure monodispersive Debye process, one expects semicircular plots with the center located on the Z' -axis whereas, for polydispersive relaxation, the argand plane plots are close to circular arcs with end-points on the real axis and the center below this axis. The complex impedance in such situation is known to be described by Cole-Cole formalism [9]

$$Z'(\omega) = Z' + iZ'' = R/[1(i\omega/\omega_0)^{1-\alpha}] \quad (3)$$

where α represents the magnitude of the departure of the electrical response from an ideal condition and can be determined from the location of the center of the Cole-Cole circles. When $\alpha \rightarrow 0$, equation.(3) reduces to the classical Debye's formalism. Fig.4 shows complex impedance plots at different temperatures. It can be seen from these plots that the data are not represented by full semicircle i.e. centre of semicircles lie below the abscissa axis ($\alpha > 0$), suggests the relaxation to be non-Debye type. Fig.5 shows the variation of $\ln \sigma_T$ with $10^3/T$. It is observed to increase with increasing temperature further confirming the NTCR behavior of BFN ceramic.

IV. CONCLUSION

It is concluded from XRD pattern that single (perovskite BFN) phase formed without pyrochlore phase with increase of sintering temperature. from 1100°C to 1300°C for 4hr. Dielectric constant at various frequencies was found to be dependent upon temperature. The transition temperature is shifted toward the lower temperature. The dielectric constant is varying with the frequency, as the frequency decreases the dielectric constant increases from 100 kHz to 1kHz. From whole experimental and characterization studied has been concluded that for preparation of barium iron niobate (BFN) solid state method is superior than the other method for obtain

the high dielectric constant and less dielectric loss. BFN Shows NTCR behavior.

V. ACKNOWLEDGEMENTS

Authors are thankful to DRDO, New Delhi (INDIA) for providing financial assistance to carry out this work.

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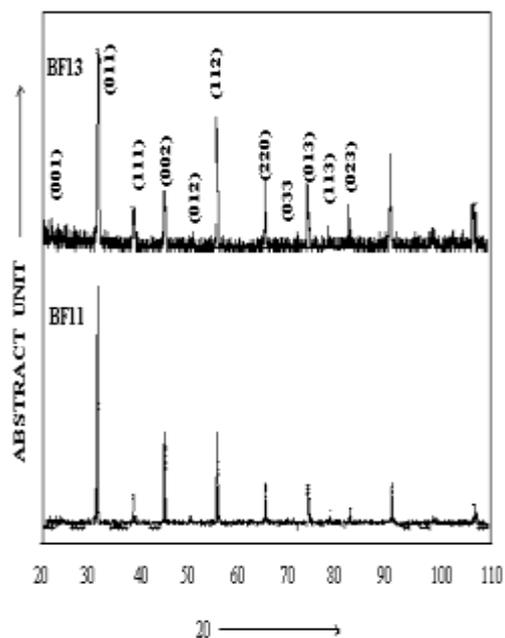


Figure 1. XRD pattern of the sample BF11 and BF13

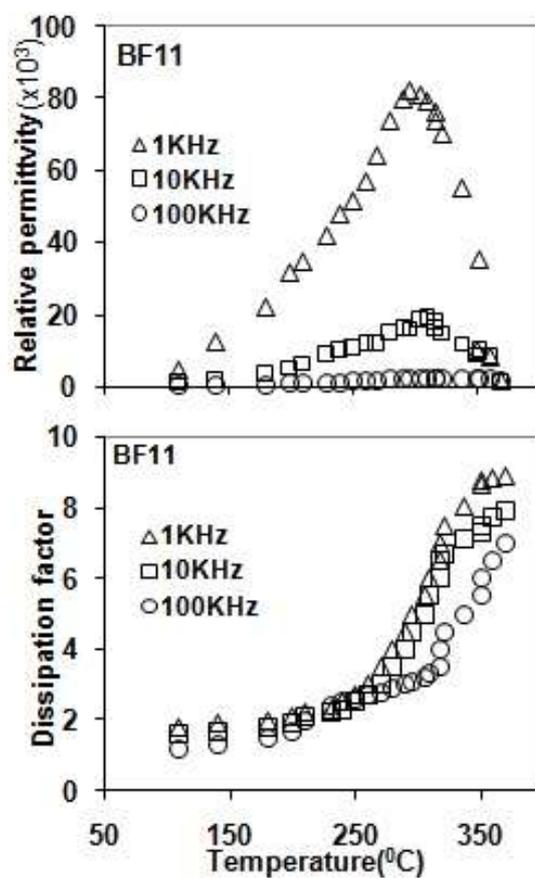


Figure 2. Relative permittivity and dissipation factor of BF11 sample

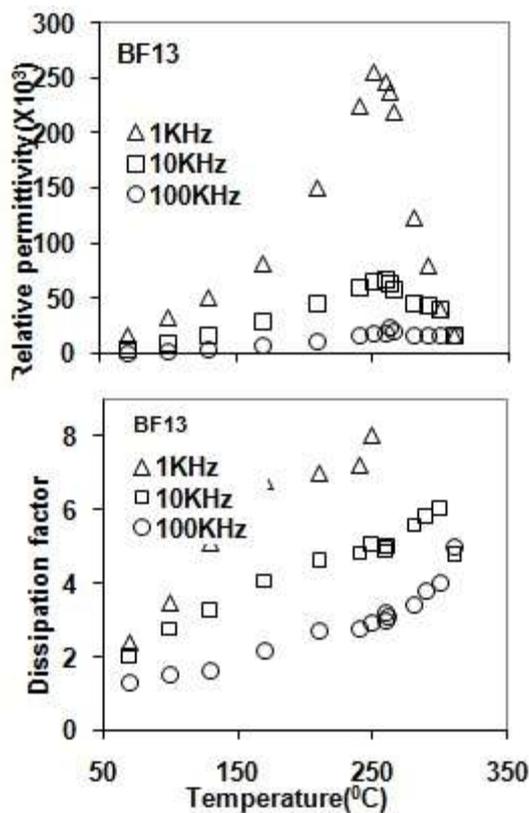


Figure 3. Relative permittivity and dissipation factor of BF13 sample

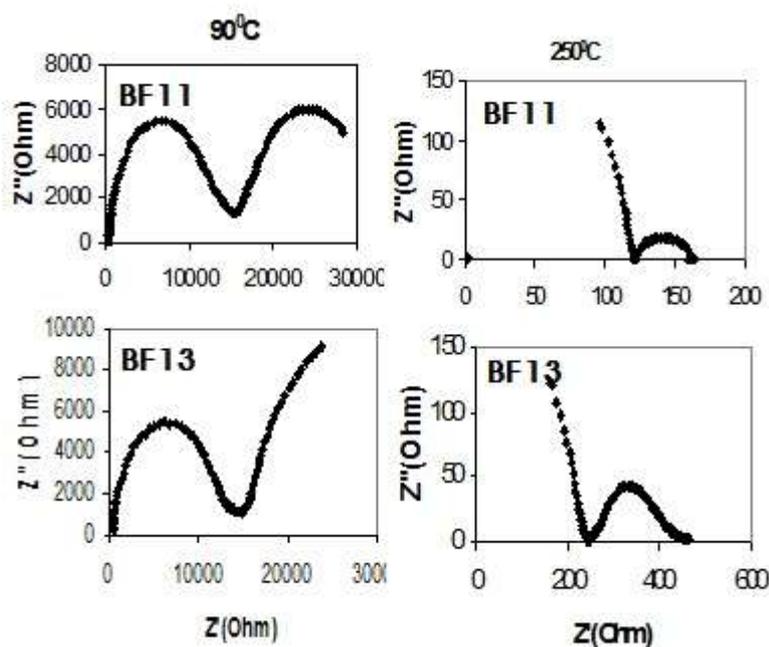


Figure 4. Variation of Z' Vs Z'' For BF11 and BF13 sample at 90°C and 250°C temperature

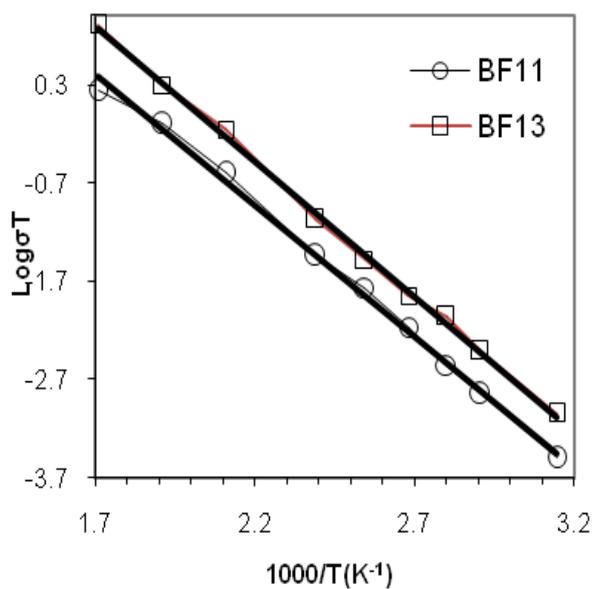


Figure 5. Variation of bulk conductivity with the temperature for sample BF11 an BF13