

Structural Microstructural and Electrical Transport Studies of Ba(Fe_{0.25}Eu_{0.25}Nb_{0.5})O₃

Devang D. Shah^{1,*}, P.K. Mehta¹, C.J. Panchal²

¹ Department of Physics, Faculty of Science, The M. S. University of Baroda, Vadodara-390002 Gujarat, India

² Department of Applied Physics, Faculty of Technology and Engineering, The M. S. University of Baroda, Vadodara-390002 Gujarat, India

(Received 15 February 2013; revised manuscript received 27 April 2013; published online 04 May 2013)

The complex multifunctional ceramic Ba(Fe_{0.25}Eu_{0.25}Nb_{0.5})O₃ (BFEN) has been synthesized. The structural studies show two iso-structured phases related with BFN and BEN co-exists in the compound. The high dielectric constant and low dielectric loss of the compound below 575 K promises industrial applications. The activation energies obtained from the Arrhenius analysis of dc conductivity supports possible ferroelectric transition at elevated temperatures. Thus the desirable properties of two different compounds viz. multiferroic properties of BFN and high quality factor of BEN are successfully incorporated in a single compound.

Keywords: XRD, Niobates and tantalates, Mobility edges, Hopping transport.

PACS numbers: 61.05.cp, 77.84.Ek, 72.20.Ee

1. INTRODUCTION

The barium based complex ceramic compounds have gathered much more attention of the researchers due to multifunctional properties and environment friendly nature of the compounds [1]. Among these the ABO₃ type Barium Iron Niobate, Ba(Fe_{0.5}Nb_{0.5})O₃ (BFN), compound has shown potential applications in the field of electro-ceramics, multiferroics and relaxor ferroelectrics [2-3]. Though, along with these properties, BFN shows high dielectric loss and poor quality factor [4-5]. The low quality factor restricts the material to be utilized for end industrial applications. On the other hand the substitution of Fe⁺³ by large lanthanide ions like Eu⁺³ changes its electrical properties drastically. The Ba(Eu_{0.5}Nb_{0.5})O₃ BEN compound shows low dielectric constant and high quality factor which is highly desirable as substrate of superconducting thin films [5]. The incorporation of multiferroic and relaxor properties of BFN ceramic with the low dielectric loss of BEN is likely to fulfill the increasing industrial demand of multifunctional ceramics.

In order to obtain desirable mixed properties of BFN and BEN compounds, we have synthesized a novel intermediate ceramic BFEN in single phase. The structural, micro structural, dielectric and electrical conductivity characterization along with its possible end applications are presented in this work.

2. EXPERIMENTAL

2.1 Sample Preparation

The conventional ceramic synthesis technique is utilized to prepare the complex ceramic compound BFEN. The extra pure (Purity > 99.99 %) basic oxides like BaCO₃, Fe₂O₃, Eu₂O₃ and Nb₂O₅ were mixed together in their stoichiometric proportion. The particle size mixing was attained through wet mixing technique using few drops of acetone. The well mixed powder was then calcined at 1200 °C in an alumina container. The

calcined powder was recrushed and sintered in the form of pallets at 1350 °C for six hours. In order to develop better growth of the grains we annealed our samples at 1300 °C for six hours. The heat treatments like; calcination, sintering and annealing were carried out in the air atmosphere.

2.2 Characterization

In order to ensure structural purity of the sample the preliminary structural characterization of the as prepared samples was carried out. The crystal structure characterization was performed using x-ray diffraction (XRD) analysis. The room temperature θ -2 θ scanning was performed using Shimadzu XRD-6000. The scanning was carried out between 10°-110° at interval of 0.02° with scanning speed of 2° per minute.

The micro structural study of the sample surface was performed using scanning electron microscopy (SEM) images. The SEM images of sample were collected under vacuum using SEM JEOL JSM 5600: F-Model at UGC-DAE-CSR Indore centre. In order to avoid charging effect on the sample surface, very thin (< 50 Å) layer of Al metal was coated.

The dielectric and electrical properties of the samples were studied through impedance spectroscopy analysis. The circular sample surfaces was polished and painted with conducting silver paint to avoid non ohmic contact between sample and electrode. The frequency as well as temperature dependent impedance data were collected using SOLARTRON 1260 impedance analyzer. The frequency response of impedance data between 100 Hz-10⁶ Hz were recorded in the temperature range of 298 K (25 °C) to 723 K (450 °C). The temperature of the sample was raised at constant and controlled heating rate of 0.5 K per minute and data were recorded at 5 K interval. The collected impedance data were converted in to dielectric and electrical conductivity data using sample dimensions and standard equations.

* devangshah_04@yahoo.co.in

3. RESULTS AND DISCUSSION

The four variety of analysis are utilized to discuss the obtained response of the sample:

1. Crystal structure analysis;
2. Microstructure analysis;
3. Dielectric spectroscopy analysis;
4. Electrical conductivity analysis.

3.1 Crystal Structure Analysis: (X-ray Diffraction – XRD Analysis):

The XRD pattern of BFEN compound with the XRD patterns of BFN and BEN ceramic are shown in the Fig. 1. For the comparison purpose, the patterns of BFEN and BEN are up-lifted by 3000 cps and 6000 cps respectively from the BFN pattern.

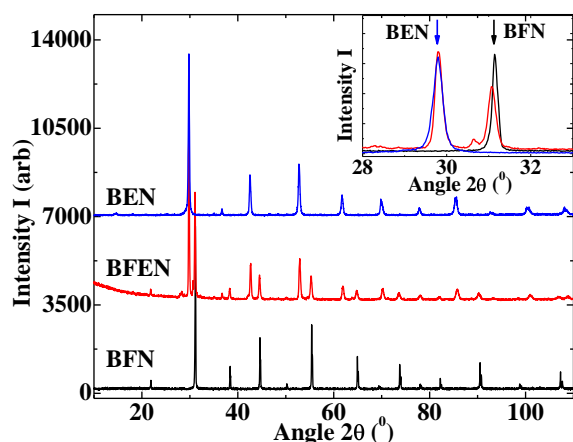


Fig. 1 – The XRD patterns of BFN, BFEN and BEN. The inset shows enlarged and superimposed patterns for main intense peak

The pure phase formation of the compound was confirmed through absence of impurity peaks. It is observed from the XRD pattern of BFEN compound that each of the peaks is split in to two. The split peaks represent presence of two iso-structured phases in a single compound. The inset of Fig.1 shows superimposed XRD patterns (enlarged for the main intense peak) of BFN, BFEN and BEN ceramics. The in-depth analysis of the observed two iso-structured phases confirms that the first phase is related to BEN and another one is related to BFN ceramics. Further it infers the presence of two separate crystallites related to BFN and BEN ceramic in a single compound.

The fitting of the XRD pattern suggests cubic phase formation for each of the BFN and BEN phases. The unit cell parameters are found to be $a = 4.0674$ and $a = 4.2363$, respectively, for BFN and BEN phase.

3.2 Microstructure Analysis: (Scanning Electron Microscopy – SEM Analysis):

The scanning electron microscopy image of BFEN compound is shown in the Fig. 2. The observed grain formation in the SEM image confirms good quality of the sample. The analysis shows that the grain size varies between $0.5 \mu\text{m}$ - $2.0 \mu\text{m}$ with average grain size of $1.2 \mu\text{m}$. The observed small amount of porosity is related to the general characteristic of ceramic compounds.

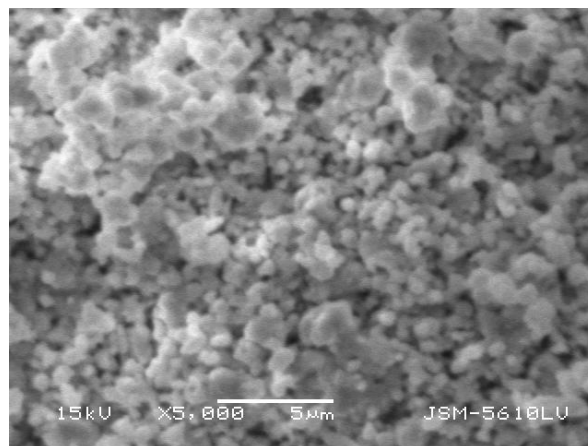


Fig. 2 – The SEM image of BFEN compound

3.3 Dielectric Spectroscopy Analysis

The dielectric response of the BFEN compound was analyzed using the complex permittivity analysis. The frequency response of real permittivity data at different temperatures are shown in the Fig.3. On decreasing the frequency of applied AC signal the corresponding values of real permittivity increases. The real permittivity further increases on rising the sample temperature up to 723 K. The temperature dispersion in the real permittivity data is found larger at lower frequencies compared to the higher frequencies.

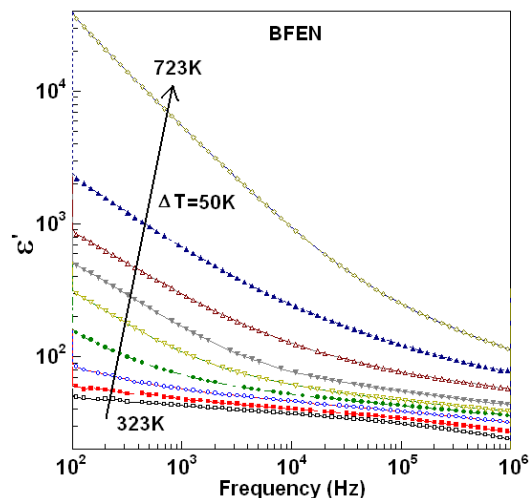


Fig. 3 – The frequency dispersion curves of real part of permittivity at different temperatures

The frequency response of imaginary permittivity data at different temperatures are shown in the Fig. 4. The data monotonously varies and no clear relaxation peak is observed in the measured frequency range. The very small values of room temperature imaginary permittivity data confirms reduced loss factor. The imaginary permittivity data increases largely at elevated temperatures ($> 600 \text{ K}$) suggest conducting nature of the sample at high temperatures [6-7].

The observed high values of permittivity and low dielectric loss up to 575 K (compared to BFN and BEN ceramic) is fulfilling the required industrial demand of multifunctional ceramic, though above 575 K the

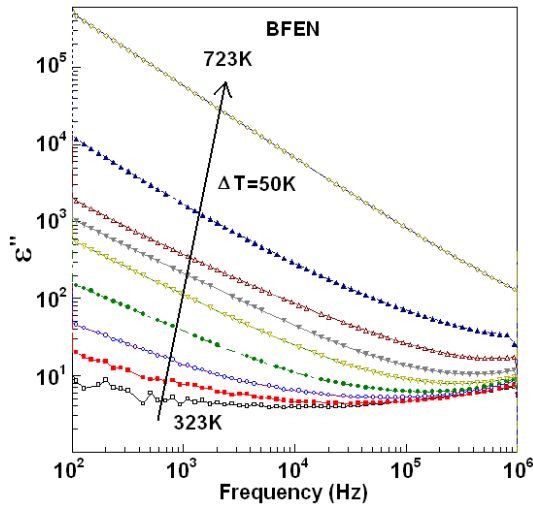


Fig. 4 – The frequency dispersion curves of imaginary part of permittivity at different temperatures

dielectric loss increases rapidly. The high values of imaginary permittivity suggest that the material becomes conducting after 575 K. The ferroelectric properties of the compound can be studied through the temperature dependent permittivity analysis.

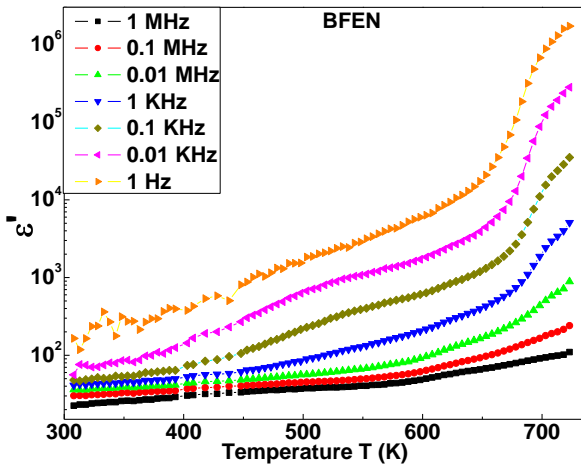


Fig. 5 – The temperature dispersion curves of real part of permittivity at few frequencies.

The Fig. 5 shows temperature dependent real permittivity data at few selected frequencies. The real permittivity gradually increases with temperature up to 600 K. It show step like increment at elevated temperatures (> 650 K) for all the frequencies. The data have not shown ferroelectric like reduction in real part of permittivity data after a sharp rise. In order to understand such sudden change at higher temperatures along with significant dielectric loss, we have carried out conductivity analysis.

3.4 Electrical Conductivity Analysis

The ac conductivity data of the sample at different temperatures are shown in the Fig. 6. The conductivity found decreases with decrease in the frequency. The conductivity continues decrement at lower frequencies suggest significant contribution of dipolar relaxation.

The observed values of conductivity data exhibits semi conducting nature of the sample. Further, at elevated temperatures the conductivity value increases and becomes nearly constant suggest dominating nature of dc conduction.

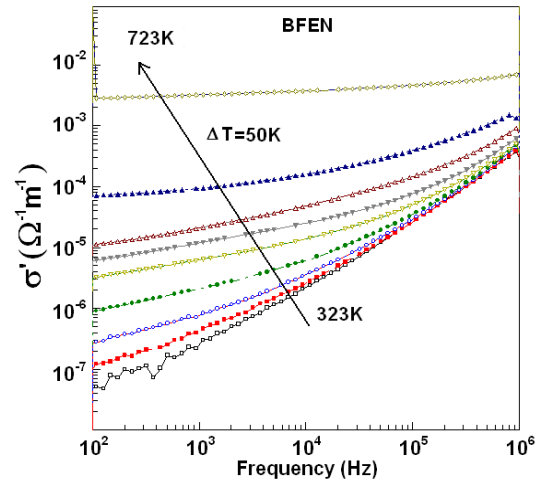


Fig. 6 – The frequency dispersion curves of ac conductivity data at different temperatures

The nearly constant values of ac conductivity at low frequencies (1 Hz) can be considered as dc conductivity [6-8]. The values of dc conductivity are useful for the analysis of conduction mechanism. Further, detail analysis using the Arrhenius law fitting of dc conductivity enables us to understand the type of carriers.

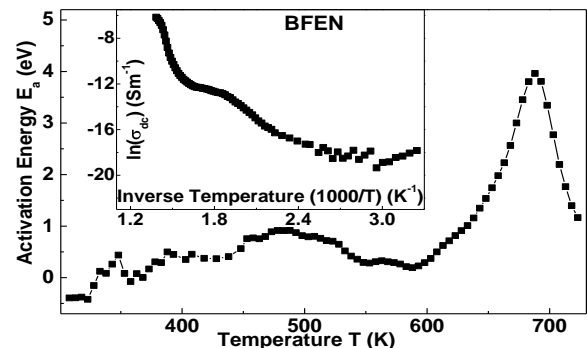


Fig. 7 – Temperature dependent activation energy values. Inset shows Arrhenius plot of dc conductivity

The Arrhenius curve between conductivity and inverse temperature is shown in the inset of Fig. 3 exhibiting nonlinear nature. The observed nonlinear nature of Arrhenius plot suggest that the conduction process is not simply thermally activated process. The activation energies of the conduction carriers vary in the different temperature segments. It may be affected by the possible thermal transitions. Therefore to investigate such conduction process we determined the temperature dependent activation energy values using the following equation [9]:

$$E_a = k_B \frac{d(\ln \sigma_{dc})}{d(1/T)}, \tag{1}$$

where E_a is activation energy and k_B is Boltzmann con-

stant. The activation energy remains below 1 eV up to 575 K, suggests that the conduction is related to the singly/doubly ionized oxygen vacancies in the entire temperature range. The observed sudden increase up to 4 eV showing a peak at higher temperatures, suggest possible structural phase transition.

4. CONCLUSIONS

The co-existence of separate crystallites related to BFN and BEN confirms the existence of iso-structured chains of – Fe – Nb – Fe – and – Eu – Nb – Eu – inside a grain. Conductivity of the sample found to be in semi conducting region. The activation energies (< 1 eV) along

with observed high dielectric constant and low loss below 575 K are promising for its applications as capacitors. Above analysis also suggests the strong interactions between iso-structured BFN and BEN crystallites via singly ionized oxygen vacancies. The rapid increase in activation energies at higher temperatures along with step like increment in dielectric constant suggests possible ferroelectric phase transition in the sample.

ACKNOWLEDGEMENTS

Authors are thankful to UGC-DAE-CSR, Indore centre and UGC-DRS program at physics department for providing measurement facilities.

REFERENCES

1. K. Uchino, *Ferroelectrics* **151**, 321 (1994).
2. N. Rama, J.B. Philipp, M. Opel, K. Chandrasekaran, V. Sankaranarayanan, R. Gross, M.S.R. Rao, *J. Appl. Phys.* **95**, 7528 (2004).
3. B. Bishnoi, P.K. Mehta, C.J. Panchal, M.S. Desai, R. Kumar, *J. Nano-Electron. Phys.* **3** No 1, 698 (2011).
4. L.A. Khalam, H. Sreemoolanathan, R. Ratheesh, P. Mohanan, M.T. Sebastian, *Mat. Sci. Eng. B* **107**, 264 (2004).
5. J. Kurian, Asha M. John, P.K. Sajith, J. Koshy, S.P. Pai, R. Pinto, *Mat. Lett.* **34**, 208 (1998).
6. K.C. Kao, *Dielectric phenomena in solids* (Elsevier: Academic Press: USA: 2004).
7. R.H. Cole, *J. Chem. Phys.* **23**, 493 (1955).
8. K.S. Cole, R.H. Cole, *J. Chem. Phys.* **9**, 341 (1941).
9. J. Jadz'yn, D. Baumen, J.-L. Déjardin, M. Ginovska, G. Czechowski, *Acta Phys. Pol. A* **108**, 479 (2005).