High Temperature Dielectric Response and AC Conductivity Mechanism of (Nd, Ni) codoped $BiFeO_3$

Mehroosh Fatema[1], Shahid Husain[1], Samiya Manzoor[1],Anand Somvanshi[1], Naima Zarrin[1] and Aref A.A. Qahtan[1]*

[1]*Department of Physics, Aligarh Muslim University, Aligarh (INDIA), 202002*

Email: s.husaincmp@gmail.com

Abstract

$BiFeO_3$(BFO)and $Bi_{0.9}Nd_{0.1}Fe_{0.9}Ni_{0.1}O_3$ (BNFNO) nanocrystalline samples have been synthesized through the sol-gel auto combustion process. Frequency and temperature dependent dielectric measurements have been performed in order to apprehend the influence of (Nd,Ni) co-doping on the conduction mechanism of pristine BFO.Thereal part of the dielectric constant is found to increase with the Nd and Ni doping, which is accredited to higher space charge polarization induced by the dopant ions.The dielectric constant measured as a function of frequency exhibits a dispersivebehaviour within low frequency region and attains a constant value at higher frequencies. A thermally activated relaxation peak is found at around 500K in the BNFNO samplewhich shifts towards lower temperatures at higher frequencies. The AC conductivity follows the Jonscher's universal dynamic law, which has been utilized to evaluate the value of frequency exponent 's'. The decrease in the value of the 's' parameter with the increase in temperature establishes that the conduction mechanism is governed by the correlated barrier hopping (CBH) model. The ac conductivity data has been utilized to evaluate the minimum hopping distance (R_{min}) and the binding energies (W_m) of the electrons in BNFNO. Arrhenius equation has been used to fit the experimental data and activation energy has been evaluated at different temperatures. The Activation energy is found to increase with the increase in the temperatures, owing to the creation of more oxygen vacancies instigated by (Nd, Ni) co-doping.

Keywords: *Dielectric constant, AC Conductivity, Activation Energy, Minimum Hopping Distance.*

1. Introduction

Multiferroic materials, exhibiting simultaneous electric and magnetic ordershave been in limelight due to their potential use in various devices.[1] The ABO_3 type perovskites have also gained immense attention owing to their unique properties[2]. A unique example of the multifunctional multiferroic material is the rhombohedrally distorted $BiFeO_3$ (BFO) perovskite which belongs to the space group *R3c.* BFO is a distinguished multiferroic as it possesses the tendency to exhibit both ferroelectric and ferromagnetic properties at room temperature[3] .This rare propensity of the material makes it a prominent prospect for sensors, modulators, waveguides and memory devices. The greatest setback involving BFO is its synthesis in a pure phase. Bismuth being volatile, gives rise to impurity in the form of secondary phases

which lead to enhanced leakage current in the sample. This condition makes it challenging to study and utilize its electrical properties. The hopping of Fe^{2+} ions create oxygen vacancies in order to compensate for the charge imbalance, which results in higher conductivity[4]. Several attempts have been made to improve the electrical properties of $BiFeO_3$ by introducing rare earth and transition metal dopants in varying concentrations at both A and B site of the perovskite [3,5].Wang. et al.[5]experimented with Nd substitution whereas Vanga et. al.[3]tried out co-doping of (Nd,Ni) in pristine $BiFeO_3$, in order to enhance its physical properties. But no significant studies have been performed, consistent with the idea of utilization of the properties of both Nd and Ni, simultaneously via their co-substitution. In this paper, the effect of (Nd, Ni) codoping on the frequency and temperature dependent dielectric properties of $Bi_{0.9}Nd_{0.1}Fe_{0.9}Ni_{0.1}O_3$(BNFNO) sample has been investigated for finding befitting applications in suitable devices.The correlated barrier hopping (CBH) model has been employed to the ac conductivity data in order to comprehend the conduction mechanism. The binding energy,minimum hopping distance and Activation energy has been found out.

2. Experimental

The sol-gel auto-combustion process has been employed to synthesize $BiFeO_3$and $Bi_{0.9}Nd_{0.1}Fe_{0.9}Ni_{0.1}O_3$ (BNFNO) samples by using $[Bi(NO_3)_3.5H_2O]$, $[Fe(NO_3)_3.9H_2O]$, $[Nd(NO_3)_2.6H_2O]$, $[Ni(NO_3)_2.6H_2O]$, as precursors. The detailed procedure has been recorded elsewhere [6]. X-ray diffraction data has been obtained in the 2θ angle range of 20°- 80° and Rietveld refinement is performed to evaluate the lattice parameters [6]. The temperature dependent dielectric properties have been analysed using the data acquired in the frequency range of 75 kHz to 5 MHz with the Agilent 4285A LCR meter (Model No. SH-1000, Wayne Kerr India). Prior to performing the dielectric measurements, the powdered material was mixed with few drops of PVA, heated at 550° C and pressed into a circular shaped pellet of 1.2 cm diameter. The opposite faces of the pallets were coated with conductive silver paste to obtain a parallel plate capacitor geometry.

3. Results and Discussion

Dielectric measurements have been carried out in order to probe the effect of (Nd, Ni) co-doping on the dielectric relaxation and conduction mechanism of BFO. The variations of the real part of the dielectric constant (ε') of BFO and BNFNO, in the frequency range 75 kHz to 5MHz, measured at varying temperatures are shown in Fig. 1 (a) and Fig. 2 (a), respectively.

The dielectric constants of both BFO and BNFNO samples have higher values in the low frequency region, which gradually declines with the rise in frequency. This dispersion is prominent within lower frequency regime but at higher frequencies the dielectric constant becomes almost independent of the frequencies. This behaviour may be accredited to the dipolar relaxation phenomena explained by the Maxwell–Wagner–Sillars polarization effect, according to which the dielectric response observed in the low frequency region is dispersive due to the interfacial or space charge polarization arising from the alignment of the space charges along the applied field [7]. As the frequency approaches a higher value, the dipoles are not able to keep up with the rapid variation of the alternating field [7], and hence register a decrease in dielectric constant.

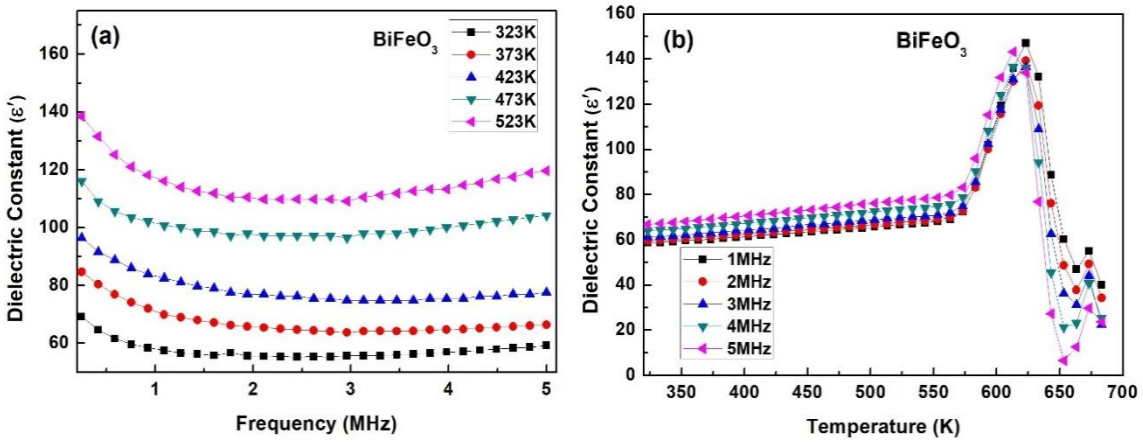

FIG 1. Plots of dielectric constant of BFO as a function of **(a)** frequency **(b)** temperature.

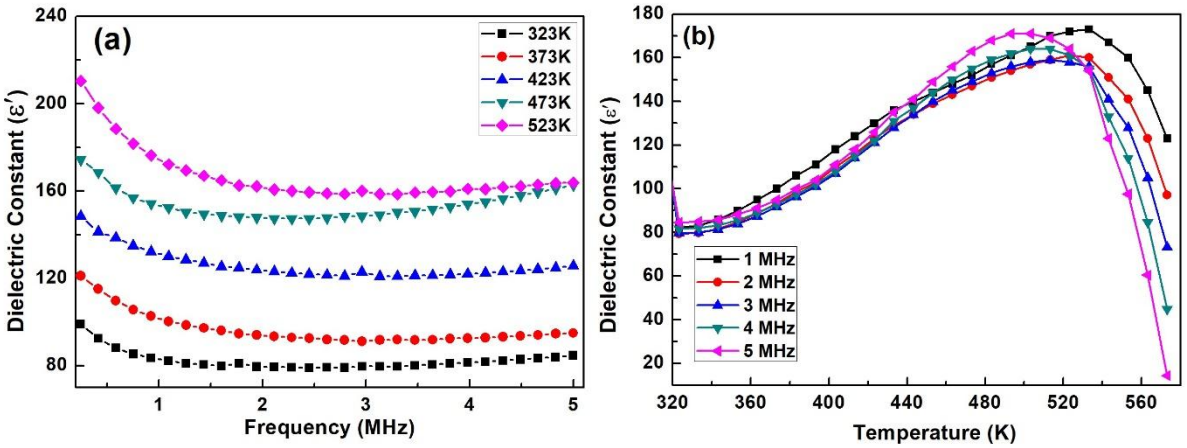

FIG 2. Plots of dielectric constant of BNFNO as a function of **(a)** frequency **(b)** temperature.

A significant increase is observed in the dielectric constant of BNFNO as compared to pure BFO, as can be observed from Fig 2 (a). This increase in the dielectric constant maybe due to Nd substitution which brings about uniformity in microstructures and alters the grain resistance, thus promoting the hopping mechanism between sites[5]. In addition, the charge imbalance arising from the substitution of Ni^{2+} dopant at Fe^{3+} site leads to the creation of oxygen vacancies.

The temperature dependent response of the BFO and BNFNOsamples are shown in Fig. 1(b) and Fig. 2(b), respectively.The variation of the dielectric constant with temperature follows a similar trend for distinct frequencies for both the samples. The dielectric constant gradually increases at low temperatures and shows a peak at 620 K in pristine BFO which shifts to lower temperatures in case of BNFNO sample. The observed anomaly in the vicinity of 620 K is very close to the Neel Temperature of BFO , indicating a transition from antiferromagnetic to paramagnetic state in the region 580-650K. The increase in the value of dielectric constant can be attributed to the increase in thermal energy, which promotes hopping between Fe^{3+}-Fe^{2+} ions, leading to increased polarization. The peak in case of BNFNO is much broader as

compared to BFO sample indicating enhanced relaxation time for the doped sample.

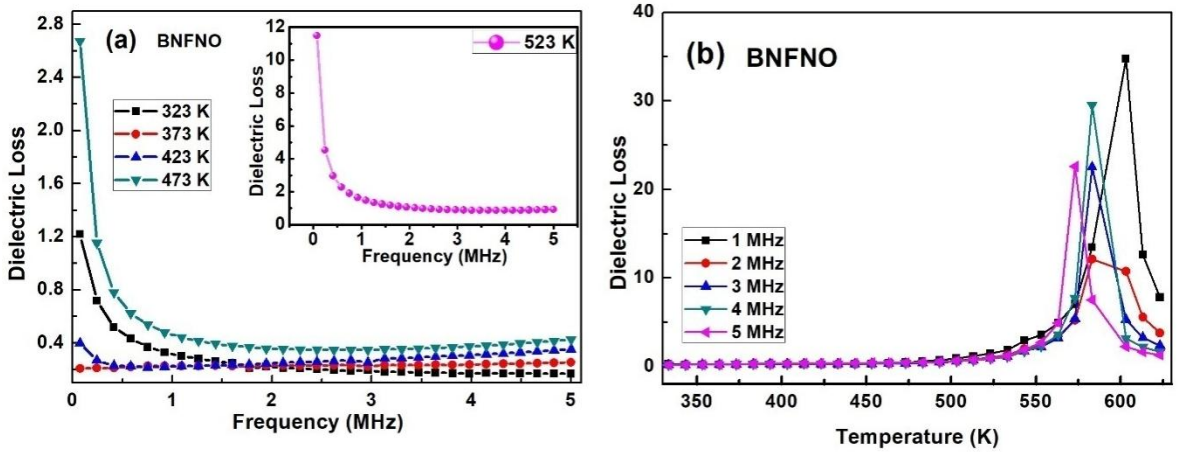

FIG 3: Plots of dielectric loss tangentof BNFNO as a function of **(a)** frequency **(b)** temperature.

Fig. 3(a) shows the variation of dielectric loss (tan δ) with frequency for the BNFNO sample at various temperatures. The dielectric loss is found to decrease with the increase in frequency. This maybe due to the decreased bismuth volatility due to (Nd, Ni) co- doping. The temperature dependent dielectric loss plot for BNFNO is shown in Fig. 3(b). The value of dielectric loss is independent of the temperature at all the frequencies within the low temperature range. It is found to increase at higher temperatures which could be due to generation of impurities and defects in the sample arising from lattice distortion caused by mismatch of the ionic radii of the dopants.The appearance of the peak at around 570K- 630K confirms the relaxor type behaviour of the sample.

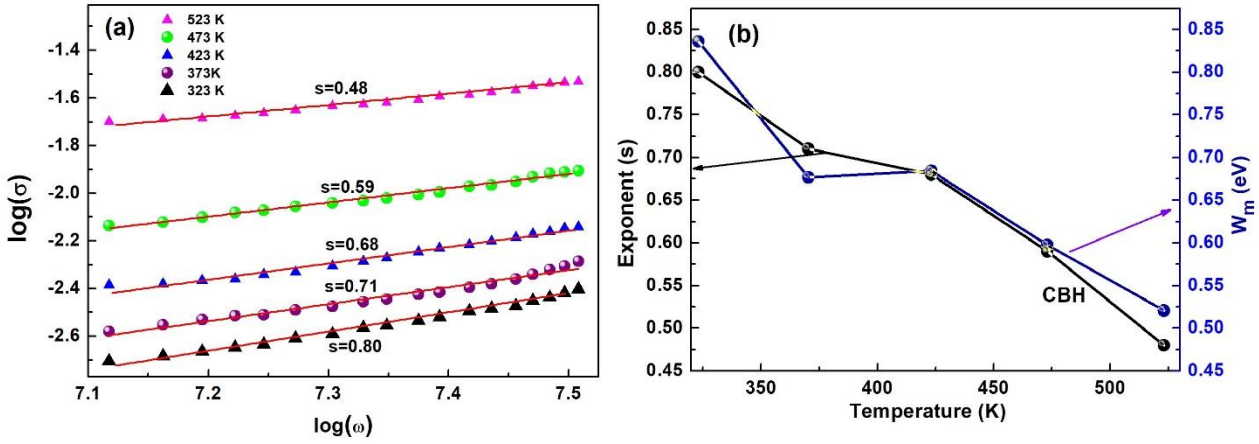

FIG 4.(a) log σ versus log ω plots at various temperatures for BNFNO **(b)** Exponent 's' and Binding Energy versus temperature plots of BNFNO .

The AC conductivity has been studied to evaluate various electrical parameters of BNFNO and their variation with frequency and temperature has been explored. It is given by the relation: $\sigma_{ac} = \varepsilon'\varepsilon_0\omega\tan\delta$, where ε', ε_0, ω and tan δ are the real part of dielectric constant, free space permittivity, angular frequency

and tangent loss factor, respectively. Various electrical parameters such as the binding energy and minimum hopping distance can be determined by applying the Jonscher's universal dynamic law stated as $\sigma_{ac}= A\omega^{s}$, where A is a constant , ω is the angular frequency and 's' is a frequency dependent parameter lying between 0 and 1 for ac conductivity[8]. From Fig 4 (a), the value of 's' has been found to lie between 0.48 to 0.80 for various temperatures. The exponent 's' exhibits a decrease with the increase in temperature, which is in accordance with the correlated barrier hopping (CBH) conduction mechanism (Fig.4 (b)). The charge carriers are thermally activated and hop over the potential barrier between different lattice sites. [9]

The exponent 's' has been used to estimate the binding energy (W_m) of the electrons in the system. It is the amount of energy required for the electron to transfer from one site to another. According to the CBH model, the binding energy is given by

$$W_m = 6k_BT/(1-s) \quad (1)$$

where, k_B is the Boltzmann's constant [2][10]. The binding energy decreases with temperature, indicating an increase in the number of hopping charge carriers and ease in the movement of the electrons which may be due to the introduction of Ni^{2+} dopant. The values of exponent 's' and binding energies of the electrons against various temperatures has been tabulated in Table 1.

TABLE 1. The values of exponent 's' and binding energies of BNFNO at various temperatures.

Temperature (K)	Exponent 's'	Binding Energy W_m (eV)
323	0.80	0.83
373	0.71	0.67
423	0.68	0.68
473	0.59	0.59
523	0.48	0.52

The binding energy has been used to evaluate the minimum hopping distance (R_{min}) which can be expressed as

$$R_{min} = 2e^2/\pi\varepsilon_{\circ}\varepsilon' W_m \quad (2)$$

where, e is electronic charge, $\varepsilon_{\circ}$ and ε' are permittivity of free space and dielectric constant respectively [2].

The value of R_{min} is observed to lie between 0.1 to 0.2 nanometers for the temperature range 323K-523K (Fig. 5 (a)). The minimum hopping distance is found to increase with frequency upto 1MHz, after which it attains almost a constant value.

The plot of ln (σ) against 1000/T at 1 MHz is shown in Fig.5 (b). Arrhenius law has been used to fit the experimental data and activation energy has been evaluated for two temperature ranges. The Activation

energy is found to increase from 0.35 eV to 2.76 eV, with the increase in the temperatures, owing to the creation of more oxygen vacancies instigated by (Nd, Ni) co-doping.

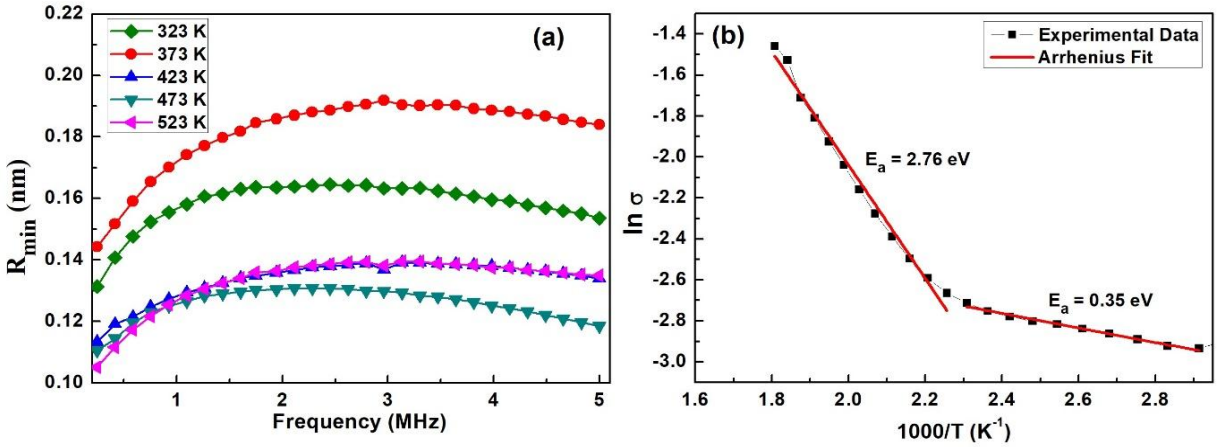

FIG 5.(a) Frequency dependence of Minimum Hopping Distance at various temperatures **(b)**ln σ vs 1000/T plots of BNFNO with Arrhenius fit.

4. Conclusions

Pristine and (Nd, Ni) co-doped BFO have been synthesized through sol-gel auto- combustion process and their temperature dependent dielectric response have been studied.The dielectric constant and dissipation factor have been found to decrease with the increase in frequency. The value of dielectric constant is increased upon doping, owing to increased number of charge carriers which contribute to orientational polarisation**.** A relaxation peak has been found at around 630 K for the BFO sample and at around 500K in the BNFNO sample which shifts towards lower temperatures at higher frequencies. The AC conductivity follows the Jonscher's universal dynamic law, that has been utilized to evaluate the value of frequency exponent 's'. The decrease in the value of the 's' parameter with the increase in temperature establishes that the conduction mechanism is governed by the correlated barrier hopping (CBH) model. The binding energies (W_m) of the electrons have been evaluated using the 's' values. The binding energy is found to decrease with the temperature, indicating an enhancement in charge transfer. The minimum hopping distance (R_{min}) calculated from the ac conductivity data comes out to be in the range of 0.1 to 0.2 nm. Arrhenius law has been used to fit the experimental data and the values of activation energy are found to increase with the increase in temperature.

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