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Tb and Ni Substituted $Bifeo_3$ Nanoparticles Best Suitable For Photo-Catalytic and Optoelectronic Devices

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Abstract:

In the present research work, we have investigated the dielectric properties of Tb and Ni substituted $BiFeO_3$ nanoparticles. The dielectric findings (100-450 K) revealed a dispersed ferroelectric phase transition. The lower temperature ac conductivity is in accord with Motts law, approving the hopping conduction mechanism.

1. Introduction

Recently, BFO with intrinsic electric polarization field, good chemical stability and ideal band gap (~2.1 eV), has also been demonstrated as a promising Visible-light driven photo catalyst [1-3]. However, their role as photo catalyst is not so significant because of rapid recombination of photo-generated electron–hole pairs in BFO [4]. But it can be improved by synthesizing its chemical composition, sintering temperature, ionic dictate dopants concentration and dispensation ambience. Consequently, approaches are required for enhancement of the photo-catalytic activity of $BiFeO_3$.

Numerous studies are available for transition metal or rare earth as dopants for BFO [5-9]. In such studies BFO has been studied in a very limited wavelength range. Also, the studies have also been done for BFO as solar cells [7], femtosecond laser pulses [6] and optoelectronic devices [8, 9] in the visible region but no fruitful results are available for BFO applications as photo catalyst and the probability of oxygen-vacancy-induced luminescence. However, this observation is very significant and show similarity with defect-induced optical behaviour of familiar various optical materials (ZnO, SnO2 and TiO2), [10, 11]. So, this will be very significant for future study in which the particle morphology has highest impact for scheming the luminescence. In gist, the rare earth and transition metal ion doped BFO studied

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for optical, photoluminescence (PL) and dielectric properties is still at an early stage and lot of new studies are required to reach at any significant result. So, the present work has been taken to explore the influence of rare earth and transition metal ion doping on the optical, photoluminescence (PL) and associated dielectric properties of $BiFeO_3$.

2. CHARACTERIZATION TECHNIQUES

The impedance analyzer has been used for dielectric study by varying temperature 90 to 350K and frequency from 20 Hz to 3 MHz.

3. Results and Discussion

Dielectric Study:

The frequency versus dielectric loss (figure 1) variation at room temperature for $Bi_{1-x}Tb_x$ $Fe_{1-x}Ni_xO_3$ (x = 0.00, 0.01 and 0.03) has been plotted. The dielectric loss first decreases rapidly owing to the low conductivity of grain boundary [14] and then decrease become almost constant and finally become independent of the frequency. Due to low conductivity, electrons need more energy for electron to swap between Fe^{2+} -Fe^{3+} ions which results heavy dielectric loss. While in the high frequency region conductivity is more so conduction of free electron is possible even with small change in energy. However, the main source of dielectric losses is presence of scums and imperfections in the crystal structure [15, 16]. The second possible reason for this behaviour is polarization mechanisms. Other than electronic, ionic and dipolar polarization, the space charge or interfacial polarisation mainly occurs in the multiferroic ceramic compounds due to the points defect formed during sintering. Three types (electronic, ionic and dipolar) of polarization exist simultaneously at low frequency, but ε significantly contributed by the space charge polarization [12]. At low frequency, the variation of applied electric field is followed by the space charges, but this behaviour is not shown at high frequencies. Hence space charges contribute to the dielectric constant decreases at high frequency. In addition, at higher frequency, the ionic as well as dipolar contributions are also small attributed to the inertia of the ions and molecules [13].

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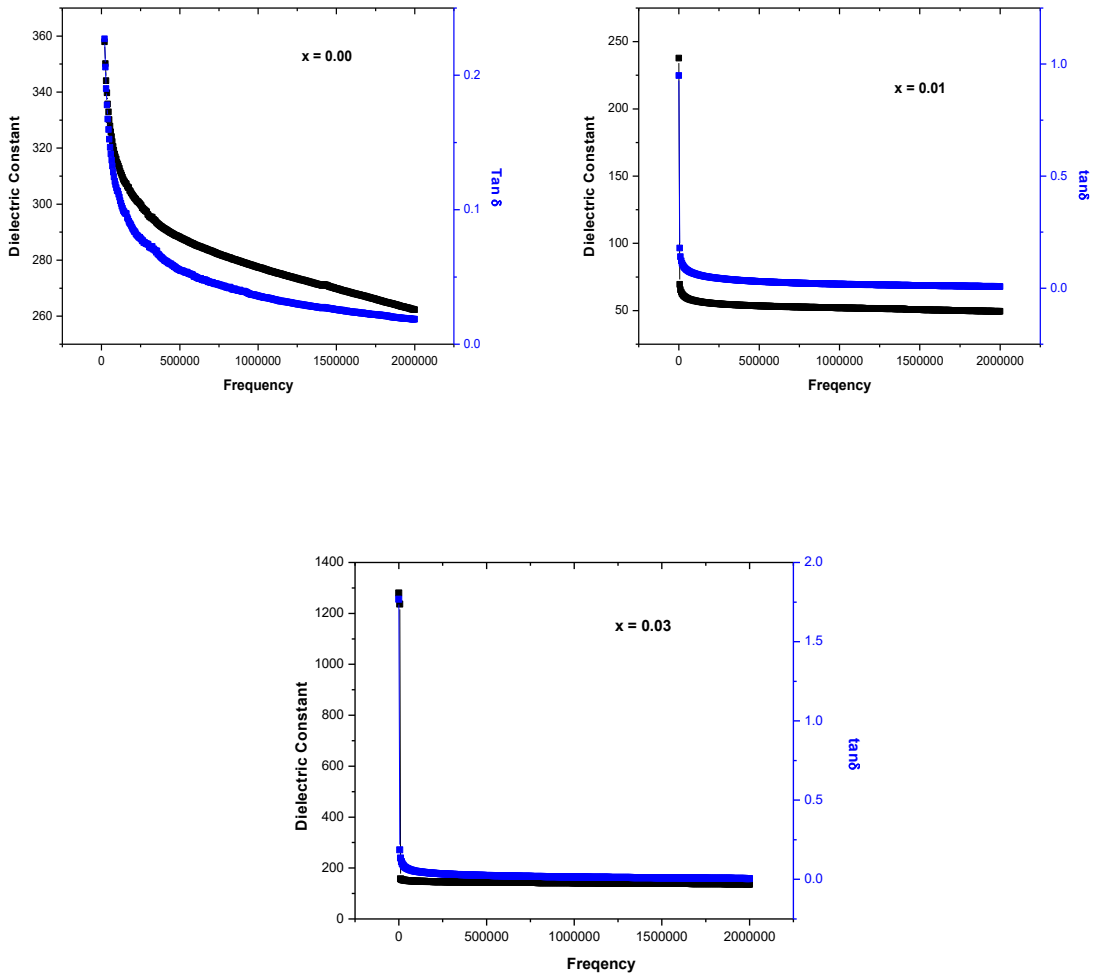

Figure 1. Frequency dependence of dielectric constant and dielectric loss of $Bi_{1-x}La_xFe_{1-x}Ni_xO_3$ (x = 0.0, 0.01 and 0.03) at RT.

The temperature versus dielectric constant $\varepsilon = \frac{Ct}{\varepsilon_\circ A}$ at different frequencies has been shown in figure 2. Form the figure it is clears that with increase in temperature at all frequencies dielectric losses decreases for all compositions. These finding has strong correlation with the koops and Maxwell-Wagner models [17, 14, 18]. On the basis of these models it can be assumed that not only electronic or ionic dipolar but also space charge polarisations contribute towards the dielectric constant. Dielectric polarizibility occurred owe to the exchange of electron and hole between the ions. This exchange is not possible at high frequency as a result dielectric loss remains almost constant. The semiconducting behaviour can be confirmed from the plot fig 2 , dielectric constant increased with temperature for all the compositions [19, 20]. Mobility is directly proportional to conductivity which increases with temperature and hence rate of hopping also increases, which results in enhanced

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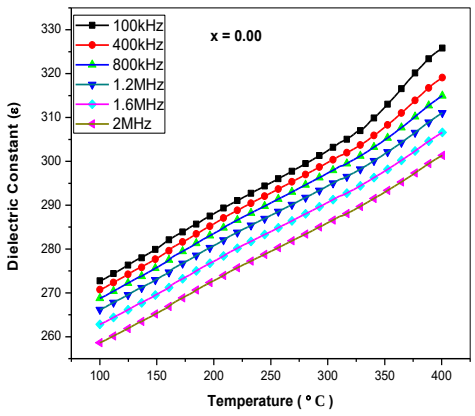
dielectric constant values. However reverse is not possible. At hopping conduction, dielectric relaxation (0.06 and 0.003) occurs at resonance frequency (100 KHz-2MHz). A diverse kind of relaxation process in the nanoregime has been noticed owe to the occurrence of relaxation peaks. In the case of nano scale sized particle one cannot neglect the influence of interfacial loss and electrical conductivity losses which found to be minimum for higher value of frequency.

Again no change in dielectric loss has been find out for high value of frequency which may be due to non-capability of electric dipoles towards the variation the applied field [21].

The variation with temperature of tan δ at different frequencies is shown in figures 3. The component tanδ exposed a relaxation. The relaxation peaks were observed in nanostructured bismuth ferrite. These peaks suggest a different kind of relaxation process was occurring in the nanoregime. As we reach to the maxima, the direct coupling between oscillating charge particle and oscillating field has been observed which further indicates maximum absorption of the electrical energy. The interfacial loss and electrical conductivity loss has great contribution in the case of nanosized particle, which found to be minimum (tan $\delta=0.003$) for higher frequency (2 MHz) and negligible for low frequency (100 KHz)((tan $\delta=0.06$) .

The hopping conduction contributes to dielectric relaxation which occurs at resonance between hopping frequency of the charge carriers and peripheral applied field. It has been observed that the relaxation value shift towards the high frequencies with increase in temperature.



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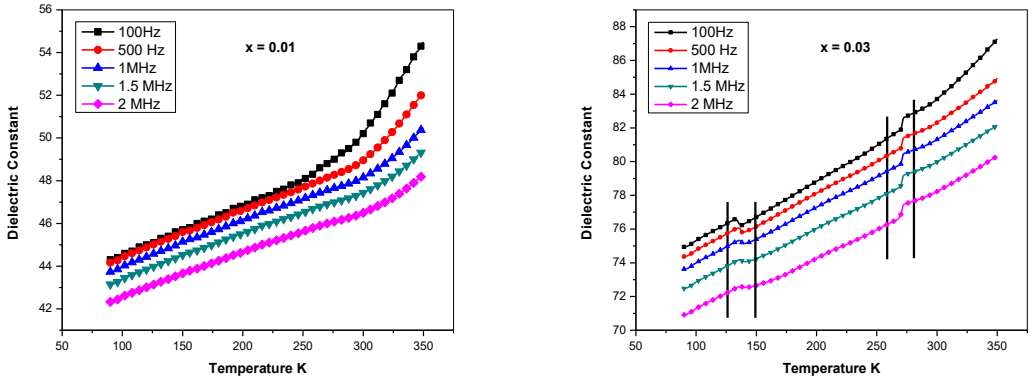
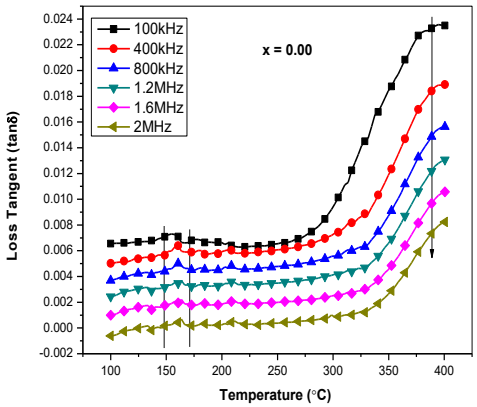


Figure 2 Temperature dependence of dielectric constant of $Bi_{1-x}Tb_xFe_{1-x}Ni_xO_3$ (x = 0.0, 0.01 and 0.03).



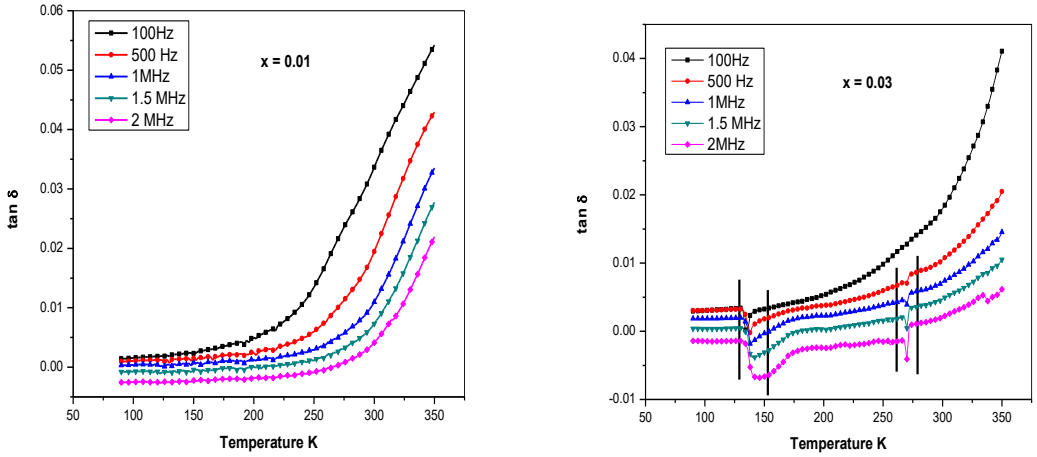


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Figure 3 Temperature dependence of dielectric loss of $Bi_{1-x}Tb_xFe_{1-x}Ni_xO_3$ (x = 0.0, 0.01 and 0.03)

Ac conductivity studies:

Figure 4 show the variation of ac conductivity at room temperature of $Bi_{1-x}Tb_xFe_{1-x}Ni_xO_3$ (x = 0.0, 0.01 and 0.03).It has been observed that ac conductivity depends upon frequency. The conductivity first increases then become maximum and then further decreases with increase in frequency. This can attributed on the basis of hopping of charge carrier. The frequency dependent ac conductivity can be expressed by the following empirical formula [22].

$$A(\omega) = A\omega^n$$

The slope of $\ln\sigma$ versus $\ln\omega$ plots gives the value of n, (Fig 8) where 'n' lies amongst 0 and 1. The n = 0 contribute that the electrical conductivity is frequency-independent, however reverse is for n >0.[23].

Koops model explain the increase in ac conductivity with frequency and temperature. According to koops model, the conductivity (which is a function of frequency) is due to the grain boundaries at low frequency. And dispersion (which occurred at higher frequencies) is basically due to the conducting grains. At interfacial states the density is higher. These high densities serve as charge carriers due to ionization. It can also contribute conduction centres which further act as a transporter of charge carriers.

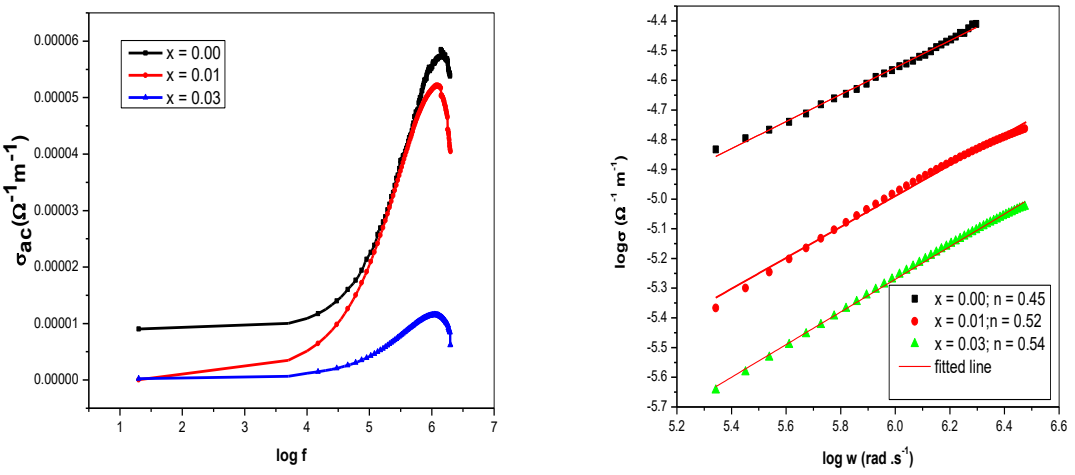

Figure:4 Plot of σ versus log f and b) log σ versus log w for $Bi_{1-x}Tb_x$ $Fe_{1-x}Ni_xO_3$ (x = 0.00, 0.01 and 0.03).

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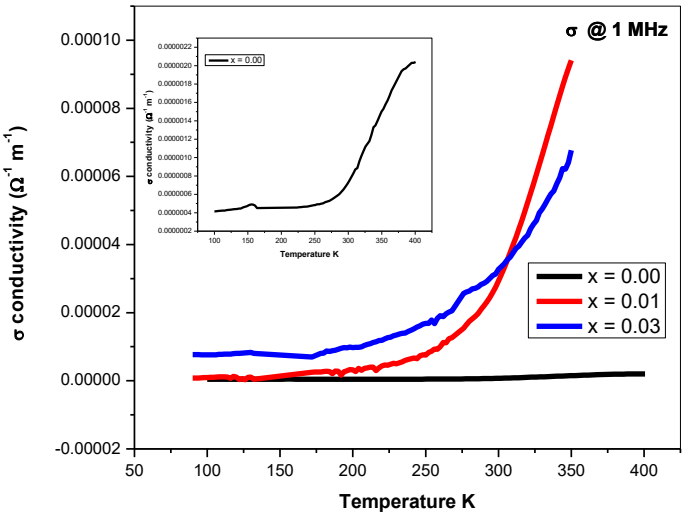
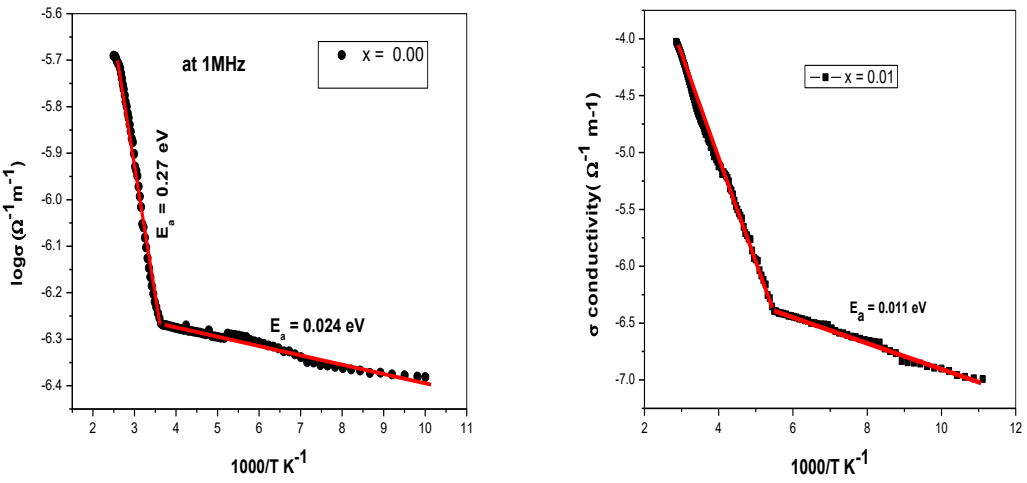


Figure:9 Plot of σ versus temperature of x = 0.00 (inset)) and σ versus temperature for $Bi_{1-x}Tb_x\ Fe_{1-x}Ni_xO_3$ (x = 0.01 and 0.03).

At sophisticated temperatures (fig 5), the ac conductivity $\sigma = A\exp^{\frac{E_a}{KT}}$ displays the activated temperature dependence. The slope of ln (σ) versus 1/T gives the value of activation energy Fig. 6. From this figure an increasing trend in activation energy with temperature has been observed.



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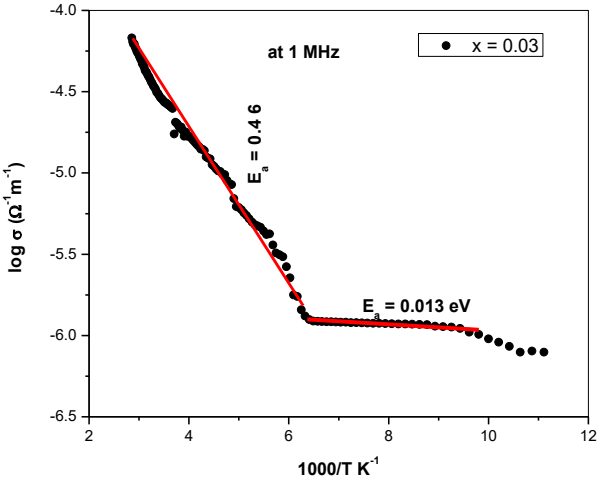

Figure 6: Plot of log σ versus 1000/T for $Bi_{1-x}Tb_x$ $Fe_{1-x}Ni_xO_3$ (x = 0.00, 0.01 and 0.03).

Conclusion:

The addition of Tb and Ni dopant significantly reduced dielectric loss and hence enhanced the dielectric properties enables the material the most probable candidate for photo-catalytic applications and optoelectronic devices.

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