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Dielectric Study of Ni Substituted Bismuth Ferrites Prepared by Sol Gel Method

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Abstract—*Ni substituted bismuth ferrites (BFNO) with compositional formula $BiFe_{1-x}Ni_xO_3$ where $0.01 \leq x \leq 0.09$ in steps of 0.02 was fabricated using Sol Gel Method. XRD confirm the phase formation of BFNO. From the Rietveld analysis of the XRD several parameter such as lattice constant, density, and crystallite size were calculated. Dielectric properties such as dielectric constant and loss factor of all the sample were studied. The dielectric constant was subjected to frequency and concentration. Frequency variation of dielectric loss was also carried out. Both the dielectric constant and dielectric loss show dispersion with frequency. Possible mechanism contributing to all the above result is being discussed.*

Keywords: *Sol Gel, Ferrite, XRD, Dielectric constant, Lattice constant.*

1. Introduction:

In recent years, Bismuth Ferrite (BFO), has attracted many researchers because of its multiferroic characteristics, ferromagnetism and ferroelectricity. BFO has rhombohedrally distorted perovskite structure with space group R3C. The Neel temperature and the Curie temperature for bulk Bismuth Ferrite is around 643 K and 1100k respectively. Magnetization arises in BFO due to exchange interaction of localized electrons in partially filled d or f shells, but the poor magnetic property is due to i) Fe-O-Fe Dzyaloshinskii-Moriya exchange interaction on B-site (Fe) which give rise to week anti-ferromagnetic ordering and ii) a magnetic cycloidal spin structure with a long periodicity of 60nm[1]. Some of its application are- magnetic data storage, sensors, spin valves, capacitor [2-5]. In addition to the potential magnetoelectric application, BFO can be used as a novel absorbent in the photocatalytic degradation of organic dynes and pollutants as it absorbed light in the range of the visible spectrum [6]. However there are certain limitations of BFO, it has low dielectric constant, large dielectric loss factor and the production of cycloid spin spiral structure. The low dielectric constant value is cause due to large leakage current which arises because of the multiple oxidation state of Fe ions which on inter-conversion of Fe^{3+} to Fe^{2+} create oxygen vacancies [6]. Researchers are using various strategies to improve the electrical properties.

In the present study Ni substituted BFNO is prepared by Sol Gel method and subjected for XRD and dielectric study.

2. Experimental

Ni substituted Bismuth Ferrite nano-powder is synthesised by Sol Gel route using Bi $(NO_3)_3.5H_2O$, $Fe(NO_3)_39H_2O$,$Ni(NO_3)_2.6H_2O$ and citric acid as the solutes and 2-methoxyethanol as the solvent. Stoichiometric amounts of the solutes are calculated by molarity method to make 100ml of 0.1M final solution. Solutions of Bismuth Nitrate and Ferric Nitrate are made in two separate beakers by taking same amount of the solvent. Both the solution are mixed thoroughly using magnetic stirrer. Stoichiometric amount of nickel(ll) nitrate hexahydrate is added to the mixture. Few drops of 3M HNO_3 acid is added to the mixture to remove the dissolve impurities. Citric acid is then added and it acts as the chelating agent to bind all the constituentions together.Finally, some amount of 2-methoxyethanol is added to the solution to make the solution of 100ml. The solution is heated at 120^0C for 2hr and a light brown colour fluffy gel is obtained. The gel is dried in a hot air oven for 3hr at around 80^0C.The dried sample is then crushed into powder and calcined at 550^0C for 30 min in a microwave oven. The calcined powder is leached with 1M HNO_3 acid then pressed into pellets of diameter 10mm and thickness 1mm using polyvinyl alcohol as the binder. Heat treatment is given to the pellets at 600°C. The samples were measured by Agilent E4980 LCR meter and the value of dielectric constants were obtained from the formula $\varepsilon' = Cd/\varepsilon_0 A$ where ε' is the dielectric constant, C is the measured capacitance, d is the thickness, A is the cross-sectional area of the sample and ε_0 is the permittivity of the free space.

3. Result and Discussion

Fig. 1 shows the Rietveld refinement of the XRD pattern of BFNO samples with different concentration. Table 1 shows the variation of crystallite size, density and the lattice constants.

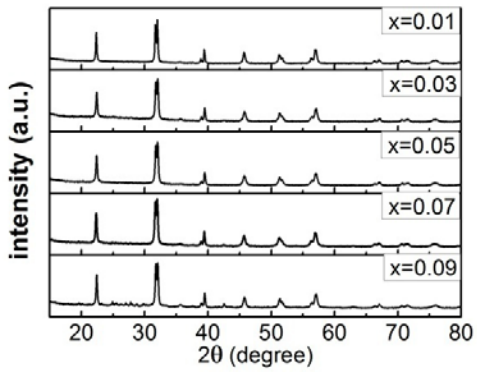

Fig. 1: Rietveld refinement of the XRD pattern of BFNO samples

Table 1: Crystallite size, density, and lattice constants of BFNO samples

Sl. No.	Concentration (x)	Crystallite Size (nm)	Density(ρ) g/cm^3	Lattice Constant (Å)		
				a	b	c
1	0.01	30	8.349	5.57673	5.57673	13.06044
2	0.03	27	8.318	5.57779	5.57779	13.86638
3	0.05	28	8.269	5.57665	5.57665	13.86362
4	0.07	28	8.235	5.57751	5.57751	13.86403
5	0.09	29	8.235	5.57756	5.57756	13.86613

The crystallite size (D) is estimated from the most intense peak using Scherer's formula as given by,

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

where β stands for Full Width at Half Maxima and λ is the wavelength of the X-ray used [7]. The crystallite size reduces with the increment in Ni concentration from x=0.01 to x=0.03 and subsequent doping slightly increase it. This reduction in crystallite size may be due to the suppression of the oxygen vacancies [6]. Replacement of the smaller cations i.e. Fe^{3+} (0.64Å) by a larger cations Ni^{2+} (0.69Å) lead to the slight increment on crystallite size for higher concentration. There is slight decrease in the density as the concentration increase due to slight increment in the lattice constant (c).

4. Dielectric properties

Fig. 2. Shows the variation of dielectric constant, ε′ and dielectric loss, tan δ as the function of frequency in the range 20Hz–2M Hz at room temperature. Both the quantities show dispersive behaviour for all the samples in the whole frequency range. The values of dielectric constant are high at low frequencies and decreases as frequency increases and beyond a particular high frequency, it has no dependence on the frequency of the applied electric field.

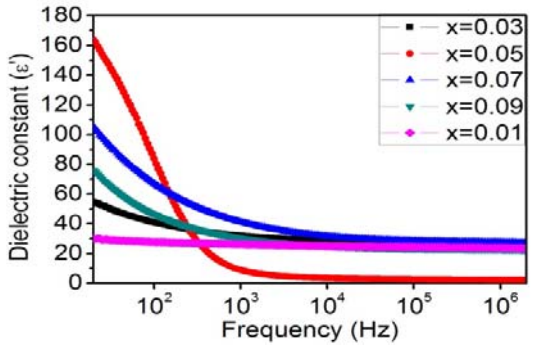

Fig. 2: Variation of dielectric constant of BFNO with frequency

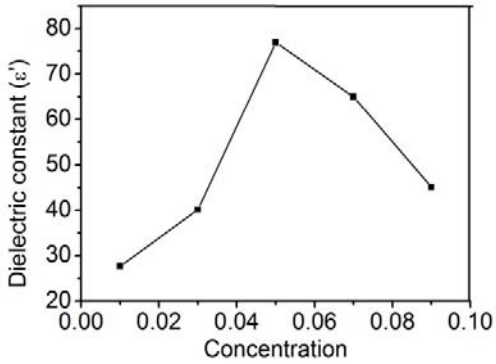

Fig. 3: Variation of dielectric constant of BFNO with the concentration of Ni content at 110 Hz

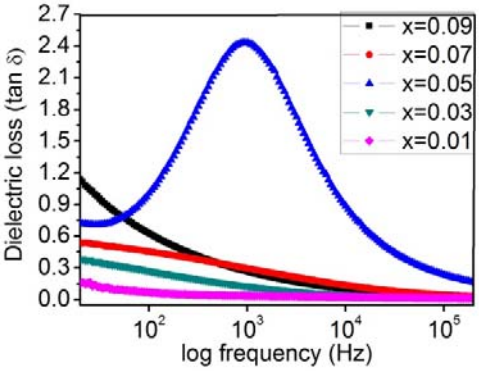

Fig. 4: Variation of dielectric loss (tan δ) of BFNO with frequency

In general, the dielectric dispersion behaviour in materials can be explained in accordance with four fundamental polarisation mechanisms. At higher frequencies, the dielectric constant of any material is contributed by the electronic and ionic polarisations. However, at lower frequencies the dipolar and interfacial polarisations (space charge polarisation) play an important role to the behaviour of dielectric response. In the present investigation, the frequency range is only up to 2 MHz and hence the contributions are expected to be made from the dipolar and interfacial polarisation mechanisms only. The high value of dielectric constant at extremely low frequency region

is attributed to Maxwell Wagner type interfacial polarisation (space charge polarisation) in connection with Koop's phenomenological two layer model. According to it, every dielectric medium is characterised by two layers, well and poor conducting layers constituted by crystallite grains and boundaries respectively. At lower frequencies, the contribution from the grain boundaries is significant and therefore the resistivity of grain boundary increases [8]. Hence, charges cannot migrate and piles up at the boundaries. This space charge piling up of electrons in low frequency region contributes to the interfacial or space charge polarisation producing a very large value of capacitance. The charge storing capacity of the sample increases and hence the value of dielectric constant is very large in low frequency region. As the value of frequency increases dipolar polarisation becomes dominant. This is due to the hopping of electrons between Fe^{2+} and Fe^{3+} ions. The presence of Fe^{2+} and Fe^{3+} ions at octahedral sites define ferrites as polar materials. The rotation or turning of dipoles can be explained as the interchange of the electrons between the ions, thus the dipoles align themselves with the field. However, the potential barrier between two types of ions (Fe^{2+} and Fe^{3+}ions) will impose an inertia to charge movement, resulting in a relaxation to the polarisation to the polarisation process and hence polarisation lagging progressively behind the field at higher and higher frequencies. Therefore at higher frequencies the value of dielectric constant decreases and finally becomes independent of the frequency of the applied electric field [8].

The dielectric constant of BFNO ceramics increases with increasing *x* from 0.01 to 0.05, and then decreases with increasing *x* from 0.05 to 0.09. There is always some relatively high conductivity in BFNO with less amount of doping, which result in small dielectric constant. The leakage current density decreases with increasing Ni content and then increases with increasing Ni content [9]. Therefore, the dielectric constant increases with increasing Ni content and then decreases. Another reason for the decrease of dielectric constant in the samples is due to the unit cell volume contraction. Since the radius of Ni^{2+} ions is larger than that of Fe^{3+} ions, the incorporation of Ni^{2+} ions is expected to obtain smaller rattle space than Fe^{3+} in the oxygen octahedron thus shows smaller polarization [9].

5. Conclusion

The dielectric measurements show that Ni substitution affect significantly the dielectric properties of Bismuth ferrite. The dielectric constant increase with increasing Ni content from 0.01 to 0.05 and then decrease with the further increase of Ni content. Frequency variation of both dielectric constant and dielectric loss show dispersion.

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