A study of dielectric relaxation properties of ZnFe$_{2-x}$Bi$_x$O$_4$ nano Ferrites synthesized by sol-gel combustion method

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Abstract. A series of bismuth doped zinc nano ferrite particles with the formula ZnBi$_x$Fe$_{2-x}$O$_4$ (x = 0.00, 0.05, 0.10, 0.15, 0.20 & 0.25) were prepared by sol-gel combustion method; and these compositions were sintered at 600°C for 5 hrs. With the effect of bismuth doping, the structural properties of all prepared samples were characterized by X-ray diffraction (XRD). The X-ray diffraction spectra analyses confirm single phase cubic (FCC) spinal structure. The average crystallite size (D) of the samples found to be in the range 17-20 nm. The dielectric properties viz., dielectric constant (ε'), dielectric loss tangent (tan δ) and AC conductivity (σ$_{AC}$) were measured at room temperature in the range 20Hz to 2MHz, which confirm the normal ferrite behavior. In the present research work, we are intended to extend dielectric relaxation studies of these samples with the help of Cole-Cole plots. The Cole-Cole plots of the bismuth doped zinc ferrites were drawn as a function of ε' and ε'' (where, ε''=ε' tan δ) and hence we have determined the spreading factor (β) for all the samples. It was observed that β decreases with the increase of the concentration of B$_2$O$_3$. It is noticed that the dielectric parameters ε', tan δ and σ$_{AC}$ have exhibited the similar trend. These samples may find suitable applications in electrolytic elements in battery technology.

Keywords: Bi-Zn nanoferrites; sol-gel combustion method, AC conductivity and dielectric constant, cole-cole plots.

1. Introduction
Nanosized ferrites are magnetic ceramics of great importance in microwave and electromagnetic applications [1-2]. The ferrite materials exhibit great physical and chemical properties specifically with nano range [3-4]. The spinal structure of any ferrite material is MFe$_2$O$_4$. Where M represent divalent metal cation and Fe$_2$ represent trivalent metal cation preferably belongs to tetrahedral and octahedral sites respectively [5-6]. The structural properties and its physiochemical properties of any ferrites can be modified by doping with different divalent and trivalent metals at A and B sites respectively like Mg, Ni, Co, Cd, Bi, Mn, Zn etc. Out of different dopent elements present in the periodic table bismuth is potential dopent element due to its high electrical resistivity with low magnetic and dielectric losses [7-10]. Hence Bismuth doped ferrites (BFO) are widely used in magnetic recording, high density data storage devices and microwave device applications. Because of this the authors are investigating the structural properties with the effect of bismuth substitution on zinc spinal ferrite synthesized by sol-gel combustion method [11-12].
2. Result and Discussion
2.1. X-ray diffraction analysis
The X-ray diffraction (XRD) patterns of Zn Bi$_x$ Fe$_{2-x}$ O$_4$ (0.00 ≤ x ≤ 0.25) nano ferrites. Which revels the diffracted peaks are found to be sharp and single phase FCC spinal structure of Zn Fe$_2$ O$_4$ with JCPDS file no.82-1049. It can be observed from the XRD pattern with the addition of bismuth in small quantity which does not alter the spinal structure of ferrite system and existence of Bi$^{3+}$ ions and indicated with ‘*’ mark [13]. The crystallite size (D) of all the compositions was determined with Debye-Scherrer formula and the crystallite size found to be gradually decreases ranges from 20 to 16 nm whereas the lattice constant (a) increases with the increases of Bi$^{3+}$ concentration. This may be attributed due to the larger ionic radii of Bi$^{3+}$ (1.30 Å) replaces the smaller Fe$^{3+}$ (0.64 Å) ions [14, 15]. It is observed that the molecular weight of the composition increases with the increase of Bi ion concentration. This is due to the lesser atomic weight of ferric ions (55.85 gm/mol) were replaced by greater atomic weight of bismuth ion (208.98 gm/mol) [13]. The microscopic SEM image of the sample (X = 0.20) from the author published paper [13] it is clear that the particles are distributed homogeneously and having almost same crystallite sizes at the sintered temperature of 600°C. It is obvious from the TEM image that, the average grain size of the composition was in 20nm. This was almost matching with the crystallite size of the sample determined from XRD pattern [13].

2.2 EDS and FTIR studies
The stoichiometric composition ZnBi$_x$Fe$_{2-x}$O$_4$ (0.00 ≤ x ≤ 0.25) sintered at 600°C. The EDS patterns reviel the presence of Zn$^{2+}$, Fe$^{3+}$, Bi$^{3+}$ and O$^{2-}$ ions in appropriate proportions as maintained in prepared samples with an error of ± 0.2%. Which is also confirm that the FTIR studies of samples are in single phase nano crystalline nature [13]. In general, any ferrite system two prominent absorption bands as high frequency band (ν$_1$) and low frequency band (ν$_2$) preferably represents two sub lattices as tetrahedral (A-site) and octahedral (B-site) respectively. The infrared spectra of nano ferrite samples show the existence of absorption bands has been located in between 300-800 cm$^{-1}$. These bands represent the higher frequency band nearby 600cm$^{-1}$ and lower frequency band nearby 400cm$^{-1}$. In the present ferrite system with Bi$^{3+}$ doping the strongest absorption bands were observed in the frequency range 543-553cm$^{-1}$ and weakest absorption bands in the frequency range 404-438cm$^{-1}$. The observed frequency absorption bands confirmed the formation of single phase nano ferrite system having tetrahedral (A-site) and octahedral (B-site) sub lattice respectively [13].

3. Dielectric Properties
3.1. Dielectric constant (ε')
The dielectric behaviour of ZnBi$_x$Fe$_{2-x}$O$_4$ (0.00 ≤ x ≤ 0.25) samples measured based on the applied frequency and Bi$^{3+}$ doping content, within the frequency ranging from 20Hz to 2MHz at 300K. Dielectric loss gives the materials inherent dissipation of electromagnetic energy, defined as either loss angle ‘δ’ or with loss tangent 'tan δ'. Figure (1) shows the behaviour of dielectric constant (ε') with applied frequency is increased the dielectric constant values are seems to be decrease in trend gradually till the maximum applied frequency of 2MHz [13]. This type of dielectric behaviour is considered to be common to any kind of ferrite material and signifies that the ferrite materials are frequency dependent [16-18]. It is observed a sharp decrease in dielectric constant (ε’) is observed at lower frequency up to 5Hz and as the frequency increases to 2MHz the dielectric values remained constant. With the increase of the Bi$^{3+}$ ion concentration in Zn ferrites, the dielectric behaviour for all the samples remains same. Similar kind of behaviour was observed in other materials and this is due to the hopping of electrons in among Fe$^{2+}$ and Fe$^{3+}$ ions taking part in the local field of electrons along with the applied electric field. This causes the displacement of charge carriers in the composition [19-21]. The relation between dielectric constant and the applied frequency was also explained by space-charge polarization mechanism [22].
Any dielectric material which has good conducting grains is separated by non conducting grain boundaries. With the applied electric field, voltage drop occurs mainly at the grain boundaries. According to the Koops phenomenology theory at grain boundaries the accumulation of space charge takes place and hence the effect grain boundary is high at lower frequencies [23]. According to Maxwell and Wanger theory the space charge polarization of any dielectric material exhibits non homogeneous structure [24, 25]. Large conducting grains in the composition are distanced by feebly conducting grain borders [26]. With all the above results, we conclude that with the application of electric field the dielectric constant ($\varepsilon'$) decreases [27].

3.2. Dielectric loss tangent $\tan \delta$

The dielectric loss tangent ($\tan \delta$) variation with log of frequency (Hz) for ZnBi$_x$Fe$_{2-x}$O$_4$ ($0.00 \leq x \leq 0.25$) samples is shown in Figure 2 (a). As observed from the figures, they showed normal dielectric behaviour as similar to any ferrite material and the dielectric loss tangent was observed to decrease exponentially by increasing frequency for both the compositions under study. A maximum was observed in the dielectric loss tangent versus frequency curves when the hopping charge carrier’s frequency coincides with frequency of the applied alternating field. The maximum in dielectric loss tangent decrease with increase in frequency and disappears at higher frequencies. A narrow peak of dielectric loss tangent indicates the existence of relaxation time rather than a single relaxation time.

3.2.1. AC Conductivity $\sigma_{AC}$

AC conductivity ($\sigma_{AC}$) versus log f (Hz) for ZnBi$_x$Fe$_{2-x}$O$_4$ ($0.00 \leq x \leq 0.25$) samples is shown in Figure 2 (b). As observed from the figures, they showed normal AC conductivity as similar to any ferrite material and the AC conductivity was observed to increase exponentially by increasing frequency for both the compositions under study. A maximum was observed in the AC conductivity versus frequency curves when the hopping charge carrier’s frequency coincides with frequency of the applied alternating field. The maximum in AC conductivity decrease with increase in frequency and disappears at higher frequencies. A narrow peak of AC conductivity indicates the existence of relaxation time rather than a single relaxation time.
3.3. AC Conductivity ($\sigma_{AC}$)

Figure 3(b) shows the variation of ac conductivity for ZnBi$_x$Fe$_{2-x}$O$_4$ (0.00 $\leq x \leq$ 0.25) samples with frequency. As observed from figure the AC conductivity values are almost independent at lower frequencies. When the frequency increased the conductivity was observed to increase slowly for all the samples. From the well known Maxwell-Wanger theory, the conductivity of all the ferrite samples were found to be low due to the existence of non conducting grain boundaries among the well conducted grains [28]. This can be explained due to the hindrance of charge carriers and thus the electrons exchange between Fe$^{2+}$ and Fe$^{3+}$ ions will be less at low frequencies. In the case of dielectric materials (such as ferrites), they exhibit frequency dependent behaviour. It is clearly observed that the ac conductivity gradually increased with increase of frequency and also it has been established that the conductivity value increases with the Bi$^{3+}$ ion concentration [13].

![Figure 3](image1.png)

**Figure 3** (a) Real part of impedance with applied frequency, (b) imaginary part of impedance with applied frequency for ZnBi$_x$Fe$_{2-x}$O$_4$ (0.00 $\leq x \leq$ 0.25).

4. Impedance studies

In order to study the electrical properties of spinel ferrites samples Impedance analysis is used to determine the involvement of conductivity for both real part and imaginary part by applying AC field [29]. Figure (4), gives the Cole-Cole plots (Complex impedance plot) give a total contribution of microstructure known as grains and grains boundary resistances and help to discriminate the grain and grain boundary resistances and interfacial resistance of conducting electrodes. It is observed from the plots shows the variations of real parts and imaginary parts of complex impedance with applied frequency (20 Hz-2MHz) and it is also observed that up to a definite limiting range (~10 kHz) $Z'$ decreases with increasing frequency subsequently they merge together and becomes nearly constant of frequency. The higher values of $Z'$ at lower frequencies shows a large polarization effect in the sample. The values of $Z''$ decreases identically monotonically up to a certain frequency limit (~100 kHz) beyond which they merge together at a very low value of $Z''$ where frequency is independent nature is observed till the highest frequency limit at room temperature for the varying concentration of bismuth doped zinc nano-ferrite samples [27].

This merging of $Z'$ and $Z''$ at higher frequencies specifies the probable discharge of space charge accumulation at the boundaries of the homogeneous phases in the sample when on application of AC field. It is observed from figure (4) that both the resistance ($Z'$) and reactance ($Z''$) values decreases with increase in applied AC field concluding that the conduction is stimulated with the effect of AC field. As observed there is a monotonic decrease in the values of $Z'$ and $Z''$ with increasing frequencies for all the samples which shows that relaxation behaviour in the material temperature dependent and no single relaxation time is observed. This is further examined and differentiates the microstructure such as grain (intrinsic) and grain boundary (extrinsic), sample-electrode surface effect, (includes crystal defects, and relaxation process etc.) Cole-Cole of impedance ($Z'$ vs. $Z''$) is plotted.
The appearance plot of semicircle in the plot represents a relaxation process, whose radius measures
the resistance of the sample and centre lies on the abscissa (Z' - axis) if the conduction is of Debye
type. In which non-Debye type conduction process, a depressed semicircle appears in the diagram.
This appearance of three distinct semicircles in the diagram, the one appears at high frequency end is
assigned to grain effect, the semicircle at intermediate frequency zone corresponds to grain boundary
effect and that of at lower frequency end is ascribed to sample surface conduction effect [30]. It is
observed that only one Cole-Cole semicircle in the plot where the radius of the semicircle decreases
with increases in Bismuth concentration indicating the decrease in resistance of the material. All the
plots show a tendency to bend towards the abscissa to form semicircles with their centers above the
real axis, having comparatively decreased in radii. It is understand that, even a single relaxation
process is observed in the experimented temperature range, it is difficult to assign that the change in
behavior is cause of intrinsic conduction effect as the resistance of the material is enough low to
prevent the arrival of extrinsic interfacial conduction effect on these samples.

5. Conclusions
A series of pH controlled bismuth doped nano ferrites were sintered at 600°C for 5 hrs in air. The X-
ray diffraction patterns confirmed the formation of single phase spinal structure of crystallite size of
the prepared samples was found to be in the range of ±17 nm. The patterns of Elemental analysis
(EDS) show the presence of stoichiometric elements in all composition samples. The dielectric
constant for all the samples were observed to decrease initially at lower frequencies and as the
frequency was increased the dielectric values were observed to be almost constant similar kinds of
trends are observed in dielectric loss also. The AC conductivity values for all the compositions
increases with the increase of frequency, however it is independent at higher frequency. Impedance
spectroscopy concluded the presence of single semicircle which indicates that there is presence of
grain interior (bulk) property in material. The samples showed presence of dielectric relaxation, which
is found to be of non-Debye type. The semicircles in the complex modulus plot indicated that both
grain and grain boundary capacitance play a vital role in the conduction mechanism of the material
system at the measured temperature.
Acknowledgements
The author (Dr. N Suresh Kumar) is grateful to Prof. K Vijaya Kumar, JNTUH Sulthanpur, sangareddy, Telangana State., and also thankful to the management of VNRVJIET, HYD for their encouragement.

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