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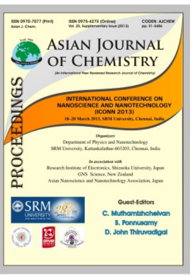

Electrical Conductivity Studies of Nanophase Copper Nickel Ferrite Prepared by Solid State Reaction Technique†

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The electrical properties of nanocrystalline copper nickel ferrites having general chemical formula $Cu_xNi_{(2-x)}Fe_2O_4$ with x varied from 0.2 to 0.9 have been studied. The AC electrical conductivity has been measured as a function of frequency in the range 50 kHz-900 kHz at room temperature 296 K. Prepared samples show the usual dielectric dispersion having Maxwell-Wagner-type interfacial polarization. Reduction in dielectric constant, loss tangent and AC conductivity has been observed with frequency. Dielectric loss tangent also increases with the increase of copper content in the sample which may be due to hopping of Fe^{2+} ions.

Key Words: Ferrite, Conductivity, Dielectric, Tangent loss.

INTRODUCTION

In recent years, spinel ferrites have been investigated because of their tremendous useful electrical and magnetic properties and applications such as information storage systems, magnetic cores, magnetic fluids, microwave absorbers and medical diagnostics[1]. Many workers have been studied the pure cobalt ferrite and the effects of cobalt substitution on the properties of nickel-copper ferrite[2,3]. Substitution of a rare earth ion into the spinel structure has been reported to lead to structural distortion and to induce strains and to significantly modify the electrical and magnetic properties[4,5]. It has been reported that the partial substitution of Fe^{3+} by rare earths (Tb^{3+}, Dy^{3+}) in cobalt ferrite[6] increases the coercive field to about 2kOe (30 % increase), due to the contribution from the large single ion anisotropy from the rare earth sublattice. Recently, Bharathi *et al.*[7,8] have reported that Ni ferrite became ferroelectric upon the substitution of small amount of Fe at the B site by Dy and Gd.

Soft magnetic ferrites with higher saturation magnetization, higher electrical resistivity and lower eddy current losses have been widely used in microwave devices such as isolators, circulators, phase shifters and gyrators[9,10]. Their electromagnetic properties can be tailored by controlling different types and amount of metal ions substitution. It is known that rare earth ions have unpaired 4*f* electrons and the strong spin-orbit coupling of angular momentum. Doping rare earth ions into spinel ferrites, the occurrence of 4*f*-3*d* couplings which determine the magnetocrystalline anisotrpy in ferrites, can also improve the electrical and magnetic properties of spinel ferrites. Therefore, rare earth ions are becoming promising additives for the improvement of electromagnetic properties and EMI shielding effectiveness of ferrites[11-15].

Remarkable electrical and magnetic properties of ferrites depend upon the nature of the ions, their charges and their distribution among tetrahedral (A) and octahedral (B) sites[16]. Nickel ferrite is one of the versatile and technologically important soft ferrite materials because of its typical ferromagnetic properties, low conductivity and thus lower eddy current losses, high electrochemical stability, catalytic behaviour, abundance in nature, *etc.*[17].

The aim of the present work is to investigate the AC conductivity and dielectric constant of nickel ferrite of the general formula $Cu_xNi_{(2-x)}Fe_2O_4$; x = 0.2-0.9. In view of this it is thought that a systematic investigation of electrical transport property would be very much useful and essential. The study would also elucidate the conduction mechanism in these materials. The present investigation is designed to examine the electrical conductivity, dielectric constant and dielectric loss tangent as a function of frequency.

EXPERIMENTAL

Synthesis: The samples having general chemical formula $Cu_xNi_{(2-x)}Fe_2O_4$; x = 0.2-0.9 were prepared by taking copper rings, $NiCl_2$ and iron powder according to stiochiometric

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ratio. The copper rings, nickel chloride and iron were weighed and dissolved in dilute nitric acid and then heated slowly to evaporate the solvent. The resulting black-brown precipitate is collected in a porcelain crucible and was kept in a furnace. It was kept in the furnace for 5 h at 50 ºC. Then it was allowed to cool slowly till it reaches the room temperature for nearly 1 h. The fired sample was ground thoroughly for an hour. It was kept in the furnace once again and heated to 85 ºC for 5 h. After cooling it was again ground for 1 h to get a fine powder. The samples were tested for nanophase using XRD analysis.

Electrical conductivity was measured in the frequency range (50 kHz-900 kHz) by modified two probe method using Zentech-3305 automatic component analyzer.

X-ray diffractogram was taken using Rigaku-mini flex system with CuK_α radiation of wavelength 1.5418 Aº. From X-ray diffraction analysis completion of solid state reaction and confirmation of single phase formation were recorded. For determining the particle size using Scherrer's formula ($t = 0.9\lambda/(B \cos\theta)$, where t = particle size of the crystal, λ = wavelength of the CuK_α radiation, B = full width at half maximum of the diffraction peak taken in radians, θ = angle at which the maximum diffraction peak seen). It was found to be in the range of 19-32 nanometers.

RESULTS AND DISCUSSION

Electrical conductivity: The conductivity studies were undertaken over a wide range of frequencies (100-1000 KHz) for $Cu_xNi_{1-x}Fe_2O_4$. As the applied frequency increases conductivity also increases from 0.12-0.36 µ S/m for x = 0.2 in copper nickel ferrite. Similar behaviour is also observed in other compositions. The variations of σ_{ac} are shown in Fig. 1 for all the compositions from frequency (100 -1000 KHz). It can be seen from these figure that the conductivity (σ) is nearly frequency dependent. However, as the frequency increases the conductivity becomes more and more frequency-dependent. The electrical conduction mechanism can be explained in terms of the electron hopping model[18].

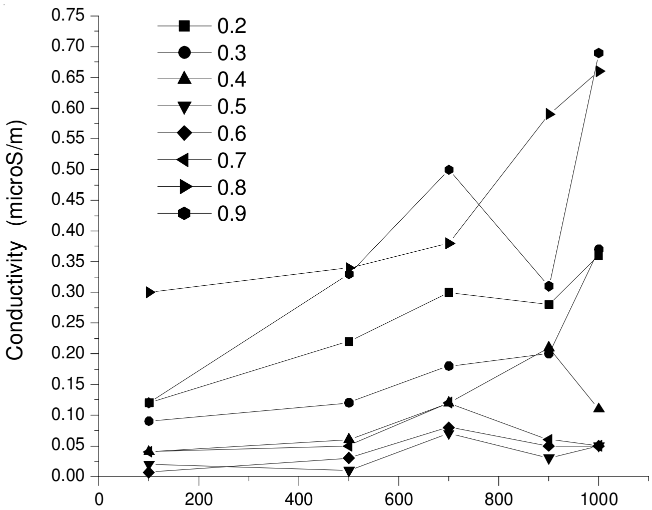

Fig. 1.

The AC conductivity σ and dielectric constant ε' were studied over a wide range of frequencies (50 Hz-5 MHz) for $Cu_x\text{-}Fe_{3\_x}O_{4+\delta}$ at room temperature[19]. The basic fact about AC conductivity in disordered solids is that σ is an increasing function of frequency (any hopping model has this feature). In a hopping model it is possible to distinguish different characteristic regions of frequency. At low frequencies where the conductivity is constant, the transport takes place on infinite paths. For a region of frequencies where the conductivity increases strongly with frequency, the transport is dominated by contributions from hopping infinite clusters.

The electrical conduction mechanism can be explained in terms of the electron hopping model by Heikes and Johnson[18]. In other words, the conduction mechanism could be due to the electron hopping between two adjacent octahedral sites (B-sites) in the spinel lattice and a transition between $Fe^{2+} \rightleftharpoons Fe^{3+}$ ions or $Cu^{2+} \rightleftharpoons Cu^+$ might take place[20].

All samples exhibit dispersion due to interfacial polarization, in agreement with Koops[22]. This behaviour of dielectric polarization may be explained qualitatively by supposing that the mechanism of the polarization process in ferrite is similar to that of the conduction process. There is a strong correlation between the conduction mechanism and the dielectric behaviour of ferrites[23]. According to the electronic exchange in this ferrite may be considered as[18].

$$Fe^{2+} + Cu^{2+} \rightleftharpoons Fe^{3+} + Cu^+$$

Dielectric constant: The variation of dielectric constant with applied frequency is shown in Fig. 2. It is clear that as applied frequency increases ε' decreases for all the compositions up to about 400 kHz. When the concentration of copper is large there is an increasing trend in dielectric constant. The variation of dielectric constant corresponding to frequency and composition of the samples. In both the cases ε' decreases. This may be ascribed to electron hopping (conduction mechanism) which increases and so ε' decreases.

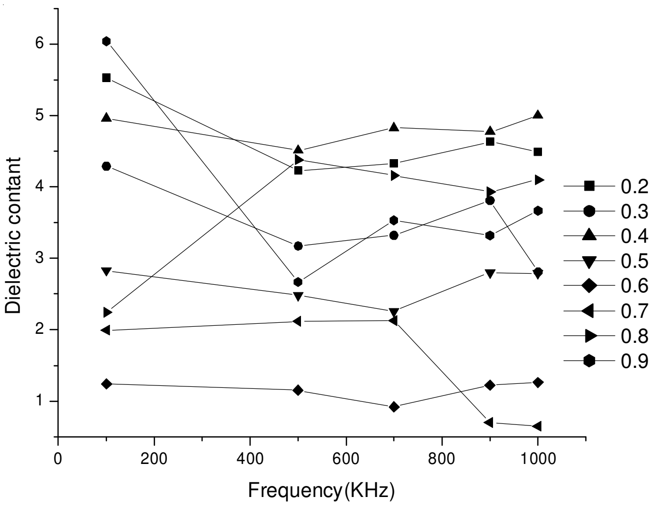

Fig. 2.

It has been reported[21] that for copper doped magnetite, one obtains local displacements of electron in the direction of the applied field. These displacements determine the polarization of the ferrite. It is known that the effect of polarization is to reduce the field inside the medium. Therefore, the dielectric constant of a substance may decrease substantially as the frequency is increased. Also, such a decrease can be attributed to the fact that the electric exchange between Fe^{2+} and Fe^{3+} ions cannot follow the external applied field beyond a certain frequency. The behaviour of ε' for the compositions under investigation can be explained on the basis of Koops work[22].

The peaks $\varepsilon'(f)$ of curves can be ascribed to the presence of collective contribution to the polarization from two different types of charge carriers[24]. For the samples under investigation, the conduction process can be attributed to the presence of two types of charge carriers, *n*-type as electron transfer between Fe^{2+} and Fe^{3+} and *p*-type as hole exchange between Cu^{+} and Cu^{2+} at the octahedral sites[25,26]. These two coupling mechanisms can be represented by the following relations:

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^{-}$$

$$Cu^{2+} \rightleftharpoons Cu^{+} + e^{+}\,(\text{hole})$$

Since the direction of displacement of electrons is opposite to that of holes under the application of external field, the mobility of holes is relatively very small with respect to that of electrons. The resultant polarization of both types of charge carriers will give peaking behaviour. The shift of the peak to higher frequency with increasing temperature may be attributed to the corresponding increase of the mobility of the charge carriers with temperature. The peaking behaviour was also observed for Cu-Ni, Cu-Mn and Cu-Zn ferrite[24] and Cu-Cr ferrite[27] and Ni-Zn ferrite[28].

Conclusion

It may be concluded that the nanophase copper nickel ferrites show a concentration dependence of AC electrical conductivity in the frequency range 100 Hz to 1000 kHz. All the sample shows interfacial polarization. Dielectric constant decreases with increasing frequency due to electron exchange interaction.

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