



Impedance Spectroscopy of Copper Substituted Nickel Ferrite Nan particles

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Abstract: Copper substituted Nickel ferrite ($\text{Cu}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$) nanoparticles with different values of x ($x=0.1, 0.2, 0.3, 0.4$, and 0.5) have been prepared by sol-gel auto-combustion

method. All the samples were annealed at 600°C for 3 hours to achieve crystal structure of spinel ferrite. Dielectric properties were studied through impedance analyzer and effect of frequency on the different parameters such as tangent loss, dielectric constant, imaginary dielectric constant, real impedance, complex impedance, electric modulus and complex electric modulus have been studied in this paper.

Keyword: Spinel ferrite, Nickel Nan particles, Sol-gel Method, Dielectric Properties.

1. INTRODUCTION

Spinel ferrites have been focused widely because of simple to achieve and used in advanced and modern allocations (El-Sayed, 2009) (Mathur, *et al.*, 2008). The helpful properties of the spinel ferrites depend on the chemical composition, preparation of samples, sintering temperature, nature of substituted elements and their composition. Spinel ferrites have face centred cubic crystal structure with general formula of AB_2O_4 where structure A represents tetrahedral sites and B is octahedral (Dias, and Moreira 1997).

Cu^{2+} is the divalent transition element which substituted basically at tetrahedral A-site depending upon the atomic radii of the replaced element (Roumaiah, 2008). (Krupicka and Novak, 2002) Among the all spine structures, nickel ferrite have been broadly utilized as a part of various types of attractive inductors, and electrical devices, for example, inductors, heads, refrigeration and attractive sound imaging. Ni-Cu doped ferrites nanoparticles have good material properties due to which can be used to find the electrical properties for advanced allocations. The electrical conductivity of spinel ferrites is of prime importance as it gives good conductive system

(Patil, *et al.*, 1991). In this way an efficient review of the electrical conductivity of the mixed Ni-Cu ferrite structure from room temperature to well past Curie temperature was attempted. Nan composite materials broadly cover a substantial scope of frameworks, for example, one-dimensional, two-dimensional, three-dimensional and formless materials made of certainly distinguishing parts and merged at the nanometer

measure. These materials are broadly utilized from the last seven decades. Currently, the utilization of the ferrite materials develops and, proceeding with scaling down pattern in electrical building. There is a need to create unique technique to prepare the ferrite nonmaterial's. In addition, Various researchers have developed the techniques to prepare nickel based ferrite nanoparticles. (Kamigaito 1991) have presented a detailed review on the nanocrystal line Nickel ferrite particles for $x=0$ to $x=1$ and co-doped Nickel ferrite for $x=0.05, 0.08, 0.1$. They were prepared these samples using wet chemical co-precipitation strategy. The particles were observed to show a spinel structure with sizes ranging from 21–51 nm. The confirmation of the spinel cubic structure with high level of crystallinity of arranged ferrites was achieved. (Song *et al.*, 2011) prepared the Nano-sized Ni-Cu ferrite nanoparticles by sol-gel auto combustion method and have studied impact of fuel proportion in auto-combustion procedure on the auxiliary, attractive and dielectric properties. (Anilkumar *et al.*, 2009) prepared Ni-Cu nanoparticles by sol-gel auto combustion method. From that mentioned analysis, the prepared ferrite nanoparticles have the effect of substitution of Ni on Cu. The increased in grain size with increase with Ni element was observed. Consequently increment of surface area with increasing the concentration of Ni was investigated. Larger surface is responsible for high coercive field of these ferrites. Ni^{2+} replaces Fe^{3+} in both [A] and [B] site diminishes the immersion polarization. The surface impact of Nickel particles diminishes immersion of charge. In this paper, co-doped substituted Nickel ferrite nanoparticles have been prepared through sol-gel auto-combustion method.

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Experimental Procedure

In the present work, ferrite nanoparticles having the general formula $\text{Ni}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x=0.1, 0.2, 0.3, 0.4, 0.5$) were prepared by sol-gel auto combustion method. The chemical used in this experiment a research based with no impurity. The chemical were chose nasnickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ferric nit rate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were mixed in distilled water with molarity ratio 1: 2 depending upon the formula. The citric acid was selected on the basis of metal nitrate. The ratio of molarity of metal nitrate to citric acid was selected as 1: 2. The solution was strongly stirred during heating from room temperature to 80°C and kept for 3 hours. The solution moved toward becoming viscous material and solis converted to gel. The solvent was evaporated form the solution when heating at 200°C Cona hot plate with continuous stirring. The gel was converted into soft powder. The samples were grinded into mortar and pestle to obtain the fine particles. The samples were then annealed at 600°C for 3 hour to achieve the crystalline nature of spinel ferrite nanoparticles.

2. RESULTS AND DISCUSSION

The impedance spectroscopy is a reasonable procedure to explore the electrical properties of materials. It can be utilized to concentrate the impedance conduct of substance and can be broke down by the perfect circuit show with discrete electrical segment. The impact of tangent loss, dielectric constant, and imaginary dielectric constant have been examined for each prepared sample, these properties of all specimens is measured in the frequency range of 600Hz to 1MHz.

The tangent loss was calculated form the given formulas

$$\tan\delta = 1 / (2\pi f R_p C) \quad (1)$$

In above formula, “f” represents the frequency, “ R_p ” represents the parallel resistance of the pellets and “C” represents the capacitance of the pellets. The frequency depending dielectric loss, also called tangent loss is measured in the range 600Hz to 1MHz as shown in Figure 1. From the figure, we conclude that the tangent loss is decreased by increasing the value of frequency. For all the samples the dielectric loss is reduced by increasing the co.er substitution in the manganese nanoparticles because loss factor is depending upon the electrical conductivity of the material. The graph shows the maximum loss is observed at lower frequency range. This shifting of the

peaks suggests that the dipole-dipole interaction is stronger at lower frequency range (Patange *et al.*, 2009).

To determine the dielectric constant, the given formulas was used as

$$\epsilon' = Cd / A\epsilon_0(2)$$

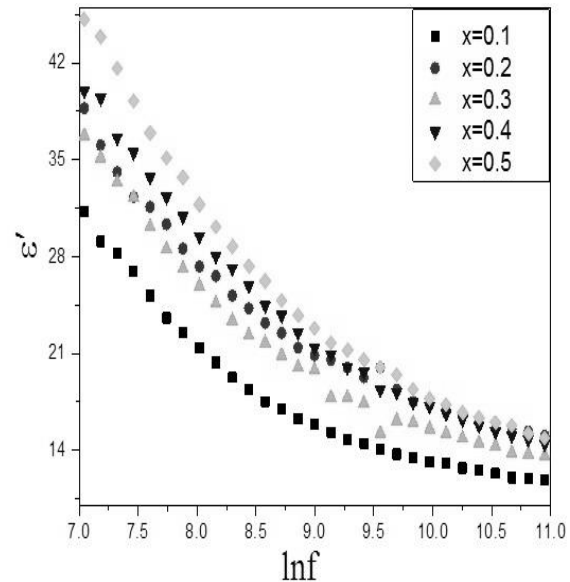


Fig.1: Frequency dependent tangent loss with different values co.er substitution in nickelferrite

Where “d” is the thickness of the pellet, “A” is the area of the pellet and “ ϵ_0 ” is the permittivity in free space whose value is $8.85 \times 10^{-12} \text{ F/m}$. The frequency dependent dielectric constant is measured in the range 600Hz to 1MHz and observed that the dielectric constant is exponentially decreased with increasing frequency and at high frequency it remains same, as shown in (Fig. 2). These varieties in the co.er substituted Nickel ferrite tests were seen because of space charge polarization. As indicated by Maxwell and Wagner two layer show, the space charge polarization is because of the in homogeneous morphology of the material. In the recurrence extend, the dielectric constant is at first exponentially diminish at lower recurrence go while at higher qualities it changes so little, consequently, becomes independent of frequency. This variety is clarified on the premise of space charge polarization which is delivered because of higher conductivity stage in the grain limits and restricted because of social occasion of charges in the region of electric field. The changing electric field will assembled the charge bearers in similar tomahawks which take limited time. Be that as it may, at the specific recurrence this marvel does not occur and this outcomes the diminishing in dielectric steady (Singh, *et al.*, 2012).

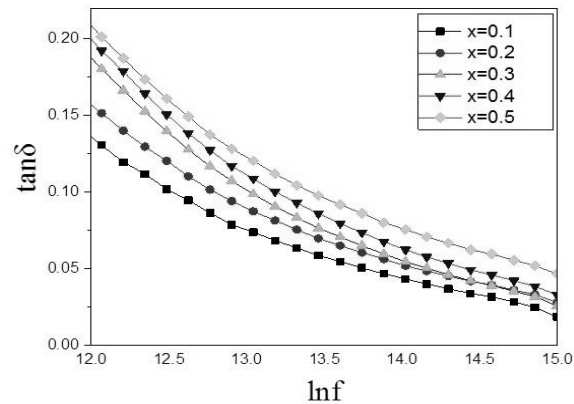


Fig. 2: Frequency dependent real part of the dielectric constant with different values co.er Substitution in nickel ferrite

The imaginary part of the dielectric constant was calculated using the following

Formula

$$\epsilon'' = \epsilon' \tan \delta(3)$$

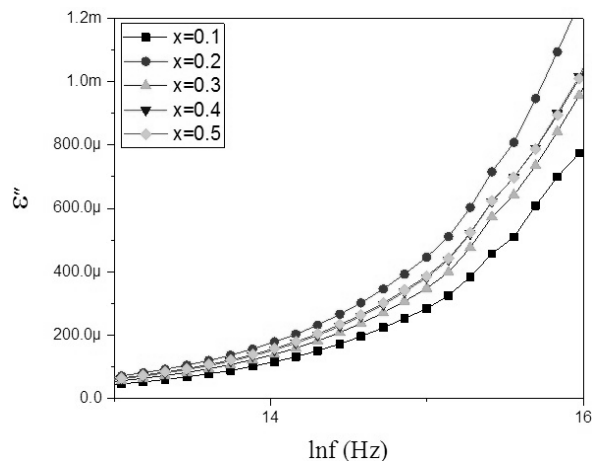


Fig.3: Frequency dependent imaginary part of the dielectric constant with different values Co.er substitution in nickel ferrite

The impedance of the material is actually based on the real and imaginary part was calculated from the formulas

$$Z' = R_s \quad (4)$$

$$Z'' = 1/2\pi f C_p(5)$$

“ R_s ” represents the resistance in series of the pellets. Equation 5 determines the imaginary impedance of the pellets where “ Z'' ” represents imaginary impedance, “ f ” stands for frequency applied on the pellets and “ C_p ” is the capacitance of the pellets. Impedance spectroscopy is the suitable technique to understand the

electrical properties of the substance; such as conductivity, dielectric and relaxation characteristics. All the samples of $\text{Ni}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ NPs ($0.0 \leq x \leq 0.5$) sintered at 600°C for 3hrs. The variation of impedance loss with increasing frequency pretends to the conduction mechanism due to the hopping of electrons, which is directly related to the frequency of applied electric field. The reduction in the curve explains the increase in the conductivity with increase in frequency (Gopalan *et al.*, 2008). It also found that the real part of impedance loss (Z') is increased by the Cu^{2+} concentration. This behavior is explained on the space charge polarization in the substance. The merger at higher frequencies is due to the release of space charges. The complex impedance loss (Z'') is observed as shown in Figure at the lower frequency range which is due to the major contribution of the grain and whereas grain boundary resistance while conduction is negligible. The observed peak pretends to the dominating of grain boundary resistivity on the conductivity while the conductivity is ignorable at the grain boundary (Farea *et al.*, 2008).

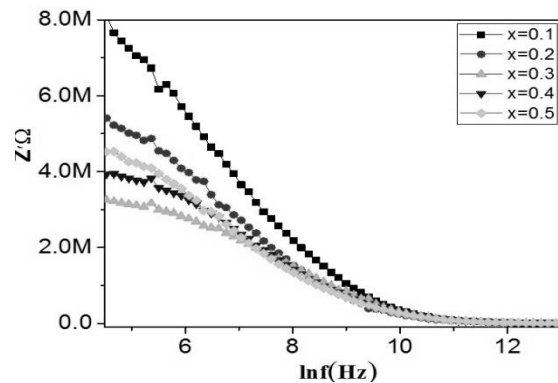


Fig.4: Frequency dependent real impedance loss with different values co.er substitution in nickel ferrite.

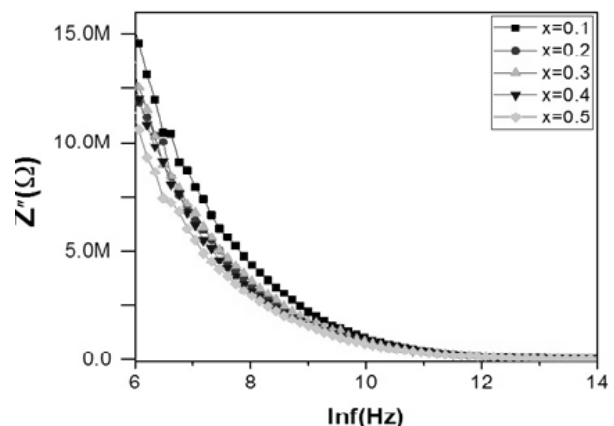


Fig.5: Frequency dependent imaginary part of impedance loss with different values co.er substitution in nickel ferrite.

Equation 6 is used to calculate imaginary modulus of the pallets while equation 7 determinesthe modulus of the pallets in which “M'''” stands for imaginary modulus and “tanδ” represents tangent loss or dielectric loss..

$$M'' = 2\pi f C_p Z' \quad (6)$$

$$M' = M'' / \tan \delta \quad (7)$$

The real part of electric modulus of co.er substituted (Ni_{1-x}Cu_xFe₂O₄) nanoparticle is observed in figure which reveals exponentially increment in the electric modulus at lower frequencies lies in the range 7 KHz to 11 KHz for all samples. The real part of electric modulus is dependent of co.er substitution in the lower frequency range. The concentration dependency is saturated and become uniform at higher frequency range.

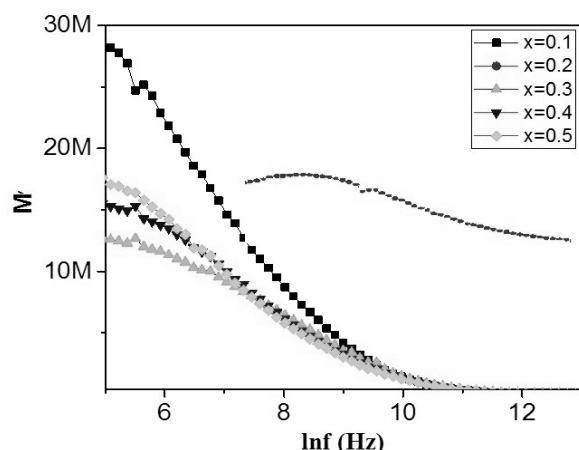


Fig.6: Frequency dependent imaginary part of impedance loss with different values co.er Substitution in nickel ferrite

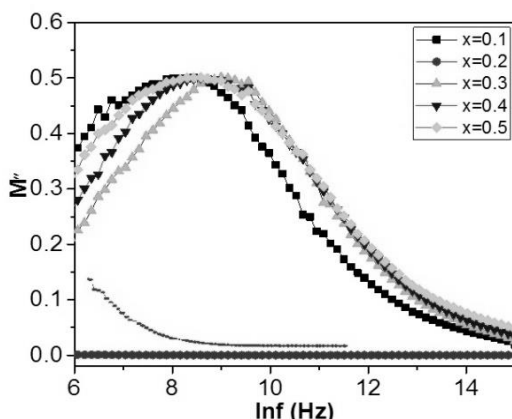


Fig.7: Frequency dependent imaginary part of Modulus with different values co.er Substitution in nickel ferrite

3. CONCLUSIONS

In this report, Cu substituted NiFe₂O₄ powders were prepared by the solgel auto combustion technique. The crystallinity was achieved with annealing of temperature at 600 °C for three hrs. The dielectric loss and the spectrum loss patterns show the reduction in as the frequency of a. l. ied electric field increase. These phenomena have been explained on the basis of space-charge polarization in the light of Maxwell-Wagner two layers model. The imaginary part of impedance indicated only one semicircle which shows the dominance of grain and the conduction of grain boundary is negligible. The real part of impedance has been found to increasing substitution of Cu²⁺ concentration as well as frequency which suggest the reduction in conductivity.

REFERENCES:

- Anilkumar R K., A. Parveen G. R Badiger. (2009) Effect of molybdenum trioxide (MoO₃) on the electrical conductivity of polyaniline. *Physica B*; 404:1664–7.
- Abbas S. M, R. Chatterjee A. K, Dixit (2007) Electromagnetic and microwave absorption properties of Nickel substituted co.er spinel ferrites and its polymer composite. *J A.I Phys* 101:074105–074111
- Blaszkiewicz M., D. S. Mclachian R. Newnham (1992). The volume fraction and temperature dependence of the resistivity in carbon black and graphite polymer composites: an effective media– percolation a.roach. *J Polym Eng Sci*; 32: 421–5.
- Chen W, W. Zhu O. K. Ta. X. F. Chen (2010) Frequency and temperature dependent impedance spectroscopy of cobalt ferrite composite thick films. *J A.I Phys* 108:034101–034118
- Chourashiya M. G., J. Y. Patil, S. H. Pawar L.D. Jadhav (2008) *Mater. Chem. Phys.* 109: 39. Alder D, Feinleib J. *Phys. Rev. B* 2. 31Pp.
- Dias, A.. and R. L. Moreira (1997) Microstructural dependence of the magnetic properties of sintered NiZn ferrites from hydrothermal powders, *JMMM*, vol. 172, no. L9. L14.
- El-Sayed, H. M. (2009) Effect of induced magnetic anisotropy on the hysteresis parameters of Co ferrite prepared from nano-sized particles, *J. Journal of Alloys and Compounds*, vol. 474, no. 1, 2, 561–564,
- Farea A.M.M., S. Kumar, K. M, Batoo A. Yousef , *J. Alloys Compd.* (2008); 464: 361.

- Krupicka S. and P. Novak, (2002) *Oxide spinels Ferroelectric Materials*, vol. 3, ed, E P Wohlforth ed., Amstermam: North-Holland0, vol. 3, 87-90.
- Kamigaito O. (1991) What can be improved by nanometer composites? *J JpnSoc Powder Metal*; 38: 315–21.
- Kryszewaski M. (1991) Heterogeneous conducting polymeric systems: dispersions, blends, crystalline conducting networks – an introductory presentation. *Synth Metals* 45: 289–96.
- Koops, C. G. (1991). “On the Dispersion of Resistivity and Dielectric Constant of Some Semiconductors at Audio frequencies”, *Physics review*. Vol. 83, 121-7
- Kambale, R. C., P. A. Shaikh, C. H. Bhosale, K. Y. Rajpure, Y. D. Kolekar, (2009). “The effect of Mn substitution on the magnetic and dielectric properties of cobalt ferrite synthesized by an auto combustion route”, *Smart Material Structure*, Vol. 18, 115028-3
- Mathur, P., A. Thakur, and M. Singh, (2008) Effect of nanoparticles on the magnetic properties of Mn-Zn soft ferrite, *JMMM*, vol. 320, no. 7, 1364-1369.
- Patil, S. A., S. M. Otari, V. C. Mahajan, M. G. Patil, A. B. Patil, M. K. Soudagar, B. L. Patil, and S. R. Sawant, (1991) Structural, IR and Magnetisation Studies on La³⁺ Sub-stituted Co_{er} Ferrite, *SolidState Communication*, vol. 78, no. 1, 39-42.
- Patil, K. C., M. S. Hegde, T. Rattan, S. T. Aruna, (2008). “Chemistry of combustion synthesis, properties and a.lications of nanocrystalline oxide materials”, World Scientific Publisher,
- Patil, N. D., R. N. Jadhav, and V Puri. (2013) "The 8–18 GHz microwave spectroscopy and conductivity of Ni_{0.4}CoxCd_{0.6-x}Fe₂O₄ nanoparticles synthesized by auto combustion method", *Advanced Science Focus*, Vol. 1, .20–25.
- Roumaiah, K. (2008) The Transport Properties of the Mixed Ni-Cu Ferrite, *Journal of Alloys and Compounds*, vol. 465,. 291-295.
- Song F., X. Shen M. Liu J. Xiang (2011) Preparation and magnetic properties of SrFe₁₂O₁₉/Ni_{0.5}Zn_{0.5}Fe₂O₄ nanocomposite ferrite microfibers via sol–gel process. *Mater Chem Phys*; 126:791–6.
- Shelar, M. B., P. A. Jadhav, S. S. Chougule, M. M. Mallapur, B. K. Chougule, (2009). “Structural and electrical properties of nickel cadmium ferrites prepared through self-propagating auto combustion method”, *Journal of Alloys and Compounds*, Vol. 476, 760-8
- Singh, N., A. Agarwal, S. Sanghi, S. Khasa, (2012). “Dielectric loss, conductivity relaxation process and magnetic properties of Mg substituted Ni–Cu ferrites”, *Journal of Magnetism and Magnetic Materials*, Vol. 324, 2506Pp.
- Ul-ain, B., S. Ahmed, Y. Huang, A. Wang and T. Zhang, (2012). “Improved structural and catalytic attributes of Ba₂Co₂Fe_{12–2x}(Zr, Ni)_xO₂₂ materials synthesized by sol–gel and microwave heating methods”, *Journal of Material Chemistry*, Vol. 22, . 22190-8
- Xiang, J., Y. Chu, X. Shen, G. Zhou, Y. Guo, “Electro spinning”s”, (2012). *Journal of Colloid and Interface Science*, Vol. 376, 57,