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# Magnetic Properties of Copper Doped Nickel Ferrite Nanoparticles Synthesized by Co Precipitation Method

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**Abstract:** Nickel ferrite nanoparticles with copper atoms as dopant have been prepared using co-precipitation method with general formula $Ni_{1-x}Cu_xFe_2O_4$ (x=0.2, 0.4, 0.6, 0.8 and 1) and are sintered at quite ambient temperature. Structural and magnetic properties were examined using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction method (XRD) and Vibrating Sample Magnetometer (VSM) to study the influence of copper doping in nickel ferrite magnetic nanoparticles. X-ray studies proves that the particles are possessing single phase spinel structure with an average particle size calculated using Debye Scherer formula. Magnetic measurements reveal that saturation magnetization value ($M_s$) decreases while magnetic coercivity ($H_c$) increases upon doping.

## 1. Introduction

Ferrite nano particles are very well established material as they exhibit unique physical peculiarities like structural, electrical and magnetic properties [1, 2]. They are also technologically important materials as they are widely utilized in magnetic, recording microwave and electronic devices [3, 4]. The properties of nickel ferrites can be greatly influenced by doping nickel atoms with other non-magnetic atoms like copper or zinc [5]. Ferrites can be prepared by various methods including sol-gel method, co-precipitation method, hydrothermal method, precursor method etc. among which co-precipitation is relatively an easier one [6]. The two important factors deciding the properties of spinel ferrites are distribution of cations among the sub lattice and interaction between magnetic dipoles [7].

Several researchers have studied the improvement of electrical and magnetic properties of nickel ferrites on doping with various metals like aluminium, zinc, cobalt, manganese and chromium [8, 9]. In the present study the effect of Cu/Ni substitution on nickel ferrite nanoparticles prepared through co-precipitation method was analyzed based on structural and magnetic properties measured at room temperature.

## 2. Experimental

Doped nickel ferrite powders were synthesized using co precipitation method with NaOH as the precipitating agent. About 0.3 g of poly vinyl pyrollidone (PVP) was dissolved in 100 ml deionized water taken in a round bottom flask. Then stoichiometric amounts of iron nitrate, nickel nitrate and cobalt nitrate were added into the PVP solution. NaOH solution was added drop wise to attain a pH around 12 with continuous stirring for 2 hours at $80^0$C. The solution containing nano powders of $Ni_{1-x}Cu_xFe_2O_4$ was centrifuged and the excess PVP was removed by washing with water and ethanol. The resultant powder was dried in the oven for 24 hours at $100^0$C. The resulting dark brown powder was crushed and calcined at $600^0$C for 3 hours [10]. The resultant compounds were characterized using FTIR and XRD to confirm the modification and particle size.

## 3. Results and discussion

*3.1. Fourier Transform Infrared Spectroscopy (FTIR)*

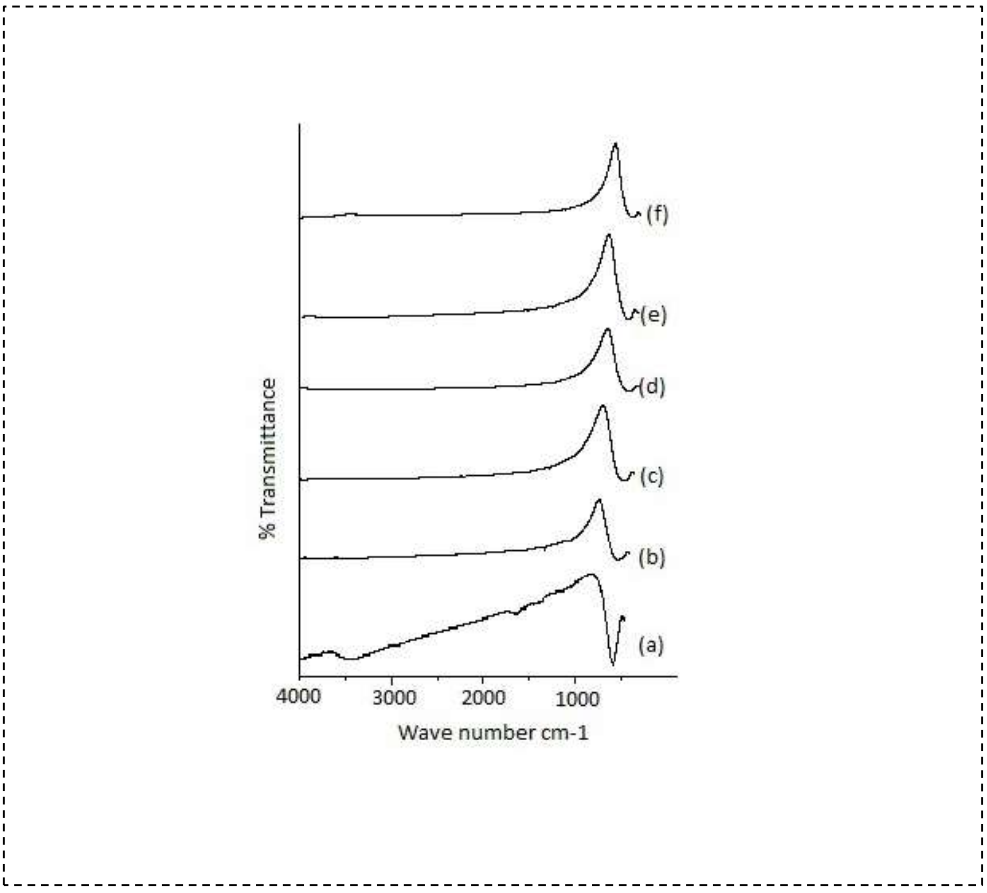


Figure 1. FTIR spectra of (a) $NiFe_2O_4$, (b) $Ni_{0.8}Cu_{0.2}Fe_2O_4$, (c) $Ni_{0.6}Cu_{0.4}Fe_2O_4$,(d) $Ni_{0.4}Cu_{0.6}Fe_2O_4$ (e) $Ni_{0.2}Cu_{0.8}Fe_2O_4$ and (f) $CuFe_2O_4$

The FTIR spectra of prepared ferrites are shown in figure 1. Two peaks at the range 540-532 cm-1 corresponds to intrinsic stretching vibrations of the metal at tetrahedral site and at 364-359 $cm^{-1}$ corresponds to octahedral stretching confirms the formation of spinel ferrite structure [11]. The presence of $Cu^{2+}$ ions in the tetrahedral site with a higher radius and atomic weight greatly influence the lattice distortions and make the $Fe^{3+}$ ions to migrate and thus decreasing the octahedral and tetrahedral vibration frequency to a greater extent. This is clear from the spectra that as copper content increases, these lattice vibrations are almost absent.

*3.2. X-ray diffraction studies (XRD)*

The preparation of ferrites include solid phase reactions among the corresponding carbonates or oxides. The synthesis involve two steps: powder formation followed by sintering step. The performance of the product depends highly on the properties of powder and any inadequacies during the powder formation can be rectified during the sintering process. The XRD patterns of synthesized nickel ferrite nano particles are depicted in figure 2. It confirms the formation of single phase spinel structure for all the samples.

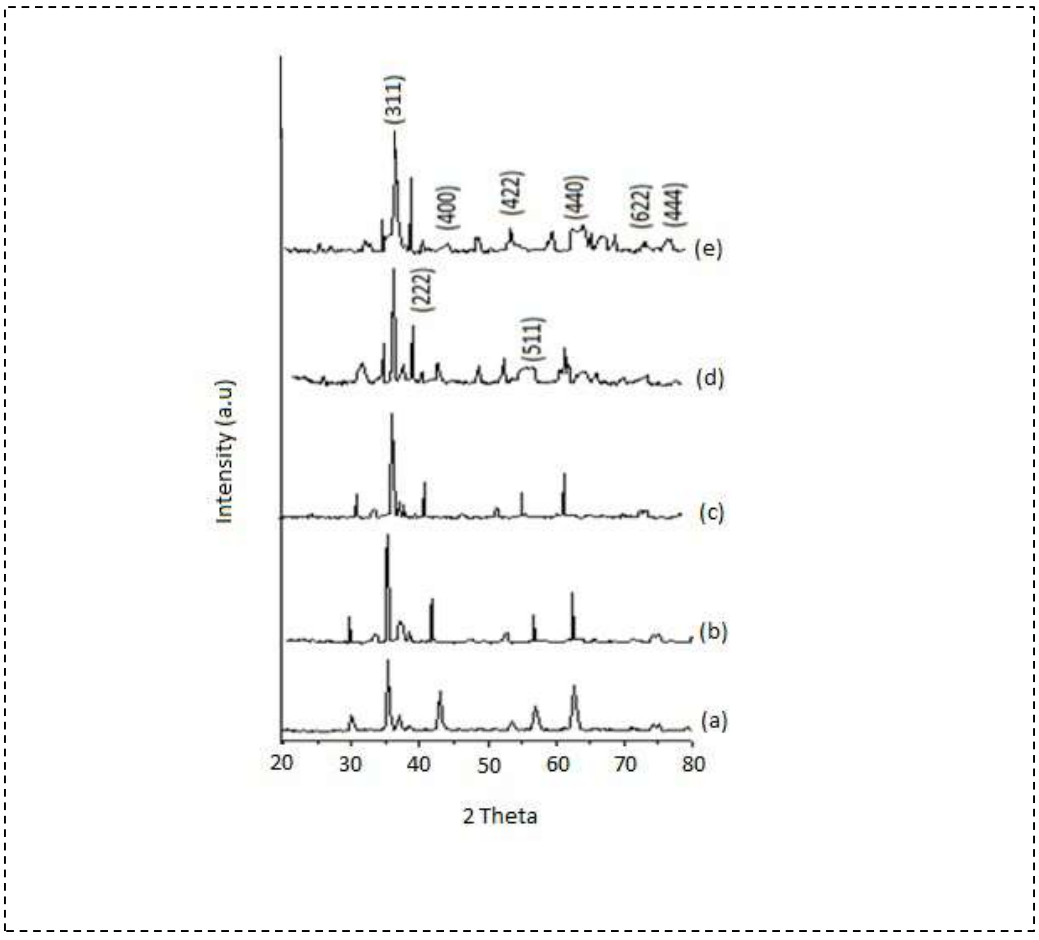


Figure 2. XRD patterns of (a) $Ni_{0.8}Cu_{0.2}Fe_2O_4$,
(b) $Ni_{0.6}Cu_{0.4}Fe_2O_4$, (c) $Ni_{0.4}Cu_{0.6}Fe_2O_4$ (d) $Ni_{0.2}Cu_{0.8}Fe_2O_4$ and (e) $CuFe_2O_4$

The formation of spinel cubic structure can be confirmed by the existence of (311), (400), (422), (511) and (440) crystal planes in the XRD patterns, which is in accordance with the JCPDS powder diffraction file. The strongest reflection comes from (311) which denotes the spinel plane [12]. The particle size was determined for all the samples based on high intensity (311) plane using Scherer formula. The average particle size was found to be 23-32 nm.

*3.3 Magnetic measurements*

Magnetic behaviour of ferrites with spinel structure rest on a numerous aspects like particle dimension, method of preparation, thermal procedures and the microstructure. The magnetic properties of the synthesized samples were determined using vibrating sample magnetometer at room temperature.

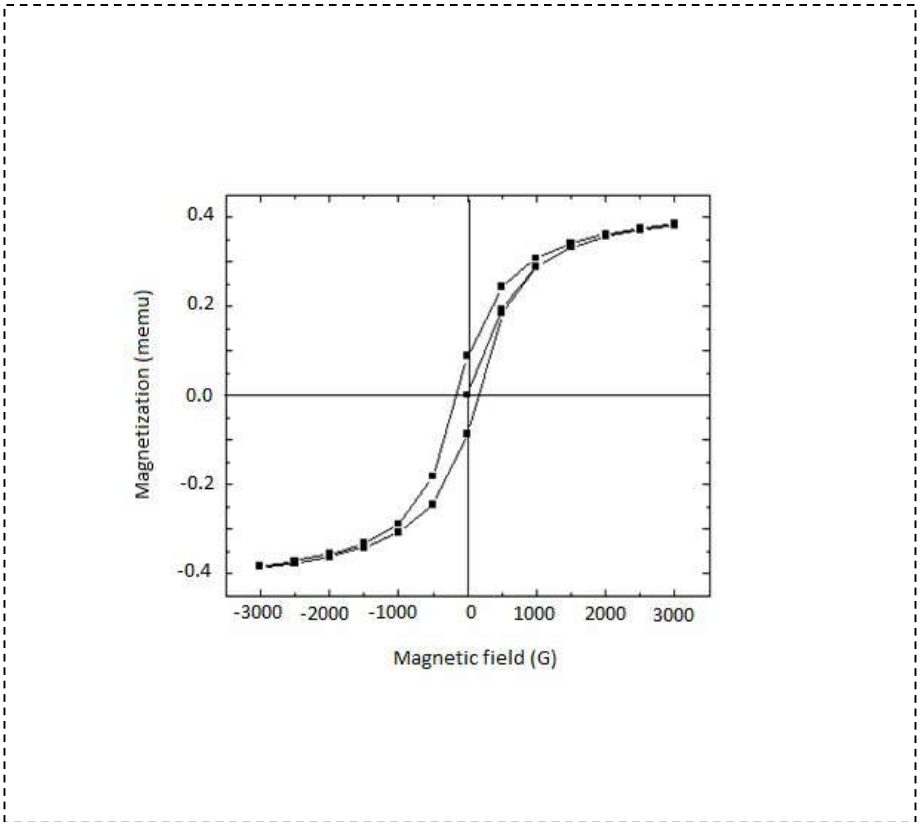


Figure 3. Hysteresis loop for $NiFe_2O_4$

The saturation magnetization of the nickel ferrite filler is estimated as 44.21 emu/g which is a smaller value when compared with the reported Ms value of the bulk counterpart [13]. The abnormality in magnetic properties may be due to numerous reasons. The arrangement of the particles possibly will be altered by the occurrence of lattice imperfections or may be due to a variation in the dispersal of the component ions among different vacant crystal sites.

The reduction in Ms value for the prepared $NiFe_2O_4$ when compared with the bulk is attributed to the small dimension influence and surface effects. Saturation magnetization of fillers falls with size of particles which may be attributed to surface spin disorder. In nano regime structures, as the surface to volume ratio is comparatively high, the amount of surface spins will be higher than the overall count of spins. This may cause disorder of surface spins leading to surface anisotropy and deviance from the usual bulk properties [14].

Table 1. Magnetic parameters at room temperature

| $Ni_{1-x}Cu_xFe_2O_4$ | Ms (memu/g) | Hc (G) | Mr (memu/g) |
|---|---|---|---|
| x = 0.2 | 0.9611 | 151.75 | 0.1644 |
| x = 0.4 | 0.8660 | 192.53 | 0.1600 |
| x = 0.6 | 0.6035 | 205.64 | 0.1491 |
| x = 0.8 | 0.3239 | 682.00 | 0.1354 |
| x = 1.0 | 0.2554 | 1020.0 | 0.1189 |

From table it is clear that saturation magnetization ($M_s$) value decreases as copper content increases. This decrease is known as spin canting occurring at the outer surface of prepared nano particles. As the copper content rises, the position of $Cu^{2+}$ ions in the tetrahedral sites leads to a decline in the probability of spin occupation in the lattice site thereby weakens the super-exchange collaborations which leads to a lessening of $M_s$value [15]. The small $M_s$value is also due to the complete substitution of $Cu^{2+}$ ions in the place of $Fe^{3+}$ ions in the octahedral sites.

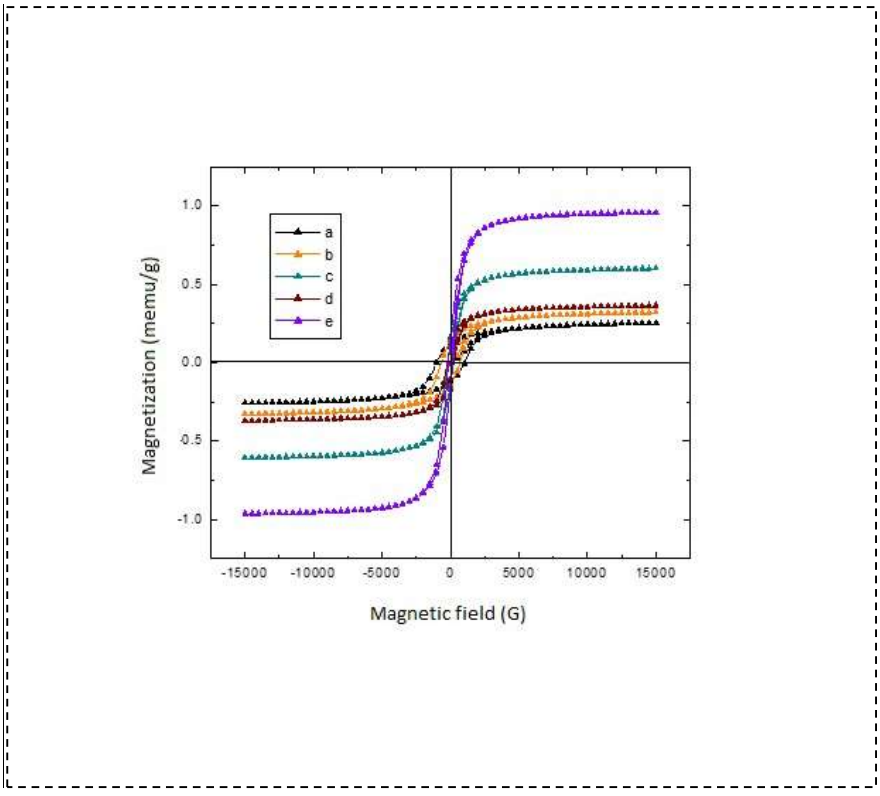


Figure 4. Hysteresis loops of copper doped nickel ferrites $Ni_{1-x}Cu_xFe_2O_4$ where x=0.2 (a), x=0.4 (b), x=0.6 (c), x=0.8 (d) and x=1 (e)

Coercivity ($H_c$) of a magnetic material is a direct measure of its magneto crystalline anisotropy. The Hc values of samples increases with copper doping. The higher magneto-crystalline anisotropy of $Cu^{2+}$ ions compared to $Ni^{2+}$ ions can be a possible explanation for this and hence the Jahn-Teller effect. The presence of copper ions as Jahn-Teller ion in the octahedral sites of nano particles leads to a lattice distortion which in turn leads to the formation of large strains in the lattice sites [16]. This makes the anisotropy and coercivity to rise with copper content.

## 4. Conclusion

Nickel ferrites doped with copper was successfully prepared by co-precipitation method. FTIR studies clearly indicates the doping level in all the prepared samples. XRD patterns shows the formation single phase spinal structure with particle size within the nano regime. Magnetic measurements indicates that there is a profound effect of copper doping in the properties of nickel ferrites. Both $M_s$ and $M_r$ values declines with increase in copper content which may be attributed to the occupation of $Cu^{2+}$ ions in the $Fe^{3+}$ pre-occupied lattice site leading to Jahn-Teller distortion.

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