



## Synthesis, Structural and Magnetic properties of $Ni_{0.8}M_{0.2}Fe_2O_4$ (M=Co,Cu) Nanoparticles synthesized by Citrate Precursor Method

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**Abstract :**  $Ni_{0.8}M_{0.2}Fe_2O_4$  (M=Co,Cu) Ferrite Nanoparticles were successfully synthesized by chemical based Citrate Precursor Method. The Citrate was annealed at temperature  $450^\circ C$  for 1hr, 3hr. The annealed powders were characterized using X-ray diffractometer (XRD) and vibrating sample magnetometer (VSM). The particle sizes was found to be 29 nm, 15nm for Ni-Co ferrites and 29 nm, 29 nm for Ni-Cu ferrite nanoparticles respectively. The magnetization values were 46.10 emu/g, 0.41 emu/g for Ni-Co ferrite and 38.01 emu/g, 0.19 emu/g for Ni-Cu ferrite respectively at annealing temperatures  $450C$  for for 1hr and 3hr.

**Key words:** Ferrites Nanoparticles, Citrate precursor method, Magnetization.

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### Introduction :

Synthesis of spinel ferrite nanomaterials has been intensively pursued because of their basic scientific importance and technological applications and due to their special Magnetic and electric properties (Gubin et al. 2005, Georgia Papaefthymiou, 2009). Magnetic ferrites such as Ni ferrite have a wide range of applications in several domains including biomedical applications, magnetic ferrofluid, microwave absorption, repulsive suspension for levitated railway systems and gas sensing capabilities towards low concentrations of chlorine gas and Similarly Co ferrite has been used for magnetic recording applications such as digital recording media which finds applications in audio and video tapes (Ishino and Narumiya, 1987; Gubin et al. 2005; Georgia 2009).

Research in this field has received a major boost in the recent years due to development of a number of preparation processes to produce pure phase ferrites in nanoparticle range (Pal and Chakravorty, 2003, Singh et al., 2010). The magnetic properties of ferrite nanoparticle are strongly influenced by the method of synthesis and process parameters even though the common

diagnostic tools like XRD show similar crystalline structure (Singh et al., 2011). The Citrate precursor method for ferrite synthesis has distinct advantages over most other chemical methods, which are maximum reactivity, short time, low temperature preparation, homogenous distributions of ions and low cost( Verma et al. 1999, Singh Shanta et al., 2011, Kumari Arpana et al. 2011 ). This method is based on chemical wet processes and one of the main controlling parameters is the annealing temperature at which the precursor powder is heated. In this present work, we report the effect of annealing hour (1hr and 3hr) on the properties of two Ni-based ferrites  $Ni_{0.8}Co_{0.2}Fe_2O_4$  and  $Ni_{0.8}Cu_{0.2}Fe_2O_4$ . Co has a strong preference for octahedral sites, Cu has preference for tetrahedral sites. Ni is known to go in octahedral sites. The magnetic properties depend on the site occupancies by the magnetic ions. As  $Cu^{2+}$  ions do not have magnetic moment, magnetic properties of the two systems will be different.

**Materials and Methods :**

Nitrates of all the three cations, Co, Cu and Fe were taken in Stoichiometric proportions as starting materials. Aqueous solutions of these salts were prepared separately by dissolving the salts in minimum amount of deionized water while stirring constantly. The solutions were then mixed together. Aqueous solution of citric acid was prepared in adequate quantity by weight and was added to the prepared salt solutions. The mixture was heated at a temperature about 60°C to 80°C for two hours with continuous stirring. This solution was allowed to cool to room temperature and finally it was dried at 60-65°C in an oven until it formed a brown color fluffy mass. This precursor was annealed at temperatures 450°C for 1hr and 3hr respectively for in a muffle furnace. During this process, the precursor thermally decomposed to give ferrite powder that was later characterized by XRD (Rikagu Miniflex, Japan) and VSM (model PAR-155).

**Results and Discussion :**

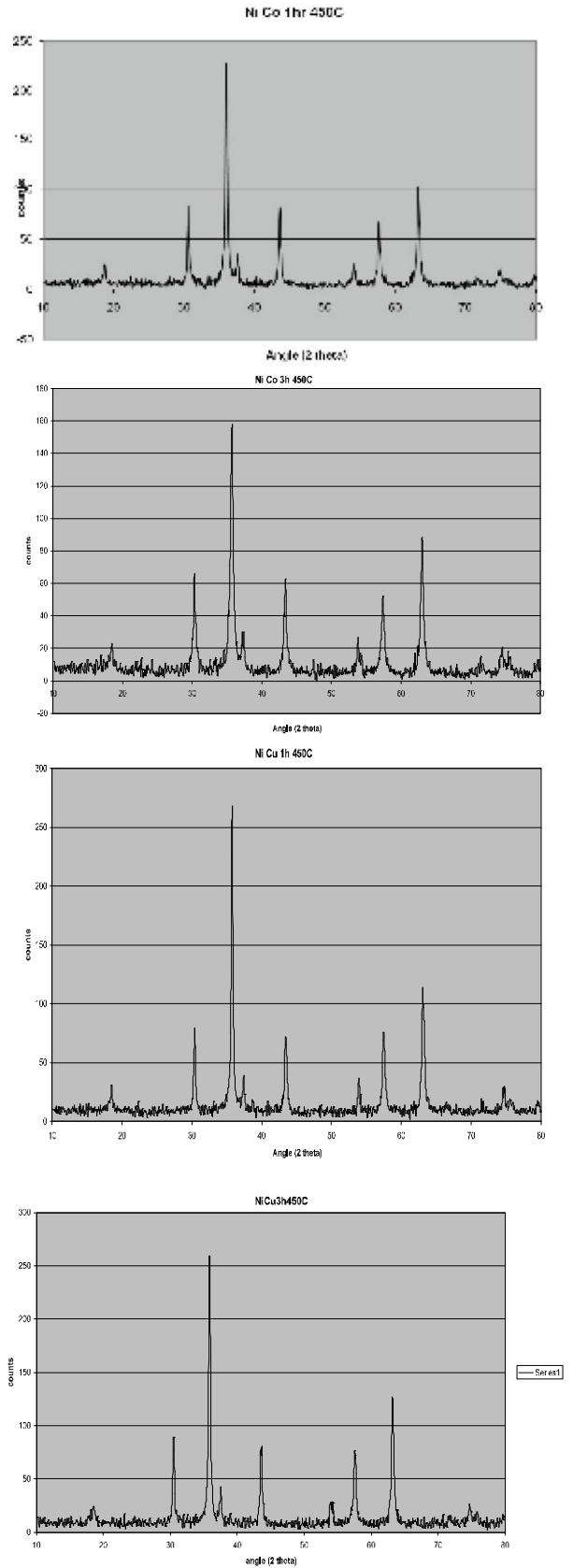


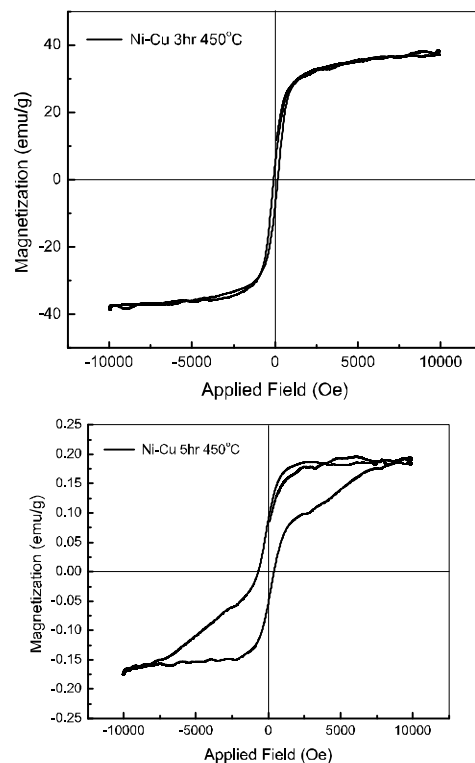
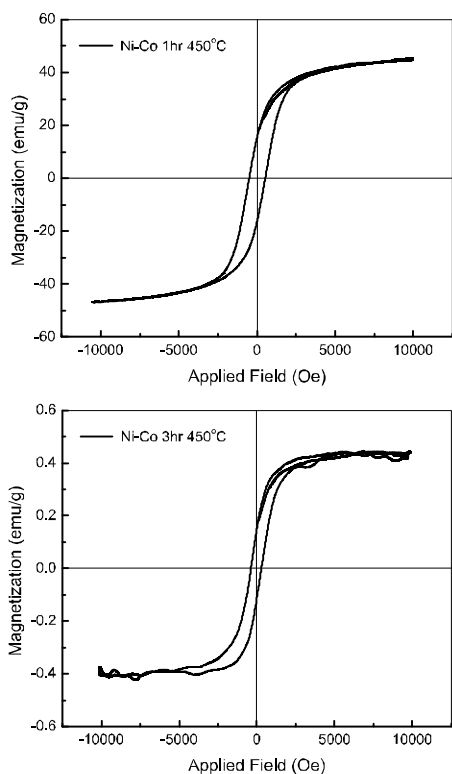
Fig.1- X-ray diffraction curve of  $Ni_{0.8}Co_{0.2}Fe_2O_4$  and  $Ni_{0.8}Cu_{0.2}Fe_2O_4$

The observed X-ray diffraction patterns of Ni-Cu and for Ni-Co ferrite samples synthesized at annealing temperature 450°C for 1hr and 3hr is shown in Fig 1. All the visible peaks, well above the background, in the XRD patterns could be identified with the spinel cubic structure (Roisnel and Rodriguez-Carvajal 2001). The average crystallite size was determined from the broadening of the most intense peak (311, angular position= 35.219 degree) using Debye-Scherrer equation (Culity 1978) and the values are given in Table 1. Crystallite size do not change for Ni-Cu ferrite (29nm and 29 nm) while particle size decreases from 29nm to 15nm for Ni-Co ferrite ). It shows that nucleation / growth mechanism is different at annealing temperatures 450°C.. The XRD analyses indicated that both Ni-Cu and Ni-Co have a cubic unit cell structure at 450°C(ICSD# 040040) .This clearly indicates that the partial replacement of  $Ni^{2+}$  ion by  $Cu^{2+}$  or  $Co^{2+}$  in the host  $NiFe_2O_4$  compound does not change the basic crystal structure to large extent. The lattice constants for  $Ni_{0.8}Co_{0.2}Fe_2O_4$  and  $Ni_{0.8}Cu_{0.2}Fe_2O_4$  8.287Å, 8.354Å and 8.333Å, 8.298Å respectively

**Table 1. Structural and magnetic characteristics of Synthesized nanomaterials**

Sample	Particle size	Lattice constant	Magnetization
$Ni_{0.8}Cu_{0.2}Fe_2O_4$ -1hr	29nm	8.287 Å	46.10 emu/g
$Ni_{0.8}Cu_{0.2}Fe_2O_4$ -3hr	15nm	8.354 Å	0.41 emu/g
$Ni_{0.8}Co_{0.2}Fe_2O_4$ -1hr	29 nm	8.33 Å	38.01 emu/g
$Ni_{0.8}Co_{0.2}Fe_2O_4$ -3hr	29 nm	8.298 Å	0.19 emu/g

M-H curves for Ni-Co and Ni-Cu ferrite samples are shown in Figure2. Table1 gives magnetization data for all samples. Cobalt substituted ferrites show well developed hysteresis loops with large magnetization. This shows strong magnetic coupling as expected as all the three cations are magnetic. On the other hand, Copper substituted ferrites show a small magnetization compared to Ni-Co ferrite. This could be related to less number of magnetic ion A-B pairs in these samples as Cu is nonmagnetic ion. Copper has stronger preference for tetrahedral sites and hence will inhibit Fe ions from coming to come a



**Fig 2. Magnetization curve for  $Ni_{0.8}Co_{0.2}Fe_2O_4$  and  $Ni_{0.8}Cu_{0.2}Fe_2O_4$**

tetrahedral sites. Ni has anyway strong preference for octahedral site. As a result the number of A-B magnetic ion pairs will be much less as compared to B-B pairs which provides only weak magnetic coupling. The substitution of Cu in Ni ferrite may create tetragonally distorted spinel oxide, which is ferromagnetic at room temperature (Roy and Ghose 2000) The magnetic properties have been seen to alter with change in cation distribution, annealing temperature and method of preparation (NA et al. 1993, Singh et al. 2012, Corr et al. 2008). In this work substitution of Cobalt by Copper changed the magnetization values.

### Conclusion :

$Ni_{0.8}Co_{0.2}Fe_2O_4$  and  $Ni_{0.8}Cu_{0.2}Fe_2O_4$  ferrite nanoparticles synthesized using citrate precursor method annealed at temperature 450C for 1hr and 3hr. Particle size was found 29nm for  $Ni_{0.8}Cu_{0.2}Fe_2O_4$  for annealing 1hr and 3hr while particle size was observed 29nm and 15nm for  $Ni_{0.8}Co_{0.2}Fe_2O_4$  for annealing 1hr and 3hr. It shows that nucleation / growth mechanism is different at temperatures 450° C. Cobalt substituted ferrites show well developed hysteresis loops with large magnetization i.e 46.10 emu/g compared to Cu substituted Ni-ferrite i.e 38.01 emu/g. The magnetization value was found 46.10 emu/g and 0.41 emu/g for  $Ni_{0.8}Co_{0.2}Fe_2O_4$  annealed for 1hr and 3hr and for  $Ni_{0.8}Cu_{0.2}Fe_2O_4$  ferrite nanoparticles magnetization was found 38. 01 and 0.19 emu/g annealed for 1hr and 3hr. This way magnetization decreases as we increase the annealing time from 1hr to 3hr.

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