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FTIR and Magnetic studies of Cu Substituted Cobalt Ferrite Nanomaterials, annealed at 650°C

Arpana Kumari • Adhishree Abha • Rakesh Kumar Singh

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Corresponding Author : Rakesh Kumar Singh

Abstract : *Magnetic nanomaterials (69nm-87nm) of $Cu_xCo_{1-x}Fe_2O_4$ (X= 0.01,0.03, 0.05, 0.07 and 0.09) annealed at 650°C were synthesized by chemical based citrate precursor method. The crystalline sizes of these materials were calculated from X-ray diffraction peaks (XRD). The bands observed in Fourier transform infrared spectroscopy (FTIR) confirmed the presence of ferrite phase. The hysteresis M-H loops for these materials were traced using the vibrating sample magnetometer (VSM) and it indicated a significant change with Cu substituation in the magnetization, retentivity, and intrinsic coercivity of the sample. $Cu_{0.07}Co_{0.03}Fe_2O_4$ ferrite nanomaterials have larger particle size (87nm) with larger retentivity and magnetization (68.35 emu/g and 29.73 emu/g) respectively in comparision with other nano ferrite samples.*

***Key words**: Ferrite, Nanomaterials, FTIR, Magnetic studies, Coercivity.*

Arpana Kumari
B.Sc III Year (Session 2008-11), Physics Honours, Patna Women's College, Patna University, Patna, Bihar, India

Adhishree Abha
B.Sc III Year (Session 2008-11), Physics Honours, Patna Women's College, Patna University, Patna, Bihar, India

Rakesh Kumar Singh
Assistant Professor, Dept. of Physics,
Patna Women's College,
Bailey Road, Patna - 800 001, Bihar, India
E-mail : rakeshsinghpu@gmail.com

Introduction :

Production mechanism and study of properties of spinel nanoferrites have been intensively pursued in recent years because of their special magnetic properties *(Sugimoto, 1999 and Ishino, et. al, 1987)*. Magnetic ferrites have a wide range of applications such as in biomedical, magnetic ferrofluid, microwave absorption, repulsive suspension for levitated railway systems, gas sensing capabilities, etc. *(Singh, et. al, 2010 and Na, J.G. et. al, 1993)*. Co ferrite has also been used for magnetic and/or digital recording applications in audio as well as video tapes. Further, it is believed that the magnetic properties are strongly dependent on particle size. Besides, the magnetic properties of ferrite nanoparticles get influenced by the method of synthesis and process parameters even though the common diagnostic tools such as XRD show similar crystalline structure *(Sugimoto, 1999 and Chinnasomy et. al, 2003)*. In recent years the development of a number of synthetic procedures to produce ferrites at nanoscale has received considerable attention *(Pal and*

Chakravorty, 2003). The synthesis of ferrites using citrate precursor method has a distinct advantage such as maximum reactivity, short time, low temperature preparation, homogenous distributions of ions and low cost compared to other chemical methods. It is based on wet chemical processes and one of the main controlling parameters is the annealing temperature at which the precursor powder is heated. It is known that the magnetic properties depend on the site occupancies by the magnetic ions.

Cu-Co are spinel ferrites whose samples have general formula $Cu_xCo_{1-x}Fe_2O_4$ which we have studied. Tetrahedral sites are called A-sites and Octahedral sites as B-sites. The metal ions can occupy either A sites or B sites. It is observed that Co^{2+} ions have a strong preference for octahedral sites while Cu^{2+} ions prefer tetrahedral sites. As Cu^{2+} ions do not have magnetic moment, magnetic properties of the two systems will be different. It will therefore, be interesting to see the effect of partial substitution of Cu^{2+} in $CoFe_2O_4$ on the structural and magnetic properties. Accordingly, present work reports the effect of Cu substitution on the structural and magnetic properties of Cu-CO ferrite using citrate precursor method. Site preference of the cations appears to play a crucial role in magnetization. The magnetic properties have been seen to alter with change in cation distribution. Cu having preference for tetrahedral sites and Co for octahedral sites result in weaker magnetic coupling giving higher coercive field, lower magnetization and retentivity in the case of $Cu_{0.05}Co_{0.05}Fe_2O_4$.

Materials and Methods

Nitrates of all the three cations (Co^{2+}/Cu^{2+} and Fe^{3+}) were taken in proper stoichiometric proportions as starting materials. Aqueous solutions of these salts were prepared separately by dissolving the salts in minimum amount of deionized water and 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 solution. The mixture was heated at 60°C-80°C for two hours with continuous stirring in Magnetic stirrer. The solutions were allowed to cool to room temperature and finally they were dried at 60°C-65°C in an oven until they turned into brown color fluffy mass. The precursors were annealed at temperatures 650°C for one hour in a muffle furnace. During this process, the precursor thermally decomposed and gave ferrite powders. The structural characterization was carried out using a X-ray Diffractometer (**Rigaku Miniflex, Japan**) with Cu K_α radiation (λ = 1.5405Å) between the Bragg angles 20° to 80°. The *XY* (*2θ vs.* intensity) data obtained from this experiment were plotted with the **WinPLOTR program** and the angular positions of the peaks were obtained with the same program *(Rodriguez. C, 2000).* The Bragg peaks were modeled with pseudo-Voigt function and the backgrounds were eliminated using linear interpolation technique.The magnetization behavior was studied by Vibrating Sample Magnetometer (**model PAR-155**).

Results and Discussion:

X-ray Diffraction analysis

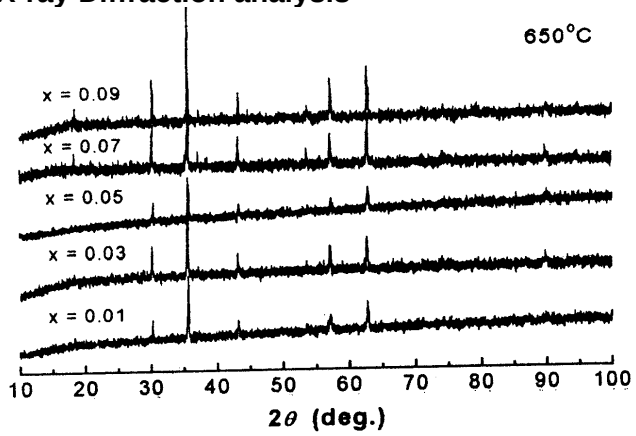

Figure1:X-ray diffraction patterns of $Cu_xCo_{1-x}Fe_2O_4$ (X=0.01,0.03, 0.05,0.07 and 0.09) annealed at 650°C

Figure1 shows the X-ray diffraction (XRD) patterns of $Cu_xCo_{1-x}Fe_2O_4$(X= 0.01,0.03, 0.05,0.07 and 0.09) annealed at 650°C. Different peaks were identified by using the JCPDS database (**JCPDS**

Card No. 25-0283). XRD pattern shows the formation of single phase cubic structure. The average particle size was determined using Scherrer formula *(Cultity, 1978)*. D= 0.9 ë/â Cosè and was found 69nm, 49nm, 34nm, 87nm and 71nm for different Cu substitution (Table 1). Their lattice constants were calculated using formula $a=d\,(h^2+k^2+l^2)^{1/2}$ and found 8.363Å, 8.377Å, 8.363Å, 8.376Å and 8.383Å respectively. It was observed that with increase in Cu content the lattice constant and crystalline size changes.

Table1: Observed data from XRD

Sample: ferrite nanomaterials	2θ (Degree)	FWHM (Degree)	Particle size	Lattice constants
$Cu_{0.01}Co_{0.09}Fe_2O_4$	35.511	0.093	69 nm	8.363 Å
$Cu_{0.03}Co_{0.07}Fe_2O_4$	35.513	0.130	49 nm	8.377 Å
$Cu_{0.05}Co_{0.05}Fe_2O_4$	35.572	0.185	34 nm	8.364 Å
$Cu_{0.07}Co_{0.03}Fe_2O_4$	35.460	0.074	87 nm	8.376 Å
$Cu_{0.09}Co_{0.01}Fe_2O_4$	35.469	0.090	71 nm	8. 383 Å

FTIR Studies: We have observed, largest particle size for $Cu_{0.07}Co_{0.03}Fe_2O_4$ (87nm) having large magnetization and retentivity (Table2). The FTIR spectra of $Cu_{0.007}Co_{0.03}Fe_2O_4$ ferrite, recorded in the range of 400-5000cm^{-1} is shown in Fig. 2. Peak recorded about 1364-84 cm^{-1} is due to NO_3 vibration and indicates the presence of nitrate ion, and the other peak shows presence of citrate ions. The band spectra near 550 cm^{-1} shows formation of ferrite. All characteristic peaks in FTIR spectrum were analyzed and confirmed the formation of ferrite phase *(Muthuroni, et. al, 2010, Mohamed, et. at., 2010, Eramanno Astorino et. al., 1994).*

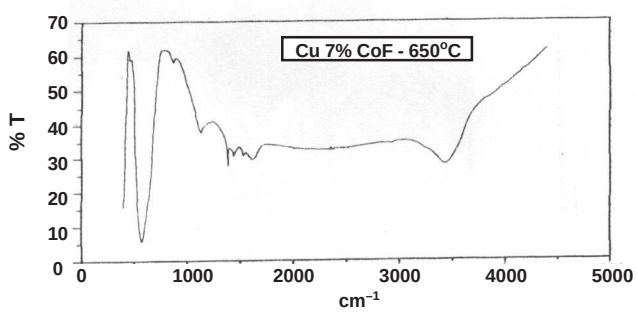

Figure 2: FTIR Spectra of of $Cu_{0.007}Co_{0.03}Fe_2O_4$ ferrite nanomaterials are recorded between 400 to 5000 cm^{-1}

Magnetic Properties:

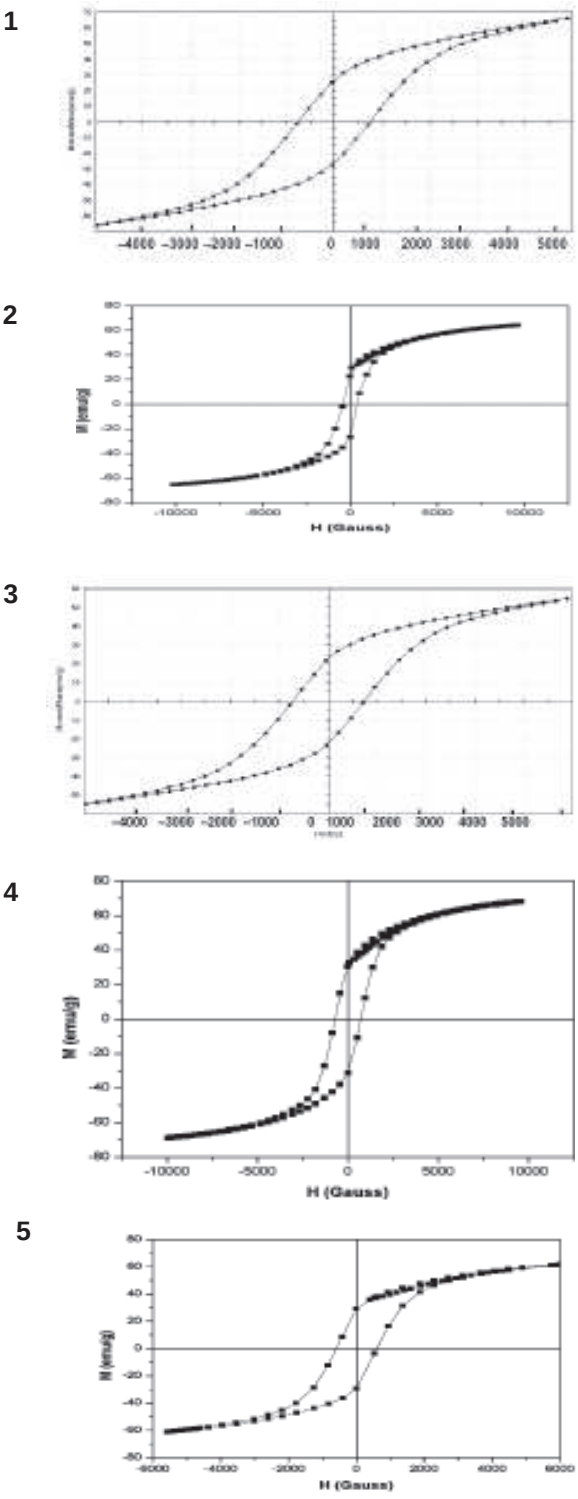

Figure 3: Magnetization curve for (1) $Cu_{0.01}Co_{0.09}Fe_2O_4$ (2) $Cu_{0.03}Co_{0.07}Fe_2O_4$ (3) $Cu_{0.05}Co_{0.05}Fe_2O_4$ (4) $Cu_{0.07}Co_{0.03}Fe_2O_4$ (5) $Cu_{0.09}Co_{0.01}Fe_2O_4$

Figure 3: shows the hysteresis loops for Cu-Co Nano Ferrite materials recorded using Vibrating sample magnetometer (**VSM**). Various magnetic parameters such as magnetization, retentivity and coercivity calculated from the hysteresis loop are given in table2.

Table 2: Magnetic parameters observed from VSM

Sample:Ferrite Nanomaterials	Magnetization	Coercivity	Retentiity
$Cu_{0.01}Co_{0.09}Fe_2O_4$	66.12 emu/g	755 G	26.35 emu/g
$Cu_{0.03}Co_{0.07}Fe_2O_4$	64.49 emu/g	416 G	22.76 emu/g
$Cu_{0.05}Co_{0.05}Fe_2O_4$	54.8 emu/g	732 G	22.46 emu/g
$Cu_{0.07}Co_{0.03}Fe_2O_4$	68.35 emu/g	690 G	29. 73 emu/g
$Cu_{0.09}Co_{0.01}Fe_2O_4$	61.83 emu/g	596 G	28.73 emu/g

Cu^{2+} ions are diamagnetic in nature therefore magnetization should decrease but in our work sample $Cu_{0.07}Co_{0.03}Fe_2O_4$ has high magnetization, i.e. 68.35 emu/g. The most interesting aspect is that this sample has all magnetic parameters of highest value except coercivity in comparison to other samples (Table2) together with pure phase of sample. Co^{2+} and Fe^{3+} are ferromagnetic in nature. Therefore in Cobalt ferrite the bonding between stetrahedral (A) and octahedral (B) sites lead to high coercivity multidomain structure. In our work we observed the same order of coercivity. In Fig. 1, Table 1, Fig. 2, Fig. 3, phase, purity, average particle size FTIR spectra and hysteresis loop support this observation. As we decreased the composition of Co^{2+} ion and increased the composition of Cu^{2+}, the coercivity was found to decrease.

The mixing of cobalt with copper ferrite changes the coercivity and magnetization values. The addition of high coercive Co^{2+} with copper ferrite, led to the A-A($Co^{2+}$and Cu^{2+}) interaction in the tetrahedral site and created the single domain system, rather than the movement of walls (multi domain). In single domain particle system, there is no domain wall motion. Thus the involvement of Cu^{2+} ions essentially decreases the net coercive values in mixed ferrites.

Conclusion:

- At the same annealing temperature of 650^{o}C, substitution of Cu altered crystalline size, lattice constant and magnetic properties.
- $Cu_{0.07}Co_{0.03}Fe_2O_4$ has largest particle size, 87 nm, magnetization and retentivity have large value comparative with other samples.
- Magnetic properties and structural properties depend upon the Cu^{2+} ions substitutation in $CoFe_2O_4$.
- Magnetic behavior depends also on crystalline size i.e different particles have different magnetic parameters.
- FTIR Spectrum shows the characteristic peak of ferrites.
- Observed magnetic parameters corresponds to soft ferrites and their values may find technological applications.
- Super exchange interaction and divalent metal ions plays crucial role in observed the magnetic properties.

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