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Synthesis, structural and magnetic studies of Cu substituted cobalt ferrite nanomaterials annealed at 750°C

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Abstract : *Cu substituted cobalt ferrite nanomaterials,* $Cu_x\ Co_{1-x}\ Fe_2O_4$ *; x=0.01,0.03,0.05,0.07 and 0.09, were prepared using chemical based Citrate precursor method. The precursor was annealed at temperature 750°C. The annealed powders were characterized using X-ray diffraction (XRD) and Vibrating sample magnetometer. XRD study shows that the synthesized samples are of cubic spinel structure. Sharp changes were observed in particle size, lattice constant, magnetization and coercivity with the increasing Cu-content.*

Key words*: Cu-Co Ferrite Nanomaterials, Particle size, Magnetic properties.*

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Introduction :

Synthesis and study of spinel nanoferrites have been intensively pursued in last two decades because of their special magnetic and electrical properties (Reed 1991; Said et al 2007). Magnetic Nano ferrites have a wide range of applications in biomedical, magnetic ferrofluid, microwave absorption, repulsive suspension for levitated railway systems, gas sensing capabilities, etc. (Sugimoto 1980; Ishino and Narumiya 1987). Also, Co ferrite has been used for magnetic and/or digital recording applications in audio as well as video tapes (Ishino and Narumiya 1987; Kumar Vinod et al 2008). Further, it is believed that the magnetic properties are strongly dependent on particle size. More over the magnetic properties of ferrite nanoparticles get influenced by the method of synthesis, substituation of divalent ions and process parameters even though the common diagnostic tools such as XRD show similar crystalline structure (Singh Rakesh Kumar et al, 2011). In recent years the development of a number of synthetic procedures to produce ferrites at nanomateric scale has received considerable attention. The synthesis of ferrites using citrate precursor method has a distinct advantage such as maximum reactivity, short time, low temperature preparation, homogenous distribution of ions and low cost over other chemical methods (Pal and Chakravorty 2003; Singh Rakesh Kumar et al, 2012). 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 (Hilpert S 1909). Cu-Co are spinel ferrites which have general formula $Cu_xCo_{1-x}Fe_2O_4$ (X= 0.01, 0.03, 0.05, 0.07 and 0.09) samples that we have studied. Tetrahedral sites are also called A-sites and Octahedral sites 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 prepared 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 (Thakhur Rashmi et al 2010; Gubin et al 2005).

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 solutions. The mixture was heated at 60ºC-80ºC for two hours with continuous stirring in Magnetic stirrer. The solutions were allowed to cool to room temperature and finally they were dried at 60ºC in an oven until they turned into brown color fluffy mass. The precursors were annealed at temperatures 750ºC 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 (**Rikagu Miniflex, Japan**) with Cu $K_á$ radiation ë = 1.5405Å between the Bragg angles 20º to 80º. The *XY* (*2è vs.* intensity) data obtained from this experiment were plotted with **WinPLOTR program** and the angular positions of the peaks were obtained with the same programme. 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 :

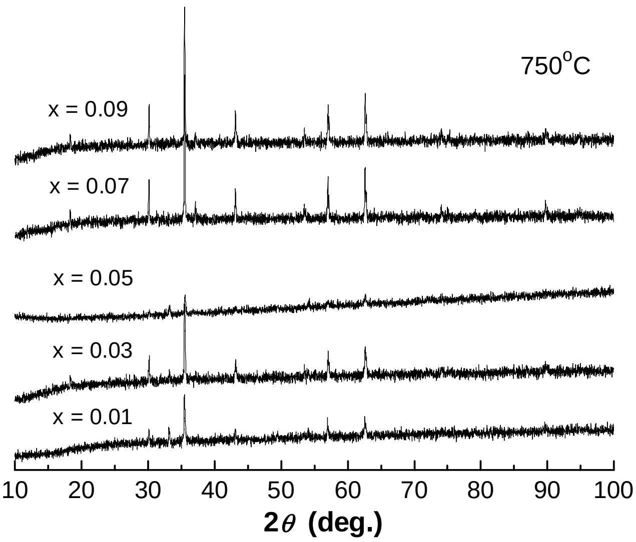

Fig 1. XRD pattern for $Cu_xCo_{1-x}Fe_2O_4$; x=0.01, 0.03, 0.05, 0.07 and 0.09, annealed at 750ºC

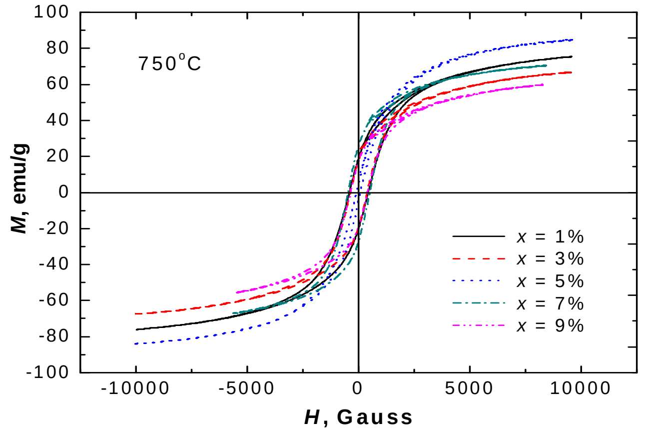

Fig 2. Magnetization curve for $Cu_x Co_{1-x} Fe_2O_4$; x=0.01, 0.03, 0.05, 0.07 and 0.09

Table 1. Structural and Magnetic properties of the Produced powder annealed at 75°C for 1h

Sample	Particle size (nm)	Magne-tization (emu/g)	Coer-civity (G)	Reten-tivity (emu/g)	Lattice constant
$Cu_{0.01} Co_{0.99} Fe_2O_4$	52	27	60	20.38	8.382 Å
$Cu_{0.03} Co_{0.97} Fe_2O_4$	49	67.18	375	20.49	8.377 Å
$Cu_{0.05} Co_{0.95} Fe_2O_4$	58	84	100	5.02	8.368 Å
$Cu_{0.07} Co_{0.93} Fe_2O_4$	87	67	486	28.98	8.381 Å
$Cu_{0.09} Co_{0.91} Fe_2O_4$	71	56.37	354	20.86	8.377 Å

All the samples $Cu_x Co_{1-x} Fe_2O_4$ (x=0.01, 0.03, 0.05, 0.07 and 0.09) are spinel ferrite (JCPDS 1977) and shown in Fig. 1. The particle sizes were obtained using Scherrer formula : D= 0.9 λ/â Cosθ (Culity 1978; West 2007) which was tabulated and given in Table 1. The particle size were found to change as we change the composition Cu. The corresponding lattice constant was also found to change. Thus we observed that the lattice constant and particle size depends on composition of Cu. The unit cell structure and lattice parameters are in very good agreement with the literature report (JCPDS file nos. 22-1086 for $CoFe_2O_4$; a= 8.391Å and JCPDS file nos. 25-0283 for $CuFe_2O_4$; a= 8.349Å). It can be seen in this work that lattice parameters of all the ferrite samples are lying between the cell parameters of $CuFe_2O_4$;a= 8.349Å and $CoFe_2O_4$; a= 8.391Å. This is due to fact that Cu^{2+} (0.730Å) has smaller ionic radius compared to that of Co^{2+} (0.745Å). Also the ferrite sample $Cu_{0.05}Co_{0.95}Fe_2O_4$ is observed to have less intense peak as well as a little poor crystallinity with respect to other ferrite magnetic nanomaterial samples.

Fig. 2 shows the magnetization curves for samples $Cu_x Co_{1-x} Fe_2O_4$ (x=0.01,0.03,0.05,0.07 and 0.09) spinel ferrite. Magnetic parameters such as magnetization, retentivity and coercivity were estimated from M-H curve depicted in Fig. 2. The observed magnetic parametric values are different for different Cu-Co ferrites. The highest magnetization was observed for $Cu_{0.05} Co_{0.95} Fe_2O_4$. The magnetic properties depend on particle size and substituation of Cu. Further study is needed for such behaviour of this sample. It can be seen that substitution of Cu^{2+} ion in Cobalt ferrite changes the magnetic parameters values. Cu^{2+} is also diamagnetic in nature, which is responsible for marked changes in the value of magnetization. Further Cu^{2+} has strong preference for tetrahedral sites and hence will inhibit Fe^{3+} ions to come to tetrahedral sites. 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. This might result in giving changes in coercivity, retentivity and magnetization values to some extent, which seems in this present case. Besides, the M-H curves show that magnetization is not completely saturated till the applied field of 10 KOe is used in this experiment. This could be due to the small (nanometric) size of the particles. It has also found, the magnetic hysteresis loops measured at room temperature revealed smaller magnetic anisotropy constant, coercivity, and remanance ratio for the samples prepared by adding the NaOH solution into the mixed solution of Co^{2+} and Fe^{3+} ions due to the formation of Co^{3+} (Zhang et al, 2010).

Conclusion :

We observed single phase copper substituted ferrite nanoparticles $Cu_x Co_{1-x} Fe_2O_4$ (x=0.01, 0.03, 0.05, 0.07 and 0.09) with cubic spinel structure using citrate precursor method and annealed at 750°C. The lattice parameters of all the nanomaterial compounds are lying between the cell parameters of $CuFe_2O_4$ and CoF_2O_4. Substituation of Cu^{2+} ions to cobalt ferrite changes the prticle size, coercivity and magnetization values of all the samples. Magnetization curves could not get saturated up to applied field 10KOe. The maximum value of magnetization 84 emu/g was observed for $Cu_{0.05} Co_{0.05} Fe_2O_4$ nano materials having particle size 58 nm.

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