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Effect of Copper Substitution on the Structural, Morphological and Magnetic properties of Nickel Ferrites

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ABSTRACT

The rich physical properties have made nano particles of spinal ferrites to be of great interest in fundamental science. Copper doped Nickel ferrites nano particles were prepared by sol- gel method under stoichiometric conditions. Here we add a nonmagnetic dopant Cu to nickel ferrite nanocrystals and characterize how relevant properties of the samples are modified accordingly. Basically, the doping causes a rearrangement of Fe+3 ions into the two pre-existing octahedral and tetrahedral sites. In the case of the Cu-doping, the Jahn-Teller effect also surfaces which is identified through the FTIR Spectroscopy of the sample. The structural, morphological and the magnetic properties of the spinal ferrite sample have been investigated by means of X-ray diffraction studies, Scanning electron microscope and the vibrating sample magnetometer studies. X-ray results confirm the single-phase cubic spinal structure. The functional groups of the magnetic material were identified from FTIR spectrum.

***Keywords*:** XRD, SEM, VSM, FTIR, Copper

1. INTRODUCTION

Nanoparticles with an average grain size ranging between 10 to 20 nm have been of utmost interest for researchers, as their physical properties can be influenced to a great extent by controlling the material at the atomic scale. Spinal ferrites with a formula of M Fe_2O_4 (M being a divalent metal ion) have numerous technological applications like high speed digital tape,ferro-fluids,rod antenna, humidity sensor, multilayer chip inductor(MLCI) [1-9] and humidity sensor. Nickel ferrites substituted with copper are an important class of spinal ferrites. As per the crystal structure, nickel ferrite is an inverse spinal ferrite and has a very high electrical resistivity and very low eddy current losses [8]. Ferrite nanocrystals are also of interest in many applications like bio separation, inter-body drug delivery [10-12] and magnetic refrigeration systems [13]. Likewise Nickel ferrites doped with copper proved to be better softer magnetic materials [14]. Both the magnetic and structural properties of the spinal ferrites depend on the magnetic interaction and cation distribution, in the tetrahedral (A) and octahedral (B) sites.

2. EXPERIMENTAL

2.1 Materials

The chemicals used were all of analytical grade having a purity≥ 99% .Citric acid C_6 H_8 O_7, Ferric nitrate $Fe(NO_3)_2.9\ H_2O$, Nickel nitrate $Ni(NO_3)_2.6\ H_2O$, Copper nitrate $Cu(NO_3)_2.3\ H_2O$ were used as the starting materials.

2.2 Experimental Procedure

Ni-Cu ferrites with a generic formula $NiCuFe_2O_4$ were synthesized by the sol gel route. This method is widely used due to its low preparation temperature and high reaction rate and production of small particles.. The stoichiometric amounts of nitrates and acid citric were dissolved separately in deionised water to make 0.5 M solutions. The mole ratio of metal nitrates to citric acid was taken as 1:1. The obtained sol was then continuously heated at 70^0C under constant stirring until a dry brown gel was formed. The gel so obtained was fired at 1000 ^{o} C for 24 hours in an oven and then finely powdered

3. RESULTS AND DISCUSSIONS

A. Structural Studies

The X ray diffraction pattern (XRD) of the pure and copper substituted as prepared nanocrystals were obtained using a Phillip PW 1800 X-ray

diffractometer with Cu Kα radiation of wavelength 1.5405 Aº operated at 40 KV and 30 ma. The X-ray diffraction analysis of the synthesized, pure and Cu doped ferrite nanocrystals as shown in figures Ia and Ib, confirm the formation of spinal cubic structure with the Fd 3m space group which is consistent with the standard data (JCPDS card No. 074-2081). As seen from the Fig 1(a) and 1(b), the XRD peaks are very broad indicating that the grain size is well within the nanoscale.Futher the XRD patterns show no excess phases ,indicating that almost all the Cu atoms have been placed in the cubic lattices. The sol gel route is usually used to produce nano size grains in the ferrite system. The Scherrer formula is used to calculate the average grain size D from the prominent (311) peak. From the particle size values indicated in table 1, it is evident that substitution of copper has indeed brought about a drastic reduction in the crystallite size.

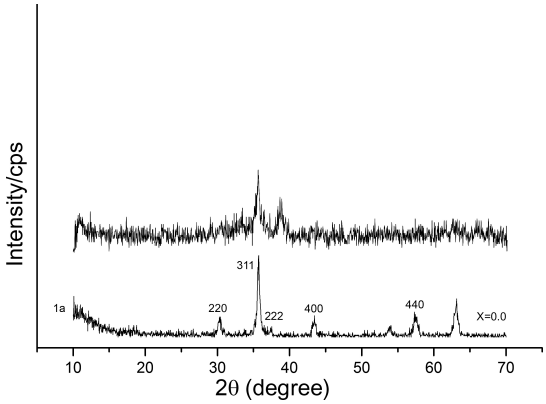


Fig. 1.XRD patterns of synthesized nanocrystals: (a) $NiFe_2O_4$, (b) $NiCuFe_2O_4$

400 cm^{-1} shows one main absorption band at 590 cm^{-1}. The vibration of the tetrahedral bonds in the lattices of the synthesized nanocrystals gives rise to this band. This band is due to the vibration of the tetrahedral bonds in the lattices of the synthesized nanocrystals. The band around 1363 cm^{-1} is attributed to the C=O stretching vibration of the carboxylate group (Co^{2-}). The light band present at 1627 cm^{-1} may be due to the adsorbed water or humidity [7]. The bands at 560 and 2337 cm^{-1} correspond to the metal ion–oxygen complexes in the tetrahedral sites (M_{tetra} <-> 0 -) and also traces of adsorbed or atmospheric Co_2. The O-H stretching vibration of the free or absorbed water gives rise to a band at 3399cm^{-1}, which indicates existence of hydroxyl groups in the synthesized ferrites.

B. FTIR Study

The Fourier Transform Infra Red (FTIR) spectral analysis of the as prepared pure and Cu doped sample as shown in Fig 2a,and 2b respectively, were done using a BRUKER TENSOR 27 FTIR spectrometer with transmissions ranging from 4000-400 cm^{-1} by using KBr pellets. The spectrum of pure nickel ferrite nanoparticles has two main broad metal oxygen bands present in the infra red spectra of all the spinal ferrites in the wave number range of 1000-300cm $^{-1}$. The highest band (γ1) which generally occurs in the range 600 – 550 cm^{-1} is due to the stretching vibration of the corresponding tetrahedral metal oxygen bond. The lowest band (γ $_2$) seen in the range 450- 385 cm^{-1} is caused by the metal – oxygen vibrations taking place in the octahedral sites(Waldron 1955). The prominent bands located around 3400 and 1600 cm^{-1} in the spectra can be attributed to the stretching and H-O-H bending mode vibrations of the free or absorbed water. The band near 1400cm^{-1} is due to the antisymmetric NO–stretching vibration arising from the nitrate group that is present as a residue in the samples. This band being very weak indicates the purity of the Ni-ferrite nanoparticles synthesised by the sol-gel route .For the copper doped nickel nanoferrites, the FTIR spectrum in the range 800-

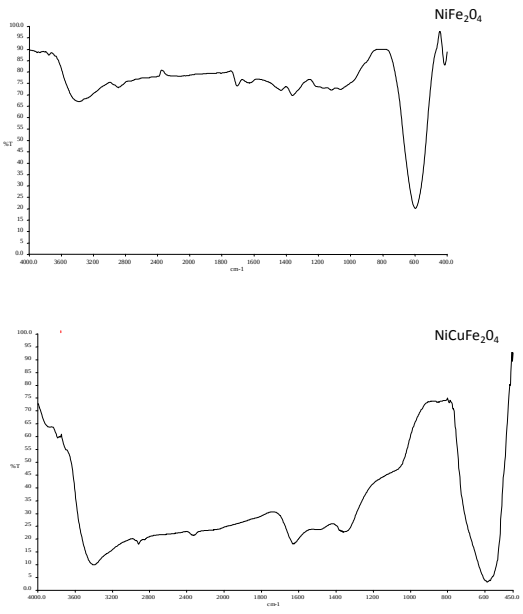


Fig.2. FTIR spectra of synthesized nanocrystals (a) $NiFe_2O_4$, (b) $NiCuFe_2O_4$

C. Morphological Study: (SEM)

The SEM images of $NiFe_2O_4$ and $NiCuFe_2O_4$ nanocrystals have been shown in Figs 3(a) and 3(b) respectively.. The average grain size of the sample obtained from the SEM images cannot be accurately calculated as the SEM micrographs don't focus on exact grain boundaries. The structure is due to the agglomeration of particles. These samples are spherical and uniform and cohesion of grains is due to the magnetic attraction.

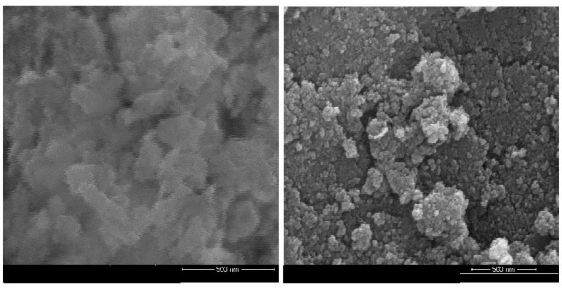


Fig.3: SEM images of synthesized nanocrystals: (a)

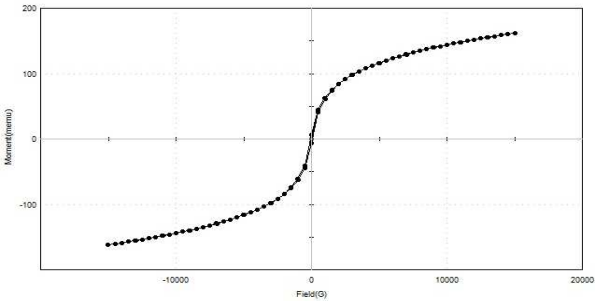


Fig.4. M-H curve of synthesized nanocrystals: (a) $NiFe_20_4$, (b) $NiCuFe_20_4$

$NiFe_20_4$, (b) $NiCuFe_20_4$

D. Magnetic Study

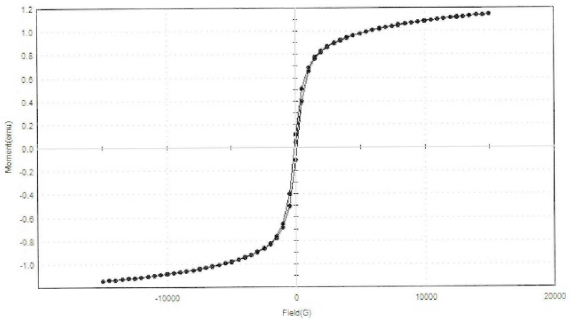
The magnetic properties of the synthesized pure and copper doped nanocrystals are analyzed using a vibrating sample magnetometer (VSM) at room temperature and represented in Fig.4a and 4b. According to Neel's ferromagnetic theory, in the spinal structure the cations on different sub lattices (tetrahedral and octahedral sites) have oppositely aligned magnetic moments [15,16] .Hence the magnetic moment per formula unit (n_B) in the μ_B units is

$$n_B = M_{oct} - M_{tet}$$

Where M_{oct} and M_{tet} are the magnetic moments of the octahedral and tetrahedral sites respectively. The magnetic behaviour of the synthesized nanocrystal measured by VSM can be attributed to the competition of ferromagnetic ions such as Fe^{3+},Ni^{2+},Cu^{2+}ions as non magnetic transition metal ions in the occupancy of the tetrahedral and octahedral sites.

The existence of Cu^{2+}ion as a Jahn ion in the octahedral sites of the $CuFe_2O_4$ nanocrystals leads to a lattice distortion, which has the effect of depleting the electronic and orbital degeneracies of Cu^{2+} cations. It is anticipated that this effect in turn creates large strains in the copper ferrite lattice and as a result modified magnetic properties .Note that the Jahn–Teller theorem does not predict the direction of the distortion; it only marks the existence of unstable lattice geometry.

The coercivity (Hc) of a magnetic material is a measure of its magneto-crystalline anisotropy. From the values listed in Table 1, it is evident that there is a rapid increase in the Hc of the sample, with Cu substitution and is significant for the same. Materials with very high coercivity are termed as magnetically hard materials and they are used in the manufacturing permanent magnets which in turn find its application in electric motors, magnetic separation and magnetic recording media. The existence of the of Cu^{2+} as a Jahn-Teller ion in the octahedral sites of the $CuFe_2O_4$ nanocrystals causes the distortion which is anticipated to create large strains in the nickel copper ferrite lattice. This in turn increases the anisotropy and coercivity of the sample, which agrees well with the FTIR analysis of Cu Fe_2O_4 nano crystals. There is a considerable reduction in the values of saturation magnetisation and retentivity when doped with copper



Composition	Crystallite size(nm)	Saturation Magnetization (emu/g)	Retentivity (emu/g)	Coercivity (Hci)
$NiFe_20_4$	17.07	16.02	0.4232	43.294
$NiCuFe_20_4$	9.9	7.044	0.2722	66.198

Table 1: Crystallite size and Magnetic parameters of $NiFe_20_4$ and $NiCuFe_20_4$

IV. CONCLUSION

The Ni-Cu Ferrites were successfully prepared by sol-gel process and they were sintered at 1000ºC for 24 hours. The sintering temperature and sintering time plays a vital role in determining the particle size. The X-ray diffraction study showed the formation of single phase spinal structure and has also indicated a drastic size reduction on substituting with copper. Magnetic studies showed an increase in the coercivity and a decrease in the saturation magnetisation and retentivity.

REFERENCES

[1] T. Pannaparayil, R. Maranle, S. Komarneni, S.G. Sankar, *A novel low-temperature preparation of several ferrimagnetic spinels and their magnetic and Mössbauer characterization*, J. Appl. Phys.64 (1988)5641.

[2] M. H. Sousa, F. A. Tourinhou, *New Electric Double-Layered Magnetic Fluids Based on Copper, Nickel, and Zinc Ferrite Nanostructures*, J. Phys. Chem. B 105 (2001) 1168-1175.

[3] F. Mazaleyrat, L.K. Varga, *Ferromagnetic nanocomposites*, J. Magn. Magn. Mater.215-216 (2000) 253-259.

[4] D. E. Speliotis, *Magnetic recording beyond the first 100 Years*, J. Magn. Magn.Mater.193 (1999) 29-51.

[5] P. C. Dorsey, P. Lubitz, D. B. Chrisey. J.S. Horwitz, *CoFe2O4 thin films grown on (100) MgO substrates using pulsed laser deposition*, J. Appl. Phys.85 (1999) 6338-6354.

[6] A.S. Vaingankar, S.G. Kulkarni, M.S. Sagare, *Humidity Sensing using Soft Ferrites*, J. Phys. IV France 07 C1 (1997) 155-156.

[7] O.H. Kwon, Y. Fukushima, M. Sugimoto, N. Hiratsuka, *Thermocouple Junctioned with Ferrites*, J. Phys. IV France 07 C1 (1997) 165-166.

[8] C.Y. Tsay, K.S. Liu, T.F. Lin, I.N. Lin, *Microwave sintering of NiCuZn ferrites and multilayer chip inductors* , J. Magn. Magn.Mater.209 (2000) 189-192.

9] T. Krishnaveni, B. RajiniKanth, V. Seetha Rama Raju, S.R. Murthy, *Fabrication of multilayer chip inductors using Ni-Cu-Zn ferrites*, J. Alloys Compd.414 (2006) 282–286. 17

[10] F. Li, H. Wang, L. Wang, J. Wang, *Magnetic properties of ZnFe2O4 nanoparticles produced by a low-temperature solid-state reaction method*, J .Magn .Magn. Mat. 309 (2007) 295-299.

[11] S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang, G. Li, *Preparation and Reversible Phase Transfer of CoFe2O4 Nanoparticles*, J. Am. Chem. Soc.126 (2004) 2782.

[12] T. Hyeon, Y. Chung, J. Park, S. S. Lee, Y. W. Kim, B. H. Park, *Monodisperse MFe2O4 (M= Fe, Co, Mn) Nanoparticles*, J. Phys. Chem. B 106 (2002) 6831.

[13] Q. Chen, Z. J. Zhang, *Size-dependent superparamagnetic properties of MgFe2O4 spinel ferrite nanocrystallites*, J. Appl. Phys. 73 (1998) 3156-3158.

[14] J.C. Aphesteguy, A. Damiani, D. DiGiovanni, S.E. Jacobo, Microwave-absorbing characteristics of epoxy resin composite containing nanoparticles of NiZn- and NiCuZn-ferrite, J. Phys. B 404 (2009) 2713–2716

[15] X. Tan, G. Li, Y. Zhao, C. Hu, Effect of Cu content on the structure of Ni1-xCuxFe2O4 spinels, Mat. Res. Bull. 44 (2009) 2160-2168

[16]L.Nèel,magnetic propertiesof ferrites:ferrimagnetism and antiferromagnetism, Ann. Phys.Paris 3(1948)137-98