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Doping Effect Of Nickel On Cobalt Ferrite At Varying Temperatures: Synthesis And Morphology Studies

Swati Gupta, Suruchi Singh, Dr. Pankaj Sharma

Department of Material Science ,Jaypee University of Information Technology, Waknaghat, Solan, H.P. (173234) India

***Abstract*--Nickel doped cobalt ferrite magnetic nano-particles were synthesized in a homogeneous aqueous solution by wet chemical method. Samples were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Effects on structural properties as a function of sintering temperature and nickel dopant have been investigated. Changes in the particle size, strain and dislocation density were observed with temperatures. The morphology of nickel doped cobalt ferrite was analyzed by TEM which showed a crystalline cubic structure.**

INTRODUCTION

Ferrites are engineering resources with Fe_2O_3 as their key constituent and find popular applications in microwave and magneto-optical technologies ([1]-[5]). The soft ferrites are mainly utilized for high frequency inductors and transformers. Hard ferrites, on the other hand, have high coercivity and high remanence are extensively used for making permanent magnets. Cobalt ferrite ($CoFe_2O_4$) is a well-known hard ferrite with high coercivity and moderate magnetization with excellent chemical stability and good mechanical hardness [6].These properties, in conjunction with great physical and chemical constancy, make cobalt ferrite ($CoFe_2O_4$) nanoparticles appropriate resources for imaging, spin electronics devices, magnetic recording and sensor applications ([7], [8]). However, adding impurity in cobalt ferrites alters its properties [9]. The magnetic characteristics of the particles meant for recording media depends on the size, shape, and purity of nanoparticles. Synthesis process should be comparatively simple and controls particle size with high yield. Synthesis techniques of nanoparticles include evaporation condensation, sol-gel processing ([10], [11]), hydrothermal method [12], reverse micelles [13], thermal treatment ([14], [15]), micro emulsions [16], laser-induced vapour phase reactions and aerosols ([17]-[19]). In this research the nickel doped cobalt ferrite nano-particles were synthesized by wet chemical method (co- precipitation). The obtained samples were sintered at different temperatures (100 ^{0}C, 400 ^{0}C and 600 ^{0}C) and characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM).

I Experimental details

A. MATERIALS

Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$); cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$); nickel (II) chloride hexahydrate ($NiCl_2.6H_2O$); sodium hydroxide pellets (NaOH). All the materials were AR grade (Merck India) and were used as received. Double distilled water was used as a solvent.

B. SYNTHESIS

Stocks of aqueous solution of iron chloride and cobalt chloride were prepared in 2:1 ratio and then mixed under constant stirring with the help of a magnetic stirrer and heated

to 60 ^{0}C. NaOH solution was slowly added to the salt solution drop wise until a pH level of 12 reached. Black precipitates appeared in the solution then the solution was kept at 80 ^{0}C for one hour with constant stirring. The precipitates were then washed twice with double distilled water and then with ethanol to get nanoparticles free from sodium and chlorine ions. The supernatant liquid was decanted after centrifugation until only thick black precipitates remained. The precipitates were then dried for twelve hours at 100 ^{0}C. The obtained samples were then grinded into a fine powder. The samples were sintered at 400 ^{0}C and 600 ^{0}C for ten hours each. Finally, blackish powder of cobalt ferrite was obtained. Magnetic nature of powder was checked using bar magnet.

Similarly, Nickel doped Cobalt ferrite had been synthesized and heat treated. $Co_{(1-x)}Ni_xFe_2O_4$ is general chemical formula used for doping where x = 0.1 M aqueous solution of nickel chloride. 0.2 M aqueous solution of cobalt (II) chloride and 0.6 M aqueous solution of Iron (III) chloride was prepared and mixed with 0.1 M aqueous solution of nickel (II) chloride at 60 ^{0}C. The overall reaction is supposed to be

$$CoCl_2.6H_2O + NiCl_2.6H_2O + 10NaOH + 2FeCl_3.6H_2Oa \longrightarrow Co_{(1-x)}Ni_xFe_2O_4 + 10NaCl + 28H_2O$$

II Characterization

X-ray diffractometer (XRD) (Panalytical's X'Pert Pro) has Cu-Ka radiation (1.54 Å). Goniometer = PW3050/60 (Theta/Theta); Minimum step size 2Theta:0.001; Minimum step size Omega: 0.001 was used to study structural parameters. Transmission electron microscopy (Hitachi, H-7500, 40-120 kV operating voltage) images of material were obtained at 90 kV.

III Results and Discussion

The fig.1 (a) and 1 (d) corresponds to temperature 100 ^{0}C , confirming the formation of cobalt ferrite and nickel doped cobalt ferrite respectively.

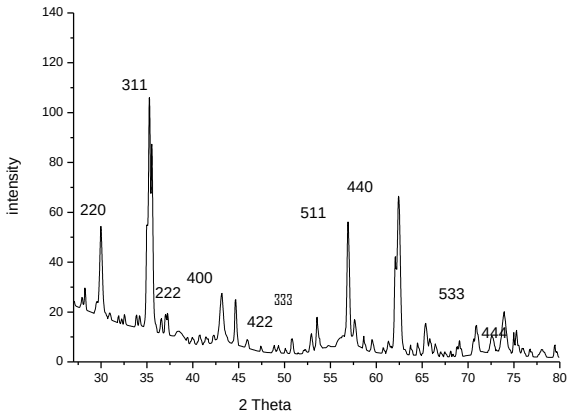

Fig1 (a): XRD Pattern of cobalt ferrite at 100◦C

The crystal structure of the $CoFe_2O_4$ has a cubic symmetry (JCPDS card No. 22-1086). In fig.1 (a) three broad lightly intense peaks at (311), (440) and (422) plane were observed confirming the formation of the nanoparticles here with peak at (220) and (440) revealing formation of CaO and CaO_3. While fig.1(b) for 400 ^{0}C contains more intense peaks, observed at (311), (400), (411), (422), (440), (511) showing the formation of fine particles at 400 ^{0}C but in fig. 1(d) the peak at (220) is much intense showing formation of oxide in large amount, and for 600^{0}C fig.1(c) gives sharp peaks of (311), (400), (411), (422), (440), (511) planes.

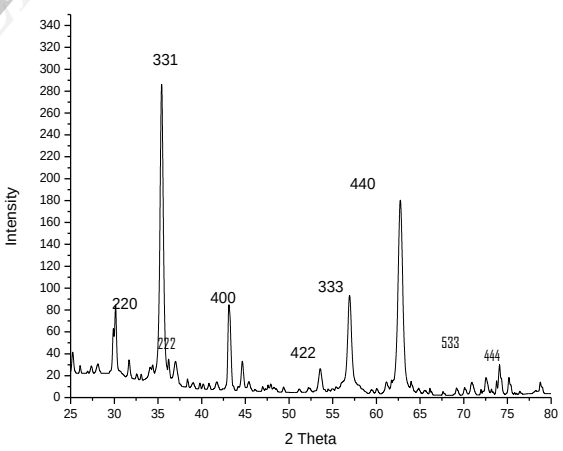

Fig1 (b): XRD Pattern of cobalt ferrite at 400◦C

Comparing fig.1 (a-c) all peaks becomes more intense and sharp with increasing sintering temperature *i.e.*, crystalline nature is increasing.

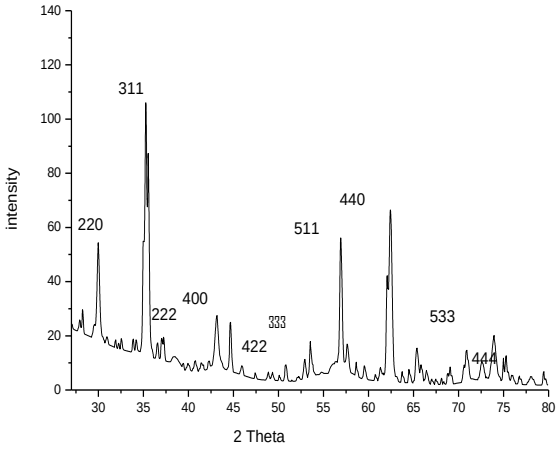

Fig1(c): XRD Pattern of cobalt ferrite at 600◦C

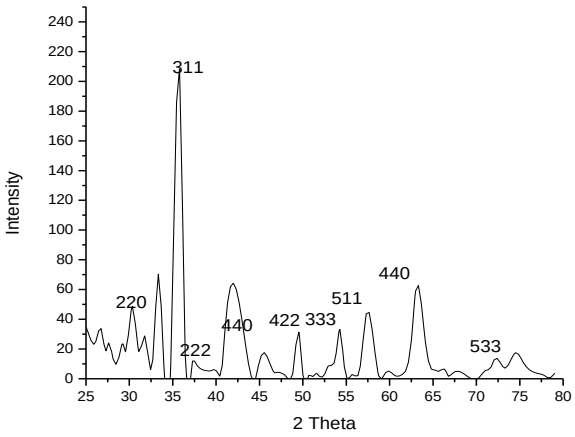

Fig1 (f): XRD Pattern of nickel doped cobalt ferrite at 600◦C

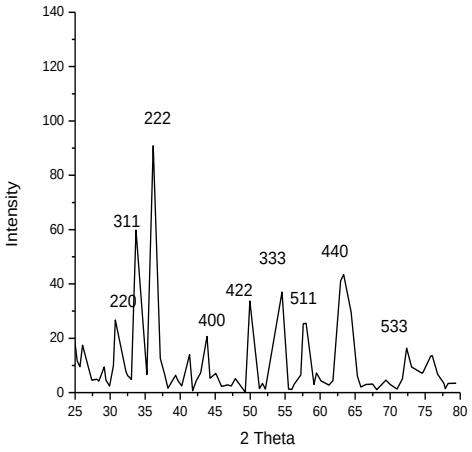

Fig1 (d): XRD Pattern of nickel doped cobalt ferrite at 100◦C

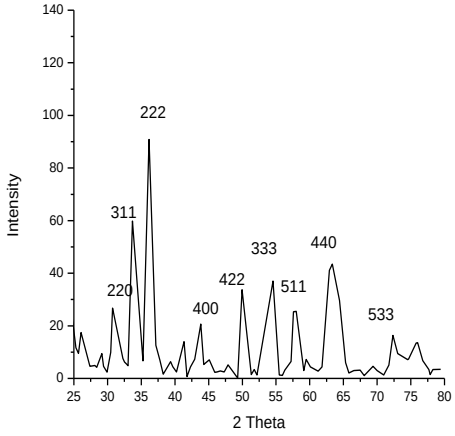

Fig1 (e): XRD Pattern of nickel doped cobalt ferrite at 400◦C

There are some extra peaks in fig.1 (e) and fig. 1(f) showing impurity in the nano powder. A comparison fig. 1(a - f) shows peaks becoming intense and sharp for 400 ^{0}C.

Grain size of the nano-crystallite calcined powder was calculated using the Scherer's formula [21].

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad (1)$$

where D is the grain size, λ is the wavelength of X-ray radiation, θ is Bragg's angle, β is the full width at half maxima of the most intense diffraction peak, and k is the instrumental constant, which is 0.94. Average particle size of cobalt ferrite nano particle was observed to be in the range 40 nm to 90 nm for samples at 100 ^{0}C, 400 ^{0}C, 600 ^{0}C. But with addition of nickel impurity it gets reduced from 20 nm to 50 nm for samples at 100 ^{0}C, 400 ^{0}C, 600 ^{0}C.

From XRD data of the powder sample, some important parameters of the prepared sample have been calculated, such as lattice parameter, strain of the crystal and dislocation density. The average strain of the sample calculated by Stokes Wilson equation [22]

$$\varepsilon = \frac{\beta}{4\cos\theta} \qquad (2)$$

Average strain increases with addition of nickel to cobalt ferrite (Table 1).

Dislocation density calculated [23] corresponding to Figure 1([a]-[f]).

$$\delta = \frac{15\varepsilon}{aD} \qquad (3)$$

where D is average grain size, a is lattice parameter [24].

$$a = d \times \sqrt{h^2 + k^2 + l^2} \qquad (4)$$

where spacing between two planes is *d*, calculated values for lattice parameters are increasing due to doping (Table 1). We observed that the lattice parameters depend on the nickel doping as well as on heat treatment.

Temperature (^{O} C)	Particle Size(Nm)	Strain	Lattice Parameters (Å)	Dislocation Density
100	58.7	6.60 x 10^{-4}	16.41	1.02 x 10^{14}
400	92.3	4.4 x 10^{-4}	18.24	3.9 x 10^{14}
600	44.0	8.8 x 10^{-4}	16.98	1.78 x 10^{14}
doped sample at 100	18.3	21.33 x 10^{-4}	16.58	1.94 x 10^{14}
doped sample at 400	44.59	8.8 x 10^{-4}	16.25	1.8 x 10^{14}
doped sample at 600	29.3	13.33 x 10^{-4}	16.38	4.5 x 10^{14}

Table 1 Lattice Parameter, Strain and Dislocation Density at 100°C, 400°C, 600°C

The morphology and particle size of nickel doped cobalt ferrite nano particles was determined by TEM.

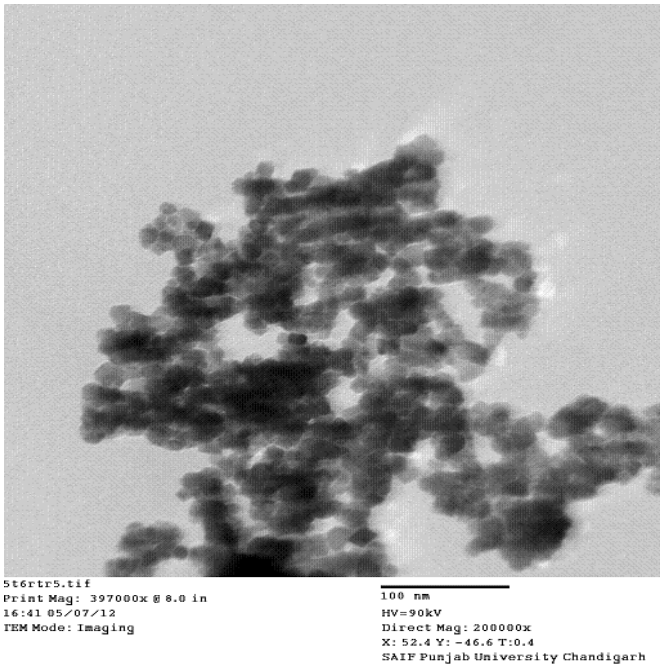

Fig2 (a): TEM image of cobalt ferrite at 400°C

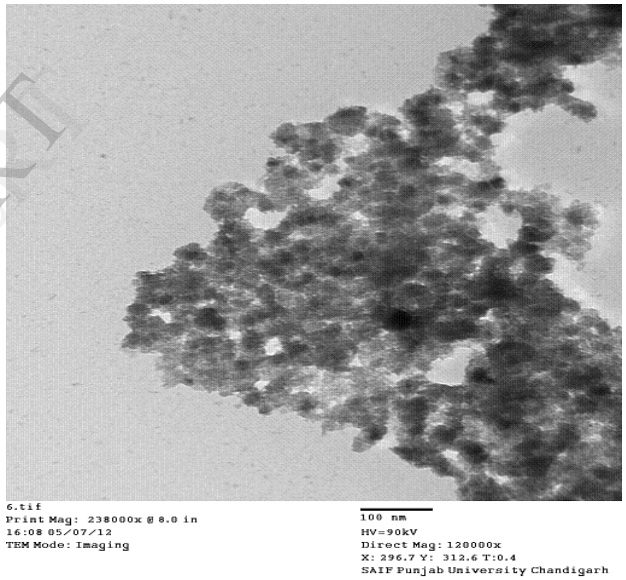

Fig2 (b): TEM images of nickel doped cobalt ferrite at 400°C.

The TEM micrograph for $CoFe_2O_4$ powder is shown in Fig. 2. The TEM micrograph of the powder sample at 400^0C in fig. 2 (a) and fig. 2 (b) shows that the particles are cubic in nature and with doping the particle size decreases.

IV CONCLUSION

Nickel doped cobalt ferrite nanocrystallite has been successfully synthesized at pH 11-12 in a range of temperature (100, 400, 600^{0}C) by co-precipitation route. Change in structural characteristics and morphology due to doping were observed by XRD and TEM, respectively. XRD pattern showed that nanocrystallite of cobalt ferrite decreased when doped with nickel. The TEM images showed that grains were regular cubic shaped nanoparticles.

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