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The effect of cobalt substitution on structure and magnetic properties of nickel ferrite

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Abstract. A series of cobalt doped nickel ferrite with composition of $Ni_{1-X}Co_XFe_2O_4$ with x ranges from 0.0 to 0.8 (in steps of 0.2) was prepared by using co-precipitation method and subsequently sintered, annealed at 600^0C for 3h. The influence of the Co content on the crystal lattice parameter, the stretching vibration and the magnetization of specimens were subsequently studied. XRD and FTIR were used to investigate structure and composition variations of the samples. All samples were found to have a cubic spinel structure. TEM was used to study morphological variations. The results indicate that the average particle sizes are between 29÷35 nm. B-H hysteresis measurement was carried out at room temperature under field of 5 kOe and this measurement with the increase of Co^{2+} concentration yields the monotonic increase of saturation magnetization (M_S) and coercive field (H_C). Ferrites with such behavior are important for magnetic recording media, microwave applications, environment and medical biology [1-3]. In view of this, we have studied the various properties of Co doped Ni ferrite.

1. Introduction

$NiFe_2O_4$ has cubic inverse spinel structure with Ni^{2+} ions occupy octahedral B – site and Fe^{3+} ions occupy both tetrahedral A – sites and octahedral B – sites [4]. Nickel ferrite has been prepared by standard ceramic route. That are particle size micrometer, low saturation magnetization and low coercivity. To our knowledge, the systematic investigation of the magnetic and electrical properties of $Ni_{1-X}Co_X Fe_2O_4$ with x varied from 0 to 0.8 in steps of 0.2 has not been reported so far. Further Ni-Co ferrite shows the good magnetostrictive properties among all the ferrite family. The studies on doping of good magnetostrictive material into the highly resistive nickel ferrite is one of the important phase for consideration of challenging magnetoelectric materials. Therefore by keeping this view in our mind we have proposed the studies on structural analysis and magnetic properties of Co–Ni ferrite with the above mentioned compositions by co – precipitation method, a new method for preparation of ferrite [5-6].

The results shown prepared $Ni_{1-X}Co_XFe_2O_4$ powder ferrite had the particle sizes in nanometers and good magnetic properties:

- Saturation Magnetization M_S about 47-67 emu/g,

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- Coercivity H_C from 31 Oe (with x=0.0) to 871 Oe (with x=0.8),
- Average longitudinal Magnetostriction $\lambda_{//} = (80\text{-}120).10^{-6}$
- Magnetomechanic Quality Q=3100 (with x=0.0)

2. Experimental

2.1. Synthesis of Ni-Co powder ferrite

A series of cobalt doped nickel ferrite with composition of $Ni_{1-x}Co_xFe_2O_4$ with x ranges from 0.0 to 0.8 (in steps of 0.2) was prepared by co-precipitation method. For the sake of simplicity, the samples are labeled viz. NF for x = 0.0, NFC02 for x = 0.2, NFC04 for x = 0.4, NFC06 for x = 0.6 and NFC08 for x = 0.8. The chemical reagents used were $NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $FeCl_3.6H_2O$. All the chemicals were dissolved in water with Fe^{3+} concentration of 0.8 mol, 0.4 mol of ions Co^{2+} and Ni^{2+}. 0.48 mol solution of sodium hydroxide was prepared and slowly added to the salt solution drop wise with steady stirring. The reaction was performed at 80^0C and pH values in the range (12-14) keep up constant for three hours. A precipitation immediately formed in the solution:

$$0.8\,NiCl_2.6H_2O + 0.2CoCl_2.6H_2O + 2Fe_2Cl_3.6H_2O + 8NaOH$$
$$\xrightarrow{80^0C} Ni_{0.8}Co_{0.2}Fe_2O_4\downarrow + 8NaCl + 22H_2O$$

After the precipitation was taken by magnet and the product was washed several time with distilled water. Finally it was annealed in oven at 600^0C for 3 hours.

2.2. Measurements of properties of Ni-Co ferrite

The morphology of the samples was performed by X-ray diffractometer (XRD), Fourier transform infrared (FT-IR) transmission spectra and Transmission Electron Microscope (TEM). Debey Scherrer formula was used to determine the particle size of the prepared samples. The magnetic characterization was performed by vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. X-ray diffraction

X-ray powder diffraction (XRD) patterns of $Ni_{1-x}Co_x\,Fe_2O_4$ (with x = 0, 0.2, 0.4, 0.6, 0.8) are shown in Fig. 1. From this Fig. the following reflection planes are showed: (111), (220), (311), (222), (400), (422), (511) and (440). These planes are indications of the presence of a spinel cubic structure. The diffraction lines corresponding to a cubic, spinel-type and crystalline phase provides clear evidence of the formation of solid solution $NiFe_2O_4$.

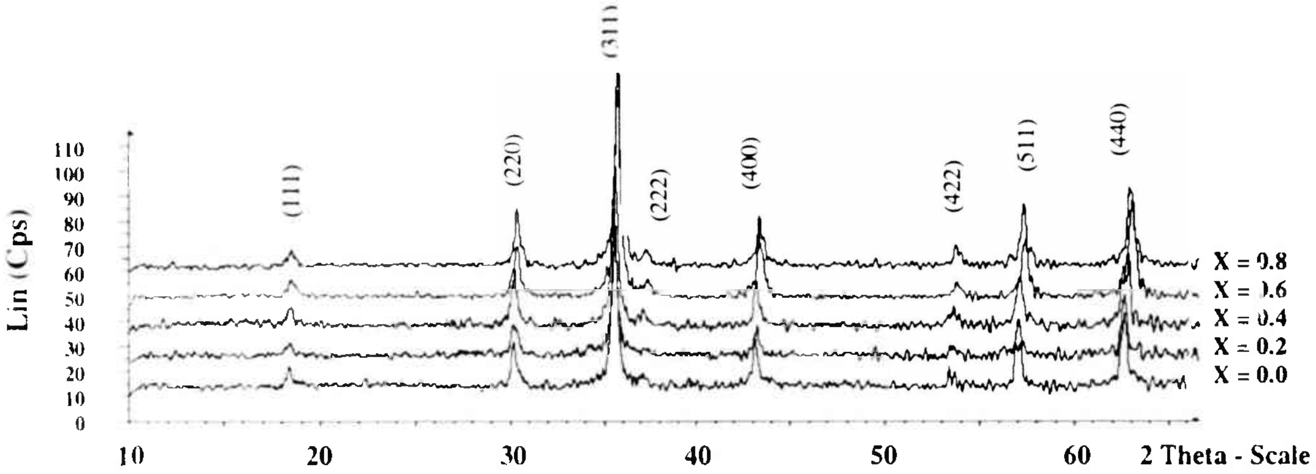

Fig. 1. XRD powder diffraction patterns of $Ni_{1-x}Co_xFe_2O_4$.

From Fig.2 it is observed that lattice parameter varies from 8.334 Å to 8.382 Å with increasing Co^{2+} content and they are tabulated in Table 1. This increase of lattice parameter with Co^{2+} due to the difference in ionic sizes of the component ions. The Co^{2+} ions have larger ionic radius (0.78 Å) than Ni^{2+} (0.74 Å) and Fe^{3+} (0.67 Å) ions.

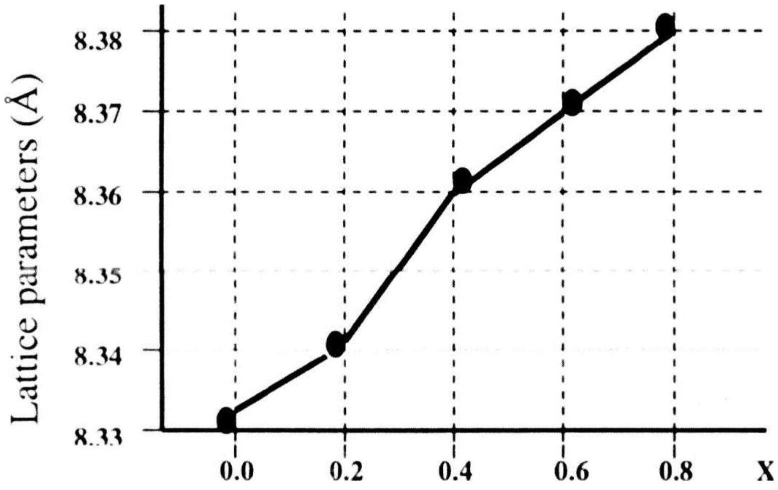

Fig. 2. Lattice parameters of $Ni_{1-x}Co_xFe_2O_4$.

Table 1. Calculated lattice parameter 'a', X-ray density 'D_X', Actual density and Relative density of $Ni_{1-x}Co_xFe_2O_4$ ferrites

Sample	Particle size (nm)	Lattice parameter (A^0)	X-ray density 'D_X' (g/cm^3)	Actual D'_x (g/cm^3)	Relative density D'_X/ 'D'_X (%)
NF	29	8.334	5.4	5.3	98.2
NFC02	33	8.343	5.4	5.2	96.3
NFC04	30	8.362	5.3	5.2	98.1
NFC06	33	8.371	5.3	5.2	98.1
NFC08	35	8.382	5.3	5.1	96.2

The X-ray density or theoretical density was estimated by using the relation [6]:

$$\text{X-ray density } D_X = \sum \frac{A}{N_A . V} \tag{1}$$

Where, A is the atomic weights of all the atoms in the unit cell, V is volume of the unit cell and N is the Avogadro's number.

Since each primitive unit cell of the spinel structure contains 8 molecules, the X-ray density 'D$_X$' was determined according to the following relation and is shown in Table1.

$$D_X = \frac{8M}{N_A . a^3} \tag{2}$$

Where, M is molecular weight of the particular ferrite, N_A is the Avogadro's number and a^3 is the volume of the cubic unit cell.

From Fig.2, it is observed that X-ray density 'D_x' decreases with addition of Co^{2+} ion content, which may be attributed to the ionic radii of constituent ions causing increase in lattice parameter and the densities of pure cobalt ferrite (5.29 g/cm^3) and pure nickel ferrite (5.38 g/cm^3).

The obtained XRD patterns of the Ni-Co ferrites are shown in Fig.1. Consequently, one can obtain the average particle size, from the broadening effect of the most intense peak employing the Scherrer formula as [6],

$$d = \frac{0.9\lambda}{B_{2\theta} \cos\theta} \tag{3}$$

where $B_{2\theta}$ is the full width half maximum (rad), λ the wavelength of the X-ray, θ the angle between the incident and diffracted beams (degree) and d the particle size of the sample (nm) (in Table 1).

3.2. FT-IR spectroscopy

The band wavenumber ν_1, ν_2, (Table 2) generally observed in the range 600-550 cm^{-1}, corresponds to an intrinsic stretching vibrations of the metal at the tetrahedral site, $M_{tetra} \leftrightarrow O$, whereas the ν_2 - lowest band, usually observed in the range 450-385 cm^{-1}, is assigned to octahedral-metal stretching, $M_{octa} \leftrightarrow O$ [6]. The decrease of wavenumber with the increase of Co^{2+} is shown in Fig.3.

Table 2. The IR spectra analysis for the studied samples

Sample	ν_1 (cm^{-1})	ν_2 (cm^{-1})
NF	596.15	428.12
NFC02	595.20	424.75
NFC04	595.37	420.65
NFC06	596.78	422.25
NFC08	593.02	420.72

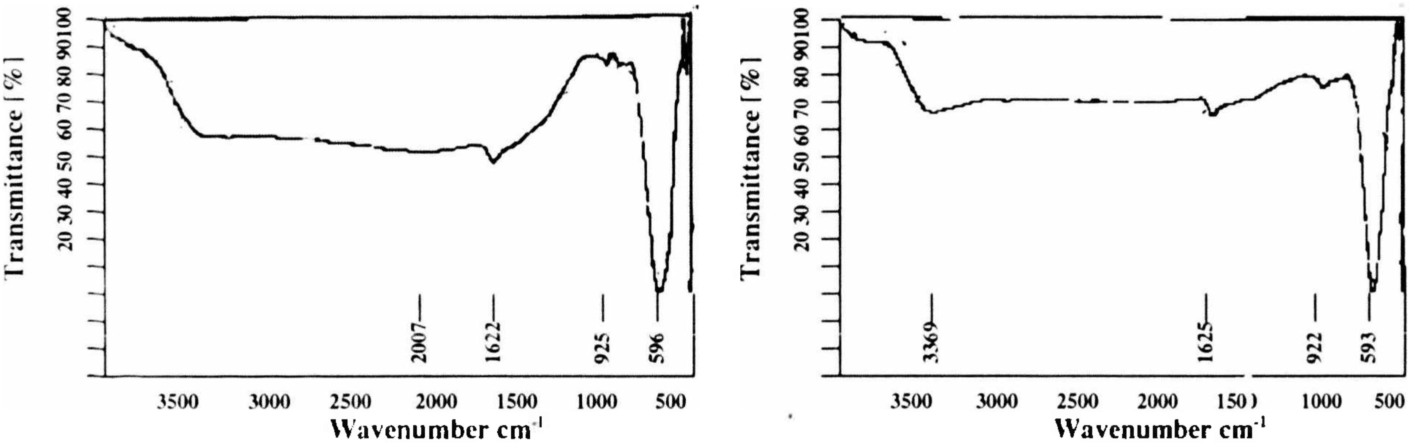

Fig. 3. FT-IR spectra of ferrite $NiFe_2O_4$ (left) and $Ni_{0.2}Co_{0.8}Fe_2O_4$ (right).

3.3. TEM analysis

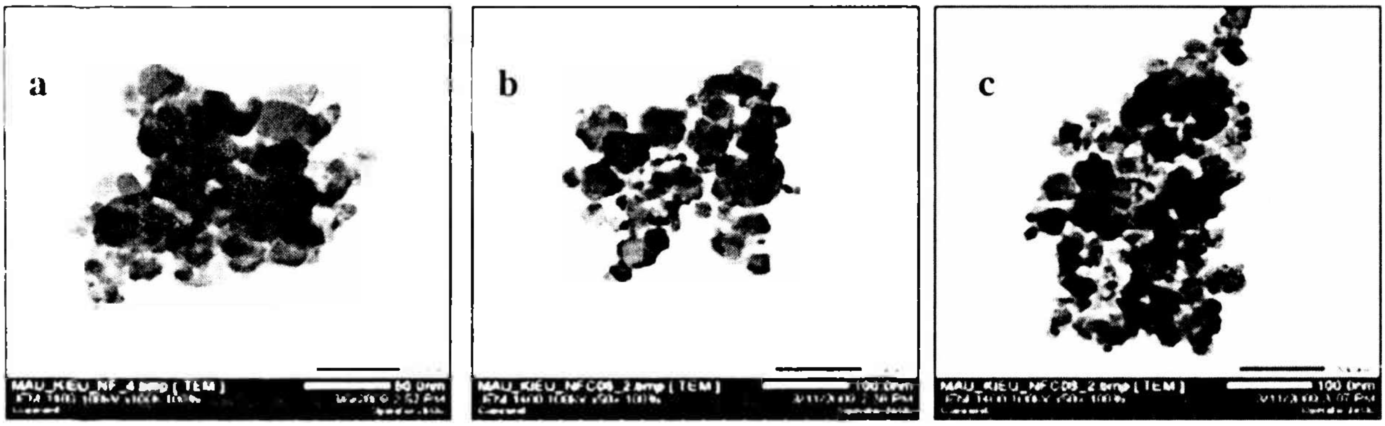

Fig. 4. TEM Micrograph of: (a) $NiFe_2O_4$, (b) $Ni_{0.4}Co_{0.6}Fe_2O_4$, (c) $Ni_{0.2}Co_{0.8}Fe_2O_4$ annealed at 600^{0}C.

TEM was used to investigate the morphology and micrographs of various samples. The micrographs are shown in Fig.4. A broad size distribution is observed with 32 ± 3 nm.

Fig.5 shows hysteresis loops for $Ni_{1-x}Co_xFe_2O_4$ nanoparticles at room temperature.These plots show that an increase in Co^{2+} doping yields monotonic increase in the saturation magnetization of Ni-ferrite which may be due to the substitution of Ni^{2+} ions by Co^{2+} on the octahedral sties. Therefore, the increasing Co^{2+} concentration (x) on the octahedral sites may result in an increasing magnetic moment per formula of $Ni_{1-x}Co_xFe_2O_4$ and equivalently, an enhancement of magnetization [7].The dependence of saturation magnetization M_s as a function of Co^{2+} concentration is shown in Fig.5. At room temperature $NiFe_2O_4$ shows a saturation magnetization M_S = 35.3 (emu/g) while $Ni_{0.2}Co_{0.8}Fe_2O_4$ exhibits M_S = 60.1 (emu/g) (in table 3).

Table 3. Room temperature parameters: Saturation magnetization (M_S), Coereivity (H_C), Remanent magnetization (M_r), Anisotropy constant (K).

X	H_C (Oe)	M_S (emu/g)	M_r(emu/g)	K (erg/g)
0.0	31	35.3	7.3	$5.5.10^2$
0.2	359	38.1	12.4	$6.9.10^3$
0.4	740	49.1	20.0	$1.8.10^4$
0.6	835	55.7	26.4	$2.3.10^4$
0.8	871	60.1	27.1	$2.6.10^5$

3.4. Magnetization measurements:

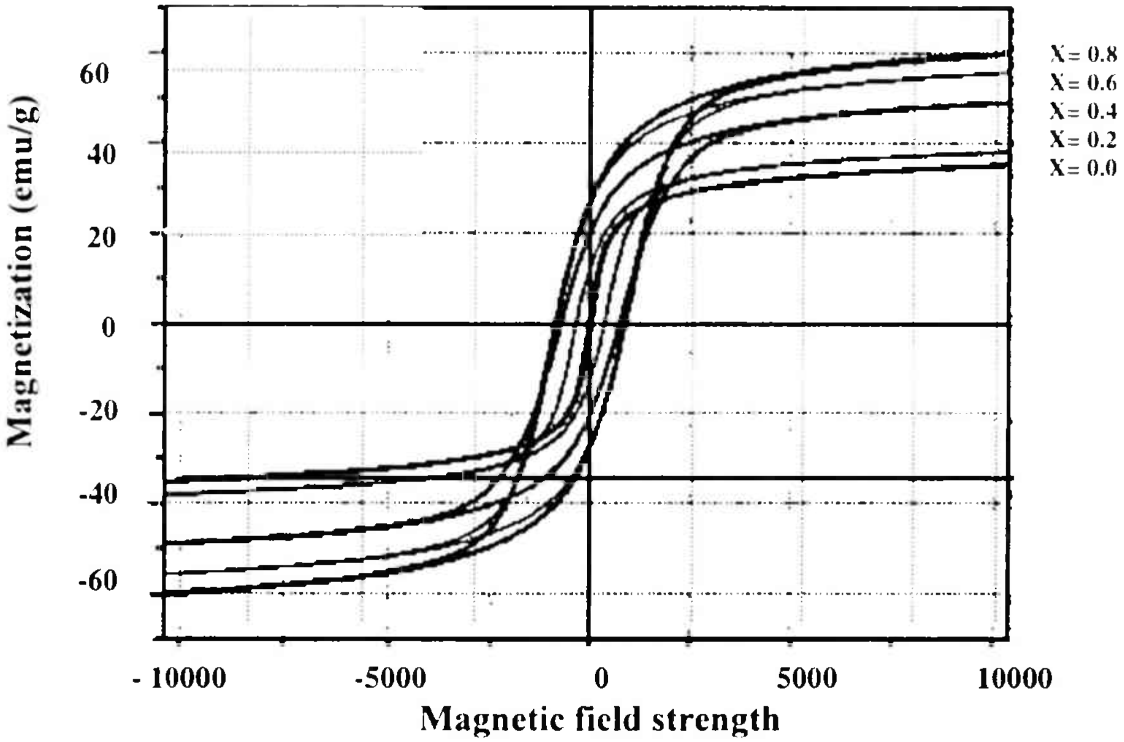

Fig. 5. Hysteresis loops for all samples of $Ni_{1-x}Co_xFe_2O_4$ ferrite system.

There will be a dependence of anisotropy constant K on the Co^{2+} ion concentration x, which can be evaluated by using the relation and is shown in table 3 with $K = \frac{H_C M_S}{2}$.

Magnetic structure of ferrite $Ni_{1-x}Co_xFe_2O_4$ is decribed following [8]:

$$\underbrace{\overrightarrow{Fe^{3+}}}_{\text{tetrahedral}}\ \underbrace{[\,\overleftarrow{Ni^{2+}_{1-x}}\ \ \overleftarrow{Co^{2+}_{x}}\ \ \overleftarrow{Fe^{3+}}\,]}_{\text{octahedral}}\,O^{2-}_{4}$$

The magnetic moment of a ion Co^{2+} is equal to 3μB, during it is 2 μB for a ion Ni^{2+} and 5 μB for Fe^{3+}. When x increased this leads to the compensation of ion Fe^{3+} in the tetrahedral and octahedral location. That led to increasing of total magnetization of a molecule $Ni_{1-x}Co_xFe_2O_4$ and hence there is increasing of M_S (table 3).

Another side, it is known that the magnetizing process of hard ferrite consisting of single domain particles is the rotation process of magnetization vectors of domain, then coercivity is determined as follows:

$$H_C = a\frac{K_1}{M_S} + b(N_1 - N_2)M_S + c\frac{\lambda_S \tau}{M_S}$$

where a, b, c are constants; N_1 and N_2 are demagnetization factors determined along two perpendicular directions; λ_S – magnetostriction and τ- mechanical strain.

The first term in above expression corresponds to the contribution of magnetocrystalline anisotropy of material, the second one is given by shape anisotropy of crystalline particles (domains) and the third one is orginated from the action of elastic mechanical deformation. In fact, the first term plays a decided role for creating high coercivity of materials, the second term can take part of several tens percent of H_C and the last one whereas can only reach several hundreds of gauss.

Thus, the increasing of Co-concentration led to the increasing of anisotropy property of ferrites $Ni_{1-x}Co_xFe_2O_4$, hence it was the increasing of H_C.

The increasing of H_C proved that the soft magnetic property of ferrite $NiFe_2O_4$ changed to the hard magnetic property of ferrite $CoFe_2O_4$.

Ni-Co ferrite samples manifested magnetostrictive property well. The longitudinal magnetostriction (was measured in accordance with sensor Wheaston bridge method [9]) of $Ni_{1-x}Co_xFe_2O_4$ ferrites was $\lambda_{//} = (80 - 120).10^{-6}$ (with $x = 0.6 - 0.8$).

The Magnetomechanic Quality was determinated by following expression: $Q = \dfrac{\omega L}{R_{Cu} - R_{Fer}}$, with L is the electric induction of a coil torus, measured on the device 819 High Precision LCR Meter in Institute of Physics in Ho Chi Minh City, ω is measured frequency, where valuable 700Hz; R_{Cu} and R_{Fer} are the resistance of the copper coil without and with ferrite toroid core, measured by the method for Wheaston bridge. The Magnetomechanic Quality of $NiOFe_2O_3$ was 3100.

4. Conclusion

Spinel ferrite $Ni_{1-x}Co_xFe_2O_4$ was synthesized successfully by co-precipitation method. X-ray diffraction study shows the presence of cubic spinel. The increase of Co^{2+} ion concentration yields the monotonic increase of M_S, H_C. Magnetic measurements show the studied system may be suitable for magnetic recording media application with some improvements.

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