

# Effects of $\text{CoFe}_2\text{O}_4$ substitution on magnetic properties of $\text{NiFe}_2\text{O}_4$ spinel ferrite

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**Abstract.** Functional magnetic materials of composition  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  ( $x=0, 0.2, 0.4, 0.6, 0.8, 1$ ) were prepared using  $\text{NiFe}_2\text{O}_4$  (soft) and  $\text{CoFe}_2\text{O}_4$  (semi-hard) nanomaterials following solid state synthesis technique. Magnetic properties of synthesized samples were studied employing XRD, FESEM, VSM and DSC techniques. Curie temperature,  $T_c$  of all the samples were determined from the temperature dependence of permeability and compared with the peak temperature of DSC thermograph.  $T_c$  is found to decrease with increasing  $\text{CoFe}_2\text{O}_4$  substitution which has been ascribed due to weakening of  $J_{AB}$  super-exchange interaction between tetrahedral and octahedral sites. The detail hysteresis parameters such as  $M_s$ ,  $M_r$ ,  $H_c$  have been determined from M-H loop measured at 80, 200 and 300K. Saturation magnetization,  $M_s$  measured at 80K was found much higher compared with data at 300K.  $M_s$  is found to increase with decreasing temperature and attained a maximum value corresponding to  $\text{CoFe}_2\text{O}_4$  at any measurement temperature which may be attributed to higher magnetic moment of  $\text{CoFe}_2\text{O}_4$  compared with  $\text{NiFe}_2\text{O}_4$ . A gradual magnetic hardening was observed to increase with increasing  $\text{CoFe}_2\text{O}_4$  content with a maximum value of  $H_c$  at  $x=0.8$ . Initial permeability as a function of frequency has been measured by an impedance analyzer. Phase transition temperature determined from DSC measurements and temperature dependence of initial permeability was found to display a good correlation. In addition, magnetic hardening of soft  $\text{NiFe}_2\text{O}_4$  with increasing amount of  $\text{CoFe}_2\text{O}_4$  substitution is also explained based on the existing theories of magnetism.

## 1. Introduction

Ferrites are commercially important magnetic materials. Ranging from the very ordinary radio sets to the complicated and exhaustive hardware involved in computers, ferrites have found their way to prove their importance. There are soft and hard magnetic ferrites. Both of these ferrites have enormous practical applications. Soft ferrites have been extensively used for many kinds of magnetic devices such as transformers, inductors, magnetic heads, in resonance circuit for high frequency (ranging from  $10^3$  to  $10^{11}$ Hz) because of their electrical resistivity higher than those of the soft magnetic alloys (ranges from  $10^3$  to  $10^{11}$   $\Omega$ -cm which is up to 15 order of magnitude higher than that of metals like iron), low eddy current losses, high initial permeability, high saturation induction, low hysteresis loss and reduced physical size. Due to these reasons extensive research activities has been carried out during the past 50 years to enhance their efficiency from the application point of view to various technical devices. Cubic spinel ferrite, has two sub-lattices, tetrahedral (A site) and octahedral (B site) in  $\text{AB}_2\text{O}_4$  crystal structure. The important structural, electrical and magnetic properties of spinels,



responsible for their application in various fields, are found to depend on the distribution of cations among the sites [1]. Therefore the estimation of the cation distribution turns out to be important. Various cations can be placed in A site and B site to tune its magnetic properties. Depending on A site and B site cations it can exhibit various magnetic structures [2]. Both Nickel and Cobalt ferrites have inverse spinel structure in bulk. Some researchers have investigated various properties of bulk Ni-Co ferrites employing co-precipitation, hydrothermal, sol-gel method but no detail study has been conducted yet to synthesize and characterize nano-power based Ni-Co mixed ferrites [3, 4].

In present work, we studied the structural and magnetic properties of functional magnetic materials of composition  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  ( $x=0, 0.2, 0.4, 0.6, 0.8, 1$ ) prepared using  $\text{NiFe}_2\text{O}_4$  (soft) and  $\text{CoFe}_2\text{O}_4$  (semi-hard) nanomaterials following solid state synthesis technique.

## 2. Experimental

Ni-Co ferrites with the composition  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  ( $x=0, 0.2, 0.4, 0.6, 0.8, 1$ ) were synthesized by solid state reaction method. The starting materials for the preparation of the studied compositions were in the form of nano powder of  $\text{NiFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  ferrites of purity 99.99% (Inframat Advanced Materials, USA). Nano powders were mixed (according to their molecular weight) using mortar and pestle and then ball milled for 10 hrs and the slurry was dried and pressed into disc shaped sample. The disc shaped samples were pre-sintered at 850 °C for 4 hrs. Final sintering of the sample was carried out at 1200°C for 4 hrs.

The structure of the sample was determined by the X-ray diffraction method using PHILIPS X'Pert Pro X-ray diffractometer. The microstructural aspects were studied with a field emission scanning electron microscope (JEOL-JSM-7600F). Curie temperature measurement was conducted by using WAYNE KERR impedance analyzer attached with an oven and compared the results obtained from DSC measurement. The magnetic measurement of the sample was carried out by a vibrating sample magnetometer (Model VSM-02, Hirstlab, UK) at 80K, 200K and 300K temperature as a function of applied field.

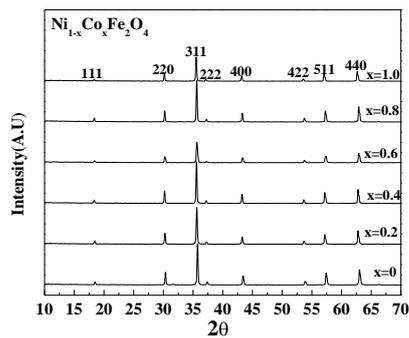
## 3. Results and discussion

### 3.1. XRD analysis

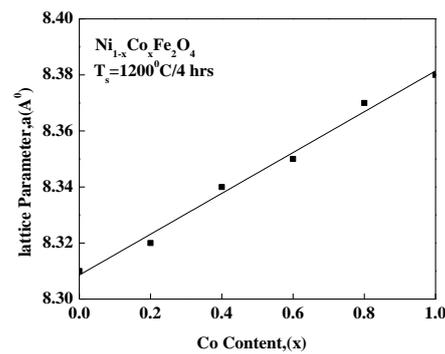
The phase identification and lattice parameter determination were performed by XRD technique. XRD patterns of  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  samples are shown in Figure 1. All the samples showed a good crystallization with well-defined diffraction lines. The XRD patterns clearly show the formation of spinel structure with identified peaks of (111), (220), (311), (222), (400), (511) and (440) planes. Obtained results are in good agreement with previously reported values [5]. Lattice parameter was determined using Nelson-Riley extrapolation method. The values of the lattice parameter obtained from each reflected planes are plotted against the Nelson-Riley function [6]

$$F(\theta) = \frac{1}{2} \left[ \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right] \quad (1)$$

where  $\theta$  is the Bragg's angle. Experimental data are fitted with a straight line. The accurate values of the lattice parameter were estimated from the extrapolation of this line to  $F(\theta) = 0$  or  $F(\theta) = 90^\circ$ .



**Figure 1.** XRD pattern of  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  ferrites.



**Figure 2.** Variation of the lattice parameters with Co content in  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  ferrites.

The variation of lattice parameter as a function of  $\text{Co}^{2+}$  content is depicted in Figure 2. It is noticed that the lattice parameter increases with the Co content, obeying Vegard's law [7]. This variation can be attributed to ionic size difference of the component ions. The  $\text{Co}^{2+}$  (0.745 Å) ions possess a larger ionic radius than  $\text{Ni}^{2+}$  (0.69 Å) and  $\text{Fe}^{3+}$  (0.645 Å) [8].

Next, the bulk density ( $d_B$ ) was measured by the usual mass and dimensional considerations whereas the X-ray density ( $d_X$ ) of the prepared samples was calculated using the following relation:

$$d_x = \frac{ZM}{Na^3} \quad (2)$$

where  $M$  is the molecular weight of the corresponding composition.  $N$  is Avogadro's number,  $V = a^3$  is the volume of the cubic unit cell and  $Z$  is the number of molecules per unit cell, which is 8 for the spinel structure. The X-ray density is expected to decrease with the Co content because the lattice parameter increases with Co content. Similar result has also been reported in Mg-Mn ferrites [9]. The bulk density is lower than the X-ray density. This may be due to the existence of pores which were formed and developed during the sample preparation or the sintering process. Table 1 shows the variation of bulk density and X-ray density of the samples.

**Table 1.** Variation of lattice parameter, X-ray density, bulk-density, porosity and Curie temperature with cobalt content in  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ .

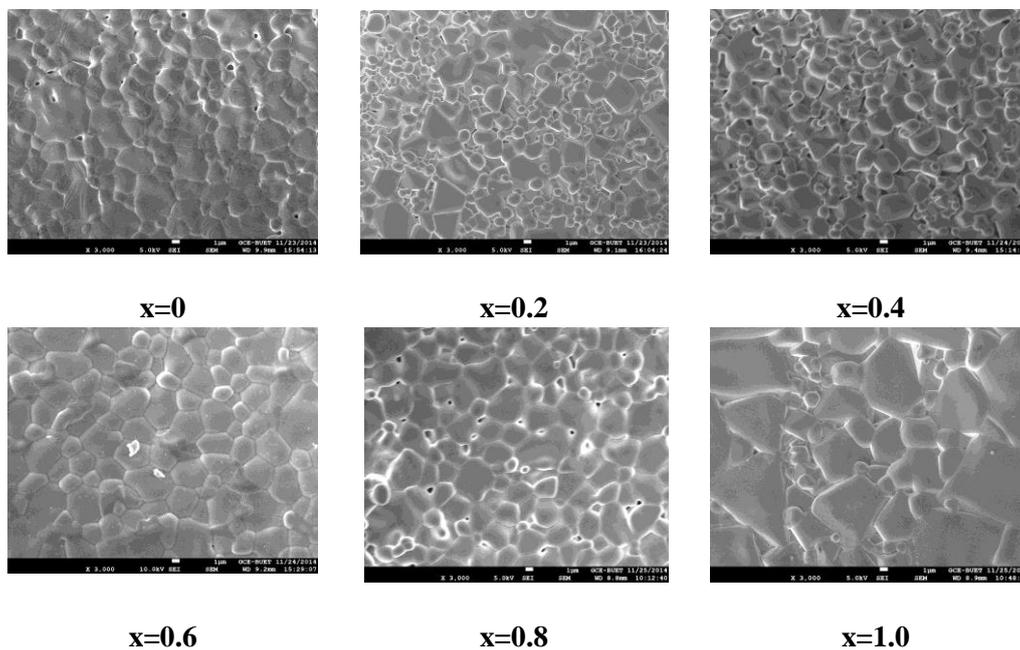
$x^a$	$a_{th} (\text{Å}^0)$	$a_{exp} (\text{Å}^0)$	$\rho_x$ ( $\text{gm}/\text{cm}^3$ )	$\rho_b$ ( $\text{gm}/\text{cm}^3$ )	P (%)	$T_c$ (C)	
						Impedence Analyzer	DSC
0	8.32	8.31	5.42	5.02	7.38	538	556
0.2	8.33	8.32	5.4	4.41	18.33	527	538
0.4	8.35	8.34	5.36	4.34	19.02	510	520
0.6	8.36	8.35	5.35	4.32	19.25	490	510
0.8	8.38	8.37	5.31	4.39	17.32	460	498
1	8.39	8.38	5.29	5.03	4.91	450	485

<sup>a</sup> Cobalt (Co) content

$a_{th}$ : theoretical lattice parameter,  $a_{exp}$ : experimental lattice parameter,  $\rho_x$ : X-ray density,  $\rho_b$ : bulk density, P: porosity,  $T_c$ : Curie temperature.

### 3.2. Microstructure

Magnetic and electrical properties of ferrites highly depend on the microstructure. Between the grain size and porosity of microstructures, the grain size is more important parameter affecting the magnetic properties of a ferrite. Grain growth is closely related to the grain boundary mobility. Recrystallization and grain growth involve the movement of grain boundaries. The grain growth being a result of inter-particle mass transport, appears to be dominated by the bimodal diffusion mechanism of lattice and grain boundary diffusion [10, 11]. Scanning electron micrographs (SEM) of  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  sintered at  $1200^\circ\text{C}$  are shown in Figure 3. As seen from the micrographs, the average dimension of the particles is below  $10\ \mu\text{m}$ .



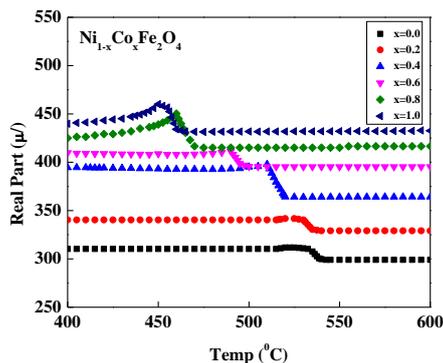
**Figure 3.** SEM micrographs of  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  samples sintered at  $1200^\circ\text{C}$ .

### 3.3. Temperature dependence of initial permeability

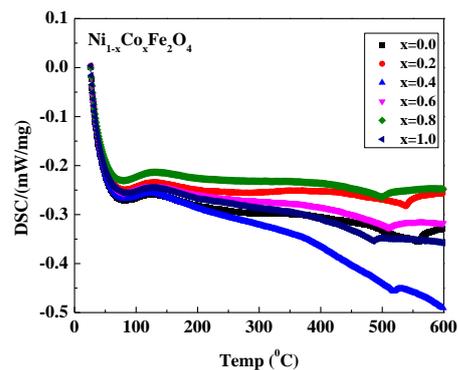
The magnitude of the initial permeability  $\mu'$  of a magnetic material is proportional to the square of the saturation magnetization and inversely proportional to the magnetic magnetocrystalline anisotropy constant. Both quantities vary with temperature, so  $\mu'$  is a complicated function of temperature [12]. The variation of  $\mu'$  with temperature is a function of the anisotropy constant ( $\kappa_1$ ) and saturation magnetization ( $M_s$ ). Both  $\kappa_1$  and  $M_s$  usually decrease with increase in temperature. However, the decrease in  $\kappa_1$  with temperature is faster than the decrease in  $M_s$ . When the anisotropy constant reaches zero,  $\mu'$  attains its maximum value and then drops off to the maximum value near the Curie point. The thermal variation of the initial permeability  $\mu'$  was recorded to determine Curie temperature,  $T_C$  for the above investigated compositions of Ni-Co ferrite in the shape of toroid samples which is shown in Figure 4.

The Curie temperature mainly depends upon the strength of the A-B exchange interaction. According to Neel's sub-lattice field model [13], the A-B exchange interaction is stronger than the A-A or B-B interaction. As the concentration of  $\text{Co}^{2+}$  increases, the amount of  $\text{Fe}^{3+}$  decreases in the B sites. This reduces the A-B interactions. From figure 4, it can be seen that  $\mu'$  increases with increasing

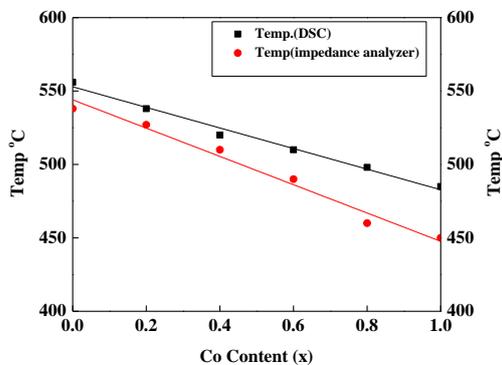
temperature, attaining a maximum value just below  $T_C$ . The maximum value of  $\mu'$  just below  $T_C$  is a manifestation of the Hopkinson peak attributed to the minimization of magneto-crystalline anisotropy energy with temperature. Beyond this peak, permeability sharply falls to a very low value indicating  $T_C$ . The sharp fall of the permeability at the Curie point indicates the degree of homogeneity in the sample composition [14]. From the curves of the initial permeability versus temperature, the Hopkinson peak is found which may be attributed to structural transformation from tetragonal to cubic in these samples [15, 16]. Figure 5 shows the phase transition temperature for different composition of  $Ni_{1-x}Co_xFe_2O_4$  determined from DSC measurements and Figure 6 shows the variation of Curie temperature with Co content.



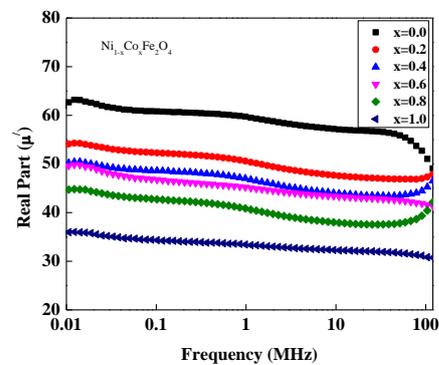
**Figure 4.** Permeability vs Temperature for different composition of  $Ni_{1-x}Co_xFe_2O_4$ .



**Figure 5.** Phase transition temperature for different composition of  $Ni_{1-x}Co_xFe_2O_4$  determined from DSC



**Figure 6.** Variation of Curie temperature with Co content.



**Figure 7.** Variation of initial permeability with Co content.

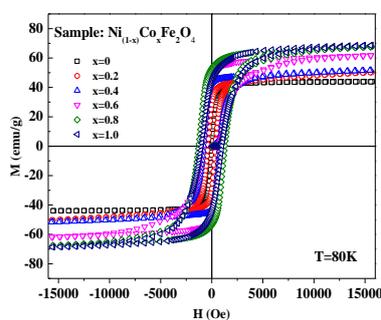
### 3.4. Frequency dependence of initial permeability

Figure 7 shows the variation of the initial permeability spectra as a function of the Co content. It is noticed that the real part of the initial permeability ( $\mu'$ ) decreases with increasing  $Co^{2+}$  substitution in  $Ni_{1-x}Co_xFe_2O_4$  samples sintered at  $1200^\circ C$ . However the decrease in  $\mu'$  with the increase of Co content was not consistent with the variation of microstructures shown in Figure 3. According to the Globus and Duplex model [14], the static permeability and their product are micro-structurally dependent. Ferrites with large grains are preferred to high permeability values because of the contribution of the domain wall motion. A decrease in the grain size results in a decrease in the number of domain walls

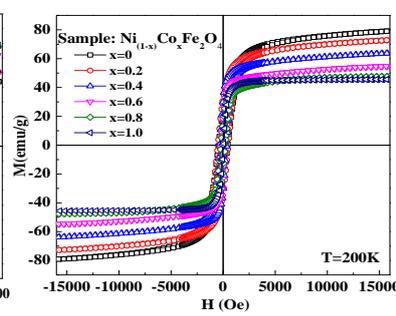
in each grain. Moreover the decrease in initial permeability is closely related to the densification of the sample. A decrease in the density of ferrites not only results in an increase of the demagnetizing field due to the presence of pores but also reduces the spin rotational contribution, which in turn decreases the permeability [17, 18]. Therefore, the decrease of the initial permeability of Ni-Co ferrites with the increase of the Co content was attributed to the decrease in bulk densities.

### 3.5. M-H loop measurement

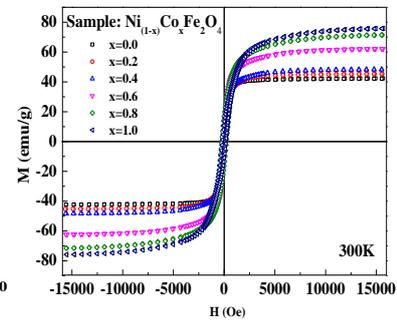
Measurement of a hysteresis loop is a very simple and fast method to characterize ferromagnetic materials. M-H loops at 80K, 200K and 300K temperature for the investigated compositions of  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  ( $x=0.0, 0.2, 0.4, 0.6, 0.8, 1$ ) sintered at  $1200^\circ\text{C}$  are depicted in figures 8 to 10.



**Figure 8.** The M-H loop for  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  at 80K.



**Figure 9.** The M-H loop for  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  at 200K.



**Figure 10.** The M-H loop for  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  at 300K.

The hysteresis curves and their properties such as the saturation magnetization ( $M_s$ ), retentivity ( $M_r$ ), coercivity ( $H_c$ ), and hysteresis loss are extracted from the application point of view. Tables 2-4 summarize hysteresis parameters such as  $M_s$ ,  $M_r$ ,  $H_c$  determined from M-H loop measured at 80K, 200K and 300K. Saturation magnetization,  $M_s$  measured at 80K was found to be much higher compared with data at 300K.  $M_s$  has shown to increase with decreasing temperature and attained a maximum value for  $\text{CoFe}_2\text{O}_4$  at any measurement temperature which may be attributed to higher magnetic moment of  $\text{CoFe}_2\text{O}_4$  compared to  $\text{NiFe}_2\text{O}_4$ . A gradual increase in magnetic hardening was observed with increasing  $\text{CoFe}_2\text{O}_4$  content attaining a maximum value of  $H_c$  at  $x=0.8$ .

**Table 2.** Saturation magnetization ( $M_s$ ), retentivity ( $M_r$ ), coercivity ( $H_c$ ), and hysteresis loss of Ni-Co ferrite samples at 80K.

Samples	$M_s$ (emu/g)	$M_r$ (emu/g)	$-H_c$ (Oe)	$+H_c$ (Oe)	$\Delta H_c$
$\text{NiFe}_2\text{O}_4$	45.58	22.55	-38.23	37.54	75.77
$\text{Ni}_{0.8}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$	47.54	31.96	-202.03	196.53	398.56
$\text{Ni}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$	54.69	33.05	-233.62	234.67	468.29
$\text{Ni}_{0.4}\text{Co}_{0.6}\text{Fe}_2\text{O}_4$	63.71	22.25	-348.28	346.57	694.85
$\text{Ni}_{0.2}\text{Co}_{0.8}\text{Fe}_2\text{O}_4$	72.77	16.02	-480.98	481.44	962.42
$\text{CoFe}_2\text{O}_4$	79.03	5.08	-434.07	429.4	863.48

**Table 3.** Saturation magnetization ( $M_s$ ), retentivity( $M_r$ ), coercivity( $H_c$ ), and hysteresis loss of Ni-Co ferrite samples at 200K.

Samples	$M_s$ (emu/g)	$M_r$ (emu/g)	- $H_c$ (Oe)	+ $H_c$ (Oe)	$\Delta H_c$
NiFe <sub>2</sub> O <sub>4</sub>	43.95	2.51	24.75	33.57	8.81
Ni <sub>0.8</sub> Co <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	50.36	28.71	373.32	361.81	11.51
Ni <sub>0.6</sub> Co <sub>0.4</sub> Fe <sub>2</sub> O <sub>4</sub>	51.59	42.59	774.74	771.74	3
Ni <sub>0.4</sub> Co <sub>0.6</sub> Fe <sub>2</sub> O <sub>4</sub>	61.74	50.67	1047.36	1038.79	8.57
Ni <sub>0.2</sub> Co <sub>0.4</sub> Fe <sub>2</sub> O <sub>4</sub>	67.7	52.84	1267.02	1266.42	0.059
CoFe <sub>2</sub> O <sub>4</sub>	68.67	43.73	100.63	1010.72	10.08

**Table 4.** Saturation magnetization ( $M_s$ ), retentivity( $M_r$ ), coercivity( $H_c$ ), and hysteresis loss of Ni-Co ferrite samples at 300K.

Samples	$M_s$ (emu/g)	$M_r$ (emu/g)	- $H_c$ (Oe)	+ $H_c$ (Oe)	$\Delta H_c$
NiFe <sub>2</sub> O <sub>4</sub>	42.16	3.16	30.41	20.82	9.58
Ni <sub>0.8</sub> Co <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	45.25	5.61	68.98	61.47	7.51
Ni <sub>0.6</sub> Co <sub>0.4</sub> Fe <sub>2</sub> O <sub>4</sub>	48.25	7.01	82.08	73.89	8.18
Ni <sub>0.4</sub> Co <sub>0.6</sub> Fe <sub>2</sub> O <sub>4</sub>	62.27	13.18	150.58	141.63	8.95
Ni <sub>0.2</sub> Co <sub>0.4</sub> Fe <sub>2</sub> O <sub>4</sub>	71.44	17.6	248.27	239.6	8.67
CoFe <sub>2</sub> O <sub>4</sub>	75.77	11.99	188.57	181.03	7.54

#### 4. Conclusions

The presence of Co ions causes appreciable changes in the physical and magnetic properties of the Ni-Co ferrites. XRD results indicate a single phase of the pure cubic spinel structure. The lattice parameter increases with the increase of Co content. The bulk density and X-ray density are found to decrease linearly with increasing Co content in the mixed Ni-Co ferrite system. The average grain size of Ni<sub>1-x</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> system increases with addition of Co. The Curie temperature has shown to decrease linearly with increasing Co content. The initial permeability was found to decrease with increasing Co content.

#### 5. Reference

- [1] Maqsood A Khan, K Rehman M A and Malik M A 2011 *Journal of Alloys and Compound*, Vol. 509 pp 7493–749.
- [2] Batoo K M et al. 2013 *Journal of Nanoparticle Research Res* Vol 15 No 2067 pp 1-9
- [3] A K M A. Hossain M Seki T Kawai H Tabata 2004 *Journal of Appl. Phys.* Vol 96 (2) No 1273.
- [4] A Meenakshisundaram N Gunasekaran V Srinivasan 1982 *Phys. Status Solidi (a)* 69 KIS
- [5] C Rath et al 2002 *Journal of Applied Physics* Vol 91 pp 2211-2215.
- [6] J B Nelson DP Riley 1945 *Proc Phys Soc (London)* Vol 57 pp 160.
- [7] L Vegard 1921 *Z. Phys.* Vol 5 pp 17-26.
- [8] R D Shannon 1976 *Acta Cryst A* Vol 32 pp 751-767.
- [9] Pandit et al 2005 *J. of Mater. Sci.* Vol 40(2) pp 423-428.
- [10] T K Gupta R L Coble 1968 *J. Am. Ceram. Soc.* Vol 51 pp 521-525.
- [11] Calton et al 2002 *J. Magn. Magn. Matter.* Vol 160 pp 242-245.
- [12] Smit J Wign 1959 *HPJ Ferrites* (New York: Wiley).
- [13] Neel, L 1948 *Magnetic properties of ferrites. Ann. Phys. Paris* Vol 3 pp 137–198
- [14] Globus A Duplex P 1966 *IEEE Trans. Magn.* Vol(3) pp 441–445.
- [15] Dawoud HA Shaat SKK 2006 *Islamic University Journal* Vol 14 pp 165–182
- [16] Bergestain A Cervinka L 1961 *Czech J. Phys. B.* Vol 11 pp 584–594.

- [17] J.J Shorti, S D.Kulkarn, C E Deshpande S K Date 1999 *Mater. Chem. Phys.* Vol 59 pp 1-5.  
[18] ST Mahmud et al 2006 *Journal of Magnetism an Magnetic Materials* Vol 305 pp 269-274.

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