Dependence of the magnetic and optical properties of Ni-Co nanoferrite on the particle shape

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Abstract. This work presents the effect of particle shape on the magnetic and optical properties of Ni-Co nanoferrite (NCF). Two series of different preparation methods were used to obtain two different shapes of Ni\textsubscript{x}Co\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{4} where x=0, 0.25, 0.5, 0.75 and 1. Sol gel was the first method used to synthesize NCF with citric acid as a fuel and the second series was synthesized by hydrothermal route and the fuel was oxalic acid. Structural characterization for NCF nanomaterials was carried out by X-ray diffraction (XRD), Energy Dispersive Spectroscopy (EDS) and Transmission Electron Microscope (TEM). Magnetic parameters were determined from Vibrating Sample Magnetometer (VSM) for all samples and it is noticed that the values of M\textsubscript{r} and M\textsubscript{r}/M\textsubscript{s} are greater in nanorod series than nanosphere series. RLC Bridge was used to obtain the Curie temperature of the polycrystalline nanomaterials by the variation of relative permeability with increasing temperature. Values of direct and indirect band gaps were determined from double beam spectrometer using Diffused Reflectance Spectroscopy (DRS) measurements. It was found that changing particle shape could change the cation distribution, magnetic and optical properties of NCF nanoparticles.

1. Introduction.
Nanoferriotes with chemical formula MFe\textsubscript{2}O\textsubscript{4} where M is any divalent metal ion have a great interest from researchers due to their unusual properties compared to bulk ferrites. They have many technological applications such as magnetic cores, sensors, permanent magnets, microwave devices, magnetic drug delivery and their catalytic activity [1,2]. There are several methods used for synthesizing nano ferrites including co-precipitation, sol-gel, microwave and hydrothermal [3]. The synthesis process may change the shape of the particle of a certain composition. The particle shape is one of the important parameters that characterize the properties of nanoferrites. It was found that NiFe\textsubscript{2}O\textsubscript{4} is a soft magnetic material and has low magnetic anisotropy [4]. On the other hand, CoFe\textsubscript{2}O\textsubscript{4} has a high magnetic anisotropy and is classified as a hard magnetic material [5]. Since the cation distribution is intermediate in most nanoferrites [6-8], the replacement of Co\textsuperscript{3+} by Ni\textsuperscript{2+} can change the magnetic and optical properties of CoFe\textsubscript{2}O\textsubscript{4} nanomaterial. Many researchers studied the mixed Ni-Co nano ferrite due to the unique magnetic coupling between transition metal ions. K. Maaz et al. [9] studied the magnetic properties of Co\textsubscript{1-x}Ni\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} (0≤x≤1) using co-precipitation method. A.B. Nawale et al. [10] measured the optical and magnetic properties of Ni-Co nanoferrite using thermal plasma technique. However, studying the dependence of the magnetic and optical properties of mixed Ni-Co nanoferrite on the particle shape has not been preceded. So, we present here the preparation of two series of Ni\textsubscript{x}Co\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{4} with x=0, 0.25, 0.5, 0.75 and 1 with different preparation techniques in order to obtain two different particle shapes and study their magnetic and optical properties.
2. Experimental.

2.1. Samples preparation.
Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ nanoferrite with $x=0, 0.25, 0.5, 0.75$ and $1$ have been synthesised by two different methods in order to obtain two different structure. The first one was Sol-gel method. Stoichiometric ratios of cobalt nitrate [Co (NO$_3$)$_2$.6H$_2$O 99.5%], nickel nitrate [Ni (NO$_3$)$_2$.6H$_2$O 99.5%] and ferric nitrate [Fe (NO$_3$)$_3$.9H$_2$O 99%] were separately dissolved in distilled water and stirred magnetically until we obtained a clear solution. A citric acid [C$_6$H$_8$O$_7$.H$_2$O 99%] was dissolved in distilled water and then added to the previous salt solution with continuous heating and stirring at 65 °C in order to make the chemical interaction goes slowly to get homogeneous precursor. Heating and stirring were continued until the formation of gel. This gel was heated at 200 °C for 1 hour to get a powder sample. This method enabled us to get the nanosphere structure.

The second series were synthesized by hydrothermal method. Cobalt nitrate [Co (NO$_3$)$_2$.6H$_2$O 99.5%], nickel nitrate [Ni (NO$_3$)$_2$.6H$_2$O 99.5%] and ferric nitrate [Fe (NO$_3$)$_3$.9H$_2$O 99%] were also taken in this interaction with stoichiometric ratios and stirred vigorously in 15 ml deionized water. Oxalic acid [C$_2$H$_2$O$_4$.2H$_2$O 99%] was dissolved in ethylene glycol and then poured to the salt solution. The mixture solution was stirred vigorously for 30 minutes to get a homogenous solution and then heated to 190 °C for 5 hours in a 80 ml Teflon-lined stainless autoclave. Afterwards, precipitate was collected and washed with distilled water for several times and then dried at 80 °C. The obtained powder was sintered at 900 °C for 3 hours with a heating rate 2 °C.min$^{-1}$. The nanorod structure was formed by this method.

2.2. Characterization of Samples.
Powder X-ray diffraction (XRD) patterns were recorded on X-ray diffractometer (X’Pert Graphics, Germany) with Cu K$_\alpha$ radiation of wavelength ($\lambda=1.54056\,\text{Å}$) between the Bragg angles 20–80°. The values of d-spacing and h k l were used to calculate the lattice parameter (a) for each sample according to the relation $a=d*(h^2+k^2+l^2)^{0.5}$. The average crystallite size (D) for each sample was calculated using high intensity peak (3 1 1) according to Sherrer equation $D=\frac{0.94\lambda}{\beta\cos\theta}$ where $\lambda$ is the used wavelength of the X-ray beam (0.154 nm), $\beta$ is the full width at half maximum (FWHM) of (3 1 1) plane and $\theta$ is Bragg’s angle. The average particle size was obtained from Transmission Electron Microscope (TEM, JEOL JEM-100CX) with voltage accelerator 120 KeV. Elemental analysis of the nanocrystalline ferrites were carried out by Energy Dispersive Spectrometer (EDS) (Tecnai G20, Super twin, double tilt (FEI, Netherland). Hysteresis loop parameters $M_s$, $M_r$ and $H_c$ were obtained using Vibrating Sample Magnetometer VSM (7410 Lakeshore, USA) with a maximum applied field of 20000 G at room temperature. The change in relative permeability $\mu_r$ with increasing temperature was carried out to obtain the Curie temperature using RLC bridge (TEGAM Inc. Model 3550, 42.0 Hz to 5.00 MHz) at constant frequency of 10 KHz knowing that $\mu/g^{3045}=\frac{L_{\text{sample}}}{L_{\text{air}}}$ where $L_{\text{sample}}$ and $L_{\text{air}}$ are the self-inductance of powder sample and air respectively [11]. The optical properties by diffused reflectance spectroscopy (DRS) analysis was carried out to determine the band gap for all samples. The optical diffused reflectance was recorded in the wavelength range 300-800 nm at room temperature using a Nordic Scientific double beam spectrophotometer.

3. Results and Discussion.
3.1. Structural Characterization.
Figure 1 shows X-ray diffraction patterns of the nanosphere and nanorod samples of NCF nanomaterials with $x=0, 0.25, 0.5, 0.75$ and $1$. It shows that each sample has a single phase cubic structure without any extra impurity peak. The lattice parameter and crystallite size were calculated from the X-ray data and their variation with increasing Ni content is shown in table 1. It can be seen that the lattice parameter decreases with increasing Ni concentration for both series. This is due to the substitution of Co$^{2+}$ ion of
ionic radius (0.78 Å) with Ni$^{2+}$ ion of smaller ionic radius (0.69 Å) [12]. Moreover, the mean values of lattice parameter and crystallite size of nanorod series are larger than those of nanosphere series. This is due to the higher temperature treatment of nanorod series (800 °C) than that of nanosphere series (200 °C) during preparation which caused an expansion for the lattice parameter and crystallite size [13].

Because of the sensitivity of the intensity ratio I(220)/I(400) to the cation distribution on tetrahedral (A) and octahedral (B) sites [14], the intensities of (220) and (400) were calculated for all samples from X-ray data. Table 2 shows the estimated cation distribution of CoFe$_2$O$_4$ for both series. This distribution is based on the preference of Ni$^{2+}$ ions to B site while Co$^{2+}$ and Fe$^{3+}$ ions prefer both A and B sites [15].

Table 1. Average crystallite size and lattice parameter of Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ nanospheres (N.S) and nanorods (N.R).

| Sample          | Crystallite size (N.S) (nm) | Crystallite size (N.R) (nm) | Lattice parameter (N.S) (Å) | Lattice parameter (N.R) (Å) |
|-----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| CoFe$_2$O$_4$   | 9.74                        | 44.27                       | 8.365                       | 8.384                       |
| Ni$_{0.25}$Co$_{0.75}$Fe$_2$O$_4$ | 10.9                        | 41.1                        | 8.373                       | 8.371                       |
| Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$   | 9.84                        | 36.09                       | 8.387                       | 8.332                       |
| Ni$_{0.75}$Co$_{0.25}$Fe$_2$O$_4$ | 12.91                       | 35.41                       | 8.356                       | 8.354                       |
| NiFe$_2$O$_4$   | 12.19                       | 33.84                       | 8.347                       | 8.349                       |

Table 2. The estimated cation distribution data of CoFe$_2$O$_4$ nanomaterials calculated from XRD pattern.

| Sample         | I(220)/I(400) | Cation distribution                       |
|----------------|---------------|------------------------------------------|
| CoFe$_2$O$_4$ (N.S) | 1.1           | (Fe)[CoFe]O$_4$                          |
| CoFe$_2$O$_4$ (N.R) | 1.5           | (Co$_{0.5}$Fe$_{0.5}$)[Co$_{0.5}$Fe$_{1.5}$]O$_4$ |

The EDS patterns of NCF nanomaterials with x=0, 0.5 and 1 for the two series are shown in Fig. 2. The patterns reveal the existence of the elemental composition of the samples Co, Ni, Fe and O. The absence of Ni peak at x=0 confirms the formation of pure CoFe$_2$O$_4$ nano ferrite and the absence of Co peak at x=1.
confirms the formation of pure NiFe₂O₄ nano ferrite for both series. On the other hand, the presence of both Co and Ni peaks at x=0.5 confirms the formation of Ni-Co mixed ferrite for both series.

![Figure 2. EDS patterns of NixCo1-xFe₂O₄ (x=0, 0.5 and 1) nanospheres (N.S) and nanorods (N.R).](image)

The TEM images of Ni₀.₅Co₀.₅Fe₂O₄ for both series are shown in figure 3. The image (a) of sol-gel sample shows that most of the particles have spherical shape and some are agglomerated. The estimated particle size from the different images of these samples lies in the range of 9 to 12 nm. On the other hand, the shape of the hydrothermal sample (b) shows the formation of rods which are composed of many end connected spherical particles. This is due to the presence of glycol which disrupts cohesive forces and hydrogen bonding between water molecules, lowers surface tension and enhances wettability on a hydrophobic surface [16]. The length of the rods is about 45 nm and thickness 8 nm.
3.2. Magnetic measurements

The variation of magnetization with the magnetic field is shown in figure 4. The saturation magnetization $M_s$, the coercivity $H_c$, and the remanence $M_r$ obtained from the hysteresis loops are given in tables 3&4. It can be seen that $M_s$ decreases with increasing Ni concentration in both series. This can be attributed to the larger magnetic moment of Co$^{2+}$ (3μB) than Ni$^{2+}$ (2μB) and the preference of Ni$^{3+}$ ions to occupy B site. This causes decreasing of $M_0$ and hence $M_s$ decreases according to the relation $M_s=M_0-M_A$. Moreover, $H_c$ has a similar trend like $M_s$ in both series which is due to the higher magnetic anisotropy of Co$^{2+}$ ions than Ni$^{2+}$ ions. Similar behaviour of decreasing $M_s$ and $H_c$ with Ni doping has been previously reported [9]. On the other hand, it is noticed that the particle shape influenced the values of remanance ($M_r$) and squareness ($M_r/M_s$). The higher values of $M_r$ in nanorod series than those of nanosphere series may be attributed to the large number of atoms within the rod shape which consists of many end-connected spheres together according to the TEM images. Moreover, the higher values of squareness ($M_r/M_s$) in nanorod series than nanosphere series may be due to its strong dependence on the magnetic anisotropy, preparation method, and particle size and shape of the samples [17]. Such a property is important in magnetic recording.

![Figure 3. TEM images of Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ (a) nanospheres and (b) nanorods.](image)

**Figure 3.** TEM images of Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ (a) nanospheres and (b) nanorods.

![Figure 4. Hysteresis loops of Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ (a) nanospheres and (b) nanorods.](image)

**Figure 4.** Hysteresis loops of Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ (a) nanospheres and (b) nanorods.
Table 3. Saturation magnetization $M_s$, remanence $M_r$ and coercivity $H_c$ of Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ nanospheres.

| Sample          | $M_s$ (emu/g) | $M_r$ (emu/g) | $H_c$ (G) | $M_r/M_s$ |
|-----------------|---------------|---------------|-----------|-----------|
| CoFe$_2$O$_4$   | 45.18         | 10.86         | 741.67    | 0.22      |
| Ni$_{0.25}$Co$_{0.75}$Fe$_2$O$_4$ | 44.54         | 11.09         | 760.42    | 0.24      |
| Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$  | 38.79         | 7.87          | 572.26    | 0.2       |
| Ni$_{0.75}$Co$_{0.25}$Fe$_2$O$_4$ | 35.83         | 7.72          | 474.35    | 0.21      |
| NiFe$_2$O$_4$   | 29.67         | 3.59          | 155.45    | 0.12      |

Table 4. Saturation magnetization $M_s$, remanence $M_r$ and coercivity $H_c$ of Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ nanorods.

| Sample          | $M_s$ (emu/g) | $M_r$ (emu/g) | $H_c$ (G) | $M_r/M_s$ |
|-----------------|---------------|---------------|-----------|-----------|
| CoFe$_2$O$_4$   | 66.62         | 26.62         | 895.49    | 0.39      |
| Ni$_{0.25}$Co$_{0.75}$Fe$_2$O$_4$ | 52.47         | 23.1          | 798.95    | 0.44      |
| Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$  | 31.45         | 14.75         | 492.42    | 0.47      |
| Ni$_{0.75}$Co$_{0.25}$Fe$_2$O$_4$ | 31.08         | 12.56         | 425.72    | 0.42      |
| NiFe$_2$O$_4$   | 29.58         | 7.59          | 215.47    | 0.24      |

Figure 5 shows the change of relative permeability $\mu_r$ with increasing temperature for NCF with $x=0$, 0.5 and 1. Curie temperature $T_c$ was obtained from the rapid decrease of relative permeability $\mu_r$ at a certain temperature. The sharp decrease of the relative permeability indicates the homogeneity and shows the ferro-paramagnetic phase transition [18]. According to Globus model, $\mu$ depends on saturation magnetization $M_s$ and magneto-crystalline anisotropy $K$ according to the relation $\mu = M_s^2/K$ [19]. Both saturation magnetization $M_s$ and anisotropy constant $K$ decrease with increasing temperature due to the thermal agitation. However, the decreasing of $K$ is faster than $M_s$ which leads to an increase in $\mu_r$. As $K$ approaches to zero, $\mu_r$ reaches its maximum value. At Curie point, the magnetization also vanishes and then $\mu_r$ decreases to zero. The most striking feature is when the Ni content increases, $T_c$ decreases in nanosphere series and increases in nanorod series. The explanation of this variation is based on the cation distribution of NCF nanomaterials. According to Neel’s theory, the Curie temperature strongly depends on the strength of A-B sublattices interaction. From the cation distribution data, calculated from XRD pattern, it can be seen that as Ni$^{2+}$ ions introduced in the system, it go to the B site instead of Co$^{2+}$ ions without migration for Fe$^{3+}$ ions from B to A site in nanosphere series. This causes a gradual decrease to A-B interaction and hence $T_c$ decreases as previously reported [20]. On the other hand, the occupation of Ni$^{2+}$ ions in nanorod series occurs through migration of Fe$^{3+}$ ions from B to A site. This migration increases the number of Fe$^{3+}$ ions at the A site and enhances the A–B interaction, due to the presence of Fe$^{3+}$ ions in B site. This results in the increase of $T_c$ with increasing Ni content. Similar increasing for $T_c$ has been reported [21].
3.3. Optical measurements.

The energy band gap of ferrites can be determined by using UV–visible absorbance spectroscopy with diffused reflectance system. According to Tauc model [22], the energy gap $E_g$ for all samples can be obtained using the relation

$$\alpha \theta = A (\theta - E_g)^n$$

where $A$ is a constant, $E_g$ is the energy gap, $n$ is the exponent factor that determines the type of transition (0.5 or 2 for direct or indirect transitions respectively), $\theta$ is the photon energy and $\alpha$ is the optical absorption coefficient which is given by

$$\alpha = \frac{(1 - R)^2}{2R}$$

where $R$ is the reflectivity. In order to determine the type of transition, we have to plot a relation between $(\alpha \theta)^{1/n}$ on the Y-axis and $\theta$ on the X-axis. The intersection of the extrapolated linear part with (hv) axis determines the values of direct and indirect $E_g$ respectively. Fig. 6 demonstrates the variation of direct and indirect band gap for nanosphere series of NCF nanomaterials. With increasing Ni concentration, the direct band gap doesn’t alter strongly but the indirect band gap increases from 1.5 to 2.05 eV which reflects the change in cation distribution. Table 3 showed that for pure CoFe$_2$O$_4$ nanosphere, Co-ferrite is an inverse spinel. Due to the preference of Ni$^{2+}$ ions to occupy B-site, the substitution of Co with Ni will not affect the A-site. Also, it was found that the majority and minority valence band edge are affected by tetrahedral and octahedral states respectively [23]. This explains the slight variation of direct band gap (majority channel) and the increasing in indirect band gap (minority channel) because of the larger band gap of NiO (4 eV) than CoO (2.4 eV) [24].

![Image of optical measurement results](image-url)
The variation of direct and indirect band gap with increasing Ni concentration for nanorod series is shown in figure 7. The direct band gap is largely affected by increasing Ni$^{2+}$ ions up to $x=0.5$ and then slightly affected till $x=1$. On the other hand, the indirect band gap exhibits a noticeable decrease with increasing Ni$^{2+}$ ions till $x=0.5$ and then increase with $x=0.75$ and 1. The explanation of this variation is also based on the change in cation distribution with increasing Ni-content. The cation distribution of pure CoFe$_2$O$_4$ in nanorod series is (Co$_{0.5}$Fe$_{0.5}$)[Co$_{0.5}$Fe$_{1.5}$]O$_4$. Then Ni$^{2+}$ ions will occupy B-site instead of Fe$^{3+}$ ions till the cation distribution be (Fe)[Co$_{0.5}$Ni$_{0.5}$Fe]$^+$O$_4$ at $x=0.5$. The larger band gap of Fe (7-8 eV) [24] than Ni (4 eV) and Co (2.4 eV) explains the variation of direct and indirect $E_g$ with increasing Ni-content. It can be seen that at $x \leq 0.5$, Fe$^{3+}$ ions increased in A-site from 0.5 to 1 instead of Co$^{2+}$ ions which decreased from 0.5 to 0 and this caused the first increase for direct $E_g$. On the other hand, the increase of Ni$^{2+}$ ions in B-site from 0 to 0.5 instead of Fe$^{3+}$ ions which decreased from 1.5 to 1 caused the first decrease of indirect $E_g$. At $x > 0.5$, the A-site didn’t alter with increasing Ni$^{2+}$ ions which explains the small variation of direct $E_g$. However, the substitution of Co$^{2+}$ with Ni$^{2+}$ in B-site caused a gradual increase to the indirect $E_g$ because of the larger band gap of NiO (4 eV) than CoO (2.4 eV). These results confirm the variation of $T_c$ with increasing Ni-content in both series.
4. Conclusion.
Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ ($x$=0, 0.25, 0.5, 0.75 and 1) ferrite nanocrystals were successfully prepared by sol-gel and hydrothermal technique. The obtained structures were nanospheres and nanorods respectively. XRD confirmed the single phase spinel structure for each sample and showed that the average lattice parameter and crystallite size of nanorod series are greater than those of nanosphere series. TEM images showed the formation of nanospheres with an average diameter ranges from 9 to 12 nm and nanorods with an average length 45 nm and thickness 8 nm. Nanorod series showed higher values for remanance and squareness than nanosphere series due to the shape dependence. Optical measurements explained the change in cation distribution between nanosphere and nanorod series from the variation of direct and indirect energy gap.

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