Co-Precipitation Synthesis of $Fe^{2+}_{1-x}Co^{2+}_xFe_2O_4$ Nanoparticles: Structural Characterization and Magnetic Properties

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Abstract: Cobalt ferrite was known as a promising magnetic material for various applications. This nano-composite ($Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4$) was synthesized via co-precipitation route, by varying the Co/Fe ratios (Co/Fe = 3, 1, and 0). The structures and magnetic properties of nano-composites were analyzed by XRD and VSM. As deduced from the XRD line broadening, the average crystallite size of the samples was found to be in the range of 13.0-15.0 nm and contain *fcc* structure with smaller lattice constant as the Co/Fe ratios increases. FESEM and TEM images revealed the morphology of the samples, which consist of irregular shapes of diameter in the range of 9.0-15.0 nm. Magnetic properties measurement shows that sample S11 with the highest Co/Fe ratio has the highest value of saturation magnetization (Ms) of 65.23 emu/g. On the other hand, increase in the concentration of cobalt ions improves the remanence magnetization (Mr) and coercivity (Hc) of the same sample to 12.18 emu/g and 238.92 Oe, respectively. It is demonstrated that the higher substitution ratio of cobalt in $Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4$ has successfully improve the magnetic properties of the samples.

Keywords: Cobalt ferrite; co-precipitation; nano-composite; magnetic properties

1. Introduction

Spinel ferrite nanoparticles have been intensively investigated in recent years due to remarkable electrical and magnetic properties, as well as enormous practical applications for information storage system, ferrofluid technology, magneto caloric refrigeration and medical diagnostics [1, 2]. The most attractive feature of ferrites is the possibility to modify the magnetic properties by varying the chemical compositions [3]. Among magnetic materials, Fe/Fe_3O_4 composite system has gained significant attention which is attributed to the remarkable magneto-electric and transport properties.

Tailoring the properties of ferrites to fulfill specific applications is possible by substituting Fe with other 3d ions [4, 5]. Substitution of cobalt, for example, has demonstrated improvement in the coercivity and chemical stability of the material due to enhancement in the magneto crystalline anisotropy

[5]. Cobalt ferrite ($Co_xFe_{3-x}O_4$) is a cubic ferrite with a spinelic inverse structure where the Co cation occupies one half of the octahedral coordination sites [6]. One-half of the Fe^{3+} cations occupy the other half of the octahedral coordination sites as well as all of the tetrahedral coordination sites [7, 8]. Particle size represents the substance performance critical factor in magnetic activity monodisperse nanoparticles. The size and magnetic properties of cobalt ferrite nanoparticles prepared by the co-precipitation method can be greatly varied depending on pH, salt concentration, temperature, stirring speed and counter-ion nature [9]. By varying the chemical composition, it is possible to control the properties of the material e.g. electromagnetic responses, crystal structure, phases, and morphology [3].

In this recent work, a new metal-ceramic composite ($Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4$) was synthesized via co-precipitation route, by varying the Co/Fe ratios

(Co/Fe = 3, 1, and 0). The effect of cobalt substitution was investigated for enhancement in its magnetic properties. The morphology, structures and magnetic properties of nano-composites were analyzed by TEM, FESEM, EDX, XRD and VSM.

2. Material and Methods
2.1 Synthesis of ferrite materials

This metal-ceramic composite ($Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4$) was synthesized by co-precipitation method. Three samples of various Co/Fe ratios (Co/Fe = 0.3, 0.2, and 0) were synthesized from the formula $Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4$ where x takes the value of 0.75, 0.50, and 0, respectively, as shown in

Table 1. Desired amount of $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$ and $CoCl_2 \cdot 6H_2O$ was mixed in deionized water according to the calculated molar concentration. All materials are reagent grade and used without further purification. Double distilled, de-ionized water was used as a solvent. Different grades of cobalt ferrite were synthesized by varying the molar concentration of $FeCl_2 \cdot 4H_2O$ and $CoCl_2 \cdot 6H_2O$; while the Fe^{3+} ion concentration remains constant for all the systems. The total molar concentration of Fe^{2+} and Co^{2+} were kept fixed to 0.1 M. Sodium hydroxide (3M) was prepared and slowly added to the salt solution drop wise. The solution was constantly stirred using a magnetic stirrer until a pH level of 11-12 was reached. A specified amount of oleic acid was added to the solution as a surfactant and coating material.

The liquid precipitate was then brought to a reaction temperature of $80°C$ and stirred for one hour. The product was subsequently cooled to room temperature. To ensure that the end product is free from sodium and chlorine compounds, the precipitate was then washed twice with distilled water and followed by ethanol to remove the excess surfactant from the solution. The beaker content was centrifuged at 3000 rpm for fifteen minutes to isolate the supernatant liquid. It was decanted afterward, and then centrifuged to leave behind thick black precipitate. The precipitate was then dried overnight at $100°C$. The acquired substance was grinded to obtain fine powder. At this stage, the product ($Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4$) contains some associated water (up to 10 wt %) which was then removed by annealing at $600°C$ for ten hours.

Table 1. Sample code for different concentration

Sample Code	Sample formula $Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4$	Co/Fe ratio
S_{11}	x = 0.75	3
S_{10}	x = 0.50	1
S_8	x = 0	0

2.2 Samples characterization

The as-synthesized nanoparticles were characterized by using X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Spectroscopy (EDX), Transmission Electron Microscope (TEM) and Vibrating Sample Magnetometer (VSM). The crystal structure, particle size and morphology of the samples were determined by XRD, TEM and FESEM. EDX analyses were conducted to investigate the composition and distribution of cobalt and iron in the composite samples. Magnetic properties measurements were carried out using a VSM at room temperature with a maximum magnetic field of 30,000 Oe.

3. Results
3.1 Structural and crystallographic properties

Figure 1 shows the XRD patterns of all samples in the 2θ range of 0-80°. It features Bragg diffraction peaks which can be indexed to the face-centered cubic structure of iron cobalt ferrite and are consistent with the standard diffraction data, i.e.,

S8 (JCPDS 76-2496(C)), S10 (JCPDS 01-1121 (D)) and S11 (JCPDS 03-0864 (N)). Sample S8 possess the properties of magnetite due to the absence of cobalt ions which lattice constant, a was found to be 8.34 Å, slightly shifted from the standard lattice constant of magnetite (a=8.3963 Å).

However, with cobalt substitution in samples S10 and S11, lattice constant was found to be in the range of 8.38-8.39 Å, which are nearly consistent with the bulk cobalt ferrite (a=8.38 Å). In agreement to the result reported by Lan et al. (2011), a slight decrease in the value of lattice constant with increase in the cobalt substitution is observed [5]. The average crystallite size of the particles, d_{XRD} was calculated using XRD line broadening technique by applying Scherer's formula at the corresponding (311) plane. From this calculation, the average crystallite sizes of the particles are in the range of 13.0-14.4 nm, as presented in Table 2.
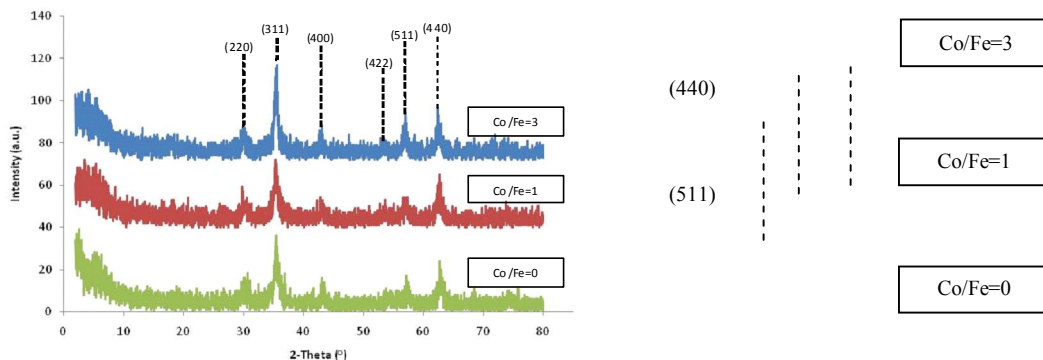
Figure 1. XRD patterns of $Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4$ samples of various Co/Fe ratios

Table 2. FWHM, d-spacing, crystallite size, lattice parameter and crystal structures of $Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4$

Sample	Diffraction (correspond to (311) plane)			
	FWHM	d-spacing (Å)	d_{XRD} (nm)	Crystal structure
S8	0.612	2.524	13.0	Face-centered cubic
S10	0.617	2.533	13.4	Face-centered cubic
S11	0.617	2.534	14.4	Face-centered cubic

3.2   Morphology and composition analysis

Surface morphology of all samples was analyzed by direct observation via TEM and FESEM analysis. In FESEM micrograph captured at 100,000X magnification as shown in Figure 2 (a), (b) and (c), the particles are found to be heavily agglomerated with almost spherical shape particles observed for all samples. Most of the particles were estimated to have diameter approximately around 9.9 to 18.0 nm, with no significant difference in the shape and distribution of the particles in all samples.

TEM micrographs shown in Figure 3 (a), (b) and (c) indicate the presence of irregular shape of circles and squares, similar to the particle shapes obtained by Li et al. (2009) which was synthesized using hydrothermal method [10]. Direct measurement on TEM micrographs revealed the size of particles which are in the range of 9.0-15.0 nm, having almost similar values as obtained from XRD measurement.
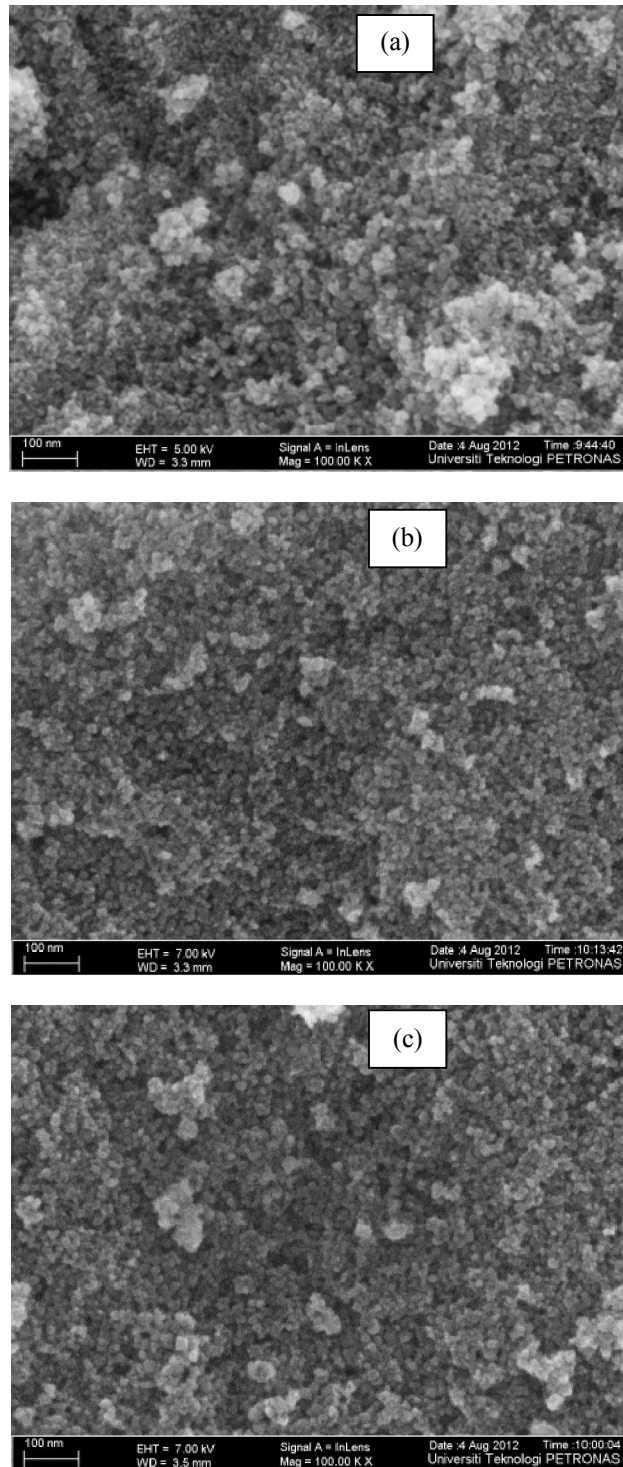
Figure 2. FESEM images of sample (a) S8, (b) S10 and (c) S11 at 100,000X magnification

From EDX analysis tabulated in Table 3, it is clearly observed that sample S8 is free from cobalt content. In sample S10, when x = 0.5, the molar ratio between Fe and Co is 5, which is clearly depicted in both atomic and weight percentage of Fe and Co elements. The molar ratio between this two elements reduces to 3 when x = 0.75,

shifting atomic and weight percentage of Co to a higher value and reduces the percentage of Fe presents in sample S11.
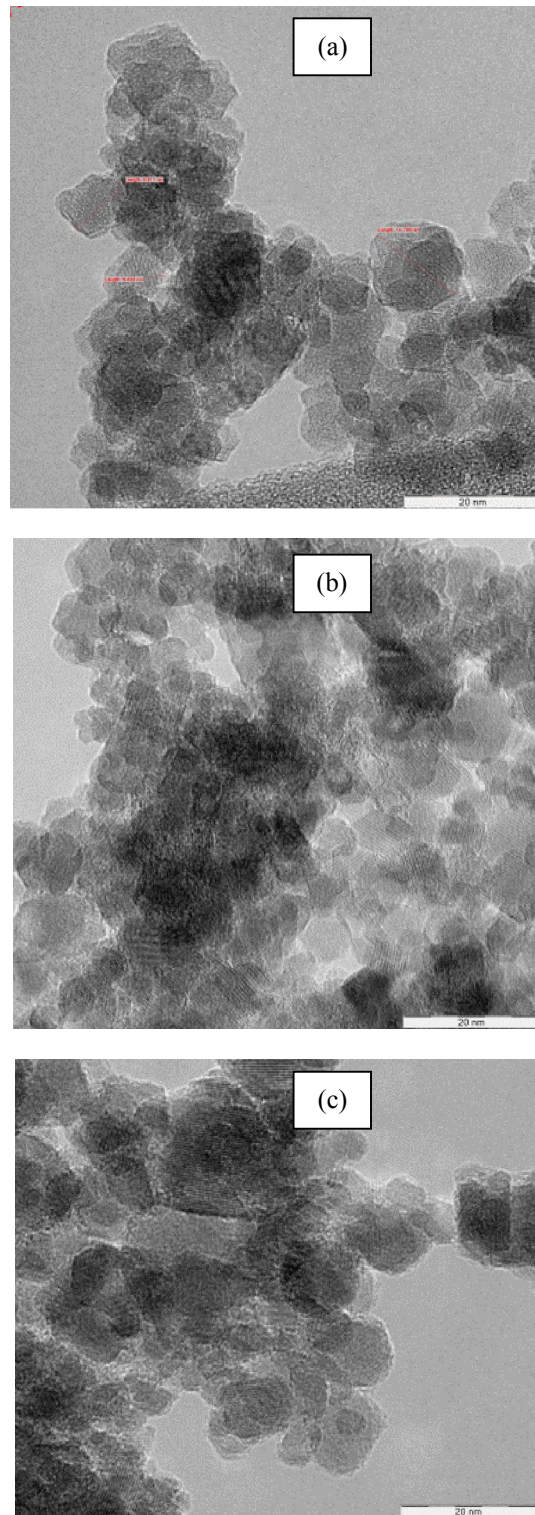

Figure 3. TEM images of samples (a) S8, (b) S10 and (c) S11 at 200,000X magnification

From EDX analysis tabulated in Table 3, it is clearly observed that sample S8 is free from cobalt content. In sample S10, when x = 0.5, the molar ratio between Fe and Co is 5, which is clearly depicted in both atomic and weight percentage of Fe and Co elements. The molar ratio between this two elements reduces to 3 when x = 0.75, shifting atomic and weight percentage of Co to a higher value and reduces the percentage of Fe presents in sample S11. Some amount of carbon was found in sample S8 and S10 as impurities that may present due to contamination during measurement.

Table 3. Chemical compositional analysis by EDX spectroscopy for all samples

	S8 (x=0)		S10 (x=0.5)		S11 (x=0.75)	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C	13.11	36.19	5.16	11.17	-	-
O	8.27	17.13	38.71	62.93	39.26	69.57
Fe	78.62	46.68	46.22	21.53	45.74	23.22
Co	-	-	9.91	4.37	15	7.21

3.3   Vibrating Sample Magnetization (VSM) Results

Magnetic properties measurement of the synthesized $Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4$ nanoparticles was conducted using VSM at room temperature and presented in the magnetization (M) versus magnetic field strength (H) curves shown in Figure 5.

From the M-H plots, magnetic parameters e.g. saturation magnetization (Ms), remanence magnetization (Mr) and coercivity (Hc) values were obtained for all samples. It is observed that the values of Ms, Mr and Hc increase as Co/Fe ratios increase. The narrow distribution of the loops is a clear evidence for soft magnetic characteristics of cobalt ferrite nanoparticles, which indicates the relative easiness of being magnetized and demagnetized in an applied magnetic field. Magnetic parameters of the synthesized samples are summarized in Table 3.
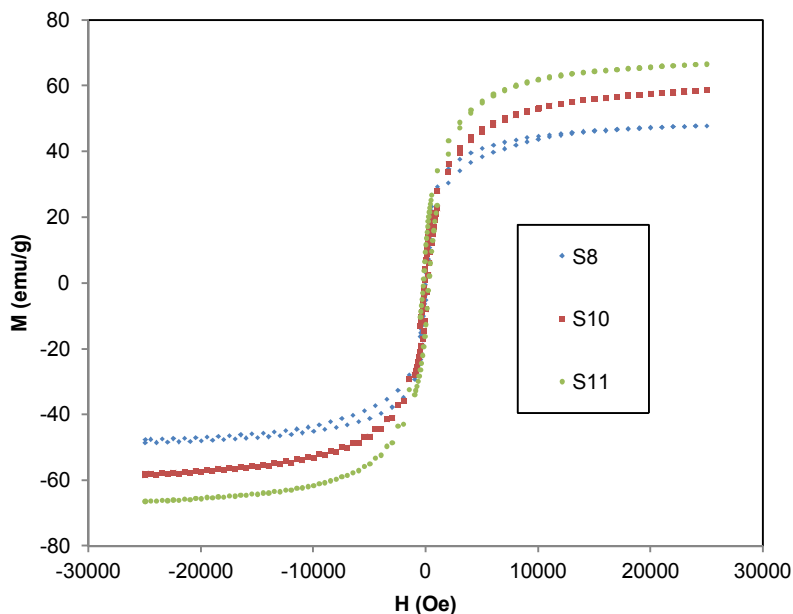
Figure 5. Magnetization (M) versus applied field (H) curves of all $Co^{2+}_xFe^{2+}_{1-x}Fe_2O_4$ samples

It is demonstrated that at higher concentration of cobalt ions (S11; x = 0.75), magnetization parameters of $Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4$ nanoparticles improved in comparison to other samples with lower cobalt concentration. Cobalt substitution enhances the magneto crystalline anisotropy of the ferrites as a result of 3d ions substitution for Fe [5]. The highest value of Ms, Mr and Hc is found on sample S11 at 65.23 emu/g, 12.18 emu/g and 239.10 Oe, respectively.

Table 3. VSM data for $Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4$ nanoparticles.

Magnetic properties	Average		
	S8	S10	S11
Hc (Oe)	55.59	135.17	239.10
Ms (emu/g)	47.35	57.13	65.23
Mr (emu/g)	4.26	7.46	12.18

4. Conclusion

Iron cobalt ferrite $(Co^{2+}_xFe^{2+}_{1-x}Fe^{3+}_2O_4)$ nanoparticles with different concentration (x = 0.75, 0.50, and 0) has been successfully obtained by co-precipitation methods. The XRD results shows that the all samples has single phase at (311) plane and the biggest particle size was observed for sample S11 (x = 0.75). The morphology analysis shown that sample S11 with higher Co/Fe ratio has the largest particle of 14.5 nm among other samples (S8 and S10). Magnetic properties of the iron cobalt ferrite nanoparticles in this work has been found remarkably high in the sample with highest Co/Fe ratio with the value of Ms of 65.23 emu/g, Mr of 12.18 emu/g and Hc of 239.10 Oe.

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References

[1]. S. Sendhilnathan and G. Vaidyanathan. Characterization of $Co_{1-x}Zn_xFe_2O_4$ nanoparticles synthesized by co-precipitation method. Physica B, Vol. 403, pp. 2157–2167, 2008.

[2]. W. Wu, Q. He and C. Jiang. Magnetic Iron Oxide Nanoparticles: Synthesis and Surface Functionalization Strategies. Nanoscale Res. Lett., pp. 397–415. Vol. 3, 2008.

[3]. A. Drmota et al. Electromagnetic wave absorption of polymeric nanocomposites based on ferrite with a spinel and hexagonal crystal structure. Journal of Magnetism and Magnetic Materials, Vol. 324, pp. 1225–1229, 2012.

[4]. Y. Koseoglu. Structural, magnetic,electrical and dielectric properties of $Mn_xNi_{1-x}Fe_2O_4$ spinel nanoferrites prepared by PEG assisted hydrothermal method. Ceramics International. http://dx.doi.org/10.1016/j.ceramint.2012.11.004, 2012.

[5]. N. T. Lan, N. P. Duong and T. D. Hien. Influences of cobalt substitution and size effects on magnetic properties if co-precipitated Co-Fe ferrite nanoparticles. Journal of Alloys and Compounds, Vol. 509, pp. 5919-5925, 2011.

[6]. M. Rajendran, R.C. Pullar, A.K. Bhattacharya, D. Das, S.N. Chintalapudi, and C.K. Majumdar. Journal of Magnetism and Magnetic Materials, Vol. 232, 71, 2001.

[7]. P.S. Haddad, T.M. Martins, L. D'Souza-Li, L.M. Li, K. Metze, R.L. Adam, M. Knobel,

D. Zanchet. Materials Science and Engineering, Vol. C28, 489, 2008.

[8]. N. Moumen, P. Veillet, and M.P. Pileni. Journal of Magnetism and Magnetic Materials, Vol. 149, 67, 1995.

[9]. A. Mohd. Hashim et al. Structural, electrical and magnetic properties of Co–Cu ferrite nanoparticles. Journal of Alloys and Compounds , Vol. 518, pp. 11-18, 2012.

[10]. S. Li et al. Magnetic properties of

[11]. $Fe_xCo_{1-x}/Co_yFe_{1-y}Fe_2O_4$ composite under hydrothermal condition. Current Applied Physics, Vol. 9, pp. 1386-1392, 2009.

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