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Crystal Structures and Magnetic Properties of Polyethylene Glycol (PEG-4000) Encapsulated $Co_{0.5}Ni_{0.5}Fe_2O_4$ Magnetic Nanoparticles

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ABSTRACT

Nanocrystalline mixed spinel ferrite of $Co_{0.5}Ni_{0.5}Fe_2O_4$ magnetic nanoparticles (MNPs) has been successfully synthesized by coprecipitation method and encapsulated by PEG-4000 with various concentrations. X-Ray Diffraction (XRD) patterns showed that nanoparticles contained $Co_{0.5}Ni_{0.5}Fe_2O_4$ spinel ferrite with crystallite size of 14.9 nm. After PEG-4000 encapsulation particles size decreased became 7.7 nm. Interaction $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles with long chain PEG-4000 caused the crystal growth trap. Lattice parameter and X-Ray density have no significant difference after encapsulated PEG-4000. The coercivity (H_c) of $Co_{0.5}Ni_{0.5}Fe_2O_4$ was 214 Oe. The H_c decreased after PEG-4000 encapsulation became 127 Oe, which is due to the decrease of crystallite size. The maximum magnetization (*Mmax*) of $Co_{0.5}Ni_{0.5}Fe_2O_4$ was 12.0 emu/g, and decreased after PEG-4000 encapsulation to 11.7 emu/g, because PEG-4000 is paramagnetic. After the concentration of PEG-4000 increased, then the amount of paramagnetic material increase which lead maximum magnetization decrease.

Keywords: Spinel Ferrite, Magnetic Nanoparticles, Coprecipitation, CoNi Ferrites.

INTRODUCTION

Ferrite nanoparticles (FNPs) belong to a broad group of magnetic nanoparticles (MNPs) due to their unique properties, such as superparamagnetism, greater surface area, and easy separation methodology [1]. The important group of ferrite is spinel ferrite with general formula MFe_2O_4 (where M = Mn, Fe, Co, Ni, Cu and Zn), and most of them show superparamagnetic (SPM) properties at the size below or about 20 nm in diameter[2]. Spinel ferrite NPs are received a considerable amount of attention due to their wide applications in various fields, which ranges from biomedical to industrial [2].

Cobalt ferrite ($CoFe_2O_4$) and nickel ferrite ($NiFe_2O_4$) are the examples of spinel ferrite NPs. Both of them have invers spinel structure [3,4]. The properties of $CoFe_2O_4$ are hard magnetic, high magnetic saturation, and high coercivity [5]. On the other hand, the properties of $NiFe_2O_4$ are soft magnetic, low magnetic saturation, and low coercivity [6]. The mixture of $CoFe_2O_4$ and $NiFe_2O_4$ with the same concentration would be $Co_{0.5}Ni_{0.5}Fe_2O_4$, which have the new properties such as mix spinel, hard magnetic, the magnetic saturation and coercivity between $NiFe_2O_4$ and $CoFe_2O_4$[7]. Due to the properties, $Co_{0.5}Ni_{0.5}Fe_2O_4$ have a possibility to be applied in biomedical application such as drug delivery.

Various synthesis routes have been studied for the preparation of $CoNiFe_2O_4$ nanoparticles, such as sol-gel[8], hydrothermal[9], co-precipitation[10], aerosol-route[11], glycol thermal-process[12], etc. The most commonly used is co-precipitation method because it have advantages over physical methods, such as low cost, simple and rapid preparation, high purity of product, and not requiring heat threatment. But, ferrite NPs prepared with co-precipitation method are easily agglomerated. So, a way to overcome this difficulty is the encapsulation of magnetic NPs with biopolimer, such as *polyethylene glycol* (PEG). Magnetic nanoparticles in their simplest form are composed of an inorganic magnetic compound (usually a ferrite such as Fe_3O_4 and MFe_2O_4 (M=Ni, Co, Mn)) core. MNPs should be pre-coated with some substance (shell) that can assure their stability, biodegradability, and non-toxicity in physiological medium and maintain the high magnetic saturation required and be a functional surface[13].

Kavas *et al.* [14], studied the magnetic characterization of ferrite nanoparticles encapsulated PEG, but this precursor has short chain polymer and high cost. So, we use PEG-4000 because it has long chain polymer and to reduce the cost incurred. Based to their paper, Kavas *et al* used hydrothermal route to encapsulating ferrite NPs, so this method requiring high temperature. Therefore, in this research, we have used co-precipitation method for making $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles. However, through the literature review, the magnetic characterization of $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles encapsulated PEG in particular has never been investigated. So, the aim of our investigation was study how variation of concentration of PEG-4000 as encapsulate substrate. In order to study the influences of encapsulate substrate on crystal structures, morphological, and magnetic properties of $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles. Further the information mechanism is discussed in detail.

EXPERIMENTAL DETAILS

The precursor such as $FeCl_3.6H_2O$ (Merck, Germany), $CoCl_2.6H_2O$ (Merck, Germany), $NiCl_2.6H_2O$ (Merck, Germany) and NaOH (Merck, Germany) were weighed carefully in accordance with the required stoichiometric proportion of salt. Mix $CoCl_2.6H_2O$ salt and $NiCl_2.6H_2O$ salt and dissolved it in 25 ml aquadest. Dissolved each $FeCl_3.6H_2O$ salt and NaOH salt in 25 ml of aquadest. Then, mix the metal solution and add 3.37 ml HCl 37% (Merck, Germany) into it. The precipitation was carried out by dropping the alloys solution into 12 M NaOH solution called sample respectively, at temperature 90°C respectively, for 1 hour and stirred at 1000 rpm. The precipitate then washed 7 times for 30 minutes and dried at 90°C for 4 hours.

The various PEG solution was dropped into 25 ml NaOH when co-precipitation process. The concentration of PEG-4000 is used as in Table 1.

Table 1. Variation of the concentration of PEG-4000

Sample	**Comparison of PEG-4000 in molarity**	
	Proportion NaOH : PEG 4000 at 2 ml aquades	**PEG Molarity mixed in NaOH (M)**
P1	12.0 gr : 0.5 gr	0.005 molar
P2	12.0 gr : 1 gr	0.011 molar
P3	12.0 gr : 1.5 gr	0.016 molar
P4	12.0 gr : 2 gr	0.021 molar
P5	12.0 gr : 2.5 gr	0.026 molar
P6	12.0 gr: 3 gr	0.032 molar

The crystal structures were analyzed by X-ray diffractometer (XRD) Shimadzu XD with CuKα1 radiation (λ = 1.5406 Å). The magnetic properties were analyzed by Vibrating Sample Magnetometer (VSM) Riken Denshi Co. Ltd. with applying external magnetic field 15 KOe at room temperature.

RESULT AND DISCUSSION

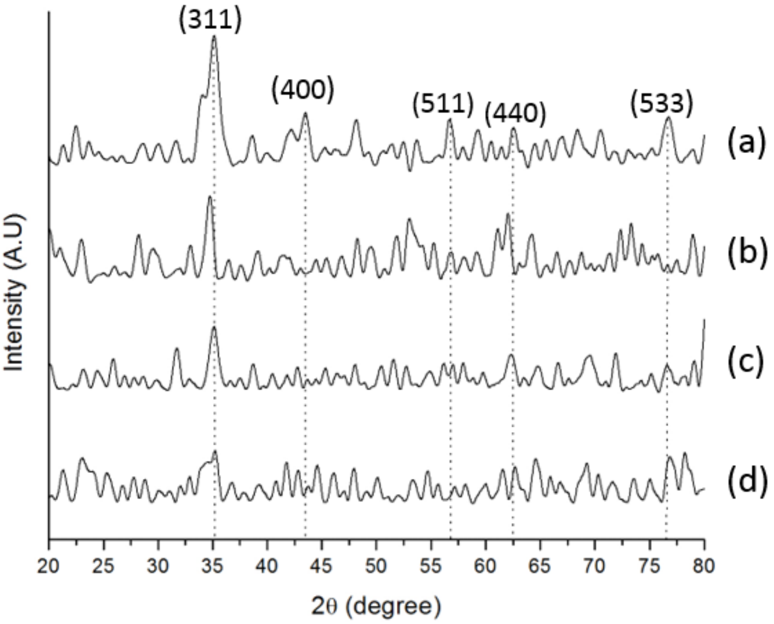

Figure 1. XRD patterns of $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles, (a) before, (b) after encapsulated 1 g PEG-4000, (c) 1.5 g PEG-4000 and (d) 3 g PEG-4000

Structural studies were done with XRD measurement and then compared to standard data (JCPDS no 45-0131) in 2θ range of 20° – 80° to $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles, as shown in Fig. 1. XRD patterns showed that nanoparticles contained $Co_{0.5}Ni_{0.5}Fe_2O_4$ spinel ferrite because all sample show the diffraction peak from (311). Table 2 show the crystallite size, X-Ray density, and lattice parameter. Crystallite size of $Co_{0.5}Ni_{0.5}Fe_2O_4$ before encapsulation is 14.9 nm. After PEG-4000 encapsulation, crystallite size decreased became 9.3 nm, 8.6 nm and 7.7 nm for PEG-4000 adding of 1; 1.5; 3 grams, respectively. Because interaction $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles with long chain PEG-4000 cause the crystal growth will trap. Lattice parameter and X-Ray density have no significant difference after encapsulated PEG-4000.

Table 2. Analysis XRD of $Co_{0.5}Ni_{0.5}Fe_2O_4$ before and after encapsulated with PEG-4000

MATERIAL	Crystallite size (nm)	X-Ray density (g/cm^3)	Lattice parameter (nm)
$Co_{0.5}Ni_{0.5}Fe_2O_4$	14.9	5.2	8.47
$Co_{0.5}Ni_{0.5}Fe_2O_4$ + 1 g PEG-4000	9.3	5.2	8.56
$Co_{0.5}Ni_{0.5}Fe_2O_4$ + 1.5 g PEG-4000	8.6	5.2	8.47
$Co_{0.5}Ni_{0.5}Fe_2O_4$ + 3 g PEG-4000	7.7	5.1	8.42

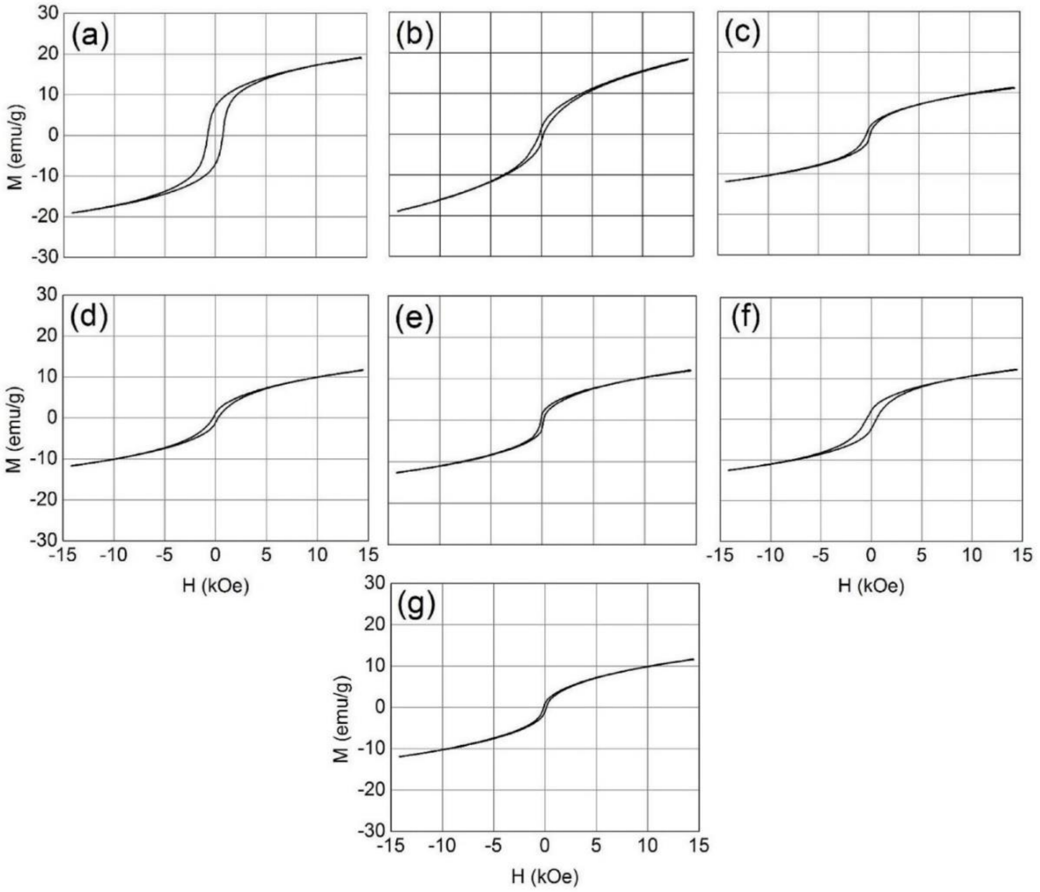

Figure 2. Hysteresis curves of $Co_{0.5}Ni_{0.5}Fe_2O_4$ encapsulated PEG-4000 (a) before, and after encapsulated (b) 0.5 g, (c) 1 g, (d) 1.5 g, (e) 2 g, (f) 2.5 g, dan (g) 3 g.

Table 3. Magnetic Properties of $Co_{0.5}Ni_{0.5}Fe_2O_4$ Before and After Encapsulated PEG-4000

PEG-4000 Concentration (gram)	**M_{max} (15 kOe) (emu/g)**	**M_r (emu/g)**	**H_c (Oe)**
0	12.0	1.1	214
0.5	9.2	0.7	197
1.0	11.4	1.1	176
1.5	11.7	1.2	231
2.0	12.1	1.6	134
2.5	12.3	2.2	450
3.0	11.7	1.0	127

The magnetic properties for all samples were studied by VSM. The magnetic hysteresis loop of $Co_{0.5}Ni_{0.5}Fe_2O_4$ before and after encapsulated with PEG-4000 as shown in Fig. 2. The result of VSM analysis are listed in Table 3. The magnetic properties of a magnetic material depend largely on the particle size distributions as the domain structure and magnetization process depends on particle size[5]. The coercivity (H_c) of $Co_{0.5}Ni_{0.5}Fe_2O_4$ was 214 Oe. The H_c decrease after PEG-4000 encapsulation became 127 Oe, respectively. It is due to the decrease of particle size. The result of this study are in the multidomain region. The multidomain particles and the energy anisotropy will be smaller so as to demagnetization require a smaller external field. Thus the value of coercivity decrease.

The maximum magnetization (M_{max}) of $Co_{0.5}Ni_{0.5}Fe_2O_4$ was 12.0 emu/g, and decrease after PEG-4000 encapsulation to 11.7 emu/g, its due to PEG-4000 is paramagnetic [15] which weaken the magnetic properties of $Co_{0.5}Ni_{0.5}Fe_2O_4$. After the concentration of PEG-4000 increased, then the amount of paramagnetic material increase which lead the value of saturation magnetization decrease by the increasing of PEG-4000 concentration.

SUMMARY

Nanocrystalline mixed spinel ferrite of $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles has been successfully synthesized by co-precipitation method. The crystallite size before encapsulation was 14.9 nm, after encapsulation PEG-4000 decreased to 7.7 nm for PEG-4000 of 3gr. Coercivity value before encapsulated was 214 Oe, after encapsulation PEG-4000 decreased to 127 Oe for PEG-4000 of 3 gr. The maximum magnetization before encapsulation was 12.0 emu/g, after encapsulation PEG-4000 decreased to 11.7 emu/g.

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