Crystal Structures and Magnetic Properties of Polyethylene Glycol (PEG-4000) Encapsulated Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ Magnetic Nanoparticles

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Abstract. Nanocrystalline mixed spinel ferrite of Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ magnetic nanoparticles (MNPs) has been successfully synthesized by coprecipitation method and encapsulated and PEG-4000 with various concentrations. X-Ray Diffraction (XRD) patterns showed that nanoparticles contained Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ spinel ferrite with the particles size of 15.2 nm. After PEG-4000 encapsulation, particles size decrease became 13.3 nm. Transmission Electron Microscopy (TEM) image showed that the nanoparticles still agglomerate after PEG-4000 encapsulation. The coercivity ($H_c$) of Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ was 50.7 Oe. The $H_c$ decrease after PEG-4000 encapsulation became 47.9 Oe, respectively. It is due to the decrease of particle size. The saturation magnetization ($M_s$) of Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ was 18.4 emu/g, and decrease to 17.1 emu/g after PEG-4000 encapsulation. This is because PEG-4000 has paramagnetic properties.

1. Introduction

Ferrite nanoparticles (MFe$_2$O$_4$, M = Zn, Ni, Mn, Co, Mg) have been attracted interest to the researchers in the field of functional materials due to their high electrical and chemical properties, and thermal stabilities [1]. Ferrite nanoparticles are widely used in technologies like drug delivery, magnetic recording media, Magnetic Resonance Imaging (MRI), contrast agent, and tomography imaging [1,2].

Zn–based ferrites is one of the spinel ferrites that attractive to researchers due to its low cost, high electromagnetic performance, and high permeability [3,4,5]. Many researchers have studied the synthesis of Ni–Zn ferrites [3,4,5]. However, for the applications, pure Ni–Zn ferrite nanoparticles usually lead to problems associated with the formation of large aggregates and the alteration of magnetic properties [6]. An encapsulation process is performed to improve the quality of Zn-Ni ferrite. This process will make Zn-Ni ferrite nanoparticles more reduce aggregates and control grain size.

Different techniques to prepare ferrite nano-particles have been reported such as low temperature solid state reaction [7], co-precipitation, sol-gel, hydrothermal, gel combustion, etc. [8], have advantages over physical methods because of low cost, the reaction taking place at room temperature and large scale possibility [9]. Among the methods, co-precipitation method is the most effective methods and relative simple.

Sertkol et al., [10] for Zn-Ni ferrite nanoparticles encapsulated with PEG have some drawbacks such as PEG used is PEG-400, it is expensive, have short chain polymer. Then we use PEG-4000 because have long chain polymer and to reduce the cost incurred. Therefore, In this research, work we
have used co-precipitation method for making $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles. The aim of our investigation was to understand the effect of variation of concentration of PEG-4000 as encapsulate substrate. To study the influences of encapsulating substrate on crystal structures, morphological, and magnetic properties of $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles. Further, the information mechanism is discussed in detail.

2. Experimental Details
The precursor such as $\text{FeCl}_3.6\text{H}_2\text{O}$ (Merck, Germany), $\text{ZnSO}_4.7\text{H}_2\text{O}$ (Merck, Germany), $\text{NiCl}_2.6\text{H}_2\text{O}$ (Merck, Germany) and $\text{NaOH}$ (Merck, Germany) was weighed carefully by the required stoichiometric proportion of salt. Mix $\text{ZnSO}_4.7\text{H}_2\text{O}$ salt and $\text{NiCl}_2.6\text{H}_2\text{O}$ salt and dissolved it in 20 ml aquadest. Dissolved each $\text{FeCl}_3.6\text{H}_2\text{O}$ salt and $\text{NaOH}$ salt in 50 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 1.5 M NaOH solution called sample respectively, at temperature 90°C respectively, for 1 hour and stirred at 1000 rpm. The precipitate then washed six times for 30 minutes and dried at 90°C for 5 hours. The various PEG solution was dropped into 20 ml NaOH when co-precipitation process. The concentration of PEG-4000 is used as in Table 1.

| Sample | Comparison of PEG-4000 in molarity |
|--------|----------------------------------|
| P1     | Proportion NaOH : PEG 4000 at 50 ml aquades |
| P2     | 2.99 gr : 0.5 gr 0.0026 molar |
| P3     | 2.99 gr : 1 gr 0.0052 molar |
| P4     | 2.99 gr : 1.5 gr 0.0079 molar |
| P5     | 2.99 gr : 2 gr 0.0105 molar |
| P6     | 2.99 gr : 2.5 gr 0.0130 molar |
| P7     | 2.99 gr : 3 gr 0.0157 molar |

The crystal structures are analyzed by X-ray diffractometer (XRD) Shimadzu XD with CuKα1 radiation ($\lambda = 1.5406$ Å). The magnetic properties are analyzed by Vibrating Sample Magnometer (VSM) Riken Denshi Co. Ltd. with $H_{\text{max}} = 15$ KOh at room temperature. The morphology was analyzed by Transmission Electron Microscopy (TEM) JEOL Jem-4000. The bonding analysis are characterized by IR spectrometer Shimadzu Prestige-21.

3. Results and Discussion
Structural Studies
Structural studies were done with XRD measurement and then compared to standard data (JCPDS no 45-0131) in 2θ range of $20^\circ – 80^\circ$ to $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles are shown in Fig. 1. XRD patterns showed that nanoparticles contained $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ spinel ferrite because all sample show peak 311. At Table 2 is the value of analysis crystallite size, X-Ray density and lattice parameter. For $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ before encapsulated crystallite size of 15.2 nm. After PEG-4000 encapsulation crystallite size decreased became 12.9 nm and 13.3 nm. This is because interaction $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles with long chain PEG-4000 that is causing the crystal growth will trap. Lattice parameter and X-Ray density constant after encapsulated PEG-4000.
Figure 1. XRD patterns of Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles, (a) before, (b) after encapsulated 1 g PEG, and (c) 3 g PEG.

**TABLE 2.** Analysis XRD of Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ before and after encapsulated with PEG

| MATERIAL          | Crystallite size (nm) | X-Ray density (g/cm$^3$) | Lattice parameter (nm) |
|-------------------|-----------------------|--------------------------|------------------------|
| Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ | 15.2 | 5.09 | 0.85 ± 0.05 |
| Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ + 1 g PEG | 12.9 | 5.07 | 0.85 ± 0.03 |
| Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ + 3 g PEG | 13.3 | 5.08 | 0.85 ± 0.02 |

**Morphological Studies**

Figure 2. Morphology, SAED pattern and histogram of the grain size from Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles, (a) before, and (b) after encapsulated 3 g PEG-4000.

The TEM images in Figure 2 show the morphology, shape and size distribution of the Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles before and after encapsulated with PEG-4000. The morphology of all samples before and after encapsulated is still agglomerated. This is due to coprecipitation method resulting small particle size and encapsulated method not enough to properly encapsulates nanoparticles, and then the concentration of PEG to much large cause nanoparticles still agglomerate because PEG-4000 have long chain polymer.
Figure 2 shows an image of a diffraction ring and a grain size distribution of Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles (a) before, and (b) after encapsulated 3 grams of PEG-4000. For the diffraction rings seen at Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ have peak diffraction (311), (400) and (333), but when encapsulated with PEG-4000 3 g still there. The obtained diffraction ring confirmed the results from the previous XRD data. The resulting grain size distribution was obtained on the Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles of 15.5 nm, which was encapsulated with PEG-4000 to 13.3 nm. The size of the grains and the crystallite size already obtained in the XRD data are almost identical.

**Magnetic behavior**

![Hysteresis curves](image)

Figure 3. Hysteresis curves of Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ 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, and (g) 3 g.

The magnetic properties for all samples were studied using VSM. The magnetic hysteresis loop of Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ before and after encapsulated with PEG-4000 as shown in Figure 3. In Table 3 as we can see the maximum magnetization ($M_{max}$) of Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ was 18.4 emu/g, and decrease after PEG-4000 encapsulation (see Table 3), its due to PEG-4000 is paramagnetic [11] which weaken the magnetic properties of Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$. 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. Magnetic anisotropy constants is not linear with the coercivity. This due to the shape of particles that has an irregular shape.
The coercivity ($H_c$) of Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ was 50.7 Oe. The $H_c$ decrease after encapsulated with variation concentration of PEG-4000. $H_c$ decrease because of the particle size decreases. The result of this study is in the multidomain region. The multidomain particles and the energy anisotropy will be smaller to demagnetization require a smaller external field. Thus the value of coercivity decrease.

| No | PEG-4000 concentration (gram) | $M_{\text{max}}$ (15 kOe) (emu/g) | $M_r$ (emu/g) | $H_c$ (Oe) | $K$ (erg/g) |
|----|--------------------------------|----------------------------------|--------------|------------|-------------|
| 1  | 0                              | 22.7                             | 0.6          | 45.8       | 0.5         |
| 2  | 0.5                            | 17.2                             | 0.3          | 47.9       | 0.4         |
| 3  | 1                              | 18.2                             | 0.3          | 48.9       | 0.4         |
| 4  | 1.5                            | 17.9                             | 0.3          | 49.2       | 0.4         |
| 5  | 2                              | 18.4                             | 0.3          | 50.7       | 0.5         |
| 6  | 2.5                            | 14.6                             | 0.1          | 43.4       | 0.3         |
| 7  | 3                              | 12.8                             | 0.2          | 44.9       | 0.3         |

4. Conclusion
Nanocrystalline mixed spinel ferrite of Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles have been successfully synthesized by coprecipitation method. The crystallite size before encapsulation was 15.23 nm. After encapsulated PEG-4000 decreased to 13.26 nm. After the encapsulated PEG-4000 nanoparticles Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ still agglomerated. Coercivity value before encapsulated was 50.7 Oe. After encapsulated PEG-4000 decreased to 47.9 Oe. The maximum magnetization before encapsulation of 18.4 emu/g After encapsulated PEG-4000 decreased to 17.1 emu/g.

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