Effect of Synthesis Parameter on Crystal Structures and Magnetic Properties of Magnesium Nickel Ferrite (Mg$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$) Nanoparticles

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Abstract. Mg$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles have been successfully synthesized by using co-precipitation method and varying the synthesis parameter, i.e. synthesis temperature and NaOH concentration. X-ray Diffraction (XRD) pattern showed that nanoparticles have cubic spinel structures with an additional phase of $\gamma$-Fe$_2$O$_3$ and particle size varies within the range of 4.3 – 6.7 nm. This variation is due to the effect of various synthesis parameters. Transmission Electron Microscopy (TEM) image showed that the nanoparticles exhibited agglomeration. The observed diffraction ring from selected area electron diffraction showed that the sample was polycrystalline and confirmed the peak appearing in XRD. The coercivities showed an increasing trend with an increase in particle size from 44.7 Oe to 49.6 Oe for variation of NaOH concentration, and a decreasing trend with an increase in particle size from 46.8 to 45.1 Oe for variation of synthesis temperature. The maximum magnetization showed an increasing trend with an increase in the ferrite phase from 3.7 emu/g to 5.4 emu/g possessed in the sample with variations on NaOH concentration. The maximum magnetization for the sample with variations on synthesis temperature varied from 4.4 emu/g to 5.7 emu/g due to its crystal structures.

Keywords: Crystal structure, Magnetic Property, Mg$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$

1. Introduction

Ferrite nanoparticles (MFe$_2$O$_4$, M = Co, Ni, Mn, Zn, Mg) have attracted the interest of researcher in the field of functional materials due to their high electrical properties, high chemical 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]. The properties of ferrite nanoparticles strongly depend on preparation method and synthesis parameter. Among ferrite nanoparticles, NiFe$_2$O$_4$ and MgFe$_2$O$_4$ have been widely investigated. NiFe$_2$O$_4$ has an inverse spinel structure with high magnetization, good conductivity and bad chemical leachability [3]. On the other hand, MgFe$_2$O$_4$ has a partial inverse spinel structure with high coercivity, high resistivity and good chemical leachability [4]. The introduction of NiFe$_2$O$_4$ to MgFe$_2$O$_4$ will provide alloy ferrite nanoparticles such as Mg$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$. The Mg$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ is a soft magnetic nanoparticle which better conductivity than MgFe$_2$O$_4$ and better chemical leachability than NiFe$_2$O$_4$ [5-7]. The Mg$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles have been synthesized by using several methods such as ceramic
method, a sol-gel method, a solvent evaporation method, combustion, and co-precipitation [8].

Coprecipitation methods have been widely used due to easier controlling particle size and crystal structure of nanoparticles. In co-precipitation methods, the concentration of coprecipitation as the source of OH\(^-\) in synthesis, and synthesis temperature that will influence the reaction rate of synthesis, were found to affect the change of the particle size [9-10]. The change of particle size and crystal structure will also change the magnetic properties of nanoparticles [11]. To explore the magnetic properties of Mg\(_{0.5}\)Ni\(_{0.5}\)Fe\(_2\)O\(_4\) nanoparticles, variations on synthesis parameter such as NaOH concentration and synthesis temperature remains to be investigated. In this paper, the effect of NaOH concentration (as co-precipitant) and temperature on crystal structures and magnetic properties of Mg\(_{0.5}\)Ni\(_{0.5}\)Fe\(_2\)O\(_4\) nanoparticles are investigated.

2. Experimental Method

The precursors such as FeCl\(_3\).6H\(_2\)O (Merck, Germany), MgCl\(_2\).6H\(_2\)O (Merck, Germany), NiCl\(_2\).6H\(_2\)O (Merck, Germany) and NaOH (Merck, Germany) were weighed carefully in accordance with the required stoichiometric proportion of salt. The MgCl\(_2\).6H\(_2\)O salt and NiCl\(_2\).6H\(_2\)O salt were mixed and dissolved them in 25 ml distilled water. Each FeCl\(_3\).6H\(_2\)O salt and NaOH salt were dissolved in 25 ml of distilled water. Then, it was mixed with the metal solution and added with 3.37 ml of HCl 37% (Merck, Germany). The precipitation was carried out by dropping the alloys solution into 3M, 6M, 10M and 12M of NaOH solution called sample A, B, C, and D respectively, at temperature of 30, 60, 90, and 150 °C called sample E, F, G and H respectively, for 1 hour and stirred at 1000 rpm. The precipitate was then washed six times for 30 minutes and dried at 95 °C for 5 hours.

The crystal structures were analyzed by using X-ray diffractometer (XRD) Shimadzu XD with CuK\(\alpha\)1 radiation (\(\lambda = 1.5406\) Å). The magnetic properties were analyzed by using Vibrating Sample Magnetometer (VSM) Riken Denshi Co. Ltd. with \(H_{\text{max}} = 15\) kOe and \(M_{\text{max}} = 2.5\) emu at room temperature. The morphology was analyzed by using Transmission Electron Microscopy (TEM) JEOL Jem-4000. The bonding analysis was characterized by using IR spectrometer Shimadzu Prestige-21. Particle size (\(D\)) was calculated from XRD peak broadening by using Scherrer formula, the values of interplanar distance (\(d\)) were estimated by using Bragg’s equation, peaks reflection (\(hkl\)) was used to estimate the lattice constant (\(a\)) [6].

3. Results and Discussion

3.1 Structural Studies

Structural studies were done by using XRD measurement and then compared to standard data (JCPDS no 17-0464) in the 2\(\theta\) range of 25° – 80°. X-ray diffraction pattern for various NaOH and temperature variations is presented in Figure 1 and in Figure 2, respectively. All the diffractograms showed the highest peak corresponding to the (311) plane which indicates the formation of cubic spinel phase with an additional peak of \(\gamma\)-Fe\(_2\)O\(_3\) phase (JCPDS no 39-1346). The broadening of diffraction peak confirms all samples experience the high value of microstrain [9]. The X-Ray density and microstrain of all samples were also calculated as shown in Table 1.

There was a peak shift at about 0.45°-0.82° from the standard data. This phenomenon may be due to the nonuniform microstrain in the crystal samples [12]. The lattice parameter of all samples were close to the value from the bulk. Lattice parameter is increasing relatively with the increase of NaOH concentration and decreasing with the increase of synthesis temperature. These could be explained as the effect of the increase of NaOH concentration leading to the decrease of cohesive energy, so the lattice parameter is increasing. The increase of synthesis temperature leads to the increase of cohesive energy, so the lattice parameter decreases [10]. The X-ray density value showed linear relation to the lattice parameter. X-ray density values tend to be constant because the composition of Mg and Ni is fixed for all samples.
Figure 1. XRD pattern of Mg$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ with NaOH concentration (A) 3, (B) 6, (C) 10, and (D) 12M.

Figure 2. XRD pattern of Mg$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ with synthesis temperature (E) 30, (F) 60, (G) 90, and (H) 150 °C.
Table 1. Particle size, lattice constant, X-Ray density and microstrain of $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles synthesized at different NaOH concentration and synthesis temperature

| Sample | Synthesis parameter variable | Temperature $^{(\circ C)}$ | NaOH Concentration (M) | Lattice constant (Å) | X-Ray Density $(g/cm^3)$ | Particle size (nm) | Microstrain |
|--------|-----------------------------|-----------------------------|------------------------|---------------------|------------------------|-------------------|-------------|
| A      | NaOH Concentration          | 90                          | 3                      | 8.534               | 4.47                   | 4.4               | 0.1059      |
| B      | NaOH Concentration          | 90                          | 6                      | 8.558               | 4.43                   | 6.8               | 0.0684      |
| C      | NaOH Concentration          | 90                          | 10                     | 8.472               | 4.57                   | 4.6               | 0.1004      |
| D      | NaOH Concentration          | 90                          | 12                     | 8.564               | 4.42                   | 5.9               | 0.0786      |
| E      | Synthesis Temperature       | 30                          | 10                     | 8.541               | 4.46                   | 5.3               | 0.0879      |
| F      | Synthesis Temperature       | 60                          | 10                     | 8.563               | 4.42                   | 4.7               | 0.0997      |
| G      | Synthesis Temperature       | 90                          | 10                     | 8.472               | 4.57                   | 4.6               | 0.1004      |
| H      | Synthesis Temperature       | 150                         | 10                     | 8.478               | 4.56                   | 5.8               | 0.0791      |

The particle size is not linear to the increase of the concentration of NaOH and the increase of synthesis temperature. This phenomenon may be due to the different stage that happens in every variation of the synthesis parameter [13]. The smaller size particles in the NaOH concentration of 3M and 10 M were nucleation stage when the structures are not crystallized better [13-15], and the values of microstrain are higher. The bigger particles in the NaOH concentration of 6M and 12M were in the crystallization stage [13-15] when the structures are crystallized better, and its microstrain values are lower. For the sample with synthesis temperature variations, at the temperature of 30 $^\circ$C to 90 $^\circ$C, the nucleation process still happens so that the structures of the samples are unstable and the microstrain values are increasing. The higher microstrain value, the more unstable particle in the nucleation process, so that the particles size decrease. The values of microstrain are not linear to the increase of synthesis parameter variations. The high value of microstrain caused by synthesis process that used low-temperature process.

3.2 Morphological Studies

The result of TEM characterization of the sample is depicted in Figure 3. Figure 3(a), and 3(b) shows the image of $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles synthesized at 90 $^\circ$C and 10M NaOH.

Figure 3.TEM Image of $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ (a) diffraction rings and (b) sample shape
The diffraction rings in Figure 3(a) confirms the peak as shown in XRD pattern. The diffraction spots are not clearly sharp due to come from not single crystal and small size of the nanoparticles. It coulds also possible that the satellites inside the grains. The image shows that the particles form an irregular shape and aggregate (Figure 3(b)). The distribution of particles size agrees well with the histograms obtained by XRD. The particles tend to aggregate because of the tiny size of particles. Smaller particles have higher surface potential energy, so they tend to aggregate to reduce it.

3.3 IR Spectral Studies

IR spectra of Mg$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles was synthesized at 90 °C and 10M of NaOH shown in Figure 4. There are two main absorptions in the wavenuber of 362 cm$^{-1}$ and band of 609.51 cm$^{-1}$ corresponding to the stretching vibration of metal ions of the tetrahedral and octahedral site, respectively [6,8]. This case confirms that all Mg$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ samples have cubic spinel structures. The absorption in 1357.89 cm$^{-1}$ and 1627.92 cm$^{-1}$ corresponds to bending vibration of O-H because of H$_2$O molecules [6]. This phenomenon may due to the sample drying process which is not perfectly done. The sharp peaks absorption in the wavenumber of 3417.86 cm$^{-1}$ corresponds to stretching O-H and may be due to the not reacted OH$^-$ because of high concentration of NaOH.

![Figure 4. IR spectra of Mg$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ systems](image)

3.4 Magnetic Behavior

The magnetic properties of all samples were studied by using VSM. The results from the measurement of coercivity ($H_c$), maximum magnetization ($M_{\text{max}}$), magnetic anisotropy constant and magnetic moment [8] are shown in Table 2. Calculation of magnetic anisotropy ($K$) constant is by using Equation 1 [6].

$$K = H_c \times M_{\text{max}}$$ (1)

The value of coercivities increases relatively with increasing particle size for the sample with variations of NaOH concentration. This phenomenon leads to the particle with variations of NaOH concentration which has single domain [16]. For the sample with variations of synthesis temperature, the coercivities relatively decrease with increasing particle size confirming that the samples have
multidomain [16]. Magnetic anisotropy constant is not linear with the coercivity. This case is due to the irregular shape of the particles [16].

| Table 2. Particle size, ferrite phase ratio, coercivity, maximum magnetization, magnetic anisotropy constant and magnetic moment of $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{Fe}_{2}\text{O}_{4}$ nanoparticles with variations of parameter synthesis |
|-------------------------------------------------|
| Synthesis parameter variable | Particle size (nm) | Ferrite Phase Ratio (%) | $H_c$ (Oe) | $M_{max}$ (emu/g) | $K$ (erg/g) | Magnetic moment ($\mu_B$) |
| NaOH Concentration | 4.4 | 54.9 | 45.18 | 3.71 | 167.89 | 0.15 |
| | 4.6 | 57.1 | 46.83 | 4.70 | 220.20 | 0.18 |
| | 5.9 | 72.8 | 44.72 | 5.47 | 244.54 | 0.21 |
| | 6.8 | 66.2 | 49.56 | 3.45 | 170.96 | 0.14 |
| Synthesis Temperature | 4.6 | 57.1 | 46.83 | 4.70 | 220.20 | 0.18 |
| | 4.7 | 46.8 | 42.97 | 4.43 | 190.48 | 0.17 |
| | 5.3 | 44.5 | 46.25 | 5.30 | 245.12 | 0.21 |
| | 5.8 | 59.9 | 45.13 | 5.77 | 260.58 | 0.22 |

4. Conclusion
Powder of $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{Fe}_{2}\text{O}_{4}$ nanoparticles has been successfully synthesized by co-precipitation method. Variations on synthesis parameter i.e. NaOH concentrations and synthesis temperature were found to influence the particle size. TEM image confirms the peaks shown in XRD. IR spectral showed vibration in tetrahedral and octahedral sites that conform spinel structures. The coercivity increases relatively by increasing particle size with variations of NaOH concentration. The coercivity for samples with variations on synthesis parameter decreases relatively by increasing particle size that leads to be varied in the magnetic properties of $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{Fe}_{2}\text{O}_{4}$ nanoparticles.

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