Crystal Structure and Magnetic Properties of Magnesium Ferrite (MgFe$_2$O$_4$) Nanoparticles Synthesized by Coprecipitation Method

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Abstract. MgFe$_2$O$_4$ has been successfully synthesized by coprecipitation method. The Precursors used are MgCl$_2$.6H$_2$O (magnesium chloride hexa-hydrate, $M_r$= 203.205 g/mol) and FeCl$_3$.6H$_2$O (ferric chloride hexa-hydrate, $M_r$= 270.19 g/mol) and NaOH (sodium hydroxide, $M_r$ = 39.99 g/mol) as coprecipitant. This synthesis process was done by varying the NaOH concentration, the synthesis temperature and the stirring duration. XRD analysis results showed that the grain size increases with synthesis temperature and decreases with the increase in the concentration of NaOH and the duration of stirring. The smallest grain size is 2.1 nm and the largest grain size is 10 nm. Analysis of magnetic properties MgFe$_2$O$_4$ by Vibrating Sample Magnetometer (VSM) showed that nanoparticles MgFe$_2$O$_4$ can be assumed in multidomain region, with relationships. Sample with the smallest particle size 2.1 nm, has highest $H_c$ value 133.9 Oe. The maximum magnetization at $H = 15$ kOe and remanent magnetization ($M_r$) increase with the degree of crystallinity of the sample. Although there is also the effect of the presence of hematite phase ($\alpha$-Fe$_2$O$_3$) and the grain size. Magnesium ferrite magnetic nanoparticles (MgFe$_2$O$_4$) has great potential to be applied as adsorption, sensors, drug delivery, semiconductor materials and other magnetic technology.

1. Introduction

Magnetic nanoparticles have been studied for a variety of applications in the study of technology and materials science, chemistry, physics, biology, and environmental science. Nanoparticles are particles with a nanometer size, which is about 1-100 nm[1]. The nanoparticles have unique physical-, chemical-, mechanical-, magnetic- and optical characteristic which are not present in other type of bulk materials[2]. Magnetic nanoparticles show a variety of unique magnetic phenomenon that differs from their bulk magnetic property, so that the properties may be advantageous for a variety of applications such as magnetic fluids, catalysts, bio-applications, magnetic resonance imaging and data storage media[3]. Magnetic properties of nanoparticles are determined by many factors, including the chemical composition, particle size and shape, morphology, particle interaction with the surrounding matrix and particles [4]. By changing the size, shape, composition, and structure of the nanoparticles, the magnetic properties of the material can be controlled[5].
Presently, much research work and numerous studies have been carried out on spinel ferrite nanoparticles due to their very wide field of application in data storage systems, transformers, computer memory, inductors, recording heads, microwave and medical diagnostics. This material has excellent magnetic properties such as high permeability, high resistivity and low coercivity. Spinel ferrite nanoparticles are soft ferrite which have a cubic crystal structure.

Among the research interests focusing on ferrite nanoparticles, the study of nanoparticles of magnesium ferrite (MgFe$_2$O$_4$) seems to stand out. Some of the reasons which led MgFe$_2$O$_4$ to attract the interest of many researchers compared to other ferrites is its wide-range application potential, because MgFe$_2$O$_4$ has a high value of saturation magnetization, Curie temperature and high electrical resistivity. MgFe$_2$O$_4$ is a soft magnetic material and one inverse spinel group are very important. MgFe$_2$O$_4$ is also an n-type semiconductor material that can be applied as an adsorption device, sensors, and used in magnetic technology. Another interesting point is that MgFe$_2$O$_4$ has unique chemical properties and thermal stability, as well as the dependence of the magnetic properties on the particle size. MgFe$_2$O$_4$ nanoparticles can also behave as superparamagnetic nanoparticles. When an external magnetic field is removed, then the sum of the magnetic moment of the magnetic nanoparticles are each pointing in different directions, thus the overall bulk magnetic moment is zero.

Various methods were employed to synthesize magnetic nanoparticles, for example, the thermal decomposition-, microemulsion-, coprecipitation-, sol gel-, hydrothermal-, and sonochemical method[7]. Among these methods, coprecipitation method is an effective method and can work at low temperatures. Moreover, because it can control the particle size, coprecipitation method can be used to evaluate the dependence of the magnetic properties of the particle size[8].

This research investigates in more details related to the influence of the grain size from magnetic properties of nanoparticles MgFe$_2$O$_4$ synthesized by coprecipitation method by varying the synthesis parameters such as NaOH concentration and synthesis temperature. The results of this study will provide information about the influence of parameter variations to magnetic properties as well as the synthesis of the acquired information about the properties of nanoparticles MgFe$_2$O$_4$, in order to improve its performance and to make it more effective in its application.

2. Materials and Methods

The material synthesis of MgFe$_2$O$_4$ nanoparticle is MgCl$_2$.6H$_2$O and FeCl$_3$.6H$_2$O as a provider of Mg$^{2+}$ ions and Fe$^{3+}$ by reaction coefficient ratio 1:2. Coprecipitation synthesis method is applied by mix 1.018 grams MgCl$_2$.6H$_2$O; 2.703 grams FeCl$_3$.6H$_2$O and 3.5 ml of HCl (37%) in 50 mL of distilled water until homogeneous. Then put that solution to 25 mL of NaOH solution by slowly droppwise while stirring use a magnetic stirrer at 1000 rpm for 60 minutes with a temperature variation of 36, 60 and 90°C (Table 1). For samples with varying concentrations of NaOH is applied in the same way at 90°C with various concentrations of NaOH as 3 M; 6 M and 10 M (Table 1).

Those solution are placed over a permanent magnet to accelerate precipitation. In order to minimize the salts dissolved in solution MgFe$_2$O$_4$, then washing approximately 7 repetitions. After the washing process is completed, then the precipitate is heated in a furnace to dry by arrange the temperatures around 95°C. Finally, black powder is succesfully made. MgFe$_2$O$_4$ samples with temperatures and concentrations variations of NaOH which has formed, then characterized by X-ray Diffraction (Shimadzu models XD-3H) with CuKα tube (wavelength 1.5406 Å) to determine the phase contained in the sample. Calculation of the sample size distribution is calculated by using Scherrer equation, as shown in equation 1 below:

$$\frac{\beta \cos \theta}{k\lambda} = t$$  \hspace{1cm} (1)

where \( t \) is the crystal grain size, \( k \) is a constant Scherrer (0.89), \( \lambda \) is the wavelength of X-rays and \( \beta \) is the width of half peak (full width at half maximum = FWHM) of the main peak. Particle morphology
will be investigated by using transmission electron microscopy (JEOL JEM 1400) and characterization of magnetic properties by vibrating sample magnetometer (Riken Denshi Co., Ltd.).

Table 1. Synthesis parameters of MgFe₂O₄ nanoparticles

| No. | Name of Sample | MgCl₂·6H₂O (g) | FeCl₃·6H₂O (g) | HCL (37%) (mL) | Concentration of NaOH (M) | duration of stirring (minute) | the synthesis temperature (°C) |
|-----|----------------|----------------|----------------|----------------|--------------------------|-------------------------------|-------------------------------|
| 1.  | A              | 1.017          | 2.703          | 3.37           | 3                        | 60                           | 90                           |
| 2.  | B              | 1.017          | 2.703          | 3.37           | 6                        | 60                           | 90                           |
| 3.  | C              | 1.017          | 2.703          | 3.37           | 10                       | 60                           | 90                           |
| 4.  | D              | 1.017          | 2.703          | 3.37           | 10                       | 60                           | 50                           |
| 5.  | E              | 1.017          | 2.703          | 3.37           | 10                       | 60                           | RT                           |
| 6.  | F              | 1.017          | 2.703          | 3.37           | 10                       | 30                           | 90                           |
| 7.  | G              | 1.017          | 2.703          | 3.37           | 10                       | 90                           | 90                           |

3. Results and Discussion

![Fig 1. XRD patterns of MgFe₂O₄ nanoparticles](image)
The value of NaOH changes the rate of solution when the temperature of the synthesis below the critical temperature and will undergo a phase change. When the temperature of the synthesis is increased, supplemental information is that the process of growing grains occurs simultaneously as a result of the high degree of supersaturated solution. The increasing concentrations of NaOH causes the rate of deposition (deposition) ion configuration is higher than the rate of soluble (dissolution) resulting in the formation and the growth rate of the core when the temperature is above the critical temperature. This is as a result of the high degree of supersaturated solution when the temperature in synthesis process is increased, supplemental information is that the process of growing grains occurs when the temperature of the synthesis below the critical temperature and will undergo a phase change or the formation of the core when the temperature is above the critical temperature ($T_c$).

At MgFe$_2$O$_4$ nanoparticles samples which are synthesized by the synthesis temperature variations, the presence of $\alpha$-Fe$_2$O$_3$ (hematite) influences the peak intensity in the sample C at which time the synthesis temperature increases, the peak intensity tends to decrease. This is as a result of the oxidation reaction between the sample ions with oxygen ions. Are shown in Table 2 are generally the ratio of the volume presentation phase presence of impurities has increased along with the increase in the synthesis temperature.

Table 2. Crystal structure of MgFe$_2$O$_4$ nanoparticles

| No | Sample | Lattice parameters (Å) | Particles Size (nm) |
|----|--------|------------------------|---------------------|
| 1. | A      | 8.57                   | 10.7                |
| 2. | B      | 8.56                   | 7.8                 |
| 3. | C      | 8.60                   | 6.4                 |
| 4. | D      | 8.58                   | 2.1                 |
| 5. | E      | 8.55                   | 6.5                 |
| 6. | F      | 8.59                   | 4.4                 |
| 7. | G      | 8.67                   | 8.4                 |

Figure 1 provides information related to the peaks of MgFe$_2$O$_4$ and obtained information related to the lattice parameters (a), grain size (t), $\alpha$-Fe$_2$O$_3$ ratio and lattice parameter deviations. It is presented in Table 2. Based on Table 2, the value of MgFe$_2$O$_4$ lattice parameter increases trend by increasing the concentrations of NaOH. Based on XRD analysis of seven samples which were synthesized by varying the NaOH concentration, synthesis temperature and stirring duration, the lattice parameter values obtained for samples A, B, C, D, E, F and G are 8.57; 8.56, 8.60, 8.58, 8.55, 8.59 and 8.67 Å. These lattice parameter values are closer to the value of the lattice parameter MgFe2O4 bulk size, 8.4 Å.[9].

Table 2 shows that the particle size of nanoparticles synthesized MgFe$_2$O$_4$ decrease by the increasing concentrations of NaOH. The highest nanoparticle size is sample A with 10.7 nm and the smallest size is sample D with 2.1 nm. Particle size variation can be attributed to the influence of the formation and the growth rate of the core particles. Rising concentrations of NaOH causes the rate of deposition (deposition) ion configuration is higher than the rate of soluble (dissolution) resulting in the nucleation stage. The nucleation stage is more dominant than the crystal growth, so that the resulting particle size is small. The more concentration of NaOH causes OH- higher. The numbers of OH- accelerate the formation of core particles, but reduces the space between the particles to grow so that the diameter is smaller. Moreover, the decreasing particle size with increasing concentrations of NaOH showed that NaOH is a good substance breaker (decomposers).

In Table 2 also shows that the particle size increased along with the increase in the synthesis temperature. This is caused by nucleation process and crystal growth that is taking place rapidly and simultaneously as a result of the high degree of supersaturated solution when the temperature in synthesis process is increased, supplemental information is that the process of growing grains occurs when the temperature of the synthesis below the critical temperature and will undergo a phase change or the formation of the core when the temperature is above the critical temperature ($T_c$).

Figure 2(a) shows that the grain sample A has a spherical shape, although not perfectly round. Samples were formed seem prone to agglomeration (clumping) resulting in low dispersibility of nanoparticles obtained. This may occur because due to the magnetic interaction between single item with other items. If this trend continues then it is predicted to lead to nanoparticle size becomes larger. So, a treatment to reduce the occurrence of agglomeration is neccessary.
TEM can also be acquired image diffraction patterns that indicate the presence of ring structures in the polycrystalline sample, as shown in Figure 2(b). The pattern of diffraction rings show rings that indicate discrete crystal planes. Diffraction rings innermost to outermost show diffraction peaks with miller index (220), (311), (511) and (440). The miller indices in accordance with \( hkl \) the diffraction pattern of XRD that are characteristic samples of MgFe\(_2\)O\(_4\) phase.

![Diffraction Patterns](image)

Fig 2. (a) morphology of MgFe\(_2\)O\(_4\) nanoparticles; (b) pattern of diffraction rings of MgFe\(_2\)O\(_4\) nanoparticles

![Hysteresis Loops](image)

Fig 3. Hysteresis loop of MgFe\(_2\)O\(_4\) nanoparticles
Characterization of magnetic properties of nanoparticles MgFe$_2$O$_4$ is investigated by using VSM. The data obtained and plotted in the form of a hysteresis curve. The hysteresis curve obtains relevant maximum magnetization data at $H = 15$ Koe, remanent magnetization ($M_r$), and the coercivity ($H_c$). The results of observations with VSM shown in Figure 3. VSM observations showed that all the samples classified into soft magnetic which are characterized by expanses of the hysteresis curve that form narrow and relatively small coercivity value. Based on Figure 3, the value of $H_c$ shown in Table 3.

| No | Sample | Particle size (nm) | $H_c$(Oe) |
|----|--------|-------------------|-----------|
| 1. | A      | 10.7              | 130.4     |
| 2. | B      | 7.8               | 123.4     |
| 3. | C      | 6.4               | 132.3     |
| 4. | D      | 2.1               | 133.9     |
| 5. | E      | 6.5               | 128.5     |
| 6. | F      | 4.4               | 129.7     |
| 7. | G      | 8.4               | 123.2     |

Based on Table 3, Sample D with the smallest particle size 2.1 nm, has highest $H_c$ value 133.99 Oe, and sample G with lowest $H_c$ value 123.18 Oe has particle size 8.4 nm. In this study, for variations in the concentration of NaOH (Table 3) the value of the highest $H_c$ was 132 Oe owned by the particles with the smallest size ($t = 6.4$ nm). As well as variations in temperature synthesis, the value of the highest $H_c$ was 133 Oe owned by the particles with the smallest size ($t = 2.1$ nm). Multidomain region $H_c$ value and particle size are inversely. Nanoparticles in this study are assumed in multidomain region. The influence of nanoparticle size on the value of coercivity can be described by the equation $H_c = 1/t$, where $t$ is the particle size and $H_c$ is the coercivity [10]. The result shows that the coercivity value will increase by the smaller size of the nanoparticles. This can be explained that the small size of nanoparticles which will provide extensive surface interaction and strong magnetic interaction between the nanoparticles.

| No | Sample | $M$ (emu/g) | $M_r$ (emu/g) |
|----|--------|-------------|--------------|
| 1. | A      | 2.7         | 0.014        |
| 2. | B      | 5.1         | 0.083        |
| 3. | C      | 4.9         | 0.062        |
| 4. | D      | 5.3         | 0.082        |
| 5. | E      | 5.1         | 0.064        |
| 6. | F      | 4.9         | 0.064        |
| 7. | G      | 6.2         | 0.094        |
Study of the relationship of $H_c$ value and particle size at multidomain region may also be caused by the movement of domain walls. Magnetization which caused by the movement of the domain wall requires energy is smaller than the magnetization caused by the rotation of the magnetic moment. In the nanoparticles multidomain region, the particle size is directly proportional to the length of the domain ($L$) and magnetization saturation ($M_s$) value of each domain.

Variations in the value of the magnetization at each sample can be linked to the presence of $\alpha$-Fe$_2$O$_3$ phase (hematite) in the sample that have different properties with MgFe$_2$O$_4$ phase. The existence of $\alpha$-Fe$_2$O$_3$ phase that is antiferromagnetic greatly affect the value of the magnetization of the sample MgFe$_2$O$_4$. When $\alpha$-Fe$_2$O$_3$ phase small amounts, MgFe$_2$O$_4$ nanoparticles towards a single phase. Phase of MgFe$_2$O$_4$ increasingly towards a single phase to create a domain-domain uniform size, it makes the dipole moments in the growing domain direction. Therefore, the value of $M$ is getting bigger. And bigger ratio of $\alpha$-Fe$_2$O$_3$ phase in the sample, then the value of $M$ will be smaller.

This can be seen in Table 4. The lowest ratio of $\alpha$-Fe$_2$O$_3$ phase obtained on the sample G is 2.59 %. The low value of the ratio of $\alpha$-Fe$_2$O$_3$ phase showed that the presence of $\alpha$-Fe$_2$O$_3$ phase in the sample only in small quantities, so it caused the value of the magnetization of the sample G is the largest value compared with other samples in the amount of 6.15 emu/g.

4. Conclusions
MgFe$_2$O$_4$ nanoparticles which have been synthesized by coprecipitation method was applied by varying the NaOH concentration, the synthesis temperature and the stirring duration. In this study, the grain size decreased by the increasing concentrations of NaOH and increases with rising temperature synthesis. Analysis of magnetic properties showed that no linear relationship between the coercivity and grain size, so it is assumed that MgFe$_2$O$_4$ nanoparticles are in multidomain region. Observation of magnetization shows higher magnetization values with increasingly smaller ratio of $\alpha$-Fe$_2$O$_3$ phase. MgFe$_2$O$_4$ nanoparticles are synthesized with a concentration of 10 M NaOH at room temperature has the smallest particle size of 2.1 nm, the highest $H_c$ value of 133.9 Oe, and the highest value of $M$ 6.1 emu/g at $H = 15$ kOe has by sample G.

Acknowledgments
The authors would like to acknowledge the Competency Research Grant (HIKOM) financial support courtesy of the Directorate General of Higher Education (DIKTI), 2015-2016.

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