Synthesis and characterization of \( \text{Mn}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4 \) based on natural iron sand prepared by Co-precipitation method

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Abstract. Magnetic nano particles, \( \text{Mn}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4 \) \((x = 0.25, 0.5 \text{ and } 0.75)\) with natural iron sand as raw material were successfully synthesized by co-precipitation method. The obtained samples were characterized by the x-ray diffractometer (XRD) and the vibrating sample magnetometer (VSM). The XRD result showed that the magnetic nano particles have a single phase of inverse-spinel face cubic center (fcc) structure. Furthermore, the lattice parameter constant, crystallite sizes and unit cell volume decrease with the increase of the \( x \) content. Contrary the dislocation density and lattice strain increase with increasing the \( x \) content. The VSM result showed that the saturated magnetization magnitude were getting high and the coercive field became low when the \( x \) were increased.

1. Introduction

Magnetic nanoparticles attract much interest in research because of their unique physical and chemical properties compared to large particles or bulk [1]. Among several magnetic nano particles, manganese ferrite (\( \text{MnFe}_2\text{O}_4 \)) nano particles has the highest magnetic moment compared to the other ferrite systems [2]. Furthermore, the \( \text{MnFe}_2\text{O}_4 \) has a high magnetic permeability, and its resistivity much lower than \( \text{CoFe}_2\text{O}_4 \) and \( \text{NiFe}_2\text{O}_4 \). Thus, the substitution of Mg ions in manganese ferrite modifies the magnetic characteristics and opens more opportunities for a superparamagnetic realization. This condition causes the thermal energy at room temperature to block the anisotropy energy to return to its low state. Here, the sum of the magnetic moments of the magnetic material are each in a different direction, thus the overall magnetic moment of the bulk is zero except under blocking temperature. This interesting property opens up application opportunities for various electronic devices such kind recording medium (data storage media) as well as a target of the drug delivery system and contrast agent at magnetic resonance imaging (MRI) system [3–8].

Various methods have been developed to synthesize the magnetic nanoparticles such as coprecipitation method, sol-gel, microemulsion, hydrothermal, and others [9–13]. The coprecipitation method is one of the best choices because it is quite effective and relatively simple compared to other methods. This method produces relatively narrow grain size distribution and can be done under atmospheric conditions. In order to realize the magnetic nano particles, the chemical with high grade qualifications for analysis are usually used. Meanwhile, the abundance of natural resources in the form of the iron sands (i.e. with the largest content of hematite, magnetite etc.) is available in almost all of Indonesia both on the coast and in the fine deposits of the river. It has also been reported that hematite content is increased after annealed at the temperature of 800°C for atmospheric conditions [14]. Furthermore, the fine sediment is so small that it is possible to extract as raw material in magnetic nano particle synthesis.
In this paper, the synthesis and characterization of nano magnetic particles of manganese magnesium ferrite, Mn\(_{1-x}\)Mg\(_x\)Fe\(_2\)O\(_4\) are presented. The natural iron sand as a raw material used the whole experimental. Then, the samples are evaluated the structural properties by using the x-ray diffractometer and FE–SEM. Whereas, the magnetic properties are characterized by the vibrating sample magnetometer at room temperature.

2. Experimental Method
The main ingredients of Mn\(_{1-x}\)Mg\(_x\)Fe\(_2\)O\(_4\) are the natural iron-sand. The natural iron sand that was used in this research was taken from Kata Beach, West Sumatera. Thus, Mn\(^{2+}\) and Mg\(^{2+}\) ions provide from MnCl\(_2\) and MgCl\(_2\). The stoichiometric \(x\) is selected to be 0.25, 0.50 and 0.75. The experimental procedure is carried out as follows the previous experimental [15]. First, 8 grams of iron sand were dissolved in 5.0 mL HCl. After filtered by using Whatman paper no 42, then amount gram equivalent to stoichiometry Mn\(^{2+}\) and Mg\(^{2+}\) are added to the solution and stirred until homogeneous. Furthermore, the solution was dropped into 100 ml of 2 M NH\(_4\)OH solution which was constantly stirred with a 200 rpm magnetic stirrer at 110°C for 2 hours. The precipitated yield was dried overnight, then washed with ethanol and de-ionized water several times until a clean product was obtained. Thus final product is dried in the oven at 70°C. Thereafter, the crystalline structure of the sample is evaluated by using x-ray diffractometer Rigaku Smart Lab from Cu K\(\alpha\) radiation source (1.5418 Å). The microstructure is studied by using field emission scanning electron microscopy (FE-SEM/EDS–JEOL JIB 4610F). Whereas the magnetic properties of the magnetic nano particles Mn\(_{1-x}\)Mg\(_x\)Fe\(_2\)O\(_4\) is performed by using vibrating sample magnetometer (VSM 250) at room temperature.

3. Result and Discussion

![Image](image-url)

**Figure 1.** X-ray diffraction (XRD) patterns for co-precipitated Mn\(_{1-x}\)Mg\(_x\)Fe\(_2\)O\(_4\) nanoparticles with \(x\) = 0.25, 0.50 and 0.75.

Figure 1 show the x–ray diffraction (XRD) patterns for co-precipitated Mn\(_{1-x}\)Mg\(_x\)Fe\(_2\)O\(_4\) nanoparticles with \(x\) = 0.25, 0.50 and 0.75 at the temperature synthesis of 110°C. The obtained of the xrd pattern typically resembles the results published by De-León-Prado et.al [16]. It was clearly observed that the strongest peak was observed at an angle of about 2\(\theta\)=35° corresponding to the Miller indices orientation.
of hkl (311). The growing crystalline structure is observed from the typical XRD curve which is less sharp considering there is no post-annealing treatment. The crystallite size \( D \) is calculated by Scherrers’ formula at the strongest peak of hkl (311)

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

(1)

where \( \beta \) is full width at half maximum (FWHM) of the peak. The lattice constant \( a \) was calculated by using

\[
a = \frac{\lambda}{2 \sin \theta} \sqrt{h^2 + k^2 + l^2}
\]

(2)

\( \lambda \) is Cu K\( \alpha \)’s wavelength, \( \theta \) is Bragg’s angle, hkl are Miller indices. The \( \delta \) is defined as

\[
\delta = \frac{1}{D^2}
\]

(3)

Whereas the lattice strain is calculated by Hall-Williamson formula by using formula [13]

\[
\varepsilon = \frac{\beta_{hkl}}{4\tan \theta}
\]

(4)

\( \varepsilon \) is the strain, \( \beta_{hkl} \) is FWHM of the peak.

Table 1 show the calculated of the crystallite size \( D \) lattice parameters \( a \), dislocation density \( \delta \) and lattice strains \( \varepsilon \) for the Mn\(_x\)Mg\(_{1-x}\)Fe\(_2\)O\(_4\) nanoparticles.

**Table 1.** Crystallite sizes \( D \), lattice parameters \( a \), dislocation density \( \delta \) and lattice strains \( \varepsilon \) of the magnetic nano particles Mn\(_x\)Mg\(_{1-x}\)Fe\(_2\)O\(_4\) synthesized with various of \( x = 0.25, 0.50 \) and 0.75.

|                      | \( x \)       | 0.25  | 0.50  | 0.75  |
|----------------------|---------------|-------|-------|-------|
| Crystallite size \( D \) (nm) | 16.284        | 15.942 | 15.911 |
| Dislocation density \( \delta \) (\( \times 10^{15} \) line/m\(^2\)) | 3.771        | 3.935  | 3.950  |
| Lattice parameter \( a \) (Å) | 8.382        | 8.364  | 8.362  |
| Lattice strain \( \varepsilon \) | 0.396        | 0.403  | 0.404  |

Crystallite size of the Mn\(_x\)Mg\(_{1-x}\)Fe\(_2\)O\(_4\) nanoparticles decrease from 16.284 nm to 15.942 nm and become 15.911 nm when the \( x \) of 0.15, 0.50 and 0.75 respectively. The reduced of the crystallite size can be attributed to the atomic radius, i.e manganese (127 pm) is smaller than magnesium (160 pm). Consequently, the crystallite formation is smaller in increasing the \( x \). The \( \delta \) of 3.771\( \times 10^{15} \) line/m\(^2\) is obtained for the \( x = 0.25 \). Thus the \( \delta \) become 3.935\( \times 10^{15} \) line/m\(^2\) and 3.950\( \times 10^{15} \) line/m\(^2\) when the \( x \) of 0.50 and 0.75 respectively. The dislocation density increases with an increase of \( x \) because of the bulk density of manganese is heavier than magnesium. The increase of the manganese content in the co-precipitated Mn\(_x\)Mg\(_{1-x}\)Fe\(_2\)O\(_4\) nanoparticles so that the dislocation density becomes larger.

Then, the lattice parameter \( a \) slightly decrease with the increase of the \( x \) parameter. This indicates that the structure of the crystal cell unit is relatively stable and insensitive to other ion substitutions. Thus, the lattice strain \( \varepsilon \) of the Mn\(_x\)Mg\(_{1-x}\)Fe\(_2\)O\(_4\) nanoparticles change from 0.396 to 0.403 and then 0.404 with increasing the \( x \) from 0.25, 0.5 and 0.75. This is attribute to the crystallite size. Thus the larger of crystallite size is reduced lattice strain. The change of the lattice strain is expected modify the magnetic properties of the Mn\(_x\)Mg\(_{1-x}\)Fe\(_2\)O\(_4\) nanoparticles.
Figure 2. (a) The FE-SEM image, (b) size particle distribution and (c) the EDS analysis for the Mn$_{x}$Mg$_{1-x}$Fe$_2$O$_4$ with x=0.25 nanoparticles.

Figure 3. Typical hysteresis curve for co-precipitated Mn$_{x}$Mg$_{1-x}$Fe$_2$O$_4$ nanoparticles with x = 0.25, 0.50 and 0.75.
The morphological analysis of the Mn$_{3}$Mg$_{1-x}$Fe$_{2}$O$_{4}$ with $x=0.25$ nanoparticles present at Figure 2. The spherical shape of the Mn$_{3}$Mg$_{1-x}$Fe$_{2}$O$_{4}$ nanoparticles are observed. The particles size distribute from about 20.00 nm to 90.00 nm with the average diameter of 46.69 nm. The agglomeration of the nano particles observe in a some part of the figure that attribute the van der Waal force [17]. The EDS analysis that the sample consist four elements i.e. manganese, magnesium, oxygen, and iron that in resonable stochiometric composition of the Mn$_{3}$Mg$_{1-x}$Fe$_{2}$O$_{4}$ with $x=0.25$.

Figure 3 show a typical hysteresis curve for Mn$_{3}$Mg$_{1-x}$Fe$_{2}$O$_{4}$ nanoparticles with $x=0.25, 0.50$ and $0.75$. It is clearly observed that the saturated magnetization increase with the increase of the $x$. The saturated magnetization of 26.39 emu/g is obtained for $x=0.25$. Then, the saturated magnetization increase of 35.89 emu/g and 40.09 emu/g for $x=0.25$ and 0.75 respectively. As is well known that the manganese has a stronger magnetic moment than the magnesium [16]. So that the presence of the manganese ion in greater amounts increases saturation magnetization.

Whereas the $H_C$ decrease with the increase of the $x$. The $H_C$ of 79.64 Oe is obtained for the $x$ of 0.25. Then, the $H_C$ are 73.91 Oe and 62.64 Oe for the $x$ of 0.50 and 0.75 respectively. In case in nano–meter–order–magnetic material/particles, when the hysteresis curve presents a near–zero coercive field, then the superparamagnetic state is achieved. Here, it is suggested that the superparamagnetic state at near room temperature occur for the Mn$_{3}$Mg$_{1-x}$Fe$_{2}$O$_{4}$ nanoparticles with $x=0.25$.

**Table 2.** Coercive field $H_C$, saturated magnetization $M_S$ and magnetization remanent $M_R$ of the magnetic nano particles Mn$_{3}$Mg$_{1-x}$Fe$_{2}$O$_{4}$ synthesized with various of $x=0.25, 0.50$ and 0.75.

| $x$    | 0.25 | 0.50 | 0.75 |
|--------|------|------|------|
| $H_C$ (Oe) | 79.64 | 73.91 | 62.64 |
| $M_S$ (emu/g) | 26.39 | 35.89 | 40.09 |
| $M_R$ (emu/g) | 3.13  | 4.28  | 4.04  |

4. Conclusion

Magnetic nano particles, Mn$_{3}$Mg$_{1-x}$Fe$_{2}$O$_{4}$ ($x=0.25, 0.5$ and $0.75$) with natural iron sand as raw material were successfully synthesized by co-precipitation method. The obtained samples were characterized by the x–ray diffracator (XRD) and the vibrating sample magnetometer (VSM). The XRD result showed that the magnetic nano particles have a single phase of inverse-spinel face cubic center (fcc) structure. Furthermore, the lattice parameter constant, crystallite sizes and unit cell volume decrease with the increase of the $x$ content. The particles size distribution is ranging from 20 nm to 90 nm with the average size of 46.69 nm. Contrary the dislocation density and lattice strain increase with increasing the $x$ content. The VSM result showed that the saturated magnetization magnitude were getting high and the coercive field became low when the $x$ were increased. The near–room–temperature of the superparamagnetic state is suggested to occur for the Mn$_{3}$Mg$_{1-x}$Fe$_{2}$O$_{4}$ nanoparticles with $x=0.25$.

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6. References

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