The Effect of Synthesis Temperature on Physical and Magnetic Properties of Manganese Ferrite (MnFe$_2$O$_4$) based on Natural Iron Sand

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Abstract. The magnetic material of Manganese Ferrite (MnFe$_2$O$_4$) based on natural Iron sand have been successfully prepared by using co-precipitation method. The natural Iron sand, MnCl$_2$·4H$_2$O, HCl and NH$_4$OH were used as raw materials to synthesize the MnFe$_2$O$_4$. The synthesis was carried out at various temperatures of 70, 100 and 130°C, respectively. The physical and the magnetic properties of the samples were analysed by using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Vibrating Sample Magnetometer (VSM). The diffraction pattern indicates that the MnFe$_2$O$_4$ is the dominant phase. The crystallite size tends to increase as the synthesis temperature increased while the saturation magnetization of MnFe$_2$O$_4$ tends to decrease.

1. Introduction

Ferrite is soft magnetic material that have spinel structure. The formula of ferrite is M-Fe$_2$O$_4$ where M is Cu, Zn, Ni, Co, Fe, Mn, and Mg. Ferrite has high permeability and thermal resistance and low coercivity [1]. Soft ferrite can be applied in many applications, such as the immobilization and the separation of proteins or enzymes, and drug administration or purification of Deoxyribonucleic Acid (DNA) [2]. Ferrite also can be used in drugs delivery, hyperthermia treatment, magnetic resonant imaging, cell membranes manipulation, biosensors, bio-labelling and metal ions adsorption [3,4,5]. In their research, Lee et al. [6] reported that the magnetic susceptility of MnFe$_2$O$_4$ (manganese ferrite, 5 $\mu_b$) was higher than others substances, such as CoFe$_2$O$_4$ and NiFe$_2$O$_4$. This can cause the magnetic moment of manganese ferrite correspond to the Neel's coupling scheme [7]. Beside that, the resistivity of MnFe$_2$O$_4$ is much lower than CoFe$_2$O$_4$ and NiFe$_2$O$_4$ [8]. The MnFe$_2$O$_4$ also have higher biocompatibility than Fe$_3$O$_4$, $\gamma$-Fe$_2$O$_3$, CoFe$_2$O$_4$, and NiFe$_2$O$_4$ to be applied as magnetic resonance imaging (MRI) [9].

The study of manganese ferrite continues to grow in recent decades. Many methods were developed to synthesize MnFe$_2$O$_4$ that resulted in various grain size, e.g. 4 nm at 320°C to 154.1 nm at temperature 420°C [10,11]. Generally, co-precipitation is often used for synthesizing MnFe$_2$O$_4$ because the method is simple, and only requires a low temperature reaction [12]. Co-precipitation
method is a chemical process that simultaneously precipitate the normally soluble component with a macro-component from the solution. This is often used to separate the solution from the impurities.

In this research, MnFe₂O₄ nanoparticles will be synthesized from natural iron sand by using co-precipitation method. The synthesis of MnFe₂O₄ was conducted using temperature variations of 70, 100, 130 °C. In order to find the characteristic of MnFe₂O₄ nanoparticles, the sample will be analysed by using XRD, SEM and VSM to determine their physical properties, morphology and magnetic properties.

2. Experimental Method
The raw materials used in the synthesis of MnFe₂O₄ were natural iron sand from Jeneberang river (Gowa district, Sulawesi Selatan) and MnCl₂·4H₂O. The synthesis process was done using co-precipitation method by mixing 8 g of iron sand, 1.017 g of MnCl₂·4H₂O and 25.5 mL of HCl (32%) in the 24.5 mL of aquades until the homogeneous solution obtained. Then, the solution was added dropwise into 100 mL of 2 M NH₂OH, followed by stirring the mixture of solution at 250 rpm for 2 hours. The synthesis temperatures were varied at 70, 100 and 130°C which was referred to T70, T100, and T130 sample, respectively.

After the precipitation of each sample was formed, the precipitation was separated from the solution. Then, the precipitate sample was washed by using aquades to purify the residue salt. Then, MnFe₂O₄ powder sample was dried in the oven at temperature of 70°C. MnFe₂O₄ sample was characterized by using X-ray Diffraction (XRD – Rigaku SmartLab) at a wavelength (λCuKα) of 1.5418 Å, Scanning Electron Microscopy (SEM - Hitachi SU 3500), Vibrating Sample Magnetometer (VSM - Electromagnetic VSM250) to obtain the physical and magnetic properties.

3. Results and Discussion
The X-ray diffraction pattern of MnFe₂O₄ sample is shown in figure 1. The crystallography database of MnFe₂O₄ show that the peaks of each three samples is related to MnFe₂O₄ phase (cubic spinel crystal structure). Based on the analysis result using XRD, the lattice parameter value, crystallite diameter and dislocation density of sample can be calculated using equations 1-3 [13] and the calculated parameters are shown in table 1.

\[ a^2 = \frac{\lambda^2}{4\sin^2\theta} (h^2 + k^2 + l^2) \]  (1)

\[ D = \frac{0.89\lambda}{b\cos\theta} \]  (2)

\[ \delta = \frac{1}{D^2} \]  (3)

where a is lattice parameter, D is crystallite diameter, \( \delta \) is dislocation density, \( \theta \) is diffraction angle, hkl is Miller index, K is Scherrer constant (0.89), \( \lambda \) is wavelength of the x-ray and B is full width at half maximum (FWHM).
Table 1. Lattice parameter, Crystallite diameter and dislocation density of MnFe₂O₄.

| Sample | Lattice parameter (α) (nm) | Crystallite diameter (D) (nm) | Dislocation density (δ) (10¹⁵ line/m²) |
|--------|---------------------------|-------------------------------|--------------------------------------|
| T70    | 0.84                      | 26.37                         | 1.44                                 |
| T100   | 0.84                      | 27.06                         | 1.37                                 |
| T130   | 0.84                      | 29.80                         | 1.13                                 |

Based on the analysis result, the three samples have an identical lattice parameter (0.84 nm). This lattice parameter value has a good agreement compared to the database value of MnFe₂O₄ (0.85 nm). This indicates that the sample of MnFe₂O₄ is well formed. The peaks of the MnFe₂O₄ suggest that higher synthesis temperature can increase the diffraction peak of MnFe₂O₄, thus larger crystallite diameter and unit cell volume could be obtained. This occurs due to the higher synthesis temperature that increases the crystal growth, thus larger diameter crystallite was formed and reduced the dislocation density [13,14].

The magnetic properties analysis are shown in figure 2 and table 2. The results suggested that the magnetisation saturation of MnFe₂O₄ in three different samples: T70, T100 and T130 are 38.75, 37.45, and 33.22 emu/g, respectively. The results shows that the magnetization saturation is inversely proportional to the grain size of the particle where the smallest grain size have a magnetic moment of MnFe₂O₄ that tends to be more unstable. The instability of the magnetic moment on the particles with smaller grain size caused by the anisotropic energy possessed by the particles is much smaller than that of large particles. As a result when an external magnetic field is given, a magnetic moment with smaller grain size will be more reactive in response to the given external field, thus the magnetic moment is easily to be switched [14]. Based on the characterization using VSM, various coercivity values have been obtained: 233.86, 172.41, and 221.71 Oe for the T70, T100, and T130 samples, respectively.

The T70 sample shows the highest value compared to the other samples (T100 and T130), this indicates that the absence of the conformity with the grain size of MnFe₂O₄. The magnitude of the external magnetic field required by the magnetized particles to return to zero is directly proportional to the size of the resulting particles that also affect the coercivity value. However, in this research, the T70 sample has the highest coercivity value caused by the agglomeration effect.
Table 2. Magnetic properties of MnFe$_2$O$_4$.

| Sample | Coercivity ($H_c$) (Oe) | Remanence ($M_r$) (Oe) | Magnetization saturation ($M_s$) (emu/g) |
|--------|-------------------------|------------------------|----------------------------------------|
| T70    | 233.86                  | 7.70                   | 38.75                                  |
| T100   | 172.41                  | 6.59                   | 37.45                                  |
| T130   | 221.71                  | 6.90                   | 33.22                                  |

The morphology analysis of the T70 sample using SEM-EDX spectrum is shown in figure 3. The results suggested that the particles tend to be round in agglomerate condition. This agglomeration occurs as a result of the interaction forces between the surfaces of the magnetic particles. This can be the cause of higher coercivity value in T70 sample compared to other samples (T100 and T130).

Based on the diameter measurement using SEM-EDX, the particle size of 26.45 nm was obtained. This is consistent with the calculation of the crystallite diameter using the scherrer equation (26.37 nm). Based on the EDX spectrum showed that the T70 sample consists of three elements: Mn, Fe, and O that have weight percentages of 6.97, 52.81 and 40.22 wt%, respectively. This corresponds to a sample molecular formula composed of the three elements.
**Table 3.** Element of MnFe$_2$O$_4$ for sample T70.

| Element | Weight (%) |
|---------|------------|
| Fe      | 52.81      |
| O       | 40.22      |
| Mn      | 6.97       |
| Total   | 100        |

**4. Conclusion**

MnFe$_2$O$_4$ based natural iron sand from the Jeneberang river, Sulawesi Selatan has been successfully synthesized using co-precipitation method with various temperatures: 70, 100 and 130°C. XRD pattern suggested that the sample have a dominant phase of MnFe$_2$O$_4$. The physical properties of the sample indicated that the crystallite diameter increase while the dislocation density decrease. The magnetic properties of the sample suggested that lower synthesis temperature have higher magnetization saturation. The morphological analysis indicated that the MnFe$_2$O$_4$ powder samples tend to be round and agglomerate.

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