Synthesis temperature and NaOH concentration dependences of microstructure and magnetic properties of MnNi-Fe$_2$O$_4$ nanoparticles

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Abstract. MnNi-Fe$_2$O$_4$ nanoparticles have been successfully synthesized by coprecipitation method in different synthesis temperatures and NaOH concentrations. Microstructure and magnetic properties of nanoparticles were characterized by X-ray diffractometer (XRD), transmission electron microscope (TEM), fourier transform infra-red (FTIR) spectroscope, and vibrating sample magnetometer (VSM). X-ray diffraction patterns confirmed the formation of spinel structure with crystallite size in the range of 7.5 nm to 14.0 nm. The spectral analysis revealed two characteristic absorption bands related to metal-oxygen vibration in tetrahedral and octahedral site that appeared at 586 cm$^{-1}$ and 432 cm$^{-1}$, respectively. The magnetization saturation within the range of 3.0-8.1 emu g$^{-1}$. The tendency to increase in coercivity from 6.5 to 17.5 Oe was due to the increase in synthesis temperature. The increase in NaOH concentration also affected coercivity to increase from 12.3 to 84.9 Oe.

1. Introduction

Nanosized ferrites have generated much attention because of their unique characteristics compared to bulk size, especially with respect to magnetic properties [1], [2]. The properties of ferrite nanoparticles can meet the need of wide range of technological application, such as: magnetic recording media, spintronic device, transformer, microwave absorber, magnetic resonance imaging (MRI) and hyperthermia therapy [3-6]. The suitability of nanoparticles in different applications also highly depends on specific characteristics, including particle size, size distribution, mechanical hardness, and chemical stability [7, 8].

Spinel ferrite which has general formula MFe$_2$O$_4$ (M = Mn, Ni, Co, Zn, etc.), is one of the ferrite structures that is widely investigated. The oxygen atoms form a cubic close packed structure consisting of two different lattice sites, tetrahedral and octahedral [9]. According to cation distribution in both lattice sites, ferrite can posses normal or invers spinel [10]. Introduction of third metal ion can change the cation occupation of tetrahedral and octahedral sites in the spinel structure [11].

Mn and Ni ferrites have a different tendency to distribute cations in tetrahedral and octahedral sites. MnFe$_2$O$_4$ shows partially inverse spinel structure and possesses characteristics of high anisotropy constant, size-dependent saturation magnetization and high Curie temperature [12], whereas NiFe$_2$O$_4$ shows an inverse spinel structure and possesses the characteristics of low coercivity, moderate magnetization, and high chemical stability [13, 14]. However, Mn-Ni ferrite nanoparticles are known to
exist as partially inverse spinel structure [15]. Replacement cations that occupy lattice sites result in
different cation distribution which enable manipulation of the ferrite properties [16].

As science develops, several methods of synthesis of Mn-Ni ferrite nanoparticles have been proposed
so far, include coprecipitation [17], sol-gel combustion [18], mechanical milling [19], glycol-thermal
[3] dan solvothermal [20]. Among these methods, the products prepared by a coprecipitation method
are relatively uniform and can be obtained in a short time and scaled up for industrial purposes [21].
Moreover, tuning coprecipitation method parameters can control the particle size that has a major
technological importance, because the magnetic properties of nanoparticles are highly size dependent
[22].

A lot of research reports that adjusting synthesis parameter present an influence on the properties
of nanoparticles. For instance, Lamdab et al. [21] prepared MnFe$_2$O$_4$ by coprecipitation method found that
increasing pH value lead to increase crystallite size, particle size, and magnetization saturation. Stein et
al. [23] synthesized CoFe$_2$O$_4$ via coprecipitation method found that increasing synthesis temperature
promoted the increase in grain size, magnetic moment and saturation magnetization.

Study of the properties of manganese ferrite and nickel ferrite have been widely reported, but lack of
investigations can be remarked on the mix manganese and nickel ferrite which obtained by
coprecipitation method. On the other hand, several studies have shown that pH value and applied
temperature in the coprecipitation process determine the physical characteristics of nanoparticles.
Therefore, this work deals with the investigation of Mn-NiFe$_2$O$_4$ nanoparticles and focusing on study of
the effect of NaOH concentration and synthesis temperature on microstructure and magnetic properties
of the nanoparticles.

2. Methods

The synthesis of polycrystalline Mn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles were carried out by coprecipitation
method. Briefly, the synthesis procedure starts with making two solutions, solution A and solution B,
with the appropriate stoichiometric ratio. The solution A was a mixture of MnCl$_2$·H$_2$O (Merck,
Germany) and NiCl$_2$·6H$_2$O (Merck, Germany) powders in 25 mL of distilled water, while the solution
B was FeCl$_2$·6H$_2$O (Merck, Germany) powder in 25 ml of distilled water. The solution A and B were
then mixed until homogeneous, and continued with the addition of 3.37 ml of HCl (Merck, Germany).
Separately, 50 ml of NaOH solution was prepared with controlled concentration (4, 6, 8, 10 M) dan
temperature (room temperature (RT), 50, 70, 120 $^\circ$C). The prepared mixed solution was added wisely
into NaOH solution drop by drop under vigorous stirring. The chemical reaction is described by equation
(1).

$$
0.5\text{MnCl}_2(aq) + 0.5\text{NiCl}_2(aq) + 2\text{FeCl}_3(aq) + 8\text{NaOH}(aq) + \text{H}_2\text{O}(l)$$

\[ \text{HCl} \]

$$\text{Mn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4(s) + 8\text{NaCl}(aq) + 5\text{H}_2\text{O}(l)$$

The synthesis temperature and stirring rate were maintained along the precipitation process which
took place within 60 minutes since the dropping starts. After precipitation process, the obtained product
was cooled down to room temperature and washed several times to removed unwanted salt which was
formed as a result of side reaction. The product was then dried at 90 $^\circ$C for 4 h in a furnace to obtain a
dried powder of Mn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles.

Crystalline phase of nanoparticles was investigated by X-ray diffractometer (XRD) Rigaku MiniFlex
600 Benchtop. The scans of diffracted x-ray were collected over a 20 range of 20$^\circ$ to 80$^\circ$ with a step size
of 0.02$^\circ$ using CuKα radiation. Scherrer equation, \( t = 0.91 \lambda/(B \cos \theta) \), was used to calculate the average
crystallite size. The chemical bonds contained in the nanoparticles were detected by Fourier transform
infra-red (FTIR) spectrometer Prestige Shimadzu-21. The infra-red transmittance spectra were measured
within the frequency range of 400 cm$^{-1}$ to 4000 cm$^{-1}$. Transmission electron microscope (TEM) Jeol
Jem-1400 was used to display morphology of nanoparticles according to the transmitted electron images in magnification up to a scale of 20 nm. Selected area electron diffraction (SAED) from TEM measurement was also recorded to study the microstructure characteristics. The magnetization measurement was performed with a Vibrating sample magnetometer (VSM) Riken Denshi Co Ltd. at room temperature and maximum magnetic field of 15 kOe.

3. Results and Discussions

3.1. Crystal structure analysis

The microstructural characteristics for all samples with different NaOH concentration and synthesis temperature were characterized by XRD, as shown in figure 1. The diffraction pattern match well with the standard reference patterns of MnFe$_2$O$_4$ (JCPDS card no. 10-0319) and NiFe$_2$O$_4$ (JCPDS card no. 10-0325). All major peaks indicate the formation of single crystalline phase of MnNi-Fe$_2$O$_4$. The peaks of (220), (311), (222), (400), (511), (440) and (622) confirm the formation of cubic spinel structure with space group Fd3m. The peak of (311) shifts at 2θ axis, suggesting that there might be distortion due to cation occupation at interstices of ferrite structure [24]. The distortion causes strain on crystal lattice of nanoparticles which is seen as lower angle of diffraction peak.

![Figure 1. X-ray diffraction pattern of MnNi-Fe$_2$O$_4$ (a) variation of NaOH concentration (b) variation of synthesis temperature.](image)

Peak of (311) in figure 1(a) clearly shows that sample with 8 M NaOH concentration possesses the highest degree of crystallinity among samples with different NaOH concentrations. As the NaOH concentration increases from 4 M to 8 M, the crystallinity of nanoparticles increases, and then decreases for further concentration. Adding more NaOH makes the number of OH$^-$ ions in the solution increase which results in a more alkaline solution. In the coprecipitation method, solutions with alkaline conditions (pH > 7) are needed to accelerate the precipitation process which leads to increasing the rate of nucleation. These results indicate a critical pH value to produce optimum degree of crystallinity of nanoparticles. Degree of crystallinity also affected by synthesis temperature, as shown in figure 1(b). The crystallinity of the nanoparticles increases with an increase in synthesis temperature due to the contribution of thermal energy to the nucleation process [25].

The relation between synthesis parameters and microstructural parameter of nanoparticles is presented by figure 2. The average crystallite size calculated using Scherrer’s formulae tends to decrease with the increase in NaOH concentration and synthesis temperature. This finding is in contrast to the
results of other studies which found that crystallite size increased by increasing NaOH concentration and synthesis temperature as a result of increased crystal growth rate [21], [26]–[28]. The lattice constants of all samples have varying values. This can happen when the obtained nanoparticles are formed not in exact same cations distribution, due to the fact that Mn and Fe ions can occupy both tetrahedral and octahedral sites. In this case, the ionic radii of Mn$^{2+}$ in tetrahedral (0.80 Å) is larger than Mn$^{3+}$ in octahedral (0.66 Å), Fe$^{3+}$ in octahedral (0.645 Å) larger than in tetrahedral (0.49 Å), while Ni$^{2+}$ (0.79 Å) [29], [30]. Larger ion substitution generally makes the lattice parameters increase, and vice versa [31].

![Figure 2](image_url)

**Figure 2.** Relation between structural parameter and (a) NaOH concentration (b) synthesis temperature.

![Figure 3](image_url)

**Figure 3.** FTIR spectra of MnNi-Fe$_2$O$_4$.

### 3.2. Functional group analysis

The confirmation about spinel structure of nanocrystalline MnNi-Fe$_2$O$_4$ was also supported by FTIR spectra, as shown by figure 3. The transmission spectra present two absorption bands in the range of 400 cm$^{-1}$ to 600 cm$^{-1}$ which are a common feature of spinel ferrite. The higher frequency of absorption band is assigned to the stretching vibration of functional groups between metal ion in tetrahedral site with oxygen ion (M$_{tet}$-O), and the lower frequency is assigned to the stretching vibration of functional
groups between metal ion in octahedral site with oxygen ion (M_{oct}-O). The vibration of the functional group in the tetrahedral sites appears at a higher frequency than those for octahedral sites as a result of the smaller bond length between M-O [32]. The absorption bands at frequency of 3387 cm\(^{-1}\) and 1628 cm\(^{-1}\) are ascribed to the bending vibration of O-H and bending vibration of H-O-H, respectively. These bands appear due to the presence of absorbed and free water molecule from the ambient atmosphere [33].

3.3. Morphology analysis

The TEM micrograph and SAED pattern for MnNi-Fe\(_2\)O\(_4\) powder synthesized at 70°C and 8 M of NaOH concentration are displayed in figure 4. The ferrite sample possesses spherical-like morphology with unclear grain boundaries and strongly agglomerated. The agglomeration tends to occur in nanosized ferrite due to magnetic interparticle interactions and large nanoparticle surface reactivity [34]. The SAED pattern shows continuous and diffuse rings that indicate fine-sized particles and low crystalline nature. Each diffraction rings correspond to crystallography planes of (311), (411) and (511) which are the characteristic planes of spinel structure and confirm the XRD measurement.

![Figure 4](image)

**Figure 4.** (a) TEM image and (b) SAED pattern of MnNi-Fe\(_2\)O\(_4\).

![Figure 5](image)

**Figure 5.** Hysteresis loop of MnNi-Fe\(_2\)O\(_4\) (a) variation of NaOH concentration (b) variation of synthesis temperature.
3.4. Magnetic measurement

The room temperature field dependent magnetic properties of all investigated samples are presented in Figure 5. All samples show ferrimagnetic behaviour with relatively low coercivity and unsaturated magnetization. The unsaturated magnetization generally attributed to the finite size effect and disordered spins at the surface paramagnetic dead layer of nanoparticles. As materials become smaller, the surface paramagnetic dead layer increases, therefore the magnetization cannot be saturated even at high magnetic fields [35].

Table 1. Crystallite size, strain, coercivity, maximum magnetization and magnetic anisotropy constant of MnNi-Fe$_2$O$_4$ nanoparticles synthesized at different NaOH concentration and synthesis temperature.

| Synthesis parameter | Sample type | Crystallite size (nm) | Strain | Coercivity (Oe) | Maximum magnetization (emu.g$^{-1}$) | $K$ (erg.g$^{-1}$) |
|---------------------|-------------|-----------------------|--------|----------------|------------------------------------|------------------|
| NaOH concentration  | 4 M         | 14.0                  | 0.03   | 122.1          | 4.9                                | 0.3              |
|                     | 6 M         | 9.6                   | 0.04   | 195.5          | 3.0                                | 0.3              |
|                     | 8 M         | 8.5                   | 0.05   | 173.5          | 4.6                                | 0.4              |
|                     | 10 M        | 8.7                   | 0.05   | 849.1          | 8.1                                | 3.4              |
| Synthesis temperature | RT         | 9.5                   | 0.05   | 64.7           | 4.2                                | 0.1              |
|                     | 50°C        | 9.3                   | 0.05   | 127.2          | 3.6                                | 0.2              |
|                     | 70°C        | 8.5                   | 0.05   | 173.5          | 4.6                                | 0.4              |
|                     | 120°C       | 7.5                   | 0.06   | 174.8          | 5.3                                | 0.5              |

The estimated values of maximum magnetization, coercivity, and anisotropy constant for all samples with various NaOH concentration and synthesis temperature are given in table 1. The increase in coercivity values have been observed from 122 Oe to 849 Oe with an increase in NaOH concentration. Similarly, the coercivity values were also found to increase from 64.7 Oe to 174.8 Oe as the synthesis temperature increases. The reason of the increase in coercivity with increase in NaOH concentration and synthesis temperature can be understood by considering multi-domain structure. For particle size above the critical limit of single domain structure, the decrease in particle size leads to the increase of magneto-static energy, hence rise the coercivity [36]. The increase in coercivity could be also related to the formation of defective structure which is directly related to the strain, as indicated by XRD analysis. Strain may induce the additional uniaxial magnetic anisotropy, i.e. stress anisotropy, which contributes to the overall magnetic anisotropy of material. As it is well known, the magnetic anisotropy is one of important parameters which induces the enhancement of coercivity.

The maximum magnetization does not show certain trend with the increase in NaOH concentration and synthesis temperature. The values are in the range of 3.0 emu g$^{-1}$ to 8.1 emu g$^{-1}$ for samples of NaOH concentration variation and in the range of 3.6 emu g$^{-1}$ to 5.3 emu g$^{-1}$ for samples of synthesis temperature variation. However, there might be different parameters which influence the value of saturation magnetization in the spinel ferrite systems, including particle size, degree of crystallinity, strain and partial amorphization at the grain boundaries [37, 38].

4. Conclusion

Powder of MnNi-Fe$_2$O$_4$ nanoparticles has been successfully synthesized by coprecipitation method. Synthesis was performed under different NaOH concentration and synthesis temperature. The average crystallite size tends to decrease with the increase of NaOH concentration and synthesis temperature. Analysis of magnetic measurement showed the increase in coercivity value due to the increase in strain and the decrease in particle size of multi-domain structure that leads to the increase of magneto-static energy.
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