

## PHASE TRANSITION IN $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ NANOCOMPOSITES BY SINTERING PROCESS

Muhammad Ghufron, Malik Anjelh Baqiya, Mashuri, Triwikantoro and Darminto

Dept. of Physics, Fac. of Math. and Natural Sciences-Sepuluh November Institute of Tech. Surabaya  
Kampus ITS Sukolilo, Surabaya 60111, Indonesia  
e-mail : darminto@physics.its.ac.id

### ABSTRACT

**PHASE TRANSITION IN  $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$  NANOCOMPOSITES BY SINTERING PROCESS.**  
 $\text{Fe}_3\text{O}_4$  powders have been successfully produced by using coprecipitation method. The characterization using X-Ray Diffraction method resulted in the size of  $\text{Fe}_3\text{O}_4$  powders of  $9.1 \pm 0.3$  nm. Samples were then formed into pellets and powders. Heat treatment at temperature  $600^\circ\text{C}$  of powder samples for 1 hour and 2 hours give maghemite and hematite phases, but heat treatment at temperature  $700\text{-}800^\circ\text{C}$  for 1 hour, 2 hours and 3 hours give only one phase namely hematite. Heat treatment at temperature  $600^\circ\text{C}$ ,  $700^\circ\text{C}$  and  $800^\circ\text{C}$  of pellets for 1 hour, 2 hours and 3 hours give also only one phase which is hematite. Quantitative analysis using MAUD program resulted in  $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$  composites with changing crystal size at increasing temperature.

**Key words :** Coprecipitation,  $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$  composites, XRD, Phase transition,  $\text{Fe}_3\text{O}_4$  powder

### ABSTRAK

**TRANSISI FASA PADA KOMPOSIT NANO  $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$  DENGAN PROSES SINTERING.**  
Dalam riset ini serbuk  $\text{Fe}_3\text{O}_4$  telah berhasil disintesis dengan menggunakan proses kopresipitasi. Karakterisasi dengan menggunakan metode difraksi sinar-X memperlihatkan ukuran kristal dari serbuk  $\text{Fe}_3\text{O}_4$  sebesar  $9,1 \pm 0,3$  nm. Sampel ini kemudian dibentuk menjadi pelet dan serbuk. Perlakuan panas pada suhu  $600^\circ\text{C}$  pada serbuk selama 1 jam dan 2 jam menghasilkan fasa *maghemite* dan *hematite*, namun perlakuan panas pada suhu  $700^\circ\text{C}$  hingga  $800^\circ\text{C}$  pada 1 jam, 2 jam dan 3 jam menghasilkan fasa tunggal yaitu *hematite*. Perlakuan panas pada  $600^\circ\text{C}$ ,  $700^\circ\text{C}$  dan  $800^\circ\text{C}$  pada pelet selama 1 jam, 2 jam dan 3 jam juga menghasilkan fasa tunggal yaitu *hematite*. Analisis kuantitatif dengan menggunakan program MAUD menghasilkan komposit  $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$  dengan perubahan ukuran kristal bila suhu dinaikkan.

**Kata kunci :** Kopresipitasi, Komposit  $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ , XRD, Transisi fasa, Serbuk  $\text{Fe}_3\text{O}_4$

### INTRODUCTION

Many researchers have recently employed various methods to obtain magnetic nanocrystal with size reduction and dimensional modification. They have tried to examine magnetic, optic, and electronic properties, and even the surface reactivity of these materials. Iron oxides are common compounds which are widespread in nature and readily synthesized in laboratories. Iron oxides in nano crystal size can improve and repair materials performance. That is why it is very important to control particle size, its morphology and texture, shape, and distribution of synthesized iron oxides [1].

Magnetite ( $\text{Fe}_3\text{O}_4$ ) is one of iron oxide phase and member of inverse spinel structure, in which the divalent ions are on octahedral sites, and the trivalent ions are equally divided between tetrahedral and octahedral sites [2]. Its general chemistry

name is *ferrous-ferric oxide*. Magnetite's chemical formula is often written in  $\text{FeO}\cdot\text{Fe}_2\text{O}_3$  form with one part is wustite ( $\text{FeO}$ ) and another part is hematite ( $\text{Fe}_2\text{O}_3$ ).

Research shows there is phase transformation from  $\gamma\text{-Fe}_2\text{O}_3$  to  $\alpha\text{-Fe}_2\text{O}_3$  in  $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$  nanocomposites at temperature  $550^\circ\text{C}$  [3]. Another study discuss the temperature effect in  $\alpha\text{-Fe}/\text{Fe}_3\text{O}_4$  composite at range  $100^\circ\text{C}$  to  $400^\circ\text{C}$  [4]. In present study, it is shown that  $\text{Fe}_3\text{O}_4$  powder and bulk (pellete) will transform completely to  $\text{Fe}_2\text{O}_3$  (hematite) in different temperature of heat treatment. In this paper,  $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$  composites were obtained from heating process of  $\text{Fe}_3\text{O}_4$  nanopowders and their bulk form in the range from  $100^\circ\text{C}$  to  $400^\circ\text{C}$ . The goal is to study the different phase transition in powder and bulk related to structural properties based on XRD analysis.

## EXPERIMENTAL METHOD

### Synthesis of Fe<sub>3</sub>O<sub>4</sub> Nanopowders

Fe<sub>3</sub>O<sub>4</sub> nanopowders were synthesized by coprecipitation technique using HCl as solvent and NH<sub>4</sub>OH as precipitate agent without calcinations. This method can be done at low temperature and give an easy and simple technique to produce nanocrystal materials quickly. Extracted iron sand was used as raw materials. It was solutted in HCl at ~ 70 °C under constant stirring. The resulted solution was added slowly with NH<sub>4</sub>OH. After 30 minutes of the digestion at the same temperature and stirring speed, the black precipitates were formed. These particles were initially washed with distilled water and then dried at 70 °C for five hours.

### Synthesis of Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub> Composites

Fe<sub>3</sub>O<sub>4</sub> nanopowders were divided into two type of samples, powder and bulk (pellete). Each sample was sintered at several temperature, that were 600 °C, 700 °C and 800 °C for 1 hour, 2 hours and 3 hours. The samples were also sintered at temperature 300 °C, 400 °C and 500 °C.

### Characterisation of Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub> Composites

After sintering process, both Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub> powder and bulk samples were analyzed by XRD. (Cu Kα 1,54 Å, 40 kV, 30 mA) for determination of phase, crystal structure and average crystal size using search match and MAUD program.

## RESULTS AND DISCUSSION

Fe<sub>3</sub>O<sub>4</sub> nanoparticles from iron sand have been synthesized using simple coprecipitation method [5]. According to qualitative analysis (search and match program), there is only one phase obtained which is magnetite (Fe<sub>3</sub>O<sub>4</sub>) with PDF Number 11-0614. XRD pattern of this initial phase is shown in Figure 1.

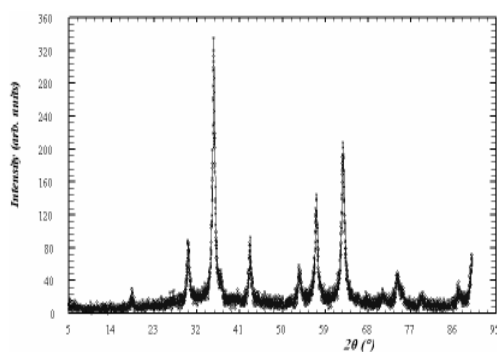


Figure 1. XRD pattern of synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

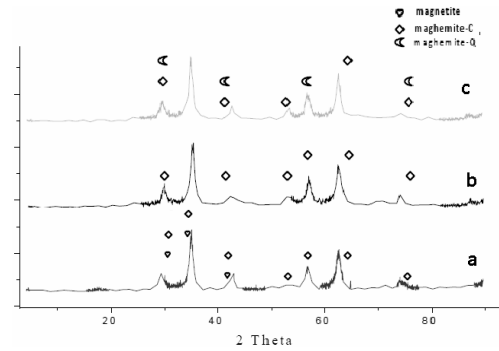


Figure 2. XRD result for pellete samples (a) sintering at temperature 300 °C, (b) sintering at temperature 400 °C, and (c) sintering at temperature 500 °C for 1 hour.

Based on quantitative analysis using MAUD Program [6], it is known that magnetite phase has crystal size  $9.10 \pm 3.25$  nm. This initial sample was then formed into two kinds, powder sample and pellete sample. Both samples were sintered at different duration time and temperature. The sintering temperature variations are 300 °C, 400 °C, 500 °C, 600 °C, 700 °C and 800 °C.

Figure 2 shows XRD result for pellete samples sintered at temperature 300 °C, 400 °C and 500 °C for 1 hour. It is known that there is phase transformation because of increasing temperature from magnetite (Fe<sub>3</sub>O<sub>4</sub>) to maghemite,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phases. When specimen is heated, the particle which initially have Fe<sub>3</sub>O<sub>4</sub> phase gets thermal energy from furnace. The increasing of heating temperature causes the increasing of thermal energy which is given so that atom will vibrate and diffuse at grain boundary.

Phase transformation process start when Fe<sup>2+</sup> ion is oxidated into Fe<sup>3+</sup> ion. These Fe<sup>3+</sup> ions diffuse so that formed  $\gamma$  Fe<sub>2</sub>O<sub>3</sub>. At temperature 300 °C, magnetite phase in pellete sample was partially oxidated, thus there are two phases in the sample, magnetite and maghemite. It might be said that composite was formed in the sample because of increasing temperature at certain value.

Maghemite-C resulted in pellete sample in Figure 2(a) and Figure 2(b) can be indexed using PDF data number 39-1346. New possible phase, maghemite-Q, seems appeared in pellete sample at sintering 500 °C and can be analized using PDF data number 25-1402. Maghemite-Q is maghemite with tetragonal crystal structure. Phase composition exists in this temperature equal to 65.23 % for maghemite-C

Table 1. Crystal size of pellete samples after sintering

T (°C)	Crystal size (nm) at holding time 1 hour		
	Magnetite	Maghemite-C	Maghemite-Q
300	19.2 ± 1.7	5.1 ± 0.5	(none)
400	(none)	9.8 ± 0.5	(none)
500	(none)	20.9 ± 2.1	8.1 ± 0.9

and 34.77 % for maghemite-Q. It should be a nanocomposite here.

From quantitative analysis using MAUD Program, phase composition of pellete sample sintered at 300 °C are magnetite and maghemite phase of 37,96 % and 62,04 %, respectively. Crystal sizes of pellete samples after sintering at 300 °C, 400 °C and 500 °C for 1 hour are shown in Table 1. Crystal size tends to increase as sintering temperature increase.

Higher sintering temperature, higher diffusion occur in all of the sample, thus higher crystal size. At constant temperature, for example 600 °C in Figure 3, diffusion took place between particle at grain boundary and resulted in larger grain. Phase transformation from magnetite to hematite happened at temperature < 500 °C for pellete samples. Below 500 °C, the phase transform slowly until reaching temperature around ~450 °C. At temperature 500 °C, crystallization of hematite will be initiated and grown to hematite phase rapidly [7]. XRD pattern of samples sintered at temperature 600 °C with different sintering time can be seen in Figure 3 and Figure 4 for powder and pellete specimen respectively.

According to Figure 3 and Figure 4, it can be observed that there are differences in the diffraction pattern between pellete (bulk) and powder sample. In bulk sample, sintering at 600 °C for 1 hour even for 2 hours, etc, will result in direct transformation from magnetite (initial) to hematite phase (PDF Number 13-0534). While for the powder sample sintering at

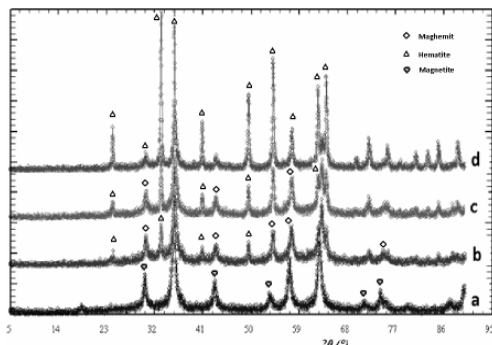


Figure 3. XRD pattern for (a) initial powder; powder sample sintered at 600 °C during (b) 1 hour, (c) 2 hours and (d) 3 hours.

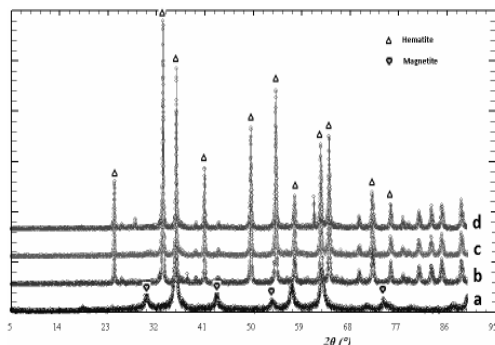


Figure 4. XRD pattern for (a) initial powder; pellete/bulk sample sintered at 600 °C during (b) 1 hour, (c) 2 hours and (d) 3 hours.

Table 2. Phase Transformation for bulk and powder samples sintered at different temperature and holding time.

T (°C)	t (h)	Initial Phase	Phase after sintering	
			Pellete (Bulk)	Powder
600	1	Magnetite	Hematite	Maghemite and Hematite
600	2	Magnetite	Hematite	Maghemite and Hematite
600	3	Magnetite	Hematite	Hematite
700	1	Magnetite	Hematite	Hematite
700	2	Magnetite	Hematite	Hematite
700	3	Magnetite	Hematite	Hematite
800	1	Magnetite	Hematite	Hematite
800	2	Magnetite	Hematite	Hematite
800	3	Magnetite	Hematite	Hematite

600 °C for 1 hour and 2 hours, will give two phases, that is maghemite and hematite. But for 3 hours sintering, the powder transform to hematite entirely. This phase transition occurs even in the same temperature because duration of sintering time also responsible for ionic diffusion in the material. Longer sintering time, it makes possible ionic arrangement to form other crystal structure which more stable in the current temperature. If the phase already reach its stability, then longer sintering time can increase crystal size. This condition can occur because of ionic vibration at grains and their boundaries.

Percentage of maghemite and hematite phase are 33.01 % and 66.99 % respectively for powder sample sintering at temperature 600 °C during 1 hour. While for sample sintered at temperature 600 °C for 2 hours, maghemite and hematite phase of 10.32 % and 89.68 % respectively are obtained. The forming of these two phases expresses that the two powder samples have come to be nanocomposite, with maghemite phase as filler and hematite phase as matrix.

Table 2 shows the result of qualitative analysis using search-match program for samples with sintering temperature of 600 °C, 700 °C, and 800 °C for 1 hour, 2 hours and 3 hours. Table 2 shows that Fe<sub>3</sub>O<sub>4</sub> nanoparticles (magnetite phase) will transform to hematite phase perfectly after sintering at temperature above 600 °C for 3 hours.

Figure 5 and Figure 6 represents that for both samples (powder and bulk), increasing temperature may cause in increasing crystal size which is signed by decreasing of FWHM values in each peak of XRD patterns. Once again, ionic (atomic) diffusion and vibration take place here.

Tables 3-4 show crystal size value for both sample (powder and bulk) analyzed using MAUD Program.

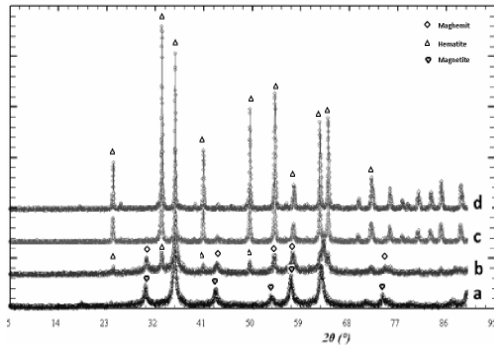


Figure 5. XRD pattern for (a) initial sampel without sintering, powder samples sintered for 1 hours at (b) 600 °C (c) 700 °C and (d) 800 °C.

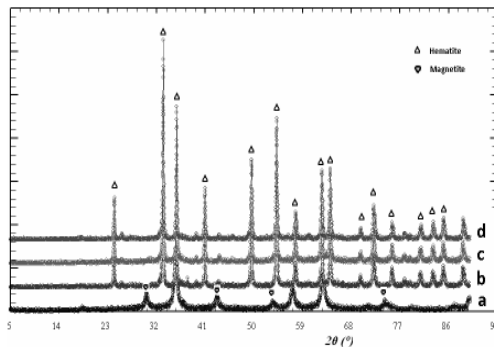


Figure 6. XRD pattern for (a) initial sampel without sintering; pellete / bulk samples sintered for 1 hour at (b) 600 °C (c) 700 °C (d) 800 °C

According to Tables 3-4, it can be observed clearly as mentioned before that the increasing of sintering temperature causes the increasing of crystal size. The increasing of holding time also yields the increasing of crystal size. Pellete samples have smaller crystal size than powder samples at the same temperature and sintering time. This may occur because pellete samples have fixed form and there is internal pressure (residual stress) in bulk samples caused by compaction, while the powder one do not have residual stress and they are not limited by room. When pellete samples are sintered at higher temperature, thermal energy activation for diffusion energy is distributed more rapid so they transform to hematite phase quicker than powder samples.

When the particle sintered at the same temperature, they have same energy for diffusion process. It should cause crystal size progressively increase, but at certain size, this increasing will reach maximal value. If the sintering still continues, pellete samples which are limited by certain available space may have large microstrain and the grain will brake (known *broken grain*) so that grain becomes apart. The higher microstrain value in pellete sample was proved by MAUD analysis. Effect of this broken grain is crystal size of pellete sample become smaller than powder sample at the same temperature with longer sintering time. This case is clearly observed at sintering

Table 3. Powder sample crystal size after sintering analyzed using MAUD software

T (°C)	Crystal size (nm)		
	1 hour	2 hours	3 hours
600°C	Maghemite 35,53 ± 0.04	Maghemite 43,70±0.03	71.5 ± 0.02
	Hematite 55,30 ± 0,03	Hematite 67,80±0,02	
700°C	88.12 ± 0.04	123.8 ± 6.30	193.5 ± 0.02
800°C	171.20 ± 0.03	205.6 ± 0.02	206.8 ± 0.03

Table 4. Pellete sample crystal size after sintering analyzed using MAUD software

T (°C)	Crystal size (nm)		
	1 hour	2 hours	3 hours
600	126.0 ± 0,03	168.8 ± 0.04	193.5 ± 0.02
700	88.5 ± 0.20	100.0 ± 0.03	119.5 ± 0.03
800	148.6 ± 0.03	176.9 ± 0.01	178.3 ± 0.01

temperature 800 °C during 1 hour, 2 hours and 3 hours for both samples.

## CONCLUSION

Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized from iron sand by coprecipitation technique result in nanomaterial which crystal size value is 9.1 ± 0.03 nm. This material was used as raw material to obtain Fe<sub>3</sub>O<sub>4</sub> / Fe<sub>2</sub>O<sub>3</sub> composites. The formed phases in the powder are hematite and maghemite-C which may occur at sintering temperature below 600 °C for 2 hours. Sintering the pellete samples at temperature between 300 °C to 500 °C may cause the formation of maghemite-C, maghemite-Q and hematite phase. Sintering the sample at temperature above 600 °C during 3 hours will result in entirely transformation of the sample to hematite phase without any other phases. Sintering at elevated temperature and sintering time can increase crystal size of the obtained phase(s). It is caused by thermal activation which affect diffusion and atomic vibration of the sample.

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