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Crystal Structure Evolution of Magnetite Ferrofluids: Effect of Heating Treatment

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Abstract. This work aimed at investigating the crystal evolution, crystallite phase, morphology, and particle size of the magnetite ferrofluids as the effects of heating temperature. The iron sand was used to prepare magnetite ferrofluids by employing a simple chemical method. The high-resolution transmission microscopy characterization presented that the particle size and morphology were expanded from small to bigger size in nanometric size with aggregation. The electron and X-ray diffractions patterns exhibited that the magnetite particles in the fluids evolved from Fe_3O_4 (cubic structure) structure to α-Fe_2O_3 (rhombohedral structure) as the effect of heating treatment. At a temperature of 500 ^{0}C, the magnetite particles had a mixed crystallite phases consisting of α-Fe_2O_3 and Fe_3O_4 structures. Interestingly, at the temperature of 600 ^{0}C or higher, the magnetite particles in the fluids changed to the pure α-Fe_2O_3 structure. Such evolution phenomenon gives significant information in designing new sophisticated application of the magnetite ferrofluids, especially for the temperature sensor.

Keywords: Crystal structure, α-Fe_2O_3, Fe_3O_4, ferrofluid, iron sand.

1. Introduction

In general, the very fast expanding of ferrofluids applications in the last 5 years have been encouraged by the advantageous performances related to their response to applied magnetic fields. Various application fields of ferrofluids that currently is intensively developed by many experts such as for heat transfer augmentations [1], heat transfer enhancements [2], biodiesel productions [3], ferrofluid shock absorbers [4], magnetic hyperthermia [5], microfluidic actuators and devices, seal technology microfluidic valves and pumps, optical applications, ferrofluid lubrication of bearings, dynamic or static magnetically driven assembly of structures, sensor applications [6], and so forth. In general, ferrofluids have been constructed by the magnetic particles in a single domain character such as magnetite (Fe_3O_4) or some metals-doped magnetite.

For specific applications such as for temperature sensor, it is significantly important to produce ferrofluids with a high stability both in physical and chemical properties. Due to the ease of oxidation of ferrofluids, especially magnetite ferrofluids, the investigations associated with the reversible conversion between iron-oxide phases have been intensively conducted by many experts. However, the

investigations focused on microscopic properties that visualize straightly the evolution of crystal structure phase, and particle size of magnetite ferrofluids, have been limited [7]. Therefore, it is essential for examining the crystal structure and particle size evolutions of magnetite ferrofluids as the effect of heat treatment based on in situ experiment. By this experiment, as one of the important fundamental characteristics, the phase stability as one of the requirements of magnetite ferrofluids to be applied in specific applications can be easily determined. Excitingly, the magnetite ferrofluids in this work were prepared from iron sand that serves inexpensive method by utilizing the natural resource.

2. Methods

The preparation of magnetite ferrofluids from iron sand was performed using a simple chemical method. Iron sand was employed as the main precursor to be reacted with chloric acid and then continued with the titration process with ammonium hydroxide to generate magnetite nanoparticles. To obtain magnetite ferrofluids, the magnetite nanoparticles were then coated by tetra-methyl ammonium hydroxide and dispersed in aqueous solution. The detailed experiment for preparing the magnetite ferrofluids was explained in our previous works [8–10]. For X-ray diffraction (XRD) characterization purpose, the samples were heated by varying temperature ranging from ambient temperature, 300, 500, and 600 ^{0}C. The samples were coded by the respective FT1, FT2, FT3, and FT4. Meanwhile, for in-situ method-based high-resolution transmission electron microscopy (HR-TEM) characterization, the magnetite ferrofluids were deposited onto subtracts. The microscopy characterization was maintained by changing the temperature experiment from ambient temperature to 1000 ^{0}C. Furthermore, all the obtained data were analyzed qualitatively and quantitatively to investigate the evolution of crystallite phase as well as lattice parameters, particle size, and morphology.

3. Results and Discussion

According to Figure 1, FT1 and FT2 samples have similar diffraction patterns. Meanwhile, FT3 presents a different pattern of diffraction peaks associated with the presence of a new phase. Furthermore, FT4 sample shows the completely different patterns compared to FT1 and FT2 diffraction patterns indicating the presence of a new phase. The diffraction patterns of FT1 and FT2 samples were identified as pure Fe_3O_4. Meanwhile, the diffraction pattern of FT3 sample presented two phases, i.e., Fe_3O_4 and α-Fe_2O_3. Interestingly, the latest sample (FT4) transformed into a pure phase of α-Fe_2O_3. This transformation or evolution was marked by the presence of new peaks indicating the formation of α-Fe_2O_3. Furthermore, the absence of original peaks in FT4 that previously occurred in FT1 originated from the absence of Fe_3O_4. It means that the heating treatment for the samples gives a significant role in constructing the structure evolution of the magnetite particles. Corresponding with this work, other groups reported that crystal phase evolution from Fe_3O_4 to α-Fe_2O_3 started form temperature of 650 °C and ended at 750 °C [11]. Moreover, Pati and co-workers found that the similar phase evolution occurred at a temperature higher than 450 °C and a pure α-Fe_2O_3 was obtained at a temperature of 600 °C [12].

Another influence of the heating treatment in the sample in this research is the growth of particle size. Referring to Table 1, the increase in sample particle size occurs with increasing heating temperature [13]. In addition, a decrease in the lattice parameters for each sample was also identified. Mahdavi and co-workers found that the decrease in lattice parameters was caused by changes in the composition of oxygen in the sample due to differences in an ambient pressure in the phase formation process [14]. Additionally, the decrease in lattice parameters also has an impact on the decrease in crystal cell volume for each sample. Statistically, all XRD data have a high compatibility with the fitting analysis model which can be determined from the value of goodness of fit (*GoF*) as shown in Figure 1 below.

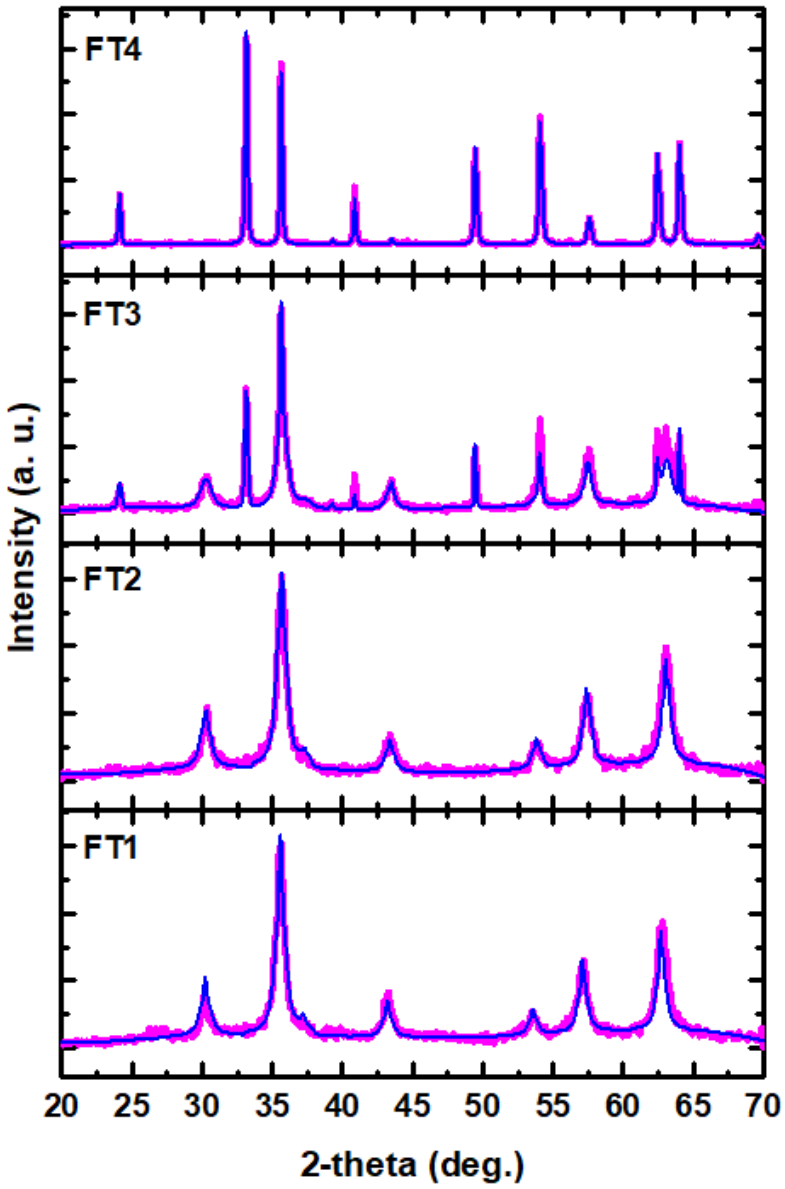

Figure 1. The X-ray diffraction patterns of dried magnetite ferrofluids (blue line represents the calculated data and the magenta line represents the experimental data)

Figure 2 shows the visualization of Fe_3O_4 and α-Fe_2O_3 crystals. In terms of crystal structure, the two phases have different space groups, namely *Fd-3m* and *R-3c* [15]. Fe_3O_4 has an inverse spinel structure while α-Fe_2O_3 has a rhombohedral structure [16,17]. Related to the increase in temperature treatment, the oxygen contained in Fe_3O_4 has a tendency to be oxidized so that Fe_3O_4 ovulates into γ-Fe_2O_3 or α- Fe_2O_3 [18]. Theoretically, Sanson and co-workers explained that the formation of α-Fe_2O_3 is a result of heating treatment resulted in the Fe atom ellipsoid having an oblate spheroid shape with shorter axes along the *c*-axis. While the absolute ellipsoid atom is in a triaxial position with the middle axis along the *a*-axis so that it causes the longest axis leading to the octahedral site empty and the shortest axis leads to the 30°-angle octahedral edge from the *c*-axis [19]. Based on the thermodynamics approach, the crystallite evolution of the magnetite particles is significantly dependent on the activation energy as the function of temperature.

Table 1. The results of refinement analysis for XRD data of the samples

Data	**FT1**	**FT2**	**FT3**		**FT4**
Phase	Fe_3O_4	Fe_3O_4	Fe_3O_4	α-Fe_2O_3	α-Fe_2O_3
a (Å)	8.36	8.34	8.33	5.04	5.04
b (Å)	8.36	8.34	8.33	5.04	5.04
c (Å)	8.36	8.34	8.33	13.76	13.75
Particle size (nm)	14.1	14.4	21.9	71.5	88.6
Gof	1.21	1.21	1.62	1.62	0.73

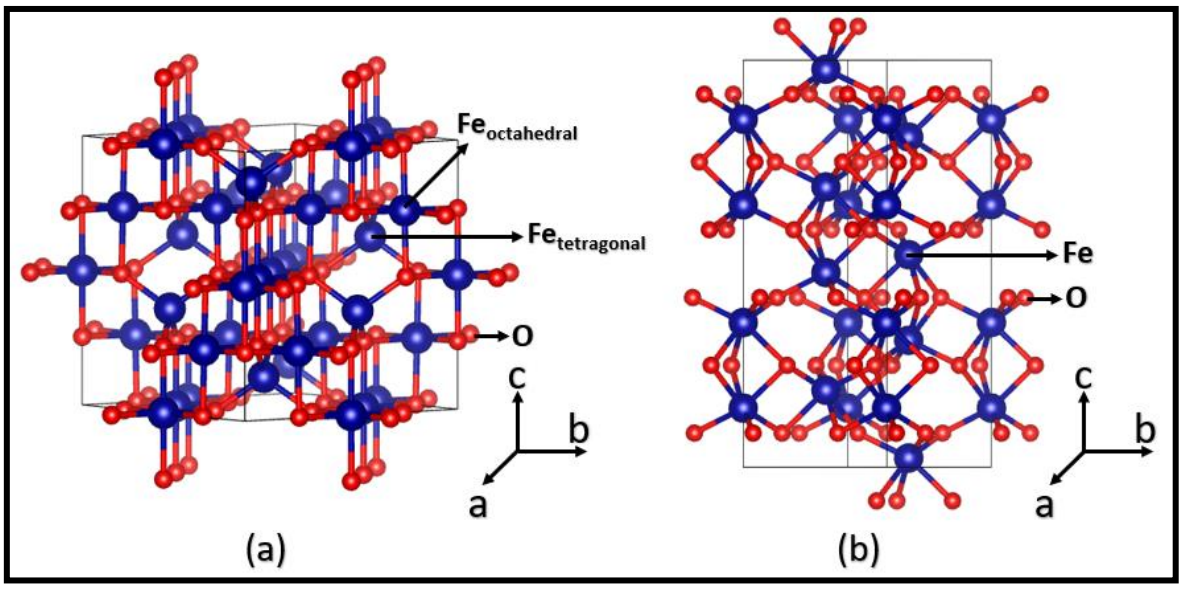

Figure 2. Crystal structures of (a) Fe_3O_4 and (b) α-Fe_2O_3

In order to investigate the phase and particle size evolution of magnetite particles in ferrofluids, we also characterized them by means of in-situ measurement using a high-resolution transmission microscopy combined with electron diffraction. The HRTEM images and electron diffraction data of the in-situ experiment are presented in Figure 3. The HRTEM experiment was conducted by varying the temperature measurement at room temperature, 300, 500, 750, and 1000 ^{0}C. Meanwhile, the electron diffraction experiment was maintained at temperatures of 300 ^{0}C and 1000 ^{0}C.

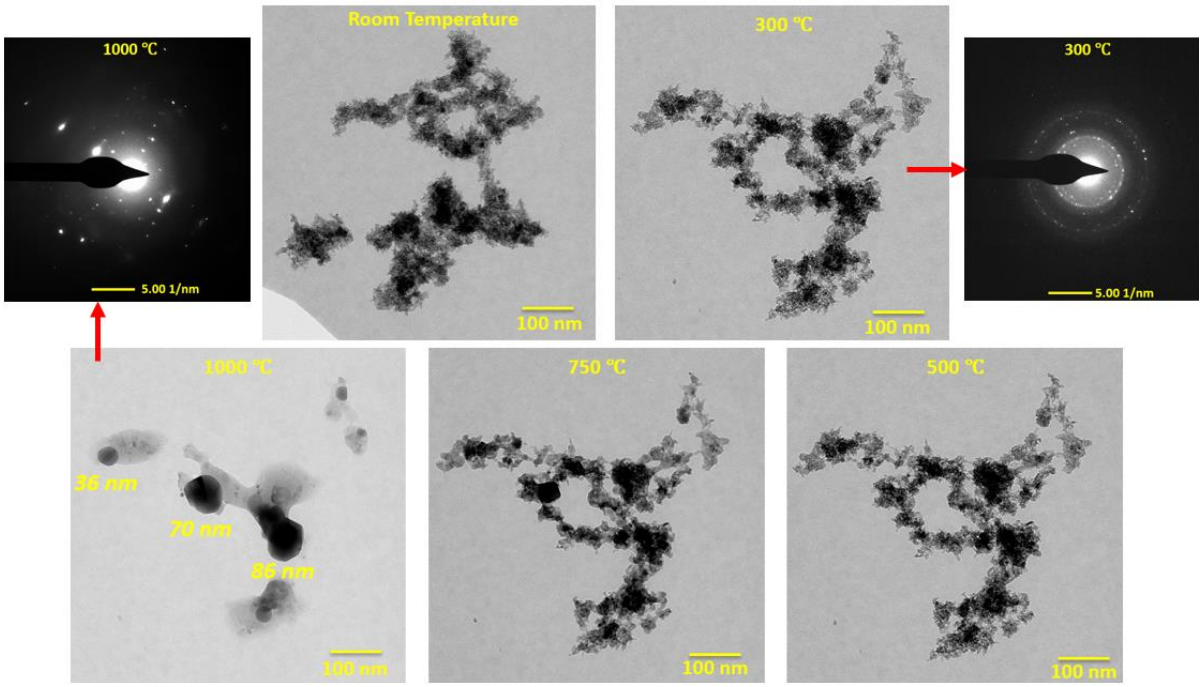

Figure 3. HRTEM images and electron diffraction patterns of magnetite ferrofluids

According to Figure 3, it is clear that the higher temperature during the in-situ experiment, the particle size, and crystallite of magnetite in ferrofluids tends to rise. The particle size of magnetite particles is approximately 10 nm at room temperature. The electron diffraction pattern for the in-situ experiment at 300 °C exhibits a single phase of the Fe_3O_4 structure. Meanwhile, when the ferrofluids heated at 1000 °C, the phase transformed to become a pure α-Fe_2O_3. At a temperature of 1000 ^{0}C, the particle size also increases constructing bigger particles with the size of about 86 nm. In general, such results are interrelated with the data analysis for the X-ray diffraction data indicated by the peaks become sharper. The broadening peaks of X-ray diffraction data for lowering temperature treatment associated with the smaller particle size of the magnetite particles. In line with these results, Sobhi *et al.* and Yuqiu *et al.* report that the increasing reaction and sintering temperature during synthesis increased the particle size of magnetic particles [20,21]. However, their works still have a limitation because they prepared magnetic particles from commercial precursors that are generally more expensive compared to that utilization of natural precursor as conducted in this work. According to the data analysis, it revealed that the particle size of the magnetic particles had still been in the nanometric size below 100 nm. We assumed that this interesting data become physical evidence that the surfactant coating the magnetic particles in the ferrofluids plays as an essential role in inhibiting the particle growth.

4. Conclusion

In this study, the crystal evolution of the magnetite ferrofluids fabricated by iron sand as the effect of heating temperature has been investigated. The electron microscopy data presented that the particle size and morphology of the magnetite particles were grown in nanometric size with aggregation along with the increase of the temperature. The patterns of electron and X-ray diffractions presented that the magnetite particles in the fluids transformed into α-Fe_2O_3 from the Fe_3O_4 structure as the increase of heating treatment. Specifically, the magnetite particles had a combined crystallite phase consisting of Fe_2O_3 and Fe_3O_4 at a temperature of 500 ^{0}C. Furthermore, the magnetite particles in the fluids changed to the pure α-Fe_2O_3 structure at the temperature of 600 ^{0}C or higher.

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