The effect of pH and sintering treatment on magnetic nanoparticles ferrite based synthesized by coprecipitation method

T Saragi1*, B Permana1, M Saputri1, B L Depi1, S W Butarbutar1, L Safriani1, I Rahayu2 and Risdiana1

1Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran, Jl. Raya Bandung-Sumedang km 21 Jatinangor, West Java, Indonesia 45363
2Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran, Jl. Raya Bandung-Sumedang km 21 Jatinangor, West Java, Indonesia 45363

*t.saragi@phys.unpad.ac.id

Abstract. Ferrite nanoparticles synthesized by coprecipitation method depend mostly on parameters synthesis such as reaction temperature, pH of the suspension, and initial molar concentration. Here, we reported the physical properties of nanoparticles magnetite (Fe3O4) synthesized by coprecipitation method with variation of pH in the range between 8 and 11, in order to investigated the effect of pH treatment to its optical properties, particles size, and phase changes after sintering treatment. The band gap parameters of magnetite nanoparticles and crystal structure of magnetite powder are determined. From UV-Vis measurement, it is found that the band gap of magnetite nanoparticles was in the range of 1.3 eV to 1.5 eV with the smallest size of nanoparticles was 9.69 nm obtained at condition of pH=10. From XRD characterization, it was found that all samples sintered at 100°C for 4h have magnetite phase of Fe3O4 with cubic structure, while all samples sintered at 1100°C for 4 h have hematite phase of α-Fe2O3 with hexagonal structure.

1. Introduction
The size of magnetic particles ferrite-based is very important for biological application. In many in-vivo biological applications, the nano-sized of materials is highly beneficial because of it properties that can penetrate cells without any agglomeration in bloodstream. In ferrite-based materials, there is a critical length showing the sized limit in which the materials have two different magnetic properties. For samples that has smaller sized than that of critical length, superparamagnetic state appears showing a strong magnetic properties under an applied magnetic field. In the case of particles size larger than critical length in the few tens of nm, the thermal agitation dominates the ferromagnetic order [1-2]. Magnetite (Fe3O4) with spherical nanoparticles and diameters less than 20 nm, for example, has advantages properties such as chemical stability, chemical and biological compatibility, non-toxicity, high saturation magnetization, Ms (90 emu/gr), environmental stability, simple preparation and can be used for biomedical applications due to their ability to affect the relaxation rate of water proton [3-4].
Controlling the size of nanoparticles in the order of critical length, several methods by using of chemical methods have been done, such as precipitation method [5], sol-gel process [6-8], and hydrothermal synthesis [9-10]. All the methods performed various experimental parameters such as the pH of the solution, ionic strength, capping agent, reaction temperature, composition and pressure. Recently, we have been synthesized iron oxide by using hydrothermal method. However the size of nanoparticles was in hundreds nm [9], so that, the effect of particles size to its phase behavior could not be observed. This nanoparticles was still in large size, due to the solubility of precursor, which is limited to the pressure in reactor [11].

In this paper, we reported the synthesis of iron oxide prepared by co-precipitation method in order to investigate the effect of pH on optical and morphology of nanoparticles and explored the sintering effect on phase change of iron oxide at sintering temperature of 100°C and 1100°C. This method is a simple, reliable and cheap process.

2. Experiment
Magnetite (Fe₃O₄) nanoparticles were synthesized by co-precipitation method. The ratio of Fe²⁺:Fe³⁺ was 1:2, with 25% of NH₃·H₂O solution. 0.033 mol FeCl₃·6H₂O and 0.016 mol FeCl₂·4H₂O were dissolved in 100 ml DI-water. The NH₃·H₂O solution was then drop wisely to the Fe²⁺/Fe³⁺ solution until pH condition reach appropriate value. In this study, we synthesized the magnetite nanoparticles at room temperature (25°C) and pH condition was varied in the range of 8-11 to investigate the effect of pH solution on optical properties, size, and morphology of synthesized magnetite nanoparticles. After the reaction, precipitates of magnetite were washed two times by using of n-hexane and ethanol, and magnetic decantation to remove all the soluble substances. Magnetite nanoparticles was re-dispersed in ethanol and characterized by UV-Vis and TEM measurement. The magnetite nanoparticles was then dried at 80°C, sintered at 1000°C for 4 hours and 1100°C for 4 hours, and characterized by XRD measurement to investigate the phase change of Fe₃O₄.

3. Result and Discussion
After synthesized by co-precipitation method, the precipitates nanoparticles were black color which indicates that the particles formed are magnetite [3]. The absorption spectra of (UV-Vis) of as-prepared nanoparticles magnetite synthesized at various pH condition is shown in figure 1. The normalized UV-Vis spectrum is shown in the left side, and the normalized tauc-plot curve (band gap dependent of (αhν)¹/²) of magnetite nanoparticles is shown in the right side. It can be seen that all samples exhibited strong absorption bands in the visible region. It was calculated that the band-gap are in the range of 1.3 eV – 1.5 eV. The lowest band-gap observed at sample prepared at pH condition of 11, while the largest band-gap observed at sample prepared at pH condition of 10. All the band-gap values were less than 2 eV and it is indicated the band-gap is in direct transition [12].

![Figure 1.](image)
The value of band-gap and the average diameter of magnetite (Fe₃O₄) nanoparticles growth at room temperature with various pH conditions is shown in table 1. The morphology and size of particles were determined by TEM. The mean particles and distribution were determined by size average of some transparent particles which are randomly selected on the TEM image. Figure 2 shows TEM image of magnetite nanoparticles synthesized at room temperature with various of pH condition of 8 (A1), 9 (A2), 10 (A3), and 11 (A4) with scale bar of 20 nm. It is found that samples are mainly composed of quasi-spherical particles. The smallest average size of magnetite nanoparticles is 9.69 ± 1.06 nm observed at pH condition of 10 and the largest size of magnetite nanoparticles is 12.48 ± 0.85 nm observed at pH condition of 9.

**Table 1.** The band-gap properties and average size of Fe₃O₄ nanoparticles growth at room temperature with various pH condition.

| Sample | pH | Band-gap (eV) | Average of Diameter (nm) |
|--------|----|---------------|--------------------------|
| A1     | 8  | 1.4           | 11.03 ± 1.06             |
| A2     | 9  | 1.4           | 12.48 ± 0.85             |
| A3     | 10 | 1.5           | 9.69 ± 1.06              |
| A4     | 11 | 1.3           | 13.24 ± 1.62             |

**Figure 2.** The TEM image of magnetite nanoparticles (Fe₃O₄) with scale bar of 20 nm growth at room temperature with various pH condition of (A1) pH = 8, (A2) pH=9, (A3) pH=10 and (A4) pH=11.
The structural analysis of a dried powder of magnetic particles was conducted by using of XRD with radiation source of Cu-Kα. Figure 3(a) illustrates the XRD pattern of iron oxide growth at room temperature with various pH condition and sintered at 100°C for 4 hours (a) and 1100°C for 4 hours, respectively. From XRD measurement, it was found that all samples sintered at 100°C for 4h have a low quality of crystal characteristics, while all samples sintered at 1100°C for 4 hours have a high quality of crystal characteristics. The XRD patterns of sample sintered at 100°C for 4 hours have all characteristic peaks of magnetite Fe₃O₄ with cubic phase and consistent with JCPDS data #11-614, and the XRD patterns of sample sintered at 1100°C for 4 hours had all characteristic peak of hematite α-Fe₂O₃ without impurity peak with hexagonal phase and consistent with JCPDS data #1309-37-1. This experiment shows that the sample sintered at 1100°C for 4 hours is hexagonal phase [9]. It was found that samples sintered at high temperature of 1100°C transformed from cubic phase of Fe₃O₄ to hexagonal phase of α-Fe₂O₃ without any influence of pH value. This transformation is probably due to the arrangement of Fe and O ions in unit cells. Compared with another report, it is found that samples sintered at 100°C have similar crystal structure of cubic phase [3], while samples sintered at 1100°C in this report, has different crystal structure with samples sintered at 1000°C [3]. It is found that crystal structure changes with increasing sintering temperature from rhombohedral α-Fe₂O₃ at sintering temperature of 1000°C to hexagonal α-Fe₂O₃ at sintering temperature of 1100°C.

![Figure 3](image_url)

**Figure 3.** The XRD pattern of iron oxide growth at room temperature with various of pH condition and (a) sintered at 100°C for 4 hours and (b) 1100°C for 4 hours respectively.

The average crystallite size in the sample was calculated using the Scherrer equation [13] and tabulated in table 2. The largest size of iron oxide was 81.02 nm. It is indicated that the sample growth at pH of 10 has the best condition.

**Table 2.** The crystal size of iron oxide sintering at 1100 °C for 4h calculated by using of Debye-Scherrer equation.

| Sample | pH  | Average of diameter (nm) |
|--------|-----|--------------------------|
| A1     | 8   | 64.80                    |
| A2     | 9   | 54.00                    |
| A3     | 10  | 81.02                    |
| A4     | 11  | 54.00                    |
4. Conclusion
The synthesis of magnetite (Fe$_3$O$_4$) has been successfully prepared by co-precipitation method. The obtained nanoparticles have been synthesized in different pH condition of 8, 9, 10 and 11, and different sintering temperature of 100°C and 1100°C. All samples were mainly composed of quasi-spherical particles with the smallest average size of magnetite nanoparticles of 9.69 nm observed at pH condition of 10 and the largest size of magnetite nanoparticles was 12.48 nm observed at pH condition of 9. It is found that samples sintered at 100°C have crystal structure of magnetite Fe$_3$O$_4$ with cubic phase, while sample sintered at 1100°C have crystal structure of hematite $\alpha$-Fe$_2$O$_3$. Samples sintered at 1100°C transformed from cubic phase of Fe$_3$O$_4$ to hexagonal phase of $\alpha$-Fe$_2$O$_3$ without any influence of pH value. Crystal structure changes with increasing sintering temperature from rhombohedral $\alpha$-Fe$_2$O$_3$ at sintering temperature of 1000°C to hexagonal $\alpha$-Fe$_2$O$_3$ at sintering temperature of 1100°C.

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