Effect of Synthesis Parameters on Crystals Structures and Magnetic Properties of Cobalt Nickel Ferrite Nanoparticles

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Abstract. Co₀.₅Ni₀.₅Fe₂O₄ magnetic nanoparticles have been successfully synthesized by co-precipitation method with varying synthesis temperature and NaOH concentration. X-ray diffraction (XRD) analysis confirmed that Co₀.₅Ni₀.₅Fe₂O₄ nanoparticles have spinel cubic crystal structure. The particle size of the sample synthesized at 3 M NaOH was 7.3 nm and then increased with the increase of NaOH concentration. It is caused by the increase of particle growth rate. The particle size of the sample synthesized at 30 °C was 10.2 nm and then increased with the increase of temperature. The lattice parameter of the sample was constant at 8.5 Å with varying synthesis temperature and NaOH concentration. The maximum magnetization and the coercivity of the sample synthesized at 3 M NaOH was 11.3 emu·g⁻¹ and 0.1 kOe, respectively, and then increased with the increase of NaOH concentration. It is caused by the increase of crystallite size in a single domain. The maximum magnetization and the coercivity of the sample synthesized at 30 °C was 9.9 emu·g⁻¹ and 0.1 kOe, respectively, and then increased with the increase of temperature. Transmission Electron Microscopy (TEM) image showed that the sample was agglomerated. Selective Area Electron Diffraction (SAED) image shows that sample is confirmed peak is appearing in XRD. The Fourier Transform Infra-Red (FTIR) spectra confirmed that vibration of octahedral and tetrahedral metal-oxide bond is 601.8 cm⁻¹ and 370.3 cm⁻¹. The purpose of this work is to investigate the effect of synthesis temperature and NaOH concentration on the relation between crystal structure and magnetic properties.

Keywords. Cobalt Nickel Ferrite, Magnetic Properties, Nanoparticles, Synthesis Parameter

1. Introduction

Recently, magnetic nanoparticles have been interested subject, because of unusual fundamental characteristic as well as their application such as magnetic drugs delivery and recording storage. MFe₂O₄ Spinel ferrite (where M = Co²⁺, Ni²⁺, Fe²⁺, Mg²⁺) is an important group of magnetic materials because of their magnetic properties and wide practical applications. Due to the unique structure, morphology, chemical, mechanical, optical, electrical and magnetic properties, the spinel ferrite magnetic nanoparticles can be studied for the next generation nanodevices [1]. Among spinel ferrites, CoFe₂O₄ is especially interesting because of their characters as inverse spinel, hard magnetic materials, high coercivities and magnetic saturation [2, 3]. High physical and chemical stability make cobalt ferrite suitable for high-density magnetic recording disk [4]. On the other hand, NiFe₂O₄ is a
well-known inverse spinel, a soft magnetic material with low coercivity and magnetic saturation that can be applied to electronic equipment such as transformation and inductor [5, 6]. If cobalt ferrite and nickel ferrite combined into Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ will present the new characteristics of crystal structure and magnetism properties [7]. The Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ characteristic can be applied to a circulator insulator device as a signal rectifier [8, 9].

Coprecipitation method is widely used for the preparation of ferrites due to the overriding advantages such as easily synthesis parameters control, homogeneity particles size distribution, effectively and relatively simple to control nucleation growth [1]. Maaz et al. successfully fabricated Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ by coprecipitation method [9]. However, the relation among preparation condition, structural and magnetic has not been investigated in detail. Therefore, it is necessary to investigate the relation between preparation condition, structural and magnetic properties. Moreover, study about a synthesis of cobalt-nickel ferrite by varying NaOH concentration and synthesis temperature by coprecipitation method on crystal structure and magnetic properties is very few. The purpose of this work is to investigate the effect of synthesis temperature and NaOH concentration on the crystal structure. The relation between crystal structure and magnetic properties of Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles is also investigated in detail to give more comprehensive information.

2. Materials and methods
Nanoparticles of Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ were synthesized by coprecipitation method with synthesis parameters variations (NaOH concentrations and temperatures). Precedors as starting material were CoCl$_2$·6H$_2$O, NiCl$_2$·6H$_2$O and FeCl$_3$·6H$_2$O (all from Merck, Germany) with dissolving in distilled water and stirring to obtain homogeneous solutions. All precursors were mixed in the calculated molar ratio 1:1:4. The solution was mixed to HCl as a catalyst to solve the ionic bond between metal cation and a chloride anion. The mix solution was added wisely drop by drop at NaOH solution (3 M, 6 M, 10 M and 12 M) for 60 min in varying temperatures (30 °C, 60 °C, 90 °C and 120 °C). The precipitate was washed several times to remove salt contents and other impurities by distilled water. The precipitate of powders was dried at 90 °C in furnace 5 h. The powders of Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles were characterized by X-ray diffractometer (XRD) Shimadzu XD with Cu-Ka radiation (1.56 Å) to confirm the crystal structure. The morphology and diffraction pattern were studied by Transmission Electron Microscope (TEM) Jeol JEM-1400. The magnetic properties were studied by Vibrating Sample Magnetometer (VSM) Riken Denshi Co Ltd. The functional groups were identified by Fourier Transform Infrared spectroscopy (FTIR) Shimadzu-21 in the wave number 4000 cm$^{-1}$ to 400 cm$^{-1}$.

3. Results and discussion
All samples exhibit a characteristic peak of crystallite plane of (311), which explain the cubic spinel structure of nanoparticles Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$, as shown in Figure 1 and Figure 2. The ferrite phase diffraction peaks were adjusted through the JCPDS CoFe$_2$O$_4$ (No. 79-1744) and NiFe$_2$O$_4$ (No. 74-2081) database as standard [9]. The several peaks of other crystallite planes, (220), (400), (511) and (440) were detected but not clearly seen in all samples. The XRD peaks become narrower and sharper with the increase of NaOH concentrations. It indicated that there is an enhancement of crystallinity. Precipitation process is accelerated with the increase of NaOH concentration. The faster precipitation process is used to increased crystallite growth. The XRD peaks become narrower and sharper with the increase of synthesis temperatures. It indicated that there is an enhancement of crystallinity [10]. The increasing synthesis temperatures attributed to increasing thermal energy and crystal growth rate.

Table. 1 shows that the crystallite size increased with the increase of NaOH concentrations (3 M, 6 M and 10 M). The increase of NaOH attributed to accelerating the rate of particles growth. Crystallite size of Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles decreased by 12 M NaOH. The solution has been saturated with the increase of nucleation rate. Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles became small and stable. Particle size and crystallinity were controlled by the OH$^-$ ions in coprecipitation. OH$^-$ ions determined the saturation level at the nucleation-growth process and crystallization [11]. The concentration of 12 M NaOH affects the stable reaction for the growth of crystallite size. The nucleation process at a lower
temperature (30 °C and 60 °C) wasn’t stable. \( \text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles at a higher temperature (90 °C) attributed to increasing of nucleation process. The increase of nucleation process causes the particles became smaller and stable. The crystallite size increased with the increase of temperature and maximum at 120 °C. It is due to the increase of thermal energy. Higher thermal energy attributed to accelerating the atomic diffusion. The particle growth rate increased by the increase of atomic motion. The changing synthesis parameters do not affect the atomic density. Because of the lattice parameters did not change with varying synthesis parameters.

![XRD pattern of Co\(_{0.5}\)Ni\(_{0.5}\)Fe\(_2\)O\(_4\) nanoparticles at (a) 3, (b) 6, (c) 10 and (d) 12 M NaOH (with synthesis temperature constant at 90 °C)](image1)

**Figure 1.** XRD pattern of \( \text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles at (a) 3, (b) 6, (c) 10 and (d) 12 M NaOH (with synthesis temperature constant at 90 °C)

![XRD pattern of Co\(_{0.5}\)Ni\(_{0.5}\)Fe\(_2\)O\(_4\) nanoparticles at (a) 30 °C, (b) 60 °C, (c) 90 °C, and 120 °C (with NaOH concentration constant at 12 M)](image2)

**Figure 2.** XRD pattern of \( \text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles at (a) 30 °C, (b) 60 °C, (c) 90 °C, and 120 °C (with NaOH concentration constant at 12 M)

From TEM images shows that nanoparticles of \( \text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4 \) are agglomerated, as shown in Figure 3 and Figure 4. Agglomeration due to the higher magnetic and interaction electrostatic forces of nanoparticles with small size and large surface [12, 13]. SAED pattern shows that nanoparticles of the \( \text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4 \) ring more prominent with the increase of NaOH concentration. Because of the higher NaOH concentration have higher crystallinity.
Table 1. Lattice parameter ($a$), crystallite size, and density of Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles

| NaOH concentration (M) | $a$ (Å) | Crystalite size (nm) | Density (g·cm$^{-3}$) | Synthesis temperature (°C) | $a$ (Å) | Crystalite size (nm) | Density (g·cm$^{-3}$) |
|------------------------|---------|----------------------|------------------------|-----------------------------|---------|----------------------|------------------------|
| 3                      | 8.5     | 7.3                  | 5.1                    | 30                          | 8.7     | 10.2                 | 4.8                    |
| 6                      | 8.5     | 7.7                  | 5.1                    | 60                          | 8.5     | 11.7                 | 5.0                    |
| 10                     | 8.5     | 10.9                 | 5.1                    | 90                          | 8.4     | 8.5                  | 5.2                    |
| 12                     | 8.4     | 8.5                  | 5.2                    | 120                         | 8.5     | 10.9                 | 5.2                    |

Figure 3. Morphology and SAED at 6 M NaOH

Figure 4. Morphology and SAED at 12 M NaOH

FTIR result shows that the vibrational spectra of Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles are present in the wave number 370.3 cm$^{-1}$, 601.8 cm$^{-1}$, 1065.4 cm$^{-1}$, 1350.2 cm$^{-1}$, 1481.3 cm$^{-1}$, 1635.6 cm$^{-1}$, 2337.7 cm$^{-1}$ and 3425.6 cm$^{-1}$, as shown in Figure 5. The band of 370.33 cm$^{-1}$ and 601, 79 cm$^{-1}$ are indicated the stretching of M-O in octahedral and tetrahedral site [14]. The band of 1064.71 cm$^{-1}$ are showed the absorption of Fe-O-H functional group. The banding in 1350.17 cm$^{-1}$ to 1635.64 cm$^{-1}$ have detected the presence of O-H banding [15]. Stretching of H-O-H appears at 3425.58 cm$^{-1}$. Hydroxyl functional groups are appeared by a not perfectly drying process of the slurry at the furnace. Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles contain a water solvent. C-H carboxyl stretching was detected in 2337.72 cm$^{-1}$ [14]. The synthesis by coprecipitation base method was allowed the Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticles by the outside air contact.
**Figure 5.** FTIR spectrum of Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ at 12 M NaOH, 90 °C

**Figure 6.** VSM hysteresis loops of Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanoparticle at a) 3, b) 6, c) 10, and d) 12 M NaOH (with synthesis temperature constant at 90 °C)

Hysteresis loops confirm that all samples do not fully saturate at a maximum external field of 15kOe, as shown in Figure 6 and Figure 7. However, all the samples have ferromagnetic behavior. Table 2 shows the coercivity increased with the increase of crystallite size. It is due to the increase of magneto crystalline energy on the surface of Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$nanoparticles by the increase of surface area and crystallite size. Small coercivity in the small crystallite size can be related to the single domain. Meanwhile, coercivity decreased with the increase of crystallite size for Synthesis temperature. This phenomenon indicated Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$nanoparticles in the multidomain structure. The maximum magnetization increased with the increase of Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$nanoparticles crystallinity. The crystallinity ofCo$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$nanoparticles depends on NaOH concentration and temperature synthesis. The higher crystallinity changes magnetic moment direction easily [16].
Figure 7. VSM hysteresis loops of Co_{0.5}Ni_{0.5}Fe_{2}O nanoparticle at a) 30 °C b) 60 °C c) 90 °C and d) 120 °C (with NaOH concentration constant at 12 M)

Table 2. Crystallite size, coercivity, and maximum magnetization of Co_{0.5}Ni_{0.5}Fe_{2}O nanoparticles

| NaOH concentration (M) | Crystallite size (nm) | Coercivity (kOe) | Maximum Magnetization (emu·g^{-1}) | Synthesis temperature (°C) | Crystallite size (nm) | Coercivity (kOe) | Maximum Magnetization (emu·g^{-1}) |
|------------------------|-----------------------|-----------------|----------------------------------|---------------------------|----------------------|-----------------|----------------------------------|
| 3                      | 7.3                   | 0.1             | 11.3                             | 30                        | 10.2                 | 0.1             | 9.9                              |
| 6                      | 7.7                   | 0.2             | 7.1                              | 60                        | 11.7                 | 0.1             | 8.4                              |
| 10                     | 10.9                  | 0.2             | 10.8                             | 90                        | 8.5                  | 0.2             | 12.0                             |
| 12                     | 8.5                   | 0.2             | 12.0                             | 120                       | 10.9                 | 0.2             | 12.3                             |

4. Conclusions

Co_{0.5}Ni_{0.5}Fe_{2}O magnetic nanoparticles have been successfully synthesized by co-precipitation method with varying synthesis temperature and NaOH concentration. Lattice parameters of Co_{0.5}Ni_{0.5}Fe_{2}O nanoparticles are constant by varying synthesis temperatures and NaOH concentrations. Crystallinity increased by the increase of NaOH concentration and synthesis temperature. The average crystallite size of Co_{0.5}Ni_{0.5}Fe_{2}O nanoparticles is in the range 7.3 nm - 11.7 nm. The density has not changed by the variation of NaOH concentrations and synthesis temperatures. The magnetization of Co_{0.5}Ni_{0.5}Fe_{2}O nanoparticles was influenced by crystallinity and crystallite size with ferromagnetic behavior. NaOH variations result shown that the Co_{0.5}Ni_{0.5}Fe_{2}O nanoparticles have single domain because of crystallite size increased by the increase of coercivity. The low-temperature variations (30 °C to 60 °C) results show that the sample has multiple domains due to small coercivity and large crystallite size. The maximum magnetization increased by the increase of crystallinity.

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