FTIR and structural properties of co-precipitated cobalt ferrite nanoparticles

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Abstract. The FTIR and structural properties in co-precipitated cobalt ferrite (CoFe$_2$O$_4$) nanoparticles are discussed in this paper. The synthesis was conducted at temperatures of 75°C and 95°C following post annealing at 1200°C for 5 hours. Other modification samples were synthesis at temperature of 95°C and then annealing at temperature of 1000°C and 1200°C for 5 hours. For both modification of synthesis and annealing temperature, FTIR result showed a metal oxide at a wave number of 590 cm$^{-1}$ which indicated cobalt ferrite nanoparticles. The crystalline structure was confirmed using x-ray diffraction that the high purity of cobalt ferrite was realized. Calculation of the cation distribution by using comparison $I_{220}/I_{222}$ and $I_{422}/I_{222}$ show that the synthesis and annealing temperature successfully modify cation occupy the site octahedral and tetrahedral.

1. Introduction

Study of ferrite based nano particles show great progress in the past decade due to the interesting techniques and developments to achieve the nano-meter order of magnetic particles. At the nanoscale, there is new behaviors and properties which is different from bulk structures [1-3]. Especially in ferrite which is materials with high chemical stability and low production cost already used for many application field [4]. Ferrite based nanoparticles currently used in application such as optical materials [5], semiconductors [6], nanofluids [7-9], and at the superparamagnetic stage [10] used for magnetic data storage [11], magnetic imaging, and biomedical applications [12].

Ferrite is spinel structured materials which is isostructural with the mineral MgAl$_2$O$_4$ and have general molecular formula (M$^{2+}$) [Fe$^{3+}$] O$_2$, with M$^{2+}$ is divalent cation and Fe$^{3+}$ is trivalent cation [13]. Its crystalline is face centered cubic containing eight formula unit [AB$_2$O$_4$] or 56 ions per unit cell. The lattice consist of 32 divalent oxygen arrange with 64 tetrahedral interstitial and 32 octahedral interstitial sites (just 8 tetrahedral and 16 octahedral sites are occupy by divalent and trivalent cations) [14]. In this large empty interstitial sites, there is possibility to cation migration [15]. For normal spinel materials such as ZnFe$_2$O$_4$, all the divalent cations occupy the tetrahedral sites (A-sites) and all the trivalent cations occupy the octahedral sites (B-sites). In contrast for inverse spinel such as MgFe$_2$O$_4$, trivalent cations are distributed at the A-sites and B-sites, whereas divalent cations have preference for B-sites. Distribution of cations in each lattice sites form materials as inverse or partially

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The distribution of cations over the two interstitial sites is strongly affected by the variations of lattice constants, size of crystallites, and bond angles - bond length between the cations [17].

One of the most interesting ferrites is cobalt ferrite (CoFe$_2$O$_4$) due to their strong magnetocrystalline anisotropy, high coercive strength and large magneto-optic coefficient [18,19]. Cobalt ferrite is a spinel structured material which is known that the Co$^{2+}$ ions have preference for the B-sites [14]. Cobalt ferrite may be complete inverse spinel or partial inverse spinel depend on cation substitution or heat treatment [16]. The cation distribution between Co$^{2+}$ ions and Fe$^{3+}$ ions over the A-sites and B-sites effect on the physical properties of cobalt ferrite spinel. In cobalt ferrite, the preference of cations is not fixed but cobalt ions show a strong preference for B-sites. The information about cation distribution can be achieved from the peaks of X-rays diagrams [20].

This study focused on the variation of heat treatment (synthesis and high annealing temperature) and a co-precipitation procedure was used to synthesize the cobalt ferrite nanoparticles due to its high simplicity procedure, low cost and good grain size control [21]. The resulting cobalt ferrite nanoparticles were then characterized using FTIR to study their infrared spectra and X-ray diffraction to study their structural properties and cation distribution.

2. Experimental procedure

2.1. Synthesis of CoFe$_2$O$_4$ nanoparticles

The synthesis of cobalt ferrite nanoparticles was prepared by co-precipitated method like as in the previous study [22]. The synthesis was conducted at temperatures of 75°C and 95°C, where the aqueous solution of 4.8 M NaOH was added dropwise to the mixed solution. The product was then cooled and washed several times with ethanol and deionised water. Precipitated solution were dried overnight at 100°C in order to remove excess water. The following post annealing has been done at 1200°C for 5 hours. Other modification samples were synthesis at temperature of 95°C and then annealing at temperature of 1000°C and 1200°C for 5 hours. The obtained samples were then characterized.

2.2. Characterization

The formation of spinel structure was characterized with Fourier Transform Infra-Red (FTIR). The X-ray diffraction (XRD) patterns of the samples were recorded with Bruker D8 Advanced system X-ray powder diffractometer using Cu Ka source (1.54 Å) radiation. The scans of the selected diffraction peaks were carried out in the step mode 0.064°.

2.3. Calculations

The force constant for the tetrahedral site ($k_t$) was calculated according to the following relation:

$$k_t = \frac{7.62 M_A v_i^2 \times 10^{-7} N}{m}$$  \hspace{1cm} (1)

where $M_A$ is the molecular weights of cations on the A-sites and $v_i$ is wave number (cm$^{-1}$).

For the calculation of the crystallite size, Scherrer’s method was applied using the following equation:

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$ \hspace{1cm} (2)

where $D$ is crystallite size, $\lambda$ is the wavelength of the X-ray radiation, $\theta$ is Bragg’s angle, and $\beta$ is the line width at half maximum height.

The lattice constant ‘a’ was determined using the following relation:

$$a = \frac{\lambda}{2 \sin \theta} \sqrt{h^2 + k^2 + l^2}$$ \hspace{1cm} (3)

where (h k l) are the miller indices. The X-ray density ($d_x$) was calculated according to the following relation:

$$d_x = \frac{Z M}{N_A a^2}$$ \hspace{1cm} (4)
where \( Z \) is number of molecule per unit cell, \( M \) is molecular weight, and \( N_A \) is Avogadro’s number [21].

3. Results and Discussion

3.1 Effect of Synthesis Temperature

The formation of the spinel structure of cobalt ferrite and its cation distribution is supported by FTIR analysis. Figure 1 presents the infrared transmittance spectra of the investigated sample cobalt ferrite which vary in the synthesis temperature. The absorption band around 3400 cm\(^{-1}\) and 1600 cm\(^{-1}\) are ascribed to the stretching mode of O-H and H-O-H bending vibration, respectively [23]. The other absorption band lies at a smaller wavenumber (see insert). The absorption band at this small wavenumber is showed in Table 1 and is the common feature in spinel ferrite oxide. The absorption band are attributed to the stretching vibration of tetrahedral group complexes [23]. This result confirms the appearance of CoFe\(_2\)O\(_4\) synthesized by co-precipitation method.

The absorption band at wavenumber around 590 cm\(^{-1}\) are slighty differ depend on the variations of synthesis temperature. At the variations of synthesis temperature (annealing temperature is constant at 1200°C), from 75°C to 95°C result on the slighty shifted absorption band to a lower frequency side. The boardening of the A-sites and B-sites attribute the different of force constant at tetrahedral sites \( k_t \). The value of force constants are listed in Table 1. It is observed that the force constant of tetrahedral sites \( k_t \) is equal 14.65 N/m for synthesis temperature of 75°C and at synthesis temperature of 95°C, the \( k_t \) decrease become 14.35 N/m. The change of the \( k_t \) is expected to modify the cation-oxygen bond length [21]. Furthermore it will modify the crystalline structure of the obtained cobalt ferrite nanoparticles.

The X-ray diffraction patterns of the CoFe\(_2\)O\(_4\) synthesized by co-precipitation vary in synthesis temperatures are shown in Fig. 2. Here, the solid line show the experimental data and the bottom line show the data peaks of the International Centre for Diffraction Data (ICDD) number 221086. This characterization shows a similarity to the data peaks of the ICDD number 221086. These result indicate that the samples are CoFe\(_2\)O\(_4\) in inverse spinel face centered cubic (fcc) structure. The similarity in the data peaks also attribute that there is no other impurities present and the CoFe\(_2\)O\(_4\) with high purity was successfully produced via co-precipitation method. All the peaks of the XRD pattern were indexed using Bragg’s law. The crystallite sizes of cobalt ferrite are becoming larger with the increasing of temperature are showed in Table 1. The crystallite size increase from 43 nm to 95 nm
for the change of temperature synthesis 75°C to 95°C. Whereas the lattice parameter a is not significantly different.

![XRD patterns](image)

**Figure 2.** XRD patterns for CoFe$_2$O$_4$ synthesized at temperature of 75°C and 95°C and annealed at 1200°C

### 3.2 Effect of Annealing Temperature

![FTIR spectra](image)

**Figure 3.** FTIR spectra of the cobalt ferrite nanoparticles synthesized at 95°C and annealed at temperature of 1000°C and 1200°C

Figure 3 presents the infrared transmittance spectra of the cobalt ferrite samples which vary in the annealing temperature. The absorption band around 3400 cm$^{-1}$ and 1600 cm$^{-1}$ are ascribed to the stretching mode of O-H and H-O-H bending vibration, respectively. Similar with the result of synthesis temperature variation, the next absorption band lies at a smaller wavenumber (see insert) is the common feature in spinel ferrite oxide. The absorption band are attributed to the stretching vibration of tetrahedral group complexes [23]. This result confirms the appearance of CoFe$_2$O$_4$ synthesized by co-precipitation method.

At the variations of annealing temperature (synthesis temperature is constant at 95°C), from 1000°C to 1200°C result on the slightly shifted absorption band to a lower frequency side which is attributed to the increase in the broadening of the A-sites and B-sites. This change show in the Figure 3 where the sample annealed at 1200°C has broad absorption band compared with the sample annealed at 1000°C which has sharper absorption band. The broadening of this band also related with the migration of cations and bond length for A-sites and B-sites complexes. The value of force constants for different annealing temperature are listed in Table 2. It is observed that the force constant of tetrahedral sites ($k_t$) is at higher level for sample annealed at 1000°C. This result consistent with variation of synthesis temperature. This behaviour show that with the increasing of synthesis or annealing temperature, $k_t$
can be attributed to the variation in cation-oxygen bond length [21]. To provide more detailed explanation on crystalline structure, samples were characterized by XRD.

### Table 2. FTIR and XRD result of sample with varied annealing temperature

| Annealing Temperature (°C) | wavenumber \( k_t \) (cm\(^{-1}\)) | 2\(\theta\) (°) | Crystallite size \( a \) (Å) | \( d_x \) (g/cm\(^3\)) |
|---------------------------|-----------------------------------|-----------------|------------------|------------------|
| 1000                      | 592                               | 14.95           | 35.67            | 8.35             |
| 1200                      | 580                               | 14.35           | 35.53            | 8.37             |

The X-ray diffraction patterns of the CoFe\(_2\)O\(_4\) synthesized by co-precipitation which vary in annealing temperatures are shown in Figure 4. This characterization shows a similarity to the data peaks of the ICDD number 221086. These result indicate that the samples are CoFe\(_2\)O\(_4\) in inverse spinel face centered cubic (fcc) structure. The similarity in the data peaks also attribute that there is no other impurities present and the CoFe\(_2\)O\(_4\) with high purity was successfully produced via co-precipitation method. All the peaks of the XRD pattern were indexed using Bragg’s law. The increment of crystallite size also happen at sample which vary in their annealing temperature. The lattice parameter and density of sample have different behaviour to their varied temperature shows in Table 2. For sample that vary in their annealing temperature show the counter behaviour from synthesis temperature due to growth of the crystal with increasing annealing temperature. These two different behaviour reflect the different cation distribution in the sample.

### 3.3 Cation distribution

From the Figure 2 and Figure 4 the relative intensity of peaks with Miller indices \((h, k, l)\) all even such as \((220), \ (222), \) and \((422)\) may be used to obtain information about sites occupancy. For all even with formula \(h+k+l=4n\), like \((220)\) and \((422)\), only tetrahedral sites \((8a)\) contribute to diffraction peaks. In contrast, for all even with formula \(h+k+l=4n+2\), like \((222)\), only octahedral sites \((16d)\) contribute to diffraction peaks [20]. The ratio of \(I_{220}/I_{222}\) and \(I_{422}/I_{222}\) are an indication of the A and B sites occupation is showed in Table 3. For these three results of comparison intensity ratios indicates clearly that in the nanoparticles especially due to the variation of heat treatment, Co\(^{2+}\) has a strong preference for tetrahedral sites, contrary with the bulk ferrite.

### Table 3. \(I_{220}/I_{222}\) and \(I_{422}/I_{222}\) ratio of cobalt ferrite vary in synthesis and annealing temperature

| Temperature (°C) | \(I_{220}/I_{222}\) | \(I_{422}/I_{222}\) |
|------------------|-------------------|-------------------|
| 75-1200          | 3.02              | 1.49              |
| 95-1200          | 2.85              | 1.52              |
| 95-1000          | 3.48              | 1.24              |

Figure 4. XRD pattern of CoFe\(_2\)O\(_4\) synthesized at 95°C and annealed at temperature of 1000°C and 1200°C.
For sample which vary in their synthesis temperature, the increasing of temperature effect to the \(I_{220}/I_{222}\) is getting smaller (from 3.02 to 2.85 for sample 75 and 95, respectively) hence \(I_{422}/I_{222}\) is getting bigger (from 1.49 to 1.52 for sample 75 and 95, respectively). This result can explain that with increasing of synthesis temperature, there is redistribution of \(\text{Co}^{2+}\) ions from A-sites back to B-sites. Same behaviour occurs at the sample which vary in their annealing temperature. Thus, it can be conclude that the increasing of temperature by heat treatment effect on the redistribution of \(\text{Co}^{2+}\) ions from A-sites back to B-sites.

4. Conclusion

\(\text{CoFe}_2\text{O}_4\) nanoparticles were successfully synthesized using co-precipitation method. FTIR result indicated the sample was spinel cobalt ferrite at wave number around 590 cm\(^{-1}\). The crystalline structure was confirmed using x-ray diffraction that the high purity of cobalt ferrite was realized. Calculation of the cation distribution by using comparison \(I_{220}/I_{222}\) and \(I_{422}/I_{222}\) showed that the synthesis and annealing tem perature succesfully modify cation occupation on the tetrahedral and octahedral sites.

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