

Effects of the Synthesis Temperature on the Crystalline Structure and the Magnetic Properties of Cobalt Ferrite Nanoparticles Prepared via Coprecipitation

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The effects of the synthesis temperature on the crystalline structure and the magnetic properties of cobalt ferrite (CoFe_2O_4) nanoparticles prepared via coprecipitation are discussed. The synthesis was conducted at temperatures of 75 °C, 85 °C and 95 °C. Fourier transform infrared spectroscopy characterization related to a stretching vibration at a wavenumber of 590 cm^{-1} indicated the formation of a CoFe_2O_4 metal oxide. In addition, powder X ray diffraction (XRD) characterization proved that the metal oxide was CoFe_2O_4 . Crystallite sizes calculated using the Scherer formula at the strongest peak of the XRD spectra of the samples synthesized at 75 °C, 85 °C and 95 °C were 32 nm, 43 nm and 50.4 nm, respectively. Finally, the results of the vibrating sample magnetometer characterization showed that the saturation magnetization decreased with increasing synthesis temperature, which is related to the dominant preference of Co^{2+} over Fe^{3+} cations at the octahedral sites.

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I. INTRODUCTION

In the last decade, nanoscience and nanotechnology have been interesting research fields due to the broad applications of nanoparticles, especially magnetic nanoparticles [1–5]. Magnetic nanoparticles have exciting properties, such as superparamagnetism, which is not present in bulk magnetic materials [6–8]. These magnetic properties are related to the single domains of particles on the nanometer scale between 10 nm and 70 nm, such in cobalt ferrite (CoFe_2O_4), which are promising for future technologies [9,10]. CoFe_2O_4 nanoparticles are particularly interesting due to their strong magnetocrystalline anisotropy, high coercive strength and large magneto optic coefficient [11,12]. CoFe_2O_4 also shows stable physical and chemical properties and is suitable for use in high frequency applications, such as magnetic recording, biomedicine and modern electronic tools [10,13–15].

Several previous studies have attempted to control the size of CoFe_2O_4 nanoparticles [16–18]. A CoFe_2O_4

nanoparticles synthesis method that allows for easier control of particle size is the coprecipitation method. This method involves mixing chemical solutions and using deposition synthesis conditions, such as the heating temperature and the heating rate, which affect the particle size and the degree of crystallinity formed [19,20]. In addition, the annealing can be modified to lead to a more homogenous nanoparticle size distribution [21].

CoFe_2O_4 has an inverse spinel face centered cubic (fcc) structure, with contributions to the magnetic moment at tetrahedral sites and octahedral sites [22]. Fe^{3+} ions are distributed at the tetrahedral and octahedral sites whereas Co^{2+} ions have a preference for octahedral sites [23]. Heat treatment during CoFe_2O_4 synthesis provides opportunities for cation substitution of Fe^{3+} at octahedral sites or for a different distribution at tetrahedral sites and octahedral sites. Therefore, the magnetic properties of CoFe_2O_4 can be changed [24–26]. In this study, the effects of the synthesis temperature on the crystalline structure and the magnetic properties of coprecipitated CoFe_2O_4 nanoparticles are discussed.

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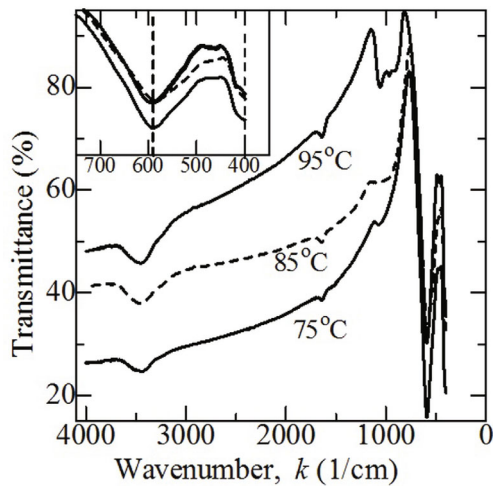


Fig. 1. FTIR results for the cobalt-ferrite nanoparticles synthesized at three different temperatures followed by annealing at 1000 °C for 5 h.

II. EXPERIMENTAL DETAILS

CoFe₂O₄ nanoparticles were synthesized using the coprecipitation method as in a previous study [21]. Mixed solutions of cobalt nitrate and iron nitrate were synthesized with a 4.8M NaOH solution. The chosen synthesis temperatures were 75 °C, 85 °C and 95 °C. The synthesis product was washed using distilled water until clean and then referred to as the precursor material. This precursor material was dried overnight at a temperature of 100 °C, and then annealed at 1000 °C for 5 h. The obtained samples were then characterized.

The crystalline structures of the samples were characterized via an X-ray diffractometer (XRD) Merck Bruker D8 Advance system with a Cu source with $\lambda = 1.54$ Å. The formation of spinel structures in the samples was characterized via Fourier-transform infrared spectroscopy (FTIR). The magnetic properties of the samples were characterized via a vibrating sample magnetometer.

III. RESULTS AND DISCUSSION

Figure 1 shows the FTIR curves for the CoFe₂O₄ nanoparticles with synthesis temperatures of 75 °C, 85 °C and 95 °C. The first characteristic absorption appears at a wavenumber of 3600 cm⁻¹, followed by a second at 1600 cm⁻¹. These bands are ascribed to the stretching mode and the H-O-H bending vibration. The next appearance of an absorption band lies at a smaller wavenumber (see insert). The band observed near 590 cm⁻¹ is a common feature in spinel ferrite oxide. The absorption band at 590 cm⁻¹ results from the intrinsic vibration of A site metal complexes, which consist of bonds between A site metal ions and oxygen ions. This result confirms the appearance of CoFe₂O₄ synthesized

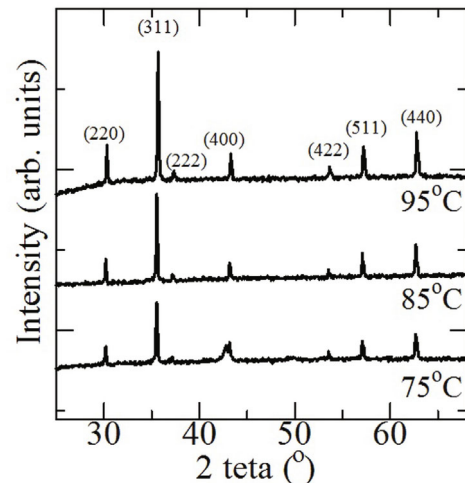


Fig. 2. XRD patterns of the CoFe₂O₄ nanoparticles synthesized at temperatures of 75 °C, 85 °C and 95 °C and then annealed at 1000 °C for 5 h.

Table 1. Crystallite size, coercive field (H_c), remanent magnetization (M_r) and saturated magnetization (M_s) for CoFe₂O₄ nanoparticle samples synthesized at temperatures of 75 °C, 85 °C and 95 °C.

	Synthesis temperature		
	75 °C	85 °C	95 °C
Crystallite size (nm)	32	43	50.4
H_c (Oe)	618	625	923
M_r (emu/cc)	140.7	156	174
M_s (emu/cc)	369.6	362.7	333.8

by coprecipitation. The absorption band near 590 cm⁻¹ is consistent with an increase in the synthesis temperature without the appearance of another metal oxide. These results can be explained by the increase in the synthesis temperature assisting the crystallisation process. To provide a more detailed explanation of the synthesis temperature's effect on the crystalline structure, we characterized the samples by using powder X-ray diffraction.

The X-ray diffraction patterns of the CoFe₂O₄ synthesized using coprecipitation at synthesis temperatures of 75 °C, 85 °C and 95 °C are shown in Fig. 2. This characterisation shows a similarity to the data peaks from the International Centre for Diffraction Data (ICDD) number 221086. These results indicate that the samples are CoFe₂O₄ in inverse spinel fcc structures. The similarity in the data peaks also indicates that no oxides or other impurities are present due to the annealing process and that CoFe₂O₄ with high purity was successfully produced via the coprecipitation method. The strongest peaks occur at an angle $2\theta = 35.54^\circ$ and are not changed by an increase in the synthesis temperature. The intensity

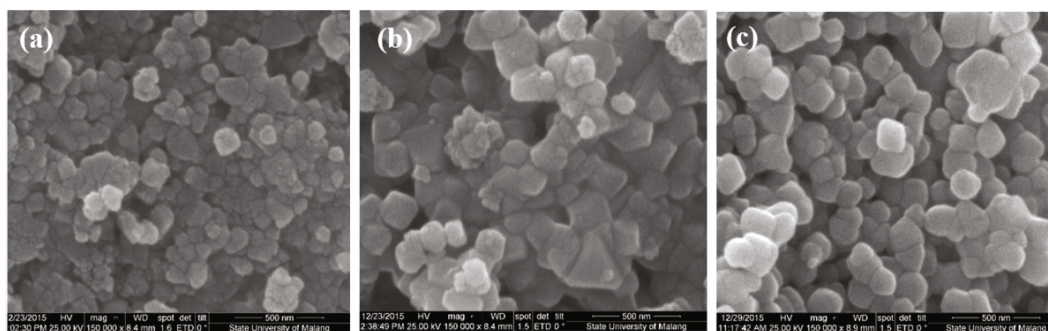


Fig. 3. Typical SEM images for cobalt-ferrite synthesized at temperatures of (a) 75, (b) 85, and (c) 95 °C and then annealed at 1000 °C for 5 h.

at this angle increases consistently with increasing synthesis temperature. The increase in the peak intensity shows that at higher synthesis temperatures, the crystalline structure is better observed, which was proved by the homogenous crystallinity of the samples. The crystallite sizes obtained using the highest XRD peak, the Miller index hkl (311) and the Scherrer formula are listed in Table 1. The crystallite sizes that are larger than those in the previous study [21] occur due to the different annealing temperatures used when synthesising the CoFe_2O_4 nanoparticles.

From the XRD results, the cations distribution for the tetrahedral and the octahedral sites are indicated by the ratios I_{220}/I_{222} and I_{422}/I_{222} , respectively [27], where I_{220} , I_{422} , and I_{222} are intensities of the XRD pattern correspond to Miller indices of (220), (422) and (222). By fitting with the pseudo-Voigt functions of Origin software, we obtained the intensities of individual peaks. The experimentally-calculated I_{220}/I_{222} ratios for CoFe_2O_4 nanoparticles synthesized at temperatures of 75 °C, 85 °C and 95 °C were 3.43, 3.40 and 3.48, respectively. The results are much larger than the theoretical value of 3.0 [27]. The I_{220}/I_{222} ratios are relatively constant with increasing synthesis temperature, which suggests that the distribution the cation of Fe^{3+} at tetrahedral sites is insensitive to the synthesis temperature. On the other hand, the experimentally calculated I_{422}/I_{222} ratios were 1.68, 1.52 and 1.24 corresponding to synthesis temperatures of 75 °C, 85 °C and 95 °C, respectively. The I_{422}/I_{222} ratios decreases with increasing synthesis temperature, and at a synthesis temperature of 95 °C was 1.24 (closer to the theoretical calculation of 1). Therefore, in cobalt ferrite samples, a cation redistribution of Fe^{3+} and Co^{2+} ions is thought to occur at the octahedral sites with increasing synthesis temperature.

Figure 3 shows the surface morphology of CoFe_2O_4 nanoparticles in scanning electron microscopy images with a magnification of 100,000 \times . It clearly shows a change in the CoFe_2O_4 nanoparticles. When the synthesis temperature is low (75 °C), the grain size is small. However, with increasing synthesis temperature, the grain size becomes larger and more homogenous.

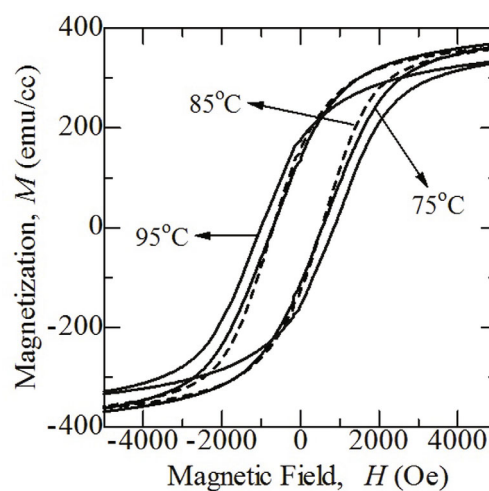


Fig. 4. Typical hysteresis curves for cobalt-ferrite nanoparticles synthesized at temperatures of 75, 85, and 95 °C and annealed at 1000 °C for 5 h.

This result is consistent with the crystalline structure measured using XRD; that is, the maximum peak increased with increasing synthesis temperature.

Figure 4 shows typical hysteresis curves for the three synthesis temperatures of 75 °C, 85 °C and 95 °C. No significant differences are seen between the hysteresis curves at 75 °C and 85 °C. The coercive field, remanent magnetization and saturation magnetization for the various synthesis temperatures are shown in Table 1. The coercive field increases with increasing synthesis temperature. At a synthesized temperature of 75 °C, the coercive field is 618 Oe, which increases to 625 Oe at 85 °C and increases drastically to 923 Oe at 95 °C. This indicates that the synthesis temperature has a role in bringing the grains of the CoFe_2O_4 nanoparticles closer to each other so that larger grain-sized particles can be obtained. In the cobalt-ferrite case, single domains are realized when the crystallite size is smaller than 70 nm [28] and in a recent study, is smaller than 45 nm [17]. When the CoFe_2O_4 crystallite size exceeds the critical size, a multi-domain configuration is realized, resulting

in small coercive field. A high-enough coercive field for the samples with synthesized at temperature of 75 °C, 85 °C, and 95 °C may be attributed to a pinning of the magnetic domains at the interface [29]. Another interesting magnetic property reflected in the hysteresis curve is the remanent magnetization M_r . A remanence M_r of 140.7 emu/cc is obtained when the synthesis temperature is 75 °C. The value of M_r increases with increasing temperature, because 156 emu/cc and 174 emu/cc for synthesis temperatures at 85 °C and 95 °C, respectively. When the magnetic nanoparticles are considered, exchange coupling between randomly-oriented nano grains may contribute to the increase in the M_r [30].

Table 1 also show the synthesis-temperature dependence of the saturation magnetization in samples fabricated using the coprecipitation procedure. The saturation magnetization M_S attains a value of 396.6 emu/cc at a synthesis temperature of 75 °C and then decreases to 362.7 emu/cc and 333.8 emu/cc at synthesis temperatures of 75 °C, 85 °C, and 95 °C, respectively. The decrease in the saturation magnetization M_S with increasing synthesis temperature can be explained as follows. As previously discussed, the tetrahedral sites are only occupied by Fe^{3+} cations, even though the synthesis temperature is increased. Meanwhile, with increasing synthesis temperature, Fe^{3+} and Co^{2+} cations share the octahedral sites. We note that the magnetic moment of Fe^{3+} is greater than that of Co^{2+} . When the redistribution of the cations at octahedral sites is discussed, the decrease in the saturation magnetization with increasing synthesis temperature indicates that a redistribution and substitution of Fe^{3+} and Co^{2+} cations occur at octahedral sites. This explanation is related to the preference of the net magnetic moment of a material with the spinel structure [25]:

$$m = \sum m_{B\text{-sites}} - \sum m_{A\text{-sites}}, \quad (1)$$

where $\sum m_{B\text{-sites}}$ is the magnetic moment of the cations in B-sites and $\sum m_{A\text{-sites}}$ is the magnetic moment of the cations in A-sites. Thus the dominant preference for Co^{2+} over Fe^{3+} cations at octahedral sites leads to a reduction in the total magnetic moment, thereby decreasing the saturated magnetization.

IV. CONCLUSION

The effects of synthesis temperature on the crystalline structure and the magnetic properties of nanoparticles were observed in this study. The spinel structure of CoFe_2O_4 was revealed at a wavenumber of 590 cm^{-1} . The result of the crystallite structure characterization demonstrated that the CoFe_2O_4 nanoparticles formed with a crystallite size of approximately 30 – 40 nm. The crystallinity of the samples increased with increasing synthesis temperature. The magnetic properties of the

formed samples demonstrated coercive field and remanent magnetization that increased consistently with increasing synthesis temperature. The saturation magnetization, which decreased with increasing synthesis temperature, indicated a dominant preference of Co^{2+} over Fe^{3+} cations at the octahedral sites.

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