

Effect of synthesis parameters on crystal structure and magnetic properties of cobalt zinc ferrite ($\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$) nanoparticles

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Abstract. $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles have been successfully synthesized by coprecipitation method with varying NaOH concentrations and synthesis temperatures. X-ray diffraction (XRD) analysis confirmed that $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles have spinel cubic crystal structure with crystallite size ranging from 7.9 to 21.4 nm. The crystallite size increase relatively by increasing NaOH concentration and synthesis temperature which related to the nucleation and crystal growth mechanism of nanoparticles during synthesis. The transmission electron microscope (TEM) image showed that the sample was agglomerated. The selected area electron diffraction (SAED) image showed the diffraction ring as representation of miller plane and confirmed that sample was polycrystalline. Magnetic measurement indicated that $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles shows ferimagnetic behaviour and tend to be superparamagnetic with decreasing crystallite size. The increase in coercivity and maximal magnetization also have been found by increasing NaOH concentration and synthesis temperature. It is attributed to single domain existence and an increasing of crystallinity degree. The Fourier transform infrared spectroscopy (FTIR) spectra also confirmed the existence of symmetric stretching vibration bands of metal ions near $563\text{--}609\text{ cm}^{-1}$ and $316\text{--}493\text{ cm}^{-1}$ in tetrahedral and octahedral sites, respectively.

1. Introduction

Studies of spinel ferrites are highly relevant to modern technologies, so the synthesis and sintering of ferrites have become an important part of modern science research. Nanosized ferrites may have extraordinary electric and magnetic properties that are comparatively different from microstructured materials, tailoring them to modern technologies, as well as providing novel applications such as ferrofluids, magnetic drug delivery, high density information storage, photocatalysis, gas sensors, etc [1]. Nano-crystalline ferrites have been widely studied and has become a field of interest of many researchers because of their unique and improved properties over the bulk crystalline materials [1]. Indrayana *et al.* have studied effects of Zn concentration and sintering temperature on crystal structure, magnetic properties and band gap energy of $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ Nanoparticles [2]. Siregar *et al.* have studied effect of synthesis temperature and NaOH concentration on microstructural and magnetic



properties of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles [3]. Praveena *et al.* have studied ferromagnetic properties of Zn substituted spinel ferrites for high frequency applications [1].

The Co substituted mixed ferrites are among those spinel ferrites which the authors are interested in. Cobalt ferrites have attracted considerable interest because of their large magnetic multi-axial anisotropy, high saturation magnetization, high Curie temperature and extraordinary chemical stability [4-7]. Cobalt ferrite nanoparticles are suitable for the isolation and refining of genomic DNA, the partitioning of polymerase chain reaction ready DNA and especially in hyperthermia treatment [1]. Zn ferrites are useful for low and high frequency applications generally for power transformers, power inductors, microwave devices, read and write heads for high speed digital tape, etc. because of their high resistivity, low losses, mechanical hardness, high Curie temperature and chemical stability [8-13]. If cobalt ferrites and zinc ferrites were combined into Co-Zn ferrites, they would present the new characteristics of crystal structure and magnetism properties which then become one of the soft ferrites used in electronic devices such as transformer cores, electric motors and generators [14]. Recently many efforts have been made to develop low power loss Co-Zn ferrites in order to miniaturize electrical devices [15, 16].

Studies on spinel ferrites synthesis methods have led to the development of different chemical synthesis techniques, all of which have a common feature, namely that all reagents are mixed at the atomic or molecular level. The most popular methods of synthesis is coprecipitation. Coprecipitation method is relatively simple, having a short reaction time, a high reaction yield, and yielding small-size particles. The microstructure of nanoparticle directly affects their magnetic, electrical, dielectric, and optical properties [17]. The microstructure of nanoparticle can be tuned by controlling the synthesis parameters, such as metal precursors type, pH, reaction temperature and reaction rate [18]. All of the parameters directly affect the crystallite size of nanoparticle [18]. Treatment temperature sintering for Co-Zn ferrite would be affected by crystal structure and magnetic properties [19]. In the case of coprecipitation synthesis, a reaction temperature of solutes and pH is very sensitive in determining the reaction yield. There has been a lot of work done toward Co-Zn ferrite, but still lack of systematic and comprehensive investigations on the preparation condition, structural and magnetic properties. To date, there has not been a single research done to study the synthesis of cobalt zinc ferrite by varying NaOH concentration and temperature synthesis by coprecipitation method on crystal structure and magnetic properties. In this study the effect of NaOH concentration and synthesis temperature on crystal structures and magnetic properties of Co-Zn ferrite nanoparticles is investigated comprehensively.

2. Experimental method

Solution prepared by dissolving stoichiometric quantities of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck, Germany) and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck, Germany) in 25 ml distilled water. Solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Merck, Germany), was also prepared in 25 ml distilled water. Both solutions were subsequently mixed into homogeneous solutions by stirring them in moderate speed for 5 minutes. Then, it was added with 3.7 ml of HCl (Merck, Germany) and it was stirred again for 5 minutes. NaOH solution was made by mixing NaOH (Merck, Germany) salts with 50 ml distilled water. The precipitation was carried out by dropping the alloys solution into 1.5 M, 3 M, 6 M and 12 M of NaOH solution at temperature 70 °C called sample M1, M2, M3, and M4 respectively for 60 minutes and stirred at 1000 rpm [20]. In the case of the synthesis temperature variations, the samples are synthesized at 30, 50, 70, and 90 °C in 6 M of NaOH solution labelled sample S1, S2, S3 and S4 respectively for 60 minutes and stirred at 1000 rpm. The synthesis reaction process was maintained until the formation of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticle product which is indicated by the forming of dark brown precipitates. Subsequently, synthesized nanoparticles were cooled to room temperature. During the cooling process, dark brown slurry of nanoparticles will separate from the solvent. To get free particles from incomplete chemical precursors compounds during synthesis, the precipitate was then washed six times with distilled water to remove the excess surfactant from the solution. Those processes will give rise to thick black precipitate which is ready to

be heated in a furnace at a constant temperature of 90 °C for 4 hours. Finally, the acquired substance was then grinded into a fine powder of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticle.

The XRD patterns of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ confirmed by Shimadzu XD X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda=1.5406\text{\AA}$) radiations. TEM and SAED methods by JEOL Jem-4000 electron microscope were used to study overall morphology of nanoparticles. For the study of functional group, FTIR analysis was performed by Shimadzu Prestige-21 IR Spectrometer. Magnetic measurements at room temperature were conducted using a vibrating sample magnetometer (VSM) of Riken Denshi Co. Ltd. All the hysteresis magnetic measurements were carried out at room temperature in the applied static magnetic fields up to 15 kOe. Particle size (t) was calculated from XRD peak broadening by using Scherrer formula, the values of interplanar distance (d) were estimated by using Bragg's equation and peaks reflection (hkl) was used to estimate the lattice constant (a).

3. Results and discussion

3.1. Crystal structure analysis

Figure 1 and Figure 2 show the XRD pattern of samples for both NaOH concentration and synthesis temperature variations. The diffraction pattern referred to the standard data of Co ferrite (JCPDS no. 22-1086) and Zn ferrite (JCPDS no. 22-1012) [1]. The profile of diffraction pattern could be indexed as (220), (311), (400), (422), (511) and (440), which are characteristics of a cubic spinel structure and some other structures, i.e. ZnO (JCPDS no.36-1451) [3]. Those phases indicate that Zn(OH)_2 were exhibited incomplete chemical reaction during synthesis.

The diffraction pattern of sample M3 has the highest degree of crystallinity due to the optimum NaOH concentration. In other hand, samples M1, M2 and M4 have a lower degree of crystallinity. Precipitation process is accelerated by the increase of NaOH concentration which lead to increase nucleation and crystal growth rate. The XRD peaks also become narrower and sharper with the increase of synthesis temperature which indicate the increase of the crystallinity degree. The increasing thermal energy has been attributed to increasing synthesis temperatures, which enables the enhancement of nucleation and crystal growth rate.

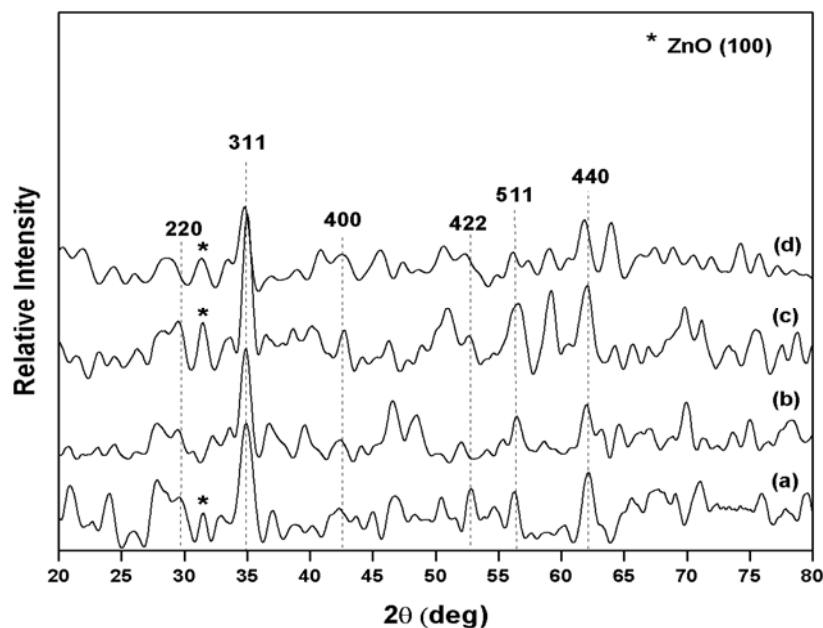


Figure 1. XRD Pattern of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ with NaOH concentration (a) 1.5 M, (b) 3 M, (c) 6 M, and (d) 12 M.

The XRD profile peaks were found to be slightly broader in the samples, because of strain effect and crystallite size. The strain is estimated to appear due to a crystal lattice defect. This defect might be caused by synthesis temperature. Increased synthesis temperature contributes to the increase of thermal energy in the process of nucleation and growth of nanoparticles which increases the reaction kinetic energy so that the nucleation becomes more effective. Nucleation process is very sensitive to reaction temperature that agitates thermal energy for the reaction [3]. Low temperature synthesis will limit the nucleation process and crystal growth resulting in a defect of the crystal lattice. The uniform strain occurring in the crystal lattice of nanoparticles brings about some changes in the site of metal cations. The ion distribution in octahedral and tetrahedral sites of crystal lattice will contribute to lattice size and crystallite size of nanoparticles [21]. Lattice parameter and X-ray density are relatively constant with the increase of synthesis temperature because of the composition of Co^{2+} , Zn^{2+} and Fe^{3+} are homogeneously in spinel structure of all samples. The crystallites size shows fluctuating results with increasing synthesis temperature. Too high or too low of synthesis temperature caused the process of nucleation and crystal growth is not optimal. The quantitative calculation results of crystallite size (t) [2], lattice constant (a) [2] and X-Ray density [2] are all presented in Table 1.

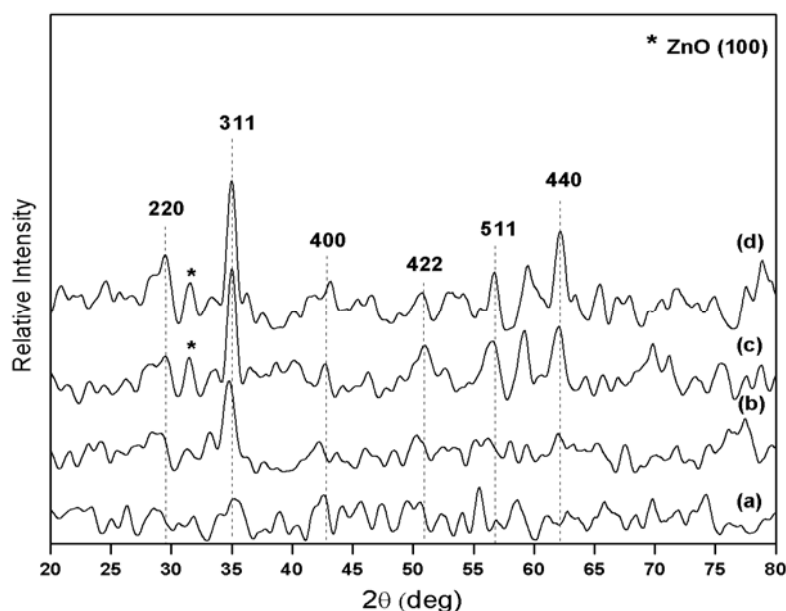


Figure 2. XRD Pattern of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ with synthesis temperature (a) 30°C, (b) 50°C, (c) 70°C, and (d) 90°C.

Table 1. Crystallite size, lattice constant and X-Ray density of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles synthesized at different NaOH concentration and synthesis temperature.

Sampel	Synthesis parameter variable	Temperature (°C)	NaOH concentration (M)	Lattice constant (Å)	X-Ray density (g/cm^3)	Crystallite size (nm)
M1	NaOH concentration	70	1.5	8.52	5.1	7.9
M2		70	3	8.54	5.0	12.4
M3		70	6	8.49	5.1	14.1
M4		70	12	8.52	5.1	15.8
S1	Synthesis Temperature	30	6	8.24	5.6	21.4
S2		50	6	8.54	5.0	9.3
S3		70	6	8.49	5.1	14.1
S4		90	6	8.50	5.1	12.9

The value of the lattice parameter is constant with increasing the NaOH concentration. The increasing of NaOH concentration is not sufficient producing significant deviation of cation distribution. The strain calculation shows a slightly decreased value with increasing NaOH concentration due to reduced defect in the crystal. Density values tend to be constant indicating volume changes followed by significant molar mass changes. It is shown in Table 1 that the crystallite size increases with increasing NaOH concentration. The availability of OH⁻ ions influences the nucleation process and enhances the crystal growth of Co_{0.5}Zn_{0.5}Fe₂O₄ nanoparticles.

3.2. Morphology analysis

The morphology of Co_{0.5}Zn_{0.5}Fe₂O₄ samples with NaOH concentration 6 M and synthesis temperature 70°C were investigated using transmission electron microscopy (TEM) and the results are shown in Figure 3. It is shown that nanoparticle is in the form of aggregate. The observation of the image reveals that the particles are approximately spherical in shape and fine particles are agglomerated. In other words, the decrease in particle size led to agglomeration of magnetic fine particles. Because of the small size, single domain particles experience a magnetic moment proportional to their volume and get permanently magnetized. The SAED image shows that the formation of diffraction rings composes the non-continuous diffraction pattern. The sample can be considered as polycrystalline Co_{0.5}Zn_{0.5}Fe₂O₄ nanoparticles which possess low crystallinity compared than bulk material [3].

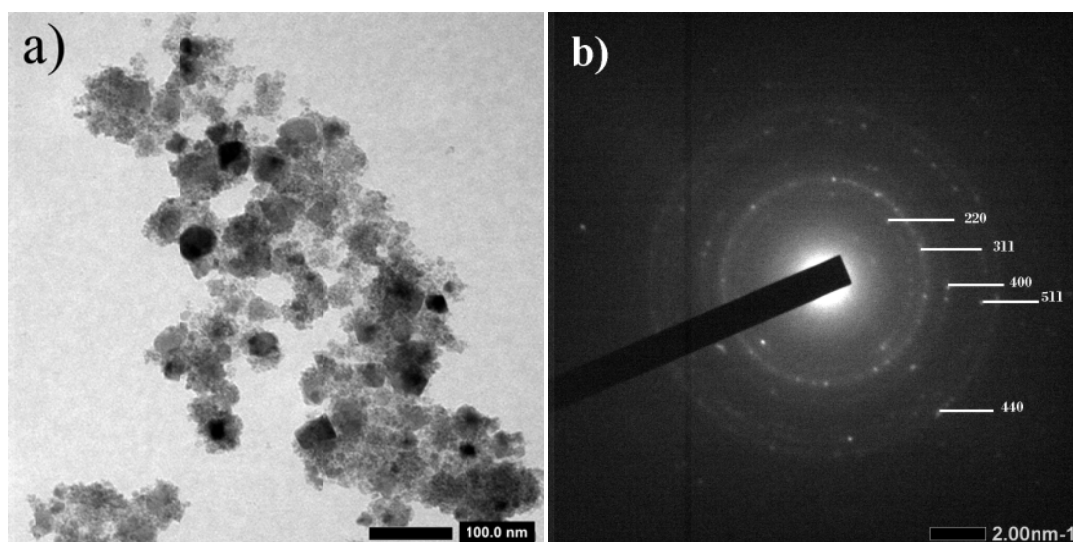


Figure 3. (a) TEM image and (b) SAED image of Co_{0.5}Zn_{0.5}Fe₂O₄.

3.3. FTIR spectrum analysis

FTIR spectra of as-synthesized Co_{0.5}Zn_{0.5}Fe₂O₄ nanoparticles are presented in Figure 4. Two main broad metal-oxygen (M-O) bands are seen in the FTIR spectra of spinel ferrites. The absorption peaks in wavenumber of 563 - 609 cm⁻¹ and 316 - 493 cm⁻¹ were observed which corresponded to intrinsic stretching vibration of metal-oxygen at tetrahedral and octahedral sites. The absorption bands of 1049.28 cm⁻¹, 1342.46 cm⁻¹, 1519.91 cm⁻¹, 1627.92 cm⁻¹ corresponds to bending vibration of O-H and 2337.72 cm⁻¹, 3356.14 cm⁻¹, 3410.15, 3749.62 cm⁻¹, 3873.06 cm⁻¹ can be assigned to hydrogen-bonded O-H stretching vibration arising from surface hydroxyl groups on nanoparticles and adsorbed water.

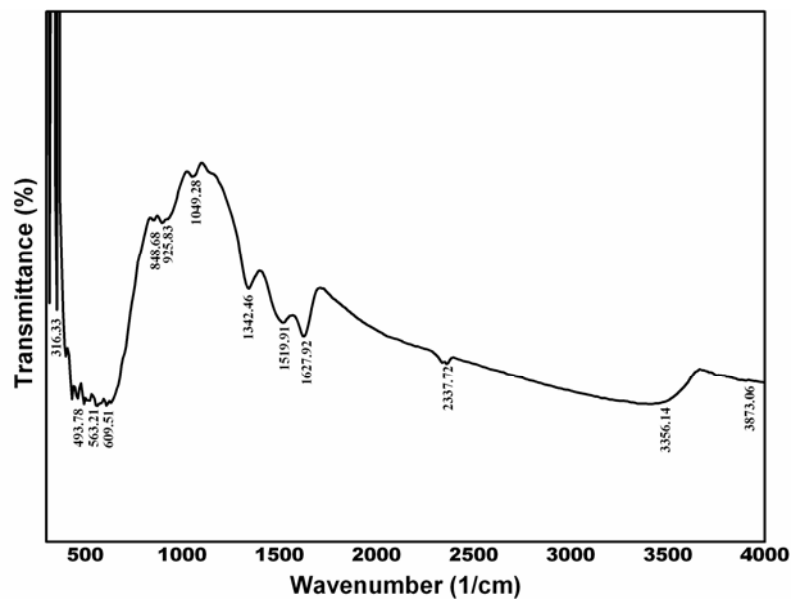


Figure 4. IR spectra of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ systems.

3.4. Magnetic measurement

The magnetic properties of samples were measured by using Vibrating Sample Magnetometer (VSM) in room temperature. Figure 5 and Figure 6 show the hysteresis loops of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples for various NaOH concentrations and synthesis temperature, which indicate that the samples have ferimagnetic behaviour with coercivity and remanent magnetization value larger than zero ($H_c > 0$ and $M_r > 0$). It also shown that they do not fully saturate at maximum external field of 15 kOe which indicated they tend to have single domain structure. These curves present very low coercivity and low residual magnetization after removal of magnetic field. This behaviour is known as superparamagnetism, which occurs only at nanoscale dimension.

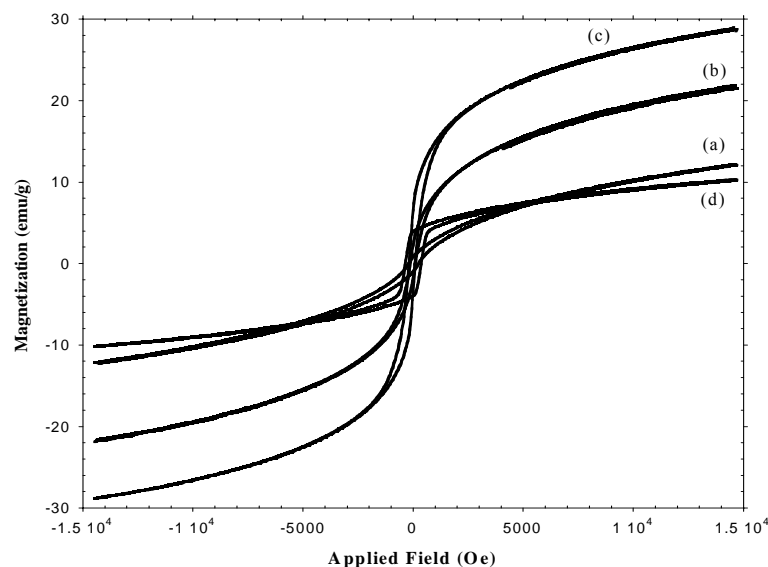


Figure 5. Hysteresis loops of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ in variation of NaOH concentrations: (a) 1.5 M, (b) 3 M, (c) 6 M, and (d) 12 M.

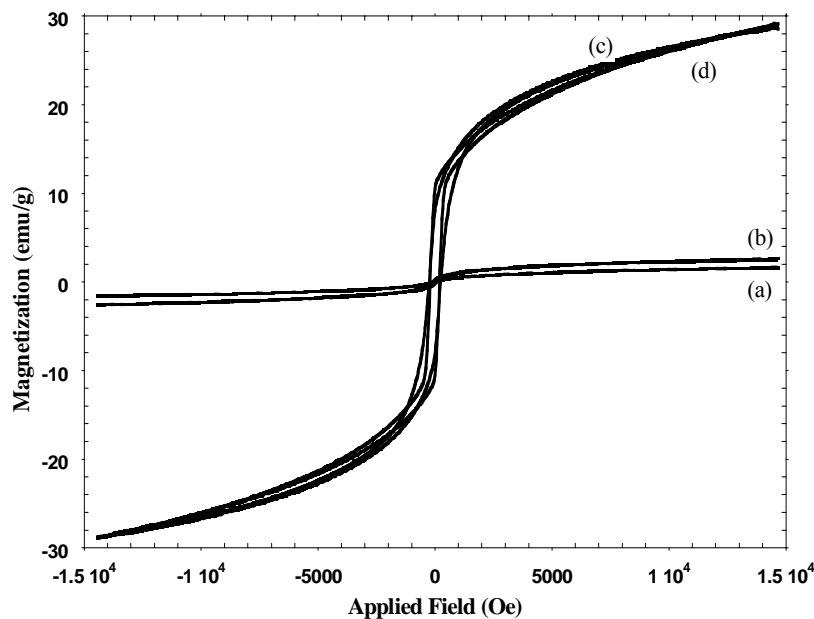


Figure 6. Hysteresis loop of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ in variation of synthesis temperatures : (a) 30°C, (b) 50°C, (c) 70°C, and (d) 90°C.

The measurement results of coercivity (H_c), maximum magnetization (M_{max}) and magnetic anisotropy constant (K) is indicated in Table 2. According to Table 2, the value of coercivities (H_c) increases in range 51.1 to 545.56 Oe with increasing crystallite size for the sample with variations of NaOH concentration. This result indicates that the coprecipitation process with increasing NaOH concentration can increase the growth rate and the crystallization progress for the magnetic nanoparticles. This variation of H_c with crystallite size can be explained on the basis of domain structure, critical diameter and the anisotropy of the crystal [22-23].

Table 2. Crystallite size, coercivity, maximum magnetization and magnetic anisotropy constant of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles synthesized at different NaOH concentration and synthesis temperature.

Sampel	Synthesis parameter variable	Temperature (°C)	Crystallite size (nm)	H_c (Oe)	M_{max} (emu/g)	K (erg/g)
M1	NaOH concentration	70	7.9	51.1	12.4	316.9
M2		70	12.4	126.9	21.9	1388.0
M3		70	14.1	257.4	29.0	3732.0
M4		70	15.8	545.6	10.3	2815.1
S1	Synthesis Temperature	30	21.4	52.5	1.6	42.8
S2		50	9.3	123.5	2.6	163.6
S3		70	14.1	257.4	29.0	3732.0
S4		90	12.8	251.3	29.2	3668.8

In the single domain region one would observe that as the crystallite size decreases the coercivity also decreases because of the thermal effect [24]. Above blocking temperature, the magnetic anisotropy energy barrier of the single domain nanoparticles is overcome by thermal energy and then the spins fluctuate randomly and will easily magnetized by an external magnetic field. The coercive field is associated with the strength of the magnetic field that is required to overcome the anisotropy

barrier. According to the Stoner - Wohlfarth theory, magnetic anisotropy energy (E_A) for non-interacting single domain particles is given by [22]

$$E_A = KV \sin^2 \theta \quad (1)$$

where K , V , and θ are magnetic anisotropy energy constant, volume of the particles and the angle between magnetization direction and the easy axis of a nanoparticle, respectively. With the reduction of magnetic anisotropy, the magnetic anisotropy energy barrier (E_A) decreases, which causes lower external magnetic field for spin reversal. When the crystallite size increases, then the volume of the nanoparticles also increases and the magnetic anisotropy energy is enhanced.

For the sample with variations of synthesis temperature the value of coercivities also increases in range 123.5 to 257.4 Oe with increasing crystallite size due to the same reason with samples of NaOH concentration. But for S1 there is some deviation which shows a larger crystallite size with lower H_c value. It could be attributed to either of two reasons. First, it may due to the expected crossover from single domain to multi domain behaviour with increasing size. Second, such phenomena can arise from crystal structure of nanoparticles. Nanoparticles which are synthesized at low synthesis temperatures may have low crystallinity degree caused by the nucleation and crystal growth process which are not optimal. The maximum magnetization shows an increasing trend with an increasing NaOH concentration and synthesis temperature. The value of maximum magnetization is strongly influenced by the degree of crystallinity of the samples.

4. Conclusion

Powder of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles has been successfully synthesized by co-precipitation method. Variations on synthesis parameter i.e. NaOH concentrations and synthesis temperature were found to influence the crystallite size and crystallinity degree due to their contribution in the nucleation and crystal growth process during synthesis. TEM image confirms the reflection peaks shown in the XRD pattern. IR spectral shows vibration in the tetrahedral and octahedral sites that confirm the spinel structures. The VSM magnetic measurement shows the hysteresis loops that indicate ferimagnetic behaviour and tend to be superparamagnetic with decreasing crystallite size. The coercivity and maximum magnetization increases relatively by increasing crystallite size with variations of NaOH concentration and synthesis temperature. It is attributed to the single domain structure existence and crystallinity degree of nanoparticles.

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