

## Crystal Structures and Magnetic Properties of Silica-Encapsulated CoZnFe<sub>2</sub>O<sub>4</sub> Magnetic Nanoparticles

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Zinc-doped cobalt ferrite magnetic nanoparticles (CoZnFe<sub>2</sub>O<sub>4</sub>) with silica encapsulation have been successfully synthesized by using coprecipitation method. The concentration of silica was varied by 0 %, 5 %, 10 %, 15 %, 20 %, 30 % and 50 % of weight. The XRD spectra show that all samples have the character of the main spinel diffraction peaks ( $2\theta$ ) attributed to the (220), (311), (400), (422), and (511) planes. The FTIR analysis shows that the intrinsic stretching vibrations of metal-oxygen at the frequency range of 393 cm<sup>-1</sup> - 401 cm<sup>-1</sup> and 470 cm<sup>-1</sup> - 563 cm<sup>-1</sup> were found at octahedral and tetrahedral sublattices, respectively. The unencapsulated CoZnFe<sub>2</sub>O<sub>4</sub> nanoparticle has coercivity ( $H_c$ ) and maximum magnetization ( $M$ ) of 251 Oe and 29.0 emu/gram, respectively. The coercivity value of the encapsulated nanoparticles increases up to 853 Oe with the increase of silica concentration, while the maximum magnetization decreases to 24.2 emu/gram.

**Keywords :** CoZnFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles, coprecipitation, encapsulation, silica

### 1. Introduction

The magnetic nanoparticle is a subject which has been studied intensively over the last few years, due to their wide applications in various fields, from industrial to biomedical such as magnetic recording, drug delivery, catalysts, sensors, microwave absorption, ferrofluids, information storage systems and magnetic resonance imaging [1]. One of the magnetic nanoparticles that attract many researcher is the spinel ferrite with molecular formula MFe<sub>2</sub>O<sub>4</sub> (where M is a divalent metal ions such as Mn<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, etc.). This is due to some ferrite spinel materials having good properties such as high saturation magnetization, high coercivity, mechanical hardness, chemical stability and strong anisotropy [2, 3]. Generally, the ferrite spinel structure is classified into normal spinel and inverse spinel, depending on the cation distribution in the crystal lattice space. For the normal spinel, all divalent

cations of Me<sup>2+</sup> occupy the tetrahedral site (A) and all trivalent cations of Fe<sup>3+</sup> reside in the octahedral site (B), whereas for the inverse spinel all divalent cations Me<sup>2+</sup> are in the octahedral lattice and the trivalent cations Fe<sup>3+</sup> are distributed in the tetrahedral (A) and octahedral (B) site [4].

Some particular spinel ferrite nanoparticles, i.e. CoFe<sub>2</sub>O<sub>4</sub> and ZnFe<sub>2</sub>O<sub>4</sub> have attracted the attention of many researchers because they have unique properties. CoFe<sub>2</sub>O<sub>4</sub> nanoparticles have inverse spinel structure, moderate saturation magnetization, good electric properties, high magnetocrystalline anisotropy, good mechanical properties and good chemical stability, whereas ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles have normal spinel structure, chemical and thermal stability properties [5], high magnetic permeability and electrical conductivity and low coercivity [6]. For certain application like hyperthermia therapy that needs nanoparticles with high magnetization saturation and low coercivity, CoFe<sub>2</sub>O<sub>4</sub> and ZnFe<sub>2</sub>O<sub>4</sub> must be combined. The combination of both nanoparticles with the same composition will produce Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanoparticle.

Recently, Zinc doped ferrites are widely studied by several researchers, Indrayana *et al.* have reported a study on Zn doped Mn mixed ferrite and found that the maximum specific magnetization of nanoparticles tends

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to increase with the increase of calcination temperature [7]. Yusmar *et al.* have synthesized Mn-Zn spinel ferrite using coprecipitation method and found that for the zinc rich Mn-Zn spinel ferrite, the dielectric parameter such as the real dielectric constant, the imaginary dielectric constant, the tangent loss and the AC conductivity decrease with the increase of Zn concentrations [8].

There are many methods that can be used to synthesize Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanoparticle, such as ceramic processing [9], reverse microemulsion [10], sol-gel method [11], hydrothermal [12], coprecipitation method [13], etc. But the coprecipitation method is the widely used method, due to its flexibility to the material composition being used, the controllable of shape and particles size, its low cost and simple technique [14, 15].

The Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles have a strong tendency to agglomerate [12], because of their magnetic interparticle interactions and large nanoparticle surface reactivity, which can give a collective or different magnetic response as compared to non-agglomerated nanoparticles. To avoid agglomeration, different routes had been adopted, e.g. dispersing nanoparticles in the non-magnetic matrix, surface silica coating, polymer coating etc [11]. Surface silica coating and polymer coating are examples of nanoparticles encapsulation treatment. These encapsulation treatments usually have other objectives, among them are to add chemical stability, dispersibility, biocompatibility, homogeneous range and morphology distribution of magnetic nanoparticles.

Silica (SiO<sub>2</sub>) is one of the nonmagnetic material that is commonly used to encapsulate magnetic nanoparticles. The advantages of using silica as encapsulated materials are to prevent nanoparticles agglomeration, improve chemical stability and create biologically friendly material [14]. The silica precursor which is commonly used is the tetraethyl orthosilicate (TEOS) as used by Girgis *et al.* [16] and Nadeem *et al.* [11]. However, TEOS has few drawbacks such as more expensive and not friendly to the environment. Therefore, other precursor of silica is needed to minimize these drawbacks, for example by using sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) which is less expensive, non-toxic and more friendly to the environment [17, 18]. In this direction some researchers have conducted research's dealing with magnetic nanoparticles encapsulated by silica using Na<sub>2</sub>SiO<sub>3</sub> as silica precursor. In this paper we present our study on the effect of silica concentration variation as encapsulating material, to the crystal structures, the morphological and the magnetic properties of CoZnFe<sub>2</sub>O<sub>4</sub> nanoparticles.

## 2. Experimental Method

### 2.1. Preparation of magnetic nanoparticle

The samples of Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanoparticles were synthesized by coprecipitation method. The precursor used in the synthesis are 2.703 g FeCl<sub>3</sub>·6H<sub>2</sub>O (Merck, Germany) dissolved in 25 mL of distilled water, 0.594 g of CoCl<sub>2</sub>·6H<sub>2</sub>O and 0.719 g of ZnSO<sub>4</sub>·7H<sub>2</sub>O also dissolved in 25 mL of distilled water, with the addition of 3.37 mL of HCl. The solution is then added in dropwise into 6 M NaOH (Merck, Germany) solution. The reaction is kept under constant stirring at 90 °C for 1 hour. Precipitated ferrite nano powder is washed with distilled water for six times. Finally, the sample is dried in a furnace at 900 °C for 5 hours.

### 2.2. Silica-encapsulated Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>

The Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanoparticles were dissolved into 30 ml of silica solution with different concentrations. The concentration of silica was varied by 5 % (1.5 mL silica and 28.5 mL distilled water), 10 % (3.0 mL silica and 27 mL distilled water), 15 % (4.5 mL silica and 25,5 mL distilled water), 20 % (6 mL SS + 24 mL distilled water), 30 % (9 mL SS + 21 mL distilled water) and 50 % (15 mL SS + 15 mL distilled water) of weight, and labeled as samples S1, S2, S3, S4, S5 and S6, respectively. The silica solution was formed from Sodium Silicate (Na<sub>2</sub>SiO<sub>3</sub>) dissolved into distilled water, stirred at room temperature for 30 minutes. Then 0.6 grams of Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanoparticles are added to the aqueous silica solution and stirred at room temperature for 5 hours so that the nanoparticles are evenly mixed and bonds formed between the nanoparticles and the silica. The precipitation process is then carried out using an external magnetic field (permanent magnet). The resulting precipitation is washed with distilled water for five times. Finally, the sample was dried at room temperature and then dried in a furnace at 50 °C for 50 minutes to ensure the sample is completely dry.

The crystalline phases of the nanoparticles powder were characterized using X-Ray diffractometer Shimadzu XD using monochromic Cu-K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation source. The vibrational spectra of nanoparticles were obtained using Fourier transform infrared spectroscopy (FTIR) Prestige Shimadzu-21 in the range of 4000-400 cm<sup>-1</sup>. The morphology and selected area diffraction (SAED) pattern were obtained using transmission electron microscope (TEM) Jeol Jem-1400. The room temperature magnetic properties measurement of the nanoparticle samples was

carried out using vibrating sample magnetometer (VSM) Riken Denshi Co Ltd.

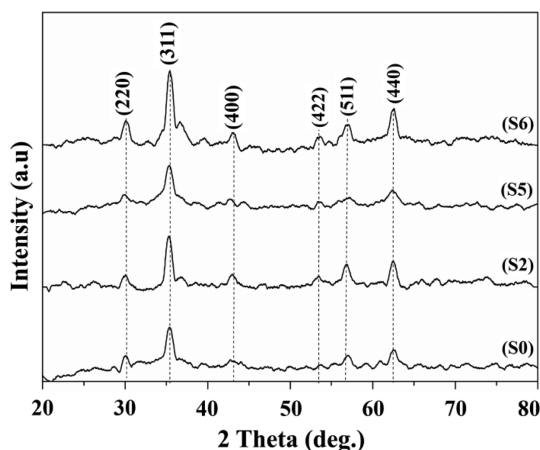
### 3. Results and Discussion

X-ray diffraction (XRD analysis) is a unique method to determine crystallinity of a compound. The XRD spectra of  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles before and after encapsulated with silica are shown in Fig. 1.

Figure 1 shows the XRD patterns of both unencapsulated and encapsulated  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles. As compared with JCPDS data (JCPDS file No. 22-1068 for  $\text{CoFe}_2\text{O}_4$  and JCPDS file No. 89-1009 for  $\text{ZnFe}_2\text{O}_4$ ), both samples show the character of the main spinel diffraction peaks ( $2\theta$ ) attributed to the (220), (311), (400), (422), (511) and (440) planes and show the characteristics of a single-phase cubic spinel structure with  $Fd\bar{3}m$  space group. The mean peak of (311) tends to shift to the lower diffraction angle due to the strain on the crystal lattice of  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles [11].

The structural parameters of  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  and Silica-encapsulated  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles is shown in Table 1.

The interplanar spacing ( $d$ ), lattice parameters ( $a$ ) and density ( $\rho$ ) tend to be constant. This is because the addition of silica layer on the surface of magnetic nanoparticles does not affect their ferrite crystal structure [19]. The average crystallite size ( $t$ ) has been calculated using Debye-Scherrer's formula [20]. The results show that the unencapsulated  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  has the particles size of 14.4 nm. The encapsulated samples have particles size which tend to increase after silica encapsulation (S2 and



**Fig. 1.** The XRD spectra of  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles encapsulated by silica with various concentrations: (S0)  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ , (S2)  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  + silica 10 %, (S5)  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  + silica 30 %, (S6)  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  + silica 50 %.

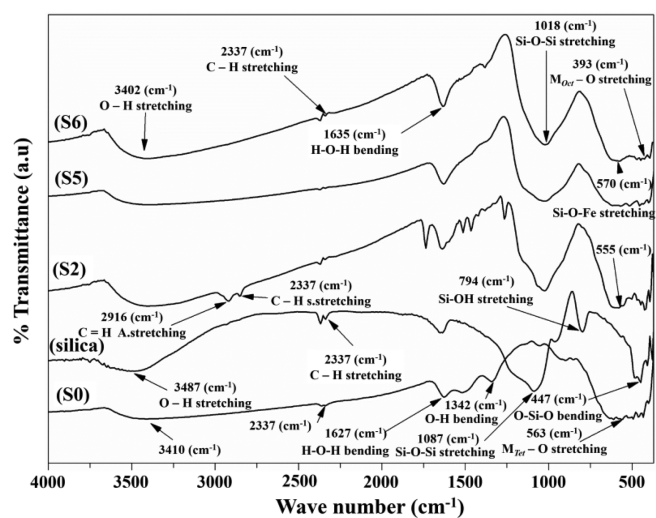
**Table 1.** Structural parameters of  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  and Silica-encapsulated  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles.

Sample	$d$ (Å)	$a$ (Å)	$\rho$ (g/cm <sup>3</sup> )	$t$ (nm)
S0	2.53	8.40	5.3	14.4
S2	2.54	8.42	5.3	18.1
S5	2.54	8.42	5.3	13.7
S6	2.53	8.39	5.4	15.4

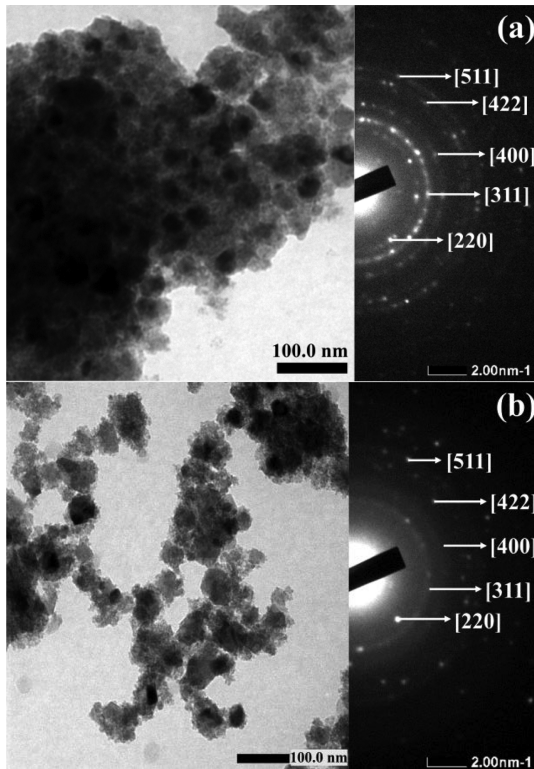
S6). This is due to the presence of silica with water molecules as an encapsulation material on the surface of nanoparticles, enabling the presence of hydrolysis and condensation reactions, thus resulting in the increase of nucleation. This in turn affects and increased the crystallite size [21]. For sample S5, there is a decrease in the size of crystallites, we think this is caused by an imperfect hydrolysis and condensation reaction, enabling the the silica to inhibit the growth of crystallites.

Bonding analysis of the samples can be performed base on the spectra provided by FTIR in Figure 2.

The bands at  $401\text{ cm}^{-1}$  and  $563\text{ cm}^{-1}$  of  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles are due to M-O tetrahedral stretching and M-O octahedral stretching vibration, respectively. These two characteristic bands show the formation of a bond between metal salt and oxygen in the entire spinel ferrite structure. After silica encapsulation, the  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticle samples show some absorption bands. Peaks at  $1087\text{ cm}^{-1}$  are due to Si-O-Si asymmetric stretching vibration. This vibrational frequency is shifted toward a lower value due to a higher bond length between Si-O after interacting with the metal ion of bare nanoparticles.

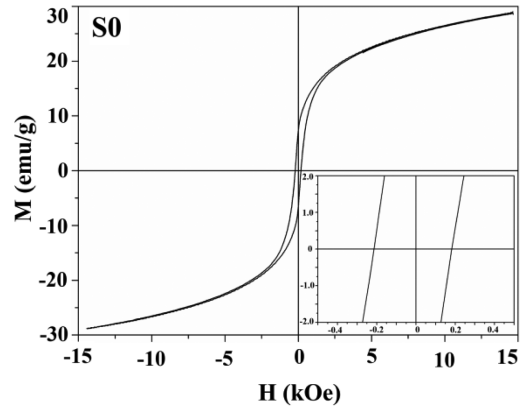


**Fig. 2.** The FTIR spectra of  $\text{CoZnFe}_2\text{O}_4$  nanoparticles encapsulated by silica with various concentration: (S0)  $\text{CoZnFe}_2\text{O}_4$ , silica, (S2)  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  + silica 10 %, (S5)  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  + silica 30 %, (S6)  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  + silica 50 %.



**Fig. 3.** TEM images of CoZnFe<sub>2</sub>O<sub>4</sub>: (a) as prepared, (b) Encapsulated by silica 50 %.

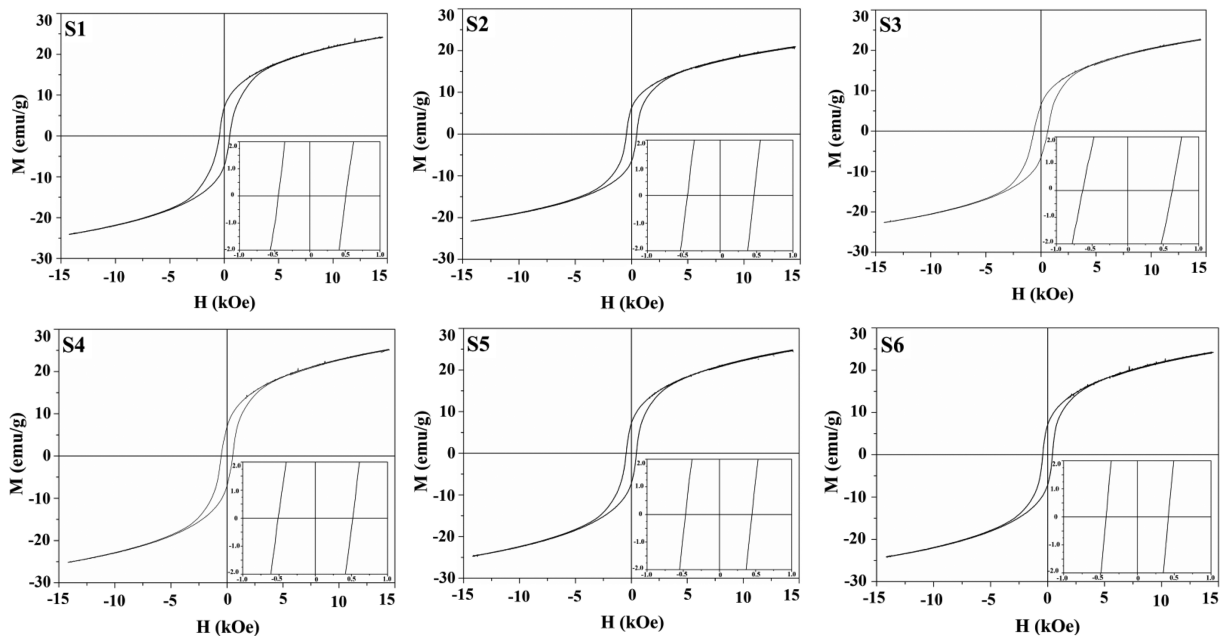
The appearance of band at 794 cm<sup>-1</sup> is due to Me-O-Si stretching which definitely shows the formation of a bond



**Fig. 4.** The hysteresis loop of CoZnFe<sub>2</sub>O<sub>4</sub> nanoparticles.

between bare nanoparticles and the silica layer [22], this is an indication that the silica layer has successfully encapsulated the surface of bare nanoparticles. Bands at 1627 cm<sup>-1</sup>, 2337 cm<sup>-1</sup>, and 3410 cm<sup>-1</sup> confirmed the existence of hydroxyl group bonds within the Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanoparticle samples.

For S2 sample, there is a kind of vibration in the 2846 cm<sup>-1</sup> and 2924 cm<sup>-1</sup> wave numbers which are identified as the symmetric stretching C-H vibration bond and the C = H antisymmetric stretching respectively [23]. The bond is associated with the presence of water molecules found in the S2 Sample, which we think to have arisen due to the imperfection in the sample drying process.



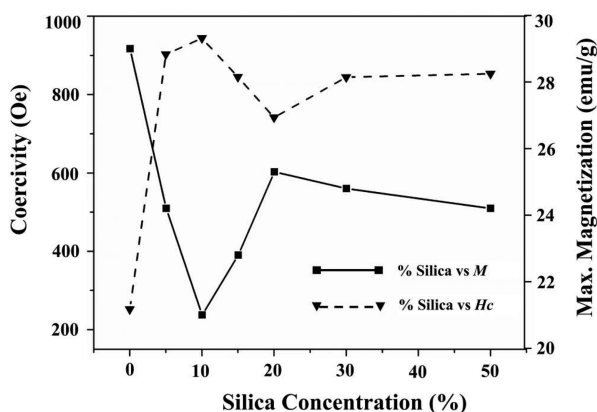
**Fig. 5.** The hysteresis loop of CoZnFe<sub>2</sub>O<sub>4</sub> nanoparticles encapsulated by silica with various concentration: (S1) CoZnFe<sub>2</sub>O<sub>4</sub> + silica 5 %, (S2) CoZnFe<sub>2</sub>O<sub>4</sub> + silica 10 %, (S3) CoZnFe<sub>2</sub>O<sub>4</sub> + silica 15 %, (S4) CoZnFe<sub>2</sub>O<sub>4</sub> + silica 20 %, (S5) CoZnFe<sub>2</sub>O<sub>4</sub> + silica 30 %, (S6) CoZnFe<sub>2</sub>O<sub>4</sub> + silica 50 %.

The morphology and selected area electron diffraction (SAED) image of  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles before and after silica encapsulation, using transmission electron microscopy (TEM), is shown in Fig. 3.

Figure 3(a) shows the TEM images of  $\text{SiO}_2$  unencapsulated  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles. It can be observed that the nanoparticles are agglomerated with the grain size of about 23.5 nm. Agglomeration is due to the strong interaction between the nanoparticles and the high reactivity of the nanoparticle surface. Fig. 3(b) shows the TEM images of  $\text{SiO}_2$  encapsulated  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles. The grain size of the nanoparticles is slightly decreases to 15.5 nm. This is due to the nanoparticles are non-agglomerated because of the presence of  $\text{SiO}_2$  as the non-magnetic material.  $\text{SiO}_2$  surface coating act as a spacer between the nanoparticles and hence reduces agglomeration [11]. The SAED image of  $\text{SiO}_2$  unencapsulated  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles shows a discontinuity pattern. This is an indication of the formation of polycrystalline materials as a result of the agglomeration of the nanoparticles. After silica encapsulation, the spots pattern was formed, which is due to the effect of the decrease of agglomeration [24].

The magnetic properties of  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles has been investigated using vibration sample magnetometer (VSM).

Figure 4 and Fig. 5 shows the hysteresis loops of unencapsulated and  $\text{SiO}_2$  encapsulate  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles, respectively. The coercivity and the maximum magnetization value of unencapsulated  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles were 251.9 Oe and 29.0 emu/g, respectively. After silica encapsulation, the coercivity tends to increase due to the increase of crystallite size. While maximum magnetization tends to decrease because silica is a non-magnetic material in nature. Fig. 6 shows the relation between the coercivity/the maximum magnetization and



**Fig. 6.** The relation between the coercivity/the maximum magnetization and the concentration of silica.

the concentration of silica.

## 4. Conclusion

The mixed spinel ferrite of  $\text{CoZnFe}_2\text{O}_4$  nanoparticles has been successfully synthesized using coprecipitation method. The structural parameters like interplanar spacing ( $d$ ), lattice parameter ( $a$ ) and density ( $\rho$ ) of  $\text{CoZnFe}_2\text{O}_4$  before and after encapsulation tends to be constant. The  $\text{SiO}_2$  unencapsulated  $\text{CoZnFe}_2\text{O}_4$  nanoparticles tend to agglomerate. After silica encapsulation, the agglomeration slightly decrease. The silica encapsulated  $\text{CoZnFe}_2\text{O}_4$  is more dispersed and agglomeration is reduced. Coercivity value before encapsulated was 251.9 Oe, and after silica encapsulation coercivity value increases. The maximum magnetization before encapsulation is 29.0 emu/g, and after silica encapsulation the maximum magnetization value decrease.

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