

Effect of Zinc on Crystal Structure and Magnetic Properties of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ Nanoparticles Synthesized by Coprecipitation Method

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Abstract. The effects of zinc (Zn) on the crystal structure and magnetic properties of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles (NPs) were investigated. $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ NPs have been successfully synthesized by co-precipitation method with synthesis temperature of 70 °C and various of x from 0.2 to 0.8. The structural and magnetic properties were determined and characterized in detail by X-ray Diffractometer (XRD), Transmission Electron Microscope (TEM), Fourier Transform Infrared (FTIR) and vibrating sample magnetometer (VSM). X-ray Diffraction analysis showed that the samples had the single phase cubic spinel structure. The crystallite size of the samples was calculated by using Scherrer's formula within the range of 9.3 nm to 11.2 nm. The increase in lattice parameter from 8.179 Å to 8.212 Å by increasing zinc content as a result of the different ionic radii. The peak of FTIR spectra observed around 478 cm^{-1} and 586 cm^{-1} was assigned to vibration of octahedral and tetrahedral sites which confirmed the presence of the metal-oxide stretching band. The decrease in saturation magnetization (M_s) from 34.3 $\text{emu}\cdot\text{g}^{-1}$ to 20.3 $\text{emu}\cdot\text{g}^{-1}$ and the decrease in coercivity (H_c) from 674 Oe to 158 Oe are significantly affected by the increase of zinc content.

Keywords. Coercivity, coprecipitation method, magnetization, nanoparticles, Scherrer's formula.

1. Introduction

The investigation of nanoparticles ferrites recently become interesting because of its broad application in various fields. Nanoparticles ferrites have been used in many electronic devices because of their high electrical resistivity, mechanical hardness, and chemical stability. According to its structure, ferrites are classified into three types [1], i.e., spinel, garnets, and hexagonal ferrites. Study of spinel ferrite to be fascinating due to its interesting properties such as superparamagnetism, quantum magnetic tunneling and surface spin canting effect [2].

Among those spinel ferrites, we are interested in cobalt ferrite (CoFe_2O_4) and zinc ferrite (ZnFe_2O_4). Cobalt ferrite is known as a hard magnetic material with high coercivity, large magnetic anisotropy, high mechanical hardness and chemical stability [3]. On the other hand, zinc ferrite is a soft magnetic material with high resistivity, and high chemical stability [4]. Hard ferrite is suitable for inductance application, while soft ferrite is suitable for high-frequency applications. The combination



of both properties will complement each other, and hence cobalt-zinc mixed ferrite becomes useful for inductance and high-frequency applications. They are used for power inductors, cores of transformers, electric motor, generator, etc. Additionally, Cobalt ferrite has inverse spinel, but zinc ferrite has normal spinel [5]. It could be inferred that studying cobalt-zinc ferrite become very interesting due to their different properties.

Deraz *et al.* [6] prepared $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ by combustion route found that increasing zinc concentration influenced the lattice constant, unit cell volume, ionic radii, the distance between magnetic ion and bond lengths on the tetrahedral and octahedral sites. Hassadee *et al.* [7] prepared $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 0.5$) by ceramic processing revealed that substitution of Co^{2+} with Zn^{2+} lead to increase the lattice parameter. Ali *et al.* [8] synthesized $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0 - 0.3$) by sol/gel method reported that the zinc substitution increases in saturation magnetization. They observed that the structural and magnetic properties could be modified by varying the concentration. Previous research has been done work with high-temperature synthesis, but lack of investigation in low temperature. The properties of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ are influenced by the shape, size, and structure which depend on the synthesis process [9-11]. In this present work, the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ NPs is synthesized by varying x from 0.2 to 0.8 using co-precipitation methods due to an easy in a homogeneous mixing the main components. The purpose of this study is to investigate the effect of Zn concentration on crystal structure and magnetic properties of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$.

2. Materials and methods

The precursor was used in the synthesis were $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Merck KGaA, Germany), NaOH and HCl. At first, we prepared two different solutions, i.e. solution A, and solution B. The solution A was a mixture of 0.2 M solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ mixed $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ and prepared in 50 mL of distilled water. Separately, the solution B was prepared using 0.4 M of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 50 mL distilled water. Then solution A and B were mixed at room temperature, stirred, followed by added 3.37 mL of HCl (37 %). This mixture was drop-by-drop into a base solution (0.6 M solution of NaOH dissolved in 50 mL distilled water) and kept 70 °C under constant stirring. The solutions were maintained at 80 °C for 60 min. Then cooled to room temperature and precipitated. The fine particles were collected by using magnetic separation. These particles were washed several times to remove salt or impurities and dried at 90 °C for 4 h to obtain a powder.

The powder samples were determined and analyzed by Rigaku MiniFlex 600 Benchtop X-Ray Diffractometer using monochromatic Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). XRD patterns were recorded in the range of 20° to 80°. The average crystallite size was calculated by applying peak broadening of (311) using Scherrer's formula. The morphology and microstructure were observed by a Transmission Electron Microscope (JEOL TEM 1400) at 200 kV. Infra-Red Spectroscopy measurement in the range of 400 cm^{-1} to 4000 cm^{-1} was measured by Fourier Transform Infra-Red (Shimadzu FTIR Spectrometer). Magnetic properties measurement was carried out by using a VSM (Riken Denshi Co., Ltd) at room temperature.

3. Results and discussion

Figure 1 shows XRD patterns of the sample. The pattern shows that all the characteristic peaks are a spinel structure. All the peaks perfectly match with the crystalline phase of cubic spinel structure as compared with JCPDS data. All XRD peaks have been matched with JCPDS file no. 82-1049 (ZnFe_2O_4) and 22-1086 (CoFe_2O_4) [7]. The estimation of the crystallite size is based on the full width half maximum (FWHM) of the highest intensity of (311) plane. The crystallite size of the samples was estimated using Scherrer's formula. The lattice parameter was also calculated from the same plane of the spinel structure using Bragg's equation.

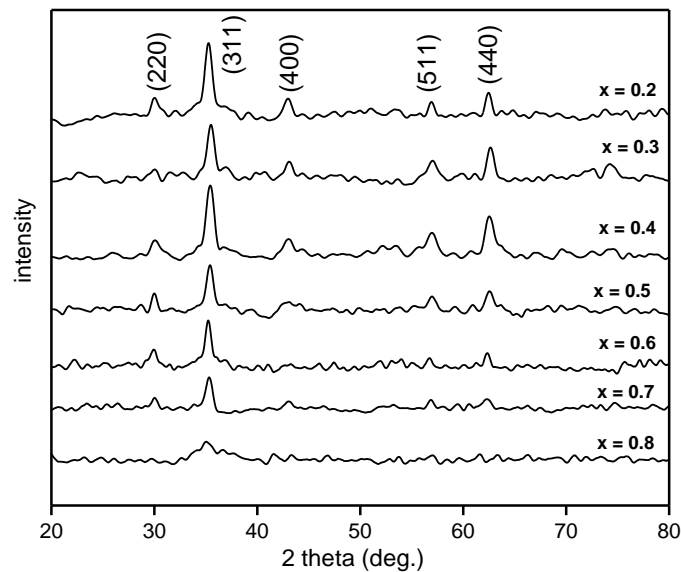


Figure 1. X-Ray Diffraction pattern for $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ with x varied from 0.2 to 0.8

Figure 2 shows the relation between zinc concentration on the crystallite size and lattice parameter. The crystallite size decreases with the increase in zinc concentration. It shows that the lattice parameter varies from 8.179 Å to 8.248 Å. It was observed that lattice parameter increases as zinc content increase. It could be explained that the ionic radii of zinc are higher than cobalt. The ionic radii of Zn^{2+} (0.88 Å) is larger than Co^{2+} (0.83 Å) [6]. Hence the lattice parameter increases as the increase in zinc content. Thus, the presence of zinc modifies in structural properties such as lattice parameter, ionic radii and the bond length on tetrahedral and octahedral sites of cubic spinel structure [8].

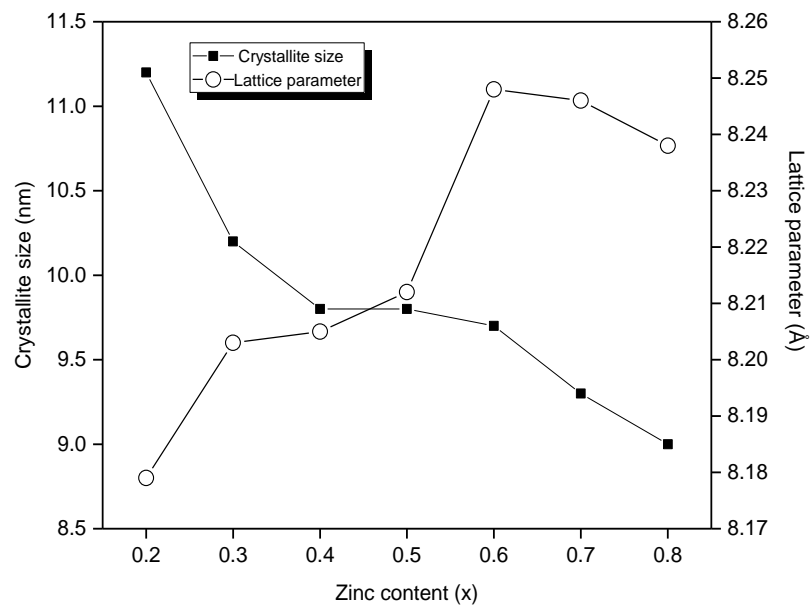


Figure 2. Crystallite size and lattice parameter of the $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$

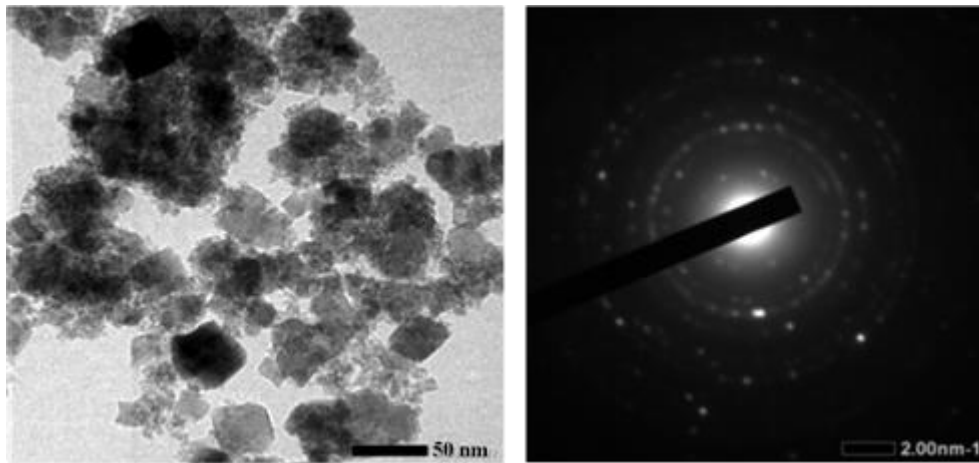


Figure 3. TEM Images of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (a) Morphology (b) SAED pattern

The TEM images are shown in the Figure 3. The selected sample is $x = 0.2$ with 20 % zinc concentration because it has the highest crystallinity and low non-ferrite phase. The indicator that sample has good crystallinity as well as regular spherical shape and size boundaries of the particles. However, the powders sample can easily agglomerate due to the nanosize effect and intrinsic magnetism. To obtain a dispersed sample, the yielded samples were ground. The SAED pattern (Figure 3.b) shows that the sample is being polycrystalline. The crystallite size of nanoparticles has a range value from 9 nm to 11 nm.

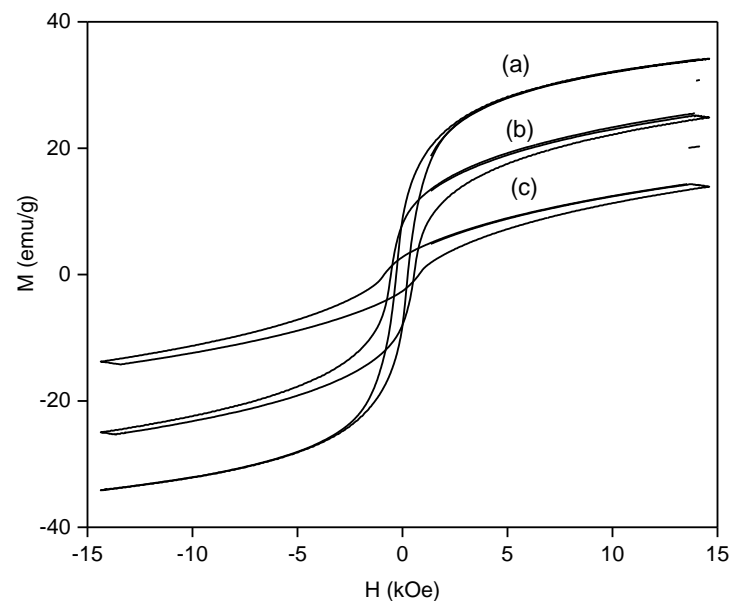


Figure 4. Hysteresis loop of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ for (a) $x = 0.2$, (b) $x = 0.5$, and (c) $x = 0.8$

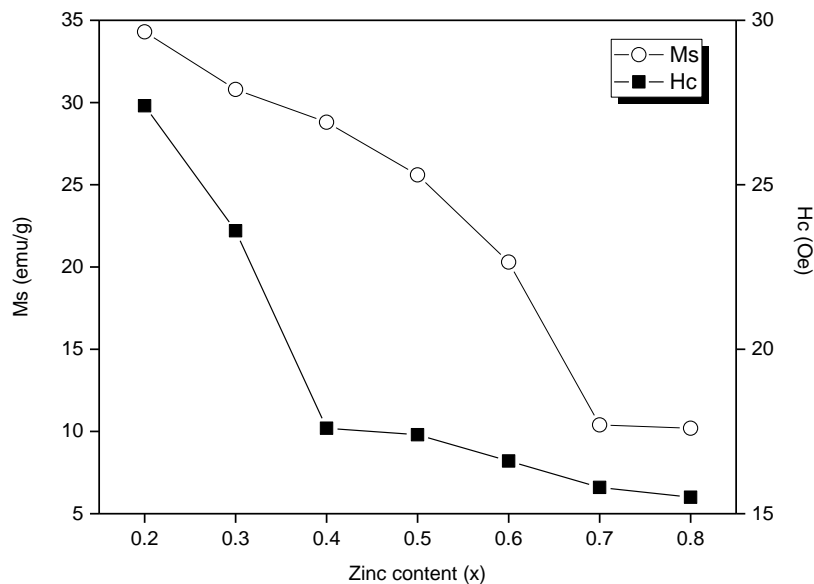


Figure 5. M_s and H_c of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ NPs

Figure 4 shows the hysteresis curve of the sample. The M_s reaches the maximum value of $34.3 \text{ emu}\cdot\text{g}^{-1}$ for $x = 0.2$ and then decrease. The M_s and H_c decrease by increasing zinc content as shown in Figure 5. The decrease in M_s due to the replacement of cations because of the changed preferential occupancy in the case of nanoparticles, a change in the distribution of Co^{2+} and Zn^{2+} in the two sites. Since zinc ions substitute for cobalt ions, the magnetic coupling weakens because of that zinc does not have an impact on the magnetic moment. The reducing of magnetic properties could be understood as a result of the relatively high orbital contribution of Co^{2+} to the magnetic moment.

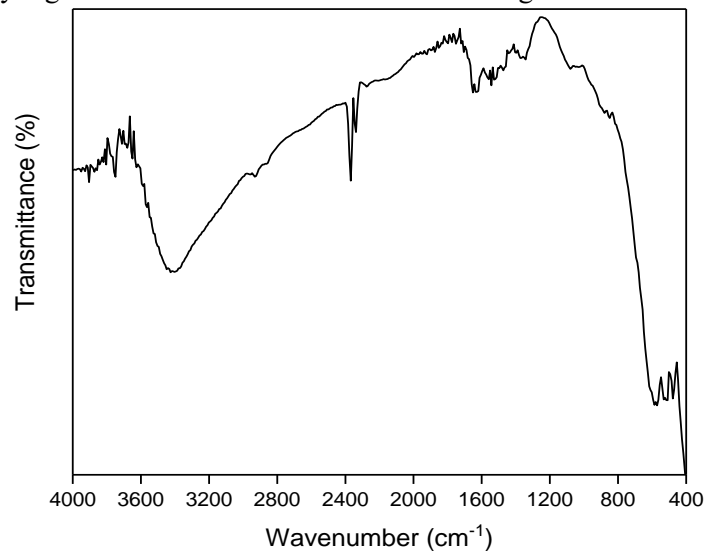


Figure 6. FTIR spectra of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$

FTIR spectra of the sample are presented in Figure 6. There are some main broads of metal-oxygen bands are shown by the FTIR spectra. The wave number observed at 400 cm^{-1} to 500 cm^{-1} are identified as a stretching vibration of metal-oxygen from the tetrahedral site. The band in the range of 500 cm^{-1} to 600 cm^{-1} are recognized as octahedral metal stretching. We observed the band at 478 cm^{-1} ,

509 cm^{-1} , 586 cm^{-1} and 393 cm^{-1} are assigned as $M_{\text{tetra}} \leftrightarrow O$. The absorption bands observed at 3404 cm^{-1} prove the presence of adsorbed water on the surface of the ferrite nanoparticles.

4. Conclusions

The samples of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ NPs have been successfully synthesized by co-precipitation methods. The XRD patterns show a cubic spinel structure for all sample. The increase in lattice parameter from 8.179 Å to 8.212 Å by increasing the zinc content as a result of Zn^{2+} substituted for Co^{2+} in the crystal structure. The crystallites size was found within the range of 9.3 nm to 11.2 nm. The decrease in magnetization saturation from 34.3 $\text{emu}\cdot\text{g}^{-1}$ to 20.3 $\text{emu}\cdot\text{g}^{-1}$ and the decrease in coercivity from 674 to 158 were affected by the increase of the zinc content. The peak observed around 478 cm^{-1} and 586 cm^{-1} of FTIR spectra were assigned to vibration of octahedral and tetrahedral sites which confirm the presence of a metal-oxide stretching band in ferrite.

Acknowledgments

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