

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

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Abstract. $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles have been successfully synthesized through coprecipitation method by varying NaOH concentrations from 0.5 M to 6 M and synthesis temperatures from 30 to 120 °C. The X-ray diffraction (XRD) pattern indicates samples consisting of multiphase structures such as spinel of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, $\alpha\text{-MnO}_2$, ZnO, $\lambda\text{-MnO}_2$, and $\gamma\text{-Fe}_2\text{O}_3$. The crystallite size of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ is in the range of 14.1 to 26.7 nm. The Transmission electron microscope (TEM) image shows that sample was agglomerate. The hysteresis loops confirm that nanoparticles are soft magnetic materials with low coercivity (H_c) in the range of 45.9 to 68.5 Oe. Those values increased relatively with increasing particles size. For NaOH concentration variation, the maximum magnetization of the sample increased from 10.4 emu/g to 11.6 emu/g with increasing ferrite content. Meanwhile, the maximum magnetization increased from 7.9 to 15.7 emu/g for samples with various synthesis temperature. The highest coercivity of 68.5 Oe was attained for a sample of 6 M NaOH under 90 °C. The highest magnetization of 15.7 emu/g was achieved for a sample of 1.5 M NaOH under 120 °C caused by the maximum crystallinity of sample.

Keywords: magnetic property, microstructural, NaOH concentration, synthesis temperature

1. Introduction

Magnetic nanoparticles have attracted interest in the field of nanomaterial because of the potential applications such as catalytic, biomedicine, magnetic resonance imaging (MRI), data storage [1]. Ferrite nanoparticle has formula MFe_2O_4 , which M is divalent metal ions i.e., Zn^{2+} , Mn^{2+} , Fe^{2+} , Cu^{2+} , Mg^{2+} , and Co^{2+} . Metal cation M can also be a combination of two different metal cations, for example, Mn^{2+} and Zn^{2+} . The $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticle is a soft magnetic material which has high initial magnetic permeability, high magnetization, high resistivity, and low power loss [2]. The nanoparticle can be prepared by using various techniques like combustion [2,3], coprecipitation [4,5], hydrothermal [6], mechanochemical processing [7], and spray pyrolysis [8]. Among of them, coprecipitation method is relatively simple, short reaction time, high reaction yield, and small particle size.

The microstructure of nanoparticle directly affects their magnetic, electrical, dielectric, and optical properties [9]. The microstructure of nanoparticle can be tuned by controlling synthesis parameters,



such as metal precursors type, pH, reaction temperature and reaction rate [6]. All of the parameters directly affect the crystallite size of nanoparticle [6]. Treatment temperature sintering for $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ would be affected by crystal structure and magnetic properties [2]. In the case of coprecipitation synthesis, a reaction temperature of solutes and pH is very sensitive in determining the reaction yield. Therefore, the presented research would like to control the synthesis temperature and pH of solutes by varying co-precipitant agent concentrations, in this case, belong to NaOH concentration.

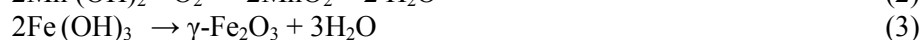
2. Experimental Method

The metal precursors such as $\text{MnCl}_2 \cdot \text{H}_2\text{O}$ (Merck, Germany), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck, Germany) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Merck, Germany) were used to prepare metal cation of Mn^{2+} , Zn^{2+} , and Fe^{3+} . Those hydroxides were dissolved in 40 mL of distilled water. The HCl solution of 3.37 mL than was added to the precursor solution. The mixture was stirred for 5 minutes at room temperature with constant stirring of 500 rpm. The obtained solution was dropped wisely to the co-precipitant solution of 50 mL NaOH (1.5 M) under the constant stirring rate of 1000 rpm and different synthesis temperature of room temperature (A5), 60 °C (A6), 90 °C (A2), and 120 °C (A7). In the case of NaOH concentration, samples were synthesized under a temperature of 90 °C and NaOH concentration of 0.5 M (A1), 1.5 M (A2), 3 M (A3), and 6 M (A4). The synthesis reaction was kept for 60 minutes until the formation of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticle formed which is indicated by the dark brown mixture. The mixture then was cooled naturally until thermal equilibrium occurred with the room temperature. During the cooling process, dark brown slurry of nanoparticles will separate from the solvent. The slurry was washed for six times to remove the incomplete chemical precursors during synthesis. Those processes will provide a dark brown slurry which is ready to be heated in a furnace to a constant temperature of 90 °C for 4 hours. At last, the dark brown powder of nanoparticles will be obtained. The crystal structure, microstructure, vibrational spectra, and magnetic properties of the powder were characterized by using XRD Shimadzu XD, TEM JEOL Jem-4000, IR spectrometer Shimadzu Prestige-21 and VSM Riken Denshi Co. Ltd., respectively.

3. Results and Discussion

3.1. X-Ray diffraction pattern of nanoparticles

The diffraction pattern of samples for both NaOH concentration and synthesis temperature variation is presented in Figure 1 and 2. The diffraction pattern referred to the standard data of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (JCPDS no. 10-0467). The profile of diffraction pattern confirmed the formation of spinel structure and some other structures, i.e. ZnO (36-1451), λ - MnO_2 (44-0992), α - MnO_2 (44-0141), γ - Fe_2O_3 (39-1346). Those phases were estimated from metal precursors which exhibited incomplete chemical reaction during synthesis. Principally, the stage of coprecipitation was initialized by the formation of hydroxide compound via coprecipitation reaction of a metal salt precursor with NaOH. The HCl solution was taken place to break the ionic bond between metal cation and chloride anions or sulfate group. Those metal cations were highly attracted by hydroxide anion OH^- to form hydroxide compound. Each hydroxide compound of $\text{Zn}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ has different reaction rate to form ferrite nanoparticles. The hydroxide which fails to form ferrite nanoparticles will be oxidized by oxygen in the atmosphere to form further oxidation state. The complete chemical reaction of formation the oxidation state can be presented in the following reactions,



Regarding Figure 1, in sample A2 (3M), the presence of ZnO phase of which composition is greater than ferrite $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and λ - MnO_2 phases are higher than α - MnO_2 is due to the maximum

oxidation process exhibited by $\text{Zn}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$. According to diffraction profile, sample A4 has the lowest degree of crystallinity due to the highest NaOH concentration that contributes to the largest number of OH^- anion that presents in solution. The number of OH^- is very sensitive to affect the environmental condition for the reaction. In other hand, samples A1 to A4 have a better degree of crystallinity and sample A3 of 1.5 M NaOH has the highest degree of crystallinity.

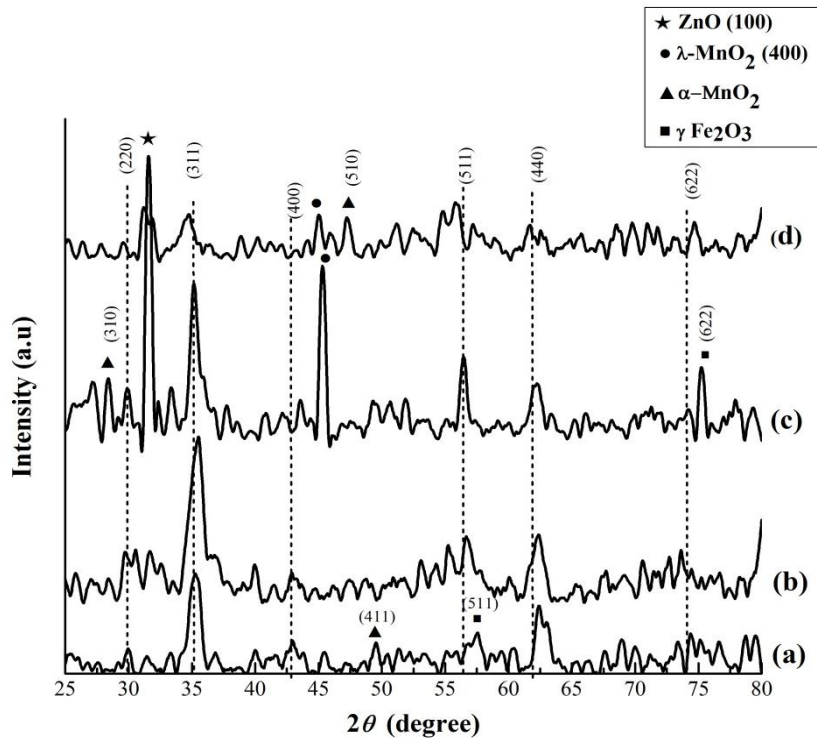


Figure 1. XRD pattern of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ with different NaOH concentration of (a) 0.5M, (b) 1.5M, (c) 3M, and (d) 6M.

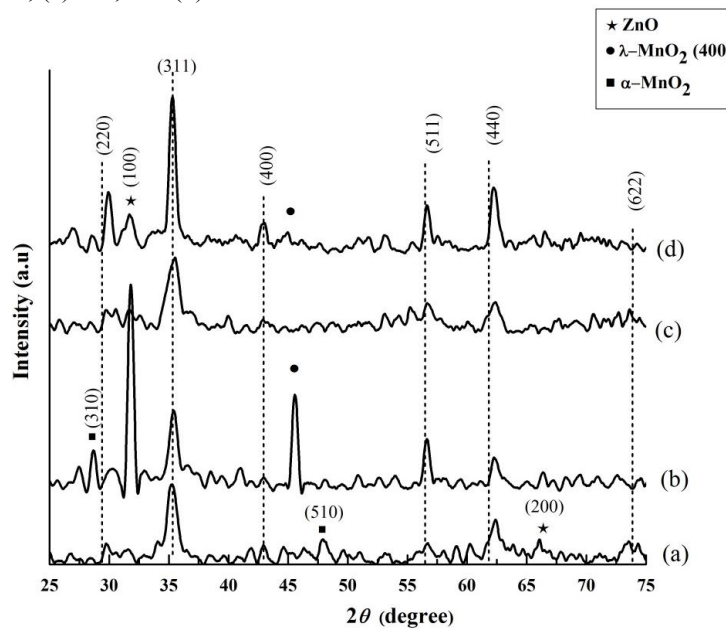


Figure 2. XRD pattern of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ with different synthesis temperature (a) 30°C, (b) 60°C, (c) 90°C, and (d) 120°C.

In relation to synthesis temperature variation, the diffraction pattern of samples can be presented in Figure 2. In diffraction data, the appearance of ZnO, λ -MnO₂, and α -MnO₂ phases were also investigated. Sample A6 was dominated by ZnO phase compared than ferrite Mn_{0.5}Zn_{0.5}Fe₂O₄ phase due to the condition for which the formation stage of ZnO phases. The diffraction pattern of sample A7 shows a clear diffraction peaks of (400). The diffraction peaks possessed by all samples were very broad due to microstrain effect and dislocation density of crystal lattice. This defect might be caused by reaction temperature. The reaction temperature gives thermal energy for metal cation to grow as nanoparticles. Nucleation process is very sensitive to reaction temperature that agitates thermal energy for the reaction. If the nucleation does not work well, so defect might occur on crystal nanoparticles. The broadening of diffraction peaks as an indication of that defect. The uninformed microstrain occurring in the crystal lattice of nanoparticles makes change the site of metal cations. The crystal site of a metal cation and also anion can determine ion distribution of nanoparticles. Thus, ion distribution will contribute to lattice size and crystallite size of nanoparticles [10]. Quantitatively, the result of calculation for crystallite size (t) by using Scherer's formula, the values of interplanar distance (d), the estimated lattice size (a), X-Ray density, and lattice microstrain can be presented in Table 1.

Table 1. Interplanar distance, lattice constant, X-Ray density and microstrain of Mn_{0.5}Zn_{0.5}Fe₂O₄ nanoparticles synthesized with different NaOH concentration and synthesis temperature

Synthesis parameter variable	Sample	Interplanar Distance (Å)	Lattice constant (Å)	X-Ray Density (g/cm ³)	Particle size (nm)	Microstrain
NaOH Cont.	A1	2.545	8.44	5.21	16.5	0.028
	A2	2.535	8.41	5.27	14.1	0.032
	A3	2.546	8.44	5.20	20.8	0.022
	A4	2.587	8.58	4.96	14.5	0.032
Synthesis Temperature	A5	2.542	8.43	5.23	16.7	0.027
	A6	2.534	8.40	5.28	22.1	0.021
	A2	2.535	8.41	5.27	14.1	0.032
	A7	2.540	8.42	5.24	26.7	0.017

The lattice sizes of samples for variation of NaOH concentration are not different significantly compared to the bulk size. In detail, the increase of NaOH concentration tends to affect to an increase of lattice size of nanoparticles. Sample A4 has the largest values of lattice parameter which can be estimated by considering the largest broadening of diffraction peaks. This phenomenon is an indication that sample A4 exhibited the largest strain and interplanar distance as discussed. The density of nanoparticles decreased with an increase of NaOH concentration. The increase of lattice size causes volume expansion of crystal lattice. The volume expansion was not followed by an increase of total weight of crystal.

Increasing synthesis temperature does not affect significantly to a change of crystal lattice nanoparticles. Lattice parameter and the crystal density are relatively constant. Both NaOH and synthesis temperature variations do not give a particular trend on crystallite size value of nanoparticles. The smallest crystallite size was attained from sample A2 which was 14.1 nm, and the greatest was achieved from samples A7 which was 26.7 nm. Increasing crystallite size of nanoparticles was followed by the decrease of lattice microstrain.

3.2. Microstructure and Morphology of nanoparticles

The TEM image of sample Mn_{0.5}Zn_{0.5}Fe₂O₄ for synthesis temperature of 120°C and NaOH concentration of 1.5 M can be shown in Figure 3. The following selected area electron diffraction (SAED) also can be shown.

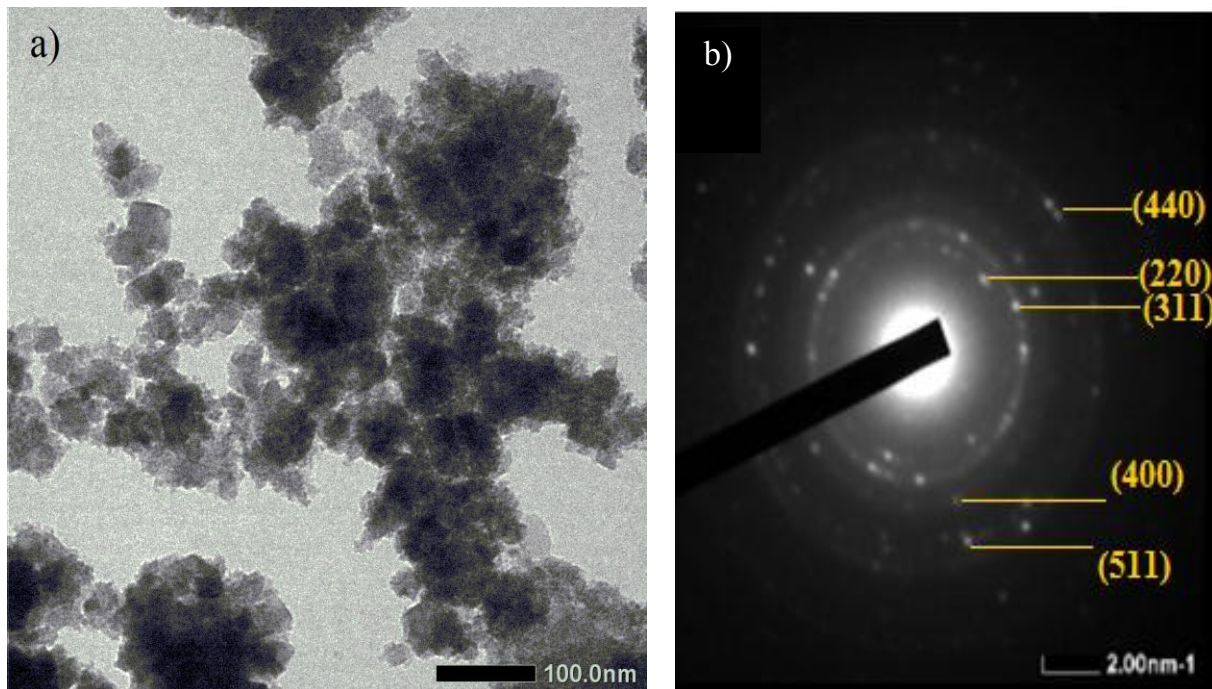


Figure 3. (a) TEM Image and (b) SAED image of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$

Figure 3 shows that nanoparticle is in the form of aggregate. The sample exhibited strongly agglomeration due to a small particle size which has higher surface energy density. The surface energy is enhanced by the largest number of charges occupying the surface of nanoparticles. Therefore, the surface tension of particle is higher than larger particles. Furthermore, the SAED image shows that the formation of diffraction rings composes the non-continuous diffraction pattern. This SAED image confirms the formation of polycrystalline $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles which possess low crystallinity compared than bulk material.

3.3. Functional group bonding spectra

Functional groups bonds between ions can be shown in Figure 4 regarding IR spectra of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles. According to Figure 4, absorption peaks in wavenumber of 455.20 cm^{-1} and 578.64 cm^{-1} were investigated which corresponded to stretching vibration of metal-oxygen at tetrahedral and octahedral sites [11]. These bands confirm that the formation of tetrahedral and octahedral sites are in the crystal lattice of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles. Band absorption of 933.55 cm^{-1} corresponds to bending vibration of Mn-O-H [8]. This band confirms that the existences of hydration and oxidation reaction between sample of nanoparticles and hydrogen in the atmosphere. This case confirms the formation of the nonspinel structure according to diffraction data. The absorption bands of 1342.46 cm^{-1} , 1627.92 cm^{-1} corresponds to bending vibration of O-H [11,12] and 3410.15 corresponds to stretching vibration of O-H [11] due to KBr oxidation state during the preparation of disk sample for FTIR characterization.

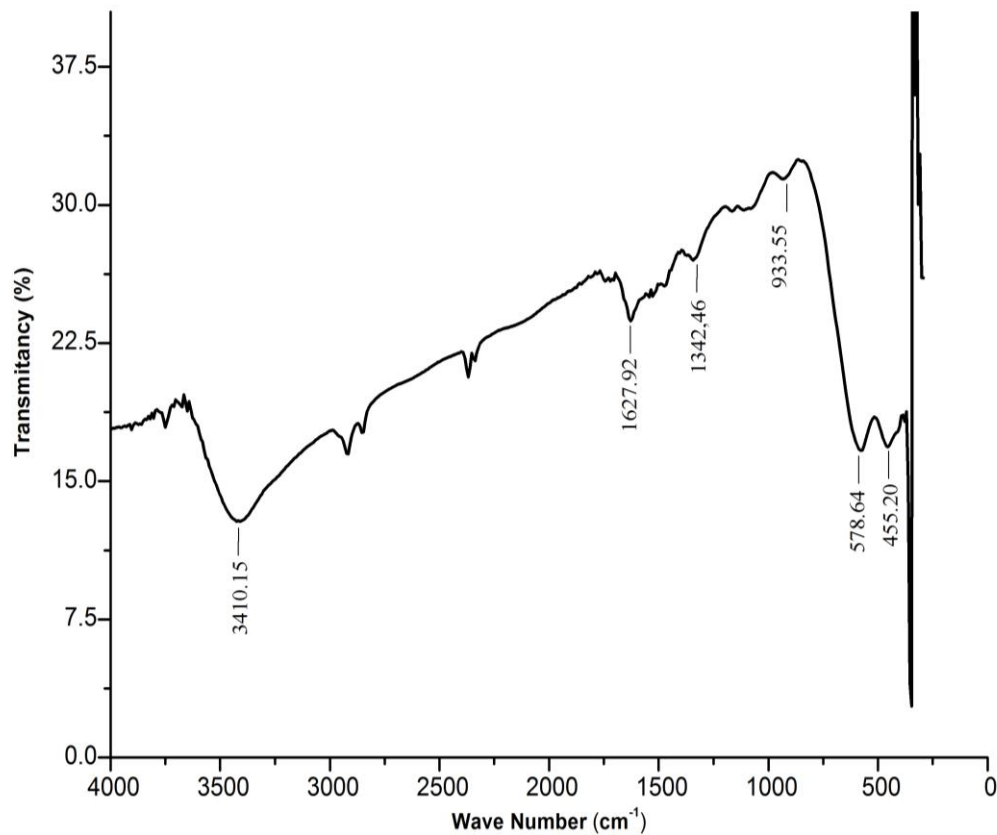


Figure 4. IR spectra of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ systems

3.4. Magnetic Measurement

The magnetic properties of samples were measured by using VSM. The examples of hysteresis loop can be shown in Figure 5. The measurement results of H_c , maximum magnetization of 15 kOe (M_{max}), and magnetic anisotropy constant (K) is indicated in Table 2.

Table 2. Ferrite phase ratio, coercivity, maximum magnetization, and magnetic anisotropy constant of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles with variations of parameter synthesis

Parameters	Sample	Ferrite Phase Ratio (%)	H_c (Oe)	M_{max} (emu/g)	K (erg/g)
Varying NaOH	A3	32.4	48.89	11.32	553.49
	A4	47.7	68.51	11.48	787.02
	A1	83.1	47.18	10.42	491.70
	A2	87.7	46.03	11.62	535.03
Varying Temperature	A6	27.3	47.85	7.87	376.34
	A5	80.2	45.95	7.99	367.15
	A2	87.7	46.03	11.62	535.03
	A7	91.9	47.53	15.69	741.41

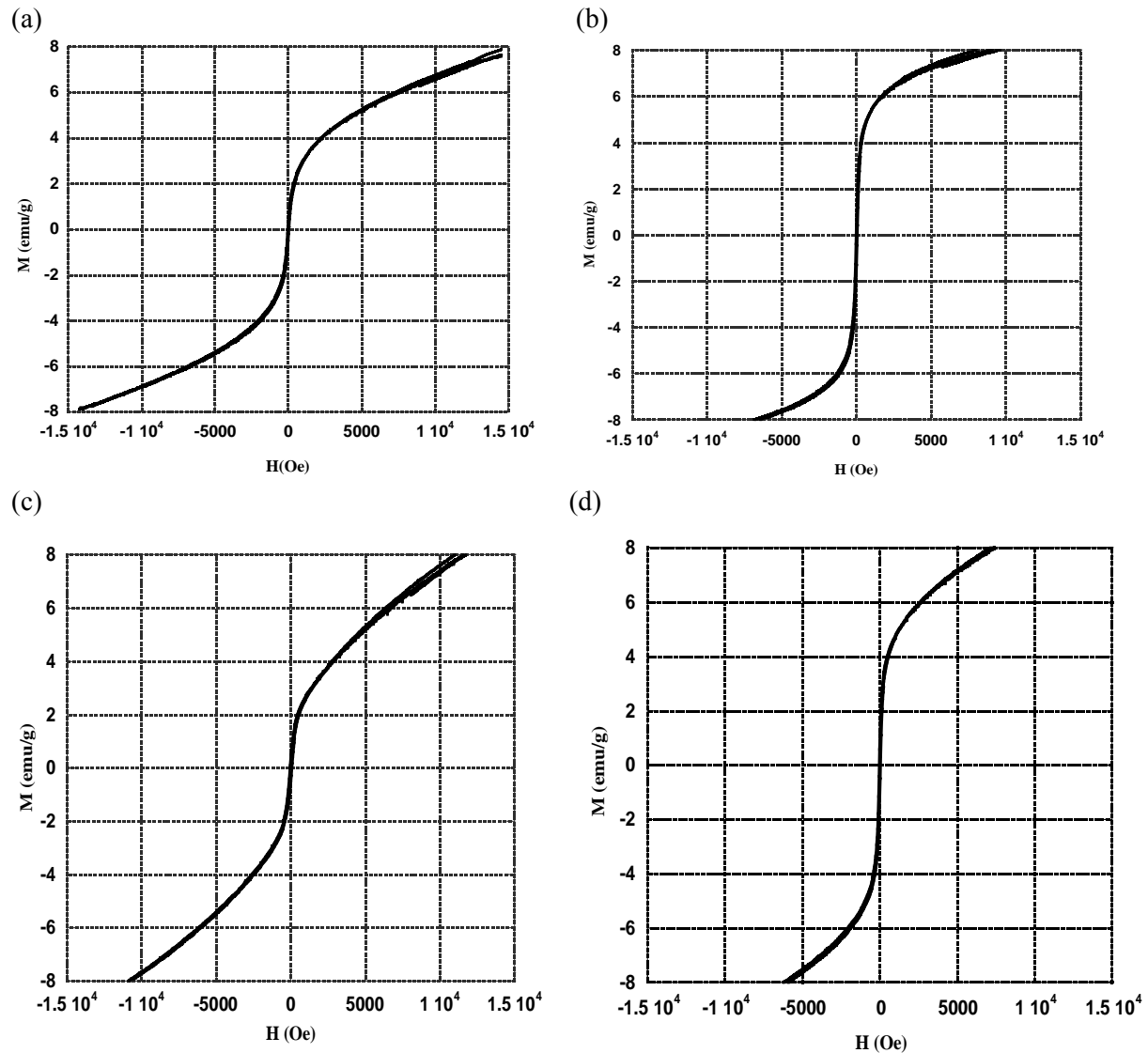


Figure 5. Hysteresis curve (a) sample A1, (b) sample A2, (c) sample A4, and (d) sample A7.

According to Table 2, the values of maximum magnetization at 15 kOe of samples increase relatively with an increase of concentration NaOH and synthesis temperature. The value of maximum magnetization is strongly influenced by the degree of crystallinity of samples. Sample A7 has the highest maximum magnetization due to the highest degree of crystallinity among all samples. The anisotropy increases with the increase of coercivity and maximum magnetization.

For NaOH variation, the coercivity of nanoparticles increase with an increase of crystallite size up to 14.6 nm [68.5 Oe] and decrease up to 20.8 nm [48.9 Oe]. Hence, for synthesis temperature variation, the increase of crystallite size is followed by the increase of coercivity. Graphically, the relation between crystallite size and coercivity for each variation can be shown in Figure 6. According to Figure 6, sample A4 has the highest coercivity. Some samples with coercivity have increased due to their cation distribution of Fe^{3+} in a spinel structure which exhibits super-exchange interaction with cations in tetrahedral and octahedral sites [3].

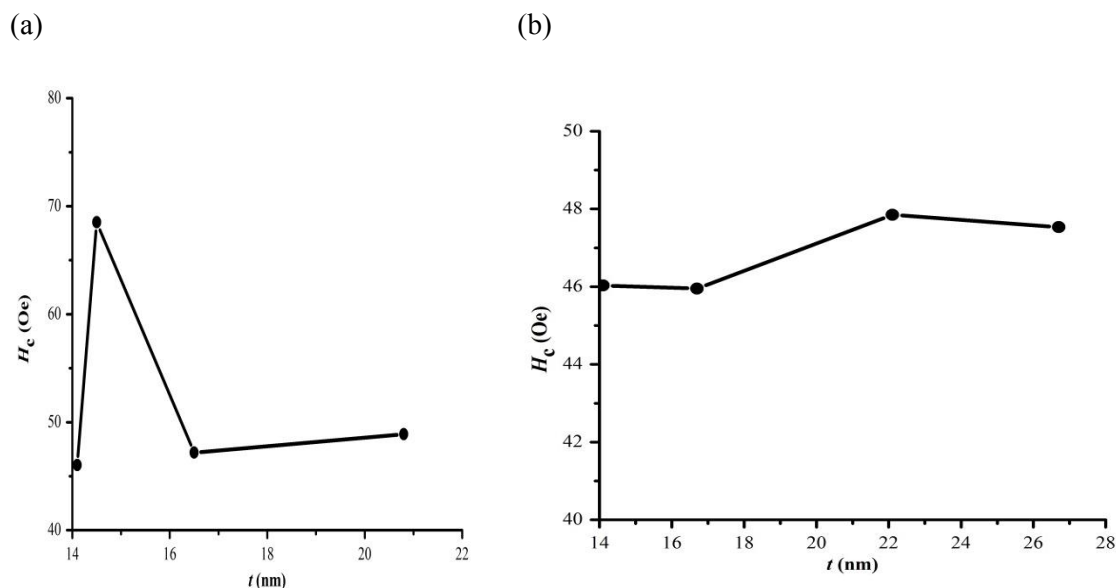


Figure 6. Correlation between grain size and coercivity of samples $Mn_{0.5}Zn_{0.5}Fe_2O_4$: a) different NaOH concentration and b) synthesis temperature.

4. Conclusion

The $Mn_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles have been successfully synthesized. The incomplete formation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ was investigated for 6M NaOH concentration and low synthesis temperature of room temperature and 60°C. The highest maximum magnetization was observed in a sample of 1.5 M NaOH and synthesis temperature 120 °C due to the highest ferrite content. The NaOH concentration and synthesis temperature strongly affected crystal structure, microstructure, crystallinity and magnetic properties of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticle.

5. References

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