The effect of synthesis parameter on crystal structure and magnetic properties of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ magnetic nanoparticles

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Abstract. Nickel Zinc Ferrite (Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$) magnetic nanoparticles have been successfully synthesized using the co-precipitation method with variation of synthesis temperature and concentration of NaOH. X-ray diffraction (XRD) analysis confirmed that Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles have spinel cubic crystal structure. The XRD profile of sample showed that the crystallinity increases with the increase of synthesis temperature. Meanwhile the XRD profile of sample showed the crystallinity decreases with the increase of NaOH concentration. Crystallite size of samples were in the range of 11.1-16.0 nm. There is no significant change in the lattice parameter size for the samples synthesized with increase of temperatures and NaOH concentrations. 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. The maximum magnetization ($\mu_0 M_r$) at 15 kOe of the samples increases with the increase of crystallite size and crystallinity. The coercivity ($H_c$) of the samples increases with the increase of crystallite size.

1. Introduction
Ferrite nanoparticles (FNPs) are one of the type of magnetic nanoparticles (MNPs) that have great attention due to their wide application in various fields. They have used for large number of application such as in high density magnetic recording, microwave device, magnetic fluid etc [1]. FNPs are metal oxide with spinel structure, we know that the spinel ferrites have a general molecular formula [M$_{1-x}$Fe$_x$]$_A$ [M$_{x}$Fe$_{2-x}$]$_B$O$_4$ where ‘A’ represents tetrahedral site, ‘B’ represents octahedral site, and ‘x’ denotes the degree of inversion [2]. Each unit cell contains eight formula unit with 32 of O$^{2-}$ anions packed in the lattice, and M$^{3+}$ and M$^{2+}$ cations occupying the 16 (tetrahedral) and 8 (oktahedral) sites. The ocupations of tetraheral site entirely with a divalent transition metal (such as Zn) produces a normal spinel structure, whereas occupation of the octahedral site with the divalent transitions metal ions (such as Ni) yields an invers spinel structure. If divalent transition metal ion are present on both A and B sub-lattice, the structure is mixed spinel [3,4]. Because of them wide application, FNPs must have specific requirement to be used in each application fields. Nickel-zinc ferrite have been extensively used in a number electronic devices due to their high electrical resistivity, large stability at high frequency, low coercivity, high magnetization, mechanical hardness, chemical stability and reasonable cost [5].
Selection of an appropriate process is an important factor to achieve ferrites with high quality. Methods and synthesis techniques conditions affect the structural, electrical and magnetic properties of ferrites [6, 7]. Kurian and Nair studied the effect of different preparation conditions on structural changes of nickel-zinc ferrite [8]. Deraz and Abd-Elkader studied the structural and magnetic properties of nickel-zinc ferrite using spinel solid solution method [9]. Both of research reported the three aspect (preparation condition, structural, and magnetic properties) separately. The purpose of this work is to investigate the effect of synthesis temperature and NaOH concentration on the crystal structure. The relation between crystal structure and magnetic properties of \( \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles were be also investigated in detail in order to give more comprehensive information.

2. Experimental detail

\( \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles were synthesized using coprecipitation method with variation of synthesis parameters (temperatures and concentrations of NaOH). Nickel chloride hexahydrate (\( \text{NiCl}_2 \cdot 6\text{H}_2\text{O} \)), zinc sulphate heptahydrate (\( \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \)), ferric chloride hexahydrate (\( \text{FeCl}_3 \cdot 6\text{H}_2\text{O} \)), chloric acid (\( \text{HCl} \)) and sodium hydroxide (\( \text{NaOH} \)) were used as starting materials.

Principally, the stage of coprecipitation was initialized by the formation of hydroxide compound via coprecipitation reaction of a metal salt precursor with \( \text{NaOH} \). The \( \text{HCl} \) solution used to break the ionic bond between metal cation and chloride anions or sulfate group. Those metal cations were highly attracted by hydroxide anion \( \text{OH}^- \) to form hydroxide compound. Each hydroxide compound of \( \text{Ni(OH)}_2 \), \( \text{Zn(OH)}_2 \) and \( \text{Fe(OH)}_3 \) has different reaction rate to form ferrite nanoparticles. According to the chemical reaction of \( \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles, the molar ratio of Ni, Zn and Fe is 1:1:4, respectively. Variation of synthesis temperature used in this work were 30, 60, 90, and 120°C (with constant of NaOH concentration at 1.5 M) and variation of NaOH concentration used in this work were 1.5, 2.5, 3.5, and 4.5 M (with constant of synthesis temperature at 60°C).

The crystal structure and phase identification were confirmed by the X-ray diffractometer (XRD). The morphology was studied by Transmission electron microscope (TEM). The magnetic measurements of \( \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles were carried out by vibrating sample magnetometer (VSM) at room temperature.

3. Result and discussion

3.1. Crystal structure from X-ray diffraction

![Figure 1](image1.png)  
**Figure 1** The XRD spectra of samples synthesized at (a) 30°C, (b) 60°C, (c) 90°C and (d) 120°C of temperatures (with constant of NaOH concentration at 1.5 M)

![Figure 2](image2.png)  
**Figure 2** The XRD spectra of samples synthesized at (a) 1.5 M, (b) 2.5 M, (c) 3.5 M and (d) 4.5 M of NaOH concentrations (with constant of synthesis temperature at 60°C)
The XRD spectra of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles that were obtained from variation of synthesis temperatures and NaOH concentrations are shown in figure 1 and 2. Analysis of XRD spectra showed that ferrite phases were obtained. The peaks identified the main diffraction plane indexed to (220), (311), (400), (511) and (440) planes, which indicated the presence of cubic spinel structure. Those diffraction planes are in good agreement with those of Ni-Zn ferrite JCPDS no 08-0234 [10]. The XRD spectra typically broad shape and low intensity reflections indicate the small of ferrite crystals [11].

Figure 1 showed that all the XRD peaks become narrower and sharper with increase of synthesis temperatures. It indicated that there is enhancement of crystallite size and crystallinity [12]. Additional peaks observed at figure 1 (c and d) indicates the impurity phase (non spinel Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$). Figure 2 showed that all the XRD peaks become broader and the intensity decreases with the increase of NaOH concentrations. It indicated that crystallite size and crystallinity decreases. Additional peaks observed at (Figure 2 b and c) indicates the impurity phase (non spinel Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$).

Table 1. Lattice parameter ($a$), crystallite size ($t$), and lattice strain ($\varepsilon$) of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles.

| Synthesis parameter | $a$ (Å) | $t$ (nm) | $\varepsilon$ | Synthesis parameter | $a$ (Å) | $t$ (nm) | $\varepsilon$ |
|---------------------|---------|---------|---------------|---------------------|---------|---------|---------------|
| Temperature (°C)    |         |         |               | NaOH Concentration (M) |         |         |               |
| 30                  | 8.56    | 12.3    | 0.04          | 1.5                 | 8.53    | 14.4    | 0.03          |
| 60                  | 8.53    | 14.4    | 0.03          | 2.5                 | 8.59    | 14.4    | 0.03          |
| 90                  | 8.54    | 15.3    | 0.03          | 3.5                 | 8.56    | 13.8    | 0.03          |
| 120                 | 8.53    | 16.0    | 0.03          | 4.5                 | 8.63    | 11.1    | 0.04          |

Table 1 shows that there is no significant change in the lattice parameter for the samples which is synthesized with increase of temperatures and NaOH concentrations. It is attributed to homogeneity of Fe$^{3+}$, Ni$^{2+}$ and Zn$^{2+}$ in spinel structure and there is a strong electrostatic force between ions [13]. The crystallite size of sample synthesized at temperature of 30°C was 12.3 nm and then increased with the increase of synthesis temperatures. The increased in crystallite size is attributed to rapid diffusion of cations at high temperature. Higher temperature might be beneficial to accelerate the rate of the diffusion and integration process, and thus, the crystallite size became larger. Meanwhile the crystallite size of sample synthesized with 1.5 M of NaOH was 14.4 nm and then it decreased with the increase of NaOH concentrations. The decrease in crystallite size is attributed to high concentration of hydroxide anions results in an extremely fast nucleation process that generate tiny nuclei [14]. Due to high concentration and small hydration sphere in solution, the sodium ions can probably be absorbed significantly onto all the facets of the nuclei, which hinder incorporation and subsequent growth of neighbouring nuclei [15].

![Figure 3](a) TEM image, and (b) SAED image of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles
3.2. Morphological studies

Morphological studies of nanoparticles \( \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) that is synthesized at 60°C with 1.5 M of NaOH was shown in Figure 3. Figure 3 (a) shows that nanoparticles are nearly spherical and agglomeration occurred. The powders of nanoparticles \( \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) are easy to form agglomerated due to nanosize effect and intrinsic magnetism. Because of very small in size, thermal energy of nanoparticles is large enough to overcome the energy of the magnetic interactions among the nanoparticles [16]. The selected area electron diffraction (SAED) image (Figure 3 (b)) showed the diffraction ring as representation of Miller plane and confirmed that sample was polycrystalline. The corresponding SAED pattern of the selected region indicates the sample is well crystallized.

![Figure 3](image-url)

**Figure 3** Hysteresis curve of samples synthesized at (a) 30°, (b) 60°, (c) 90° and (d) 120°C of temperatures (with constant of NaOH concentration at 1.5 M)

![Figure 4](image-url)

**Figure 4** Hysteresis curve of samples synthesized at (a) 30°, (b) 60°, (c) 90° and (d) 120°C of temperatures (with constant of NaOH concentration at 1.5 M)

![Figure 5](image-url)

**Figure 5** Hysteresis curve of samples synthesized at (a) 1.5, (b) 2.5, (c) 3.5 and (d) 4.5 M of NaOH concentrations (with constant of synthesis temperature at 60°C)

![Table 2](image-url)

**Table 2.** Crystallite size \((t)\), maximum magnetization \((\sigma_s)\), and coercivity \((H_c)\) of \( \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles

| Variable of Synthesis | \( t \) (nm) | \( \sigma_s \) (emu/g) | \( H_c \) (Oe) | Variable of Synthesis | \( t \) (nm) | \( \sigma_s \) (emu/g) | \( H_c \) (Oe) |
|-----------------------|--------------|----------------------|---------------|-----------------------|--------------|----------------------|---------------|
| temperature           |              |                      |               |                       |              |                      |               |
| temperature           | 12,3         | 21,9                 | 99,6          | 14,4                  | 43,3         | 112,5                |
|                       | 14,4         | 43,3                 | 112,5         | NaOH                  | 14,4         | 30,3                 | 84,6          |
|                       | 15,3         | 36,8                 | 86,9          | Concentration         | 13,8         | 29,9                 | 91,7          |
|                       | 16,0         | 32,2                 | 108,3         |                       | 11,1         | 26,9                 | 53,3          |

3.3. Magnetic properties

The magnetic properties of all samples were investigated with a vibrating sample magnetometer (VSM) at room temperature. Figure 4 and figure 5 shows hysteresis curve of \( \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles synthesized with variation of synthesis temperatures and NaOH concentrations.

All samples were not fully saturate at maximum external field of 15kOe. Lack of saturation magnetization can be related to single domain nature of the particles and magnetocrystalline anisotropy energy of the nanoparticles. Maximum magnetization \((\sigma_s)\) increase with the crystallite size mainly due to the spin non-colinearity at the surface [17]. Lower \( \sigma_s \) that is associated with the smaller crystallite size could be attributed to magnetocrystalline anisotropy of the particles that depends on the crystallinity. Coercivity \((H_c)\) shows the fluctuate value with the increase of crystallite size, for the samples with variation of temperature. It occure due to the different of magnetocrystalline anisotropy energy. The difference of magnetocrystalline anisotropy energy may due to the irregular shape of the particles. Meanwhile coercivity increased with the increase of crystallite size for the sample synthesized with variations of NaOH concentrations. This phenomena indicated that the samples have...
single domain structure. The $H_c$ is in direct proportion to the volume single-domain grains. Therefore, $H_c$ become gradually larger as the single-domain particle size increase. Particles which has single domain, have the magnetostatic energy dominant at the surface of particles, so the coercivity increases with the increase of crystallite size.

4. Conclusion
Nickel zinc ferrite (Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$) magnetic nanoparticles have been successfully synthesized using the co-precipitation method with variation of synthesis temperatures and NaOH concentrations. Crystallite size of samples were in the range of 11.1-16.0 nm. The XRD studies confirm the presence of cubic spinel structure. The SAED image showed the diffraction ring as representation of Miller plane and confirmed that sample was polycrystalline. The VSM analysis showed that all samples were not fully saturate at maximum external field of 15kOe. The maximum magnetization increases with the increasing of crystallite size. The coercivity increases with the increasing of crystallite size.

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