Synthesis and characterization of nanoparticles
Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_{2}$O$_{4}$ using the co-precipitation method

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Abstract. This research was conducted to see the nanostructure and magnetic properties of nanoparticle Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_{2}$O$_{4}$. Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_{2}$O$_{4}$ has been successfully synthesized at 100°C using co-precipitation method. After synthesized, it was dried at 80°C. The second step, nanoparticle powder was characterised by X-Ray Diffraction (XRD) to determine the structure and phases formation of Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_{2}$O$_{4}$. FE-SEM was used to analyze the morphology of Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_{2}$O$_{4}$. To find out the elements contained in the sample, EDAX testing was conducted. X-Ray Diffraction (XRD) results showed that Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_{2}$O$_{4}$ in the shape of cubic spinel with the main peak at (311). There was a hematite phase (Fe$_2$O$_3$) with low intensity. Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_{2}$O$_{4}$ crystallizes well indicated by $2\theta = 35.385^\circ$. The crystal size on the nano scale has been formed, which was 14.5087 nm. The FE-SEM results showed that the morphology of Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_{2}$O$_{4}$ was spherical and has agglomerated. The elements contained in these nanoparticles were Zn, Ni, Cu, Fe and O. There were no other impurities indicated from the EDAX test results. This indicated that the elements contained were already in accordance with the chemical formula. Magnetic hysteresis curves showed that Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_{2}$O$_{4}$ was softmagnetic.

1. Introduction

In recent years researchers have focused on developing research on spinel ferrite nanoparticles. Spinel ferrite nanoparticles have many uses that can be applied in microwaves, gas sensors, biomedicals, transformers, sensors, digital diary, floppy disk drives [1,2]. Ni-Zn is very beneficial in the electronics industry because it has high magnetization, high permeability, low power loss, high resistivity, low dielectric loss. Copper (Cu) has a high conductivity, good magnetic susceptibility, high permeability and low coercivity, which is good for use in microwave absorption [3]. The addition of Cu$^{2+}$ ions to Ni-Zn affects the structure, microstructure and electrical properties. Resistivity, permeability and magnetization increase with the addition of Cu$^{2+}$ ions to Ni-Zn. The addition of Cu$^{2+}$ ions can also decrease dielectric loss [2,4]. The magnetic properties of nanoparticles can be improved by substituting various types of Me$^{2+}$ metal ions such as Zn$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$, etc. Where the ferrite spinel nanoparticles have a common formula MeFe$_{2}$O$_{4}$. Me is a divalent metal ion as in the Me$^{2+}$ metal ions...
type [5,6]. Me$^{2+}$ and Fe$^{3+}$ at two different crystallographic sites. These sites have tetrahedral and octahedral oxygen coordination (A sites and B sites). There are 8 A sites which are coordinated tetrahedral with oxygen and 16 B sites which are octahedral coordination. Spinel ferrite consists of three types of structure, namely normal spinel structure, reverse spinel structure and mixed spinel structure. The normal spinel structure occurs when A sites is occupied by the Me$^{2+}$ cation and B sites is occupied by the Fe$^{3+}$ cation. The reverse spinel structure occurs if A sites is occupied by Fe$^{3+}$ and B sites is occupied by Me$^{2+}$ and Fe$^{3+}$ randomly. Whereas the mixed spinel structure occurs when the Me$^{2+}$ and Fe$^{3+}$ cations become A sites and B sites [7]. Spinel ferrite nanoparticles can be synthesized using several methods namely co-precipitation, hydrothermal, sol-gel, high-energy ball milling, micro-emulsion, auto-combustion, etc [5, 6, 8]. The co-precipitation method is an excellent method of producing materials at a nanoscale. In addition to producing at a nanoscale, the method can also produce nanoparticles with high crystallization [8]. The co-precipitation method is the safest method to use, economical, requires less time and high productivity [9]. Maulinda et al [10] reported that the coprecipitation method also has the advantage of producing high purity, having an easy procedure, and using a low the synthesis temperature. By dissolving several substances, the co-precipitation method has the result in the form of sediment.

This method uses mixing distilled water with divalent metal and stirring continuously. In this method, maintaining the pH value obtained to produce high quality ferrite spinel. Therefore in this study using the method of co-precipitation. The magnetic properties of the spinel ferrite are grouped into two parameters. These two parameters are intrinsic magnetic parameter and extrinsic magnetic parameter. Intrinsic magnetic parameters obtained by crystal structure and material composition. Examples of intrinsic magnetic properties are curie temperature $T_c$, saturation magnetization $M_s$, stiffness exchange A, magneto crystalline anisotropy $K$. While extrinsic magnetic properties are related to microstructure which is influenced by particle size and shape. Examples of extrinsic magnetic properties are coercivity $H_c$, remanent magnetization $M_r$, and magnetic susceptibility. The amount of cation concentration given affects the properties of the magnet as well [9].

Indonesia is rich in natural resources, one of them is iron sand (Fe$_2$O$_4$). Iron sand can be used as a raw material for making magnets because it has advantages. Some of the advantages possessed by iron sand are soft magnetic, low price, increase absorption of microwaves [11]. Magnetite is a mineral content found in iron sand (Fe$_2$O$_4$). Therefore, iron sand (Fe$_2$O$_4$) can be applied for ferroelectric materials, as a catalyst for magnesium-based hydrogen storage materials, and as a material for making cement [12]. In this study, iron sand from Lombok was used because it has high magnetic properties.

2. Materials and methods

Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$ nanoparticles were synthesized using the co-precipitation method. The main ingredients in the manufacture of these nanoparticles are ZnCl$_2$, CuCl$_2$, NiCl$_2$, HCl 37%, and iron sand. About 16 g of iron sand were dissolved with 50 ml of HCl 37% and then stirred until homogeneous. After being homogeneous, it is filtered using paper to get solution 1. After that ZnCl$_2$, CuCl$_2$, NiCl$_2$ are dissolved with 25 ml of aquades and stirred until homogeneous. The results of the homogeneation were given the name solution 2. The solutions 1 and 2 were mixed and homogenized again. Once homogeneous, drop by drop is mixed with NaOH 3M solution along with stirrer process at 500 rpm. This synthesis process was carried out for two hours at a temperature of 100°C. After being synthesized, it was washed with aquades for seven times. This washing is carried out to obtain a neutral PH. Then dried in an oven at 80°C. The dried samples were mashed and then characterized using X-ray Diffraction (Rigaku Smartlab), Field Emission - Scanning Electron Microscope (JEOL) and Vibrating Sample Magnetometer (VSM250 Dexion Magnet Ltd).

3. Results and discussions

Figure 1 is the result of the X-Ray Diffraction (XRD) characterization. The peaks identified in Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$ are (111), (220), (311), (400), (422), (511), (440), (620), (533), (444), (642), (731). The highest peak is at the angle of $2\theta = 35.385^\circ$. This value indicates that Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$
has crystallized well. XRD test results showed that the nanoparticles contained an impurity phase (Fe$_2$O$_3$). This is likely due to the oxidation during sample preparation. The grain size obtained was 14.5087 nm using Scherrer’s formula.

\[ D = \frac{K\lambda}{\beta \cos \Theta} \]  

(1)

Where D is crystal size, \(\beta\) is line broadening in radians (FWHM), \(\Theta\) is bragg angle, \(\lambda\) is wavelength x-ray (1.54 Å), and K is constanta (0.9) [13]. The lattice parameter value obtained is 8.410 Å as calculate by the equation (2).

\[ a = d_{hkl} \left( h^2 + k^2 + l^2 \right)^{1/2} \]  

(2)

Where hkl is miller’s index and \(d_{hkl}\) is interplanar spacing [14]. The lattice parameter value \(a = b = c\) at Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$ states that the nanoparticles are cubic spinels. The nanoparticles have a true density value of 3.0396 g/cm$^3$, while the x-ray density is 8.9728 g/cm$^3$. The x-ray density (\(\rho_{x\text{-ray}}\)) has been calculated using the equation (3).

\[ \rho_{x\text{-ray}} = \frac{8M}{Na^3} \]  

(3)

Where M is molecular weight, N is Avogadرو number, a is lattice constant [15]. The dislocation density of these nanoparticles is $4.7505 \times 10^{15}$ line/m$^2$ with the equation (4).

\[ \delta = \frac{1}{D^2} \]  

(4)

Where D is the crystal size. The unit cell volume and the crystal volume of these nanoparticles are $5.9484 \times 10^{-3}$ nm$^3$ and $1.5998 \times 10^3$ nm$^3$. 

![Figure 1 XRD diffraction of Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$.](image)

Figure 1 shows the print out of Field Emission-Scanning Electron Microscope (FE-SEM) and the particle distribution histogram. These results indicate the morphology of Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$ in the form of spheres with particle sizes on the nano scale. The particle size obtained was 33.6399 nm. The addition of Cu$^{2+}$ can increase the crystal size of the nanoparticles. This occurs because the nucleation
center has decreased in density during the ion substitution process. So that a large crystal size was formed [16]. The particle size in the FE-SEM test was different from the XRD results due to the agglomeration that might occur during the synthesis process. Agglomeration occurs because cells are not fully formed when small particles combine into larger structures [6]. Where the ionic radius of Cu\(^{2+}\) is greater than the ionic radius of Ni\(^{2+}\), so that ionic Ni\(^{2+}\) is substituted by Cu\(^{2+}\). The ionic radius of Cu\(^{2+}\) is 0.73 Å while the ionic radius of Ni\(^{2+}\) is 0.69 Å [2].

![Figure 2](image2.png)

**Figure 2** The FE-SEM images and the histogram of the particle size distribution of Zn\(_{0.7}\)Ni\(_{0.15}\)Cu\(_{0.15}\)Fe\(_{2}\)O\(_4\).

Figure 3 is the EDAX test result which shows the elements contained in Zn\(_{0.7}\)Ni\(_{0.15}\)Cu\(_{0.15}\)Fe\(_{2}\)O\(_4\). The test results showed that there were no impurities in the sample. The elements contained in the sample are Zn, Ni, Cu, Fe and O.

![Figure 3](image3.png)

**Figure 3** EDAX spectra of Zn\(_{0.7}\)Ni\(_{0.15}\)Cu\(_{0.15}\)Fe\(_{2}\)O\(_4\).

In Table 1 we can see the percentage of the number of atoms (at%) and weight percentage (wt%) contained in the Zn\(_{0.7}\)Ni\(_{0.15}\)Cu\(_{0.15}\)Fe\(_{2}\)O\(_4\) nanoparticles. The data in Table 1 shows the results in accordance with the chemical formula used for Zn\(_{0.7}\)Ni\(_{0.15}\)Cu\(_{0.15}\)Fe\(_{2}\)O\(_4\) nanoparticles. Figure 4 shows that the results of the vibrating sample magnetometer (VSM). From the VSM results, the saturation magnetization value (Ms) of the nanoparticles was 26.27 emu/g. Meanwhile, the remanent magnetization (Mr) and coercivity (Hc) values obtained in the VSM test were 2.91 emu/g and 92.62 Oe. The addition of Cu\(^{2+}\) influences the saturation magnetization value. This is due to the addition of Cu\(^{2+}\) increasing the crystal size so that the crystallization process increases [4]. The magnetic hysteresis curves of Zn\(_{0.7}\)Ni\(_{0.15}\)Cu\(_{0.15}\)Fe\(_{2}\)O\(_4\) nanoparticles shows that this nanoparticles is soft magnetic.
Table 1. The elemental composition of synthesized Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$ nanoparticles.

| Ferrite Composition | At% | Wt% |
|---------------------|-----|-----|
| Zn                  | 6.0 | 12.7|
| Ni                  | 0.8 | 1.6 |
| Cu                  | 1.8 | 3.7 |
| Fe                  | 26.3| 48.0|
| O                   | 65.2| 34.1|

Figure 4 Magnetic hysteresis curves of Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$ nanoparticles.

Conclusion
Synthesis and characterization of Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$ nanoparticles were carried out using the co-precipitation method. The synthesis has successfully obtained particles on nanoscale. The characterization results showed that Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$ was in the form of cubic spinel. Nanoparticles have crystallized well with the main peak 311 with an angle of $2\Theta = 35.385^\circ$. The FE-SEM test results showed agglomeration of Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$ nanoparticles. This is probably due to imperfect cell formation during the synthesis process. There are no impurities in the Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$ nanoparticles. The elements contained are Zn, Ni, Cu, Fe and O which are shown in the EDAX test results. Based on VSM results, Zn$_{0.7}$Ni$_{0.15}$Cu$_{0.15}$Fe$_2$O$_4$ nanoparticles can be categorized as softmagnetic.

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