Phase analysis and magnet properties of \( \text{Zn}_x\text{Fe}^{(3-x)}\text{O}_4 \) prepared by milling process

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Abstract

Phase analysis and magnetic properties of \( \text{Zn}_x\text{Fe}^{(3-x)}\text{O}_4 \) (\( x = 0.25, 0.50, 0.75 \) and 1.0) have been analyzed. The synthesis of \( \text{Zn}_x\text{Fe}^{(3-x)}\text{O}_4 \) was carried out using a solid reaction with the \( \text{ZnO} : \text{Fe}_2\text{O}_3 \) material composition (\( x = 0.25, 0.50, 0.75 \) and 1.0) according to the mole ratio of each, then being milled for 5 hours and sintered at a temperature of 1200 °C for 3 hours. Phase identification by XRD (X-ray Diffractionometer) shows that \( \text{Zn}_x\text{Fe}^{(3-x)}\text{O}_4 \) milling results form the diffraction peak of the \( \text{NiFe}_2\text{O}_4 \) and \( \text{Fe}_3\text{O}_4 \) phases, the greater the value of \( x \) (the \( \text{Zn} \) atom content) the less \( \text{Fe}_3\text{O}_4 \) % phase while the % phase \( \text{ZnFe}_2\text{O}_4 \) is getting bigger and even for \( x = 1.0 \) only \( \text{ZnFe}_2\text{O}_4 \) phase is formed (\( \text{ZnFe}_2\text{O}_4 \) formed 100% of single phase). Surface morphological observations with SEM (Scanning Electron Microscope) show the formation of an increasingly homogeneous structure along with the addition of \( \text{Zn}^{2+} \) ion content and varying sizes ranging from 1 μm to 100 nm. The properties magnetic of \( \text{ZnFe}_2\text{O}_4 \) with VSM (vibrating sample magnetometer) showed that the sample behave ferromagnetically with \( \text{Ms} \) higher (in the range 1.89 - 21.10 emu/g) while the \( \text{Hc} \) value is smaller (in the range 243 - 107 Oe) with the addition of \( \text{Zn}^{2+} \) ion content. Thus, the presence of the \( \text{Fe}_3\text{O}_4 \) phase can decrease the magnetic properties of the material.

Keywords: Crystal structure, zinc ferrite, magnet properties, milling process

INTRODUCTION

In recent years, researcher’s attention to ferrite spinel nanoparticles has been increasing for industrial applications. The ferrite spinel nanoparticles with the structural formula of \( \text{MFe}_2\text{O}_4 \) (M is a divalent metal ion, such as \( \text{Ni}, \text{Co}, \text{Cu}, \text{Mn}, \text{Mg}, \text{Zn}, \text{Fe} \)) also have spinel cubic crystal structure [1]. Ferrite spinel nanoparticles have superior properties such as high electrical resistivity, high permeability, and eddy current losses that can be ignored by the propagation of high frequency electromagnetic waves. Its properties give it the potential to have applications in data storage technology, microwave equipment, telecommunication equipment, drug delivery system, ferrofluid technology and gas sensor [2]. One of the ferrite spinel magnetic nanoparticles of interest today is the Zinc ferrite nanoparticles \( \text{ZnFe}_2\text{O}_4 \). This nanoparticle has an inverse spinel structure, is all \( \text{Zn}^{2+} \) ions are in the octahedral site and \( \text{Fe}^{3+} \) ions are distributed evenly on the tetrahedral and octahedral sites. The \( \text{ZnFe}_2\text{O}_4 \) nanoparticles show the ferromagnetic properties derived from the anti-parallel magnetic moment pair between the magnetic moment of the \( \text{Fe}^{3+} \) ion at the tetrahedral site with the magnetic moment of \( \text{Zn}^{2+} \) and \( \text{Fe}^{3+} \) ions at the octahedral site [3,4]. \( \text{ZnFe}_2\text{O}_4 \) nanoparticles are soft magnetic materials with low coercivity and saturation magnetization but have high electrical resistivity making them highly suitable for magnetic and magneto-optical applications. The \( \text{ZnFe}_2\text{O}_4 \) Nanopaths displays narrow hysteresis curves so that these materials are widely applied as gas sensors, catalysts, photocatalyst, microwaves and so on [5]. Various methods have been developed for the synthesis of \( \text{ZnFe}_2\text{O}_4 \) nanoparticles, such as solid reactions, sol-gel methods, coprecipitation methods, hydrothermal techniques and others [6,7]. In this study, \( \text{ZnFe}_2\text{O}_4 \) nanoparticles have been synthesized through solid reaction using milling technique. In the previous study, milling techniques using HEM (High Energy Milling) for 5 hours have been successfully synthesized \( \text{NiFe}_2\text{O}_4 \) spinel which has a single phase [8]. This method is chosen because the preparation is very simple and does not require a long time. It is expected that the results of this research can add information to obtain the properties of \( \text{ZnFe}_2\text{O}_4 \) nanoparticles effective for the purposes of it’s application.

EXPERIMENTAL

Materials

The materials used in this study are \( \text{ZnO} \) powder from Merck with 99.9% purity, \( \text{Fe}_2\text{O}_3 \) powder with 99% purity. Equipment used, Thermoline furnace for heating \( \text{ZnFe}_2\text{O}_4 \) powder formed, XRD (X-Ray Diffractometer) brand PANalytical Empyrean for phase identification and structural analysis. Surface morphological observations were performed by JEOL JSM-6510 LA SEM (Scanning Electron Microscope), and magnetic properties measurements by Oxford Tesla's VSM (Vibrating Sample Magnetometer) with 1 Tesla magnetization.

Synthesis of \( \text{Zn}_x\text{Fe}^{(3-x)}\text{O}_4 \)

\( \text{Zn}_x\text{Fe}^{(3-x)}\text{O}_4 \) (\( x = 0.25, 0.50, 0.75 \) and 1.0) compounds are synthesized by solid reaction using milling technique. \( \text{Fe}_2\text{O}_3 \) and \( \text{ZnO} \) powders are each weighed in accordance with the mole ratio of a total
weight of 10 grams. The chemical composition for the Zn$_x$Fe$_{3-x}$O$_4$ ($x = 0.25$, $0.5$, $0.75$ and $1.0$) samples is synthesized according to the following reaction equation:

$$(3-x)\text{Fe}_2\text{O}_3 + 2x\text{ZnO} \rightarrow 2\text{Zn}_x\text{Fe}_{3-x}\text{O}_4 \quad (1)$$

Each of these powder mixtures was inserted into the Stainless Steel vial and added a steel ball with weight ratio of the sample to the weight of the steel balls at 1:5 and 50 ml of ethanol solution was added. Furthermore, the process of milling each for 5 hours. The milled powders were dried at a temperature of 100 °C (for 2 hours). The dried powder was ground and heated for 5 hours at 1200 °C. Crystalline phase were identified by XRD. The surface morphology was investigated by SEM and the magnetic properties of samples were measured with VSM. The research and characterization of the samples were conducted at the laboratory of the Center for Advanced Materials Science and Technology, BATAN.

RESULTS AND DISCUSSION

The synthesis of Zn$_x$Fe$_{3-x}$O$_4$ ($x = 0.25$, $0.5$, $0.75$ and $1.0$) by milling process using the HEM technique which is the solid state reaction has been done. The resulting diffraction pattern along with its relative intensity is matched to the diffraction pattern database named Crystallography Open Database (COD).

The result of the phase identification has been done using the Match 3rd Edition software shown in Figure. 1 shows that for the values $x = 0.25$ to $0.75$ indicates the presence of two main peaks at the angle of diffraction 20 around the corner 32° and 35°, this indicates the second phase formation. The main peaks formed have the diffraction angle position and the intensity corresponding to the Zn$_2$O$_3$ and Fe$_2$O$_3$ phases. ZnFe$_2$O$_4$ phase compared to the crystallographic data from Crystallography Open Database (COD) with number 96-900-5113, while Fe$_2$O$_3$ phase compared with reference data number 96-901-5965. Based on the analysis of the formed phase it is known that, Fe$_2$O$_3$ phase has the highest relative intensity at the position of 20 about 32° corresponding to the trigonal structure (104). The results of the analysis show that the peaks which are characteristic of the Fe$_2$O$_3$ phase are the tops of the plane (012) at an angle of about 24°, (104) at an angle of about 33°, (110) at an angle of about 36°, (113) at an angle of about 41°, (024) at an angle of about 49°, (018) at an angle of about 58°, (214) at an angle of about 61° and (300) at an angle of about 64° corresponding to the data reference from COD with number 96-901-5965. The ZnFe$_2$O$_4$ phase has the highest relative intensity at the 20 position corner position at about 350 with the crystallographic area of [311] spinel-shaped cubic. This analysis is reinforced by the appearance of other peaks which are also characteristic of ZnFe$_2$O$_4$ is the top of the field 111 at an angle of about 18°, (220) at an angle of about 30°, (222) at an angle of about 37°, (400) at an angle of about 42°, (422) at an angle of about 53°, (511) at an angle of about 56°, (440) at an angle of about 62° and (533) at an angle of about 73° corresponding to the reference data of the Crystallography Open Database (COD) with number 96-901-5113.

The diffraction peak at an angle of 32° is lower while the diffraction peak at an angle of 35° increases with the increase in the value of $x$, and even disappears in the sample with the composition of the value $x = 1.0$. The diffraction pattern for $x = 1.0$ is seen only one major peak in the angle position 20 around the 35° angle which is the top of the field 311 of ZnFe$_2$O$_4$ indicates the indication of the formation of a single phase with a ferrite spinel structure having a cubic crystal structure with space group Fd3m with lattice parameter is $a = b = c = 0.58836$ nm at room temperature.

![Fig. 1 XRD pattern of Zn$_x$Fe$_{3-x}$O$_4$ powder ($x = 0.25$, 0.50, 0.75 and 1.0) milling result for 5 hours.](image-url)
Fig. 2 Identification phase of ZnFe(3-x)O₄ powder (x = 0.25; 0.50; 0.75 and 1.0) milling result for 5 hours.

Fig. 3 Refinement XRD pattern of ZnₓFeₓFeₓO₄ powder (x = 0.25, 0.50, 0.75, and 1.0) milling result for 5 hours.
Further analysis to show that the powders have multi phase for the value of $x = 0.25$ to 0.75 whereas for the value $x = 1.0$ is a single phase of ZnFe$_2$O$_4$. Figure 3 shows the refinement of the X-ray diffraction pattern of Zn$_{3-x}$Fe$_x$O$_4$ ($x = 0.25$, 0.50, 0.75, and 1.0) powder results. The results of crystal structure analysis in the form of refinement fitting of X-ray diffraction pattern of Zn$_{3-x}$Fe$_x$O$_4$ ($x = 0.25$ to 0.75) powder shows that multiphase peaks have been formed which belong to the phase of Fe$_2$O$_3$ and ZnFe$_2$O$_4$. As shown in Table 1, the results of this refinement resulted have an excellent fitting quality with a very small R factor. The R factor is the criteria of fit and the S factor is the goodness of fit which is of very small value. and according to Izumi the value of S or $\chi^2$ (chi-squared) is allowed to maximum 1.3 [13].

The result of observation of surface morphology of Zn$_{3-x}$Fe$_x$O$_4$ ($x = 0.25$, 0.50, 0.75, and 1.0) with SEM at 5000x magnification is shown in Figure 4. It shows that Zn$_{3-x}$Fe$_x$O$_4$ powder with $x = 0.25$ to 0.75 has non-homogeneous particles and begins to homogeneously along with an increase in the value of $x$ with a particle size in the range of from 300 nm to 1 μm. As for the value $x = 1.0$ looks homogeneous and uniform particles with a size of about 200 nm. In accordance with the results of observation by XRD that for $x = 0.25$ - 0.75 formed ZnFe$_2$O$_4$ phase and Fe$_2$O$_3$ phase. The Fe$_2$O$_3$ phase decreases with the increase of $x$ value so that the particles formed are almost homogeneous. On the contrary, in the composition of $x = 1.0$ almost uniform shaped nanoparticles were formed. The greater homogeneity in the composition of $x = 1.0$ happened due to the single-phase formation of ZnFe$_2$O$_4$ with spherical crystallite appearance. This results correspond with the research which has been done by Lazarevic who studied the formation of nano ferrites [14].

![Fig. 4 SEM profile of Zn$_{3-x}$Fe$_x$O$_4$ powder (x = 0.25; 0.50; 0.75 and 1.0) milling result for 5 hours.](image)

The results of observation of Zn$_{3-x}$Fe$_x$O$_4$ powder magnetic properties shown in Figure 5. Figure 5 shows the MH hysteresis curve in magnetic field range -1 Tesla to 1 Tesla. which gives information magnetization value of remanent (Mr), saturation magnetization (Ms) and the coercivity field (Hc).

![Fig. 5 M-H curva of Zn$_{3-x}$Fe$_x$O$_4$ powder (x = 0.25; 0.50; 0.75 and 1.0) milling result for 5 hours.](image)

The results of this observation indicate that all samples showed behavior of ferromagnetic properties with relatively small coercivity value. For more details, the hysteresis curve is magnified and the values of the magnetic parameters of each sample are shown in Table 2.

<table>
<thead>
<tr>
<th>X</th>
<th>Sample</th>
<th>Value of Magnetic parametrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>Zn$<em>{2.25}$Fe$</em>{0.75}$O$_4$</td>
<td>1.89</td>
</tr>
<tr>
<td>0.50</td>
<td>Zn$<em>{1.5}$Fe$</em>{1.5}$O$_4$</td>
<td>4.03</td>
</tr>
<tr>
<td>0.75</td>
<td>Zn$<em>{0.75}$Fe$</em>{2.25}$O$_4$</td>
<td>14.10</td>
</tr>
<tr>
<td>1.00</td>
<td>ZnFe$_2$O$_4$</td>
<td>21.10</td>
</tr>
</tbody>
</table>

According to research results reported by Swamy et. al (2011) [1] and Xue et. al. (2007) [6] that ZnFe$_2$O$_4$ synthesized with combustion method showed Ms values of 7 emu / g and 20 emu / g respectively.

**CONCLUSION**

The single phase of ZnFe$_2$O$_4$ have succesfully synthesized in the composition of Zn$_{3-x}$Fe$_x$O$_4$ for $x = 1.0$ and exhibit homogeneous morphological structure. This composition also has the best magnetic property among all compositions and exhibit ferrimagnetic behavior.

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REFERENCES


