The effect of calcination temperature on the formation and magnetic properties of ZnMn$_2$O$_4$ spinel

B Hermanto, Ciswandi, F Afriani, D Aryanto and T Sudiro

Research Center for Physics, Indonesian Institute of Sciences, Kawasan Puspiptek Serpong, Tangerang Selatan 15310, Indonesia

E-mail: toto011@lipi.go.id

Abstract. The spinel based on transition-metal oxides has a typical composition of AB$_2$O$_4$. In this study, the ZnMn$_2$O$_4$ spinel was synthesized using a powder metallurgy technique. The Zn and Mn metallic powders with an atomic ratio of 1:2 were mechanically alloyed for 3 hours in aqueous solution. The mixed powder was then calcined in a muffle furnace at elevated temperature of 400, 500 and 600 °C. The X-ray Diffractometer (XRD) was used to evaluate the formation of a ZnMn$_2$O$_4$ spinel structure. The magnetic properties of the sample at varying calcination temperatures were characterized by a Vibrating Sample Magnetometer (VSM). The results show that the fraction of ZnMn$_2$O$_4$ spinel formation increases with the increase of calcination temperature. The calcination temperature also affects the magnetic properties of the samples.

1. Introduction

The spinel structure based on transition metal oxides having a general formula of AB$_2$O$_4$ (A and B = a transition metal but not in same element) is a promising material for wide range applications. The one of an attractive oxide spinel is ZnMn$_2$O$_4$. Due to its thermal and electrochemical properties, the zinc manganese oxide spinel materials have been used in practical devices such as negative temperature coefficient (NTC) thermistor, catalyst, high temperature materials, cathode and anode electrode for battery, supercapacitor applications, and solar energy fields [1-11].

The various methods have been used to synthesize the ZnMn$_2$O$_4$ spinels as: sol-gel [12], hydrothermal [4, 8, 10, 13], polymer-pyrolysis [1], solvothermal reaction [2, 5, 9, 11], flame spray pyrolysis [3], reactive template route combined with a post-calcination process [4], oxalate decomposition [6], and solid state reaction [14]. Nevertheless, the properties of ZnMn$_2$O$_4$ oxide spinel is often affected by its purity and crystalline structure. Accordingly, the appropriate method and processing parameter used are important to obtain the high purity and crystallinity of oxide spinel.

In this study, we synthesized the zinc manganese oxide spinel from Zn and Mn metallic powders using a powder metallurgy technique. The effect of calcination temperature on the formation of ZnMn$_2$O$_4$ spinel was studied by X-ray diffractometer and magnetic properties was investigated by Vibrating Sample Magnetometer (VSM).
2. Experimental

2.1. Material preparation and synthesis
The ZnMn₂O₄ samples were prepared using Zn (≥95%) and Mn metallic powders (≥99%) from Merck and Sigma-Aldrich, respectively. Initially, the Zn-Mn powder mixture with an atomic ratio of 1:2 (at%) was prepared by a mechanical alloying technique. The powder was mixed under wet milling condition in steel vial using a shaker mill with a powder to ball ratio of 1:10 for 3 h. After powder mixing was conducted, the Zn-Mn powder mixture was dried to evaporate the milling solution. In order to form the ZnMn₂O₄ oxide spinel, the mixture powder was then calcined in muffle furnace at elevated calcination temperature of 400, 500 and 600 °C in an air atmosphere. Prior to powder characterization, the calcined powder was crushed using a mortar.

2.2. Characterization examination
A Smartlab-Rigaku X-ray diffractometer with CuKα radiation was used to analyze the formation of ZnMn₂O₄ spinel phases after the powders were calcined at different temperature. The X-ray diffraction measurement was carried out in the angle range of 10° - 90°. In this study, we estimated the average crystallite size (D) using Debye Scherer’s formula [15], as shown below:

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]  
(1)

The λ, β and θ represent the wavelength of X-ray used (1.541862 Å), the full width at half maximum (FWHM) diffraction peak of ZnMn₂O₄ and the Bragg’s diffraction angle, respectively. While the lattice strain (ε) was calculated using the following formula [15],

\[
\varepsilon = \frac{\beta}{4 \tan \theta}
\]  
(2)

The magnetic properties of calcined powder was characterized using a Vibrating Sample Magnetometer Model VSM-250 Dexing Magnet Tech. Co., Ltd. at room temperature.

3. Results and discussion

3.1. Spinel formation at varying calcination temperature
Figure 1 shows the X-ray diffraction patterns of Zn, Mn powders as a starting material and Zn-Mn mixture after mechanical alloying. It can be seen that the starting material of the powder as shown in figure 1a and 1b is composed mainly by Zn and Mn phases, respectively. After mixing by a shaker mill for 3 h, X-ray diffraction analysis shows a main peak in the diffraction angle of 43.16° (figure 1c). This suggest that the Zn and Mn powder form the (Zn, Mn) solid solution. There are no other phase formed in the powder after mechanical milling. The ball and powder collison during milling enhance the complete mixing of the starting powder materials.

Figure 2 shows the XRD patterns of formed ZnMn₂O₄ oxide spinel synthesized at varying calcination temperature. The results reveal that small diffraction peaks of ZnMn₂O₄ can be observed at calcination temperature of 400 ºC. The other diffraction peaks were identified as MnO and ZnO phases. Accordingly, it can be predicted that during calcination, Zn and Mn elements are preferentially oxidized to form its oxide as shown in equation 3 and 4. While, the formation of ZnMn₂O₄ oxide spinel may take place in the two ways according to equation 5 and 6.

\[
2Zn + O₂ → 2ZnO
\]  
(3)

\[
2Mn + O₂ → 2MnO
\]  
(4)

\[
Zn + 2Mn + 2O₂ → ZnMn₂O₄
\]  
(5)
2\text{ZnO} + 4\text{MnO} + \text{O}_2 \rightarrow 2\text{ZnMn}_2\text{O}_4 \quad (6)

At higher calcination temperature of 500 and 600 °C, the formation of \text{ZnMn}_2\text{O}_4 oxide spinel tends to raise. The small amounts of \text{MnO} and \text{ZnO} phases are still observed at 500 °C. The \text{ZnMn}_2\text{O}_4 spinel was observed as a major phase after calcined at 600 °C for 18 h. Since the formation of \text{ZnO} and \text{MnO} decreases with the increase of calcination temperature, the formation of \text{ZnMn}_2\text{O}_4 is likely to occur due to the reaction between \text{ZnO} and \text{MnO}, as shown in equation 6.

![Figure 1](image1.png)

**Figure 1.** X-ray diffraction patterns of (a) Zn, (b) Mn starting materials, and (c) Zn-Mn powder after mechanical alloying.

![Figure 2](image2.png)

**Figure 2.** X-ray diffraction patterns of formed \text{ZnMn}_2\text{O}_4 prepared at varying calcination temperature of 400, 500 and 600 °C.

The crystallite size of synthesized powder was estimated using a Scherer formula based on the Full Width Half Maximum (FWHM) of X-Ray diffraction data. According to the results as presented in table 1, the crystallite size of \text{ZnMn}_2\text{O}_4 increases with an increasing calcination temperature. It is about
14 - 28 nm. It seems that the crystallite size of ZnMn$_2$O$_4$ spinel tends to grow with the increase of calcination temperature. On the contrary, the lattice strain is gradually decreased by increasing calcination temperature.

3.2. Effect of calcination temperature on the magnetic properties

Figure 3 shows the magnetization curves of formed ZnMn$_2$O$_4$ synthesized at elevated calcination temperatures of 400, 500 and 600 °C. The corresponding magnetic properties of the magnetization measurement are listed in table 1. Initially when the external field was applied to the sample, the hysteresis curve looks like it has not been saturated. But the line between magnetization and demagnetization has a coincided. This indicates that the measurement has undergone magnetization saturation state. These results correspond to the magnetization measurement of ZnMn$_2$O$_4$ studied by Song et al. [5]. The magnetization curve first shows an extremely increases as the external field increases approximately a hundred Oersteds, and then a slow increase with the increases of external field. In the present study, the maximum external field which can be applied is up to 22 kOe (2.2 Tesla). The magnetization curve was possible to rise slowly with increasing external magnetic field when it was compared to the previous study [5] which was measured for up to 7 T.

![Figure 3](image.png)

**Figure 3.** Hysteresis curve of formed ZnMn$_2$O$_4$ prepared at elevated calcinations temperatures of 400 °C, 500 °C and 600 °C.

As can be seen in table 1, the saturation magnetization of the samples decreases from 2.08 to 0.82 emu/g and for the remanance magnetization is decreased from 0.14 to 0.03 emu/g when the calcination temperature increases from 400 to 600 °C. Meanwhile, the coercivity of the sample is varied between 120–133 Oe. It was known that Mn [16] and Zn [17] as a starting materials in this study are paramagnetic and diamagnetic, respectively. The Zn oxide (ZnO) and Mn oxide (MnO) exhibit diamagnetic [18] and antiferromagnetic [19], respectively. The table 1 shows that the formed ZnMn$_2$O$_4$ prepared at varying calcinations temperature has a low magnetic saturation, remanence and coercivity. Obviously from figure 2, the calcination temperature of 600 °C leads to the formation of high purity ZnMn$_2$O$_4$ spinel oxide, while at 400 and 500 °C, the small amount of MnO and ZnO can still be found. In addition, table 1 indicates that the crystallite sizes of ZnMn$_2$O$_4$ are also depended on the calcinations temperature. The aforesaid evidences strongly suggest that the magnetic properties of synthesized sample are affected by the phase composition and crystallite size. At calcination temperature of 600 °C, the synthesized material consisting of ZnMn$_2$O$_4$ spinel shows antiferromagnetic behavior [20] with low magnetic saturation, remanence and coercivity. Thus,
according to the magnetic properties classification as reported in Ref. [21], the ZnMn$_2$O$_4$ oxide spinel can be classified as semi-hard magnetic (jHc between 25 to 700 Oe).

### Table 1. Crystallite size, lattice strain and magnetic properties of formed ZnMn$_2$O$_4$ prepared at varying calcination temperature.

| Calcination temperature T (°C) | Crystallite size D (nm) | Lattice strain ε [%] | Saturation magnetization $\sigma_s$ (emu/g) | Remanence magnetization $\sigma_r$ (emu/g) | Coercivity jHc (Oe) |
|-------------------------------|------------------------|----------------------|-------------------------------|-------------------|-----------------|
| 400                           | 15                     | 0.763                | 2.08                          | 0.14              | 133             |
| 500                           | 25                     | 0.444                | 1.34                          | 0.07              | 120             |
| 600                           | 29                     | 0.386                | 0.82                          | 0.03              | 124             |

### 4. Conclusions

The ZnMn$_2$O$_4$ spinel was successfully synthesized using powder metalurgy technique. The phase formation and stability of ZnMn$_2$O$_4$ spinel were affected by calcination temperatures. At low calcination temperature (400 and 500 °C), instead of ZnMn$_2$O$_4$ oxide spinel, the phase characterization indicates the formation of ZnO and MnO phases. A high purity of ZnMn$_2$O$_4$ spinel was mostly formed after calcined at 600 °C. The crystallite size of the sample increases while the lattice strain decreases with the increase of calcination temperature. Few hundred Oerstead in coercivity of ZnMn$_2$O$_4$ oxide spinel reveals that this material can be classified as semi-hard magnetic material.

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