

Fabrication of Oxide Ceramic MgFe_2O_4 Using Iron Oxide Isolated from Lapindo Mud as a Raw Material

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ABSTRACT

The quite high content (28.8%) of iron oxide (Fe_2O_3) in Lapindo Sidoarjo's mud promotes as a potential raw material for fabrication of oxide ceramics. The preeminence magnetic properties of iron oxide materials have led to be widely used for preparation of noteworthy product i.e semiconductor ceramics. However, the high band gap of iron oxide results in high resistivity, limiting its application as semiconductor ceramics. The addition of other oxides to iron oxide is able to reduce the energy gap of resulted oxide ceramics. Accordingly, in this study, MgO is added to Fe_2O_3 isolated from Lapindo mud for preparation of the oxide ceramic MgFe_2O_4 . The products are characterized, which include crystal structure, crystal size and resistivity. It was found that the addition of MgO decreased the volume fraction of spinel structure formation, the average of crystal size, and the resistance value. The ratio $\text{MgO}/\text{Fe}_2\text{O}_3$ of 3:7 and a sintering temperature of 1300°C show the optimum composition for fabrication of MgFe_2O_4 with the volume fraction of 0.72 and the crystal size of 49.06 nm as characterized by XRD.

Keywords: Lapindo mud, Fe_2O_3 , MgO, MgFe_2O_4 , oxide ceramics.

INTRODUCTION

Nowadays, the iron oxide materials come into great popularity on the research activities especially in the fields of material science and technology. Due to the magnetic properties preeminence, iron oxide materials have been widely used for many products such as ceramics, inks, catalysts, thin films, nano-particles technological and semiconductor ceramics. Solikha et al [1] used a semiconductor ceramic as a sensitive gas sensor in the environment. However, a semiconductor ceramic made of iron oxide as a raw material possesses high resistivity caused by the high energy gap (3.1 eV) of iron oxide itself [2], which may confine for further applications in this field.

The addition of copper oxide (CuO) to the iron oxide (Fe_2O_3) in the fabrication of ceramic oxide semiconductor CuFe_2O_4 , produce ceramic CuFe_2O_4 with the energy gap value of 2.4 eV. In this work, ceramic oxide CuFe_2O_4 , whose has spinel structure, is sintered at 1000 and 1100 °C for one hour [3]. Such results proved that the mixing other oxides with iron oxide can decrease energy gap ferrite compounds to be used as the raw material of the ceramic oxide semiconductor. Similarly, magnesium oxide can be added to iron oxide to form oxide ceramic of MgFe_2O_4 with energy gap of 2.18 eV [4].

Lapindo Sidoarjo's mud consist of some major oxides, such as 40.1% SiO_2 , 28.8% Fe_2O_3 , and 15% Al_2O_3 [5]. Several studies have been conducted to isolate silica (SiO_2) and alumina (Al_2O_3) in the Lapindo mud, and they were applied as raw materials for ceramic [5]

and silica aerogel [6]. However, to best of our knowledge, there is no research dealing with isolation of Fe_2O_3 from Lapindo mud to be utilized as a raw material for fabrication of some valuable materials with can increase its economic value. Therefore, in this study, Fe_2O_3 from Lapindo mud is isolated using the acidic method, and subsequently applied as a raw material for the formation of oxide ceramic MgFe_2O_4 after reacted with MgO . The ratio of Fe_2O_3 to MgO as well as sintering temperature is studied in detail. The resulted oxide ceramic MgFe_2O_4 is characterized which includes the measurement of spinel volume's fraction, crystal size, morphology, and resistivity.

EXPERIMENT

Chemicals and instrumentation

Some chemicals used in this experiment are HCl 37% $\rho = 1,19 \text{ g/mL}$, HNO_3 66% $\rho = 1,51 \text{ g/mL}$, MgO and NH_4OH 21% . All chemicals were of analytical grade and purchased from Merck (Germany).

The sample in this study is a chunk of Lapindo's mud and mud liquid which was taken in the Porong subdistrict of Sidoarjo Siring with coordinates of $07^\circ 31.480'$ LU and $112^\circ 42.274'$ LS, is 2.7 meter from the edge of the embankment and the distance from the center of the hot blast of 1.5 km and a depth of 75 cm. Prior to use, Lapindo mud sample is dried in an oven at 110°C for 24 hours. Then, the sample is finely crushed in a mortar and stored in a sealed container. The metal contents in dried Lapindo mud are analyzed using X-ray Fluorescence (XRF).

The instrumentations used in study include Oven Fisher Scientific 655 F, Furnace Nabertherm N-31 model, German; Pressing tools Paul Otto Weber GmbH, German, multimeter Sanwa CD800a, XRF PANanalytical type Minipal 4, United States; Scanning Electron Microscope (SEM) Tabletop Microscope TM3000 type Hitachi, Japan; XRD X'pert type Philips, The Netherlands.

Procedure reaction

Isolation of Fe_2O_3 form Lapindo

A 10-mg of dried sample is dissolved in 20 ml of aqua regia. After agitation and heating the sample for 1 h, the obtained precipitate is separated by filtration. Then, the filtrate is added with excess amounts of NH_4OH to precipitate $\text{Fe}(\text{OH})_3$. After filtration, $\text{Fe}(\text{OH})_3$ is dried at 110°C to form Fe_3O_4 . The latter iron oxide is calcinated at 600°C for 1 h to form Fe_2O_3 , which then analyzed by XRF to measure the iron oxide content.

Table 1. Ceramics MgFe_2O_4 composition.

| Ceramic | Concentration of MgO (w/w) (%) | Mass (g) | | T ($^\circ\text{C}$) |
|---------|---|-------------------------|--------------|------------------------|
| | | Fe_2O_3 | MgO | |
| A | 0 | 1.0 | 0.0 | 1000 |
| B | 20 | 0.8 | 0.2 | 1000 |
| C | 50 | 0.5 | 0.5 | 1000 |
| D | 70 | 0.3 | 0.7 | 1000 |
| E | 100 | 0.0 | 1.0 | 1000 |
| F | 70 | 0.3 | 0.7 | 1300 |

Fabrication of MgFe₂O₄ ceramics

Magnesium oxide is added into Fe₂O₃ at various concentration of 0, 20, 50, 70 and 100% by weight (w/w), with a total weight of ceramic MgFe₂O₄ to be made as much as 1 g. Ceramic powder composition is shown in Table 1. The mixing is performed in mortar and stirred for 1 h. The pressing process is performed in uniaxial with a compressive load of 2×10^3 kg/cm² to produce ceramic pellets. Then raw ceramic pellets is sintered at 28 - 1000 °C (and 28 - 1300 °C) for 2 h. The resulted ceramic is characterized, which include the measurement of spinel volume's fraction, crystal size, resistivity and micro-picture (morphology).

RESULT AND DISCUSSION

Isolation of Fe₂O₃ of mud Lapindo with acidic method

The principle of isolation of iron(III) oxide (Fe₂O₃) with acidic method is to separate the Fe(III) from samples of sludge extraction with Lapindo using acid solution, then it is conducted the precipitation of Fe(III) in the form of hydroxide (Fe(OH)₃) using a solution of ammonium hydroxide. Calcination temperature affect formation of structure of Fe₂O₃. Temperatures above 500 °C produced the Hematite (α -Fe₂O₃) which is an isostructural of corundum [8]. Then iron oxide obtained is characterized using XRF. Level of iron oxide obtained from this method as shown in Table 2.

Table 2. The analyze result of the content of metal oxides (Si, Al and Fe) from acidic method using XRF.

| Sample | Percentage (%) | | |
|--|----------------|-------|-------|
| | Al | Si | Fe |
| Lapindo's mud sample | 13.00 | 38.20 | 32.60 |
| Precipitation from the result of Acidic Method | 5.60 | 0.00 | 79.62 |

Characteristics of Ceramics MgFe₂O₄

In this study, MgFe₂O₄ ceramics are made using raw materials of Fe₂O₃ which is the result of the isolated Lapindo's mud, while MgO is analytical grade. To determine the optimum composition in the fabrication of ceramics, characterization MgFe₂O₄ then it is performed to look at the most optimum results. The characterizations were performed such that the calculation of the volume fraction of spinel structure formation, crystal size and resistivity of ceramics at each composition.

To find out how many spinel structure is formed on the ceramic structure MgFe₂O₄ made, it is performed an analysis using XRF. From the analysis, it can be calculated volume fraction of the spinel structure ceramics B, C and D based on equation 1 [9], and obtained the results as shown in Table 4.

$$R_x = \frac{\text{MgFe}_2\text{O}_4 (2\ 2\ 0)}{\text{MgFe}_2\text{O}_4 (2\ 2\ 0) + \text{Fe}_2\text{O}_3 (1\ 0\ 4)}$$

$$\alpha = -1,564R_x^4 + 3,210R_x^3 - 1,304R_x^2 + 0,647R_x - 0,004 \quad (\text{Equation 1})$$

Where MgFe_2O_4 (220) is the peak intensity of the (220) of MgFe_2O_4 and Fe_2O_3 is the peak intensity of the (104) of Fe_2O_3 .

Table 3. Intensity ratio and the volume fraction of the ceramic spinel formation MgFe_2O_4 .

| Ceramic | R_x (Intensity ratio) | A (Volume fraction) |
|---------|----------------------------|------------------------|
| B | 0.1272 | 0.0634 |
| C | 0.2476 | 0.1191 |
| D | 0.2495 | 0.1201 |

Based on Table 3 it can be shown that the more increased volume fraction and the more MgO 's concentration used.

The resistivity is represented by the symbol ρ and defined as a measure of whether or not the electrons to move easily within a material. The result of resistivity calculation's characteristic shows that the resistivity of the ceramic MgFe_2O_4 decreases as shown in Figure 1.

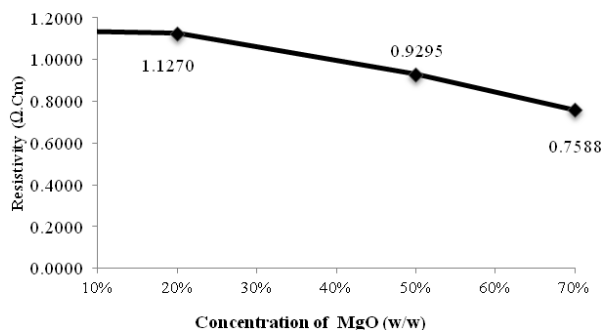


Figure 1. Curve concentration MgO vs resistivity of ceramics MgFe_2O_4

Resistivity decreases with the increasing of MgO 's concentration used due to the increasing concentration of MgO is added, the formation MgFe_2O_4 gets increased. This is proven by the result of the fraction volume's calculation of spinel is also increasing. Magnesium oxide is an oxide that do not have a free electron. This means that MgO in the solid state can not conduct electricity. This causes that the concentration of MgO ceramics E with 100% (w/w) resistance can not be measured.

Crystal size of the ceramic MgFe_2O_4 can be calculated based on the Debye Schererr equation based on data analysis using XRD. The result of calculations using the crystal size Debye Schererr modification equation is shown in Table 5. Its equation is presented in equation 2 [10].

$$\ln \beta = \ln \frac{K\lambda}{L \cos\theta} = \ln \frac{K\lambda}{L} + \ln \frac{1}{\cos\theta} \quad (\text{Equation 2})$$

Where L is the crystal size in the nanometer scale, K is a constant of 0.9, λ is the wavelength used during testing XRD (0.154056), β is the value of FWHM (Full Width at

Half Maximum) in units of radians and θ is bragg angle. By plotting $\ln 1/\cos\theta$ values on the x-axis and y-axis $\ln \beta$, the intercept obtained a value of $\ln (K \lambda / L)$, and the size of the crystal (L) can be determined.

Table 4. Crystal sizes of MgFe₂O₄ ceramic B, C and D

| Ceramic | Average crystal size (nm) |
|---------|---------------------------|
| B | 87.80576 |
| C | 39.58408 |
| D | 39.20589 |

Based on Table 4 it can be shown that the average size of crystallite on ceramics MgFe₂O₄ get decreased with the increasing concentration of MgO added. This is due to that the increasing number of MgO added in the ceramic matrix is MgFe₂O₄ whereas magnesium oxide is the second phase. Magnesium oxide has a relatively small size compared to the oxide Fe₂O₃ and MgFe₂O₄. Therefore, with the increasing addition of MgO in the fabrication of ceramics MgFe₂O₄, MgO crystal size affects the value of the average crystal size ceramic MgFe₂O₄ is getting smaller.

Based on the result calculation of XRD and resistivity of the data is showed that the optimum composition is found in concentrations of 70% MgO (the biggest volume fraction, average sized crystall and the smallest resistivity).

Effect of Sintering Temperature

Value of the volume fraction of the ceramic spinel MgFe₂O₄ sintered at 1000 °C (Ceramic B, C and D) are still too small, this is allowed since the used sintering temperature which is not high so the forming of the spinel's new structure cannot move optimally. Therefore the sintering process is performed at a temperature of 28 °C - 1300 °C and then held for 2 hours at a temperature of 1300 °C. It performed on the pellets with 70% MgO concentration. MgFe₂O₄ ceramics obtained from the sintering process (Ceramic F) characterized to determine the character of the ceramic.

Table 5. Comparison of the average crystallite size ceramic D and F.

| Ceramic | Crystallite size (nm) |
|---------|-----------------------|
| D | 39.20589 |
| F | 49.06407 |

Based on the results of the characterization of ceramics F using XRD, obtained spinel volume fraction is amount 0.72. This value is much greater than in the ceramic D (Table 5). It means that the sintering temperature increases the formation of spinel structure in the forming of MgFe₂O₄. At temperatures 1000 °C, a used mixture of iron oxide and magnesium oxide is a few parts which have formed MgFe₂O₄'s spinel structure. In the sintering process work out a of diffusion of atoms to achieve the equilibrium structure of the most stable form. At temperatures of 1300 °C, the diffusion of Fe(III), Mg(II) and O(II) is increase, so the process to form a spinel structure is faster than that in 1000 °C. This causes the volume

fraction of the ceramic spinel F is greater than the ceramic D. Temperature also affects the average crystal size of the resulting ceramic MgFe_2O_4 as shown in Table 5, which shows the comparative crystallite sizes of ceramic D and F.

Average crystal size on ceramics F is increased compared to ceramic D. Formation of spinel structure affects the average crystallite size on ceramics MgFe_2O_4 . Based on the calculation it is known that the ceramic volume fraction F has a value greater than ceramic D. It means that the ceramic D, MgFe_2O_4 is formed more. Magnesium ferrite has relatively larger size, with the more formation of ceramics MgFe_2O_4 F causes an increase in the average sized crystal.

Resistance measurement on ceramics F is also performed, but the resistance value can not be measured directly. Heating the ceramics is also conducted with the expectation that the increase of temperature can improve the mobility of the electron. So, it can analyze the electricity and the resistance of the ceramic cannot be measured. This is possible because the energy gap of the resulting MgFe_2O_4 still too width.

The density of crystalline structure can also inhibit the mobility of electrons, thus affects its resistance. This is supported by the calculation of shrinkage of the ceramic fuel MgFe_2O_4 . Loss of mass and volume values on ceramic D of 29.4 and 31%, whereas the F ceramic mass and volume shrinkage of 64.40 and 76.30%.

At the sintering temperature 1000 °C, exsiccate fuel values of ceramic is still smaller than the temperature of 1300 °C. It means that the crystal structure of the ceramic at 1000 °C is not too tight. So the electron mobility is quite high and can be measured. At temperature 1300 °C while the treatment is more tightly structured so that the low electron mobility so the resistance can not be measured directly. It is also supported by data of the calculation result of both ceramics, the density of ceramics at the sintering temperature of 1300 °C is greater (2.4038 g/cm^3) than at 1000 °C (1.3453 g/cm^3)

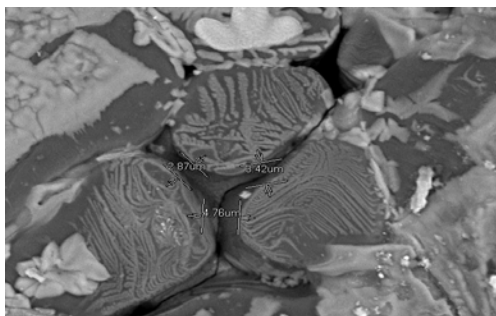


Figure 2. Micro image MgFe_2O_4 at 3000x magnification.

The surface area of contact between the electrode and ceramic MgFe_2O_4 can also affect the resistance measurement. Electrode coatings on ceramic F can increase the interfacial surface area contact between the MgFe_2O_4 with a multimeter measuring instrument. On the ceramic F, it is performed the micro picture analyze by SEM. Based on the imaging, there are a sphere with the various sizes as shown in Figure 4. Grain size of the ceramic MgFe_2O_4 are variability caused by the mixing process Fe_2O_3 and MgO aren't homogeneous.

CONCLUSION

Based on the results of this, the conclusion is that after the magnesium oxide into iron oxide sintering then it is performed at a temperature of 1300 °C to produce ceramic oxides with spinel structure. The optimum composition of the ceramic forming $MgFe_2O_4$ the addition of MgO concentration of 70% by spinel volume fraction values formed by 0.72, but the value of the resistivity can not be measured directly. The micro structure of ceramics $MgFe_2O_4$ spheres with the various sizes.

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