Cu-Mn Co-doped NiFe$_2$O$_4$ based thick ceramic film as negative temperature coefficient thermistors

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Abstract. NTC (Negative Temperature Coefficient) thermistors are widely used as temperature sensors in industrial and medical applications due to their high-temperature sensitivity, durability, and low cost. Generally, NTC thermistors are made from spinel structured ceramics formed by transition metal oxides with the general formula AB$_2$O$_4$. One of the spinel structured ceramics that can be made for NTC thermistors is NiFe$_2$O$_4$ nanoparticles. This work aimed to prepare Cu-Mn co-doped NiFe$_2$O$_4$ based thick ceramic film using Jarosite mineral as a precursor. The synthesis method used was a simple coprecipitation method, while the technique used in making a thick ceramic film was a simple screen printing technique. The sintering temperatures used were 1000 ℃, 1100 ℃, and 1200 ℃. Based on x-ray diffraction analysis, the thick films consist of spinel phase, hematite phase, and some unidentified phase. The constant thermistor values (B) for thick films obtained with 1000, 1100, and 1200 ℃ sintering temperatures were 4740 K, 5669 K, and 5731 K, respectively. These results showed that all obtained thick films had passed the minimum value in market needs (B ≥2000 K).

1. Introduction

A thermistor, which comes from a thermally sensitive resistor, is a type of resistor sensitive to temperature changes. The principle of the thermistor is to provide a change in resistance which is proportional to the change in temperature. A significant change in resistance to a relatively small change in temperature makes thermistors widely used. Thermistors usually use semiconductor materials, and there are two types of materials, namely metal oxide and semiconductor single crystals [1].

One type of thermistor widely used in the world of electronics is the NTC thermistor. NTC (Negative Temperature Coefficient) thermistors are widely used as temperature sensors in industrial and medical applications because of their high-temperature sensitivity, durability, and low cost [2]. It is well known that most NTC thermistors are made from ceramics with a spinel structure, formed by transition metal oxides with general formula AB$_2$O$_4$ where A is a metal ion in the tetrahedral position and B is a metal ion in the octahedral position [3,4]. NTC thermistors can be made in various forms such as disc, CD, bulk, or pellet film and film either thick film [5] or thin film [6]. One of the most common forms of a thermistor is thick ceramic film. The thick ceramic film has the advantage of...
requiring very little material and can be applied in a compact integrated circuit with a small volume (hybridization and miniaturization) [7].

Research on thick film ceramics NiFe$_2$O$_4$ has been carried out by Koli et al. [7] with the precipitation method for gas sensors. It is said that there is a decrease in the electrical resistivity of the NiFe$_2$O$_4$ thick ceramic film when the temperature increases, which indicates that the NiFe$_2$O$_4$ thick ceramic film can be used as an NTC (Negative Thermal Composite) type thermistor.

A thermistor with good quality is a thermistor with a fast response to changes in temperature. A thermistor has two critical constants: the thermistor constant (B) and the thermistor sensitivity ($\alpha$). There are two critical constants in a thermistor: the thermistor constant (B) and the thermistor sensitivity ($\alpha$).

There have been many studies on NTC thermistors to produce the best quality thermistors. The manufacture of NTC thermistors with iron minerals as the primary material is still being developed, such as in the manufacture of thick film ceramics FeTiO$_3$ by Denny [8] and the manufacture of thick ceramic film Fe$_2$O$_3$-MnO-ZnO carried out by Sari et al. in 2016 [9].

This work aimed to study NiFe$_2$O$_4$ thick ceramic film made from Jarosite mineral as NTC thermistors based on the background described. However, to reduce the resistance value, three strategies were chosen: the use of Fe$_2$O$_3$ from Jarosites local mineral, the addition of Cu and Mn as dopant, and the variations in sintering temperature. In this research, the electrical resistivity characteristics of thick film ceramic NiFe$_2$O$_4$ and its relationship with temperature were also carried out.

2. Research methods

The method used in this research to synthesize NiFe$_2$O$_4$ nanoparticles was the precipitation method. NiFe$_2$O$_4$ nanoparticles were prepared by mixing NiCl$_2$.6H$_2$O, Fe$_2$O$_3$ from Jarosite, CuO, and MnO minerals with mole ratios of 30%, 30%, 30%, and 10%. The solution was then precipitated with NH$_4$OH while stirring with a magnetic stirrer until the pH of the solution approached pH 10. The precipitate was then washed with distilled water and dried in an oven at 100 ºC. Then the precipitate was calcined in a furnace at 600 ºC for 2 hours to get brown NiFe$_2$O$_4$ nanoparticle powder.

Furthermore, the NTC thermistor thick film NiFe$_2$O$_4$ was made using a screen printing technique by adding inorganic and organic components with a ratio of 70:30. The inorganic part contains NiFe$_2$O$_4$ nanoparticle powder, while the organic part contains 90% $\alpha$-terpineol and 10% ethyl cellulose. All of these components are combined to form a solid paste. The paste was printed on a cut alumina substrate with a size of ± 1.25 x 0.5 cm using a T90 screen. Then the film plates were sintered with temperature variations, namely 1000 ºC, 1100 ºC, and 1200 ºC.

The NiFe$_2$O$_4$ thick ceramic film formed then characterized its crystal structure using X-Ray Diffraction analysis with Cu Kα radiation. For electrical properties measurement, a couple of parallel electrodes Ag paste was coated on each side of NiFe2O4 thick film and then heated at 600ºC for 10 minutes. The electrical properties (resistance) were carried out using a digital multimeter and a laboratory-made chamber equipped with a digital temperature controller. The resistance value was measured at a temperature range of 180 to 240 ºC with a step size of 5 ºC.

3. Results and discussion

3.1. Crystal Analysis of Cu-Mn co-doped NiFe2O4 ceramic thick film

Identification of the NiFe$_2$O$_4$ thick ceramic film crystallinity doped with Cu and Mn was carried out using X-Ray Diffraction (XRD). Characterization using XRD aims to determine the form of crystals formed.

The x-ray diffraction pattern of Cu-Mn co-doped NiFe$_2$O$_4$ sintered at 1000 ºC, 1100 ºC, and 1200 ºC are shown in Figure 1. It indicates that besides the cubic spinel NiFe$_2$O$_4$ phase, there is an additional hexagonal Fe$_2$O$_3$ phase and other phases. Based on Figure 1, it can be seen the NiFe$_2$O$_4$ phase peaks of the fields (111), (220), (311), (222), (400), (422), (511), and (440) appear, which correspond to the literature data (JCPDS card no. 10-0325). Whereas in the additional phase of Fe$_2$O$_3$,
the peaks of fields (012), (104), and (024) appear, which correspond to the literature data (9000139 COD). The presence of the Fe$_2$O$_3$ phase in NiFe$_2$O$_4$ was probably due to the incomplete reaction. In addition, there are other additional peaks of impurities that have not been identified yet, but it was suspected that these peaks originate from CuO and MnO, which partially were insoluble in NiFe$_2$O$_4$, or from alumina substrate, which was analyzed by XRD. There is no significant change in the x-ray diffraction pattern with the increase of sintering temperature, and the changes were only on the intensity occur at the peaks. Peak intensity shows the crystallinity of a material, the higher and tapering the peak intensity, the higher the crystallinity of a material, whereas if the peak and intensity are widening, this shows that the amorphous properties of the material also increase. In addition, the narrower and sharper diffraction peaks also showed an increase in particle and crystal size [10]. Therefore, it can be seen that the XRD patterns on the Cu-Mn co-doped NiFe$_2$O$_4$ thick ceramic film which sintered at a temperature of 1200 °C showed the XRD pattern results were narrower and sharper than the XRD pattern results on Cu-Mn co-doped NiFe$_2$O$_4$ thick ceramic film which sintered at a temperature of 1000 °C and 1100 °C. This shows that at a temperature of 1200 °C NiFe$_2$O$_4$ crystals are more crystalline.

3.2. Electrical properties of Cu-Mn co-doped NiFe$_2$O$_4$ ceramic thick film ceramic

Before testing the characterization of electrical properties, the ceramic coating of thick film NiFe$_2$O$_4$ doped with Cu and Mn was carried out with silver paste on both ends of the thick film ceramic, then sintered at 600 °C for 10 minutes, as shown in Figure 2. This silver plating functions as a metal contact or ohmic contact so that the resistance of thick film ceramics can be measured when heated [4].

![X-ray diffraction pattern of Cu-Mn co-doped NiFe$_2$O$_4$ thick film ceramics sintered at 1000 °C, 1100 °C, and 1200 °C.](image)

Figure 1. X-ray diffraction pattern of Cu-Mn co-doped NiFe$_2$O$_4$ thick film ceramics sintered at 1000 °C, 1100 °C, and 1200 °C.
Figure 2. A ceramic thick film of Cu-Mn co-doped NiFe₂O₄ coated with silver paste.

The electrical characterization test was carried out using a multimeter, in which a thick film ceramic NiFe₂O₄ doped with Cu and Mn was heated on a hotplate and the resistance or resistance value was recorded every 5 °C temperature increase. Measurements were made from a temperature of 180 °C to 240 °C. The data obtained from this measurement is in the form of resistance data (R) in ohms (Ω) to temperature (T) in Kelvin (K) (Figure 3).

Figure 3. Graph of the relationship between temperature resistance values on thick film ceramic NiFe₂O₄ doped with Cu and Mn.

From Figure 3 it can be seen that there is a decrease in the resistance value of the thick film ceramic NiFe₂O₄ doped with Cu and Mn along with the increase in temperature. This proves that what is formed is a true NTC type thermistor, according to the literature where it is said that the NTC thermistor is a type of thermistor where when the temperature increases, the resistance will decrease.

To get the thermistor constant value, the data is converted into ln R and \( \frac{1}{T} \) form and graphed. The graph of the relationship between ln R to \( \frac{1}{T} \) can be seen for each combustion temperature in Figure 4.
Figure 4. The relationship between ln R and $\frac{1}{T}$ thick film ceramic NiFe$_2$O$_4$ doped with Cu and Mn which was sintered at a temperature of (a) 1000 °C; (b) 1100 °C; and (c) 1200 °C

From the graph of the ln R to $\frac{1}{T}$ relationship, the thermistor constant (B) can be obtained by determining the slope of the line equation formed by equation (1).

$$B = \frac{\ln(R)}{\frac{1}{T}}$$

Where $B$ is the thermistor constant (K), $R$ is the resistance (Ω), and $T$ is the temperature (K).

After obtaining the constant thermistor value, the following can be calculated the resistance value at room temperature ($R_{RT}$), namely by extrapolating the graph to the line equation formed on the graph with $T = 300$ K; The thermistor sensitivity value is obtained using the equation (2).

$$\alpha = \frac{B}{T^2} \times 100\%$$

Where $\alpha$ is the thermistor sensitivity (%/K); and the value of the activation energy using the equation (3).

$$B = \frac{\varepsilon_A}{K}$$

Where $\varepsilon_A$ is the value of activation energy (eV).

| Sintering temperature (°C) | B (K) | $R_{RT}$ (MΩ) | $\alpha$ (%/K) | $\varepsilon_A$ (eV) |
|---------------------------|------|---------------|----------------|---------------------|
| 1000                      | 4740 | 25591         | -5.3           | 0.4                 |
| 1100                      | 5669 | 25591         | -6.3           | 0.5                 |
| 1200                      | 5731 | 76175         | -6.4           | 0.5                 |

From Table 1 it can be seen that the thermistor constant (B) resulting from the three variations in the sintering temperature of the NiFe$_2$O$_4$ thick film ceramic doped Cu and Mn were sufficiently large to meet the demand of the wide range thermistors [11]. B value located in the range of 2000-7000 K is desirable for NTC thermistor applications [12]. These results are also comparable with other reports on nickel ferrite thermistors [13].
In addition, it can also be seen that an increase in the combustion temperature of 1000 °C and 1100 °C has the same resistance value at room temperature \( R_{RT} \), which then increases with the combustion temperature of 1200 °C. This shows that the combustion temperatures of 1000 °C and 1100 °C are the optimal temperatures in preparing thick film ceramic thermistor NiFe\(_2\)O\(_4\) doped with Cu and Mn because at that temperature the resistance value at room temperature \( R_{RT} \) shows the smallest resistance value, so its use requires high power. Smaller than the thick film ceramic NiFe\(_2\)O\(_4\) doped with Cu and Mn which was sintered at a temperature of 1200 °C. The use of large amounts of power can result in self-heating which can affect the accuracy of the thermistor [13].

However, when viewed from the thermistor sensitivity value \( \alpha \), thick film ceramic NiFe\(_2\)O\(_4\) doped Cu and Mn sintered at 1200 °C has the best sensitivity because the thermistor sensitivity value is related to the speed of detecting temperature changes. The greater the sensitivity value, the better the thermistor's response to changes in ambient temperature. A good thermistor has a sensitivity value greater than -2.2%/K, so it can be seen that the three variations in the sintering temperature of NiFe\(_2\)O\(_4\) thick ceramic film doped with Cu and Mn have good electrical characteristics.

Seeing the results of the resistance value at room temperature \( R_{RT} \) and thermistor sensitivity \( \alpha \), from the three combustion temperatures, it can be concluded that the 1100 °C combustion temperature has the best results because it has a low resistance value at room temperature \( R_{RT} \), namely 25591 MΩ, however, it also has a high thermistor \( \alpha \) sensitivity value of -6.3% K\(^{-1}\).

4. Conclusion

Cu-Mn co-doped NiFe\(_2\)O\(_4\) thick film ceramics have been successfully prepared using precipitation and screen printing method. By increasing the sintering temperature from 1000 to 1200 °C, the crystallinity also increased. The electrical properties characterization showed that Cu-Mn co-doped NiFe\(_2\)O\(_4\) sintered at 1100 °C has the potential to be used as NTC thermistor with thermistor constant (B) 5669 K, resistant at room temperature \( R_{RT} \) 25591 MΩ, and thermistor sensitivity \( \alpha \) -6.3% K\(^{-1}\).

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