Synthesis and Characterization of $CuFe_2O_4$ Thick Film Ceramics for NTC Thermistor Using Yarosite Mineral as Raw Material

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ABSTRACT

A study on fabrication of $CuFe_2O_4$ thick film ceramics for NTC (Negative Thermal Coefficient) thermistor by applying yarosite mineral has been carried out. This study was to know if there was a possibility to step up the added value of the mineral abundant in Indonesia. Powder of yarosite (mainly composed of Fe_2O_3) and CuO with composition proportional to $CuFe_2O_4$ was crushed and sieved using a 38 µm sieve. The fine mixed powder was then mixed with 5 weight % glass frit. The powder containing glass frit was mixed with 30 weight % organic vehicle to form a paste. The paste was screen printed using screen printing technique on alumina substrates. The films were fired at 900-1100^oC for 1 hour in air. Electrical characterization was done by measuring electrical resistance of the thick film ceramics at various temperatures. Microstructure and crystal structure analyses were done by using a scanning electron microscope (SEM) and an x-ray diffractometer (XRD). The XRD analyses showed that the thick film ceramics had tetragonal spinel structure. The SEM images showed that the thick film ceramics were porous with relatively small grains. The grain was larger for higher firing temperature. From the electrical characteristics data, it was known that the electrical characteristics of the $CuFe_2O_4$ thick film ceramics followed the NTC characteristic. The optimum firing temperature was 1000^oC. The thick film fired at 1000^oC had characteristics namely B = 3027K and R_{RT} = 7.8 MOhm which fitted the market requirement.

Key words: *Thermistor, NTC, thick film, yarosite,* $CuFe_2O_4$.

Introduction

NTC thermistors are widely used in the world and the need for them is still increasing due to its potential use for many sectors such as biomedical, aerospace, instrumentation, communications, automotive and HVACR (Heating, Ventilation, Air conditioning and Refrigeration) [Betatherm, 2008, Na, et al., 2001]. Some areas for NTC thermistor applications are temperature measurement, circuit compensation, suppression of in rush-current, flow rate sensor and pressure sensor [Park and Han, 2005]. It is traditionally known that most NTC thermistors are produced from spinel ceramics based on transition metal oxides forming general formula AB_2O_4 where A is metal ion in tetrahedral position and B is metal ion in octahedral position [Na, et al., 2001, Park, 2003, Matsuo, 1982, Jung, 1993, Hamada, 2001, Park and Han, 2005, Park and bang, 2003, Fritsch, 2004, Schmidt, 2004]. One of the spinel ceramics that can be used for NTC thermistor is $CuFe_2O_4$.

In Indonesia many electronic components are generally imported. In order to decrease the dependency of Indonesia to the imported product and get capability in self producing the NTC thermistor as well as increase the added value of mineral abundant in Indonesia, a study on fabrication of $CuFe_2O_4$ NTC thermistor in the form of pellet or disk has been carried out by utilizing yarosite as raw material [Wiendartun, 2007, Wiendartun, 2008]. However, the application of the $CuFe_2O_4$ thermistor in the form of pellet is more limited. In order to extend the area of application, it is required to also produce the thermistor in another form that more practical and profitable economically. Here, the form of thick film is considered as the choice. The thermistor in the form of thick film is possible for miniaturization and integration.

Technology generally used for fabrication of thick film thermistor is screen printing which is technically simple. Some parameters in the screen printing namely viscosity of paste, screen size, paste composition and firing parameter such as time and temperature significantly influence the characteristic of the thick film produced. In this work, a study on fabrication of thick film thermistor based on $CuFe_2O_4$ by utilizing yarosite as raw material was performed. The effect of firing temperature on the characteristics, especially the electrical characteristics, of the $CuFe_2O_4$ thick film ceramics for NTC thermistor is the focus of the study.

Materials and Methods

Powder of Fe_2O_3 derived from yarosite mineral (chemical composition is shown in Table 1) and glass frit made of SiO_2, B_2O_3 and PbO were crushed and sieved with a sieve of 38 μm (Hole size of 38μm). The method for processing the Fe_2O_3 powder is described elsewhere [Wiendartun,2007]). The sieved Fe_2O_3 powder and 5 weight % glass frit was mixed. The mixture of Fe_2O_3 and glass frit was mixed with organic vehicle containing alpha terpineol and ethyl cellulose with composition of 90 weight % and 10 weight %, respectively, to form a paste. The paste was screen printed on alumina substrates using screen printing technique. The films were fired at 900-1100°C for 1 hour in air. The crystal structure of the fired thick films was analyzed with x-ray diffraction (XRD) using Kα radiation. The films were investigated by SEM to evaluate their microstructure (morphology). A couple of parallel electrodes which is 1 mm apart are made on the sensor side of the fired thick film by using Ag paste. After the paste was dried at room temperature, the Ag coated-thick films were heated at 600°C for 10 minutes. The resistance was measured at various temperatures from 25 to 100°C in steps of 5°C using a digital multimeter and a laboratory made chamber equipped with a digital temperature controller. Thermistor constant (B) was derived from Ln resistivity vs. $1/T$ curve where B is the gradient of the curve based on (1)[Park, 2003,Park and Han, 2005]:

$$\rho = \rho_o .\exp (B/T) \qquad (1)$$

where, ρ is the electrical resistivity, ρ_o is a constant or the resistivity at T is infinite, B is the thermistor constant and T is the temperature in Kelvin.

Room temperature resistance (R_{RT}) was determined as the electrical resistance at room temperature (25°C) and sensitivity (α) was calculated using (2) [Moulson and Herbert, 1990].

$$\alpha = B/T^2 \qquad (2)$$

where, α is the sensitivity, B is the thermistor constant and T is the temperature in Kelvin.

Results and Discussion

Fig. 1 shows the appearance a typical thick film. Fig.2, Fig.3. and Fig.4 show the XRD profiles of $CuFe_2O_4$ thick film ceramics fired at 900°C, 1000°C and 1100°C, respectively. As shown in the figure Fig.2, Fig.3. and Fig.4, the profiles are similar. The XRD profiles show that the structure of the thick film ceramics is tetragonal spinel after being compared to the XRD standard profile of $CuFe_2O_4$ from JCPDS No. 34-0425). No peaks from second phases observed. It may be due to the small concentration of impurities which is smaller than the precision limit of the x-ray diffractometer used. The XRD data of Fig.2, Fig.3. and Fig.4 indicates that the synthesis of the $CuFe_2O_4$ films has been well prepared from CuO and Fe_2O_3 powder at 900°C-1100°C.

Table 1. Chemical composition of Fe_2O_3 powder derived from yarosite.

Component	Concentration (Weight %)
Fe_2O_3	93.80
SiO_2	1.15
Al_2O_3	2.54
TiO_2	1.02
MgO	0.19
MnO	0.09
K_2O	0.12
Na_2O	0.50
CaO	0.59

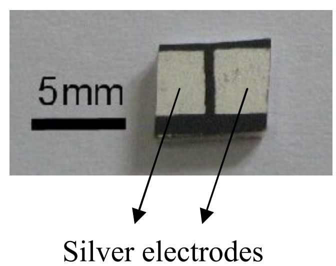

Fig.1. A typical thick film thermistor.

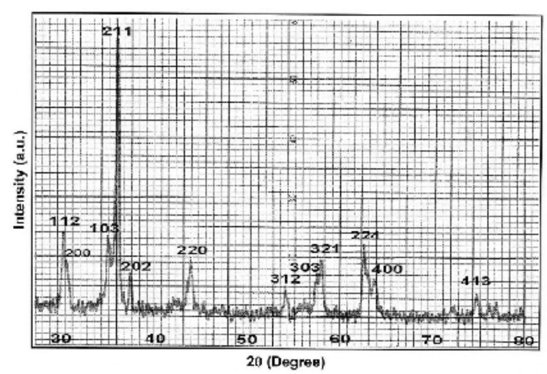

Fig. 2. XRD profile of $CuFe_2O_4$ based-thick film fired at 900°C.

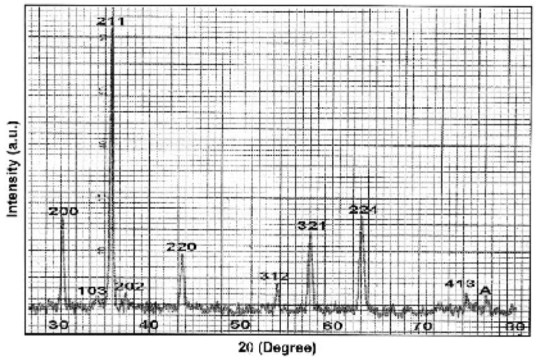

Fig. 3. XRD profile of $CuFe_2O_4$ based-thick film fired at 1000°C.

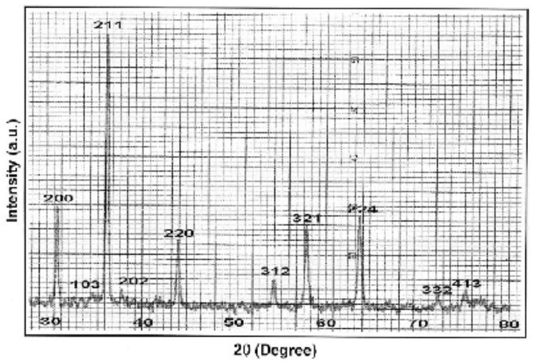

Fig. 4. XRD profile of $CuFe_2O_4$ based-thick film fired at 1100°C.

Microstructures of the $CuFe_2O_4$ film ceramic fired at 900°C, 1000°C and 1100°C, respectively, are depicted in Fig.5, Fig.6 and Fig. 7. All of the thick films are characterized in porous structure with different grain size depending on the firing temperature. The grain size becomes larger following the increase of the firing temperature. This is a consequence of the higher mobility of ions at the higher firing temperature. The higher the mobility of ions is, the larger the grain growth.

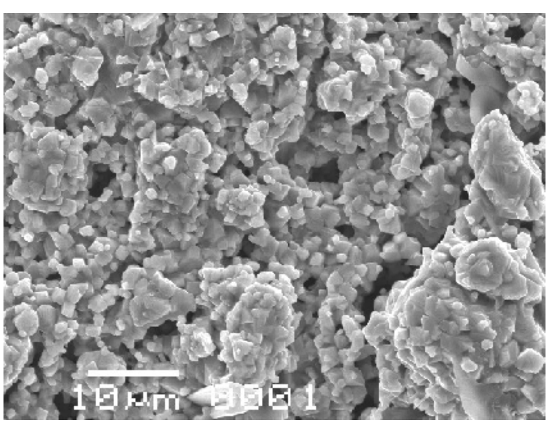

Fig. 5. Microstructure of $CuFe_2O_4$ thick film fired at 900°C.

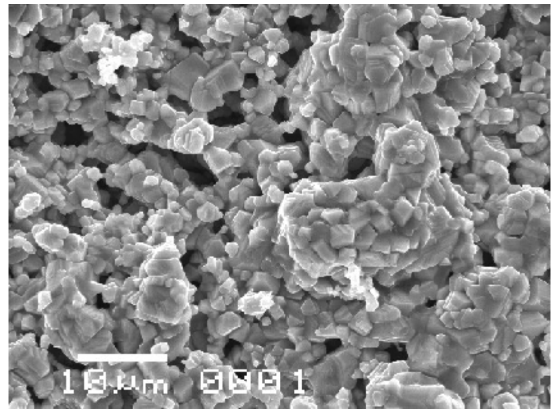

Fig. 6. Microstructure of $CuFe_2O_4$ thick film fired at 1000°C.

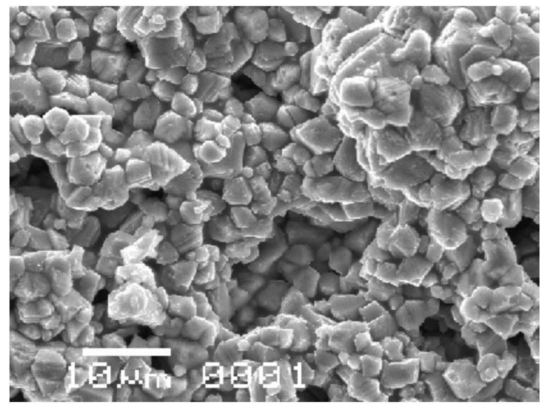

Fig. 7. Microstructure of $CuFe_2O_4$ thick film fired at 1100°C.

The electrical data of the $CuFe_2O_4$ thick film ceramics is shown in Fig. 8 and Table 2. The electrical data of Fig. 8 shows that the Ln resistivity increases linearly as the $1/T$ increasing, indicating that the electrical characteristics of the ceramics follows the NTC tendency expressed by equation (1).

As shown in Table 2, the increase of firing temperature from 900°C to 1000°C decreases the room temperature resistance (R_{RT}), thermistor constant (B) and sensitivity (α). Meanwhile, the increase of firing temperature from 1000°C to 1100°C increases the room temperature resistance (R_{RT}), thermistor constant (B) and sensitivity (α). It is clearly seen that there is an optimal value of the firing temperature, namely 1000°C. The mechanism of this condition can be explained as follow. At 900°C, due to relatively low temperature, the grains of the film are relatively small and interconnection among the grains is few. This situation produces many scattering centers for charge carrier resulting in high resistance. When the temperature is increased to 1000°C from 900°C, the grains are larger and the interconnection among grains increases resulting in fewer scattering center for charge carrier and lower resistance. For further increasing temperature from 1000°C to 1100°C, there is a different tendency in electrical characteristic change. Although the grains of the thick film are larger than that of the films fired at 900°C and 1000°C, the resistance is higher than that of the film fired at 1000°C. At 1100°C, there may be an aggressive penetration of glass frit among the grains, so many grains are covered by the layer of glass resulting in high resistance. There is a possibility that the penetrated glass among the grains also reacted with the $CuFe_2O_4$ making the film is more resistive.

From the (B) value, the activation energy has been calculated by using (3) [Park, 2003,Park and Han, 2005] below:

$$Ea = B/k \qquad (3)$$

where, Ea is the activation energy, B is the thermistor constant and k is the Boltzmann constant. The calculated activation energies are listed in Table 1. The small value of the activation energy exhibits the extrinsic property of the ceramics.

Compared to the B and Ea value for market requirement where B is 2000-7000°K and Ea is 0.1 - 1.5eV[Hamada and Oda,2001, Park,2003, Park and Bang, 2003], the value of B and Ea of the ceramics in this work is large enough and fits the market requirement. If the market requirement for the room temperature resistance is considered, a calculation has to be done. By taking the thickness of the films of 70 μm, distance between electrodes of 1 mm, width of the films of 3.5 mm and the maximum room temperature resistivity for market requirement of 1 MOhm.cm [Matsuo et al., 1982, Jung, et al., 1993], the maximum room temperature resistance for market requirement should be around 41 MOhm. So, only the thick film fired at 1000°Cand 1100°C fit the market requirement.

Table 2. Electrical characteristics of the $CuFe_2O_4$ thick film ceramics.

Firing Temp. (°C)	B (°K)	α (%/°K)	R_{RT} (M.Ohm)	Ea (eV)
900	4857	5.4	125.6	0.42
1000	3027	3.4	7.8	0.26
1100	3596	4.0	37.6	0.31

Market requirement for room temperature resistivity ($\rho_{RT)}$ = 10 ohm.cm-1Mohm.cm [Matsuo et al., 1982, Jung,et al.,1993,].

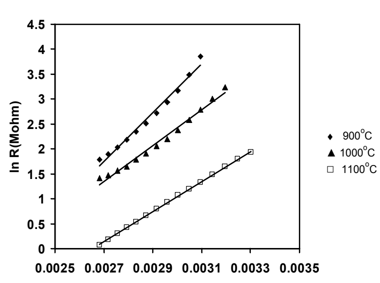

Fig.8. Ln resistivity (ρ) vs. 1/*T* of the $CuFe_2O_4$ thick film ceramics.

Conclusion

$CuFe_2O_4$ thick film ceramics utilizing Fe_2O_3 derived from yarosite mineral have been well prepared at 900°C to 1100°C with interval of 100°C. All of the thick films crystallize in tetragonal spinel. The increase of firing temperature till 1000°C decreases the resistance and thermistor constant of the thick films, however, a further increase to 1100°C increases the resistance and thermistor constant of them. So, 1000°C is the optimum firing temperature for preparing the thick films in this work. The thick film fired at 1000°C has optimal characteristic namely thermistor constant (B) = 3150K and room temperature resistance (R_{RT}) = 7.9 MOhm. These values fit the market requirement for NTC thermistor.

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