Effect of Heat Treatment on the Characteristics of SiO_2 Added-$ZnFe_2O_4$ Ceramics for NTC Thermistors

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ABSTRACT-**A study on the effect of heat treatment on the characteristics of SiO_2 added - $ZnFe_2O_4$ ceramics for NTC thermistor has been carried out. The ceramics were produced by pressing an homogenous mixture of ZnO, Fe_3O_4 and SiO_2 (0,5 weight %) powders in appropriate proportions to produce $ZnFe_2O_4$ based ceramics and sintering the pressed powder at 1200°C for 2 hours with cooling rate of 6°C in air. Some sintered pellets were heat treated by heating them at 1000°C for 10 minutes with cooling rate of 2°C/minutes, 10°C/minutes and quenching. Electrical characterization was done by measuring electrical resistivity of the ceramics at various temperatures. Microstructure and crystal structure analyses were done by using an optical microscope and x-ray diffractometer (XRD). The XRD analyses showed that the $ZnFe_2O_4$ ceramics with and without addition of 0,5 w/o SiO_2 had cubic structure. No peak from second phase was observed from the XRD profiles. From the electrical characteristics data, it was known that the heat treatment could change the electrical characteristics of the $ZnFe_2O_4$ based-thermistor. The resistivity decreased with the cooling rate of 10°C/minutes and quenching, and increased with the cooling rate of 2°C/minutes. All ceramics made had thermistor characteristics that fit the market requirement namely B = 3014-3978K and ρ_{RT} = 12 - 154 kΩcm. It was known that the addition of 0,5 w/o SiO_2 increased the B and ρ_{RT} of the $ZnFe_2O_4$ based-ceramics.**

Key words-Thermistor, NTC, heat treatment, $ZnFe_2O_4$, SiO_2

I. INTRODUCTION

NTC thermistors are widely used in the world due to their potential use for many applications such as temperature measurement, circuit compensation, suppression of in rush-current, flow rate sensor and pressure sensor in many sectors [1]. It is well known that most NTC thermistors are produced from spinel ceramics based on transition metal oxides with general formula of AB_2O_4 where A is metal ion in tetrahedral position and B is metal ions in octahedral position [2-10]. Many studies have been done to improve the characteristics of the spinel based-NTC thermistors [6, 7, 10 and 11]. However, the study on the effect of heat treatment on $ZnFe_2O_4$ spinel ceramics added with 0,5 mole % SiO_2 has not been reported yet. In our previous work, it has been known that the resistance of the $ZnFe_2O_4$ ceramics added with 0,5 mole % SiO_2 was high, although the ceramic can be applied as the NTC thermistor.

The electrical characteristic of the NTC ceramic theoretically can be controlled using several methods. One of the methods is a heat treatment. The heat treatment theoretically can change the electrical characteristics such as electrical resistivity and thermistor constant [12] because the charge carrier of the ceramic is dependent to the surrounding environment. In this research the heat treatment was done by heating the $ZnFe_2O_4$ ceramics added with SiO_2 at 1000°C in air with different cooling rates. The electrical characteristics of the ceramics were studied after the heat treatment.

II. THEORETICAL BACKGROUND

An NTC thermistor has a special characteristic as shown in Fig.1 below:

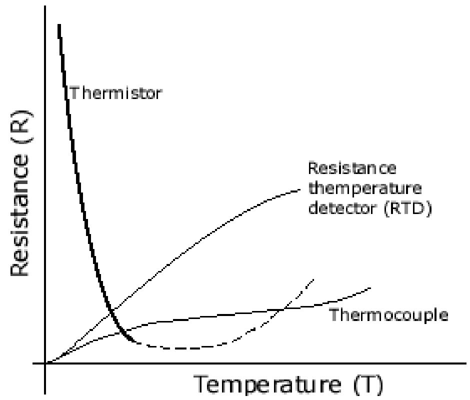

Fig.1. The relation between resistance and temperature for several temperature sensors.

As can be seen from Fig.1, the resistance of a NTC thermistor decreases exponentially with the increase of temperature. The relation between the resistance and temperature can be expressed by equation 1 [1-12] :

$$R = R_0.\ \mathrm{Exp.}(\frac{B}{T}) \qquad (1)$$

where, R is thermistor resistance (Ohm), R_0 is a constant which is the same with the resistance at the infinite temperature (ohm), B is thermistor constant (K) and T is temperature of thermistor (K)

The relation between the thermistor constant and the activation energy can be written as : [10],

$$B = Ea/k \qquad (2)$$

where, B is the thermistor constant, Ea is activation energy (eV) and k is the Boltzmann constant (eV/K)

Sensitivity of a thermistor can be calculated using equation 3 below [11,12]:

$$\alpha = - B/T^2 \qquad (4)$$

where, α is sensitivity of thermistor, B is the thermistor constant (K) and T is the temperature in Kelvin (K). The larger the value of α and B, the higher the quality of the thermistor.

III. METHODOLOGY

Powders of ZnO, Fe_3O_4 and SiO_2 were weighed in appropriate proportions to fabricate SiO_2 added-$ZnFe_2O_4$ ceramics where the SiO_2 concentration was 0,5 weight %. The homogeneous mixture of powders was calcined at 800°C for 2 hours. After calcination, the powder was crushed and sieved with a siever of < 38 μm. The sieved powder was then pressed with pressure of 4 ton/cm^2 into green pellets. The green pellets were sintered at 1200°C for 2 hours in air with cooling rate of 6°C/minutes. The sintered pellets were subjected to some heat treatments. The heat treatments were heating at 1000°C for 10 minutes with heating and cooling rate of 10°C/minutes (which then written as 1000°C / 10min / 10°C/10°C), 1000°C / 10min/ 10°C / 2°C and 1000°C / 10min / 10°C / quenching.

The crystal structure of the sintered pellets was analyzed with x-ray diffraction (XRD) using Kα radiation at 40KV and 25mA. After grinding, polishing, etching the pellets, the microstructure of the pellets was investigated by an optical microscope. The opposite-side surfaces of the sintered pellets were coated with Ag paste. After the paste was dried at room temperature, the Ag coated-pellets were heated at 750°C for 10 minutes. The resistivity was measured at various temperatures from 25 to 100°C in steps of 5°C.

IV. RESULTS AND DISCUSSION

4.1 Visual appearance and XRD analyses

Fig. 2 shows the appearance of typical SiO_2 Added-$ZnFe_2O_4$ ceramics**.** The ceramics are visually good. Fig. 2, and Fig. 3 show the XRD profiles of $ZnFe_2O_4$ ceramic with and without addition of 0.5 weight % SiO_2, respectively. As shown in the figure 2 and 3, the profiles are similar. The XRD profiles show that the crystal structure of the ceramics is cubic spinel after being compared to the XRD standard profile of $ZnFe_2O_4$ from JCPDS no.22-1012. No peaks from second phases are observed. It may be due to the small concentration of the added SiO_2 which is smaller than the precision limit of the x-ray diffractometer used. From a calculation of lattice parameter, there is no significant effect on the lattice parameter can be observed where the lattice parameter of the $ZnFe_2O_4$ is 8.4354Å and that of the 0.5 weight % SiO_2 added-$ZnFe_2O_4$ is 8.4359Å. The added SiO_2 may be dissolved or not. It cannot be concluded from the XRD profiles in this works. The microstructure and electrical data may be used to evaluate whether the SiO_2 added was dissolved or not.

Fig. 2. Visual appearance of typical SiO_2 Added-CuF_2O_4 ceramics.

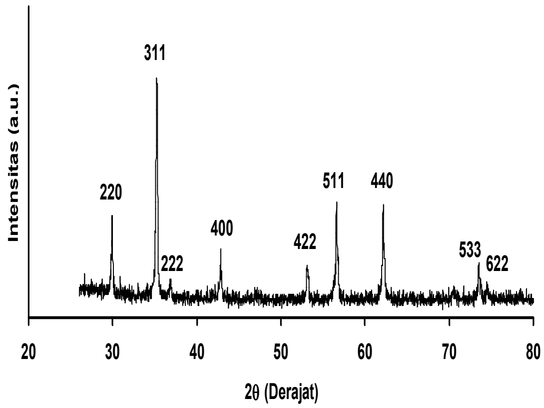

Fig. 3. XRD profile of $ZnFe_2O_4$ without addition of SiO_2 sintered at 1200^0C for 2 hours with heating and cooling rate of 6^0C/minutes, showing a cubic crystal structure.

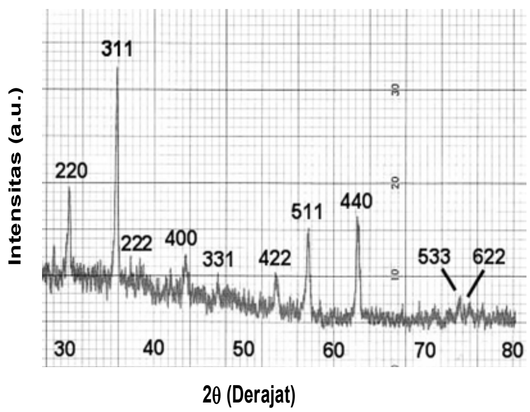

Fig. 4. XRD profile of $ZnFe_2O_4$ added with 0.5 weight % SiO_2 sintered at 1200^0C for 2 hours with heating and cooling rate of 6^0C/minutes, showing a cubic crystal structure.

4.2 Microstructure

Microstructures of the $ZnFe_2O_4$ with and without addition of 0.5 weight % SiO_2 are depicted in Fig. 5 and 6, respectively. From Fig. 5 and 6, it can be seen that the grains of the ceramic added with SiO_2 are smaller than those of the ceramic without SiO_2 addition. This may be due to segregation of the added SiO_2 in grain boundaries which then inhibits the grain growth during sintering. If this is true, it means that the added additive of SiO_2 is not dissolved in the $ZnFe_2O_4$ ceramic.

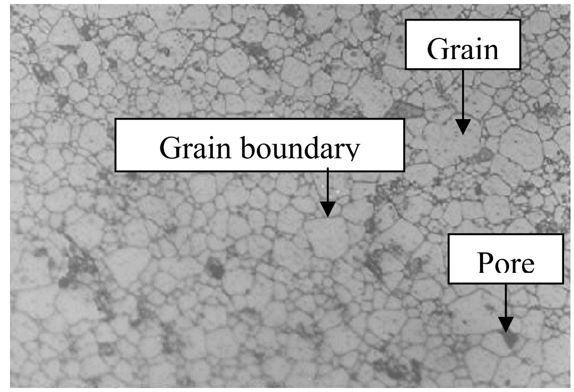

Fig. 5. Microstructure of $ZnFe_2O_4$ ceramic without SiO_2 addition) sintered at 1200^0C for 2 hours in air with heating and cooling rate of 6^0C/minutes.

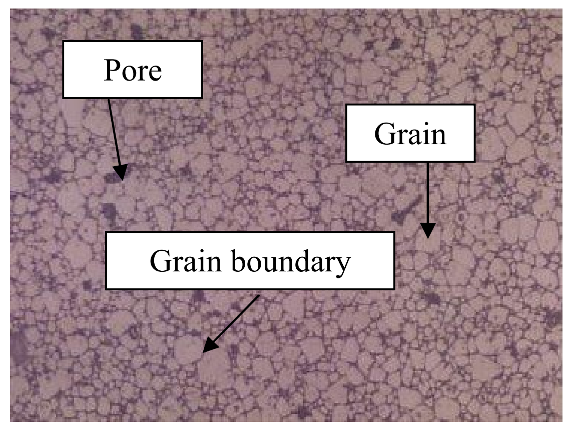

Fig. 6. Microstructure of $ZnFe_2O_4$ ceramic added with 0.5 weight % SiO_2 1200^0C for 2 hours in air with heating and cooling rate of 6^0C/minutes.

From Fig. 5 and 6, it can be seen that the grains of the ceramic added with SiO_2 are smaller than those of the ceramic without SiO_2 addition. This may be due to segregation of the added SiO_2 in grain boundaries which then inhibits the grain growth during sintering. If this is true, it means that the added additive of SiO_2 is not dissolved in the $ZnFe_2O_4$ ceramic.

4.3 Electrical Characterization

Fig. 7. shows the relation between ln resistivity and 1/T of the SiO_2 added-$ZnFe_2O_4$ ceramics and Table 1 shows the electrical characteristics of the ceramics. The linear curves in Fig. 7 show that the resistivity follows the Arhennius equation of equation 1. It is clearly seen that the initial room temperature electrical resistivity of the SiO_2 added-$ZnFe_2O_4$ ceramic is high (98 Kohm). After heat treatment with step of 1000^0C /10min/10^0C/10^0C and 1000^0C/10min/10^0C/quenching,

the electrical resistivity decreases to 38 kohm and 12 kohm respectively and after step of $1000^0C/10min/10^0C/2^0C$ the electrical resistivity increases to 154 kohm. This fact indicates that the resistivity is cooling rate dependent. As the cooling rate increases, the resistivity decreases. In Fig. 7, the higher position means high resistivity and the lower position means low resistivity. During process, the ceramic which is cooled with high cooling rate has no chance to interact with oxygen, making the ceramic is lack of oxygen and the oxygen vacancies are formed inside the ceramic. These oxygen vacancies are compensated by a formation of electron in conduction band. Therefore, the ceramics that are processed with higher cooling rate have smaller electrical resistivity. The activation energy of the ceramics having many charge carrier is small as shown in Table 1. The values of the thermistor constant (B), sensitivity (α) and room temperatura resistivity (ρ_{RT}) of 0.5 weight % SiO_2 added-$ZnFe_2O_4$ ceramics can be seen in Table 1. As shown in Table 1, the value of the thermistor constant (B), sensitivity (a) and ρ_{RT} fit the market requirement where B is about 2000K, α (alpha) is about 2,2%/K and ρ_{RT} is from 10 ohm.cm to 10^6 ohm.cm.

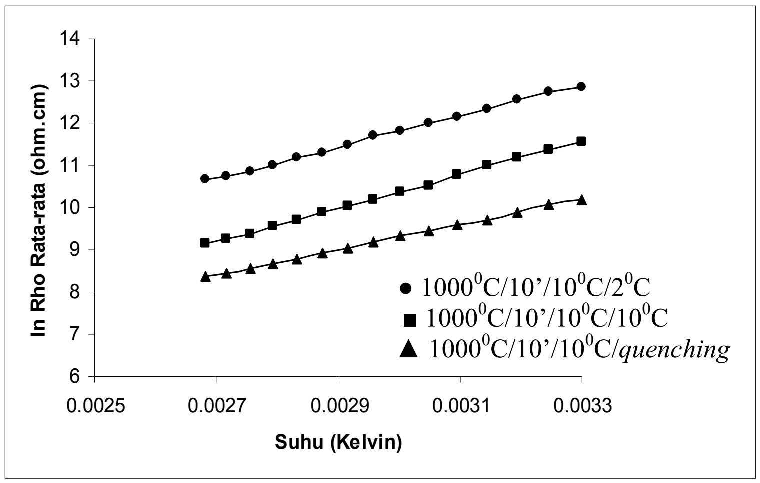

Fig. 7. The relation between ln ρ and 1/T of heat treated SiO_2 added-$ZnFe_2O_4$ ceramics.

Tabel 1. The value of the thermistor constant (B), sensitivity (α) and room temperature resistivity (ρ_{RT}) of 0.5 weight % SiO_2 added-$ZnFe_2O_4$ ceramics.

No.	Heat treatment	B (^{0}K)	Ea (eV)	α (%/ ^{0}K)	ρ_{RT} (kOhm-cm)
1	Sintered at $1200^0C/2hours/6^0C/6^0C$) (Initial)	-	-	-	98
2	$1000^0C/10min/10^0C/10^0C$	3978	0.34	4.42	38
3	$1000^0C/10min/10^0C/2^0C$	3705	0.32	4.12	154
4	$1000^0C/10min/10^0C/$*quenching*	3014	0.26	3.35	12

V. CONCLUSION

The grain size of the $ZnFe_2O_4$ ceramics decreases by addition of SiO_2 because the added SiO_2 segregated at grain boundaries and inhibited grain growth during sintering. The heat treatment influences the electrical characteristics of the 0.5 weight % SiO_2 added-$ZnFe_2O_4$ ceramics. The high cooling rate during heat treatment decreases the electrical resistivity of the ceramics while low cooling rate increases the electrical resistivity. The heat treatment can be adopted in thermistor fabrication to control the electrical characteristics of the thermistor. The values of the thermistor constant (B) 3014-3978K and the room temperature resistivity (ρ_{RT}) of 12–154 kΩcm fit the market requirement.

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