

# The effect of SiO<sub>2</sub> addition on the characteristics of CuFe<sub>2</sub>O<sub>4</sub> Ceramics for NTC Thermistor

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## Abstract.

The effect of SiO<sub>2</sub> addition on the characteristics of CuFe<sub>2</sub>O<sub>4</sub> ceramics for NTC thermistors has been studied. The ceramics were produced by pressing a homogeneous mixture of CuO, Fe<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub> (0-0.75 w/o) powders in appropriate proportions to produce CuFe<sub>2</sub>O<sub>4</sub> based ceramics and sintering the pressed powder at 1100°C for 2 hours in air. Electrical characterization was done by measuring electrical resistivity of the ceramics at various temperatures (25°C-100°C). Microstructure and structural analyses were also carried out by using optical microscopy and x-ray diffraction (XRD), respectively. The XRD analyses showed that the CuFe<sub>2</sub>O<sub>4</sub> and SiO<sub>2</sub> added-CuFe<sub>2</sub>O<sub>4</sub> ceramics have crystal structure of cubic spinel. The presence of second phase could not be identified from the XRD analyses. According to the electrical data, it was known that the SiO<sub>2</sub> addition increased the thermistor constant (B) and the room temperature electrical resistivity ( $\rho_{RT}$ ). The value of B and  $\rho_{RT}$  of the produced CuFe<sub>2</sub>O<sub>4</sub> ceramics namely B = 2548-3308°K and  $\rho_{RT}$  = 291-9400 ohm's, fitted market requirement.

**Key words:** *Thermistor, NTC, CuFe<sub>2</sub>O<sub>4</sub>, SiO<sub>2</sub>.*

## 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 inrush-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<sub>2</sub>O<sub>4</sub> 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, 11]. However, the study on the effect of SiO<sub>2</sub> addition on the characteristics of CuFe<sub>2</sub>O<sub>4</sub> spinel ceramics for NTC thermistor has not been reported yet.

Generally, the CuFe<sub>2</sub>O<sub>4</sub> ceramics used as soft magnet [12-15] as well as catalyst [16-18], however, potentially, the CuFe<sub>2</sub>O<sub>4</sub> ceramics have capability of being NTC thermistors due to its semi conductive property. According to CuO-Fe<sub>2</sub>O<sub>3</sub> phase diagram [19], there is an area where the

ceramic composing of CuO and Fe<sub>2</sub>O<sub>3</sub> heated at 1100°C will have a microstructure containing liquid phase. In room temperature, the liquid phase may be a boundary material. This boundary material theoretically will influence the characteristics of the ceramics, especially the electrical characteristics. Since an additive such as SiO<sub>2</sub> is added, the characteristics of the CuFe<sub>2</sub>O<sub>4</sub> may change because two conditions may happen. The conditions are, the first, the SiO<sub>2</sub> dissolves in the CuFe<sub>2</sub>O<sub>4</sub> by substituting Cu ions or Fe ions, the second, the SiO<sub>2</sub> does not dissolve but segregated at grain boundaries and it may react with the liquid phase that originally exists.

Since the first condition happens, the CuFe<sub>2</sub>O<sub>4</sub> ceramics may have a lower electrical resistivity when the substitution of Fe<sup>3+</sup> and /or Cu<sup>2+</sup> creating free electron in the conduction band. Meanwhile, since the second one happens, the electrical resistivity may be higher because the segregated SiO<sub>2</sub> may change the microstructure. In our previous study [12], it was known that TiO<sub>2</sub> tend to increase the room temperature resistivity and thermistor constant. This work is to know the effect of SiO<sub>2</sub> addition on the characteristics of the CuFe<sub>2</sub>O<sub>4</sub> ceramics for NTC thermistors, especially the electrical characteristic based on the above mentioned hypothesis. The results were compared to our previous study.

## II. METHODOLOGY

Powders of CuO, Fe<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub> were weighed in appropriate proportions to fabricate SiO<sub>2</sub> added-CuFe<sub>2</sub>O<sub>4</sub> ceramics where the SiO<sub>2</sub> were 0, 0.25, 0.5 and 0.75 weight %. The 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<sup>2</sup> into green pellets. The green pellets were sintered at 1100°C for 2 hours in air.

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.

### III. RESULTS

Fig.1 shows appearance of typical  $\text{SiO}_2$  Added- $\text{CuFe}_2\text{O}_4$  ceramics. The ceramics are visually good. Fig.2, Fig.3, and Fig.4 show the XRD profiles of  $\text{CuFe}_2\text{O}_4$  ceramic added with 0, 0.25 and 0.75 weight %  $\text{SiO}_2$ , respectively. As shown in the figure 2 - 4, the profiles are similar. The XRD profiles show that the structure of the ceramics is cubic spinel after being compared to the XRD standard profile of  $\text{CuFe}_2\text{O}_4$  from JCPDS No. 22-1012. No peaks from second phases observed. It may be due to the small concentration of  $\text{SiO}_2$  added which smaller than the precision limit of the x-ray diffractometer used. The added  $\text{SiO}_2$  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  $\text{SiO}_2$  added was dissolved or not.



Fig. 1. Visual appearance of typical  $\text{SiO}_2$  Added- $\text{CuFe}_2\text{O}_4$  ceramic.

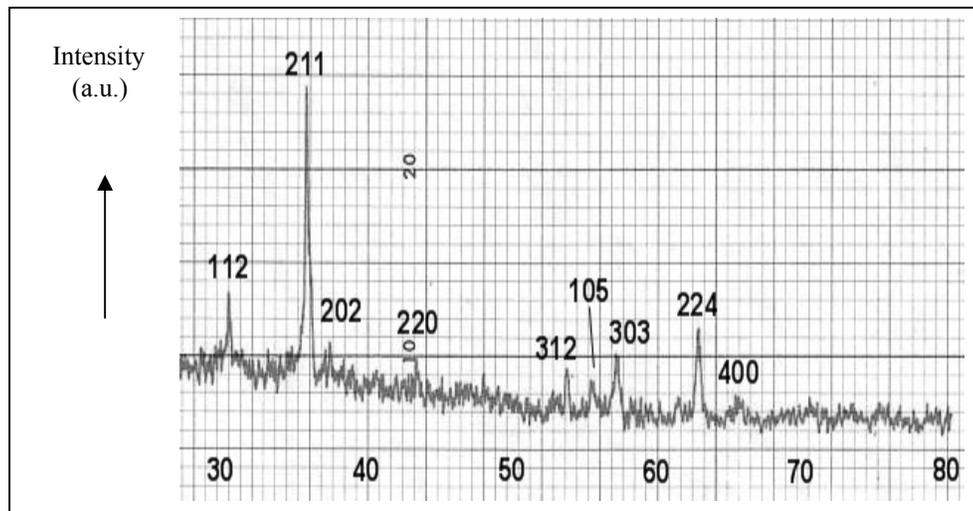


Fig. 2. XRD profile of  $\text{CuFe}_2\text{O}_4$  ceramic.

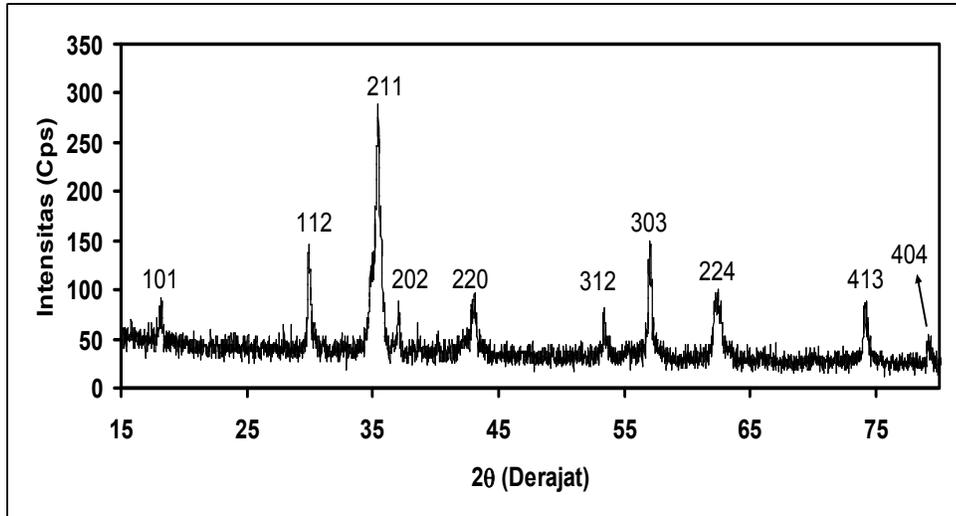


Fig. 3. XRD profile of 0.25 w/o SiO<sub>2</sub> added-CuF<sub>2</sub>O<sub>4</sub> ceramic.

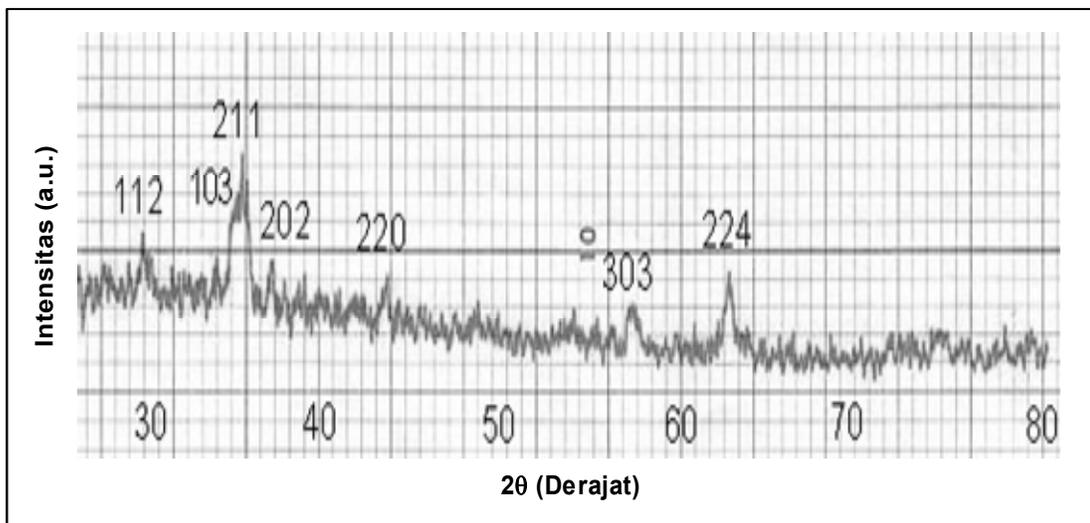


Fig. 4. XRD profile of 0.50 w/o SiO<sub>2</sub> added-CuF<sub>2</sub>O<sub>4</sub> ceramic.

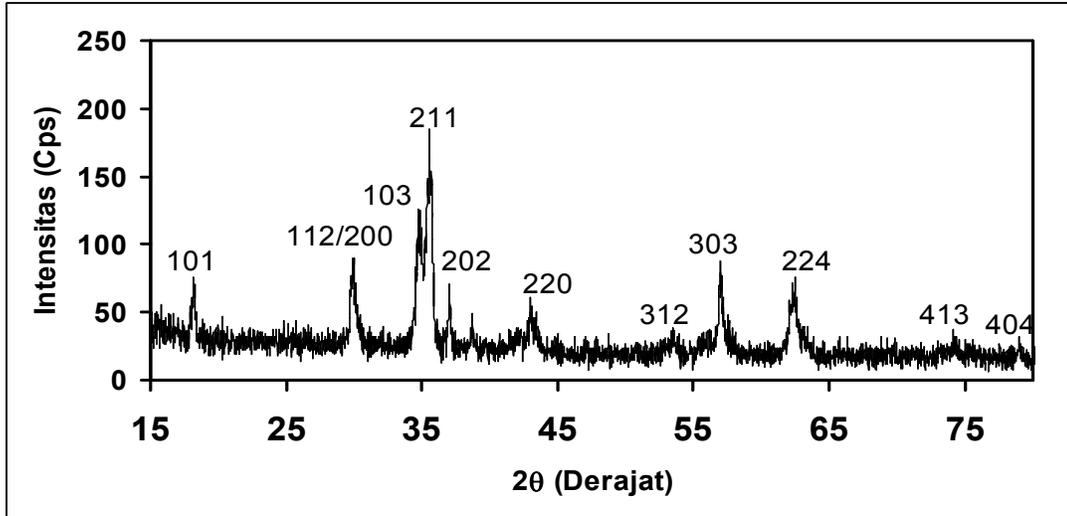


Fig. 5. XRD profile of 0.75 w/o SiO<sub>2</sub> added-CuFe<sub>2</sub>O<sub>4</sub> ceramic.

Fig.6, Fig.7 and Fig. 8 are microstructures of the CuFe<sub>2</sub>O<sub>4</sub> ceramics added with 0, 0.25, and 0.75 weight % SiO<sub>2</sub>, respectively.

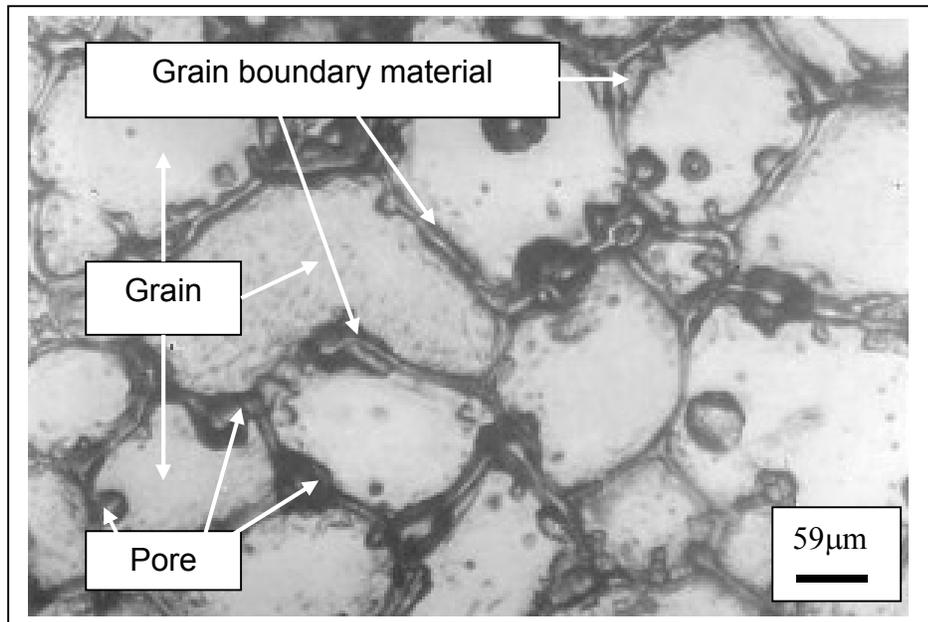


Fig. 6. Microstructure of the CuFe<sub>2</sub>O<sub>4</sub> ceramic.

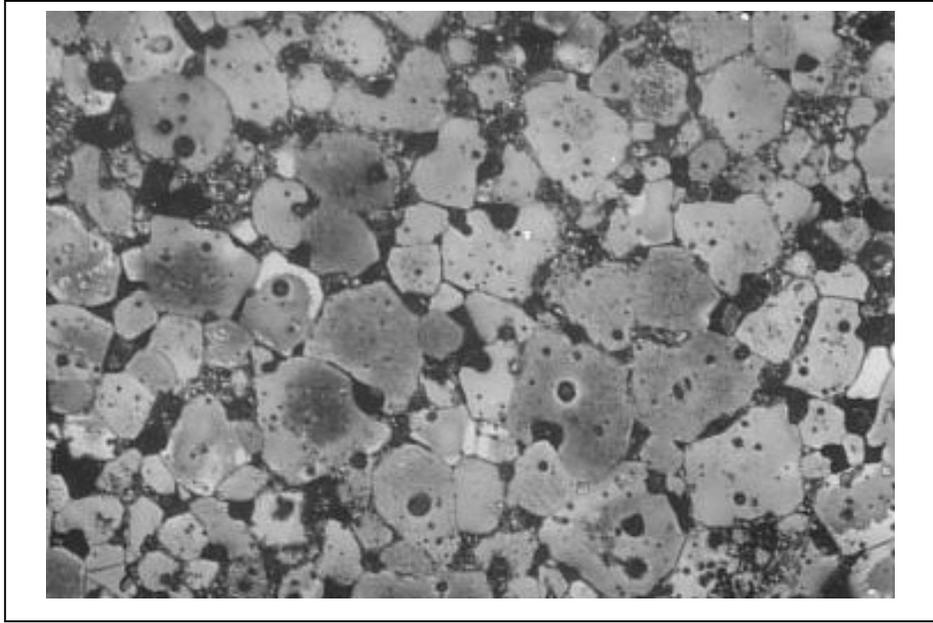


Fig. 7. Microstructure of the 0.25 w% SiO<sub>2</sub> added-CuFe<sub>2</sub>O<sub>4</sub> ceramic.

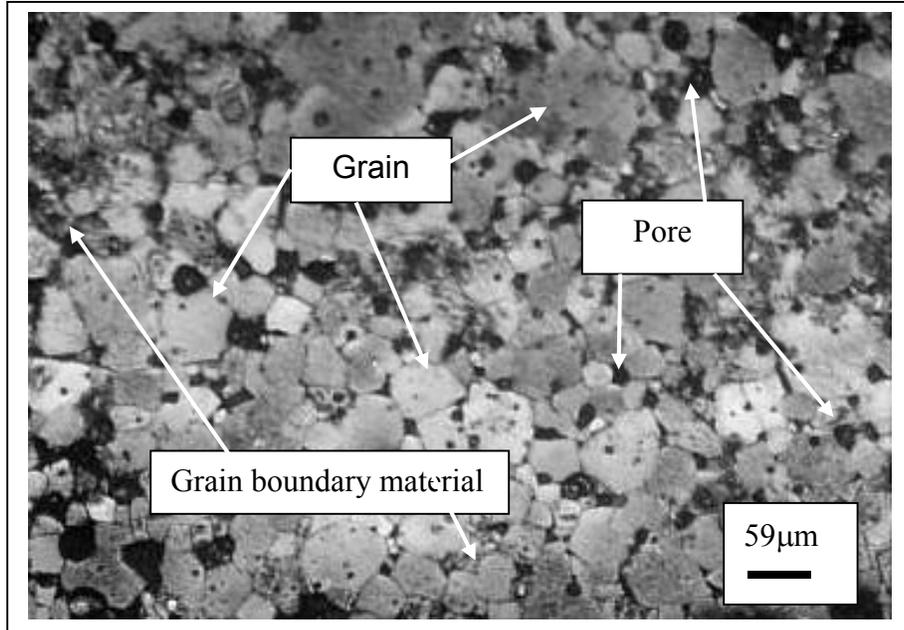
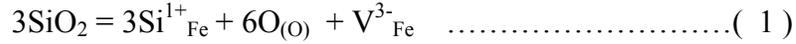
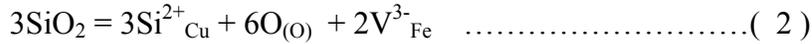


Fig. 8. Microstructure of the 0.75 w% SiO<sub>2</sub> added-CuFe<sub>2</sub>O<sub>4</sub> ceramic.

From Fig. 6-8, it is clearly shown that the addition of SiO<sub>2</sub> decreases the size of grains. The decrease of the grain size is due to the segregation of the SiO<sub>2</sub> at grain boundaries. Since the SiO<sub>2</sub> dissolved in CuFe<sub>2</sub>O<sub>4</sub> the grains should become larger when Si<sup>4+</sup> creates iron vacancy following reactions (1) and (2):

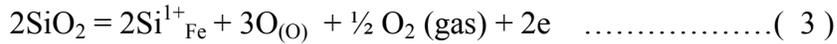


where,  $\text{Si}_{\text{Fe}}^{1+}$  = Ion Si<sup>4+</sup> occupies Fe sublattice,  $\text{O}_{(\text{O})}$  = Oxygen ion occupies oxygen sublattice and  $\text{V}_{\text{Fe}}^{3-}$  = Iron vacancy.



where,  $\text{Si}_{\text{Cu}}^{2+}$  = Ion Si<sup>4+</sup> occupies Cu sublattice,  $\text{O}_{(\text{O})}$  = Oxygen ion occupies oxygen sublattice and  $\text{V}_{\text{Fe}}^{3-}$  = Iron vacancy.

Since the accomodation of Si<sup>4+</sup> follows reaction (3) and (4), it will be no effect on the grain growth.



where,  $\text{Si}_{\text{Fe}}^{1+}$  = Ion Si<sup>4+</sup> occupies Fe sublattice,  $\text{O}_{(\text{O})}$  = Oxygen ion occupies oxygen sublattice,  $\frac{1}{2} \text{O}_2 (\text{gas})$  = Released oxygen and  $\text{e}$  = Released electron.



where,  $\text{Si}_{\text{Cu}}^{2+}$  = Ion Si<sup>4+</sup> occupies Cu sublattice,  $\text{O}_{(\text{O})}$  = Oxygen ion occupies oxygen sublattice,  $\frac{1}{2} \text{O}_2 (\text{gas})$  = Released oxygen and  $\text{e}$  = Released electron.

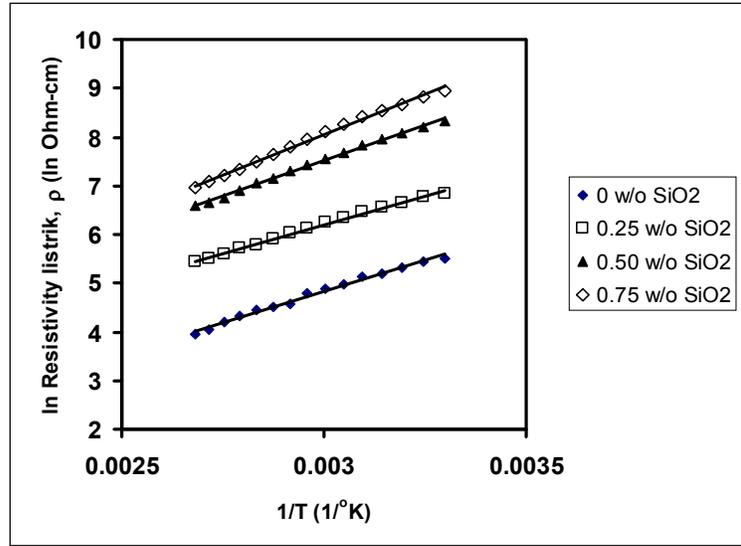


Fig.9. Ln resistivity ( $\rho$ ) vs  $1/T$  of  $\text{SiO}_2$  added- $\text{CuFe}_2\text{O}_4$  ceramics.

The electrical data of Fig. 9 shows that the electrical characteristics of the ceramics follow the NTC tendency expressed by eq. 6. As shown in Table 1, the addition of  $\text{SiO}_2$  increases the room temperature resistivity ( $\rho_{\text{RT}}$ ) and thermistor constant ( $B$ ). Compared to the ( $B$ ) value for market requirement where  $B \geq 2000^\circ\text{K}$ , the value of  $B$  for our ceramics is larger and it means better.

$$\rho = \rho_0 \exp.(B/T) \dots\dots\dots( 5 )$$

where,  $\rho$  = Electrical resistivity,  $\rho_0$  = Electrical resistivity at infinite temperature,  $B$  is the thermistor constant and  $T$  is the temperature in Kelvin.

Table 1. Electrical characteristics of the  $\text{SiO}_2$  added- $\text{CuFe}_2\text{O}_4$  ceramics.

No.	Additive $\text{SiO}_2$ (w/o)	$B$ ( $^\circ\text{K}$ )	$\alpha$ ( $\% / ^\circ\text{K}$ )	$\rho_{\text{RT}}$ (ohm-cm)
1.	0	2548	2,83	291
2.	0,25	2358	2,62	1079
3.	0,50	2884	3,20	4788
4.	0,75	3308	3,68	9400

## IV. DISCUSSION

The decrease of the grain size is caused by the segregation of the added SiO<sub>2</sub>. The segregated SiO<sub>2</sub> inhibits the grain growth during sintering. This data confirms that the added-SiO<sub>2</sub> is not dissolved in the CuFe<sub>2</sub>O<sub>4</sub> ceramics which could not be concluded from the XRD data.

The change of the electrical characteristics is controlled by the change of the microstructure due to the SiO<sub>2</sub> addition. Since the SiO<sub>2</sub> dissolved in CuFe<sub>2</sub>O<sub>4</sub> by substituting Cu and/or Fe following eq. (3) and (4), the room temperature resistivity ( $\rho_{RT}$ ) and thermistor constant (B) should decrease. The increase ( $\rho_{RT}$ ) and (B) as shown by our data indicates that the added SiO<sub>2</sub> is not dissolved and tends to segregate at the grain boundaries.

The other reactions following eq. (1) and (2) may also happen when the added SiO<sub>2</sub> dissolved in CuFe<sub>2</sub>O<sub>4</sub> by substituting Cu and/or Fe. The possibility of the reactions of (1) – (4) to occur can be evaluated using data of ionic radii. The ionic radius of Cu<sup>2+</sup>, Fe<sup>3+</sup> and Si<sup>4+</sup> is shown in Table 2.

Table 2. Ionic radius of Cu<sup>2+</sup>, Fe<sup>3+</sup>, Si<sup>4+</sup> and Ti<sup>4+</sup> with 6 coordination number [20].

No.	Ion	Radius (pm)
1.	Cu <sup>2+</sup>	87
2.	Fe <sup>3+</sup>	69
3.	Si <sup>4+</sup>	54
4.	Ti <sup>4+</sup>	74.5

The ionic radius difference between Si<sup>4+</sup> and Cu<sup>2+</sup> is too large, so the possibility of the reaction (3) and (5) to occur is small. The ionic radius difference between Si<sup>4+</sup> and Fe<sup>3+</sup> is smaller than that between Si<sup>4+</sup> and Cu<sup>2+</sup>, however, this difference is still large. So, the possibility of the reaction (2) and (4) to occur is also small. The microstructure data showed that the SiO<sub>2</sub> addition decreased the grain size. So, therefore it can be concluded that the reaction of eq. (1) - (4) do not occur. As mentioned before, the added SiO<sub>2</sub> is segregated at the grain boundaries and the electrical characteristic is controlled by the microstructure.

Compared to the previous study about the effect of TiO<sub>2</sub> on electrical characteristic of CuFe<sub>2</sub>O<sub>4</sub> [12], there is a significant difference in electrical resistivity. The room temperature

resistivity of the SiO<sub>2</sub> added-CuFe<sub>2</sub>O<sub>4</sub> ceramics is larger than that of the TiO<sub>2</sub> added-CuFe<sub>2</sub>O<sub>4</sub> ones [12]. It may be due to the difference effect of the different additive. There is a high possibility that a part of added TiO<sub>2</sub> was dissolved in the CuFe<sub>2</sub>O<sub>4</sub> ceramics, so that the resistivity of the TiO<sub>2</sub> added-CuFe<sub>2</sub>O<sub>4</sub> lower than that of the SiO<sub>2</sub>-added CuFe<sub>2</sub>O<sub>4</sub> ceramics in the current work. Considering the ionic radius of the Ti<sup>4+</sup> ion i.e. 74.5 pm [20] which is close to that of Fe<sup>3+</sup> ion, it is possible that TiO<sub>2</sub> dissolved in CuFe<sub>2</sub>O<sub>4</sub> where the Ti<sup>4+</sup> substitutes the Fe<sup>3+</sup> decreasing the resistivity of the ceramics.

## V. CONCLUSION

The grain size of the CuFe<sub>2</sub>O<sub>4</sub> ceramics decreases by addition of SiO<sub>2</sub> because the added SiO<sub>2</sub> segregated at grain boundaries and inhibited grain growth during sintering. The addition of SiO<sub>2</sub> increased the room temperature resistivity ( $\rho_{RT}$ ) and the thermistor constant (B) of the CuFe<sub>2</sub>O<sub>4</sub> ceramics through changing the microstructure. The value of ( $\rho_{RT}$ ) and (B) of the CuFe<sub>2</sub>O<sub>4</sub> ceramics made in this work fits the market requirement.

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