Electrical Characteristics CuFe$_2$O$_4$ Ceramics With and Without Al$_2$O$_3$ for Negative Thermal Coefficient (NTC) Thermistor

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ABSTRACT

In order to get capability in thermistor production in Indonesia, a study on electrical characterization of CuFe$_2$O$_4$ based-ceramics with Al$_2$O$_3$ addition has been performed. The Al$_2$O$_3$ addition was done with various concentrations namely 0, 1 dan 5 mole %. Powder of CuO, Fe$_2$O$_3$ and Al$_2$O$_3$ was mixed and ground. The mixture was pressed with pressure of 3.9 ton/cm$^2$ to form pellets. The pellets was then sintered at 1100$^\circ$C for 2 jam in air. After sintering, two sides of some sintered pellets were coated with silver paste and fired at 600$^\circ$C for 10 minutes. Some of coated samples were heat treated at 500$^\circ$C for 5 minutes in N$_2$ gas. These pellets were analyzed using x-ray diffraction (XRD). R-T and ageing characteristics were evaluated. From the XRD data, it was known that the CuFe$_2$O$_4$ ceramics produced crystallized in tetragonal spinel. According to the electrical data, the thermistor constant (B) and sensitivity (a) increases due to the addition of Al$_2$O$_3$. It was known from the ageing test that only the ceramics with 0 and 1 mole % Al$_2$O$_3$ fit the electrical stability condition.

Keywords: Ceramic, CuFe$_2$O$_4$, Al$_2$O$_3$, thermistor, NTC, ageing.

1. INTRODUCTION

NTC thermistor are widely used due to its capability to be applied in many applications such as temperature sensor, electric current limiter, flowrate meter and pressure sensor[1]. It is known that generally the NTC thermistor is made of ceramic having structure of spinel of AB$_2$O$_4$ where A is the ion occupies tetrahedral position and B is the ion occupies octahedral position[2-10]. Many works have been performed in order to improve the characteristic of the NTC thermistor having spinel structure [6,7,11]. Theoretically, the addition of additive such as Al$_2$O$_3$ may change the electrical characteristics of CuFe$_2$O$_4$ ceramic.

When the additive of Al$_2$O$_3$ is added to the CuFe$_2$O$_4$ ceramic, the characteristics of the CuFe$_2$O$_4$ ceramic may change because two conditions may occur namely, the first, Al$_2$O$_3$ dissolves in the CuFe$_2$O$_4$ through substituting Cu ions or Fe ions, the second, Al$_2$O$_3$ does not dissolve and segregate at grain boundaries. When the substitution of Fe or Cu ions results in an increase of electron in the conduction band, the electrical resistivity of the CuFe$_2$O$_4$ will decrease. On the contrary, when the second condition occurs, the electrical resistivity may increase due to a change in microstructure. In this work, the effect of the Al$_2$O$_3$ addition on the electrical characteristics, especially the electrical stability, of the CuFe$_2$O$_4$ ceramic was studied.

2. METHODOLOGY

Powder of CuO, Fe$_2$O$_3$ and additive of Al$_2$O$_3$ (0, 1 and 5 mole %) were mixed and ground. The composition is shown at Table 1. After calcination at 800$^\circ$C for 2 hours, the mixture was ground. The ground powder was pressed with pressure of 3.9 ton/cm$^2$ to form pellets. The green pellets were sintered at 1100$^\circ$C for 2 hours in furnace air. Two sides of some sintered pellets were coated with silver paste. Some silver coated samples were heat treated at 500$^\circ$C for 5 minutes in N$_2$ gas. Structure of the sintered pellet was analyzed using x-ray diffraction (XRD). For electrical characterization, the electrical resistance of the pellets was measured at various temperatures. The measurement was done before and after ageing test. The ageing test was conducted by measuring the resistance of the pellet at room temperature after heating at 150$^\circ$C in every several hours.
Thermistor constant (B) is the gradient of the ln Resistivity vs 1/T curve which is constructed based on equation (1) [2-11] expressing NTC characteristic. Sensitivity (α) was calculated using equation (2)[6].

\[ R = R_0 \cdot e^{B/T} \]  ……..(1)

where \( R \) = thermistor resistance (Ohm), \( R_0 \) = a constant (Ohm), \( B \) = Thermistor constant (K) and \( T \) = Temperature (K).

\[ \alpha = \frac{-B}{T^2} \]  ……..(2)

where \( \alpha \) = Sensitifitas termistor,
\( B \) = Koefisien termistor dalam °K
\( T \) = suhu dalam °K

Activation energy can be calculated using equation (3)[6],

\[ B = \frac{\Delta E}{k} \]  ……..(2)

Dengan \( B \) = Konstanta termistor (°K)
\( \Delta E \) = Energi aktivasi (eV),
\( k \) = Konstanta Boltzmann (\( \frac{eV}{°K} \))

Table 1. Sample composition in mole %.

<table>
<thead>
<tr>
<th>No.</th>
<th>CuO</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>40</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>40</td>
<td>59</td>
<td>1</td>
</tr>
<tr>
<td>3.</td>
<td>40</td>
<td>55</td>
<td>5</td>
</tr>
</tbody>
</table>

### 4. RESULTS AND DISCUSSION

#### 4.1 XRD Analyses

XRD profiles of CuFe₂O₄ base-ceramics added with Al₂O₃ are shown at Fig. 1 and Fig.2 as the representative. All the CuFe₂O₄ base-ceramics crystallized in tetragonal structure (JCPDS No.34-0425). In all XRD profiles peak of Fe₂O₃ was observed indicating that a part of the Fe₂O₃ could not form CuFe₂O₄ solid solution. Peak from Al₂O₃ was not observed in all XRD profiles. This fact gives a possibility that the Al₂O₃ was dissolved.

![Fig.1. XRD profile of CuFe₂O₄ base-ceramic (40CuO-60Fe₂O₃) without Al₂O₃ addition. F is peak from Fe₂O₃.](image)

![Fig.2. XRD profile of CuFe₂O₄ base-ceramic (40CuO-60Fe₂O₃) with 1 mole % Al₂O₃. F is peak from Fe₂O₃.](image)

#### 4.2 Electrical Characteristics

Curves of ln Resistivity vs 1/T in Fig. 3 are linear indicating that the CuFe₂O₄ base-ceramics obey the NTC characteristic of the thermistor. As shown in Table 1, thermistor constant (B) and sensitivity (alpha) of the ceramics added with Al₂O₃ are larger than those of the ceramics without Al₂O₃. This means that the addition of Al₂O₃ increased the thermistor constant and sensitivity of the ceramics. Large B and α is good for the NTC thermistor. The value of B and α of the ceramics fit the market requirement (larger than or equal 2000K(B) and 2.2%/K(α,α)).
mechanism of the increasing the thermistor constant and sensitivity is as follow. The $\text{Al}_2\text{O}_3$ segregates at grain boundaries and impeded grain growth during sintering. The ceramics then contains small grains or many grain boundaries. Because the grain boundaries are scattering center for electron, the electrical resistivity and thermistor constant of the ceramics increase.

The ageing test result is shown in Fig. 4. As can be seen, for sample without $\text{Al}_2\text{O}_3$, from 0 to 100 hours ageing test, the resistivity change rapidly following the aging time. From 100 hours to 1000 hours, the resistance tends to stable. Below 100 hours, the ions in the ceramics tend to rearrange during heating at 150°C[12]. Here, some $\text{Fe}^{2+}$ oxidizes to $\text{Fe}^{3+}$. So, the resistance has not been stable. In the range 100-1000 hours, the resistance tends to stable though slightly fluctuates. The time to reach a stability condition is different depending on the concentration of $\text{Al}_2\text{O}_3$. For sample added with $\text{Al}_2\text{O}_3$ the time to reach the stable condition is about 200 hours. It is clear that the addition $\text{Al}_2\text{O}_3$ worsen the stability. The fluctuation of the resistance becomes larger as the concentration of $\text{Al}_2\text{O}_3$ increases. The value of 200 hours can be taken as a time for preparing a stable CuFe$_2$O$_4$ base-ceramics for NTC thermistor.

![Fig.3. The relation between ln Electrical Resistivity and 1/T.](image)

Table 1. Electrical characteristics of the ceramics.

<table>
<thead>
<tr>
<th>No.</th>
<th>Penambahan $\text{Al}_2\text{O}_3$ (mole %)</th>
<th>$B$ (°K)</th>
<th>$\alpha$ (%/°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0</td>
<td>2862</td>
<td>3.22</td>
</tr>
<tr>
<td>2.</td>
<td>1</td>
<td>3208</td>
<td>3.61</td>
</tr>
<tr>
<td>3.</td>
<td>5</td>
<td>3958</td>
<td>4.46</td>
</tr>
</tbody>
</table>

![Fig. 4. Electrical resistance as function of time as the result of ageing test.](image)
5. CONCLUSION

All CuFe$_2$O$_4$ base-ceramic crystallized in tetragonal structure. Thermistor constant (B) and sensitivity (a) of the CuFe$_2$O$_4$ base-ceramics increase with the increase of Al$_2$O$_3$ concentration. This means that the addition of Al$_2$O$_3$ can be used as a controlling parameter. However, the addition of Al$_2$O$_3$ decreases the electrical stability of the CuFe$_2$O$_4$ base-ceramics. Only sample without Al$_2$O$_3$ and that added with 1 mole % Al$_2$O$_3$ fit the electrical stability condition. Heating at 150°C for 200 hours can be used to make CuFe$_2$O$_4$ base-ceramic stable electrically.

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