ISSN 2616-5880 Vol. 4, Issue 2: 26-30, DOI: 10.25236/AJMC.2023.040205

Influence of the preparation conditions on the electrical properties with negative temperature coefficient

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Abstract: *The $CaCu_3Ti_4O_{12}$ ceramics have been successfully prepared by the sol-gel method. We have set four different temperature gradients (950℃, 1000℃, 1050℃, 1100℃) as the sintering temperatures for $CaCu_3Ti_4O_{12}$ ceramics to study the influence of different temperatures on the thermistor. The effects of different sintering temperatures on the structure of $CaCu_3Ti_4O_{12}$ ceramics were analyzed by X-ray diffraction (XRD). Scanning electron microscope (SEM) images demonstrate that the grain size of ceramic samples will increase with the increase of the sintering temperature. X-rayphotoelectron spectroscopy (XPS) has been used to study the chemical states on the surface of ceramic samples. It is confirmed that the coexistence of Cu^+/Cu^{2+} and Ti^{3+}/Ti^{4+} is the cause of the conductivity of $CaCu_3Ti_4O_{12}$ ceramics. All ceramic samples have NTC behavior, room temperature resistivity (ρ_{25}), material constant (B) and the relationship between the nature logarithm of the resistivity and the temperature has been studied in this paper.*

Keywords: *CCTO Ceramic; Temperature gradients; Sintering; Temperature sensor*

1. Introduction

A thermistor with a negative temperature coefficient (NTC) is sensitive to temperature and its resistance decreases with increasing temperature. Its main functions are temperature measurement, temperature control, temperature compensation, and a temperature sensor. At the same time, the condition of negative temperature coefficient is the jump of electrons between adjacent ions of the same type and different valences [1,2]. $CaCu_3Ti_4O_{12}$ has semiconductor grains and insulating grain boundaries that can be used as a negative temperature coefficient thermistor[3]. At present, Most of the studies on CCTO focused on improving its dielectric and nonlinear electrical properties by element doping, there are relatively few reports on the NTC characteristics of CCTO ceramics. Therefore, we want to understand the effect of preparation conditions, especially sintering temperature, on the NTC characteristics of CCTO ceramics. In this paper, four different sintering temperatures were selected for the sintering of CCTO ceramics. By comparing the phase structure, ceramic grains, ceramic surface chemical states, and electrical properties, the effect of sintering temperature on CCTO ceramics was further understood, and the material constants B and resistivity ρ at different sintering temperatures were obtained.

2. Experimental procedure

The $CaCu_3Ti_4O_{12}$ samples were prepared by the sol-gel method. According to stoichiometry, calcium acetate monohydrate ($C_4H_6CaO_4$.H2O, chemically pure) and copper nitrate trihydrate ($Cu(NO_3)$.$3H_2O$, analytically pure)are dissolved in distilled water to form liquid A, Tetrabutyl titanate ($C_{16}H_{36}O_4Ti$, analytical pure) was dissolved in the mixed solution of glacial acetic acid and ethanol to form liquid B, and then liquid A was poured into liquid B to dissolve, stirring while dissolving. Lastly, crosslinked in a water bath at 80-90°C to form a wet gel. The wet gel was dried by a rotary evaporator, and then the dried powder was calcined for 4h in an oven at 700°C. The calcined powder is ground in an agate mortar for 30 minutes, then pressed into ceramic discs with a diameter of about 10mm and a thickness is about 1mm under a pressure of 15MPa.$CaCu_3Ti_4O_{12}$ polycrystalline ceramic samples were obtained by sintering ceramic discs at different sintering temperatures for 4h.

The crystal structure of sintered samples was studied by X-ray diffraction(XRD, DX-2700,

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Dandong, China), using Cu K_{α} radiation with a size of 0.01° and 1 second for each step in a range of 2θ=20°-80°at 40kV. The surface microstructure of the ceramic sample was analyzed by scanning electron microscopy (SEM, Hitachi S-3400N), and the chemical states of the ceramic sample were analyzed by X-ray photoelectron spectroscopy (XPS, AXIS Supra, Kratos, Germany). Brushing quick-drying silver electrodes on both sides of the ceramic sample can facilitate the measurement of ceramic samples. Then the ceramic samples were tested at 25-250℃ in the high-temperature chamber and the DC resistance was tested with an electrometer (Keithley Model 6517B).

3. Results and discussion

Figure 1 shows the XRD patterns of $CaCu_3Ti_4O_{12}$ ceramic sintered for 4h at different sintering temperatures. The XRD peaks of the samples are $CaCu_3Ti_4O_{12}$ phase with body-centered cubic structure and Im-3 space group.We can see that the sintering temperature is from 950℃ to 1100℃, the phase structure of the ceramic samples does not change, and they are all pure CCTO phases.

Figure 2 is the SEM morphology at different sintering temperatures. It is obvious that, with the increase of sintering temperature, the grain size of $CaCu_3Ti_4O_{12}$ ceramic samples increases. The grains are very fine about 0.5-2um and have many holes at 950℃. This is because the grain growth is not sufficient and grain has not grown normally under the condition of sintering at 950 ℃.

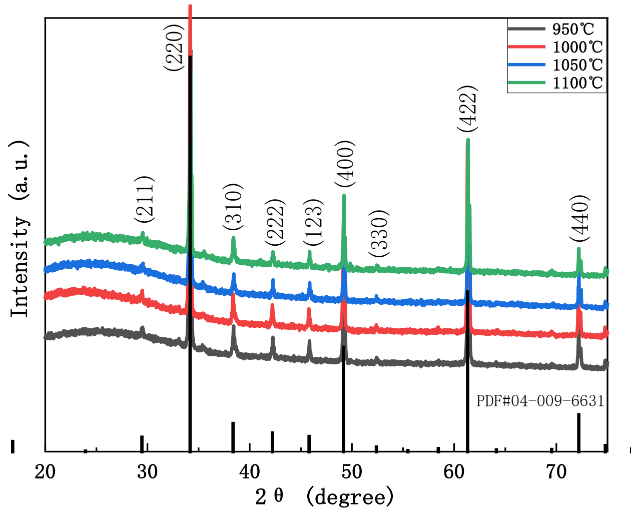

Figure 1: XRD patterns of $CaCu_3Ti_4O_{12}$ ceramics

However, at 1000℃, large grains appear and the grain size is 1-4um. There are obvious grain boundaries between grains, and the porosity is reduced. What's more, there are many abnormally grown grains at 1050℃ or 1100℃, large grains have dozens of microns, small grains only a few microns, and the uniformity of grains is not good. The above phenomenon can be explained by the CCTO sintering mechanism[3 4]: With the increase of sintering temperature, CuO with a relatively low melting point will melt into a liquid phase, and densification will be improved through particle rearrangement and mass transport. The migration rate of grain boundary will be accelerated due to the presence of the liquid phase, resulting in abnormally large grains.

Figure 3 shows the XPS spectrum of Cu $2p_{3/2}$ in the CCTO ceramic sample. It can be seen from the spectrum that three peaks represent three different chemical states, they belong to different Cu-O complexes [5]. The three peaks also correspond to three kinds of binding energy, and the lowest binding energy state is mainly related to Cu^+; The highest and intermediate binding energy states are mainly related to Cu^{2+}[6]. According to our test results, copper ions with intermediate binding energy and high binding energy are mainly distributed on the surface of ceramic samples sintered at 950℃and 1000℃, which represents Cu^{2+}.The surface of the ceramic samples sintered at 1050℃and 1100℃ can see the presence of copper ions with low binding energy, which represents Cu^+. The reasons for the above phenomenon are as follows: CuO can be decomposed into Cu_2O and O_2 when the temperature is higher than 1026℃ (decomposition temperature of CuO)[7].

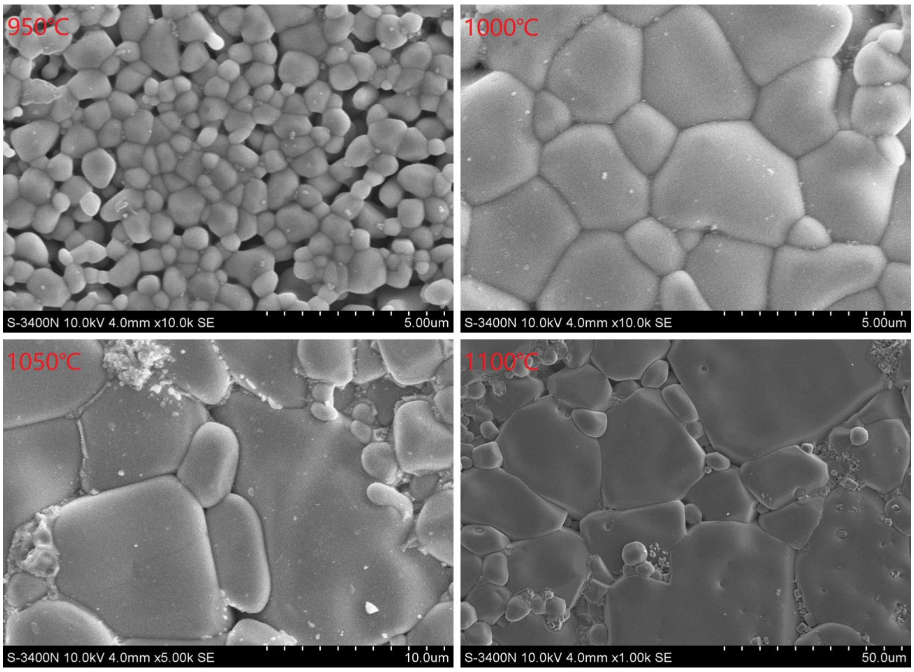

Figure 2: The SEM morphology of CaCu3Ti4O12 ceramics

Therefore, Cu^{+} can be observed in the ceramic samples sintered at 1050℃ and 1100℃. It can be concluded from these results that Cu^{+} and Cu^{2+} coexist in CCTO ceramic samples.

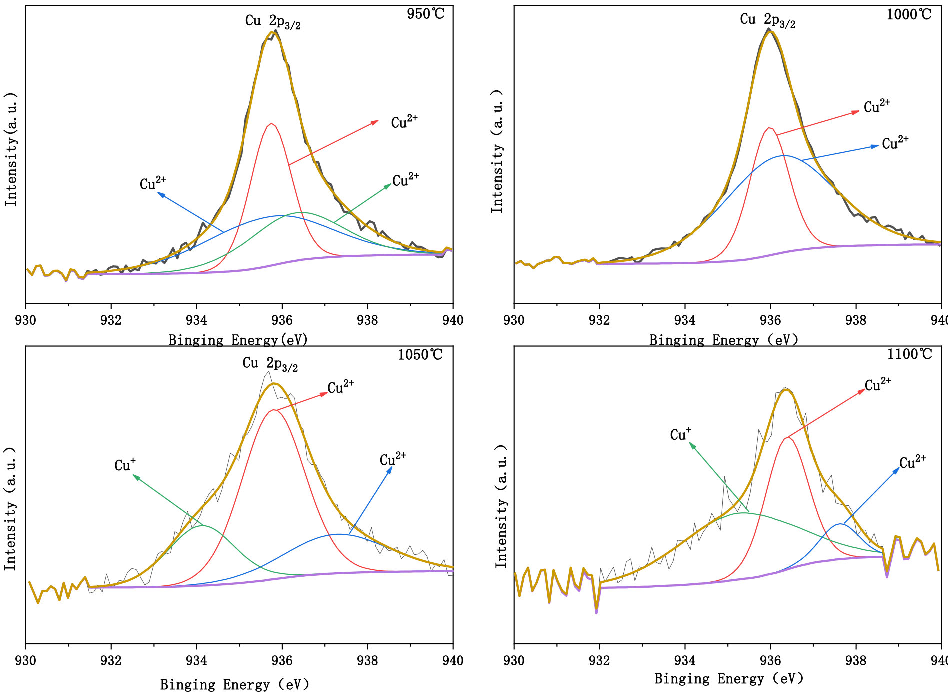

Figure 3: The spectrum of Cu 2p3/2 in CaCu3Ti4O12 ceramic samples

Figure 4 is the XPS spectrum of Ti 2p in $CaCu_3Ti_4O_{12}$ ceramic samples. It can be seen from the spectrum that the $2p_{3/2}$ and $2p_{1/2}$ peaks of Ti are divided into two peaks, indicating that Ti^{3+} and Ti^{4+} coexist in the $CaCu_3Ti_4O_{12}$ ceramic sample [8].

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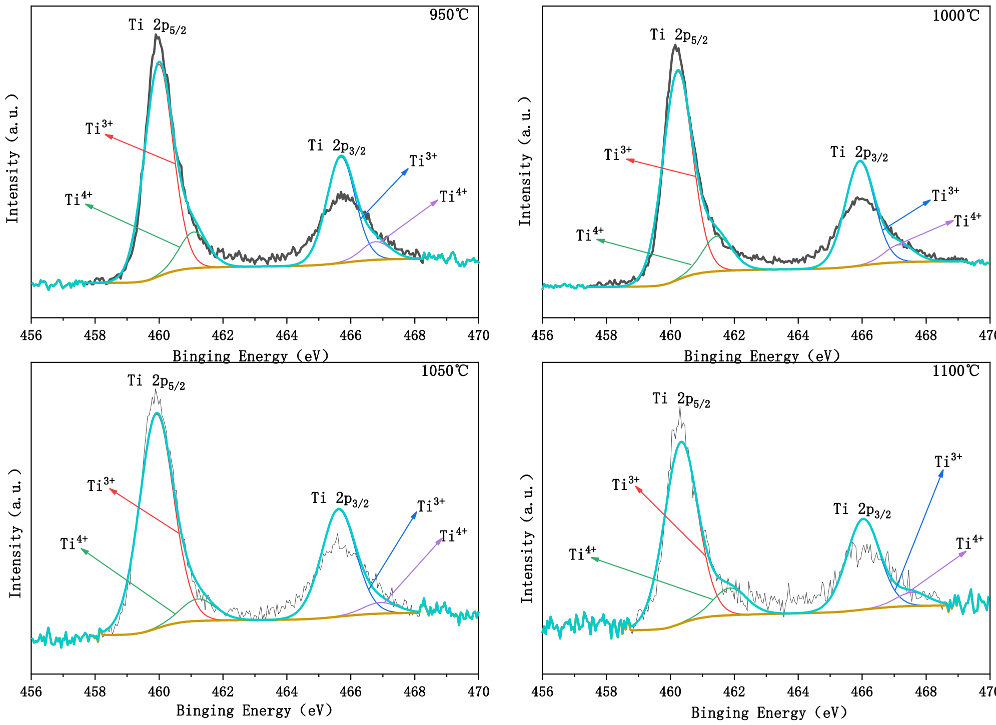

Figure 4: The spectrum of Ti 2p in CaCu3Ti4O12 ceramic samples

Figure 5 shows the relationship between the natural logarithm of resistivity and temperature. In the range of 25°C to 250°C, the resistivity decreases linearly with the rise of temperature, which is consistent with the behavior of NTC. Besides, it is intuitively that the resistivity decreases with the increase of sintering temperature. The four sintering temperatures have a great influence on the grain size of CCTO, leading to a great difference in grain boundary area, as shown by SEM. The carriers in CCTO ceramic samples are mainly electrons, and the increase in the grain boundary area results in a decrease in the time between the electron scattering events of the charge carriers [9]. It decreases the electron concentration and increases the resistivity. At the same time, according to Slater's theory [10], the energy barrier is related to grain boundaries and can be changed. Barrier thickness φ can be calculated by $\varphi \propto (\chi - \int L)$, where χ is the barrier width, L the grain size, and $\int$ is a fraction between 1/15 and 1/50. It can be concluded from this calculation that the smaller the grain size, the higher the energy barrier, the more grain boundaries, the more difficult for carriers to cross the grain boundaries, and the higher the resistivity. Therefore, grain size increases gradually at 950°C, 1000°C,1050°C and 1100°C, grain boundary area decreases the energy barrier of charge carriers across grain boundary decreases, and resistivity decreases.

In addition, table1 lists the resistivity at room temperature (ρ_{25}), and B at four different sintering temperatures.The calculation formula of ρ_{25} is $\rho_{25} = R_{25} \bullet (S / L)$. Where R_{25} refers to the resistance of the ceramic samples at 25°C, S refers to the surface area of the ceramic samples, and L refers to the thickness of the ceramic samples.Similarly,B is calculated according to the formula $B = (\ln R_1 - \ln R_2)/(1/T_1 - 1/T_2)$, where R_1 and R_2 are resistances , and T_1 and T_2 are the Kelvin temperatures corresponding to them.

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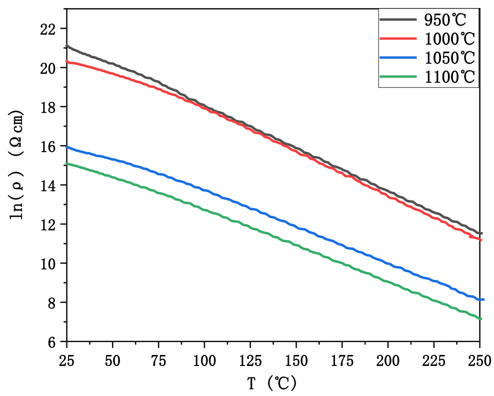

Figure 5: Plots of the lnρ versus T for the CCTO NTC thermistors

Table 1: ρ25 and B at different temperature ranges of CCTO ceramic

T (°C)	ρ_{25}(Ωcm)	$B_{25\text{-}50}$	$B_{50\text{-}75}$	$B_{75\text{-}100}$	$B_{100\text{-}125}$	$B_{125\text{-}150}$	$B_{150\text{-}175}$	$B_{175\text{-}200}$	$B_{200\text{-}225}$	$B_{225\text{-}250}$
950	1.483×10^9	3533	4174	6333	6245	7568	8234	9357	10324	11021
1000	6.633×10^8	2455	3578	5129	6363	7533	8440	10184	10379	11371
1050	8.337×10^6	2438	3391	4301	5651	6228	6942	8099	8357	9896
1100	3.566×10^6	2703	3608	4492	5325	6064	6984	8082	9074	9535

4. Conclusion

In this paper, the influence of sintering temperature gradients (950℃, 1000℃, 1050℃ and 1100℃) on $CaCu_3Ti_4O_{12}$ ceramics was studied. With the increase in sintering temperature, the grain size of ceramic samples increased accordingly, which changed the NTC performance of $CaCu_3Ti_4O_{12}$ ceramics. The results show that the room temperature resistance of ceramic samples can be adjusted from 3.566×10^6 to 1.483×10^9Ωcm by changing the sintering temperature, and the B-value constant can also be adjusted at different temperature ranges from 25 to 250. This research provides a way of thinking about a new temperature sensor.

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