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CCTO Giant Dielectric Ceramic Prepared by Reaction Sintering

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Abstract

In present research, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) giant dielectric ceramics were prepared by solid phase reaction sintering method. Two ways of sintering were used: 1) the sintering temperature was risen to 1100°C directly, hold on 2, 3, 6, 8 hours respectively; 2) first, the temperature was heated to 1150°C , then decreased to 1000°C immediately and hold on 3, 6, 9 hours separately. The sintering performance, dielectric properties and impedance characteristics, as well as the relationship between the characteristics were investigated. The experiments show that, the density of the CCTO ceramics prepared via the first routine raised with increasing soaking time. Meanwhile the radial shrinkage rate had a significant increase. But via the second routine, the radial shrinkage rate had a slight increase. In both processes the dielectric constant and dielectric loss of all samples were decreased with the test frequency increase. With the soaking time increased, the downtrend of the dielectric constant was also found.

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1. Introduction

Recent reports show that perovskite structure $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ material with cubic structure have the dielectric constant of 80000 at room temperature and a strong current-voltage nonlinear effects^[1-2]. In the range of temperature from room temperature to 600K, the dielectric constant of the material kept a certain value. With the temperature dropped below 100k, the dielectric constant drops to around 100K. On the other hand, the dielectric constant of the material in infrared frequencies at room temperature only 80. Currently there are several models to explain this specific permittivity characteristics. Some people thought that high dielectric CCTO was caused by intrinsic lattice

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structure of the material. Some people thought that high dielectric properties of CCTO caused by the depletion layer(SBLC) between the sample and the electrodes [3-4]. But more people believe that a high dielectric constant may caused by the internal barrier layer capacitance [5-6].Therefore, the internal barrier layer capacitance model was received more attention.

High dielectric materials had huge potential applications in the microelectronics devices, especially its key roles on reducing the size of microelectronic devices. In recent years, CCTO as one giant dielectric material was subjected to a concern that the material not only its high dielectric constant (104-105), but also the dielectric constant maintained in a wide temperature with low dielectric loss. For this reason, preparation, performance and theory about CCTO material studied by growing number of domestic and international scholars, in order to make the material as soon as possible to get the actual application. Currently, most studies on giant dielectric CCTO ceramics were focused on the conventional synthesis that sintered after burning. The conventional synthesis is a long time sintering followed by a long burning. As its known, microstructure and dielectric properties of CCTO ceramics have extremely sensitive on its sintering process. Therefore, in this paper, solid-state reaction sintering was used to simplify the preparation process, to prepare CCTO ceramics, to study of its sintering characteristics, dielectric properties and impedance characteristics, and to analyze the relationship between each other.

2. Experimental

Traditional solid-phase sintering was used to prepare CCTO ceramics. The raw materials, such as CaCO_3 , TiO_2 and CuO powder were commercially available with purity of 99%. These powders were weighed in accordance with stoichio metry of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. Powder was loaded into the mill pot adding appropriate amount of distilled water, milled 8h with ZrO_2 balls, dried after being milled, passed through a 120 mesh sieve. The power sieved was added about 5wt% PVA binder to granulated and passed through a 40 mesh sieve, then dry-pressed to 10mm cylindrical embryo molds under 70 MPa pressure. Two sintering routine were used: 1)the sintering temperature was risen to 1100°C directly, then held on 3, 6, 9 hours separately; 2) first, the temperature is heated to 1150°C, then decreased to 1000°C immediately, then held on 2, 3, 6, 8 hours separately. The performances of sintered samples were investigated. The density after sintering was tested via Archimedes method and the shrinkage was measured with multiple caliper whose accuracy was 0.02. Sample pieces sintered was painted by silver, silver electrode was formed on the surfaces of samples heated at 550°C for 30min. Finally, WAYNE KERR 6540A impedance analyzer was used to detect impedance spectroscopy of the sample electrodes.

3. Results and Discussion

3.1 .Density and shrinkage

Table 1 shows the densities and shrinkage of sintered samples at different soaking time. It can be seen that density increases slightly with the holding time increases, but the shrinkage increases sharply.

Table 1. Density and shrinkage of the CCTO ceramic prepared at 1100°C with different soaking times

Soaking time	2h	3h	6h	8h
Density(g/cm^3)	4.035	4.064	4.076	4.112
Shrinkage (%)	18.7	19.9	22.8	24.2

Table 2 shows the densities and shrinkage of the ceramics which increased to 1150°C and then cooled to 1000°C then holding at different times. It can be seen that the density increased sharply as the holding time varied length, but the shrinkage changed slightly. So the density as CCTO holding time increases changed significantly.

Table 2. Density and shrinkage of the CCTO ceramic increased to 1150°C and then cooled to 1000°C then holding at different times

Soaking time	3h	6h	9h
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Density (g/cm ³)	3.578	4.210	4.440
Shrinkage (%)	21.5	22.7	22.9

3.2. Phase composition

It can be seen clearly that there is a new phase $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ occurred, at different soaking time (Fig.1).

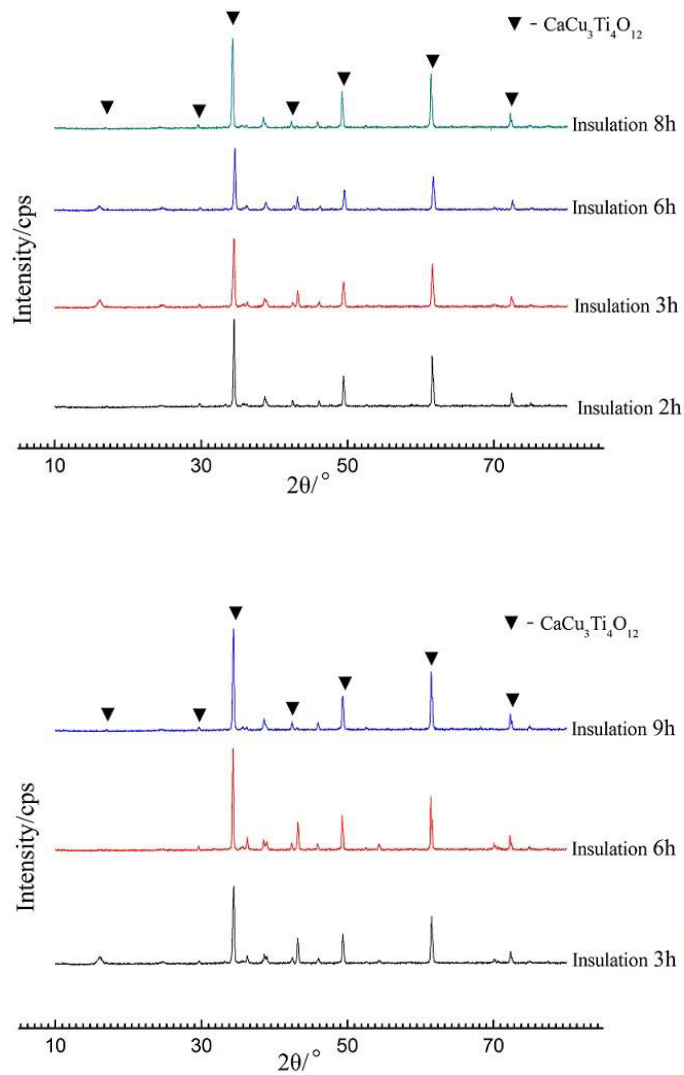


Fig.1. XRD pattern of samples with different soaking times

3.3. Dielectric performance analysis

The two pictures in Fig. 2 respectively show the dielectric spectra and dielectric loss of CCTO ceramic prepared at 1100°C for different soaking times. It can be seen that the dielectric spectra and dielectric loss of CCTO ceramic decreased as frequency increased. At low frequencies, the dielectric spectra of the ceramics with 3 hours soaking time runs up to the maximum. At 1 kHz, the dielectric spectra achieve 310. However, with the frequency increases, the dielectric constant of the ceramic of 3 hours soaking time are lower than that sintered at 1100°C. Dielectric loss has a similar trend.

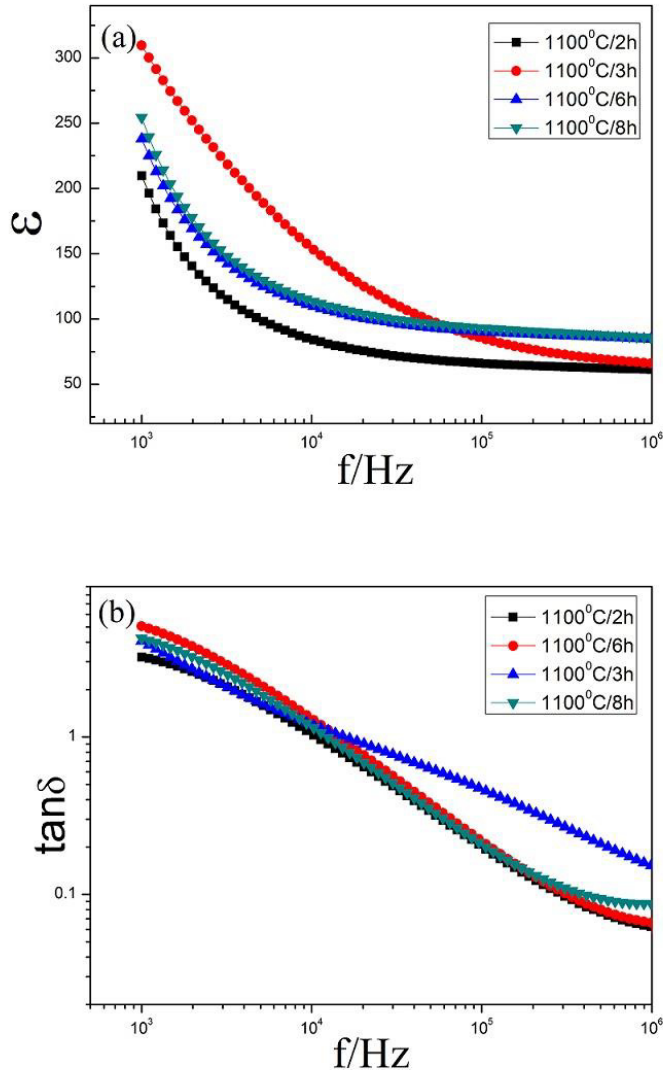


Fig. 2. The CCTO ceramic prepared at 1100°C for different soaking times. (a) dielectric spectra; (b) dielectric loss.

Fig. 3 show the dielectric spectra and dielectric loss of CCTO ceramic that heated to 1150°C and then cooled to 1000°C with different soaking times followed. It can be seen that the dielectric spectra and dielectric loss of CCTO

ceramic decrease with frequency increasing. At low frequencies, the dielectric spectra of the samples whose soaking time is 3 hours reach the maximum dielectric ceramic CCTO. At 1 kHz, the dielectric spectra of the samples achieve 785. This trend is similar to what is described above.

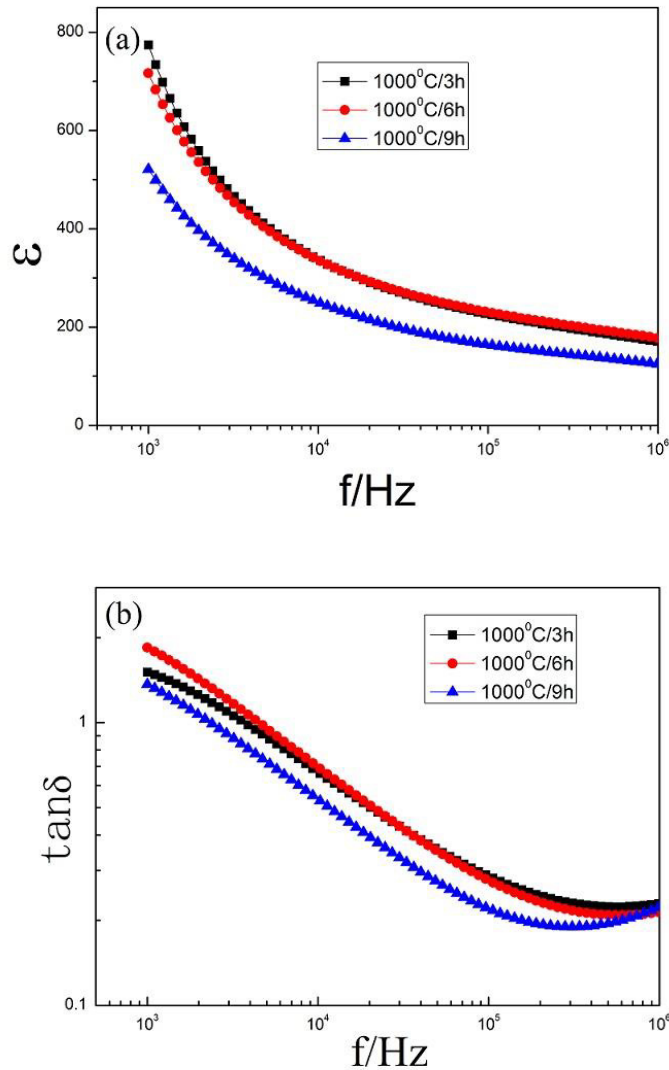


Fig. 3. The CCTO ceramic first increased to 1150°C and then cooled to 1000°C after holding at different times. (a) dielectric spectra, (b) dielectric loss.

3.4. Impedance spectroscopy

AC impedance spectroscopy is an effective evaluation for the material properties and microstructure analysis. Impedance spectroscopy measured by impedance spectroscopy analyzer: WAYNE KERR 6540 A, can reflect the difference between the internal and the grain boundary. Therefore, impedance spectroscopy of CCTO ceramics

prepared by solid-state reaction sintering was measured. Fig. 4 shows the impedance spectroscopy of CCTO ceramic prepared at 1100°C with different soaking times. It can be seen that the difference of the impedance spectrum among the samples with 3h, 6h, 8h soaking times is small. Impedance spectroscopy of the sample soaking for 2 hours was significantly greater than the other three samples, its maximum value can achieve 160 kΩ. Its trends have significant differences with the previous three. But these four kinds of ceramics have its own features: the slope of the curve of impedance spectroscopy at different frequencies did not differ significantly which showed that the existence of an order of magnitude difference on conductive properties between the grain interior and boundaries in CCTO ceramics prepared by reaction sintering. I believe that internal barrier layer capacitor of the samples with the holding time of 2h are more obviously.

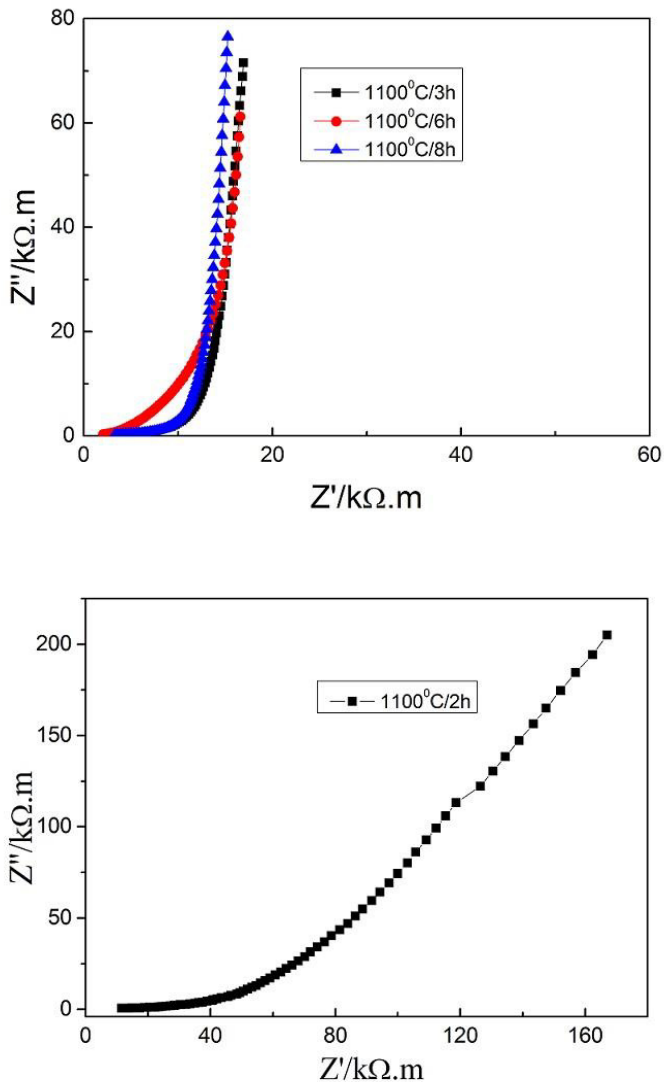


Fig. 4. The impedance spectroscopy of CCTO ceramic prepared at 1100°C for different soaking times.

Fig. 5 shows the impedance spectroscopy of CCTO ceramic first increased to 1150°C and then cooled to 1000°C after holding at different times. As can be seen from the figure, at different holding time the change trend is similar.

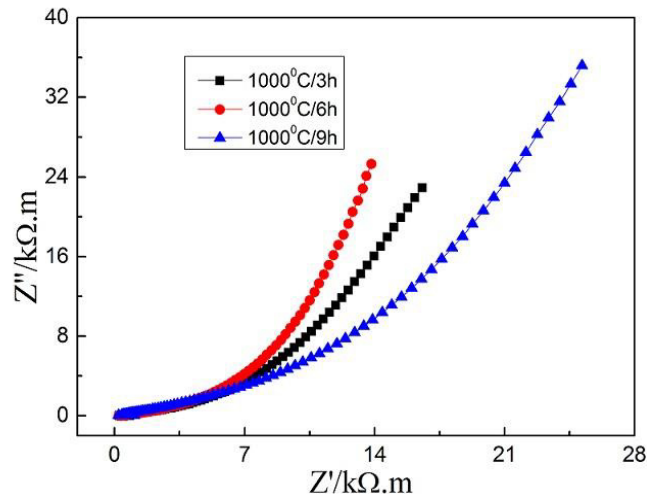


Fig.5. The impedance spectroscopy of CCTO ceramic first increased to 1150°C and then cooled to 1000°C after holding at different times.

4. Summary

With the extension of the holding time, the density and shrinkage of the CCTO ceramic increased slightly. At high frequencies, permittivity of the CCTO ceramics were tested, dielectric loss of samples show ceramics that first increased to 1150°C and then cooled to 1000°C after insulation 2h, their dielectric constant containing a maximum and decreases rapidly with the frequency increasing. Their dielectric loss is relatively small. Based on this characteristic, it can be applied to the microelectronic components.

Acknowledgements

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