Article ID: 1000-324X(2014)11-1228-05 **DOI:** 10.15541/jim20140255

Preparation and Electrical Properties of $CaCu_3Ti_4O_{12}$ Thin Ceramic Sheets *via* Water-based Tape Casting

LI Wei, XIONG Zhao-Xian, XUE Hao

(College of Materials, Xiamen University, Xiamen 361005, China)

Abstract: Thin ceramic sheet of $CaCu_3Ti_4O_{12}$ has a great significance for preparation of multiplayer ceramic chip capacitors. In this work, a simple plan was made to achieve $CaCu_3Ti_4O_{12}$ thin ceramic sheets with excellent dielectric properties. Thin ceramic sheets of $CaCu_3Ti_4O_{12}$ were prepared *via* water-based tape casting at various sintering temperatures. The $CaCu_3Ti_4O_{12}$ samples sintered at 1080℃ exhibit a great performance on dielectric properties with high permittivity (ε_r=98605) and low dielectric loss (tanδ=0.028) which are better than those of samples prepared by conventional dry pressing. Meanwhile, the complex impedance spectra were measured to explain the mechanism of special electrical behaviors of $CaCu_3Ti_4O_{12}$ ceramics. These testing results indicate that the $CaCu_3Ti_4O_{12}$ ceramics *via* tape casting exhibits a better performance of giant permittivity and lower dielectric loss than other reports, which provides a possibility for the application of the $CaCu_3Ti_4O_{12}$ in modern micro-electronics technology.

Key words: perovskite; tape casting; dielectric properties; grain boundary

Tape casting technique has got attention, due to the high production efficiency, good products uniformity and stable performance[1]. Tape casting is a kind of molding ceramic method of thin film to control thickness of ceramic chip. Tape casting is first used to produce ceramic layer capacitor by Howatt, *et al* in 1947[2]. Now, tape casting has been widely used in the ceramics material forming process, mainly concentrated in the field of functional ceramics. In general, the slurry system is divided into water-based and solvent-based systems. Polyvinyl alcohol (PVA) is usually used for the water-based system, while polyvinyl butyral (PVB) is used for the solvent-based system.

The ceramics $CaCu_3Ti_4O_{12}$, *i.e.*, CCTO has attracted ever-increasing attention, due to the practical microelectronic applications including capacitors and memory devices. Although CCTO ceramics have attracted considerable attentions recently due to its unusual high dielectric constant (ε=10^4–10^5) in a wide range of the frequency and the temperatures (100–600 K)[3-6], its relatively high dielectric loss (tanδ) restricts their applications[7-10]. At present, the internal barrier layer capacitance (IBLC) model representing semiconducting grains and insulating grain boundaries confirms the electrical heterogeneities in the microstructure of CCTO[11-13]. And, the insulating grain boundaries acted as Schottky-type potential barriers in CCTO ceramics[14]. It is revealed that the high permittivity of CCTO is not only due to the intrinsic nature of the polarization or ferroelectricity, but also related to an extrinsic effect of the potential barriers[10-13, 15-16].

Thin ceramic sheet of CCTO has a great significance for the development of multiplayer ceramic chip capacitors (MLCC). So it is necessary to study thin CCTO ceramic sheet *via* tape casting in details to improve its dielectric loss. In this study, the thin CCTO ceramic sheets with high performance are prepared by using water-based tape casting, and its structure, composition and dielectric properties are studied in details.

1 Materials and methods

CCTO samples were prepared by the solid state method. All the starting materials used were of analytical grade: $CaCO_3$ (99%), TiO_2 (99%) and CuO (99%). Stoichiometric ratios of the reagents ($CaCO_3$: TiO_2: CuO =1: 4: 3) were mechanically ball milled in an alcohol medium for 6 h in a polyethylene bottle, using zirconium balls, with ball to powder ratio of 10:1. A powder exhibiting free flowing characteristics was then obtained by sieving the dried milled powders. Subsequently, the powder was sintered at

Received date: 2014-05-19; **Modified date:** 2014-07-16; **Published online:** 2014-09-01
Foundation item: Fundamental Research Funds for the Central Universities(2010121052); National Natural Science Fund of China(51202204)
Biography: LI Wei(1988–), male, candidate of master degree. E-mail:welllee1988@gmail.com
Corresponding author: XIONG Zhao-Xian, professor. E-mail: zxxiong@xmu.edu.cn

900℃ for 3 h in air to form CCTO phase. Next, CCTO samples were formed by tape casting. These pellets were sintered at 1020℃, 1040℃, 1060℃, 1080℃ and 1100℃ in air for 5 h, respectively, and then cooled down to room temperature in a furnace.

Crystal structures of the CCTO ceramics were identified by using automatical X-ray diffraction (Panalytical, χ'pert PRO, Holland) with CuK radiation. The microstructures of ceramics were observed by a scanning electron microscope (Philips, XL30, Holland). Dielectric properties of the samples were performed at 1 V from 20 Hz to 1 MHz by a LCR precision meter (HP 4284A, USA). Impedance measurements of the samples were performed from 0.1 Hz to 0.1 MHz by a type of electrochemical workstation (EG&G263A, Princetion Applied Reaseach). *I-V* characteristics of CCTO samples were measured by Digital Source Meters (model 2400, Keithley, Cleveland, OH) connecting to a computer.

2　Results and discussion

Figure 1 shows the X-ray diffraction patterns of CCTO sintered at different temperatures. The diffraction peaks could be indexed to single perovskite structure of $CaCu_3Ti_4O_{12}$ without noticeable minor phases for all specimens. Peaks of the ceramics were matched well with the standard pattern of cubic structured CCTO (PDF 01-075-1149)[17].

The scanning electron micrographs of the ceramics are displayed in Fig. 2. Microstructures of these samples exhibit that grain size increases gradually with the increase of sintering temperature. When the sintering temperature was at 1040℃, grains were discreted and there were a lot of big pores inside the sample. In Fig. 2 (b), the sample sintered at 1060℃ shows that the grain size increases dramatically. And the sample sintered at 1080℃ shows the largest grain size (100–150 μm). However, the grain

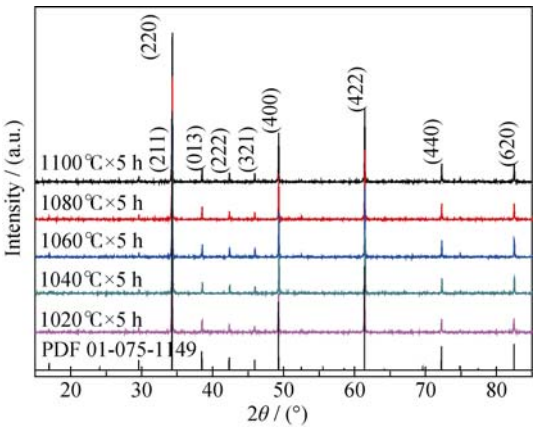

Fig. 1　XRD patterns of thin CCTO ceramic sheets sintered at different temperatures, comparing with CCTO (PDF 01-075-1149)

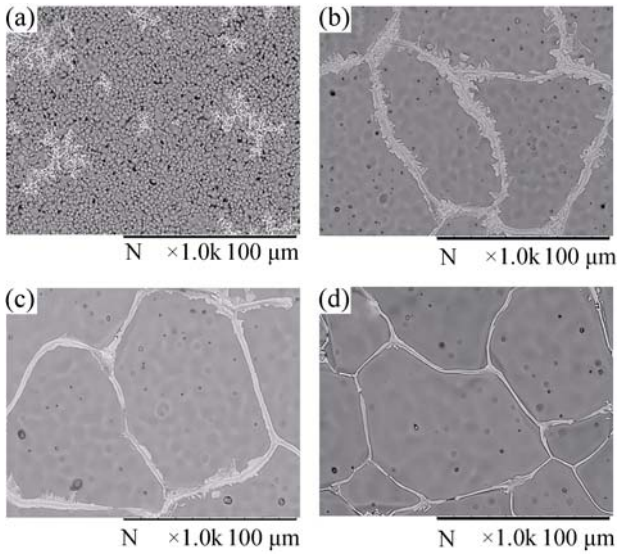

Fig. 2　SEM images of the $CaCu_3Ti_4O_{12}$ samples sintered at (a) 1040℃, (b) 1060℃, (c) 1080℃ and (d) 1100℃

boundaries of sample sintered at 1100℃ are more narrow than those of the others, while the highly active area of grain boundary is sagged. It is revealed that the connection of grain boundary is unstable and the specimen is slightly over-burn. When increasing sintering temperature, the glass phase increases and the viscosity of liquid phase reduces. Meanwhile, the sintering driving force is improved with the increasing of sintering temperature and the migration of grain boundary increases, which leads to the increase of the grain size of CCTO.

EDX analysis was carried out on the grain and grain boundary regions of the sample sintered at 1080℃ in Fig. 3. EDX results clearly indicates that the grain region is lack of Cu (Ca: Cu: Ti = 1: 2.2: 4) (Seen in Fig. 3(c)), while the grain boundary region is enriched in Cu, as shown in Fig. 3(d). It is determined that Cu-rich phases are segregated at grain boundaries, which has also been reported in some reports[18-20].

Frequency dependent permittivity and dielectric loss of all samples at room temperature are shown in Fig. 4. CCTO samples sintered at 1080℃ shows the best dielectric properties: the highest permittivity (ε_r=98605.9) and the lowest loss (tanδ=0.028). Although permittivity of the sample sintered at 1100℃ is almost the same with that of the sample sintered at 1080℃, its dielectric loss is slightly higher, especially at low frequencies.

About the IBLC model, the permittivity at low frequencies is given by

$$\varepsilon_r = \frac{R_g^2 C_g + R_{gb}^2 C_{gb}}{C_0 (R_g + R_{gb})^2} \tag{1}$$

When $R_g \ll R_{gb}$, formula (1) is approximate to

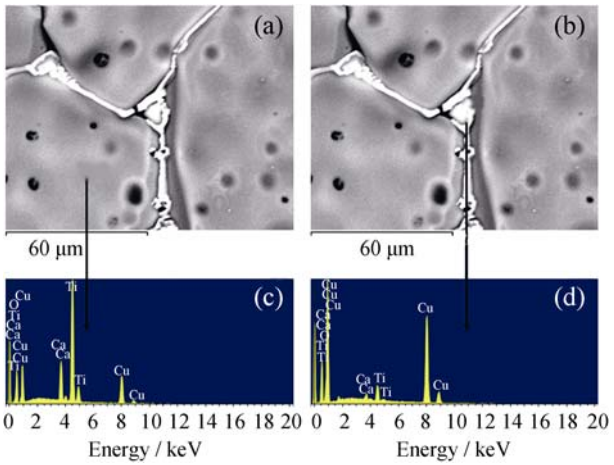

Fig. 3 SEM images of the sample sintered at 1080℃ (a and b), EDX patferns of grain (c) and grain boundary region (d)

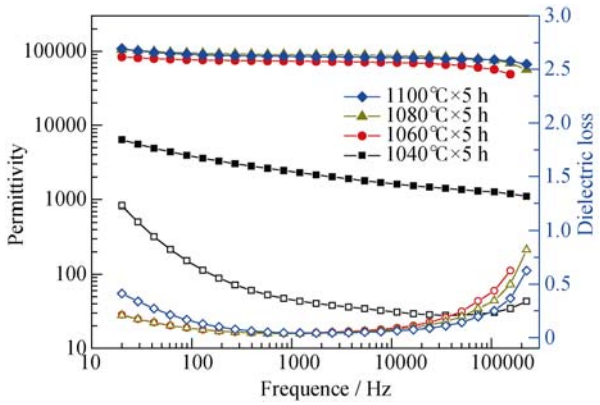

Fig. 4 Frequency dependence of permittivity and loss of samples sintered at different temperatures at room temperature

$$\varepsilon_r \propto \frac{C_{gb}}{C_0} \propto \varepsilon_{gb}(D/d) \tag{2}$$

$$\varepsilon_r \propto D/d \tag{3}$$

Where D and d are the diameter of grain and the thickness of grain boundary, respectively. It is clear that the permittivity of CCTO at 1 kHz increases with the rising of grain size, as shown in Fig. 2.

In this paper, CCTO ceramics prepared *via* tape casting exhibits much lower dielectric loss than other reports[21], while retaining a giant permittivity. However, in some reports[22], reduction in the loss in CCTO also affected the permittivity to a large extent.

Temperature dependent (–20~120℃) characteristics of permittivity and dielectric loss at 1 kHz are shown in Fig. 5. With increasing the test temperature, there is a slight rise in permittivity of all samples below 60℃. But, the permittivity of these samples increase remarkably above 60℃. Meanwhile, dielectric loss appears a relaxation peak at high test temperatures and the relaxation peaks move

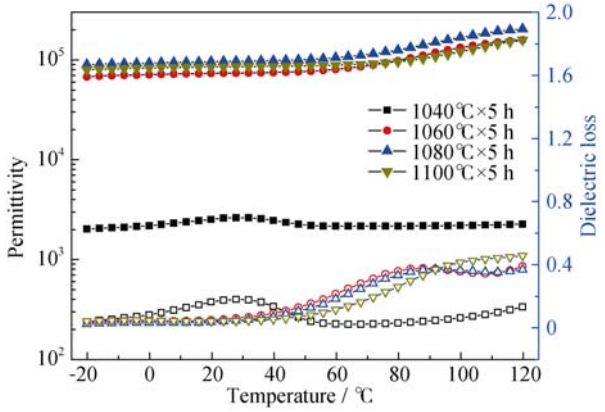

Fig. 5 Temperature dependence of permittivity and loss of samples sintered at different temperatures

to high test temperature with the increasing of sintering temperature.

The complex impedance spectra of all specimens are shown in Fig. 6, in which there are semi-circular arcs with non-zero intercept on the Z' axis at high frequencies. According to the complex impedance analysis based on the

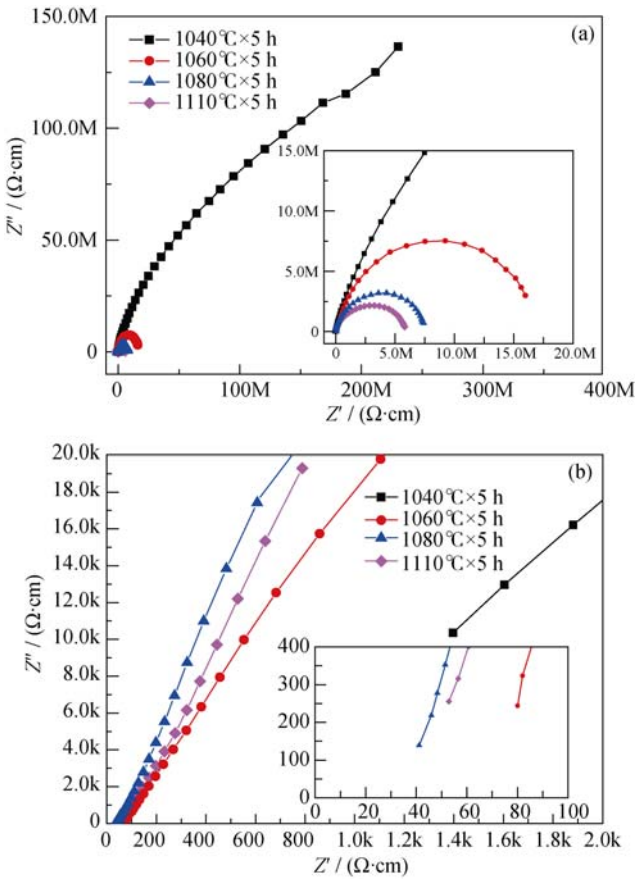

Fig. 6 Complex impedance plane measured at room temperature (25℃) for $CaCu_3Ti_4O_{12}$ samples sintered at different temperatures

Inset in (a) shows an expanded views of the high-frequency data and in (b) shows an expanded views of the high-frequency data close to the origin

model of IBLC, the values of the resistivity of grain and grain boundary are 70 Ω·cm and 17 MΩ·cm for the sample at 1060℃, 38 Ω·cm and 7.5 MΩ·cm for the sample at 1080℃, and, 32 Ω·cm and 5.5 MΩ·cm for the sample at 1100℃, respectively. With the increasing of sintering temperature, the resistivity of grain and grain boundary reduces. It is the presence of high resistance area at grain boundaries that enhanced the varistor performance. The microstructure of CCTO ceramics is consisted of semi-conducting grains and insulating grain boundaries, which verifies the IBLC model further.

Grain boundaries and defects of CCTO ceramics exhibit a very high resistance which are far higher than the resistance of grains. If these high resistance regions and grains are independent, the Fermi levels of these regions would be below that of grains. However, when the high resistance region is contacted with grain, the difference of energy is transferred from these high resistance regions to grains until realizing the dynamic equilibrium. These interfaces accept many electrons and negatively charge, and then the energy band bend upwards. Then the Fermi level of grain is equal to that of these high-resistance regions. It is similar to the metal contacting with the semi-conductor, forming a potential barrier at the interfaces. There is both a potential barrier at the plus and minus directions of the interfaces with an asymmetric relationship. So there is a back-to-back Schottky potential barrier at the interfaces[23], which generates nonlinearity of CCTO ceramics. Based on the analysis above, IBLC model is combined with the back-to-back Schottky barrier model, which deduces an equivalent circuit diagram of CCTO ceramics, and grains, grain boundary and domain boundary are respectively corresponded to a RCD element in Fig. 7. Giant permittivity and varistor characteristic of the CCTO ceramics are semi-quantitatively explained by the IBLC model with Schottky barriers.

It is pointed out that CCTO has rather high permittivity of about 10^5 but high dielectric loss. The CCTO specimens via tape casting technique presented a colossal permittivity and very low dielectric loss, which provides a possibility for the application of CCTO in modern microelectronics.

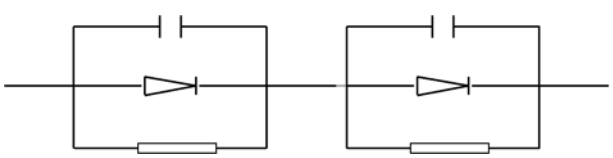

Fig. 7　Improved equivalent circuit model according to the IBLC and Schottky barrier model

Grains and grain boundaries respectively correspond to a RCD element. Diode stand for a Schottky-type potential barrier

3　Conclusions

Dielectric properties of thin CCTO ceramic sheets prepared by water-based tape casting were investigated in details. The CCTO sheets were obtained by sintering at 1020℃, 1040℃, 1060℃, 1080℃ and 1100℃ for 5 h, respectively. The microstructures of samples showed the grain size increased gradually with the increase of sintering temperature. EDX studies revealed that Cu-rich phases were segregated at grain boundaries. The best sample sintered at 1080℃ for 5 h exhibited a high permittivity (ε_r) of 98605 with a very low dielectric loss, tanδ= 0.028 at 1 kHz, which provides a possibility for the application of CCTO in modern microelectronics. Meanwhile, the complex impedance spectra were measured to discuss the mechanism of the special electrical behaviors of $CaCu_3Ti_4O_{12}$ ceramics.

References:

[1] HOTZA D, GREIL P. Review: aqueous tape casting of ceramic powders. *Mater. Sci. Eng.*, 1995, **202(1):** 206–217.

[2] HOWATT G, BRECKENRIDGE R, BROWNLOW J. Fabrication of thin ceramic sheets for capacitors. *J. Am. Ceram. Soc.*, 1947, **30(8):** 237–242.

[3] HOMES C, VOGT T, SHAPIRO S, *et al*. Optical response of high-dielectric-constant perovskite-related oxide. *Science*, 2001, **293(5530):** 673–676.

[4] SUBRAMANIAN M, LI D, DUAN N, *et al*. High dielectric constant in $ACu_3Ti_4O_{12}$ and $ACu_3Ti_3FeO_{12}$ phases. *J. Solid State Cherm.*, 2000, **151(2):** 323–325.

[5] LIU J, DUAN C G, MEI W N, *et al*. Dielectric properties and Maxwell-Wagner relaxation of compounds $ACu_3Ti_4O_{12}$ (A=Ca, $Bi_{2/3}$, $Y_{2/3}$, $La_{2/3}$). *J. Appl. Phys.*, 2005, **98(9):** 093703–093705.

[6] MAZUMDER R, SEAL A, SEN A, *et al*. Effect of boron addition on the dielectric properties of giant dielectric $CaCu_3Ti_4O_{12}$. *Ferroelectrics*, 2005, **326(1):** 103–108.

[7] JIN S, XIA H, ZHANG Y. Effect of La-doping on the properties of $CaCu_3Ti_4O_{12}$ dielectric ceramics. *Ceram. Int.*, 2009, **35(1):** 309–313.

[8] YU H, LIU H, HAO H, *et al*. Dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics modified by $SrTiO_3$. *Mater. Lett.*, 2008, **62(8):** 1353–1355.

[9] Kobayashi W, Terasaki I. $CaCu_3Ti_4O_{12}$/$CaTiO_3$ composite dielectrics: Ba/Pb-free dielectric ceramics with high dielectric constants. *Appl. Phys. Lett.*, 2005, **87(3):** 032902–032903.

[10] PATTERSON E A, KWON S, HUANG C C, *et al*. Effects of ZrO_2 additions on the dielectric properties of $CaCu_3Ti_4O_{12}$. *Appl. Phys. Lett.*, 2005, **87(18):** 182911–182913.

[11] SINCLAIR D C, ADAMS T B, MORRISON F D, *et al*. $CaCu_3Ti_4O_{12}$: one-step internal barrier layer capacitor. *Appl. Phys. Lett.*, 2002, **80(12):** 2153–2155.

[12] ADAMS T B, SINCLAIR D C, WEST A R. Giant barrier layer capacitance effects in $CaCu_3Ti_4O_{12}$ ceramics. *Adv. Mater.*, 2002, **14(18):** 1321–1323.

[13] CHUNG S Y, KIM I D, KANG S J L. Strong nonlinear current–voltage behaviour in perovskite-derivative calcium copper titanate. *Nat. Mater.*, 2004, **3(11):** 774–778.

[14] YU R, XUE H, CAO Z, *et al*. Effect of oxygen sintering atmosphere on the electrical behavior of CCTO ceramics. *J. Eur. Ceram. Soc.*, 2012, **32(6):** 1245–1249.

[15] RAMIREZ A, SUBRAMANIAN M, GARDEL M, *et al*. Giant dielectric constant response in a copper-titanate. *J. Solid State Cherm.*, 2000, **115(5):** 217–220.

[16] DE LA RUBIA M A, LERET P, DE FRUTOS J, *et al*. Effect of the synthesis route on the microstructure and the dielectric behavior of $CaCu_3Ti_4O_{12}$ ceramics. *J. Am. Ceram. Soc.*, 2012, **95(6):** 1866–1870.

[17] MCGUINNESS C, DOWNES J E, SHERIDAN P, *et al*. X-ray spectroscopic study of the electronic structure of the high-dielec tric-constant material $CaCu_3Ti_4O_{12}$. *Phy. Rev. B*, 2005, **71(19):** 195111.

[18] CAPSONI D, BINI M, MASSAROTTI V, *et al*. Role of doping and CuO segregation in improving the giant permittivity of $CaCu_3Ti_4O_{12}$. *J. Solid State Cherm.*, 2004, **177(12):** 4494–4500.

[19] PRAKASH B S, VARMA K. The influence of the segregation of Cu-rich phase on the microstructural and impedance characteristics of $CaCu_3Ti_4O_{12}$ ceramics. *J. Mater. Sci.*, 2007, **42(17):** 7467–7477.

[20] FANG T T, MEI L T. Evidence of Cu deficiency: a key point for the understanding of the mystery of the giant dielectric constant in $CaCu_3Ti_4O_{12}$. *J. Am. Ceram. Soc.*, 2007, **90(2):** 638–640.

[21] JO SOO KYONG, HAN YOUNG HO. Sintering behavior and dielectric properties of polycrystalline $CaCu_3Ti_4O_{12}$. *J. Mater. Sci.: Mater. Electron.*, 2009, **20:** 680–684.

[22] THOMAS P, DWARAKANATH K, VARMA K. Effect of calcium stoichiometry on the dielectric response of $CaCu_3Ti_4O_{12}$ ceramics. *J. Eur. Ceram. Soc.*, 2012, **32(8):** 1681–1690.

[23] MARQUES V, BUENO P, SIMOES A, *et al*. Nature of potential barrier in $CaCu_3Ti_4O_{12}$ polycrystalline perovskite. *J. Solid State Cherm.*, 2006, **138(1):** 1–4.

流延法制备片式 $CaCu_3Ti_4O_{12}$ 陶瓷及其性能研究

李 伟, 熊兆贤, 薛 昊

(厦门大学 材料学院, 厦门 361005)

摘 要: 片式 $CaCu_3Ti_4O_{12}$ 陶瓷由于其巨介电效应, 用于制备多层陶瓷片式电容具有重大意义。通过水基流延法并在不同的烧结温度下制备的片式 $CaCu_3Ti_4O_{12}$ 陶瓷具有优异的介电性能。其中在 1080℃下烧结的样品在保持巨电容率(98605)的同时, 降低了介电损耗, 其值只有 0.028, 远低于其他报道的损耗值。同时, 测试了 CCTO 陶瓷薄片的复阻抗图谱, 讨论了 CCTO 陶瓷的特殊的电学性能。实验结果表明, 通过流延成型制备的 CCTO 陶瓷薄片在保持巨电容率的同时具有很低的介电损耗, 这为 CCTO 陶瓷在微电子工业上的应用提供了可能性。

关 键 词: 钙钛矿; 流延法; 介电性能; 晶界

中图分类号: TQ174 **文献标识码:** A