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Trans. Nonferrous Met. Soc. China 21(2011) s400−s404

Transactions of Nonferrous Metals Society of China
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Effects of synthesis technique on dielectric properties of $CaCu_3Ti_4O_{12}$ ceramic

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Received 10 May 2011; accepted 25 July 2011

Abstract: $CaCu_3Ti_4O_{12}$ powder was prepared by sol-gel technique, and the $CaCu_3Ti_4O_{12}$ composites were sintered at 1 000 °C for different time after cold pressing with the same pressure and time. The results exhibit that the grain size is affected by the pressure and sintering time. The impedance spectrum measurement results show that both the dielectric constant and dielectric loss have a weak frequency dependence over large frequency region of 50 Hz to 100 kHz, and not only does the dielectric loss decrease but also the dielectric constant remains high sufficiently. The most suitable sintering time is 6 h.

Key words: $CaCu_3Ti_4O_{12}$ ceramics; dielectric constant; dielectric loss; sintering time

1 Introduction

Both of the $CaCu_3Ti_4O_{12}$ (CCTO) ceramics [1−5] and the thin film of CCTO [6−10] have still attracted ever-increasing attentions for their practical microelectronic applications including capacitors and memory devices. CCTO has a body-centered cubic perovskite-related structure with the space group *Im*3 down to 35 K [11]. Despite the centrosymmetric nature of the polycrystalline, CCTO possesses colossal dielectric constant $>10^3$ in the frequency range of 100 Hz−1 MHz and exhibits a dielectric relaxation above this frequency.

Internal barrier layer capacitance (IBLC) model has been employed to explain the colossal dielectric constant of CCTO ceramics [12]. It has been revealed that the high dielectric constant of CCTO is not only due to the intrinsic nature of the polarization or ferroelectricity, but also is related to an extrinsic effect from the barriers [1]. The impedance spectroscopic (IS) data of CCTO ceramics have indicated that the extrinsic nature is due to the huge difference that exists in the resistivity of grain and the grain boundary, leading to the barrier layer capacitor-like situation [6, 13].

Incidentally, reported colossal dielectric values are also associated with high dissipation factor. For practical applications of CCTO, along with huge dielectric values, low dielectric loss is also of paramount importance [14] that has not yet been modified heartily. This has led to a quest among the scientific community to improve the dielectric loss of CCTO, because the small dielectric loss of CCTO ceramics is very important for the device applications. It can be concluded from some researches [1, 5, 14−16] that the dielectric loss of CCTO ceramics is mainly contributed from the semiconductive grain and grain boundary leakages. The processing conditions have strong effects on the dielectric properties of CCTO [6]. The studies, concerning on different processing and preparation conditions such as sol-gel derivation [17−18], sintering temperature and time [10, 19], doping [8, 20], electrode material and pellet thickness [6, 11] and the dielectric characteristics of CCTO, demonstrated their strong influence on the dielectric properties of CCTO ceramics.

In this work, an attempt was made to prepare CCTO particles, and the details pertaining to the influence of short sintering time on the microstructural features of sol-gel derived CCTO ceramics were studied to make a new simple technology for CCTO ceramics preparation.

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In this method, not only does the dielectric loss decrease, but also the dielectric constant remains high sufficiently. Ceramics with low dielectric loss and high dielectric constant were synthesized, and the relationship between the microstructure and properties of CCTO ceramics was also analysized.

2 Experimental

The CCTO ceramics used in this work were prepared by sol-gel technology using starting materials of $Ca(NO_3)_2·4H_2O$ (≥99%, mass fraction), $Cu(NO_3)_2·3H_2O$ (≥99.5%), $[CH_3(CH_2)_3O]_4Ti$ (98%), with ethylenglycol monomethylether ($C_3H_8O_2$, 95%) as solvent. CCTO sol was dried at 200 °C for 780 min and then sintered at 800 °C for 240 min in air atmosphere to prepare CCTO powders. Prepared CCTO powders were milled carefully and resintered at 450 °C for 30 min. The CCTO powders were milled again, and cold pressed into disks of ~9.5 mm in diameter and 0.5−0.7 mm in thickness at a pressure of 10 MPa for 90 s. These disks were sintered at 1 000 °C for different time in air atmosphere and then cooled to room temperature in the conventional furnace. The densities of samples were obtained by calculations.

The crystalline phases were identified by X-ray diffraction (XRD) analysis on a Philips X'Pert diffractometer with the Cu K_α radiation operated at 40 kV and 40 mA. Microstructure and elemental distribution of the polished pellets were analyzed using field-emission scanning electron microscope (SEM, FEI COMPANY and Hitachi S-3400 N). All pellet ceramics were polished and thinned to low thickness before impedance spectroscopy (IS) measurement and their surfaces were coated by magnetron plasma sputtering system of silver as capacitor electrodes.

The dielectric properties and impedance analyses of the present ceramics were determined using an impedance gain phase analyzer (Agilent 4294A) at signal strength of 0.5 Vrms. For this purpose, the frequency was ranged from 50 Hz to 100 MHz at 300 K.

3 Results and discussion

3.1 Phase composition

Figure 1(a) shows the XRD patterns obtained for the CCTO ceramics sintered at 1 000 °C for 4 h, 6 h and 8 h. The diffraction positions and intensities of the CCTO standard peaks are also indicated in the figure for each specimen. The results were identified according to the JCPDS files of 75−1149 and 33−0784. Using the Bragg's law, the lattice constants of CCTO were calculated using high angle diffraction peaks, and the results indicate that the lattice constants for all specimens are 0.739 4 nm, which indicates that all specimens are well crystallized. Good matching between the observed and calculated interplanar spacing (*d*-values) suggests that the compounds are with a single-phase cubic structure. The lattice parameters were calculated using

$$a_0 = \frac{\lambda\sqrt{h^2+k^2+l^2}}{2\sin\theta}$$

for all samples. The obtained lattice parameter is similar to the literature values (0.739 nm and 0.737 nm) [1, 21].

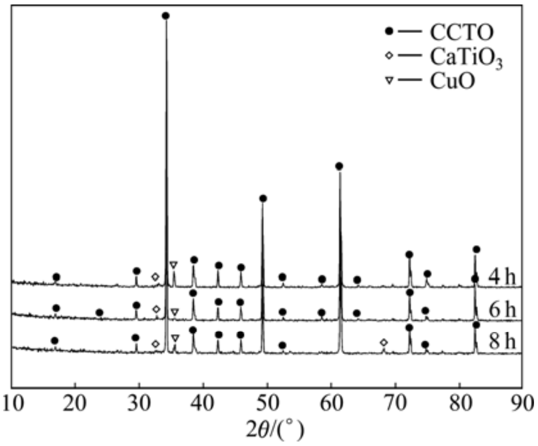

Fig. 1 Comparison of X-ray diffraction (XRD) patterns of all specimens

The densities of the disks were measured to be 4.13, 4.47 and 4.11 g/cm^3 for the samples sintered for 8 h, 6 h and 4 h, as shown in Fig. 2, which corresponds to relative density of 84.2%, 91.2% and 83.9%, respectively, considering the theoretical density of 4.9 g/cm^3 for CCTO [22]. This small variation in density of the three samples may be sufficient to cause the difference in their electric properties. The increase of density with sintering time is attributed to the decrease of porosity in the samples sintered for 6 h and 8 h.

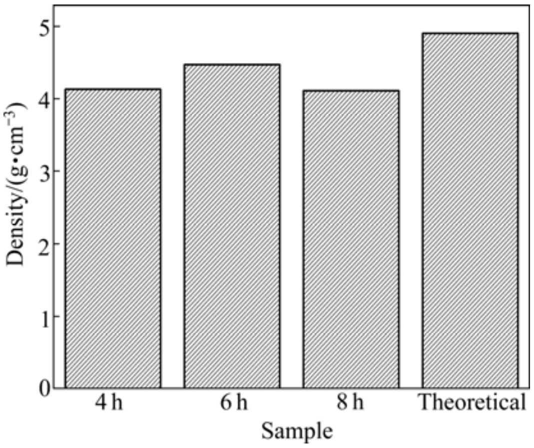

Fig. 2 Density comparison of samples with theoretical density

The diffraction peaks show that a small amount of $CaTiO_3$ (CTO) secondary phase and CuO exist in the CCTO ceramics, which may be due to the decomposition of CCTO phase at high temperature. Nevertheless sintering time increases in the ceramics, the content of CTO and CuO phases changes, which may make a variation in grain size. The role of CTO secondary phase in the giant dielectric response for the CCTO samples cannot be ignored, if considering that the segregated CTO content is dispersed at the grain boundaries. CTO has a dielectric insulator of ε=200. It is suggested that CTO secondary phase acts as the barrier layers at the grain boundaries, which contribute largely to the high dielectric constant observed in the CCTO ceramics [23]. As can be observed, the maximum relative intensity (RI) of CTO and the minimum RI of CuO in the samples sintered for 6 h can be considered a reason of the best dielectric properties.

3.2 Microstructure

Microstructure features of the samples were investigated using SEM images of the fresh fractured surface, as shown in Fig. 3.

It is obvious that the CCTO has an equiaxed grain shape. The grains are almost evenly distributed throughout the ceramics with different sintering time. SEM analysis of these specimens confirms the above judgment of XRD. Moreover, the average-largest grain size is 1.5−2 μm (6−9 μm in Ref.[18]) for the specimen with different sintering time. It can be observed that the increase of grain size is not considerable with increasing the sintering time.

The interface thickness can be approximately calculated using SEM images of the samples. The interface thickness values are 0.107 7, 0.061 6 and 0.076 9 μm for the samples sintered for 4 h, 6 h and 8 h, respectively. Considering the IBLC model, the relative rates of t_g/t_{gb} are 18.57, 24.35 and 23.4, respectively (t_g is the thickness of grain or grain size and t_{gb} is the interface thickness), which indicate the best dielectric properties of 6 h-sintered sample.

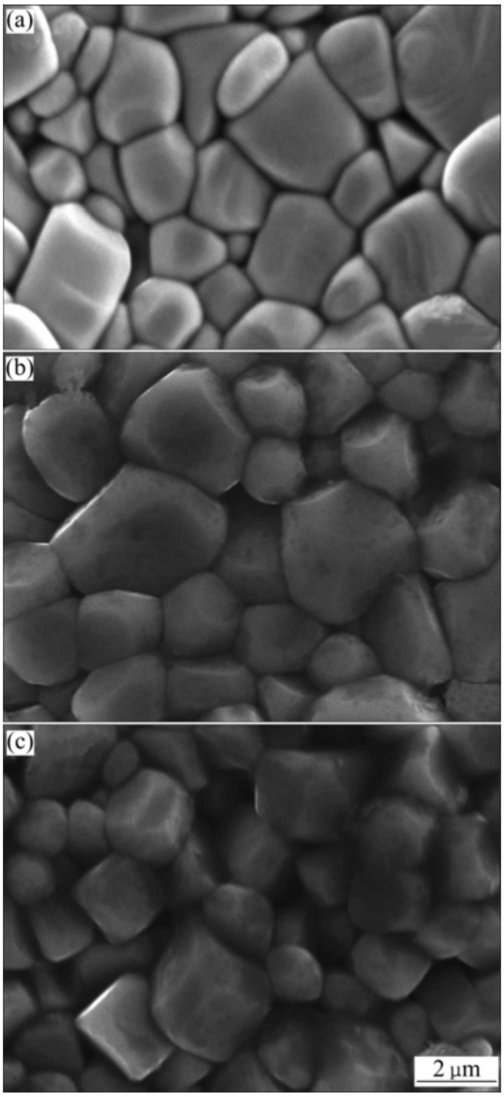

Fig. 3 SEM images of ceramics sintered for different time: (a) 4 h; (b) 6 h; (c) 8 h

3.3 Dielectric properties

Figure 4 shows the frequency dependence of the dielectric constant and dissipation factors at room temperature for the three samples. It is explicitly observed that the dielectric constant of CCTO ceramics increases for 6 h-sintered sample with increasing the sintering time and then a little decrease for 8 h-sintered sample. The ceramic sintered for 6 h has the lowest dielectric loss and the highest dielectric constant over all the frequency region of 50 Hz to 100 MHz. As can be seen in Fig. 5, the highest dielectric constant is shown in 6 h-sintered sample in all frequency range, but the dielectric loss of ceramics with medium sintering time is the best in low and middle frequency range and the ceramic with the shortest sintering time has the best dielectric loss in the high frequency range.

As can be observed, the 6 h-sintered sample exhibits the highest permittivity and the lowest dielectric loss. The highest CTO phase rate and the lowest CuO rate formed in the interface of CCTO ceramics may cause the variation of energy bond structure of CCTO ceramics, which results in the lower dielectric constant. The high CTO rate in the interface means that more Ti forms on the interface, which can enhance the dielectric properties. When the sintering time increases, the oxide phases may change the interfacial structure and damage the IBLC effect, which results in the decreasing of dielectric constant of CCTO ceramics.

In contrast to the published data, the dielectric loss for each CCTO ceramic is similar to the literature values

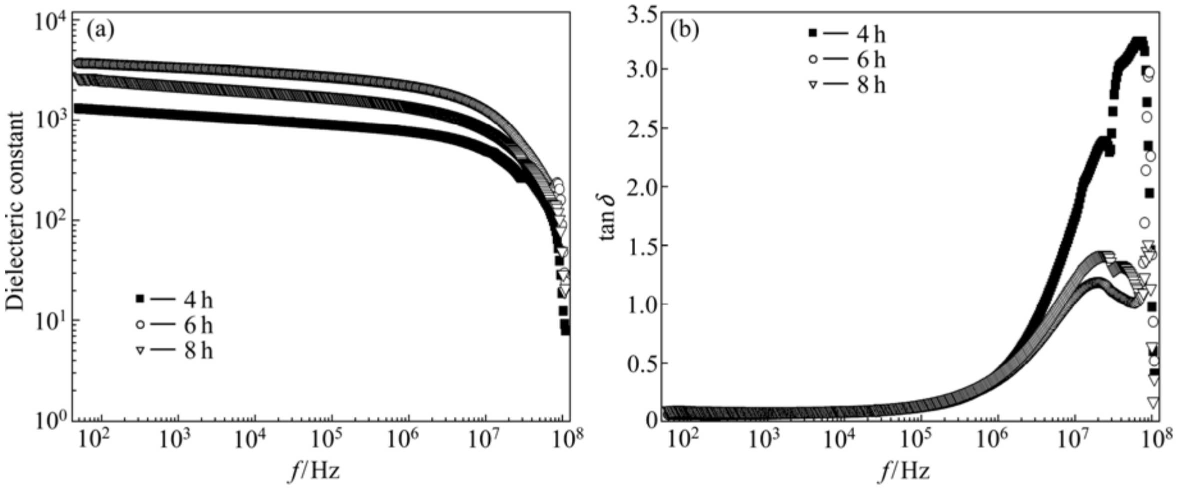

Fig. 4 Comparison of frequency dependences of dielectric properties of CCTO ceramics with different sintering time: (a) Dielectric constant; (b) Tangent of dielectric loss angle

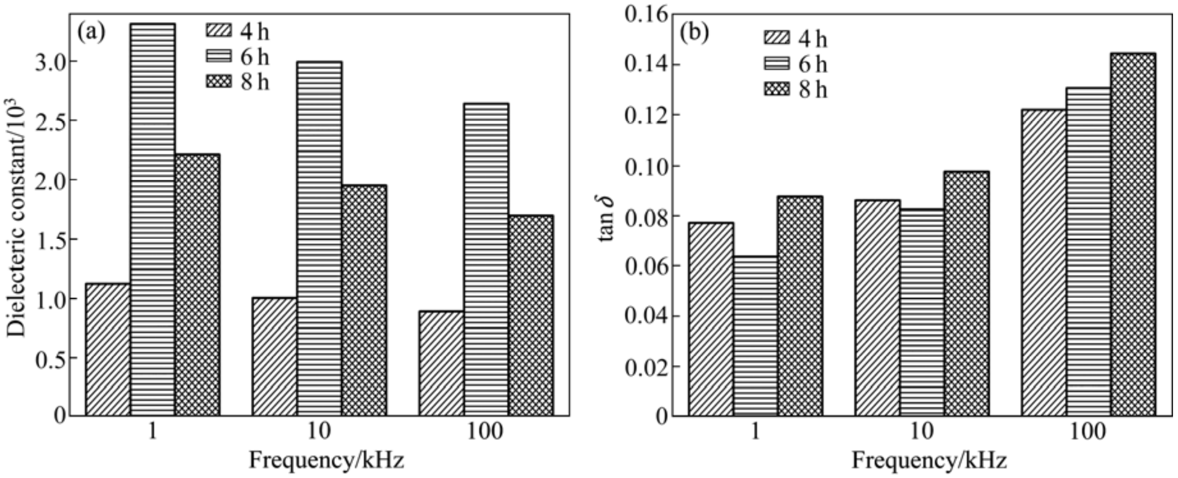

Fig. 5 Comparison of frequency regions of dielectric properties of CCTO ceramics with different sintering time: (a) Dielectric constant; (b) Tangent of dielectric loss angle

for large frequency region of 50 Hz to 100 MHz at room temperature, and is better than them under 100 Hz or between 1 MHz and 100 MHz [18]. On the basis of these observations, a good modification was performed on the dielectric loss of pure CCTO with different sintering time. The present technology has three advantages over the above mentioned good results. Firstly, the ceramics were prepared with a short sintering time. Secondly, the sintering temperature (1 000 °C) is lower than other published data (more than 1 100 °C) [10−11, 19−20, 24], and the present technology is more simple than these technologies that prepare ceramics with powder for sintering. Thirdly, the materials have a very good academically advantage: both of the dielectric constant and dielectric loss have a weak frequency dependence over all the large frequency region of 50 Hz to 100 kHz. It is believed that the present studies would help in providing more insight and rationalizing the dielectric behavior of these ceramics.

4 Conclusions

1) CCTO powder is prepared by sol-gel and formed into ceramics using cold pressing with different sintering time to construct a good interface of CCTO ceramics. A simple technology, short sintering time and low sintering temperature are utilized to prepare the ceramics.

2) With increasing the sintering time, the grain size of CCTO ceramics decreases and the density of specimens increases, but not linearly. The CCTO ceramic sintered for 6 h has the lowest dielectric loss and the highest dielectric constant overall the frequency range of 50 Hz to 100 MHz.

3) Both of the dielectric constant and dielectric loss have a weak frequency dependence over all the large frequency region of 50 Hz to 100 kHz.

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合成工艺对 $CaCu_3Ti_4O_{12}$ 陶瓷介电性能的影响

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摘　要：利用溶胶−凝胶工艺制备 $CaCu_3Ti_4O_{12}$ 粉体，经相同压力和时间冷压后，于 1 000 °C 下进行烧结，制备 $CaCu_3Ti_4O_{12}$ 陶瓷。微观组织观察表明，烧结时间对复合陶瓷的晶粒尺寸有显著的影响；烧结不同时间的复合陶瓷的介电常数和介电损耗在 50 Hz 到 100 kHz 的范围内表现出弱的频率相关性。随着频率的增加，复合材料的介电损耗降低，而介电常数保持在一个较高值。最佳的烧结时间为 6 h。

关键词：$CaCu_3Ti_4O_{12}$ 复合陶瓷；介电常数；介电损耗；烧结时间

(Edited by HE Yun-bin)