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LETTER

Sintering effects on structure and dielectric properties of dielectrics $CaCu_3Ti_4O_{12}$

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Introduction

Due to the continuous demand for miniaturization of electronics, there is an interest in developing dielectric materials with higher permittivity. Recently, the $CaCu_3Ti_4O_{12}$ (CCTO) has been reported [1–3], has a very high permittivity (~10^4) at room temperature and very small temperature dependence in a broad temperature range. However, it appears that the dielectric properties of CCTO are very sensitive to processing. [4–7] Permittivities from 478 to 300,000 have been obtained for CCTO prepared by different routes. The original work, done by Subramanian et al. [1] and Ramirez et al. [2] using conventional mixed-oxide processing via mortar and pestle, showed that room temperature permittivities ranged from 10,000 to 20,000. Other researchers using the same technique have reported permittivities of 478, 2400 and 18,700 [8–10]. The highest permittivity reported as derived from impedance spectroscopy measurements was 300,000 for CCTO made from powder that was mixed via ball milling and sintered for 24 h at 1100 °C [11].

Though different hypotheses have been put forth to explain the high permittivity of CCTO, its origin is still not fully justified. At present, the grain boundary barrier layer capacitance model of extrinsic mechanism is the most favorable one [12–19]. It is believed that insulating surfaces form on semi-conducting grains during the sintering of CCTO ceramics, which results in an electronically heterogeneous material very similar to the nature of internal barrier layers capacitors (IBLC). The dielectric properties of these IBLCS are very sensitive to different processing parameters.

In the present work, the CCTO ceramics are prepared by the solid-state reaction method. The sintering effects on the phase evolution, structure and dielectric properties of CCTO ceramics have been investigated.

Experimental

CCTO ceramics were prepared by the conventional solid-state reaction method using starting materials of $CaCO_3$ (>99%), CuO (>99%), TiO_2 (>99%). Stoichiometric amounts of powders were mixed in distilling water by ball milling with zirconia media for 12 h. After drying, the mixed powder was calcined in air at 950 °C for 2 h. The calcined powder was milled again, added about 5 wt% PVA as binder and pressed into disks of 13 mm in diameter and 1–2 mm in thickness. These disks were sintered at temperatures range from 1100 °C to 1150 °C for different times and then cooled to room temperature in the furnace.

The densities of samples were measured by Archimedes method. The crystalline phases were identified by powder X-ray diffraction analysis with Cu Kα radiation (XRD, D/max-IIIC). Microstructure of the ceramics was carried out in a scanning electron microscope (SEM, Philips XL30 ESEM-TMP). The dielectric properties and impedance analyses of the present ceramics were determined using the precision LCR meter (Agilent 4284A) in the frequency range from 20 Hz to 1 MHz over the temperature range of 25–150 °C.

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Results and discussion

The densities and relative densities of CCTO ceramics prepared at different processes are listed in Table 1. The data of CCTO ceramics sintering below 1120 °C and above 1140 °C are not shown because they are either too low density or over sintering. It clearly shows that density increases with sintering time and reach a maximum value for 6 h, beyond which the density decreases slightly. Meanwhile, sintering temperature has the similar effect.

Figure 1 shows SEM images of CCTO ceramics prepared at different processes. There are two classes of different grain sizes in the microstructure of the present ceramics. A small amount of small grains exist in the grain boundary of large grains for the ceramics sintered at 1120 °C for 6 h and 12 h. The large and relatively uniform grain is in the order of some tens of micrometers. And the average grain size increases with the increasing sintering time. But the bimodal distribution of grain sizes and pores are clearly observed in the ceramics sintered at 1130 °C for short time 3 h. One class has the grain sizes of several micrometers; the other has the larger grains sizes of about 10 micrometer.

Figure 2 illustrates the room temperature XRD patterns of CCTO ceramics prepared at different processes. Apparently, all these samples reveal the quite similar diffraction profiles and diffraction peaks corresponding to CCTO phase (JCPDS No. 75-2188) with cubic perovskite related structure. In addition, little $CaTiO_3$ and CuO phases presents in the ceramics sintered at 1120 °C for 3 h. With prolong sintering, CuO disappears, while very little $CaTiO_3$ still exists. Besides, sparklet of TiO_2 appears in the longest sintered ceramics. As a certain sintering time 3 h, the similar phases are observed in the ceramics with sintering temperature from 1120 to 1140 °C. TiO_2 phase appears in the ceramics due to CCTO decomposition and CuO volatilization [20].

Table 1 Densities of CCTO ceramics prepared at different processes

Sintering process	1120 °C/ 3 h	1120 °C/ 6 h	1120 °C/ 12 h	1130 °C/ 3 h	1140 °C/ 3 h
Density (g/cm^3)	4.53	4.80	4.74	4.62	4.47
Relative density (%)	89.2	95.5	94.1	89.7	88.9

Figure 3 represents the room temperature permittivity and loss for CCTO ceramics prepared at different processes. It is clear that all of these samples exhibit the giant permittivity at low frequency. As the frequency increases, permittivity drastically decreases in the frequency range below 1 kHz; and then becomes flat. There are wide dielectric loss peaks around 1 kHz for the present ceramics. The permittivity increases with decreasing frequency suggests the possibility of the presence of interfacial polarization. It is possible that the charge carriers may be blocked at an electrode interface when migrated under the influence of an electric field, which results in interfacial polarization. At the same time, the frequency dependence of dielectric properties of CCTO ceramics is closely related to the polycrystalline microstructure. At present, most of the investigations [3–6, 12–19] point out that CCTO ceramics consist of insulating grain

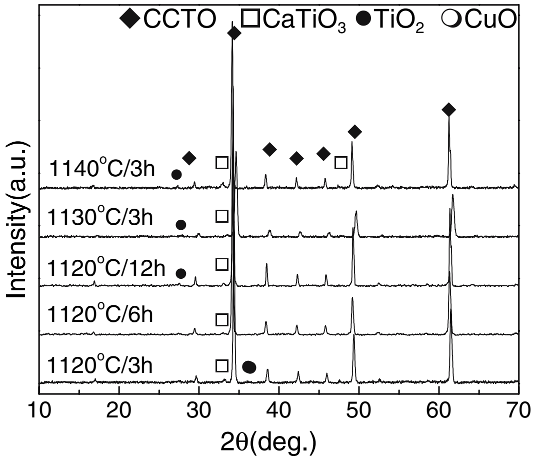

Fig. 2 XRD patterns of CCTO ceramics prepared at different processes

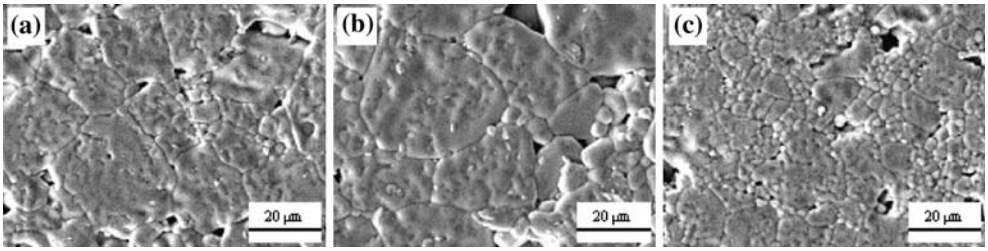

Fig. 1 SEM images of various CCTO ceramics sintered at different processes: 1120 °C for (**a**) 6 h and (**b**) 12 h; (**c**) 1130 °C for 3 h

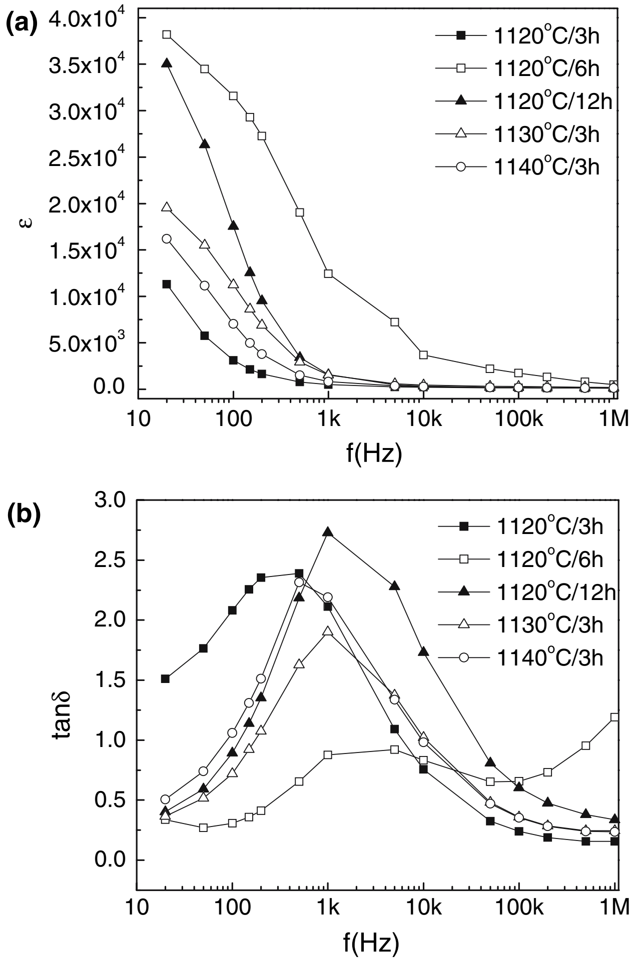

Fig. 3 Frequency dependence of permittivity (**a**) and loss (**b**) of CCTO ceramics prepared at different processes

boundaries and semi-conducting grains. The difference of conductivity between grain boundary and grain volume causes the charge accumulation on the grain boundary, which results in large quantity boundary barrier layer capacitors, that is the famous Maxwell–Wagner effect. These capacitors connect in parallel or series, so the CCTO ceramics represents very high permittivity, especially performances more obviously under lower frequency.

Moreover, the dielectric properties are found to strongly depend on the sintering process. The sample sintered at 1120 °C for 3 h shows the lowest permittivity of about 514 at 1 kHz, and the one sintered at 1120 °C for 6 h gives the highest value over 12,400. The significant difference is due to the different microstructure. As stated above, there displays different microstructures for the ceramics sintered with different processes. It is well known that the microstructure remarkably influences the dielectric properties of ceramics, especially for the CCTO ceramics with internal barriers.

The changes in the permittivity and loss, measured at 1 kHz, versus the temperature (25–150 °C), are given in Fig. 4 for the CCTO ceramics prepared at different processes. As can be seen, the temperature dependence of dielectric properties can be classed three categories. The first is the specimen sintered at 1120 °C for 3 h. Permittivity linearly increases with the increasing temperature. The dielectric loss decreases at first and then turns to increase with the increasing temperature. But the category has the largest dielectric loss and the lowest permittivity. The second is the specimen sintered at 1120 °C for 6 h. Permittivity quickly increases below 20 °C and reaches one plateau, then rapidly increases again above 110 °C. This phenomenon is similar with previous report [21], however, different from most reports [1–3]. And this exhibits a similar dielectric loss variation with temperature. The dielectric loss is the lowest. The last is the other specimens with intermediate dielectric loss. The variation of permittivity is similar that of the second. While the plateau is not obvious, especially for the specimen prepared at 1140 °C for 3 h, whose permittivity shows little change with increasing temperature.

Recently, most of reports point out that the large dielectric responses in CCTO ceramics are associated with the grain boundary barrier layer capacitor. The grain boundary barrier layer capacitor usually consists of conducting or semi-conducting bulk grains and insulating grain boundary layers. This structure can be modeled by using an equivalent impedance circuit that consists of two parallel RC elements in series; R and C represent resistance and capacitance. One pair of the parallel RC elements represents the grain boundary layers, while the second pair of the parallel RC elements represents the bulk grains. Figure 5 shows the room temperature complex impedance spectroscopy for CCTO ceramics prepared at different processes. For all the samples, there are two clear semicircular arcs in the complex impedance spectroscopy at room temperature within the measuring frequency range of 20 Hz–1 MHz, corresponding to two parallel RC elements in series. The large arc is due to the insulating grain boundary responses at low frequencies and the small arc is due to the semi-conducting bulk grain responses at high frequencies. So, there generates large quantity boundary barrier layer capacitors in CCTO ceramics, which lead to high permittivity. Though this phenomenon is different from most reports [1–3], it is similar with the observation reported by Matos and Walmsley [22].

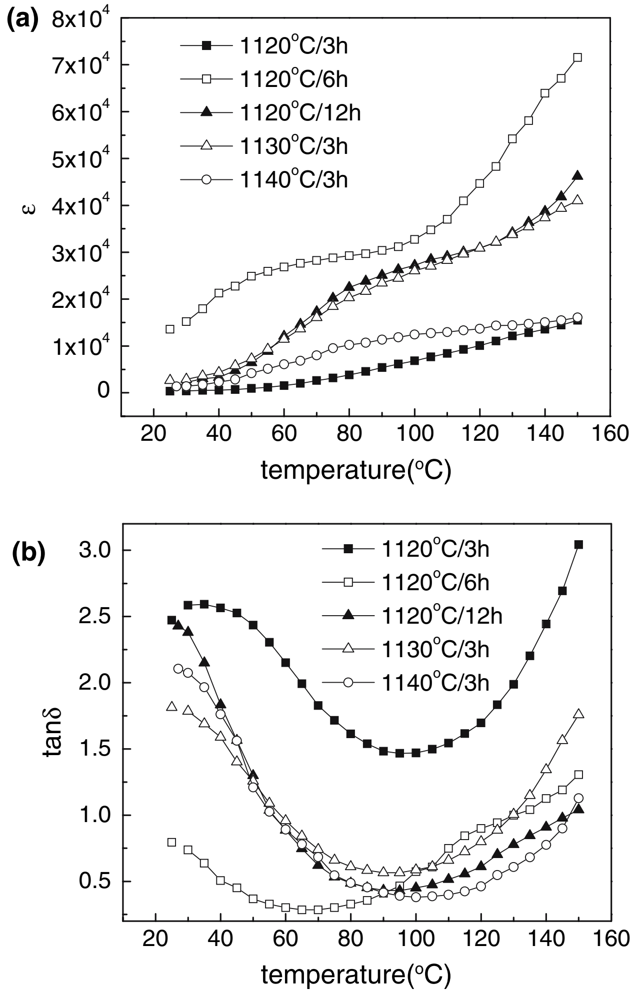

Fig. 4 Temperature dependences of permittivity (**a**) and loss (**b**) at 1 kHz for CCTO ceramics prepared at different processes

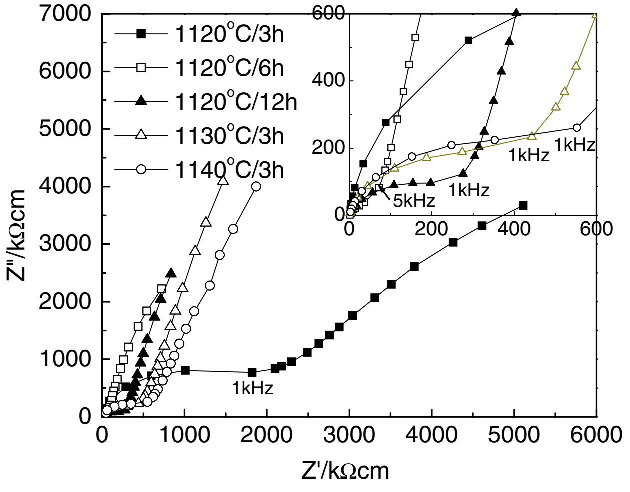

Fig. 5 Impedance Spectroscopy of CCTO ceramics prepared at different processes. The inset shows an enlarged view of high frequency data close to the origin

Generally, the grain resistance is much smaller than the boundary resistance and decreases with the sintering temperature and sintering time. As shown in Fig. 5, it's clearly shown that the grain resistance of the sample sintered at 1120 °C for 6 h is much lower than that of the sample sintered at 1120 °C for 3 h. It seems the phenomenon that grain resistance decreases with sintering temperature and sintering time, might be understood from the viewpoint of oxygen vacancies, which are considered to have the close relationship with the conducting carriers.

Fang et al. [23] study the theoretical electronic structure in CCTO and $CdCu_3Ti_4O_{12}$ by using the extend Hückel method within a paramagnetic electronic configuration and find that breaking cation-O and –Ti bonds in CCTO is easier than in the Cd compound. It could be expected that oxygen vacancy formation is more likely to occur in CCTO. In another study [24], CCTO thin films with high dielectric constants were successfully grown on $Pt/Ti/SiO_2/Si(100)$ substrates. Larger dielectric relaxation, both for the permittivity and loss tangent, was observed when the sample was post-annealed at 550 °C in N_2 atmosphere. This effect was attributed to the generation of oxygen vacancies. After annealing the sample in an oxygen atmosphere at high temperature, which leads to oxygen vacancies compensation, the dielectric relaxation disappeared. We have prepared CCTO ceramics by sintered in O_2-riched atmospheres at 1120 °C for 6 h. The dielectric properties of ceramics are strongly dependent of atmosphere, the permittivity is only 346 at room temperature in 1 kHz, and the resistivity of grains higher than the ceramics of sintered at air. These results show that oxygen in CCTO was easier to lose in sintering, so lead to lower resistivity of grains. At the same time, the grain boundaries were reoxidation during cooling. So, the more internal resistive barriers are gained, which results in the larger effective permittivity in CCTO ceramics.

The most interesting feature of these results in the large enhancement of permittivity at 1 kHz from ~1500 for ceramics sintered at 1130 °C for 3 h to ~12,400 for ceramics sintered at 1120 °C for 6 h (Fig. 3a). This enhancement is clearly linked to the differences in ceramic microstructure and in particular, even in the grain size. Li et al. [25] point out that the permittivity (ε) of CCTO ceramics, which capacitance is contributed by the grain boundary capacitance, was calculated by using following formula.

$$\varepsilon = \frac{D}{d}\varepsilon_b$$

where D is the grain size, d the boundary layer thickness and ε_b the permittivity of the insulating layer. So increasing the grain size and decreasing the boundary layer thickness would produce an increase in the permittivity. For sample sintered at 1130 °C for 3 h, there exist two classes of different grain sizes (~3 μm and 10 μm, Fig. 1c). As exhibited in Fig. 1(a), samples sintered at 1120 °C for 6 h display the large grain size (~19 μm) and the comparatively uniform distribution. So, the permittivity of CCTO ceramics sintered at 1120 °C for 6 h higher than that of others.

Conclusions

$CaCu_3Ti_4O_{12}$ (CCTO) ceramics were sintered with different temperatures or durations. Strong sintering effect on microstructure was found in CCTO ceramics. To appropriately extend sintering time would benefit the densification and formation of bigger and uniform grain of CCTO ceramics. The samples sintered at 1120 °C for 3 h showed the lowest permittivity of about 514 at 1 kHz, and the ones sintered at 1120 °C for 6 h gave the highest value large than 12,400. Furthermore, larger grains resulted in higher permittivity. According to the impedance spectroscopy of CCTO ceramics, the high permittivity could be associated Maxwell–Wagner model, which was result from semiconducting grains and insulating grain boundaries.

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References

1. Subramanian MA, Li D, Duan N, Reisner BA, Sleight AW (2000) J Solid State Chem 151:323
2. Ramirez AP, Subramanian MA, Gardel M, Blumberg G, Li D, Vogt T (2000) Solid State Commun 115:217
3. Homes CC, Vogt T, Shapiro SM, Wakimoto S, Ramirez AP (2001) Science 121:625
4. Ni L, Chen XM, Liu XQ, Hou RZ (2006) Solid State Commun 139:45
5. Almeida AFL, Fechine PBA, Kretly LC, Sombra ASB (2006) J Mater Sci 41:4623
6. Guillemet-Fritsch S, Lebey T, Boulos M, Durand B (2006) J Eur Ceram Soc 26:1245
7. Shri Prakash B, Varma KBR (2006) Phys B 382:312
8. Choudhary RNP, Bhunia B (2002) Mater Sci 37:5177
9. Jha P, Arora P, Ganguli AK (2003) Mater Lett 57:2443
10. Sinclair DC, Adams TB, Morrison FD, West AR (2002) Appl Phys Lett 80:2153
11. Adams TB, Sinclair DC, West AR (2002) Adv Mater 14:1321
12. Zhang L, Tang ZJ (2004) Phys Rev B 70:174306
13. West AR, Adams TB, Morrison FD, Sinclair DC (2004) J Eur Ceram Soc 24:1439
14. Chiodelli G, Massarotti V, Capsoni D, Bini M, Azzoni CB, Mozzati MC, Lupotto P (2004) Solid State Commun 132:241
15. Capsoni D, Bini M, Massarotti V, Chiodelli G, Mozzatic MC, Azzoni CB (2004) J Solid State Chem 177:4494
16. Homes CC, Vogt T, Shapiro SM, Wakimoto S, Subramanian S (2003) Phys Rev B 67:092106
17. Cohen MH, Neaton JB, He LX, Vanderbilt D (2003) J Appl Phys 94:3299
18. Fang TT, Shiau HK (2004) J Am Ceram Soc 87:2072
19. Zhang L (2005) Appl Phys Lett 87:022907
20. Lu FH, Fang FX, Chen YS, (2001) J Eur Cream Soc 21:1093
21. Zhang JL, Zheng P, Wang CL, Zhao ML, Li JC, Wang JF, (2005) Appl Phys Lett 87:142901
22. Matos M, Walmsley L (2006) J Phys: Condens Matter 18:1793
23. Fang L, Shen M, Cao W (2004) J Appl Phys 95:956483
24. Shao SF, Zhang JL, Zhang P, Zhong WL, Wang CL, (2006) J Appl Phys 99:084106
25. Li JR, Cho K, Wu NJ, Ignatiev A (2004) IEEE T Dielect El In 11:534