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Influence of sintering atmosphere on dielectric properties and microstructure of $CaCu_3Ti_4O_{12}$ ceramics

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Abstract

$CaCu_3Ti_4O_{12}$ (CCTO) ceramics were sintered in the mixed gases flow of O_2 and N_2 with different volume ratios by the solid state reaction method, the volume ratios were strictly controlled by a gas mixture proportioner during sintering. The effects of different volume fractions of O_2 (x) on the microstructure and dielectric properties of CCTO ceramics were investigated. The appearance of Cu_4O_3 phase in the XRD patterns when $x \geq 20\%$, suggests that a chemical reaction had occurred between Cu_2O and O_2. The Gibbs energy of formation of CCTO was closely related to the ternary phase relations of system CaO–CuO/Cu_2O–TiO_2, and the decrease of x promoted the decomposition of CCTO. All the samples showed high dielectric constant ($\geq 5 \times 10^3$) in a broad frequency range from 20 Hz to 100 kHz, which decreased gradually with increasing x. Cole–Cole plots of conductivity suggested that the resistivity of grain and grain boundary both increased with increasing x. With the variation in the conductivity of grain boundary which is caused by the increasing x.

Keywords: A. Grain growth; B. Grain boundaries; C. Dielectric properties; C. Impedance

1. Introduction

The perovskite-like CCTO ceramics have attracted increasing interests because of the giant dielectric constant (of the order of 10^4) with weak frequency and temperature dependence in these years [1–3]. The effective dielectric constant (ε_{eff}) of CCTO is directly proportional to the ratio of the average grain size (t_g) to average thickness of the insulating layer (grain boundary, t_{gb}) [3–5]. Andreja et al. [6] found that postannealing atmosphere (N_2 or O_2) governed the distinctive contributions of insulating grain boundaries and semiconducting grains in different temperature and frequency ranges. The suppression (and recovering) of the colossal dielectric constant effect of CCTO thin films on annealing under O_2 (N_2) atmosphere have been reported by Rubinger et al. [7]. Therefore, focused research on microstructure and electrical properties of the grain/grain boundary becomes the key important method in exploring the dielectric properties of CCTO ceramics, additionally, improving our understanding of how to process CCTO ceramics to optimize the internal barrier layer capacitance (IBLC) effects [5,8,9]. In this paper, we prepared the CCTO ceramics in the mixed gases flow of O_2 and N_2 with different volume ratios, the volume ratios were strictly controlled by a gas mixture proportioner during sintering, mainly focused on exploring the dielectric responses of CCTO ceramics, which was affected by x.

2. Material and methods

CCTO ceramics were prepared by a solid state reaction process using the high purity materials of $CaCO_3$, CuO and TiO_2. The raw materials were weighed according to the stoichiometric ratios and mixed in ethanol, ball milled for 24 h. The dried mixtures were calcined at 950 and 1000 °C for 12 h in air. The CCTO powders with 3 wt% polyvinyl alcohol (PVA) were pressed into disks under a pressure of 60 MPa. The disk samples were sintered at

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1100 °C in a tube oven for 12 h. The tube oven was connected with a gas mixture proportioner to obtain a mixed gases flow of O_2 and N_2 ($x=10\%$, 15%, 17.5%, 20%, 22.5% and 25%). The crystal structures of samples were confirmed by powder X-ray diffraction (XRD; Cu Kα, 50 kV, 100 mA, Model Rad; Rigaku, Tokyo, Japan). The microstructures were evaluated by scanning electron microscopy (SEM; JEOL JSM-T330, Japan).

For the electrical and dielectric measurements, Ag electrodes were screen printed with Ag pastes on both sides of the pellets and heat treated at 650 °C for 20 min. The frequency dependence of the dielectric properties was measured by a precision LCR meter (Agilent E4980A) in a frequency range from 20 Hz to 2 MHz. The Cole–Cole plots of conductivity were measured and fitted by an HP 4192A impedance analyzer (Palo Alto, CA) in a frequency range from 40 Hz to13 MHz.

3. Results and discussion

Fig. 1 shows the XRD patterns of the CCTO samples sintered in different sintering atmospheres. The results indicate the presence of small amounts of CuO, $CaTiO_3$ and TiO_2 phases in these patterns, it is due to the decomposition of CCTO, which is consistent with previous reports [10]. Because of the oxidation-reaction of CuO at 1100 °C [11], cuprite phase (Cu_2O) appears in all the XRD patterns. Paramelaconite phase (Cu_4O_3) appears in the XRD patterns when $x \geq 20\%$, it is indicated that a chemical reaction had occurred between Cu_2O and O_2 during sintering. The pseudo-ternary system CaO–CuO/Cu_2O–TiO_2 is formed in the samples at 1100 °C [12], the ternary phase relations were very sensitive to x. The Gibbs energy of formation of CCTO was closely related to the ternary phase relations of system CaO–CuO/Cu_2O–TiO_2, and the decrease of x promoted the decomposition of CCTO, so the peak intensities of the $CaTiO_3$ and TiO_2 weakened in the patterns with increasing x.

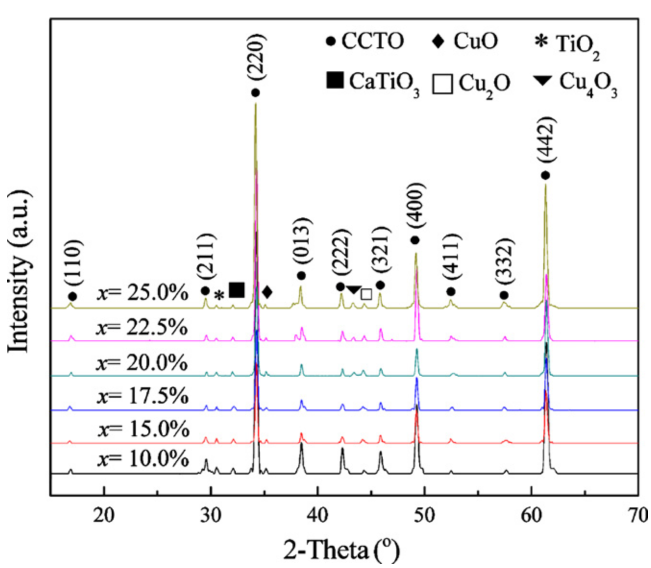

Fig. 1. X-ray diffraction patterns of CCTO samples sintered at 1100 °C for 12 h in different sintering atmospheres.

The evolution of the polished of the CCTO ceramics with various sintering atmospheres is shown in Fig. 2. The CCTO samples all show the microstructure consisting of coarse grains (10–25 μm) surrounded by fine grains (2–3 μm), and the approximate percentage of fine grains increase with increasing x. When the oxygen partial pressure was very low in the sintering atmosphere, oxygen atoms separated from the ceramic lattice, the oxygen vacancies formed at the grain surface, the increase of oxygen vacancy promote the substances exchange between the grains, so the grain size of sample ($x=10\%$) increased to 10–30 μm. As x increased, the number of oxygen vacancies decreased gradually, which led to the grain growing slowly, so the average grain size decreased.

Fig. 3 shows the Cole–Cole plots of conductivity of the CCTO samples sintered in different sintering atmospheres. The Cole–Cole plots of conductivity can reflect the resistivity variation of the grain and grain boundary (R_g, R_{gb}). The radiuses of the semicircular arcs decrease with increasing x, it is indicated that the conductivity of the grain decreases, which can figure out R_g increases from 75 to 400 Ω cm (13 MHz). The low-frequency region (40 Hz) show that conductivity at crossing point (between real axis and arc) decreases from about 1.07×10^{-5} to 5.16×10^{-7} S cm^{-1}, it can figure out the value of R_g+R_{gb} increases from about 2.84×10^{4} to 1.93×10^{6} Ω cm with increasing x. It can be estimated that R_{gb} predominate in the value of R_g+R_{gb}, so the R_{gb} also increases with

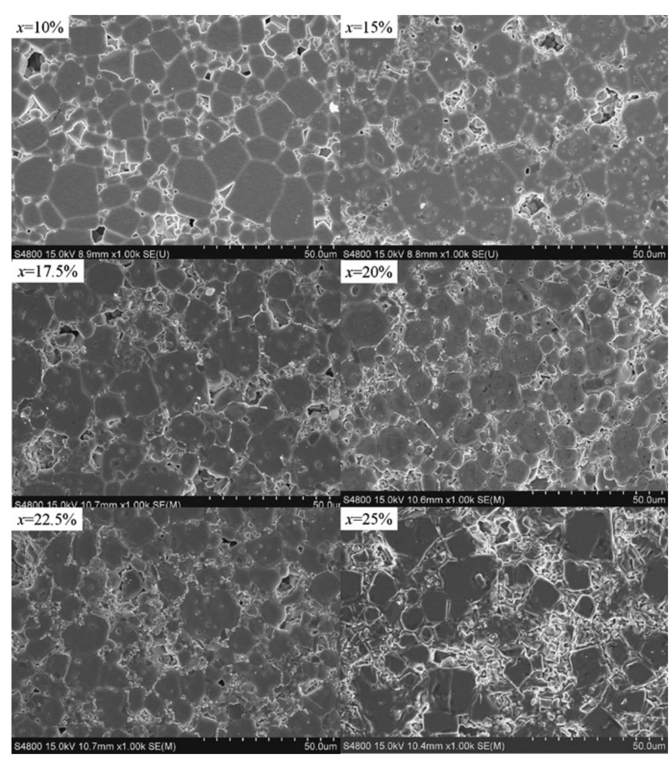

Fig. 2. SEM images of CCTO samples sintered at 1100 °C for 12 h in different sintering atmospheres.

increasing x. The variations of the R_g and R_{gb} are caused by the activities of the oxygen vacancies and free electrons, which correspond to different x.

Fig. 4 shows the frequency dependence of the dielectric properties of the CCTO samples sintered in different sintering atmospheres. All the samples show high dielectric constant (≥ 5000) in a broad frequency range from 20 Hz to 100 kHz, which decreases gradually from 2×10^4 to 5×10^3 with increasing x. When $x\leq17.5\%$, oxygen vacancies and free electrons are formed more in these CCTO samples according to Eq. (1):

$$O \rightarrow V_o^{\bullet\bullet} + 2e + (1/2)O_2 \quad (1)$$

The free electrons cause space charge distribution at grain boundary [13], and the high value in dielectric constant is attributed to a major contribution from the space charge polarization [14]. Fig. 4(b) shows the CCTO sample (when $x=10\%$) having the lower dielectric loss (0.05–0.01) over the frequency range from 1 kHz to 1 MHz, it is due to the relatively more coarse-grained microstructure of this sample [15]. From Fig. 4(b), we can see that when the frequency was lower than the range from 20 kHz to 40 kHz, the dielectric loss decreases with increasing x, but when the frequency was higher than this frequency range, it showed an opposite phenomenon. According to Fig. 3, the complex admittance Y^* can be shown as Eq. (2) [16]:

$$Y^* = [1-\omega^2 R_g R_{gb} C_{gb} + i\omega(R_g + R_{gb} C_{gb})]/(R_g + i\omega R_g R_{gb} C_{gb}) \quad (2)$$

where ω is the angular frequency, C_{gb} is the effective capacitance of grain boundary. Because $R_g \ll R_{gb}$, the admittance G is shown as Eq. (3):

$$G = (1+\omega^2 R_g R_{gb} C_{gb}^2)/(R_{gb} + \omega^2 R_g^2 R_{gb} C_{gb}^2) \quad (3)$$

and $\omega R_{gb} C_{gb} \ll 1$, $C_{gb} \approx C_p$, C_p is the measurement capacitance. The dielectric loss can be shown as Eq. (4):

$$\tan\delta = G/(\omega C_p) \quad (4)$$

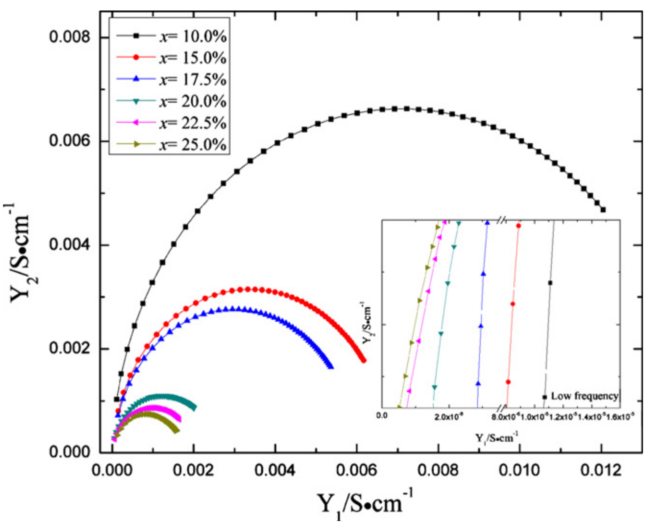

Fig. 3. Cole–Cole plots of conductivity at 300 K for the CCTO samples sintered at 1100 °C for 12 h in different sintering atmospheres.

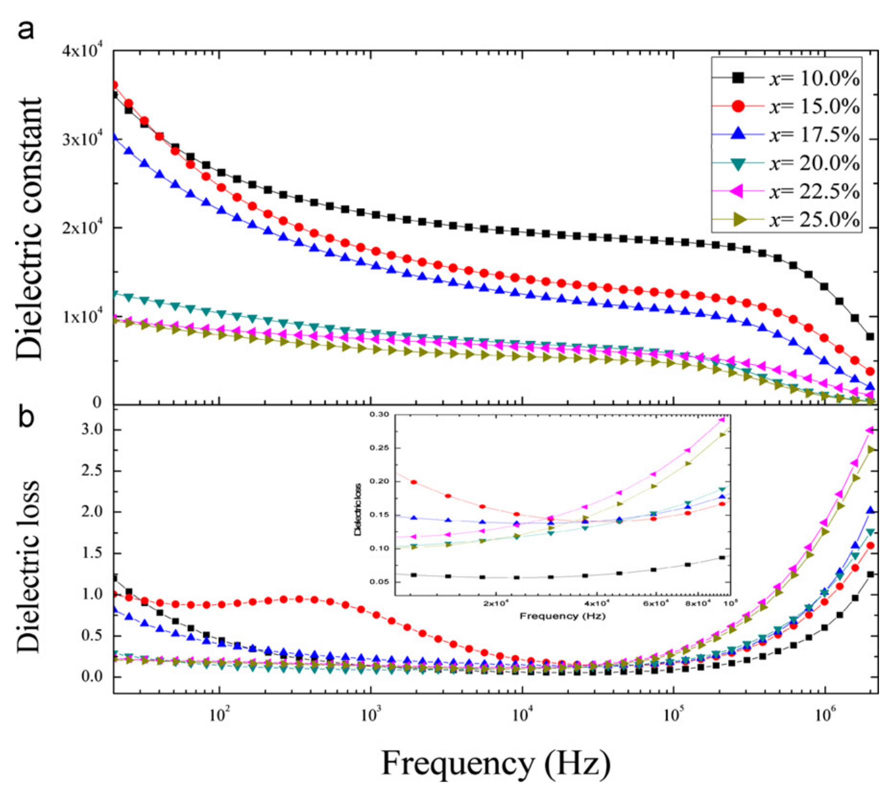

Fig. 4. Frequency dependence of dielectric constant (a) and dielectric loss (b) of the CCTO samples sintered at 1100 °C for 12 h in different sintering atmospheres.

so,

$$\tan\delta = 1/\left(R_{gb}C_p\right) + \omega R_{gb}R_gC_{gb}/C_p \approx 1/\left(\omega R_{gb}C_p\right) + \omega R_{gb} \quad (5)$$

when the frequency is <20–40 kHz, the dielectric loss depends on the first part of Eq. (5), R_{gb} and C_p increased, so the dielectric loss decreased with increasing x. By the same reasoning method, we can know that the dielectric loss increased with increasing x when the frequency is greater than the range of 20–40 kHz.

4. Conclusions

The microstructure and dielectric properties of CCTO ceramics prepared in the mixed gases of O_2 and N_2 were investigated. With the increasing x, the dielectric constant decreased gradually from 2×10^4 to 5×10^3. Cole–Cole plots of conductance suggested that the resistivity of grain and grain boundary both increased with increasing x (volume fractions of O_2 in atmosphere).

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