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Decrease of dielectric loss in giant dielectric constant $CaCu_3Ti_4O_{12}$ ceramics by adding $CaTiO_3$

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Abstract

$CaCu_3Ti_4O_{12}$–$x$$CaTiO_3$ ceramics ($x = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5) was studied by X-ray diffraction, scanning electron microscope and dielectric measurements. It was indicated that some $CaTiO_3$ entered the boundaries of $CaCu_3Ti_4O_{12}$ grains and/or subgrains. Dielectric measurement showed that the addition of $CaTiO_3$ lowered the dielectric loss remarkably, especially at low frequencies, while the giant dielectric constant still remained. At room temperature, the dissipation factor of the $x = 0.5$ sample was decreased to ~0.02 over the frequency range from 50 to 2000 Hz, and the dielectric constant was kept to be 4000. We explain this phenomenon in terms of internal barrier layer capacitance model by using the impedance spectroscopy analysis.

Keywords: Dielectric loss; Dielectric constant; $CaCu_3Ti_4O_{12}$ ceramics

1. Introduction

The complex titanate $CaCu_3Ti_4O_{12}$ (CCTO) has recently attracted particular attentions in the field of dielectric materials. The provskite-like compound shows temperature independent giant dielectric constant over a wide temperature range [1–3]. This dielectric property makes CCTO a promising material in the area of micro-electronic techniques. Nevertheless, the relatively high dissipation factor in CCTO is not desirable for the practical applications.

To find a rational route to lower the dielectric loss, one needs to understand the mechanism of the giant dielectric response in CCTO. Based on the impedance spectroscopy (IS) measurement, Sinclair et al. [4] proposed an internal barrier layer capacitance (IBLC) model. They suggested that the CCTO ceramics were electrically heterogeneous and consisted of semiconducting grains with insulating grain boundaries. By using micro-contact current–voltage measurements, Chung et al. [5] showed that there did exist an intrinsic electrostatic barrier at the grain boundaries. Very recently, Li et al. [6] investigated the IS spectrum on CCTO crystals, giving the evidence of internal barriers within a crystal. In a word, the IBLC mechanism has been commonly accepted as the origin of the giant dielectric constant in the CCTO material.

According to the IBLC picture, the dissipation factor is closely related to the insulation of the barrier layers. The conductance of the barriers leads to the leakage loss. However, the nature of the internal barriers is not clear up to present. Plan-view TEM studies [7] showed that the CCTO films, whose composition was $Ca_{1.5}Cu_3Ti_{5.5}O_{16}$, had orthogonal nano-size domain structures with the edge nearly parallel to either the [1 0 0] or the [0 1 0] direction. Considering the obviously excess Ca and Ti in the sample, we speculate that the barrier layers may be associated with the $CaTiO_3$-like matter. Therefore, we tried to add small amount of $CaTiO_3$ into CCTO to increase the insulation of the internal barriers. As a result, we found that the dielectric loss of the $CaCu_3Ti_4O_{12}$–$x$$CaTiO_3$ (CCTO–CTO) ceramics was really lowered remarkably, compared with the parent material, while the giant dielectric property still remained.

2. Experimental

Ceramic samples of $CaCu_3Ti_4O_{12}$–$x$$CaTiO_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) were prepared by a conventional solid-state reaction. Stoichiometric amounts of high purity $CaCO_3$ (99.99%), CuO (99.99%) and TiO_2 (99.99%) were mixed thoroughly in an agate mortar. The mixture was pressed into pellets and calcined at 1273 K for 12 h in air. This procedure was

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repeated twice for the adequate reaction. Finally, the pressed disks of 10 mm in diameter and about 2 mm in thickness were sintered in air for 24 h and furnace-cooled to room temperature. In order to obtain the comparable samples that have the similar density and grain size, the sintered temperature was 1373 K for $x = 0, 0.1, 0.2$ and 0.3, 1383 K for $x = 0.4$ and $x = 0.5$. All the samples were characterized by X-ray diffraction (XRD) at room temperature using Cu Kα radiations as the X-ray source. In addition, we also employed field-emission scanning electron microscope (SEM, SIRION FEI, Netherlands) to investigate the microscopic morphology of the samples.

The dielectric properties were obtained by using the ordinary capacitive technique. The disk samples were polished and then electroded with silver paste to form a parallel plate capacitor. The capacitance C_p and the dissipation factor D of the capacitor were directly measured in the frequency range of 20–10^6 Hz and the temperature range of 90–330 K with the four-terminal coaxial cables connected to an Agilent 4284A precision LCR meter at an ac voltage of 1 V. Suppose the sample's thickness and the area of the electrodes are d and A, respectively, the relative dielectric constant ε_r can be obtained by

$$\varepsilon_r = \frac{d}{\varepsilon_0 A} C_p, \tag{1}$$

where ε_0 is the dielectric constant of vacuum. The complex impedance can be calculated by

$$Z^* = \frac{1}{i\omega C^*}, \tag{2}$$

where C^* represents the complex capacitance, $C^* = C_p - iDC_p$; and ω is the angular frequency of the applied electric field, $\omega = 2\pi f$.

3. Results and discussion

Fig. 1 shows the XRD patterns for the powdered samples of $CaCu_3Ti_4O_{12}$–$x$$CaTiO_3$ (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5). As can be seen, the samples of $x < 0.3$ are in single CCTO phase. For the samples of $x \geq 0.3$, small amount of $CaTiO_3$ impurity phase starts to appear (see the inset). However, even in the case of $x = 0.5$, in which the initial volume ratio of $CaTiO_3$ to CCTO is about 1:8 (=12.5%), the volume fraction of $CaTiO_3$ in the resultant sample is less than 5%, as estimated by comparing the heights of the strongest peaks of CCTO and $CaTiO_3$. This indicates that part of the $CaTiO_3$ does incorporate with CCTO. If some Ca^{2+} substituted for Cu^{2+}, one would expect the substantial increase of the cell constant. However, all the samples have the identical lattice constant of $a = 7.391(1)$ Å. This fact suggests that the incorporated $CaTiO_3$ enters the barrier layers of subgrain boundaries and/or grain boundaries.

Fig. 2 shows SEM images of the surface of $CaCu_3Ti_4O_{12}$–$x$$CaTiO_3$ ceramics. The morphology is characterized by the close packing of shaped grains with the size ranging from 3 to 10 μm. It can be seen that the grain size does not change so much from sample to sample. No secondary phase can be seen for the samples of $x \leq 0.3$, in agreement with the XRD result, while small amount of secondary phase in polyhedral shape with the grain size of ~1 μm appears in the cases of $x = 0.4$ and 0.5. The composition of the impurity was determined to be approximately "$CaTiO_3$" by the energy dispersive X-ray spectroscopy. Considered the well lattice-match between CCTO and $CaTiO_3$, and from the hint of the TEM study in CCTO films [7], the microstructure inside the CCTO–CTO grains can be speculated as orthogonal submicron-size CCTO subgrains wrapped by $CaTiO_3$-like layers. A detailed TEM study is expected to confirm this picture.

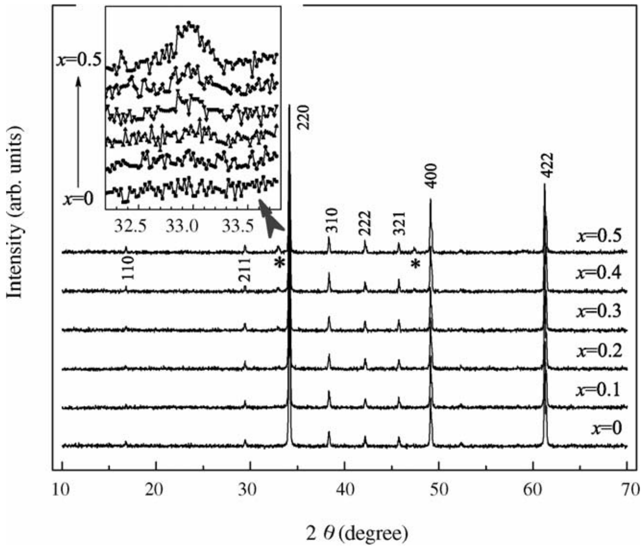

Fig. 1. XRD patterns of $CaCu_3Ti_4O_{12}$–$x$$CaTiO_3$ powdered samples at room temperature. The inset is an expanded view, showing the appearance of small mount (<5%) of $CaTiO_3$ for $x \geq 0.3$ samples.

Fig. 3 shows the temperature dependence of the dielectric constant and the dissipation factor at 1 kHz for the CCTO–CTO ceramics. In the upper panel, one can see that all the samples show very large dielectric constant (over 3500) above 100 K. The dielectric constant decreases with the addition of $CaTiO_3$. According to the IBLC model, the apparent dielectric constant can be magnified by the formula $\varepsilon_{r,app} = \varepsilon_b(L/t)$, where ε_b is the relative dielectric constant of the barriers, L and t represent the size of the CCTO grains/subgrains and the thickness of the corresponding boundaries (probably $CaTiO_3$-like layers), respectively. Since the average grain size does not vary so much, the decrease of ε_r is mainly ascribed to the increase of t due to the incorporation of $CaTiO_3$. If so, compared with the parent sample t value will increase by about four times for the $x = 0.5$ specimen, according to the change of ε_r. In Fig. 3(b), it can be seen that the tan δ values decrease remarkably in the whole temperature range with the addition of $CaTiO_3$. Above 180 K, the $x = 0.4$ and 0.5 samples have the dissipation factors 5–14 times lower than those of CCTO. For example, the tan δ value at 330 K decreases from about 0.28 to about 0.02 as x increases from 0 to 0.5. We will discuss this issue in some details later.

The frequency dependence of ε_r and tan δ at 300 K is shown in Fig. 4. As can be seen, all the samples show giant dielectric constant over 3500 in the frequency range from 20 to 10^6 Hz, though ε_r tends to decrease with increasing x. On the other hand, the tan δ value is remarkably decreased in the whole measured frequency range by the addition of $CaTiO_3$. It is noted that the