SCIENCE CHINA
Technological Sciences

April 2012 Vol.55 No.4: 879–882
doi: 10.1007/s11431-011-4738-9

Characterization of individual grain boundaries and grains of $CaCu_3Ti_4O_{12}$ ceramic

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Received February 15, 2011; accepted August 31, 2011; published online January 19, 2012

Microcontact measurement is employed to locally investigate the electric and dielectric properties of individual grains and grain boundaries in $CaCu_3Ti_4O_{12}$ ceramic. The measurements give more detail of the impedance spectroscopy, capacitance, and *I-V* characteristics of the microstructure, and will help with further understanding of the mechanism of the electric and dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics.

microcontact measurement, $CaCu_3Ti_4O_{12}$, individual grain boundary

Citation: Luo F C, He J L, Hu J, et al. Characterization of individual grain boundaries and grains of $CaCu_3Ti_4O_{12}$ ceramic. Sci China Tech Sci, 2012, 55: 879–882, doi: 10.1007/s11431-011-4738-9

1 Introduction

The $CaCu_3Ti_4O_{12}$ ceramic has drawn much attention for its colossal relative permittivity of more than 10^4 which is steady in a wide temperature range [1–3]. The mechanism of the unusual dielectric response has been uncertain till now. The “internal barrier layer capacitance (IBLC)” model is currently the most accepted theory to explain the colossal permittivity [4]. The ceramic is considered to be composed of semiconductive grains separated by insulating grain boundaries with Schottky barriers on both sides in this model [4]. This model was supported by conventional impedance measurements [4, 5], and was also supported by the experimental results that the electric and dielectric properties depend highly on the ceramic’s grain size [6]. Two theories were put forward to explain the conducting mechanism of the bulk. In the first theory, the oxygen is considered to be lost during the sintering process, and electrons are given out as charge carriers [4, 6]. In the second theory, Cu^{2+} ions are reduced to Cu^+ ions during sintering, and Cu^+ ions give out electrons as charge carriers during the cooling process [5, 7]. Besides the dielectric behavior, the ceramic was also discovered to have non-ohmic current-voltage property [8], which was also supposed to originate from the electrical barriers at the grain boundaries.

The grain boundaries play a key functional role according to the IBLC theory. To take a closer look at the electric properties of the grain boundaries, the microcontact method is proved a direct and effective method, which was ever performed on various materials like ZnO varistors, $SrTiO_3$, AgCl, etc. [9–12].

In this research, microcontact measurements were applied to locally investigate the properties of the bulk and individual grain boundaries, and detailed properties of the microstructures were revealed.

2 Experiment platform and procedure

$CaCu_3Ti_4O_{12}$ ceramic samples were prepared by the sol-

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id-state reaction and sintering process. $CaCO_3$, CuO and TiO_2 powders were weighed and ball-milled for 24 h with ethanol as liquid medium. The slurry was dried and calcined at 900°C for 12 h and then ball-milled for 24 h. The powders were then dried and sieved and pressed into discs of 12 mm in diameter. 1wt% of polyvinyl alcohol was employed as the binder. The pellets were sintered in air for 3 h at 1050°C.

The as-sintered sample had typical polycrystalline structure. The average grain size was about 100 μm. The surface of the sample was then polished, and round-shaped silver electrodes of 40 μm in diameter and 40 μm in distance were patterned on the surface by lithography and vacuum vapor plating technology (See Figure 1). The microcontact measurement was performed on a microprobe station (Summit 11000M, Cascade Microtech Inc. Beaverton) with probes connected to the electrodes across individual grain boundaries as well as within single grains. The *I-V* characteristic curves were tested by using a digital source meter (Model 2410, Keithley Instruments, Cleveland). The impedance spectroscopy and capacitance tests were performed by using a broadband dielectric measurement system (Concept 80 Broadband Dielectric Spectrometer, Novocontrol GmbH, Germany). Data were collected from a number of points on the sample surface. The macroscopic impedance was also tested in order to compare with the parameter obtained by microcontact measurements.

3 Results and discussion

The complex impedance plots at room temperature across individual grain boundaries and within single grains are shown in Figure 2. The magnitude of the resistance across a single grain boundary is 10^7 to 10^8 ohms, while that of the bulk is 10^4 to 10^5 Ω, with the distance between the electrodes kept the same. This result gives direct evidence to the existence of the grain boundary barrier. The single grain boundary impedance is also obtained from the macroscopic measurement by using the IBLC model. The result is depicted with solid line in Figure 2(b). It is seen that the microscopic and macroscopic measurement results are in reasonable consistence.

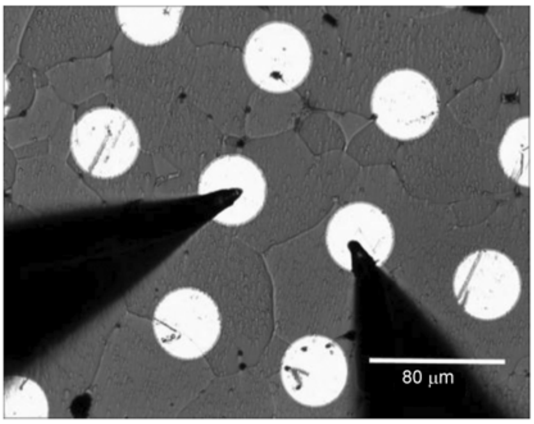

Figure 1 The sample with patterned silver electrodes and the microcontact probes.

It is seen from Figure 2 that there are differences among the resistances measured at different points. Also, we notice that the points that have relatively larger resistance have smaller capacitance. The reason is probably that the size of the residual grains under the electrodes varies, and then the areas of the grain boundaries between these grains are different. According to

$$R = \rho l / A, \tag{1}$$

and

$$C = \varepsilon A / l, \tag{2}$$

where R is the resistance, C the capacitance, l the length and A the cross section area of the current path, the grain boundaries with smaller area have relatively larger resistance and smaller capacitance.

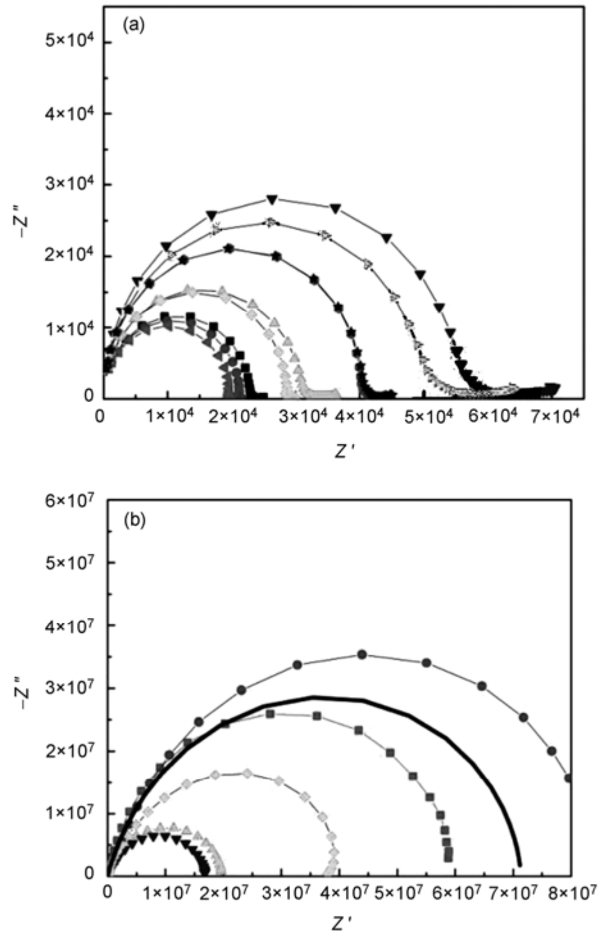

Figure 2 The complex impedance plots measured (a) within individual grains and (b) across individual grain boundaries. The curves within one figure were measured at different points under the same measurement condition. The solid line in (b) is the individual grain boundary impedance obtained from the macroscopic impedance data, assumed that the grains are cubic with 100 μm sides.

The capacitances within single grains and across single grain boundaries are shown in Figure 3. It is seen in Figure 3(b) that the capacitance of the individual grain boundary is around 100 pF at the measuring frequency of 10^3 Hz and below. Here the capacitance across the grain boundary is taken directly as the capacitance of the grain boundary. Actually, the bulk between the electrodes also contributes to the capacitance. We demonstrate by calculation that the capacitance measured across the grain boundary is almost the capacitance of the grain boundary below the measuring frequency of about 10^4 Hz.

The bulk obviously has a different dielectric behavior from those of the grain boundaries (see Figure 3(a)). The capacitance decreases from more than 100 nF to less than 100 pF when the measuring frequency increases from 1 to 1000 Hz. This behavior, recoganized as the "low frequency dispersion (LFD)", was ever described and discussed by Joscher in his work [13]. Joscher also explained that the LFD behavior was observed typically in a carrier-dominated system, and it was supposed to be related to the short-range migration process of the hopping carriers, which is captured and released repeatedly by other particles while moving. In the $CaCu_3Ti_4O_{12}$ bulk, it is supposed that electrons hop between Ti^{3+} and Ti^{4+} as charge carriers, which probably causes the LFD behavior. Wang et al. [14] also reported that there probably exist "hopping localized carriers" that contribute to the permittivity of $CaCu_3Ti_4O_{12}$, which is consistent with the result presented here.

The *I-V* characteristic curves of the bulk and individual grain boundaries are shown in Figure 4. The *I-V* curves of the bulk are almost linear, while those across single grain boundaries exhibit obvious non-ohimic property. It demonstrates directly that the non-ohmic *I-V* characteristic originates from the grain boundaries. No sign of domain boundaries with high resistance was observed. The non-linear coefficients are around 4 for the *I-V* curves across the individual grain boundaries. The same curve can be obtained when the voltage is applied repeatedly, indicating that the breakdown of the grain boundaries is recoverable. The variation of the *I-V* curves measured across the grain boundaries indicates that the grain boundaries may have quite different properties, while the *I-V* curves of the bulk are close to each other.

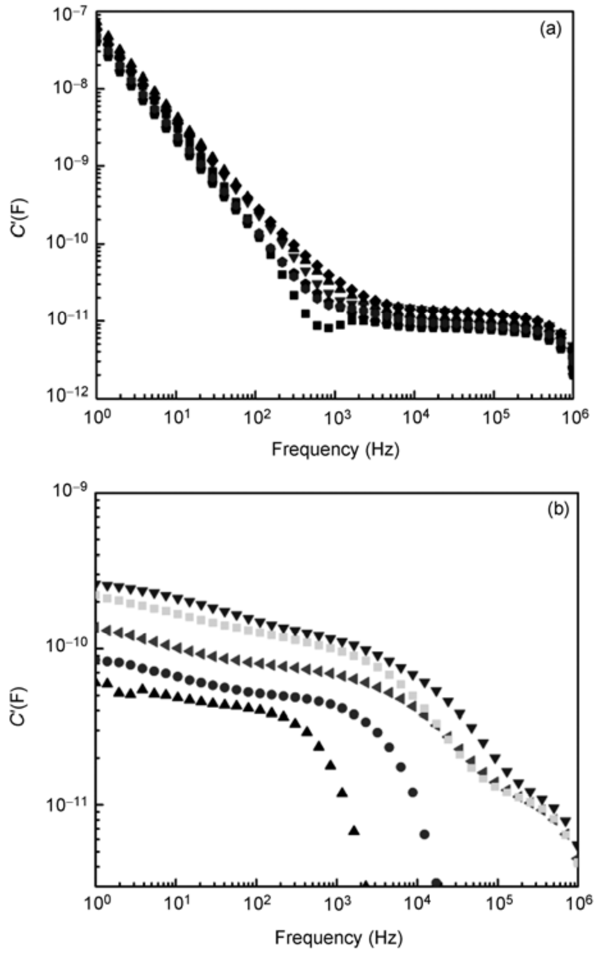

Figure 3 The capacitance spectroscopy measured (a) within individual grains and (b) across individual grain boundaries. The curves within one figure were measured at different points under the same measurement condition.

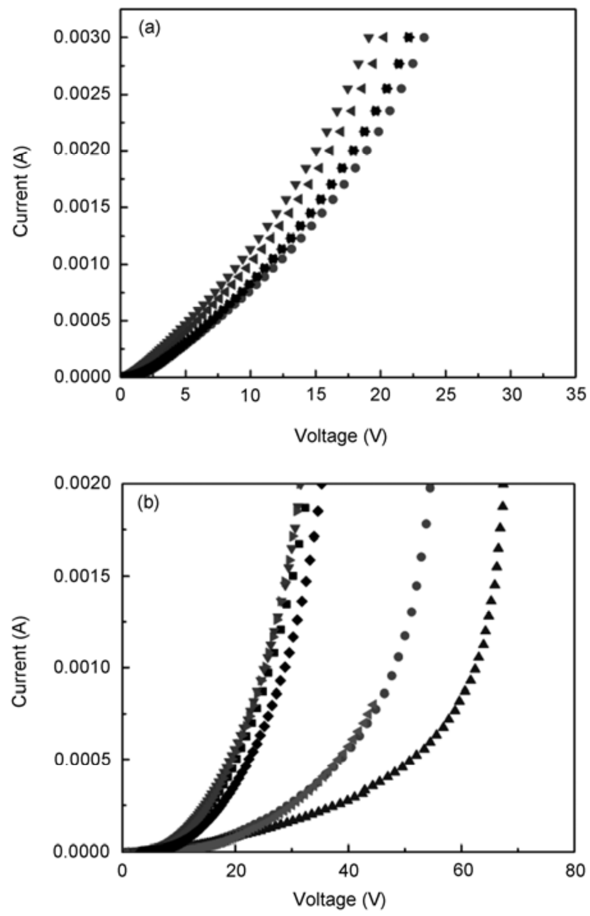

Figure 4 The *I-V* characteristic curves measured (a) within individual grains and (b) across individual grain boundaries. The different curves within one figure were measured at different points under the same measurement condition.

The individual grain boundary capacitance under applied dc voltage is shown in Figure 5. As other materials (e.g., ZnO varistor) with resistive grain boundaries, the capacitance goes down a little with the increase of applied dc voltage in the beginning. Then the capacitance rises until the breakdown takes place, and then goes downward to below zero [15]. As the measuring frequency rises, the decline section at the beginning of the curve extends, which is similar to the ZnO varistor capacitance-voltage curves. The capacitance-voltage relationship can be used to calculate the height of the grain boundary barrier. Previous researches have shown that the dependence of the grain boundary capacitance under a DC bias can be described as the following equation [15]

$$(1/C-1/2C_0)^2 = A(\Phi_b + V), \quad (3),$$

where C_0 is the capacitance of a single grain boundary under 0 V DC bias, A the constant related with the material nature, Φ_b the barrier height of the grain boundary, and V the applied dc voltage. The $(1/C-1/2C_0)^2$ vs. V plot for one single grain boundary measured under 500 Hz is shown in Figure 5(b), which exhibits excellent linear relationship as described in eq. (3). The barrier height is about 1.0 eV for this grain boundary.

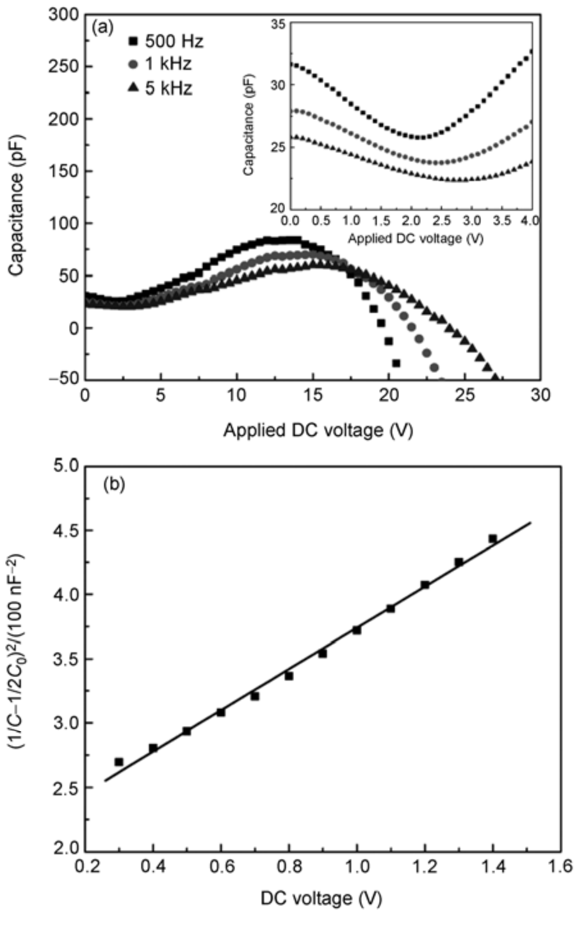

Figure 5 The capacitance-DC voltage relationship of an individual grain boundary. The inset of (a) is a close view of the beginning of the curves.

4 Conclusion

The electric and dielectric properties of individual grains and grain boundaries are measured directly by using the microcontact probes. The magnitudes of the parameters of the grains and grain boundaries were effectively obtained. The origin of the colossal permittivity and the non-ohmic *I-V* characteristic is strongly proved to be the existence of the potential barrier at the grain boundaries. The height of the barrier was also obtained by *C-V* measurement of individual grain boundaries. These detailed microstructure properties will help with a further understanding of the conductive mechanism.

This work was supported by the National Nature Science Foundation of China (Grant Nos. 50425721, 50677029 and 50737001).

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