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High dielectric and nonlinear electrical behaviors in TiO_2-rich $CaCu_3Ti_4O_{12}$ ceramics

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We present a TiO_2-rich $CaCu_3Ti_4O_{12}$ polycrystalline ceramic with high dielectric and nonlinear electrical properties. Analysis of the ceramic microstructure and composition indicates that obvious grain boundaries are formed. Our results demonstrate that all the ceramic samples exhibit high dielectric permittivity and remain almost constant over the frequency range from 100 Hz to 1 MHz, which could be attributed to an internal boundary layer capacitance effect. The current-density–electric-field characteristics prove that the excessive TiO_2 in the $CaCu_3Ti_4O_{12}$ ceramics can efficiently improve varistor voltage and nonlinear coefficient. *© 2006 American Institute of Physics*. [DOI: 10.1063/1.2198479]

It is generally believed that high dielectric ceramic capacitors with Ba/Pb-based perovskite oxides are indispensable to modern electronic devices and have been obtained wide applications. However, the high dielectric permittivities are always associated with ferroelectric or relaxor properties and exist a peak as a function of temperature due to ferroelectric phase transition.[1] Recently, the perovskite-based compound $CaCu_3Ti_4O_{12}$ (CCTO) has attracted considerable attention due to its high dielectric permittivity, which is almost constant over a wide temperature range from 100 to 400 K below 1 MHz.[2,3] This unusual dielectric property has been observed in the CCTO single crystal,[4] thin film grown on the (001) $LaAlO_3$ substrate,[5] and polycrystalline ceramics,[6] which is rarely influenced by the processing routes. Up to now, the origin of anomalously high dielectric constant of the CCTO is not fully understood. Most researchers considered that the large dielectric response is not intrinsic, and should be extrinsic and related to the special microstructure.[7] The high dielectric constant is probably caused by an internal boundary layer capacitance (IBLC) effect, which is proved by density functional theory calculations[8] and impedance spectroscopy measurements.[9] Recently, Patterson *et al.*[10] investigated that effects of ZrO_2 additions on the dielectric properties of the CCTO ceramics, and found that ZrO_2 doping is an effective method for maintaining a high dielectric permittivity and low loss over a broad range in temperature, bias, and frequency.

In this letter, we report TiO_2-rich $CaCu_3Ti_4O_{12}$ (TCCTO) ceramics with nonlinear electrical and high dielectric behaviors.

$CaCO_3$, CuO, and TiO_2 were employed as raw materials. The specimens with the nominal composition $CaCu_3Ti_{4+x}O_{12+2x}$ (x=0.0, 0.5, 1.0, and 1.5, abbreviated as TCCTO-0, TCCTO-1, TCCTO-2, and TCCTO-3) were prepared by a solid-state sintering method. Firstly, the raw materials were mixed homogenously and calcined at 900 °C for 4 h, and then the preclacined CCTO powders were pressed to green pellets by using polyvinyl alcohol as a binder. Finally, the pellets were sintered at 1100 °C for 3 h in air to form the TCCTO ceramics, and the final color of the sintered ceramics is grayish black.

X-ray diffraction (XRD) with a Rigaku D/MAX-2550V diffractometer at 40 kV and 100 mA (Cu $K\alpha$ radiation), and scanning electron microscopy (SEM) with energy dispersive x-ray spectrometer (EDS) were employed to reveal microstructure and phase composition of the TCCTO ceramics. The ceramic samples were polished and electroded by silver paint on both sides of the disk-shape samples fired at 600 °C for 30 min. The dielectric response of the specimens was measured using a HP 4192A gain phase analyzer over a frequency range from 100 Hz to 1 MHz and at an oscillation voltage of 1.0 V. The nonlinear coefficient and varistor voltage of samples were measured by using current-voltage measurements (Model 2410 source measurement unit, Keithley).

Figure 1 shows the XRD patterns of as-sintered TCCTO ceramic samples. The results indicate that the TCCTO ceramics consist of the CCTO crystal phase and the second phase (e.g., TiO_2), especially the TCCTO-2 and TCCTO-3 samples. Typical SEM micrographs of the TCCTO-1 sample

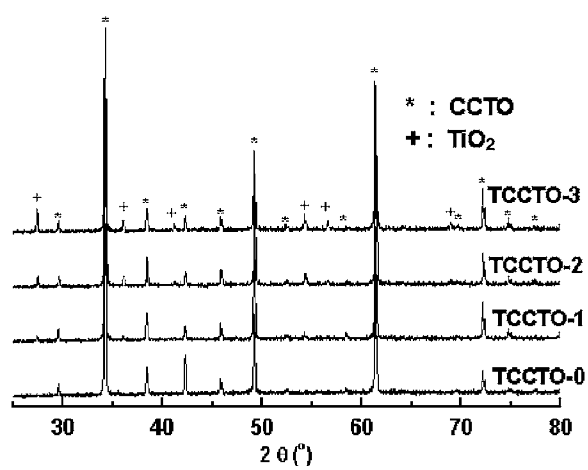

FIG. 1. XRD patterns of various TCCTO samples.

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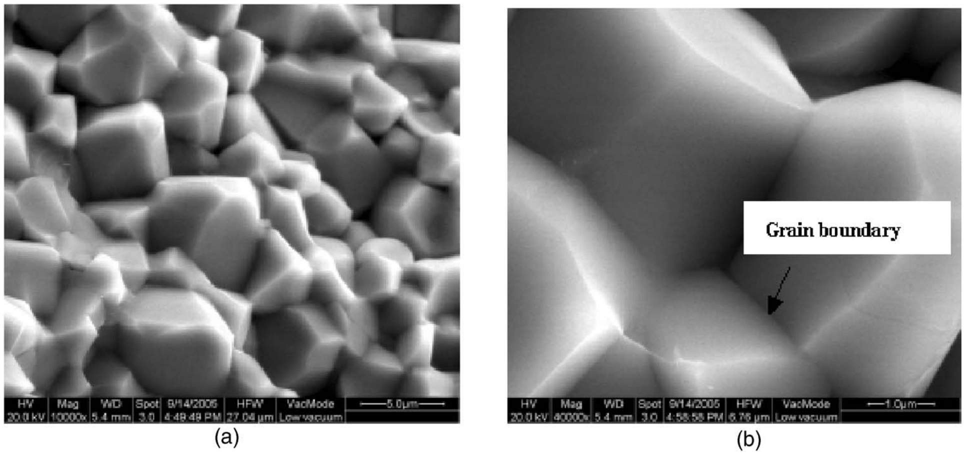

FIG. 2. SEM microstructure graphs of the TCCTO-1 sample.

in Fig. 2 prove that the TCCTO ceramics have obvious grain and grain boundary structures.

Figure 3 illustrates the frequency dependence of the dielectric constant of the TCCTO samples at room temperature. The dielectric constant at 1 kHz for the TCCTO-0, TCCTO-1, TCCTO-2, and TCCTO-3 samples are 17 550, 7113, 5559, and 4233, respectively, which decreases obviously as the addition content of TiO_2 increasing, and the dielectric loss also decreases from 0.07 to 0.03. Additionally, in the frequency range from 100 Hz to 1 MHz, the dielectric constant remains almost constant for all the TCCTO samples, which has also been observed in the pure CCTO polycrystalline ceramics.[11]

It is well known that the complex impedance spectroscopy is a powerful tool in separating out the grain and the grain boundary effects.[12] As previously reported,[13] impedance data on dielectric TCCTO ceramics can be analyzed using an equivalent circuit consisting of resistor-capacitor (*RC*) elements as shown in Fig. 4(a). The complex impedance can be expressed as the following:

$$Z(\omega) = R_g + \left(\frac{1}{R_{\text{gb}}} + j\omega C_{\text{gb}}\right)^{-1}, \qquad (1)$$

where $\omega = 2\pi f$ is the angular frequency. R_g and R_{gb} represent the resistance of grain and grain boundary, respectively.

Based on Eq. (1), we can get the real part of complex impedance spectra,

$$Z'(\omega) = R_g + R_{\text{gb}}/[1 + (\omega C_{\text{gb}} R_{\text{gb}})^2]. \qquad (2)$$

Obviously, as $\omega \rightarrow 0$ and $\omega \rightarrow \propto$, we can get $Z'(0) = R_g + R_{\text{gb}}$, and $Z'(\propto) = R_g$. Figure 4 shows the Cole-Cole graphs for TCCTO samples at room temperature. It can be seen that the addition concentration of TiO_2 has influence on the resistivity of the grain and grain boundary, especially for the grain boundary. Similar phenomena have been observed in the modified $(Pb,Sr)TiO_3$,[14] $SrTiO_3$,[15] $BaTiO_3$ (Ref. 16) polycrystalline ceramics. In the CCTO polycrystalline ceramics, the semiconductivity of the grains may arise from a small amount of oxygen loss during ceramic processing in air at elevated temperatures, as is known to occur in other titanate-based materials.[17,18] In our samples, the grain boundary effect on electric conductivity should originate from a grain boundary potential barrier, which could be attributed to the TiO_2-rich boundary. As seen from in Fig. 4, we can observe that the R_{gb} value of the TCCTO ceramics increased as the addition content of TiO_2 increases, which should be related to the amount and microstructure of grain boundaries. Similar phenomenon has also been observed by Patterson *et al.*[10] in ZrO_2-doped CCTO-based ceramics, and an order of magnitude increased in the static resistivity in the

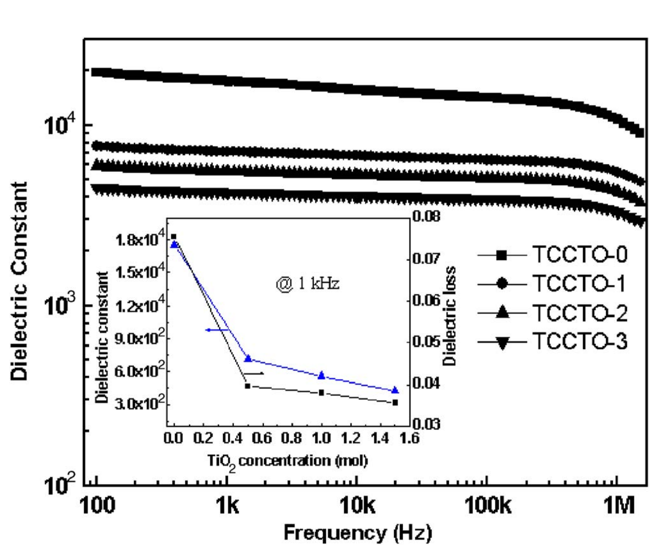

FIG. 3. Frequency dependence of dielectric constant of various samples; the inset is the composition dependence of dielectric properties.

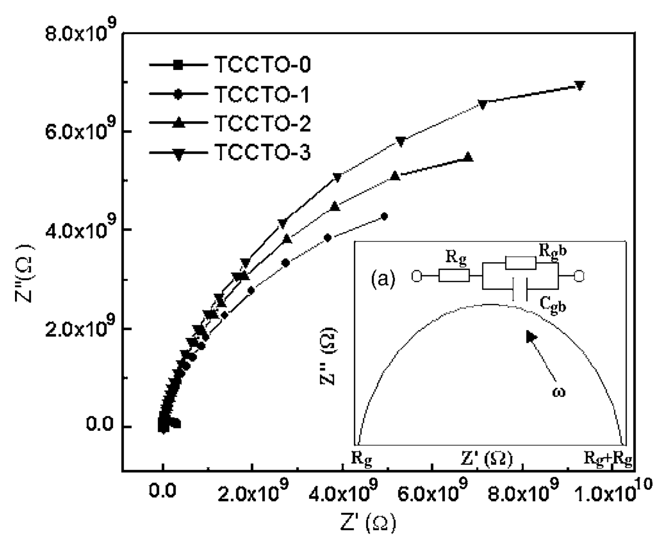

FIG. 4. Impedance complex plane plots for the TCCTO ceramics at 300 K. The inset (a) is the *RC* effective circuit, and *g* and gb represent grain and grain boundary, respectively.

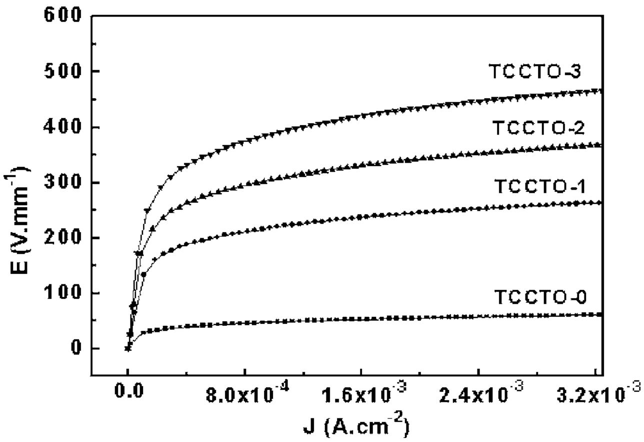

FIG. 5. Current-density–electric-field (J-E) characteristics of the TCCTO ceramic samples.

ZrO_2-doped samples as compared to the undoped samples due to the presence of ZrO_2 at the grain boundaries.

Now, we consider that the BLC structured TCCTO ceramics consist of the conducting grains, CCTO, and nonconducting grain boundary layers (e.g., TiO_2). According to the simple series-layer model for the IBLC, the dielectric constant of the TCCTO ceramic specimens can be simply expressed as[19]

$$\varepsilon^* \approx d\varepsilon_2/t, \tag{3}$$

here d is the grain size, t is the boundary-layer thickness, and ε_2 is the dielectric constant of the boundary layer.

Equation (3) indicates that the dielectric constant can be controlled by the thin nonconducting grain boundary layer, and reverse to the thickness of grain boundary. As for the TCCTO-1 ceramic sample, the average grain size is about 2.0 μm, and the thickness of grain boundary region is about 25 nm, and the dielectric constant of TiO_2 is about 100.[20] Therefore, the dielectric constant at low frequency will be 8000, which is in good agreement with our experimental data. As the thickness of grain boundary layer increases with the addition content of TiO_2 increasing, it will lead to the decrease of dielectric constant, which is also good consistent with our experiment results.

The current-voltage characteristic of varistors is nonlinear and empirically expressed by the equation[21]

$$I = KV^{\alpha}, \tag{4}$$

where K is a constant related to the electrical resistivity of the material, and α is the nonlinear coefficient which is one important parameter of a varistor.

The current-density–electric-field curves of the TCCTO samples and fitted results by Eq. (4) are shown in Fig. 5 and listed in Table I, respectively. It can be seen that the TCCTO-3 sample has a larger varistor voltage of 391 V/mm and a nonlinear coefficient of 7.9. As compared to TCCTO-0 sample, the varistor voltage can be increased by more than a factor of 8 as the addition content of TiO_2 increasing, but only ~1.5 times for the nonlinear coefficients. Previous investigation proved that there are sufficient mobile charge carriers in the CCTO lattice.[5,9] Chung *et al.*[22] measured the thermoelectric power and found that n-type conduction by electrons existed in bulk CCTO ceramics with a negative Seebeck coefficient. Therefore, they deduced that the electron energy-band structure across an insulating grain boundary in the CCTO specimens is likely to be equivalent to n-i-n with acceptorlike interface traps for electrons within the band gap at the boundary regions. In our TCCTO samples, we also got a negative Seebeck coefficient for the bulk TCCTO ceramics. The nonlinear electrical properties may be attributed to the similar n-i-n structure, and can be adjusted by the addition content of TiO_2.

TABLE I. The nonlinear coefficient fitted by J-E curves and varistor voltage of samples.

Samples	Nonlinear coefficient	Varistor voltage (V/mm)
TCCTO-0	5.1	48
TCCTO-1	6.8	220
TCCTO-2	7.1	308
TCCTO-3	7.9	391

In conclusion, TiO_2-rich $CaCu_3Ti_4O_{12}$ ceramics have been prepared by a solid-state sintering method. Microstructure and phase composition analyses indicate that the TCCTO ceramics consist of the CCTO crystal phase and the TiO_2 phase. All of these TCCTO ceramics exhibit high dielectric properties due to the internal boundary layer capacitance effect. The TCCTO-3 sample has a large varistor voltage ~391 V/mm and a nonlinear coefficient ~7.9, which indicate that the excessive TiO_2 in the CCTO ceramics can improve the varistor voltage and the nonlinear coefficient.

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