Dielectric spectroscopy analysis of CaCu$_3$Ti$_4$O$_{12}$ polycrystalline systems

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Dielectric spectroscopy was used in this study to examine CaCu$_3$Ti$_4$O$_{12}$ polycrystalline samples. The analysis involved systems presenting low non-Ohmic properties, and the grain's internal domain was evaluated separately from the contribution of barrier-layer capacitances associated with Schottky-type barriers in this type of material. The effect of oxygen-rich atmosphere and high cooling rate was evaluated, revealing a strong increase in the dielectric properties of the CaCu$_3$Ti$_4$O$_{12}$ system under these conditions. This effect was attributed to a chemical change in the grain's internal domain, which may be considered an internal barrier-layer capacitance of the polycrystalline material. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2386916]

A number of theoretical studies and experimental observations have attempted to elucidate the remarkable (ultrahigh) dielectric property of (Ca$_{0.25}$,Cu$_{0.75}$)TiO$_3$ perovskite-like material (alternatively CaCu$_3$Ti$_4$O$_{12}$).[1–10] In addition to the remarkable and intriguing dielectric property, Chung *et al.*[2] recently observed that a large potential barrier exists intrinsically in the grain boundary region. The importance of the work of Chung *et al.*[2] is its ability to support important proposals. For instance, it is now generally accepted that the ultrahigh dielectric response is not an intrinsic behavior.[11] Rather, the dielectric response is due to barrier-layer capacitances associated with one or more of the following grain boundaries: twin boundaries (or domain boundaries), dislocation networks, and/or Schottky-type barrier or interfacial polarization effects.[11,12] To support this interpretation and the extrinsic origin of the dielectric features, a detailed first-principles study did not reveal any unusual features for the bulk. Based on the work of Chung *et al.*,[2] we have recently shown that the non-Ohmic electrical properties in such polycrystalline ceramics likely originate from Schottky-type potential barriers,[13] according to a chemical model for barrier formation in non-Ohmic devices in which oxygen plays a key role.[14]

In the present letter, we analyze the dielectric spectroscopy features of CaCu$_3$Ti$_4$O$_{12}$ (CCTO) polycrystalline ceramics obtained under different sintering conditions and cooling rates. The literature reports the frequent use of impedance spectroscopy analyses to reveal and study the mechanisms responsible for the dielectric properties of CCTO polycrystalline materials,[9,12,15,16] particularly to obtain information on nonintrinsic dielectric effects. The purpose of using dielectric spectroscopy analysis[17,18] instead of the traditional impedance spectroscopy approach is to demonstrate that dielectric complex diagrams of the frequency response of polycrystalline materials can sometimes reveal more about the relaxation processes involved with grain boundaries and dielectric dipolar relaxation than impedance diagrams can.[17,18] Thus, the dielectric spectroscopy analysis carried out here revealed that non-Ohmic features can be separated from grain (or the domain contained in the grain)

dielectric relaxation, although they must be associated, and that both relaxations contribute to the total dielectric response. Dielectric spectroscopy analyses were also made here to study the effect of sintering conditions and cooling rates on the ultrahigh dielectric response. Oxygen-rich atmospheres and high cooling rates were found to be determining factors in activating the nonintrinsic effect in polycrystalline devices, which leads to the ultrahigh dielectric properties of CCTO polycrystalline systems.

The CCTO polycrystalline samples were prepared by solid-state reaction. All the starting materials used were of analytical grade: CaCO$_3$ (Aldrich, 99.99%), TiO$_2$ (Aldrich, 99.8%), and CuO (Riedel, 99%). These materials were ball milled in an alcohol medium for 24 h in a polyethylene bottle, using zirconium balls, after which the slurry was dried and heat treated at 900 °C in an ambient atmosphere for 12 h. The heat-treated powders were lightly compressed into 8-mm-diameter, 1-mm-thick disks and then isostatically pressed under 210 MPa. The pellets were sintered at 1100 °C for 3 h in a conventional furnace using ambient and oxidizing atmospheres (constant oxygen flow of 5 l/h). The heating and cooling rates applied were 5 °C/min under both conditions. For purposes of comparison with ambient atmosphere sintering, quenching to ambient temperature was also applied. The fast cooling rate applied here proved highly instrumental in attaining ultrahigh dielectric properties, as will be discussed later.

Gold contacts were deposited by sputtering on the samples' surfaces for the electrical measurements. Current-tension measurements were taken using a high voltage measure unit (Keithley Model 237). The breakdown electric field (E_b) was obtained at a current density of 1 mA cm^{-2}. Numerical values for the nonlinear coefficient α were obtained by a linear regression of the log J vs log E plot within the range of $1–10$ mA cm^{-2}. The dielectric spectroscopy measurements were taken with a frequency response analyzer (HP 4294 A), at frequencies ranging from 100 Hz to 15 MHz.

Figure 1 shows the J vs E for the quenched, ambient, and oxygen-rich atmosphere CCTO samples. Note the strong influence of the sintering conditions on the J vs E pattern, particularly in terms of leakage current (l_{leak}) and breakdown voltage (E_b) (see Table I). In addition, according to Table I no significant differences were observed in the nonlinear co-

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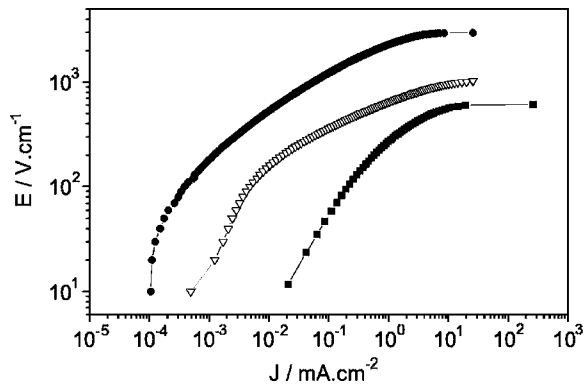FIG. 1. J vs E of polycrystalline CCTO devices: (●) ambient sintering, (▽) oxygen-rich atmosphere sintering, and (■) quenched sample.

efficient values (α) as a function of sintering conditions or cooling rates. It can also be observed that E_b values increase as the mean grain size decreases, a behavior expected for variable resistor devices. The great differences in E_b values are found by comparing the ambient CCTO with oxygen-rich and quenched samples. However, the most important point worth mentioning is the importance of the sintering features and rapid cooling rates on the dielectric feature of the CCTO system, which can be evaluated by the complex capacitance plane, according to Fig. 2. From an analysis of Fig. 2 one can see that the material sintered in an ambient atmosphere presents a dielectric constant value, ε', of about 9.000. The ε' values are around 50.000 for the quenched sample and 46.000 for the sample sintered in oxygen-rich atmosphere. In other words, the sintering and rapid cooling rate can increase the ε' values by at least fivefold.

The high frequency region of the complex capacitance diagrams shows the presence of a dipolar relaxation process possessing a near-Debye pattern (see Bode capacitive diagrams of Fig. 3). The three systems exhibited near-Debye relaxation, and the fast cooling rate or sintering atmosphere variable did not interfere in the relaxation symmetry pattern. The differences were related mainly to the value of the capacitance ($C_0 - C_\infty$) or dielectric constant ($\varepsilon_0 - \varepsilon_\infty$) associated with dipolar relaxation. In other words, a strong increase occurred in the dielectric constant associated with the increase of a relative increment in the value of the real part of the capacitance ($C_0 - C_\infty$)/C_∞, which reached higher values in samples sintered in an oxygen-rich atmosphere and in the sample subjected to the fast cooling rate. It is important to emphasize here that, in the present discussion, because the dielectric properties may be strongly related to the a multi-junction domain,[11,19] it is inappropriate to use parameters such as dielectric permittivity or susceptibility, since it is almost impossible to know enough about the geometry, i.e., the thickness of the region in question (domain boundaries

TABLE I. α (nonlinear coefficient), E_b (breakdown voltage), mean grain size (d), and relative densities (ρ_r) of polycrystalline CCTO samples.

System	α	E_b (V/cm)	I_{leak} (μA)	d (μm)	ρ_r (%)
Ambient	6	2290	240	15	95
Oxygen-rich	7	650	220	40/20[a]	95
Quenching	3	270	515	30	95

[a]This sample presents bimodal grain size distributions or mean values (40 and 20 μm).
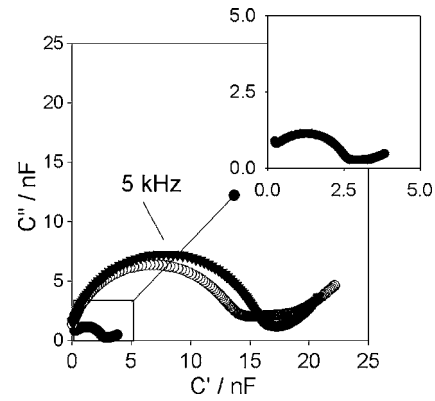

FIG. 2. Complex capacitance diagram for the CCTO polycrystalline sample. The low frequency region shows the response relating to grain boundary relaxation and the Schottky-type barrier contribution. At high frequencies one can see the near-Debye relaxation relating to dipolar effects, which are likely due to the grain's internal domain. (●) Ambient sintering, (○) oxygen-rich atmosphere, and (▼) quenched sample. Note that the axis indicates the exponent of decimal base.

existing in the grain), to determine the complex permittivity. That is why we prefer to express the response in terms of complex capacitance (C^*) instead of complex dielectric form (ε^*).[18] However, it should be noted that all the polycrystalline materials displayed about the same dimensions (0.95 mm thickness and 0.65 mm diameter), so they could be compared and the changes observed were only morphological or due to heterogeneities such as domain structures inside the grains.
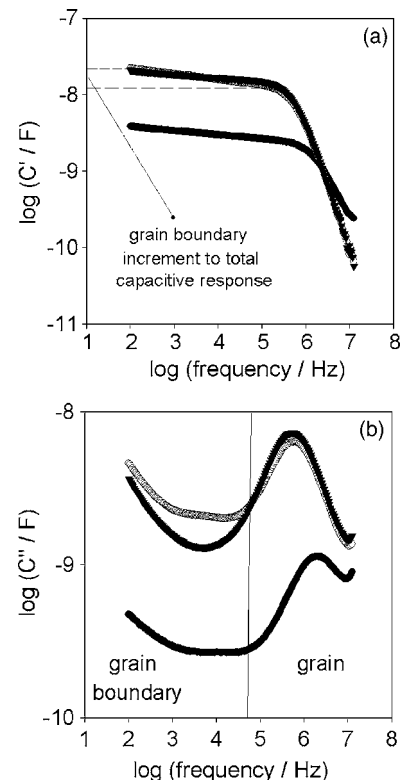

FIG. 3. Bode dielectric diagram, i.e., (a) real (C') and (b) imaginary (C'') parts of the complex capacitance as a function of frequency, for the CCTO polycrystalline sample showing the contribution of the grain boundary and grain to the total dielectric response. (●) Ambient sintering, (○) oxygen-rich atmosphere, and (▼) quenched sample. Note that the axis indicates the exponent of decimal base.

Apparently, the Debye-type dielectric relaxation [see Fig. 3(b)] observed in the high frequency region is the same as that reported by Zhang *et al.*,[20] who studied its dependence on temperature. According to the relaxation pattern in Figs. 2 and 3, it can be stated that the equivalent circuit representation of the frequency response analysis is more complicated than the equivalent circuit that has so far been proposed in the literature,[11,20] particularly in the case of responses at ambient temperature, in which the non-Ohmic components strongly influence the responses in the low frequency region.[21] In other words, the dipolar relaxation is clearly visible in the high frequency region.[21] However, the low frequency region is dominated by the presence of grain boundary capacitances and likely the presence of deep trap states related to the Schottky-type barriers, which contribute to the total barrier-layer capacitive response of polycrystalline CCTO.[21]

With regard to the approximately fivefold increase in the dielectric properties caused by the high cooling rate or oxygen atmosphere during sintering, it can be inferred that both treatments exert a particularly marked influence on the grain's internal domain. Hence, they are able to increase the number of "active" domains, so that the cause of the strong increase in the dielectric properties is here mainly related to the number of active internal domains. The chemistry of dielectric internal domains most likely depends on the oxygen and cooling rates to increase its effectiveness. In the particular context reported here, in which the non-Ohmic properties are not very strong, the grain boundary contribution is lower than the total dielectric response. For instance, the contribution of the grain boundary effect represents about 10.000 out of the total value of 50.000 in the case of the sample sintered in an oxygen-rich atmosphere and cooled. In the case of the sample sintered in ambient air, the contribution is about 2.000 out of a total of 9.000.

In summary, we use dielectric spectroscopy here to demonstrate that it is possible to separate the contribution of the grain boundary from the total dielectric response. We consider that the grain's internal domain contributes strongly to the total ultrahigh dielectric response of polycrystalline CCTO samples, particularly since our samples present low non-Ohmic properties, so that the contribution of barrier-layer capacitances associated to Schottky-type barriers is minimal. Based on this finding, we also studied the effect of sintering in an oxygen atmosphere on the near-Debye dipolar relaxation of the polycrystalline samples compared with sintering in an ambient atmosphere. The effect of the cooling rate (quenching) also contributes strongly to the total dielectric response and was found to be associated with internal barrier-layer capacitances in the grain's internal domain.[11] Both effects lead to an approximately fivefold increase in the dielectric constant and are presumably related with a chemical change in the grain's internal domain rather than with grain boundary contribution, in the particular case of samples possessing low non-Ohmic properties.

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