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Non-Ohmic and dielectric properties of a $Ca_2Cu_2Ti_4O_{12}$ polycrystalline system

M. A. Ramírez, P. R. Bueno,[a] J. A. Varela, and E. Longo
Departamento de Físico-Química, Instituto de Química, Universidade Estadual Paulista, P.O. Box 355, 14800-900 Araraquara, São Paulo, Brazil

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An investigation was made into the non-Ohmic and dielectric properties of a $Ca_2Cu_2Ti_4O_{12}$ perovskite-type system. Compared to the traditional $CaCu_3Ti_4O_{12}$-based composition, the imbalance between the Ca and Cu atoms caused the formation of a polycrystalline system presenting ~33.3 mol % of $CaCu_3Ti_4O_{12}$ (traditional composition) and ~66.7 mol % of $CaTiO_3$. As for non-Ohmic properties, the effect of this Ca and Cu atom imbalance was that a nonlinear electric behavior of ~1500 was obtained. This high nonlinear electrical behavior emerged in detriment to the ultrahigh dielectric property frequently reported. The high non-Ohmic property was explained by the existence of Schottky-type barriers, whose formation mechanism may be similar to that proposed for traditional metal oxide non-Ohmic devices, according to similarities discussed herein. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2393122]

$CaCu_3Ti_4O_{12}$ (CCTO) has attracted considerable attention recently thanks to its ultrahigh dielectric property, whose origin has been investigated exhaustively.[1–6] Currently, the most widely accepted hypothesis is that this ultrahigh dielectric property originates from extrinsic defects caused by barrier-layer capacitances associated with internal barrier domains inside the grain.[5,7] In addition to the intriguing and remarkable dielectric property, Chung *et al.*[8] have observed that a large potential barrier exists intrinsically in the grain boundary region, causing the existence of non-Ohmic behavior combined with the ultrahigh dielectric property. Marques *et al.*[9] showed that, in CCTO systems, this non-Ohmic property depends on the oxygen heat treatment, which increases low frequency capacitance values as a function of oxygen partial pressure. A similar behavior is observed in metal oxide varistor systems, leading to the inference that a Schottky-type barrier is probably the potential barrier type responsible for non-Ohmic properties and that it must be located at grain boundary junctions.[10]

Furthermore, dielectric properties in CCTO systems are highly sensitive to processing parameters, and dielectric constant values from $\sim 10^2$ to $\sim 10^6$ have been reported.[11] Besides, nonlinear coefficient values from ~10 to ~900 have also been reported as a consequence of different processing strategies.[12] Although a correlation between high dielectric and non-Ohmic properties does appear to exist,[8,9,12] it is not always observable. Therefore, it is still not evident if the nonlinear electrical response is directly related to the extrinsic mechanism responsible for the ultrahigh dielectric properties, a mechanism still poorly understood,[3,4,8,9,11,13–16] despite the fact that it appears to be related to barrier-layer capacitances,[17] as previously mentioned here. Based on this picture, it can be inferred that more than one type of barrier can contribute to the extrinsic dielectric properties: different internal barriers inside the grain and even Schottky-type barriers in the grain boundary junctions.[8,17,18]

Changes in the compositions of CCTO polycrystalline systems may help explain how chemistry and stoichiometry affect these properties. In this context, Lin *et al.*[12] recently investigated TiO_2-rich CCTO systems and found high dielectric properties.[12] However, the nonlinear electrical properties declined sharply compared to traditional compositions, reaching low values of around 7.[12] Moreover, an x-ray diffraction analysis indicated that the excess of TiO_2 precipitated as a second phase.[12] Additional important information provided by the work of Lin *et al.*[12] is that an increase in TiO_2 content decreases the dielectric constant of polycrystalline materials.

The main goal here is to describe the response of the dielectric and non-Ohmic properties when Ca and Cu atoms are imbalanced in relation to the 1/4 Ca and 3/4 Cu stoichiometries. To this end, we investigated the 1/2 Ca and 1/2 Cu stoichiometries ($Ca_2Cu_2Ti_4O_{12}$ or alternatively $Ca_{0.5}Cu_{0.5}TiO_3$).

The polycrystalline CCTO modified stoichiometry was prepared based on traditional reagent mixture processing. All the precursors were of analytical grade: $CaCO_3$ (J. T. Baker—99.99%), TiO_2 (Aldrich—99.8%), and CuO (Riedel—99%). The mixed reagents were ball milled for 24 h in isopropylic alcohol using a polyethylene bottle and zirconium balls, followed by drying at 110 °C and heat treating at 900 °C in an ambient atmosphere for 12 h. The stoichiometrically modified CCTO system (CCTO-*m*) was previously slightly compressed into disks of 10 mm in diameter and about 1 mm in thickness, and then isostatically pressed under 210 MPa. The pellets were sintered at 1050 °C for 30 min at a heating rate of 230 °C/min in a domestic microwave oven (CCE, M301, 2.45 GHz, 900 W, GL107 magnetron). The phases were analyzed by x-ray diffraction using a Rigaku diffractometer. The 2θ angle ranged from 15° to 120°, using incremental steps of 0.02°. The radiation employed was based on a Cu $K\alpha$ source. To take the electrical measurements, gold contacts were deposited on the samples' surfaces. E vs J plots were obtained using a high voltage measurement unit (Keithley model 237). The impedance measurements were taken with a frequency response ana-

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[a] Author to whom correspondence should be addressed; electronic mail: prbueno@iq.unesp.br

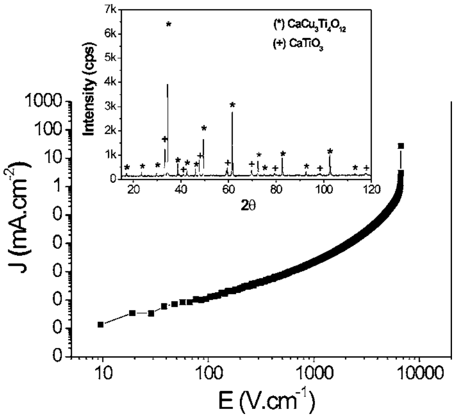

FIG. 1. *E* vs *J* plot obtained for the CCTO-*m* polycrystalline system. The inset shows the Rietveld refinement based on the XRD pattern.

lyzer HP 4294 A, in a frequency ranging from 40 Hz to 110 MHz and an ac amplitude perturbation voltage of 0.5 V.

Figure 1 shows the *E* vs *J* plot for the CCTO-*m* composition. The non-Ohmic parameters are shown in Table I for different current or current density values. Note that the nonlinear coefficient value (α) is very high for this composition. The inset of Fig. 1 shows the x-ray diffraction pattern. The x-ray diffraction (XRD) analysis indicated that the CCTO-*m* composition did not stabilize into one single-phase system. Furthermore, the quantitative XRD Rietveld phase analysis of the CCTO-*m* system indicated that the system was comprised of ~33.3 mol % of $CaCu_3Ti_4O_{12}$ (traditional CCTO composition) and ~66.7 mol % of $CaTiO_3$. The dielectric constant obtained for this CCTO-*m* composition was found to be about 1300. This value is very low compared to the traditional CCTO compositions, in which the dielectric constant is generally higher than 10.000.[5,6,8,15]

On the one hand, based on the results described earlier herein and those reported by Lin *et al.*,[12] it possible to infer that the excess of Ti does not decrease the dielectric constant values as markedly as Ca atoms do. On the other hand, an excess of Ca atoms causes an increase of non-Ohmic properties compared with Ti atoms existing in excess in traditional CCTO compositions. Evidently, based on these combined results, it can be stated that the relationship between dielectric properties and non-Ohmic behavior pointed out by Chung *et al.*[8] is not so easy to establish. One may argue that the α values and dielectric constant obtained by Chung *et al.*[8] are much higher than the value reported by Lin *et al.*[12] or the value presented here. With regard to the dielectric constant values, the value found by Chung *et al.*[8] is indisputably higher than that reported by Lin *et al.*[12] (or by us[9]), but this does not hold true with respect to the α value obtained here for the CCTO-*m* system. For instance, Chung *et al.*[8] found a value of 900 using a current range of 5–100 mA. Generally, α values are reported for non-Ohmic devices using current densities starting at 1 mA/cm^2 and ranging up to 10 mA/cm^2. In this letter, we report an α value of 65 for the traditional current density range of 1–10 mA/cm^2. On the other hand, the α value can reach values even higher than 900 if one considers, for example, a current range of 3–30 mA. For instance, in this current range, we obtained a value of ~1500. This result reinforces the argument that it is not as easy to establish the correlation between non-Ohmic and ultrahigh dielectric properties as Chung *et al.* suggest,[8] although the non-Ohmic properties can contribute to the total dielectric constant value.

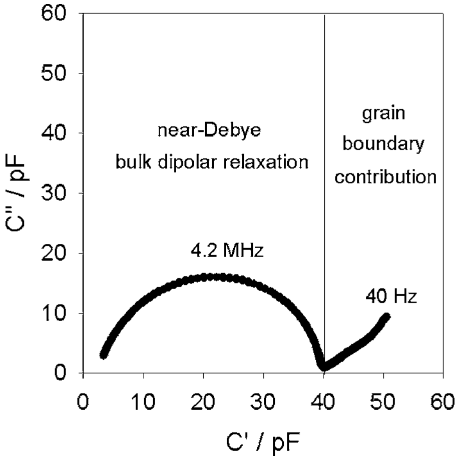

FIG. 2. Complex capacitance diagrams for the CCTO-*m* polycrystalline system, showing the relaxation in the polycrystalline material. The higher frequency region exhibits a near-Debye relaxation pattern relating to the system's dielectric feature.

Figure 2 shows the complex capacitance diagram of the CCTO-*m* composition. The dipolar relaxation associated with the system's dielectric property is visible in the higher frequency region. This dipolar relaxation presents a near-Debye pattern and is likely due to intrinsic dipolar relaxation existing in bulk of the polycrystalline device. Near-Debye-type relaxation has already been described in CCTO systems.

On the other hand, in the lower frequency region there is a relaxation relating to the grain boundary. This relaxation is probably due to a Schottky-type barrier existing in this type of polycrystalline material. The Bode capacitive diagram in Fig. 3 provides a better vision of the different relaxations existing in this polycrystalline system and their respective frequency ranges in the CCTO-*m* system.

Finally, it is now possible to make inferences about the potential barrier formation mechanism in CCTO polycrystalline materials. This mechanism may be similar to the potential barrier formation mechanism proposed for other traditional metal oxide non-Ohmic based systems.[10] In other words, a large body of evidence indicates that nonlinear electrical properties arise in non-Ohmic devices due to oxygen

TABLE I. Nonlinear coefficient (α) obtained in two different ranges of current, breakdown electrical field (E_b), and leakage current (I_l) calculated at 20% of the breakdown electrical field, mean grain size values (d), and relative density for the CCTO-*m* system.

System	α (1–10 mA/cm^2)	α (3–30 mA)	E_b (V/cm)	I_l (mA)	d (μm)	ρ_r[a] (%)
CCTO-*m*	65	1535	6560	60	7	97

[a] This value was obtained by considering ideal theoretical density values of $CaCu_3Ti_4O_{12}$ and $CaTiO_3$ mixtures (5.07 g/cm^3 for CCTO and 4.67 g/cm^3 for CTO).

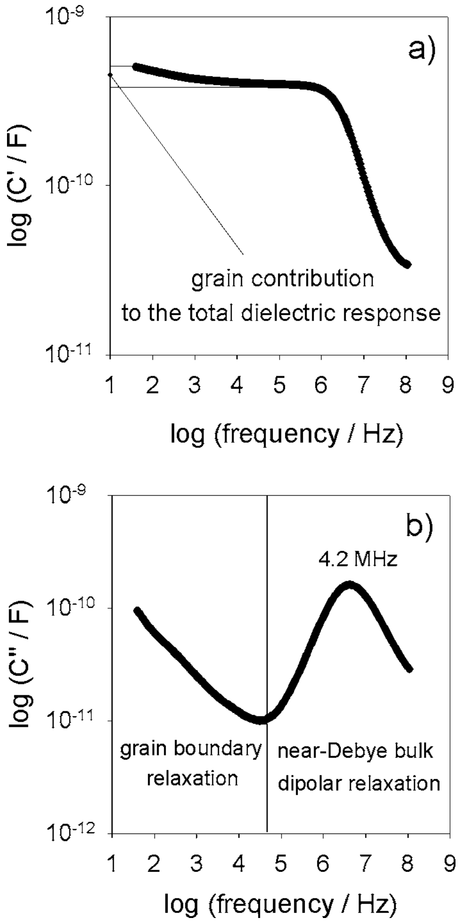

FIG. 3. Bode capacitive diagrams for the CCTO-*m* system. Logarithm of (a) real and (b) imaginary parts of the complex capacitance as a function of frequency.

enrichment at the grain boundary due to the formation of a metal oxide segregation region or precipitated phases.[10] Such a grain boundary region may possess a high "*p*-type semiconductor nature" (metal deficient and oxygen rich) phase compared with the *n*-type semiconductor nature of the grains.[10] Therefore, TiO_2-rich CCTO systems (presented by Lin *et al.*[12]) may have an excess of Ti atoms that form TiO_2 *n*-type phases and contribute to the segregation of Ti atoms, which can dilute the grain boundary *p*-type semiconductor nature, thereby decreasing the non-Ohmic properties.[10,12] On the other hand, Ca-rich systems may have (as demonstrated here) an imbalance between Ca and Cu atoms. To establish ~33.3 mol % of $CaCu_3Ti_4O_{12}$ in the total composition, excess of Cu and Ca may exist in the grain boundary regions. We have confirmed such segregation by TEM analysis and will discuss this point in detail in a future paper.

To conclude, it is possible to affirm that the dielectric and non-Ohmic properties of CCTO polycrystalline materials are strongly dependent on the distribution of Ca, Cu, and Ti atoms in the polycrystalline microstructure. Imbalances between Ca and Cu atoms with Ca in excess may favor the non-Ohmic properties in detriment to the dielectric property, due to phase separation and segregation. Furthermore, it can be stated that non-Ohmic properties, according to the potential barrier formation mechanism,[10] will be favored by Ca or Cu segregation in the grain boundary region. All the results indicate that the correlation between non-Ohmic and dielectric properties is not easily established.

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