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Citation: Appl. Phys. Lett. **98**, 132906 (2011); doi: 10.1063/1.3574016
View online: http://dx.doi.org/10.1063/1.3574016
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v98/i13
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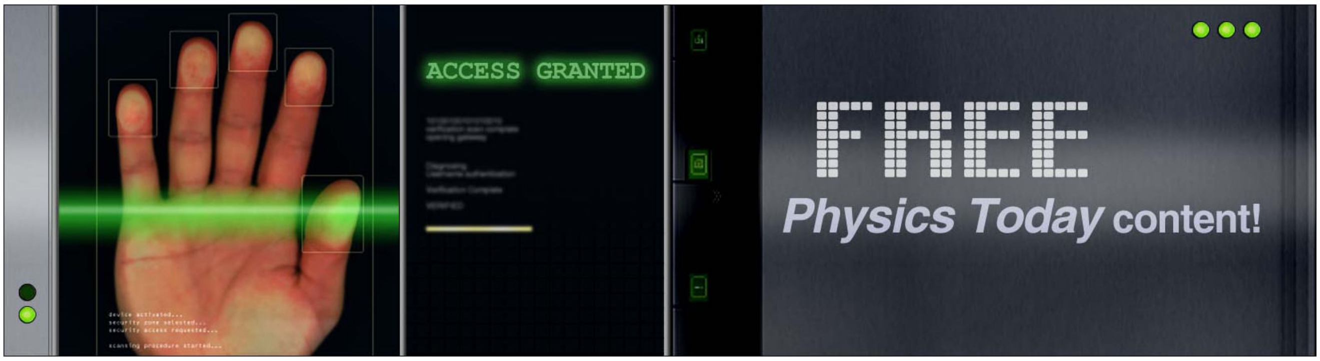

APPLIED PHYSICS LETTERS **98**, 132906 (2011)

# The dielectric suppress and the control of semiconductor non-Ohmic feature of $CaCu_3Ti_4O_{12}$ by means of tin doping

Willian C. Ribeiro, Rafael G. C. Araújo, and Paulo R. Bueno[a]
*Departamento de Físico-Química, Instituto de Química, Universidade Estadual Paulista, P.O. Box 355, 14800-900 Araraquara, São Paulo, Brazil*

(Received 25 August 2010; accepted 15 March 2011; published online 31 March 2011)

In this work it was demonstrated that the addition of Sn on $CaCu_3Ti_4O_{12}$ material improved non-Ohmic behavior by suppressing dielectric properties. It was noted that the improvement of the varistor characteristics, monitored by the increase in nonlinear coefficient, occurs with the disappearance of the grain dielectric relaxation process with concomitant decreasing of both dielectric constant and dielectric loss values. By forming a solid solution, $Sn^{4+}$ was incorporated into $CaCu_3Ti_4O_{12}$ matrix deforming the crystal lattice and restricting the formation of polaronic stacking faults. Thus, the dielectric relaxation due to polaronic defects is believed to be the origin of the huge dielectric properties disappearance. This framework is in agreement with the nanosized barrier layer capacitor model. © *2011 American Institute of Physics*. [doi:10.1063/1.3574016]

Dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO) have attracted much interest since its discovery by Subramanian *et al.*[1] This dielectric material has a high value of permittivity over a wide temperature range,[2,3] which is desirable for electronic devices miniaturization.[4] In addition, the non-Ohmic behavior was observed by Chung *et al.*,[5] showing the existence of insulating grain boundaries which could act as potential barriers, very similar to metal oxide varistors. Marques *et al.*[6] identified the Schottky-type nature of the potential barrier in CCTO when they observed the dependence between oxygen partial pressure in sintering process and varistor behavior. In a different work, Marques *et al.*[7] corroborated this fact by using vacuum heat treatment to decrease the varistor's properties. It is possible to attain good non-Ohmic characteristics by modifying the stoichiometry of the system. Ramírez *et al.*[8] presented a ceramic composed by 66.7% of $CaTiO_3$ (CTO) and 33.3% of $CaCu_3Ti_4O_{12}$ (CCTO/CTO) with high nonlinear coefficient ($\alpha \sim 1500$) that is even higher than the value find out by Chung *et al.*[5] calculated in the same current density range. However, the improvement of the varistor's properties decrease the dielectric constant value.[8] The correlation between non-Ohmic and dielectric properties was discussed by Marques *et al.*[6] using the IBLC model proposed by Sinclair *et al.*[9] to explain the increase in low frequency capacitance and high values of $\alpha$ on the oxygen heat treatments. The possibility to conciliate non-Ohmic and dielectric properties were reported in others works.[5,10,11]

Recently, a model based on the existence of stacking faults associated with polaronic defects has been reported to explain the semiconducting and dielectric coexistence characteristics in CCTO compounds, named nanosized barrier layer capacitor (NBLC). This model operates simultaneously with the IBLC model so that the dielectric relaxations of the grain boundary and polaronic defect were used to explain the high permittivity values.[12] The permittivity and dielectric losses increase proportionally, indicating that the process of energy storage is related to the mechanisms of energy dissipation (conduction process). Many applications of dielectric materials need low dielectric losses because of the heating (energy losses). In the literature, the decrease in dielectric loss is attained by addition of impurities.[13–19] Thus, herein it was aimed to show the possibility of improving the non-Ohmic behavior by suppressing the dielectric properties with the addition of Sn into the CCTO material. Moreover, the effects of doping were discussed considering dielectric relaxation processes and the mechanisms involved in the NBLC model.

CCTO polycrystalline bulk samples were prepared by solid-state reactions. Analytical grade $CaCO_3$ (Aldrich, 99%), $TiO_2$ (Aldrich, 99%), CuO (Riedel, 99%) and $SnO_2$ (Aldrich, 99%) powders were used to sintering $CaCu_3Ti_4O_{12}$ (CCTO) and $CaCu_3Ti_{3.8}Sn_{0.2}O_{12}$ (CCTO-Sn), i.e, 0.2 mol/mol of Sn. The precursor's materials were milled in isopropanolic media for 24 h with zirconia balls inside a polyethylene bottle. The resulting product was dried at room temperature and heat-treated at 900 °C for 12 h, using ambient atmosphere. After repeating the ball-milling operation, the powders were uniaxially pressed (1 MPa) into 12 mm diameter and 1 mm thick bulk samples, followed by 210 MPa isostatic pressing. The disks were sintered at 1100 °C for 3 h using ambient atmosphere, with heating and cooling rates of 5 °C/min. Finally, a polishing process was employed in order to obtain samples with plane and parallel faces.

The sintered samples backscattered images were obtained by electron scanning microscope (ZEISS DSM 940 A) and mean grain size were determined by the intercept method. X-ray diffraction patterns of the two systems (CCTO and CCTO-Sn) were recorded at room temperature with a RIGAKU RINT 2000 42 kV/120 mA powder diffractometer with Cu $K\alpha$ radiation over a wide range of Bragg angles $2\theta$ ($20° \leq 2\theta \leq 80°$). For the electrical characterization, sputtered gold contacts were deposited on the flat surfaces of the samples. Current-tension measurements were taken using a high-voltage source-measure unit (Keithley model 237). Impedance and capacitance spectroscopy measurements were carried out in the frequency range from 40 Hz to 110 MHz, with an amplitude voltage of 500 mV (rms),

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

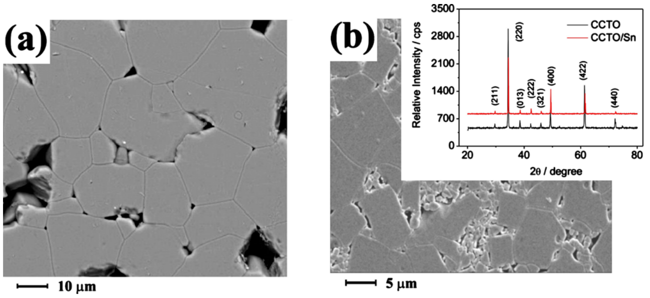

FIG. 1. (Color online) (a) CCTO and (b) CCTO-Sn micrographs exhibiting the grain grow inhibition with $SnO_2$ addition. Inlay: the x-ray diffractions patterns of the sintered samples.

employing a frequency response analyzer (HP model 4294A).

Figure 1 shows the micrographs of CCTO and Sn doped-CCTO samples. The inset exhibits the x-ray diffraction patterns. The micrographs indicate that the grain growth is inhibited by Sn addition (with average grain size $d_{\mathrm{CCTO}} = 14\ \mu\mathrm{m}$ and $d_{\mathrm{CCTO\text{-}Sn}} = 2\ \mu\mathrm{m}$). Ni and co-workers[19] have also showed the same trend in the decrease in grain size with increasing Sn content. Besides, there was no existence of precipitates in the microstructure and diffraction pattern shows only diffraction peaks related to CCTO crystallographic planes. This evidences that the Sn is forming a solid solution with CCTO phase. It is likely that $Sn^{4+}$ occupies the position of $Ti^{4+}$ in the crystalline lattice to form a solid solution because of the similarities in ionic radius and electronegativity. The results published by Parkash *et al.*[16] corroborated this assumption. They showed that there is only a single phase in $CaCu_3Ti_{4-x}Sn_xO_{12}$ compounds when $0 \leq x \leq 1.0$.

The addition of Sn increases the grain's and the grain's boundary resistance about one order of magnitude, as shown in the impedance diagrams of Fig. 2(a). The increase in the grain's boundary resistance was consistent with the decrease in the average grain size, showed in Fig. 1. Regarding the non-Ohmic behavior, there was an increase in the electrical breakdown field and a significant improvement in the coefficient of nonlinearity, according to *E-J* curves in Fig. 2(b). However, the leakage current was slightly changed. It is interesting to note that dielectric property is harmed if non-Ohmic properties are improved, as can be seen in Figs. 2(c) and 3.

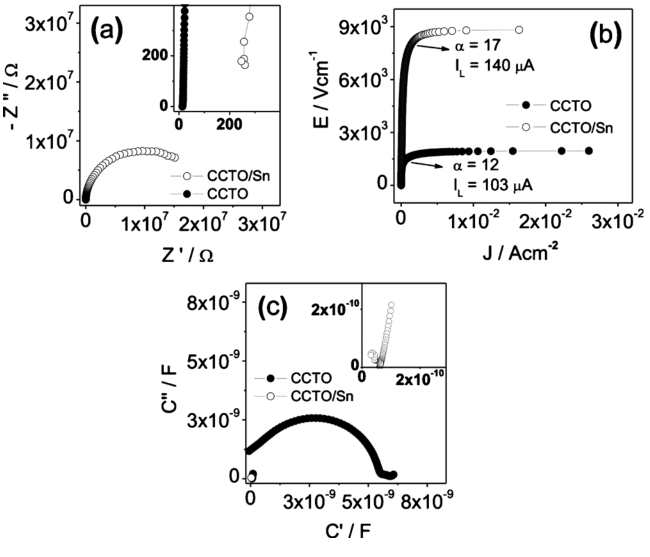

FIG. 2. Sn addition into a CCTO system (a) increased grain's and grain's boundary resistances, (b) improved non-Ohmic behavior, and (c) suppressed dielectric relaxation process in high frequency.

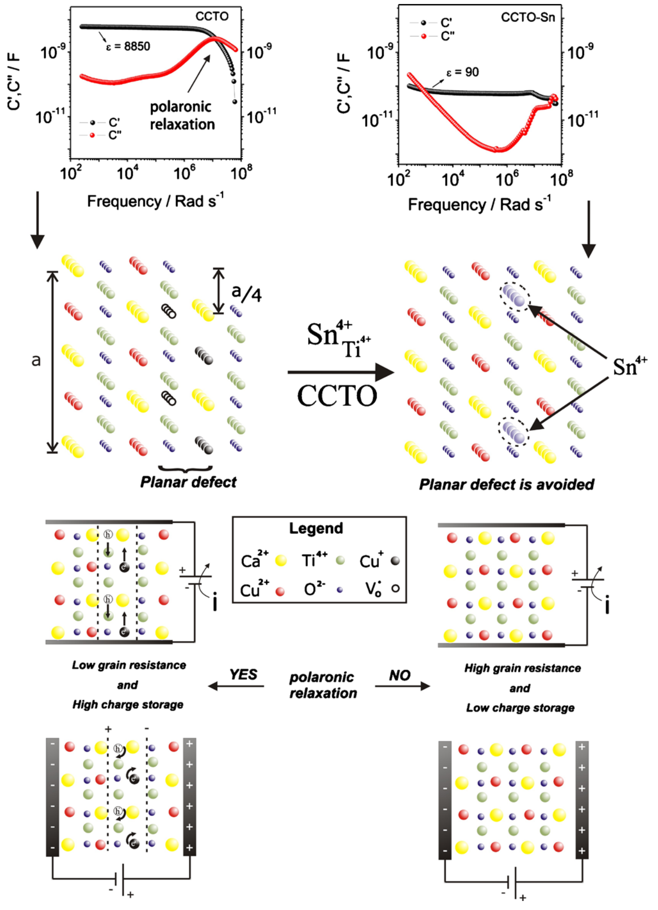

FIG. 3. (Color online) The high frequency relaxation peak in C″ plot disappeared when some Sn atoms replaced Ti atoms in the CCTO system. Note that the real capacitance value diminished in the absence of this peak. Below each graph there is a figure that ascribes the atomic structure of CCTO and CCTO-Sn systems and the electrical properties of a CCTO system caused by planar defect.

The Nyquist capacitive diagram [see Fig. 2(c)] shows the dielectric relaxation processes occurring in CCTO and CCTO-Sn systems. It was observed that the shape of the capacitance curves is quite different. The dielectric relaxation process corresponding to the grain response stands out in the CCTO system. Nevertheless, details given for the curve corresponding to the CCTO-Sn [inset in Fig. 2(c)] shows that the capacitive response in CCTO-Sn system is caused by polarization of the charges in grain boundary. This statement is confirmed in Fig. 3, where there is a decrease in dielectric constant of two orders of magnitude on Sn-doped CCTO (from about 9000 to 90 at 1 kHz). The decreasing in permittivity occurs in high frequency region of the real part of complex capacitive response, indicating the importance of the grain polarization phenomena for the occurrence of huge dielectric features in CCTO.

The dielectric loss curve, C″ plot in Fig. 3, follows the same trends in intermediate and high frequency. However, the values converge in low frequency and are approximately the same at 100 Hz. The decrease in the dielectric constant in CCTO is related to the suppressing of dielectric relaxation phenomenon which is represented by the peak in the curve of dielectric loss at high frequency. Ramírez *et al.*[20] showed that CCTO systems with high amount of calcium present low dielectric constants which are related to the disappearance of the high frequency relaxation peak of dielectric loss curves. They proposed the reduction in stacking faults in CCTO grains and low content of CCTO phase to explain the disappearance of the dielectric loss peak. Ribeiro *et al.*[21] characterized the dielectric relaxation process related to this peak and they associated to polaronic defects based on NBLC model.

According to the NBLC model, the origin of the remarkable CCTO dielectric property is due to the appearance of polaronic planar defects that act as nanosized bulk barriers. It was observed that the high dielectric constant is attained when high frequency dielectric loss peak appears, i.e., if polaronic defects in grain reply to the external electric field. So, the polaronic defects associated with stacking faults may be related to the dielectric loss peak. As mentioned previously, $Sn^{4+}$ and $Ti^{4+}$ ionic radii are very similar, but it is slightly higher for $Sn^{4+}$ ($R_{Ti^{4+}}=0.61$ Å e $R_{Sn^{4+}}=0.69$ Å).[22] The structure twists due to the insertion of $Sn^{4+}$ in CCTO crystal lattice and the sliding motion of one atomic plane can be, as a consequence, inhibited. Therefore, the absence of this peak indicates that Sn addition could inhibit the formation of stacking faults. The dielectric loss of CCTO is related to the conduction paths that arise from polaronic defects, leading to higher conductive in grains, as commented by Bueno *et al.*[12]

As mentioned, the dielectric response of doped CCTO was given only by intrinsic effects. Bueno *et al.*[23] showed that grain boundary contributes approximately with 25% of the total CCTO dielectric constant, but when polaronic relaxation is not present, the dielectric response is weak. The permittivity value in this work decreases about 100 times when $SnO_2$ was added to the CCTO, reinforcing the idea that localized charges in polaronic planes control the dielectric phenomenon in this system. Therefore, the grain polarization phenomena have great influence on the storage of charges at grain boundary and its suppression appears to be beneficial to provide pure non-Ohmic behavior.

In summary, Sn addition into CCTO systems inhibited the grain growth and did not modify the crystalline structure. Small grain size microstructures presented higher grain and grain boundary resistivity in agreement with $E_r$ value. Moreover, CCTO-Sn exhibited better non-Ohmic behavior than stoichiometric CCTO but dielectric properties were suppressed (the permittivity value diminished two orders of magnitude). The disappearance of the peak at high frequency on $C''$ plot suggested that the formation of stacking faults and thus the polaronic defects polarization were inhibited. As a result, it was shown herein that the dielectric properties can be modulated and suppressed by doping strategies, leading to pure varistor features in CCTO materials when Ti is replaced by Sn.

The financial support of this research project by the Brazilian research funding agencies CNPq and FAPESP is gratefully acknowledged.

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