Nanoscale effects and polaronic relaxation in CaCu₃Ti₄O₁₂ compounds

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ABSTRACT

In the present communication, by using dielectric spectroscopy measurement, the correlations between Nanosized Barrier Layer Capacitance (NBLC) (Bueno et al. (2009) [7]) and the high frequency polaronic near-Debye dipolar relaxation found in CaCu₃Ti₄O₁₂ compounds was discussed. The polaronic process was confirmed to be closely associated with the ultrahigh dielectric features of CaCu₃Ti₄O₁₂ materials and its concomitant dielectric loss. Herein, the shift in relaxation frequency as a function of temperature was used for calculating the activation energy for hopping electronic conduction. The value obtained was 33 meV, an energy whose magnitude is compatible and confirmed the hypothesis of polaronic features for this high frequency dipolar relaxation process. Furthermore, it is shown that the nanosized barrier inferred from the NBLC model has a polaronic feature with dielectric permittivity exiting orthogonally to dielectric loss, a phenomenological pattern that contradicts the normally observed behavior for traditional dielectrics but explain the dielectric and conductivity feature of CaCu₃Ti₄O₁₂ compounds.

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Both mono and polycrystalline CaCu₃Ti₄O₁₂ (CCTO) structures show a huge dielectric constant value [1] (larger than 10^4) over a wide temperature range, i.e. from 100 to 400 K [2–4]. Due to its weak temperature and frequency dependence, this dielectric behavior has great technological importance, being a promising feature for low frequency microelectronic applications, i.e. decoupling capacitors. However, since the first report by Subramanian et al. [4], the origin of the huge dielectric response for CCTO ceramics is still unclear and there is a strong debate regarding the intrinsic or extrinsic origin of this unusual dielectric performance.

The Internal Boundary Layer Capacitor (IBLC) model states that the dielectric behavior of CCTO does not have an intrinsic origin [5] or intrinsic space charge polarization mechanisms, its nature arising from the extrinsic heterogeneities of the ceramic itself. Stoichiometry has also been referred to as another important point in the CCTO debate, playing a crucial role in obtaining ultrahigh permittivity values [6].

One of the main attributes of the CCTO compound is related to its dual nature: dielectric features combined with semiconductor characteristics. It has been demonstrated that an increase in the dielectric properties lead to a simultaneous increase in the dielectric loss, i.e. an increase of the electronic conduction [7]. Indeed, dielectric and/or capacitance spectroscopy analyses have shown that the grain boundaries contribute to this dielectric behavior [8,9]. However, this contribution represents only about 25% of the total dielectric response, indicating that the grain boundaries *per se* cannot account for the unusual dielectric performance [8]. In

the high frequency region, the grain region, a dipolar relaxation in bulk CCTO ceramics was observed by Bueno et al. [9]. This phenomenon, related to the dielectric behavior of the system, presents a near-Debye pattern and its existence was attributed to an "intrinsic" dipolar relaxation occurring in the bulk of the polycrystalline device [9]. Zhang and Tang attributed such relaxation to the existence of polarons with a variable-range-hopping conducting mechanism [10].

More recently, the NBLC model [7] proposed that polaronic electronic defects, present in bulk CCTO, and associated with stacking faults, are involved in the mechanism for the huge dielectric properties. The model explains the observation of both dielectric and conductive features increasing concomitantly, which is not a characteristic that can be explained only by the traditional IBLC model. For this model, the origin of the electrostatic barriers (dielectric barriers) are not necessarily associated to a parallel electronic conduction mechanism, although the barriers can be associated to extrinsic space charge regions (grain boundary potential barriers), for instance. The polaronic defects, proposed in the NBLC model, shows a preferential conduction direction parallel to stacking faults (perpendicular to the dielectric barrier), creating nanoscale barriers. Even though the nature of the NBLC and IBLC models is different, they can work concomitantly, completing each other [7].

Subramanian et al. [11] have briefly described the existence of twinning planar defects in CCTO monocrystalline ceramics, suggesting that such defects could contribute as a capacitive barrier. From all the evidence, it is clear that the key to understand the ultrahigh dielectric properties of CCTO compounds is related to its bulk characteristics, although the grain boundaries have a prominent percentage in the whole dielectric feature.

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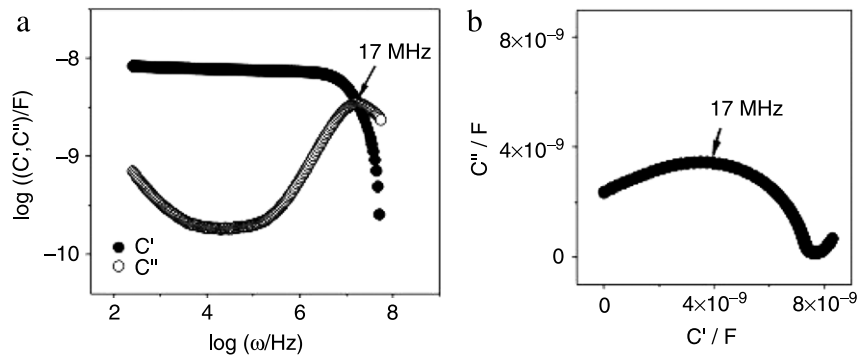 *E-mail address:* prbueno@iq.unesp.br (P.R. Bueno).

Fig. 1. (a) Bode complex capacitive diagrams and (b) Nyquist capacitive diagram for CCTO. The diagrams show the dipolar relaxation process causing an abrupt increase in the permittivity values in the high frequency region.
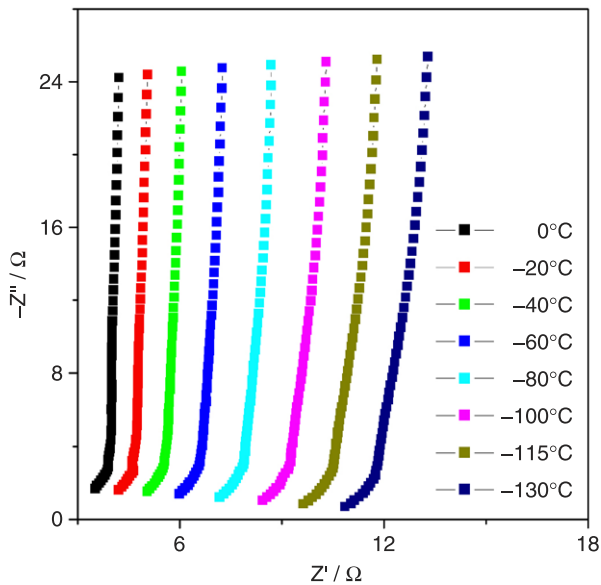

Fig. 2. Nyquist diagrams obtained from 320 kHz to 3.2 MHz at different temperatures. The plot shows an increase in the real part of the impedance as the temperature decreases. There are no changes in the dipolar relaxation pattern (the shape of the curves remain the same).

In order to support the NBLC model and understanding its correlation with polarons, it is important to mention the presence of sub-grain microstructures that can act as domain boundaries, this configuration being denominated layered domains [12,13]. The nature of these layered domains is still unclear, but it could be related to different structural regions separated by stacking faults inside a single grain, as proposed by the NBLC model. These structural regions have been pointed out as the origin of other types of disordered domains (bump domains and terrace-ledge domains) observed in CCTO ceramics [13].

The main goal of the present paper is to confirm the polaronic nature of the high frequency dipolar relaxation and discuss its correlation with NBLC model. Particularly, the confirmation of polaronic nature reinforces the NBLC model as a plausible phenomenological and physical explanation for the huge dielectric features and co-existing semiconducting properties in CCTO ceramics.

CCTO polycrystalline bulk samples were prepared by solid-state reactions. Analytical grade $CaCO_3$ (Aldrich–99%), TiO_2 (Aldrich–99%) and CuO (Riedel–99%) powders, with the appropriate molar ratio, were used. The raw materials were milled in alcohol 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 uniaxial pressed (1 MPa)

into 12 mm diameter and 1 mm thick bulk samples, followed by 210 MPa isostatic pressing. The discs 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. For the electrical characterization, sputtered gold contacts were deposited on the flat surfaces of the samples. Impedance and capacitance spectroscopy measurements were carried out in the frequency range from 250 Hz to 50 MHz, employing a frequency response analyzer (Solartron model SI 1260) coupled to a dielectric interface (Solartron model 1296). In order to perform the measurements between 0 and −130 °C, a cryostat filled with liquid nitrogen was used. Before each measurement, the impedance of the sample holder was compensated in order to minimize any resonance effects.

Fig. 1(a) shows a typical room temperature Bode capacitive diagram for CCTO bulk systems. The real part of the complex capacitive response exhibits a near constant value (plateau) in the low frequency region, showing an abrupt decrease for the higher frequencies. Clearly, one can observe that the decrease from low to high frequencies is associated to a relaxation process. This phenomenon was previously conferred as being a dipolar relaxation within the grains of a CCTO polycrystalline system [8,9]. The dipolar relaxation feature is confirmed by the peak in the imaginary part of the capacitive Bode diagram. In this figure it is also possible to notice that the main increment in the permittivity value is related to the dipolar relaxation process. As mentioned previously, this phenomenon is a near-Debye relaxation (Fig. 1(b)) [8,9], with its characteristic frequency between 2 MHz ($\omega = 2\pi f \sim 12$ MHz) and 4 MHz ($\omega = 2\pi f \sim 25$ MHz). For the capacitive response in particular, the characteristic frequency is about $\omega \sim 17$ MHz. The results are in total agreement with the work of Zhang and Tang [10].

The behavior of the relaxation process as a function of temperature was studied with the purpose of confirming its nature by means of dielectric spectroscopy. The analysis are in agreement with the scientific literature [14]. Zhang et al. [15] suggested the existence of two relaxation processes: a low frequency grain boundary process and a high frequency grain-linked process (about 10^6 Hz). In Fig. 2 it is shown the high frequency impedance spectra, from 320 kHz up to 3.2 MHz, as a function of temperature, using a Nyquist representation. One can observe that the resistive part, the real part of the diagram, is the main component changing in the temperature range from 0 to −130 °C. The capacitive pattern is maintained and no changes are observed in the low frequency region of the spectra. This pattern is expected for a polaronic activated hopping conduction process [10]. Therefore, the elected frequency range was suitable for identifying grain related processes in CCTO bulk ceramics, as intended. The impedance pattern as a function of temperature (Fig. 2) demonstrates a typical
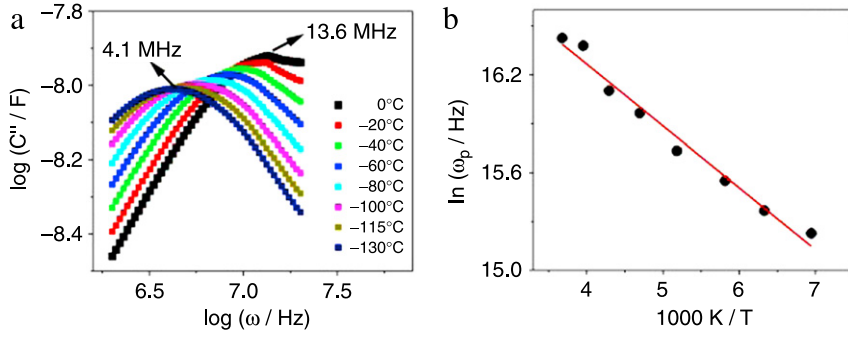
Fig. 3. (a) Bode capacitive diagram (imaginary part—C'') showing the temperature-dependent displacement of the polaronic relaxation process at high frequencies. (b) Arrhenius-type dependence of ω_p as a function of $1/T$. The Pearson coefficient for the linear dependence was 0.976.
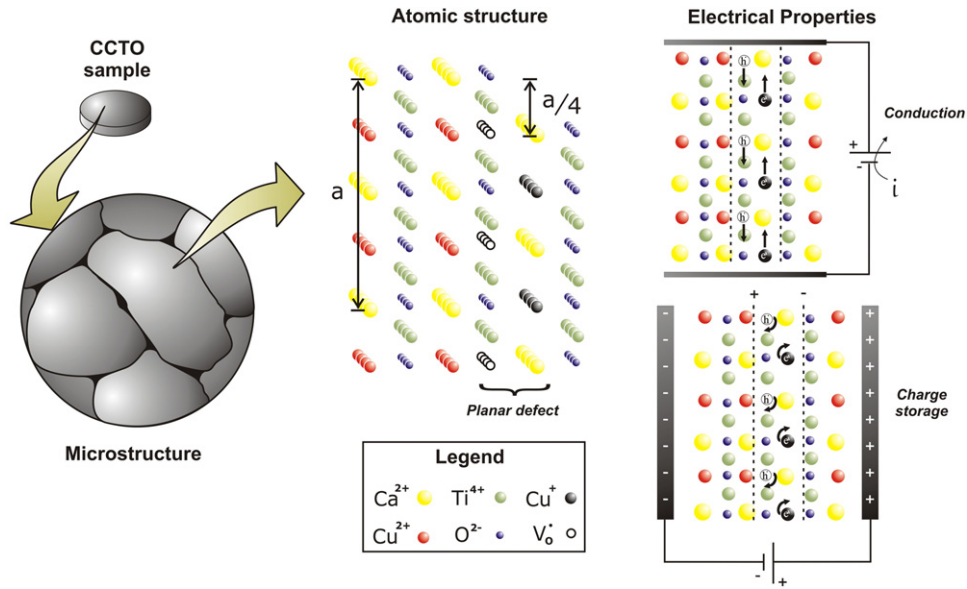

Fig. 4. Schematic representation of bulk polaronic defect that correlates the NBLC model and variable-range-hopping mechanism observed in CCTO compounds.

polaronic relaxation process, characterized by low hopping activation energy. The near-Debye relaxation, a relaxation very close to the ideal, is a result of a slight distribution of relaxation times. Adams et al. [3] cited that a study of the chemical defects in CCTO bulk ceramic should lead to the origin of its semiconducting grain properties that was suggested by Zhang and Tang [10] as being due to Mott's variable-range-hopping mechanism.

Fig. 3(a) shows the Bode capacitive diagram (C''), with the temperature dependent frequency peak of the imaginary part (entitled ω_p). This Arrhenius-type dependence can be expressed as:

$$\omega_p = \frac{1}{\tau_p} = \omega_0 \exp\left(-\frac{E_a}{kT}\right) \tag{1}$$

in which τ_p is the relaxation time, ω_0 is a pre-exponential factor, E_a is the activation energy of the process and k is the Boltzmann's constant. The linearization of Eq. (1) is shown in Fig. 3(b). The activation energy calculated for this relaxation process was $\sim$33 meV. This value, characteristic of polaronic processes, is very close to the ones reported in literature [16].

Bidault et al. [17] studied the activation energy for conduction in different perovskite systems and observed anomalous dielectric behavior at low temperatures, i.e. $\sim$5 K. The authors raised the possibility of ionic dipolar defects introduced by dopants as responsible for this phenomenon. Due to the activation energy of 0.2 eV, with mean value around 0.075 eV for the

different perovskite systems studied, the hypothesis of an ion-jumping relaxation process was discarded. Dominik and MacCrone [18] attributed the polaronic activated hopping conduction process in rutile TiO_2 to oxygen vacancy defects, this process having an activation energy of 20 meV at low temperatures. The polaronic conduction is usually proved by means of optical absorption. Homes et al. [19] performed optical infrared absorption measurements in CCTO monocrystals that proved the existence of a dipolar relaxation process with nanometric scale, attributing this phenomenon to the ultrahigh dielectric properties of the material. The authors calculated an energy value of 54 meV, this value having the same order of magnitude as the one obtained in this work.

By comparing different perovskite systems, Li et al. [20] postulated the presence of atomic defects capable of explaining the conductivity of CCTO. The authors suggested that, at high temperatures and in oxidizing atmospheres, Cu^{2+} can be reduced to Cu^+ and Ti^{4+} substitutes the copper in the CCTO structure. The high conductivity would arise during cooling when Cu^+ oxidizes to Cu^{2+} and, in order to compensate the charges, the Ti^{4+} will reduce to Ti^{3+}. This mechanism is similar to the one proposed by Bueno et al. [7], where the formation of stacking faults are the structural origin of the polaronic conduction. Therefore, the relationship between structural dielectric barrier and electronic defects that cause electronic hopping parallel to the dielectric barriers, could explain the ultrahigh dielectric properties

associated to semiconducting features in CCTO systems (see Fig. 4). Li et al. [20] suggested that the variations in the dielectric constant value in CCTO systems were due to the presence of nanoscale capacitive barriers located in the bulk of the material. In common perovskite systems, there are only capacitive barriers at grain boundaries and, therefore, the electronic charge storage is low. Although the authors show the existence of nanoscale capacitive barriers in the bulk, they do not associate them with the presence of polaronic defects. The correlation between these defect types could be the key for understanding the mutual dependence of the dielectric and semiconducting properties.

In Fig. 4 it is shown the specific bulk polaronic defect that is able to lead to a high dielectric feature combined with hopping conductivity. The conductivity is confined in a plane and it can be polarized orthogonally to this plane, generating a capacitance, i.e. a nanosized capacitance whose associated effective permittivity is $k_{ef} = (L/\overline{n})\,k$. $\overline{n}$ is the distance between these nanoscale defects and L is the sample's thickness. Supposing a 10 nm length for $\overline{n}$, a value of 100 to the intrinsic permittivity, k, and a distance between electrodes around 1 mm, one will have a 10^5 order of magnitude for the k_{ef} which is in good agreement to the values found in CCTO. Note that both dielectric and conductivity properties are orthogonal each other, explaining why both are in phase during ac perturbation meaning that this defect is able to increase concomitantly the permittivity and dielectric loss in a particular way that is not observed in other materials.

In conclusion, our results confirm that the high frequency near-Debye relaxation process in CCTO has a polaronic nature. This is in agreement with the NBLC model which postulates the existence of nanoscale capacitive barriers and electronic conduction in bulk CCTO, explaining both its dielectric and semiconducting properties. Moreover, the bulk stacking faults, located at nanometric distances from each other, could account for the dielectric and conductive properties concomitantly observed. An energy value of 33 meV was obtained for the polaronic relaxation process in the high frequency region (MHz). This reinforces the hypotheses of polaronic origin for the abrupt increase in dielectric properties observed at high frequencies.

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