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## Separation of dielectric and space charge polarizations in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{CaTiO}_3$ composite polycrystalline systems

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The complex analysis of dielectric/capacitance is a very useful approach to separate different polarization contributions existing in polycrystalline ceramics. In this letter, the authors use this type of spectroscopic analysis to separate the bulk's dielectric dipolar relaxation contributions from the polarization contribution due to space charge in the grain boundaries of a  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{CaTiO}_3$  polycrystalline composite system. The bulk dielectric dipolar relaxation was attributed to the self-intertwined domain structures from the  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  phase coupled to the dipole relaxation from the  $\text{CaTiO}_3$  phase, while the space charge relaxation was attributed to the Schottky-type potential barrier responsible for the highly non-Ohmic properties observed in this composite polycrystalline system. © 2007 American Institute of Physics. [DOI: 10.1063/1.2720301]

The huge dielectric constant ( $>10,000$  over a wide temperature range of 100–400 K) of a  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  perovskite-like material was discovered by Subramanian *et al.*<sup>1</sup> and, as foreseen, the discovery of such an intriguing dielectric property soon led  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  materials to become important candidates for ceramic capacitors, attracting the technological<sup>2–4</sup> and scientific<sup>2,5–9</sup> interest of many researchers. At present, it is generally accepted that the ultrahigh dielectric response is not an intrinsic behavior.<sup>10,11</sup> 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, etc.<sup>10–12</sup> Specifically, the grain boundary barrier-layer capacitances are generally associated with non-Ohmic properties in metal oxide polycrystalline semiconductors.<sup>13–16</sup> Indeed, in addition to the remarkable and intriguing dielectric property, Chung *et al.*<sup>12</sup> observed that potential barrier exists intrinsically in the grain boundary region, likely possessing a Schottky-type nature, according to Refs. 12 and 17. This Schottky-type barrier or the grain boundary interfacial polarization effects also contribute to the total dielectric response, and recently, based on impedance and dielectric (or capacitance) complex analysis, our research group<sup>18,19</sup> demonstrated that the grain boundary contribution can be responsible for up to 25% of the total dielectric response of this type of material.<sup>18,19</sup> However, most results have led to the conclusion that the correlation between non-Ohmic and dielectric properties (i.e., the higher the non-Ohmic property, the higher the dielectric response) is not easily established mainly because of the presence of other kinds of barrier-layer capacitances inside the grain, e.g., self-intertwined domain structures inside the grains of polycrystalline  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  materials.<sup>10,11,18,19</sup> Therefore, although the grain boundary contributes to a large extent to the total dielectric constant value at ambient temperature, it is not the major effect contributing to this property.

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{CaTiO}_3$  composites are also very promising Ba-/Pb-free dielectric materials<sup>20</sup> due to their lower dissipation factor at room temperature compared with

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  pure and stoichiometric materials, even though their dielectric constant at ambient temperature is much lower, i.e., around 1300–1800. Recently, we have also shown that such composites also present remarkable non-Ohmic properties<sup>19</sup> (i.e., a nonlinear coefficient value  $\alpha$  of  $\sim 65$  in the traditional current density range of 1–10 mA/cm<sup>2</sup> and

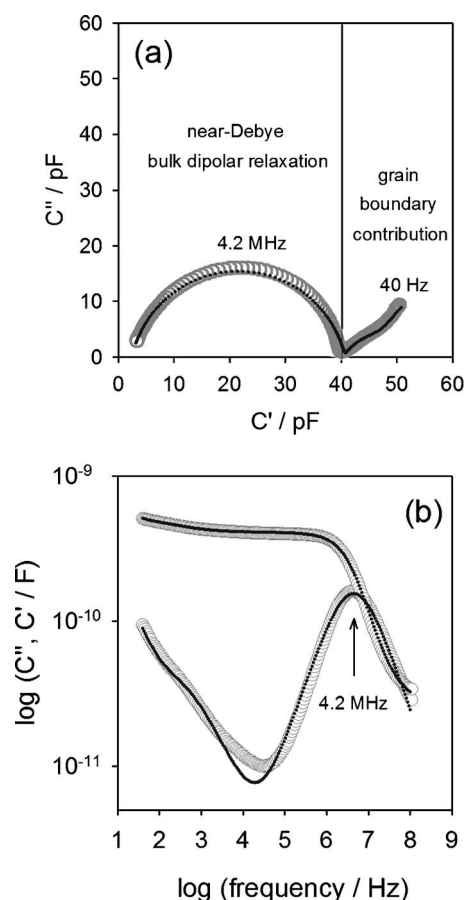


FIG. 1. (a) Complex capacitance diagrams for the CCTO-CTO composite, showing the whole relaxation pattern in this polycrystalline material. The higher frequency region exhibits a near-Debye relaxation pattern relating to the bulk dielectric features. (b) Bode capacitive diagrams, real ( $C'$ ) and imaginary ( $C''$ ) parts. (o) Experimental data and (continuous line) the result of the fitting to the theoretical function.

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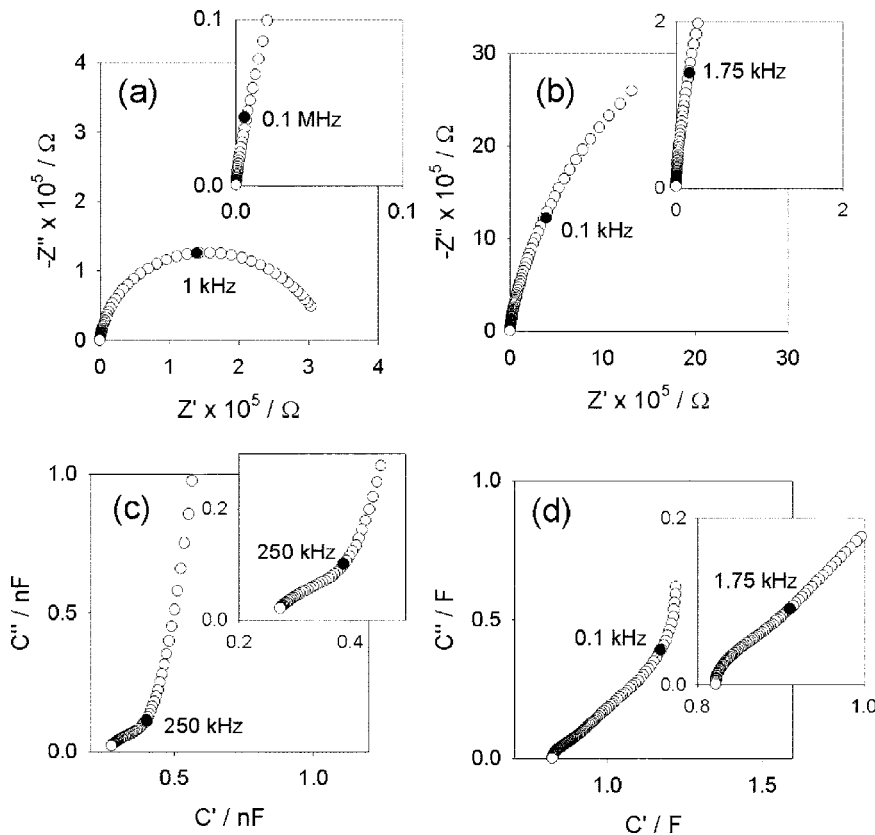


FIG. 2. Comparison of impedance and capacitance complex diagrams in the low frequency region (from about 0.5 MHz to 40 Hz) of the frequency response data for the  $\text{SnO}_2$ -based varistor system and the CCTO-CTO composite. (a) and (c) are, respectively, the impedance and capacitance complex diagrams for the  $\text{SnO}_2$ -based varistor system. (b) and (d) are, respectively, the impedance and capacitance complex diagrams for the CCTO-CTO composite.

$\sim 1500$  in the current range of 3–30 mA, the same range used by Chung *et al.*<sup>12</sup>.

This letter proposes a methodology to separate the dielectric polarization response elicited by the grain's internal capacitance barriers (i.e., self-intertwined domains) and dipolar relaxation from that of the grain boundary space charge region, using dielectric/capacitance spectroscopy.<sup>3</sup> Based on such a physical analysis, we also propose an adequate equivalent circuit that can take into account the capacitance-voltage dependence of the Schottky-type barrier existing in metal oxide dielectric materials with highly non-Ohmic properties.<sup>19</sup> The Mott-Schottky straight-line behavior was constructed from a complex capacitance analysis and displayed via  $C_{\text{gb}}^{-2}$  (grain boundary capacitance) versus  $V_{\text{dc}}$ , proving the existence of potential barriers in the grain boundary region.

The  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{CaTiO}_3$  polycrystalline composite was prepared based on traditional oxide mixture processing. All the precursors were of analytical grade:  $\text{CaCO}_3$  (J. T. Baker, 99.99%),  $\text{TiO}_2$  (Aldrich, 99.8%), and  $\text{CuO}$  (Riedel, 99%). The mixed oxides were ball milled for 24 h in isopropyl 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  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{CaTiO}_3$  polycrystalline composite system (CCTO-CTO) was first slightly pressed into disk shaped pellets 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).

Gold contacts were deposited by sputtering on the samples' surfaces for the electrical measurements. Current-tension measurements were taken using a high-voltage source-measure unit (Keithley model 237). The breakdown electric field ( $E_b$ ) was obtained at a current density of

$1 \text{ mA cm}^{-2}$ . Numerical values for the nonlinear coefficient  $\alpha$  were obtained by a linear regression of the  $\log J$  vs  $\log E$  plot within the range of 1–10  $\text{mA cm}^{-2}$ , and the  $\alpha$  values were calculated at around 62–68 in this current density range. The dielectric spectroscopy measurements were taken with a frequency response analyzer (HP 4294 A), at frequencies ranging from 40 Hz to 110 MHz, with an amplitude voltage of 500 mV. For the capacitance-voltage analysis, a bias dc potential of 0–40 V was applied.

It is widely known that dielectric relaxation can be empirically described by Debye-type or Cole-Cole relaxation functions,<sup>21</sup>  $C^*(\omega) = C_\infty + \Delta C / (1 + (\omega\tau)^{1-\beta})$ , in which  $\beta$  approaches the zero value for pure Debye relaxation. Figure 1(a) shows the typical dielectric or capacitance complex diagrams for the CCTO-CTO polycrystalline composite. Note the Debye-type relaxation<sup>21</sup> ( $\beta \sim 0.1$ ) in the frequency range of 0.1–110 MHz, which we attribute to the grain dielectric response; i.e., it is likely due to the dipolar relaxation of CCTO-CTO composite grains related to self-intertwined domains<sup>10,11</sup> from the CCTO phase coupled to the dipole relaxation from the CTO phase. The characteristic frequency of this dipolar relaxation was found to be around 4.2 MHz, as indicated in Figs. 1(a) and 1(b).

The complex analysis of capacitance is useful to separate distinct relaxation processes and can sometimes be useful to separate different polarization effects that contribute to the global frequency response or to the total relaxation response.<sup>22–24</sup> Based on this approach, an example of the usefulness of this methodology is the  $\text{SnO}_2$  non-Ohmic basic varistor system,<sup>13,14,22–24</sup> in which the influence of trapping activity associated with the conductance term can be eliminated, as observed via the depression angle of a semicircular relaxation in the complex capacitance plane.<sup>13,22–24</sup> This methodology allows one to construct the “true” Mott-Schottky pattern,<sup>13,22–24</sup> i.e., a frequency-independent Mott-

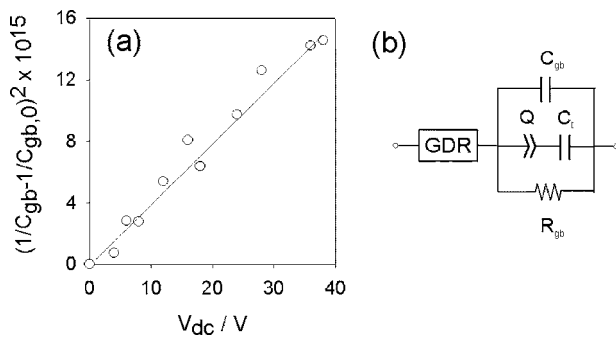


FIG. 3. (a) Mott-Schottky representation of the CCTO-CTO composite, which is an indication of the potential barrier in the grain boundary region responsible for the non-Ohmic properties found in this system.  $C_{gb,0}$  is the grain boundary capacitance at zero potential bias. (b) Equivalent circuit representing the grain boundary region considering the influence of trapping states. GDR accounts for grain dielectric relaxation.  $Q$  is the constant phase element representing the distribution of trapping states or energy levels in the gap of the semiconductor.

Schottky representation, which requires that the maximum slope of the straight-line behavior be attained. This implies reaching the minimum value of the  $C_{gb}$ , which is due only to the net/total geometric capacitance.

As previously discussed, the CCTO-CTO composite possesses both non-Ohmic and good dielectric properties.<sup>19</sup> Therefore, if one eliminates the dipolar dielectric response from the whole frequency response data (using an appropriate software after fitting to the theoretical function, see Fig. 1), one can better visualize the response due only to the nonlinear electrical response (grain boundary response associated with the space charge polarization and Schottky-type potential barriers responsible for the highly non-Ohmic properties). The complex capacitance plane without the dielectric response of the CCTO-CTO composite is shown in Fig. 2(d) and compared with the usual non-Ohmic response of the  $\text{SnO}_2$ -based polycrystalline system shown in Fig. 2(c). The impedance diagrams in Figs. 2(a) and 2(b) correspond to the  $\text{SnO}_2$  and CCTO-CTO systems, respectively. The similarities between Figs. 2(c) and 2(d) lead one to infer that the range of frequencies of around 40 Hz to 0.1 MHz corresponds to the frequency region in which space charge relaxation occurs in the CCTO-CTO systems and that this region is equivalent to the one observed in  $\text{SnO}_2$ -based non-Ohmic systems.<sup>13,15</sup> This space charge relaxation is coupled to the dc grain boundary resistance  $R_{gb}$ ; i.e., at lower frequencies, one finds that the conductive term ( $G/\omega$ ) is related to  $R_{gb}$  [see Fig. 3(b)]. At this point, it is important to emphasize that in ZnO- or  $\text{SnO}_2$ -based varistor systems, at higher frequencies (usually  $10^6$  to  $10^9$ ), a resonance phenomenon emerges as a circle possessing negative values<sup>13,25</sup> of the terminal parallel capacitance in the  $C^*$  plane. A detailed description of resonance events is given in Ref. 25. However, as stated previously, in the case of metal-oxide varistor/dielectric systems such as the CCTO-CTO composite described here, the high frequency region is dominated by the dipolar dielectric relaxation of the grains, which is related to self-intertwined domain structures.<sup>10,11</sup>

Figure 3 depicts the  $C$ - $V$  or Mott-Schottky pattern constructed from the grain boundary capacitance value as a function of bias voltage. The grain boundary capacitance values were extracted from the fitting of the data to the theoretical relaxation function (see Fig. 1 to visualize this fitting).

This Mott-Schottky-type response of the  $C$ - $V$  pattern proves the existence of the charge space region relating to potential barriers. Note that the equivalent circuit for this region considers the existence of trap effects (i.e., energy levels existing in the gap), which is quite acceptable for  $\text{ATiO}_3$ -based oxides,<sup>2</sup> since low concentrations of oxygen vacancies (lower than 0.0002) cause a huge decrease in the grain's resistivity.<sup>2</sup> Figures 1(a) and 1(b) compare the fitting of the theory and the experimental data.

In conclusion, dielectric/capacitance or impedance spectroscopy can be used to separate the different types of relaxation existing in CCTO-based polycrystalline ceramics, i.e., separate the contributions from dipolar relaxation and the space charge region. Dipolar relaxations likely occur due to self-intertwined domain structures in the bulk region of the CCTO phase coupled to the dipole's relaxation in the bulk of the CTO phase, while space charge polarizations likely come from grain boundary regions due to Schottky-type potential barriers. It is important to stress that due to the composite's low dielectric constant, the influence of self-intertwined domain structures in the relaxation is not as strong as that expected for the CCTO pure phase. This will be the subject of a future investigation.

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