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Effects of cation stoichiometry on the dielectric properties of $CaCu_3Ti_4O_{12}$

Seunghwa Kwon[a,*], Chien-Chih Huang[a], M.A. Subramanian[b], David P. Cann[a]

[a] *Materials Science, School of Mechanical, Industrial, and Manufacturing Engineering, 204 Rogers Hall, Oregon State University, Corvallis, OR 97331, United States*
[b] *Department of Chemistry, 153 Gilbert Hall, Oregon State University, Corvallis, OR 97331, United States*

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ABSTRACT

Compositions based on $CaCu_{3+x}Ti_{4+y}O_{12}$ ($x = +0.06, 0, -0.06$; $y = +0.08, 0, -0.08$) with varying cation stoichiometry were prepared via the conventional solid state synthesis methods. No significant changes in the perovskite crystal structure were observed via diffraction compared to stoichiometric $CaCu_3Ti_4O_{12}$ (CCTO). However, a CuO phase was detected on the surface of all compositions and the presence of Cu_2O was observed in the inner region of the sample for both Cu- and Ti-excessive CCTO. From the results of dielectric measurements, Cu- and Ti-deficient CCTO showed a higher dielectric constant than undoped CCTO. Due to the presence of Cu_2O, both Cu- and Ti-excessive CCTO yielded low values of the dielectric constant. Using impedance spectroscopy, the improvement in dielectric constants and low $\tan\delta$ values in the Cu- and Ti-deficient CCTO compositions can be traced to the lower grain resistivities compared to stoichiometric CCTO.

1. Introduction

In recent years, $CaCu_3Ti_4O_{12}$ (CCTO) has attracted a significant amount of attention based on its extraordinary dielectric properties. The dielectric constant of CCTO is about 10,000 at room temperature and is independent of temperature over the range of 100–400 K [1–3]. This feature makes it applicable to a variety of microelectronic device applications for capacitive elements. In addition, this cubic perovskite material lacks the presence of structural transitions as is the case with ferroelectric materials [1,2] such as the common ferroelectric perovskite $BaTiO_3$. For the unusually high dielectric constant in CCTO, there have been many attempts to explain the origin of this phenomenon. Based on the microstructural evidence including domain boundaries [4] in polycrystalline CCTO and twin boundaries [5] in single crystal CCTO, it has been generally understood that a purely intrinsic model cannot be used to explain the origin of the high dielectric constant [6]. Rather, it has been proposed that the reason for the abnormally large dielectric constant is due to Maxwell–Wagner relaxation [7], which was supported by a first-principles study [8]. Here, the electrical heterogeneity originating from the mobile charged species and the internal interfaces in polycrystalline CCTO gives rise to the polarization in semiconducting grains and insulating grain boundaries [9,10]. The grain boundary inhomogeneity was confirmed by the existence of electrical potential barriers via current–voltage measurements [11]. So far, the internal barrier layer capacitor (IBLC) model has been widely accepted as the most likely mechanism to elucidate the high dielectric constant in CCTO.

In order to account for the semiconductivity in CCTO, two models have been proposed so far. First, it is known that TiO_2-based perovskite ceramics such as $BaTiO_3$ and $SrTiO_3$ become more conductive during sintering under reducing conditions due to a small amount of oxygen loss occurring at high temperatures [12]. On the other hand, a cation non-stoichiometry model was suggested by Li et al. [13]. From their studies on $ACu_3Ti_4O_{12}$ (A = Ca, Sr), Cu^{2+} reduces to Cu^{1+} upon heating along with a charge balanced substitution of Ti^{4+} on the Cu site. These reduced monovalent Cu ions are reoxidized into divalent Cu ions during the cooling stage along with the reduction of Ti^{4+} to Ti^{3+} where the electrons move into the 3d conduction band, which in turn contribute to the rise in conductivity. With the recent report that a Cu_2O phase was observed inside a decomposition zone with a negligible change in bulk resistivity during a nitrogen or oxygen annealing [14], the cation non-stoichiometry model is likely to be the reasonable explanation for semiconducting behavior in CCTO.

Since cation instability has an influence on the defect equilibrium (including processing condition) and that in turn has a significant effect on the dielectric properties of CCTO [15], it is crucial to understand the influence of the cation non-stoichiometry on the dielectric response. There have been reports that confirmed the existence of Cu deficiency in CCTO [14,16], but the detailed mechanisms of the stoichiometric effects governed by both Cu and Ti stoichiometry has not been well established. In this study, the effects of Cu and Ti non-stoichiometry on the dielectric properties

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* Corresponding author. Tel.: +1 541 737 8896; fax: +1 541 737 2600.
E-mail address: kwonse@onid.orst.edu (S. Kwon).

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of CCTO are investigated and compared with stoichiometric CCTO. The frequency and temperature dependence of the dielectric constant and loss tangent was measured and analyzed in terms of the stoichiometric deviations.

2. Experimental

The preparation of both stoichiometric and non-stoichiometric CCTO pellets was carried out via solid state synthesis. First, high purity powders of $CaCO_3$, CuO, and TiO_2 were mixed together and milled using a vibratory mill with yttria-stabilized zirconia media to obtain stoichiometric CCTO (i.e. $CaCu_3Ti_4O_{12}$). The process was repeated for the non-stoichiometric CCTO powders based on the calculations of 2 at% deficient Cu and Ti (i.e. Cu2.94 and Ti3.92) as well as 2 at% excessive Cu and Ti (i.e. Cu3.06 and Ti4.08). Then, each powder was calcined in air at 1000 °C for 24 h. After the second milling of the calcined powders, 12.7 mm diameter CCTO pellets were made with the help of approximately 3 wt% organic binder through a cold uniaxial press. Those pellets were then sintered in air at 1100 °C for 2 h, followed by density measurements via Archimedes method which confirmed that the density of all pellets was over 95% compared to the theoretical value. For the examination of phase equilibria and lattice parameter changes, an X-ray diffractometer (Bruker-AXS D8 Discover) was used for the calcined powders, as-sintered and polished pellets. For the dielectric measurements, an Agilent 4284A LCR meter was used with an environmental chamber for the temperature measurements after the samples were sputtered with gold electrodes. Also, the electrical properties of CCTO samples were measured by using an HP 4194A impedance analyzer over the frequency range from 10 Hz to 5 MHz.

3. Results and discussion

The X-ray diffraction patterns of polished stoichiometric (i.e. undoped) and non-stoichiometric CCTO samples are plotted in Fig. 1. As can be seen on the plots, all diffraction peaks were matched with known peaks of the pseudo-cubic structured CCTO based on the Powder Diffraction File data (PDF #75-2188). Also, the lattice parameter of the CCTO phase among the different chemical stoichiometric CCTO samples varied less than 0.08%. Diffraction measurements on as-sintered (i.e. unpolished) stoichiometric and non-stoichiometric specimens revealed the existence of a tenorite CuO phase. This evidence suggests that during sintering decomposition reaction drives Cu out of the CCTO phase. Equilibrium thermodynamics would suggest that, in air, CuO will reduce to Cu_2O at temperatures just above 1000 °C. Thus during sintering, a conversion of Cu^{2+} to Cu^{1+} occurs and given the strict ionic size limitations within the CCTO crystal structure the majority of the relatively large Cu^{1+} must reside in a Cu_2O secondary phase. Consequently, this suggests that the Cu/Ti stoichiometry of the CCTO phase changes during processing. Upon cooling, a reoxidation reaction occurs which coverts Cu_2O to CuO, though at relatively rapid cooling rates such as those used in this study (~10 °C/min), the reformation of the CuO phase is mostly limited to the surface. It is likely that reoxidation reactions also occur on a finer scale within grain boundary networks and other high oxygen diffusion paths. This ultimately contributes to the electrical heterogeneity observed via the space charge polarization.

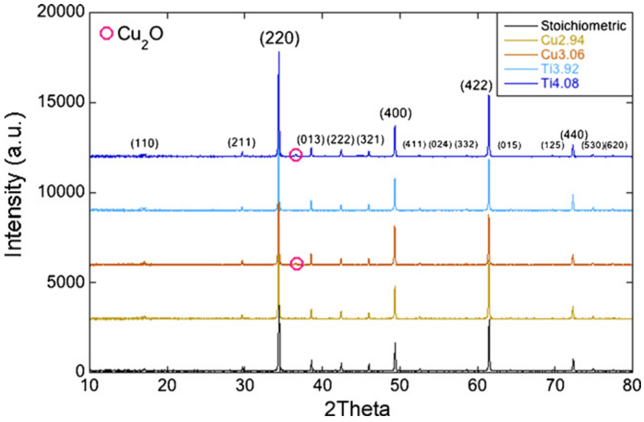

Fig. 1. XRD patterns for stoichiometric (undoped), Cu-deficient (Cu2.94), Cu-excessive (Cu3.06), Ti-deficient (Ti3.92), and Ti-excessive (Ti4.08) CCTO.

Interestingly, in diffraction measurements on polished ceramics it was found that both the Cu-excessive (Cu3.06, hereafter) and Ti-excessive CCTO (Ti4.08, hereafter) compositions exhibited one unknown peak at $2\theta \approx 36.58°$ and 36.54°, respectively. Both peaks are in the vicinity of a strong reflection matched with the cuprite Cu_2O phase ($2\theta \approx 36.52°$, PDF #05-0667). Considering that all the as-sintered CCTO samples (both stoichiometric and non-stoichiometric) exhibited the presence of surface CuO ($2\theta \approx 35.6°$, PDF #45-0937) but not Cu_2O via XRD measurements (not shown), it can be inferred that both Cu3.06 and Ti4.08 have an inner layer which contains a Cu_2O-rich phase. This result has been confirmed by other authors with sintering temperatures below 1100 °C [16–18]. Since Adams et al. [14] reported that a Cu_2O peak (~36.5°) was found on the surface of undoped CCTO sample after sintering at a slightly higher sintering temperature of 1115 °C, there might be a transition temperature where either CuO or Cu_2O secondary phase is favorable depending on sintering temperatures and times. This might help shed light on the great variability of dielectric properties reported in the literature. Further study based on the sintering temperatures is necessary to evaluate the presence of the CuO and Cu_2O phases in non-stoichiometric CCTO.

The plot of dielectric constant versus frequency for non-stoichiometric CCTO samples is shown in Fig. 2. Compared to the undoped CCTO, both the Cu3.06 and Ti4.08 sample have lower dielectric constants through the entire range of frequency. Considering that the Cu_2O phase has a low permittivity ($\varepsilon' \sim 8$) [19] and is relatively insulating ($\sigma \sim 10^{-3}\ \Omega^{-1}\ cm^{-1}$) [20], the observed decrease in the dielectric constant of the Cu3.06 and Ti4.08 compositions might be explained by a simple mixing rule. For a heterogeneous material having phase 1 (Cu_2O) and phase 2 (CCTO), the effective dielectric constant ($\varepsilon'_{\rm eff}$) can be expressed by the logarithmic mixture rule, known as Lichtenecker formula [21]:

$$\ln\ \varepsilon_{\rm eff} = v_1 \ln \varepsilon_{r1} + v_2 \ln \varepsilon_{r2} \tag{1}$$

where v_1 and v_2 are the volume fractions of phases 1 and 2. A volume percent of about 2.2% of the Cu_2O could explain the

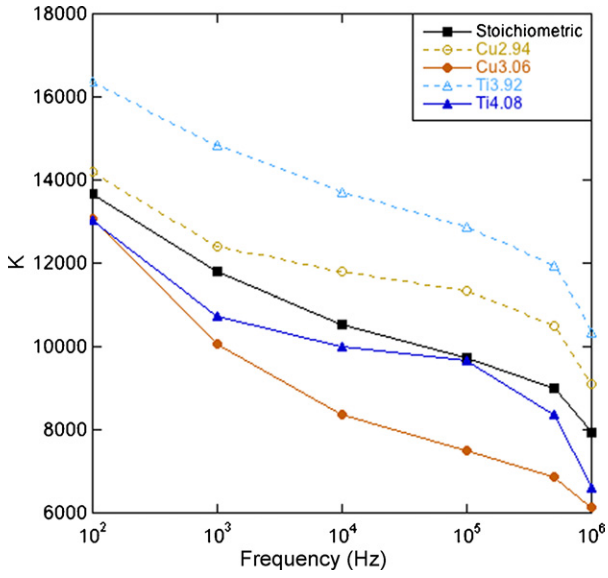

Fig. 2. Dielectric constant versus frequency for stoichiometric and non-stoichiometric $CaCu_{3+x}Ti_{4+y}O_{12}$ (x = 0, −0.06, +0.06; y = 0, −0.08, +0.08).