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Microstructures and dielectric relaxation behaviors of pure and tellurium doped $CaCu_3Ti_4O_{12}$ ceramics prepared via vibro-milling method

Worawut Makcharoen[a,*], Tawee Tunkasiri[b,c]

[a]College of Data Storage Innovation, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand
[b]Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[c]School of Science, Mae Fah Luang University, Chiang Rai 57100, Thailand

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Abstract

In this work, we have reported microstructures and the dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO) ceramics doped with different proportions of TeO_2 dopant (mol%, $x=0$, 0.5%, 1.0%, 2.0%). The pure and tellurium doping CCTO ceramics were prepared by a conventional solid-state reaction method and the effects of TeO_2 doping on the electrical properties and microstructures of these ceramics were investigated. XRD analysis confirmed the formation of single-phase material in samples. Scanning electron microscopy (SEM) is used in the micro structural studies of the specimens, which showed that TeO_2 doping can reduce the mean grain size and increasing size of an abnormal grain growth. Lattice parameter increases slightly with tellurium doping in CCTO, the dielectric constant reached a value as high as 18,000 (at 1 kHz) at a tellurium-doping concentration of 2.0 mol% and showed temperature stability at high frequency. The loss tangent of Te-doped CCTO ceramics was less than 0.05 at 1 kHz region below 105 °C. The loss tangent properties could be interpreted by the internal barrier layer capacitor model and the impedance measurement data.

Keywords: C. Dielectric properties; D. Perovskites; E. Capacitors

1. Introduction

$CaCu_3Ti_4O_{12}$(CCTO) ceramics have attracted the considerable interests due to their high dielectric constant of 10^4–10^5 and a good stability until 1 MHz, they have a large dielectric constant. They have independence from temperature over the range of 100–400 K [1–5]. These properties make it applicable to a variety of the microelectronic device applications for a capacitive element [3]. CCTO has a complex cubic perovskite like structure with a lattice parameter, $a \sim 7.393$ Å [6]. It is now widely accepted that the high dielectric constant at the room temperature is associated with the internal barrier layer capacitance (IBLC) effect [7,8]. It is believed that, insulating surfaces were formed on the semiconducting grains during the sintering process [15]. It is also reported that, electrical properties of CCTO depend on many factors such as processing conditions, doping, and chemical stoichiometry. Some successful routes reduce dielectric loss that has been reported [9]. CCTO microstructure and its dielectric properties are strong, dependent on the doping elements and their concentrations. In this study, the influences of Te ion doping on the microstructures and dielectric properties of CCTO were investigated. TeO2 is glass former characterized by a low melting point (T = 733 °C), it was used for preparing CCTO composites, expecting that changes induced on grain boundaries could increase grain boundaries resistance, lower tan δ. In the present work, the dielectric properties of CCTO ceramics modified by TeO2 have been studied. The electrical properties of the Tellurium modified CCTO have been reported.

2. Experimental procedure heading

The $CaCu_3Ti_4O_{12}$ (CCTO) powder was prepared with the mixed-oxide route. High purity (> 99.9%) $CaCO_3$ (Riedel-de Haen), TiO_2 (Riedel-de Haen) and CuO

*Corresponding author. Tel.: +66 86 9017322; fax: +66 2 3298263.
E-mail address: warmak77@hotmail.com (W. Makcharoen).

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(Aldrich) powders were weighed in the desired ratio. The samples were mixed with the vibratory milling for 6 h for using yttria-stabilized zirconia balls in the ethanol media. After being dried, the powders were calcined at 900 °C for 2 h to form the CCTO powders.In the doping study, TeO_2 powders were added to CCTO at the calcination stage based on the stoichiometry in concentrations of 0.5, 1.0 and 2.0 mol%. The calcined powder was granulated using polyvinyl alcohol (PVA) 3% binder and formed under a uniaxial pressure of 1500 kg/cm^2 into discs, typically 10 mm in diameter and 2.0 mm in thickness. The discs were sintered in the air at 1100 °C (with soaking time of 4 h). The ramping and the cooling rates were 5 °C/min. The polished CCTO pellets under different Te concentrations were examined via an X-ray diffractometer (Bruker D8 Discover) for their phase evolution. The crystallite sizes and the strain of the powders prepared through both methods were calculated using the Scherrer equation and the formula derived from Bragg's equation, respectively. Density of the polished CCTO samples was measured by using the Archimedes method. Silver paste was used as the electrical contact. The painted samples were dried at 750 °C for 20 min, and the dielectric constant and the loss tangent was measured in terms of the frequency (f=102–106 Hz) with an Agilent 4284A LCR meter in the room temperature. Microstructure of the crack ceramics were studied using SEM (JEOL JSM-5910LV). The impedance spectroscopy measurements of the ceramics were made at 500 kHz–1 MHz (HP 4194A impedance analyzer).

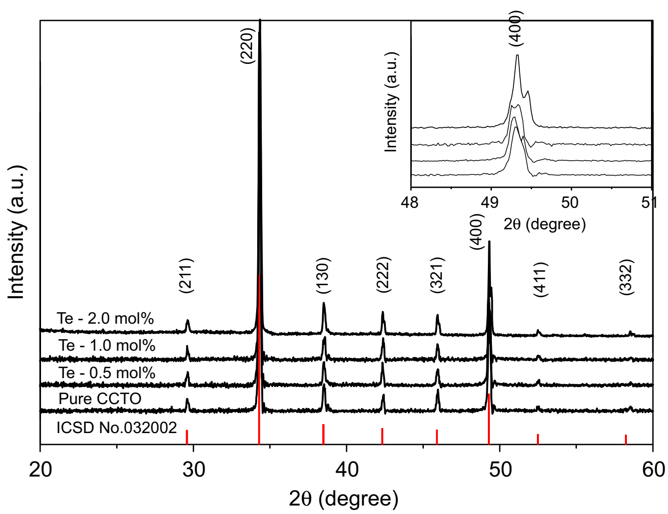

Fig. 1. XRD patterns of pure and modified CCTO: pure CCTO, 0.5 mol% Te doped CCTO, 1.0 mol% Te doped CCTO and 2.0 mol% Te doped CCTO.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns for the CCTO ceramic samples with various Te doping and sintered at 1100 °C. The following XRD peaks obtained agree with CCTO, that obtain with Yang et al. [8] and Brize et al. [9].

All peaks can be exactly matching with the data in the Inorganic Crystal Structure Database (ICSD) file no. 032002, which is cubic perovskite. According to the file, the density and lattice parameter (a) of CCTO are 5.053 g/cm^3 and 7.371 Å respectively. The lattice constants and the densities of the ceramics of various Te doping were determined and tabulated in Table 1.

The lattice constant slightly increased as the amount of TeO_2 increased (inset Fig. 1). This implies that small amount of Te ions could go into solid solution with the CCTO lattices. Te addition, density and shrinkage slightly increased and decreased grain size with the concentration (Fig. 2), suggesting that the doping oxide slightly promoted the densification.

Fractured surfaces of the CCTO ceramics are displayed in Fig. 3. TeO2 doping produced a notable decrease in the grain size. In the average values of grain size, as measured by the linear intercept method, decreased from ~20.4 μm for unmodified CCTO to ~2.5 μm for the 1.0 mol% sample and increased to ~3.2 μm for the 2.0 mol% sample. Hence, TeO2 doping inhibited grain growth and generate the abnormal grain growth, when increasing percentage of Te doping to 2.0 mol%.

The important parameters should be considered in abnormal grain growth at 2.0 mol% Te are the interface structure and the presence of a liquid phase. When the grains are spherical, the interface is atomically rough. There is no barrier for atomic attachment when a large grain grows at the expense of a small grain via Ostwald ripening. Grain growth becomes the diffusion controlled, which induces a normal grain growth behavior. On the other hand, in the angular grains with an atomically flat (singular) interface, there is an appreciable energy barrier for an atomic attachment because a ledge generating sources such as 2-D nucleation is necessary. Due to the significant energy barrier for 2-D growth, only small

Table 1
Relative density, lattice parameter (a) and average grain size of the prepared CCTO ceramics at various conditions.

TeO_2 doped CCTO (mol% Te)	Density* (%)	Lattice parameter (a (Å))	Average grain size (μm)
0	97.40	7.391	20.41
0.5	97.80	7.394	5.12
1.0	98.13	7.396	2.51
2.0	98.27	7.398	3.23

numbers of grains which are significantly larger than the average grain size can grow rapidly. The existence of a liquid phase is another important factor [10].

The result suggested most of the doped oxide still presented out size the lattices the from a glass phase. It may be a cause of segregation of the doping oxide and/or forms secondary phases on a very small scale at the grain boundaries which cannot be detected with XRD. The segregation phases can prevent grain boundary movement during the processing [11] as a result of the grain growth inhibition.

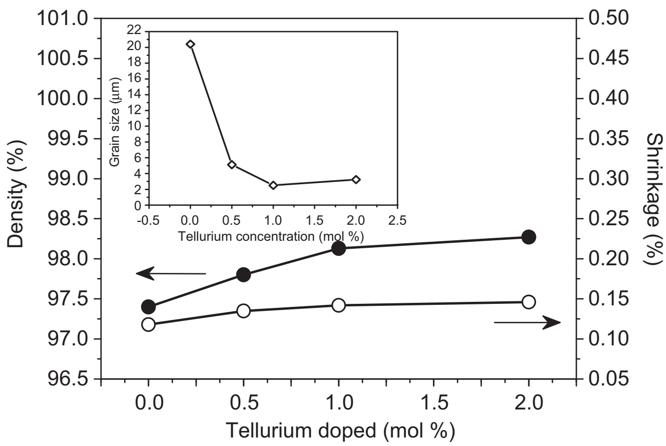

Fig. 2. Density and shrinkage as a function of the doping concentration of the samples.

The temperature dependence on the dielectric constant and loss tangent at various frequencies of the ceramic samples are presented in Fig. 4. For the unmodified CCTO, the dielectric constant exhibited a stronger dielectric-frequency dependence while the doped samples showed a weaker dielectric-frequency dependence. It should be noted that at a high frequency, all samples showed a dielectric independence of temperature. The dielectric constant at the room temperature and at 1 kHz decreased from 36,000 for the unmodified sample to 18,000 for the 2.0 mol% sample.

The reduction in the dielectric constant has been observed for many modified CCTO ceramics [8]. However, the doping improved in the loss tangent performance. The loss tangent at the room temperature, at 1 kHz decreased from 0.14 for the unmodified sample to 0.07 for the 2.0 mol% sample while at 500 kHz, it decreased from 0.51 for the unmodified sample to 0.24 for the 2.0 mol% sample. However, the lowest loss tangent was 0.01 at 1 kHz and at ~65 °C.

Plots of the dielectric constant and loss tangent as a function of a frequency at the room temperature are illustrated in Fig. 5. The dielectric constant decreased with increasing frequency. For frequencies 100 Hz–10 kHz, however, the loss tangent decreased with increasing the frequency (until 10 kHz), it increased with further frequencies.

The IBLC model was recently supported by the different observations of a defect inside both single crystals [11] and grains of polycrystalline CCTO [12,13] by complex impedance spectroscopy measurements on a CCTO crystal [14].

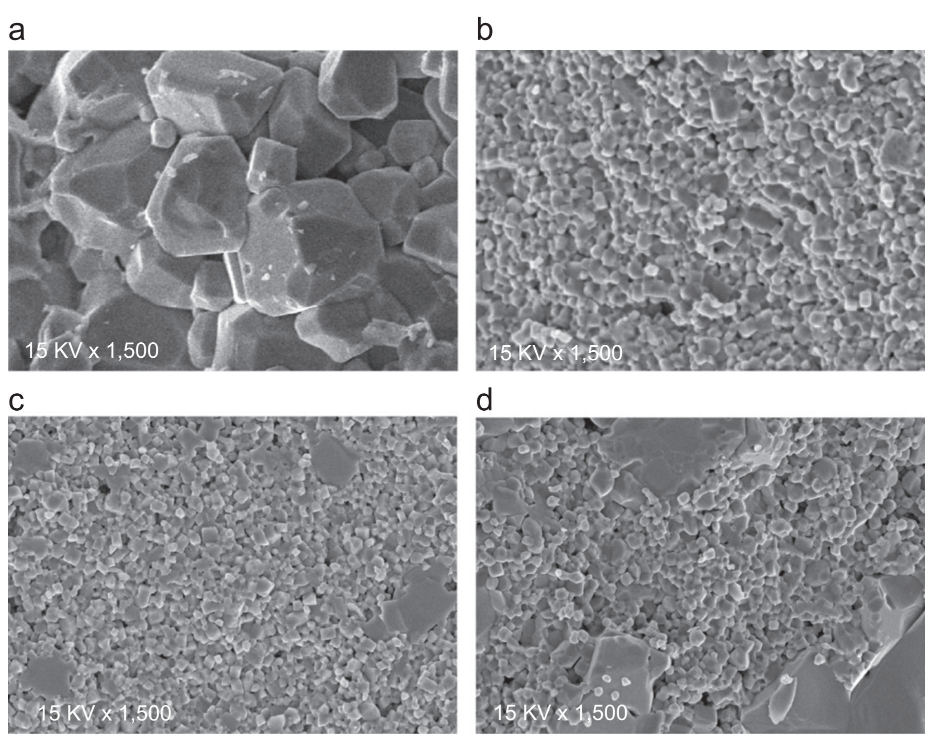

Fig. 3. Fracture surfaces of selected samples: (a) pure CCTO, (b) 0.5 mol% Te doped CCTO, (c) 1.0 mol% Te doped CCTO and (d) 2.0 mol% Te doped CCTO.

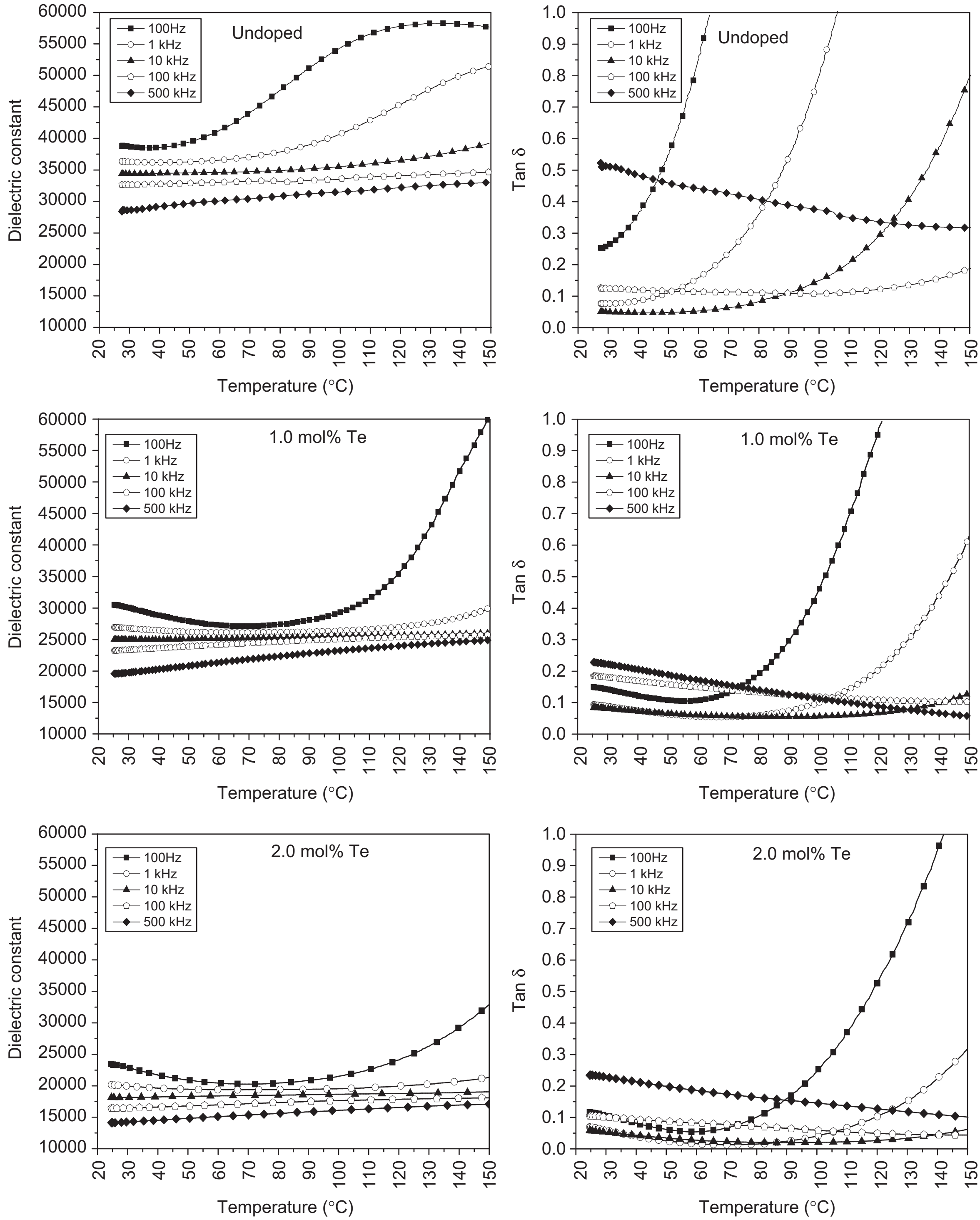

Fig. 4. Dielectric constant and loss tangent as a function temperature of the samples: pure CCTO, 1.0 mol% Te doped CCTO and 2.0 mol% Te doped CCTO.

The dielectric properties of CCTO ceramics are very sensitive to processing parameters. Values between 5.0×10^2 and 2.0×10^4 are usually reported [15,16]. In this work, the impedance plot of the Te doped CCTO sample is revealed in Fig. 6 and the inset shows the impedance on high frequency.

It can be seen that by extrapolation the resistance of the grain boundaries (R_{gb}) decrease from 4000 kΩ to 2000 kΩ and it decreases the grain resistance (R_g) from 46 kΩ to 80 kΩ, when Te concentration is increased accordingly. Based on the R_{gb} and R_g values in this experiment, the Te doped CCTO ceramics, with decreased average grain size,

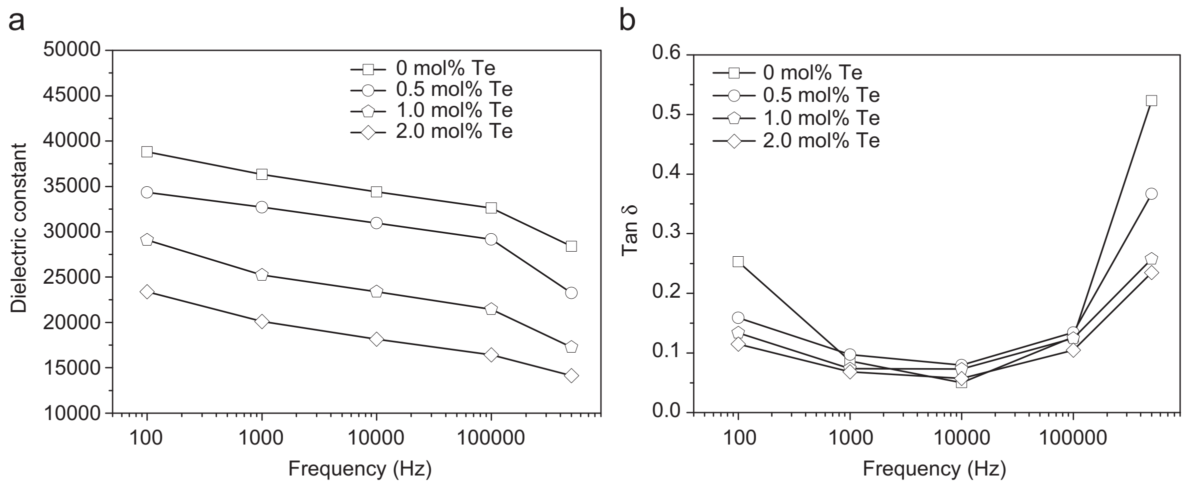

Fig. 5. Dielectric properties of the samples as a function of frequency: (a) dielectric constant and (b) loss tangent.

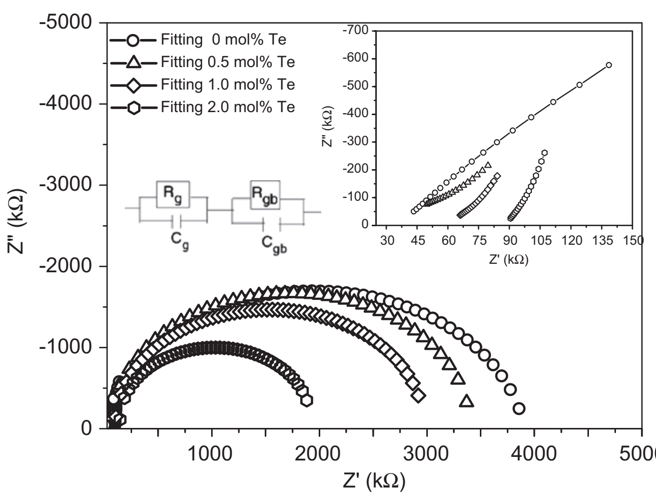

Fig. 6. Impedance complex plane plot of the samples.

have decreased dielectric constant and dielectric loss compared to those of the undoped CCTO ceramics samples.

4. Conclusions

Dielectric properties of pure CCTO and Te doped CCTO were reported in this article. The doping produced the reduction of the dielectric constant. However, the better loss tangent performance was observed after doping. The loss tangent frequency characteristic at the room temperature was agreeable with the IBLC model. The significant change in the microstructure of the doped samples suggested that the loss tangent performance should be related with the characteristic of the grain boundary.

Acknowledgments

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