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Letter

# Structure and electrical response of $CaCu_3Ti_4O_{12}$ ceramics: Effect of heat treatments at the high vacuum

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ABSTRACT

In this work, $CaCu_3Ti_4O_{12}$ (CCTO) ceramics based perovskite varistors were prepared using the solid-state reaction method, and effects of heat treatments at the high vacuum on their microstructures and electrical properties were investigated experimentally. Two conditions of heat treatment, i.e., calcining at 950 °C for 10 h and then sintering at 1100 °C for 20 h, and at 900 °C for 2 h in $10^{-4}$ Pa vacuum level were used. It was found from the X-ray diffraction (XRD) that for the former condition, the single phase of CCTO based on the perovskite structure was formed, whereas for the later condition, multiple phases were detected due to the decomposing of CCTO. The electrical response of both conditions was monitored using the dielectric spectroscopy and was revealed that varistor voltage increased remarkably due to the heat treatments at the high vacuum.

## 1. Introduction

The miniaturization and integration of electronic devices requires new materials with multiple functions, which have attracted great attention for both scientific research and numerous technological applications. Recently $CaCu_3Ti_4O_{12}$ (CCTO) based perovskite is extensively investigated due to its giant dielectric constant ($\varepsilon' \sim 10^4$ to $10^5$), nonlinear varistor behavior and weak temperature dependence [1–3] of the electrical properties in the range from $100\,K \le T \le 600\,K$. It was suggested that La doping can control the CCTO ceramic's grain size and electrical performance consequently [1], and some researchers reported that the high dielectric constant behavior should be attributed to local dipole moments associated with off center displacement of Ti ions [2]. Recently, a nonlinear current–voltage characteristic with the nonlinear coefficient about 900 was also found, Chung et al. [3] reported that CCTO exhibits nonlinear current–voltage characteristics even in the absence of any dopants. Atomic force microscopy revealed the presence of an intrinsic electrostatic potential barrier at the grain boundaries that is considered to be responsible for the varistor properties [3]. These outstanding electrical performance is quite unusual since CCTO exhibits a body centered cubic perovskite structure with slightly tilted [$TiO_6$] octahedra facing each other [4], i.e. the compound is not ferroelectric.

Till now, the underlying operative mechanisms in these systems are not well established. The giant dielectric response is found to be very sensitive to the processing conditions. Various electrical transport behavior within a grain and across a grain boundary is proposed to derive from the oxygen content between the grain and the grain boundary. Impedance spectroscopy, which is a powerful tool to study the dielectrics, has proven that such ceramics consist of semiconducting grains and insulating grain boundaries [5–9].

Several previous reports [10,11] reveal that annealing of the CCTO varistor materials in vacuum (≈1 Pa) chemisorbed oxygen at the grain boundaries plays a key role in determining nonlinear coefficient, $\alpha$. During heat treatment in vacuum chemisorbed oxygen departs from the grain boundaries which can be detected by the degradation of the nonlinear coefficient. It is considered that oxygen is partially extracted from the grain and grain boundaries leaving oxygen vacancies [10]. This process increases conductivity of the CCTO material.

In the present investigation, preliminary study shows that annealing in vacuum results in drastic changes in dielectric behavior including current–voltage ($I$–$V$) response at elevated temperatures. The results of two different CCTO samples, which were designated as A and B and prepared in normal and vacuum conditions respectively, showed quite different dielectric behavior when evaluated with their electrical responses.

## 2. Experimental

Proper amounts of high-purity (>99%) $CaCO_3$, CuO, and $TiO_2$ were used to prepare CCTO ceramics following solid-state reaction as:

$$CaCO_3 + 3CuO + 4TiO_2 \rightarrow CaCu_3Ti_4O_{12} + CO_2\uparrow .$$

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These raw materials were mixed in a ball mill and milled with $ZrO_2$ balls for 4 h. The mixed slurry was dried and then calcined at 950 °C for 10 h in air. The polyvinyl alcohol (PVA) was added as binder to the calcined powder and then dried to obtain pressable powder for making pellets of 12 mm diameter and 1.6 mm thickness at 85 MPa pressure. The pellets were heated to 500 °C to get burn-out of the binder, and then sintered in air at 1100 °C for 20 h to obtain sample A. From these samples some are heat treated at 900 °C for 2 h in vacuum ($10^{-4}$ Pa) to obtain sample B for investigation. The opposite parallel surfaces were polished smoothly and deposited sputtered gold as electrode for electrical measurements.

The formation of the CCTO compound was confirmed via X-ray powder diffraction (XRD) using Cu $K_\alpha$ radiation. The compositional information of grains and grain boundaries were detected through energy dispersive spectroscopy (EDS). The current–voltage ($I$–$V$) response was measured by HP 34401A multimeter and WWWL-LDG precision linear high-voltage direct current power. The dielectric measurement was carried out at with 1 V peak-to-peak ac small-signal for the frequency range $0.1\ \text{Hz} \le f \le 10\ \text{MHz}$ using a Novocontrol broadband dielectric spectrometer with an Alpha-A high performance frequency analyzer.

The nonlinear coefficient $\alpha$ is obtained by the following expression:

$$\alpha = \frac{1}{\lg(V_1/V_{0.1})}, \tag{2}$$

where $V_1$ and $V_{0.1}$ are varistor voltage referring to the applied voltages corresponding to the currents 1 and 0.1 $\mu A/mm^2$, respectively.

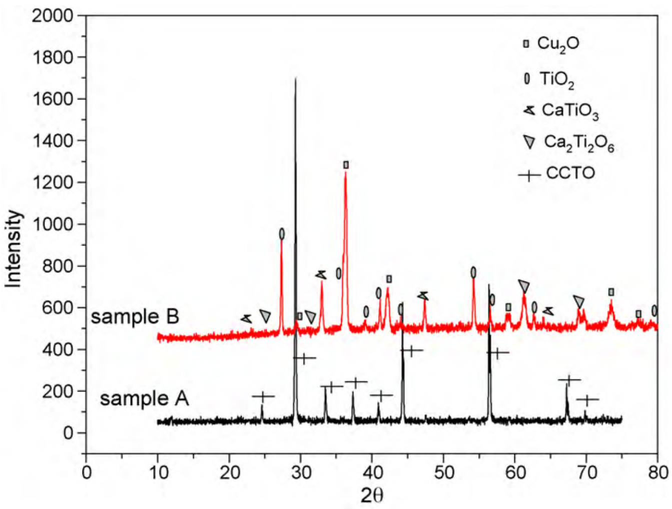

**Fig. 1.** XRD (X-ray diffraction) analysis for sample A and sample B.

## 3. Results and discussion

Fig. 1 shows the room temperature XRD results of samples A and B. Only the perovskite phase was detected for sample A while for sample B there are $Cu_2O$, $TiO_2$, $CaTiO_3$, and $Ca_2Ti_2O_6$ phases without the CCTO phase. Thus, in the present study CCTO single phase appears to have completely decomposed into four separate phases when heat treated at vacuum. This situation is not reported earlier.

Fig. 2 shows the SEM micrographs of sample A in (a) and sample B in (b). From Fig. 2(a) no secondary phase is observed from any cross-section of the SEM micrograph. In the case of sample B melting grain growth and variation in elemental distribution are prominent in Fig. 2(b). Considering these results it is noted that the high vacuum environment for the heat treatment plays an important role for multiple phases and variation in the elemental distribution.

Table 1 shows two selected values of current density corresponding to the electric field and the nonlinear coefficient for samples A and B. The electric field gradient of sample B is much higher than sample A while the nonlinear coefficient remains nearly identical. The internal barrier layer capacitor (IBLC) [11,12] model plays a key role in determining the dielectric behavior for the CCTO ceramics or crystals. For sample B, the IBLC model is presumed to be destroyed with the evolution of multiple phases due to the heat treatment in vacuum.

Fig. 3 shows the Bode plot comprising of the real part of the complex dielectric constant ($\varepsilon'$) indicating parallel capacitance as a function of measurement frequency at different temperatures for the sample A in (a) and sample B in (b). Fig. 4 shows the dielectric loss ($\tan\delta$) as a function of measurement frequency at various temperatures for sample A in (a) and sample B in (b). The temperature dependence of both $\varepsilon'$ and $\tan\delta$ indicates thermal activation of the operative relaxation processes. The primary peak in the high frequency side of Fig. 4(a) indicated dielectric relaxation and thermally activated in the range $\sim 10^5\ \text{Hz} \le f \le \sim 10^6$ Hz. The secondary peak in the low frequency side indicated similar relaxation in the range $\sim 10\ \text{Hz} \le f \le \sim 5 \times 10^2$ Hz at low temperatures. Each of these relaxations provide parallel R–C (resistance–capacitance) configuration

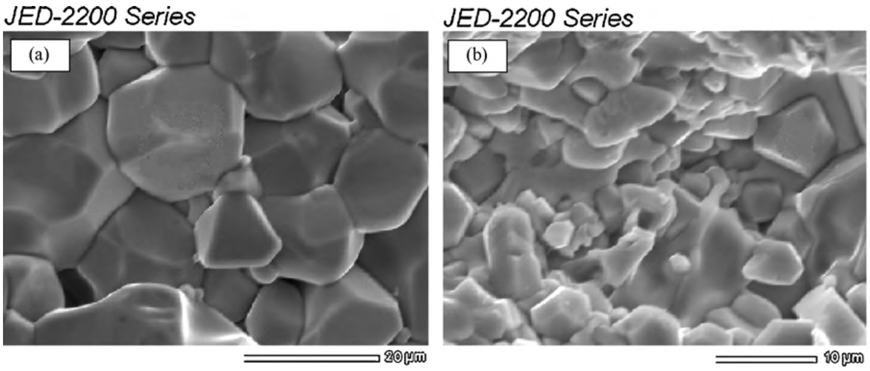

**Fig. 2.** SEM micrographs of sample A in (a) and sample B in (b).

**Table 1**
Electrical parameters of sample A and sample B.

| Current density ($J$) ($\mu A/mm^2$) | Electric field ($E$) for sample A (V/mm) | Electric field ($E$) for sample B (V/mm) |
|---|---|---|
| 0.1 | 12.5 | 220 |
| 1.0 | 27.2 | 479 |
| Nonlinear coefficient $\alpha$ | Sample A – 2.97 | Sample B – 2.96 |

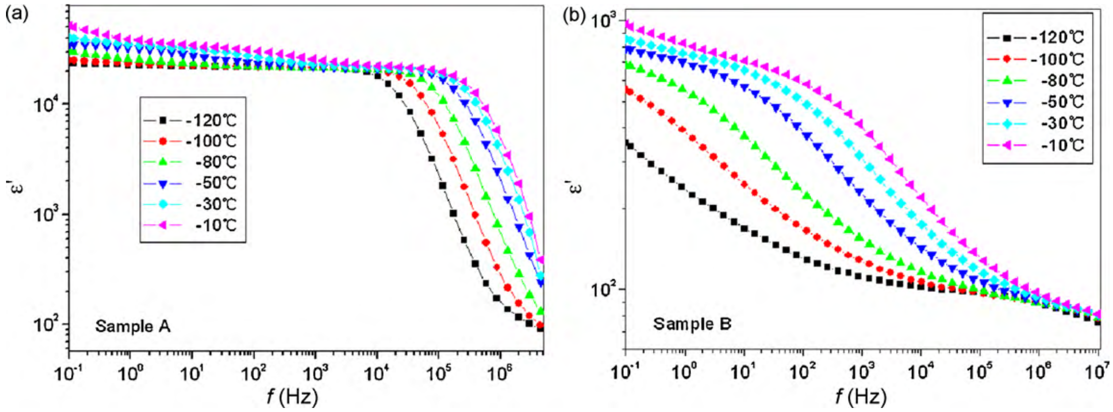

**Fig. 3.** Dielectric constant (real part of complex permittivity) as a function of frequency for sample A in (a) and sample B in (b).

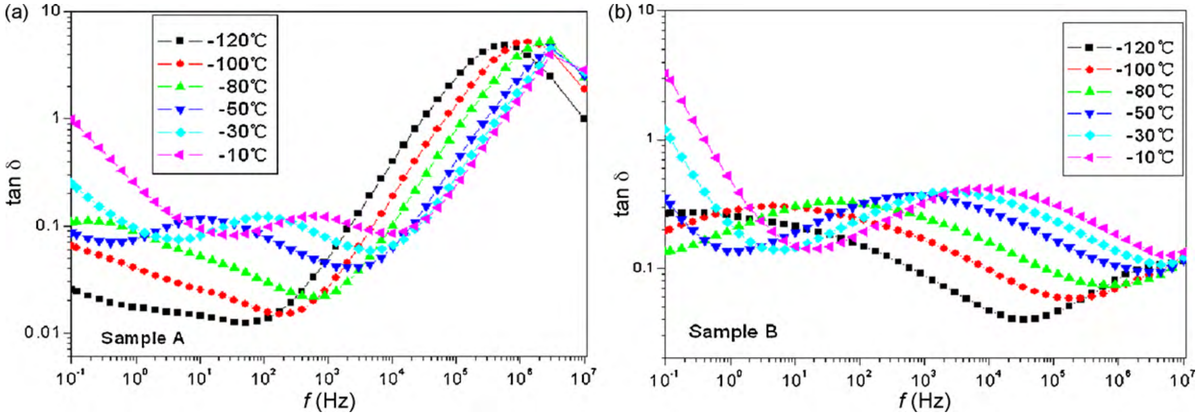

**Fig. 4.** Dielectric loss (tan δ) as a function of frequency for sample A in (a) and sample B in (b).

in series with another parallel R–C combination. Nevertheless, two simultaneous relaxation processes indicate usual polycrystalline behavior attributing to the response of lumped grains at high frequencies and lumped grain boundaries at low frequencies [13–17]. In Fig. 4(b) for sample B, lumped dielectric relaxation is visible around $\sim 2 \times 10^4$ Hz at the low temperature end which gradually drifts toward the low frequency side as the temperature increases. The internal construction of these phases in the form of microstructures is tedious to visualize as single lumped grains or single lumped grain boundaries. However, the relaxation as a whole lumps to a single distinct relaxation. The origin for the single lumped relaxation in sample B is not clear at this time although multiple phases have been detected for sample B. Overall as the temperature increases, the relaxation processes drifts toward the high frequency side, which is the usual dielectric characteristic for both samples. Usually the trapping behavior within the polycrystalline CCTO is not recognized via the Bode plots for $\varepsilon'$ or tan δ as it is identified only in the complex capacitance [or dielectric constant, $\varepsilon^* = \varepsilon' - j\varepsilon''$ with $j = \sqrt{(-1)}$] plane and/or admittance [or conductivity, $\sigma^* = \sigma' + j\sigma''$] plane formalisms [8,9].

Both sample A and sample B possess frequency dependent dielectric constant as a function of temperature. The variation in relaxation time $\tau$ with temperature follows an Arrhenius law [18,19] with activation energies of 0.1 and 0.505 eV for sample A which are in accordance with the reported values [20,21], and 0.318 eV for sample B. The values of these activation energies strongly suggest that the associated relaxation processes originate from different sources, presumably from some kind of charge carriers in conjunction with the physical regions within the microstructures which are attributed to the heat treatment under vacuum.

## 4. Conclusions

$CaCu_3Ti_4O_{12}$ (CCTO) ceramics based perovskite varistors have been prepared using the solid-state reaction method, and effects of heat treatments at the high vacuum on their microstructures and electrical properties have been investigated. The investigation reveals that simultaneous multiple phases result from the decomposing of the CCTO single phase due to the heat treatment at the high vacuum. Furthermore, the heat treatment conditions affect strongly the relaxation process and the elemental distribution. In addition, the varistor voltage has increased remarkably, which has not been reported previously.

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