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High Permittivity and Dielectric Response of $CaCu_3Ti_{3.9}(Y_{0.5}Nb_{0.5})_{0.1}O_{12}$ Ceramics

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Abstract

$CaCu_3Ti_{3.9}(Y_{0.5}Nb_{0.5})_{0.1}O_{12}$ (CCTYNO) ceramics were prepared with the conventional solid-state method. Dielectric properties and electric responses at temperatures from - 80 to 200 °C were investigated in the frequency range of 100 – 1 MHz. A body-centered cubic structure was confirmed by means of X-ray diffraction. High dielectric permittivity (~ 6000) and low dielectric loss (~ 0.082) were observed at room temperature. Impedance spectroscopy measurements showed the resistance of the grain boundaries is higher by 2 – 3 orders of magnitude than that of the grains, indicating the different microstructure and electric property. The activation energy for the dc conduction process (0.593 eV) is comparable to that for the relaxation process (0.662 eV), implying that strong interfacial polarization at insulating grain boundaries may be responsible for the dielectric response of CCTYNO ceramic. Polyvalent cations (i.e. Cu^+, Cu^{2+}, Ti^{3+} and Ti^{4+}) may cause changes in the conduction of semiconducting grains at high temperature.

Keywords: Dielectric properties, impedance, co-doping, grain boundary, interfacial polarization

I. Introduction

Colossal dielectric materials have attracted wide attention over past decades for potential application in electronic devices such as memories, capacitors and filters [1–4]. $CaCu_3Ti_4O_{12}$ (CCTO) is a representative example of these materials, exhibiting colossal and nearly temperature-independent dielectric permittivity (ε') over a wide temperature range [1,2]. However, its relatively high dielectric loss (tan δ) limits its further application [5,6]. In order to understand the origin of its dielectric response, some possible mechanisms for intrinsic or extrinsic effects have been proposed [7–10]. The most widely accepted of these is the internal barrier layer capacitor (IBLC) model. It demonstrates that CCTO has a special electrically heterogeneous microstructure, revealing the different electric responses at the grains and grain boundaries [11]. It is claimed that the excellent dielectric property is related to the electric properties of the grain boundaries [8, 11]. A lot of work has been done on improving the performance of CCTO. Doping with a single element or oxide is a common approach, but it has been found that the effects of such doping are uncertain. A few reports have recently been published about CCTO co-doped with two elements. J. Boonlakhorn *et al.* discovered that the dielectric properties of Y+Mg-co-doped CCTO were improved based on the control of the geometric and intrinsic properties of grain boundaries [12]. H.A. Ardakani *et al.* found Cr+La-co-doped CCTO ceramics could reduce the dielectric loss effectively [13]. Wen *et al.* demonstrated the effect of Al+Nb co-doping on the dielectric response, especially the dielectric loss [14]. It is considered that CCTO ceramic co-doped with two elements at one site is worthwhile with regard to improving the dielectric responses.

In this work, Y+Nb-co-doped CCTO ceramics were successfully prepared with the conventional solid-state method. The dielectric properties were investigated in wide ranges of frequency and temperature. A high ε' ~ 6000 and low tan δ ~ 0.082 at 10 kHz were achieved by using Y+Nb co-doping ions. The possible mechanism for the origin of the dielectric response was discussed.

II. Experimental

In this work, $CaCO_3$ (99.99 % purity), CuO (99 % purity), Y_2O_3 (99.9 % purity), Nb_2O_5 (99.9 % purity) and TiO_2 (99.99 % purity) were weighed according to the stoichiometry of $CaCu_3Ti_{3.9}(Y_{0.5}Nb_{0.5})_{0.1}O_{12}$(CCTYNO). The mixture of starting raw materials was ball-milled with ethanol in a polytef jar for 6 h. After calcination at 950 °C for 5 h, the calcined powders were ground and 4 % polyvinyl alcohol (PVA) was added. Then pellets were pressed at 200 MPa by means of cold isostatic pressing (CIP). Finally, the pellets (10 mm in diameter and ~1 mm in thickness) were sintered at 1060 – 1100 °C for 4 h in a muffle furnace, before being cooled to room temperature naturally. Both surfaces of the sintered ceramics were polished and coated with silver paint, then fired at 550 °C for 1 h.

X-ray diffraction (XRD) (D8 Advance, Bruker) was used to analyse the phase purity. The microstructure was characterized with a scanning electron microscope (SEM) (S4800, HITACHI). The dielectric properties and electric responses were measured using a WK6500 LCR meter in the frequency range of 100 – 1 MHz. The measurements were performed at temperatures ranging from – 80 °C to

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240 °C. The valence states of cations in CCTYNO were studied using X-ray photoelectron spectroscopy (Thermo ESCALAB 250XI).

III. Results and Discussion

Fig. 1 shows the frequency dependence of the dielectric responses at room temperature for the CCTYNO ceramics sintered at different temperatures. High dielectric permittivity (ε') was observed in all samples. Both ε' and tan δ increase slightly with increasing sintering temperature, and become more frequency-dependent in a wide frequency range. The values of ε' at 10 kHz were found to be 5721, 6041 and 6168 for 1060, 1080 and 1100 °C respectively. A drastic drop of ε' corresponding to a sudden increase in tan δ was observed above 100 kHz. It indicates that a relaxation process occurred at high frequency in the CCTYNO ceramics. In many CCTO-related ceramics, this is called Debye-type relaxation. It probably results from intrinsic properties, i.e. the dielectric response of the bulk or grains [15–17].

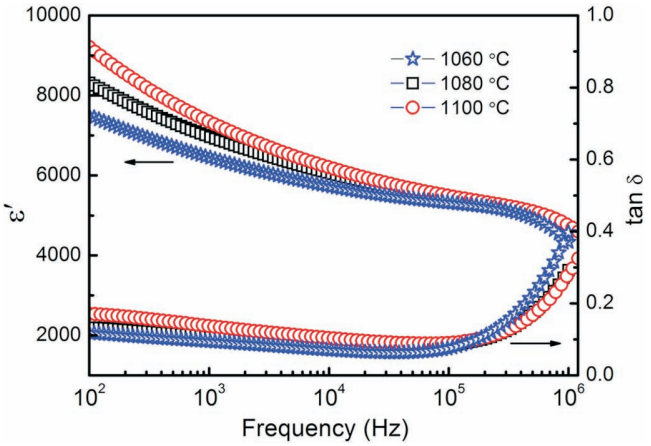

Fig. 1: Frequency dependence of the dielectric responses at room temperature for the CCTYNO ceramics sintered at different temperature.

Fig. 2 presents X-ray diffraction (XRD) patterns of all sintered CCTYNO ceramics. All diffraction peaks consisted of a body-centered cubic structure of CCTO (JCPDS No.75–2188). A single phase with space group Im 3 was observed, indicating successful preparation of the CCTYNO ceramics. The inset in Fig. 2 shows the surface microstructure of the CCTYNO ceramic sintered at 1080 °C. The average grain size was 8–10 μm. Some grains grow rapidly to sizes of ~20 μm, and other grains with 2–4 μm were observed as well. This abnormal grain growth behavior was considered to have originated from a eutectic reaction between CuO and TiO_2 [18]. On account of the similar dielectric behavior and phase formation at room temperature, the ceramic sintered at 1080 °C for 4 h was chosen as the representative to undergo further detailed investigation.

Figs. 3a and b show the frequency dependence of ε' and tan δ at different temperatures for the CCTYNO ceramic. At low temperature (< 40 °C), ε' depends slightly on frequency from 100 to 100 kHz, and then decreases sharply. ε' begins to increase dramatically in the frequency range of 100–1 kHz when the temperature is increasing. This dielectric behavior is usually attributed to an extrinsic response such as electrode or surface polarization [19,20]. In Fig. 3b, the sudden enhancement of tan δ occurs at high frequency. As temperature increases, the point at which enhancement starts shifts gradually to higher frequencies. This corresponds to a step-like decrease in ε', indicating a thermally activated relaxation process.

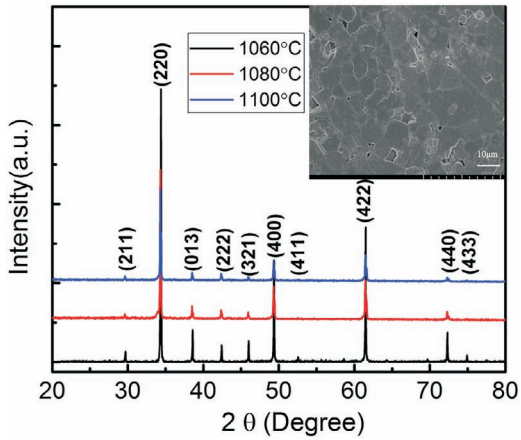

Fig. 2: XRD pattern and surface morphology of the CCTYNO ceramic sintered at different temperature. Inset shows the surface microstructure of the CCTYNO ceramic sintered at 1080 °C.

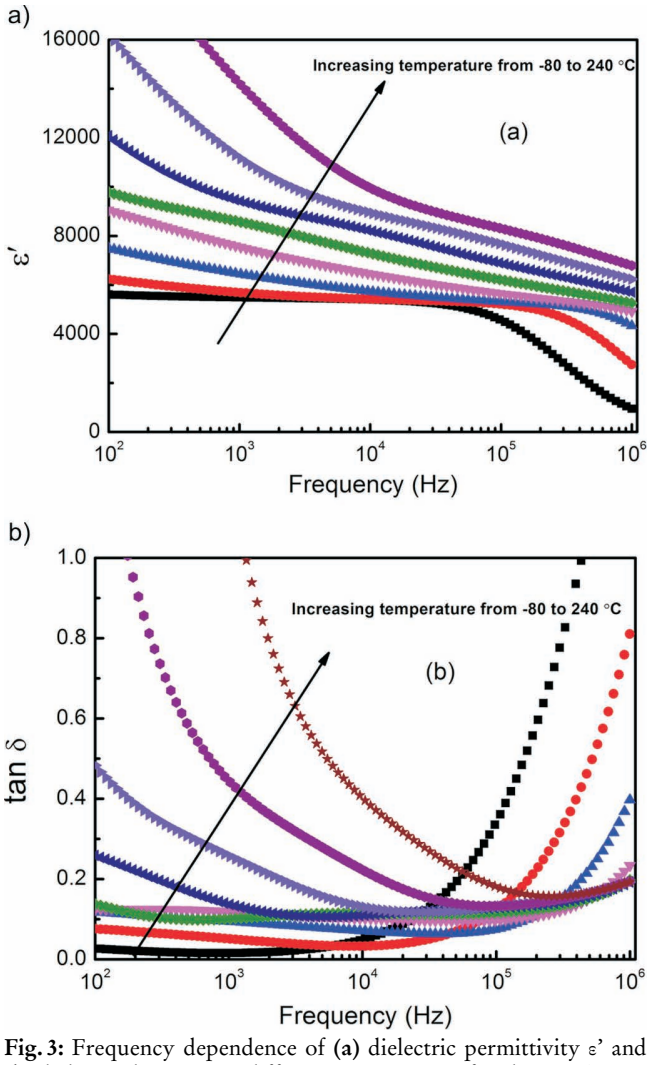

Fig. 3: Frequency dependence of **(a)** dielectric permittivity ε' and **(b)** dielectric loss tanδ at different temperatures for the CCTYNO ceramic sintered at 1080 °C.

Spectroscopic plots of the imaginary of electric modulus (M'') at a few temperatures are studied in Fig. 4. A typical broad peak of M'' for the CCTYNO ceramic was observed. It is clear that this M'' peak shifts to the high frequency side with the increasing temperature in the 100 – 100 kHz range. This temperature-activated relaxation process that appears at intermediate frequencies can be attributed to the Maxwell-Wagner effect, which suggests the grain boundaries have a crucial influence on dielectric response [15, 21]. This dielectric behavior was described with the Arrhenius equation:

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (1)$$

where E_a is the activation energy, τ_0 is the mean relaxation time and k_B is the Boltzmann constant. Generally, the dielectric relaxation time τ is determined with the relation $\tau=1/2\pi f$, where f is the M'' peak at various temperatures. The inset in Fig. 4 demonstrates the relationships between log (τ) and 1,000/T for the CCTYNO sample. The value of E_a was calculated to be 0.662 eV. It is comparable with those values reported in many CCTO-related materials for extrinsic relaxation [22, 23].

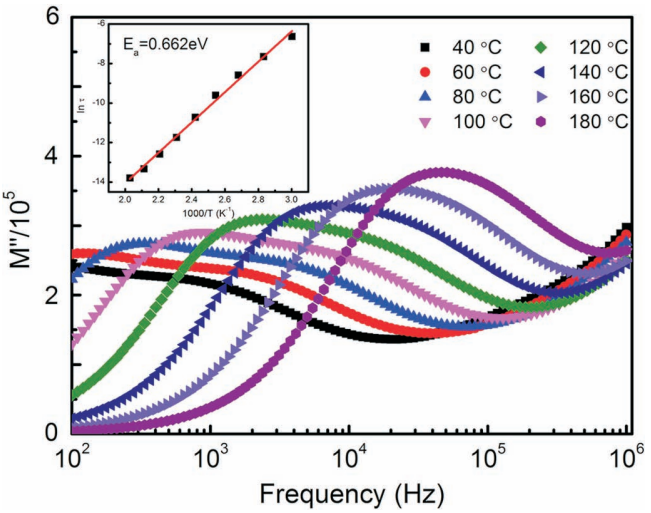

Fig. 4: Spectroscopic plots of the imaginary of electric modulus (M'') at a few temperatures for the CCTYNO ceramic sintered at 1080 °C. Inset shows the Arrhenius plot of the relaxation time.

Impedance spectroscopy measurement is widely accepted to further discuss the origin of dielectric response for high dielectric permittivity materials, especially CCTO-related structural ceramics. According to the equivalent circuit model, it mainly contains two parallel RC elements (R_gC_g and $R_{gb}C_{gb}$). The element R_gC_g usually describes the dielectric response of grains, while the element $R_{gb}C_{gb}$ delineates the effect caused by grain boundaries (GBs). Fig. 5 demonstrates impedance complex plane plot in the temperature range of 100 – 180 °C for the CCTYNO ceramic. A large semicircle arc of Z^* is clearly observed, indicating the grain boundary response [24]. The resistance of the grain boundary is larger by 2 – 3 orders of magnitude than that of the grain, this illustrates that the CCTYNO ceramic has a heterogeneous microstructure consisting of semiconducting grains and insulating grain boundaries. Furthermore, the values of R_{gb} decrease with increasing temperature. It is concluded that charges inside the semiconducting grains moved actively at high temperatures, and accumulated continually at the insulating grain boundaries [25]. The observed high dielectric properties may therefore be attributed to a strong interfacial polarization at grain boundaries.

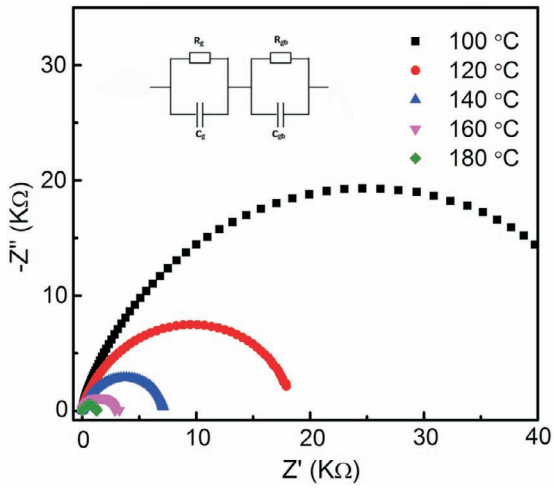

Fig. 5: Temperature dependence of complex impedance plots for the CCTYNO ceramic sintered at 1080 °C.

To better understand the conductivity on the dielectric response of the CCTYNO ceramic, the frequency dependence of ac conductivity (σ_{ac}) over the temperature from 60 to 200 °C was studied. In general, σ_{ac} is an increasing function of frequency, and ac power law shows the variation:

$$\sigma_{ac} = \sigma_{dc} + Af^n \quad (2)$$

where A is a constant, f is the frequency, and the exponent n varies between 0 and 1. As shown in Fig. 6a, the plot of σ_{ac} at room temperature is mainly divided into three parts [26]. In part I, the frequency is low, the electric field does not perturb the hopping conduction, and hopping is not active. As the frequency increases shown in part II, σ_{ac} begins to increase moderately, and presents a nonlinear trend. This is because the capacitor admittance becomes larger with increasing frequency. In part III, σ_{ac} is proportional to frequency due to nearly constant loss (NCL), which dominates σ_{ac} at high frequency and low temperature relatively [27, 28]. Fig. 6b shows the frequency dependence of σ_{ac} at different temperatures. It is obvious the value of σ_{ac} in low frequency ranges becomes invariable at high temperatures. This means the low frequency σ_{ac} can be approximately equal to σ_{dc}. It is found that the curves of the dependence of logarithmic dc conductivity on the inverse of temperature follow the Arrhenius law:

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-E_{dc}}{k_B T}\right) \quad (3)$$

where E_{dc} is the activation energy for the dc conduction process. As demonstrated in the inset of Fig. 6b, the calculated E_{dc} was 0.593 eV, which is comparable to E_a (0.662 eV), this means that the dielectric response of CCTYNO ceramic is associated with the properties of grain boundaries.

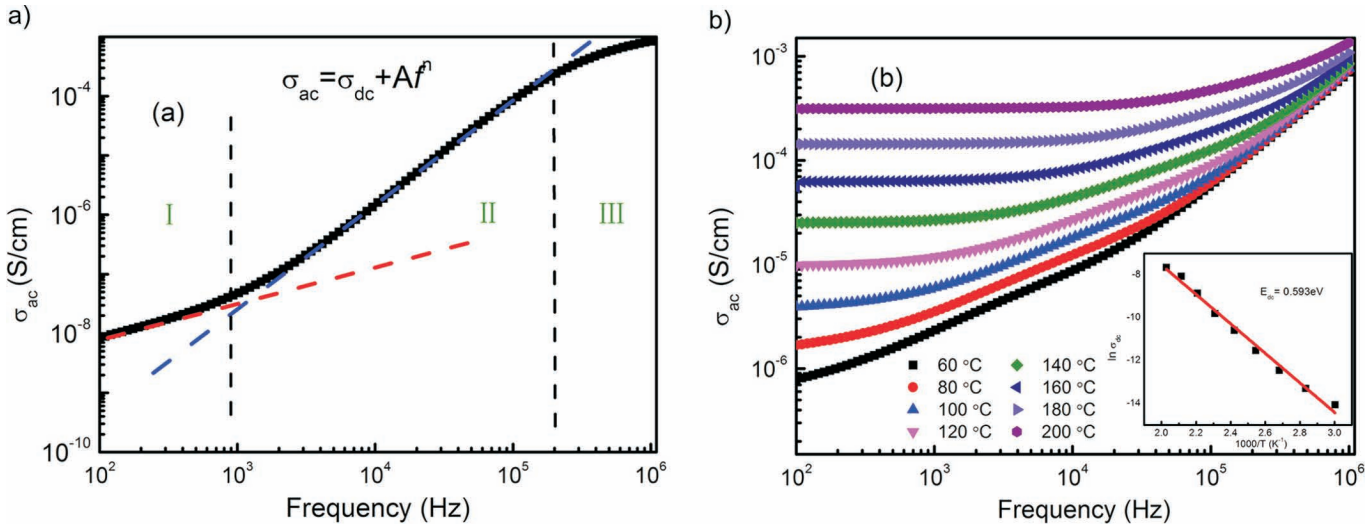

Fig. 6: (a) Typical conductivity spectrum of CCTYNO ceramic at room temperature. **(b)** Frequency dependence of ac conductivity at various temperatures. Inset shows Arrhenius plots of the temperature dependence of dc conductivity.

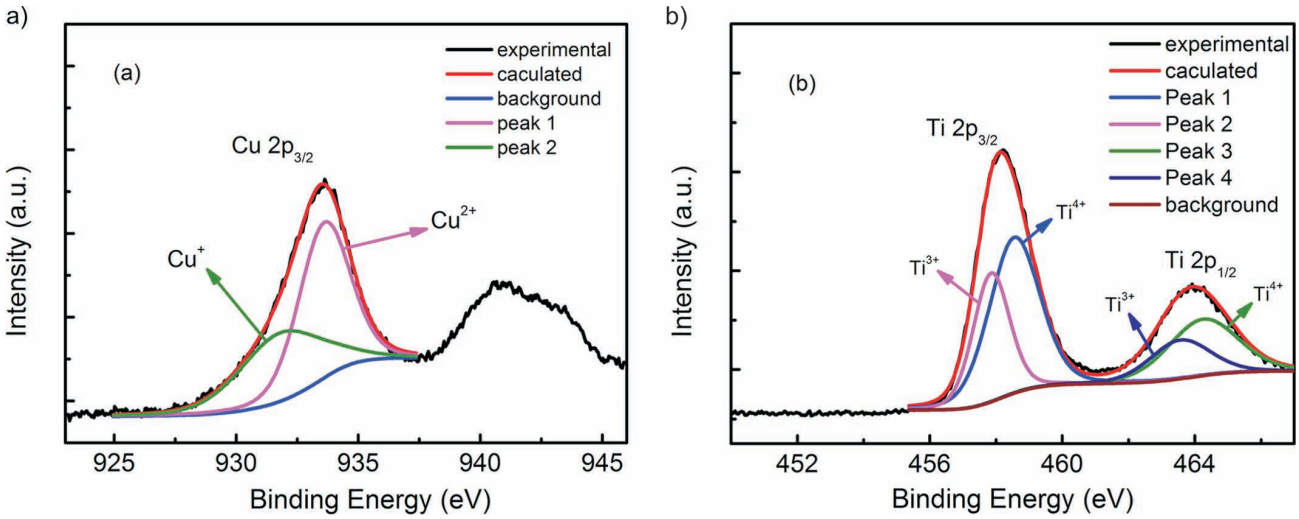

Fig. 7: XPS spectrum of **(a)** Cu 2p and **(b)** Ti 2p electron of the CCTYNO ceramic sintered at 1080 °C.

Figs. 7a and b show the XPS spectra of Cu 2p, Ti 2p peaks for the CCTYNO ceramic. The Cu 2p peak can be extracted into two peaks by means of Gaussian-Lorentzian profile fitting. The highest peak observed at a binding energy of 933.67 eV represents Cu^{2+}, while the peak at 931.81 eV corresponds to Cu^{+}. The existence of Ti^{3+} and Ti^{4+} is also found in the CCTYNO ceramic, as shown in Fig. 7b. For CCTO-related ceramics, the presence of polyvalent cations (i.e., Cu^{+}, Cu^{2+}, Ti^{3+}, and Ti^{4+}) may cause changes in the dielectric properties of the grains, especially at high temperature [29]. In this work, doping of Y^{3+} and Nb^{5+} ions on Ti sites may induce the defect clusters, i.e. Y_{Ti}' and $Nb_{Ti}^{\bullet}$, in the grains. When the temperature increases, movement of defect clusters becomes faster, indicating an active polaron hopping process. This implies the conduction mechanism inside the semiconducting grains of the CCTYNO ceramic.

IV. Conclusions

CCTYNO ceramics were fabricated with the conventional solid-state reaction method, and their dielectric properties were studied as functions of frequency and temperature. High dielectric permittivity (~6000) and low dielectric loss (~0.082) were observed at room temperature. The activation energy for the dc conduction process (0.593 eV) is comparable to that for the relaxation process (0.662 eV), implying that the dielectric response is associated with the properties of the grain boundaries.

Acknowledgements

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