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Colossal dielectric permittivity and relevant mechanism of $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics

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ABSTRACT

$Bi_{2/3}Cu_3Ti_4O_{12}$ (BCTO) ceramics with pure perovskite phase were successfully prepared by traditional solid-state reaction technique. Uniformly distributed and dense grains with the grain size of 2–3 μm were observed by SEM. A giant low-frequency dielectric permittivity of $\sim 3.3\times10^5$ was obtained. The analysis of complex impedance revealed that $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics are electrically heterogeneous. There are three kinds of dielectric response detected in $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics, which existed in the low-frequency range, middle-frequency range, and high-frequency range, respectively. Through the study of dielectric spectrum at different temperatures, the relatively low activation energy of 0.30 eV for middle-frequency dielectric response was calculated, which suggested that this Middle-frequency dielectric response can be ascribed to grain boundaries response. In view of the analysis of dielectric spectrum at low temperatures, the activation energy of 0.07 eV for high frequency dielectric response was found. This value illustrated that dielectric response at high frequencies was associated with grains polarization effect. The comparison of dielectric spectra of $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics with different types of electrodes revealed that giant low-frequency dielectric constant was attributed to the electrode polarization effect.

1. Introduction

Over the past few years, $CaCu_3Ti_4O_{12}$ (CCTO) has attracted great interest due to its exceptionally high dielectric permittivity of 10^4, which is stable over a wide temperature range of 100–600 K [1]. It shows high potential for technological applications, such as memory devices based on capacitive components and microwave devices. It is now widely accepted that the high dielectric constant of polycrystalline CCTO ceramics is associated with internal barrier layer capacitor (IBLC) structure, consisting of semiconducting grains and insulating grain boundaries [2,3]. In addition, a sample-electrode interface effect has been suggested to contribute to the high permittivity of single crystals where grain boundaries are absent [4].

Recently, several CCTO-like oxides that can be generally described with a compositional formula of $Acu_3Ti_4O_{12}$ (A=Sr, $Bi_{2/3}$, $Bi_{1/2}Na_{1/2}$, $La_{2/3}$, etc.) have been reported and confirmed to show the colossal dielectric properties [5–11]. $Bi_{2/3}Cu_3Ti_4O_{12}$ (BCTO), as a member of $ACu_3Ti_4O_{12}$ family, has a similar structure with CCTO. It was reported that BCTO ceramics had a grain size of ~2 μm [9,12,13]. The small grain size reveals a promising application for thin-film capacitor. A low dielectric constant of ~2000 with the same temperature and frequency stable as CCTO was obtained through traditional solid state technique. The systematical investigation of impedance and electric modulus revealed this low permittivity can be ascribed to an internal barrier layer capacitance (IBLC) effect [9]. Moreover, through a rapid cooling temperature process, a very large low-frequency dielectric constant of $\sim 1.5\times10^5$ was obtained. The comparison experiment of different electrodes illustrated this large value was attributed to sample-electrode interface polarization effect [12]. Furthermore, a series of high density BCTO ceramics were synthesized by the sol-gel method. They showed an outstanding dielectric constant of $\sim 1.2\times10^4$ at 1 kHz [13].

In the present work, $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics were prepared via the traditional solid-state reaction method. A giant dielectric permittivity of $\sim 3.3\times10^5$ was obtained. The crystalline structure, microstructure, dielectric properties, and complex impedance were investigated in detail. In addition, three dielectric responses, which existed in low-frequency range, middle-frequency range, and high-frequency range, respectively, were systematically studied.

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2. Experimental

$Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics were prepared by a conventional solid-state reaction technique. The stoichiometric amounts of Bi_2O_3 (99.0%), CuO (99%), TiO_2 (99.99%) were mixed and ball-milled in ethanol for 24 h. Subsequently, the mixtures were dried and calcined at 800 °C for 10 h in air. The calcined powders were blended with approximately 5 wt% polyvinyl alcohol (PVA) and pressed into disk pellets (15 mm diameter and 1.5 mm in thickness) with a uniaxial pressure of 100 MPa after sufficient grounding. These disk pellets were sintered at 1000 °C for 10 h in air. For electrical characterization, the sintered disk pellets were surface-polished in most cases and then coated with silver paint and fired at 600 °C for 20 min.

The phase structures of the sintered specimens were identified by X-ray diffraction (XRD, D/max-2550/PC, Rigaku, Japan) with Cu K radiation and the microstructures were studied by scanning electron microscope (SEM, Quanta 200, Philips, Netherlands). Dielectric spectra and complex impedance at room temperature were measured by Agilent 4294 A precise impedance analyzer within the frequency range of 40 Hz to 110 MHz. The measurement of dielectric properties with varied temperatures was carried out with the LCR meter (Agilent E4980A).

3. Results and discussion

Fig. 1 illustrates X-ray diffraction pattern of BCTO ceramics at room temperature. As shown in Fig. 1, no detectable impurity phase is observed. XRD pattern can be assigned to the body-centered cubic structure with the space group *Im3* according to JCPDS #75-2188 [14]. The SEM images of the fresh surface of BCTO ceramics at room temperature are present in inset of Fig. 1. Compacted textures and uniformly distributed grains can be observed. The grain size is about 2–3 µm. The relative density of BCTO ceramics is found to be 96.7%.

Fig. 2 exhibits the frequency dependence of ε' and $\tan\delta$ at room temperature for $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics. Interestingly, two obvious step-like decreases and three dielectric plateaus can be found in the plot of the frequency dependence of ε'. At 1 kHz, a giant ε' of $\sim 3.3\times10^5$ is obtained, which is much larger than permittivity values of 2000 [9], 1.2×10^4 [13], and 1.5×10^5 [12]. However, $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics obtained here present a narrow frequency-stability range below 3 kHz, which is smaller than that of previous $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics showing the frequency-stability range below 1 MHz [9,13]. In addition, two $\tan\delta$ peaks are clearly discerned in the frequency dependence of $\tan\delta$. From the view of positions where peaks occur, these two loss peaks are corresponding to two step-like decreases in the frequency dependence of ε'.

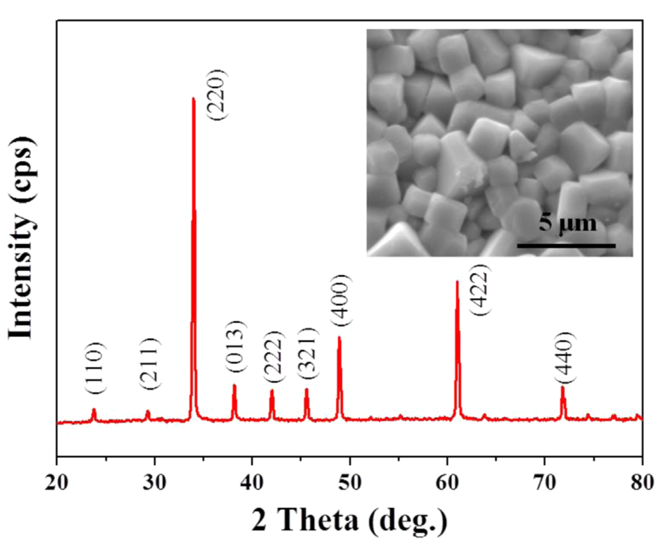

Fig. 1. XRD pattern of BCTO ceramics. Inset is the SEM micrograph of the surface of BCTO ceramics.

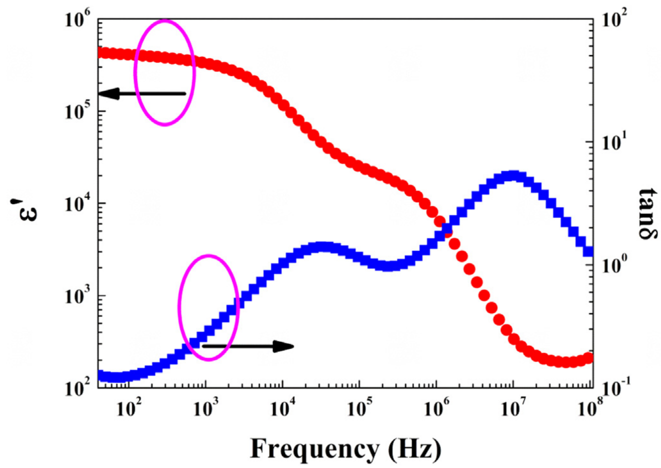

Fig. 2. Frequency dependence of dielectric constant and dielectric loss for BCTO ceramics at room temperature.

Fig. 3 demonstrates the complex impedance of $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics measured in the frequency range from 40 Hz to 110 MHz at room temperature. As shown in Fig. 3, three clearly semicircles are observed, indicating that $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics are electrically heterogeneous. The complex impedance can be explained by an equivalent circuit consisting of three parallel resistor–capacitor (R–C) elements connected in series, where R–C elements at different frequencies represent different electrical responses. Therefore, the complex impedance reveals there are three electrical responses in $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics, which exist at low frequencies, middle frequencies, and high frequencies, respectively.

In order to interpret the giant low-frequency dielectric constant, a comparison of dielectric spectra with different types of electrodes is performed. As shown in Fig. 4, dielectric spectra of same BCTO ceramic with different electrodes overlap in the frequency range above $\sim$3 kHz. However, a low-frequency dielectric spectrum displays an obvious discrepancy. The dielectric constant of BCTO with Au electrode is larger than that with Ag-paint in the

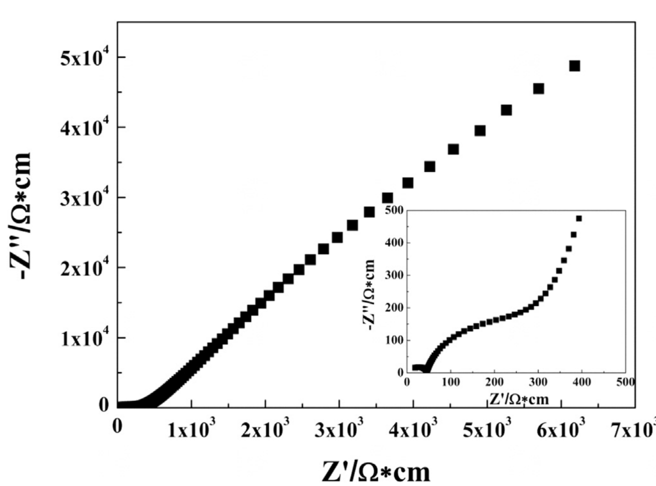

Fig. 3. Complex impedance plots for BCTO ceramics at room temperature. The inset shows an expanded view of the high frequency data close to the origin.