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Dielectric constant versus voltage and non-Ohmic characteristics of $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics prepared by different methods

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Abstract

$Bi_{2/3}Cu_3Ti_4O_{12}$ (BCTO) ceramics were successfully prepared by traditional solid-state reaction method (BCTO-SS) and sol–gel method (BCTO-SG). Pure perovskite phase and dense structure were obtained in BCTO ceramics prepared by both methods. BCTO-SG ceramics showed a large dielectric constant of $\sim 1.1\times10^4$ while BCTO-SS ceramics exhibited a low dielectric constant of $\sim$3200. At 100 kHz, the dielectric constant of BCTO-SS ceramics decreased with applied voltage increasing, while the dielectric constant of BCTO-SG ceramics increased with applied voltage increasing. Further study of the relationship between dielectric constant and voltage suggested BCTO-SG ceramics had larger defect concentration than BCTO-SS ceramics. The investigation of complex impedance indicated that the electrical properties of grain boundaries for all BCTO ceramics were evidently affected by applied voltages and the electrical properties of grains were independent of applied voltages. In addition, the non-Ohmic properties of BCTO ceramics were studied in detail. The non-linear coefficients of BCTO-SS and BCTO-SG ceramics were 1.65 and 1.01, respectively. The breakdown electric fields of BCTO-SS and BCTO-SG ceramics were found to be 1.21 and 0.48 kV/cm, respectively. The potential barrier heights of BCTO-SS and BCTO-SG ceramics were calculated to be 0.549 and 0.485 eV, indicating that the potential barriers at the grain boundaries for BCTO-SS and BCTO-SG ceramics are the Schottky-type barrier.

Keywords: C. Dielectric properties; $Bi_{2/3}Cu_3Ti_4O_{12}$; Impedance spectroscopy; Non-Ohmic properties

1. Introduction

Materials with high dielectric constant and good thermal stability have attracted considerable attention particularly for their practical applications in microelectronics such as capacitors and memory devices. Recently, giant dielectric permittivity with weakly temperature-dependent permittivity has been observed in TiO_2-based ceramics and $CaCu_3Ti_4O_{12}$ (CCTO) -like compounds. For TiO_2-based ceramics, a very large permittivity of 2.2×10^5 was observed in the TiO_2 ceramics by doping (Sm, Ta) and (Bi, Nb)-modified TiO_2 ceramics showed a dielectric constant of 4.2×10^4 [1,2]. CCTO-like compounds 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 extensively studied [3–9]. As a member of CCTO-like compounds, $Bi_{2/3}Cu_3Ti_4O_{12}$ (BCTO), which is isostructural with CCTO, has been reported in the literatures [10–12]. It exhibited the same temperature and frequency dependence of the dielectric constant as CCTO. A very large low-frequency dielectric constant (12,000) of BCTO ceramics was obtained through sol–gel method [10], which was much larger than that of $\sim$2000 for BCTO ceramics prepared by a solid-state reaction technique [11,12]. Though the large dielectric constant of BCTO ceramics prepared by the solid-state reaction technique and sol–gel method has been well explained by Maxwell–Wagner relaxation, it is very necessary to deeply investigate the essential mechanism of BCTO ceramics prepared by both methods.

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For CCTO, the capacitance versus voltage (*C–V*) characteristic of CCTO was investigated lately in order to further study the mechanism of huge dielectric constant [13–15]. It is now believed that the huge permittivity is related to defects, especially to rechargeable defects, i.e., trap states [16]. In addition to the giant dielectric properties, CCTO ceramics also exhibit remarkably non-Ohmic electrical behavior. This is due to the existence of intrinsic potential barriers at the grain boundaries. The non-Ohmic characteristics of CCTO make it suitable for varistor applications [17,18]. A Schottky-type potential barrier was proposed to explain the non-Ohmic electrical properties [19]. Therefore, in order to reveal the essential difference in mechanism between BCTO ceramics prepared by solid-state reaction method and sol–gel method, it is a very meaningful work to investigate the capacitance–voltage (*C–V*) and non-Ohmic characteristics of BCTO ceramics prepared by both methods.

In the present work, $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics were prepared by the traditional solid-state reaction method and sol–gel method. The crystalline structure and microstructure were analyzed. Dielectric properties and complex impedance with applied voltages were systematically investigated. In addition, the non-Ohmic characteristics of BCTO ceramics prepared by both methods were studied in detail.

2. Experimental

In this work, $Bi_{2/3}Cu_3Ti_4O_{12}$ ceramics were prepared by a conventional solid-state reaction technique (BCTO-SS) and sol–gel method (BCTO-SG). All raw materials used in this work were purchased from Sinopharm Chemical Reagent Co., Ltd, China. For the solid-state reaction method, the stoichiometric amounts of highly pure Na_2CO_3 (99.8%), Bi_2O_3 (99.0%), CuO (99%) and TiO_2 (99.99%) were mixed and ball-milled in ethanol for 10 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 in 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 20 h in air. For a sol–gel method, according to the appropriate molar ratio, bismuth nitrate ($Bi(NO_3)_3\cdot 5H_2O$, 99%), copper nitrate ($Cu(NO_3)_3\cdot 3H_2O$, 99%) and tetrabutyl titanate ($Ti(OC_4H_9)_4$, 98%) were weighed as starting materials. $Cu(NO_3)_3\cdot 3H_2O$ and $Bi(NO_3)_3\cdot 5H_2O$ were dissolved in the buffer mixed solution of ethanol and deionized water (C_2H_5OH:H_2O = 1:1), which formed solution A. Particularly, $Bi(NO_3)_3\cdot 5H_2O$ had to been dissolved in 2 mol/L HNO_3 due to its hydrolyzation. Tetrabutyl titanate ($Ti(OC_4H_9)_4$), glacial acetic solution (CH_3COOH) and ethanol (C_2H_5OH) were mixed to obtain solution B. These two solutions of A and B were mixed and stirred by a magnetic stirrer. Subsequently, the mixed solution was held in a water bath at 40 °C until it turned completely to a gel. The gel was then aged for 16 h. After that, the gel was dried and calcined at 800 °C for 10 h. The obtained powders were blended with polyvinyl alcohol and compacted into pellets (15 mm in diameter and 1.5 mm in thickness). These pellets were fired at 1000 °C for 7.5 h. For electrical characterization, the sintered disk pellets were surface-polished in most cases and then coated with silver paint and fired at 840 °C for 30 min.

For ceramics prepared by both methods, the phase structures were identified by X-ray diffraction (XRD, D/max-2550/PC, Rigaku, Japan) with Cu Kα radiation and the microstructures were studied by scanning electron microscope (SEM, Quanta 200, Philips, Netherlands). The densities of the sintered pellets were measured with Archimedes method. The dielectric properties and complex impedance with applied voltages were measured by Agilent 4294A precise impedance analyzer at room temperature. The current–voltage properties of the samples were measured by using current–voltage measurements (Model 610E, TREK). These measurements were performed at temperatures of 30 °C, 50 °C, 70 °C, and 90 °C, which were kept constant with an accuracy of ±1 °C.

3. Results and discussion

Fig. 1 illustrates X-ray diffraction patterns of BCTO-SS and BCTO-SG ceramics at room temperature. As shown in Fig. 1, no detectable impurity phase is observed for both ceramics. XRD patterns can be assigned to the body-centered cubic perovskite phase with the space group *Im3* according to JCPDS 75-2188 [20]. In addition, the peak shift for different preparation methods can be found if a careful observation is taken. Compared to BCTO-SS, all positions of BCTO-SG peaks shift to lower angle, indicating that the lattice constant of BCTO-SG is larger than that of BCTO-SS. The relative densities of BCTO-SS and BCTO-SG ceramics are found to be 95.3% and 97.2%, respectively. Fig. 2(a) and (b) are SEM images of BCTO-SS and BCTO-SG ceramics, respectively. For both samples, compacted textures and uniformly distributed grains can be observed. The grain size of BCTO-SG ceramics is a little larger than that of BCTO-SS ceramics if a careful observation is taken. Therefore, it can be concluded that BCTO-SG ceramics reveal more dense structure than BCTO-SS ceramics.

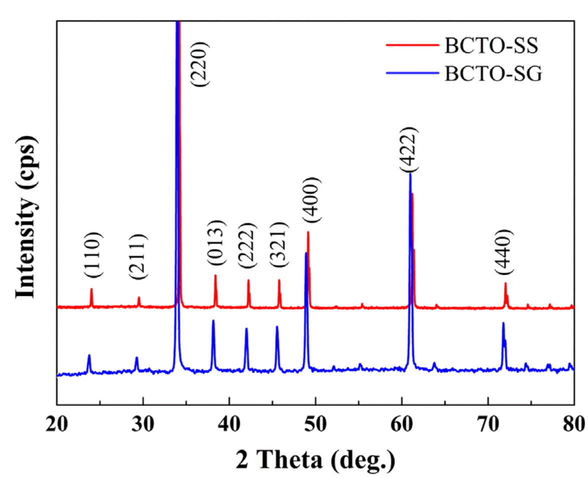

Fig. 1. XRD patterns of BCTO-SS and BCTO-SG ceramics.