

Effects of Bi^{3+} doping on microstructure and dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{CaTiO}_3$ composite ceramics

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Abstract

The effects of Bi^{3+} doping ions on the microstructure and dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{CaTiO}_3$ (CCTO/CTO) composites prepared by using a conventional solid state reaction method were investigated. Microstructure analysis revealed that Bi^{3+} doping ions can be substituted into Ca^{2+} sites in both the CCTO and CTO phases. It is notable that the value of ϵ' at 1 kHz and 30 °C of the CCTO/CTO composite was greatly increased to 4.1×10^4 by doping with Bi^{3+} ions, compared to the un-doped sample ($\epsilon' \sim 1.8 \times 10^3$). Non-Ohmic properties of Bi^{3+} -doped CCTO/CTO composites were also investigated. The electrical responses of grains and internal interfaces were investigated using impedance spectroscopy. Strongly enhanced dielectric responses and variation in nonlinear electrical properties can be well described based on the electrical responses at internal interfaces of the composites.

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1. Introduction

In recent years, giant dielectric materials, especially $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO), have been intensively investigated due to their very high dielectric permittivity (ϵ') and novel physical behavior [1–10]. The electrical responses of different internal interfaces in CCTO polycrystalline ceramics and related $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ compounds ($\text{A}=\text{Bi}_{2/3}, \text{La}_{2/3}, \text{Na}_{1/2}\text{Bi}_{1/2}, \text{Na}_{1/2}\text{Sm}_{1/2}$, etc.) were investigated in order to clarify the unexpected appearance of giant dielectric properties [2,3,7,11–15]. The internal interfaces studied were domain boundaries (DBs) [16], grain boundaries (GBs) [2,3,7], planar defects due to stacking faults in the grains [17], and interfaces between the CCTO grain matrix and secondary phases of other substances [18–21]. Furthermore, CCTO can exhibit electrical properties that show a nonlinear relationship between

current density and electric field strength (J – E) [2]. Most results suggested that the observed nonlinear J – E behavior of CCTO polycrystalline ceramics was caused by the electrical response of the insulating GBs [2–5,12,20]. Unfortunately, the loss tangent ($\tan\delta$) of CCTO is still too large [1,4–7,21], which is undesirable for many applications such as capacitors and memory devices.

To improve the dielectric properties of CCTO ceramics, Kobayashi and Terasaki [18] reported a strategy to greatly reduce $\tan\delta$ of CCTO ceramics by producing a composite system of CCTO/ CaTiO_3 (CCTO/CTO) from a starting composition with a nominal formula of $\text{Ca}_2\text{Cu}_2\text{Ti}_4\text{O}_{12}$. The nonlinear J – E properties of this composite system were improved [19,22]. Generally, $\tan\delta$ values of CCTO/CTO composites are very low ($\tan\delta \sim 0.02$) [23,24]. Moreover, very high breakdown electric field (E_b) and large nonlinear coefficient (α) values were achieved in this composite system compared to a single phase of CCTO ceramics [19,22]. Enhancement of nonlinear electrical properties of CCTO/CTO composites was mainly attributed to the electrical response of

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the CTO–CCTO interface [19,23,24], which does not appear in a single phase CCTO ceramic. It is often observed that substitution of metal ions into CCTO ceramics significantly changes both the dielectric response and nonlinear properties. Changes in properties of CCTO ceramics were ascribed to the changing electrical properties of grains and GBs as a result of dopants [4,5,25–27].

In this work, we substituted aliovalent Bi^{3+} ions in various concentrations into Ca^{2+} sites of material with a starting composition of $\text{Ca}_2\text{Cu}_2\text{Ti}_4\text{O}_{12}$. Two CCTO and CTO phases were observed in the XRD patterns. It was found that Bi^{3+} doping ions had remarkable effects on the microstructure, dielectric response, and electrical properties of CCTO/CTO composites. Very large changes in dielectric properties were described based on interfacial polarization at internal interfaces.

2. Experimental details

In this work, ceramic powders with nominal compositions of $\text{Ca}_2\text{Cu}_2\text{Ti}_4\text{O}_{12}$ (CCTO/CTO), $\text{Ca}_{1.95}\text{Bi}_{0.05}\text{Cu}_2\text{Ti}_4\text{O}_{12}$ (Bi_05), $\text{Ca}_{1.90}\text{Bi}_{0.10}\text{Cu}_2\text{Ti}_4\text{O}_{12}$ (Bi_10), and $\text{Ca}_{1.7}\text{Bi}_{0.30}\text{Cu}_2\text{Ti}_4\text{O}_{12}$ (Bi_30) were prepared by using a solid state reaction method. CaCO_3 (99.9% purity), Bi_2O_3 (99.99% purity), TiO_2 (99.9% purity), and CuO (99.9% purity) were used as starting raw materials. First, stoichiometric amounts of these raw materials were mixed by ball milling in ethanol for 24 h using 2 mm in diameter ZrO_2 balls. Next, each slurry mixture was dried and calcined in air at 900 °C for 15 h. Then, the calcined powders were ground and pressed to form green bodies each with a diameter of 9.5 mm and a thickness of ~ 1.2 mm. Finally, the green bodies were sintered in air at 1100 °C for 24 h at heating and cooling rates of 5 °C/min.

Phase compositions of sintered ceramics were investigated by X-ray diffraction spectrometer (XRD; Philips PW3040). Scanning electron microscopy (SEM; LEO 1450VP; Cambridge, UK) and energy-dispersive X-ray spectrometry (EDS) were used to reveal the distribution of CCTO and CTO phases as well as the chemical elements in the sintered ceramics at different areas. The dielectric properties of the sintered ceramics were measured using an Agilent 4294A Precision Impedance Analyzer over a frequency range of 10^2 – 10^7 Hz with an oscillation voltage of 0.5 V. The dielectric properties were measured over the temperature range of -70 to 150 °C. Each step increase in measurement temperature was 10 °C with a precision of ± 0.1 °C. J – E measurements were determined at room temperature using a high voltage measurement unit (Keithley Model 247). The value of E_b was obtained at $J=1$ mA cm^{-2} . α values of all the samples were calculated over the range of $J=1$ – 10 mA cm^{-2} . Before electrical and dielectric measurements, Au was sputtered onto each pellet face at a current of 25 mA for 8 min using a Polaron SC500 sputter coating unit (Sussex, UK).

3. Results and discussion

The XRD patterns of Bi-doped CCTO/CTO composites are illustrated in Fig. 1. It is clearly seen that all of the composite

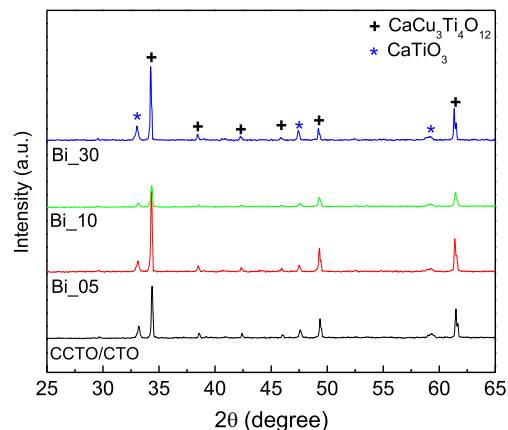


Fig. 1. XRD patterns of Bi-doped CCTO/CTO composites.

samples consisted of two phases of CTO (JCPDS 82-0231) and CCTO (JCPDS 75–2188). This result is similar to those reported in the literature [19,23,24,28]. Considering the nominal formula of $\text{Ca}_2\text{Cu}_2\text{Ti}_4\text{O}_{12}$, ~ 66.7 mol% of CTO and ~ 33.3 mol% of CCTO should be created during the sintering process due to an imbalance between Ca^{2+} and Cu^{2+} ions. The creation of CCTO/CTO composites was confirmed by a Rietveld quantitative analysis of synthesized $\text{Ca}_2\text{Cu}_2\text{Ti}_4\text{O}_{12}$ ceramics as reported in the literature [19]. The formation can be explained as follows. Due to a relatively large ionic radius of Ca^{2+} compared to that of Cu^{2+} , Ca^{2+} cannot enter into Cu^{2+} sites in a planar square to form a $\text{Ca}(\text{CaCu}_2)\text{Ti}_4\text{O}_{12}$ structure [23,24].

Fig. 2 shows surface morphologies of CCTO/CTO and Bi-doped CCTO/CTO composites. It was found that some grains in the microstructure of Bi-doped CCTO/CTO grew rapidly. This indicates that an abnormal grain growth occurred in the Bi-doped CCTO/CTO composites [29]. Such grain growth may be related to the liquid phase sintering behavior as a result of a Bi-related liquid phase. This is reasonable because the melting point of Bi_2O_3 is lower than the sintering temperature of CCTO/CTO composites (1100 °C). As revealed in the insets of Fig. 2(a) and (b) for the backscattered SEM images, two phases with different contrasts were observed, i.e., darker and lighter phases in the CCTO/CTO sample. This observation is consistent with the XRD results and similar to those reported in the literature for un-doped CCTO/CTO [19,23,24]. The darker and lighter phases were CTO and CCTO phases, respectively [19,23,24]. However, varying contrast could not be clearly observed in the Bi_05 sample as well as in other Bi-doped CCTO/CTO samples. As depicted in Fig. 3(a) and (b), EDS peaks corresponding to Bi, Ca, Ti, and O appeared in the EDS spectra measured in a small grain (point 2). All EDS peaks for Bi, Ca, Cu, Ti, and O were detected in the larger grain. This clearly indicates that Bi^{3+} doping ions preferentially formed solid solution within both the CCTO and CTO phases.

Fig. 4 and its inset show the frequency dependence of ϵ' and $\tan\delta$ at 30 °C. Clearly, Bi^{3+} doping ions have a great influence on the dielectric properties of CCTO/CTO composites. The values of ϵ' and $\tan\delta$ of CCTO/CTO composites were strongly

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