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Microstructural evolution and strongly enhanced dielectric response in Sn-doped $CaCu_3Ti_4O_{12}/CaTiO_3$ ceramic composites

Jutapol Jumpatam[a], Bundit Putasaeng[b], Teerapon Yamwong[b], Prasit Thongbai[c,*], Santi Maensiri[d]

[a] *Materials Science and Nanotechnology Program, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand*
[b] *National Metal and Materials Technology Center (MTEC), Thailand Science Park, Pathumthani 12120, Thailand*
[c] *Integrated Nanotechnology Research Center (INRC), Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand*
[d] *School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand*

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ABSTRACT

Sn^{4+}-doped $CaCu_3Ti_4O_{12}/CaTiO_3$ composites were prepared using a solid state reaction method employing a simple one-step process. A minor phase of $CaTiO_3$ grains was very well dispersed into the $CaCu_3Ti_4O_{12}$ matrix and these two phases were clearly separated from each other in $CaTiO_3/CaCu_3Ti_4O_{12}$. The grain size of the $CaCu_3Ti_4O_{12}$ phase was largely enhanced by Sn^{4+} doping. Furthermore, $CaTiO_3$ grains were also found inside the enlarged $CaCu_3Ti_4O_{12}$ grains. The microstructural evolution can be described based upon liquid phase sintering and the pinning effect by second-phase particles. The dielectric permittivity of Sn^{4+}-doped $CaCu_3Ti_4O_{12}/CaTiO_3$ was greatly enhanced from $\sim 2 \times 10^3$ to $\sim 0.6–1.3 \times 10^4$ at 10^3 Hz, while, the dielectric loss tangent was still low. The nonlinear properties were degraded as a main result of microstructural evolution. These results strongly indicated an extrinsic effect upon both of the giant dielectric response and nonlinear properties of $CaCu_3Ti_4O_{12}$-based compounds.

1. Introduction

Recently, investigations to reduce the dielectric loss tangent ($\tan\delta$) of $CaCu_3Ti_4O_{12}$ (CCTO) ceramics and related compounds have been intensively conducted [1–10]. Although CCTO ceramics can exhibit high dielectric permittivity values (ε') of about 10^4–10^5, their $\tan\delta$ values are still too large [3,4,11–14]. CCTO ceramics with a high ε' value and low $\tan\delta$ may be desirable for multilayer ceramic capacitors. It was found that improved dielectric and electrical properties of CCTO were obtained by deliberately creating a composite system of CCTO/$CaTiO_3$ (CTO) with the nominal chemical formula of $Ca_2Cu_2Ti_4O_{12}$ [1,6,9,15–17]. CCTO/CTO composites have very low $\tan\delta$ of $\sim$0.02 compared to CCTO ceramics ($\tan\delta$ >0.5) [1]. Moreover, improved nonlinear current density–electric field (or non-Ohmic) properties were achieved in this composite system. Very high breakdown electric field (E_b) and nonlinear coefficient (α) values were observed in CCTO/CTO [15].

Recently, many metal ions were substituted into Cu^{2+} or Ti^{4+} sites of a single phase of CCTO ceramics in order to improve their dielectric properties [2–4,11,18–20]. It was reported that doping CCTO with suitable ions such as Mg^{2+} [20], Zr^{4+} [2], and Sn^{4+} [4] can reduce $\tan\delta$ values. Unfortunately, the reduced values of $\tan\delta$ due to substitution of these ions were still higher than the standard value for capacitor applications. This may be due to a large initial $\tan\delta$ value of CCTO. According to our previous research, ε' values of CCTO/CTO composites prepared using a nominal formula of $Ca_2Cu_2Ti_4O_{12}$ were greatly enhanced by doping Zn^{2+} and Mg^{2+} ions into Cu^{2+} sites. Notably, its $\tan\delta$ value was still low [9,17]. These may be desirable for capacitor applications. Simultaneously, the nonlinear current density–electric field properties of the composites were significantly improved. Using this concept, substitution of Sn^{4+} into Ti^{4+} sites in $Ca_2Cu_2Ti_4O_{12}$ may also lead to improved dielectric properties of CCTO/CTO composites. This is because $\tan\delta$ values of single phase CCTO ceramics can be reduced by Sn^{4+} doping ions [4]. It was suggested that variation in dielectric properties of Sn-doped CCTO ceramics was attributed to intrinsic effects, existing inside the grains [4,21]. While it is widely believed that the giant dielectric behavior of CCTO polycrystalline ceramics was attributed to the extrinsic effect of the electrical response of internal interfaces (e.g., grain boundary or domain boundary) [2,11,19,22,23]. Ribeiro et al. [21] found that the non-Ohmic properties of CCTO ceramics can be enhanced by Sn^{4+} doping ions. Systematic investigation of the dielectric properties and electrical

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* Corresponding author. Fax: +6643202374.
E-mail addresses: pthongbai@kku.ac.th, prasitphysics@hotmail.com (P. Thongbai).

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responses of internal interfaces of Sn^{4+}-doped CCTO/CTO composites may provide important clues supporting the intrinsic or extrinsic model for clarifying the giant dielectric response in CCTO ceramics. To the best of our knowledge, dielectric and electrical properties of the composite system of CCTO/CTO substituted by Sn^{4+} ions have never been reported.

Therefore, the aim of this work is to study the effects of Sn^{4+} doping ions on the microstructure and dielectric properties of CCTO/CTO composites. Sn^{4+}-doped CCTO/CTO composites were produced using a one-step process for ceramics with the nominal formula of $Ca_2Cu_2Ti_{4-x}Sn_xO_{12}$. Interestingly, improved dielectric properties with a strong increase in ε' and slight increase in $\tan\delta$ were achieved. However, the nonlinear electrical properties were degraded. The possible mechanisms are discussed in detail.

2. Experimental details

Sn^{4+}-doped CCTO/CTO composites were prepared by using a starting nominal formula of $Ca_2Cu_2Ti_{4-x}Sn_xO_{12}$ (where $x = 0$, 0.1, 0.20, and 0.30, referenced as CCTO/CTO, Sn10, Sn20, and Sn30 composites, respectively). Ceramic powders were prepared using a conventional solid state reaction method. First, a stoichiometric mixture of $CaCO_3$ (99.95% purity), CuO (99.9% purity), SnO_2 (99.9% purity), and TiO_2 (99.9% purity) specific for each composition was ball milled in ethanol for 24 h using ZrO_2 balls. Second, all resulting slurries were dried and carefully ground. Third, dried mixed powders were calcined at 900 °C for 15 h. Then, the calcined powders were ground and pressed into pellets of 9.5 mm in diameter and ~1.0 mm in thickness to produce the green body. Usually, to accomplish a dense ceramic microstructure, the sintering temperatures of CCTO and CTO ceramics are of about 1050 – 1100 °C and ≈1300 °C, respectively. When the sintering temperature of CCTO ceramics was higher than 1100 °C, CuO becomes to decompose from CCTO lattice [24]. Thus, finally, these green body pellets were sintered in air at 1100 °C for 6 and 24 h using a heating rate of 5 °C/min.

Phase composition and crystal structures were characterized using an X-ray diffraction (XRD; Bruker, 2D phaser) technique. Scanning electron microscopy (SEM; LEO 1450VP) coupled with energy dispersive X-ray spectrometry (EDS) were used to characterize the composite microstructures. Elemental distribution in the sintered Sn-doped CCTO/CTO composites was examined to reveal mapping images using a field-emission scanning electron microscopy (FE-SEM, HITACHI SU8030, Japan). For the dielectric and electrical measurements, ceramic samples were polished and coated by sputtering Au on their surfaces. The dimensions of samples used for the measurements are of about ~9.4 mm in diameter and ~0.8 mm in thickness. The dielectric properties were measured using an Agilent 4294A Precision Impedance Analyzer over the frequency range of 100 Hz–10 MHz. The dielectric properties were investigated as a function of temperature in the range from −70 to 220 °C. The amplitude of an applied oscillation voltage was 500 mV. Current–voltage characteristics were investigated at room temperature using a high voltage measurement unit (Keithley Model 247). The electric field strength (E) and current density (J) were calculated from the applied voltage and measured current values, respectively. E_b is defined as an electric field at which $J = 1\ mAcm^{-2}$. α was calculated in the range of $J = 1 - 10\ mAcm^{-2}$.

The complex impedance (Z^*) was calculated from the complex dielectric permittivity (ε^*) using the following relationship:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \frac{1}{i\omega C_0 Z^*} = \frac{1}{i\omega C_0 (Z' - iZ'')} \qquad ,(1)$$

where ε' and ε'' are the real (dielectric constant) and imaginary parts (dielectric loss factor) of ε^*, respectively. ε' was calculated from $\varepsilon' = C'd/\varepsilon_0 S$, where S is the area of electrode, d is the sample thickness, and ε_0 is the permittivity of free space ($\varepsilon_0 = 8.854 \times 10^{-12}$ F/m). ω is the angular frequency of an applied AC electric field ($\omega = 2\pi f$) and $i = \sqrt{-1}$. $C_0 = \varepsilon_0 S/d$ is the empty cell capacitance.

3. Results and discussion

Fig. 1 shows the XRD patterns of the composite ceramics sintered for 6 h with nominal compositions of $Ca_2Cu_2Ti_{4-x}Sn_xO_{12}$ ($x = 0$–0.3). Two phases of CCTO (JCPDS 75-2188) and CTO (JCPDS 82-0231) were detected in all samples, indicating the existence of a CCTO/CTO composite system as reported in published literature [1,9,15–17]. Impurity phases were not observed in the XRD patterns of the composites sintered for 6 and 24 h. Generally, the composite samples can also present other phases in amount below the detection limit of the XRD analysis. As shown in Fig. 2 and EDS result, Cu-rich phase particles were observed in the microstructure of Sn^{4+}-doped CCTO/CTO samples. However, an impurity of Sn-related phase cannot be detected in both of the XRD and EDS results. Thus, it is likely that Sn^{4+} could substitute into Ti^{4+} sites in CCTO and/or CTO structures. The lattice parameters (a) of the CCTO phase of CCTO/CTO, Sn10, Sn20, and Sn30 composites sintered for 6 h were found to be 7.4040, 7.4066, 7.4057, and 7.4098 Å, respectively. a values of the composites sintered for 24 h were found to be 7.3891, 7.4011, 7.3958, and 7.4075 Å, respectively. Values of a tended to increase with increasing Sn^{4+} content. This might be due to the larger ionic radius of Sn^{4+} (0.69 Å) compared to Ti^{4+} (0.605 Å) [25].

Fig. 2a–d show backscattered SEM images of polished surfaces of all composite samples sintered for 6 h. In each sample, at least two phases with different contrasts were observed, supporting the XRD results. Fig. 3 shows EDS spectra of the Sn30 composite measured in darker and lighter contrast regions, clearly indicating CTO and CCTO phases. This result is similar to that reported in published literature [9,15–17]. In the lighter grains, a small intensity EDS-peak of Sn was detected as well as main EDS-peaks for Ca, Cu, Ti, and O. The EDS-peak for Sn was not observed in the darker CTO grain.

In principle, Sn^{4+} can also substitute into CTO lattice structure. To further analyze the distribution of each element in Sn^{4+}-doped CCTO/CTO composites, mapping of all elements was performed, as shown in Fig. 4. In Fig. 4b, it is clear that Sn^{4+} doping ions are not homogeneously distributed in the CCTO/CTO composites. A large

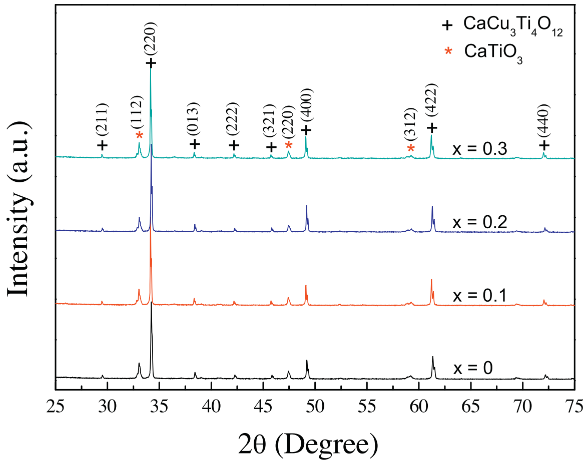

Fig. 1. XRD patterns of $Ca_2Cu_2Ti_{4-x}Sn_xO_{12}$ ($x = 0$–0.3) ceramics sintered for 6 h.