



# Grain size independence of giant dielectric permittivity of $\text{CaCu}_3\text{Ti}_{4-x}\text{Sc}_x\text{O}_{12}$ ceramics

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## Abstract

The dielectric and electrical properties of  $\text{CaCu}_3\text{Ti}_{4-x}\text{Sc}_x\text{O}_{12}$  ( $x=0, 0.04, 0.08,$  and  $0.20$ ) ceramics prepared by a solid-state reaction method were investigated. Grain sizes of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  were greatly reduced by doping with  $\text{Sc}^{3+}$ . Surprisingly, the dielectric constant of  $\text{CaCu}_3\text{Ti}_{4-x}\text{Sc}_x\text{O}_{12}$  ceramics with  $x=0-0.08$  largely increased as the mean grain size decreased. This behavior was extremely hard to produce in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  ceramics. The nonlinear current–voltage properties  $\text{CaCu}_3\text{Ti}_{4-x}\text{Sc}_x\text{O}_{12}$  ceramics were significantly degraded. The grain boundary (GB) resistance decreased with increasing  $\text{Sc}^{3+}$  concentration even though the density of GB layer increased. This resulted in enhancement of a low-frequency loss tangent due to increased dc conduction. Substitution of some  $\text{Sc}^{3+}$  ions into Cu sites was proposed as the cause of reduction of the potential barrier height at GBs. The possible mechanisms of giant dielectric response in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  ceramics are discussed.

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## 1. Introduction

Materials with giant–dielectric permittivity have attracted considerable attention since an ultra high dielectric permittivity ( $\epsilon'$ ) was discovered in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) polycrystalline ceramics [1]. This is because CCTO has high potential for use in many electronic devices, especially for multilayer ceramic capacitors (MLCCs). CCTO is a body-centered cubic perovskite–related material with slightly tilted  $\text{TiO}_6$  octahedra facing each other and producing square planar  $\text{CuO}_4$  [1–3]. It is now widely accepted that the giant dielectric response in CCTO is due to the extrinsic effect rather than the intrinsic effect [4–8].

The internal barrier layer capacitor (IBLC) effect based on interfacial polarization (Maxwell–Wagner polarization) at grain boundaries (GBs) is widely used to describe the giant dielectric behavior in CCTO ceramics [4,7,9–15]. However, it is difficult to use the IBLC model to describe the giant dielectric response in single CCTO crystals even though the dielectric response at twin boundaries was proposed [16,17].

Although the mechanism of the giant dielectric response in CCTO is still unclear, it has been certainly shown that CCTO polycrystalline ceramics are electrically heterogeneous, consisting of  $n$ –type semiconducting grains and insulating layer of GBs [4,5]. The primary cause of giant dielectric response in CCTO may either be due to this special electrically heterogeneous microstructure or other intrinsic effects. Considering the IBLC model, the dielectric response in polycrystalline ceramics is primarily due to the electrical response at GBs

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[11]. Changes in electrical properties of GB should have some effects on the material's dielectric properties. If the giant dielectric response in a CCTO polycrystalline ceramic is caused by polarization at GBs, changes of dielectric properties are related to changes in electrical properties in GB regions [18].

It is interesting that CCTO polycrystalline ceramics can also exhibit non-Ohmic properties, which is widely accepted to be the cause by the formation of intrinsic electrostatic potential barriers at the GBs, i.e., the Schottky barrier [5]. The nonlinear electrical response originates in the GB region as does its giant dielectric behavior. Data obtained from nonlinear  $J-E$  behavior of CCTO ceramics are widely believed to strongly relate the electrical properties of GBs to the overall dielectric response [7,19,20]. However, some literature suggests that there is no relationship between the giant dielectric response and nonlinear properties in CCTO ceramics [21,22]. Therefore, the giant dielectric response in CCTO ceramics may not be described by the IBLC model of Schottky barriers at the GBs. The exact origin of giant dielectric properties in CCTO ceramics is difficult to completely explain.

Thus, the aim of this work is not to provide the exact origin of giant  $\epsilon'$  in CCTO ceramics. We provide some important information about the giant dielectric and electrical properties in CCTO ceramics. We systematically investigated the effects of  $\text{Sc}^{3+}$  doping ions on the microstructure, dielectric properties, and electrical response at GBs for CCTO ceramics prepared using a solid-state reaction method. An enormous dielectric behavior was observed. The dielectric permittivity ( $\epsilon'$ ) greatly increased as the mean grain size markedly decreased.

## 2. Experimental procedure

In this work,  $\text{CaCu}_3\text{Ti}_{4-x}\text{Sc}_x\text{O}_{12}$  ( $x=0, 0.04, 0.08, \text{ and } 0.20$ ) ceramic powders were prepared using a conventional solid-state reaction method. These material compositions are abbreviated as CCTO, CCTSO-1, CCTSO-2, and CCTSO-3 ceramics, respectively.  $\text{CuO}$  (Cerac, 99.9% purity),  $\text{TiO}_2$  (Sigma–Aldrich, 99.9% purity),  $\text{CaCO}_3$  (Cerac, 99.95% purity), and  $\text{Sc}_2\text{O}_3$  (Sigma–Aldrich, 99.99% purity) were used as starting raw materials. First, a stoichiometric mixture of the starting materials for each composition was ball-milled in ethanol for 24 h using  $\text{ZrO}_2$  balls. Second, the mixed slurries were dried and then calcined at  $800^\circ\text{C}$  for 6 h. Then, the calcined powders were ground and pressed into pellets (without a binder) of 9.5 mm in diameter and 1.5 mm in thickness. Finally, the green bodies were sintered at  $1090^\circ\text{C}$  for 6 h with a heating rate  $5^\circ\text{C}/\text{min}$  followed by natural furnace cooling to room temperature.

X-ray diffraction (XRD; Bruker, D2 phaser) was used to characterize the phase compositions and crystal structures of the sintered  $\text{CaCu}_3\text{Ti}_{4-x}\text{Sc}_x\text{O}_{12}$  ceramics. Scanning electron microscopy (Hitachi S–3400, Japan) and energy-dispersive X-ray spectrometry (EDS) were used to characterize the microstructure of  $\text{CaCu}_3\text{Ti}_{4-x}\text{Sc}_x\text{O}_{12}$  ceramics. Valence states of cations in CCTO and Sc-doped CCTO ceramics were

investigated using X-ray photoelectron spectroscopy (XPS) (AXIS Ultra DLD, UK). An Agilent E4980A Precision LCR Meter was used to measure the dielectric properties. The measurement was performed in the temperature and frequency ranges of  $-70$ – $200^\circ\text{C}$  and  $10^2$ – $10^6$  Hz, respectively. Non-linear electrical properties were measured at various temperatures using a high voltage measurement unit (Keithley Model 247). Au was sputtered on each pellet face at a current of 25 mA for 8 min using a Polaron SC500 sputter coating unit before measurements. The breakdown electric field strength ( $E_b$ ) was achieved from the current density–electric field ( $J-E$ ) curves at  $J=1$  mA/cm<sup>2</sup>. The nonlinear coefficient ( $\alpha$ ) was calculated in the range of  $1$ – $10$  mA/cm<sup>2</sup>.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of  $\text{CaCu}_3\text{Ti}_{4-x}\text{Sc}_x\text{O}_{12}$  ( $x=0, 0.04, 0.08, \text{ and } 0.20$ ) ceramics, confirming the presence of the main phase consisting of CCTO (JCPDS 75–2188) in all ceramic samples. All the diffraction peaks in XRD patterns are perfectly indexed to the body-centered cubic structure with space group  $Im\bar{3}$ . A second phase consisting of  $\text{Cu}_2\text{O}$  appeared in the XRD patterns of the CCTSO-2 and CCTSO-3 samples. Furthermore, impurities consisting of  $\text{CaTiO}_3$  were also observed in the CCTSO-3 sample. The lattice parameters ( $a$ ) were calculated for CCTO, CCTSO-1, CCTSO-2, and CCTSO-3 samples and were found to be  $7.392 \pm 0.001$ ,  $7.394 \pm 0.001$ ,  $7.397 \pm 0.001$ , and  $7.403 \pm 0.0005$  Å, respectively. Chung et al. [23] investigated the effects of initial cation stoichiometry on current–voltage behavior and electrical response at a single GB layer of Sc-doped CCTO ceramics. According to their experimental results, they proposed that  $\text{Sc}^{3+}$  ions occupied both  $\text{Cu}^{2+}$  and  $\text{Ti}^{4+}$  sites in a  $\text{CaCu}_3\text{Ti}_{3.8}\text{Sc}_{0.2}\text{O}_{12}$  ceramic composition. The increase in the value of this cell parameter of CCTO ceramics was attributed to the larger ionic radius of the  $\text{Sc}^{3+}$  dopant ( $0.745$  Å) compared to the host ions,  $\text{Ti}^{4+}$  ( $0.605$  Å) and  $\text{Cu}^{2+}$  ( $0.570$  Å) [24].

The observation of a  $\text{Cu}_2\text{O}$  phase was similar to that observed in a  $\text{CaCu}_3\text{Ti}_{3.8}\text{Sc}_{0.2}\text{O}_{12}$  ceramic reported by Chung and coworkers [23]. Kwon and Cann [25] observed a second phase of  $\text{Cu}_2\text{O}$  in pure CCTO ceramics that were sintered in air

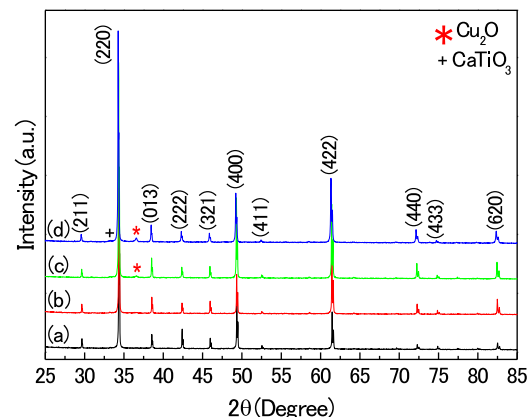


Fig. 1. XRD patterns of (a) CCTO, (b) CCTSO-1, (c) CCTSO-2, and (d) CCTSO-3 ceramic samples.

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