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(Al^{3+}, Nb^{5+}) co–doped $CaCu_3Ti_4O_{12}$: An extended approach for acceptor–donor heteroatomic substitutions to achieve high–performance giant–dielectric permittivity

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ABSTRACT

Substitution of (Al^{3+}, Nb^{5+}) co–dopants into TiO_6 octahedral sites of $CaCu_3Ti_4O_{12}$ ceramics, which were prepared by a solid state reaction method and sintered at 1090 °C for 18 h, can cause a great reduction in a low–frequency loss tangent ($\tan\delta \approx 0.045$–0.058) compared to those of Al^{3+} or Nb^{5+} single–doped $CaCu_3Ti_4O_{12}$. Notably, very high dielectric permittivities of $2.9 - 4.1 \times 10^4$ with good dielectric–temperature stability are achieved. The room–temperature grain boundary resistance ($R_{gb} \approx 0.37$–1.17×10^9 Ω.cm) and related conduction activation energy ($E_{gb} \approx 0.781$–0.817 eV), as well as the non–Ohmic properties of the co–doped ceramics are greatly enhanced compared to single–doped ceramics ($R_{gb} \approx 10^4$–10^6 Ω cm and $E_{gb} \approx 0.353$–0.619 eV). The results show the importance of grain boundary properties for controlling the nonlinear–electrical and giant–-dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics, supporting the internal barrier layer capacitor model of Schottky barriers at grain boundaries.

1. Introduction

Since the giant dielectric behavior of the most studied $CaCu_3Ti_4O_{12}$ (CCTO) ceramics was reported by Subramanian et al. [1], many giant–dielectric oxides have been extensively investigated. Giant–dielectric oxides that can exhibit unusually high dielectric permittivities (ε') of $\approx 10^3$–10^6 without detectable ferroelectric phase transitions found in CCTO and its isostructural–type perovskites [1–17], Zr–doped $SrTiO_3$ [18], $La_{2-x}Sr_xNiO_4$ [19], SnO_2–Zn_2SnO_4 [20], PZN–PZT/Ag [21] and $\mathbf{A}Fe_{1/2}\mathbf{B}_{1/2}O_3$ (**A** = Ba, Sr, Ca; **B** = Nb, Ta, Sb) [22], among others. In addition to their potential applications in electronic and high energy–dense storage devices, the origins of giant–dielectric behavior have also been intensively studied in detail. Many elegant models were proposed to describe the giant–dielectric properties of these oxides such as the internal barrier layer capacitor (IBLC) [23], surface barrier layer capacitor (SBLC) [24], and small polaron hopping models [19] as well as the non–Ohmic sample–electrode contact model [25]. Actually, the origin(s) of the giant–dielectric responses of these materials is still open to scientific debate. Based on the applications point of view, unacceptably high values of the dielectric loss tangent (tanδ) of these giant–dielectric oxides is considered the most serious problem. A large high temperature value of the temperature coefficient, *i.e.*, variation of ε' or capacitance (at 1 kHz) at any temperature compared to room temperature (RT), is one of the most difficult parameters to improve. Generally, if a parameter can be successfully improved, other dielectric parameters are simultaneously was worsened.

Recently, a newly discovered (In^{3+}, Nb^{5+}) co–doped rutile TiO_2 ceramic can exhibit a low tanδ (≈ 0.02) and very high ε' ($\approx 6 \times 10^4$) with good frequency and temperature stability [26]. Simultaneously, a new elegant model, *i.e.*, the electron-pinned defect–dipole (EPDD) model, was proposed to explain the underlying mechanisms of the high dielectric performance of INTO ceramics. In this EPDD model, free electrons in the TiO_2 structure are produced by doping with Nb^{5+}. Under an applied electric field, such localized electrons were freely polarized in triangular shaped $In_2^{3+}V_O^{\bullet\bullet}Ti^{3+}$defect complexes of the In^{3+} defect environments. However, it was further suggested that the giant–dielectric behavior in INTO ceramics originated from the IBLC and/or SBLC effects [27,28]. Although a controversy about the origin of the giant–dielectric response of INTO currently exists, the acceptor–donor co–doping concept can successfully be used to achieve high–performance giant–dielectric properties in other co–doped TiO_2 systems such as (Al^{3+}, Nb^{5+}) [29], (Mg^{2+}, Nb^{5+}) [30] and (Ga^{3+}, Ta^{5+}) [28], among others. Interestingly, this strategy for obtaining high ε' values while retaining a very low tanδ can be applied to SnO_2

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ceramics by co–doping them with (Al^{3+}, Nb^{5+}) [31]. Enhanced ε′ values of $\approx 10^3$ with low tanδ values ≈ 0.03 at 1 kHz and RT were achieved in an $Al_{0.03}Nb_{0.05}Sn_{0.92}O_2$ ceramic. However, to achieve a highly dense microstructure with a very high ε′ value in these co–doped TiO_2 and SnO_2 ceramics, high sintering temperatures of 1400–1500 °C were employed [26,29,31].

In the current work, we have successfully used the co–doping concept to significantly improve the dielectric properties of $CaCu_3Ti_4O_{12}$ prepared using a mixed oxide method and sintering at a relatively low temperature of 1090 °C. Through optimization of dopant concentration and sintering conditions, high–performance giant–dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics were obtained by co–doping for substitution (Al^{3+}, Nb^{5+}) into TiO_6 octahedral sites. The possible origin of the giant-dielectric properties is systematically investigated and discussed in detail.

2. Experimental details

$CaCu_3Ti_{4\text{-}x}(Nb_{1/2}Al_{1/2})_xO_{12}$ ceramics, where $x = 0.025$–0.2, as well as single-doped $CaCu_3Ti_{3.975}Nb_{0.025}O_{12}$ (Nb025) and $CaCu_3Ti_{3.975}Al_{0.025}O_{12}$ (Al025) ceramics were prepared via a solid state reaction method. The starting raw materials consisted of $CaCO_3$ (99.0%), CuO (99.9%), TiO_2 (99.99%), Al_2O_3 (99.99%) and Nb_2O_5 (99.99%). First, a stoichiometric mixture of the starting materials corresponding to each doping composition was mixed by wet–ball milling in ethanol for 24 h. Second, the mixed raw materials were dried at 80 °C for 24 h to remove ethanol from the media. Third, the resulting dried precursors were ground and calcined at 850 °C for 12 h. Then, the resulting calcined powders were ground and pressed by uniaxial compression at ≈180 MPa into pellet shaped disks, 9.5 mm in diameter and ≈1.2 mm in thickness. These pellets were sintered at 1050–1090 °C for 3–36 h using a heating rate 2 °C/min followed by natural cooling in a furnace to room temperature (RT).

The phase composition and crystal structure of these ceramics were characterized using X-ray Diffractometry (PANalytical, EMPYREAN). The diffraction spectra were collected over the 2θ range of 25°–65v with s step size of 0.02°/min. The Rietveld refinement was carried out using X'Pert HighScore Plus software and compared with the crystallographic structure of CCTO. Surface morphologies were characterized using scanning electron microscopy (SEM; LEO 1450VP). The distribution of all elements used in the sintered ceramics was examined using field–emission scanning electron microscopy (FE–SEM) with energy–dispersive X-ray analysis (EDX) (HITACHI SU8030, Japan). X–ray Absorption Near Edge Structure (XANES) and X-ray photoelectron spectroscopy (XPS) spectra were collected at the SUT-NANOTEC–SLRI XAS and beamline (BL5.2) (electron energy of 1.2 GeV; bending magnet; beam current 80–150 mA; 1.1–1.7×10^{11} photon.s^{-1}) and BL5.1 XPS machine (PHI5000 VersaProbe II, ULVAC–PHI) at the SUT-NANOTEC–SLRI at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand. Details of this characterization technique and analysis are given elsewhere [8].

To measure dielectric and electrical properties, both surface sides of the sintered samples were carefully polished to obtain smooth and clean surfaces. After that, all the samples were dried overnight at 100 °C. Both top and bottom sample surfaces were coated by Au sputtering using a Polaron SC500 sputter coating unit with an electric current ~25 mA for 4 min. The dielectric properties of the sintered ceramics were measured using a KEYSIGHT E4990A unit with an oscillation voltage of 500 mV. These measurements were done in range of 40–10^6 Hz and −60 to 210 °C. Nonlinear current density–electric field (J–E) characteristics were measured at room temperature (RT) using a high voltage measurement unit (Keithley 247). The rate of increase in source voltage was 1.33 V/s. The E_b value was defined as the electric field breakdown at which $J = 1\ \text{mA/cm}^2$. The nonlinear coefficient (α) was calculated in the range of 1–10 mA/cm^2.

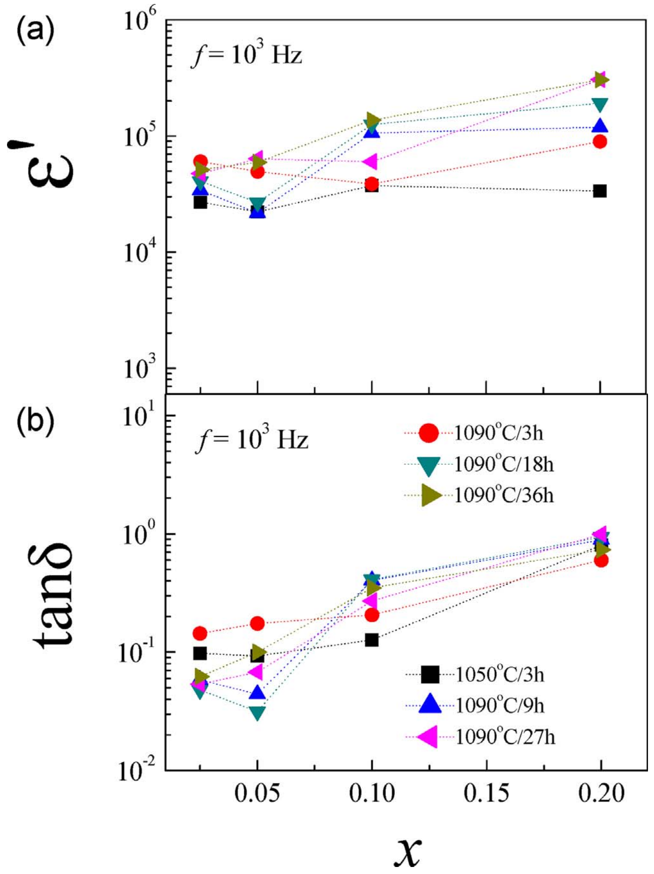

Fig 1. (a − b) ε′ and tanδ values at 10^3 Hz for $CaCu_3Ti_{4\text{-}x}(Nb_{1/2}Al_{1/2})_xO_{12}$ ($x = 0.025 - 0.20$) sintered under various conditions.

3. Results and discussion

Typical ε′ and tanδ values at 10^3 Hz and RT for the co–doped $CaCu_3Ti_{4\text{-}x}(Nb_{1/2}Al_{1/2})_xO_{12}$ ($x = 0.025$–0.2) sintered under different conditions are shown in Fig. 1. Both ε′ and tanδ values remarkably changed, irrespective of the sintering conditions or co–dopant concentration. All of co–doped samples exhibited very large ε′ values ($> 10^4$). This is similar to that observed in a pure CCTO ceramic, since very high ε′ values can easily be produced, but it is usually accompanied by quite large tanδ values, especially in a low frequency range ($\leq 10^3$ Hz) [1,8,10,23,25]. Therefore, the composition and sintering optimization should first focus on the reduction of tanδ. Substitution of CCTO with high concentrations of co–dopants ($x \geq 0.1$) likely gives rise to very high tanδ > 0.1. Low tanδ < 0.1 values were obtained in the co–doped ceramics with $x \leq 0.05$. These interesting dielectric properties can be comparable to those reported in literature [32–35]. The ceramic compositions with $x \leq 0.05$ can be further optimized by sintering at 1090 °C for 18 h. Interestingly, low tanδ values can also be achieved even at frequencies as low as 40 Hz (as represented in Fig. 4). This is very hard to accomplish in CCTO–based ceramics. Thus, the co–doped $CaCu_3Ti_{4\text{-}x}(Nb_{1/2}Al_{1/2})_xO_{12}$ ceramics with $x = 0.025$ and 0.05 sintered under this condition (referred to as the NA025 and NA05 ceramics, respectively) were selected to further investigate the underlying mechanisms of the origin of the significantly improved dielectric response.

The diffraction peaks of all single–doped (Nb025 and Al025) and co–doped (NA025 and NA05) ceramics were consistent with standard peaks of CCTO (JCPDS 75–2188). A secondary Cu_2O phase was detected in the Al025 ceramic, as shown in Fig. S1(a) (*Supplementary Information*). No impurities (i.e., CuO, Cu_2O, TiO_2, $CaTiO_3$ and related–oxide Nb/Al phases) were detected in other sintered ceramics.