Nonlinear electrical properties and giant dielectric response in $Na_{1/3}Ca_{1/3}Y_{1/3}Cu_3Ti_4O_{12}$ ceramic

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ABSTRACT

A new isostructural $CaCu_3Ti_4O_{12}$–type perovskite, $Na_{1/3}Ca_{1/3}Y_{1/3}Cu_3Ti_4O_{12}$, was successfully synthesized using a solid state reaction method. In this material, Ca–sites in the $CaCu_3Ti_4O_{12}$ structure were occupied by Na^+, Ca^{2+}, and Y^{3+} ions, each at a level of $\sim$33.3 at.%. The dielectric and non –Ohmic properties were investigated. The mean grain sizes of the $Na_{1/3}Ca_{1/3}Y_{1/3}Cu_3Ti_4O_{12}$ ceramics sintered at 1100–1110 °C for 10–15 h were of about $\approx$15 μm. All of the sintered ceramics exhibited high dielectric permittivities (ε') and low loss tangents ($\tan\delta$). By optimizing sintering conditions, a high $\varepsilon' \approx 1.2 \times 10^4$ and low $\tan\delta \approx 0.04$ were achieved. $Na_{1/3}Ca_{1/3}Y_{1/3}Cu_3Ti_4O_{12}$ ceramics can exhibit nonlinear current-voltage behavior. The existence of Cu^+, Cu^{3+}, and Ti^{3+} ions was confirmed using an X-ray Absorption Near Edge Structure (XANES) and X–ray photoelectron spectroscopic analyses. The n–type semiconductivity inside the grains was primarily caused by the presence of Ti^{3+} ions, while the existence of Cu^+ and Cu^{3+} may also have an effect on conduction inside the grains. Using impedance and admittance spectroscopy analyses under different conditions (i.e., varying frequency, temperature and DC bias), the giant dielectric response and nonlinear electrical properties could be well explained based on the internal barrier layer capacitor model.

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1. Introduction

The dielectric response of $CaCu_3Ti_4O_{12}$ was first reported by Subramanian et al. [1]. $CaCu_3Ti_4O_{12}$ has attracted a great deal of interest owing to its exceptionally giant dielectric constant (ε') values, on the order to 10^3–10^5, depending on sintering duration and temperature, electrode material, cooling rate, doping ions, and preparation method [2–16]. A high ε' value was observed over a wide temperature range of 100–400 K. Usually, the loss tangent ($\tan\delta$) of the $CaCu_3Ti_4O_{12}$ ceramics, over 0.05 at 1 kHz, was still too high for practical capacitor applications [17]. In addition to $CaCu_3Ti_4O_{12}$, isostructural $CaCu_3Ti_4O_{12}$–type perovskite materials (i.e., the $ACu_3Ti_4O_{12}$ family, where A = $La_{2/3}$, $Bi_{2/3}$, $Y_{2/3}$, $Na_{1/2}La_{1/2}$, $Na_{1/2}Bi_{1/2}$, $Na_{1/2}Sm_{1/2}$, $Na_{1/2}Y_{1/2}$, and $Na_{1/3}Ca_{1/3}Bi_{1/3}$) [18–27] as well as $NaCu_3Ti_3BO_{12}$ (B = Nb^{5+}, Ta^{5+}, and Sb^{5+}) [28–30] have gained considerable attention because of their giant dielectric properties. Notably, $\tan\delta$ of these $CaCu_3Ti_4O_{12}$–related compounds are lower than that of $CaCu_3Ti_4O_{12}$ ceramics [19–23]. These interesting properties are important for practical applications in capacitors and memory devices.

Nowadays, the origin of giant ε' of $CaCu_3Ti_4O_{12}$ and related materials is still debated. The extrinsic origin of the internal barrier layer capacitance (IBLC) model is widely accepted as an explanation of the giant ε' of these materials [10,15,20,30,31]. The electrically heterogeneous microstructure of $CaCu_3Ti_4O_{12}$ polycrystalline ceramics consists of semiconducting grains and insulating grain boundaries (GBs). Alternatively, their intrinsic origin cannot be ignored [32,33]. In addition to a giant ε' response, $CaCu_3Ti_4O_{12}$ and related $ACu_3Ti_4O_{12}$ ceramics demonstrate a nonlinear relationship between current density (J) and electric field strength (E) [8,19,20,34]. This behavior may be important for practical applications in varistor devices if the nonlinear coefficient and electric breakdown strength can be suitably tuned.

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It is very impressive that many isostructural $CaCu_3Ti_4O_{12}$–type perovskite oxides partially containing Na^+ in A–sites exhibit good dielectric properties. Large ε' values of $\approx 10^4$ with low $\tan\delta$ values ≈ 0.02–0.031 at 10 kHz were achieved in $Na_{1/2}Bi_{1/2}Cu_3Ti_4O_{12}$ ceramics [21,35]. $Na_{1/2}Y_{1/2}Cu_3Ti_4O_{12}$ has been extensively investigated because it exhibits a giant $\varepsilon' \approx 10^4$ and low $\tan\delta < 0.1$ [36]. Good dielectric properties were also achieved in $Y_{2/3}Cu_3Ti_4O_{12}$ [23]. Most recently, the dielectric and nonlinear electrical properties of a new isostructural $CaCu_3Ti_4O_{12}$–type perovskite, $Na_{1/3}Ca_{1/3}Y_{1/3}Cu_3Ti_4O_{12}$, were investigated [19]. Its Ca-sites were occupied by Na^+, Ca^{2+}, and Y^{3+} ions, each at a level of $\sim$33.3 at.%. This ceramic can exhibit a giant $\varepsilon' \approx 2.5 \times 10^4$ and low $\tan\delta \approx 0.038$ at 1 kHz. Furthermore, ε' was slightly dependent on temperature over a wide range. According to interesting dielectric properties of $Na_{1/2}Y_{1/2}Cu_3Ti_4O_{12}$, good giant dielectric and non –Ohmic properties of a new isostructural – $CaCu_3Ti_4O_{12}$ oxide may be achieved, with mixed valence states of Na^+, Ca^{2+}, and Y^{3+} in the A–sites.

In this work, we synthesized a perovskite–like structure as $(Na_{1/3}Ca_{1/3}Y_{1/3})Cu_3Ti_4O_{12}$ ceramics using a conventional solid–state reaction method under different sintering conditions. The giant dielectric properties were investigated as functions of frequency, temperature and DC bias. The nonlinear current density–electric field properties were also investigated. Interestingly, the giant ε' and low $\tan\delta$ values at 1 kHz were found to be 1.2×10^4 and 0.04, respectively. The origins of the giant dielectric response and nonlinear electrical properties are discussed in detail.

2. Experimental details

$Na_{1/3}Ca_{1/3}Y_{1/3}Cu_3Ti_4O_{12}$ (NCYCTO) was prepared using a conventional solid–state reaction method. Na_2CO_3 (99.9% purity), $CaCO_3$ (99.9% purity), Y_2O_3 (99.99% purity), CuO (99.9% purity) and TiO_2 (99.9% purity) were used as the starting raw materials. First, a stoichiometric mixture of the starting materials was ball–milled in ethanol for 24 h using ZrO_2 balls. Second, the mixed slurry was dried and calcined at 1000 °C for 20 h. Then, the resulting calcined powder was carefully ground and pressed into pellets of 9.5 mm in diameter and $\sim$1–2 mm in thickness by uniaxial compression. Finally the pellets were sintered at different temperatures. A dense microstructure was obtained by sintered at 1100 °C. It was found that the NCYCTO ceramics started to decompose when they were sintered at temperatures $\geq$1120 °C, as was observed for $Na_{1/2}Sm_{1/2}Cu_3Ti_4O_{12}$ [27]. Thus, the sintering conditions used were 1100 °C for 10, 15 h and 1110 °C for 10 h. The sintered ceramics produced under these conditions are referred to as the NCY1, NCY2 and NCY3 samples, respectively.

Phase composition and crystal structure of the sintered ceramics were studied using X-ray diffraction (XRD; PANalytical EMPYREAN). Scanning electron microscopy (SEM; SEC SNE4500M) was used to reveal the polished–surface morphology of the sintered NCYCTO ceramics. Valence states of Ti were characterized using an X–ray absorption near edge structure (XANES) technique. XANES spectra were collected at the SUT–NANOTEC–SLRI XAS beamline (BL5.2) at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand. Details of this characterization technique and analysis are given elsewhere [37]. The normalized XANES data were processed and analyzed after background subtraction in the pre–edge and post–edge regions using ATHENA software included in an IFEFFIT package [38]. Characterization of oxidation states of Cu and Ti was done using X–ray photoelectron spectroscopy (XPS; PHI5000 VersaProbe II, ULVAC–PHI, Japan) at the SUT–NANOTEC–SLRI Joint Research Facility, Synchrotron Light Research Institute (SLRI), Thailand. The experimental curves were fitted with PHI MultiPak XPS software using a combination of Gaussian-Lorentzian lines.

For dielectric and electrical measurements, surfaces of the sintered ceramics were polished and sputtered with Au at a current of 25 mA for 4 min. A KEYSIGHT E4990A and an Agilent 4294A Precision Impedance Analyzer were used to measure the dielectric properties of sintered ceramics. The measurements were done over the frequency range of 10^2–10^7 Hz using an oscillation voltage of 0.5 V. Dielectric properties were measured in the temperature range from −60 to 200 °C with step increases of 10 °C. Temperatures were held constant with an accuracy of ±0.1 °C for each step. The nonlinear J–E properties were measured at room temperature (RT) using a high voltage measurement unit (Keithley Model 247). Breakdown electric field strength (E_b) was obtained at $J = 1$ mA cm^{-2}. The nonlinear coefficient (α) was calculated in the range of 1–10 mA cm^{-2}.

3. Results and discussion

The XRD patterns of NCYCTO ceramics sintered under different conditions are shown in Fig. 1. All XRD patterns show a single phase with no diffraction peaks of an impurity phase. Additionally, the lattice parameters of the NCY1, NCY2 and NCY3 samples were calculated and found to be nearly the same in value, $\approx$7.386 Å. The lattice parameters of $CaCu_3Ti_4O_{12}$ and $Na_{1/2}Y_{1/2}Cu_3Ti_4O_{12}$ ceramics were about 7.391 Å (JCPDS 75–2188) [1] and $\approx$7.378–7.379 Å, respectively [1,26]. This means that the ionic radius of Ca^{2+} in A–sites of the $CaCu_3Ti_4O_{12}$ structure was larger than that of the average ionic radius of Na^+ and Y^{3+} in the $Na_{1/2}Y_{1/2}Cu_3Ti_4O_{12}$ structure, which randomly occupied A–sites. Reasonably, the ionic radius of NCYCTO ceramics is intermediate between the $CaCu_3Ti_4O_{12}$ and $Na_{1/2}Y_{1/2}Cu_3Ti_4O_{12}$ because Na^+ and Y^{3+} ions in $Na_{1/2}Y_{1/2}Cu_3Ti_4O_{12}$ structure were partially replaced by Ca^{2+}, leading to an enlarged lattice parameter of the NCYCTO structure.

Fig. 2 shows the polished–surface morphologies of NCYCTO ceramics sintered under various conditions. The average grain sizes of the NCY1, NCY2 and NCY3 samples were estimated to be $\sim$15.9 ± 5.9, $\sim$15.1 ± 6.8 and $\sim$14.9 ± 4.9 μm, respectively. The mean grain size was slightly changed by increasing the sintering temperature from 1100 to 1110 °C. Sintering at 1100 °C for a longer time had also slight impact on the microstructure. A small number of pores were observed in all the samples. Commonly, the densification and grain growth processes in polycrystalline ceramics are primarily caused by the diffusion of atoms, ions and charged species during sintering process. For $CaCu_3Ti_4O_{12}$ ceramics, diffusion can be promoted by the presence of a liquid phase along the grain boundaries. In the current study, the large grain sizes of NCYCTO ceramics might therefore be caused by a CuO–related liquid phase, since the eutectic temperature of CuO–TiO_2 is $\approx$919 °C [16,39]. Note that the mean grain size slightly decreased with increasing temperature from 1100 to 1110 °C. This
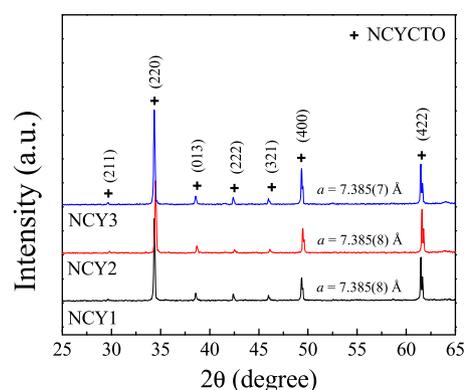
Fig. 1. XRD patterns of NCYCTO ceramics sintered under different conditions.