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Effect of Cu-stoichiometry on the dielectric and electric properties in $CaCu_3Ti_4O_{12}$ ceramics

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Abstract

$CaCu_{3+y}Ti_4O_{12}$ ($y = 0$, ±0.025, ±0.05, ±0.1 and −0.15) ceramics are prepared by the conventional solid-state reaction technique under sintering condition of 1050 °C, 10 h. X-ray diffraction shows that they all have the good crystalline structure. Cu-deficient ceramics exhibit the microstructures of uniform grain size distribution, whereas both Cu-stoichiometric and Cu-rich ceramics display microstructures of bimodal grain size distribution. The largeness of low-frequency dielectric permittivity at room temperature is found to be very sensitive to the Cu-stoichiometry. Upon raising the measuring temperature, all of the ceramics present commonly three semicircles in the complex impedance plane. It indicates that there exist three distinct contributions, which are ascribed to arising from domains, grain boundaries and domain boundaries. In addition, the influence of CuO segregation on the dielectric and electrical properties is also discussed.

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Keywords: A. CCTO; B. Microstructure; C. Dielectric properties; E. Complex impedance

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1. Introduction

Recently, there has been considerable interest in the cubic perovskite-related $CaCu_3Ti_4O_{12}$ (CCTO), [1–5] because of its unusual dielectric property. It exhibits an enormously large low-frequency dielectric permittivity (ε' is of the order of 10^4) in both forms of single crystals and ceramics at room temperature, and keeps almost constant at low frequencies over the wide temperature region from 100 to 380 K [1–3]. With decreasing temperature or increasing frequency, ε' drops rapidly to a value of about 100 and shows the Debye-type relaxation behaviour, and the characteristic relaxation frequency follows approximately the Arrhenius-law [2,3]. Nevertheless, neither a phase transition nor a detectable long-range crystal structure change has been observed in high-resolution X-ray and neutron powder diffractions and Raman-phonon measurement [1,2].

The controversial problem for this material has been whether the large dielectric response is intrinsic or extrinsic [1–7]. Sinclair et al. proposed that the giant-dielectric phenomenon is attributed to a grain boundary (internal) barrier layer capacitance (IBLC) [4,5]. To date, the IBLC explanation seems to be plausible [8–13]. On the other hand, although oxygen vacancies, CuO-segregation and aliovalences of Ti and Cu ions are considered to play important roles in interpreting the semiconducting and insulating phenomenon of grains and grain boundaries, [4,8,14–20] detailed mechanisms still remain unsettled.

In our previous work, we studied the influence of sintering conditions on the microstructure and dielectric and electrical properties of CCTO ceramics at high temperatures [21, 22]. It has been found that high-temperature dielectric and electrical properties are much more complicated than those at room temperature and low temperatures. In this letter, we concentrate investigation on the Cu-stoichiometry effect on the microstructure, polycrystallinity, and dielectric and electric properties in $CaCu_{3+y}Ti_4O_{12}$ ceramics.

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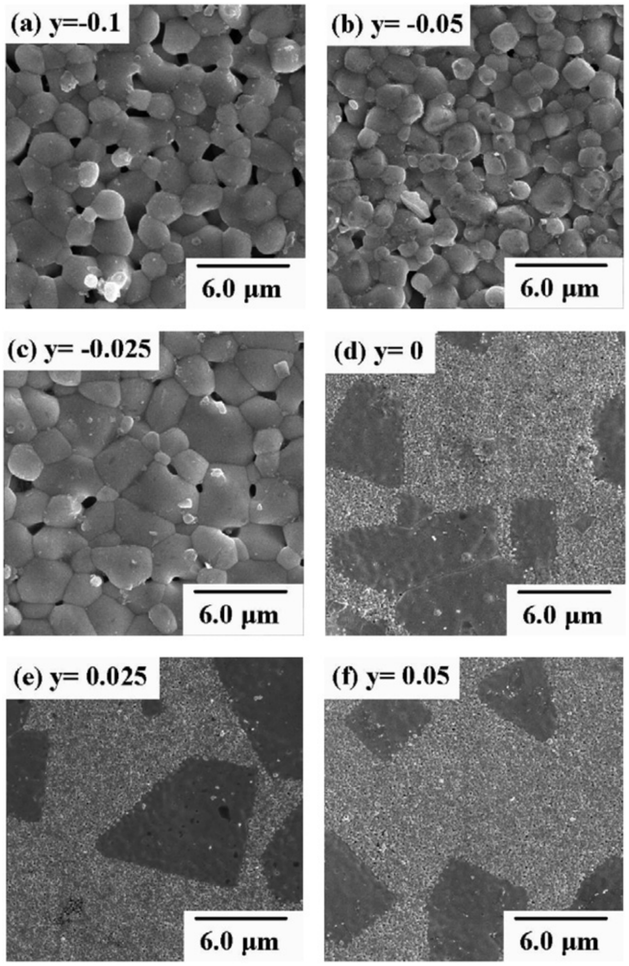

Fig. 1. SEM images of $CaCu_{3+y}Ti_4O_{12}$ ceramics with different Cu-contents.

2. Experimental

Ceramic specimens are prepared by the conventional solid-state reaction method using starting materials of $CaCO_3$ (99.0%), CuO (99.0%) and TiO_2 (99.8%). The raw materials are weighed according to the formulas $CaCu_{3+y}Ti_4O_{12}$ ($y = 0$, ± 0.025, ± 0.05, ± 0.1 and -0.15). They are ball-milled, pressed into a block, and calcined at 650 °C for 8 h. The calcined mixture is again ball-milled and pressed into pellet disks (15 mm in diameter, 1.5 mm in thickness), and these disks are sintered at 1050 °C for 10 h. For electrical characterization, silver paint is coated on both surfaces of the sintered disks and fired at 570 °C for 20 min.

Crystalline structures are examined by X-ray diffraction (XRD) with Cu Kα radiation on an MSAL–XD2 diffractometer at room temperature. Surface microstructures are investigated on a scanning electronic microscope (SEM). Dielectric dispersion and complex impedance are measured using an Agilent 4294A impedance analyser within the frequency range of 40 Hz–110 MHz at room temperature and within the frequency range of 40 Hz–4.5 MHz at higher temperatures up to 280 °C.

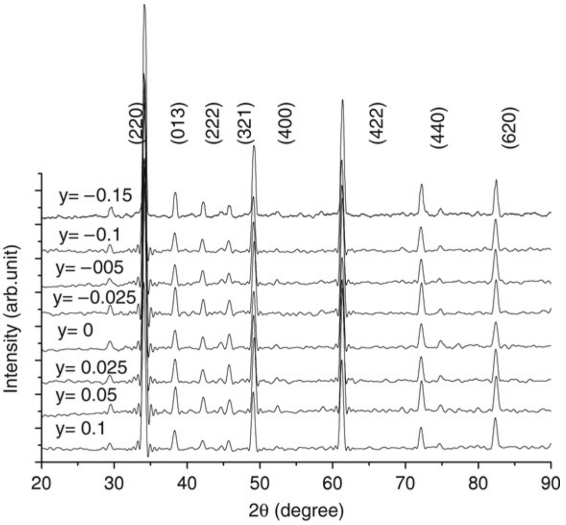

Fig. 2. XRD profiles for the various $CaCu_{3+y}Ti_4O_{12}$ ceramics.

3. Results and discussion

Fig. 1 reveals a series of SEM images of surface microstructures for the various compositional ceramics. Apparently, the morphologies change significantly with the Cu-stoichiometry. As shown in Fig. 1(a)–(c), ceramics with $y < 0$ show the microstructures of uniform grain size distribution. When increasing the Cu-content, there is a subtle increase in the grain size and an obvious decrease in the porosity. However, ceramics with Cu-content either in or over stoichiometry exhibit the distinctly different type of microstructures, shown in Fig. 1(d)–(f). Discontinuous grain growth and bimodal grain size distribution, which were obtained in CCTO ceramics sintered at temperatures around 1050 °C for moderate sintering durations, [14,20,22,23] are observed. The present result is generally consistent with the reported microstructures for the ceramics with $y = -0.10$ and 0.10 recently by Fang et al. [18].

Fig. 2 presents the XRD profiles for the various compositional ceramics. As can be seen, these profiles are quite similar to each other. It is found that all of diffraction peaks could be indexed by a body-centred cubic perovskite-related structure of space group $Im3$ according to ICSD #032002, which indicates that all of the ceramics prepared in the present study have the good polycrystalline structure despite of the different Cu-content and microstructures. Similar to Ref. [18], no secondary phase could be directly discerned from the XRD profiles, which might be because of the detecting accuracy limitation of the XRD apparatus used. However, it is worth noting that the existence of CuO secondary phase is indeed confirmed by further careful analyses of XRD profiles with the Rietveld method and energy-dispersive X-ray spectroscopy [11,18,19].

Fig. 3 demonstrates the dielectric dispersion for the $CaCu_{3+y}Ti_4O_{12}$ ceramics measured at room temperature. As can been seen, all of the ceramics display the similar spectra and their values of dielectric permittivity ε_r at low frequencies are larger than 2500. In particular, the one with