Effect of doping ions on the structural defect and the electrical behavior of $CaCu_3Ti_4O_{12}$ ceramics

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ABSTRACT

The microstructure, dielectric and electrical properties of $CaCu_3Ti_{4-x}R_xO_{12}$ (R = Y, Zr, Ta; $x = 0$ and 0.005) ceramics were investigated by XRD, Raman spectra, SEM and dielectric spectrum measurements. Positron annihilation measurements have been performed to investigate the influence of doping on the defects. The results show that all samples form a single crystalline phase. Y and Ta doping cause different defect types and increase the defect size and concentration, which influence the mobility of grain boundary and result in the different grain size. Y doping increases the dielectric constant and decreases the nonlinear property while Ta doping lead to an inverse result. Zr-doped sample has nearly the defect type, grain morphology and dielectric properties as pure $CaCu_3Ti_4O_{12}$. The effects of microstructure including the grain morphology and the vacancy defects on the mechanism of the dielectric and electric properties by doping are discussed.

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1. Introduction

Materials with high dielectric constant have great potential for the decrease in the dimensions of electronic devices. The cubic perovskite oxide $CaCu_3Ti_4O_{12}$ (CCTO) has attracted much attention owing to its high dielectric constant which is in the range of 10^3–10^5, depending on their fabrication process [1–3]. Moreover, a large number of reports have showed that dielectric constant of CCTO varies weakly with frequency and temperature between 100 K and 400 K, which makes it desirable for commerical applications. However, the high dielectric loss in CCTO is an important factor affecting the use in devices.

In order to understand the origin of giant dielectric response in CCTO, extensive work has been carried out and various model such as intrinsic and extrinsic mechanisms have been put forward. Among them, internal boundary layer capacitor (IBLC) model is the most widely accepted one for CCTO ceramic, which is the nature of the Maxwell-Wagner relaxation as well known [4]. According to the IBLC model, the dielectric response in CCTO ceramic originates from the insulating grain boundary (GB) and the semiconducting grains, thus the change on microstructure can make a considerable impact on dielectric behaviors. For example, the dielectric constant can be enhanced significantly when the grain size increases. In addition, the composition variation at GB also has a great effect on dielectric properties [5–8]. Therefore, it is very important to investigate the effect of interfacial modification to obtain lower dielectric loss with higher dielectric constant. Perovskite structure is flexible. Doping can modify the chemical compositions and change its property, which is the most important means changing the intrinsic semiconducting properties of CCTO ceramics [9,10]. Till now, a large number of doping studies have been performed to improve the dielectric properties of CCTO, such as La^{3+}, Cr^{3+}, Fe^{3+}or Nd^{5+} substitution at A or B sites in CCTO, which have a critical influence on dielectric response [11–17]. Recently, several papers describing Y, Zr and Ta doped CCTO samples have been published. But the results in these papers differ each other. Thongbai et al. [18] found that Ta doping causes decreasing dielectric while the dielectric constant of the samples increases with increasing tantalum concentrations reported by Rai et al. [19]. Jesurani et al. [20] doped 0.1 mol% Zr to improve the permittivity and dielectric loss while Zhang et al. [21] got $CaCu_3Ti_{3.96}Zr_{0.04}O_{12}$ ceramics with decreasing dielectric constant at low frequency ($f \leq 10^5$ Hz) and unchanged one at high frequency ($f \geq 10^7$ Hz). Luo et al. [22] show Yttrium addition reduced the dielectric loss remarkably while maintaining colossal permittivity. The results of Saji and Choe [23] indicate the dielectric constant and loss increased with Y substitution.

Vacancies are normally assumed to be the dominant point defects in perovskite oxide ABO_3 materials and often strongly

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influence the material properties [24]. Positron annihilation spectroscopy (PAS) techniques have been applied to identify defects in semiconductors and superconductor on the atomic scale. Based on its positive charge and annihilating with electrons, the positron annihilation method has ability to selectively detect vacancy-type defects. An energetic positron which has penetrated into a solid rapidly loses its energy and then lives for a few hundred picoseconds in thermal equilibrium with the environment. During its thermal motion the positron interacts with defects, which may lead to trapping into a localized state. Thus, the final positron annihilation with an electron can happen from various states. The positron lifetime is inversely proportional to the electron density encountered by the positron.

To our knowledge, PAS is not used in CCTO with different valence ion doping. Thus, the aim of this work is to study the effect of a small amount of Y^{3+}, Zr^{4+} and Ta^{5+} substitution Ti^{4+} sites on the microstructure and dielectric properties as well as the electrical response in CCTO ceramics. XRD, Raman spectra, SEM and PAS were employed to reveal characteristics of the phase structure, grain morphology, size and type of the defect of a small amount of Y^{3+}, Zr^{4+} and Ta^{5+} doped CCTO.

2. Experimental procedure

Samples of $CaCu_3Ti_{4-x}R_xO_{12}$ (R = Y, Zr, Ta; $x = 0$ and 0.005) were synthesized by solid state reaction method. The analytical grade $CaCO_3$, TiO_2, CuO, Y_2O_3, ZrO_2, and Ta_2O_5 (99.99% in purity) powders were used as raw materials. The powder mixtures were thoroughly ground for 4 h together according to the stoichiometric ratio using agate mortar and pestle and then calcined at 950 °C in air in a box furnace for 8 h. The calcined mixtures were reground for 2 h and then pressed into disk shaped pellets with a diameter of 10 mm and a thickness of 2 mm at a pressure of 15 MPa. Finally, the pellets were sintered at 1050 °C for 12 h in air and then cooled down with furnace to room temperature. The sintered pellets were polished and coated with silver paste on both sides for use as electrodes and cured at 500 °C for half an hour. Diffractograms of the sintered samples were recorded using X-ray powder diffraction (XRD) to identify the phase. Lattice parameters were calculated by the least-square method with Powder X program [25]. The fracture surface of the samples was observed by a scanning electron microscope (SEM) (JSM-7000F, JEOL) equipped with energy-dispersive X-ray spectroscopy (EDS) operated at 25 kV. Furthermore, the mean grain sizes for all sintered pellets were determined from the respective backscattered SEM images by averaging the size of 100 randomly selected CCTO grains on each sample. The Raman measurement was performed in the quasi-backscattering geometry using 50 mW of the 532 nm line of a semiconductor laser via a Renishaw in Via spectrometer with the resolution of 0.5 cm^{-1}. A positron annihilation lifetime spectrum was measured using an American ORTEC fast-slow coincidence lifetime spectrometer at room temperature. A 22Na positron source with intensity of about 13 μCi was sandwiched between two identical sample pellets for measurements. Every spectrum containing about 10^6 counts was modeled with a three-component fit using the LT9.0 software. The deviation of the fit is better than 1.1. The current–voltage (I–V or J–E) characteristics were measured by using a high voltage measuring unit (Radaint American). The nonlinear coefficient (α) was calculated from the following formula:

$$\alpha = \frac{\log(J_2/J_1)}{\log(E_2/E_1)} \tag{1}$$

Here E_1 and E_2 are, respectively, the electric fields corresponding to $J_1 = 1$ and $J_2 = 10$ mA cm^{-2}. The breakdown electric field (threshold electric field) (E_b) was achieved at $J = 1$ mA cm^{-2}. The dielectric properties and impedance spectrum of the varistors were determined using an Agilent 4294A precision impedance analyzer from 40 Hz to 110 MHz.

3. Results and discussion

Fig. 1 shows XRD patterns of $CaCu_3Ti_{4-x}R_xO_{12}$ (R = Y, Zr, Ta; $x = 0$ and 0.005) samples sintered at 1050 °C for 8 h. All samples exhibit a cubic perovskite CCTO phase according to JCPDS75-2188 without second phases of raw materials. The values of lattice parameters calculated by the least-square method with Powder X program are 7.3924(2), 7.4014(2), 7.3988(3) and 7.3973(2) for pure, Y-, Zr- and Ta-doped CCTO, respectively. In an octahedrally coordinated site, Ti^{4+}, Y^{3+}, Zr^{4+} and Ta^{5+} ions have the ion diameters about 0.61, 0.90, 0.72 and 0.64 Å, respectively. It is noted that the lattice parameter increases monotonically with increasing doping ion radius, revealing that Y^{3+}, Zr^{4+} and Ta^{5+} ions have entered the lattice of CCTO, leading to large cell volume.

The room temperature Raman spectra of all ceramic samples are shown in Fig. 2. Before discussing our results we briefly summarize some characteristics of CCTO. Standard group theory analysis predicts that Raman active modes of CCTO are distributed among the irreducible representation as $2A_g + 2E_g + 4F_g$ [17]. But
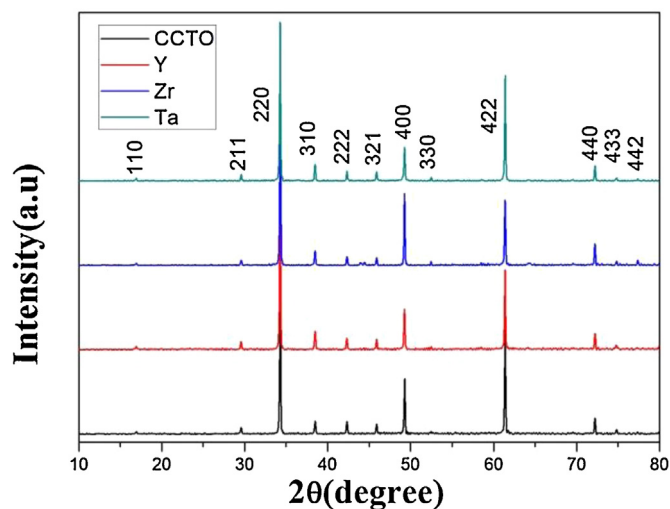

Fig. 1. XRD patterns for the $CaCu_3Ti_{4-x}R_xO_{12}$ (R = Y, Zr, Ta; $x = 0$, 0.005) ceramics.
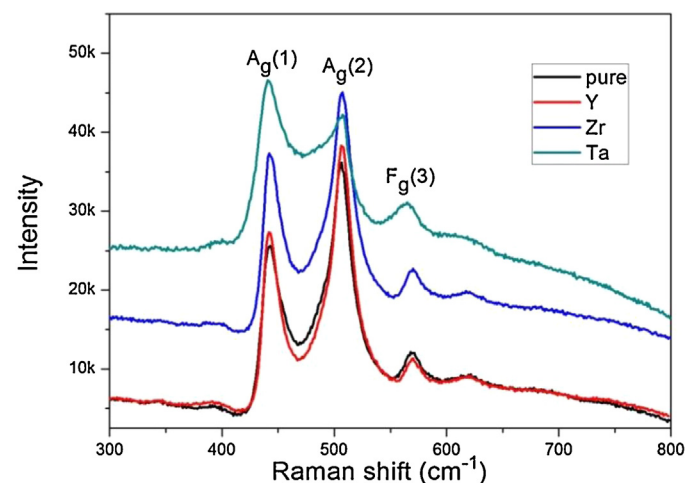

Fig. 2. Raman spectra of $CaCu_3Ti_{4-x}R_xO_{12}$ (R = Y, Zr, Ta; $x = 0$, 0.005) ceramics.