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Review

An effective method to decrease dielectric loss of $CaCu_3Ti_4O_{12}$ ceramics

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ABSTRACT

Ceramics with the chemical compositions of $CaCu_{3-x}Sr_xTi_4O_{12}$ ($0 \leq x \leq 0.4$) (CCSTO) were prepared by the conventional solid-state reaction method and the dielectric properties were investigated. It is found that the dielectric loss decreases with increasing x and reaches 0.03 for $x = 0.4$, meanwhile, the permittivity remains above 3000. Scanning electron microscopy and Energy Dispersive X-ray results indicate the solutions of $SrTiO_3$ and $CaTiO_3$ emerge at grain boundaries. Correspondingly, the impedance spectroscopy analysis confirms that the decrease of dielectric loss is mainly attributed to the increase in the resistivity of the grain boundary. The permittivity and dielectric loss of CCSTO ceramics exhibit very little dc bias dependence ($\Delta\varepsilon'/\varepsilon' < 3\%$ up to 0.8 kV/cm) at 10 kHz. These results indicate that CCSTO ceramics have a promising applied prospect with high-permittivity, sufficiently low dielectric loss, and better dc bias voltage stability.

Contents

1. Introduction

Materials with high dielectric constants are widely used in microelectronic devices, such as capacitors, resonators and filters, as demanded by miniaturization of microelectronic devices. High dielectric constants allow smaller capacitive components, thus offering the opportunity to decrease the size of electronic devices. Recently, the perovskite-related body-centered-cubic compound $CaCu_3Ti_4O_{12}$ (CCTO) has attracted much interest because of its extraordinarily high permittivity (ε') of $\sim 10^5$ at room temperature and very small temperature dependence in a broad temperature range from 100 K to near 400 K [1,2]. Furthermore, the dielectric constant is almost frequency independent below 10^6 Hz, which is desirable for many micro-electronic applications [3]. However, the dielectric loss ($\tan\delta$) of CCTO is relatively too high to apply commercially. For CCTO ceramics, the typical value of $\tan\delta$ is about 0.1 at 1 kHz at room temperature.

It is necessary to know the origin of dielectric loss in CCTO ceramics to find an effective method to lower it. The Maxwell–Wagner relaxation [4] is widely accepted as the primary mechanism for the giant dielectric constant in CCTO ceramics. Accompanied by a strong Maxwell–Wagner relaxation, the dielectric loss mainly originates from the conductivity of insulating barriers, which is called leakage loss. On the other hand, the alternate current within the conducting region also produces dissipation as the Joule heat [4]. Up to present, substituting, doping and two-phase composites are the mainly methods to decrease $\tan\delta$, e.g., $Ca_{1-x}La_xCu_3Ti_4O_{12}$ [5], $CaCu_{3-x}La_{2x/3}Ti_4O_{12}$ [6], Cr_2O_3-doped CCTO [7], ZrO_2-doped CCTO [8], CCTO/$CaTiO_3$ composite [9], CCTO/SiO_2/CCTO multilayered [10] and CCTO–$SrTiO_3$ composite [11]. All these studies mentioned herein aimed to decrease dielectric loss by controlling the chemistry and structure of interfacial regions at grain boundaries. Recently, Yeoh et al. [12] in using a

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wet chemical method for synthesizing $CaCu_3Ti_4O_{12}$ found the content of Cu would effect the dielectric properties. Moreover, the second phase $CaTiO_3$ are found in nonstoichiometric $CaCu_{3x}Ti_4O_{12}$ ceramics [13], which has been proved to decrease dielectric loss of CCTO. Thus, Sr doping in Cu-deficiency $CaCu_{3-x}Sr_xTi_4O_{12}$ ceramics was carried out in this work. It has been found that this design can decrease dielectric loss and improve voltage property of CCTO ceramics by decreasing grains sizes and increasing the impedance of grain boundary. So, we can conclude that Sr-doped CCTO ceramics have outstanding electrical properties for practical applications.

2. Experimental procedures

Ceramic samples of $CaCu_{3-x}Sr_xTi_4O_{12}$ (CCSTO, $x = 0$, 0.05, 0.1, 0.2 and 0.4) were prepared by using the conventional ceramic solid-state reaction. Stoichiometric amounts of $CaCO_3$ (99.99%), CuO (99.9%), $SrCO_3$ (99.61%) and TiO_2 (99.99%) were mixed and milled in ethanol using a planetary mill with zirconia media for 10 h and prefired in air at 850 °C for 6 h. The prefired mixtures were ball milled and pressed into pellet disks with 15 mm in diameter. These disks were sintered at 1050 °C, 1080 °C, and 1100 °C for 12 h, respectively. The crystalline structure and microstructure of the sintered specimens were characterized by X-ray diffraction (D/max-2550/PC, Rigaku, Japan) and scanning electron microscopy (SEM, Quanta 200, Philips, Netherlands), respectively. The ceramic density measured by Archimedes method are over 95% of the theoretical density for all of the ceramics prepared in this study. Especially, the ceramics sintered at 1080 °C have the highest density above 97% of the theoretical values. The samples sintered at 1080 °C were painted with Ag-electrodes for dielectric properties, which were measured by Agilent 4294A impedance analyzer in the frequency range from 40 Hz to 110 MHz. The permittivity and dielectric loss versus dc bias voltage were measured utilizing a TH2816 LCR meter combined with Delta Design 9023 environmental test chamber in the voltage range from 0 V to 400 V.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns obtained for $CaCu_{3-x}Sr_xTi_4O_{12}$ (CCSTO) ceramics ($x = 0$, 0.05, 0.1, 0.2 and 0.4) after sintering at 1080 °C for 12 h. The diffraction peaks could be indexed to a cubic perovskite-related structure according to JCPDS-05-0566, except that additional small diffraction peaks around at $2\theta \sim 32.5^\circ$, 46.7°, 58.1° well coincide with (1 1 0), (2 0 0) and (2 1 1) peaks of $SrTiO_3$. From the insert of Fig. 1, the (2 2 0) peaks of CCSTO ceramics shift towards low angles as x increasing except the composition of $x = 0.4$, indicating that a little amount of Sr enter the lattice of CCTO and induce the lattice constant larger. As compared with Ca^{2+} ($r_{Ca^{2+}} = 1.34$ Å), Sr^{2+} ($r_{Sr^{2+}} = 1.44$ Å) is too large to substitute Cu^{2+} ($r_{Cu^{2+}} = 0.57$ Å), thus, the (2 2 0) peak shift is the result of substituting Ca^{2+} with Sr^{2+}, while both have the comparable ionic radius.

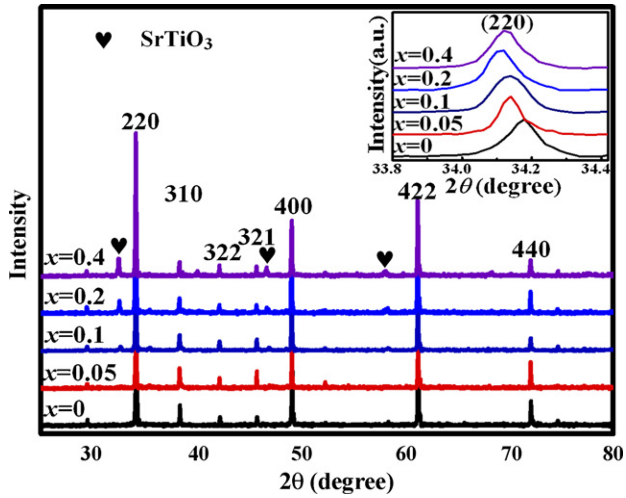

Fig. 1. XRD results of $CaCu_{3-x}Sr_xTi_4O_{12}$ ceramic samples. The top right inset is an expanded view of the XRD patterns around 34.1°, showing the shift of (2 2 0) peaks.

Fig. 2(a)–(e) present SEM images of surface microstructure for CCSTO ceramics characterized in Fig. 1. In order to validate the exist of the secondary phases, the SEM micrograph of fracture surface of CCSTO ($x = 0.4$) is shown in Fig. 2(f) followed with energy dispersive X-ray (EDX) analysis for the different regions as shown in Fig. 2(g) and (h). As observed, the microstructures of CCSTO ceramics change significantly with the increasing of Sr content. Obviously, CCTO ceramics show the microstructure distributed uniformly with the grain size of 100–200 μm and the clear grain boundaries. In contrast, the abnormally large grains gradually disappear by increasing the content of Sr. When $x = 0.4$, the evenly distributed grains of CCSTO ceramics have an average size smaller than 10 μm. The size distributions with x can be attributed to the secondary phase that is observed in cross micrograph of CCSTO ($x = 0.4$) (Fig. 2(f)). For clarity, the element proportion (Ca:Cu:Sr:Ti:O=1:0.27:1.20:2.19:8.95) at circular area indicates that the white particle in grain boundaries is mainly composed of the solutions of $CaTiO_3$ and $SrTiO_3$, exactly whose presence restrained the egregious growth of grain. Fig. 2(h) illuminates that the main body of ceramic is CCTO with less than stoichiometric content of Sr. Moreover, the deficiency of oxygen (Ca:O = 1:10) consists with previous investigations [14–17].

Fig. 3 demonstrates the frequency dependence of ε' and $\tan\delta$ for the CCSTO ceramics. All the samples show giant dielectric constant of $\varepsilon' \geq 3000$ in a broad frequency range, which decreases gradually with increasing x. Moreover, the CCSTO ceramics show the broader ε' plateaus than the CCTO ceramic. Fig. 3(b) shows the higher frequency peaks of $\tan\delta$ at around 30 MHz depress and shift to higher frequency. The result is beneficial for utilization of this material in a wider and higher frequency. The inset in Fig. 3(b) describes the frequency dependence of $\tan\delta$ in the frequency range of 500 Hz to 5 MHz. It reveals $\tan\delta$ decreases and the lower $\tan\delta$ expands to higher frequency with increasing x. Especially, for the sample of $x = 0.4$, the $\tan\delta$ is less than 0.05 in the frequency range of 20–200 kHz with the minimum of 0.03 at 53 kHz. Compared with the parent CCTO sample, the dielectric loss is reduced by 62%.

To understand the effect of the secondary phases at grain boundaries on decreasing the dielectric loss, we provide the Cole–Cole plot of the impedance at room temperature for CCSTO ceramic samples in Fig. 4. The inset of Fig. 4 shows Cole–Cole plot in the highest frequency range. The results show that all ceramics reveal three semicircular arcs, whose diameters increase with Sr doping. As we know, the DBLC [16] structure has an equivalent circuit consisting three parallel RC elements connected (R_g, C_g), (R_{gb}, C_{gb}) and (R_s, C_s). Concretely, (R_g, C_g) represents the impedance and capacitance of semiconducting grain measured at the highest frequency, while (R_{gb}, C_{gb}) and (R_s, C_s) correspond to the insulating grain boundary and surface oxidation layer measured at medium-frequency and low-frequency regions, respectively. We have fit the arcs with semicircles for the curves and the values of R_g and R_{gb} are listed in Table 1. Take CCSTO ($x = 0.05$) as an example shown in Fig. 4, the intersection point of semicircular arcs at the highest frequency is at 1.8 Ω. Similarly, fitting of semicircular arcs at medium-frequency is performed and the intersection point is at 1.1×10^4 Ω at Z' axis. So R_g and R_{gb} of CCSTO ($x = 0.05$) are 1.8 Ω and 1.1×10^4 Ω, respectively. Moreover, impedance R_s is too large and appears beyond the frequency range, so it is difficult to fit out complete

Table 1
The resistivity of grain and grain boundary of $CaCu_{3-x}Sr_xTi_4O_{12}$ ceramics

x	R_g Ω	R_{gb} ($\times 10^4$ Ω)
0.05	1.8	1.1
0.1	2.0	1.7
0.2	2.6	2.3
0.4	3.8	4.2