Effect of ZrO_2 Doping on the Microstructure and Dielectric Properties of $\text{Ca}_{0.97}\text{Y}_{0.03}\text{Cu}_3\text{Ti}_{4-x}\text{Zr}_x\text{O}_{12}$ Ceramics

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Abstract

Dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramics were studied by doping amount of Zr^{4+} donor on the basis of doping Y^{3+} donor. $\text{Ca}_{0.97}\text{Y}_{0.03}\text{Cu}_3\text{Ti}_{4-x}\text{Zr}_x\text{O}_{12}$ ($x=0, 0.005, 0.010, 0.015$, CYCTZO) ceramics were prepared by reaction sintering method, and the phase structure, microstructure and dielectric properties of the ceramics were studied. The single phase CCTO was detected in all ceramic samples. SEM images of samples showed a high density and uniform-sized microstructure, and the average grain sizes of the ceramics was reduced with increasing content of Zr^{4+} donor. Interestingly, the dielectric constant (ϵ_r) was increased significantly while the dielectric loss tangent ($\tan\delta$) was decreased with the suitable doping amount of Zr^{4+} . CYCTZO ceramics with $x=0.010$ exhibited a relatively high ϵ_r value of 1.02×10^5 at 1kHz. Meanwhile, the improved grain boundaries response and dielectric properties were closely related to the strengthened grain boundaries resistance (R_{gb}). The present results indicate that the ϵ_r was improved and the $\tan\delta$ was reduced by doping Zr^{4+} donors in $\text{Ca}_{0.97}\text{Y}_{0.03}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (CYCTO) ceramics and explained that the electrical properties were closely related to the electrical heterogeneity of ceramic grains and grain boundaries.

1 Introduction

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramics, due to its giant dielectric constant (ϵ_r) and simple preparation method, have been widely studied [1–5]. However, the practical application of CCTO ceramics is limited due to its high dielectric loss [4–14]. Many experiments focus on the reduction of dielectric loss tangent ($\tan\delta$) in CCTO ceramics from the following three methods. Firstly, the $\tan\delta$ of CCTO ceramics is reduced by decreasing the grain size. The $\tan\delta$ in the low frequency range is connected to grain boundaries resistance (R_{gb}) [6]. The decrease in grain size means that the number of series insulating grain boundaries increases, which leads to an increase in the resistance of the ceramic [3]. Sol-gel and hydrothermal methods are to synthesize ceramics with nanoscale grains [7–9]. There are also emerging synthetic methods used to synthesize ceramics with nanoscale grains, such as accelerated sintering using electric fields [10]. However, owing to the complex process of the above methods, solid-state synthesis is widely used to synthesize CCTO ceramics. CuO is used as a raw material for the synthesis of CCTO ceramics and forms a liquid phase during the sintering process. The liquid phase, the driving force of grain growth, promotes grain growth [5]. By introducing sintering additives such as P_2O_5 [11], Bi_2O_3 [7] and halogen element [8], the formation of the liquid phase can be suppressed. Secondly, the $\tan\delta$ is reduced by enhancing the heterogeneity between grains and grain boundaries. Some ions, such as Zr^{4+} [12–14], Al^{3+} [15], Mg^{2+} [16], Zn^{2+} [9], Sr^{2+} [17] and rare earth ions [18–20], are introduced into the lattice structure to successfully reduce the internal conductivity of the grains as well as to increase the R_{gb} , achieving lower the $\tan\delta$ of the ceramic. In addition, smaller $\tan\delta$ and larger ϵ_r are also obtained in CCTO ceramics by the doping of binary elements, such as Y^{3+} and Mg^{2+} [21], Zr^{4+} and Nb^{5+} [22], Al^{3+} and Ta^{5+} [23]. Thirdly, the dielectric properties of CCTO ceramics are influenced by the generation of intergranular phases. When the concentration of the dopant increases, the inclusion phases are segregated out in

CCTO to form the intergranular phase, such as Ba^{2+} [24], SrTiO_3 [25], etc. These intergranular phases inhibit crystal growth and increase the resistance of grain boundaries. These studies not only provided experimental basis for the mechanism of giant permittivity, but also provided ideas and methods for improving the ϵ_r and reducing the $\tan\delta$ of CCTO ceramics [7–25].

In the light of the internal barrier layer capacitance (IBLC) theory model, the giant dielectric properties of CCTO ceramics come from heterogeneity of insulating grain boundaries and the n-type semiconducting grains [26–28]. As a result, the ϵ_r of CCTO are improved by increasing semiconductivity of grains and resistance of grain boundaries. Lu Tang et al. [29] reported that ϵ_r was increased and $\tan\delta$ was decreased by doping Y^{3+} into CCTO ceramics. The doping of the Y^{3+} donor results in a reduction in oxygen vacancies, which leads to a significant reduction in mobility at grain boundaries and consequently a reduction in grain size [29]. The decrease in grain size inevitably causes an increase in the density of grain boundaries with large potential barriers, meanwhile the Y^{3+} donor promotes the separation of the liquid phase copper from the grains and adheres to the grain boundaries, thus the impedance of the ceramics is increased [12, 29]. According to reports, single doping of Zr^{4+} in the B-site (Ti^{4+}) of perovskite structure changed the electrical heterogeneity of the grains and grain boundaries, thus the dielectric properties were changed [13]. To achieve CCTO ceramics with giant ϵ_r and low $\tan\delta$, CCTO ceramics were studied with different contents of ZrO_2 on the basis of 3% Y^{3+} doping.

2 Experimental

The synthesis of $\text{Ca}_{0.97}\text{Y}_{0.03}\text{Cu}_3\text{Ti}_{4-x}\text{Zr}_x\text{O}_{12}$ (CYCTZO) was carried out by reaction sintering method. High purity powders including CaCO_3 (99.0%), Y_2O_3 (99.0%), CuO (99.0%), TiO_2 (99.0%), ZrO_2 (99.0%) were used as raw materials [29]. CaCO_3 , Y_2O_3 , CuO , TiO_2 and ZrO_2 were weighed according to the stoichiometric ratio of formula $\text{Ca}_{0.97}\text{Y}_{0.03}\text{Cu}_3\text{Ti}_{4-x}\text{Zr}_x\text{O}_{12}$ ($x=0, 0.005, 0.010, 0.015$). The weighed powder, zirconia ceramic ball and anhydrous ethanol were put into agate ball mill, and then ground on planetary ball mill for 8h. The mixture was dried at 70°C for 6h, and the uniform powder mixture was obtained by grinding and sieving. 3% polyvinyl alcohol binder (PVA) was added to the powder mixture, which was grinded into granules in a mortar and granulated through a 100 mesh sieve. The granular material was pressed into disc shape with diameter of 12 mm and thickness of 1 mm by uniaxial compression. After molding, the samples were kept in air at 550°C for 2 hours to discharge the binder. The sample obtained was calcined in the air at 1080°C for 10 hours in the crucible and cooled to room temperature in the furnace. After the surface of the sample was ground to a smooth surface. The silver oxide paste was coated on both sides of the sample, heated at 550°C for 20 minutes after drying, and then formed a silver electrode after cooling.

The crystal structure and phase structure of the ceramics were analyzed by X-ray diffraction (XRD-7000X, Japan) with a $\text{CuK}\alpha$ ($\lambda = 0.15406\text{nm}$). The microstructure of ceramic samples was examined by scanning electron microscope (SEM, JSM-7610F, Japan). The types and contents of elements inside the grains and grain boundaries were detected by energy dispersive spectrometer (EDS, JSM-7610F, Japan). The

dielectric constant, dielectric loss tangent and impedance performance of samples were measured at room temperature in the range of 10^2 - 10^6 Hz by using a precision impedance analyzer (Agilent 4294A, Agilent Inc., American).

3 Results And Discussion

Figure 1 shows the XRD patterns of different doping amount of CYCTZO ceramics in the 2θ range of 20 to 80 at room temperature. XRD curves were basically consistent with the peak shape of single-phase CCTO (JCPDS 75-2188), and no impurity phase was detected [29]. Each diffraction peak in the XRD pattern of CYCTZO ceramics perfectly matched with a body-centered cubic perovskite-like structure [22]. The figure on the right side of Figure 1 shows diffraction peaks (220) pattern when different amounts of ZrO_2 were doped. With the increase of ZrO_2 , the diffraction peaks (220) shifted to a large angle. As doping amount from 0.010 to 0.015, diffraction peaks (220) shifted to a small angle [22]. This phenomenon suggests that Zr^{4+} entered the lattice structure, which caused lattice shrinkage [29].

Figure 2 is the SEM image of CYCTZO ceramic sample at 1080°C for 10h. As shown in Fig. 2, all samples had clear grains, and the grain size of the samples was relatively small. The average grain size of the samples was 3.05 μm without doping Zr^{4+} . Smaller fine grains were adhered to larger coarse ones, which was similar to the pinning effect of the second phase [22]. For the doped CYCTZO ceramics with $x=0.005$, 0.010 and 0.015, the average grain size was 2.16 μm , 2.13 μm and 2.11 μm respectively. Compared to the grain size interval (~ 1.20 -5.78 μm) of the undoped sample, grain size interval (~ 1.16 -4.96 μm) of sample with $x=0.005$ was narrower. The uniformity of the ceramic grains was improved by doping Zr^{4+} . The reduction of grain sizes in CYCTZO ceramics may be related to the inhibition of the formation of liquid phase during sintering and consequently hinders the movement of grain boundaries [30, 31]. In addition, the lattice strain energy is diminished as a result of the mismatch of ionic radii between the dopants of Zr^{4+} and host Ti^{4+} in CCTO, resulting in the smaller grain size [22]. This is also confirmed by the deviation of diffraction peaks (220) in the XRD pattern.

The EDS spectra of CYCTZO ceramics with $x = 0.005$ and $x = 0.015$ are shown in Fig. 3 Pt-1 and pt-2 respectively represent grains and grain boundaries grain boundary. The spectra showed the changes of element type and content in the grains and grain boundaries of the samples doped with Zr^{4+} . The content of copper elements in the grain was higher than that in the grain boundaries for both, which was due to Y^{3+} promoting the liquefaction of Cu in the grain and precipitation at the grain boundaries. Zr elements appear in the grains and the grain boundaries, and the content of Zr elements was similar for doping concentration $x=0.005$. When the doping content increases to $x=0.015$, the Zr^{4+} content at the grain boundaries was obviously higher than that inside the grain.

The ϵ_r and $\tan\delta$ of CYCTZO ceramics as a function of frequency in the range of 10^2 - 10^6 Hz are shown in Fig. 4. The ϵ_r was decreased slowly in the range of 10^2 - 10^5 Hz, and decreased sharply in the range of 10^5 - 10^6 Hz. The rapid decrease in the ϵ_r of ceramic samples at high frequencies could be explained by typical

Debye-related behavior [22]. For doping amount of Zr^{4+} from $x=0$ to $x=0.010$, the ϵ_r value of CYCTZO ceramic was gradually increased. The highest ϵ_r value was 1.02×10^5 at a frequency of 1KHz for doping content $x=0.010$. Compared with Y^{3+} single-doped [29] and Zr^{4+} single-doped [32], (Y^{3+} , Zr^{4+}) co-doped CCTO ceramics had a larger ϵ_r value. It was noted that the ϵ_r of the ceramic sample was dropped drastically and was lower than that of the Zr^{4+} non-doped sample. The result shows that the ϵ_r of ceramics could be raised by doping Zr^{4+} donor of suitable amount. To further explore the influence of Zr^{4+} donor on the dielectric properties of ceramics, it is also necessary to investigate the change of $\tan\delta$ value. Fig. 4b showed the frequency dependence of $\tan\delta$ with different doping amount. Without doping Zr^{4+} , the ceramics had lower $\tan\delta$ value at low and medium frequencies. For the ceramic samples with the doping amount $x=0, 0.005, 0.010$, overall trend of $\tan\delta$ curves was almost same. In the frequency range of 10^2 - 10^3 Hz, the $\tan\delta$ value was showed a slow increase trend as the doping content increases. In the frequency range of about 10^3 - 10^5 Hz, the $\tan\delta$ value of CYCTZO ceramics with the doping content $x=0.005$ and $x=0.10$ were lower than the $\tan\delta$ of undoped Zr^{4+} ceramics. The ceramic sample with doping amount $x=0.005$ had the lowest $\tan\delta$ value of 0.078 in this experiment at 6×10^3 Hz. The $\tan\delta$ value of CYCTZO ceramics was successfully reduced by doping appropriate content of Zr^{4+} .

Based on the IBLC model, the value of ϵ_r is inversely proportional to the grain size [33]. However, CYCTZO ceramic with a doping amount $x=0.010$ had a smaller grain size and maximum ϵ_r . As the amount of doping increases, the crystal grain size was decreased and the ϵ_r was increased, which was contrary to IBLC model. As we all know, the giant dielectric effect of CCTO ceramics is considered to be caused by the external polarization of the n-type semiconductor and insulating grain boundaries [34, 35]. A larger number of free electrons usually enhances the conductivity of n-type semiconducting grains [22]. The grade of the grain semiconductor was improved by doping Zr^{4+} . Therefore the ϵ_r of the CYCTZO ceramics with doping amount increases from $x=0$ to $x=0.010$ is raised. The ϵ_r was decreased as the Zr^{4+} content continues to increase, due to the decrease of the carrier concentration inside the crystal grain and the change of the conduction mechanism. The carriers inside the CCTO ceramic grains are mainly provided by oxygen vacancies and the charge transfers between $Cu^{2+} \rightarrow Cu^+$ and $Ti^{4+} \rightarrow Ti^{3+}$ [36–38]. Increasing Zr^{4+} in CCTO ceramics would lead to the decrease of oxygen vacancies [22, 39]:

(1)

(2)

According to Eq. (1), Eq. (2), the transmission effect between $Ti^{4+} \rightarrow Ti^{3+}$ also was weakened with the increase of Zr^{4+} content [22].

The impedance spectrum of CYCTZO ceramics at room temperature is shown in Fig. 5. The non-zero intercept on the Z' axis and the diameter of the semicircle formed by the impedance line at low frequency represent the grain resistance (R_g) and the R_{gb} of the ceramic sample, respectively [34, 35]. The impedance diagram showed that R_{gb} was decreased with increasing Zr^{4+} doping content. According to the EDS results, the decrease of R_{gb} is related to the increase of Zr element content at the grain boundaries. It is easy to find that the trend of R_{gb} is consistent with trend of the $\tan\delta$ in the low frequency region in Fig. 4(b). Interestingly, in the med-frequency region, the $\tan\delta$ values of CYCTZO ceramics with doping content $x=0.005$ and $x=0.010$ were lower than that of undoped Zr^{4+} . Not only the ϵ_r was increased, but also the $\tan\delta$ value was reduced doping appropriate amount of Zr^{4+} .

4 Conclusions

In conclusion, CYCTZO ceramics were successfully synthesized by reaction sintering method at 1080°C. The phase composition, microstructure and dielectric properties of the ceramics were studied. The experimental results show that the donor Zr^{4+} doping has little effect on $Ca_{0.97}Y_{0.03}Cu_3Ti_4O_{12}$ (CYCTO) ceramic phase composition, but reduces the crystal grain size and improves the dielectric properties of the ceramic. For Zr^{4+} donor doping amount $x=0.005$, CYCTZO ceramic had larger ϵ_r value of 1.02×10^5 at 1KHz and the lowest $\tan\delta$ value of 0.078. In addition, the highest ϵ_r value of 1.03×10^5 at 1KHz and smaller $\tan\delta$ value of 0.08 were obtained for ceramic doped with Zr^{4+} amount of 0.010. Our results further strengthen the argument for optimizing the dielectric properties of ceramics by adjusting the properties of grains and grain boundaries.

Declarations

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Figures

Figure 1

XRD pattern of $\text{Ca}_{0.97}\text{Y}_{0.03}\text{Cu}_3\text{Ti}_{4-x}\text{Zr}_x\text{O}_{12}$ ceramics with (a) $x=0$, (b) $x=0.005$, (c) $x=0.010$, (d) $x=0.015$, and the position of (220) diffraction peak change with X content.

Figure 2

SEM image of $\text{Ca}_{0.97}\text{Y}_{0.03}\text{Cu}_3\text{Ti}_{4-x}\text{Zr}_x\text{O}_{12}$ ceramics with (a) $x=0$, (b) $x=0.005$, (c) $x=0.010$, (d) $x=0.015$.

Figure 3

SEM-EDS analysis of $\text{Ca}_{0.97}\text{Y}_{0.03}\text{Cu}_3\text{Ti}_{4-x}\text{Zr}_x\text{O}_{12}$ ceramics with (a) $x=0.005$, (b) $x=0.015$. Pt-1 and pt-2 represent grains and grain boundaries, respectively.

Figure 4

Dielectric constant (a) and dielectric loss tangent (b) of $\text{Ca}_{0.97}\text{Y}_{0.03}\text{Cu}_3\text{Ti}_{4-x}\text{Zr}_x\text{O}_{12}$ ceramics with $x=0 \sim 0.005 \sim 0.010 \sim 0.015$.

Figure 5

the impedance spectrum of $\text{Ca}_{0.97}\text{Y}_{0.03}\text{Cu}_3\text{Ti}_{4-x}\text{Zr}_x\text{O}_{12}$ ceramics with $x=0 \sim 0.005 \sim 0.010 \sim 0.015$.