Influence of interface point defect on the dielectric properties of Y doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics

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Received 13 December 2015; Revised 5 February 2016; Accepted 13 February 2016; Published 11 April 2016

$\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ($0 \leq x \leq 0.12$) ceramics were fabricated with conventional solid-state reaction method. Phase structure and microstructure of prepared ceramics were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The impedance and modulus tests both suggested the existence of two different relaxation behavior, which were attributed to bulk and grain boundary response. In addition, the conductivity and dielectric permittivity showed a step-like behavior under 405 K. Meanwhile, frequency independence of dc conduction became dominant when above 405 K. In CCTO ceramic, rare earth element Y^{3+} ions as an acceptor were used to substitute Ti sites, decreasing the concentration of oxygen vacancy around grain-electrode and grain boundary. The reason to the reduction of dielectric behavior in low frequencies range was associated with the Y doping in CCTO ceramic.

Keywords: $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$; grain boundary; bulk conduction; electrochemical techniques; dispersion; dielectric properties.

1. Introduction

Over the past decade, the perovskite-related material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has gained considerable attention as a nonferroelectric due to its high ($\sim 10^5$) and almost temperature-independent dielectric constant.^{1–3} CCTO could be considered as a promising candidate for the miniaturization of electronic devices such as dynamic random access memory (DRAM) devices and multi-layer ceramic capacitors (MLCC). However, high dielectric loss of CCTO materials has limited their commercial applications.

In view of these properties of CCTO materials, the scientific community has been focusing its attention on efforts to understand the origin of the giant dielectric constant. In the past several years, many models have been proposed to illustrate the origin of giant dielectric constant.^{4–7} However, it is still questionable whether the high dielectric constant is intrinsic to a perfect crystal or extrinsic and related to the material microstructure (such as grain size) and processing conditions (such as sintering temperature and time, cooling rate, etc.). According to these models, the method for depressing dielectric loss could be found. The high dielectric loss could be contributed to the hopping of charged carriers

(such as oxygen vacancy), especially at high temperatures, nevertheless, the relaxations from ceramic–electrode interface and grain boundary resulting from point defects is rarely investigated. In this context, a detailed temperature-dependent dielectric behavior was analyzed to understand the mechanism of conduction and to determine the electrical behavior of bulk and grain boundaries.

In the present work, rare earth Y was employed to substitute Ti in CCTO as an acceptor in order to modify the concentration of oxygen vacancy. The ceramics were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) for structural and microstructure analysis, respectively. The dielectric relaxation characterization were subsequently investigated using impedance analyzer at various temperatures.

2. Experimental Procedure

$\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramics with different mol% of dopant ($x = 0, 0.02, 0.05, 0.08$, and 0.12) were prepared using conventional solid-state processing method. The stoichiometric amounts of highly pure CaCO_3 (99%), CuO (99%), TiO_2

(99.99%) and Y_2O_3 (99.99%) were mixed and ball-milled in ethanol for 10 h, dried, and then calcined in air at 930°C for 2 h. The phase formation of calcined powders were investigated and characterized by X-ray diffraction (XRD PANalytical X-Pert-PRO) technique using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The calcined powder was remilled for 4 h again to eliminate the agglomerates and granulated by adding PVA, then pressed into pellets with a diameter of 12.0 mm and thickness of 2.0 mm under 350 MPa pressure. The pellets sintered in air at 1080°C for 12 h.

XRD was used to identify the phase purity and crystal structure of the sintered samples. Meanwhile, the surface microstructure of the samples was observed using SEM (JSM-6380, Japan). The samples were polished, and both surfaces were coated with silver paste for the dielectric measurement. The dielectric properties of the samples were measured through Impedance Analyzer (Agilent 4294A) at frequency range from 40 Hz to 110 MHz at different temperatures.

3. Results and Discussion

Figure 1 shows XRD patterns of the $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramics at room temperature. No second phase was observed for all of the samples. All the major diffraction peaks in the XRD patterns can be indexed by a body-centered cubic perovskite-related structure of space group $Im-3$ [ICDD-JCPDS card 75-2188]. These results indicate that Y^{3+} for all samples has completely diffused into the CCTO lattice to form a solid solution. With increasing Y^{3+} concentration, all diffraction peaks shift toward lower angle, indicating the lattice parameter increases. Through Rietveld refinement (Topas software), the lattice parameter of the samples were calculated $7.3966 \text{ \AA}$, $7.3972 \text{ \AA}$, $7.3982 \text{ \AA}$, $7.4023 \text{ \AA}$, $7.4061 \text{ \AA}$

for $x = 0, 0.02, 0.05, 0.08$ and 0.12 , respectively. Normally, Y^{3+} ion prefers to occupy Ca site due to the smaller difference of ionic radius between them. However, the Ca/Ti ratio plays an important role on the substitution of Y^{3+} . In this work, since the radius of Y^{3+} ion ($r = 1.02 \text{ \AA}$, CN = 8) is smaller than that of Ca^{2+} ($r = 1.34 \text{ \AA}$, CN = 12), Y^{3+} occupies Ca site will lead to a decrease of lattice parameter, which disagrees our XRD results. While the substitution of Y^{3+} ($r = 0.9 \text{ \AA}$, CN = 6) to Ti^{4+} ($r = 0.605 \text{ \AA}$, CN = 6) results in the increase of lattice parameter, which is inconsistent with the XRD refinement results.

Figure 2 shows SEM photographs of selected undoped and Y-doped CCTO ceramics. The mean grain size of the CCTO ceramic significantly reduced for doping with Y^{3+} ions. The morphology of the undoped CCTO sample is characterized by the grain size of the order of $50\text{--}200 \mu\text{m}$ with the big grains inlaying some several micrometer grains, as shown in Fig. 2(a). Liquid phase sintering mechanism is likely to be the main cause of increase in the grain growth process.^{8,9} The presence of liquid phase during sintering process could enhance the diffusion rate of ions across grain boundaries or/and weld the smaller grains. However, Y-doped ceramics display uniformly distributed grains with the grain size of approximately $1\text{--}2 \mu\text{m}$. Smaller grain sizes of Y-doped ceramics may be due to the ability of Y^{3+} to suppress the grain growth rate of CCTO ceramics.

Figure 3 shows the frequency dependence of (a) the real part (ϵ'), (b) the imaginary part (ϵ'') of the dielectric constant, and (c) dielectric loss ($\tan\delta$) for $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramics at room temperature in the frequency range of 40 Hz–110 MHz. It can be seen that all samples exhibit considerable high dielectric permittivity at room temperature. Furthermore, compared with undoped CCTO, the dielectric permittivity of Y-doped CCTO is not sensitive to frequency in the range from 10 kHz to 10 MHz. The results demonstrate that all Y-doped samples have good frequency stability of dielectric constant below 10 MHz. The sample with $x = 0.02$ show the lowest ϵ' value of about 32,000. As the measurement frequency increases to 1 kHz, the dielectric constant of all samples decreases rapidly, which accompanies with low-frequency relaxation peaks appeared in the imaginary part ϵ'' of the dielectric constant in Fig. 3(b). These features are attributed to the Maxwell–Wagner relaxation. An equivalent circuit consisting of the grain boundary contribution is connected in series to a parallel RC circuit where R and C are much greater than the corresponding grain boundary quantities. The high-resistance thin layers that generate this RC circuit could be surface layers, grains, depletion layers or planar defects.^{10–14} In addition, the high-resistance thin layers generating this RC circuit are shorted via their capacitance, and intrinsic response is detected at high frequency. The lower value of ϵ' at higher frequency ($> 10 \text{ MHz}$) are associated with the intrinsic response which is not sensitive to the Y^{3+} substitution content. It can also be found in Fig. 3(b) that with the increasing x , ϵ'' value of the doped samples

Fig. 1. XRD patterns of $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramics with $x = 0, 0.02, 0.05, 0.08$ and 0.12 . The lattice planes were indexed according to ICDD-JCPDS card 75-2188.

Fig. 2. The SEM photographs of the surface of $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramics: (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.05$, (d) $x = 0.08$ and (e) $x = 0.12$.

increased significantly in the frequency range from 40 to 1 MHz, and ε'' peak amplitude monotonically decreases in the higher frequency range. It could be caused by the change of the conductivity of grain boundaries and grains, respectively. According to the equation $\sigma_{ac} = \varepsilon''\varepsilon_0\omega$ (ε_0 is the static dielectric constant and ω is the angular frequency), ε'' is proportional to the electrical conductivity in the ac field. As shown in Fig. 3(c), the dielectric loss measured at higher frequency ranging from 100 kHz to 1 MHz decreases dramatically with increasing x , which suggests that the resistance of grain boundaries increases dramatically. Furthermore, the dielectric loss peak measured around 40 MHz monotonically shifts to higher frequency region, indicating the decrease of

the grains resistance. The variation trend of dielectric loss with Y^{3+} substitution content is consistent with the ε'' results shown in Fig. 3(b).

Generally, impedance spectroscopy is a powerful tool to reveal the mechanism of dielectric response in CCTO system, particularly to obtain information on nonintrinsic dielectric effects.^{15–17} Figure 4 demonstrates the complex impedance for $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramics measured in the frequency range from 40 Hz to 1 MHz at room temperature. Only one large arc is observed in the complex impedance of the undoped sample. It can be seen that the complex impedance plots for Y-doped samples show two semicircles: one in the high frequency range is associated with grain response

Fig. 3. The frequency dependence of (a) the real part ε' , (b) the imaginary part ε'' of the dielectric constant and (c) dielectric loss ($\tan\delta$) for $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramics with $x = 0, 0.02, 0.05, 0.08$ and 0.12 .

Fig. 4. Complex impedance plots of the $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramics at room temperature. The inset shows an expanded view of the plots at high frequency.

Table 1. The calculated R_g and R_{gb} for $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramics at room temperature.

Samples	$x = 0.00$	$x = 0.02$	$x = 0.05$	$x = 0.08$	$x = 0.12$
R_g (k Ω)	0.002	1.228	0.512	1.504	0.324
R_{gb} (k Ω)	3.220	4.647	4.480	5.733	4.203

(Fig. 4, inset); while the other one is related to grain boundary response at low frequencies. The equivalent circuit of the complex impedance can be expressed as follows:

$$Z(\omega) = \frac{R_g}{1 + i\omega C_g R_g} + \frac{R_{gb}}{1 + i\omega C_{gb} R_{gb}}, \quad (1)$$

where $\omega = 2\pi f$ is the angular frequency. R_g (C_g) and R_{gb} (C_{gb}) represent the resistances (capacitances) of the grains and grain boundaries, respectively. The grain resistances R_g and

Fig. 5. Frequency dependence of imaginary part $-Z''$ of the $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramics at different temperatures. (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.05$, (d) $x = 0.08$ and (e) $x = 0.12$.

grain boundaries resistances R_{gb} have been calculated and the results are shown in Table 1. It is evident as shown in Table 1 that the R_{gb} values for all ceramics are slightly different. The result is consistent with the small change of $\tan\delta$ for these samples. R_g of the undoped sample monotonically increases with the substitution of Y^{3+} ions. Interestingly, at room temperature, R_g of the Y-doped samples are much higher than that of the undoped sample by a factor of ~ 150 . The difference indicates that the Y^{3+} doping makes a remarkable influence on the electrical transport in the grain interiors, but slightly affect conduction at grain boundaries.

Figure 5 shows frequency dependence of imaginary part Z'' of impedance of the $CaCu_3Ti_{4-x}Y_xO_{12}$ ceramics at various temperatures. The Z'' data exhibit Debye-like peaks with characteristic frequency maximum (f_{max}) above 346 K. No such peaks were observed at temperatures below 346 K in the measured range of frequency due to the high total samples resistance. The apparent Z'' peak shifts to higher frequencies with increasing temperature, indicating a thermally activated electrical response. The Z'' peak is related to the large semicircle observed in Fig. 4. Thus, these apparent peaks of Z'' represent the electrical response of grain boundaries. As shown in Fig. 6, it was found that the grain boundaries conduction, $\sigma_{gb} = 1/R_{gb}$, follows the Arrhenius law,¹⁸

$$\sigma_{gb} = \sigma_0 \exp\left(\frac{-E_{gb}}{k_B T}\right), \quad (2)$$

where σ_0 is pre-exponential term, E_{gb} is the activation energy for conduction at the grain boundaries, k_B is the Boltzmann constant and T is absolute temperature. From the slope of the plots, E_{gb} values of $CaCu_3Ti_{4-x}Y_xO_{12}$ ceramics with $x = 0, 0.02, 0.05, 0.08$ and 0.12 are 0.693, 0.692, 0.668, 0.583 and 0.638 eV, respectively. E_{gb} of the doped samples lower than that of the CCTO ceramic. The substitution of Y^{3+} into Ti^{4+} in CCTO ceramic makes positive influence on the migration of oxygen vacancy at grain boundaries. This result is consistent with the Maxwell–Wagner relaxation model proposed by Liu *et al.*¹⁹

Figure 7 shows the Cole–Cole plots of complex impedance data (the imaginary part Z'' and the real part Z') of $CaCu_3Ti_{4-x}Y_xO_{12}$ ceramics at different temperatures. It can be seen from the figure that the feature of impedance spectra is almost similar at different temperatures, except for a decrease in radius of curvature of the arcs with the increasing temperature, which reveals that the resistance of the sample decreases as the temperature increases. As shown in Fig. 7(a), only one semicircle arc can be observed at different temperatures and this semicircle arc could arise from the grain boundary effect. The grain boundary resistance (R_{gb}) could be obtained directly from the intercept on the Z' -axis. The semicircle radius decreases with the increase of temperature, which suggests the decrease of the grain boundary resistance. As can be seen in Figs. 7(b)–7(d), each complex impedance plot shows two semicircles, it is considered that there are two dielectric relaxations, corresponding to grain and grain

boundary. One corresponds to the small arc is associated with grain response in the high frequency range, the other is related to grain boundary response at low frequencies. These two semicircular arcs can be modeled as equivalent circuit consisting of two parallel RC elements connected in series: one RC element, i.e., $R_g C_g$, represents the semiconducting grains, and the other, i.e., $R_{gb} C_{gb}$, represents the insulating grain boundary regions, as shown in the inset of Fig. 7(b). For such an equivalent circuit, each RC element ideally arises semi-circular arc in complex impedance plane Z^* ²⁰ described as follows:

$$Z^* = Z' - iZ''. \quad (3)$$

In AC circuits, for a pure resistor and capacitor, $Z^* = R$ and $1/i\omega C$, respectively. Therefore, the impedance can be expressed as Eq. (4) for each RC element.

$$Z^* = \frac{1}{1/R + i\omega C} = \frac{R}{1 + i\omega RC}. \quad (4)$$

In our experiment, the impedance spectrum can be modeled as two RC elements connected in series. Therefore, the complex impedance ($Z^* = Z' - iZ''$) here can be expressed as

$$Z' = \frac{R_g}{1 + (\omega R_g C_g)^2} + \frac{R_{gb}}{1 + (\omega R_{gb} C_{gb})^2} \quad (5)$$

and

$$Z'' = R_g \left[\frac{\omega R_g C_g}{1 + (\omega R_g C_g)^2} \right] + R_{gb} \left[\frac{\omega R_{gb} C_{gb}}{1 + (\omega R_{gb} C_{gb})^2} \right], \quad (6)$$

where R and C are the resistance and capacitance, respectively, the subscripts g and gb refer to the grains and grain boundaries, respectively, and ω is the angular frequency. Based on Eq. (6), the response peaks of the grains and the grain boundaries are located at $1/(2\pi R_g C_g)$ and $1/(2\pi R_{gb} C_{gb})$, respectively, and the peak value is proportional to the associated resistance. The above results demonstrate that the

Fig. 6. Arrhenius plots of temperature dependence of the grain boundary conductivity for the $CaCu_3Ti_{4-x}Y_xO_{12}$ ceramics.

Y-doped samples are electrically heterogeneous, which is well consistent with the internal barrier layer capacitance (IBLC) model.^{21–23}

The giant dielectric response in CCTO should be contributed either from grain boundary or grain interior or from both of them. The brick layer model is the most popular model to simulate the frequency-dependent electrical behavior of polycrystalline electroceramics.²⁴ There is only one arc in the impedance spectrum for the ceramics, and this arc is often related to the contribution from the grain boundary.

Actually, the modulus spectrum maybe the most powerful tool to analyze the dielectric behavior of electroceramics for the modulus is directly linked to the capacitance, and in some cases, more arcs may appear in the modulus spectrum which has the obvious merit to analyze the contribution from different factors.²⁵ So the modulus spectrum is used to analyze the dielectric behavior of the sample. The modulus spectra at various temperatures for the $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramic with $x = 0.08$ are shown in Fig. 8. The figure shows two arcs and a tail are found in the M^* plots below 345 K; this observation,

Fig. 7. Impedance complex plane plots for $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramics at different temperatures. The inset shows an expanded view of the plots at high frequency. (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.05$, (d) $x = 0.08$ and (e) $x = 0.12$.

Fig. 8. Complex modulus plots of $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramics with $x = 0.08$ at different temperatures. Arrow represents the direction of increasing frequency and the inset shows the equivalent circuit.

combined with the Z^* data is consistent with an equivalent circuit consisting of two parallel RC elements and resistor-inductor all placed in series as shown in the inset in Fig. 8. The subsequent data analysis is based on this equivalent circuit model. The idealized response of the equivalent circuit is shown along with the experimental approximation used to extract R and C values. As described later, the series $RsLs$ represents the contribution of measuring leads and electrodes, which is responsible for the high frequency nonzero intercept in Z^* plots and upturn in M^* data. Here, the low frequency arc corresponds to the grain boundary response, $R_{gb}C_{gb}$, representing the grain boundary regions and the high frequency arc corresponds to the grain response, R_gC_g , representing the grain interiors. The fitting results are shown in Table 2. The resistances of both grain and grain boundary decrease with increasing temperature, and the ratio of R_{gb}/R_g is much lower than that of the other giant dielectric constant materials, such as $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$,²⁶ so the dielectric contribution from the grain boundary barrier layer capacitor model may be suppressed.²⁷ The capacitances of grain boundaries significantly increase with increasing temperature, while the capacitances of grain interiors first slightly increase and then

Table 2. Parameter of $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramic with $x = 0.08$ fitted from the modulus curve as shown in Fig. 8.

Temperature (K)	$R_{gb}(\Omega)$	$C_{gb}(\text{nF})$	$R_g(\Omega)$	$C_g(\text{nF})$
300	5733 ± 24	689 ± 15	1504 ± 8	45.81 ± 0.35
325	2259 ± 12	762 ± 14	496.9 ± 6.1	46.70 ± 0.37
345	951.9 ± 3.2	792 ± 12	211.5 ± 2.4	47.55 ± 0.39
365	380.5 ± 2.2	813 ± 12	88.11 ± 0.92	48.67 ± 0.40
385	164.5 ± 1.7	829 ± 12	40.06 ± 0.38	49.83 ± 0.43
405	74.69 ± 0.58	853 ± 10	19.63 ± 0.56	51.54 ± 0.46
425	33.29 ± 0.22	881 ± 10	9.95 ± 0.04	52.14 ± 0.48
445	14.92 ± 0.08	924 ± 10	5.422 ± 0.03	52.77 ± 0.54
465	7.60 ± 0.03	968 ± 10	3.27 ± 0.02	52.27 ± 0.62
485	4.17 ± 0.01	1016 ± 9	1.963 ± 0.009	49.01 ± 0.73

Fig. 9. Frequency dependence of the ac conductivity at different temperatures for $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramic with $x = 0.08$.

decrease when the temperature above 445 K, which is similar to that of the temperature dependence for dielectric constant although the occurred temperature is somewhat different. The above results show that the origin of giant dielectric constant of the sample should be dominated by grain interior instead of grain boundary.

Figure 9 shows the frequency dependence of the ac conductivity σ_{ac} for $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramic with $x = 0.08$ at different temperatures. The curves tend to flatten with increasing temperature, especially in the low frequency regions, suggesting dc conduction behavior. The figure shows that, below 405 K, the data exhibits step-like behavior characteristic of a multiple relaxation process. The frequency-independent plateau in the 1–10 kHz range indicates relaxation of the bulk conduction $\sigma_g = 1/R_g$, while at lower frequency there is a strong frequency dependence associated with the dispersion toward relaxation of the grain boundary and total dc conduction $\sigma_{total} = \sigma_{dc} = 1/(R_g + R_{gb}) \approx 1/R_{gb}$ as $R_{gb} \gg R_g$. On the other hand, the frequency-independent behavior of dc conduction becomes dominant above 405 K. The dispersion at the highest frequency is related to the relaxation of R_g and R_s . The full expression for the total conductivity is actually $\sigma_{total} = \sigma_{dc} = 1/(R_s + R_g + R_{gb})$ and the “bulk” relaxation is $\sigma_g = 1/(R_s + R_g)$, but the contribution of R_s has been ignored for simplicity as $R_s \ll R_g$, R_{gb} . Extrapolation of this part towards lower frequency will obtain direct current conductivity σ_{dc} . The ac conductivity σ_{ac} could be described by the so-called “universal dielectric response” law²⁸:

$$\sigma'(f) = \sigma_{dc} + \sigma_0 f^s, \quad (7)$$

where σ_{dc} is the dc bulk conductivity, f is the frequency, σ_{dc} is a constant, and $0 \leq s \leq 1$. The $\sigma_0 f^s$ term is an empirical expression representing the transport properties of polarons, electrons and ions. The temperature variation of σ_{dc} thus

obtained follows the Arrhenius law given by:

$$\sigma_{dc} = T^{-1} \sigma_0 \exp\left(-\frac{E_{con}}{k_B T}\right), \quad (8)$$

where σ_0 is the preexponential factor, and E_{con} is the dc conduction activation energy. E_{con} was calculated for the sample with $x = 0.08$ at different frequencies from the slopes of straight lines obtained from $\ln\sigma_{dc} \sim 1000/T$ plot in Fig. 10. The plot exhibits two distinct regimes: one with activation energy for grain boundary conduction $E_{gb} \sim 0.583$ eV above 405 K and another with bulk conduction $E_g \sim 0.367$ eV over 300–405 K. The nature of the plot simply suggests that frequency-independent regions are indicative of the grain boundary and bulk relaxation processes, rather than a change in the conduction mechanism.

Previous studies made by Fang *et al.*²⁹ suggested that the spectral intensity of the dielectric relaxation was activated thermally by virtue of hopping process of charge carriers and small polarons in polycrystalline ceramics. However, in the present case it is likely that the high frequency dispersion could well be due to the relaxation of resistance (R_s) than a separate conduction mechanism.

The calculated activation energy (E_a) of 0.583 eV which was obtained from the data on the higher temperature side is comparable to activation energy of 0.547 eV for diffusion of oxygen ions in bismuth-based bulk materials $\text{Na}_{0.05}\text{Bi}_{0.65}\text{Cu}_3\text{Ti}_4\text{O}_{12}$.³⁰ Similar to many other perovskite-type oxide polycrystalline ceramics, oxygen vacancies in the samples are believed to create charge carriers via a defect compensation mechanism and thus play an important role in resistance and dielectric degradation.

As seen in Fig. 11, The low frequency upturn, as evidenced by the increase in the $\epsilon'(f)$ and $\epsilon''(f)$ corresponding to dipolar relaxation becomes more pronounced as it shifts

Fig. 10. Semi-log plot of temperature dependence of dc conductivity of $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramic with $x = 0.08$ depicting two regions for which activation energies are estimated using Arrhenius equation.

Fig. 11. Frequency dependence of (a) real and (b) imaginary parts of complex effective permittivity at different temperatures for $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ceramic with $x = 0.08$.

towards higher frequencies with increasing temperature. In Fig. 11(b), the slope of the log-log plots at high temperature and low frequency is close to -1 indicating frequency-independent conduction, i.e., dc conduction at low frequencies. There was a strong low frequency dielectric dispersion in the high temperature region (above 405 K) where the frequency dependence of ac conductivity reduced gradually. Hence the dc conduction mechanism is not that of a simple metal-semiconductor-metal structure because this should not contribute to any polarization and thus to the dielectric constant. A possibility for the origin of this polarization process at the electrode is that can be accumulation of carriers either due to acceptor states trapping electrons at a depletion layer or a diffusion limited transfer process through the metal electrode for ionic species such as oxide ions. In the low temperature region (below 385 K), the conduction behavior of electrode-sample-electrode junction may be ascribed to the trap controlled space charge. For the sample, the space charge could be created by migration of oxygen vacancies toward various trap sites such as interfaces/electrodes.

4. Conclusions

Structure, microstructure and dielectric properties of $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12}$ ($x = 0, 0.02, 0.05, 0.08$ and 0.12) ceramics were investigated. Combination of impedance and electric modulus showed the presence of low-frequency grain boundary relaxation at high temperature and high-frequency bulk relaxation at low temperature. Y plays an acceptor to modify the concentration of oxygen vacancy both in grains and at grain boundaries. Grain resistance increases obviously in Y doped CCTO samples, which indicates the concentration of oxygen vacancy decreases in grain. While according to activation energy of grain boundary, the substitution of Y^{3+} into Ti^{4+} in CCTO ceramic makes positive influence on the migration of oxygen vacancy at grain boundaries.

The high-frequency dielectric loss was depressed for all Y doped samples. The ceramic with $x = 0.08$ exhibits a step-like behavior in both conductivity and dielectric constant below 405 K from 1 to 10 kHz. The behavior associates with the migration of oxygen vacancy either in grains or at grain boundaries occurred at different temperatures or frequency ranges. The frequency-independent conduction at low frequency and high frequency corresponds to dc conduction and grain-boundary-associated conduction, respectively. The dielectric constant of the sample $x = 0.08$ shows frequency independence above 400 K, which could be used in high-temperature capacitor field.

Acknowledgments

This work was financially supported by the Natural Science Foundation of China (Grant Nos. 11564010, 11264010, 21061004 and 50962004), and by the Natural Science Foundation of Guangxi (Grant No. GA139008).

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