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Enhancement of giant dielectric response in Ga-doped $CaCu_3Ti_4O_{12}$ ceramics

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Abstract

The influences of Ga^{3+} doping ions on the microstructure, dielectric and electrical properties of $CaCu_3Ti_4O_{12}$ ceramics were investigated systematically. Addition of Ga^{3+} ions can cause a great increase in the mean grain size of $CaCu_3Ti_4O_{12}$ ceramics. This is ascribed to the ability of Ga^{3+} doping to enhance grain boundary mobility. Doping $CaCu_3Ti_4O_{12}$ with 0.25 mol% of Ga^{3+} caused a large increase in its dielectric constant from 5439 to 31,331. The loss tangent decreased from 0.153 to 0.044. The giant dielectric response and dielectric relaxation behavior can be well described by the internal barrier layer capacitor model based on Maxwell–Wagner polarization at grain boundaries. The nonlinear coefficient, breakdown field, and electrostatic potential barrier at grain boundaries decreased with increasing Ga^{3+} content. Our results demonstrated the importance of ceramic microstructure and electrical responses of grain and grain boundaries in controlling the giant dielectric response and dielectric relaxation behavior of $CaCu_3Ti_4O_{12}$ ceramics.

Keywords: B. Grain boundaries; C. Dielectric properties; C. Electrical properties; Impedance spectroscopy

1. Introduction

Since an anomalously giant dielectric constant (ε') of $CaCu_3Ti_4O_{12}$ (CCTO) was first reported by Subramanian et al. [1], CCTO has attracted considerable attention [2–21]. It was reported that CCTO can exhibit high and nearly temperature independent dielectric constants of $\sim 10^3$–10^5 over the range of 100–600 K. Due to these unique dielectric properties, it is theorized that CCTO ceramics are a promising material for capacitor applications.

It is now widely accepted that the giant dielectric response in CCTO ceramics originates from an extrinsic effect [2–6]. Maxwell–Wagner polarization at grain boundaries (GBs) is believed to be the primary source of the giant dielectric response in CCTO ceramics [2,3]. However, there are other important factors that significantly influence the total dielectric response of CCTO. These include polarization at domain boundaries (DBs) [4], the sample–electrode effect [5], stacking fault defects [6], and a variety of chemical defects introduced into CCTO ceramics during the sintering process. It is interesting that CCTO ceramics can also exhibit nonlinear current–voltage behavior [3]. This is due to the existence of intrinsic potential barriers at the GBs, i.e., the Schottky barrier [3,15,22]. This electrical behavior may have potential for applications in varistors. Unfortunately, the loss tangent ($\tan\delta$) of CCTO ceramics is still too large ($\tan\delta > 0.05$ at 1 kHz), making them unsuitable for many applications. Considering the possibility of using CCTO in electronic applications, reduction of $\tan\delta$ in CCTO ceramics is very important. It is likely that a high $\tan\delta$

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value is the only major problem preventing the use of CCTO in electronic applications.

It was demonstrated that the electrical properties of CCTO ceramics are strongly dependent upon their microstructure [3,14–16]. These observations support the internal barrier layer capacitor (IBLC) model of Schottky barriers at the GBs between semiconducting grains. Adams et al. [15] suggested that the IBLC model can be used to explain both the giant dielectric properties and nonlinear current–voltage characteristics of CCTO ceramics. According to this model, if a high ε' value of CCTO ceramics is attributed to the electrical response of GBs, variations of dielectric properties must be systematically correlated to changes in electrical properties at the GBs. Conversely, it was shown that the relationship between the giant dielectric response and non-Ohmic properties of CCTO ceramics is still not easy to predict using the IBLC model [22].

To improve the dielectric properties of CCTO ceramics and to elucidate their electrical properties, substitution of metal ions and an anion (F^{1-} for O^{2-}) into Ca^{2+}, Cu^{2+}, Ti^{4+}, and O^{2-} sites for CCTO ceramics has been extensively investigated [7,18,19,23–33]. All substitution ions have effects on all electrical parameters. Therefore, the influences of any doping ion on microstructure, dielectric response, electrical properties of grains and GBs, and nonlinear current–voltage characteristics of CCTO ceramics should be investigated systematically. Such a systematic investigation will yield more understanding of the physical mechanisms affecting giant dielectric properties. To our knowledge, there is no report on the synthesis, dielectric and non-Ohmic properties of Ga^{3+} substituted-CCTO ceramics.

In this work, we systematically investigated the dielectric and electrical properties of Ga^{3+} doped-CCTO ceramics. The results revealed that Ga^{3+} doping ions have remarkable effects on the microstructure, nonlinear electrical properties, giant dielectric response and dielectric relaxation behavior of CCTO ceramics. The experimental observations are well described by the IBLC model to explain the giant dielectric response in CCTO ceramics.

2. Experimental

$CaCu_3Ti_{4-x}Ga_xO_{12}$ ($x=0$, 0.01, 0.05, and 0.1) ceramics were prepared by a solid state reaction method. These materials are referred to as CCTO, CCTO-Ga01, CCTO-Ga05, and CCTO-Ga10 samples, respectively. $CaCO_3$ (Cerac, 99.95% purity), CuO (Cerac, 99.9% purity), TiO_2 (Sigma-Aldrich, 99.9% purity), and Ga_2O_3 (Sigma-Aldrich, 99.99% purity) were used as starting raw materials. Each stoichiometric mixture of the starting materials was mixed while ball milling with zirconia media in ethanol for 24 h. The mixed slurries were dried and then calcined at 900 °C for 15 h. The calcined powders were ground and pressed into pellets (without a binder) of 9.5 mm in diameter and ~1 mm in thickness by uniaxial compression at 200 MPa. Finally, these pellets were sintered at 1050 °C for 5 h.

The phase composition and microstructure of the sintered $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics were characterized using x-ray diffraction (XRD) (PW3040 Philips; Eindhoven, the Netherlands) and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) (Hitachi S-3400, Japan), respectively. The dielectric properties of the samples were measured using an Agilent E4980A (Hayward, CA) Precision LCR Meter over a frequency range from 10^2 to 10^6 Hz and an oscillation voltage of 0.5 V. The measurements were performed at temperatures ranging from −70 to 150 °C. Experimental temperatures were kept constant with an accuracy of ±1 °C. Current–voltage measurements were made using a high voltage measurement unit (Keithley Model 247, Estado St. Pasadena, CA). The rate of increase in source voltage was 0.45 V/s. Prior to measurements, the ceramic samples were polished. Au was sputtered onto each pellet surface at a current of 25 mA for 8 min using a Polaron SC500 (Sussex, UK) sputter coating unit.

3. Results and discussion

Fig. 1 shows the XRD patterns of $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics, revealing the phase formation and crystal structure of sintered CCTO and Ga^{3+}-doped CCTO ceramics. The main phase of CCTO was observed in all ceramics. However, the CuO impurity phase was detected in the CCTO-Ga01, CCTO-Ga05, and CCTO-Ga10 ceramic samples, but was not observed in the CCTO ceramic sample. It was observed that the intensity of (411) diffraction peak changes with concentration of Ga^{3+} doping ions. Generally, the variation of relative peak intensities indicates the existence of preferential orientation in polycrystalline ceramics. In this work, it was shown that Ga^{3+} substitution into CCTO ceramics can cause an

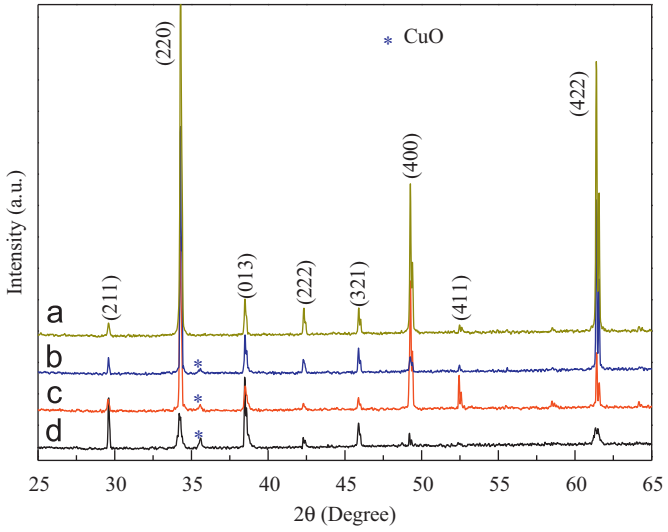

Fig. 1. XRD patterns of (a) CCTO, (b) CCTO-Ga01, (c) CCTO-Ga05, and (d) CCTO-Ga10 ceramic samples.

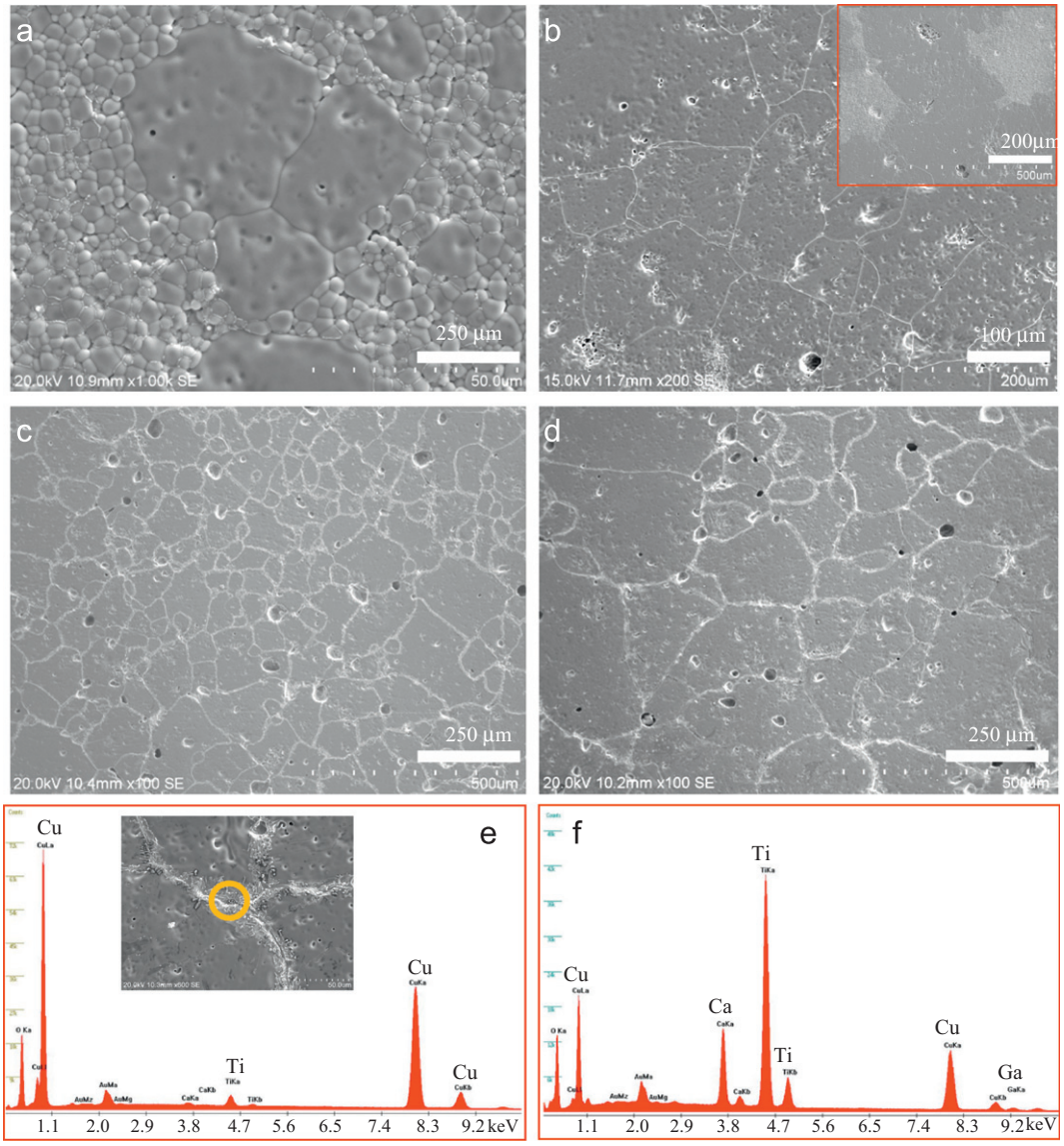

Fig. 2. (a–d) SEM images of surface morphologies of CCTO, CCTO-Ga01, CCTO-Ga05, and CCTO-Ga10 ceramic samples; inset of (b) reveals surface morphologies of the CCTO-Ga01 ceramic consisting of large-grained region (darker region) and fine-grained region (lighter region). (e,f) EDS spectra of CCTO-Ga10 sample detected at GB region and on grain region, respectively; inset of (e) shows an expanded view of surface morphology of the CCTO-Ga10 sample, revealing the detection point of EDS.

increase in the grain size (data shown in Fig. 2). This result might be responsible for the preferential orientation in $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics. However, this observation is still not proven to be correct so further investigation is needed.

Surface morphologies of the sintered $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics are shown in Fig. 2(a)–(d). Ga^{3+} has great influence on the microstructure of CCTO ceramics. The mean grain size of CCTO was greatly enhanced by doping with Ga^{3+}. Abnormal grain growth was observed in the CCTO ceramic sample. Some grains of undoped CCTO ceramic grew rapidly to sizes of ~28.7 µm, which is significantly greater than the average size of a matrix of fine grains (~5.5 µm). The mean grain sizes of the CCTO-Ga01, CCTO-Ga05, and CCTO-Ga10 ceramic samples were found to be about 138, 136, and 199 µm, respectively. Note that fine-grained region is still observed in surface area of the CCTO-Ga01 ceramic, as revealed in the inset of Fig. 2(b). The enhancement of the grain size due to the effect of Ga^{3+} doping ions indicates that Ga^{3+} doping ions play some important roles to promote the grain growth rates of CCTO ceramics. There have been several reports investigating the effects of metal ions substituted into CCTO ceramics. Before the current study, it was found that only Zn^{2+} and Fe^{3+} doping ions can significantly increase the grain size of CCTO ceramics [26,34].

As shown in Fig. 2(e) and its inset, the SEM-EDS results reveal that CuO is segregated along the GB regions of the CCTO-Ga10 sample. This is confirmed by a relatively high Cu peak measured at the GB region. No evidence of enhanced Cu concentration was observed in the EDS spectrum measured in the grain region of the CCTO-Ga10

sample, as shown in Fig. 2(f). Note that the EDS peak corresponding to Ga^{3+} was detected in the grain region of the CCTO-Ga10 sample, confirming the existence of Ga^{3+} inside grains.

To clarify the effects of Ga^{3+} doping ions on the dielectric and electrical properties of the sintered $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics, measurements were performed at different temperatures as a function of frequency. First, to exclude the possible effects of the sample–electrode interface that usually occur in a low-frequency range at temperatures greater than room temperature, the dielectric properties are presented at −70 °C in Fig. 3(a) and (b). A low-frequency ε' value increases with increasing Ga^{3+} doping concentration. The insets of Fig. 3(a) and (b) show expanded views of ε' and ε'' at −70 °C for the CCTO sample. The values of ε' at 1 kHz and 20 °C for all samples are summarized in Table 1. According to the IBLC model, the effective dielectric constant (ε'_{eff}) of a material can be expressed as [30]

$$\varepsilon'_{eff} = \varepsilon_{gb} t_g / t_{gb} \quad (1)$$

where ε_{gb}, t_g, and t_{gb} are the dielectric constants of the GB, the average grain size, and the thickness of the GB, respectively. Using Eq. (1) for the IBLC model, the observed increase in ε' of the $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics may be related to the enhancement of the grain size. However, it is premature to suggest that the giant dielectric response of $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics is primary caused by the IBLC effect because ε' of the CCTO-Ga05 sample is higher than that of the CCTO-01 sample. The mean grain size of the CCTO-Ga05 sample is slightly smaller than that of the CCTO-01 sample. This observation is still insufficient to explain the origin of dielectric response in CCTO ceramics. To resolve and confirm the IBLC effect as the main source of giant ε', changes of other parameters caused by Ga^{3+} substitution must be further explored to provide explanation based on this model.

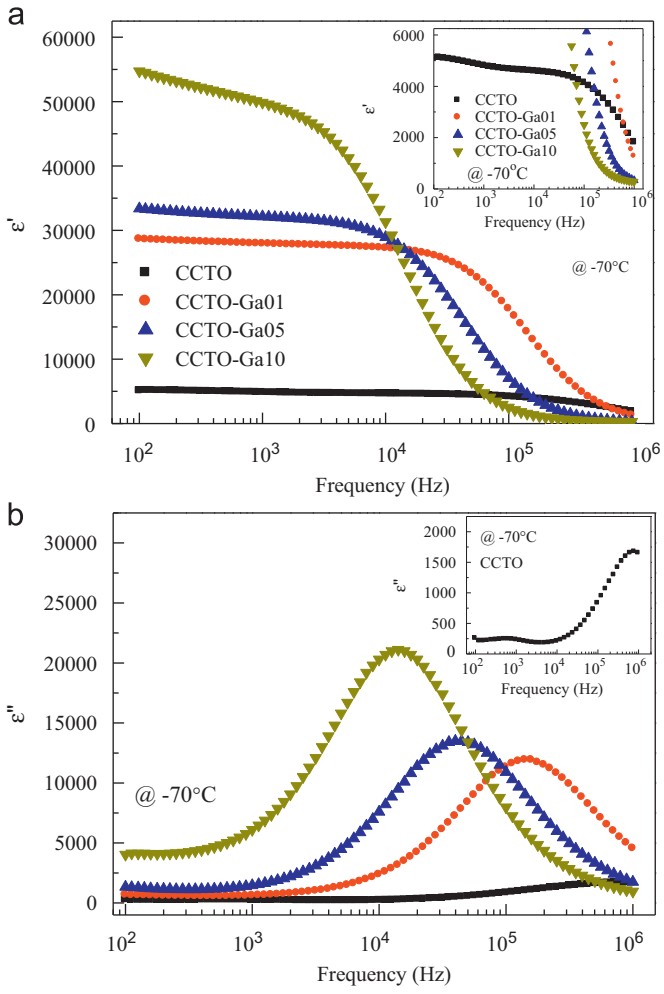

Fig. 3. Frequency dependence of (a) ε' and (b) ε'' at −70 °C for $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramic samples; insets of (a) and (b) show expanded views of ε' and ε'' data to show the dielectric data of the CCTO sample.

As seen in Fig. 3(a) and (b), the step-like decrease in ε' and corresponding ε'' peak shift to lower frequencies with increasing concentration of Ga^{3+}. This indicates an effect of Ga^{3+} substitution on the dielectric relaxation behavior of CCTO ceramics. The existence of dielectric relaxation behavior in dielectric materials is undesirable for electronic applications. This is because the relaxation process is certainly associated with extreme changes in ε' and ε'' (or tan δ). However, it is particularly valuable for investigating the possible physical mechanisms related to dielectric responses in the materials. In the absence of sample–electrode contact effect, the electrical microstructure of CCTO ceramics can be represented by the equivalent circuit consisting of two parallel resistance–capacitance ($R-C$) elements (grain and GB responses) connected in series [2]. Based on the Maxwell–Wagner polarization model for CCTO ceramics and the equivalent circuit model [12], a relaxation time (time constant, τ) of the dielectric relaxation process and the value of low-frequency ε' were respectively estimated to be $\tau \approx R_g C_{gb}$ and $\varepsilon' \approx C_{gb}/C_0$ (R_g, C_{gb}, and C_0 are the resistance of semiconducting grains, capacitance of insulating GBs, and the empty cell capacitance, respectively). The results reveal that ε' and hence

Table 1
ε' and tan δ values (at 20 °C and 1 kHz), relaxation activation energy (E_a), resistance of grains (R_g) (at −70 °C), nonlinear coefficient (α), breakdown field (E_b), and potential barrier height at GB (Φ_B) for $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics.

Sample	ε'	tan δ	E_a (eV)	R_g (Ω cm)	α	E_b (V cn^{-1})	Φ_B (eV)
CCTO	5439	0.153	0.096	~500	6.65	3177	0.765
CCTO-Ga01	31,330	0.044	0.095	~500	4.39	647	0.692
CCTO-Ga05	38,011	0.066	0.102	~1250	4.09	438	0.552
CCTO-Ga10	66,736	0.102	0.108	~2000	3.42	238	0.524

parameters related to C_{gb}, were enhanced by doping with Ga^{3+}. As shown in Fig. 4 and R_g data in Table 1, R_g tends to increase with increasing Ga^{3+} concentration. The increase in τ is therefore attributed to increases in C_{gb} and R_g. As demonstrated in Fig. 3, ε' of the CCTO-Ga05 ceramic was slightly increased even though grain size decreased slightly compared to the CCTO-Ga01 ceramic. This result may be due to the presence of fine-grained region in the CCTO-Ga01 ceramic. Thus, the true mean grain size of the CCTO-Ga01 ceramic should be smaller than 138 μm. Both the giant dielectric response and dielectric relaxation behavior of $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics are well described by the IBLC electrically heterogeneous model based on Maxwell–Wagner polarization at GBs.

Fig. 5 shows the frequency dependence of tan δ at 20 °C for all ceramic samples. Low-frequency tan δ values (<1 kHz) of CCTO ceramics are reduced by substitution of Ga^{3+}. The values of tan δ at 20 °C and 1 kHz for all samples are summarized in Table 1. tan δ of the CCTO-Ga01 sample was found to be lower than 0.05 over a wide frequency range. These are important results because the substitution of Ga^{3+} into CCTO ceramics not only enhances ε' greatly, but also decreases tan δ. As shown in the inset of Fig. 4, it was found that the total resistance of CCTO ceramics, which is governed by the total resistivity of GBs (R_{gb}), was enhanced by substitution of Ga^{3+} ions. This can cause a decrease in tan δ of Ga^{3+}-CCTO ceramics. As revealed in the inset of Fig. 2(e), CuO secondary phase was observed along the GB regions. The increase in R_{gb} may be attributed to the segregation of CuO phase at GBs.

It is also found that ε' of the CCTO-Ga01 and CCTO-Ga05 samples is nearly independent of temperature over the range from −70 to 100 °C, as shown in Fig. 6. Comparison of ε' values (1 kHz) at different temperatures to the value at 20 °C reveals that the variations of ε' for the CCTO-Ga01 and CCTO-Ga05 samples are found to be less than ±15% in the temperature range from −70 to 100 °C, as shown in the inset of Fig. 6. The variation of ε' for the undoped CCTO sample strongly depends on temperature when the temperature is higher than 50 °C. This result indicates that substitution of Ga^{3+} into CCTO ceramics can improve their dielectric properties, i.e., increase ε', reduce tan δ, and enhan1ce thermal stability of ε'. High ε' and low tan δ with good thermal stability in the CCTO-Ga01 are basic requirements for capacitor applications.

To study the effect of Ga^{3+} doping ions on the electrical response of GBs for the $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics, the current density−electric field strength ($J-E$) characteristics were investigated at various temperatures. We found that all ceramic samples exhibit nonlinear $J-E$ characteristics. The nonlinear coefficient (α) and the breakdown field (E_b) for the $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics were calculated from the $J-E$ curves. As summarized in Table 1, α values were determined in the current density range of 1−10 mA cm^{-2} and found to be 6.65, 4.39, 4.09, and 3.42 for the CCTO, CCTO-Ga01, CCTO-Ga05, and CCTO-Ga10 samples, respectively. E_b values obtained at $J=1$ mA cm^{-2}

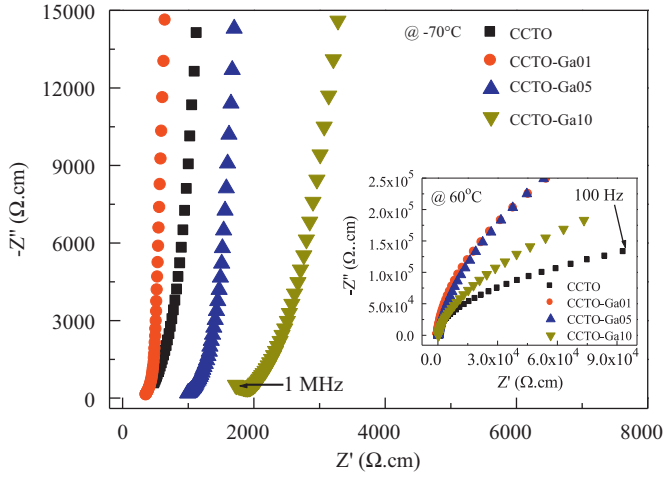

Fig. 4. An expanded view of high-frequency data of impedance complex plane (Z^*) plot at −70 °C for $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics; inset shows low-frequency data of impedance complex plane (Z^*) plot at 60 °C.

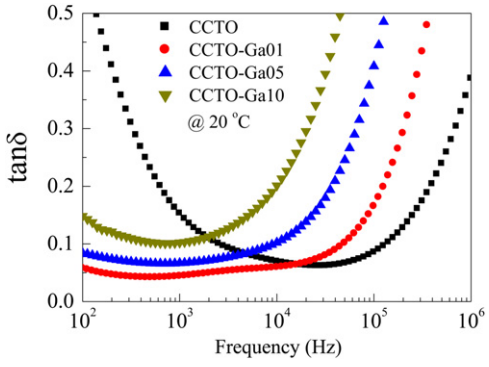

Fig. 5. Frequency dependence of tan δ at 20 °C for $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramic samples.

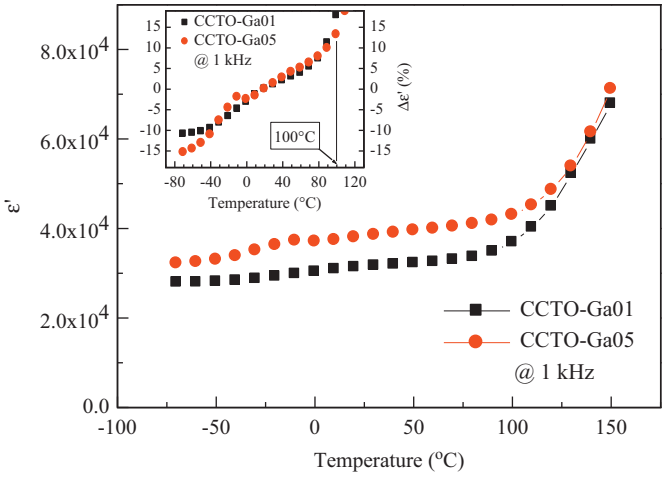

Fig. 6. Temperature dependences of ε' at 1 kHz for CCTO-Ga01 and CCTO-Ga05 samples; inset shows the variations of ε' for the CCTO-Ga01 and CCTO-Ga05 samples in the temperature range from −55 to 120 °C evaluated at the frequency of 1 kHz.

were 3177, 647, 438, and 238 V cm^{-1}, respectively. Both α and E_b decrease with increasing concentration of Ga^{3+} doping ions. Reduction of E_b is likely caused by the increase in the mean grain size, resulting in reduction of GBs density. In this work, the rate of increase in source voltage was 0.45 V/s. It was found that the $J-E$ characteristic tested at this rise rate was affected by Joule self-heating [10]. Thus, α values summarized in Table 1 may be overvalued.

As shown in Fig. 7(a) and (b), E_b decreases with increasing temperature. Non-Ohmic behavior tends to become linear Ohmic in nature as temperature is increased. This indicates the effect of temperature on the Schottky barrier [19,20]. The electrical response of GBs for CCTO polycrystalline ceramics is closely associated with the existence of Schottky barriers at the GBs [3,15,19,20,22]. Electrical conduction in the pre-breakdown region is dominated by the Schottky emission, which is associated with the electric field and temperature. As a result, J and E will follow the relationship [19,20]:

$$J = AT^2 \exp\left(\frac{\beta E^{1/2} - \Phi_B}{k_B T}\right) \tag{2}$$

$$\ln J = \frac{\beta E^{1/2}}{k_B T} + \left[\ln AT^2 - \frac{\Phi_B}{k_B T}\right] \tag{3}$$

where Φ_B is the barrier height of electrostatic potential at the GBs, A is the Richardson constant, E is the electric field, and β is a constant related to the potential barrier width. From Eq. (3), the last term on the right hand side can be expressed as

$$\ln J_0 = \ln AT^2 - \frac{\Phi_B}{k_B T} \tag{4}$$

According to Eq. (3), values of $\ln J_0$ at different temperatures can be calculated from the plots of $\ln J$ vs. $E^{1/2}$ by the linearly fitting of data. Then, the value of $\ln J_0$ can be obtained at $E=0$. As demonstrated in Fig. 7(c) and (d), the fitted results display a linear relationship between $\ln J$ vs. $E^{1/2}$. Using Eq. (4), Φ_B values for the $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics can be calculated from the slopes of the plots of $\ln J_0$ vs. $1000/T$, as shown in Fig. 8. The values of Φ_B were calculated to be 0.765, 0.692, 0.552, and 0.524 eV for the CCTO, CCTO-Ga01, CCTO-Ga05, and CCTO-Ga10 ceramics, respectively. Φ_B decreases as the concentration of Ga^{3+} doping ions was increased. In the absence of a dc bias, Φ_B is expressed as [15]

$$\Phi_B = \frac{qN_s^2}{8\varepsilon_0 \varepsilon' N_d}, \tag{5}$$

where q is the electronic charge, N_s is the acceptor (surface charge) concentration, ε' is the relative permittivity of materials, and N_d is the charge carrier concentration in the semiconducting grains. From Eq. (5), the reduction of Φ_B for $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics is likely to be caused by changes in N_s and N_d. As seen in Fig. 4, R_g tends to

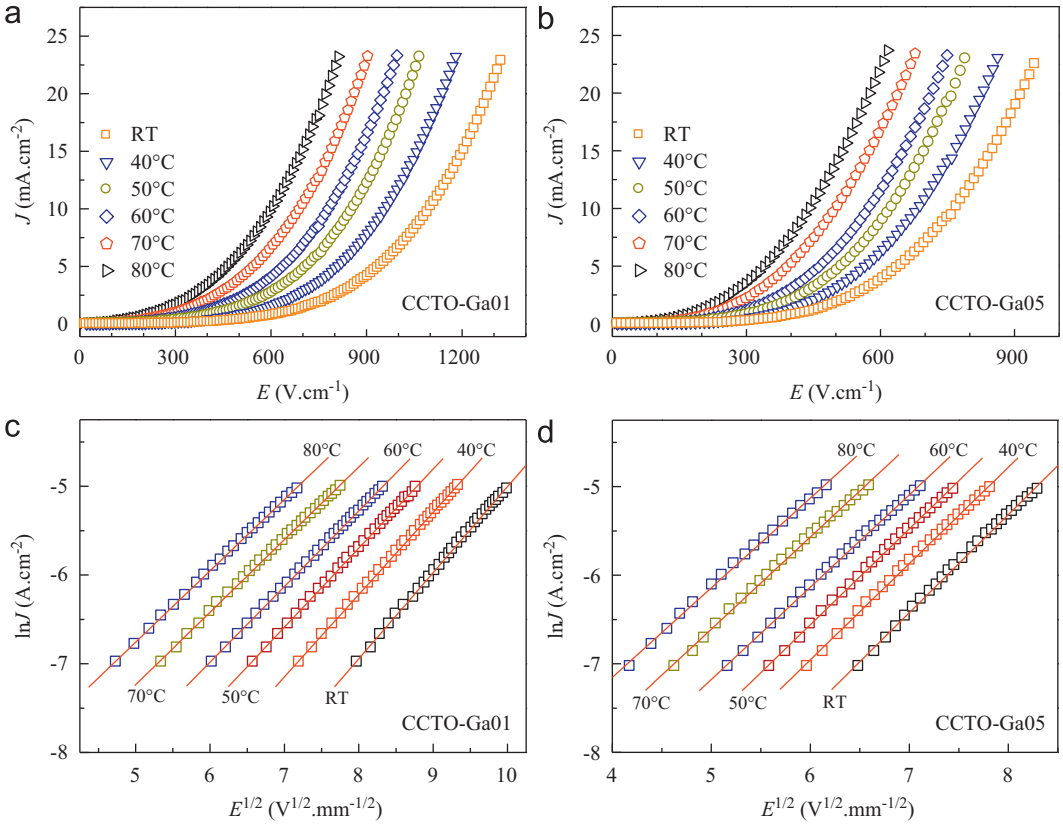

Fig. 7. (a,b) J–E curves of CCTO-Ga01 and CCTO-Ga05 samples at various temperatures, revealing non-Ohmic characteristics. (c,d) Plots of $\ln J$ vs. $E^{1/2}$ for the CCTO-Ga01 and CCTO-Ga05 samples.

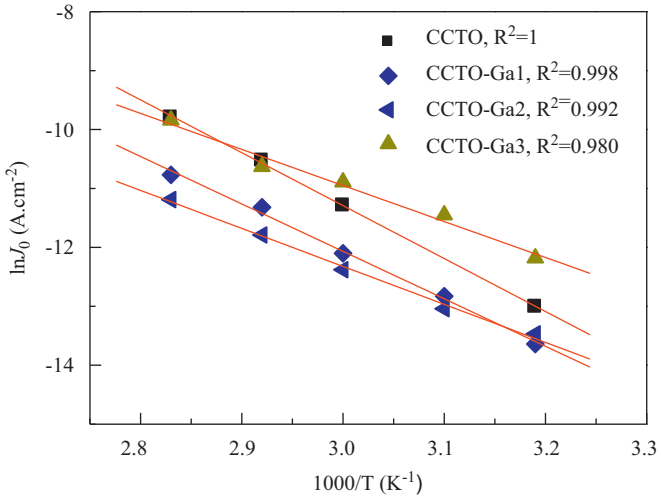

Fig. 8. Plots of ln J_0 vs. 1000/T for $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramic samples; the solid lines are fitted results using Eq. (4).

increase with increasing Ga^{3+} content, indicating a decrease in N_d. This results in enhancement of Φ_B. However, the experimental results reveal that Φ_B of $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics was decreased as the concentration of Ga^{3+} increased. Therefore, it is possible that the decrease in Φ_B for $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics may be attributed to a decrease in N_s. Generally, it is believed that the mechanism of potential barrier formation in CCTO ceramics is attributed to oxygen enrichment at the GBs [22]. Thus, the GB region may possess the *p*-type semiconductor nature, resulting from vacancies of metal ions and high oxygen content along the GBs compared with the *n*-type semiconductor nature inside the grains [22]. For Ga^{3+} substitution into CCTO ceramics, the creation of oxygen vacancies possibly results from charge compensation. The presence of oxygen vacancies can degrade the *p*-type semiconductor nature of GBs. We hypothesize that the observed decrease in Φ_B might be primarily caused by the enhancement of oxygen vacancies at the GBs due to the effect of Ga^{3+} substitution.

4. Conclusions

In conclusion, the microstructure, dielectric properties, and nonlinear $J-E$ characteristics of $CaCu_3Ti_{4-x}Ga_xO_{12}$ ceramics were investigated systematically. We found that Ga^{3+} doping ions have remarkable influences on the microstructure and electrical properties of CCTO ceramics. Ga^{3+} substitution into CCTO can cause a significant increase in the mean grain size. Substitution of 0.25 mol% Ga^{3+} in CCTO ceramics resulted in a large increase in ε' from 5439 to 31,331. Concurrently, $\tan\delta$ was reduced from 0.153 to 0.044 (at 20 °C and 1 kHz). The giant dielectric properties and relaxation behavior can be well described by the IBLC model based on Maxwell–Wagner polarization at GBs. It was found that the nonlinear coefficient, breakdown field, and potential barrier height at GBs decreased as Ga^{3+} content was increased.

Acknowledgments

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