Dielectric Properties of Eu-Doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ with Different Compensation Mechanisms

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Abstract To get a better understanding of the influence of rare-earth element doping, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) samples with a partial substitution of Ca with Eu with different compensation mechanisms were designed and prepared by solid-state reaction. All the ceramics were single phase, while the dielectric constants and thermally activated energy values for dielectric relaxation in Eu-doped ceramics were both lower than those of CCTO. $\text{Ca}_{0.875}\text{Eu}_{0.1}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (CECT1) exhibited a slight decrease in both the permittivity and electric resistance of grain boundaries compared with CCTO, while $\text{Ca}_{0.85}\text{Eu}_{0.1}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (CECT2) underwent a sharp decrease in permittivity associated with an abnormally large resistance. The different dielectric behavior indicates that the dielectric properties of CCTO are sensitive to the valence states of cations and defects. The variation of permittivity is related to the localization of carriers, which, according to the XPS results, should be caused by the presence of oxygen vacancies. The formation of defect complexes between cations and oxygen vacancies leads to the increase in resistance and prevents the hopping between Cu^+ and Cu^{2+} , which is an important source of the polarization in grain boundaries.

KEY WORDS: $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$; Compensate doping; Carrier localization; Oxygen vacancy

1 Introduction

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has attracted great interest for the giant dielectric constant (10^3 – 10^5) [1] and strong nonlinear current–voltage behavior [2] in recent years. Various

models such as internal barrier layer capacitance (IBLC) [3], intrinsic local dipole fluctuation [4], Cu deficiency [5], internal domains [6] have been proposed to interpret the origin of the unusual dielectric properties. Among them, the extrinsic IBLC model, which is composed of semi-conducting grains and insulating grain boundaries (GBs), is widely accepted. In this model, the interfacial Maxwell–Wagner polarization is responsible for the high dielectric constant of polycrystalline CCTO. Despite the huge efforts in the explanation of colossal dielectric constants, the properties of CCTO are still not ideal for application because of the amplitude of its dielectric loss. To make use of CCTO for technical applications, various efforts have been developed to reduce the high dielectric loss and maintain a relative high permittivity.

As widely used to optimize the dielectric behavior in BaTiO_3 , rare-earth (RE) elements such as La, Nd, Yb are also adopted for CCTO dielectric properties tailoring [7–9]. Considering the ionic radii and the charge neutrality, rare-

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earth elements are often used for Ca substitution according to the formula $\text{Ca}_{1-3x/2}\text{RE}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$. In most cases, CCTO ceramics undergo a sharp decrease in permittivity after the RE doping, while the resistance of GBs is ~ 3 – 5 orders of magnitude higher than for undoped CCTO [10]. The large decrease in permittivity is attributed to the decrease in the grain size [9]. Conversely, in other conditions, the reduction in the grain size is not the dominant factor compared with the thickness of GBs or space-charged layers at the interface between grains [10]. So, the origin of the decrease in permittivity is still controversial. Meanwhile, the abnormal increase in resistance in GBs is confusing and less addressed. On the other hand, the reduction in permittivity in RE-doped CCTO according to another formula of $\text{Ca}_{1-x}\text{RE}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ is less significant [7]. In this case, to maintain the electroneutrality, the concentration of low-valence species of Cu and Ti (Cu^+ and Ti^{3+}) or of oxygen vacancies will increase to compensate the higher valence of the RE elements compared to Ca^{2+} . This suggests that the valence states of cations and oxygen vacancies play an important role in the dielectric properties of CCTO. Although the influence of defect and valence has been studied [11], no convincing conclusion has been obtained so far.

To clarify the different behavior of RE-doped CCTO, we carried out a partial substitution of Ca by Eu according to two different charge compensation mechanisms: $\text{Ca}_{1-5x/2}\text{Eu}_{2x}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ($x = 0.05$, CECT1) with a mixture of ionic and electronic compensation and $\text{Ca}_{1-3x/2}\text{Eu}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ($x = 0.1$, CECT2) with ionic compensation. Since the mixed valence was proved to play an important role in the polarization of CCTO [4], the polyvalent Eu cation [12] seems more suitable than other RE elements for the charge compensation and polarization in CCTO. In these two samples, the total amount of Eu ions is the same, but the valence of polyvalent Eu ion will be different to maintain the charge neutrality. Samples of the former type contain the same amount of Eu^{2+} and Eu^{3+} , while in those of the latter type, Eu adopts the designed valence $+3$. In this work, the effects of Eu substitution on the microstructure, dielectric response and electric properties of CCTO have been investigated and discussed. Moreover, the dielectric properties were also studied as functions of temperature and frequency.

2 Experimental

2.1 Materials Preparation

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, $\text{Ca}_{0.875}\text{Eu}_{0.1}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (CECT1) and $\text{Ca}_{0.85}\text{Eu}_{0.1}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (CECT2) ceramics were prepared using the conventional solid-state reaction method.

Stoichiometric amounts of CaCO_3 ($>99\%$), CuO ($>99\%$), TiO_2 ($>99.9\%$) and Eu_2O_3 ($>99.9\%$) were used as reagents. The starting materials were mixed in an agate mortar and calcined at 950°C for 5 h, and then, the calcined powder was milled again and pressed into disk-shaped pellets (12 mm in diameter and 2 mm in thickness) at 200 MPa. Finally, these pellets were sintered at 1100°C for 12 h in air and then cooled at a rate of 100°C/h .

2.2 Characterization

Powder X-ray diffraction (XRD) (DX-2700, Dandong, China) using $\text{Cu } K_\alpha$ radiation was performed to confirm the crystal structure of the sintered ceramics with a step of 0.02° and count time of 3 s. The morphologies of the pellets were examined by scanning electron microscopy (SEM) (EVO MA10, Zeiss, Germany). The dielectric characteristics such as dielectric constant (ϵ), ac conductivity (σ_{ac}), impedance (Z) and modulus (M) of the ceramics were recorded with a broadband dielectric spectrometer (Turkey Concept 41, Novocontrol Technologies, Germany) in a range of temperature (173–473 K) and frequency (1 Hz–15 MHz), using silver paste as electrode. Valence states of cations in the ceramics were investigated using X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Scientific, USA).

3 Results and Discussion

3.1 Structural Characteristics

The powder XRD patterns for CCTO, CECT1 and CECT2 are shown in Fig. 1a. All the XRD results exhibit a single phase without any detectable secondary phase and can be indexed based on a cubic structure with the space group $\text{Im}\bar{3}$, which is in good agreement with the reported literature [13]. Secondary phases such as CuO were observed by some authors and are considered to play an important role in forming the insulating grain boundaries and to have a significant influence on ϵ' [14], but in our XRD results, there is no clear evidence of CuO segregation, which suggests that the content of CuO is very low and beyond the limit of detectability of the XRD measurement. The calculated lattice constants of CCTO, CECT1 and CECT2 are 7.3902, 7.3860 and $7.3860 \text{ \AA}$, and these values are in good agreement with those reported in literature [9]. The slight decrease in the lattice parameter for the doped samples can be attributed to the smaller ionic radii of Eu ($0.974 \text{ \AA}$) [8], but there is no difference between CECT1 and CECT2, probably as a consequence of the low content of Eu.

Fig. 1 XRD patterns **a** and SEM images for CCTO **b**, CECT1 **c**, CECT2 **d**

3.2 Microstructure

SEM images for each sample are presented in Fig. 1b–d: Large-size grains surrounded by a fine-grained matrix with relatively smaller grains were observed in the surface morphologies. The average grain sizes are estimated from the area in SEM images and can be divided into two size groups: the large and small grain sizes for CCTO, CECT1 and CECT2 are 20.1 ± 2.3 and 4.5 ± 0.7 μm , 5.5 ± 1.0 and 2.0 ± 0.5 μm , 4.3 ± 1.2 and 2.1 ± 0.6 μm , respectively. The great decrease in grain size in Eu-doped CCTO is common in CCTO substituted with rare-earth elements such as La^{3+} , Nd^{3+} , Y^{3+} and Sm^{3+} and has been attributed to the solute drag mechanism caused by segregation of the doping ions [15]. The segregation of rare-earth cations and of the CuO phase may play an important role in the solute drag mechanism.

3.3 Dielectric Properties

Two dielectric relaxations are observed from the temperature dependence of the dielectric constant and loss in the measurement range (Fig. 2), one at low temperature and high frequencies, and the other at high temperature and low frequencies. Figure 3 presents the frequency dependence of the real (ϵ') part of the complex permittivity at 173 K for the ceramics. All the ceramics exhibit a higher dielectric constant plateau in the low-frequency range which decrease rapidly to a lower plateau at high frequency. In the framework of dielectric relaxations represented by IBL model, the high-permittivity plateau at low frequencies primarily originates from the GB contribution, whereas the low-permittivity plateau at high frequencies primarily originates from the bulk contribution [16]. The ϵ' of CCTO, CECT1 and CECT2 at 10^3 Hz is about 5000, 4000 and 240. For the high-

Fig. 2 Temperature dependence of the dielectric constants of CCTO at different frequencies

Fig. 3 Frequency dependence of ϵ' at 173 K for CCTO, CECT1 and CECT2. Symbols are experimental data, and lines are fitting results by the modified Debye's model

frequency plateau, the ϵ' values of CCTO, CECT1 and CECT2 at 10^7 Hz are 117, 97 and 70, respectively. The above results suggest that Eu ions have a significant effect on the dielectric properties of both GBs and the bulk. It is meaningful to note that the permittivity of CECT1 is about 15 times higher than that of CECT2 at 10^3 Hz: Since the amount of Eu ions is the same and there is little difference in the average grain size between CECT1 and CECT2, the reason of the drastic decrease in ϵ' for CECT2 compared with CECT1 may be related to the defect state, so that the electrical properties and the ion valence need to be studied carefully. Since the grains and GBs behave different in structure and electric properties, they will be discussed separately in the following.

According to Grubbs [17], the activation energy of grain is related to the dielectric relaxations: So, the conduction of

grains could be reflected by the study of relaxation process. The plots of ϵ' are fitted by a modified Debye's equation:

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \quad (1)$$

where $\omega = 2\pi f$ is the angular frequency, τ is the relaxation time, ϵ_0 is the static dielectric constant, and ϵ_∞ is the dielectric constant at high frequency. The value $\alpha < 1$ stands for the deviation from Debye behavior, while the condition of $\alpha = 0$ indicates standard Debye behavior. The relaxation times (τ) at different temperatures calculated using Eq. (1) can be well fitted by the Arrhenius law with $1/T$:

$$\tau = \tau_0 \exp(-E_a/\kappa_B T) \quad (2)$$

where E_a is the activation energy required for the thermally activated process, τ_0 represents the pre-exponential factor, κ_B is the Boltzmann constant, and T is the absolute temperature. The values of E_a calculated from the slope of the fitted line are equal to 97 ± 1 meV for CCTO, 89 ± 1 meV for CECT1 and 77 ± 2 meV for CECT2, respectively, which are comparable with the reported values of 102 meV [18] and 98 meV [19]. It is noteworthy that CECT2 with ionic compensation has the minimum E_a , while CECT1 has a larger value but smaller than that of CCTO. This can be interpreted by the incorporation into the crystal lattice of Eu cations, since Eu^{3+} in CCTO plays a role of donor, leading to semiconductor grains.

The frequency dependence of the imaginary part Z'' of complex impedance Z^* is used to study the electrical properties of GBs. According to the equivalent circuit based on two parallel RC elements connected in series, Z'' can be expressed as follows:

$$Z'' = R_g \left[\frac{\omega R_g C_g}{1 + (\omega R_g C_g)^2} \right] + R_{gb} \left[\frac{\omega R_{gb} C_{gb}}{1 + (\omega R_{gb} C_{gb})^2} \right] \quad (3)$$

The frequency dependence of Z'' at different temperatures for CECT1 is shown in Fig. 4. R_{gb} can be calculated from the maximum value of Z'' ($Z''_{\max}$) using the relationship $R_{gb} = 2Z''_{\max}$ [20]. The R_{gb} values of CCTO, CECT1 and CECT2 at 413 K are found to be $2.3 \times 10^4 \Omega \text{ cm}$, $6.1 \times 10^3 \Omega \text{ cm}$ and $2.6 \times 10^7 \Omega \text{ cm}$, respectively. The Z'' peaks shift to higher frequencies with increasing temperature, indicating a thermally activated electrical response. The intensity of the Z'' peaks decreases with increasing temperature indicating a semiconductor behavior, but the grain boundary conductivity, $\sigma_{gb} = 1/R_{gb}$, is much lower than that of the bulk. The σ_{gb} also follows the Arrhenius law: The values of the activation energy E_{gb} calculated from the slope of the plot of $\ln(\sigma_{gb})$ versus $1000/T$ for CCTO, CECT1 and CECT2 are equal to 601 ± 8 meV, 523 ± 5 meV and 765 ± 12 meV, respectively.

Fig. 4 Frequency dependence of Z'' at 173 K for CECT1: The inset shows the Arrhenius plots of σ_{gb} for CCTO, CECT1 and CECT2

At high temperature, the ac conductivity (σ_{ac}) exhibits a nearly constant value at low frequencies and then increases moderately with increasing frequency (Fig. 5). So, the value of σ_{ac} at 1 Hz is estimated to be the value of the dc conductivity (σ_{dc}). Using the Arrhenius law, the calculated values of the activation energy E_{cond} required for the dc conduction process are 595 ± 3 meV, 524 ± 2 meV and 679 ± 8 meV, respectively, which are similar to the E_{gb} value. This result indicates that the dc conduction process is closely related to the electrical response of GBs. Interestingly, the GBs of CECT2 show different behaviors compared with the bulk: The anomalous increase of E_{gb} may be the main cause of the low permittivity. According to the IBLC model, the high permittivity is dominated by the space polarization in GBs, so that the permittivity plateau seems to be suppressed by the larger E_{gb} and E_{cond} , which is related to the localization of carriers. To confirm

Fig. 5 Frequency dependence of σ_{ac} at 473 K for CCTO, CECT1 and CECT2

the degree of localization, the combined plots of M'' and Z'' versus frequency are used to distinguish whether the short-range or long-range movement of charge carriers is dominant in the relaxation process [21]. In Fig. 6c, the peaks of M''/M''_{max} and Z''/Z''_{max} for CECT2 separate from each other at 473 K, indicating that the short-range movement of charge carriers cannot be neglected even at high temperature, while the mismatch of the peaks for CCTO (Fig. 6a) is slight, which means that both long- and short-range movements of carriers exist. For the sample of CECT1 in Fig. 6b, the peaks of M'' and Z'' almost collapse into one curve, indicating that the long-range movement of carriers is more important compared with CCTO and CECT2. So, the difference of E_{gb} and resistivity can be well interpreted

Fig. 6 Frequency dependence of normalized peaks M''/M''_{max} and Z''/Z''_{max} for a CCTO, b CECT1, c CECT2 at 473 K

by the localization of space charge: In CECT2, the hopping of carriers will be more difficult than those in the other two samples, so CECT2 possesses the largest E_{gb} and resistivity, while the long-range movement of carriers in CECT1 results in a minimum activation energy.

3.4 XPS Analysis

However, the reason of the huge difference of the localization of carriers for CECT1 and CECT2 is still unclear. To clarify this problem, the oxidation states of polyvalent cations were investigated by XPS. The $Cu2p$, $Ti2p$ and $Eu4d$ signals were recorded. Use of the Gaussian-Lorentzian curve fitting shows that both the $2p_{3/2}$ peaks for Ti and Cu are asymmetrical and can be split into two peaks: Ti^{3+}/Ti^{4+} and Cu^+/Cu^{2+} , while the $Eu\ 4d$ peaks can be fitted by a combination of Eu^{2+}/Eu^{3+} . The ionic ratios of Ti^{3+}/Ti^{4+} are calculated to be 0.47, 0.48 and 0.48 for CCTO, CECT1 and CECT2 (Fig. 7a), while the ratios of

Cu^+/Cu^{2+} are 0.48, 0.54 and 0.61 (Fig. 7b), respectively. The Eu^{2+}/Eu^{3+} ratio is 0.68 for CECT1 and 3.3 for CECT2 (Fig. 7c). This result suggests that all of the cations exhibit variable valence behavior except Ca. Meanwhile, the Eu ions have a more significant effect on the relative amount of Cu^+ , while the Ti^{3+}/Ti^{4+} ratios remain the same for the three samples. From the point of view of defect chemistry, the lower valent states of Ti^{3+} and Cu^+ in CCTO can be compensated by the oxygen vacancies to maintain the charge neutrality, but the simultaneous increase of Eu^{2+} and Cu^+ in CECT2 compared with CCTO means that more oxygen vacancies must be produced to compensate the valence change. For CECT1, the increase of the Cu^+ content is compensated by the formation of more Eu^{3+} , so that the production of oxygen vacancies will be much less than that for CECT2. The increase of the Cu^+ content will contribute to the long-range migration of charge carriers, which leads to n-type conduction, which is consistent with the decrease in activation energy of grains [22]. Conversely, the defects, including oxygen vacancies and low-valence cations, tend to segregate in grain boundaries [11], so that metal–oxygen vacancy defect complexes tend to form. Thus, the increases in resistivity and E_{gb} in CECT2 may be related to the formation of associated defects pairs such as $(Cu_{Cu}^+)'-V_O^{\bullet}$ [23], which result in the localization of carrier and also influence the space charge polarization. On the other hand, due to the long-range movement of carriers in CECT1, the dipoles led by the hopping of electrons among copper ions with various valences will contribute to the higher permittivity.

4 Conclusion

Single-phase Eu-doped CCTO ceramics were successfully prepared by solid-state reaction. The lattice constant and average grain size decreased simultaneously after Eu doping. The dielectric constants of grain and GBs for Eu-doped ceramics were both lower than those of CCTO. The drastic decrease in permittivity observed for $Ca_{0.85}Eu_{0.1}Cu_3Ti_4O_{12}$ is associated with the localization of charges at GBs, which also result in the large resistance of GBs. According to XPS results, this low permittivity may be attributed to the production of defect complexes between cations and oxygen vacancies. On the other hand, $Ca_{0.875}Eu_{0.1}Cu_3Ti_4O_{12}$ can maintain a relatively high permittivity due to the low content of oxygen. The mixed valence and oxygen vacancies are proved to play crucial roles in the polarization of grain boundaries. Larger contents of multivalent cations with less oxygen vacancies will result in a high permittivity, providing clues for the optimization of CCTO dielectric performance.

Fig. 7 XPS spectra of the CCTO, CECT1 and CECT2 ceramics

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