1 **Enhanced intrinsic permittivity and bulk response in**

2
3 **$\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics**

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Abstract

Considering the contribution of the mixed valence structure of Ti^{3+} and Ti^{4+} to the semiconductivity of grain, compositions with the formula of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ were designed and prepared. The dielectric bulk responses of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics were explored in detail. Changing Ti stoichiometry gives rise to an increase of the intrinsic permittivity. $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{3.925}\text{O}_{12}$ ceramic exhibits a higher intrinsic permittivity of ~ 120 at 60 MHz than that of pure $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics (87 at 60 MHz). Additionally, the activation energies of bulk responses are significantly enhanced by changing Ti stoichiometry, which is closely linked with the increase of $\text{Ti}^{3+}/\text{Ti}^{4+}$.

Keywords: Intrinsic permittivity; Bulk response; Ti stoichiometry; Mixed valence structure.

1. Introduction

$\text{Y}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (YCTO) is isostructural with $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) and can therefore be described as a perovskite-related phase with the general formula of $\text{AA}'_3\text{B}_4\text{O}_{12}$ and space group $\text{Im}\bar{3}$ with $a=2a_p$, where a_p is the aristotype perovskite cell edge [1,2]. The crystal structure of CCTO has been proved to retain centrosymmetric and cubic symmetry down to at least 37 K without evidence for a structural phase transition to lower symmetry [3,4]. With the similar electronic and crystal structure of CCTO, YCTO also exhibits similar phase structure. In recent years, YCTO ceramics were reported to exhibit a giant dielectric constant ($\epsilon' > 10000$), a relatively low dielectric loss (0.033 at 1 kHz) and a good temperature stability of dielectric response [5]. Based on combined impedance and electric modulus spectroscopy, it has been certified that YCTO ceramics consist of semiconducting grains and insulating grain boundaries. In other word, the giant permittivity in YCTO ceramics stems from an “extrinsic”, internal barrier layer capacitance effect, as opposed to an intrinsic, bulk effect. Owing to the semiconductivity of grains, it is difficult to establish its bulk dielectric response at near-ambient temperatures. Only at low temperature or high frequency range, the intrinsic dielectric constant of $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ (ACTO) can be measured [2,4,6].

Low temperature impedance spectroscopy and fixed frequency measurements show the bulk permittivity of CCTO and $\text{Na}_{1/2}\text{Bi}_{1/2}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (NBCTO) to be 100 and 200, respectively [6]. These values are higher than those calculated based on the Clausius-Mossotti equation or from

density-functional theory, suggesting that a different mechanism contributes to the high intrinsic permittivity of these two materials [7-9].

It is known that the core, fundamental question for CCTO and related ACTO materials is the origin of the bulk semiconductivity. Without the semiconducting grains there would be no high dielectric constant observed in ACTO. It is generally agreed that deviations from the nominal CCTO stoichiometry must occur in bulk areas to explain their semiconductivity. Several defect mechanisms have been proposed. However, they demonstrate opposite types of bulk semiconductivity, i.e. n-type electron or p-type hole conduction. Thus, bulk semiconductivity of CCTO could potentially rely on mixed valence $\text{Ti}^{3+}/\text{Ti}^{4+}$ or $\text{Cu}^+/\text{Cu}^{2+}$ (n-type), or $\text{Cu}^{2+}/\text{Cu}^{3+}$ (p-type) conduction [10-14].

In this work, considering the substantial contribution of the mixed valence structure of $\text{Ti}^{3+}/\text{Ti}^{4+}$ to the bulk response of YCTO ceramics, the compositions were designed and prepared according to the formula of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ to systematically investigate the effect of Ti stoichiometry on the bulk response of YCTO ceramics.

2. Experimental Procedure

$\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ polycrystalline bulk samples were prepared by solid-state reaction. Appropriate amounts of high-purity Y_2O_3 (99.9%), TiO_2 (99.99%), and CuO (99%) reagents were mixed by ball milling in alcohol for 10 h using agate balls. After drying, the mixed powders were then calcined at 910-950 °C for 10 h in air. The calcined mixture was ball-milled again for another 10 h and then pressed into disk pellets with a diameter of 15 mm under 100 MPa pressure. The pellets were sintered in air at 1050-1080 °C for 25 h, respectively.

The phase structures of sintered ceramics were characterized by X-ray diffraction (XRD, D/max-2550/PC, Rigaku, Japan) technique using $\text{Cu } K\alpha$ radiation. After being polished and then silver pasted on both sides, the ceramic samples were treated at 840 °C for 30 min to form the electrodes for electrical measurements. Dielectric dispersion and complex impedance were measured by Agilent 4294A (Palo Alto, CA) impedance analyzer in the frequency range of 40–110 MHz at ambient temperature. Temperature dependence of dielectric constant and loss was measured by the LCR meter (Agilent E4980A) from 80 to 375 K at 100, 300, 500, 700, and 1000 kHz, respectively. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCAPHI5400 (PerkinElmer, Santa Clara, CA) photoelectron spectrometer.

3. Results and Discussion

Fig. 1 shows the XRD patterns of the as-sintered $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics. All the major diffraction peaks in the XRD patterns can be indexed by a body centered cubic perovskite-related structure with space group $Im\bar{3}$ according to JCPDS # 75-2188. Furthermore, obvious secondary phase (TiO_2) is observed in the composition with $x \geq 0.050$ as indicated by the red arrow in Fig. 1(b).

Fig. 2 exhibits the frequency dependence of dielectric constant of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics, and the inset shows a magnified view of dielectric constant at high frequency range. As shown in Fig. 2 clearly, all ceramics exhibit considerable high dielectric constants and the dielectric constant is nearly frequency independent in the low frequency range from 40 Hz to ~100 kHz. As the measuring frequency increases to 1 MHz, the dielectric constant of all samples decreases rapidly and gradually approaches to another dielectric constant plateau above 30 MHz, which is frequently observed in ACTO ceramics. These features are attributed to Maxwell-Wagner relaxation behavior. Based on the IBLC model, the low-frequency giant dielectric constant plateau is mainly dominated by grain boundary effect, and the high-frequency dielectric constant plateau is closely linked with bulk response [15-17]. Herein, we mainly concentrate on the bulk response of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics, i. e. high-frequency dielectric response. It can be seen in the inset of Fig.2 that changing Ti stoichiometry gives rise to a significant increase in bulk permittivity of YCTO ceramics. Among the $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ compositions, the sample with $x = -0.075$ shows the highest bulk permittivity of about 120 at 60 MHz, which is much

higher than that of pure YCTO ceramics (87 at 60 MHz) and CCTO materials (~110 at 100 K).

It is well known that the dielectric polarizability is closely related to the intrinsic dielectric constant by the Clausius-Mosotti (C-M) equation [18]:

$$\alpha_D = 1/b[(V_m)(\epsilon' - 1)/(\epsilon' + 2)] \quad (1)$$

where V_m is the molar volume in $\text{\AA}^3$ and b is defined as $4\pi/3$. Based on Shannon's research basis [18], the ion polarizabilities of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics could be approximately calculated according to

$$\alpha(\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}) = 2/3\alpha(\text{Y}^{3+}) + 3\alpha(\text{Cu}^{2+}) + 4\alpha(\text{Ti}^{4+}) + 12\alpha(\text{O}^{2-}) \quad (2)$$

Where $\alpha(\text{Y}^{3+})$, $\alpha(\text{Cu}^{2+})$, $\alpha(\text{Ti}^{4+})$ and $\alpha(\text{O}^{2-})$ represent the polarizability of Y^{3+} , Cu^{2+} , Ti^{4+} and O^{2-} , respectively. And the values of $\alpha(\text{Y}^{3+})$, $\alpha(\text{Cu}^{2+})$, $\alpha(\text{Ti}^{4+})$ and $\alpha(\text{O}^{2-})$ are 3.84, 2.11, 2.94 and 2.00, respectively. According to Eq. (2), the ion polarizabilities of $x=-0.075$, 0.00 and 0.075 are 44.43, 44.65 and 44.87, respectively. Based on Eq.(1), the dielectric constants of $x=-0.075$, 0.00 and 0.075 are separately calculated to be 38.71, 41.26 and 44.50, which are almost identical to dielectric constants expected either based on the Clausius-Mosotti equation or from density functional theory ($\epsilon' \sim 40-50$ for CCTO) [7,8]. Like CCTO and NBCTO, It is noted that the intrinsic permittivity of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics in the insets of Fig. 2 is much higher than that from the Clausius-Mosotti equation, suggesting that other polarizations, apart from ionic polarization, may also play important roles in the dielectric polarization of these compounds [4,6]. To explain this high bulk permittivity, Matthew et al. proposed one possible mechanism. The Ti–O–Ti bonds in ACTO

lattice depart significantly from a linear arrangement with an angle of 180° and flexural polarizability linked with these nonlinear bonds could be responsible for the high bulk permittivity [6].

In order to further elucidate the bulk response of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics, the low temperature dielectric responses were studied. Fig. 3 demonstrates the temperature dependence of dielectric constant of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics at the temperature range from 80 to 375 K at different frequency. It can be clearly observed that dielectric constants of all samples show step-like decreases with decreasing the temperature at different measurement frequency. The step-like decreases of dielectric constant gradually shift to high temperature with increasing the measurement frequency. Similar with the frequency dispersion of dielectric constant in Fig. 2, the giant permittivity plateau observed from 200 to 375 K is mainly attributed to grain boundary effect, and the permittivity plateau observed from 80 to 100 K is mainly dominated by the bulk response. Corresponding to the step-like decrease of dielectric constant, obvious dielectric loss factor peaks are observed in Fig. 4 which shows the temperature dependence of dielectric loss factor of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics from 80 to 375 K at different frequencies. As can be seen in Fig. 4, the dielectric loss factor peaks shift to high temperature with increasing the measurement frequency, indicating a thermally activated dielectric behavior. The relations between the observed temperature and frequency of ϵ'' peak (T_{max}) obey the Arrhenius law, which is shown in Fig. 5. It can be seen that the Arrhenius plots ($\ln(f_{\text{max}})$ versus $1/T$) of all the samples exhibit linear relationship. The activation

energies for the relaxation process of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics with $x = -0.10, -0.05, 0.00, 0.05,$ and 0.10 are $0.123, 0.120, 0.112, 0.119,$ and 0.121 eV, respectively. It is evident that these activation energies are associated with the bulk response of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics, and the variation of Ti stoichiometry gives rise to a slight increase of the activation energy of bulk response. As we know, the semiconductivity of grain in ACTO is mainly attributed to the electron hopping between Ti^{3+} and Ti^{4+} [10-14]. Therefore, it can be concluded that the activation energy of bulk response should be closely linked with $\text{Ti}^{3+}/\text{Ti}^{4+}$. To further explore the mixed valence structure of $\text{Ti}^{3+}/\text{Ti}^{4+}$, the XPS measurement was carried out. The XPS spectra of all $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ samples suggest the coexistence of Ti^{3+} and Ti^{4+} . Fig. 6 exhibits the calculated area ratio of Ti^{3+} to Ti^{4+} . It can be seen that changing Ti stoichiometry induces an increase of $\text{Ti}^{3+}/\text{Ti}^{4+}$, which will generate more polar clusters to intensify the interaction between micro-domains [19,20]. This could extend the relaxation process and enhance the activation energy of bulk response as shown in Fig. 5.

Conclusion

Dielectric bulk response of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics was effectively modified by slightly tuning Ti stoichiometry. The variation of Ti stoichiometry results in a significant increase of intrinsic permittivity of YCTO ceramics. Among the $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ compositions, the sample with $x=-0.075$ shows the highest intrinsic permittivity of about 120 at 60 MHz, which is much higher than that of pure $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics (87 at 60 MHz). Moreover, the $\text{Ti}^{3+}/\text{Ti}^{4+}$ is enhanced by changing Ti stoichiometry, which is responsible for the increased activation energies of bulk response.

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Figure captions

Fig. 1. XRD patterns of the as-sintered $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ($-0.10 \leq x \leq 0.10$) ceramics.

Fig.2. Frequency dependence of the real part of dielectric constant for $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ($-0.10 \leq x \leq 0.10$) ceramics.

Fig.3. Low-temperature dependence of the real part of dielectric constant for $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics: (a) $x=-0.10$, (b) $x=-0.05$, (c) $x=0.00$, (d) $x=0.05$ and (e) $x=0.10$, respectively.

Fig.4 Low-temperature dependence of the imaginary part of dielectric constant for $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics: (a) $x=-0.10$, (b) $x=-0.05$, (c) $x=0.00$, (d) $x=0.05$ and (e) $x=0.10$, respectively..

Fig.5. Arrhenius plots of $\ln(f_{\text{max}})$ versus $1000/T$ for the grain response of $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{4+x}\text{O}_{12}$ ceramics: (a) $x=-0.10$, (b) $x=-0.05$, (c) $x=0.00$, (d) $x=0.05$ and (e) $x=0.10$, respectively. The solid line is linear-fitting line..

Fig.6. Ti^{3+} to Ti^{4+} as a function of Ti stoichiometry.

Figure 1

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