Dielectric and Nonohmic Properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{SrTiO}_3$ Ceramics

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In this work, $(1-x)\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ - $x\text{SrTiO}_3$ [$(1-x)\text{CCTO}/x\text{ST}$, $x = 0\%$ to 2%] ceramic samples were prepared by the solid-state reaction method. The dielectric and electrical properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{SrTiO}_3$ (CCTO/ST) ceramics were investigated. The results show that a small amount of Sr^{2+} can enter the lattice of CCTO. The mean grain size of the ceramic samples increased greatly for $x = 0.5\%$ and then decreased for $x = 0.75\%$ to 2% . ST addition and Sr^{2+} preferential occupancy in CCTO grains should be responsible for the change of the microstructure. Interestingly, the dielectric constant (ϵ) of the 0.5% ST-added sample increased significantly while the dielectric loss ($\tan \delta$) remained low. With further increase of the ST content, the ϵ and $\tan \delta$ values of the CCTO ceramics decreased monotonically while the nonlinear current-voltage properties were significantly enhanced. The change in the potential barrier height is thought to be the main cause for the opposite behaviors in the dielectric properties and nonohmic characteristics.

Key words: Composite ceramics, microstructure, grain boundary, electrical properties

INTRODUCTION

Recently, the perovskite material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has attracted considerable attention from researchers in scientific fields due to its giant dielectric constant ($\sim 10^3$ Hz to 10^5 Hz).^{1–3} High dielectric constant ϵ is essential to allow smaller capacitive components, which offers an opportunity to decrease the dimensions of electronic devices.^{4–6} The origin of the giant dielectric constant effect has been extensively investigated. To date, various mechanisms such as intrinsic polarization, relaxation, or the internal barrier layer capacitor (IBLC) model have been put forward. Among these, the IBLC model is the most widely accepted mechanism for CCTO ceramics, based on impedance spectroscopy (IS) measurements.^{7–9} Based on the IBLC model, the dielectric property depends strongly on

aspects of the material microstructure such as the grain size and high resistivity at grain boundaries (GBs). It has been reported that CCTO ceramics with larger grain size usually have higher dielectric constant.^{10–12} Therefore, the effect of grain size on the dielectric constant is one of the pieces of evidence for the extrinsic mechanisms as elucidated by the IBLC model.^{13,14}

However, its relatively high dielectric loss is one of the main problems regarding use of CCTO in practical applications. In particular, an enhancement of ϵ is usually accompanied by an increase in $\tan \delta$. It is essential to decrease the dielectric loss if CCTO ceramics are to be introduced into commercial applications such as barrier layer capacitors. Therefore, studies on the dielectric loss of CCTO have received much attention.^{1,13,14} The relationship between the dielectric loss and frequency has been clearly shown in some research results.^{1,5,6,10,11} From these studies, it can be concluded that the dielectric loss in CCTO ceramics mainly originates from

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semiconducting grains and insulating GBs. Numerous attempts have been made to reduce the current leakage by modifying the semiconducting properties and the interfacial structure of CCTO ceramics. One effective approach is the use of elemental substitution such as La at Ca site or Zr and Ta at Ti site, which has been reported to reduce the dielectric loss in CCTO.^{11,13} Another proposed approach for reducing the dielectric loss is to combine the high-dielectric-constant material with another insulating oxide with low tangent loss to improve the final material characteristics, e.g., GeO_2 , Cr_2O_3 , and CaTiO_3 .^{15–17} These results suggest that the appropriate amount of dopant can give rise to an increase of the GB resistance, which contributes to low dielectric loss. GBs are the main source of internal barrier layers in CCTO ceramics, and hence characterization of the GBs of CCTO ceramics is very important. In addition to high ϵ values, CCTO ceramics can also exhibit nonlinear current–voltage characteristics. This special behavior is believed to originate from the existence of intrinsic potential barriers at GBs, i.e., Schottky barriers. This behavior might be desirable for varistor applications.^{13,18,19}

SrTiO_3 (ST) has a low dielectric loss as an incipient ferroelectric, though it does not possess attractive properties in the pure form.²⁰ Therefore, it would be interesting to add a small amount of ST to CCTO and investigate the dielectric and electric properties of such composite materials. In this work, polycrystalline $(1-x)\text{CCTO}/x\text{ST}$ ($x = 0\%$ to 2%) ceramics were synthesized using a conventional solid-state synthesis method. The effect of ST addition on the microstructure and the dielectric and electrical properties of CCTO ceramic was investigated.

EXPERIMENTAL PROCEDURES

Samples of $(1-x)\text{CCTO}/x\text{ST}$, where $x = 0.0\%$, 0.5% , 0.75% , 1% , 1.5% , and 2% (referred to as ST0, ST1, ST2, ST3, ST4, and ST5, respectively), were synthesized by the solid-state reaction method. First, high-purity (99.99%) chemicals CaCO_3 , CuO , and TiO_2 in powder form were mixed and ground together according to the stoichiometric ratio using an agate mortar and pestle for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ synthesis. The mixed powders were then calcined at 950°C for 8 h, followed by grinding for 4 h. Then, the calcined powder was pressed into pellet form and sintered at 1050°C for 8 h. Secondly, high-purity (99.99%) chemicals SrCO_3 and TiO_2 in powder form were mixed according to the stoichiometric ratio and ground well for 4 h. For synthesis of SrTiO_3 , calcination and sintering were applied at high temperature of 1150°C and 1400°C , respectively. Thirdly, the powders of CCTO and ST in stoichiometric proportions were mixed and thoroughly ground for 4 h to achieve good homogenization, then calcined at 950°C in air for 8 h. The calcined mixtures were reground for 2 h, then

pressed at 15 MPa into disk-shaped pellets. The pellets were sintered at 1050°C for 8 h in air, followed by furnace cooling. The sintered pellets were polished to thickness of 2 mm and coated with silver paste on both sides to act as electrodes and cured at 500°C for half an hour. Diffractograms of the sintered samples were recorded using x-ray powder diffraction (XRD) to identify the phase. Lattice parameters were calculated by the least-squares method using the Powder X program.²¹ The fracture surface of the samples was examined by scanning electron microscopy (SEM). The dielectric properties and impedance spectrum of the ceramics were determined using a precision impedance analyzer (Agilent 4294A) from 100 Hz to 1 MHz at room temperature. The current–voltage (I – V or J – E) characteristics were measured by using a high-voltage measuring unit (American Radiant). The nonlinear coefficient (α) values were calculated from the following formula:

$$\alpha = \frac{\log(I_2/I_1)}{\log(V_2/V_1)}, \quad (1)$$

where V_1 and V_2 are the voltages at current values of $I_1 = 0.1$ mA and $I_2 = 1$ mA, respectively. The breakdown electric field (threshold electric field) (E_b) was obtained when a current density of 1 mA flowed through the ceramics.

RESULTS AND DISCUSSION

Figure 1 shows powder XRD spectra measured at room temperature for the CCTO and CCTO/ST ceramic samples. All of the XRD patterns exhibit the main phase of CCTO with cubic perovskite structure [Joint Committee on Powder Diffraction Standards (JCPDS) card no. 75-2188] with no second phases of raw materials. This result is similar to those in published literature.²² The lattice constant

Fig. 1. XRD patterns of CCTO/ST ceramics with different ST contents.

Table I. Lattice parameter, dielectric constant (ϵ), dielectric loss ($\tan \delta$) (at 10 kHz and room temperature), nonlinear coefficient (α), breakdown voltage (E_b), and barrier height (Φ_b) of CCTO and CCTO/ST ceramics

Sample	Lattice Parameter ($\text{\AA}$)	ϵ	$\tan \delta$	α	E_b (V/cm)	Φ_b (eV)
ST0	7.3930(2)	7372	0.14	2.44	343	0.650
ST1	7.3936(2)	11,683	0.16	2.59	268	0.642
ST2	7.3938(3)	4725	0.12	2.09	537	0.664
ST3	7.3940(3)	2883	0.09	2.36	677	0.675
ST4	7.3941(2)	1972	0.04	3.18	716	0.724
ST5	7.3940(2)	1431	0.03	9.48	1387	0.765

of the samples calculated by the least-squares method using the Powder X program is listed in Table I. The results indicate that the lattice constant of samples ST1, ST2, and ST3 was increased compared with that of sample ST0, indicating that a small amount of Sr^{2+} can enter the lattice of CCTO. With further increase of the ST content ($x > 1\%$), the lattice constant remained nearly unchanged, suggesting that no more Sr^{2+} enters the CCTO grains. On the other hand, the second phase of ST was not observed in the XRD patterns of the ceramic samples, which should be due to its low content.

Figure 2 presents SEM images of the fracture surfaces of the CCTO and CCTO/ST ceramic samples. The ceramic samples exhibited a bimodal grain size distribution with small grains of several micrometers and large grains of size from 10 μm to 150 μm . The mean grain size of the CCTO ceramic was greatly increased by addition of 0.5% ST. Then, it decreased with increasing ST content from 0.75% to 2%. Although the bimodal distribution of CCTO grains remained apparent, the grain size became more homogeneous within this weight ratio range. Hence, a small amount of ST addition ($x \leq 0.5\%$) improved grain growth in the CCTO/ST ceramics during the sintering stage, while further ST addition ($x > 0.5\%$) inhibited the GB mobility in CCTO. Yang²³ and Vangchangyia²² reported that the mean grain size in $\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics first increased and then decreased with increasing Sr^{2+} doping content, while a monotonically increasing mean grain size with increasing Sr content x to 0.3 was observed by Li et al.²⁴ Despite these different results, they all agree that a small amount of Sr doping causes abnormal grain growth. However, the mechanisms behind this relation remain to be resolved. The presence of CuO liquid phase in CCTO and BaTiO_3 -based ceramics has been acknowledged as the main parameter promoting grain growth and ceramic densification because of its low melting point and liquid-phase effect.^{11,15,22} Based on these results, a small amount of Sr^{2+} entering the lattice of CCTO should enhance segregation of Cu-rich phase and promote grain growth since ST has a relatively high melting point, over 2000°C. Furthermore, a small additional amount of ST also assists in inducing better contact between neighboring grains and enhancing the

mobility of GBs. Both of these effects result in larger grains and thin interfaces in sample ST1. However, further ST addition causes increased thickness of the interfaces, and no more Sr ions enter the lattice, which is not beneficial to segregation of Cu-rich phase. From the insets in Fig. 2c and f, it is obvious that the GB thickness of CCTO increases with increasing ST content from 0.75% to 2%, and consequently, the contact of CCTO particles would be more restrained. The abnormal grain growth is greatly suppressed, leading to a small mean grain size in CCTO ceramics.

Figure 3a illustrates the frequency dependence of the dielectric constant ϵ of the CCTO and CCTO/ST ceramic samples with different x values measured at room temperature. It is clearly observed that the dielectric constant of ceramic sample ST1 was greatly increased compared with that of sample ST0. When the ST content was further increased from 0.75% to 2%, the dielectric constant decreased rapidly and was almost frequency independent. The frequency dependence of $\tan \delta$ in all the CCTO ceramics is shown in Fig. 3b. It is found that the $\tan \delta$ value of sample ST1 is slightly increased compared with that of sample ST0. With further increase of the ST content, $\tan \delta$ decreased continuously. There are two Debye-like relaxations, one at low and the other at high frequencies, which can be observed in the dielectric loss plot shown in Fig. 3b. The ϵ and $\tan \delta$ values of all the samples at 10 kHz are summarized in Table I. The $\tan \delta$ values of samples ST3, ST4, and ST5 were greatly reduced to 0.09, 0.04, and 0.03, respectively, while ϵ remained above 10^3 . These ϵ and $\tan \delta$ values are acceptable for ceramic capacitor applications.²⁵

According to the IBLC model, the dielectric constant is related to the microstructure, and the effective dielectric constant can be calculated from the expression $\epsilon_{\text{eff}} = \epsilon_{\text{gb}}(d_g + d_{\text{gb}})/d_{\text{gb}}$, where d_g , d_{gb} , and ϵ_{gb} are the mean grain size, the thickness of the GB layer, and the dielectric constant in the GB layer, respectively.²⁶ Addition of 0.5% ST increases d_g and decreases d_{gb} , corresponding to an improvement of the dielectric constant of CCTO. However, further ST addition ($x = 0.75\%$ to 2%) results in a decrease of d_g . Meanwhile, more ST resides at GBs, increasing d_{gb} and decreasing ϵ_{gb} , since the ST phase at the GBs has a low dielectric constant value

Fig. 2. Surface SEM images of CCTO and CCTO/ST ceramics: (a) ST0, (b) ST1, (c) ST2, (d) ST3, (e) ST4, and (f) ST5. Insets of (c, f) show high-magnification SEM images for samples ST2 and ST5, respectively.

of about 300 at low frequency.²⁷ As a result, the dielectric constant of the composite ceramics decreases monotonically with increasing ST content from 0.75% to 2%. In addition, grain refinement can enhance the specific surface area, resulting in an increase of the material resistivity. This will contribute to the frequency independence of the ST-added samples.²⁸

According to the IBL model, CCTO ceramics are electrically heterogeneous and consist of semiconducting grains with insulating GBs. As mentioned above, the dielectric loss in CCTO mainly originates from the conductivity of grains as well as that of the insulating barriers. The impedance of electroceramics has been modeled using an equivalent circuit

consisting of two parallel RC elements connected in series: one for the semiconductive grain contribution, and the other for the GB response. In some cases, only the semicircular arc at a low frequency range is observed. In these cases, the nonzero intercept of the large arc at high frequencies usually represents the resistance of grains (R_g) while that at low frequency represents the resistance of GB (R_{gb}). In general, the higher the R_{gb} value, the lower the dielectric loss in the low-frequency region. Figure 4 shows Z^* (Z' versus $-Z''$) plots for the CCTO and CCTO/ST ceramics at room temperature. The impedance spectroscopy (IS) results reveal that the low-frequency impedance corresponding to R_{gb} decreases slightly for ST1, then increases with

Fig. 3. Frequency dependence of dielectric constant (a) and dielectric loss (b) of CCTO and CCTO/ST ceramics at room temperature.

increasing ST content, whereas the diameter of the high-frequency arc corresponding to R_g changes little. A small amount of ST addition improves the grain growth and decreases R_{gb} . As the ST addition increases, more insulating ST resides between CCTO grains, causing an increase of R_{gb} which narrows the leakage loss. The SEM micrographs (Fig. 2) also suggest that addition of $\geq 0.75\%$ ST causes a reduction in the mean grain size and thereby increases the density of GBs in the samples, contributing to the significant drop in the dielectric loss of the ST-added samples. The IS results can well explain the variation of the dielectric loss. Therefore, the change in the dielectric loss in the CCTO/ST system can be attributed to the variation of R_{gb} with ST addition.

In this work, we also investigated the effects of ST addition on the nonlinear current–voltage properties of the CCTO ceramics. As shown in Fig. 5, all the ceramic samples exhibited nonohmic properties. The breakdown voltage E_b and nonlinear coefficient α calculated from the J – E curves are listed in Table I. With increasing ST content, the E_b and α values first decrease and then increase. Especially for samples ST4 and ST5, the E_b and α values are larger than those of the CCTO ceramic sample.

It has been proposed that the nonlinear J – E property of CCTO ceramics originates from Schottky barriers at GBs.^{29,30} A double Schottky barrier is normally created in electroceramics between grains and GBs, while GBs act as an extrinsic source of impedance. The electric conduction in the

Fig. 4. Complex impedance (Z' versus $-Z''$) plots for CCTO and CCTO/ST ceramics at room temperature.

Fig. 5. Nonohmic characteristics (J versus E) of CCTO and CCTO/ST ceramics at room temperature.

prebreakdown region is dominated by thermionic emission of Schottky type, which is related to the electric field and temperature. Therefore, the electric current density (J) and electric field (E) will follow the relationship³¹

$$\ln\left(\frac{J}{AT^2}\right) = \left(\frac{\beta}{k_B T}\right) E^{\frac{1}{2}} - \frac{\Phi_b}{k_B T}, \quad (2)$$

where A is Richardson's constant, Φ_b is the potential barrier height, k_B is the Boltzmann constant, T is the temperature (K), and β is a constant related to the potential barrier width. According to the Schottky conduction model, plots of $\ln J$ against $E^{1/2}$ for the CCTO ceramics can be used to determine the potential barrier height in the low current density range. The electric current density (J) versus the electric field (E) was measured at room temperature. As shown in Fig. 6, a good linear relationship between $\ln J$ and $E^{1/2}$ was obtained for each sample, indicating that a Schottky barrier should exist at

Fig. 6. Plots of $\ln(J/AT^2)$ versus $E^{1/2}$ for CCTO and CCTO/ST ceramics.

GB regions. The Φ_b values obtained from Fig. 6 for the CCTO and CCTO/ST ceramics are listed in Table I. Addition of 0.5% ST results in a slight decrease of Φ_b , while further ST addition causes an increase of Φ_b . From Table I, it can be found that the dielectric constant as well as the dielectric loss are inversely proportional to the height of the Schottky barriers Φ_b .

The barrier can typically be characterized as a GB impedance, since it is resistive (in comparison with the grain) and has high capacitance owing to the thin width of the depletion region with respect to the grain size. In the absence of a direct-current (dc) bias, Φ_b can be expressed as³²

$$\Phi_b = \frac{eN_s^2}{8\epsilon_0\epsilon_r N_d}, \quad (3)$$

where e , ϵ_0 , and ϵ_r are the electronic charge, vacuum dielectric constant, and material dielectric constant, respectively. N_s is the concentration of effective surface states, and N_d is the concentration of ionized donors. From Eq. 3, it is easy to see that the dielectric constant ϵ_r is inversely proportional to the height of the Schottky barriers Φ_b , which is consistent with the results in Table I. In addition, it is observed that the variations in E_b are consistent with the changes in Φ_b , indicating that the breakdown voltage is closely correlated with the barrier height. Therefore, the opposite behaviors for the dielectric properties and nonohmic characteristics can be ascribed to the change in the height of the Schottky barriers Φ_b . An increase in Φ_b is thought to be the main cause for the improvement of both R_{gb} and E_b for CCTO ceramics. According to the dielectric and nonlinear current-voltage properties, it can be concluded that the dielectric constant of CCTO ceramics can be significantly improved by addition of 0.5% ST, whereas $\tan \delta$ and the nonlinear properties are improved by further ST

addition. All of the experiments were repeated several times with similar results.

CONCLUSIONS

$(1 - x)\text{CCTO}/x\text{ST}$ ceramics were successfully prepared by the solid-state synthesis method to study the effects of ST addition on the microstructure and the dielectric and nonohmic properties of CCTO. The results show that the ceramic samples form a single crystalline phase and that a small amount of Sr^{2+} ($x \leq 1\%$) can enter the lattice of CCTO. The mean grain size of the ceramic samples greatly increased for $x = 0.5\%$ and then decreased for $x = 0.75\%$ to 2% . ST addition and Sr^{2+} preferential occupancy in CCTO grains should be responsible for the change of the microstructure. The ϵ value of the 0.5% ST-added sample increased significantly, while the dielectric loss $\tan \delta$ remained low. Further ST addition caused the dielectric constant to decrease but significantly improved the frequency stability compared with the CCTO ceramic sample. The $\tan \delta$ values of samples ST3, ST4, and ST5 were greatly reduced to 0.09, 0.04, and 0.03, respectively, while ϵ remained above 10^3 at 10 kHz, being acceptable for ceramic capacitor applications. The IS results can well explain the variation of the dielectric loss. Addition of ST ($x = 0.75\%$ to 2%) can also significantly enhance the breakdown voltage of CCTO ceramic. A double Schottky barrier is evidenced by the linear behavior between $\ln J$ and $E^{1/2}$ in GB regions. An increase in Φ_b is thought to be the main cause for the improvement of both R_{gb} and E_b of the CCTO ceramics. These improvements of dielectric and electric characteristics have great significance for potential applications.

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