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Effect of different pH values adjusted by ammonia on the

dielectric properties of CaCu₃Ti₄O₁₂ ceramics prepared by a

sol-gel method

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Abstract

To investigate the effect of different pH values (pH = 1, 3, 5, 7) of a solution used to prepare CaCu₃Ti₄O₁₂ (CCTO) ceramics on the microstructure and dielectric properties of the resultant ceramics, the acid regulator in the solutions was replaced with an alkaline regulator, ammonia water, and CCTO ceramics were prepared through a sol-gel method. The data show that the dielectric constants of the as-prepared samples maintained relatively high values in the frequency range from 1 to 10⁷ Hz. In addition, the dielectric loss decreased to 0.028 at 10³ Hz for the sample prepared at pH = 5. Moreover, the results reveal that the grain size, porosity and content of the CuO phase at the grain boundaries of the CCTO ceramics varied with the pH value. Our results indicate that using an alkaline regulator to adjust the pH value of the synthesis solution is an effective method for reducing the dielectric loss of CCTO ceramics.

Keywords: CaCu₃Ti₄O₁₂(CCTO); Sol-gel processes; pH value; Alkaline regulator; Dielectric response.

1. Introduction

Since CaCu₃Ti₄O₁₂ (CCTO) ceramics were discovered in 2000 [1], extensive research has been devoted to them because of their high dielectric constant (ϵ_r) of approximately 10⁴–10⁵ and phase-transition stability over a wide temperature range from 100 to 400 K [2]. CCTO ceramics also exhibit non-ohmic characteristics, which makes these ceramics promising for applications such as energy storage capacitors and over-voltage protection devices [3, 4]. However, the relatively high dielectric loss (tan δ) of CCTO ceramics limits their application in devices. Although the origin of the promising properties of CCTO ceramics are not yet well understood [5], both the giant dielectric constant and non-ohmic characteristics of CCTO have been tentatively attributed to an internal barrier layer capacitor (IBLC) effect originating from extrinsic polarization at the grain boundaries [6, 7]. In this model, bulk grains behave as a semiconductor and grain boundaries exhibit insulating behavior with high resistance. Generally, the high resistance of the grain-boundary layer corresponds to a low conductance, which means a low tan δ . Therefore, the tan δ can be reduced by methods that increase the grain-boundary resistance [8].

Thus far, modification of the preparation process has been demonstrated to be one of the most effective methods for controlling the structure of the interfacial regions at the grain boundaries. In addition, the dielectric properties of CCTO ceramics have been found to be highly sensitive to the structure of the grain boundaries [9]. Among the methods for fabricating CCTO ceramics, the sol-gel method has been commonly used because of the good chemical uniformity of the product, low-temperature synthesis conditions and ease of controlling the components. The preparation of CCTO ceramics via the sol-gel method involves several key processes, including solution preparation, gel formation, pre-sintering and sintering [10]. Most of the previously related research has been focused on the sintering process, whereas little has considered the effect of the pH value of the solution on the dielectric performance of the products. In previous works, when certain elements such as Sr, Mg and Pr were added by doping, the pH value was usually adjusted to 3 and only the

effects of the sintering temperature and/or the dopants were investigated [10-14]. In another work, the pH value of the solution was varied from 1.0 to 1.8 with an acidity regulator, nitric acid, and the sample exhibited the highest ε_r when the pH was 1.6 [15]. Notably, the pH interval was narrow, only between 1 to 3, when acidity regulators were used, and the effect of larger pH values on the microstructure and dielectric properties of CCTO ceramics warrants further exploration. Therefore, in this paper, CCTO ceramics were prepared through the sol-gel method. An alkaline regulator, ammonia water, was used to adjust the pH of the solution from 1 to 7, and the influences of different pH values on the microstructure and dielectric properties and dielectric properties were investigated.

2. Experimental

CCTO precursor powders were prepared by the sol-gel method using solutions with different pH values. The raw materials included Cu(NO₃)₂·3H₂O (99 wt%), Ca(NO₃)₂·4H₂O (99 wt%) and Ti(OC₄H₉)₄ (99 wt%). Citric acid was used as a complexing agent. First, appropriate amounts of Ca(NO₃)₂·4H₂O and Cu(NO₃)₂·3H₂O were dissolved in ethanol to form solution A and Ti(OC₄H₉)₄ was immixed into ethanol to form solution B. Solution B was then added into a citric acid solution immediately with vigorously stirring by a magnetic stirrer to obtain solution C. The two solutions A and C were mixed in a beaker under stirring, and the pH was adjusted to 1, 3, 5 or 7 by addition of ammonia water to obtain a sol. The sol was subsequently heated to 80 °C for 12 h to prepare the dry gel. The precursor powders were obtained by drying the gel in a crucible at 700 °C in air; the organic matter was fired for 2 h at 750 °C. The as-prepared powders were pressed into 30 mm diameter pellets under 200 MPa pressure, and the CCTO ceramics were finally fabricated by sintering the pellets at 1050 °C for 12 h.

The phase structures of the sintered specimens were identified by X-ray diffraction with Cu K_{α} radiation (MSAL–XD2). The fractured cross-sectional microstructures were observed by scanning electron microscopy (SEM, TESCAN VEGA SBU) and Energy-dispersive X-ray spectroscopy (EDS) was conducted using a spectrometer attached to the scanning electron microscope to analyze

the chemical composition. Electronic backscattered micrographs were performed through the field emission scanning electron microscopy (FE-SEM, JSM-6700F). To measure the dielectric properties, both sides of the samples were coated by silver paste and fired at 620 °C to form electrodes. The dielectric dispersion spectra and complex impedance spectra were collected using an impedance analyzer (NOVOCONTROL Concept 80) in the frequency range from 1 to 10^7 Hz at different temperatures. The current-voltage (*J-E*) characteristics were recorded using a precision high-resistance meter (Keithley 6517b).

3. Results and Discussion

3.1 Structural studies

Fig. 1 shows the XRD patterns for calcinated CCTO powders with different pH values. The XRD analysis confirms pseudo-cubic CCTO phase is clearly the main phase in all the samples by comparison with the standard powder diffraction file database (JCPDF File No. 75-1149), while CuO phase was also present in all the sample powders. When the pH value of the sol was 1, an impurity phase of TiO_2 appeared in the product, and both the CaTiO₃ and TiO_2 phases were found in the sample prepared using a sol with pH = 7, suggesting that an excessively low or excessively high sol pH value adversely affects the formation of the pure CCTO phase powders.

Fig. 2 shows the XRD patterns of CCTO ceramics prepared from sols with different pH values, after the ceramics were sintered at 1050 °C for 12 h. The cubic perovskite CCTO phase as the main phase and the CuO phase as the secondary phase were detected in all the samples. A comparison with Fig. 1 reveals that the mixed phases CaTiO₃ and TiO₂ disappeared after the sintering process, whereas the peaks of the CuO phase become more intense. Through the full width at half maximum of XRD pattern, the lattice parameters for the samples prepared from sols with pH = 1, 3, 5 and 7 were calculated to be 7.389, 7.390, 7.392 and 7.392 Å, respectively. These lattice parameters of the samples are not substantially different (<0.002 Å) from the value of 7.391 Å reported in the literature [16].

3.2 Morphology

Fig. 3 presents SEM and backscattered micrographs of the ceramic samples prepared from sols with different pH values, after the samples were sintered at 1050 °C for 12 h. All the CCTO ceramics are composed of particles with sizes that range from several to more than 10 μ m. In the samples prepared from sols with pH \leq 3, no grains of large size are present; by contrast, grains with both large and small sizes are observed in the samples prepared from sols with pH \geq 5. The average grain sizes estimated using the program Nano-measurer are listed in Table 1. With increasing pH of the sols, the grain size first decreases to the minimum (1.14 μ m for the sample prepared from a sol with pH = 3) and then increases again. The SEM images show that the sample prepared from a sol with pH = 5 shows a uniform grain microstructure with a grain size of approximately 4.39 μ m. We attributed the wide range of grain sizes for these samples to the different pH values of the sols, which may lead to different contents of the CuO phase at the grain boundary during the formation of the CCTO ceramics [9, 17-19].

Table 1

Average grain size estimated using the Nano-measurer program, and the density measured by Archimedes' method for CCTO ceramics prepared by sols with different pH values.

4.41
4.09

Table 1 also lists the densities of the samples prepared from sols with different pH values measured by Archimedes' method. The density increases to the maximum for the sample prepared from the sol with pH = 5 and then decreases to the minimum for the sample prepared from the sol with pH = 7. The variation of the density may be related to the different concentrations of CuO at the grain boundary as a result of the variation of the pH of the solution. During the sintering process,

the CuO phase melts first; the liquid phase subsequently promotes grain growth and influences the density of the samples [7, 20-22].

To confirm the concentration of CuO at the grain boundary, EDS for all samples was conducted at A, B, C and D point, respectively. As shown in Fig. 2, the CuO phase exists in all the sintered ceramic samples. Combined with the EDS data shown in Table 2, the results in Fig. 3 confirm that the content of CuO at the grain boundary first decreases and then increases with increasing pH of the sol, indicating that pH of the sol plays an important role in determining the CuO concentration at the grain boundaries. It also can find from the electron backscattered micrographs of all the samples (Fig 3 a'-d') that no obvious second phase was observed except for the grain boundaries, indicating all the secondary CuO phase existed at the grain boundaries.

Table 2

EDS analysis results for the marked points in Fig. 3.

_	Element/at.%	А	В	С	D
_	0	64.86	61.89	65.24	64.258
	Ca	4.92	8.79	2.32	3.282
	Ti	19.47	20.69	21.47	21.67
	Cu	10.75	8.63	10.97	10.79

3.3 Complex impedance spectroscopy

To further study the effect of the pH value on the electrical properties of the CCTO ceramics, the complex impedance properties of the samples were analyzed. In accordance with the IBLC model, a series circuit of two RC parallel circuits can be used to illustrate the electrical heterogeneity of the grains and grain boundaries in polycrystalline ceramics. The complex impedance (Z^*) of the equivalent circuit can be calculated by [7, 23]

$$Z^{*} = Z' - iZ'' = \frac{R_{gb}}{1 + i\omega R_{gb}C_{gb}} + \frac{R_{g}}{1 + i\omega R_{g}C_{g}}$$
(1)

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

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

where R_{gb} and C_{gb} are the resistance and capacitance, respectively, of the grain boundaries; and R_g and C_g are the resistance and capacitance of the grains, respectively. The complex impedance spectra for the CCTO ceramics at room temperature in the 0.01 Hz to 10 MHz frequency range are shown in Fig. 4. According to Eq.(1), R_g and R_{gb} can be obtained from the intercepts on the Z axis. The figure suggests that the R_{gb} of the sample first decreases and then increases with the increase of the pH value, and the R_{gb} of the sample with pH = 3 is the minimum. A comparison of the results of the EDS and impedance analysis shows that the trend in the Cu content at the grain boundary is basically in line with the trend in R_{gb} with the increasing pH value. This indicates that the pH value has a great influence on R_{gb} .

In general, the R_g and R_{gb} follow the Arrhenius laws [24]:

$$R_g = R_0 \exp(E_g / K_B T) \tag{4}$$

$$R_{gb} = R_0 \exp(E_{gb} / K_B T)$$
⁽⁵⁾

where R_0 is the pre-exponential constant term, the values of E_g and E_{gb} represent the activation energies at grain and grain boundaries, respectively, k_B is the Boltzmann constant, and T is the absolute temperature. The E_g and E_{gb} could be calculated from the slopes of the linear fitting results. In order to determine the E_g and E_{gb} for all the samples, complex impedances spectra were conducted at different temperatures (not shown here). Fig 5 shows the dependence of $\ln R_{gb}$ and $\ln R_g$ on the 1000/T. With the rising of pH values, it can be found that the E_{gb} for different samples increased to a maximum of 0.66 eV for the CCTO ceramics prepared with sol of pH=5 at first, and then decreased. While the E_{gb} varies with pH value, the E_g remains 0.081-0.089 eV, with negligible differences, which is consistent with other reported literature [25]. It can be inferred that different

pH values for CCTO ceramics adjusted by ammonia has obvious impact on properties of grain boundaries rather than grains, and appropriate pH value facilitates the improvement of E_{gb} for CCTO samples. Usually, high activation is associated with low tan δ , and the CCTO ceramic sample with pH=5 with the lowest tan δ would be expected, as described below in Section 3.4.

3.3 Current-voltage characteristics

The current–voltage characteristics are also affected by R_{gb} [26]. As shown in Fig. 6, nonlinear *J–E* characteristics are observed for all the CCTO samples at room temperature. Breakdown electric field (E_b) is defined when the leakage current density is 10 mA/cm². The nonlinear coefficient (α) of all the samples are calculated from these curves via the equation [27]

$$\alpha = \frac{\log(I_2 / I_1)}{\log(U_2 / U_1)} \tag{6}$$

where U_1 and U_2 are the voltages corresponding currents I_1 and I_2 , respectively; α is calculated when $I_1 = 0.1$ mA and $I_2 = 1$ mA. The results are summarized in Table 3. Generally, a large R_{gb} , a large number of grain boundaries, lower dc conduction and low porosity improve the E_b [28, 29]. According to the results in Fig. 6, the sample prepared from a sol with pH = 3 exhibits the lowest E_b , and the smallest R_{gb} even though it has the largest number of grain boundaries. Meanwhile, the sample prepared from a sol with pH = 5 exhibits the maximum E_b , while it behaves a larger R_{gb} and the highest density. Although the sample prepared from a sol with pH = 7 has the largest R_{gb} , the higher porosity and the small number of grain boundaries lead to a reduction of the E_b . In this work, the obtained α values are consistent with those of the original CCTO ceramics reported in the previous literatures[18, 30].

Generally, the formation of the grain-boundary Schottky potential barrier is attributed to the difference of electronic structures between grain and grain boundary: the chemical heterogeneity can lower the local Fermi energy of grain boundary and can trap the flowing electrons till the Fermi energy in grain and grain boundary become equal. This separation and accumulation of charges can

produce a depletion layer at grain boundary, and the inner electric field in the depletion layer forms the grain-boundary Schottky potential barrier. Hence, increasing the barrier height (Φ) would make the hopping or migration of charge carriers over the potential barrier in CCTO ceramics more difficult, indicating a larger Φ can decrease the α , improve the E_b , and effectively restrain the leakage conductance, which may be a critical factor responsible for the low tan δ of CCTO ceramics [31, 32]. In present work, the pH causes the variation of the amount of Cu at grain boundary, which can affect the Fermi energy at grain boundary and introduce electronic traps, which might induce the variation of Φ . According to the *J*–*E* characteristics measured at 298–358 K (not shown here), the Φ of CCTO ceramics were calculated by the equations [33]:

$$J = AT^{2} \exp\left[\left(\beta E^{1/2} - \boldsymbol{\Phi}\right) / k_{B}T\right]$$
(7)

$$InJ_0 = -\Phi / k_B T + In(AT^2)$$
(8)

where *A* and *T* are the Richardson constant and absolute temperature, respectively, β and k_B are the pre-exponential factor and Boltzmann constant, and Φ is the Schottky barrier height of the grain boundary, J_0 is the current density at zero electric field. As shown in the inset of Fig. 6, a good linear relationship between $\ln J$ and $E^{1/2}$ can be obtained at the low electric field region in the range 298–338 K, which indicates that the *J*–*E* characteristics of the CCTO ceramics can be well elucidated based on the field-assisted thermionic emission mechanism [34]. The Φ was obtained at 0.38, 0.55, 0.57, and 0.31 eV for the CCTO samples prepared from sols with different pH values. Φ of different samples increased with the rise of pH values at lower pH, then sharply dropped when pH=7. The sample prepared from the sol with pH = 5 exhibits the largest Φ , which means that its dc conduction is suppressed and E_b will be improved, which is consistent with the analysis of aforementioned E_b data. The results indicate that the pH change caused by adding ammonia greatly effects on grain boundary properties.

Table 3 The ε_r and tan δ values at room temperature and 1 kHz, nonlinear coefficient (α), and DC breakdown electric field (E_b) of CCTO ceramics prepared from sols with different pH values; the

pH value	$\varepsilon_r \times 10^3 (1 \text{ kHz})$	$\tan\delta$ (1 kHz)	α	E_b (V/cm)
1	7.92	0.052	3.81	1272.79
3	2.73	0.030	3.37	494.97
5	28.70	0.028	4.46	1725.34
7	126.73	0.354	4.16	636.40

samples were sintered at 1050 °C for 12 h.

3.4. Dielectric properties

The ε_r and tan δ as functions of the frequency are shown in Fig. 7 and Fig. 8, respectively. Notably, the pH value of the sol strongly influences not only the morphologies of the CCTO ceramics but also their dielectric properties. The ε_r and tan δ of all the samples at room temperature and 1 kHz are listed in Table 3. The ε_r of all the CCTO ceramic samples decrease slowly over the frequency range from 1 to 400 kHz, and a sharp decreased is observed at frequencies greater than 400 kHz, except for the sample prepared from a sol with pH = 7. Moreover, the ε_r decreases first and then increases with increasing sol pH value. The sample prepared from a sol with pH = 3 exhibits the minimum ε_r , which is approximately 2500 in most of the frequency range of the test. The maximum ε_r is observed for the sample prepared from the sol with pH = 7. However, it exhibits poor frequency stability. The difference in ε_r is attributed to the various grain size distributions. According to the IBLC model, the ε_r can be obtained by the equation [23, 35]

$$\varepsilon_r = \varepsilon_{gb} \frac{d_g + d_{gb}}{d_{sb}} \tag{9}$$

where ε_{gb} is the dielectric constant of the grain boundary; and d_g and d_{gb} are the sizes of the grain and grain boundary, respectively. The ε_r is closely related to d_g , as d_g is much larger than d_{gb} . Therefore, with increasing sol pH value, the ε_r changes because of the variation of the grain size, which results in the minimum ε_r of the sample prepared from the sol with pH = 3 which has the smallest grain size. This observation is consistent with the SEM results presented in Fig. 3 and Table 1.

In Fig.8, tan δ decreases first and then increases with increasing pH value. Among the samples,

the sample prepared from a sol with pH = 5 presents the lowest tan δ , approximately 0.028 at room temperature and 1 kHz, and its ε_r is maintained at approximately 2 × 10⁴. Generally, a lower tan δ is closely correlated with a large number of grain boundaries, high density, low dc conduction of the grain barrier layer and high R_{gb} [36-41]. Therefore, the sample prepared from a sol with pH = 5, which possesses a high R_{gb} , the largest observed density and the maximum barrier height, has the lowest tan δ .

4. Conclusions

CCTO ceramics were prepared by the sol-gel method from solutions with 4 different pH values, where the pH of the solution was adjusted with ammonia water as an alkaline regulator. With increasing sol pH value, both the ε_r and the tan δ of the obtained CCTO first decrease and then increase, exhibiting similar trends. The sample prepared from a sol with pH = 5 exhibits the lowest tan δ of 0.028, and its ε_r , α and E_b were 2×10^4 , 4.46 and 1725.34 V/cm, respectively. This material may thus be a promising variator material for over-voltage protection in electronic systems. Our results demonstrate that adjusting the pH value of the sol using an alkaline regulator is an effective method for reducing the tan δ of CCTO ceramics.

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Figure Captions

Fig.1. XRD patterns of the as-prepared CCTO powders prepared via the sol-gel method from sols with different pH values.

Fig.2. XRD patterns of CCTO ceramic samples prepared from sols with different pH values.

Fig.3. SEM and electronic backscattered images of CCTO ceramics prepared from sols with different pH values: (a), (a') pH = 1; (b), (b') pH = 3; (c), (c') pH = 5; (d), (d') pH = 7.

Fig.4. Impedance spectroscopy plots for all the CCTO ceramics at room temperature.

Fig.5. Arrhenius plots of the relaxation behavior of CCTO ceramics with different pH values: (a) grain boundaries; (b) grains.

Fig.6. Current–voltage characteristics of CCTO ceramic samples. The inset shows the calculation of the Φ in the temperature range from 298 to 338 K for all the CCTO ceramics.

Fig.7. ε_r as a function of the frequency measured at room temperature for all CCTO ceramics.

Fig.8. Frequency dependence of $tan\delta$ measured at room temperature for all CCTO ceramics.



















Highlights:

- The pH values of CCTO sol was adjusted by alkaline regulator from 1 to 7.
- ε_r for the sample prepared from the sol with pH = 5 maintained 2.87× 10⁴ at 1K Hz.
- The tan δ for the sample prepared from the sol with pH=5 was 0.028 at 1 kHz.
- The tan δ decreasing may be attributed to the increasing $R_{\rm gb}$ and lower porosity.