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Improved dielectric properties of the CaCu₃Ti₄O₁₂ composites using BaTiO₃-coated powder as precursor



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Hui Eun Kim^a, Soon-Mi Choi^a, Youn-Woo Hong^b, Sang-Im Yoo^{a,*}

^a Department of Materials Science and Engineering, Research Institute of Advanced Materials (RIAM), Seoul National University, Seoul 151-742, Republic of Korea ^b Electronic Materials Convergence Division, Functional Module Team, Korea Institute of Ceramic Eng. & Tech., Seoul 153-801, Republic of Korea

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ABSTRACT

A high dielectric loss and a large leakage current of CaCu₃Ti₄O₁₂ (CCTO) ceramics could be greatly suppressed by using BaTiO₃ (BTO)-coated CCTO powder as precursor. BTO-coated CCTO precursors with 5, 10, and 15 mol% BTO relative to CCTO were prepared by a sol–gel process and a subsequent calcination at 850 °C for 3 h in pure oxygen gas atmosphere. All samples were sintered at 1060 °C for 12 h in air. Compared with pure CCTO sample of $\varepsilon_r \sim 52,000$ and $\tan \delta \sim 0.38$ at 100 kHz, all CCTO composite samples exhibited significantly reduced dielectric losses and leakage currents. Among all CCTO composite samples, the sample using 5 mol% BTO-coated CCTO powder exhibited the most improved properties of the dielectric loss ($\tan \delta \sim 0.04$ up to 100 kHz) and the leakage current (less than 1% up to DC field of ~1 kV/cm) although a large suppression in its dielectric constant ($\varepsilon_r \sim 6000$ up to 100 kHz) was unavoidable. This improvement is mainly attributed to a relatively uniform distribution of the second phases such as Ba₄Ti₁₂O₂₇ and CaTiO₃ at the CCTO grain boundary, which were formed by the chemical reaction between CCTO and BTO during the sintering process.

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1. Introduction

A miniaturization of electronic devices increases the demand of dielectric materials with high dielectric constant, low dielectric loss, low leakage current, and good temperature stability. Recently, CCTO ceramics have drawn a large attention of researchers due to their extraordinary high dielectric constants of 10^4 – 10^5 in the temperature region of 100–500 K below 1 MHz. However, a real application of CCTO ceramics has been hindered by the fatal problems of the high dielectric loss and the large leakage current [1–4].

In order to overcome these problems, CCTO ceramics has been doped with some other materials such as $MnCO_3$ [5] and ZrO_2 [6], and the CCTO composites with other oxides of low dielectric loss, including SiO₂ [7], SrTiO₃ [8], CaTiO₃ [9], and BaTiO₃ [10,11], have been prepared. While the electrical resistivity of 2 mol% Mn-doped CCTO ceramics at room temperature was abruptly increased around six orders of magnitude compared with that of pure CCTO, the capacitance was reduced from 0.3 nF/cm for pure CCTO to ~4 pF/cm for Mn-doped CCTO ceramics below ~50 kHz [5], implying that the degradation in the dielectric constant is so serious that the Mn doping is undesirable. For Zr-doped CCTO

ceramics, Patterson et al. [6] reported that 5 wt% ZrO₂-doped CCTO ceramics exhibited the dielectric constant of ~ 5000 and the dielectric loss below 0.05 over the frequency region of 50 Hz-30 kHz. Unfortunately, the leakage current of this sample was not reported in their paper. Kim et al. [7] reported that 2 wt% SiO₂-CCTO composite ceramics showed the high dielectric constants of 26,000-32,600 at 1-100 kHz whereas the dielectric losses were insignificantly reduced. For 60 vol% CCTO-SrTiO₃ composite sample, the dielectric constant of ~2000 and the dielectric loss of <0.03 with a good temperature stability from $-55 \,^{\circ}$ C to 150 °C at 1–100 kHz were reported by Yu et al. [8]. Thongbai et al. [9] reported that 33.3 mol% CCTO–CaTiO₃ composite ceramics prepared by a polymer pyrolysis method showed the dielectric constant of \sim 2500 below 1 MHz and the dielectric loss of <0.05 in the frequency range of 160 Hz-177 kHz. From these previous literature, one can see that a significant degradation in the dielectric constant below \sim 5000 is unavoidable in order to achieve low dielectric loss of <0.05, and the leakage current characteristics are not reported even though those are very critical for capacitor applications.

On the other hand, in our previous report on 5–15 mol% BTO– CCTO composite samples [11], we reported significantly reduced dielectric losses of < 0.05 up to 100 kHz although their dielectric constants were largely suppressed to 3000–4000. In addition, although the BTO additive was effective for the improvement of



^{*} Corresponding author. Tel.: +82 2 880 5720; fax: +82 2 887 6388. *E-mail address:* siyoo@snu.ac.kr (S.-I. Yoo).

the dielectric loss (<0.05), the leakage currents could be improved only in a limited DC field region of 0.1-2 kV/cm. As an alternative approach to reduce the dielectric loss and the leakage current of CCTO ceramics without a serious degradation in the dielectric constant, we tried to prepare BTO-coated CCTO powder as precursor in this study since the leakage current would be effectively suppressed if a core-shell structure, composed of semiconducting CCTO powder [12-17] covered with insulating layer, could be formed. For the BTO coating on the surface of CCTO powder, we selected the sol-gel process since it had been used for the fabrication of BTO films and powder [18-22].

2. Experimental

CCTO ceramics sintered at 1060 °C for 12 h in air were pulverized into fine particles for BTO coating. Details for the fabrication of CCTO ceramics are reported in our previous paper [13]. The 5, 10, and 15 mol% BTO coating on CCTO powder were performed using the sol-gel process as the following; Barium acetate, $Ba(CH_3COO)_2$ (Sigma Aldrich, 99%), was first dissolved in acetic acid, (CH₃COOH). Titanium isopropoxide, [Ti(OCH(CH₃)₂]₄ (Sigma Aldrich, 99.999%), including acetylaceton (C₅H₈O₂, Sigma Aldrich, 99%) as a stabilizer, was added drop by drop to the Ba-dissolved solution which was constantly being stirred and thus the sol was made. The sol might be stabilized since [Ti(OCH(CH₃)₂]₄ was known insensitive to moisture if it was chelated with acetylacetone [23]. Then, CCTO powder were put into a yellow solution containing Ba and Ti elements, and dried at 200 °C in an oven. The dried powder was calcined at 850 °C for 3 h in pure oxygen gas atmosphere. Finally, CCTO powder coated with 5, 10, and 15 mol% BTO were pressed into pellets and sintered at 1060 °C for 12 h in air (hereafter, 5BTOC, 10BTOC, and 15BTOC, respectively)

X-ray diffraction (XRD, D8-Advance) analyses were performed for all samples using Cu K α radiation. The microstructures of samples were observed by scanning electron microscopy (SEM, JSM-5600) after the thermal etching process at 1050 °C for 30 min in air. A high-resolution transmission electron microscope (HR-TEM, JEM-3000F) and an analytical transmission electron microscope (TEM, FEI Technai F20) with energy dispersive spectroscopy (EDS) mapping were also employed for the microstructure analysis. For the measurements of electrical properties, the Ag electrode was deposited on samples by the screen printing method, and the frequency-dependent dielectric constant, ε_r and dielectric loss, $tan \delta$ were measured by an impedance/gain-phase analyzer (HP 4194a) in the frequency regime of 1 kHz-15 MHz. To determine the leakage currents under a DC bias condition, the current-voltage (I-V) curves of samples were measured with a LCR (L: Inductance, C: Capacitance, R: Resistance) source meter (Keithley-4200). The Z* and M* spectroscopy analyses for identifying the resistivity (ρ) and C values of grain and grain boundary were performed using Solatron 1260 and Agilent E4991a at relatively low frequency region (10⁻²-10⁶ Hz) and high frequency region (10⁶-10⁹ Hz), respectively. All data from the Z^* and M^* spectroscopy were obtained using the equivalent circuit with two parallel *R* and *C* elements of grain and grain boundary.

3. Results and discussion

The XRD patterns of BTO-coated CCTO powder calcined at 850 °C for 3 h in pure oxygen gas atmosphere are represented in Fig. 1(a). It is obvious that there exist two phases of CCTO (ICDD card No. 01-075-2188) and BTO (ICDD card No. 01-078-4475), indicating that no chemical reaction occurs between CCTO and BTO at 850 °C for 3 h in pure oxygen gas atmosphere. With increasing the amount of BTO, the peak intensities of the BTO phase are increased. However, as shown in Fig. 1(b), the second phases such as Ba_4Ti_{12} O₂₇ (ICDD card No. 01-089-6712) and CaTiO₃ (ICDD card No. 00-042-0423) are observed for CCTO composite samples after sintering at 1060 °C for 12 h in air, and their peak intensities are increased with increasing the BTO content from 5 to 15 mol%. These results show that the CCTO phase is no more compatible with the BTO phase but chemically reacts with it to form the $Ba_4Ti_{12}O_{27}$ and $CaTiO_3$ phases at the sintering conditions. These second phases have also been detected in the BTO-added CCTO ceramics sintered at 1060 °C for 12 h in air [11]. Though not presented here, our independent study on the 15 mol% BTO-added CCTO composite showed that CCTO was compatible with BTO up to 925 °C in air since these second phases began to appear above 950 °C in air. This result is in good agreement with the previous paper by Fechine et al. [10] since they reported a thick film



Fig. 1. The XRD patterns of BTO-coated CCTO powder after calcination at 850 °C for 3 h in pure oxygen gas atmosphere (a), and those of CCTO composite samples after sintering at 1060 °C for 12 h in air (b).

(thickness $\sim 150 \,\mu\text{m}$) of 50 wt% CCTO-BTO composite with no chemical reaction between CCTO and BTO at 900 °C in air.

The SEM micrographs of pure CCTO and BTO-coated CCTO powder are shown in Fig. 2. Compared with pure CCTO particles in Fig. 2(a), BTO-coated CCTO particles in Fig. 2(b-d) exhibit much more small particles on the surfaces of large CCTO particles, and their areal density is increased with increasing the BTO content. These small particles are presumed to be sol-gel coated BTO particles. To fully identify these small particles, we analyzed them with HR-TEM. The results are shown in Fig. 3. Fig. 3(a) shows a low magnification image of a particle sampled out of 15 mol% BTO-coated CCTO powder. One can see that many small particles are attached to the particle surface. The red square area in Fig. 3(a) was magnified by HR-TEM as shown in Fig. 3(b). From the Fast Fourier Transformation (FFT) patterns of (1), (2), and (3), it is obvious that the small particle within the red square area is the BTO nanoparticle and it forms a clear interface with CCTO. Therefore, it is clear that the small particles observed in Fig. 3(a) are the BTO nanoparticles attached to the surface of CCTO. Unfortunately, from the micrographs in Figs. 2 and 3(a), the BTO-coating of CCTO particles by the sol-gel process does not form a uniform core-shell structure but a non-uniform covering of CCTO with BTO nanoparticles.

Fig. 4 shows the SEM micrographs of all samples sintered at 1060 °C for 12 h in air. While pure CCTO sample is composed of abnormally grown large grains with the average grain size of \sim 50 µm as shown in Fig. 4(a), CCTO composite samples in Fig. 4(b-d) consist of fine grains, representing that the abnormal



Fig. 2. The SEM micrographs of pure CCTO (a), 5BTOC (b), 10BTOC (c), and 15BTOC (d) powder after calcination at 850 °C for 3 h in pure oxygen gas atmosphere.



Fig. 3. The TEM bright-field image of a particle sampled out of 15BTOC sample (a) and HR-TEM image (b) of the square area related by red line in (a). (1), (2), and (3) represent the FFT patterns of the square area related by blue line in the image (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

grain growth of CCTO can be suppressed by the BTO-coating on CCTO. With increasing the BTO content, however, the average grain sizes of CCTO samples were slightly increased from ${\sim}1.4\pm0.5~\mu{\rm m}$ (5BTOC) to ${\sim}2\pm0.8~\mu{\rm m}$ (15BTOC), suggesting that the BTO interaction with CCTO to form the second phases might be responsible for

this grain growth. Furthermore, their microstructures are composed of round-shaped grains while those of BTO-added CCTO ceramics [11] consist of faceted grains, which is surely related to a difference in the BTO addition to CCTO between BTO coating and BTO mixing.

Fig. 4. The SEM micrographs of pure CCTO (a), 5BTOC (b), 10BTOC (c), and 15BTOC (d) samples after sintering at 1060 °C for 12 h in air.

The dielectric properties of sintered samples are represented in Fig. 5. As shown in Fig. 5(a), the dielectric constants of CCTO composite samples (6000-8000) are largely suppressed in comparison with that of pure CCTO sample (\sim 52,000) below 100 kHz. According to the grain boundary internal barrier layer capacitance model



Fig. 5. The frequency dependent dielectric constants (a) and dielectric losses (b) of CCTO composite samples.

[4], the dielectric constant values are strongly dependent on the microstructure and the electrical properties of grain boundary with the following equation of $\varepsilon_r \sim d\varepsilon_{\rm gb}/t$, where *d* is the average grain size, ε_{gb} is the dielectric constant of grain boundary, and t is the grain boundary thickness. Therefore, the large suppression in the dielectric constants of CCTO composite samples can be explained by their smaller grain sizes as shown in Fig. 4. Although the dielectric constants of pure CCTO sample are abruptly decreased at \sim 100 kHz, those of CCTO composite samples are maintained up to 1 MHz. On the other hand, the dielectric losses of CCTO composite samples (0.02-0.07) are lower than those of pure CCTO sample $(tan \delta \sim 0.1)$ below 10 kHz in Fig. 5(b). While pure CCTO sample exhibits a rapid increase in the dielectric loss at ~ 10 kHz, CCTO composite samples show such an abrupt increase at much higher frequency of ~100 kHz. The lowest dielectric losses up to 200 kHz are obtained from 5BTOC sample. However, with increasing the BTO content from 5 to 15 mol%, the dielectric losses of CCTO composite samples are increased from 0.04 to 0.075 in the region of 1-100 kHz, respectively. The dielectric constants of ~6000 with low dielectric losses ($tan \delta < 0.05$) up to 200 kHz from this CCTO composite sample of 5BTOC are superior to any data previously reported for CCTO-based ceramics [5-11].



Fig. 6. I-V measurement under a DC bias condition of CCTO composite samples.

Figure 6 represents the leakage currents versus applied DC electric field for all samples. The leakage currents of all samples are gradually increased with increasing the DC field. Compared with pure CCTO sample, CCTO composite samples show the lower leakage currents over the whole DC field region. Particularly, 5BTOC sample shows the lowest leakage currents among all samples.

In our previous paper [11], we reported the dielectric properties of CCTO composite samples fabricated by sintering the BTO-CCTO powder mixture. For CCTO composite samples with the same amount of 5 mol% BTO, the dielectric constants of CCTO composite sample (\sim 6000) using BTO-coated powder are higher than those of the composite sample (\sim 4000) using BTO-CCTO powder mixture at 100 kHz while both CCTO composite samples show the lower dielectric loss (<0.05) at the same frequency. Moreover, the sample using BTO-coated powder exhibits the tens of times lower leakage currents than those of the sample using BTO-CCTO powder mixture at the whole range of the applied DC field. Consequently, the BTO coating is surely more effective for the improvement of the electrical properties of pure CCTO sample.

The significant reduction in the dielectric loss and the leakage current for CCTO composite samples may be explained by their microstructure. The STEM images of CCTO composite samples with the EDS elemental mapping are represented in Fig. 7. The particles consisted of Ba and Ti components, which are confirmed to be the $Ba_4Ti_{12}O_{27}$ phase from FFT patterns (not shown), are located at the CCTO grain boundaries. The CaTiO₃ and CuO phases are also observed around the $Ba_4Ti_{12}O_{27}$ phases. The $Ba_4Ti_{12}O_{27}$ and CaTiO₃

phases must be formed by the chemical reaction between CCTO and BTO and infiltrated into the CCTO grain boundary during the sintering of BTO-coated CCTO powder. In the case of 5BTOC sample, as shown in Fig. 7(a and b), the Ba₄Ti₁₂O₂₇ phase is unobservable at thsse CCTO grain boundary although it is detectable on the XRD patterns in Fig. 1(b), which is probably due to its relatively smaller amount uniformly distributed at the CCTO grain boundary. Whereas, the Ba₄Ti₁₂O₂₇ phase agglomerated at the CCTO grain boundary is easily observed for 15BTOC sample in Fig. 7(c and d). Consequently, this agglomeration of the Ba₄Ti₁₂O₂₇ phase rather than more uniform distribution at the CCTO grain boundary is considered to be responsible for the degradation in the dielectric loss and leakage current properties of CCTO composite sample with higher BTO contents.

In order to identify the effect of the BTO coating on CCTO sample, we performed Z^* and M^* spectroscopy analyses to evaluate the R and C values of both grain and grain boundary using the following equations,

 $M^* = jwC_0 Z^* = M' + jM''$ (1)

$$Z_{\max}'' = \frac{R}{2} \tag{2}$$

$$M''_{\rm max} = \frac{C_0}{2C} \tag{3}$$

$$\omega \tau = 2\pi f_{\text{max}} R C = 1 \tag{4}$$



Fig. 7. The Z-contrast STEM images of 5BTOC (a) and 15BTOC (c) samples. Ca, Cu, Ba, and Ti spectral images of 5BTOC (b) and 15BTOC (d) samples analyzed for the square area related by the orange line in (a) and (c), respectively.

Table 1 The ρ_{g} , ρ_{gb} , C_{g} , and C_{gb} values of CCTO composite samples sintered at 1060 °C for 12 h in air. The data were evaluated from the data measured by Z^* and M^* spectroscopy.

Sample	$ ho_{ m g} \left(\Omega { m cm} ight)$	$C_{\rm g}~({\rm pF/cm})$	$ ho_{ m gb}({ m M}\Omega{ m cm})$	$C_{\rm gb}~({\rm pF/cm})$
ССТО	36	966	43	2,26,600
5BTOC	62	2,266	81	34,820
10BTOC	64	795	15	19,460
15BTOC	109	4	12	18,880

where Z''_{max} and M''_{max} are the peak values of the imaginary parts of Z^* and M^* spectroscopy, respectively, C_0 is the vacuum capacitance $(8.854 \times 10^{-14} \text{ [F/cm]})$, and w is the angular frequency. The $\rho_{\rm g}$, $\rho_{\rm gb}$, $C_{\rm g}$, and $C_{\rm gb}$ values are the ρ and C values of grain and grain boundary. The values calculated from the data with the Eqs. (1)-(4) are summarized in Table 1. 5BTOC sample shows the highest ρ_{gb} value in all samples. With increasing the BTO content from 5 to 15 mol%, the $\rho_{\rm gb}$ values of CCTO composite samples are decreased from 81 to 12 M Ω cm, respectively, which is considered to be closely related to the distribution of the second phases in the microstructure of sintered CCTO composite samples since as previously mentioned, while the second phases of 5BTOC sample are somewhat uniformly distributed at CCTO grain boundary in Fig. 7(a and b), those of 15BTOC sample are segregated at CCTO grain junction in Fig. 7(c and d). Interestingly, although the $ho_{
m gb}$ values of 10BTOC and 15BTOC samples are lower than that of pure CCTO sample, those composite samples exhibit lower leakage currents above 5 V/cm compared with that of pure CCTO sample. The reason is that the total grain boundary areas of these composite samples are much larger than that of pure CCTO sample due to their much smaller average grain sizes. On the other hand, compared to the $C_{\rm gb}$ value of pure CCTO sample with higher dielectric constant (>10,000) below 100 kHz, CCTO composite samples with lower dielectric constant (\sim 6000) at the same region of frequency exhibit the reduced $C_{\rm gb}$ values. This tendency is in good agreement with previous study [4,12–17]. Lee et al. [17] reported that the improvement of dielectric constants in the CCTO ceramics was surely attributable to the high $C_{\rm gb}$ values. With increasing the BTO content from 5 to 15 mol $\overset{\circ}{}$, the $ho_{
m g}$ values are increased from 62 to 109 Ω cm while the C_g values are decreased from 2266 to 4 pF/cm, respectively, representing that those values might be affected by the diffusion of the Ba elements into the CCTO compound due to the chemical reaction between CCTO and BTO.

4. Conclusion

To overcome the large dielectric loss and the large leakage current of CCTO ceramics, we tried to employ the BTO additive using sol–gel coating in this study. Compared with pure CCTO sample of $\varepsilon_r \sim 52,000$ and $tan \delta \sim 0.38$ at 100 kHz, the sintered CCTO composite sample with applied the 5 mol% BTO-coating for CCTO powder,

which was composed of fine grains (<2 μ m) after sintering at 1060 °C for 12 h in air, exhibited the reduced dielectric constant (~6000) and dielectric loss (~0.04). With increasing the BTO content up to 15 mol%, however, the CCTO composite samples showed the insignificantly varied dielectric constants with increased dielectric losses (>0.05) at 100 kHz. CCTO composite sample using 5 mol% BTO-coated CCTO powder showed the lowest leakage currents among all samples, which is attributed to better distribution of the second phases at the CCTO grain boundary. Further improvement is expected for real application like multilayer ceramic capacitors if BTO coating on CCTO powder becomes more uniform enough to form the core–shell microstructure through a noble processing route, since the reaction between BTO and CCTO can be prevented below 950 °C in air.

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