Materials Research Express

PAPER

Significantly improved non-ohmic and giant dielectric response in CaCu$_3$Ti$_4$O$_{12}$ ceramics by incorporating Portland cement

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Keywords: CaCu$_3$Ti$_4$O$_{12}$, Portland cement, dielectric properties, impedance spectroscopy, nonlinear I–V characteristic

Abstract

The giant dielectric and nonlinear current–voltage properties of CaCu$_3$Ti$_4$O$_{12}$ (CCTO) incorporating Portland cement (PC) were investigated. Analysis revealed that the microstructure of the CCTO/PC ceramics was highly dense. Using the microstructure analysis and theoretical calculation, the elements in PC (i.e., Al, Si, Fe, K, Cr, and Mg) can substitute into the CCTO structure, giving rise to enhanced electrical properties of the grains and grain boundaries. As a result, the giant dielectric and nonlinear current–voltage properties of CCTO/PC were significantly improved. The low–frequency loss tangent of CCTO/PC was greatly reduced, by a factor of 10, while the dielectric permittivity of the ceramics was still large ($\sim 10^4$) over a frequency range of $10^2$–$10^6$ Hz. Interestingly, the nonlinear coefficient ($\alpha$) and electric field breakdown ($E_b$) of the CCTO/PC ceramics were greatly enhanced by factors of 2 and 30, respectively. Impedance spectroscopy analysis revealed large increases in $\alpha$ and $E_b$, as well as a decrease in the loss tangent due to a significant increase in the grain boundary resistance of CCTO/PC ceramics. Changes in giant dielectric and nonlinear electrical properties can be well described by the internal barrier layer capacitor model based on space charge polarization at the internal interfaces.

1. Introduction

Recently, giant dielectric oxides, which are oxide materials that can exhibit high dielectric permittivity ($\varepsilon'\sim 10^4$) without a detectable phase transition (e.g., CaCu$_3$Ti$_4$O$_{12}$ (CCTO) and related Cu$_3$TiO$_4$O$_{12}$ compounds, such as CuO, and NiO–based ceramics, among others), have been widely reported [1–11]. This discovery has stimulated significant research activity. Generally, the dielectric loss tangent ($\tan\delta$) and $\varepsilon'$ values of dielectric oxides are the primary parameters determining the suitability of a material for fabricating a ceramic capacitor. A high $\varepsilon'$ value with a low $\tan\delta$ are required for capacitor applications. Therefore, investigations on enhanced $\varepsilon'$ with reduced $\tan\delta$ values in many kinds of giant dielectric oxides are important.

CCTO is one of the most interesting giant dielectric oxides. It has been intensively studied for purely scientific and technological reasons [1, 12–18]. This is because CCTO and related ACu$_3$Ti$_4$O$_{12}$ (A = Cd$^{2+}$, Na$^{+}$, Bi$^{3+}$, Na$_{1/2}$Bi$_{1/2}$, Na$_{1/2}$Y$^{3+}$, Na$_{1/2}$Ca$_{1/2}$Bi$_{1/2}$$^{3+}$, etc.) ceramics can exhibit very high $\varepsilon'$ values of about $10^3$–$10^5$ at room temperature, depending on sintering conditions [12–14]. For a pure CCTO ceramic, some minor problems should be resolved before practical applications can be achieved. Its low-frequency $\tan\delta$ is very high. Various methods to reduce the $\tan\delta$ values must be investigated.

Besides the giant dielectric properties, nonlinear current density–electric field ($J$–$E$) properties are also found in CCTO polycrystalline ceramics, which can be useful in applications of varistor devices [16]. According
to impedance spectroscopy analysis [16] and studies using Kelvin probe microcontact [19], it has been clearly shown that the microstructure of CCTO ceramics consists of semiconducting grains and insulating grain boundaries. These special behaviors, i.e., giant dielectric and nonlinear electrical properties, are widely suggested to originate from the presence of Schottky barriers at the grain boundaries [19–21]. The resistivity of the grain boundaries is therefore very high compared to that of the grains. Thus, the grain boundaries of CCTO ceramics have two major roles. The first is to control energy loss in the material. A low—frequency tanδ can be reduced by increasing the total grain boundary resistance (Rgb). This can be accomplished by introducing insulating particles into CCTO bulk ceramics or by reducing the mean grain size to increase the grain boundary density. It is possible that increased Rgb values can be simultaneously obtained using these two methods. Another role of the grain boundaries is to produce interfacial polarization, giving rise to the giant dielectric response, and hence high ε′ values.

In this work, CaCu3Ti4O12 (CCTO) ceramics incorporating Portland cement (PC) at various levels (0, 1, 2.5, and 5 wt.%) were prepared by a conventional mixed—oxide method. The microstructure of the sintered ceramics was investigated. Both the dielectric and electrical properties of CCTO ceramics were improved by adding PC at a suitable concentration. The mechanisms resulting in the improved dielectric and electrical properties are discussed.

2. Experimental & theoretical details

CCTO powders were prepared using a solid—state reaction method. Details of the preparation method are given elsewhere [22]. A dried mixture of starting raw powders (CaCO3, CuO, and TiO2) was ground and calcined in air at 850 °C for 12 h. Then, the obtaining calcined powder was ground. PC/CCTO composite powders with various contents of PC (0, 1, 2.5, and 5 wt.%) were prepared by a conventional mixed—oxide method using a dry ball—milling procedure for 6 h. These samples are referred to as the CCTO, CCTO/Cement 1%, CCTO/Cement 2.5%, and CCTO/Cement 5% samples, respectively. The resulting mixed PC/CCTO powders were pressed into pellets (9.5 mm diameter and ~1.0–1.5 mm in thickness) by uniaxial compression at ≈160 MPa. Finally, the pellets were sintered in air at 1100 °C for 3–6 h.

The sintered ceramics were characterized using X—ray diffractometry (PANalytical, EMPYREAN) and scanning electron microscopy (SEC, SNE–4500M). The distribution of all elements was examined using field—emission scanning electron microscopy (FE—SEM) with energy—dispersive x—ray analysis (EDX) (HITACHI SU8030, Japan). For dielectric and electrical measurements, the sintered samples were polished to remove their outer surface layer and to obtain smooth surfaces. The polished samples were cleaned and dried at 100 °C overnight. Both sides of polished surfaces were coated by sputtering Au on them (Polaron SC500 sputter coating unit) to form a parallel plate capacitor. The capacitance and dissipation factor were measured using a KEYSIGHT E4990A unit with an oscillation voltage of 500 mV. The measurements were performed over the frequency range of 102–106 Hz and in the temperature range from −60 to 200 °C. The nonlinear J–E characteristics were measured at room temperature (RT) using a high voltage measurement unit (Keithley 247). The E0 value was defined as the electric field breakdown at which J = 1 mA cm−2. The nonlinear coefficient (α) was calculated in the range of 1–10 mA cm−2.

In this work, we also used the theoretical calculation to predict the substitution of many kinds of ions in the PC phase, which can enter into the CCTO structure. The theoretical calculation was performed using the Vienna Ab initio Simulation Package (VASP) code [23]. Details of the calculation were given elsewhere [24].

3. Results and discussion

The XRD patterns of the PC, CCTO, CCTO/Cement 1%, CCTO/Cement 2.5%, and CCTO/Cement 5% samples are illustrated in figure 1. The main phase of CCTO (ICPDS No.75–2188) was found in the XRD patterns of all of these samples. The PC phase was not detected in any of the XRD patterns of the CCTO/Cement samples. This result might have been due to the small amounts of PC in CCTO ceramics. Furthermore, this may have occurred since the crystallinity of the PC phase was much lower than that of the CCTO phase. Instead, secondary phases of TiO2 and CuO were detected in the CCTO/Cement 5% sample at 2θ angles between 30–35° and 35–50°, respectively. Likely, some elements (e.g., Al, Si, and Fe) in the PC phase were substituted into the Cu and Ti sites of the CCTO structure.

The microstructures of the sintered CCTO and CCTO/Cement samples were investigated to describe the variation in the dielectric and electrical properties. Figure 2 shows the SEM images of the polished samples. In figure 2(a), the overall microstructure of the CCTO sample is similar to that reported in the literature [16, 25, 26], consisting of grains and grain boundaries. Pores were also observed in the microstructure. After
addition of PC into the CCTO ceramics, secondary phase particles were observed, as seen in figures 2(b)–(c). Furthermore, large grains were more apparent compared to the CCTO sample.

Figures 3(a) and (b) show SEM images of PC powder and EDS mapping images of the elements in the PC powder. Figures 3(c) and (d) show the EDS mapping images of each element in the PC powder and EDS
spectrum detected in the PC powder, respectively. Major elements (i.e., O, Ca, Si, Al, and Fe) and minor elements (i.e., Ti, Cu, S, Mg, Cr, and K) were detected. It is important to note that these elements can substitute into CCTO ceramics, giving rise to changes in their dielectric and electrical properties.

Figures 4(a) and (b) show the EDS mapping images of a pure sintered CCTO ceramic for all elements and each element, respectively. As can be clearly seen, all elements (i.e., Ca, Cu, Ti, and O) were homogeneously
dispersed in the microstructure of the CCTO ceramic. Figure 4(c) illustrates the EDS spectrum of the CCTO ceramic, confirming the presence of Ca, Cu, Ti, and O in the CCTO structure.

To understand the microstructural changes in CCTO/Cement samples, the sintered samples, as well as PC particles, were characterized using an EDS–SEM mapping technique. As illustrated in figure 5, all major metal elements in CCTO ceramics (i.e., Ca, Cu, and Ti) can be detected, but they were not homogeneously dispersed in the microstructure of the CCTO/Cement 5% sample. In regular grains of a CCTO phase (a smooth surface grain), all major metal elements were observed and homogeneously dispersed. In contrast, Cu can largely be observed in the region of the secondary phase grain (in the square area), while Ti and Ca phases were observed little in this area. This result confirmed that this phase was not in the CCTO grain. Thus, this area can be considered a Cu–rich phase, as has been reported in the literature [7, 27]. Other elements were dispersed in both the CCTO and secondary phase grains. This result also indicated that Fe, Zn, V, and Al can be substituted into the CCTO structure. The results of this substitution are changes in the dielectric properties, as reported in the literature [28–32]. A Si–rich phase can enhance a liquid phase sintering mechanism [33].

The ionic radius of K$^+$ ion ($r = 1.64$ pm) was much larger than that of the Cu$^{2+}$ ($r = 57$ pm) and Ti$^{4+}$ ($r = 60.5$ pm) ions. Thus, it is likely that K$^+$ ions can substitute in the Ca$^{2+}$ ($r = 134$ pm) site. Furthermore, due to the same valence state, Si$^{4+}$ ions should prefer to substitute in the Ti$^{4+}$ site. For other ions (e.g., Fe$^{3+}$, Cr$^{3+}$, Mg$^{2+}$, and Al$^{3+}$ ions), the ionic radii of these ions and the host ions (Cu$^{2+}$ and Ti$^{4+}$) are not much different in size. They can substitute in either of the Cu$^{2+}$ or Ti$^{4+}$ site. The theoretical calculation was performed to predict the preferential substitution of Fe$^{3+}$, Cr$^{3+}$, Mg$^{2+}$, and Al$^{3+}$ ions in the CCTO structure. First, the intrinsic structure of the CCTO was optimized. Second, three structures for the replacement of dopants in the Ca, Cu, and Ti sites were also optimized. Third, the total energy for each structure was calculated. Then, the difference in
cohesive energy was determined \([24]\). The theoretical calculation results were demonstrated in figure 6. The preferential site of all the dopants (Fe\(^{3+}\), Cr\(^{3+}\), Mg\(^{2+}\), and Al\(^{3+}\) ions) in the CCTO structure was on the Cu site because of the largest cohesive energy.

The effects of the addition of PC on the dielectric properties of CCTO ceramics were investigated. As shown in figure 7(a), \(\varepsilon'\) values in the frequency range of 40–10⁶ Hz of the CCTO/Cement ceramics decreased with increasing amounts of PC. Nevertheless, the \(\varepsilon'\) values in the frequency range of 40–10⁶ Hz for the CCTO/Cement 1% and CCTO/Cement 2.5% ceramics were still very high (>10⁹), and they can still be classified as giant dielectric materials. However, the \(\varepsilon'\) value of the CCTO/Cement 5% ceramic greatly decreased to <10⁹ at frequencies higher than 10⁶ Hz. At 1 kHz and room temperature, the \(\varepsilon'\) values of the CCTO, CCTO/Cement 1%, CCTO/Cement 2.5%, and CCTO/Cement 5% samples were 2.4 \(\times\) 10⁵, 4.4 \(\times\) 10⁴, 1.8 \(\times\) 10⁴, and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_5.png}
\caption{EDX–SEM mapping of elements in the CCTO/Cement 5% sample.}
\end{figure}
It is likely that the frequency dependence of the CCTO/Cement ceramic $\varepsilon'$ values was more stable than that of the CCTO ceramics. According to a previous report, the $\varepsilon'$ values of the CCTO ceramics were greatly decreased by doping with Fe$^{3+}$ ions [28, 29], while the $\varepsilon'$ value of the CCTO ceramics was not significantly reduced by doping with Al, Si, Mg, Cr, and K$^+$ ions [17]. Thus, the significant reduction of $\varepsilon'$ for the CCTO/Cement 5% ceramic should be due to a large amount of Fe dopant ions.

As demonstrated in figure 7(b), a low–frequency tanδ value of CCTO/Cement ceramics can be significantly reduced by adding PC. Interestingly, tanδ of the CCTO/Cement 1% and CCTO/Cement 2.5% samples was much lower than that of the CCTO ceramic over the measured frequency range. The low–frequency tanδ of the
CCTO/Cement 5% sample was very high. The observed tanδ peak was due to the presence of a low–frequency dielectric relaxation, corresponding to a dramatic decrease in the ε′ value of the CCTO/Cement 5% sample. At 1 kHz, the tanδ value of the CCTO/Cement 2.5% sample was reduced by more than a factor of 3 compared to that of the CCTO ceramic. At 40 Hz, the tanδ value was greatly decreased, by one order of magnitude. A decrease in the low–frequency tanδ usually results from increased grain boundary resistance [34, 35]. The increase in tanδ in a high frequency range for the CCTO, CCTO/Cement 1%, and CCTO/Cement 2.5% samples, which was accompanied with the rapid decrease in ε′, signifies a dielectric relaxation behavior [36, 37]. These results indicated that addition of PC can effectively improve the giant dielectric properties of CCTO ceramics. Kotb et al [38], Zhang et al [9], and Choi et al [31] reported a significant decrease in the tanδ values of CCTO ceramics by doping with Al³⁺ ions. Wang et al [39] also reported that the tanδ values of CCTO ceramics prepared by a sol-gel method can be reduced by doping with K⁺ ions. Furthermore, it was also widely reported that substitution of Mg²⁺ ions into the CCTO structure can effectively decrease tanδ [34, 40, 41]. Most recently, Swatsitang and Putjuso [42] showed a decrease in the tanδ values of CCTO ceramics by doping with Cr³⁺ ions. Thus, the decrease in tanδ of the CCTO/Cement 1% and CCTO/Cement 2.5% samples should be attributed to the substitution of Al, Mg, Cr, and K ions into the CCTO structure, as reported in the literature.

Besides the improved dielectric properties, the nonlinear J–E properties of the CCTO/Cement ceramics were also studied. As illustrated in figure 8, all the sintered ceramic samples show nonlinear J–E characteristics. Notably, the electric field breakdown (E₀) of CCTO ceramics was greatly enhanced by incorporation of PC. This result directly indicates that the grain boundary response of CCTO ceramics was enhanced, since the nonlinear J–E properties originate at the grain boundaries [19]. From the nonlinear J–E behavior, the nonlinear coefficients (α) of the CCTO, CCTO/Cement 1%, CCTO/Cement 2.5%, and CCTO/Cement 5% samples were calculated and found to be 2.2, 2.8, 4.1, and 2.2, respectively. Their E₀ values were found to be 43.0, 264.1, 1295.3, and 1859.6 V cm⁻¹, respectively. Notably, the incorporation of PC has remarkable influences on both of the giant dielectric and nonlinear electrical properties of CCTO ceramics. The α value of the CCTO/Cement 2.5% sample was larger than that of the CCTO sample by a factor of 2. According to the microstructure analysis and theoretical calculation, it can be confirmed that many ions in the PC phase can substitute in the CCTO structure. Among them, the Cr³⁺, Al³⁺, and Mg²⁺ doping ions can enhance the nonlinear electrical properties of CCTO ceramics due to the improved electrical properties of the grain boundaries [24, 34, 42]. The increase in E₀ value can be described by the enhancement of electrostatic potential barrier at the grain boundaries [20, 21]. Variations in the dielectric and nonlinear electrical properties of the CCTO, CCTO/Cement 1%, and CCTO/Cement 2.5% are closely correlated. Thus, the giant dielectric properties should be caused by the internal barrier layer capacitor (IBLC) effect [19, 34]. Under an applied electric field, free charge carriers were trapped at the insulting grain boundary layers. This produces a space charge polarization, giving rise to a giant dielectric response.

To describe the origin of the enhanced dielectric and nonlinear electrical properties, impedance spectroscopy analysis was performed on the CCTO and CCTO/Cement samples. Accordingly, the electrical properties of the grains and grain boundaries of all sintered ceramic samples were characterized [20]. For CCTO ceramics, generally, the grain resistance and grain boundary resistances at room temperature can be calculated from the nonzero intercept of the Z' axis and the diameter of the large semicircular arc of the complex impedance plane.
Hence, the effects of substituted ions on the variation in dielectric and electrical properties can be explained. As illustrated in figure 9(a) and its inset, a portion of the large semicircle arcs can be observed at room temperature for the CCTO, CCTO/Cement 1%, and CCTO/Cement 2.5% samples. As previously reported [20, 22, 30], the observed large semicircular arc in the $Z^*$ plot of the CCTO sample at room temperature and higher was ascribed to the grain boundary response. It is likely that there were two large semicircular arcs, marked #A and #B, in the CCTO/Cement 5% sample. These two large semicircular arcs were confirmed to exist in the CCTO/Cement 5% sample with increased temperature to 80°C, as shown in figure 9(b) and its inset.

Figure 9(c) shows an expanded view of $Z^*$ plots at 20°C for high-frequency data close to the origin. Obviously, the nonzero intercept on the $Z'$-axis can be observed in the CCTO, CCTO/Cement 1%, and CCTO/Cement 2.5% samples only. The grain resistance values of these samples can be calculated from the nonzero intercepts. Alternatively, it is likely that the high-frequency data for the CCTO/Cement 5% sample tends to reach the origin of $Z^*$ plot. Thus, the #A and #B semicircular arcs likely result from the electrical responses of the grains and grain boundaries, respectively. The grain resistance of the CCTO/Cement 5% sample was calculated from the relationship $R_g = 2\pi^{n\max}$, where $Z^{\prime\max}$ is the maximum value obtained in the $Z^*$ plot [43].

It was found that the grain and grain boundary resistances of the CCTO/PC samples increased with the PC content. The calculated grain resistance values at 20°C of the CCTO, CCTO/Cement 1%, CCTO/Cement 2.5%, and CCTO/Cement 5% samples were found to be ~60, ~125, ~375, and 1.5 x 10^6 Ω·cm, respectively. This result is similar to that observed in Fe-doped CCTO ceramics, in which the grain resistance of CCTO ceramics greatly increased with the level of Fe^{3+} dopant ions [28]. Thus, the large increase in the grain resistance of the CCTO/Cement 5% sample should be attributed to the greater level of Fe^{3+} dopant ions. According to the impedance spectroscopy analysis and the IBLC model, it can be suggested that the large decrease in the $\varepsilon'$ value of the CCTO/Cement 5% sample was associated with a significant increase in the grain resistance, resulting in a greatly reduced concentration of free charge carriers inside the grains of this sample. Therefore, under an applied electric field, the interfacial polarization intensity at the grain boundaries of the CCTO/Cement 5% sample was very low due to a small amount of accumulated charges at the interface between the grains and grain boundaries.
According to the IBLC model, the total resistance of polycrystalline ceramics was governed by the grain boundary resistance. A low-frequency tanδ value, which was directly caused by the conduction of free charges, can be reduced by increasing the grain boundary resistance [44]. Thus, significantly reduced tanδ values of the CCTO/Cement 1% and CCTO/Cement 2.5% ceramics were attributed to the increased grain boundary resistance. Note that a large tanδ value of the CCTO/Cement 5% ceramic was caused by the existence of a low-frequency dielectric relaxation.

As shown in figure 7(a), the frequency dispersion in the CCTO/Cement 1% and CCTO/Cement 2.5% ceramics was less than that of the pure CCTO ceramic. This observation can be well described using an impedance spectroscopy analysis, which was due to the different values of the grain boundaries between the CCTO and CCTO/PC ceramics. It was theoretically demonstrated that a low-frequency dielectric response in CCTO ceramics was attributed to the sample-electrode contact (SEC) effect [43]. The SEC cannot appear when the grain boundary resistance significantly increased. As shown in figure 9, the grain boundary resistance of the CCTO ceramics can be significantly enhanced by incorporating with PC. Thus, the SEC effect and correlated additional low-frequency dielectric response cannot exist in the CCTO/PC ceramics, giving rise to the slight frequency dependence of ε′. Furthermore, the significantly enhanced resistance of the grain boundaries in the CCTO/PC ceramics can cause an increase in the Eδ values.

4. Conclusions

We successfully prepared CCTO/PC ceramics using a conventional mixed-oxide method. The microstructure of the sintered CCTO/PC ceramics was dense. Al, Fe, Si, K, Cr, and Mg were confirmed present in the PC powder. These elements can substitute into the CCTO structure, resulting in significantly improved giant dielectric and nonlinear I−V properties. High ε′ ∼ 10⁶ over a frequency range of 10⁵–10⁷ Hz and greatly reduced tanδ values, by a factor of 10, were obtained. Addition of PC into the CCTO ceramics can cause an increase in the α and Eδ values by factors of 2 and 30, respectively. Using impedance spectroscopy, it was found that the significant enhancement of α and Eδ as well as the reduction in the tanδ value, were due to the great increase in the grain boundary resistance of the CCTO/PC ceramics. This was due substitution of many suitable ions in PC such as Al<sup>3+</sup>, Si<sup>4+</sup>, Fe<sup>3+</sup>, K<sup>+</sup>, Cr<sup>3+</sup>, and Mg<sup>2+</sup> ions into the CCTO structure.

Acknowledgments

This work was financially supported by the Thailand Research Fund (TRF) under the TRF Distinguished Research Professor Grant No. DPG6180002. It was partially supported by the Research Network NANOTEC (RNN) program of the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, and by Khon Kaen University, Thailand. This work received a scholarship under the Post-doctoral Program from Research Affairs and Graduate School, Khon Kaen University (60170).

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