Enhanced dielectric response and non-Ohmic properties of Ge-doped CaTiO$_3$/CaCu$_3$Ti$_4$O$_{12}$

Jirata Prachamon$^a$, Jakkree Boonlakhon$^a$, Narong Chanlek$^b$, Nutthakritta Phromviyo$^c$, Viyada Harnchana$^b$, Pornjuk Sreeparawat$^a$, Ekaphan Swatsitang$^a$ and Prasit Thongbai$^b$.

$^a$Giant Dielectric and Computational Design Research Group (GD–CDR), Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen, Thailand; $^b$Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima, Thailand; $^c$Research and Innovation, Faculty of Science, Khon Kaen University, Khon Kaen, Thailand.

ABSTRACT

We present a method for increasing the dielectric constant of CaTiO$_3$/CaCu$_3$Ti$_4$O$_{12}$ (CTO/CCTO) composites and retaining a low-loss tangent (tan$\delta$) by doping with Ge dopant. The Ge-doped CTO/CCTO composites were fabricated using a one-step processing method. The phase composition and microstructure analyses confirmed the existence of CTO and CCTO phases, in which Ge doping ions can be substituted into both phases. The mean grain sizes of the two phases were slightly reduced by decreasing the porosity. Doping the CTO/CCTO with Ge doping ions resulted in a high dielectric constant by ~ two times, while a very low tan$\delta$ value of ~0.01 did not change. Furthermore, the dielectric constant changed by less than ±15% in the temperature range of ~60 – 150°C. The nonlinear current-density–electric field properties of CTO/CCTO can also be enhanced. Impedance spectroscopy showed a heterogeneous microstructure with enhanced grain boundary properties after doping with Ge dopants, giving rise to enhanced nonlinear electrical properties. The decreased grain resistivity due to Ge substitution is confirmed to originate from the increase in the Ti$^{4+}$/Ti$^{3+}$ ratio, which was analyzed using X-ray photoelectron spectroscopy.

1. Introduction

Dielectric materials are essential for technology development [1–3], and can be used in various applications, such as memory devices, capacitors, and electric energy storage equipment [3]. Therefore, dielectric materials with high dielectric constants ($\varepsilon'$) play an essential role in developing these technologies. A huge $\varepsilon'$ value of the capacitor material can reduce the capacitor size with maintaining the original capacitance [2,3].

Recently, materials with high $\varepsilon'$ values have been extensively studied to support the development of these technologies. One of the most studied materials is ACu$_3$Ti$_4$O$_{12}$, where A = Ca (CTO), Cd, Bi$_{2/3}$, Y$_{2/3}$, Na$_{1/2}$ Bi$_{1/2}$ and etc [4–19]. These materials have $\varepsilon'$ values of $10^5$–$10^6$ and vary only slightly $\varepsilon'$ according to the temperature. A suitable dielectric material for application must have a high $\varepsilon'$, low tan$\delta$, and slightly dependent temperature of $\varepsilon'$ [1,3]. Researchers believe that these materials will be able to replace traditional materials in the invention of ceramic capacitors such as BaTiO$_3$, where the $\varepsilon'$ value is strongly dependent on temperature near the Curie temperature point. However, CTO and related composites still exhibit above-standard tan$\delta$ values, which are unacceptable for practical use [15,19–21].

At present, strategies for reducing tan$\delta$ by various methods, such as metal ion doping, have been studied at various structural positions [6,12,15,19–21]. A unique structural design with a small grain size to increase the grain boundary density was also designed to reduce tan$\delta$ [22,23]. The fabrication of CTO ceramic composites reinforced with other ceramic materials with low $\varepsilon'$ tan$\delta$ values, such as SrTiO$_3$, TiO$_2$, and CaTiO$_3$ (CTO), has also been studied [19,24–28]. One of the most widely studied composites systems is the CTO/CTO system [19,24,26,27,29]. Such a ceramic composite system can be fabricated in only one step by adjusting the molar proportions of Ca and Cu [30]. The altered proportion resulting in a new phase was CTO. This material phase has a very low tan$\delta$ value. Therefore, the CTO/CTO composite system had a lower tan$\delta$ value. However, the $\varepsilon'$ value for the composite system decreased. Many researchers have attempted to find ways to increase the $\varepsilon'$ value of this ceramic composite system by doping with metal ions such as Zn$^{2+}$ and Sn$^{4+}$ [19,26,31].

On the other hand, it has been shown that CTO doping with Ge$^{4+}$ metal ions can improve the dielectric properties of the material. By reducing tan$\delta$ and increasing the $\varepsilon'$ value of CTO, Ge$^{4+}$ is a potential metal ion that improves the dielectric properties of
CCTO [32]. However, no research has been conducted on the dielectric properties of CTO/CCTO composite systems doped with Ge$^{4+}$ ions. Therefore, the aim of this research is to enhance the dielectric response of CTO/CCTO ceramic composites by substituting the Ge dopant.

In addition, non-Ohmic properties and nonlinear current density-electric fields (J-E) are also observed in CTO and CTO/CCTO [14,19,20,25]. Nonlinear J-E properties can be used to fabricate essential electronic components, such as varistors. Therefore, it was expected that Ge$^{4+}$ doping would also be able to improve their nonpathogenic properties.

In this study, we synthesized Ge$^{4+}$-doped CTO/CCTO ceramic composites using a solid-state reaction (SSR) route [33]. We studied the microstructural changes in the ceramic composites due to the doped ions. These ceramic composites have low tanδ values, which can be significantly increased by doping them with Ge metal ions. The conductivity of the composite materials can be explained using the internal barrier layer capacitor (IBLC) model.

### 2. Experimental details

CTO/CCTO ceramic composites were prepared by the SSR method using a single-step processing method from the formula Ca$_3$Cu$_2$Ti$_4$O$_{12}$. Accordingly, the CTO and CCTO phases with ~66.7 and ~33.3 mol%, respectively, should be obtained due to the deviation Ca$^{2+}$:Cu$^{2+}$ ratio of 1:3 (for CTO) to 2:2 (for CTO/CCTO) [31]. Excessive Ca$^{2+}$ and Ti$^{4+}$ preferentially formed the CTO phase. Ca$_3$Cu$_2$Ti$_4$Ge$_{0.025}$O$_{12}$ powders (x = 0–0.1) were synthesized using the SSR route. The starting raw materials were TiO$_2$ (Sigma-Aldrich, 99.9% purity), GeO$_2$ (Sigma-Aldrich, 99.99%), CuO (Merck, 99.0% purity), and CaCO$_3$ (Sigma-Aldrich, 99.9% purity). First, for each composition, the starting materials were mixed by ball-milling in ethanol for 6 h. Second, the ZrO$_2$ balls were separated from the mixed powders. Third, ethanol was removed by evaporation in an oven at 100°C for 12 h. Next, the powders were calcined at 850°C for 12 h to form CCTO and CTO phases. The composite powder was carefully ground and pressed into pellets. Finally, ceramic composite samples were obtained by sintering for 6 h at 1,060°C. The sintered Ca$_3$Cu$_2$Ti$_4$Ge$_{x}$O$_{12}$ ceramics with x = 0 (CTO/CCTO), 0.025 (Ge025), and 0.10 (Ge10) were obtained.

The sintered ceramic composites were characterized using X-ray diffraction (XRD, PANalytical, EMPYREAN) and field-emission scanning electron microscopy (FESEM; HITACHI SU8030, JAPAN) with energy-dispersive X-ray analysis. The sintered ceramic composites were characterized using the X-ray photoelectron spectroscopy (XPS) technique (PHIS000 VersaProbe II, ULVAC- PHI, Japan) at the SUT–NANOTEC–SLRI Joint Research Facility, the Synchrotron Light Research Institute (SLRI), Thailand. The XPS spectra were analyzed using PHI MultiPak XPS software with Gaussian-Lorentzian lines.

A KEYSIGHT E4990A impedance analyzer was used to measure the dielectric properties. The samples were polished and coated with silver paint on both sides of the surface to create a parallel-plate capacitor. The samples were then fired at 600°C for 30 min in air. The capacitance ($C_p$) and tanδ were measured at an oscillation voltage of 0.5 V. The dielectric data were tested in the frequency and temperature ranges of 10$^2$–10$^6$ Hz and −60 − 220°C, respectively. The J-E characteristics were measured at −25°C using a high-voltage measurement unit (Keithley Model 247, Estado St. Pasadena, CA). The electric field at which $J = 1$ mA cm$^{-2}$ was defined as the breakdown electric field ($E_b$). The nonlinear coefficient (a) was calculated in the range of $J_1 = 1$ to $J_2 = 10$ mA cm$^{-2}$, using the following formula:

$$a = \log(J_2/J_1) \over \log(E_2/E_1),$$

where $E_1$ and $E_2$ are the electric fields at $J_1$ and $J_2$, respectively.

### 3. Results and discussion

The XRD patterns of all composites are shown in Figure 1(a), confirming the two phases of CTO (JCPDS 82–0231) and CCTO UCPDS 75–2188. Only the CTO and CCTO phases were observed, which are similar to those reported in previous studies [30,34–36]. For CCTO, the Ca$^{2+}$:Cu$^{2+}$:Ti$^{4+}$ ratio is 1:3:4. When this ratio deviates from 1:3:4 to 2:2:4 (Ca$_3$Cu$_2$Ti$_4$O$_{12}$), the required ratio of Ca$^{2+}$:Cu$^{2+}$:Ti$^{4+}$ for the formation of the CCTO phase is (2/3):2:(8/3). The formation of the CTO phase was due to the reaction between excessive (4/3)Ca$^{2+}$ and (4/3)Ti$^{4+}$. Thus, CCTO and CTO phases with ~33.3 and ~66.7 mol% should be formed and confirmed by Rietveld quantitative analysis, as reported in a previous work [30]. The lattice parameters of the CCTO phases of CTO/CCTO, Ge025, and Ge10 obtained from Rietveld refinement (Figure 1(b)) were 7.391, 7.392, and 7.390 Å, respectively. According to our previous studies [37,38], the mixed oxidation states of the Ge dopant were Ge$^{2+}$ and Ge$^{4+}$ [37]. DFT calculations showed that the Ge dopant can substitute in the Cu and Ti sites of the CTO structure but is a more preferential substitution on the Cu site [38]. Theionic radii of Cu$^{2+}$ ($r_a$) and Ti$^{4+}$ ($r_d$) are 57 and 60.5 pm, respectively, while the radii of Ge$^{2+}$ ($r_a$) and Ge$^{4+}$ ($r_d$) are 73 and 53 pm, respectively [39]. Theionic radius of Ge$^{2+}$ was larger than that of Cu$^{2+}$, whereas the ionic radius of Ti$^{4+}$ ($r_d$) was larger than that of Ge$^{4+}$. Thus, the average lattice parameter of the CTO phase changes slightly.
This result clearly indicates the presence of the CTO phase. For the lighter grains, all the elements (i.e., Ca, Cu, Ti, and O) were observed, confirming the CTO phase. These observations were similar to those observed for Ge10, as shown in Figure 3(b). Furthermore, Ge dopant can be observed in both the CTO and CTO phases, as indicated by the circular areas.

The average grain sizes (G) of the CTO and CTO phases were calculated from backscattered SEM images. The G values of the CTO phase in the CTO/CTO, Ge025, and Ge10 are 2.5 ± 1.4, 1.6 ± 0.4, and 1.7 ± 0.7 µm, respectively, while the G values of the CTO phases are 1.5 ± 0.9, 1.0 ± 0.6, and 1.1 ± 0.5 µm, respectively. The G values of the CTO and CTO phases were slightly decreased by Ge substitution. The porosity was reduced by doping with Ge. This result is caused by the liquid-phase sintering (LPS) mechanism, as observed in Ge-doped CTO ceramics [32,38]. However, in the Ge-doped CTO, the G values significantly increased owing to the LPS. The suppressed grain growth of the CTO phase in the Ge-doped CTO/CTO composites was attributed to the pinning effect of the CTO particles [40]. Thus, densification can be enhanced by the Ge dopant, whereas grain growth is inhibited by the CTO-phase particles.

The dielectric properties of the Ge-doped CTO/CTO composites at 20°C are shown in Figure 4. As clearly seen, the ε’ value of the CTO/CTO composites in the measured frequency range increased with increasing Ge doping concentration. The ε’ values of all composites varied slightly with frequency. At 1 kHz, the ε’ values of CTO/CTO, Ge025, and Ge10 were 1.784, 2.095, and 3.377, respectively. The ε’ value of CTO/CTO is nearly equal to that reported by Kobayashi and Terasaki (ε’ ~ 1,800) [29]. The ε’ value of Ge10 significantly increased by nearly a factor of 2. As displayed in the inset of Figure 4, although the tanδ value at 1 kHz of the Ge025 was as low as 0.044, the low-frequency tanδ value of Ge025 increased with decreasing frequency, which resulted from the motion of charge carriers [41]. The tanδ values at 1 kHz for CTO/CTO and Ge10 are 0.012 and 0.010, respectively. It is worth noting that doping Ge ions into the CTO/CTO composites not only increased the ε’ value but

![Figure 1](image1.png)

**Figure 1.** (a) XRD patterns of Ge-doped CTO/CTO composites. (b) Rietveld refinement of CTO/CTO composite.

The microstructures of the ceramic composites were analyzed using backscattered SEM images, as shown in the Figure 2(a–d). Before characterization, the composite samples were polished and thermally etched at 1,000°C for 30 min. The two different contrast zones in the images, lighter and darker, indicate two phases corresponding to the XRD patterns. According to previous reports [19,24,26,30], the lighter and darker zones were the CTO and CTO phases, respectively, confirming the presence of two phases in the ceramic samples. To confirm the existence of CTO and CTO phases in the observed microstructure, SEM-EDS mapping was performed. As shown in Figure 3(a), Cu was not observed in the darker grains of CTO/CTO, whereas Ca, Ti, and O were observed.

![Figure 2](image2.png)

**Figure 2.** Backscattered SEM images of the polished samples: (a) CTO/CTO, (b) Ge025, and (c) Ge10.
also inhibited the increased tanδ value. The high-frequency tanδ uptrend is attributed to the dielectric relaxation of the primary contributors to the overall dielectric response. Considering the starting Ca$_2$Cu$_2$Ti$_4$O$_{12}$ composition, CCTO and CTO phases with \( \sim 33.3 \) and 66.7 mol\% were obtained, respectively. The volume fractions of these phases were calculated and found to be \( f_{\text{CCTO}} = 0.642 \) and \( f_{\text{CTO}} = 0.358 \). Thus, the CCTO phase was the ceramic matrix. For a pure CCTO ceramic sintered at 1,060°C, the \( \varepsilon' \) value was \( \sim 10^4 \) [42], while that of the CTO ceramic sintered at 1100°C was \( \sim 80 \) [35]. Therefore, the reduced \( \varepsilon' \) value of the CTO/CCTO composite was caused by the low \( \varepsilon' \) value of the CTO phase.

To clearly explain the dielectric properties of the CTO/CCTO and Ge-doped CTO/CCTO composites, the effective dielectric constant (\( \varepsilon_{\text{eff}} \)) was calculated using the Lichtenecker logarithmic model [29,43]:
\[
\ln \varepsilon'_{\text{eff}} = (1 - f_{\text{CTO}})\ln \varepsilon'_{\text{CCTO}} + f_{\text{CTO}}\ln \varepsilon'_{\text{CTO}}
\]  

(2)

where \(\varepsilon'_{\text{CCTO}}\) and \(\varepsilon'_{\text{CTO}}\) are the \(\varepsilon'\) values for the CCTO (10\(^5\)) and CTO (80) phases, respectively. The calculated \(\varepsilon'_{\text{eff}}\) of the undoped CTO/CCTO composite was 1,755, which corresponds to the experimental \(\varepsilon'\) value for the undoped CTO/CCTO composite (1,784). According to a previous work [32,37], the \(\varepsilon'\) value of CTO ceramics was increased by doping with Ge. Thus, the increased \(\varepsilon'\) values of the Ge025 and Ge10 composites are primarily attributed to the increased \(\varepsilon'\) value of the Ge-doped CTO phase in the ceramic composites.

In addition to the enhanced \(\varepsilon'\) and low \(\tan\delta\) values, the variation of with temperature must be investigated to verify the performance of the dielectric composites. Figure 5 shows the temperature coefficient of the \(\varepsilon'\) (\(\Delta\varepsilon'\)) compared to that of the \(\varepsilon'\) value at 30°C. Notably, the \(\Delta\varepsilon'\) of the CTO/CCTO and Ge025 was < ±15% in the temperature range from −60 to 140°C, meeting the requirement for application in the X7R capacitor with the temperature dependence of the capacitance of less than 15% in the temperature range from −55 to 125°C [1,3]. Furthermore, the \(\Delta\varepsilon'\) of Ge10 was < ±15% in the temperature range of −60 – 150°C, following the requirement for application in the X8R capacitor, whose temperature dependence of the capacitance must be < ±15% in the temperature range from −55 to 150°C [1,3].

To clearly explain the dielectric behavior of the Ge-doped CTO/CCTO composites, the electrical properties of the grains and grain boundaries were studied using impedance spectroscopy. For a coarse-grained CTO ceramic, the large semicircular arcs of the impedance complex plane (\(Z^*\)) plot, which is typically observed at room temperature in the frequency range below 5–10\(^5\) Hz [44,45], represents the insulating grain boundary (or internal interface) response. For fine-grained CTO ceramics, only parts of large arcs are usually observed [45]. On the other hand, the electrical response of grains with relatively low conductivity was indicated by the observed nonzero intercept at high frequencies [45]. In this case, the grain boundary resistance (\(R_{\text{gb}}\)) and grain resistance (\(R_{\text{g}}\)) can be calculated from the diameter of the large semicircular arc and nonzero intercept on the \(Z^*\) axis, respectively. Figure 6 shows the \(Z^*\) plots of all the ceramic composites at 25°C in the frequency range of 10\(^2\)–10\(^6\) Hz. Only parts of the large semicircular arcs can be observed, which are attributed to the large \(R_{\text{gb}}\) values of all the ceramic composites. At 25°C, it was difficult to verify the relative \(R_{\text{gb}}\) values of the CTO/CCTO and Ge10 composites. \(R_{\text{gb}}\) values were reduced by increasing the temperature. Therefore, the \(Z^*\) plots at high temperatures clearly show the different \(R_{\text{gb}}\) values of all composite samples. The inset (1) of Figure 6 shows the \(Z^*\) plots of the CTO/CCTO and Ge-doped CTO/CCTO composites at 130°C. Large semicircular arcs are clearly observed. The \(R_{\text{gb}}\) values of all the composites were very large (> 1 MΩ·cm) even at a high temperature of 130°C. The \(R_{\text{gb}}\) value of Ge025 decreased, while the \(R_{\text{gb}}\) value of Ge10 increased significantly compared to that of the undoped CTO/CCTO composite. The variation in the \(R_{\text{gb}}\) values is consistent with their \(\tan\delta\) values in a relatively low-frequency range, following the relation [20]

\[
\tan\delta \approx \frac{1}{\omega C_{\text{gb}} R_{\text{gb}}},
\]

(3)

where \(C_{\text{gb}}\) is the grain-boundary capacitance. The \(\tan\delta\) value is inversely proportional to \(R_{\text{gb}}\). As shown in inset (2) of Figure 6, the nonzero

![Figure 5](image-url)  

Figure 5. Temperature coefficient (\(\Delta\varepsilon'/\varepsilon'_{30}\)) at 1 kHz for Ge-doped CTO/CCTO composites.
intercept at high frequencies can be observed with $R_g \sim 80–125$ $\Omega$.cm. Thus, the composites consisted of low-conductivity grains and very-high-conductivity grain boundaries (IBLC structure). This enhanced $\varepsilon'$ value should be described using the IBLC model. The $R_g$ values of the CTO/CCTO composites decrease with increasing Ge doping concentration. This result indicates that the conductivity and free charges inside the semiconducting grains of Ge025 and Ge10 increased, corresponding to an increase $\varepsilon'$ in. When an electric field was applied to the composites, a large number of free electrons inside the semiconducting grains of the Ge-doped CTO/CCTO accumulated more at the internal interfaces than that in the undoped CTO/CCTO, leading to enhanced space charge polarization and $\varepsilon'$. Therefore, an increased dielectric response in the CTO/CCTO composites was obtained by changing the electrical conductivity of the semiconducting grains.

To confirm the increase in free charges inside the semiconducting grains of Ge025 and Ge10 compared to that of the CTO/CCTO composite, the XPS spectra of Ti 2p of all samples were measured. Figure 7 shows the XPS spectra of the Ti 2p$_{3/2}$ peaks of Ge025 and Ge10, which can be separated into two peaks using a Gaussian-Lorentzian fitting. The primary peak with a binding energy of ~458 eV is typically assigned to Ti$^{4+}$ [21]. The additional peak with a lower binding energy of ~456.8 eV was assigned to Ti$^{3+}$ [21]. Accordingly, the Ti$^{3+}$/Ti$^{4+}$ ratios of Ge025 and Ge10, which can be calculated from the area ratio, were approximately 5.95.

![Figure 6](image1.png)

**Figure 6.** Impedance complex plane ($Z'$) plots at 20°C for Ge-doped CTO/CCTO composites; insets (1) and (2) show $Z'$ plots at 130°C and 20°C, respectively, for high-frequency data.

![Figure 7](image2.png)

**Figure 7.** XPS spectra of Ti 2p for (a) Ge025 and (b) Ge10.
Figure 8. Nonlinear J-E characteristics of CTO/CCTO, Ge025, and Ge10 at 25°C.

and 8.41%, respectively. Note that the Ti$^{3+}$ peak in the XRS spectrum of CTO/CCTO cannot be separated (not shown), which may be because the Ti$^{3+}$/Ti$^{4+}$ ratio is lower than the resolution limit of this technique. Nevertheless, the increased Ti$^{3+}$/Ti$^{4+}$ ratio is in accordance with the decreased $R_g$ value. The increased Ti$^{3+}$/Ti$^{4+}$ ratios of the Ge-doped CTO/CCTO composites were similar to those observed in the Ge-doped CCTO ceramics [32], which was attributed to the presence of oxygen vacancies during the sintering process at high temperatures.

It was demonstrated that the electrical responses of the CCTO-CTO and CCTO-CTO interfaces were electrically active, while the CTO-CTO was electrically inactive [30]. The significantly increased $R_{gb}$ value of Ge10 may be caused by the improved electrical properties of the active interfaces owing to the Cu- and Ge-related phases that were segregated at the grain boundaries, similar to the case of Ge-doped CCTO [32,38]. Furthermore, as shown in the SEM-EDS mapping images, the Ge dopant was also observed in the CTO grains. It is possible that, but not proven, the CTO-CTO interface became an electrically active interface owing to the substitution of Ge in the CTO phase when the doping concentration increased.

In addition to the significantly improved dielectric properties, the nonlinear electrical properties of the CTO/CCTO composites also improved. The nonlinear electrical characteristic of polycrystalline ceramics is used as a varistor device to protect the electric circuit from rapid changes in voltage [3]. As displayed in Figure 8, the CTO/CCTO and Ge-doped CTO/CCTO composites showed nonlinear J-E characteristics, which were caused by the Schottky barrier at the interface between the adjacent $n$-type semiconducting grains [26,45]. The $E_b$ values of the CTO/CCTO, Ge025, and Ge10 composites were 5,224, 5,903, and 6,386 V cm$^{-1}$. The $E_b$ values of Ge025 and Ge10 are larger than those of the CTO/CCTO composites. This result was attributed to the decreased $G$ values of the CTO and CTO phases of Ge025, and Ge10 as shown in Figure 2. The $\alpha$ corresponding values were 10.4, 7.4, and 12.7, respectively. The nonlinear electrical properties of Ge10 can be significantly improved by increasing $E_b$ and $\alpha$ compared to those of the undoped CTO/CCTO composites.

4. Conclusion

The phase composition, microstructure, nonlinear J-E characteristics, dielectric response, and electrical properties of the grains and grain boundaries of the Ge-doped CTO/CCTO composites fabricated using the SSR method were systematically investigated. Ceramic composites can be synthesized by a one-step processing method using the formula Ca$_2$Cu$_2$Ti$_4$Ge$_{10}$O$_{27}$. The CTO and CCTO phases were confirmed by XRD and SEM-EDS mapping techniques. Ge dopants can be observed in both the CTO and CCTO phases, which inhibited the grain growth of the two phases but promoted the densification process. The $\varepsilon'$ of the CTO/CCTO composites can be increased by ~2 times with retaining a low tanδ value of ~0.01 at 1 kHz. Notably, $\Delta\varepsilon' < \pm 15\%$ was obtained in the temperature range of ~60 – 150°C, meeting the temperature-dependent requirement for the XBR capacitor. Furthermore, the $E_b$ and $\alpha$ values of the CTO/CCTO composites could also be improved by doping with Ge. An electrically heterogeneous microstructure with an enhanced $R_{gb}$ and reduced $R_g$ was observed in the Ge-doped CTO/CCTO composites. The enhanced electrical properties of the grain boundaries may be attributed to the improvement of the active electrical interfaces of CCTO-CTO and CTO-CCTO, while the inactive interface of the CTO-CTO might be electrically active, but not...
proven, owing to the substitution of Ge into the CTO phase.

Acknowledgments

This project was funded by the National Research Council of Thailand (NRCT): (N41A640084). Funding support was also received from the National Science, Research, and Innovation Fund (NSRF) and the Basic Research Fund of Khon Kaen University. J.P. expresses her gratitude to the Institute of Nanomaterials Research and Innovation for Energy (IN–RIE) for a master’s degree scholarship in Physics.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the National Research Council of Thailand [N41A640084]; Basic Research Fund of Khon Kaen University [:]; National Science, Research and Innovation Fund (NSRF) [:].

ORCID

Narong Chanlek (http://orcid.org/0000-0002-8025-1293)
Prasit Thongbai (http://orcid.org/0000-0001-7658-6165)

References

[1] Pan M, Randall CA. A brief introduction to ceramic capacitors. IEEE Electr Insl Mag. 2010;26(3):44–50.
[2] Wang Y, Jie W, Yang C, et al. Colossal permittivity materials as superior dielectrics for diverse applications. Adv Funct Mater. 2019;29(27):1808118.
[3] Moulson AJ, Herbert JM. Electroceramics: materials, properties, applications. 2nd ed. West Sussex (New York): Wiley; 2003.
[4] Li W, Tang L, Xue F, et al. Large reduction of dielectric losses of CaCu3Ti4O12 ceramics via air quenching. Ceram Int. 2017;43(8):6618–6621.
[5] Li Y, Li W, Du G, et al. Low temperature preparation of CaCu3Ti4O12 ceramics with high permittivity and low dielectric loss. Ceram Int. 2017;43(12):9178–9183.
[6] Du G, Wei F, Li W, et al. Co-doping effects of A-site Y3+ and B-site Al3+ on the microstructures and dielectric properties of CaCu3Ti4O12 ceramics. J Eur Ceram Soc. 2017;37(15):4653–4659.
[7] Peng Z, Wang J, Lei X, et al. Colossal dielectric response in CdAl2Cu3Ti4O12 perovskite ceramics. Mater Chem Phys. 2021;258:123940.
[8] Peng Z, Wang J, Zhou X, et al. Grain engineering inducing high energy storage in CdCu3Ti4O12 ceramics. Ceram Int. 2020;46(10, Part A):14425–14430.
[9] Peng Z, Zhou X, Wang J, et al. Origin of colossal permittivity and low dielectric loss in Na0.5Y2/3Ca1/3Cu3Ti4O12 ceramics. Ceram Int. 2020;46(8, Part A):11154–11159.
[10] Kotb HM, Khater HA, Saber O, et al. Sintering temperature, frequency, and temperature dependent dielectric properties of Na0.5Sm0.5Cu3Ti4O12 ceramics. Materials. 2021;14(17):4805.
[11] Ahmad MM, Kotb HM, Joseph C, et al. Transport and dielectric properties of mechanosynthesized La2/3Cu3Ti4O12 ceramics. Crystals. 2021;11(3):313.
[12] Kotb HM, Ahmad MM, Alshoaiabi A, et al. Dielectric response and structural analysis of (A3+, Nb5+) cosubstituted CaCu3Ti4O12 ceramics (A: Al and Bi). Materials. 2020;13(24):5822.
[13] Peng Z, Wang J, Liang P, et al. A new perovskite-related ceramic with colossal permittivity and low dielectric loss. J Eur Ceram Soc. 2020;40(12):4010–4015.
[14] Xue R, Chen Y, Li T, et al. Effects of Lu3+ doping on microstructures and electrical properties of CaCu3Ti4O12 ceramics. J Supercond Novel Magn. 2021;34(12):3297–3309.
[15] Mao P, Wang J, Xiao P, et al. Colossal dielectric response and relaxation behavior in novel system of Zr4+ and Nb5+ co-substituted CaCu3Ti4O12 ceramics. Ceram Int. 2021;47(1):111–120.
[16] Chinnathambi M, Saktisabarimoothi A, Jose M, et al. Study of the electrical and dielectric behaviour of selenium doped CCTO ceramics prepared by a facile sol-gel route. Mater Chem Phys. 2021;272:124970.
[17] Liu Z, Chao X, Liang P, et al. Differentiated electric behaviors of La2/3Cu3Ti4O12 Ceramics prepared by different methods. J Am Ceram Soc. 2014;97(7):2154–2163.
[18] Yang Z, Ren H, Chao X, et al. High permittivity and low dielectric loss of Na0.5Bi0.5-La3Cu3Ti4O12 ceramics. Mater Res Bull. 2012;47(5):1273–1277.
[19] Cortés JA, Moreno H, Orrego S, et al. Dielectric and non-ohmic analysis of Sr2+ influences on CaCu3Ti4O12-based ceramic composites. Mater Res Bull. 2021;134:111071.
[20] Boonlakhorn J, Chanlek N, Manyam J, et al. Enhanced giant dielectric properties and improved nonlinear electrical response in acceptor-donor (Al3+, Ta5+)–co-substituted CaCu3Ti4O12 ceramics. J Adv Ceram. 2021;10(6):1243–1255.
[21] Jumpatam J, Putasaeng B, Chanlek N, et al. Significantly improving the giant dielectric properties of CaCu3Ti4O12 ceramics by co-doping with Sr2+ and F- ions. Mater Res Bull. 2021;133:111043.
[22] Thongbai P, Yamwong T, Maensiri S, et al. Improved dielectric and nonlinear electrical properties of fine-grained CaCu3Ti4O12 ceramics prepared by a glycerine-nitrate process. J Am Ceram Soc. 2014;97(6):1785–1790.
[23] Boonlakhorn J, Kiddkhunthod P, Thongbai P. A novel approach to achieve high dielectric permittivity and low loss tangent in CaCu3Ti4O12 ceramics by co-doping with Sm3+ and Mg2+ ions. J Eur Ceram Soc. 2015;35(13):3521–3528.
[24] Jumpatam J, Putasaeng B, Chanlek N, et al. Influences of Sr2+ doping on microstructure, giant dielectric behavior, and non-ohmic properties of CaCu3Ti4O12/CaTiO3 ceramic composites. Molecules. 2021;26(7):1994.
[25] Saengvong P, Chanlek N, Putasaeng B, et al. Significantly improved colossal dielectric properties and Maxwell–Wagner relaxation of TiO2–rich Na2/3Y1/3Cu3Ti4O12 ceramics. Molecules. 2021;26(19):6043.
[26] Cotrim G, Cortés JA, Moreno H, et al. Tunable capacitor-varistor response of CaCu3Ti4O12/CaTiO3 ceramic composites with SnO2 addition. Mater Charact. 2020;170:110699.
[27] Maleki Shahraki M, Daeijavad H, Emami AH, et al. An engineering design based on nano/micro-sized composite for CaTiO3/CaCu3Ti4O12 materials and its dielectric and non-Ohmic properties. Ceram Int. 2019;45(17):21676–21683.

[28] Xue R, Liu D, Chen Z, et al. Dielectric and nonohmic properties of CaCu3Ti4O12/SrTiO3 ceramics. J Electron Mater. 2015;44(4):1088–1094.

[29] Kobayashi W, Terasaki I. CaCu3Ti4O12/CaTiO3 composite dielectrics: Ba/Pb-free dielectric ceramics with high dielectric constants. Appl Phys Lett. 2005;87(3):032902.

[30] Ramirez MA, Bueno PR, Tararam R, et al. Evaluation of the effect of the stoichiometric ratio of Ca/Cu on the electrical and microstructural properties of the CaCu3Ti4O12 polycrystalline system. J Phys D: Appl Phys. 2009;42(18):185503.

[31] Jumpatam J, Putasaeng B, Yamwong T, et al. A novel route to greatly enhanced dielectric permittivity with reduce loss tangent in CaCu3+2ZnTi4O12/CaTiO3 composites. J Am Ceram Soc. 2014;97(8):2368–2371.

[32] Boonlakhorn J, Thongbai P, Putasaeng B, et al. Microstructural evolution, non-Ohmic properties, and giant dielectric response in CaCu3Ti1-xGeO12 ceramics. J Am Ceram Soc. 2017;100(8):3478–3487.

[33] Chao X, Wu P, Zhao Y, et al. Effect of CaCu3Ti4O12 powders prepared by different synthetic methods on dielectric properties of CaCu3Ti4O12/polyvinylidene fluoride composites. J Mater Sci: Mater Electron. 2015;26(5):3044–3051.

[34] Ramirez MA, Bueno PR, Longo E, et al. Conventional and microwave sintering of CaCu3Ti4O12/CaTiO3 ceramic composites: non-ohmic and dielectric properties. J Phys D: Appl Phys. 2008;41(15):152004.

[35] Cheng B, Lin Y-H, Yang H, et al. High dielectric permittivity behavior in Cu-doped CaTiO3. J Am Ceram Soc. 2009;92(11):2776–2779.

[36] Oliveira LH, Paris EC, Avansi W, et al. Correlation between photoluminescence and structural defects in Ca11+4Cu9−xTiO12 systems. J Am Ceram Soc. 2013;96(1):209–217.

[37] Boonlakhorn J, Chanlek N, Srepusharawoot P, et al. Controlling microstructure and significantly increased dielectric permittivity with largely reduced dielectric loss in CaCu3.2Ge1.8Ti4O12 ceramics. Appl Phys A. 2020;126(11):897.

[38] Boonlakhorn J, Chanlek N, Thongbai P, et al. Strongly enhanced dielectric response and structural investigation of (Sr2+, Ge4+) Co-doped CCTO ceramics. J Phys Chem C. 2020;124(38):20682–20692.

[39] Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in Halides and Chalogenides. Acta Cryst. 1976;A32:751–767.

[40] Rahaman MN. Ceramic processing and sintering. 2nd ed. New York: M. Dekker; 2003.

[41] Emmert S, Wolf M, Gulich R, et al. Electrode polarization effects in broadband dielectric spectroscopy. Eur Phys J B. 2011;83(2):157–165.

[42] Boonlakhorn J, Chanlek N, Manyam J, et al. Simultaneous two-step enhanced permittivity and reduced loss tangent in Mg/Ge-doped CaCu3Ti4O12 ceramics. J Alloys Compd. 2021;877:160322.

[43] Hennings D, Schreinemacher H. Temperature dependence of the segregation of calcium titanate from solid solutions of (Ba, Ca) (Ti, Zr)O2 and its effect on the dielectric properties. Mater Res Bull. 1977;12(12):1221–1226.

[44] Sinclair DC, Adams TB, Morrison FD, et al. CaCu3Ti4O12: one-step internal barrier layer capacitor. Appl Phys Lett. 2002;80(12):2153.

[45] Adams T, Sinclair D, West A. Characterization of grain boundary impedances in fine- and coarse-grained CaCu3Ti4O12 ceramics. Phys Rev B. 2006;73(9):094124.