Enhanced giant dielectric properties and improved nonlinear electrical response in acceptor–donor (Al$^{3+}$, Ta$^{5+}$)-substituted CaCu$_3$Ti$_4$O$_{12}$ ceramics

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Abstract: The giant dielectric behavior of CaCu$_3$Ti$_4$O$_{12}$ (CCTO) has been widely investigated owing to its potential applications in electronics; however, the loss tangent (tan$\delta$) of this material is too large for many applications. A partial substitution of CCTO ceramics with either Al$^{3+}$ or Ta$^{5+}$ ions generally results in poorer nonlinear properties and an associated increase in tan$\delta$ (to $\sim$0.29–1.15). However, first-principles calculations showed that self-charge compensation occurs between these two dopant ions when co-doped into Ti$^{4+}$ sites, which can improve the electrical properties of the grain boundary (GB). Surprisingly, in this study, a greatly enhanced breakdown electric field ($\sim$200–6588 V/cm) and nonlinear coefficient ($\sim$4.8–15.2) with a significantly reduced tan$\delta$ ($\sim$0.010–0.036) were obtained by simultaneous partial substitution of CCTO with acceptor–donor (Al$^{3+}$, Ta$^{5+}$) dopants to produce (Al$^{3+}$, Ta$^{5+}$)-CCTO ceramics. The reduced tan$\delta$ and improved nonlinear properties were attributed to the synergistic effects of the co-dopants in the doped CCTO structure. The significant reduction in the mean grain size of the (Al$^{3+}$, Ta$^{5+}$)-CCTO ceramics compared to pure CCTO was mainly because of the Ta$^{5+}$ ions. Accordingly, the increased GB density due to the reduced grain size and the larger Schottky barrier height ($\phi_b$) at the GBs of the co-doped CCTO ceramics were the main reasons for the greatly increased GB resistance, improved nonlinear properties, and reduced tan$\delta$ values compared to pure and single-doped CCTO. In addition, high dielectric constant values ($\varepsilon'$ $\approx$ (0.52–2.7) $\times$ 10$^4$) were obtained. A fine-grained microstructure with highly insulating GBs was obtained by Ta$^{5+}$ doping, while co-doping with Ta$^{5+}$ and Al$^{3+}$ resulted in a high $\phi_b$. The obtained results are expected to provide useful guidelines for developing new giant dielectric ceramics with excellent dielectric properties.

Keywords: CaCu$_3$Ti$_4$O$_{12}$ (CCTO); impedance spectroscopy; nonlinear electrical properties; dielectric constant; loss tangent; first-principles calculations

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1 Introduction

The giant dielectric properties (GDPs) of dielectric materials with a high dielectric constant ($\varepsilon'$) have been extensively studied for use in electronics applications, such as capacitive devices used in high-energy storage devices [1–13]. Most recently, giant dielectric materials have been proposed as potential epsilon-negative or mu-negative materials [14–16]. High $\varepsilon'$ values of $\sim 10^3$–$10^7$ in the low-frequency range without detectable phase transitions have been reported for a wide range of functional electroceramics, such as doped TiO$_2$ [4,17], doped SnO$_2$ [18], doped NiO [19], CaCu$_3$Ti$_4$O$_{12}$ (CCTO) and its related structures [3,5,20–23], and La$_{2-x}$Sr$_x$NiO$_4$ [24]. These ceramic oxides can be used in electronic devices, such as capacitors, sensors, and varistors. However, these materials still have several serious limitations that restrict their use in electronic devices. The most critical challenge is the high loss tangent ($\tan\delta$) of these materials [4,5,18,20,21]. Furthermore, for use in capacitor applications, a low frequency- and temperature-dependence of $\varepsilon'$ (at 1 kHz) is important [4,5].

In addition to potential applications, the primary mechanisms of the GDPs have been widely investigated. The surface/internal barrier layer capacitor (SBLC/IBLC) model [18,20,25], polaron-hopping model [24], electron pinned defect dipole (EPPD) model [4], and non-ohmic sample–electrode contact model [26] have been used to describe the contributions to the GDPs in simple and complex oxides. However, the origin of the GDPs of these dielectric oxides is still unclear and is a current research focus.

In recent years, the dielectric properties of a range of ceramic materials have been improved by substituting pairs of metal ions into their crystalline structures [1,4,5,17,18,27]. Newly discovered $\text{A}^{3+}$ ($\text{Al}^{3+}$, $\text{In}^{3+}$, $\text{Ga}^{3+}$) and $\text{B}^{5+}$ ($\text{Nb}^{5+}$, $\text{Ta}^{5+}$) acceptor–donor co-doped rutile TiO$_2$ and SnO$_2$ ceramics were reported to show GDPs $\varepsilon'$ with very low $\tan\delta$ values in the Ti sites, namely CaCu$_3$Ti$_4$–$x$Ta$_x$O$_{12}$ samples with $x = 0.025$, 0.05, 0.10, and 0.20 are henceforth abbreviated as TaAl$_{0.5}$, TaAl$_{1.0}$, and TaAl$_{2.0}$, respectively. The starting raw materials used to synthesize the powders were $\text{Al}_2\text{O}_3$ (99.99%), $\text{Ta}_2\text{O}_5$ (99.99%), $\text{CaCO}_3$ (99.0%), and $\text{TiO}_2$ (99.99%), which were all purchased from Sigma Aldrich. CuO (99.9%) was purchased from Merck. Details of the preparation steps were comprehensively provided in the previous work [29]. The starting powders were weighed to give the desired nominal compositions, and the powder mixtures were calcined at 850 °C for 12 h. The ceramic samples were obtained by sintering in air at 1090 °C for 9 h using a 5 °C/min heating rate. The sintered CaCu$_3$Ti$_4$–$x$Ta$_x$O$_{12}$ samples with $x = 0.05$, 0.10, and 0.20 are henceforth abbreviated as TaAl05, TaAl10, and TaAl20, respectively.

Scanning electron microscopy (SEM; SNE-4500M), field-emission SEM (FE-SEM) with energy-dispersive X-ray spectroscopy (EDS; Hitachi SU8030), X-ray diffraction (XRD; PANalytical model Empyrean), and X-ray photoelectron spectroscopy (XPS; PHI5000...
VersaProbe II, ULVAC-PHI) were used to characterize the sintered ceramics. The XRD patterns were analyzed using the X'Pert High Score Plus v3.0e software package with the Rietveld refinement technique, where the optimized structural parameters and coefficients were reported in the previous work [30]. Before SEM characterization, the top surface of the as-sintered samples was coated with Au using DC sputtering at 25 mA for 3 min.

To prepare the parallel electrodes for measuring the dielectric and electrical properties, the sample surfaces were polished until clean and smooth. The surfaces were then coated with Au in the same way as the SEM samples. The dielectric properties were measured using an E4990A impedance analyzer (Keysight Technology) with an oscillation voltage of 0.5 V over frequency and temperature ranges of $10^2$–$10^7$ Hz and ($-60$)–$210$ °C, respectively. The $J$–$E$ field characteristics were tested at $25$ °C (Keithley model 247). The breakdown electric field ($E_b$) was obtained at $J = 1$ mA/cm$^2$. The nonlinear coefficient ($\alpha$) was calculated over the $J$ range of 1–10 mA/cm$^2$.

Density functional theory calculations were used to calculate the most preferential configuration for the Al and Ta dopants occupying the Ti sites of the CaCu$_3$Ti$_4$O$_{12}$ structure. The calculation details are described in the previous work [31]. The 3s and 3p valence states were chosen for the Al pseudopotential. For Ta, the 5p, 6s, and 5d states were used. In the current research, the unit cell of the CaCu$_3$Ti$_4$O$_{12}$ structure with 40 atoms was used.

3 Results

The XRD patterns of all samples are shown in Fig. 1(a). The XRD peaks of all samples corresponded to the characteristic peaks of the main CCTO phase (JCPDS No. 75-2188), with a body-centered cubic (bcc) structure with a space group of $Im\overline{3}$ [32]. All samples showed the presence of only CCTO, with no remaining unreacted precursor materials or secondary phases. The Rietveld refinement method was successfully used to analyze the XRD patterns, where the pattern for the TaAl20 ceramic is shown in Fig. 1(b) as a representative example. The obtained results are summarized in Table 1. The $R$-factors ($R_{exp}$, $R_p$, and $R_w$) obtained by Rietveld refinement were $\sim$3.4%–6.1%, and the goodness of fit values were $\sim$1.1–1.5. By considering the local environment of the metal ion M (reference coordinates: 0.25, 0.25, 0.25), where $M = Ti$, Al, or Ta, the bond lengths M–O and M–Cu of the (Al$^{3+}$, Ta$^{5+}$)–CCTO ceramics were the same as those in the undoped CCTO ceramic. Furthermore, the bond angles (i.e., O–M–O, O–Cu–O, and Cu–M–Cu) in the CCTO structure either did not change after co-doping with Al$^{3+}$ and Ta$^{5+}$. The $a$ values of the Al025 and Ta025 ceramics were smaller and larger than that of the undoped CCTO ceramic, respectively, with the $a$ values of the co-doped TaAl05, TaAl10, and TaAl20 ceramics between these extremes. The $a$ values of all samples were similar to those presented in other studies [5,27,32].

The SEM images of the surface morphologies of all samples are shown in Fig. 2. The mean grain size ($G$) values of all samples are summarized in Table 1. Doping CCTO ceramics with Al$^{3+}$ and/or Ta$^{5+}$ greatly affected the microstructure. Compared with the pure CCTO ceramic, the $G$ of Al025 was higher after partial substitution with Al$^{3+}$, while doping with Ta$^{5+}$ resulted in a decrease in $G$. The changes in the $G$ values of the Al$^{3+}$ and Ta$^{5+}$ single-doped CCTO ceramics were similar to those observed previously [5,33]. In addition, our findings are similar to the experimental results for the CaCu$_3$Ti$_{3.95}$(Nb$_{0.5}$Al$_{0.5}$)$_{0.05}$O$_{12}$ ceramic [5]. However, the $G$ of the TaAl10 and TaAl20 ceramics were much smaller than that of the Ta025 ceramic.

Fig. 1 (a) XRD patterns of the CCTO, Al025, Ta025, TaAl05, TaAl10, and TaAl20 ceramics. (b) Rietveld profile of TaAl20.
Table 1  Lattice parameter and structural data obtained from the Rietveld refinement, and the calculated grain size and relative density of the CCTO, Al025, Ta025, TaAl05, TaAl10, and TaAl20 ceramics

| Sample  | CCTO     | Ta025     | Al025     | TaAl05    | TaAl10    | TaAl20    |
|---------|----------|-----------|-----------|-----------|-----------|-----------|
| $a$ (Å) | 7.394(4) | 7.395(5)  | 7.390(3)  | 7.393(0)  | 7.393(0)  | 7.393(9)  |
| $R_{exp}$ (%) | 5.280(8) | 4.156(0)  | 4.306(6)  | 4.284(5)  | 4.127(5)  | 4.214(1)  |
| $R_p$ (%) | 3.818(1) | 3.499(2)  | 3.639(5)  | 3.767(2)  | 3.524(1)  | 3.489(5)  |
| $R_w$ (%) | 6.182(8) | 5.006(1)  | 5.007(4)  | 5.201(2)  | 4.824(4)  | 4.501(7)  |
| GOF    | 1.370(8) | 1.450(9)  | 1.352(0)  | 1.473(7)  | 1.366(2)  | 1.141(1)  |

Bond length (Å)  
$\{M = \text{Ta, Al, Ti}\}$

| Bond length (Å) | (M = Ta, Al, Ti) |
|-----------------|------------------|
| $M$–O           | 1.959(0)         | 1.959(0)         | 1.958(0) | 1.959(0) | 1.959(0) | 1.959(0) |
| $M$–Cu          | 3.202(0)         | 3.202(0)         | 3.200(0) | 3.201(0) | 3.201(0) | 3.202(0) |

Bond angle (°)  

| Bond angle (°) | |
|----------------|---------|
| $O$–$M$–$O$   | 89.422(4) |
| $O$–$Cu$–$O$  | 116.693(2) |
| $Cu$–$M$–$Cu$ | 109.471(2) |

$G$ (µm)  

| $G$ (µm) | 67.3 ± 21.9 |
|----------|-------------|

$\rho$ (%)  

| $\rho$ (%) | 94.60 |
|------------|-------|

In addition, the apparent density values of all samples were measured using the Archimedes method. The relative densities of the sintered ceramics were calculated by dividing the apparent density by the theoretical density, as shown in Table 1. The relative densities of all samples were above 94%. Hence, sintering at 1090 °C for 9 h was considered acceptable for obtaining sufficiently dense ceramics.

The elemental distribution in all samples was evaluated using EDS mapping, as shown in Fig. 3. The distributions of Ca, Cu, Ti, Ta, and Al were very homogeneous for the TaAl20 ceramic. According to the XRD and EDS results, it is reasonable to conclude that the Ta and Al dopants were substituted well into the CCTO lattice.

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Figure 4(a) and its inset show the frequency-dependent $\varepsilon'$ and tan$\delta$ of the undoped CCTO, and single-doped Al0.25 and Ta0.25 ceramics. The low-frequency $\varepsilon'$ values of both Al0.25 and Ta0.25 were larger than that of the CCTO ceramic. The $\varepsilon'$ values of the single-doped samples were frequency-dependent in the low-frequency range ($10^2$–$10^3$ Hz). As shown in the inset of Fig. 4(a), the low-frequency tan$\delta$ values of both Al0.25 and Ta0.25 were higher than that of pure CCTO. The $\varepsilon'$ and tan$\delta$ values at 1 kHz of the CCTO, Al0.25, and Ta0.25 ceramics are summarized in Table 2, and showed that GDPs can be achieved with these three ceramics ($\varepsilon'>10^4$). Nevertheless, the tan$\delta$ values are still too high for practical applications [34].

The frequency dependence of $\varepsilon'$ and tan$\delta$ of the co-doped Ta0.05, Ta0.10, and Ta0.20 ceramics measured at 20 °C are shown in Fig. 4(b). Interestingly, their $\varepsilon'$ values showed a wider range of frequency stability than those of the undoped and single-doped samples. Furthermore, over the measured frequency range, the tan$\delta$ values of the co-doped CCTO ceramics were much lower than those of the undoped and single-doped samples. Significantly, the tan$\delta$ values in the low-frequency range ($<10^3$ Hz) of the co-doped CCTO ceramics were low, indicating their improved dielectric properties, similar to the results of (Al$^{3+}$, Nb$^{5+}$) co-doped CCTO [5]. The $\varepsilon'$ and tan$\delta$ values at 1 kHz for Ta0.05, Ta0.10, and Ta0.20 are also listed in Table 2. Notably, large $\varepsilon'$ values of $\sim$(0.52–2.7) $\times$ 10$^4$ and very low tan$\delta$ values of $\sim$0.010–0.036 were obtained with the co-doped CCTO ceramics. The high-performance dielectric properties of (Al$^{3+}$, Ta$^{5+}$) co-doped CCTO ceramics may be the first step to improve their properties sufficiently for use in capacitor applications.

In addition to their high $\varepsilon'$ and very low tan$\delta$ values, Fig. 5 shows that the $\varepsilon'$ values of the (Al$^{3+}$, Ta$^{5+}$) co-doped CCTO ceramics were much less temperature dependent than the pure and single-doped CCTO ceramics. The greatly improved thermal stability of $\varepsilon'$ could be associated with the enhanced GB response as a result of co-doping. Interestingly, the variations in $\varepsilon'$ of the Ta0.10 and Ta0.20 ceramics are consistent with the required standards for capacitor applications [34]. The improved temperature stability of $\varepsilon'$ for the co-doped CCTO ceramics is consistent with that reported for co-doped TiO$_2$, and single- and co-doped CCTO ceramics [4,5,28,35,36].

In general, the $\varepsilon'$ values of the undoped and doped CCTO ceramics are considered high. Therefore, the origin of the GDPs in this material may differ from that

Table 2 $\varepsilon'$ and tan$\delta$ values measured at 1 kHz and 20 °C, grain resistance ($R_g$) at 20 °C, grain boundary resistance ($R_{gb}$) at 110 °C, conduction activation energies of the grain ($E_g$) and grain boundary ($E_{gb}$), breakdown electric field ($E_b$), and nonlinear coefficient ($\alpha$) of the CCTO, Al0.25, Ta0.25, Ta0.05, Ta0.10, and Ta0.20 ceramics

| Sample   | $\varepsilon'$ | tan$\delta$ | $R_g$ (Ω-cm) | $R_{gb}$ (Ω-cm) | $E_g$ (eV) | $E_{ gb}$ (eV) | $E_b$ (V·cm$^{-1}$) | $\alpha$ |
|----------|----------------|-------------|---------------|----------------|------------|---------------|---------------------|---------|
| CCTO     | 9.15 $\times$ 10$^4$ | 0.121       | 33            | 5.08 $\times$ 10$^4$ | 0.086      | 0.682         | 200.71              | 4.82    |
| Al0.25   | 2.55 $\times$ 10$^3$ | 0.289       | 46            | 5.96 $\times$ 10$^3$ | 0.111      | 0.656         | 77.09               | 4.75    |
| Ta0.25   | 9.44 $\times$ 10$^4$ | 1.147       | 37            | 4.06 $\times$ 10$^2$ | 0.091      | 0.416         | 22.50               | 2.24    |
| Ta0.05   | 2.70 $\times$ 10$^4$ | 0.036       | 82            | 8.49 $\times$ 10$^6$ | 0.095      | 0.732         | 491.57              | 5.19    |
| Ta0.10   | 5.15 $\times$ 10$^3$ | 0.017       | 145           | 1.81 $\times$ 10$^8$ | 0.094      | 0.724         | 497.87              | 2.86    |
| Ta0.20   | 5.98 $\times$ 10$^3$ | 0.010       | 170           | 1.31 $\times$ 10$^9$ | 0.097      | 0.713         | 6588.38             | 15.20   |
of co-doped TiO$_2$ ceramics [4,17]. Furthermore, doping CCTO with only Ta$^{5+}$ or Al$^{3+}$ cannot enhance the dielectric properties above those of undoped and co-doped CCTO. Thus, the reduction of tan$\delta$ is attributed to the synergistic effect of the A1$^{3+}$ and Ta$^{5+}$ dopants.

Impedance spectroscopy was used to clarify the possible mechanisms of the GDPs in each ceramic. The resistance of the grain ($R_g$) and GB ($R_{gb}$) was estimated from the nonzero intercept at high frequency and the semicircular arc of the complex impedance ($Z^*$) plot, respectively [37]. Heterogeneous ceramic components consisting of semiconducting grains and insulating GBs were identified for all of the prepared ceramics [5,37], as shown in Figs. 6 and 7. As shown in Fig. 6, the $R_{gb}$ values of the co-doped CCTO ceramics were much larger than those of CCTO, Al025 (inset (1) of Fig. 6), and Ta025 (inset (2) of Fig. 6). The $R_g$ values at 20 °C of all the co-doped CCTO ceramics were also larger than those of the undoped and single-doped CCTO ceramics, as shown in the inset (1) of Fig. 7 and listed in Table 2. The variations in the $R_{gb}$ and $R_g$ values of the TaAl20 ceramic at different temperatures are shown in Fig. 7 and its inset (2). As shown in these two figures, the $R_{gb}$ and $R_g$ values decreased significantly with even small increase in temperature. The trends in the $R_{gb}$ and $R_g$ values at different temperatures are consistent with the characteristic dielectric behavior observed for CCTO and its related structures [2,5,21,33,37]. As shown in Figs. 8(a) and 8(b), the temperature dependence of $R_g$ and $R_{gb}$ followed the Arrhenius law well. The conduction activation energies of the grains ($E_g$) and GBs ($E_{gb}$) were calculated from the slopes of the lines of best fit, and are listed in Table 2. The obtained $E_g$ values of the ceramics were all slightly different, while the $E_{gb}$ values of the co-doped CCTO ceramics were significantly larger than those of undoped and single-doped ceramics [4,17].
single-doped CCTO ceramics.

Nonlinear $J$–$E$ properties were observed for all samples, as shown in Fig. 9. The $E_b$ values of all co-doped CCTO ceramics were significantly larger than those of undoped and single-doped CCTO ceramics. Furthermore, $E_b$ significantly increased with increasing dopant content. The lowest $E_b$ value was measured for the single-doped Ta025 ceramic. Among the samples analyzed in this study, the best nonlinear $J$–$E$ properties were observed for all co-doped CCTO ceramics, with an $E_b$ of $\sim 6.59 \times 10^3$ V cm$^{-1}$ and $\alpha$ of $\sim 15.20$, measured for the TaAl20 ceramic. The improved nonlinear $J$–$E$ properties imparted by co-doping was consistent with previous results for (Al$^{3+}$, Nb$^{5+}$), (Zn$^{2+}$, Mn$^{4+}$), and (Y$^{3+}$, Zr$^{4+}$) co-doped CCTO ceramics [5,12,35]. According to the dielectric and nonlinear results, it can be considered that the primary benefits of the (Al$^{3+}$, Ta$^{5+}$) co-doped CCTO ceramics are their reduced tan$\delta$ and improved nonlinear properties. The dielectric and nonlinear electrical properties of the TaAl20 ceramic were compared to those of other co-doped CCTO ceramics with various pairs of ions co-substituting the B-site Ti$^{4+}$, as summarized in Table 3. TaAl20 showed the best overall performance of all CCTO ceramics, with the lowest tan$\delta$ value and the highest $E_b$ and $\alpha$ values.

The valence structures and charge compensation mechanisms for the CCTO, TaAl10, and TaAl20 ceramics were systematically investigated using XPS. As shown in Figs. 10(a)–10(c), Gaussian–Lorentzian profile fitting was used to reproduce the Cu$^{2+}$ peaks for the CCTO, TaAl10, and TaAl20 ceramics. The asymmetric shape of the Cu$^{2+}$ peaks indicates several overlapping peaks, i.e., the presence of both smaller Cu$^+$ and larger Cu$^{2+}$ peaks. The smaller peak of Cu$^+$ was observed at a binding energy (BE) of $\sim 931.85$–$932.30$ eV, while the larger peak of Cu$^{2+}$ was detected at $\sim 933.99$–$934.33$ eV. The ratios between Cu$^+$/Cu$^{2+}$ for the CCTO, TaAl10, and TaAl20 ceramics were 5.76/14.19%, 15.20/7.69, and 15.20/8.73, respectively.

To investigate the possible configurations of the defect structures in the (Al$^{3+}$, Ta$^{5+}$) co-doped CCTO ceramics, first-principles calculations were performed. Two initial defect configurations were set up, as shown in Fig. 11. We first created structure I by replacing two Ti ions with Al and Ta ions in the CCTO structure; however, Al and Ta ions in the octahedral sites were placed far apart. The total energy of structure I was calculated and compared with that of the undoped CCTO structure.

### Table 3 Comparison of the dielectric properties (at 1 kHz and $\sim 25^\circ$C) and nonlinear properties of (Al$^{3+}$, Ta$^{5+}$)–CCTO ceramics with other CCTO ceramics with other ion pairs co-substituted for the B-site Ti$^{4+}$

| Sample | $\varepsilon'$ | tan$\delta$ | $E_b$ (V/cm) | $\alpha$ | Ref. |
|--------|----------------|-----------|-------------|---------|-----|
| CaCu$_3$Ti$_{1.35}$Nb$_{0.025}$Al$_{0.025}$O$_{1.925}$ | 2.90 x 10$^4$ | 0.045 | $-0.72 \times 10^3$ | $-5.76$ | [5] |
| CaCu$_3$Ti$_{1.35}$Al$_{0.025}$O$_{1.925}$ | $-3.00 \times 10^4$ | $<0.49$ | — | — | [6] |
| CaCu$_3$Ti$_{1.35}$Zn$_{0.025}$O$_{1.925}$ | $-4.54 \times 10^4$ | $-0.266$ | — | — | [7] |
| CaCu$_3$Ti$_{1.35}$Ta$_{0.0125}$In$_{0.0125}$O$_{1.925}$ | $3.86 \times 10^4$ | 0.075 | — | — | [8] |
| CaCu$_3$Ti$_{1.35}$Ta$_{0.0125}$O$_{1.925}$ | $2.36 \times 10^3$ | 0.024 | $-9.67 \times 10^3$ | $-6.69$ | [9] |
| CaCu$_3$Ti$_{1.35}$Nb$_{0.025}$O$_{1.925}$ | $-10^3$ | $-0.2$ | — | — | [10] |
| CaCu$_3$Zn$_{0.06}$Nb$_{0.04}$O$_{1.98}$ | $2.0 \times 10^3$ | $-0.23$ | — | — | [11] |
| CaCu$_3$Ti$_{1.35}$Ta$_{0.0125}$Zr$_{0.0125}$O$_{1.935}$ | $-1.15 \times 10^4$ | $-0.05$ | $-1.21 \times 10^4$ | $-4.5$ | [12] |
| CaCu$_3$(Ta$_{0.5}$Fe$_{0.25}$Nb$_{0.25}$)O$_{1.92}$ | $-10^3$ | $-1.2$ | $-35$ | $-2.27$ | [13] |
| CaCu$_3$(Ta$_{0.5}$Al$_{0.5}$)O$_{1.92}$ (TaAl20) | $5.98 \times 10^3$ | 0.010 | $-6.6 \times 10^3$ | 15.20 | This work |

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then calculated. Then, the total energy was calculated for structure II with the two Al and Ta dopant ions in adjacent octahedral sites. Figure 11 clearly shows that the total energy of structure II is lower than that of structure I by 7.68 meV. Hence, the Al and Ta dopants in the CCTO host prefer to be in proximity. Generally, the substitution of Ta$^{5+}$ for Ti$^{4+}$ requires charge compensation by the formation of free electrons according to the following relations.

$$24\text{TiO}_2 + \text{Ta}_2\text{O}_3 \rightarrow 2\text{Ti}^{4+} + 2\text{Ta}^{5+} + 8\text{O}_2 + \frac{1}{2}\text{O}_2$$ (1)

$$\text{Ti}^{4+} + e \rightarrow \text{Ti}^{3+}$$ (2)

In contrast, the substitution of Ti$^{4+}$ with Al$^{3+}$ requires the formation of oxygen vacancies ($V_0^-$) for charge compensation, according to the relation:

$$\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}^{3+}_\text{Ti} + V_0^- + 3V_O$$ (3)

In the case of structure II, when the two octahedral sites of the CCTO structure containing the Al and Ta dopants are close together, there is no need for charge compensation, as shown by the following relation:

$$4\text{TiO}_2 + \text{Ta}_2\text{O}_5 \rightarrow 2\text{Al}^{3+}_\text{Ti} + 2\text{Ta}^{5+}_\text{Ti} + 8\text{O}_2$$ (4)

Consequently, self-charge compensation between these two ions occurs in our structure without the formation of free electrons or oxygen vacancies.
4 Discussion

4.1 Structure and phase formation

Changes in the $a$ values of both the single- and co-doped ceramics were consistent with the differences between the ionic radii of Al$^{3+}$ ($r_b = 0.535 \, \text{Å}$) and Ta$^{5+}$ ($r_b = 0.72 \, \text{Å}$) doping ions and Ti$^{4+}$ ($r_b = 0.605 \, \text{Å}$) host sites [39]. Variations in the $a$ values of the Al025 and Ta025 ceramics compared to that of the CCTO ceramic were caused by the different ionic radii between the dopant and host ions. The ionic radii of all co-doped ceramics were slightly smaller than that of the CCTO ceramic because the average ionic radius of the co-dopants (0.588 Å) was slightly smaller than that of Ti$^{4+}$. The same $a$ for the TaAl05 and TaAl10 ceramics and slightly higher $a$ of TaAl20 were because of the average ionic radius of the co-dopants being similar to that of Ti$^{4+}$.

4.2 Microstructural evolution

Generally, the grain growth in polycrystalline ceramics is associated with GB mobility ($M_b$), which is dependent on the diffusion of ions, atoms, and/or charged species across the GB [40]. It was previously shown that the grain-growth and densification rates of CCTO ceramics were lower when sintering in an oxidizing atmosphere than a reducing atmosphere [41]. Thus, the diffusion of oxygen ions (O$^{2-}$), which is directly dependent on the $V_o^-$ concentration, is an important factor influencing the higher grain-growth rate. According to Eq. (3), the large increase in $G$ for the single-doped Al025 ceramic (~127 μm) compared to that of the CCTO ceramic (~67.3 μm) was likely associated with the higher diffusion coefficient of O$^{2-}$ due to the increase in $V_o^-$ as a result of the partial substitution of Al$^{3+}$ on Ti$^{4+}$ sites. This could also be attributed to the presence of liquid-phase sintering. The eutectic liquid in CCTO ceramics can be formed above 919 ºC, facilitating the diffusion of ions across the GBs [42].

In contrast, the smaller $G$ of the single-doped Ta025 ceramic (~15.9 μm) compared to the Al025 ceramic was because of Ta$^{5+}$ ions inhibiting the grain growth, as demonstrated previously for CCTO-based ceramics [33]. According to Eq. (1), the grain growth of the Ta025 ceramic was not increased by the increased diffusivity of O$^{2-}$, resulting in a relatively low grain-growth rate compared to that of Al025. Furthermore, the $G$ value of Ta025 was much smaller than that of CCTO. Similarly, the decrease in $G$ of BaTiO$_3$ ceramics doped with Nb$^{5+}$ (> 0.5 at%) was explained based on the space-charge and defect-chemistry concepts [43]. The $R_g$ of Ta025 was slightly larger than that of CCTO, which does not obey Eq. (1), and is instead explained by Eq. (5), where most of the Ta$^{5+}$ ions are ionically compensated by cation vacancies ($V_{Ti}^{\text{V}}$).

$$2\text{Ta}_2\text{O}_5 + 3\text{TiO}_2 \rightarrow 4\text{Ta}^{\text{IV}} + V_{Ti}^{\text{V}} + 3\text{Ti}^{\text{IV}} + 16\text{O}_2\text{O}$$

In this case, $V_{Ti}^{\text{V}}$ and electrons were expected to accumulate in the negative space-charge region [44]. The accumulated $V_{Ti}^{\text{V}}$ are likely related to a depletion of the oxygen vacancies in the space-charge region, where the diffusivity of O$^{2-}$ across the GB was slow because of the large ionic size of O$^{2-}$. This resulted in the reduction of $M_b$, which was a possible reason for the significantly reduced $G$ value of Ta025 compared to that of CCTO. According to the first-principles calculations and Eq. (4), the decrease in $G$ of the co-doped TaAl10 and TaAl20 ceramics with increasing the doping content was because of self-charge compensation between Al$^{3+}$ and Ta$^{5+}$ on the Ti$^{4+}$ sites. The $G$ values of the co-doped TaAl10 and TaAl20 ceramics were between those of the single-doped Al025 and Ta025 ceramics, indicating the balance between driving and inhibiting forces for GB migration. Thus, the charge compensation by the formation of oxygen vacancies did not occur in these materials. Furthermore, the Cu-rich phase was not observed for TaAl10 and TaAl20, as confirmed by EDS maps (Fig. 3).

4.3 Origins of the GDPs and enhanced grain and GB properties

The strong frequency dependence of the low-frequency $\varepsilon'$ for the Al025 ceramic (Fig. 4(a)) was considered to originate from the dielectric response of the sample–electrode interface [5]. This result is consistent with the appearance of a low-frequency dielectric relaxation peak in the tan$\delta$ curve (10$^5$−10$^3$ Hz) (inset of Fig. 4(a)). These results clearly indicate the additional dielectric response from the sample–electrode interface, which was dominant when the $R_{gb}$ of the Al025 ceramic significantly decreased from 5.08×10$^4$ to 5.96×10$^3$ Ω·cm at 110 ºC [45,46]. Furthermore, the $\varepsilon'$ of Ta025 was frequency independent over a wide range of frequencies, while the low-frequency tan$\delta$ significantly increased with decreasing frequency from 10$^5$ to 10$^2$ Hz. A shoulder of the tan$\delta$ peak was observed at 10$^{-3}$–10$^{-4}$ Hz, indicating
a hidden peak. The strong increase in tan$\delta$ below $10^2$ Hz was because of the long-range migration of charges or DC conduction in Ta025 [5,33], corresponding to its lowest $R_{gb}$ value (4.06 $\times$ 10$^2$ $\Omega$ cm).

According to the IBLC structure [19], a simple series layer model can be developed for explaining the giant dielectric response: $\varepsilon' = \varepsilon_{gb} G / t_{gb}$, where $\varepsilon_{gb}$ and $t_{gb}$ are the dielectric constant and thickness of the GB, respectively. Thus, the lower $\varepsilon'$ values of all of the (Al$^{3+}$, Ta$^{5+}$)–CCTO ceramics than that of pure CCTO were because of their lower $G$ values. In contrast, the much higher $\varepsilon'$ value of the Al025 ceramic was attributed to its high $G$ value. However, the $\varepsilon'$ of Ta025 was slightly higher than that of CCTO, even though its $G$ value was much smaller. In addition to the mean $G$, the $\varepsilon'$ was also determined from $\varepsilon_{gb}$, which is associated with the GB capacitance ($C_{gb}$). The $C_{gb}$ per unit GB area, which was equal to $G$, can be expressed as [37]:

$$C_{gb} / G = \left( \varepsilon' q N_d / 8 \Phi_b \right)^{1/2}$$  

(6)

Here, $C_{gb} / G$ is inversely proportional to $\Phi_b$, which was clearly shown to be closely correlated with the $E_{gb}$ value ($C_{gb} / G \propto 1 / E_{gb}$). Although $C_{gb} / G$ is proportional to the charge carrier concentration inside the semiconducting grains ($N_d$) or inversely proportional to $R_g$, the different $R_g$ values of the CCTO and Ta025 ceramics are too small. As shown in Table 2, the $E_{gb}$ value of Ta025 was the lowest of all samples (0.416 eV), giving rise to the largest $C_{gb} / G$, and hence, highest $\varepsilon'$ value.

According to impedance spectroscopy results, the improved dielectric properties observed for the co-doped ceramics may have been a result of a greatly enhanced GB response [5]. The increases in $R_{gb}$ and $E_{gb}$ in the co-doped CCTO ceramics originated from the reduction in $G$ and improved electrical properties of the GBs owing to co-doping. The low-frequency tan$\delta$ of the co-doped ceramics was closely related to their large $R_{gb}$ and $E_{gb}$ [5,27]. Due to the IBLC structure, $R_g << R_{gb}$, where the correlation between tan$\delta$ in the low-frequency range and $R_{gb}$ is described as follows:

$$\tan \delta \approx \frac{1}{w \varepsilon_d \varepsilon' C_0 R_{gb}}$$  

(7)

where $\varepsilon_d$ is the dielectric constant in the low-frequency range, and $C_0 = \varepsilon_0 A / t$ is the free space capacitance, where $A$ and $t$ are the area of electrodes and the sample thickness, respectively. The lower tan$\delta$ values of the (Al$^{3+}$, Ta$^{5+}$)–CCTO ceramics at low frequencies, which was compared to the undoped, observed here are consistent with Eq. (7), where tan$\delta$ is associated with DC conductivity ($\sigma_{dc} \propto 1 / R_{gb}$). As shown in the inset of Fig. 4(b), the tan$\delta$ values at $10^2$ Hz of TaAl10 and TaAl20 were significantly lower than that of TaAl05. This was attributed to the remarkable decrease in $\sigma_{dc}$, observed by the significant increase in $R_{gb}$, which resulted in the long-range motion of free charge carriers being completely inhibited by the GBs with very high resistance and $\Phi_b$. Note that, the lower $R_{gb}$ of the single-doped Al025 and Ta025 ceramics compared to CCTO, which resulted in the higher tan$\delta$ value, was similar to the behavior reported for Nb$^{5+}$ and Ta$^{5+}$ single-doped CCTO ceramics [5,33,47,48]. The improved temperature dependence of the $\varepsilon'$ of the co-doped ceramics was because of the high $R_{gb}$.

The different $E_b$ values measured for the ceramic samples evaluated here may be because of differences in their microstructure and the electrical properties of the GBs. The higher $\alpha$ values measured for TaAl20 may have been a result of the high $E_{gb}$ and $R_{gb}$ that indicate a high $\Phi_b$ at the GBs that the charges need to overcome [49]. Several previous studies reported that $\alpha$ simultaneously increases with $E_b$ [5,29,49–51]. For such ceramics, $E_b = N_{gb} E_{gb} = (t E_{gb}) / G$, where $N_{gb}$ is the number of GBs and $E_{gb}$ is the breakdown field of an individual GB layer. Therefore, the macroscopically enhanced $E_b$ value of the (Al$^{3+}$, Ta$^{5+}$)–CCTO ceramics should be primarily correlated to the microstructure because of a significant decrease in $G$ (or significant increase in $N_{gb}$). The low $E_b$ value of Al025 was its high $G$ value, while the lowest $E_b$ value of Ta025 (despite its small $G$ value) was a result of its lowest $\Phi_b$.

The XPS results showed the presence of Cu$^+$ and Ti$^{3+}$ ions, which may have been formed as a charge-compensation mechanism due to oxygen loss during sintering, following the relationship:

$$2O_2^+ \rightarrow O_2 + V_0^* + 2e'$$  

(8)

corresponding to the formation of the IBLC structure [52]. This gave rise to the presence of Cu$^+$ and Ti$^{3+}$, as shown in Eq. (2) and Cu$^{2+} + e \rightarrow Cu^+$. Interestingly, an increase in $R_g$ is highly consistent with a decrease in the concentration of Cu$^+$ and Ti$^{3+}$ in the sintered samples. It is reasonable to suggest that co-substitution of Ta$^{5+}$ and Al$^{3+}$ can suppress oxygen loss during sintering at high temperature. When the co-dopants were close together in the CCTO structure, fewer $V_0^*$ defects.
tended to form, resulting in a decrease in the Cu$^{2+}$/Cu$^{3+}$ and Ti$^{3+}$/Ti$^{4+}$ ratios. According to the first-principles calculations (Fig. 11), self-charge compensation between Al$^{3+}$ and Ta$^{5+}$ ions probably occurred, which prevented the formation of further $V_O^-$ and enhanced free charge carriers. Therefore, co-doping can result in an increase in $R_{gb}$ and $R_{g}$, which greatly decreases tan$\delta$.

5 Conclusions

In conclusion, we confirmed that acceptor–donor co-doping of CCTO ceramics to reduce tan$\delta$ and improve the nonlinear properties is also effective for (Al$^{3+}$, Ta$^{5+}$) dopants, where wide regions of frequency- and temperature-independent dielectric properties were observed. The substitution of (Al$^{3+}$, Ta$^{5+}$) dopants into the TiO$_6$ octahedral sites of the CCTO ceramics greatly reduced tan$\delta$, compared to the single-doped counterparts, indicating the synergistic effect of the dopants. The nonlinear $J$–$E$ properties of the (Al$^{3+}$, Ta$^{5+}$) co-doped CCTO ceramics were also greatly improved and attributed to the enhanced electrical properties of the GBs, which were well described by the IBLC model. Although the tan$\delta$ values are quite high for practical applications, our results further strengthen the argument for acceptor–donor co-doping of CCTO ceramics for producing electroceramics with excellent GDPs.

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