Giant dielectric behavior and non-ohmic properties in Mg$^{2+}$+F$^-\,$ co-doped \(\text{CaCu}_3\text{Ti}_4\text{O}_{12}\) ceramics

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ABSTRACT
A solid–state reaction method was used to produce \(\text{CaCu}_3\text{Mg}_x\text{Ti}_4\text{O}_{12-2x/2}\text{F}_{2x}\) with \(x\) values of 0, 0.05, and 0.10. A \(\text{CaCu}_3\text{Ti}_4\text{O}_{12}\) phase was detected in the absence of impurities. The \((\text{Mg}^{2+}+\text{F}^-)\) co–doping ions inhibited the grain growth of the \(\text{CaCu}_3\text{Ti}_4\text{O}_{12}\) ceramics because of the solute drag mechanism. The dielectric and non–Ohmic electrical properties of \(\text{CaCu}_3\text{Mg}_x\text{Ti}_4\text{O}_{12-2x/2}\text{F}_{2x}\) ceramics were studied. Intriguingly, the ceramic with \(x = 0.05\) enhanced the dielectric properties with a considerably decreased loss tangent (\(\text{tan}\delta \approx 0.06\)) while retaining a high dielectric permittivity (\(\varepsilon' \approx 10^5\)) at 1 kHz. The nonlinear current density–electric field (\(J-E\)) properties of the ceramic with \(x = 0.05\) were also successfully improved. However, the dielectric and nonlinear properties deteriorated when \(x = 0.10\). The variations in the low–frequency \(\text{tan}\delta\) and electric breakdown strength were primarily associated with the grain size and Schottky barrier height at the grain boundaries. The relevant mechanisms for these improved dielectric and non–Ohmic properties are discussed based on the effect of the internal barrier layer capacitor.

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1. Introduction

Electronic technology plays an important role in daily life. Therefore, the performance of electronic devices and important internal components should be updated along with the development to reduce the size of these devices. Ceramic dielectrics are one of the crucial materials utilized in the electronics industry. Numerous simple and complex oxides, such as \(\text{TiO}_2\) [1], \(\text{SnO}_2\) [2,3], and \(\text{BaTiO}_3\) [4], have been extensively investigated for their dielectric and electrical properties to optimize their performance in electronic applications. \(\text{CaCu}_3\text{Ti}_4\text{O}_{12}\) (CCTO), a material in the perovskite–related family of \(\text{ACu}_3\text{Ti}_4\text{O}_{12}\) compounds, has attracted considerable attention owing to its giant dielectric permittivity (\(\varepsilon'\)) of approximately \(10^4\)–\(10^5\) in the radio frequency range [5–14]. No phase transitions were detected in these materials. Thus, the giant dielectric response was not related to ferroelectricity. Additionally, when compared to other ceramics, such as \(\text{BaTiO}_3\) [4], polycrystalline CCTO ceramics show non–ohmic behavior, referred to in some articles as nonlinear current–voltage properties [12–17]. These interesting giant dielectric properties and nonlinear behaviors are promising for use in capacitor and varistor applications. Numerous theories, both extrinsic and intrinsic, have been suggested to describe the complex colossal dielectric responses observed in CCTO ceramics [5,6,18–20]. Although the precise mechanism of the colossal dielectric response is unclear, it is largely agreed that the extrinsic effect, particularly the internal layer barrier capacitor (IBLC) effect, might be the cause. The IBLC structure consists of \(n\)-type semiconducting grains and insulating grain boundaries (GBs). The giant dielectric response of this unique IBLC structure can be tuned by fine–tuning the microstructure of polycrystalline ceramics. However, the intrinsic defects existing in the grains, such as point defects that result in the formation of a nanoscale barrier layer capacitor (NBLC) and the charge compensation mechanisms of CCTO, cannot be ignored [18–20].

Although a very high \(\varepsilon'\) value of CCTO ceramics can be obtained, the loss tangent (\(\text{tan}\delta\)) remains larger than the acceptable value for use in multilayer ceramic capacitor applications [21]. To date, many studies have reported strategies for reducing the \(\text{tan}\delta\) value, such as doping CCTO with \(\text{Mg}^{2+}\) [20,22,23], \(\text{Zn}^{2+}\) [15,18,24], \(\text{Al}^{3+}\) [9] cations, \(\text{I}^-\) [14], \(\text{Br}^-\) [14], and \(\text{F}^-\) [9,14] anions. For example, the low–frequency \(\text{tan}\delta\) value of \(\text{Mg}^{2+}\)-doped CCTO ceramics decreased slightly to \(\approx 0.05\) with increasing \(\text{Mg}^{2+}\) dopant concentration [22]. Although a reduction in \(\text{tan}\delta\) values of \(\text{Mg}^{2+}\)-doped
CCTO ceramics was accomplished, their ε’ values also decreased, resulting from the increase in resistance inside the grains ($R_p$). The use of the sol–gel method to prepare Mg$^{2+}$–doped CCTO ceramics ε’ can be enhanced [23]. Moreover, a significantly reduced tanδ <0.015 with good temperature stability ε’ was achieved in Mg$^{2+}$–doped CaCu$_3$Ti$_4$O$_{12}$/CaTiO$_3$ composites [25].

On the other hand, the replacement of fluorine (F⁻) ions as anion dopants in CCTO ceramics causes an increase in GB resistance ($R_{gb}$) and a decrease in $R_p$, leading to a reduction in tanδ values [26]. CCTO ceramics co-doped with metal cations and anions exhibit significantly enhanced dielectric characteristics, such as (Li⁺+F⁻) [27], (Sr$^{2+}$+F⁻) [28], (Al$^{3+}$+F⁻) [9], and (Cd$^{2+}$+F⁻) [29]. To the best of our knowledge, the dielectric properties of (Mg$^{2+}$+F⁻) co-doped CCTO ceramics have never been reported. As a result, the goal of this research is to examine the effects of Mg$^{2+}$ and F⁻ co-doping on the microstructure, giant dielectric properties, electrical responses, and nonlinear current–voltage properties.

In this study, a solid–state reaction method was used to produce (Mg$^{2+}$+F⁻) co-doped CCTO ceramics with the nominal formula CaCu$_{3-x}$Mg$_x$Ti$_{4-2x}$F$_{2x}$. A significant reduction in the low–frequency tanδ value was accomplished by (Mg$^{2+}$+F⁻) co-doping ions with a proper doping concentration (x = 0.05), which was related to the improved grain size and Schottky barrier height at the GBs compared to pure CCTO ceramic. The possible mechanisms underlying the giant dielectric response are thoroughly discussed.

2. Experimental details

The solid–state reaction method was used to prepare CaCu$_{3-x}$Mg$_x$Ti$_{4-2x}$F$_{2x}$ ceramics with x = 0, 0.05, and 0.10. In this study, an undoped ceramic is referred to as CCTO. Also, the codoped CaCu$_{3-x}$Mg$_x$Ti$_{4-2x}$F$_{2x}$ ceramics with x = 0.05 and 0.10 are named CCTO–MgF05 and CCTO–MgF10 samples, according to their compositions. The raw materials were MgF$_2$ (99.9% purity), CuO (99.0% purity), CaCO$_3$ (99.0% purity), and TiO$_2$ (99% purity). Plastic bottles were used to mix the stoichiometric weights of all raw materials in ethanol and then ball–milled at 200 rpm for 24 h. It was then dried and ground into powder. Third, the dried mixtures were calcined in air at 900°C. The calcined powder was then crushed finely. Subsequently, the resultant fine powders were compacted using a uniaxial pressure of 200 MPa into pellets with a diameter of 9.5 mm and a thickness of 1.0 mm. Finally, the pellets were sintered in air for 6 h at a temperature of 1075°C.

X–ray diffraction (XRD, PANalytical, EMPYREAN) was used to analyze the phase composition and crystal structure of the sintered ceramics. The parameters of the XRD measurements and the Rietveld refinement technique for the analysis of the XRD data are discussed in the previous work [15]. Scanning electron microscopy (SEM, SEC, SNE4500M) was used to examine the morphologies of the sintered ceramics. The dielectric parameters were examined using a capacitor – loss tangent, $C_p$ – tanδ, mode on a KEYSIGHT E4990A impedance analyzer ($V_{rms}$ = 500 mV). The experiment was conducted over frequency and temperature ranges of 10$^2$–10$^3$ Hz and 70–220°C, respectively. A high–voltage measurement instrument (Keithley Model 247) was used to investigate the non-linear characteristics of the current density–electric field (J–E curve). The breakdown electric field ($E_b$) and nonlinear coefficient (a) can be calculated using a technique described in the literature [25].

3. Results and discussion

The XRD patterns of the sintered ceramics are shown in Figure 1(a). The Rietveld profile fitting of the XRD patterns compared to the standard structure for the undoped CCTO and the co–doped CCTO–MgF05 and CCTO–MgF10 samples is shown in Figures 1(b–d). Compared to the standard structure, which ignores the influence of charge states, all XRD patterns can be well–fitted using the Rietveld method of analysis. In all the ceramics, the profile fits verified the presence of a major CCTO phase (JCPDS No. 75–2188). No impurity phases were detected (e.g. CuO, TiO$_2$, or CaTiO$_3$) in any of the XRD spectra. The observed XRD findings were consistent with those previously published, showing the presence of a body–centered cubic structure parted in the Im3 No. 204 space group [20,24]. Lattice parameters (a) were obtained from the fitted data based on the Rietveld approach and were found to be 7.391(9), 7.393(8), and 7.392(0) Å for the CCTO, CCTO–MgF05, and CCTO–MgF10 samples, respectively. These a values are comparable to the 7.391 Å for the CCTO structure (JCPDS No. 75–2188) [22,23,26].

Figures 2(a–c) show the surface morphologies of the undoped CCTO and (Mg$^{2+}$+F⁻) co–doped CCTO ceramics. After sintering at 1075°C for 6 h, the SEM images demonstrate that the grain size ranges in all samples appear to be uniform. In addition, the microstructures revealed that all–ceramic compositions have a microstructure that is quite dense. When the effect of dopants on the microstructural evolution is considered, it is discovered that these co–doped ions have little effect on the crystal structure of CCTO ceramics, but they have a significant impact on the microstructure of CCTO ceramics because of their co–dominance. The grain growth of CCTO ceramics is suppressed by the substitution of (Mg$^{2+}$+F⁻) ions. As shown in Figures 2(d–f), the average grain sizes of the CCTO, CCTO–MgF05, and CCTO–MgF10 samples were approximated by the line intercept technique and were found to be $\approx$114.2 ± 36.7, 48.5 ± 17.6, and
51.1 ± 19.1 μm, respectively. This result is in contrast to those observed for F− single–doped and LiF co–doped CCTO ceramics [27,28]. The mean grain size of the CCTO ceramics was significantly enlarged by doping with F and LiF owing to the low melting points of CuF2 (~836°C) and LiF (~848°C), which were used as the starting raw materials. The enlarged grain size was due to the existence of liquid phases of CuF2 and LiF during sintering at 1,075°C. However, the grain growth of the SrF2 co–doped CCTO ceramics was not promoted because of the high melting point of SrF2 (~1,477°C) [29], which was used as the raw material. In this current study, although the melting point of MgF2 is 1,263°C, abnormal grain growth was observed in these two samples. The abnormal grain growth is a typical result of liquid–phase sintering. Thus, the abnormal grain growth in the sintered CCTO–MgF05 and CCTO–MgF10 samples was specified to liquid phase sintering caused by F–rich addition. The decrease in the mean grain size of the (Mg2+ + F−) co–doped CCTO ceramics may have resulted from the solute drag mechanism. When the mixed starting powders were calcined, the dopants were attracted to the GB because of the interaction potential [30]. The lattice strain energy resulting from the size mismatch between the host and doping ions causes interactions between them. Upon heating, the GB starts to move because of the diffusion of ions across the GB, whereas a retarding force on the GB occurs owing to solute drag, resulting in inhibited grain growth. However, when the driving force for GB migration is sufficiently high, the GB breaks away from the dopant. In this case, the grain growth rate approaches that of the un–doped sample, as observed in the Mg2+–doped CCTO ceramics that were sintered at a sufficiently high temperature of 1,100°C [21]. Thus, the Mg2+ and F− co–doping ions might inhibit the motion of the GBs and suppress the grain growth rate in doped ceramics [17,20]. However, there are also small grains around the large grains of the CCTO–MgF05 and CCTO–MgF10 samples, indicating abnormal grain growth [30]. The sintering conditions should be optimized to balance the densification and grain growth rates in CaCu3+2x Mg2Ti4O12+2xF2x ceramics.

The dielectric properties (ε′ and tanδ) as a function of frequency for the sintered ceramics at room temperature (RT) are shown in Figure 3(a) and its inset. Clearly, the Mg2+ and F− doping ions have an impact on the dielectric properties of CCTO ceramics. The ε′ value of the CCTO–MgF05 samples varied slightly with frequencies between 102 and 105 Hz. At RT and 1 kHz,
The ε′ values for the CCTO, CCTO–MgF05, and CCTO–MgF10 samples were approximately $2.00 \times 10^5$, $8.08 \times 10^4$, and $1.99 \times 10^5$, respectively. The variations in the ε′ and tanδ values with co–doping concentration are shown in the inset of Figure 3(b).

This work is comparable to that of Liu et al. [31], who reported the dielectric properties of $M_{1/2}$La$_{1/2}$Cu$_3$Ti$_4$O$_{12}$ ($M =$ Li, Na, and K) with various additive elements. The tanδ value of the CCTO ceramics was reduced by (Mg$^{2+}$+F$^-$) co–doping ions with a proper doping concentration ($x = 0.05$). As shown in the inset of Figure 3(a), the large tanδ values of all the ceramic samples appeared in both the low– and high–frequency ranges. The low–frequency and low–frequency dielectric relaxations (L–FDR and H–FDR) were caused by the non–Ohmic sample–electrode contact [32,33] and the primary polarization relaxation that gives rise to the giant dielectric response, i.e. Maxwell–Wagner polarization at the GBs, respectively [5,33,34]. At 1 kHz and RT, tanδ values were 0.144, 0.060, and 0.251 for the CCTO, CCTO–MgF05, and CCTO–MgF10 samples, respectively. The improved dielectric properties of the CCTO–MgF05 sample are comparable to those observed in earlier studies described in the literature [9,27–29].

The temperature dependence of the ε′ of (Mg$^{2+}$+F$^-$) co–doped CCTO ceramics at 1 kHz is shown in Figure 3(b). Evidently, the temperature dependence of ε′ for the
CCTO–MgF05 and CCTO–MgF10 samples was improved compared to that of the undoped CCTO sample. When the temperature exceeded ~50°C, the ε’ value of the CCTO sample changed significantly. Among the three samples, the CCTO–MgF05 sample exhibited the best temperature stability of the ε’ value. As illustrated in Figure 3(a), the observed L–FDR may be the source of instability of the ε’ value at L–F and high–temperature regions. This explanation is confirmed by the results in Figures 3(c–d) and their insets. The circle cross marks in Figure 3(c) and its inset represent the same ε’ value at 10^4 Hz and 150°C in different points of view. For the CCTO sample, the intense temperature–dispersion of the ε’ response in a L–F range (inset of Figures 3(c)) is related to the remarkable frequency–dispersion of the ε’ response in a high–temperature range (Figures 3(c)). This observation contrasts with that observed in the CCTO–MgF05 sample, as illustrated in Figure 3(d) and its inset. Remarkably, the temperature stability of ε’ for the CCTO ceramics can be improved by substituting Mg^2+ and F− with a proper concentration. This finding is consistent with those published in the literature [7–9], demonstrating the positive effect of doping on improving the dielectric stability with frequency and temperature.

The plateau of the primary dielectric response, which was due to the Maxwell–Wagner polarization at the GBs [5,26,35], can be clearly observed at ~60°C because the L–F polarization at the sample–electrode interface is not dominant, as illustrated in Figure 4. Therefore, only the H–FDR was observed with the ε’ values at 1 kHz of 1.30 × 10^3, 5.42 × 10^3 and 1.14 × 10^4 for the CCTO, CCTO–MgF05, and CCTO–MgF10 ceramics.

Figure 3. (a) Frequency dependence of ε’ at RT for CaCu3−xMg2xTi4O12−2x/2F2−x ceramics; inset shows tan δ as a function of frequency at RT. (b) Temperature dependence of ε’ at 1 kHz for CaCu3−xMg2xTi4O12−2x/2F2−x ceramics; inset shows the values of ε’ and tan δ at RT and 1 kHz. (c–d) Temperature dependence of ε’ for various frequencies for CCTO and CCTO–MgF05 samples, respectively; their insets show the frequency dependence of ε’ from 10^6 to 10^7 Hz at the selected temperatures. The circle cross marks in Figure 3(c) and its inset represent the ε’ value at 10^4 Hz and 150°C.

Figure 4. Frequency dependence of ε’ at ~60°C for the CaCu3−xMg2xTi4O12−2x/2F2−x ceramics.
Thus, changed respectively. As shown in Figures 3(b–d), the \( \varepsilon' \) values in a low–temperature range of all the samples changed slightly owing to the elimination of L–FDR. Thus, in a relatively high–temperature range, the strong temperature dependence of the \( \varepsilon' \) value at 1 kHz for the CCTO and CCTO–MgF10 samples is attributed to the dominant effect of L–FDR, which was due to the sample–electrode effect [32,33].

Impedance spectroscopy has been used to investigate the electrical characteristics of \( n \)–type semiconducting grains and insulating GBs in (Mg\(^{2+}\) + F\(^{-}\)) co–doped CCTO ceramics to understand the mechanism of the colossal dielectric response [5,17,26]. Without the sample–electrode effect, the electrical structure of the IBLC model can be defined by an equivalent circuit consisting of two parallel resistor–capacitor (RC) components linked in series. The semiconducting grains are represented by a single RC element, which consists of \( R_g \) and grain capacitance (C\(_g\)). The other was for insulating GB regions, which were composed of \( R_{gb} \) and GB capacitance (C\(_{gb}\)) [5,35]. For CCTO ceramics, \( R_{gb} \) and \( R_g \) can be estimated by measuring the diameter of a large semicircular arc at L–Fs and a nonzero intercept on the \( Z' \)–axis at high frequencies, respectively [5]. As shown in Figure 5(a), the calculated \( R_{gb} \) values at 120°C are 5.80, 6.63, and 1.42 kΩ–cm for the CCTO, CCTO–MgF05, and CCTO–MgF10 samples, respectively. The variance in \( R_g \) was proportional to the variation in tan\( \delta \). As shown in the inset of Figure 5(a), the \( R_g \) value of the CCTO–MgF05 sample was changed compared to that of the CCTO sample. At −60°C, the \( R_g \) values of CCTO, CCTO–MgF05, and CCTO–MgF10 were approximately 103, 140, and 96 Ω–cm, respectively. The small increase in \( R_g \) is most likely due to a reduction in electrical transport within the semiconducting grains.

Usually, changes in the \( \varepsilon' \) values of CCTO ceramics are closely correlated with their microstructural changes. Thus, the suppressed \( \varepsilon' \) value of the CCTO–MgF05 sample was primarily caused by a decrease in the mean grain size. However, the \( \varepsilon' \) value of the CCTO–MgF10 sample is not consistent with the microstructural effect. The different \( \varepsilon' \) values between the CCTO–MgF05 and CCTO–MgF10 samples, despite their microstructures being practically identical, may be caused by the different C\(_{gb}\) values. The increased charge carrier density (decreased \( R_g \)) in CCTO–MgF10 sample compared to CCTO–MgF05 sample may be the primary reason for the increase in \( \varepsilon' \), which could be due to the different doping concentrations. The \( \varepsilon' \) value of the CCTO sample was larger than that of the CCTO–MgF10 sample, despite their \( R_g \) values being practically identical, may be due to the larger mean grain size in accordance with the IBLC structure [5,21]. This can be explained as follows: the L–F \( \varepsilon' \) was calculated as \( \varepsilon' \approx C_{gb}/C_0 \) (where \( C_0 \) is the capacitance of free space) [17]. Using impedance spectroscopy, the estimated C\(_{gb}\) values for the CCTO, CCTO–MgF05, and CCTO–MgF10 samples at 20°C were approximately 10.24, 4.26, and 8.32 nF, respectively. Clearly, the variation in \( \varepsilon' \) is related to C\(_{gb}\).

According to the IBLC model of Schottky barriers at the GBs [36], the C\(_{gb}\) values are correlated with the charge carrier concentration in the semiconducting grains (\( N_d \)), as determined by the varied \( R_g \) of each sample, following the equation.

\[
C_{gb/S} = \sqrt{\frac{q\varepsilon^2N_d}{80\Phi_b}}
\]

where C\(_{gb/S}\) is the GB capacitance per unit area, \( q \) is the electronic charge, and \( \Phi_b \) is the effective potential barrier of height at the GBs. Now, there are two

Figure 5. (a) Impedance complex plane (\( Z' \)) plot at 120°C; inset shows high–frequency data of the \( Z' \) plot at −60°C. (b–c) Arrhenius plots of \( R_g \) and \( R_{gb} \).
possible origins of the semiconducting grains [5,35]. First, it was due to oxygen loss during sintering, as shown in the following equation:

$$O_2^\infty \rightarrow \frac{1}{2} O_2(g) + V_0 + 2e^- \quad (2)$$

$$2Cu^{2+} (2Cu^{x}_C) + 2e^- \rightarrow 2Cu^{+} (2Cu^{x}_C)$$

$$2Ti^{4+} (2Ti^{x}_B) + 2e^- \rightarrow 2Ti^{3+} \quad (3)$$

where, $V_0$ is an oxygen vacancy. Second, it was due to the non–stoichiometry associated with the instability of $Cu^{2+}$ and the partial substitution of $Cu^{2+}$ by $Ti^{4+}$, giving rise to the existence of $Cu^+$ and $Ti^{3+}$ in the heating and cooling stages, respectively [35]. For the CCTO–MgF05 sample, the decreased $\epsilon'$ and $C_{gb/s}$ values resulted from the decrease in $N_d$ (or increased $R_g$) value owing to the reduced $V_0$ concentration as follows:

$$MgF_2 + [2V_0 + 4Cu^{x}_C] \xrightarrow{ScCuO} Mg^{x}_C$$

$$+ [2O_2 + 2Cu^{x}_C + 2Cu^{x}_C + 3O_2^\infty \quad (4)$$

Accordingly, the concentration of free electron or $Cu^+$ ($Cu^{x}_C$) was reduced by co–doping with $(Mg^{2+} + F^-)$, leading to a decreased $C_{gb}$ value for the CCTO–MgF05 sample. When the concentration of $F^-$ doping ions is higher than that of $V_0$ for the CCTO–MgF10 sample, free electrons were re-generated by the excessive MgF dopant, as shown in the following equation:

$$MgF_2 + 2Cu^{x}_C \xrightarrow{3Cu^{x}_C} Mg^{x}_C + 2F_0 + 2Cu^{x}_C + O_2^\infty \quad (5)$$

Thus, the increased $N_d$ (or decreased $R_g$) value was obtained in the CCTO–MgF10 sample (compared to that of the CCTO–MgF05 sample), resulting in an increased $C_{gb}$ value.

Additionally, the temperature dependences of $R_g$ and $R_{gb}$ were determined to match Arrhenius law [15,17]:

$$R_{gb} = R_0 \exp \left( \frac{E_{gb} \cdot \alpha}{k \cdot T} \right) \quad (6)$$

where $R_0$ is a term corresponding to the pre–exponential constant, $T$ is the absolute temperature (K), and $k_b$ is the Boltzmann constant. Calculations of the activation energies involved in the charge carrier conduction within grains ($E_g$) and at GBs ($E_{gb}$) can be performed using the linear fitting data. As shown in Figures 5(b,c), the $E_g$ values determined for the CCTO, CCTO–MgF05, and CCTO–MgF10 samples were 0.084, 0.081, and 0.080 eV, respectively. The $E_{gb}$ values of all the ceramics varied slightly. The $E_{gb}$ values were 0.625, 0.685, and 0.437 eV, respectively. Interestingly, the change in $E_{gb}$ was closely correlated with $R_{gb}$. The calculated $E_g$ values are comparable to those published by Ni et al. [20], 0.1 eV. It is well known that monovalent ($V_{O}$) and bivalent $V_0$ can easily occur during sintering. $V_0$ has a donor energy level of less than 0.07 eV, while $V_{O}$ has a donor energy level of 0.1 eV [37]. Thus, an $E_g$ of 0.08 eV might have been generated by the electrical reaction occurring inside the semiconducting grains of $(Mg^{2+} + F^-)$ co–doped CCTO ceramics. Additionally, the large difference between $E_g$ and $E_{gb}$ implies the formation of an IBLC structure, which is a significant cause of the giant dielectric response observed in CCTO.

In general, the variation in $R_{gb}$ is primarily associated with the geometric (volume fraction of GBs, $f_{gb}$) and intrinsic properties ($E_{gb}$ and $\alpha_{gb}$) of GBs [15]. The significantly increased $R_{gb}$ of the CCTO–MgF05 samples compared with that of the undoped CCTO sample was dominated by the increased $f_{gb}$ because of the reduced mean grain size. The $R_{gb}$ of the CCTO–MgF10 sample was reduced by one order of magnitude compared to that of the CCTO sample even though its $f_{gb}$ was increased, corresponding to the reduced $E_{gb}$.

Typically, the L–F tanδ value of CCTO ceramics is governed by $R_{gb}$, which is proportional to the DC conductivity [9,15]. The influences of the DC conduction and dielectric relaxation processes on the tanδ values can be described as follows [34]:

$$\tan \delta = \frac{(\epsilon'_s - \epsilon'_\infty) \cdot \omega^2 \cdot \epsilon_0 \cdot \tau + (1 + \omega^2 \cdot \tau^2) \cdot \sigma_{dc}}{\omega \cdot \epsilon_0 (\epsilon'_s + \epsilon'_\infty) \cdot \omega^2 \cdot \tau^2} \quad (7)$$

where $\epsilon'_s$ and $\epsilon'_\infty$ denote the high–frequency and static dielectric constants, respectively, $\tau$ denotes the relaxation time, $\epsilon_0$ denotes the permittivity of vacuum, and $\sigma_{dc}$ denotes the DC conductivity. When $\omega \tau < 1$, the correlation of tanδ and $\sigma_{dc}$ in Eq. (2) can be written as [23],

$$\tan \delta \approx \frac{\sigma_{dc}}{\omega \cdot \epsilon_0 \cdot \epsilon_\infty} \quad (8)$$

When the hypothesis $R_g \ll R_{gb}$ is established, $\sigma_{dc}$ can be approximated as [15],

$$\tan \delta \approx \frac{1}{\omega \cdot \epsilon_0 \cdot \epsilon_\infty \cdot R_g} \quad (9)$$

According to Equation (9), tanδ can be diminished by increasing the $R_{gb}$ value if the L–F tanδ is solely due to DC conduction. The correlation between tanδ and 1/$R_{gb}$ values (at 80°C) of all the samples is clearly shown in Figure 6, following Equation (9). Note that the $R_{gb}$ values at RT cannot be obtained.

The effect of $(Mg^{2+} + F^-)$ co–doping ions on the non–Ohmic curves of undoped and co–doped CCTO ceramics at RT is shown in Figure 7. Values of $E_{gb}$ were calculated and found to be 108.15, 346.96, and 44.48 V/cm² for the CCTO, CCTO–MgF05, and CCTO–MgF10 samples, while $\alpha$ were approximately about 3.42, 4.32, and 3.17, respectively. Both the $E_g$ and $\alpha$ values of the CCTO and $(Mg^{2+} + F^-)$ co–doped CCTO ceramics were closely related to their dielectric
electrical responses. The co–dopants can improve both the dielectric and non–Ohmic properties of CCTO ceramics when doping with a proper doping concentration. The variations in $E_b$ values are also correlated to changes in tanδ values, as shown in Figure 6. The lowest tanδ of the CCTO–MgF05 sample is related to its highest $E_b$ value.

The nonlinear $J–E$ properties are attributed to the formation of Schottky barrier height at the GBs [36,38]. Generally, the $E_{gb}$ value is closely related to the $\Phi_b$ value [39]. Thus, the variations in $E_b$ values of all the samples are related to their $E_{gb}$ (or $\Phi_b$) values and the mean grain sizes (or $f_{gb}$). As shown in Figure 8, the significantly increased $E_b$ value of the CCTO–MgF05 sample compared to that of the CCTO sample is clearly attributed to the mutual contribution of the intrinsic ($E_{gb}$) and extrinsic (grain size) effects. It is worth noting that the reduction in $E_b$ for the CCTO–MgF10 sample, whose grain size was remarkably reduced compared to the CCTO sample, arises from the significant decrease in $\Phi_b$.

4. Conclusions

In conclusion, we systematically investigated the influence of Mg$^{2+}$ and F$^–$ substitution in CCTO ceramics prepared using the solid–state reaction method. A primary CCTO–like phase without impurities was obtained for all ceramics. The mean grain sizes of the CCTO ceramics were degraded by the co–doping with Mg$^{2+}$ and F$^–$. Notably, the dielectric properties and

Figure 6. Correlation between $1/R_{gb}$ at 80°C, tanδ (at 1 kHz and 80°C), and $E_b$ at RT for CaCu$_{3-x}$Mg$_x$Ti$_4$O$_{12-2x}$F$_{2x}$ ceramics.

Figure 7. Nonlinear $J–E$ characteristics at RT of CaCu$_{3-x}$Mg$_x$Ti$_4$O$_{12-2x}$F$_{2x}$ ceramics.

Figure 8. Correlation between $E_b$ at RT, grain size ($G$), and $E_{gb}$ for CaCu$_{3-x}$Mg$_x$Ti$_4$O$_{12-2x}$F$_{2x}$ ceramics.
nonlinear J–E characteristics of the CCTO ceramics were successfully improved by co-doping with Mg2+ and F- with a proper doping concentration. When CCTO ceramics were compared to CCTO–MgF0.5 samples, the L–F tanδ value was significantly lowered. The increase in $E_p$ was due to the reduced grain size and increased Schottky barrier height at the GBs. The importance of the geometric and intrinsic properties of the GB was represented to control the nonlinear electrical and giant-dielectric properties of CCTO ceramics.

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Disclosure statement

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