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Selectivity of doping ions to effectively improve dielectric and non-ohmic properties of $CaCu_3Ti_4O_{12}$ ceramics

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Abstract

We provide two separate strategies to improve the dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics. First, substitution of La^{3+} ions can reduce the loss tangent ($\tan\delta < 0.03$) and increase the temperature stability of the dielectric constant ($\Delta\varepsilon'(\%)$) of $CaCu_3Ti_4O_{12}$ ceramics. The dielectric constant of $CaCu_3Ti_4O_{12}$ was greatly reduced from ~17500 to ~5300 and ~2700 for $Ca_{0.775}La_{0.15}Cu_3Ti_4O_{12}$ and $Ca_{0.70}La_{0.2}Cu_3Ti_4O_{12}$, respectively. The $\Delta\varepsilon'(\%)$ values of these two ceramics were found to be approximately $\pm$ 15% over the temperature ranges of −55–125 °C and −55–150 °C, meeting X7R and X8R temperature characteristics for capacitor applications, respectively. Second, substitution of Sr^{2+} at concentrations of 5–15 at% can significantly reduce $\tan\delta$ (< 0.04). Interestingly, the dielectric constant decreased slightly and was found to be higher than 10^4. However, the requirement for $\Delta\varepsilon' < \pm$ 15% was obtained only over the −60–90 °C temperature range. The effects of La^{3+} and Sr^{2+} doping ions on the nonlinear current–voltage properties were also investigated. Both doping ions were observed to significantly enhance nonlinear electrical properties.

Keywords: B. Grain boundaries; C. Dielectric properties; C. Electrical properties; Impedance spectroscopy

1. Introduction

In recent years, the demand for electronic components that can be operated at high temperatures has dramatically increased due to rapid development of new technologies. One result is that sizes of electronic components have to be smaller. This is needed to support new technologies requiring low-weight electronic devices and/or to increase functions of communication devices such as smartphones. Among basic electronic components, multilayer ceramic capacitors (MLCCs) are widely used as passive components in electronic systems [1]. New dielectric materials with better performance and lower costs have therefore gained attention [2–14]. Usually, three basic factors are considered to determine suitability of a material for use in fabrication of MLCCs. These are the values of a dielectric constant (ε'), the loss tangent ($\tan\delta$), and the temperature stability of ε' ($\Delta\varepsilon'(\%)$) or the temperature stability of capacitance ($\Delta C/C_{25}$ (%)) [15].

Since giant dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO) were discovered [10], CCTO has been intensively investigated [11,16–36]. CCTO ceramics can exhibit very high ε' values, in the range of 10^3–10^5, depending on microstructure and sintering conditions. Unfortunately, $\tan\delta$ of CCTO ceramics was found to be higher than 0.05 at room temperature and a frequency of 10^3 Hz, which is too large. Many investigations focused on strategies to reduce the value of $\tan\delta$ while retaining a high ε' value [16,22,25,27–31,35]. Most researchers believe that high $\tan\delta$ values are a serious problem that prevents

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practical applications of CCTO ceramics. In MLCCs, the temperature coefficient of capacitance (or ε') of a dielectric material is one of the most important factors that must be considered [15]. For an X7R capacitor, $\Delta\varepsilon'(\%)$ or $\Delta C/C_{25}$ (%) (compared to the ε' value at 25 °C and 10^3 Hz) of a dielectric material used to fabricate this type of capacitor must be less than $\pm$ 15% over the temperature range of −55–125 °C. This is necessary to achieve capacitance values that vary less than $\pm$ 15% with temperature over this range. For X5R and X8R capacitors, $\Delta\varepsilon'(\%)$ has to be less than $\pm$ 15% over the ranges of −55–85 °C and −55-150 °C, respectively [15].

It was also found that substitution of La^{3+} or Sr^{2+} into CCTO ceramics can improve the dielectric properties of CCTO ceramics [25,28]. For instance, tanδ of CCTO ceramics substituted by La^{3+} ions was significantly reduced to a value of 0.03 [25]. Substitution of Sr^{2+} ions into CCTO ceramics can greatly reduce tanδ while retaining a high ε' value [28]. This suggests that La^{3+} and Sr^{2+}-doped CCTO ceramic materials have high potential for use in practical applications as capacitive elements. Unfortunately, systematic investigations to study the possibility for practical capacitor application of these materials have rarely been done. The effects of La^{3+} or Sr^{2+} doping concentrations on the values of ε' and tanδ as well as the temperature coefficient of capacitance must be investigated before practical developments are possible. According to previous work [18,31], CCTO ceramics prepared using Ca- and Cu-acetates exhibited interesting dielectric properties including high ε' and low tanδ. The results revealed that CCTO ceramics prepared using these raw materials may have potential for capacitor applications. We hypothesized that metal ions substituted to CCTO ceramics prepared using Ca- and Cu-acetates as starting raw materials may provide good dielectric properties, especially for La^{3+} and Sr^{2+}-doped CCTO ceramics. Thus, we prepared La^{3+} and Sr^{2+}-doped CCTO ceramics using a simple thermal decomposition method. Ca- and Cu-acetates were used as sources of Ca^{2+} and Cu^{2+} ions, respectively. The influences of these doping ions on the dielectric properties and nonlinear current–voltage properties of CCTO ceramics were investigated.

2. Experimental details

$Ca_{1-3x/2}La_xCu_3Ti_4O_{12}$ and $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ ceramics, where x=0.05, 0.10, 0.15, and 0.20 (referred to as La05, La10, La15, La20 samples and Sr05, Sr10, Sr15, Sr20 samples, respectively), were prepared using a simple thermal decomposition method. Undoped $CaCu_3Ti_4O_{12}$ was referred to as the CCTO sample. $Ca(C_2H_3CO_2)_2 \cdot H_2O$ (99+%, Sigma-Aldrich), $Cu(CH_3COO)_2 \cdot H_2O$ (98−102.0%, Carlo Erba), $C_{16}H_{28}O_6Ti$ (75 wt% in isopropanol, Sigma-Aldrich), $(C_2H_3O_2)_2Sr$ (99.995%, Sigma-Aldrich), $(C_6H_9O_6)La.xH_2O$ (99.9%, Sigma-Aldrich), citric acid, and ethanol were employed as starting raw materials. Details of the preparation were previously reported [31]. Mixed solutions of each composition were reacted at 900 °C for 4 h. The resulting powders were ground and pressed into pellets using a 9.5 mm diameter die set, samples of ~1–2 mm in thickness were obtained by uniaxial compression at 200 MPa. Finally, these disks were sintered in air at 1070 °C for 9 h.

X-ray diffraction (XRD; Philips PW3040, the Netherlands) and scanning electron microscopy (SEM; Hitachi S-3400, Japan) were used to characterize the phase composition and microstructure of the sintered $CaCu_3Ti_4O_{12}$ ceramics. The dielectric response of the samples was measured using an Agilent E4980A (Hayward, CA) Precision LCR Meter over the frequency and temperature ranges of 10^2–10^6 Hz and −70–150 °C, respectively. An oscillation voltage of 0.5 V was used in each case. Each temperature was held constant with an accuracy of $\pm$ 1 °C. Current–voltage measurements were made using a high voltage measurement unit (Keithley Model 247, Estado St Pasadena, CA). The breakdown electric field (E_b) was achieved at J=1 mA cm^{-2}. The nonlinear coefficient (α) was calculated from the following formula:

$$\alpha = \frac{\log(J_2/J_1)}{\log(E_2/E_1)}, \quad (1)$$

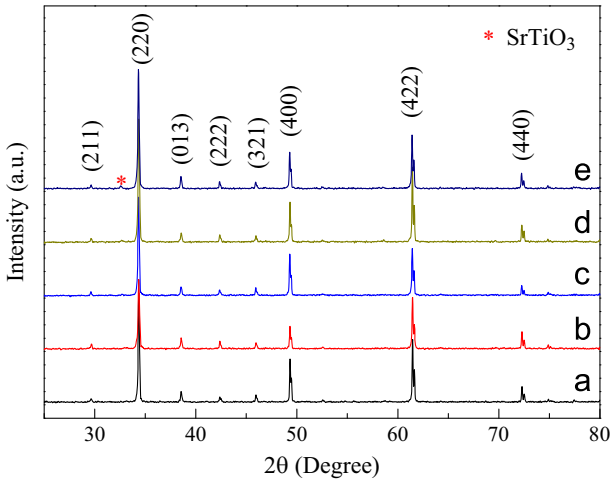

Fig. 1. XRD patterns of (a) CCTO, (b) Sr05, (c) Sr10, (d) Sr15, and (e) Sr20 ceramic samples.

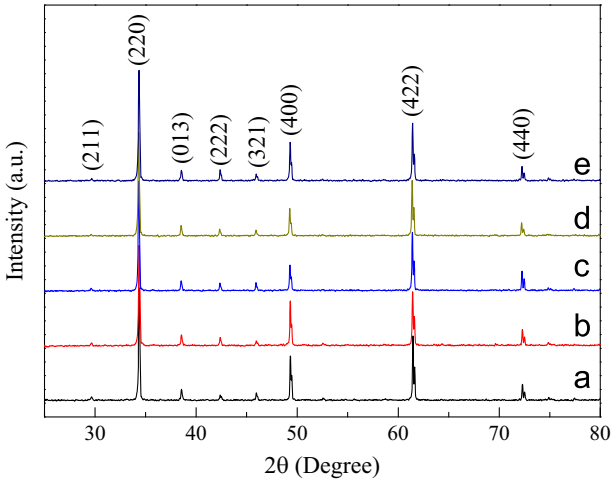

Fig. 2. XRD patterns of (a) CCTO, (b) La05, (c) La10, (d) La15, and (e) La20 ceramic samples.

where E_1 and E_2 are, respectively, the electric fields corresponding to $J_1=1$ and $J_2=10$ mA cm^{-2}. Prior to measurements, Au was sputtered onto each pellet face at a current of 25 mA for 8 min using a Polaron SC500 (Sussex, UK) sputter coating unit.

3. Results and discussion

Figs. 1 and 2 show the XRD patterns of Sr^{2+}- and La^{3+}-doped CCTO ceramics, respectively. All of the XRD patterns exhibited the main phase of CCTO with centered-cubic perovskite structure. Pure phase of CCTO was detected in the XRD patterns of all compositions of La^{3+}-doped CCTO ceramics without impurity phases. This result is similar to those in published literature [25]. The second phase of $SrTiO_3$ was only observed in the XRD pattern of the Sr20 sample. Other Sr^{2+}-doped CCTO samples showed only the pure phase. This observation of Sr^{2+}-doped CCTO ceramics prepared using a thermal decomposition method is consistent with Sr^{2+}-doped CCTO ceramics prepared using a solid state reaction method [28]. Lattice parameters of the CCTO, Sr05, Sr10, Sr15, and Sr20 samples were calculated and found to be 7.392, 7.393, 7.392, 7.392, and 7.396 Å, respectively. Lattice parameters of the La05, La10, La15, and La20 samples were calculated to be 7.394, 7.394,

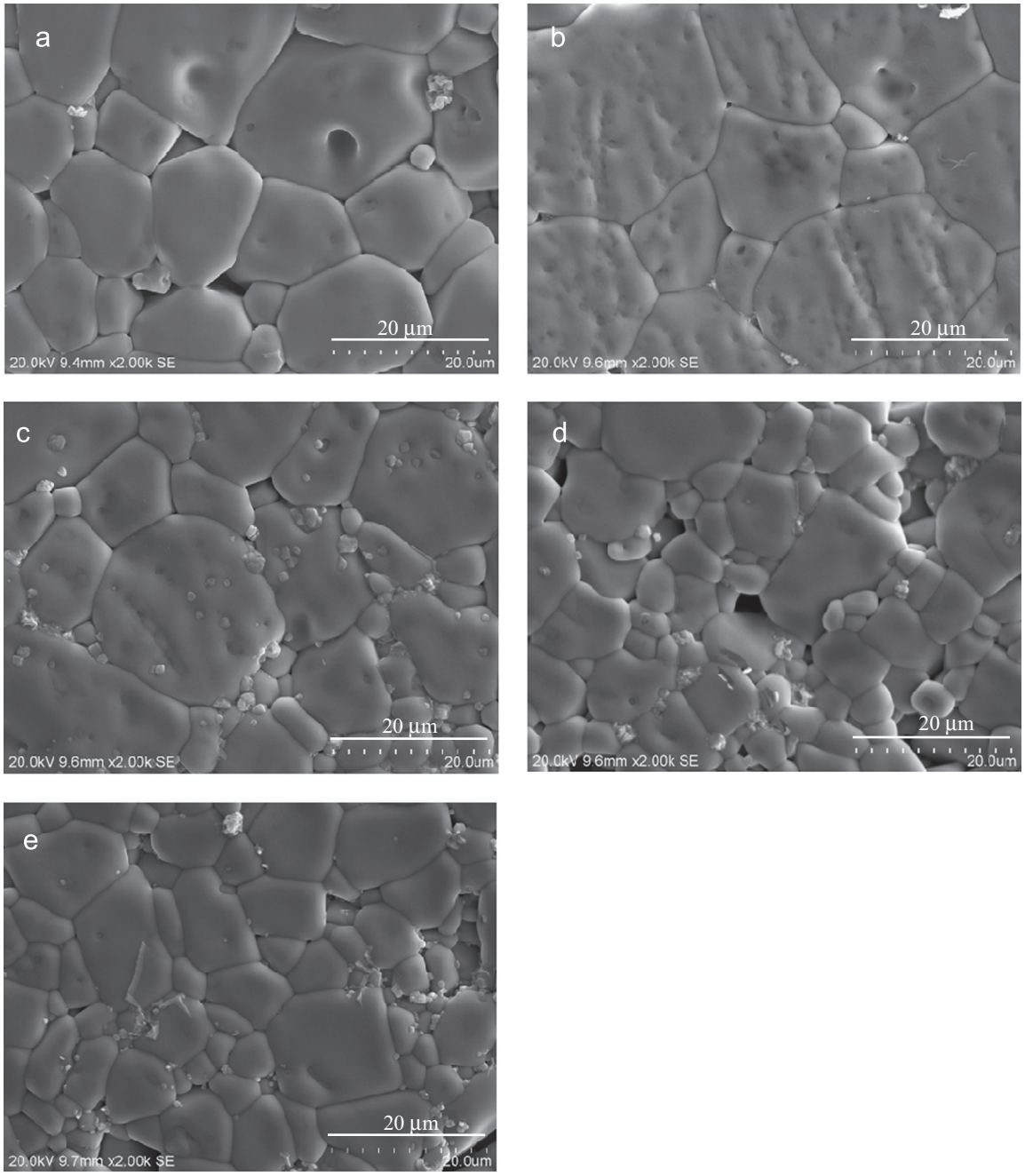

Fig. 3. SEM images of polished surface morphologies of (a) CCTO, (b) Sr05, (c) Sr10, (d) Sr15, and (e) Sr20 ceramic samples.

7.398, and 7.398 Å, respectively. The lattice parameter of the La^{3+}-doped CCTO ceramics significantly increased as the concentration of La^{3+} increased. The lattice parameters of the Sr05, Sr10, and Sr15 samples were nearly constant compared to that of the CCTO sample. The lattice parameter of the Sr20 sample increased significantly.

Fig. 3 shows surface morphologies of the CCTO and Sr^{2+}-doped CCTO ceramics, revealing grain and grain boundary (GB) microstructure. The mean grain size of CCTO ceramics increased slightly when doping with 5 at% Sr^{2+} for the Sr05 sample. Then it gradually decreased as the concentration of Sr^{2+} doping ions increased from 10 to 20 at%. This result is similar to that found in published reports [28]. The microstructures of the La^{3+}-doped CCTO ceramics are shown in Fig. 4. Low concentration of La^{3+} doping content in the La05 sample has no significant influence on the microstructure of CCTO ceramics. With increasing La^{3+} doping content, the mean grain size was greatly decreased. This decrease in the mean grain size of La^{3+}-doped CCTO may be attributed to the ability of La^{3+} doping ions to inhibit the GB mobility during the sintering process. Note that porosity is observed in the La10, La15, and La20 samples.

Fig. 5a and c shows ε' values at 20 °C as a function of frequency for the La^{3+}- and Sr^{2+}-doped CCTO ceramics. ε' of the CCTO and La05 samples gradually decreased as the frequency increased. Frequency independence of ε' over the measured range was observed in the La10, La15, and La20 samples. It was found that ε' of the La^{3+}-doped CCTO ceramics decreased with increasing La^{3+} doping concentration. For the Sr^{2+}-doped CCTO ceramics, ε' decreased continuously as the Sr^{2+} doping content increased from 5 to 15 at% for the Sr05, Sr10, and Sr15 samples. Then, ε' increased slightly when Sr^{2+} content was further increased from 15 to 20 at%. The frequency dependence of tanδ for La^{3+}- and Sr^{2+}-doped CCTO ceramics is shown in Fig. 5b and d, respectively. It was found that low-frequency tanδ values (in the range of 10^2–10^4 Hz) for the La05 sample slightly increased compared to the CCTO sample. With increasing La^{3+} content, the low-frequency tanδ decreased as La^{3+} doping content increased. Substitution of Sr^{2+} into CCTO ceramics at concentrations of 5–15 at% (the Sr05, Sr10, and Sr15 samples) greatly decreased the low-frequency tanδ. However, substitution of Sr^{2+} at the highest concentration (20 at%) for the Sr20 sample resulted in an increase in tanδ. The tanδ values at 1 kHz of all samples are summarized in Table 1. Interestingly, substitution of Sr^{2+} or La^{3+} ions with suitable concentrations can greatly reduce tanδ. For La^{3+}-doped CCTO ceramics, higher concentrations of La^{3+} doping ions are likely suitable. However, for Sr^{2+} doping ions, high doping concentration is unsuitable. A small concentration of Sr^{2+} is recommended for improving dielectric response in CCTO ceramics prepared using a simple thermal decomposition method. This result is consistent with observations of Sr^{2+}-doped CCTO ceramics prepared by a solid state reaction method [28]. The ε' values at 20 °C and 10^3 Hz of all samples

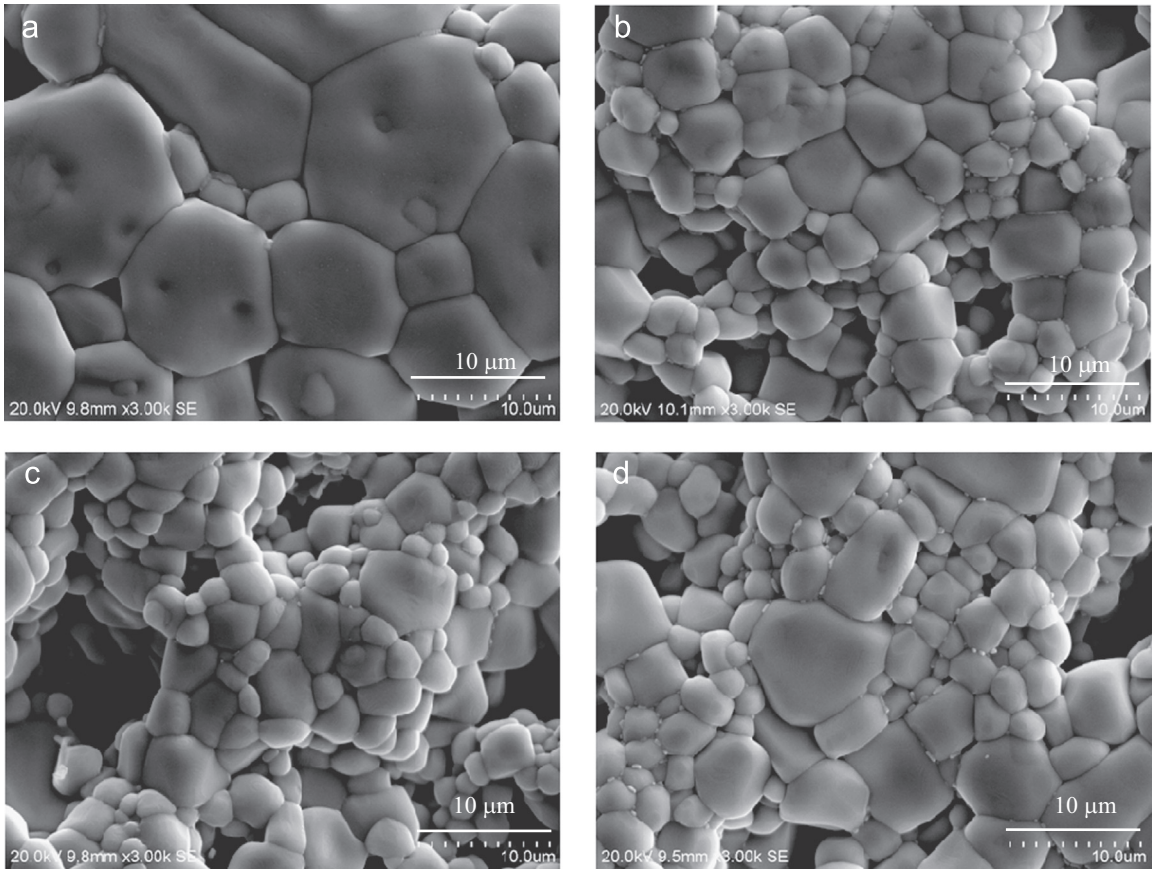

Fig. 4. SEM images of polished surface morphologies of (a) La05, (b) La10, (c) La15, and (d) La20 ceramic samples.

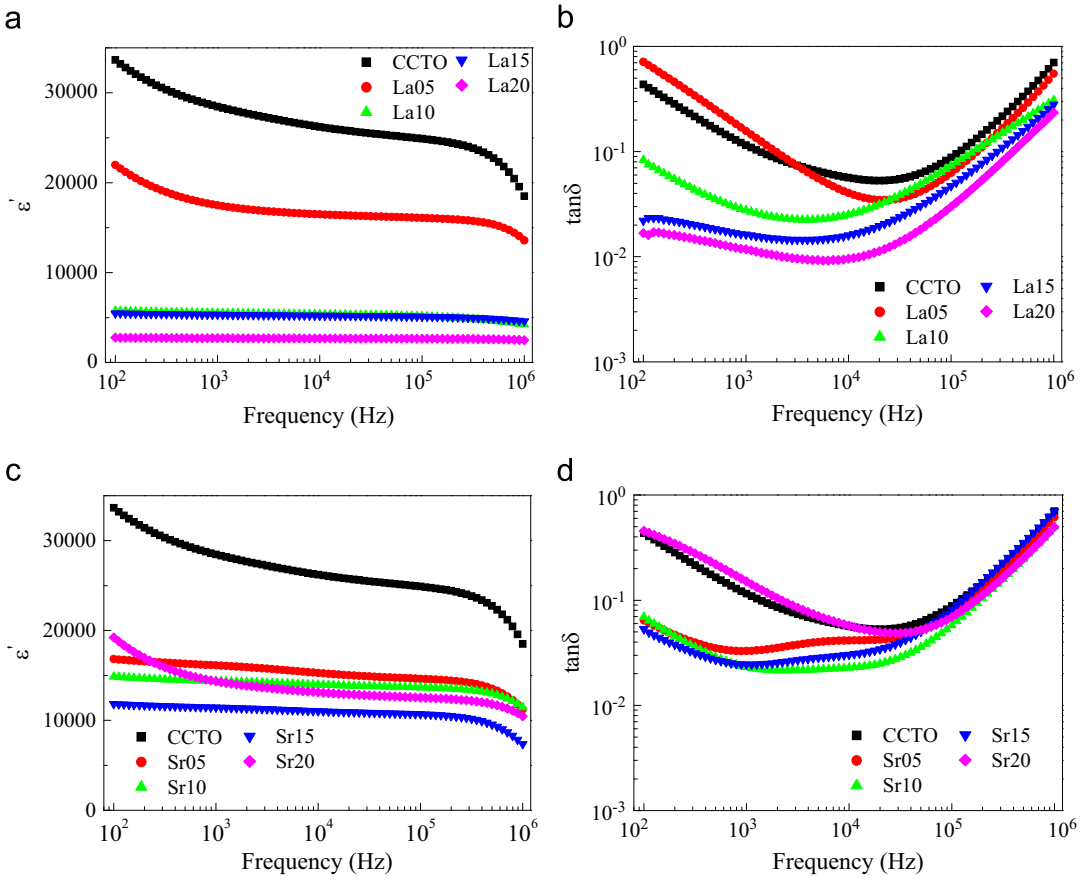

Fig. 5. (a and c) Frequency dependence of ε' at 20 °C for La-doped CCTO and Sr-doped CCTO ceramics. (b and d) Frequency dependence of tanδ at 20 °C for La-doped CCTO and Sr-doped CCTO ceramics.

Table 1
Dielectric properties (ε' and tanδ at 20 °C and 1 kHz), temperature coefficient of capacitance ($\Delta C/C_{20}$°C (%)), nonlinear coefficient (α), and breakdown field (E_b) for the CCTO, La-doped CCTO, and Sr-doped CCTO ceramics.

Sample	ε'	tanδ	$\Delta C/C_{20\,°C}$ (%)				α	E_b (V cm^{-1})
			−60 °C	90 °C	130 °C	150 °C		
CCTO	28,473	0.116	−11.67	43.85	107.33	173.01	3.53	582
La05	17,498	0.157	−8.50	77.80	128.86	144.01	2.96	562
La10	5,508	0.028	−3.97	13.36	42.64	55.42	6.11	2,832
La15	5,311	0.016	−1.33	5.00	12.21	23.22	6.98	4,149
La20	2,704	0.012	0.28	3.11	7.77	13.67	7.19	5,242
Sr05	16,131	0.033	−8.56	11.80	40.74	49.19	5.02	1,436
Sr10	14,369	0.023	−3.81	15.15	61.89	87.61	5.37	1,850
Sr15	11,432	0.025	−3.82	14.77	69.69	114.76	6.90	3,402
Sr20	14,348	0.151	−11.92	122.71	310.35	370.07	3.53	513

are summarized in Table 1. As reported by Yang et al. [28], tanδ of CCTO ceramics was decreased significantly by substitution of 10 at% Sr^{2+}, tanδ~0.022 at 1 kHz. They also found that the GB resistance (R_{gb}) of CCTO ceramics increased when doping with 10 at% Sr^{2+}. Thus, we attribute the large decrease in tanδ of Sr^{2+}-doped CCTO ceramics to the enhancement of R_{gb} as reported by Yang et al. [28].

As shown in Table 1, tanδ values of the La10, La15, and La20 samples were greatly reduced to 0.028, 0.016, and 0.012, respectively. ε' remained higher than 10^3 (at 20 °C and 1 kHz). These values of ε' and tanδ are acceptable for ceramic capacitor applications [15]. However, the temperature coefficient of ε' or capacitance is still one of the most important parameters to be considered before their use as materials to fabricate capacitors. Fig. 6 shows $\Delta C/C(\%)$ for the La^{3+}-doped CCTO ceramic samples compared to the value obtained at 20 °C and 1 kHz. It was found that the temperature coefficient of the La10 sample satisfies the EIA X5R capacitor specification, i.e., $\Delta C/C < \pm 15\%$ in the temperature range from −55-85 °C. Interestingly, $\Delta C/C(\%)$ of the La15 and La20 samples

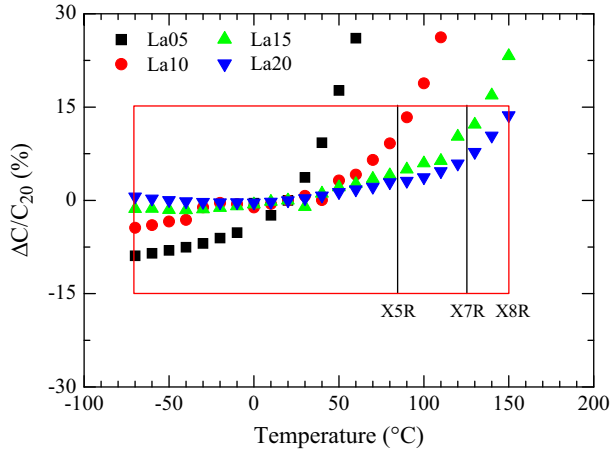

Fig. 6. Temperature coefficient of capacitance for La-doped CCTO ceramic samples in the temperature range of −70–150 °C evaluated at the frequency of 1 kHz.

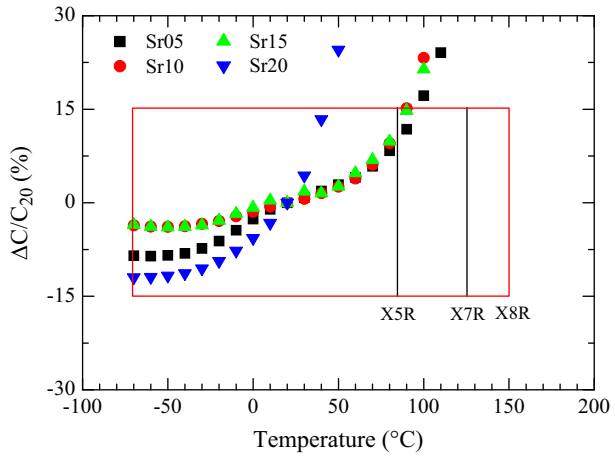

Fig. 7. Temperature coefficient of capacitance for Sr-doped CCTO ceramic samples in the temperature range of −70–150 °C evaluated at the frequency of 1 kHz.

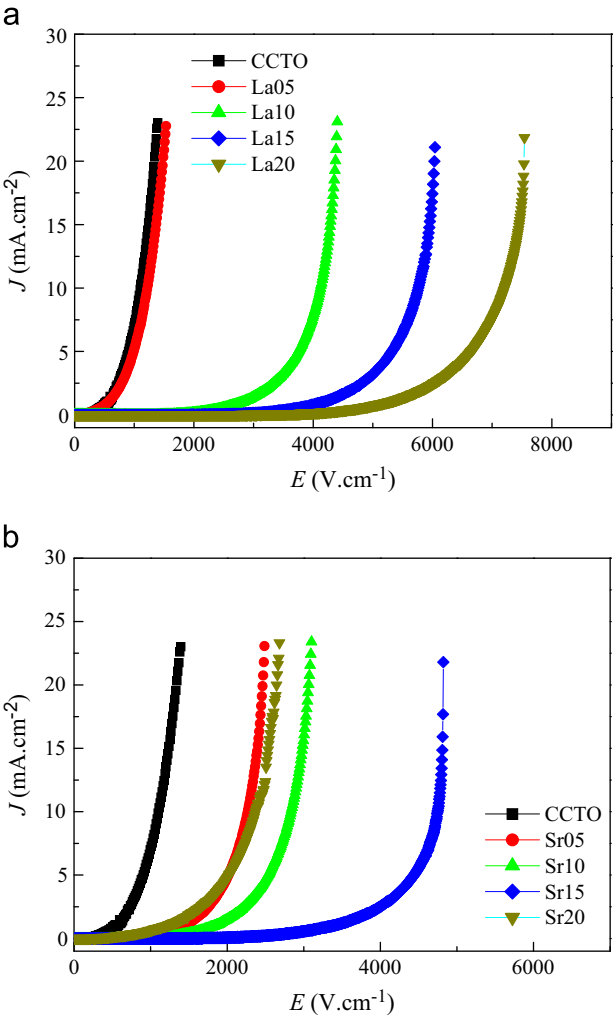

Fig. 8. Non-ohmic characteristics (J vs. E) of (a) La-doped CCTO and (b) Sr-doped CCTO ceramics at room temperature.

were found to be $< \pm 15\%$ over the temperature ranges of −55-125 °C and −55-150 °C, respectively. Therefore, the dielectric properties of the La15 and La20 samples satisfy the X7R and X8R capacitor specifications, respectively. This is the first report of CCTO with performance sufficient for fabrication of X8R capacitors. Fig. 7 shows ΔC/C(%) of the Sr^{2+}-doped CCTO ceramic samples. It was found that the condition of $\Delta C/C < \pm 15\%$ for the Sr05, Sr10, and Sr15 samples occurred only in the range of −55-85 °C. This indicates that these three ceramics may have potential for fabrication of X5R capacitors. From the overall dielectric properties of the La^{3+}-doped CCTO and Sr^{2+}-doped CCTO ceramics, it can be postulated that if it is desirable to fabricate temperature stable capacitors without reducing their size, the former material group may be used. In contrast, if the goal is to reduce capacitor size and if performance at extra high temperatures is not necessary, the later material group may be satisfactory due to their high ε' values.

In this work, we also investigated the effects of La^{3+} and Sr^{2+} doping ions on the nonlinear current–voltage properties of CCTO ceramics. As shown in Fig. 8, all ceramic samples exhibit non-ohmic properties. E_b and α values were calculated from the J–E curves. These calculated values for all samples are summarized in Table 1. It was found that both the E_b and α values of the La10, La15, La20 samples as well as the Sr05, Sr10, Sr15 samples increased with increasing La^{3+} and Sr^{2+} concentrations. E_b and α values of these samples were larger than the values of the undoped CCTO ceramic sample. It was observed that suitable doping concentration ranges of La^{3+} or Sr^{2+} exist for simultaneously improving both dielectric and nonlinear properties.

4. Conclusion

We successfully improved the dielectric and nonlinear electrical properties of CCTO ceramics by substitution of La^{3+} or Sr^{2+}. The results revealed that these two substituted ions have different influences on the overall dielectric properties. It was found that doping with La^{3+} to CCTO ceramics can reduce tanδ (< 0.03). Furthermore, this can cause an increase in the temperature–capacitance coefficient. A slight disadvantage of La^{3+} substitution is that ε' of CCTO ceramics was

greatly reduced from ~17,500 to ~5300 and ~2700 for $Ca_{0.775}La_{0.15}Cu_3Ti_4O_{12}$ and $Ca_{0.70}La_{0.2}Cu_3Ti_4O_{12}$ ceramics, respectively. However, these two ceramics still satisfied the EIA X7R and X8R temperature specifications for capacitor applications, respectively. Substitution of Sr^{2+} at concentrations of 5–15 at% can significantly reduce tanδ (< 0.04). Interestingly, ε' was slightly reduced and still found to be higher than 10^4. The temperature-capacitance coefficients were found to be less than $\pm 15\%$ in the range from −60-90 °C only. We also found that substitutions of La^{3+} and Sr^{2+} doping ions have remarkable effects on the nonlinear current-voltage properties of CCTO ceramics.

Acknowledgments

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