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Improved dielectric and non-ohmic properties of $Ca_2Cu_2Ti_4O_{12}$ ceramics prepared by a polymer pyrolysis method

Prasit Thongbai[a,*], Bundit Putasaeng[b], Teerapon Yamwong[b], Santi Maensiri[c]

[a] Integrated Nanotechnology Research Center (INRC), Department of Physics, Khon Kaen University, Khon Kaen, 40002, Thailand
[b] National Metals and Materials Technology Center (MTEC), Thailand Science Park, Pathumthani, 12120, Thailand
[c] School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand

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ABSTRACT

Non-ohmic and dielectric properties of $Ca_2Cu_2Ti_4O_{12}$ ($CaCu_3Ti_4O_{12}/CaTiO_3$ composite) ceramics prepared by a polymer pyrolysis method (PP-ceramic samples) are investigated. The PP-ceramics show a highly dense structure and improved non-ohmic and dielectric properties compared to the ceramics obtained by a solid state reaction method (SSR-ceramic samples). ε' ($\tan\delta$) of the PP-ceramic samples is found to be higher (lower) than that of the SSR-ceramic samples. Interestingly, the PP-ceramic sintered at 1050 °C for 10 h exhibits the high ε' of 2530 with weak frequency dependence below 1 MHz, the low $\tan\delta$ less than 0.05 in the frequency range of 160 Hz–177 kHz, and the little temperature coefficient, i.e., $|\Delta\varepsilon'| \leq 15\,\%$ in the temperature range from −55 to 85 °C. These results indicate that the $CaCu_3Ti_4O_{12}/CaTiO_3$ composite system prepared by PP method is a promising high-ε' material for practical capacitor application.

1. Introduction

Recently, $CaCu_3Ti_4O_{12}$ (CCTO) has gained considerable interest both scientifically and technologically because its dielectric constant (ε') is very high ($\varepsilon' \sim 10^3$–10^5) [1–13] and nearly independent of temperature in the range of 100–600 K [4]. Such dielectric properties of the CCTO ceramics are useful for applications in capacitors and memory devices. Up to now, although several investigations have been reported on the dielectric properties of the CCTO ceramics and single crystal as well as related materials, the high loss tangent ($\tan\delta$) of the CCTO ceramics ($\tan\delta > 0.05$ at 1 kHz) is still the most serious problem for applications based on capacitive components. Besides the giant dielectric properties, it is interesting that this material can also exhibit strong non-linear electrical behavior, which is due to the existence of intrinsic potential barriers at the grain boundaries, making it suitable for application in varistors [6].

Kobayashi and Terasaki [14] have reported that the dielectric properties of the CCTO ceramics could significantly be improved by tuning the molar ratio of Ca:Cu atoms ($Ca_{1+x}Cu_{3-x}Ti_4O_{12}$). The ceramic with nominal composition of $Ca_2Cu_2Ti_4O_{12}$ (Ca:Cu = 2:2) was found to exhibit the best dielectric properties, i.e., $\varepsilon' \sim 1800$ and $\tan\delta \sim 0.02$, in this ceramic system. Considering the nominal composition of $Ca_2Cu_2Ti_4O_{12}$ and compared to the $CaCu_3Ti_4O_{12}$ composition, this ceramic consists of ~33.3 mol% of CCTO and ~66.7 mol% of $CaTiO_3$ (CTO), resulting from the imbalance between the Ca and Cu atoms [15]. Besides such improved dielectric properties, it was revealed that the CCTO/CTO composite ceramics also exhibited high non-linear coefficient values ($\alpha \sim 42$–65) with high breakdown field extracted from the *J*–*E* curves [16,17]. Furthermore, the sintering temperature of the CCTO/CTO ceramic composites (~1050–1100 °C) is much lower than that of $BaTiO_3$ (~1350 °C), which is the ferroelectric ceramic that can exhibit the high ε' and low $\tan\delta$ values of about 2000 and 0.02, respectively [14]. Consequently, it is believed that this CCTO/CTO ceramic composite is a promising material system for capacitor and varistor applications. Actually, the CCTO/CTO ceramics still have to pass through extensive compatibility test before its availability for commercial applications in devices. Unfortunately, the investigation of the temperature coefficient of the temperature variation of ε' – the important parameter that determines dielectric materials to be used for capacitor applications – of the CCTO/CTO ceramics is still missing and important to be studied.

Generally, the CCTO ceramics are prepared by the conventional solid state reaction (SSR) method, and high-sintering temperatures and long reaction times are required for this method [1,2,4–11]. To obtain a dense ceramic microstructure, certainly, the sintering temperature (reaction time) of the CCTO/CTO ceramics must be higher (longer) than that of the CCTO ceramics because of the relative high-sintering temperature of CTO (~1300 °C). Therefore, the synthesis of the CCTO/CTO composite ceramics from chemical solution routes is very important because wet chemical methods can offer homoge-

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[*] Corresponding author. Tel.: +66 84 4190266; fax: +66 43 203359.
E-mail addresses: prasitphysics@hotmail.com, pthongbai@kku.ac.th (P. Thongbai).

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neous mixing of the metal ions at the atomic scale. This can reduce the diffusion path length of the ions; thus, the shorter reaction times and lower temperatures are required [18,19]. The obtained homogeneous powders can be used to form the high-performance green body by pressing; consequently, high-performance sintered body (dense ceramic) can be achieved. Up to now, there have been several chemical solution routes that have been used to prepare CCTO such as pyrolysis of an organic solution method [18], wet-chemistry method [19], semi-wet route [20], ethylenediaminetetraacetic acid gel combustion method [21], co-precipitation method [22], soft chemical method [23], and combustion of an aqueous-solution [24]. However, to our knowledge, there is no report on the preparation of CCTO/CTO by a chemical solution route.

In this work, we investigated the dielectric and non-linear properties of the CCTO/CTO ceramics prepared by a polymer pyrolysis (PP) route compared to those of the ceramics prepared by SSR method. Based on the same preparing conditions, dense ceramic microstructure and improved breakdown voltage and dielectric properties were achieved in the PP-ceramic samples. The results revealed that our PP-ceramics have a potential for practical capacitor application.

2. Experimental details

In this work, the $Ca_2Cu_2Ti_4O_{12}$ ceramics were prepared by PP and SSR methods. For the PP method, $Ca(NO_3)_2 \cdot 4H_2O$ (99.9% purity), $Cu(NO_3)_2 \cdot 4H_2O$ (99.5% purity), $C_{16}H_{28}O_6Ti$ (75 wt.% in isopropanal), $(NH_4)_2S_2O_8$, and acrylic acid were employed as starting raw materials. Firstly, stoichiometric amount of $C_{16}H_{28}O_6Ti$ was dissolved in acrylic acid aqueous solution under constant stirring and at 30 °C. Secondly, stoichiometric amounts of $Ca(NO_3)_2 \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot 4H_2O$ were dissolved in the above solution under constant stirring at 100 °C until the clean solution was obtained. Then, several drops of 5% $(NH_4)_2S_2O_8$ aqueous solution as the initiator were added to the mixed acrylic acid solution to promote the polymerization [25,26]. The obtained gel precursor was dried at 350 °C for 1 h. The dried gel was ground and later calcined at 950 °C for 5 h. The calcined powder was pressed into pellets of 9.5 mm in diameter and ~1 mm in thickness by a uniaxial pressing method at 200 MPa. Finally, these pellets were sintered at 1050 °C for 5 and 10 h (abbreviated as PP-5 and PP-10 samples, respectively).

For SSR method, $CaCO_3$ (99.95% purity), CuO (99.9% purity) and TiO_2 (99.9% purity) were employed as starting raw materials. A stoichiometric mixture of the starting materials was ball-milled in ethanol for 24 h. The mixed slurry was dried and then calcined at 950 °C for 5 h. The calcined powder was ground and pressed into pellets of 9.5 mm in diameter and ~1 mm in thickness by a uniaxial pressing method at 200 MPa. Finally, these pellets were sintered at 1050 °C for 5 and 10 h (abbreviated as SSR-5 and SSR-10 samples, respectively).

X-ray diffraction (XRD) (Philips PW3040, The Netherlands) and scanning electron microscopy (SEM) (LEO 1450VP, UK) were used to characterize the phase composition and microstructure of the sintered $Ca_2Cu_2Ti_4O_{12}$ ceramics. The ceramics were polished and electroded by silver paint on both sides of the disk-shape samples. The dielectric response of the samples was measured using an Agilent E4980A Precision LCR Meter over the frequency and temperature ranges of 10^2–10^6 Hz and −70–200 ° C at the oscillation voltage of 1.0 V. Each measuring temperature was kept constant with an accuracy of ±1 °C. Current–voltage measurements were taken using a high voltage measurement unit (Keithley Model 247). The breakdown electric field (E_b) was obtained at a current density of 1 mA cm^{-2}. Numerical values for the non-linear coefficient (α) were obtained by a linear regression of the log J vs. log E plot within the range of validity of the $I = V^{\alpha}$ equation [16,17].

3. Results and discussion

Fig. 1 shows the XRD patterns of the sintered $Ca_2Cu_2Ti_4O_{12}$ ceramics prepared by PP and SSR methods. All of the $Ca_2Cu_2Ti_4O_{12}$ ceramics consist of two main phases of $CaCu_3Ti_4O_{12}$ (JCPDS card no. 75-2188) and $CaTiO_3$ (JCPDS card no. 82-0231), which are similar to CCTO/CTO composites as reported in literatures [14–17]. Additionally, a small amount of CuO phase can be observed in the XRD patterns of the SSR-ceramics, corresponding to the result observed in the TEM micrograph of the CCTO/CTO ceramic reported in Ref. [17]. Considering the nominal composition of $Ca_2Cu_2Ti_4O_{12}$, the formation of the CCTO/CTO composite consisting of ~33.3 mol% of CCTO and ~66.7 mol% of CTO is caused by the imbalance between the Ca and Cu atoms [15]. The lattice parameters of the $CaCu_3Ti_4O_{12}$ phase presented in the SSR-5, SSR-10, PP-5, and PP-10 samples are calculated from the XRD patterns and found to be 7.387, 7.385, 7.389, and 7.388 Å, respectively. These values are slightly lower than the 7.391 Å reported in JCPDS card no. 75-2188. Fig. 2 depicts the SEM images of the CCTO/CTO ceramics, revealing the surface morphologies of the ceramics prepared by SSR and PP methods. Interestingly, the amounts of pores observed in the microstructure of the PP-5 and PP-10 samples are less than in the SSR-5 and SSP-10 samples, respectively.

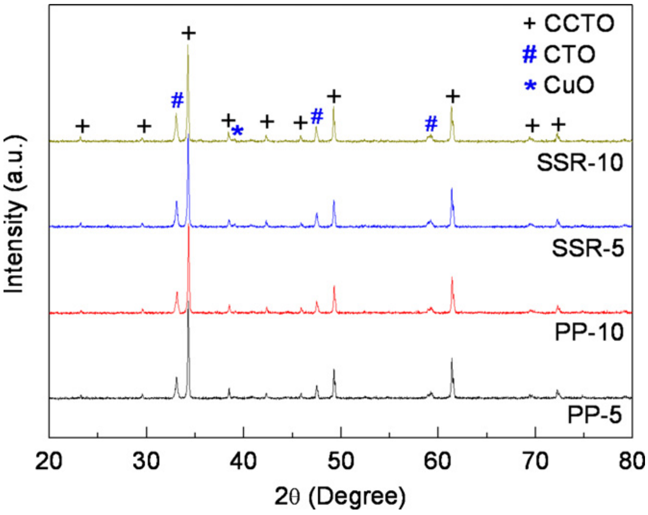

Fig. 1. XRD patterns of CCTO/CTO ceramic samples prepared by PP and SSR methods.

Fig. 3(a) illustrates the frequency dependence of ε' and tan δ at 30 °C for the SSR-10 and PP-10 samples. ε' of the SSR-10 and PP-10 samples is nearly independent of frequency in the range of 10^2–10^6 Hz, and tan δ of these two samples is found to be lower than 0.05 in the frequency range of 10^2–10^5 Hz. The large increase in tan δ at frequencies higher than 10^5 Hz is attributed to the dielectric relaxation process [27], which is mainly due to the dielectric response in the CCTO phase. It is worth noting that the high-frequency dielectric relaxation process of the CCTO ceramics has recently been proposed to be attributed to the nanoscale barrier layer capacitance (NBLC) effect and is related to the existence of polarons on the material [28,29]. The values of ε' and tan δ at the selected frequencies of all samples are summarized in Table 1. Obviously, the dielectric properties of the CCTO/CTO ceramics prepared by PP method are found to be better than those of the ceramics prepared by SSR method. The ε' values of the PP-10 and PP-5 samples are respectively higher than those of the SSR-10 and SSR-5 samples, whereas the tan δ values are lower. These results may be attributed to the dense microstructures of the PP-ceramics compared to the SSR-ceramics. Note that, ε' of the PP-10 sample (~2530 at 1 kHz) is higher than that of 1800 as reported in Ref. [14] for the CCTO/CTO ceramic prepared by SSR method, whereas the tan δ values of these two ceramics are not different. Although ε' of the CCTO/CTO ceramic sintered at 1100 °C for 3 h reported in Ref. [16] (ε' ~2960 at 1 kHz) is higher than that of the PP-10 ceramic, unfortunately, tan δ of this ceramic is not reported.

For capacitor applications, besides the values of ε' and tan δ, the temperature coefficient ($\Delta\varepsilon'$) – the temperature dependence of ε' in a certain temperature range – is one of the most important parameter that must be considered. $\Delta\varepsilon'$ is evaluated at the frequency of 1 kHz and defined as $\varepsilon'_T - \varepsilon'_{20}/\varepsilon'_{20} \times 100[\%]$, ε'_T and ε'_{20} are ε' at a temperature (°C) and 20 °C, respectively [14]. As illustrated in Fig. 3(b), $|\Delta\varepsilon'|$ values of both the SSR-10 and PP-10 samples are lower than 15% in the temperature range from −55

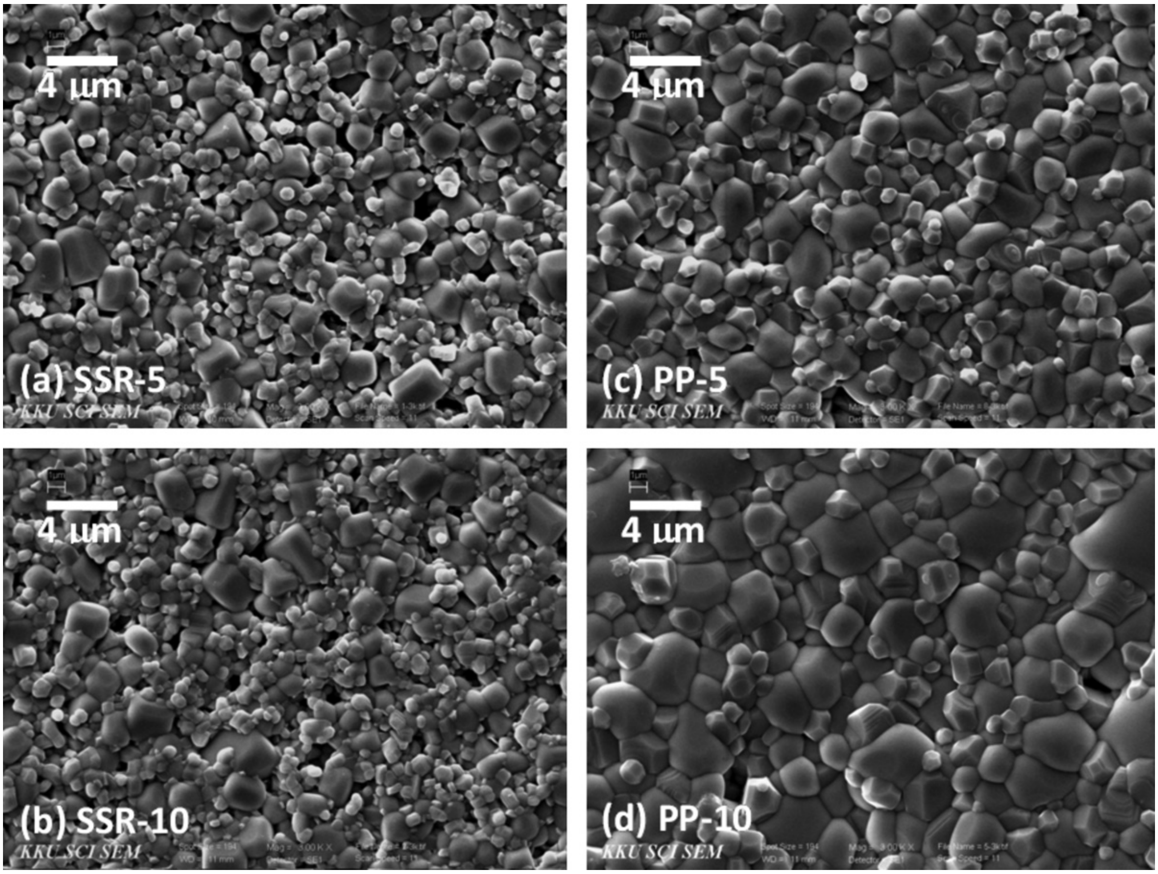

Fig. 2. SEM images of CCTO/CTO ceramic samples for (a) SSR-5, (b) SSR-10, (c) PP-5, and (d) PP-10 samples.

Table 1
Dielectric properties of CCTO/CTO ceramics prepared by PP and SSR methods.

Frequency (kHz)	ε'				$\tan\delta$			
	SSR-5	PP-5	SSR-10	PP-10	SSR-5	PP-5	SSR-10	PP-10
0.1	1732	1861	2171	2595	0.128	0.046	0.072	0.065
1	1625	1815	2104	2530	0.037	0.018	0.027	0.021
10	1556	1779	2021	2470	0.037	0.017	0.034	0.020
100	1486	1739	1935	2404	0.033	0.034	0.037	0.035

to 90 °C. This indicates that both ceramics have the potential to be used to fabricate the X5R standard-capacitor, which is defined as the capacitor that exhibits $|\Delta\varepsilon'| \leq 15\,\%$ in the temperature range from −55 to 85° C. When the temperature is higher than 90 °C, it is found that $|\Delta\varepsilon'| > 15\,\%$. This large increase in $\Delta\varepsilon'$ is attributed to the high-temperature relaxation effect, as demonstrated in the inset of Fig. 3(b). This effect strongly inhibits the application of the (33.33 mol%)CCTO/(66.67 mol%)CTO ceramics for the fabrication of the X7R standard-capacitor—the capacitor that exhibits $|\Delta\varepsilon'| \leq 15\,\%$ in the temperature range from −5 to 125 °C.

Besides the low- and high-temperature dielectric relaxations exhibited in the CCTO/CTO ceramics (inset of Fig. 3(b)), the middle-temperature relaxation indicated by a small $\tan\delta$-peak of the SSR-10 sample in the frequency range of 10^3–10^4 Hz is additionally observed (Fig. 3(a)). Although the occurrence of these three sets of dielectric relaxations is particularly valuable for investigation of the possible physical mechanisms related to dielectric response(s) in materials, these are undesirable for applications based on capacitive components because the relaxation process is certainly associated with the extreme change in ε'. The study on the dielectric relaxations observed in the CCTO/CTO composite system is out of the scope of this work, and more details will be reported elsewhere.

The non-ohmic characteristics (J vs. E) of the SSR- and PP-ceramics are demonstrated in Fig. 4. Accordingly, the two most important parameters related to the non-ohmic properties, i.e., non-linear coefficient (α) and breakdown field (E_b), of the CCTO/CTO ceramics are calculated from these curves. α calculated in the range of 1–10 mA/cm^2 of the SSR-5, SSR-10, PP-5, and PP-10 samples are found to be 6.48, 11.36, 10.87, and 10.59, respectively. These values are much lower than the values of 42–65 as reported in the literatures [15–17]. The E_b values of the samples obtained at J = 1 mA/cm^2 are 5953, 10385, 12083, and 10616 V/cm, respectively. It is found that the E_b values of the PP-10 and SSR-10 samples are not significantly different, whereas the PP-5 sample exhibits the highest E_b among these four samples. This highest E_b might be attributed to its high α value [17] and the dense microstructure of the PP-5 sample, i.e., a small amount of pores and small grain size (compared to the PP-10 sample). It is important to note that the E_b value of the SSR-5 sample is found to be lower than that of

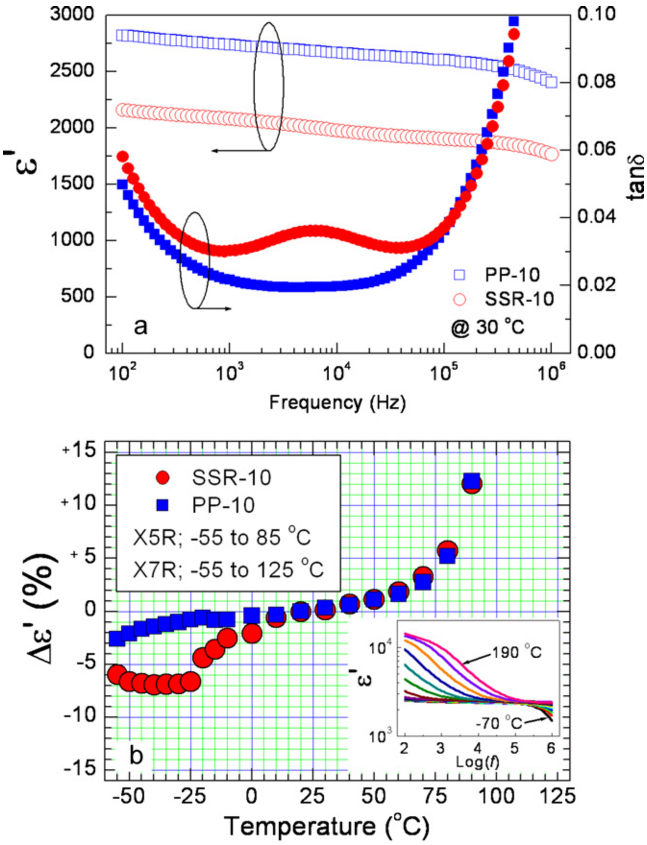

Fig. 3. (a) Frequency dependence of ε' and tan δ for the SSR-10 and PP-10 samples. (b) Temperature coefficient of the SSR-10 and PP-10 samples in the temperature range of −55–125 °C evaluated at the frequency of 1 kHz; inset illustrates the frequency dependence of ε' for the SSR-10 sample at the temperature range of −70–190 °C.

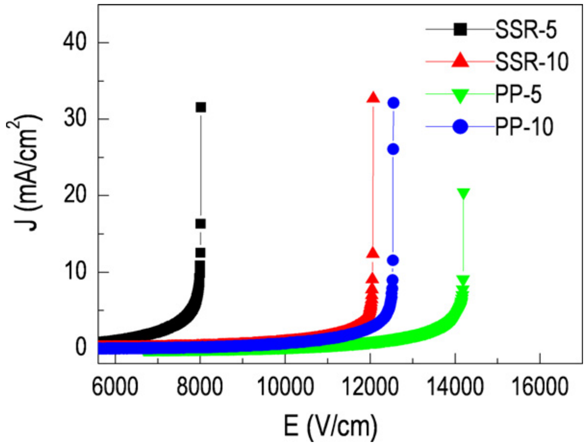

Fig. 4. Non-ohmic characteristics (J vs. E) of CCTO/CTO ceramic samples.

the SSR-10 sample. This result may be attributed to the member of pores presented in the microstructure of the SSR-5 sample compared to the SSR-10 sample. It is due to the fact that the sintering time of the SSR-5 sample is shorter than that of the SSR-10 sample. The presence of pores in the microstructure can cause a decrease in the number of active barriers between electrodes, resulting in the reduction of E_b.

Although the internal barrier layer capacitor effect is now widely accepted to be the origin of the giant ε' response in the CCTO ceramics [5,6], there is still controversy in some literatures [15,17] about this and the question is still open to be answered. In contrast, the dielectric response in the CCTO-based composites can easily be understood by using simple mixing rules such as Maxwell–Garnett's, Yamada's, and Lichtenecker's rules [14,30,31]. Based on these models, the effective dielectric constant (ε'_{eff}) of composite materials depends on the volume fractions and the ε' values of two phases (a matrix and filler particles) composing the composite material. In the case of our CCTO/CTO composite ceramics sintered at different duration times, ε'_{eff} of both SSR- and PP-ceramics increases with the increasing sintering time, as demonstrated in Table 1. According to these models, such enhanced ε'_{eff} is therefore attributed to the increase in the ε' values of the CCTO and CTO phases. However, it is reasonable to believe that the increase in ε'_{eff} of the CCTO/CTO composite is mainly due to the increase in ε' of the CCTO phase. This is due to the fact that ε' of the CCTO ceramics is strongly dependent on the sintering time [32]. Both grain size and density of defects in the grain interiors of the CCTO ceramics can be enhanced by increasing the sintering time [33], which in turn can cause an increase in ε' of the CCTO ceramics.

4. Conclusions

In conclusion, the non-linear and dielectric properties of the CCTO/CTO ceramics with the nominal composition of $Ca_2Cu_2Ti_4O_{12}$ prepared by PP and SSR methods were studied. Ceramic microstructure, dielectric response, and non-linear properties were successfully improved by preparing the ceramics with PP method. It was suggested that the CCTO/CTO ceramics had a potential for practical application in X5R standard-capacitor.

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