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$CaCu_3Ti_4O_{12}$ ceramics from basic co-precipitation (BCP) method: Fabrication and properties

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ABSTRACT

High dielectric $CaCu_3Ti_4O_{12}$ (CCTO) ceramics have been successfully prepared by a novel basic co-precipitation (BCP) method. Compared with the conventional solid-state and/or soft chemistry methods, the BCP method has many advantages such as relatively lower sintering temperature, shorter sintering time and lower costs. The XRD patterns confirm the formation of CCTO crystal phase in the as-prepared samples. Influences of initial ingredients and sintering condition on phase composition, microstructure and dielectric property have been investigated through series of trials. The correlation between the process of the grain growth and dielectric properties of final products has been explored. The final products exhibit the dielectric constants higher than 10,000 and the dielectric losses lower than 0.15 at 1 KHz.

1. Introduction

The rapid development of the microelectronic devices such as capacitors, resonators and filters not only accelerates the miniaturization of passive components but also increases the active demands of the high dielectric permittivity materials. $CaCu_3Ti_4O_{12}$ (CCTO) has received much attention because of its high dielectric constant over a wide range of temperature. Since the discovery of high permittivity ($\sim 10^4$ at 1 kHz) in CCTO by Subramanian et al. [1], CCTO has become a promising candidate to replace commonly used high-dielectric materials (e.g. $BaTiO_3$, PCT) with relatively low dielectric constants [2–4]. A wealth of theoretical investigation has been carried out in order to account for the origin of the giant dielectric permittivity of CCTO. Polarization mechanism [5], boundary mechanism [6], Maxwell–Wagner relaxations [7] were once used to elucidate the special properties of CCTO ceramic. Recently, many valuable works [8–15] have been reported on the Internal Barrier Layer Capacitor (IBLC) effect which has been generally accepted as a well-founded explanation for the origin of the giant permittivity. On the other hand, numerous works on the performance enhancement of CCTO ceramic have been reported. CCTNO (Ni-doped) [16] and B_2O_3 doped CCTO [17] considerably increase the dielectric constant because the dopants enhance the grain growth rate in the sintering process. Sr-CCTO [18] exhibits current–voltage nonlinearity, for impedance characteristics of grain and grain boundary of CCTO ceramics are apparently adjusted by Sr doping. Dielectric loss effectively decreases when CuF_2 [19] or MnO_2 [20] is added. Rare earth elements such as Eu [21] and La [22] are also found benefit to the dielectric properties especially the frequency stability.

With respect to fabrication, CCTO ceramics were normally prepared by solid-state reaction method at high temperature for a long sintering time. However, the conventional solid method may cause uneven powders which have negative effects on the properties of the final products. Wet chemistry methods have been studied in recent years. With a homogenous liquid solution of ingredients, stoichiometric particles of nano-scale can be obtained under lower sintering temperature for shorter sintering time. Sun et al. [23] reported a sol–gel method in which acetates were used as precursor, and calcined powder was sintered at 1050 °C for 3 h. Zhu et al. [24] reported an oxalate co-precipitation method in which calcined powder was sintered at 1000 °C for 2 h. Both of them obtained high-grade CCTO ceramics with dielectric constants reaching a high level.

In this work, CCTO ceramics of high dielectric constant (above 10^4) had been successfully prepared by a novel basic co-precipitation (BCP) method. Initial soluble ingredients were co-precipitated in a basic solution. Then, homogeneous suspension could be achieved under quick agitation. The as-prepared powder was fine and even. Also, the correlation between the initial ratio of the starting materials and the composition of as-prepared powder had been explored as well as the influence of sintering time on the grain growth process.

2. Experimental

A basic co-precipitation (BCP) method was used to synthesize CCTO powder. $CaCl_2$ (>96%), $Cu(NO_3)_2 \cdot 3H_2O$ (>99.5%), $TiCl_4$ (49.5% in hydrochloric acid saturated solution) and the precipitator NaOH (>99%) were initial ingredients. The $CaCl_2$ and

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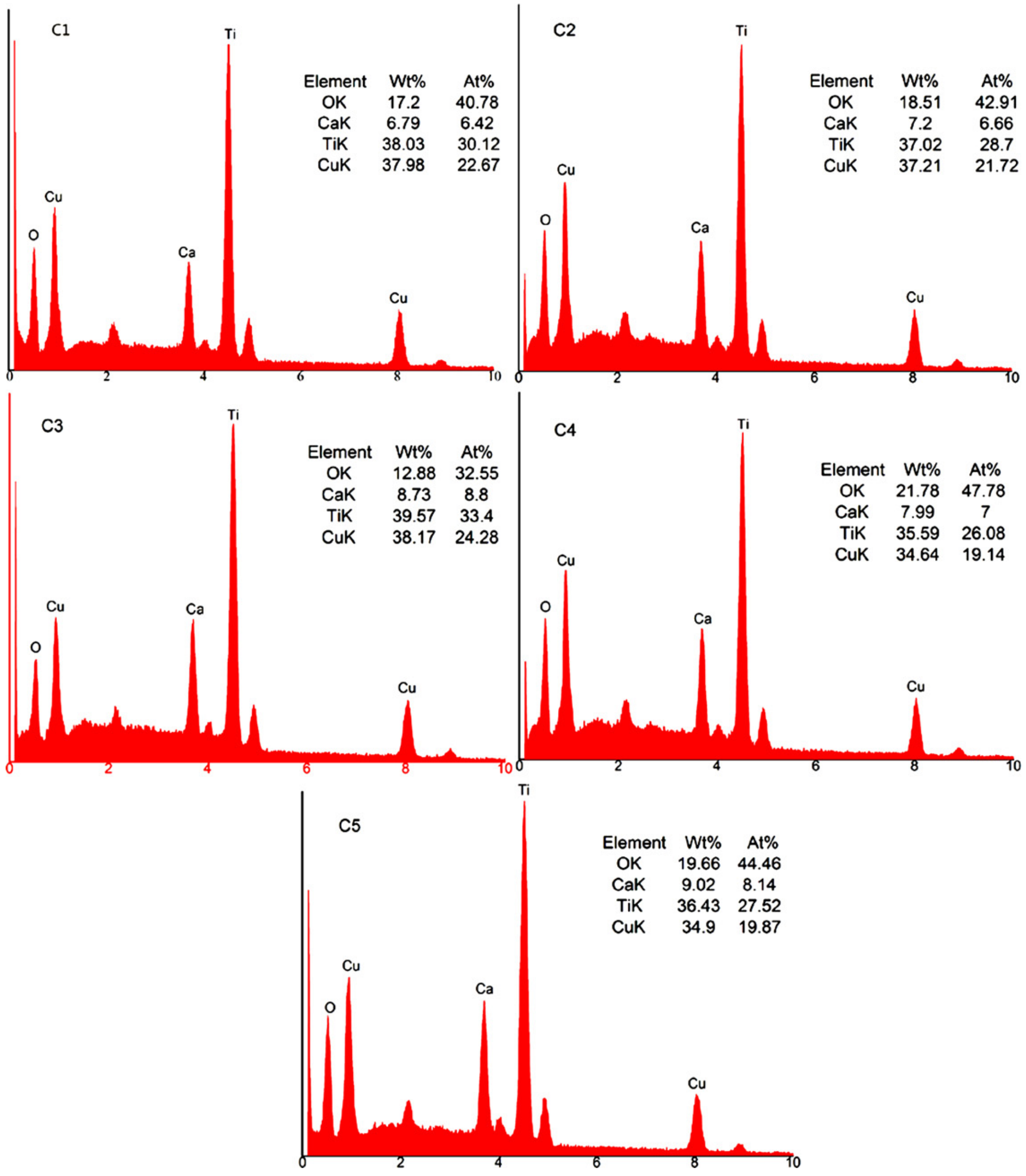
Table 1
Contents of initial ingredients and ratio of Ca/Cu/Ti.

$CaCl_{2(g)}$	$Cu(NO_3)_2$	$3H_2O_{(g)}$	$TiCl_{4(g)}$	$NaOH_{(g)}$	Ratio (Ca:Cu:Ti)	Calcined powder (Ca/Cu/Ti)
C1	2.9	18.2	38.3	27	1:3:4	0.85:3:4
C2	3.2	18.2	38.3	27	1.10:3:4	0.92:3:4
C3	3.4	18.2	38.3	27	1.17:3:4	1.05:3:4
C4	3.5	18.2	38.3	27	1.20:3:4	1.07:3:4
C5	4.0	18.2	38.3	27	1.38:3:4	1.18:3:4

$Cu(NO_3)_2{\cdot}3H_2O$ were dissolved in the de-ionized water and then $TiCl_4$(dissolved in hydrochloric acid saturated solution) was mixed with the solution. After agitated for about 10 min, the solution was dropped into the NaOH aqueous solution slowly so that ingredients could be co-precipitated fully and homogeneously.

Samples with various $CaCl_2$ contents were obtained by a co-precipitation method. Different from the sol–gel or acid precipitation process, the Ca^{2+} precipitate is hard to control in the BCP method. In order to obtain the designed ratio (theoretical ratio, Ca/Cu/Ti = 1:3:4), we adjusted the $CaCl_2$ content (abbreviated as C1, C2, C3, C4, C5) respectively, while keeping the Cu^{2+} content constant. Besides, a filter washing procedure with de-ionized water was applied to wipe off the Na^+ in the precipitate. The precipitate filter was dried at 80 °C for 24 h and porphyrized into fine powder. Then the powder was calcined at 850 °C for 2 h. The obtained initial powder was then pressed into disks of 20 mm in diameter and 1 mm in thickness. These disks were sintered at 1050 °C for 0.5 h, 1 h, 2 h, 4 h, 6 h, respectively, with the heating rate of 200 °C/h and the cooling rate of 100 °C/h.

The constitution of the initial calcined powder was analyzed by the energy-dispersive X-ray spectroscopy (EDS, JSM-6360LV, EDAX Ltd., America). The phase formation of the sintered samples was confirmed by X-ray diffraction (XRD, focus-D8, BRUKER OPTICS Ltd., Germany) in a 2θ range 20–80°. The morphology and microstructure of the ceramic samples were characterized by scanning electron



C1

Element	Wt%	At%
OK	17.2	40.78
CaK	6.79	6.42
TiK	38.03	30.12
CuK	37.98	22.67

C2

Element	Wt%	At%
OK	18.51	42.91
CaK	7.2	6.66
TiK	37.02	28.7
CuK	37.21	21.72

C3

Element	Wt%	At%
OK	12.88	32.55
CaK	8.73	8.8
TiK	39.57	33.4
CuK	38.17	24.28

C4

Element	Wt%	At%
OK	21.78	47.78
CaK	7.99	7
TiK	35.59	26.08
CuK	34.64	19.14

C5

Element	Wt%	At%
OK	19.66	44.46
CaK	9.02	8.14
TiK	36.43	27.52
CuK	34.9	19.87

Fig. 1. EDS results of calcined powders C1–C5.

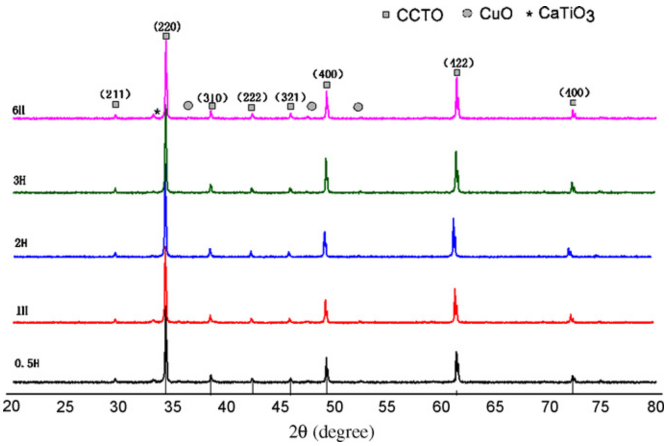


Fig. 2. X-ray diffraction patterns of CCTO multiphase powder sample sintered at 1050 °C for different time.

microscope (SEM, JSM-6360LV, JEOL Ltd., Japan) where EDS was used together to compare the grain and grain-boundary compositions.

For dielectric measurements, both surfaces of the disks were sputtered with nano gold powder as electrodes. The dielectric measurements were performed over the frequency range of 10 Hz–10^4 Hz (Concept 40, NOVOCONTROL Ltd., Germany) at room temperature.

3. Results and discussion

3.1. EDS analysis

The contents of initial ingredients were listed in Table 1 where the molar ratio of Ca/Cu/Ti was also presented. Fig. 1 showed the weight and atom content of each sample. Final ratio of Ca/Cu/Ti in C1–C5 (calcined powder) was calculated and listed in the last column of Table 1 as comparison.

Much attention had been paid to the sodium element in EDS analysis and no sodium residue in the calcined powder was observed after filter washing procedure which indicated that NaOH may be an ideal choice as a precipitator.

As shown in Table 1, the calcium content decreased during the basic co-precipitation process because the calcium hydroxide precipitate was partly dissolved in the suspension (solubility = 0.15 g/100 g H_2O at 20 °C). As the whole volume of de-ionized water in the liquid system was about 300 ml, 0.5 g excess $CaCl_2$ should be added on the basis of theoretical ratio to balance the dissolved calcium hydroxide precipitates. Finally, the calcined powder of C3 (Ca/Cu/Ti = 1.05:3:4) exhibited the nearest ratio to the theoretical one, which was consistent with our speculation above.

3.2. XRD and SEM analysis

According to the results of the EDS analysis, C3 was chose to synthesize the initial powder. In order to explore the influence of different sintering conditions on the phase composition, grain growth, and dielectric property, the initial powder was pressed into pellets after porphyrization and then sintered at 1050 °C for 0.5 h, 1 h, 2 h, 4 h, 6 h respectively (marked as C-0.5H, C-1H, C-2H, C-4H, C-6H).

Fig. 2 showed the X-ray diffraction patterns of C-0.5H ~ C-6H. The main diffraction peaks corresponded to the standard diffraction patterns of CCTO phase (JCPDS No.75-2188) as shown in the bottom of Fig. 2 by vertical lines. The results also indicated that small amount of CuO ($2\theta = 36^\circ$, 48°) and $CaTiO_3$ ($2\theta = 33^\circ$) existed in addition to a dominant pure CCTO phase, similar to several previously work [13,25,27]. Besides, CCTO phase was obtained after sintered at 1050 °C for only 0.5 h and remained steady with the increasing sintering temperature and duration. Therefore, 1050 °C was enough to form the CCTO phase by the BCP method.

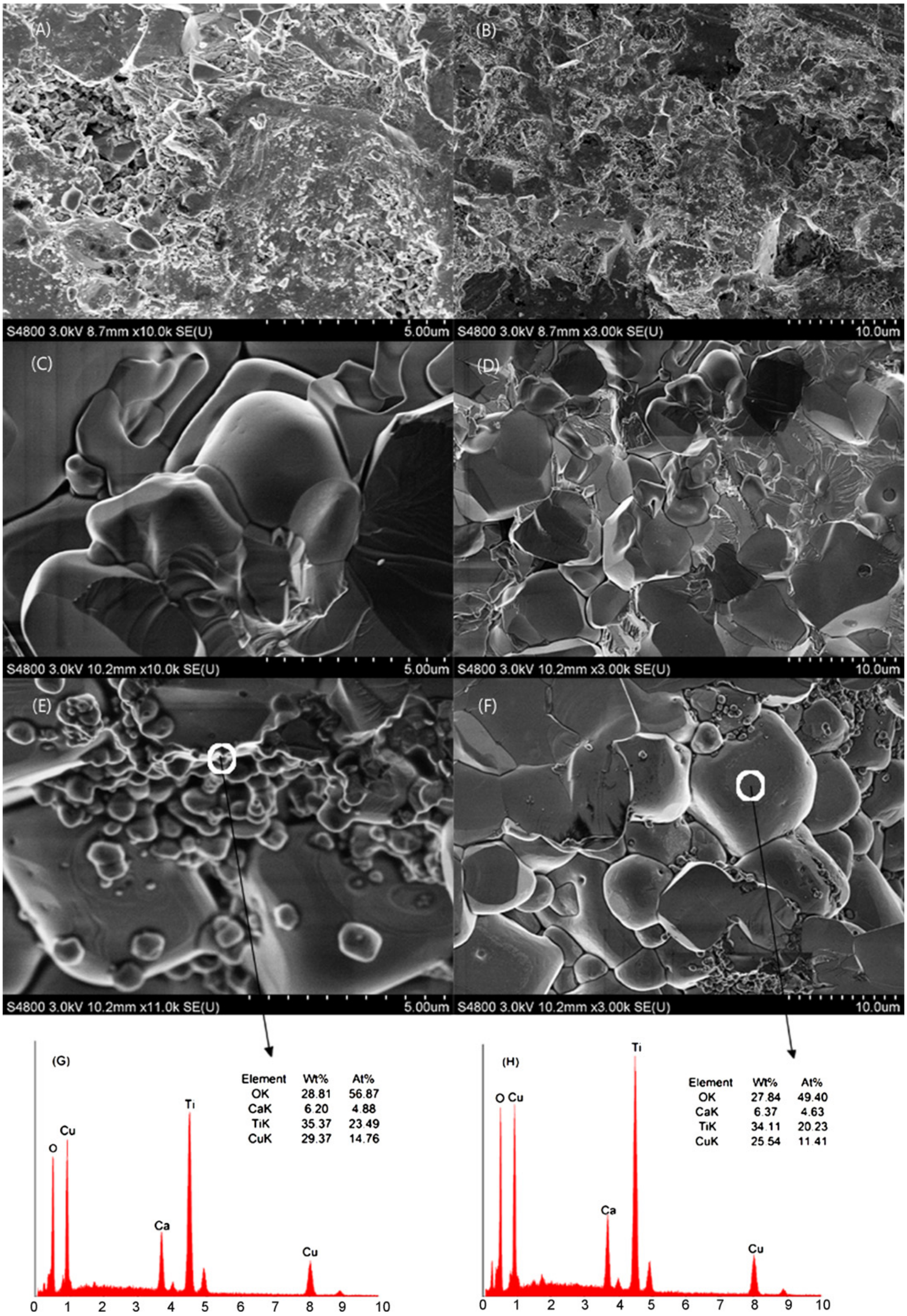
Fig. 3 showed the SEM images of CCTO sintered at 1050 °C for different time (0.5 h, 2 h, 6 h), from which an evolution of grain growth could be observed. At the preliminary stage of sintering (Fig. 3A and B), although the CCTO phase had already been formed as confirmed by the XRD patterns, the oxide ingredients in initial powder had not yet grown and shaped into the large and mature crystal grain, thus causing an inhomogeneous microstructure. With the sintering time increasing from 2 h to 6 h, distinct CCTO grains had gradually taken tangible shape and occupied the whole ceramic. In this stage, CCTO ceramics emerged as a homogeneous microstructure with the uniformly-distributed crystal grains of 5–10 μm in size, which demonstrated that the sintering temperature (1050 °C) could provide sufficient energy for the grain growth. At this temperature, the grain size increased with the sintering time. However, there existed several white and bright particles around the main crystal body (Fig. 3D) as well as much tiny ball-like segregation on the grain boundary (Fig. 3E and F). In order to validate these secondary phases and explore the difference between grain and grain boundary, EDS analysis was carried out for specific dots (marked in Fig. 3E).

The EDS analysis of the selected dot in bulk grain showed the Cu/Ca molar ratio was 2.46 (other selected dots centered in 2.4–2.5) while Cu/Ca molar ratio in grain boundary was 3.03 (in 3–3.1) in the CCTO crystal grain. Meanwhile, the oxygen and titanium contents in grain boundary were 11.5% and 11.6% higher than that in grain, which indicated that a little amount of CuO and $CaTiO_3$ segregated around the growing CCTO grain combined with the XRD analysis (the $CaTiO_3$ and CuO still existed in sample 6H). According to the phase diagram [27] for the system CaO–TiO_2–CuO, temperature and partial pressure of oxygen were critical factors in the sintering process. In our work (1050 °C, oxygen rich atmosphere), TiO_2 totally changed into $CaTiO_3$, Cu_2O could not exist (the XRD pattern also confirmed the truth). The system presumably consisted of CCTO grain and a mixture of CuO and $CaTiO_3$ around the grain boundary. The amounts of CuO were responsible for the LPSR (liquid phase secondary recrystallization) effect mentioned by Wang et al. [28]. CuO began to melt when the sintering temperature was above 1000 °C, the liquid region expanded with the increasing sintering temperature. This phenomenon was consistent with the previously reported work so that the effect of secondary phase such as CuO and $CaTiO_3$ should be taken into consideration in the process of sintering. For example, Loic et al. [25] found that the CuO content in the powder correlates with the grain growth. Lu et al. [26] explained a formation of CuO–TiO_2 eutectic during the sintering process.

3.3. Dielectric property analysis

The frequency dependence (10–10^4 Hz in this work) of the dielectric constant and dielectric loss at room temperature for C-0.5H ~ C-6H was shown in Fig. 4. As shown in Fig. 4, the dielectric constant of CCTO ceramic increased and the dielectric loss decreased with the increasing sintering time. When the sintering time was less than 1 h, the dielectric constant was relatively low ($\sim 5 \times 10^3$) and the dielectric loss was higher than 0.3 at 1 kHz. The turning point emerged at 2 h when the DC (dielectric constant) increased rapidly to 10^4 level and the DL (dielectric loss) reached a very low level below 0.15. These results were similar to those of many other wet chemical methods [12,25,26].

Variation of dielectric properties of CCTO ceramics with the sintering time could be explained from a micro structural point of view. The tendency of the DC and DL curve accorded with the process of CCTO grain growth. As shown in SEM images, the initial powder sintered at 1050 °C had not grown into the integrated grain until after sintered for 2 h. CuO (liquid phase above 1000 °C) facil-



Element	Wt%	At%
OK	28.81	56.87
CaK	6.20	4.88
TiK	35.37	23.49
CuK	29.37	14.76

Element	Wt%	At%
OK	27.84	49.40
CaK	6.37	4.63
TiK	34.11	20.23
CuK	25.54	11.41

Fig. 3. SEM images of CCTO ceramics sintered at 1050 °C for (A) and (B) 0.5H, (C) and (D) 2H, (E) and (F) 6H followed with (G) and (H) EDS analysis of selected dots in (E) and (F).

itated the grain growth. During the melting and diffusion of the liquid phase, $CaTiO_3$ gradually segregated at the grain boundary together with CuO. After the intrinsic-extrinsic "movement" completed (Cu cation excess in boundary and deficiency in bulk grain in the EDS selected dots), the bulk of the grains would behave like other semiconducting perovskite while the grain boundaries would be insulating layers. This contributed to an IBLC Model in which the ratio of thickness of the insulating layer to the grain size was inversely proportional to dielectric constant [29]. In the case of certain amounts of CuO liquid phase segregating around the grain, the grain was growing rapidly while the grain boundary thickness kept constant, so the ratio was gradually decreasing during the sintering process. But if the excess Cu content in the initial powder increased, the CuO phase would thicken the grain boundary, resulting in the increased ratio (boundary thickness/grain size) and the decreased permittivity. Chang et al. [30] established two mod-

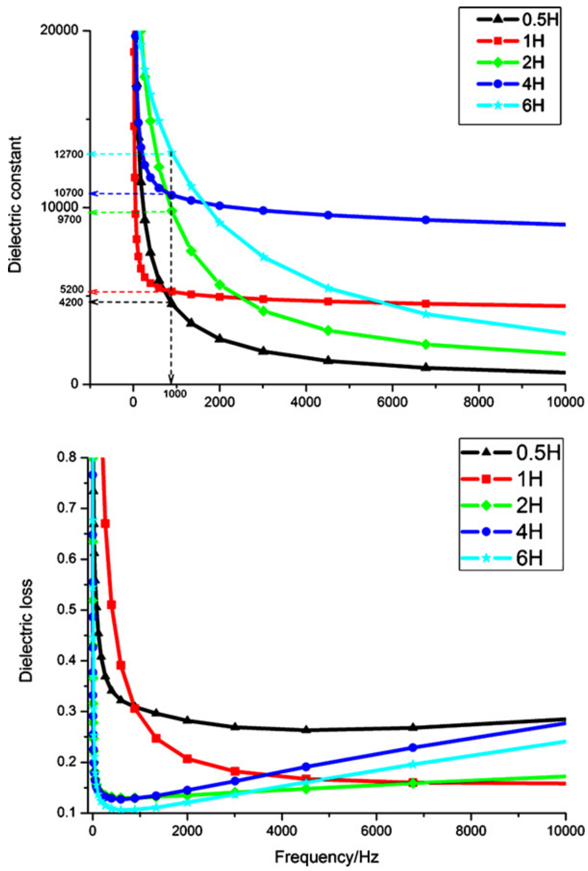


Fig. 4. Frequency dependence of the dielectric constant and dielectric loss for CCTO with different sintering time.

els (MFA, SFA) and demonstrated that the dielectric loss decreases with the increased ratio of boundary thickness to the grain size. Romero et al. [31] found the IBLC model reveal the change of the intergranular phase, caused by a compositional change due to the incorporation of Cu into the CCTO grains. Kim et al. [32] did lots of work about Cu/Ca ratio and found the CuO composition a key parameter that determines the microstructure and dielectric properties of CCTO ceramics which also accorded with our work.

4. Conclusions

In summary, CCTO ceramics with high dielectric constant and low loss had been successfully prepared by the basic co-precipitation (BCP) method. The sintering temperature at 1050 °C was enough to shape the initial powder into the CCTO phase. When the sintering time was above 2 h, the initial powder had grown into relatively integrated CCTO grain and the grain size became larger with the sintering time. Moreover, the dielectric constant (DC) was above 10^4 and the dielectric loss (DL) was below 0.15 at 1 KHz. The turning point emerged at about 2 h when DC decreases and DL increases rapidly. This indicated that the process of grain growth and the CCTO microstructure had great influences on its dielectric properties. In view of its lower cost and lower sintering temperature for shorter time, BCP method might be another practical approach for fabrication of CCTO ceramics.

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