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Microwave dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics: A clue to its intrinsic dielectric response

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$CaCu_3Ti_4O_{12}$ (CCTO) is a potential dielectric material with giant permittivity, good stability over the wide temperature and frequency range. However, the dielectric responses of CCTO-based ceramics are mainly investigated in the frequency of 10^2–10^6 Hz, which is far low to clarify the intrinsic dielectric feature. So, microwave dielectric properties have been investigated for the CCTO porous ceramics sintered at low temperature (≤1000°C). Good microwave dielectric properties of permittivity ε = 62.7, quality factor Qf = 3062 GHz and temperature coefficient of the resonant frequency τ_f = 179 ppm/°C are achieved for the CCTO ceramics sintered at 1000°C, the dielectric loss significantly decreases two orders to 0.002 compared to that of CCTO ceramics sintered at critical temperature of 1020°C confirmed by differential scanning calorimetry (DSC). This clue indicates that giant permittivity and high loss is not intrinsic for CCTO ceramics, but derives from composition segregation, liquid phase and defects associated with internal barrier layer capacitor (IBLC). It suggests that CCTO-based ceramics is a promising microwave dielectric materials with high permittivity.

Keywords: CCTO; microwave dielectric properties; sintering temperature; dielectric mechanism.

1. Introduction

In the past two decades, tremendous attention has paid to $CaCu_3Ti_4O_{12}$ (CCTO) with giant permittivity (10^4–10^5) and temperature independence of permittivity in the low frequency,[1–5] which suggests the potential application in capacitor-based devices for miniaturization. Therefore, a lot of investigations have focused on the origin of the giant permittivity of CCTO materials in terms of academic significance and technology fundamental.[4–12] Some possible mechanisms, such as internal barrier layer capacitor (IBLC) effect[5–7] and surface barrier layer capacitor (SBLC) effect,[7,8] have been proposed. The extrinsic effect of IBLC model is now widely accepted to be responsible for the giant permittivity. However, now there is no perfect model to clarify the dielectric responses of both CCTO single crystal and ceramics.

CCTO ceramics, usually sintered at about 1100°C, generally displays the particular microstructure of huge grains of 100–200 μm and intergranular phase. It implies that the liquid phase and composition segregation appear during the sintering of CCTO-based ceramics, which induce the abnormal grain growth, formation of some secondary phases such as TiO_2, Cu_2O, CuO and $CaTiO_3$, and reductions of Cu^{2+} and Ti^{4+}.[9,10,23,26–31] These induce not only space charge polarization, but also electronic and ion relaxation polarization. With the frequency rising, the slower polarization such as space charge polarization gradually disappears, which is the major contribution to some giant permittivity dielectric materials such as CCTO. These fast polarizations of electronic and ion polarization gradually dominate with frequency increasing up to 10^7 Hz. In general, the characterization frequency of electronic and ion relaxation polarization is well falling in the low range of microwave frequency[23]; therefore, which significantly affects the dielectric response of CCTO at microwave frequency. So, to better understand the physical nature of CCTO-based materials, it is important to investigate the dielectric properties at high frequency up to microwave frequency. Although some work has addressed the microwave dielectric properties of CCTO materials: permittivity of about 80 and high dielectric loss of 10^{-1}.[18–25] This indicates that the permittivity has a significant decrease of two orders and high dielectric loss.

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As stated above, CCTO ceramics sintered at about 1100°C displays electronic and ion relaxation polarizations due to the composition segregation and ion reductions. This does not well reflect the intrinsic dielectric properties. To better clarify the nature of dielectric response, the key issue is to prepare the suitable CCTO ceramics with less or no electronic and ion relaxation polarization. In our previous investigation,[25] it suggests that the particular structure and giant permittivity of CCTO ceramics are only observed when sintering temperature is over 1025°C. Thus, based on the above stated, CCTO ceramics without the abnormal grain growth, composition segregation and reductions is expected to sinter at relatively low temperature, which is not above 1000°C in this work. It has been found that the pure phase CCTO ceramics displays porous microstructure with uniform and small grain. And the permittivity of about 80 and dielectric loss as low as 0.002 have been achieved. Dielectric mechanism and structure evolution have also been discussed based on DSC results of calcined CCTO powder, microstructure and dielectric properties of CCTO ceramics sintered at 1020°C. The clue suggests that CCTO-based ceramics is a new low loss microwave dielectric ceramics with high permittivity.

2. Experimental Methods

$CaCu_3Ti_4O_{12}$ powder was calcined at 950°C and 1050°C for 6 h from the mixture of $CaCO_3$ (99.5%), TiO_2 (99.5%) and CuO (99%). The CCTO powder calcined at 950°C was pressed into pellets, and then sintered at 950°C and 1000°C for 6 h, respectively. For comparison, some CCTO ceramics were sintered at 1020°C for different holding time. Densities were measured with Archimedes method. Crystal phase and microstructures were identified by using X-ray diffraction (XRD, Model D/max-IIIC, Rigaku) and the environmental scanning electron microscope (ESEM, Philips XL30 ESEM-TMP). In the temperature range from room temperature to 1190°C, DSC of CCTO calcined powder was carried out using a synchronous thermal analyzer (Netzsch STA 449C) in air with heating rate of 10°C/min. For CCTO ceramics sintered at 1000°C, the dielectric properties as a function of frequency and temperature at low frequencies were measured by a LCR meter (Tonghui 2828). $TE_{01\delta}$ dielectric resonator method was adopted to measure microwave dielectric properties of CCTO ceramics with a network analyzer (Agilent 8720ES). The temperature coefficient (τ_f) of the resonant frequency was measured in the temperature range of 25°C to 85°C.

3. Results and Discussion

Table 1 lists densities and microwave dielectric properties of CCTO ceramics sintered at different temperature. These relative densities are 66.4% and 87.6% for the porous CCTO ceramics sintered at 950°C and 1000°C, respectively. As mentioned above, the chosen sintering temperature in the present work is much lower than the generally sintering temperature (~1100°C) of CCTO ceramics, which results in the lower relative density. Microwave dielectric properties of ε = 37.5, Qf = 1560 GHz and temperature coefficient τ_f = 246 ppm/°C are achieved for the CCTO ceramics sintered at 950°C. When sintering temperature arises to 1000°C, microwave dielectric properties are considerably improved to ε = 62.7, Qf = 3062 GHz and τ_f = 179 ppm/°C. This is significantly different from these previous investigations.[7–18] In previous investigations, giant permittivity of 10^4 and high dielectric loss of about 10^{-1} are generally reported at the frequency range of 1k–1MHz. Microwave dielectric properties, permittivity of about 80 and dielectric loss of 10^{-1}, have been only reported in some investigations.[18–24] Taking into account of porosity,[32–34] the permittivity at microwave frequency will be 75.6 and 77.0 for the present CCTO ceramics sintered at 950°C and 1000°C, respectively. This value is close to the previously reported permittivity of about 80 for CCTO ceramics at low temperature (below 100K) or microwave frequency.[3,10,16,18–24] But it should be noted that the present CCTO ceramics exhibits a very low dielectric loss, which is calculated as 0.0050 and 0.0021 at resonance frequency from Qf values, respectively. Dielectric loss at microwave frequency is effectively reduced by about two orders compared to the previously reported values.[18–24] Generally, significant effect of porosity on Qf value or dielectric loss has been reported when relative density is below 90% for the microwave dielectric ceramics.[32,33] So the intrinsic dielectric loss of CCTO ceramics should be far below 0.0021 at

Table 1. Densities and microwave dielectric properties of CCTO ceramics in the present work and Ref. 22. The theoretical density is 5.05g/cm^3 according to the JCPDS No. 75-2188. And the ε_c is calculated from the formula $\varepsilon/(1\text{-}1.5p)$,[32–34] where p is the porosity of CCTO ceramics.

ε	Qf (GHz)	f_r (GHz)	τ_f (ppm/°C)	ρ (g/cm^3)	ρ_r (%)	ε_c	tanδ (at f_r)	Sintering condition
37.5	1560	7.839	246	3.356	66.4	75.6	0.0050	950°C/6 h
62.7	3062	6.548	179	4.423	87.6	77.0	0.0021	1000°C/6 h
~83.9	38.0	3.4	—	—	~96	89.3	0.089	1050°C/3 h[22]
~84.5	17.1	3.4	—	—	~96	89.9	0.20	1100°C/3 h[22]
83.4	18.0	3.4	—	—	~96	88.7	0.19	1100°C/3 h[22] + O_2 annealed

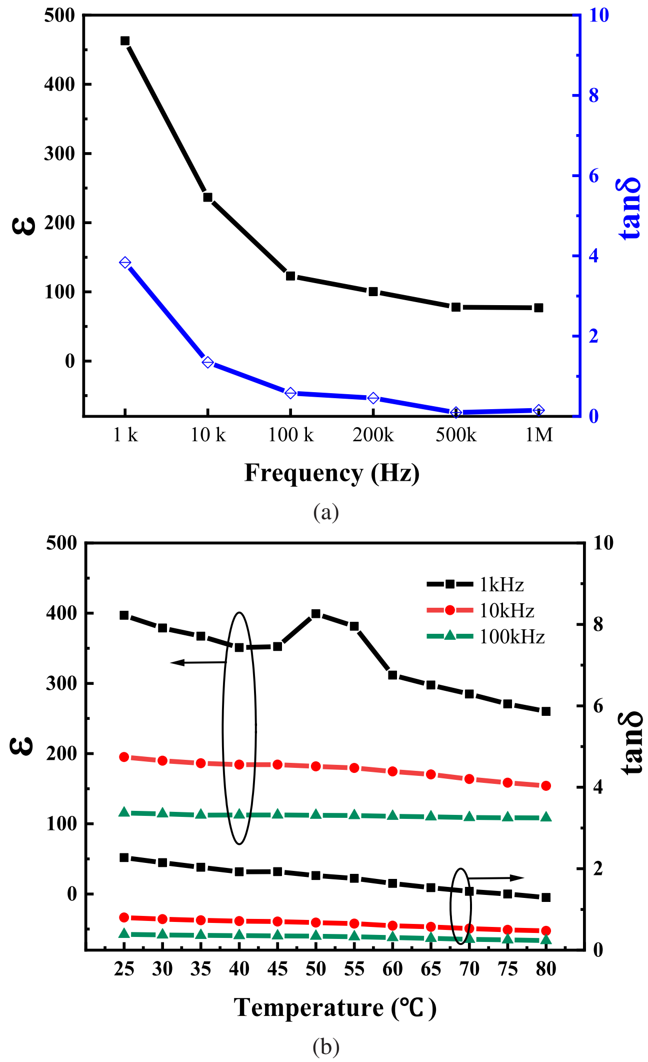

Fig. 1. Dielectric properties of the CCTO ceramics sintered at 1000°C for 6 h as the functions of frequency (a) and temperature (b).

microwave frequency. This is similar to that of Mn substituted CCTO ceramics. Microwave dielectric properties of $CaCu_{2.85}Mn_{0.15}Ti_4O_{12}$ are ε = 93, Qf = 3950 GHz at 3.95 GHz.[3] A very small amount of Mn substitution in CCTO, for example $CaCu_3Ti_{3.996}Mn_{0.004}O_{12}$, results in uniform and fine grain, high bulk resistivity and good microwave dielectric properties of $\varepsilon = 68.1$, $Qf = 4030$ GHz and $\tau_f = 220$ ppm/°C.[25] Therefore, it means that CCTO-based ceramics is a promising low loss dielectric material with high permittivity.

For CCTO ceramics sintered at 1000°C, Fig. 1 gives the dielectric properties as a function of frequency and temperature at low frequencies. Due to too low density, the dielectric properties at low frequencies are not measured for CCTO ceramics sintered at 950°C. From Fig. 1, the permittivity and loss gradually decrease with the elevating frequency. The room temperature permittivity is only 76.9 at 1 MHz, which is very close to the permittivity at microwave frequency. With the elevating temperature, gradual decrease is also observed

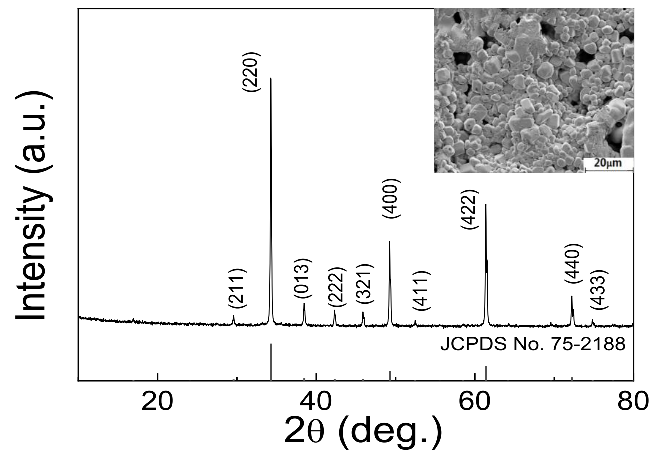

Fig. 2. XRD patterns and SEM image (inset) of the CCTO ceramics sintered at 1000°C for 6 h.

for the permittivity and loss. The temperature stability has obviously improved when the frequency increases.

XRD patterns and SEM image of CCTO ceramics sintered at 1000°C for 6 h are shown in Fig. 2. Only CCTO phase (JCPDS No.75-2188) is observed. No secondary phase such as TiO_2, Cu_2O, CuO and $CaTiO_3$ has been observed, which often appears in the CCTO ceramics sintered at about 1100°C for long holding time.[5–16] And the SEM image displays the porous microstructure with uniform and fine grains. This is obviously different from the microstructure of huge grains and intergranular CuO-rich phase for the CCTO sintered at about 1100°C. This difference of microstructure suggests no formation of CuO-rich liquid phase and CCTO phase decomposition in the CCTO ceramics during the sintering at 1000°C. Therefore, it also means that the relative low sintering temperature can effectively suppress composition segregation and ion reductions in CCTO ceramics. This agrees well with the liquid phase may be the CuO-TiO_2 eutectic phase with low melting temperature of ~1020°C in air.[25,35]

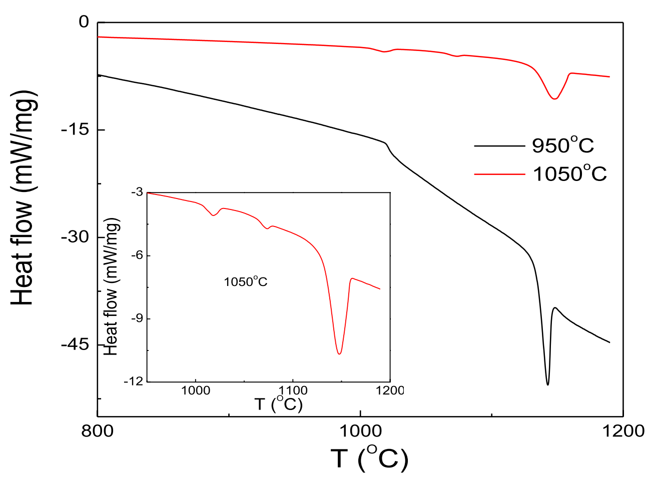

Fig. 3. DSC curves of CCTO powder calcined at 950°C and 1000°C.

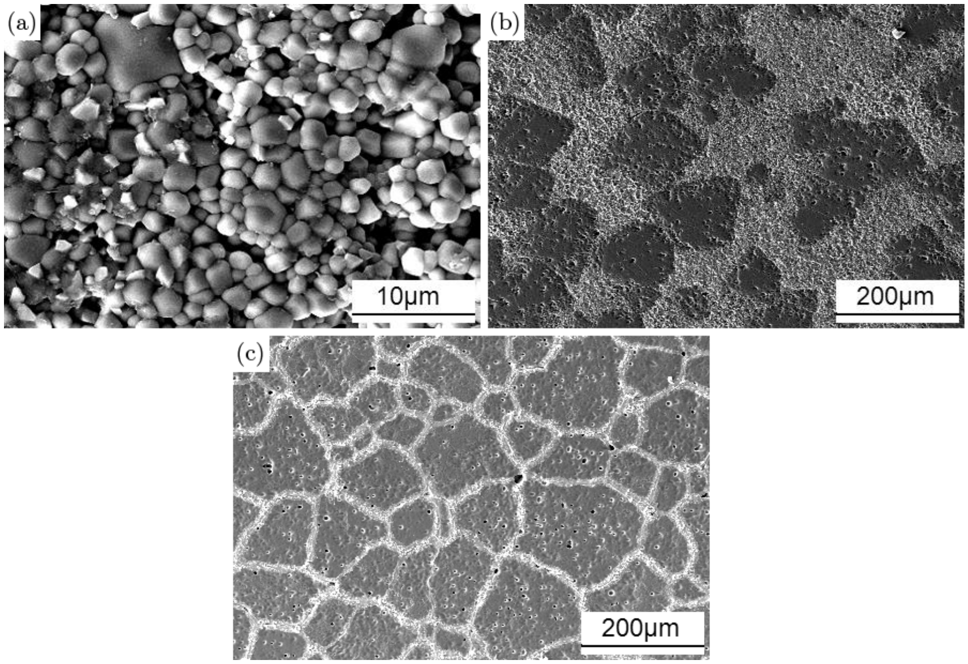

Fig. 4. SEM images of CCTO ceramics sintered at 1020°C for (a) 3 h (b) 6 h (c) 24 h.

To better understand the significant variation of dielectric properties, DSC was carried out in air for the calcined CCTO powder. As shown in Fig. 3, a large endothermic peak around 1150°C is both observed for the calcined powder at 950°C and 1050°C, which is corresponding to the melting point of CCTO phase. Besides the sharp endothermic peak, however, it is obvious to note difference between the two curves for the CCTO calcined powder. Two weak endothermic peaks are detected for the CCTO powder calcined at 1050°C. One is at around 1020°C, the other appears about 1075°C. For the former, a similar abnormity also appears in the CCTO powder calcined at 950°C. The endothermic trend of beyond 1020°C is more obvious for the CCTO powder calcined at 950°C. This means that the composition segregation occurs at about 1020°C, which results in the formation of CuO-rich liquid phase. Because the calcining temperature 1050°C is above 1020°C, the composition segregation may obviously occur in the calcined CCTO powder. The CuO-rich phase corresponding to composition segregation melts at around 1020°C, so a weak endothermic peak is correspondingly observed. However, the reduction of Cu^{2+} in the CCTO powder calcined at 1050°C is corresponding to the weak endothermic peak at 1075°C. So, Cu_2O phase was often observed in the CCTO ceramics.[11,13,30] Due to the two endothermic peaks of the CCTO powder calcined at 1050°C, the peak corresponding to the melting of CCTO phase is obviously weaker and broader.

To confirm the DSC results, some CCTO ceramics was sintered at a critical temperature of 1020°C for 3–24 h. As shown in the Fig. 4 of SEM images, with prolonging the holding time, the microstructure of CCTO ceramics varies from the fine grains of 2–3 μm with a litter abnormal grain growth to huge grains of 100–200 μm and intergranular phase, which indicates that the liquid phase is formed. The variation of microstructure confirms that the composition segregation gradually occurs during the sintering of CCTO ceramics at 1020°C. As mentioned above, giant permittivity and high loss of CCTO ceramics may be derived from the composition segregation and reduction at 1020°C and 1075°C, respectively. Therefore, the permittivity of CCTO ceramics at 1 kHz is enhanced from 1720 to 57,035 listed in Table 2 when the holding time varies from 3 h to 24 h. Unfortunately, the no resonant peak for theses ceramics sintered at 1020°C has been observed at the microwave frequency due to the high dielectric loss. This consists well with the previous reports.[18–25] For the evaluation of microwave dielectric properties of giant permittivity materials with high loss is required to develop a modified resonant cavity method, which has been reported by Li *et al.*[20] From the considerable differences of microstructure and dielectric properties, it can be concluded that the dielectric response of giant permittivity and high loss is not intrinsic for CCTO ceramics. On the contrary, low dielectric loss (~0.002) and high permittivity (~77) of the CCTO ceramics sintered at 1000°C (<1020°C) suggests that

Table 2. Densities and dielectric properties of CCTO ceramics sintered at 1020°C.

ρ (g/cm^3)	ρ_r (%)	ε (1kHz)	tanδ (1kHz)	Sintering condition
4.552	90.1	1720	0.19	1020°C/3 h
4.587	90.8	11768	0.15	1020°C/6 h
4.741	93.9	57035	0.10	1020°C/24 h

CCTO-based ceramics is a potential candidate for microwave dielectric ceramics with high permittivity.

4. Conclusions

In order to investigate the intrinsic dielectric feature and physical nature, microwave dielectric properties have been investigated for CCTO ceramics sintered at relative low temperature (≤1000°C). Although the CCTO ceramics exhibits porous microstructure, very low dielectric loss (~0.002) and high permittivity (~77) are achieved, which suggests CCTO is a promising low loss microwave dielectric materials with high permittivity and low sintering temperature. The sintering mechanisms and dielectric response have been discussed based on the DSC results of the calcined powder, microstructure evolution and dielectric variations CCTO ceramics sintered at critical temperature of 1020°C. Therefore, it clarifies that the intrinsic dielectric properties of CCTO ceramics are high permittivity of about 80 and low loss below 0.002.

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