

# Dielectric Properties of Composites in the CaO-CuO-TiO<sub>2</sub> System

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## Abstract

Since ultra-high dielectric constants ( $> 10^4$ ) with weak temperature and frequency dependence were observed in non-ferroelectric materials such as  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  and  $\text{CuO}$ , it is very meaningful to study the dielectric properties not only of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  and  $\text{CuO}$ , but also of other members in the  $\text{CaO-CuO-TiO}_2$  system in order to find other compositions with similar characteristics, to discover the underlying mechanisms and to search for new composites with even better dielectric properties.

The dielectric properties of the composites in ternary systems  $\text{CuO-CaCu}_3\text{Ti}_4\text{O}_{12}\text{-CaTiO}_3$  and  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}\text{-CaTiO}_3\text{-TiO}_2$  have been tentatively investigated in the present study. The frequency and temperature dependences of permittivity and impedance in the range of  $10^2\text{-}5 \times 10^6$  Hz and  $25\text{-}130^\circ\text{C}$  were investigated in the representative high permittivity ( $> 10^4$ ) composite with molar fraction of  $\text{Cu/Ti/Ca}$  of  $\sim 85/10/5$  in the ternary  $\text{CuO-CaCu}_3\text{Ti}_4\text{O}_{12}\text{-CaTiO}_3$  system. Strong hints suggest an important effect of grain boundary contributions on dielectric properties. Preliminary results demonstrated that a multiphase microstructure consisting of larger grains with predominant phase surrounded by smaller grains with secondary phases played an important role for enhancing the dielectric response due to possible barrier layer effects caused by the grain boundary of the composites.

**Keywords:**  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ,  $\text{CuO}$ , Dielectric properties, Composite, Microstructure

## WŁAŚCIWOŚCI DIELEKTRYCZNE KOMPOZYTÓW W UKŁADZIE CaO-CuO-TiO<sub>2</sub>

Od kiedy zaobserwowano ultra wysokie stałe dielektryczne ( $> 10^4$ ), przy słabej zależności od temperatury i częstotliwości, w nieferroelektrycznych materiałach takich jak  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  i  $\text{CuO}$ , zasadnym stało się badanie właściwości dielektrycznych nie tylko  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  i  $\text{CuO}$ , ale także innych członków układu  $\text{CaO-CuO-TiO}_2$  po to, aby znaleźć inne składy o podobnej charakterystyce, aby odkryć podstawowe mechanizmy, i aby poszukiwać nowe kompozyty o nawet lepszych właściwościach dielektrycznych.

W prezentowanej pracy zbadano wstępnie właściwości dielektryczne kompozytów w układach potrójnych  $\text{CuO-CaCu}_3\text{Ti}_4\text{O}_{12}\text{-CaTiO}_3$  i  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}\text{-CaTiO}_3\text{-TiO}_2$ . Częstotliwościowe i temperaturowe zależności przenikalności dielektrycznej i impedancji w zakresie  $10^2\text{-}5 \times 10^6$  Hz and  $25\text{-}130^\circ\text{C}$  zbadano w przypadku reprezentatywnego kompozytu o wysokiej przenikalności ( $> 10^4$ ) o udziale molowym  $\text{Cu/Ti/Ca}$  wynoszącym  $\sim 85/10/5$  w układzie trójskładnikowym  $\text{CuO-CaCu}_3\text{Ti}_4\text{O}_{12}\text{-CaTiO}_3$ . Mocne przesłanki sugerują ważny wpływ przyczynków związanych z granicami międzyziarnowymi na właściwości dielektryczne. Wstępne wyniki pokazały, że wielofazowa mikrostruktura składająca się z większych ziaren dominującej fazy otoczonych przez mniejsze ziarna fazy drugorzędnej odgrywała ważną rolę w przypadku podniesienia odpowiedzi dielektrycznej, w związku z możliwymi efektami warstwy barierowej wywołanymi przez granicę międzyziarnową kompozytów.

**Słowa kluczowe:**  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ,  $\text{CuO}$ , właściwości dielektryczne, kompozyt, mikrostruktura

## 1. Introduction

Electroceramics exhibiting high dielectric constants ( $\epsilon'$ ) accompanied by low loss tangent ( $\tan \delta$ ) and good temperature stability have attracted considerable attention due to their practical applications in microelectronics such as capacitors and memory devices, etc. [1]

The unusual and promising ceramic material  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  was found to possess giant dielectric constants with values of above  $10^4$ , which is frequency independent in the range between dc and  $10^6$  Hz. Furthermore, the permittivity of this material has good temperature stability over a wide temperature range from 100 to 600 K [2, 3]. Recently, other materials with giant dielectric constants were also reported,

for example Li or Ti doped NiO [4],  $\text{CuO}$  [5] or (Ca, Ta)-doped  $\text{TiO}_2$  ceramics [6]. Interestingly, similar dielectric behaviour to  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  has been found in these materials. Though the origin of this specific dielectric behaviour is still unknown, an internal barrier layer capacitor is generally considered as the most probable mechanism [4-6].

From our first study in the ternary system  $\text{CaO-CuO-TiO}_2$ , the phase relations and their dielectric properties after sintering at  $950^\circ\text{C}$  in air were preliminarily determined [7]. Two potentially interesting combinations were found, namely  $\text{CuO-CaCu}_3\text{Ti}_4\text{O}_{12}\text{-CaTiO}_3$  and  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}\text{-CaTiO}_3\text{-TiO}_2$ . In such combinations, each phase possesses a particular dielectric property.  $\text{CaTiO}_3$  was used to produce dielectric composites due to its low  $\tan \delta$  [8]. It might be very useful

to further focus on the composites in such combinations in order to find the common characteristics in the high- $\epsilon'$  materials and also to search for new composites with optimal dielectric properties. In the present study, the frequency and temperature dependences of permittivity and impedance in the range of  $10^2$  to  $5 \times 10^6$  Hz and 25-130°C were investigated in the representative high permittivity composites with Cu/Ti/Ca (mol%) of ~85/10/5 in the ternary system CuO-CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-CaTiO<sub>3</sub>. Room temperature dielectric responses in the composites in the CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-CaTiO<sub>3</sub>-TiO<sub>2</sub> ternary system have been studied. The detailed results concerning the correlation between dielectric properties, micro-structure and phase distribution have been tentatively discussed. Grain boundary effects might have an important effect on the dielectric property.

## 2. Experimental

The variation of the compositions in the systems CuO-CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-CaTiO<sub>3</sub> and CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-CaTiO<sub>3</sub>-TiO<sub>2</sub> was realized by parallel synthesis in the system CaO-CuO-TiO<sub>2</sub> by injection moulding. In short, three triangular pyramid-shaped layers of CaCO<sub>3</sub>, CuO and TiO<sub>2</sub>, which were individually produced by the injection moulding technique, were combined in the final shape of a triangular prism, followed by subsequent dividing (by honeycomb board), mixing and thermal treatments. The as-obtained powdered materials were pressed into pellets. The pellets were sintered at 950°C (some at 1050°C) for 70 h, followed by cooling in the furnace. The detailed procedures were described elsewhere [7, 9].

X-ray powder diffraction (XRD) measurements were carried out using Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å) in a Siemens D-500 diffractometer equipped with a graphite monochromator. A SEM instrument equipped with energy-dispersive X-ray spectroscopy (EDX) was used to observe the microstructure and compositions of the sintered pellets.

Room-temperature capacitance,  $C$ , and loss tangent,  $\tan\delta$ , of the samples were measured with a parallel-plate capacitor arrangement using Agilent 4284A precision LCR meter in the range from  $10^2$  to  $10^6$  Hz. The sample surfaces were coated with silver conducting paint to ensure good electrical contacts. The capacitance and loss tangent were measured as a function of frequency ( $10^2$  Hz –  $5 \times 10^6$  Hz) and temperature (25-130°C), using an Agilent 4294A precision impedance analyzer at an oscillation voltage of 100 mV. The complex permittivity  $\epsilon^*$  was calculated as follows:

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (1)$$

$$\epsilon' = \frac{Cd}{\epsilon_0 A} \quad (2)$$

$$\epsilon'' = \epsilon' \tan \delta \quad (3)$$

where  $\epsilon_0$  is the permittivity in free space,  $A$  is the sample area and  $d$  is the sample thickness.

The complex impedance  $Z^*$  was calculated as follows:

$$Z^* = Z' - iZ'' = \frac{1}{i\omega C_0 \epsilon^*} \quad (4)$$

where  $\omega$  is the angular frequency ( $\omega = 2\pi f$ ).  $C_0 = \epsilon_0 A/d$  is the capacitance of free space.

## 3. Results and discussion

### 3.1. Composites in the CuO-CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-CaTiO<sub>3</sub> system sintered at 950°C

Based on the dielectric property investigations within the ternary CuO-TiO<sub>2</sub>-CaO system [7], the most promising candidates with high dielectric constants were observed in two regions. One is the CuO-rich region sintered at 950°C; the other is the CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-rich region sintered at 1050°C. A particular microstructure of bigger grains of the predominant phase surrounded by smaller grains of secondary phases was observed. This microstructure seems to be a type of structure which provides the internal barrier layers, which are supposed to be the most probable mechanism for giant dielectric constants [10]. Herein, in order to reveal the possible mechanism for the giant dielectric response in the composites in the ternary system CuO-CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-CaTiO<sub>3</sub>, an investigation of the detailed temperature dependence of the dielectric response was carried out on the composite with the molar fraction of Cu/Ti/Ca of ~85/10/5, which was designated as "CuO-a". This composite shows a giant dielectric constant above  $10^4$ , with minor frequency dependence below  $10^5$  Hz.

Fig. 1 shows the microstructure of the sample CuO-a. The sample exhibits a bimodal grain size distribution with small grains of approximately 300 to 600 nm and large grains between 2 and 5  $\mu$ m. The XRD pattern of CuO-a is shown in Fig. 2. Three phases coexist as CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>, CaTiO<sub>3</sub> and CuO, in which CuO is the main phase. Fig. 3 shows the frequency dependence of the  $\epsilon'$  and  $\epsilon''$  of the sintered sample at various temperatures between 25 and 130°C. A Debye-like relaxation with a steep decrease in  $\epsilon'$  was observed in the frequency region where  $\epsilon''$  displays a relaxation peak. Fig. 3(a) illustrates that CuO-a has a very high dielectric constant with a value of  $\epsilon' > 10^4$  and weak frequency and temperature dependence at frequencies below 100 kHz. With increasing temperature, the relaxation peak shifted to higher frequencies (see Fig. 3 (b)), which reveals a thermally activated relaxation process.

The dielectric relaxation time  $\tau$  ( $\tau = 1/(2\pi f)$ , where  $f$  is the response frequency at which the dielectric loss has a maxi-

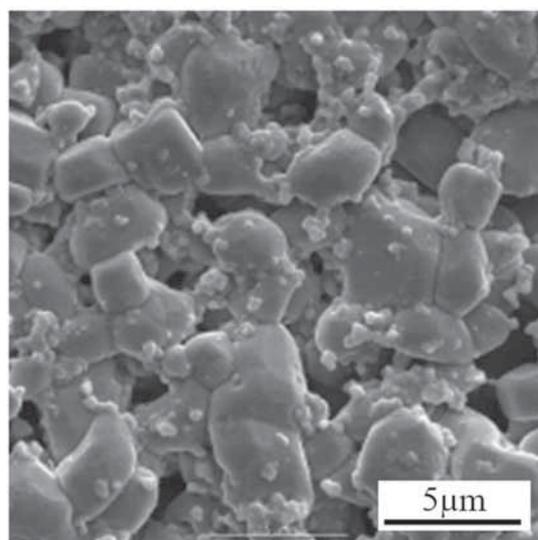


Fig. 1. SEM micrograph of the sample CuO-a sintered at 950°C in air.

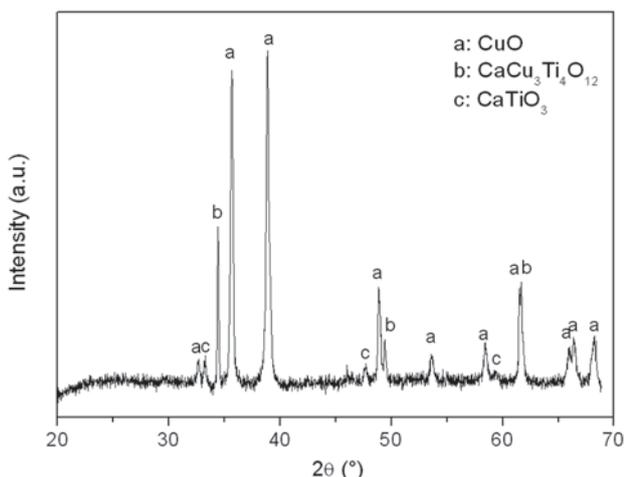
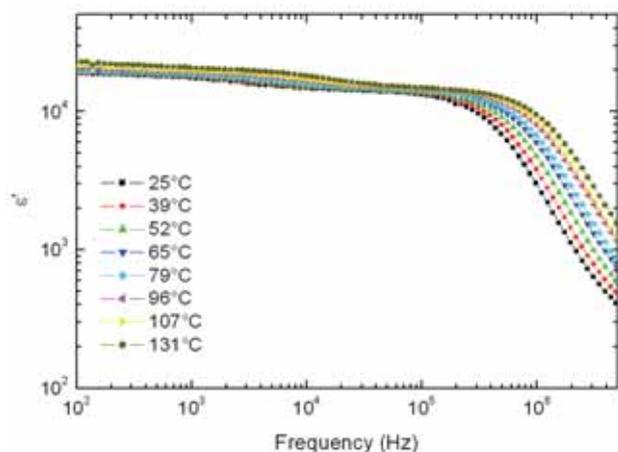


Fig. 2. XRD pattern of the sample CuO-a sintered at 950°C in air.

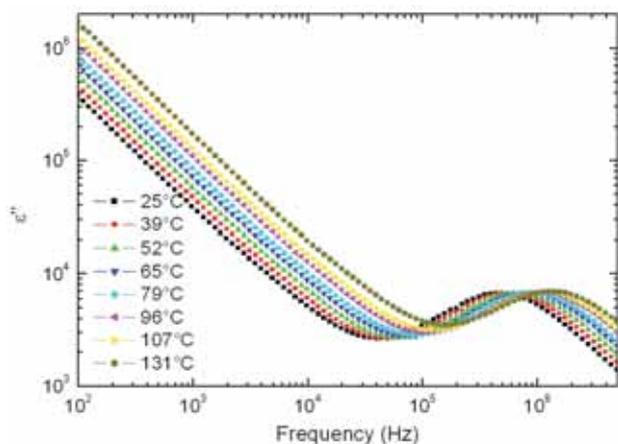
mum, can be determined by the Arrhenius law of

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (5)$$

where  $\tau_0$  is the pre-exponential factor,  $E_a$  the activation energy for the relaxation,  $k_B$  the Boltzmann constant and  $T$  the absolute temperature. In Fig. 4, the relaxation time has been plotted as a function of inverse temperature. The experimental data fit well with the Arrhenius relation, within the



a)



b)

Fig. 3. The frequency dependence of (a)  $\epsilon'$  and (b)  $\epsilon''$  at temperatures between 25 and 130°C for sample CuO-a sintered at 950°C in air.

temperature range of 25-130°C. The activation energy of the electrical response at different temperature can be derived from the fitting curve (solid line) according to equation (5) and is found to be 0.103 eV.

The secondary phases located at the grain boundaries might provide a significant contribution to the observed high dielectric response of the sample CuO-a. The charge carriers pile up at the interfaces where different conductive materials coexist which exhibit high dielectric constants. The electrically heterogeneous microstructure consisting of semiconducting grains with insulating grain boundaries might associate to the high dielectric constant observed in CuO-a due to the internal barrier layer effect [10]. As the permittivity of the CuO-a composite increases slightly with an increase of temperature over the whole frequency range, the thermally activated mechanism also plays its role partly in the high dielectric response of CuO-a.

In the low frequency region, dielectric loss is quite high and increasing with temperature, which is possibly due to the increase of the dc conductivity. The expression describing the losses is

$$\tan \delta = \frac{\epsilon''}{\epsilon'} = \frac{\left(\epsilon_r'' + \frac{\sigma}{\omega \epsilon_0}\right)}{\epsilon'}, \quad (6)$$

where  $\epsilon_r''$  corresponds to the part of the losses associated with the relaxation phenomena and  $\sigma/\omega \epsilon_0$  corresponds to

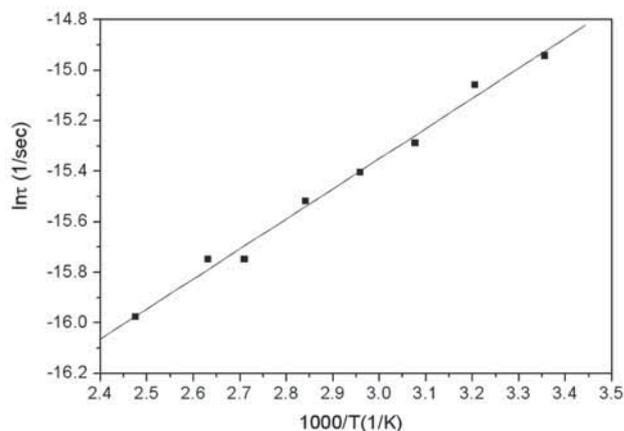


Fig. 4. Arrhenius plot of dielectric relaxation time  $\tau$  for the sintered sample CuO-a.

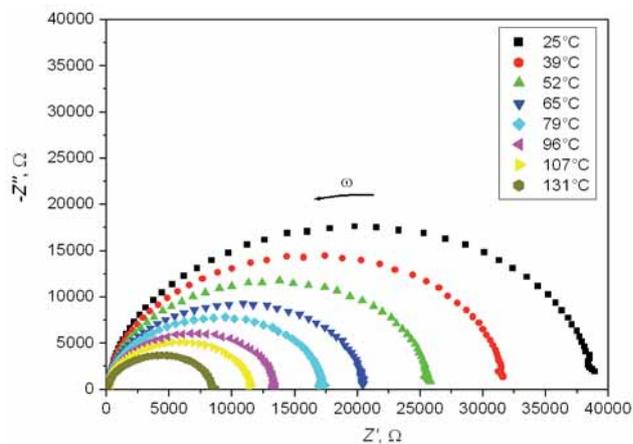


Fig. 5. Impedance complex plane plot  $Z^*$  at different temperatures for the sintered sample CuO-a.

the part due to a pure conduction mechanism, with  $\sigma$  being the conductivity,  $\omega$  the angular frequency and  $\varepsilon_0$  the vacuum permittivity [11]. Therefore, the plot of  $\varepsilon''$  versus the frequency for various temperatures gives a hint to the possible coexistence of these two mechanisms.

In polycrystalline solids, complex impedance spectra usually contain features that can be directly related to the microstructure. The equivalent circuit associated with the microstructure consists of series-connected parallel RC elements of grain and grain boundary [10]. In this case, the complex impedance plot should in principle reveal two semicircles, corresponding to the contributions of grain and grain boundary, respectively. Fig. 5. shows the impedance spectra of the sintered sample CuO-a at various temperatures. Only one semicircle is found in the complex plot. Due to the big difference of the resistivities between grain and grain boundary, the higher resistivity of the grain boundary is dominating the overall conductivity and thus leading to the appearance of only one semicircle in the complex impedance plots. Further studies on the temperature dependence of the bulk and grain boundary resistances and details of the curve fitting of impedance spectroscopic data are going on and will be reported elsewhere. A thermally activated process of conduction of the grain boundaries was revealed (Fig. 5). With increasing temperature, the conductivity of the grain boundaries increases, which explains the high dielectric loss observed in the low frequency range (Fig. 3 (b)).

### 3.2. Composites in the system $\text{CaCu}_3\text{Ti}_4\text{O}_{12}\text{-TiO}_2\text{-CaTiO}_3$

The composites in the  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}\text{-TiO}_2\text{-CaTiO}_3$  region did not show a giant dielectric behaviour when sintered at  $950^\circ\text{C}$ , which is probably due to the microstructure and the lower densities. When the composites were sintered at  $1050^\circ\text{C}$ , a giant dielectric response was observed. Preliminary results show also that the grain boundary effect exists on the obtained high dielectric constant composites. Based on the present investigations, the following discussions will focus on the dielectric behaviour of the bi-phasic composites of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}\text{-CaTiO}_3$  and  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}\text{-TiO}_2$  and a tri-phasic composite of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}\text{-CaTiO}_3\text{-TiO}_2$ . For simplification, the bi-phasic ( $\text{CaCu}_3\text{Ti}_4\text{O}_{12}\text{-CaTiO}_3$ ) composites with the molar fraction of Cu/Ti/Ca of

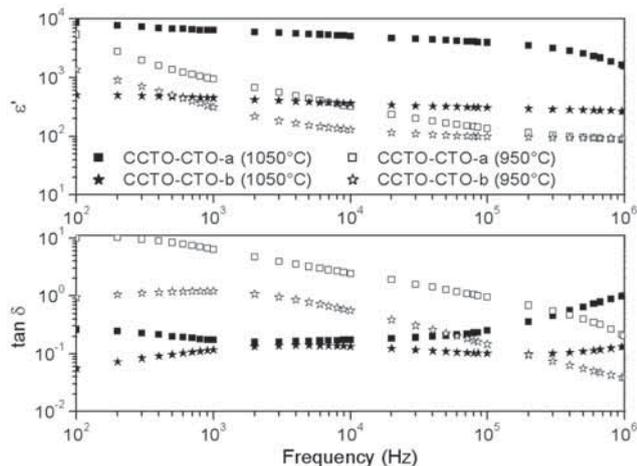
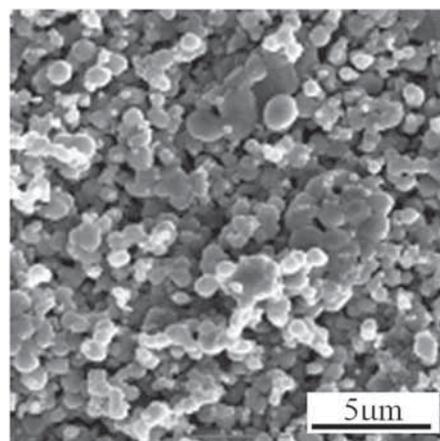
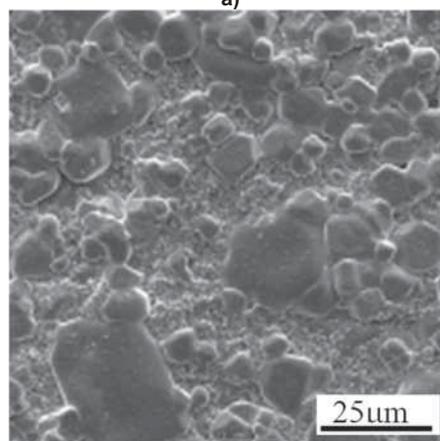


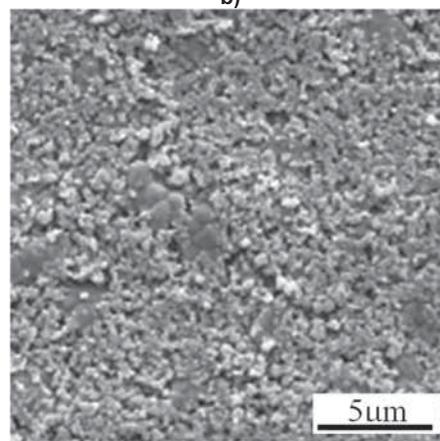
Fig. 6. The frequency dependence of  $\varepsilon'$  (top) and  $\tan \delta$  (bottom) of composites CCTO-CTO-a, CCTO-CTO-b, both of which sintered at  $950^\circ\text{C}$  and  $1050^\circ\text{C}$ , respectively.



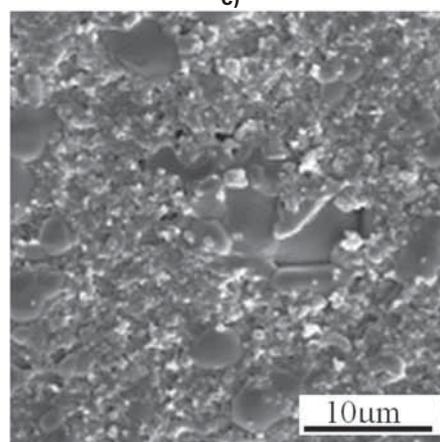
a)



b)



c)



d)

Fig. 7. SEM images of samples CCTO-CTO-a sintered at: a)  $950^\circ\text{C}$  and b)  $1050^\circ\text{C}$ , and samples CCTO-CTO-b sintered at: c)  $950^\circ\text{C}$  and d)  $1050^\circ\text{C}$ .

~32.3/50/17.7 and ~11.2/50/38.8 were designated as sample CCTO-CTO-a and CCTO-CTO-b, respectively. The bi-phasic (CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-TiO<sub>2</sub>) composites with the molar fraction of Cu/Ti/Ca of ~31.3/59.2/9.5 and ~17.5/77.3/5.2 were designated as sample CCTO-TiO<sub>2</sub>-a and CCTO-TiO<sub>2</sub>-b, respectively. The tri-phasic (CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-TiO<sub>2</sub>-CaTiO<sub>3</sub>) composite with the molar fraction of Cu/Ti/Ca of ~31.8/54.7/13.5 was designated as sample CCTO-CTO-TiO<sub>2</sub>-a.

Fig. 6 presents the dielectric constant and dielectric loss dependence on frequency at room temperature for bi-phasic (CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-CaTiO<sub>3</sub>) composites of CCTO-CTO-a and CCTO-CTO-b with sintering temperature of 950°C and 1050°C, respectively. A weak dependence of  $\epsilon'$  on frequency was observed in these samples. Composites sintered at 1050°C exhibited a much better dielectric behaviour, *i.e.*, higher a dielectric constant and a lower dielectric loss, than those sintered at 950°C. Great differences in the microstructure and densification might explain such differences.

Fig. 7 shows the SEM images of the composites of CCTO-CTO-a and CCTO-CTO-b with sintering temperature of 950°C and 1050°C, respectively. For both composites

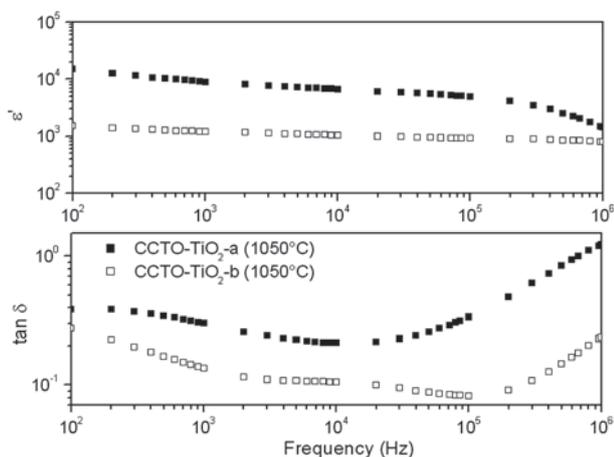
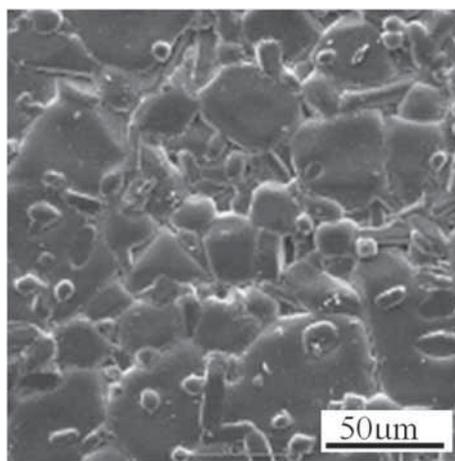
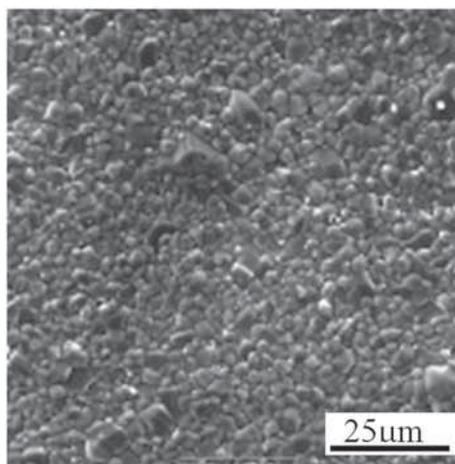


Fig. 8. The frequency dependence of  $\epsilon'$  (top) and  $\tan \delta$  (bottom) of composites CCTO-TiO<sub>2</sub>-a, CCTO-TiO<sub>2</sub>-b, sintered at 1050°C.

sintered at 950°C, the grains are relatively homogeneous in shape and size, approximately ranging from 0.15 to 1.50  $\mu\text{m}$  and 0.15 to 1.20  $\mu\text{m}$  for sample CCTO-CTO-a and CCTO-CTO-b, respectively. The average grain size in CCTO-CTO-b is much smaller than that in CCTO-CTO-a. In comparison, when they are sintered at 1050°C, quite different microstructures were observed in both composites. The typical bimodal grain size distribution was observed in both samples sintered at 1050°C. EDX analysis reveals different compositions in the bigger grains and smaller grains, which were found to be CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> and CaTiO<sub>3</sub>, respectively. It can be clearly seen that the smaller grains of CaTiO<sub>3</sub> became dominant when the sample contains more CaTiO<sub>3</sub>, as in sample CCTO-CTO-b (Fig. 7d). Kobayashi *et al.* [8] investigated the dielectric properties of two phase composites of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> and CaTiO<sub>3</sub> and found that CaTiO<sub>3</sub> could effectively decrease the dielectric loss of the composite. A high  $\epsilon'$  ( $\approx 1800$ ) with a low  $\tan \delta$  ( $\leq 0.02$ ) below 100 kHz was obtained at a CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> : CaTiO<sub>3</sub> ratio of 2 : 1. A barrier layer of CaTiO<sub>3</sub> on the surface of the CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> grains was proposed to be the possible contribution to the high dielectric performance [8]. In the present study, smaller dielectric loss was observed



a)



b)

Fig. 9. SEM images of samples sintered at 1050°C: a) CCTO-TiO<sub>2</sub>-a and b) CCTO-TiO<sub>2</sub>-b.

in the sample CCTO-CTO-b, which has a higher CaTiO<sub>3</sub> content. This is in good agreement with the previous report. However, the dielectric constant values in CCTO-CTO-b are much smaller than those in the sample CCTO-CTO-a with higher CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> content due to the major dielectric contribution from CaTiO<sub>3</sub>.

Another comparison between two bi-phasic (CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-TiO<sub>2</sub>) composites has been tentatively investigated. Fig. 8 presents the dielectric constant and the dielectric loss dependence on frequency at room temperature for sample CCTO-TiO<sub>2</sub>-a and CCTO-TiO<sub>2</sub>-b sintered at 1050°C. A weak dependence on frequency of  $\epsilon'$  was observed in both samples. Higher dielectric constants were observed in the CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-richer composite. The morphology differences between such two composites are shown in Fig. 9. In composite CCTO-TiO<sub>2</sub>-a, smaller particles located at the grain boundaries were observed and found to be a Cu-rich phase, although no additional copper oxide phase was examined in XRD pattern in this composite. Quite homogeneous grains in size and shape were observed in composite CCTO-TiO<sub>2</sub>-b. No clear boundary phase has been detected. Lin *et al.* [12] investigated TiO<sub>2</sub>-rich CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> systems and found that an increase in TiO<sub>2</sub> content decreases the dielectric constant of polycrystalline materials. In our study, similar results were obtained. It is proposed that grain boundary phases of the

composites have an influence on the dielectric behaviour of the composites.

Fig. 10 presents the dielectric constant and dielectric loss dependence on frequency at room temperature for tri-phasic ( $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ - $\text{TiO}_2$ - $\text{CaTiO}_3$ ) composite of CCTO-CTO- $\text{TiO}_2$ -a in comparison to the bi-phasic composites of CCTO-CTO-a and CCTO- $\text{TiO}_2$ -a sintered at 1050°C. Comparable dielectric constant values were observed in these three composites. In addition, the typical bimodal grain size distribution (Fig. 11) was observed in composite CCTO-CTO- $\text{TiO}_2$ -a. Compared with the microstructures of CCTO-CTO-a (Fig. 7b) and CCTO- $\text{TiO}_2$ -a (Fig. 9a), the tri-phasic composite CCTO-CTO- $\text{TiO}_2$ -a exhibited more evenly distributed smaller grains and bigger grains. This investigation further confirms the importance of the grain boundary effect on the dielectric behaviour of the composite.

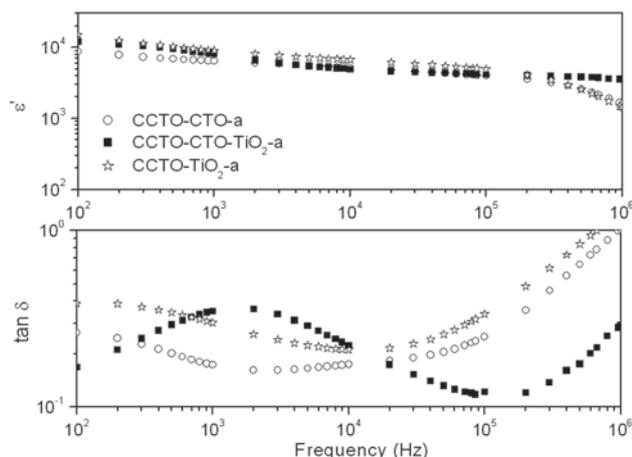


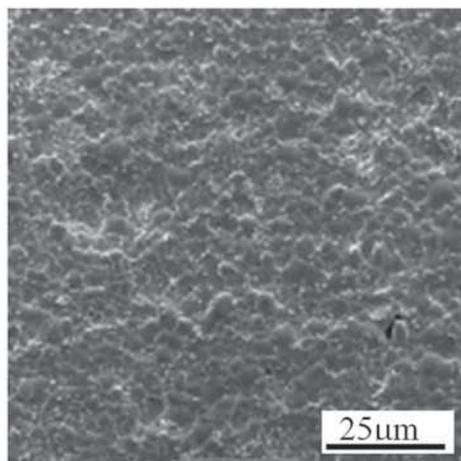
Fig. 10. The frequency dependence of  $\epsilon'$  (top) and  $\tan \delta$  (bottom) of composites CCTO-CTO-a, CCTO-CTO- $\text{TiO}_2$ -a, CCTO- $\text{TiO}_2$ -a, sintered at 1050°C.

#### 4. Conclusions

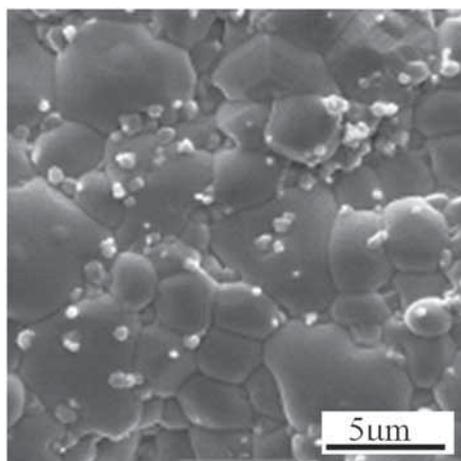
The dielectric properties of the composites in the ternary systems  $\text{CuO}$ - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ - $\text{CaTiO}_3$  and  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ - $\text{CaTiO}_3$ - $\text{TiO}_2$  have been tentatively investigated in the present study. The frequency and temperature dependences of the representative high permittivity ( $> 10^4$ ) composite with the molar fraction of Cu/Ti/Ca of  $\sim 85/10/5$  deduced the possible existence of the barrier layers, which is probably located at the interfaces between grain and grain boundary. The dc conductivity and Debye relaxation might be two main contributions to the high dielectric losses.

A giant dielectric behaviour was observed in the composites with the distinct grain boundary microstructure. The  $\text{CaTiO}_3$  phase can effectively reduce the dielectric loss in the composite but it also decreases the dielectric constants. From the preliminary results, strong hints suggested that an internal barrier layer effect, possibly located at the interface between grain and grain boundary, was the main contribution to the observed high dielectric constants in the composites in both  $\text{CuO}$ - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ - $\text{CaTiO}_3$  and  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ - $\text{CaTiO}_3$ - $\text{TiO}_2$  systems.

To conclude, the dielectric properties of  $\text{CuO}$ -rich and  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ -rich polycrystalline materials are strongly dependent on the microstructure. How to alter and perhaps control the microstructure and therefore modify the dielectric



a)



b)

Fig. 11. SEM images in magnifications of (a)  $\times 1000$  and (b)  $\times 5000$  of the composite CCTO-CTO- $\text{TiO}_2$ -a sintered at 1050°C.

behaviour of the composites will be an interesting subject for further investigations.

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