

## Investigation of Grain Size Effect on the Impedance of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ From 100 Hz to 1 GHz of Frequency

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**Abstract.**  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) is a cubical perovskite phase and sintered ceramics exhibit very high dielectric constant at room temperature. The speculated origins of the high dielectric constant are the existence of insulative barrier layer at grain boundaries and domain boundaries which created an internal barrier layer capacitance (IBLC) at the microstructure of CCTO. The relation of grains and domains electrical resistance were studied in this work by using impedance spectroscopy (IS). A series of samples with different heat treatment temperature were tested to investigate their microstructure by using field emission scanning electron microscopy (FESEM). The grains and domains resistance was calculated from a wide frequency range of impedance complex plane measurement (100 Hz to 1 GHz). The FESEM and IS analyses showed the dependency of grains and domains resistance to average grains size of CCTO microstructure.

### Introduction

Recent researches show that perovskite-related materials  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) exhibit an extraordinarily high dielectric constant ( $10^4$ - $10^5$ ) at room temperature but nearly constant between 100 and 400 K. These features make it applicable to a variety of microelectronic device applications. The origins of high dielectric constant of CCTO were proposed by many researchers and recently they agreed that IBLC with two types of barrier layer were the reliable mechanism.

Sinclair et al. [1] initially reported the electrical heterogeneity of CCTO structure in term of semiconducting grains and insulative grain boundaries of polycrystalline CCTO. Later Fang et al. [2] have found domains and domain boundaries within grains and solved interpretation difference between the single crystal and polycrystalline of CCTO.

Previously we reported that pure CCTO and Nb-doped CCTO have the microstructures of the twin domains distributed within grains from FESEM micrograph and the size is ranging from 20 to 180 nm measured by AFM [3]. The domains existences also have been proved by the existing of high frequency curve as the respond of domain resistivity from Impedance Spectroscopy (IS) measurement [4].

Brize et al. [5] reported the large grain size increased the dielectric constant of CCTO at low frequency region. The high frequency region which associated with the domains existence was not much reported. Most researchers have focused on the domain structures/formations and the electrical properties of the domains and domain boundaries were not widely discussed.

In this study, we reported the effect of different grain size (obtained from specific calcination and sintering temperature) to impedance complex plane at a wide frequency (100 Hz to 1 GHz). The curve fitting technique was applied in order to observe the resistivity of constituent elements inside the bulk of CCTO. Other electrical properties were also studied.

### Materials and Methodology

First, the raw materials of  $\text{CaCO}_3$ ,  $\text{CuO}$  and  $\text{TiO}_2$  were prepared and weight according to the stoichiometric ratio for pure CCTO. The raw materials were mixed via ball milling process for an hour using an alumina jar. The well mixed raw material was heat treated with a series of calcination and sintering temperature to get different grain size/structure. FESEM analysis (Zeiss SUPRA 35VP) was performed to observe the grain size. Three of samples which significant difference in grain size or structures were chosen (abnormal grains: calcined at  $900^\circ\text{C}$  for 12 hours and sintered at  $1040^\circ\text{C}$  for 10 hours, normal grains : calcined at  $1000^\circ\text{C}$  for 3 hours and sintered at  $1040^\circ\text{C}$  for 4 hours and fine grains : calcined at  $900^\circ\text{C}$  for 6 hours and sintered at  $1010^\circ\text{C}$  for 4 hours). An X-ray diffraction (XRD) analysis (Bruker Advance D8) was used for the examination crystallographic structures of the sintered pellets. Dielectric constant, dielectric loss, bulk resistivity and impedance complex plane of CCTO were measured using the Impedance/Gain Phase Analyzer for a range of 100 Hz to 1 MHz and RF Impedance/Material Analyser 4291B Hewlett Packard for a range of 1 MHz to 1 GHz.

### Result and Discussion

Fig. 1 shows the XRD patterns of the sintered CCTO samples with the different grain structures. All of the patterns indicate single phase of CCTO (ICSD 01-075-2188). The obtained single phase structure is important to eliminate the effect of secondary phase to the studied CCTO electrical properties.

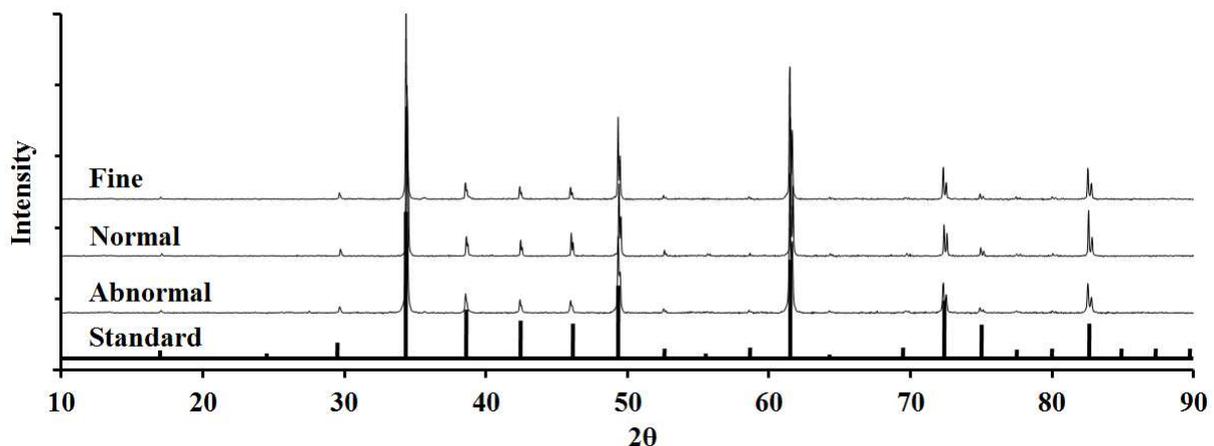


Fig. 1: XRD pattern of the three grain structures of abnormal, normal and fine.

Most of reported CCTO electrical impedance planes are consisting one or two semi-circle curves only (measured at 10 MHz or below). However, few researchers investigated the impedance at higher frequency (till 110 MHz) [6] and they found incomplete additional curve at the high frequency region. This incomplete additional curve was resulting insufficient of data to analyse the curve fitting to observe the resistivity of the domains. Our previous report [4] indicated the complete high frequency curve and found the domains resistance about  $1\ \Omega$ .

Wide frequency range of measurement (till to GHz range) is very important to observe the impedance responds of constituent elements inside of CCTO. The elements electrically can form an equivalent circuit of two or more sets of parallel resistor and capacitor ( $RC$ ) and connected in series. Some literatures [7,8], showed the domain related curve at medium frequency by cooling their samples at low temperature and increased the overall bulk electrical resistivity. The advantage of the wide range of frequency measurement is the capability to reveal the curves at room temperature and the resistivity of the constituent elements at room temperature can be identified.

FESEM micrographs on Fig. 2, Fig 3 and Fig. 4 show the as sintered surface and fracture surface of abnormal, normal and fine grains of the CCTO electroceramic, respectively. The average grain size of abnormal, normal and fine grain are  $\sim 120\ \mu\text{m}$ ,  $\sim 8\ \mu\text{m}$  and  $\sim 3\ \mu\text{m}$  respectively with both as sintered surface and fracture surface indicate the nearly same the average size. Different size of grains was obtained from different calcination and sintering temperature and soaking time.

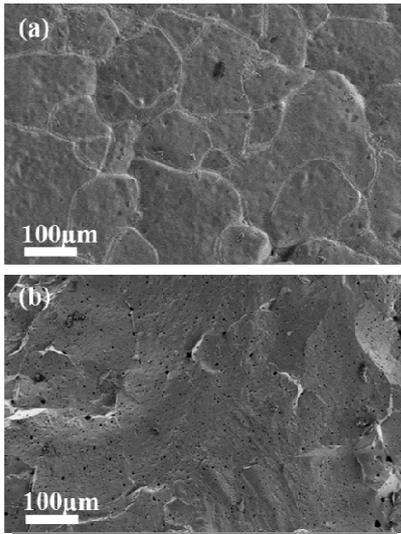


Fig. 2: Microstructure of abnormal grains: (a) surface area and (b) fracture surface

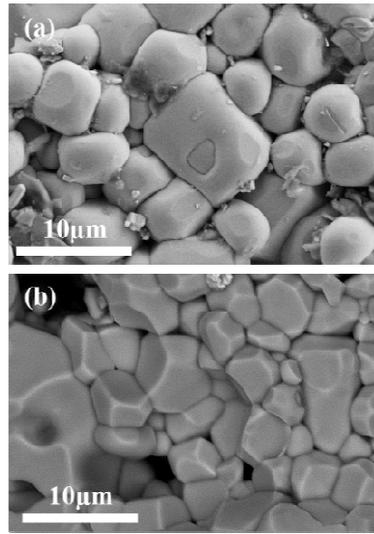


Fig. 3: Microstructure of normal grains: (a) surface area and (b) fracture surface

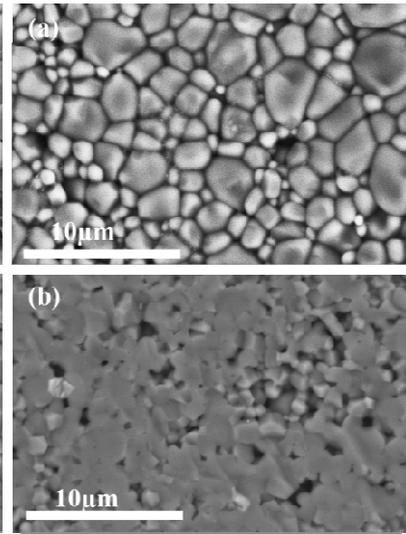


Fig. 4: Microstructure of fine grains: (a) surface area and (b) fracture surface

Different grains size affects significantly the electrical properties. Fig. 5 and Fig. 6 show dielectric constant of different grain size of CCTO ceramics at low and high frequency. The dielectric constant was increasing with the increasing of average grains size. High dielectric constant can be seen on the sample of abnormal grains which is about 36,000 and nearly constant till 31 kHz of frequency. Sample of normal and fine grains show dielectric constant of  $\sim 8,700$  and  $\sim 1,400$  respectively.

The differences of dielectric constant can be described from twin barrier layer capacitance which arise from grain boundaries and domain boundaries of CCTO structure. Previous researchers [4,9,10] have reported the samples with large grains contained many domains compared to the normal or fine grains. The domain structures can be observed when the samples were thermal etched and two types of domain, bumped and terraced like shape were also reported. Large amount of tiny domains inside the large size grains produced high dielectric constant because of the IBLC effects.

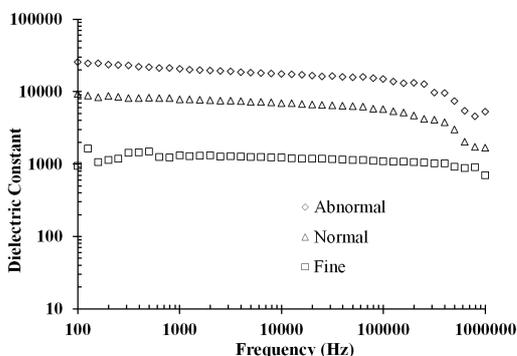


Fig. 5: Dielectric constant of different grain size of CCTO at low frequency.

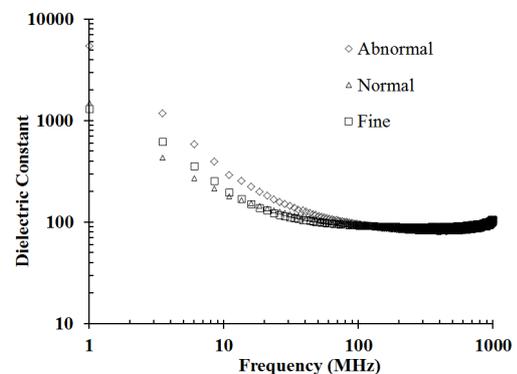


Fig. 6: Dielectric constant of different grain size of CCTO at high frequency.

Dielectric loss at low and high frequency are shown in Fig. 7 and Fig. 8 respectively. The dielectric loss followed the same trend of the dielectric constant over frequency which the increasing of grain size increases the magnitude of dielectric loss. Large bandwidth relaxation occurred from 100 kHz to

100 MHz and the 10 MHz is the peak of the highest dielectric loss (~4 for abnormal, ~2 for normal and ~1.5 for fine grain). Low frequency are not affected too much which all the samples share a constant dielectric loss (below 0.2). High dielectric loss at higher frequency is unfavourable in high frequency electronic and device applications. From the observation, finer grain size improve the dielectric loss but the low dielectric constant is the drawback.

However normal grain size possesses the best combination of both properties which high dielectric constant (nearly constant at 10,000) and low dielectric loss (below 0.2 at outer of relaxation frequency).

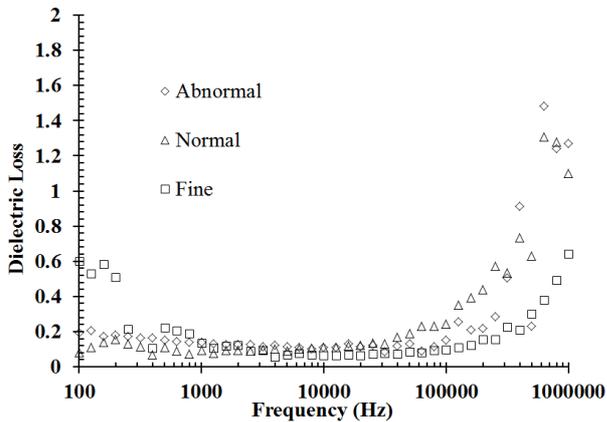


Fig. 7: Dielectric Loss of different grain size of CCTO at low frequency.

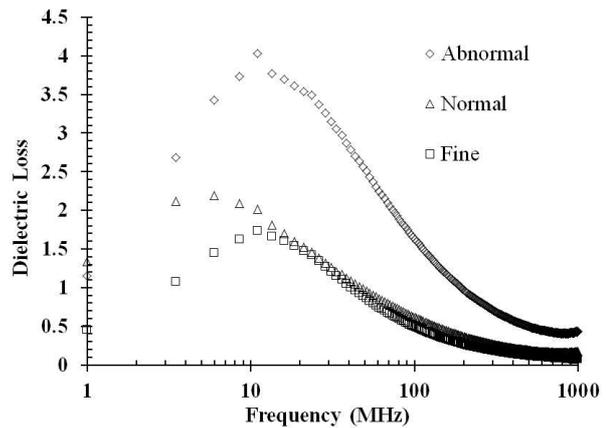


Fig. 8: Dielectric loss of different grain size of CCTO at high frequency.

Fig. 9 shows low frequency impedance complex plane of the CCTO sample with different grain structure. The large curve at lower frequencies was attributed to the grain boundaries resistance,  $R_{gb}$  and the non-zero intercept on the  $Z''$ . On the other hand, the low frequency curve also can be attributed to the electrodes contacts resistivity,  $R_x$  of the samples. However, due to the value of  $R_{gb}$  is much larger than  $R_x$ , the curve of  $R_x$  will disappear because overlapping with  $R_x$  curve.  $R_x$  can be measured by lowering the  $R_{gb}$  via doping process as reported previously [4].

The samples with abnormal grain has lower grain boundaries resistivity,  $R_{gb}$  compared to the normal and fine grain. From curve fitting measurements (not shown) obtained  $R_{gb}$  of 3.6 M $\Omega$ .cm, 4 M $\Omega$ .cm and 4.2 M $\Omega$ .cm for abnormal, normal and fine grain were calculated respectively. The capacitances of the grain boundaries,  $C_{gb}$  were unable to be calculated because of lower frequency measurements are required.

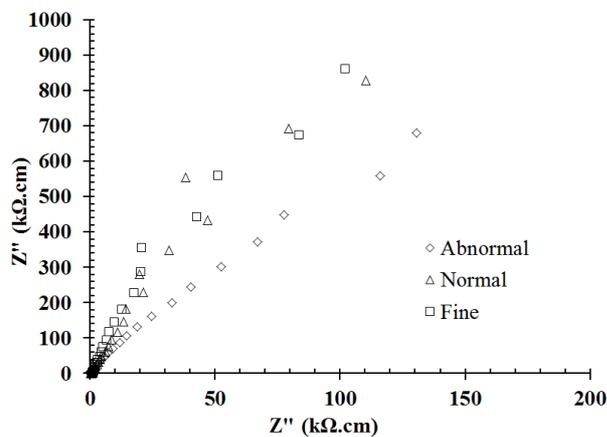


Fig. 9: Impedance complex plane of different size of CCTO at low frequency

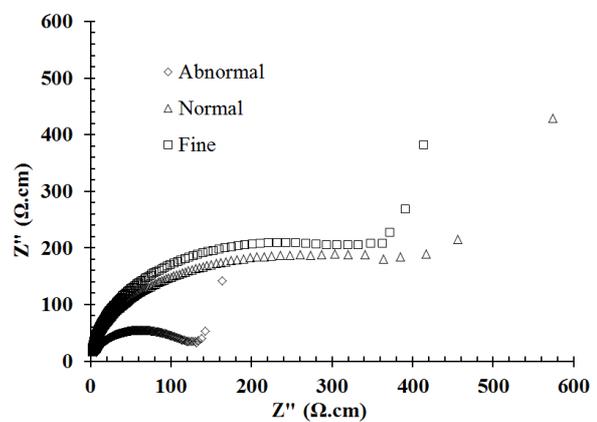


Fig. 10: Impedance complex plane of different size of CCTO at high frequency

The bulk resistivity of the samples at low and high frequency are shown in Fig. 11 and Fig. 12 respectively. The bulk resistivity is the total resistivity of phases inside of CCTO and it was found that sample with abnormal grain possess lower resistivity. Low resistivity of grains boundaries and bulk of abnormal structure can be described by high oxygen vacancies formed during the sintering process which increase the mobility of carriers inside the CCTO bulk sample[11].

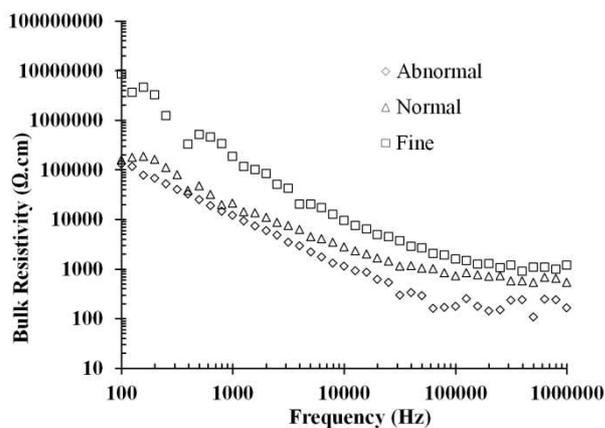


Fig. 11: Bulk resistivity of different grain size of CCTO at low frequency.

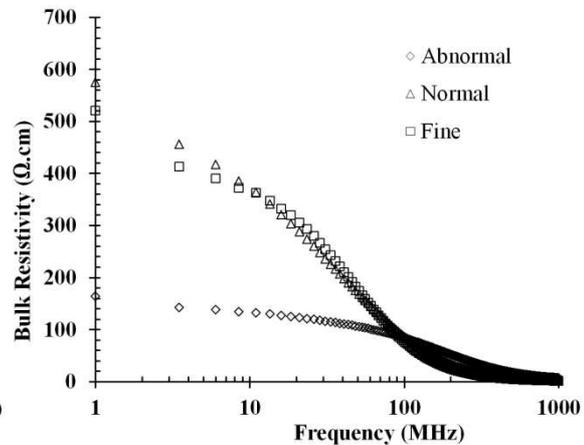


Fig. 12: Bulk resistivity of different grain size of CCTO at high frequency.

Zheng et al. [12] reported the conduction activation energies of electron from the second ionization of oxygen vacancies are about 0.70 eV which indicates that dielectric relaxation produced in the grain boundaries. The report by Bidault et al. [13] shows a correlation between the dielectric relaxation and the conductivity by using space-charge model and found that an increase in the oxygen vacancies leads to an increase in both the conductivity and the dielectric relaxation.

At high frequency impedance complex plane of the difference grain structure as shown in Fig. 10, the curve fitting (not shown) indicated the resistivities of domain boundaries are 140  $\Omega$ .cm, 480  $\Omega$ .cm and 500  $\Omega$ .cm for abnormal, normal and fine structure respectively. It was suggested that the high frequency impedance complex planes were contributed to the domain boundaries resistivity as discussed previously [4].

## Conclusion

The observation on this study was point out the dielectric constants and dielectric losses are proportional to the grain size. The grain boundaries and domain boundaries resistivity are inversely proportion to grain size. The resistivity of abnormal grain structure is the lowest and suggested originating from oxygen vacancies formation as longer sintering time was applied. Oxygen vacancies inside the lattice structure promoted hopping mechanism which increases the conduction [13] of carriers inside the CCTO structure.

## Acknowledgment

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**Reference**

- [1] D.C. Sinclair, T.B. Adams, F.D. Morrison and A.R. West: *Appl. Phys. Lett.* Vol. 80 (2002), p. 2153.
- [2] T.T. Fang, H.K. Shiau, *J. Am. Ceram. Soc.* 87 Vol. (2004), p. 2072–2079.
- [3] M.A. Sulaiman, S.D. Hutagalung and Z.A. Ahmad: *Advanced Materials Research* Vol. 364 (2012), p. 455–459.
- [4] M.A. Sulaiman, S.D. Hutagalung, J.J. Mohamed, Z.A. Ahmad, M.F. Ain and B. Ismail: *J. Alloys Compd.* Vol. 509 (2011), p. 5701–5707.
- [5] V. Brizé, G. Gruener, J. Wolfman, K. Fatyeyeva, M. Tabellout, M. Gervais and F. Gervais: *Materials Science and Engineering: B* Vol. 129 (2006), p. 135–138.
- [6] S.F. Shao, J.L. Zhang, P. Zheng, W.L. Zhong and C.L. Wang: *J. Appl. Phys.* Vol. 99 (2006), p. 084106.
- [7] D.-L. Sun, A.-Y. Wu and S.-T. Yin: *J. Am. Ceram. Soc.* Vol. 91 (2007), p. 169–173.
- [8] R. Bodeux, M. Gervais, J. Wolfman, C. Autret-Lambert, G. Liu and F. Gervais: *Thin Solid Films* Vol. 520 (2012), p. 2632–2638.
- [9] L.-T. Mei, H.-I. Hsiang and T.-T. Fang: *J. Am. Ceram. Soc.* Vol. 91 (2008), p. 3735–3737.
- [10] T.-T. Fang and L.-T. Mei: *J. Am. Ceram. Soc.* Vol. 90 (2007), p. 638–640.
- [11] T. Adams, D. Sinclair and A.R. West: *Advanced Materials* (2002), p. 2001–2003.
- [12] Q. Zheng, H. Fan and C. Long: *J. Alloys Compd.* Vol. 511 (2012), p. 90–94.
- [13] O. Bidault, P. Goux, M. Kchikech, M. Belkaoumi and M. Maglione: *Physical Review B* Vol. 49 (1994), p. 7868–7873.