



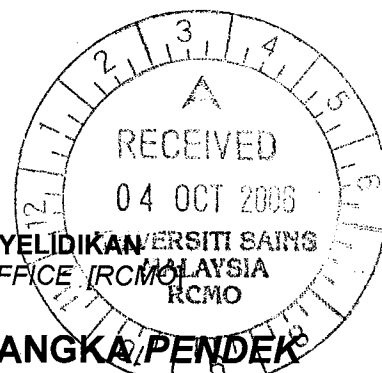
# **Laporan Akhir Projek Penyelidikan Jangka Pendek**

## **Effect of Annealing Condition on the Electrical and Structural Properties of Ferroelectric CCTO Prepared by Mechanical Alloying Technique**

**by**

**Dr. Sabar Derita Hutagalung  
Khatijah Aisha Yaacob**

**2006**



PEJABAT PENGURUSAN & KREATIVITI PENYELIDIKAN  
 RESEARCH CREATIVITY AND MANAGEMENT OFFICE (RCMO)

**LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA PENDEK**  
**FINAL REPORT OF SHORT TERM RESEARCH PROJECTS**

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*Name of Research Leader :*

Ketua Penyelidik <i>Research Leader</i>	PTJ <i>School/Centre</i>
Dr. Sabar Derita Hutagalung	PPK. Bahan dan Sumber Mineral

**Nama Penyelidik Bersama**  
*(Jika berkaitan) :*  
*Name/s of Co-Researcher/s*  
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Penyelidik Bersama <i>Co-Researcher</i>	PTJ <i>School/Centre</i>
Khatijah Aisha Yaacob	PPK. Bahan dan Sumber Mineral

2) **Tajuk Projek :** .....  
*Title of Project:*

.....  
 Effect of Annealing Condition on the Electrical and  
 .....  
 Structural Properties of Ferroelectric CCTO Prepared by  
 .....  
 Mechanical Alloying Technique  
 .....  
 .....  
 .....

3)

### **Abstrak untuk penyelidikan anda**

(Perlu disediakan di antara 100 – 200 perkataan di dalam Bahasa Malaysia dan Bahasa Inggeris. Ini kemudiannya akan dimuatkan ke dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & luar).

#### *Abstract of Research*

*(Must be prepared in 100 – 200 words in Bahasa Malaysia as well as in English. This abstract will later be included in the Annual Report of the Research and Innovation Section as a means of presenting the project findings of the researcher/s to the university and the outside community)*

### **Abstrak**

Bahan elektroseramik ferroelektrik  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) telah disediakan dengan teknik pengalioan mekanikal terubahsuai dan tindak balas pepejal. Kesan keadaan sepuhlindap (suhu dan masa pengkalsinan, suhu dan masa pensinteran) dan pendopan telah dikaji keatas pembentukan fasa, mikrostruktur dan sifat-sifat elektrik (pemalar dielektrik, lesapan dielektrik dan rintangan) bahan CCTO. Teknik pengalioan mekanikal terubahsuai meliputi proses penyediaan bahan mentah, pencampuran dan pengisaran selama 5 jam, pengkalsinan dan pensinteran. Teknik ini telah dipilih untuk membolehkan proses pengkalsinan dan pensinteran dapat dilakukan pada masa yang pendek dan suhu rendah untuk menjimatkan masa dan tenaga. Hasil kajian menunjukkan bahawa parameter terbaik untuk menghasilkan CCTO melalui teknik pengalioan mekanikal terubahsuai ialah pengisaran selama 5 jam, pengkalsinan  $750^\circ\text{C}$  selama 9 jam dan pensinteran  $950^\circ\text{C}$  selama 12 jam. Walaubagaimanapun, kesan ketumpatan dopan zink keatas sifat dielektrik CCTO didapati tidak mantap, dimana bahan yang didop 5% Zn memberikan nilai pemalar dielektrik terendah tetapi menunjukkan lesapan dielektrik terbaik. Sampel ini juga memberikan nilai rintangan tertinggi. Oleh itu dapat disimpulkan bahawa pendopan dengan Zn dapat meningkatkan sifat dielektrik CCTO. Bagi CCTO yang disediakan dengan tindak balas pepejal, hasil pengamatan menunjukkan bahawa terjadi pertumbuhan butiran yang luar biasa dan berliang besar. Pertambahan suhu pensinteran telah meningkatkan ketumpatan dan menghasilkan pembentukan fasa  $\text{Cu}_2\text{O}$ . Sampel yang disinter pada  $1040^\circ\text{C}$  selama 10 jam menghasilkan saiz butiran yang seragam dan nilai pemalar dielektrik tertinggi iaitu 33210.

### **Abstract**

*Electroceramic ferroelectric material of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) was synthesized by modified mechanical alloying and solid state reaction techniques. The effects of annealing condition (calcinations temperature and time, sintering temperature and time) and doping concentration to the phase formation, microstructure and electrical (dielectric constant, dielectric loss and resistance) properties of CCTO have been studied intensively in this work. The modified mechanical alloying technique is covers preparation of raw material, mixing and ball milling for 5 hours, calcination, pellet forming and sintering processes. This technique was chosen for this work to enable the calcination and sintering processes in future carried out in shorter time and lower temperature, therefore it can be save time and energy. The results show that optimum parameter to synthesized CCTO via modified mechanical alloying technique are milling time 5 hours, calcination at  $750^\circ\text{C}$  for 9 hours, and sintering at  $950^\circ\text{C}$  for 12 hours. However, the effect Zn-doping concentration on the dielectric constant CCTO is not consistent, which was found that 5 % dopant give a lower dielectric constant value but shows the best dielectric loss properties if compared to others samples. Besides that, this sample also shows the highest resistance value. Therefore, it can be concluded that by doping with certain amount of zinc, the electrical and dielectric properties of CCTO can be improved. For CCTO prepared by the solid state reaction technique, the microstructure observation shows abnormal grain growth and large pores. Increasing sintering temperature enhances the density and secondary formation of  $\text{Cu}_2\text{O}$ . The results show that the sample sintered at  $1040^\circ\text{C}$  for 10 hours yields a clearly uniform grain size with the highest dielectric constant value of 33210.*

- 4) Sila sediakan Laporan teknikal lengkap yang menerangkan keseluruhan projek ini.  
[Sila gunakan kertas berasingan]  
*Kindly prepare a comprehensive technical report explaining the project  
(Prepare report separately as attachment)*

Senaraikan Kata Kunci yang boleh menggambarkan penyelidikan anda :  
*List a glossary that explains or reflects your research:*

Bahasa Malaysia

CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (CCTO),  
Bahan elektroseramik,  
Pengalioan mekanikal terubahsuai,  
Tindak balas pepejal,  
Pengkalsinan,  
Pensinteran,  
Pemalar dielektrik tinggi,  
Lesapan dielektrik rendah.

Bahasa Inggeris

CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (CCTO),  
electroceramic material,  
modified mechanical alloying,  
solid state reaction,  
calcination,  
sintering,  
high dielectric constant,  
Low dielectric loss.

- 5) **Output Dan Faedah Projek**  
*Output and Benefits of Project*

- (a) \* **Penerbitan (termasuk laporan/kertas seminar)**  
*Publications (including reports/seminar papers)*  
*(Sila nyatakan jenis, tajuk, pengarang, tahun terbitan dan di mana telah diterbitkan/dibentangkan).*  
*(Kindly state each type, title, author/editor, publication year and journal/s containing publication)*

1. Preparation of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (CCTO) by modified mechanical alloying technique, S. D. Hutagalung, J. J. Mohamed, Z. A. Ahmad, presented at 3<sup>rd</sup> International Conference on Materials for Advanced Technologies (ICMAT 2005), Singapore, 3-8 July 2005.
2. Microwave characteristic of CCTO dielectric resonators, Julie J. Mohamed, Sabar D. Hutagalung, Mohd. Fadzil Ain, Zainal A. Ahmad, Proceedings of the International Conference on Robotics, Vision, Information and Signal Processing (ROVISP 2005), Penang (2005) 931-933.
3. The effect of compaction pressure on the CCTO formation and dielectric properties via solid state technique, Julie J. Mohamed, Sabar D. Hutagalung, Zainal A. Ahmad, Proceedings of the 6<sup>th</sup> National Seminar on Neutron and X-Ray Scattering, Serpong, Indonesia (2005) 79- 81.
4. Different sintering time effect on the formation and dielectric properties of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>, Julie J. Mohamed, Sabar D. Hutagalung, Zainal A. Ahmad, Proceedings of the 6<sup>th</sup> National Seminar on Neutron and X-Ray Scattering, Serpong, Indonesia (2005) 82-85.
5. The effect of CuO addition in CCTO on the dielectric properties and microstructure, Julie J. Mohamed, Hairol. A. Rahman, Zainal A. Ahmad, Proceedings of the 14<sup>th</sup> Scientific Conference of Electron Microscopy Society of Malaysia, Penang (2005) 51-54.
6. Microstructure and dielectric properties of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> ceramic, Julie J. Mohamed, Sabar D. Hutagalung, M. Fadzil Ain, Karim Deraman, Zainal A. Ahmad, Materials Letters xx (2006) xxx-xxx, Elsevier, in press.

- (b) **Faedah-Faedah Lain Seperti Perkembangan Produk, Prospek Komersialisasi Dan Pendaftaran Paten atau impak kepada dasar dan masyarakat.**  
*Other benefits such as product development, product commercialisation/patent registration or impact on source and society*

.....  
Produk bertajuk: **"Super-K CCTO"**.

Produk ini telah berjaya memenangi pingat perak pada pameran ITEX 2005.

Produk ini sesuai digunakan sebagai resonator untuk peranti gelombang mikro (Microwave Devices).

.....

- \* Sila berikan salinan  
\* *Kindly provide copies*

(c) **Latihan Gunatenaga Manusia**  
*Training in Human Resources*

i) Pelajar Siswazah : .....  
*Postgraduate students:*  
*(perincikan nama, ijazah dan status)*  
*(Provide names, degrees and status)*

.....  
1). Julie Juliewatty Mohamed, calon PhD., sedang menulis tesis.  
.....  
.....

ii) Pelajar Prasiswazah : .....  
*Undergraduate students:*  
*(Nyatakan bilangan)*  
*(Provide number)*

.....  
Enam (6) orang pelajar telah menyelesaikan projek penyelidikan tahun  
akhir mereka dibawah geran penyelidikan ini.  
.....  
.....

iii) Lain-Lain : .....  
*Others:*

.....  
Pembantu Projek: 2 orang

- 1. Mohd. Hafizi Md. Ramly (1 Oktober 2004 – 31 Disember 2004)
  - 2. Malihah Mat Yusof (23 April 2005 - 30 Jun 2005)
- .....

6. **Peralatan Yang Telah Dibeli :**  
*Equipment that has been purchased:*

.....  
Alat yang dibeli hanya peralatan kaca yang dapat dikategorikan sebagai alat pakai habis iaitu:  
Vacuum desiccator 210 mm (2 unit), glass tube (1 unit), dan three-neck round-bottom flask  
1000 mL (1 unit).  
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**KOMEN JAWATANKUASA PENYELIDIKAN PUSAT PENGAJIAN**  
*Comments of the Research Committees of Schools/Centres*

Dari laporan yang diterima didapati projek ini telah berjaya dilaksanakan.

Output projek ini juga amat baik dengan berjaya menghasilkan 6 kertas kerja dan telah memenangi pingat Perak, di ITEX 2006.



TANDATANGAN PENERUSI  
JAWATANKUASA PENYELIDIKAN PUSAT PENGAJIAN  
*Signature of Chairman*  
*[Research Committee of School/Centre]*

2-10-2006

TARIKH  
*Date*

PROF. MADYA DR. AZIZAN BIN AZIZ  
Timbalan Dekan  
(Pengajian Siswazah dan Penyelidikan)  
P.P. Kejuruteraan Bahan & Sumber Mineral  
Universiti Sains Malaysia

# **TECHNICAL REPORT**

Project Title:

**EFFECT OF ANNEALING CONDITION ON THE  
ELECTRICAL AND STRUCTURAL PROPERTIES OF  
FERROELECTRIC CCTO PREPARED BY MECHANICAL  
ALLOYING TECHNIQUE**

Project Leader:

**Dr. Sabar Derita Hutagalung**  
School of Materials and Mineral Resources Engineering,  
Universiti Sains Malaysia

Grant:

**USM Short Term Research Grant  
Project No. 304/PBAHAN/6035119  
(01 September 2004 - 31 August 2006)**

Amount of Grant:

**RM 15,645.00**

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# EFFECT OF ANNEALING CONDITION ON THE ELECTRICAL AND STRUCTURAL PROPERTIES OF FERROELECTRIC CCTO PREPARED BY MECHANICAL ALLOYING TECHNIQUE

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## ABSTRACT

Electroceramic ferroelectric material of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) was synthesized by modified mechanical alloying and solid state reaction techniques. The effects of annealing condition (calcinations temperature and time, sintering temperature and time) and doping concentration to the phase formation, microstructure and electrical (dielectric constant, dielectric loss and resistance) properties of CCTO have been studied intensively in this work. The modified mechanical alloying technique is covers preparation of raw material, mixing and ball milling for 5 hours, calcination, pellet forming and sintering processes. This technique was chosen for this work to enable the calcination and sintering processes in future carried out in shorter time and lower temperature, therefore it can be save time and energy. The results show that optimum parameter to synthesized CCTO via modified mechanical alloying technique are milling time 5 hours, calcination at 750 °C for 9 hours, and sintering at 950 °C for 12 hours. However, the effect Zn-doping concentration on the dielectric constant CCTO is not consistent, which was found that 5 % dopant give a lower dielectric constant value but shows the best dielectric loss properties if compared to others samples. Besides that, this sample also shows the highest resistance value. Therefore, it can be concluded that by doping with certain amount of zinc, the electrical and dielectric properties of CCTO can be improved. For CCTO prepared by the solid state technique, the microstructure observation shows abnormal grain growth and large pores. Increasing sintering temperature enhances the density and secondary formation of  $\text{Cu}_2\text{O}$ . A clear grain boundary and dense microstructure were observed. The results show that the sample sintered at 1040 °C for 10 hours yields a clearly uniform grain size with the highest dielectric constant value of 33210.

### Keywords:

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO), electroceramic material, modified mechanical alloying, solid state reaction, calcination and sintering condition, high dielectric constant, low dielectric loss.

## INTRODUCTION

High dielectric constant and ferroelectric materials are increasingly important for pushing the state of art in semiconductor integrated circuits. There are necessary in applications that require high capacitance values per lateral area. Ceramic materials are also can be used in the microelectronic industries as dielectric substrates, due to their high reliability, high integration potential, good dielectric properties, excellent thermal conductivity and their thermal expansion coefficient close to silicon [1]. It is known that some ceramic compounds with perovskite structures are found to be very interesting dielectric properties. In particular, one of the members,  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO), was recently studied to investigate the origin of the so-called colossal permittivity, and Chidelli et. al. [2] was reported the dielectric properties result of CCTO for single crystal, powders and thin films.

The electroceramic compound CCTO has been found as a material exhibit a giant dielectric constant with relatively temperature independent over a wide temperature range between 100 and 600 K. Its dielectric constant value up to  $10^5$ . However, below 100 K its value drops abruptly almost three orders of magnitude. Local structural properties of CCTO system as a function of temperature was investigated within a range from 50 K up to room temperature [3,4]. The temperature dependence of the nearest neighbor Cu-O distance is very flat, supporting the idea that this is bracing the structures. However, unusual temperature dependence for the atomic displacement parameters of calcium and copper is observed. Temperature dependent modeling, suggests that the Ca atoms become under bonded at low temperature. This unique property makes CCTO a promising material for microelectronic and microwave device applications.

The dielectric properties of electroceramic materials are depends on the phase transition phenomena, and that is closely related to the crystal structure. On the other hand, the crystal structure is closely dependent on the thermal history and the fabrication method. Therefore, the properties of a certain electroceramic materials will finally affected by the sintering condition, including sintering temperature and time.

Mechanical alloying technique has been used to produce CCTO by using two different experimental procedures [5]. The advantage of this procedure remains on the fact that melting is not necessary; the powders are nanocrystalline and exhibits extraordinary mechanical properties. It can also be easily shaped (injected, compacted, etc.) into any geometry or used in others procedures of film preparation [5]. Although this technique is able to produce nanocrystalline powders of CCTO, but this process need a very long milling time up to 100 hours to obtain a single-phase of CCTO formation. On the other hand, a conventional ceramic solid state reaction technique is one of the promising technique to prepared CCTO, but again, this process need a relatively high calcination temperature, normally in the range of 1000-1100 °C. To solved these problems, in this work we try to reduce the milling time to 5 hours only and then following by calcination process at 600-900 °C for different soaking time to produce a single-phase CCTO formation [6]. A novel technique that using in this work to prepare the  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) is called modified mechanical alloying technique. For comparison purpose, another technique namely solid state reaction method was employed to prepare CCTO.

## EXPERIMENTAL

There are two (2) techniques were employed to prepare ferroelectric  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) electroceramics are modified mechanical alloying and solid state reaction techniques. The

first stage in these techniques is  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) was prepared by a modified mechanical alloying technique. This technique is a modification technique from the original method that was reported by Almeida et al. [5]. The starting materials of  $\text{Ca}(\text{OH})_2$  (Aldrich, 99%),  $\text{CuO}$  (Aldrich, 99%) and  $\text{TiO}_2$  (Merck, 99%) powders were weighed according to the stoichiometric ratio. Mixed powders were subject to a fast ball milling process (1500 rpm) in sealed alumina vial under ambient condition for 5 hours. The milled powders then were put in an alumina crucible and submitted to calcination process at temperature of 600, 700, 800 and 900 °C in air for 12 hours, respectively. The calcined powders were reground and pressed into a disc shape pellets with diameter of 6 mm and 1 mm in thickness using a stainless steel die set. The pellets were sintered in the presence of air at 1050 °C with soaking time of 24 hours. Phase analysis was conducted on the both calcined powders and sintered pellets by using

The second stage in the modified mechanical alloying technique is the preparation of CCTO with optimum calcinations' time. Because in the first stage, the calcinations' time was fixed at 12 hours that is may be too long or too short. Similar with first stage, raw materials for preparation of undoped CCTO are  $\text{Ca}(\text{OH})_2$ ,  $\text{CuO}$  and  $\text{TiO}_2$ . The CCTO processing process was done by using so-called modified mechanical alloying technique, which covers preparation of raw material, mixing and ball-milling process for 5 hours, calcination, pellet forming and sintering.

In the stage 2, which is the undoped CCTO sample preparation, the starting materials of  $\text{Ca}(\text{OH})_2$ ,  $\text{CuO}$  and  $\text{TiO}_2$  powders were weighed according to the stoichiometric ratio and fast ball milling (1500 rpm) in sealed alumina vial under ambient condition for 5 hours. The mixed powder was submitted to calcination at 750°C in air for 6, 9, 12, 16, 24 hours respectively. The calcined powder was then pressed into a pellet using a stainless steel die. The prepared pellets were sintered in air at 900°C and 1050°C with soaking time of 24 hours. Phase analysis was conducted on those calcined powders by XRD analysis. From the result, the optimum calcinations time will be applied in the preparation of zinc-doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ . Preparation process of zinc-doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  samples are almost same but different in term of raw materials (with doping additional), calcination time and sintering temperature using the optimum parameters obtained from stage 2.

The second technique namely solid state reaction was also employed to prepare CCTO in this project. High purity  $\text{CaCO}_3$  (Aldrich, 99%),  $\text{TiO}_2$  (Merck, 99%) and  $\text{CuO}$  (Aldrich, 99%) were used as starting materials. A stoichiometric ratio of the reagents was milled for 1 hour using zirconia balls. The powders exhibiting free flowing characteristics were then obtained by sieving the dried milled powders. The mixed powder was calcined in air at 900 °C for 12 hours. Cylindrical shape specimens with 5 mm in diameter and approximately 0.5 - 1 mm thick were then pressed with 300 MPa compaction pressure. The samples were sintered in air at 1050 °C with different sintering time (1, 3, 6, 12, 18 and 24 hours) and heating rate of 5°C/minutes.

The X-Ray Diffraction (XRD) analysis was done to the calcined powder and different duration sintered pellets by using D8 Bruker diffractometer machine. Density and porosity of the samples were obtained by Archimedes method. The microstructures were investigated on the fracture surface of the sintered specimens using SEM (FE-SEM, Zeiss SUPRA 35VP). The electrical and dielectric properties (resistivity, dielectric constant and dielectric loss) of the sintered pellets were measured by using Agilent 4284A Precision LCR meter at 1 kHz frequency in ambient temperature and Hewlett-Packard 4912 Impedance Spectroscopy at frequency range of 1 Hz to 10 GHz. The samples for measuring electrical and dielectric properties were polished to ensure surface flatness and then painted with silver paste on both surfaces as electrodes.

## RESULTS AND DISCUSSION

Figure 1 show a color transformation from a black color of mixed powder raw materials to yellow-brown of calcined CCTO powder and then change to a grey color after sintering process.

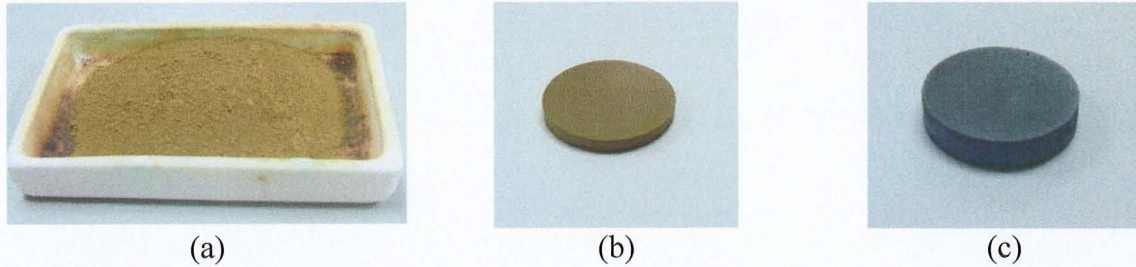


Figure 1. Obtained  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ : (a) calcined powder, (b) calcined pellet, (c) sintered pellet.

### Modified Mechanical Alloying Technique Results

Figure 2 shows the XRD analysis results for the calcined powders at different temperature of 600 °C, 700 °C, 800 °C and 900 °C for 12 hrs. The patterns shows that the formation of single-phase polycrystalline CCTO has been formed completely starting in the sample calcined at 700 °C. The degree of crystal structure was improved as calcination temperature increasing to 800 °C and 900 °C. All of the detected peaks were identified and found to be corresponding to CCTO phase (JCPDS File No. 21-0140). This phenomenon was confirmed that calcination temperature of 700 °C has been enough to form CCTO single-phase by modified mechanical alloying technique. It is very interesting, because this calcination temperature is much lower if we compared to the other methods. The calcination temperature of CCTO preparation by using conventional solid state reaction technique is normally in the range of 900-1100 °C [2,5,7,8].

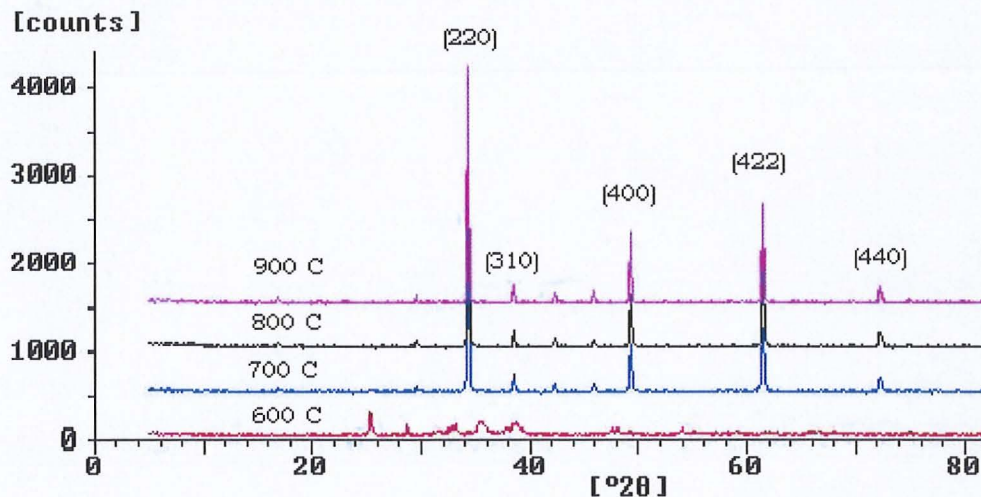


Figure 2. XRD patterns of the calcined powders at different temperature in the range of 600-900 °C for 12 hrs.

The XRD pattern result of sintered pellet is almost similar with those calcined powders. This indicates that the CCTO phase formed during the calcination processing has been complete and very stable. See Figure 3 and compare to Figure 2. There is no additional major peak was detected that would indicate the formation of secondary phase after the higher temperature sintering of 1050 °C.

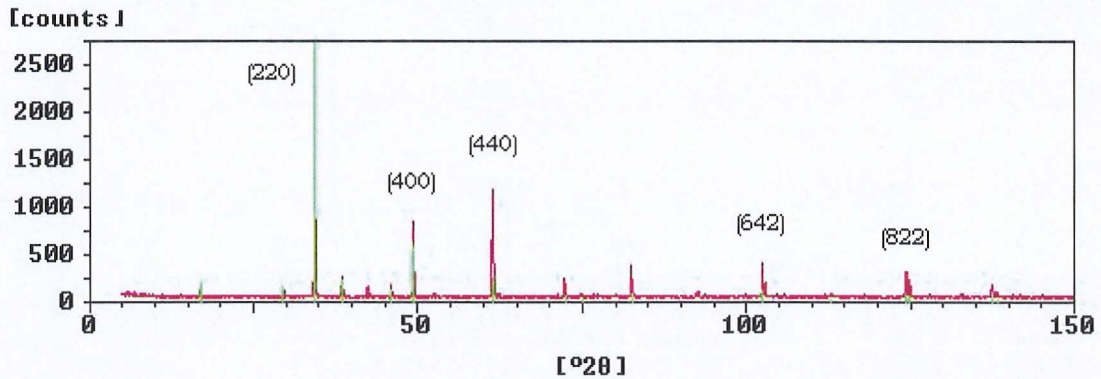


Figure 3. XRD pattern of sintered pallet at 1050 °C for 24 hours. Pellet was formed from the calcined powders at 900 °C for 12 hrs.

Figure 4 shows the XRD analysis results for samples calcined at 750°C for 6, 9, 12, 16 and 24 hours by using Siemens D-5000 diffractometer. The XRD patterns shows that the formation of single-phase  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  has been formed completely at 750°C starting at calcination time 9 hours and the crystalline structure was improved as calcined time increasing to 12 hours, 16 hours and 24 hours. All the peaks detected are corresponded to  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  “Referance Pattern” with ID card number: 01- 075- 2188. The position of diffraction peak can be detected by the overlapping of compound’s peak with the standard peak at 34.289°, 49.2762°, 61.487° and 82.4704° angles with (220), (400), (422), (440) and (620) peaks. It is thus confirmed that calcination time of 9 hours has been enough to form  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  by modified mechanical alloying technique. This calcination time is much shorter than calcination time of via conventional solid state reaction. Calcination temperature at 750°C with calcination time of 9 hours had been applied on the preparation of the doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ .

The dielectric constant testing was conducted by using Agilent 4284A Precision LCR meter, which can be conducted at different frequencies, between the 10Hz and 1MHz range. In this work, 4 parameters of frequencies had been fixed up during conducting the tests which are 50 Hz, 100 Hz, 1000 Hz and 1000000 Hz. Figure 5 shows the dielectric constant versus log of frequency graph for samples samples calcined at 750°C for 9 hours with different percentage moles of zinc. For that graph, the dielectric constants keep on decreasing by increasing the frequency.

The mechanisms of polarization have varying time response capability to an applied field frequency, and the net contribution of polarization to the dielectric constant is therefore frequency dependent. Electronic displacement responds rapidly to the field reversals, and no lag of the polarization contribution occurs at higher frequency. As is expected, ions, which are larger and must shift within the crystal structure, are less mobile, and have a less rapid response. At high frequency, the ionic displacement begins to lag the field reversals, increasing the loss factor and contributing less to the dielectric constant. At higher frequency, the field reversals are such that the ions no longer see the field (the

natural frequency of ions is less than the applied frequency), and no polarization (or loss factor) contribution is made by ionic displacement.

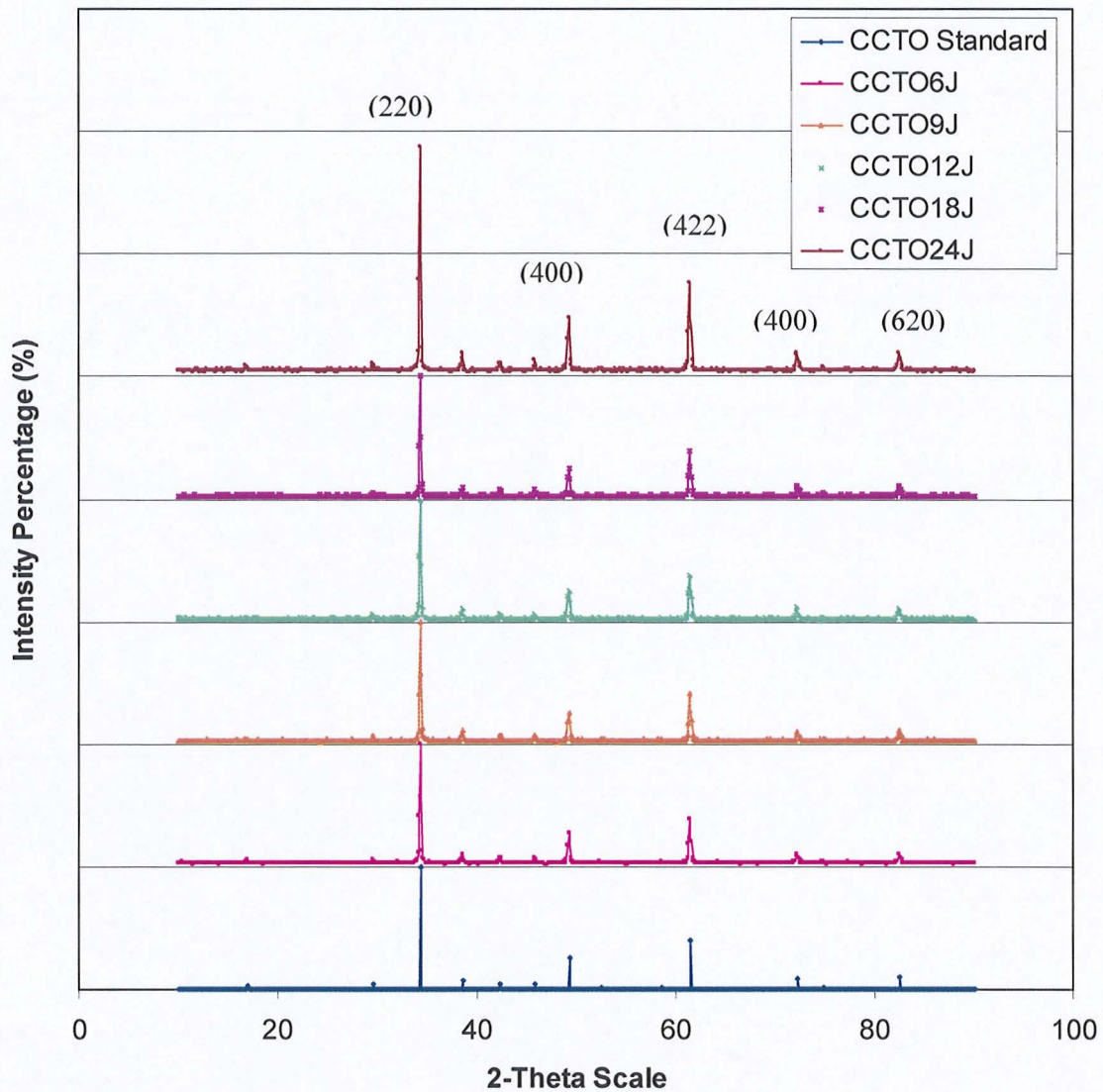


Figure 4. XRD Patterns of the calcined powders at different calcination time.

To look into the effect of the doping of zinc, Figure 6 shows the dielectric constant versus percentage moles of zinc, which are 1, 2, 3, 5 and 10% at 1000 Hz. The dielectric constant of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  pellets was found to be increasing with molarities percentages of zinc. This trend is well correlated to the relative microstructure of the pellet where the grain size had increased with the molarities percentages of zinc. From the SEM image, which is doped with 10% moles of zinc, has a larger and more integral grain size than the others. The surface analysis of SEM images shows that the giant dielectric constant of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is dependent on the grain size. The larger and more integral grain can contribute the higher dielectric properties.

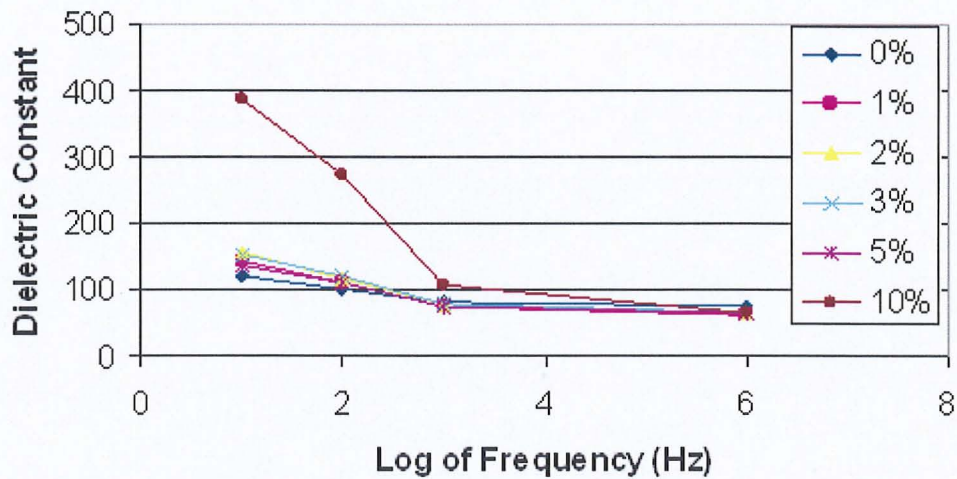


Figure 5. Dielectric Constant versus Log of Frequency graph for samples calcined at 750°C for 9 hours with different percentage moles of zinc.

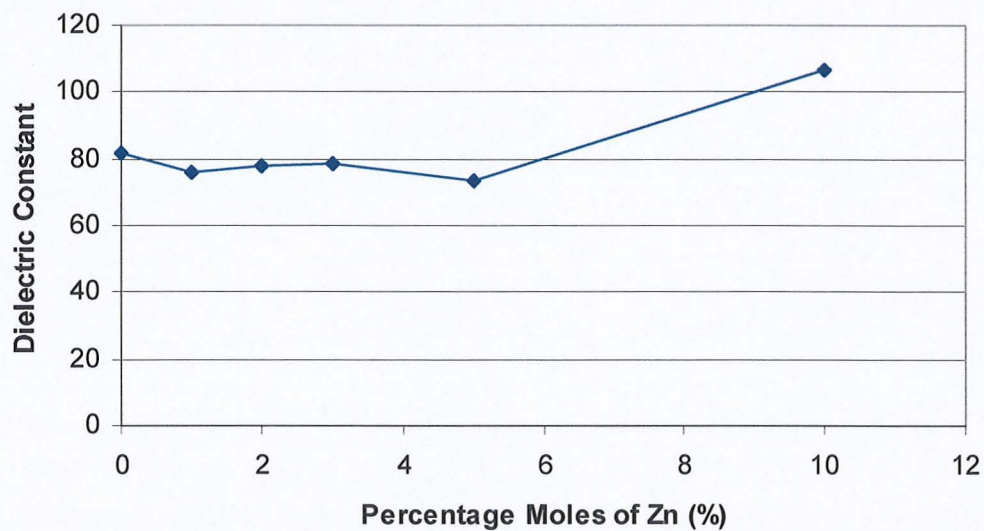


Figure 6. Dielectric constant value as a function of the molarities percentages of zinc.

The dielectric loss is closely related with the mechanism of the dielectric response. Based on the widely-accepted internal-barrier-layer-capacitance (IBLC) model, the dielectric loss mainly originates from the conductivity of the  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  conducting crystalline grains/subgrains as well as that of the insulating barriers. The conductance of the barriers leads to the leakage loss.  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  exhibits very high dielectric constant, which is desirable for many micro-electric applications. However, the dielectric loss of the material is relatively high. Therefore, in this work,  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is doped with zinc in the hope of lowering the dielectric loss.

The dielectric loss testing is also being conducted by using the Agilent 4284A Precision LCR machine, which can be conducted at different frequencies, between the 10Hz and 1MHz range. In this work, the dielectric loss is being expressed in dissipation factor and Q factor. Figure 7 shows the dissipation factor versus log of frequency graph for samples  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  calcined at  $750^\circ\text{C}$  for 9 hours with different percentage moles of zinc. The graph shows the decreasing of dissipation factor by increasing of frequency. While, Figure 8 shows the Q factor versus log of frequency graph for samples  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  calcined at  $750^\circ\text{C}$  for 9 hours with different percentage moles of zinc. By increasing the frequency, the Q factor of the doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  also increased. These unique properties of the doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  to the frequency make it a very promising material for microwave application which need a high Q factor over a wide range of frequency.

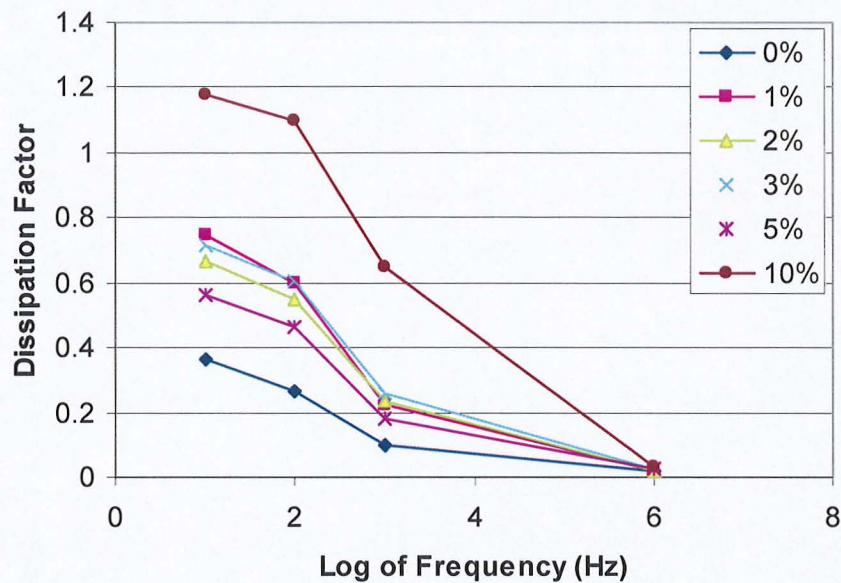


Figure 7. The dissipation factor versus log of frequency graph for samples  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  calcined at  $750^\circ\text{C}$  for 9 hours with different percentage moles of zinc.

To study the effects of the doping, Figure 9 shows the dissipation factor versus percentage moles of zinc graph at 1000 Hz. While, Figure 10 shows the Q factor versus percentage moles of zinc graph at 1000 Hz. From the rise and fall of the curve in Figure 9 and Figure 10, we can find out that by doping with certain amount of zinc dopant, the properties for dielectric loss can be improved. The sample of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  doped with 5 % Zn shows good dielectric loss properties, which is giving the lowest dissipation factor or the highest Q factor if compared to others doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ .



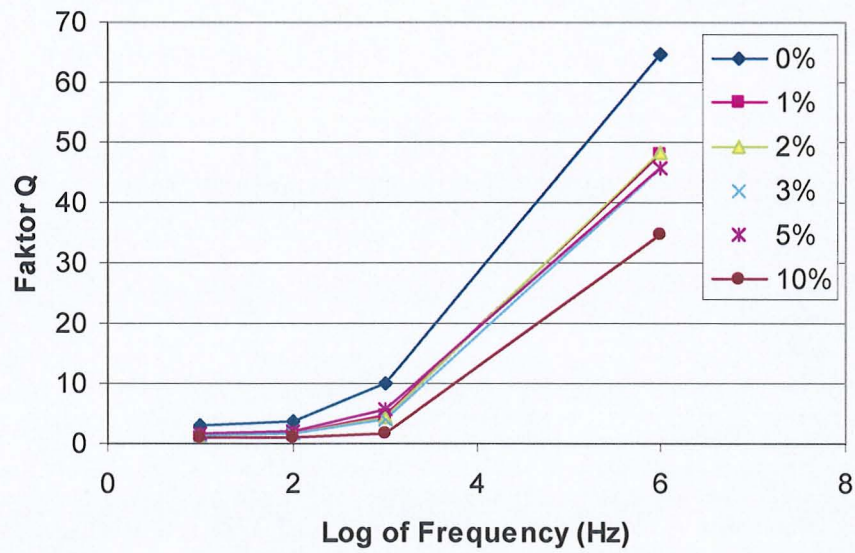


Figure 8. The Q factor versus log of frequency graph for samples  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  calcined at  $750^\circ\text{C}$  for 9 hours with different percentage moles of zinc.

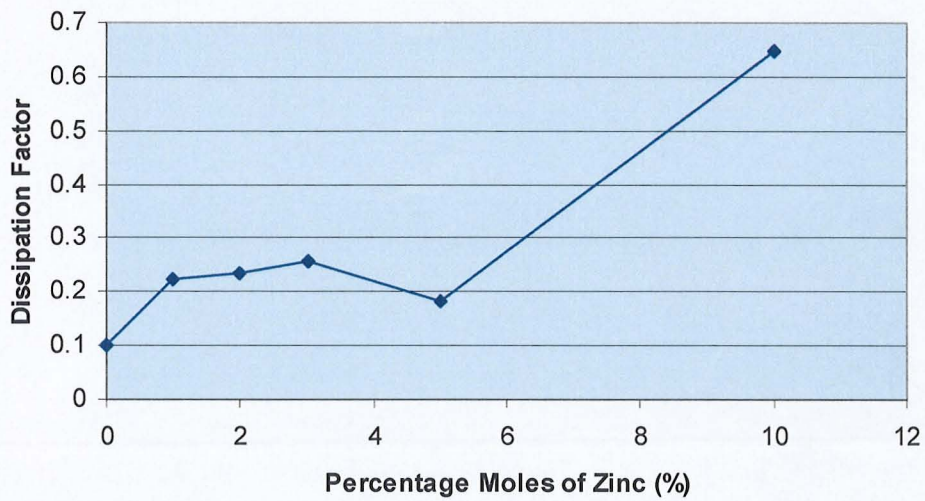


Figure 9. The dissipation factor versus percentage moles of zinc graph at 1000 Hz.

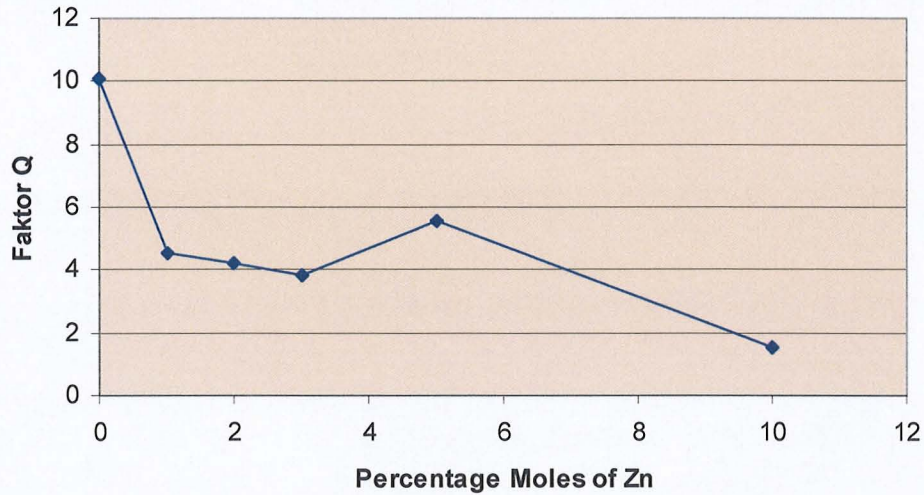


Figure 10. The Q factor versus percentage moles of zinc graph at 1000 Hz.

Electrical resistivity also known as specific electrical resistance is a measure of how strongly a material opposes the flow of electric current. A low resistivity indicates a material that readily allows the movement of electrical charge. Figure 11 shows the resistivity versus log of frequency graph for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  samples calcined at  $750^\circ\text{C}$  for 9 hours with different percentage moles of zinc dopant. The graph shows that the resistivity is decreasing by increasing the frequency. To study on the effect of doping, Figure 10 shows the resistivity versus percentage moles of zinc graph at 1000 Hz. Metals like zinc have very low resistivities and are known as conductors which contain some electrons that can move rather freely. Therefore, by increasing the percentage moles of zinc, the resistivity for doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  will be reduced. However, the rise and fall of the curve in Figure 12 is the amount of zinc dopant effect.

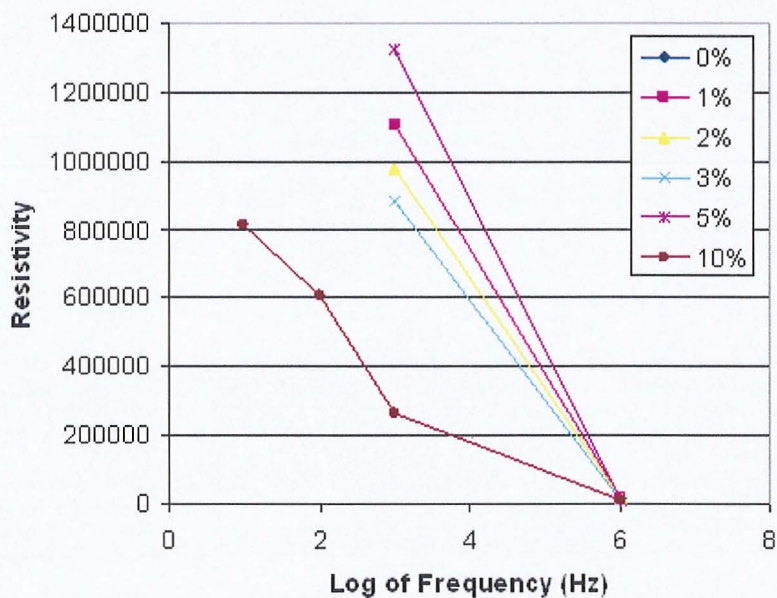


Figure 11. The resistivity versus log of frequency graph for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  samples calcined at  $750^\circ\text{C}$  for 9 hours with different percentage moles of zinc dopant.

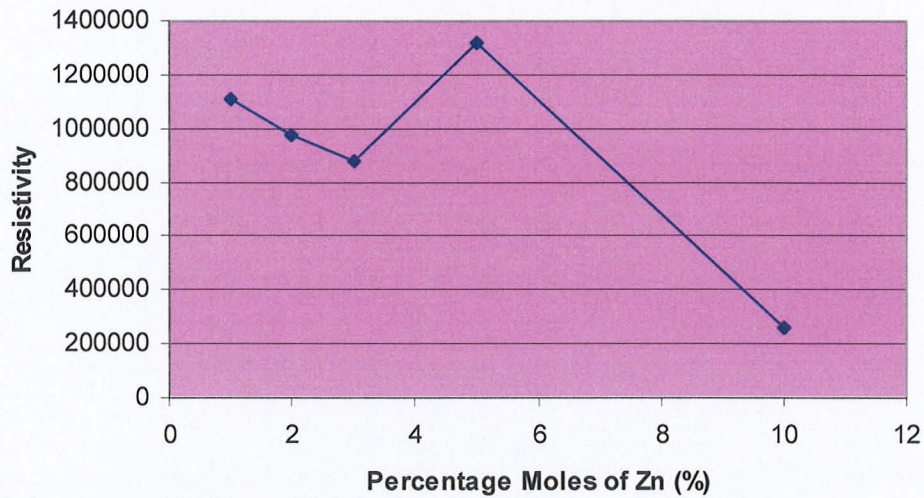


Figure 12. The resistivity versus percentage moles of zinc graph at 1000 Hz.

Surface observation and analysis of the grain-boundary-grained structure were carried out by using scanning electron microscopy. Figure 13 shows the SEM image for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  samples sintered at  $900^\circ\text{C}$  for 24 hours with 15000 magnifications, while Figure 14 shows the SEM image of sample  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  sintered  $1050^\circ\text{C}$  for 24 hours with 1000 magnification. For the sintering temperature at  $900^\circ\text{C}$ , the temperature is too low and the grain of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is not growing enough. In the other hand, for the sintering temperature at  $1050^\circ\text{C}$  at 24 hours, the grain begins to be destroyed which may be due to the high sintering temperature and time.

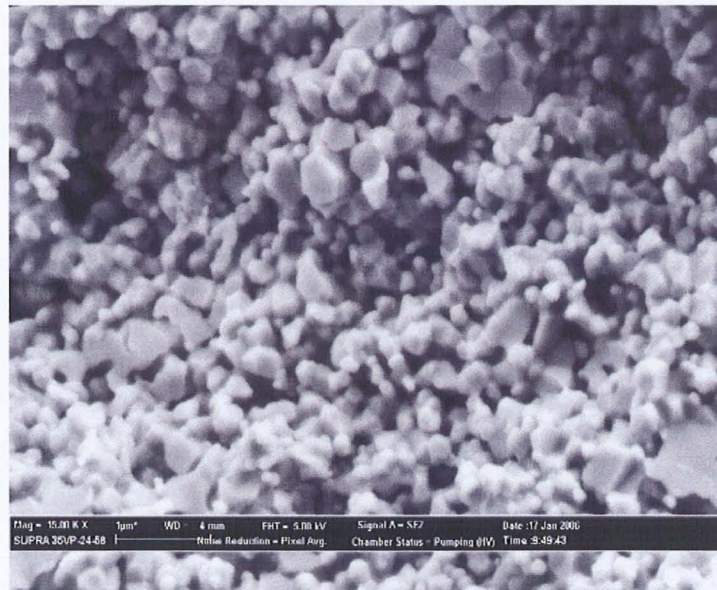


Figure 13. SEM image of sample  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  sintered  $900^\circ\text{C}$  for 24 hours

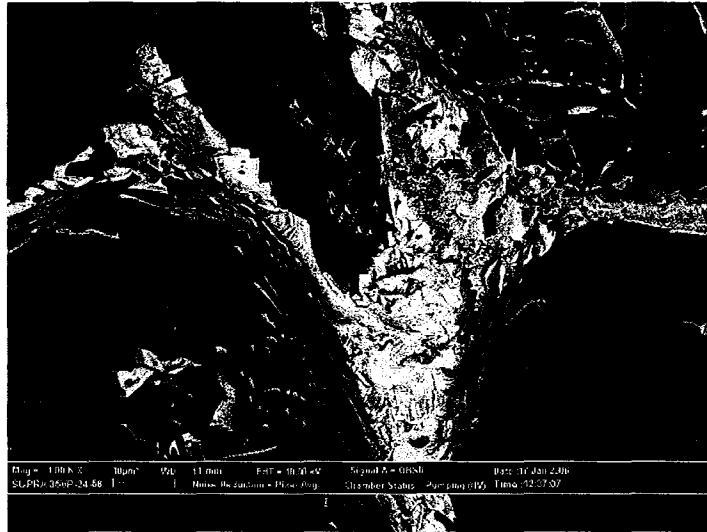


Figure 14. SEM image of sample  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  sintered  $1050^\circ\text{C}$  for 24 hours

Looking for better sintering parameters, another 2 parameters were being tried out. Figure 15 shows the SEM image of sample  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  sintered  $950^\circ\text{C}$  for 24 hours with 30000 magnifications. While, Figure 16 shows the SEM image of sample  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  sintered  $1050^\circ\text{C}$  for 4 hours with 500 magnifications. From the SEM images, it is found that SEM image of sample  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  sintered  $950^\circ\text{C}$  for 24 hours shows a very clear microstructure. In the other hand, the SEM image of sample  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  sintered  $1050^\circ\text{C}$  for 4 hours shows that the grain begins to be destroyed due to the high sintering temperature. Therefore, for the stage 2 which is the preparation of doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ , sintering parameter of  $950^\circ\text{C}$  for 24 hours was being applied on all doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ .

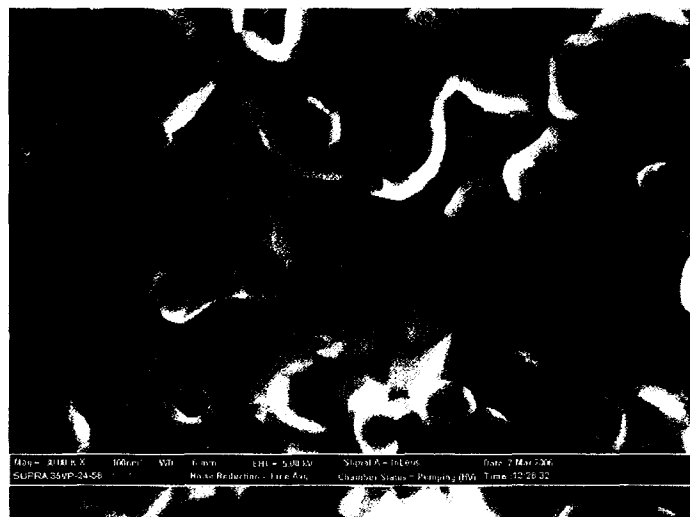


Figure 15. The SEM image of sample  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  sintered  $950^\circ\text{C}$  for 24 hours

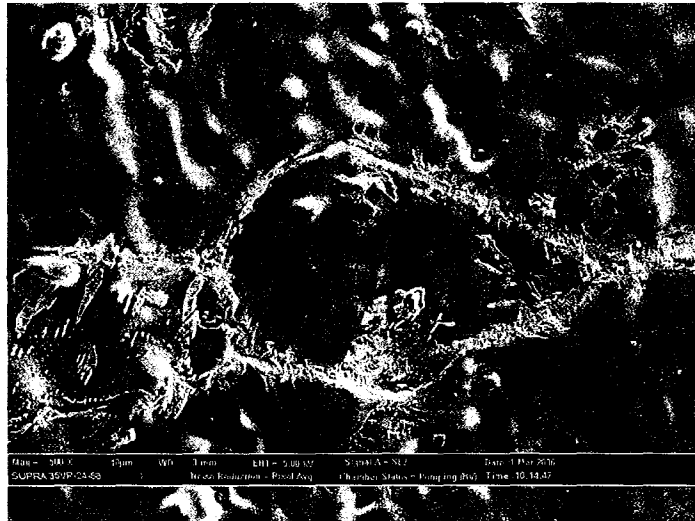


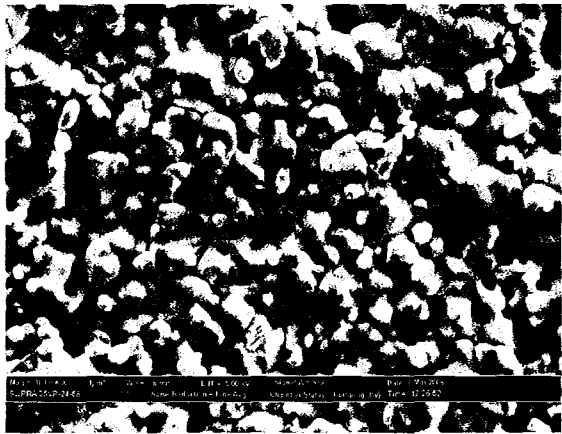
Figure 16. The SEM image of sample  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  sintered  $1050^\circ\text{C}$  for 4 hours

Looking for the effect of doping zinc in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ , Figure 17 show the SEM image of sample  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  sintered  $950^\circ\text{C}$  for 24 hours with different percentage moles of zinc which are 0, 1, 2, 3, 5 and 10%. From the SEM images, it is found that sample  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  doped with 10% Zn sintered  $950^\circ\text{C}$  for 24 hours has a larger and more integral grain size than the others doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ . The surface analysis of SEM images shows that the giant dielectric constant of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is dependent on the grain size.

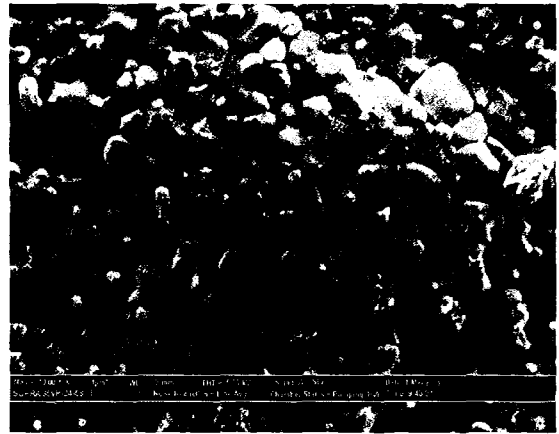
### Solid State Reaction Technique Results

In the solid state reaction technique, the sample was calcined at  $900^\circ\text{C}/12$  hours and sintered at  $1050^\circ\text{C}/24$  hours, then subjected to XRD to ensure CCTO formation. The microstructure was observed by SEM. XRD results identified both samples were single phase CCTO, whereas the microstructure shows abnormal grain growth and large pores. Sintering was studied in the temperature range of  $950\text{--}1050^\circ\text{C}$  for 3–12 hours. Increasing sintering temperature enhances the density and secondary formation of  $\text{Cu}_2\text{O}$ . A clear grain boundary and dense microstructure were observed. The results show that the sample sintered at  $1040^\circ\text{C}/10$  hours yields a clearly uniform grain size with the highest  $\epsilon_r$  (33210) [9].

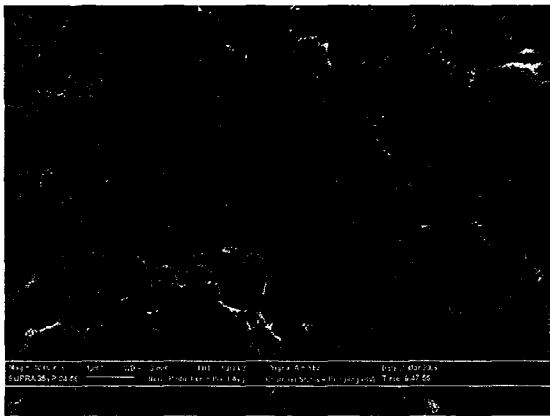
The sintering parameter of  $1050^\circ\text{C}$  for 24 hours was applied in this work. Single phase CCTO was identified in both calcined and sintered powders. We have tried to keep our experimental condition quite close to those reported for formation of CCTO, but SEM observation only shows evidence for melting and abnormal grain growth, with large pores (Figure 18). Figure 19 shows the XRD analysis for the samples sintered at different temperature for the same soaking time. The samples sintered at  $950\text{--}1030^\circ\text{C}$  show the single phase CCTO, but a minor phase was detected for the sample sintered at  $1050^\circ\text{C}$ . XRD analysis shows the presence of  $\text{Cu}_2\text{O}$ . Theoretically, the  $\text{Cu}^{2+}$  cations are reduced at  $T \approx 1000^\circ\text{C}$  into  $\text{Cu}^+$ . The  $\text{Cu}^+$  will reoxidize during the cooling [11]. Subramaniam et. al., also reported the existence of impurity  $\text{CuO}$  in their samples of CCTO. Initial assumption made based on XRD analysis was that for samples sintered at  $1050^\circ\text{C}/24$  hours only consist of a CCTO single phase due to undetected  $\text{Cu}_2\text{O}$  glassy phase.



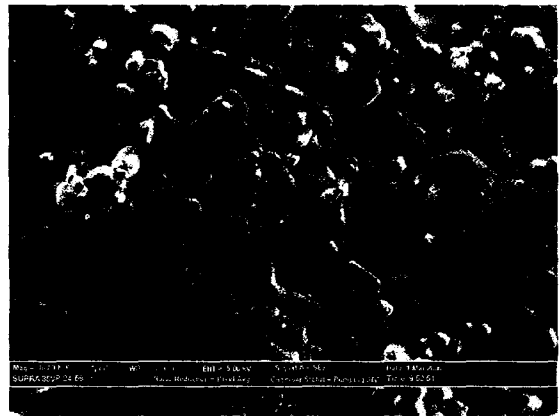
Undoped



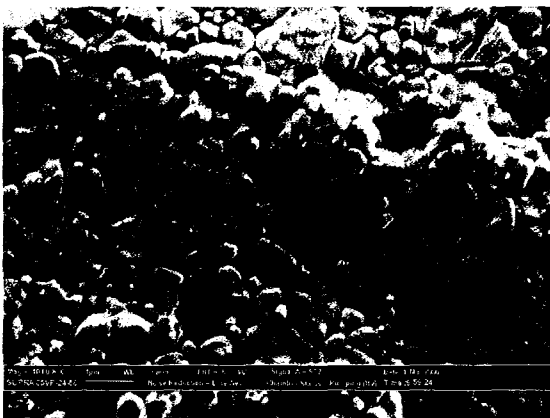
1% Zn



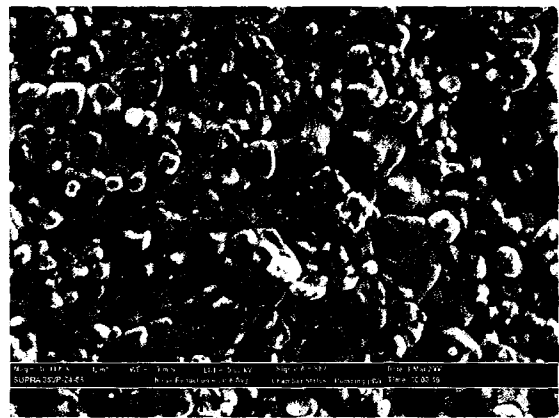
2% Zn



3% Zn



5% Zn



10% Zn

Figure 17. SEM image of undoped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  and Zn-doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  sintered  $950^\circ\text{C}$  for 24 hours.



Figure 18. The microstructure of the melt and abnormal grain growth for sample sintered at 1050°C for 24 hours (Mag: 1000X).

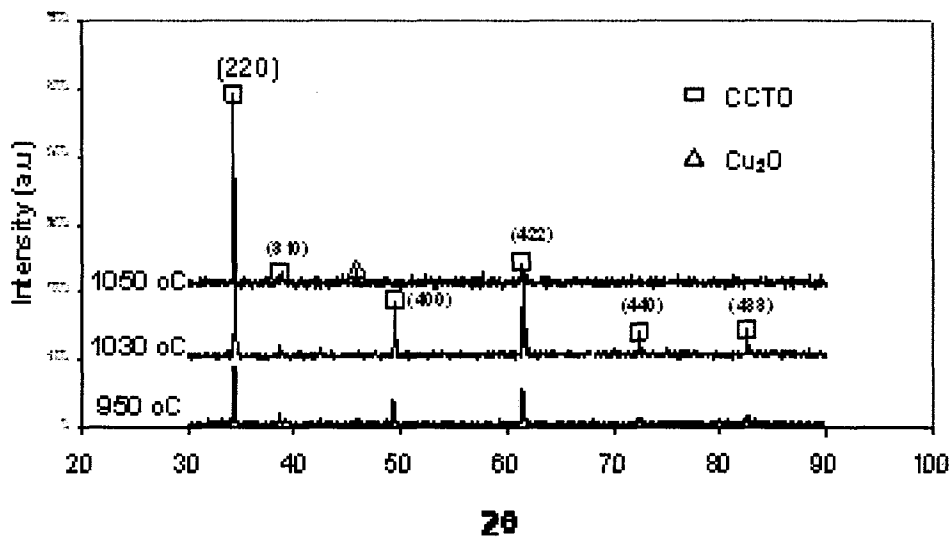


Figure 19. XRD analysis for samples sintered at different temperature for 12 hours.

Figure 20(a) shows the SEM micrographs of CCTO sintered at different temperatures. A porous microstructure with small grain size is observed in the specimen sintered at 950°C. Increasing the sintering temperature significantly promotes the grain growth and microstructural densification. The grain growth in the sintered specimens sintered above 1030°C implies an increase in the amount of liquid phase. The 1050°C for 12 hours samples show the liquid phase phenomena. When the soaking time was increases to 24 hours, the whole structure melt. Further study was made by sintering the samples at 1040°C with different soaking time (Figure 20(b)).

The 3 and 6 hours sintered samples show fairly uniform grain sizes with clear grain boundaries. The densest microstructure was obtained for a sample sintered for 10 hours. The grain size is in the range of 1-3μm. With further sintering to 12 hours, the sample

began to melt. This may have happened due to the secondary recrystallization and possible vaporization of Cu during the very long sintering time. The presence of Cu was confirmed by EDX analysis. Fritsh et. al., (2006) reported that the huge grains observed for the CCTO that contain CuO are also probably related to the appearance of a liquid phase that wets the grain during the sintering. Small amounts of CuO are believed to be responsible for the abnormal grain growth.

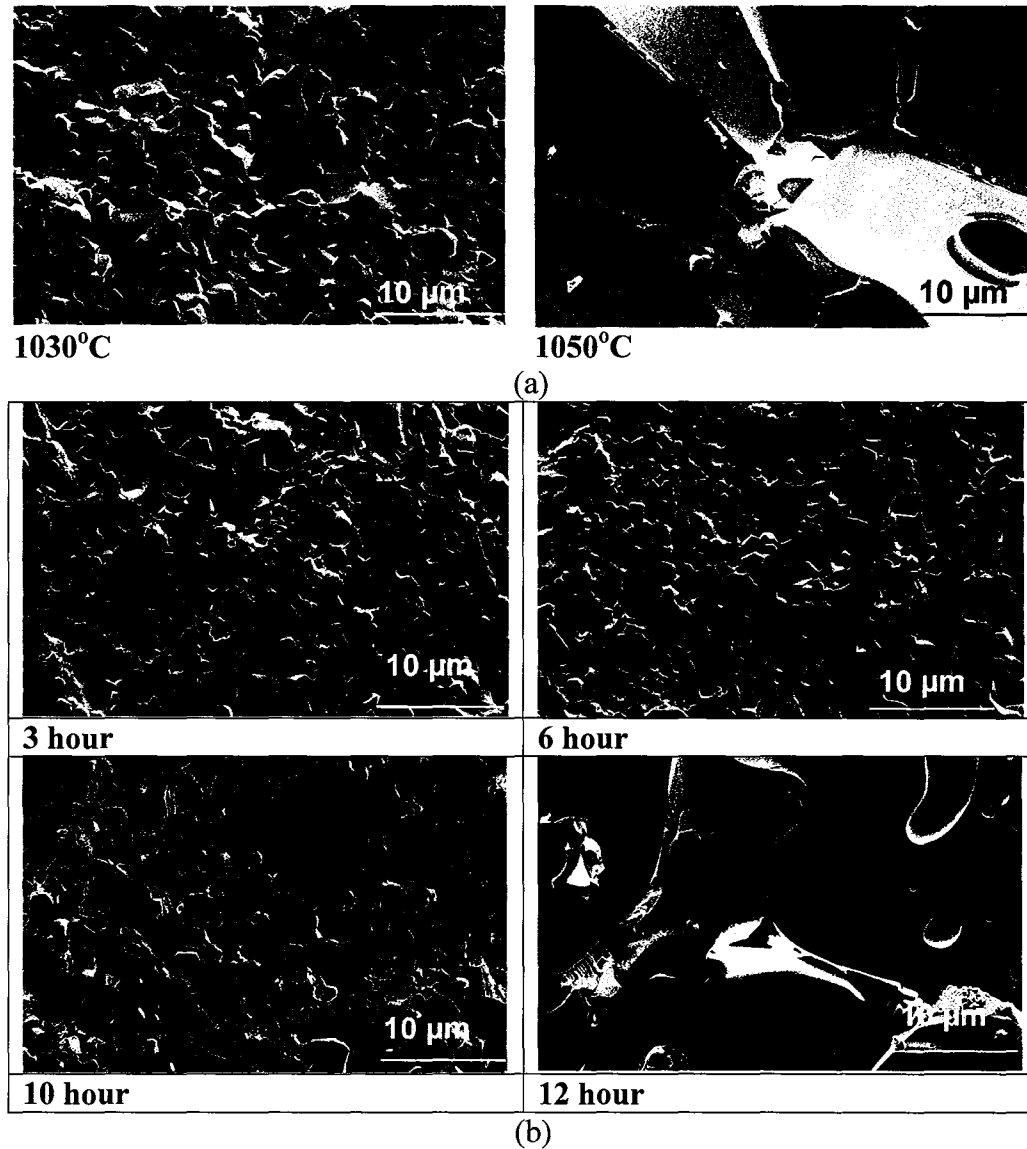


Figure 20. SEM micrographs of CCTO ceramics sintered (a) at different temperatures for 12 hours and (b) at 1040°C with different sintering times.



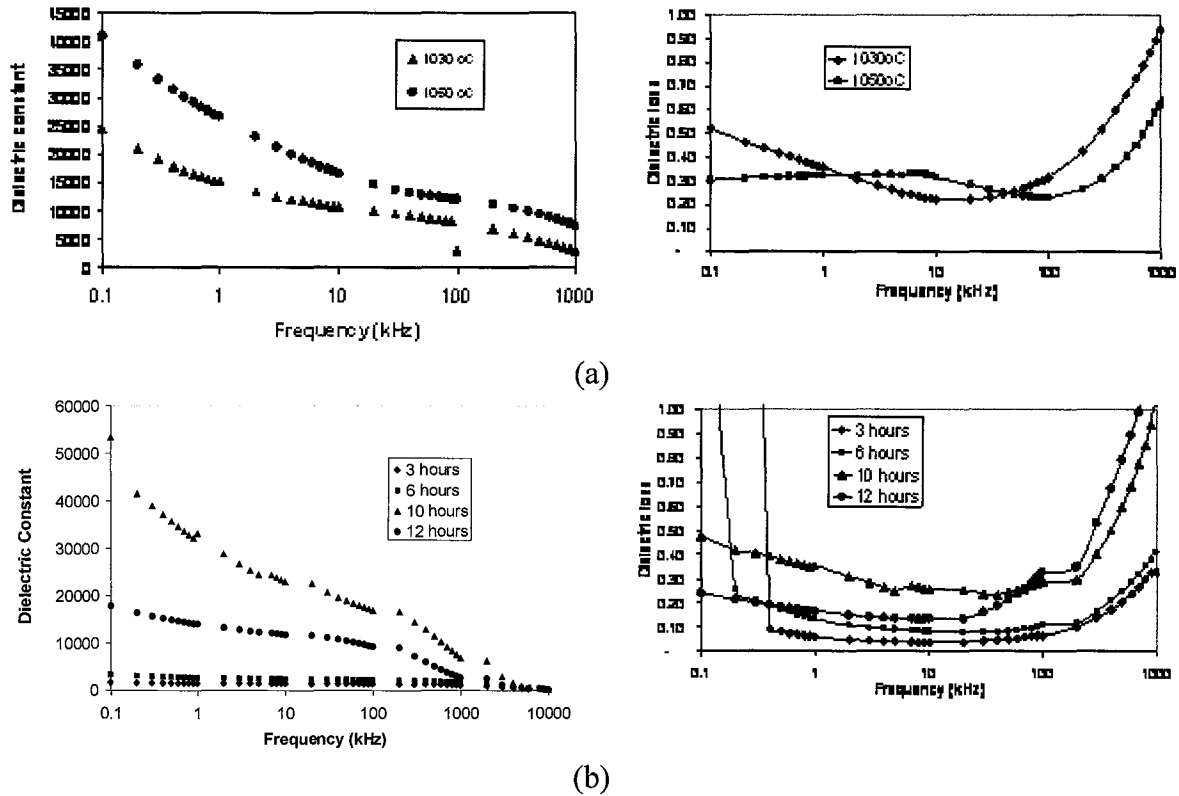


Figure 21. The  $\epsilon_r$  and dielectric loss value against frequencies for samples sintered at different (a) temperatures and (b) soaking times.

Figure 21 shows the results of  $\epsilon_r$  and dielectric loss for CCTO samples. For  $\epsilon_r$ , as the frequency increased, each curve presents a plateau followed by a drop for 1 GHz. At 1 kHz, the  $\epsilon_r$  for the samples sintered at 1030 and 1050°C, were 15218 and 26743, respectively (Figure 21 (a)). For Figure 21(b), at 1 kHz, the  $\epsilon_r$  for samples sintered at 1040°C for 3, 6, 10, and 12, were 1569, 2720, 33210 and 14117, respectively. The dielectric loss is around 0.2-1.0, and the value starts to increase at higher frequency. The highest  $\epsilon_r$  value obtained in this study and measured at room temperature was 33210 i.e. for the sample sintered at 1040°C for 10 hours. Subramaniam et. al. [3], first reported that  $\epsilon_r$  for bulk CCTO at 1 kHz was around 10000–12000. The value from our experiment was three times higher than earlier reported.

## CONCLUSION

This modified mechanical alloying technique is chosen for this work to enable the calcination and sintering process in future carried out in shorter time and lower temperature, so that can save money and energy. For dielectric properties, the dielectric constant increased by molarities percentage dopant of zinc. The increasing of dielectric constant is not consistent, as the  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  doped with 5 % Zn will give a lower dielectric constant value. However, the sample of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  doped with 5 % Zn shows good dielectric loss properties, which is giving the lowest dissipation factor or the highest Q factor if compared to others doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ . Besides that, it also shows high resistance and low conductance value. Therefore, it can be concluded that by doping with

certain amount of zinc dopant, the properties for dielectric and dielectric loss can be improved.

In solid state reaction technique, sample sintered at 1050°C for 24-hour shows the melting and abnormal grain growth. The effects of different sintering conditions on density, phase formation, microstructure and dielectric properties were discussed. Increasing sintering temperature enhances the density. A clear grain and dense microstructure were observed for the samples sintered at 1000 and 1030°C for 12 hours, and for the samples sintered at 1040°C for 3, 6 and 10 hours. The melting grains in sample sintered at 1050°C for 12 hours show the existence of new phase, Cu<sub>2</sub>O. The highest  $\epsilon_r$  (33210) with clearly uniform grain was obtained by the sample sintered at 1040°C for 10 hours.

## ACKNOWLEDGEMENTS

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 TEMPOH BERAKHIR 31 OGOS 2006

DR SABAR DERITA HUTAGALUNG

304.PBAHAN.6035119

**EFFECT OF ANNEALING CONDITION ON THE ELECTRICAL & STRUCTURAL PROPERTY OF FERROE**

JUMLAH GERAN :-

Tempoh Projek:01/03/2004 - 31/08/2006

NO PROJEK :-

PANEL :- JIPEDEK

PENAJA :-

Vot

	Peruntukan (a)	Perbelanjaan sehingga 31/12/2005 (b)	Tanggungan semasa 2006 (c)	Belanja Semasa 2006 (d)	Jum. Belanja 2006 (c + d)	Jumlah Belanja Terkumpul (b+c+d)	Baki Peruntukan Semasa 2006 (a-(b+c+d))
11000: GAJI KAKITANGAN AWAM	3,150.00	2,390.52	0.00	0.00	0.00	2,390.52	759.48
21000: PERBELANJAAN PERJALANAN DAN SARAHAI	4,100.00	2,996.99	0.00	360.00	360.00	3,356.99	743.01
23000: PERHUBUNGAN DAN UTILITI	145.00	0.00	0.00	0.00	0.00	0.00	145.00
24000: SEWAAN	100.00	0.00	0.00	0.00	0.00	0.00	100.00
26000: BAHAN MENTAH & BAHAN UNTUK PENYELE	700.00	0.00	0.00	0.00	0.00	0.00	700.00
27000: BEKALAN DAN ALAT PAKAI HABIS	4,500.00	6,186.27	4.80	(339.25)	(334.45)	5,851.82	(1,351.82)
29000: PERKHIDMATAN IKTISAS & HOSPITALITI	2,950.00	3,130.67	15.00	900.00	915.00	4,045.67	(1,095.67)
	<u>15,645.00</u>	<u>14,704.45</u>	<u>19.80</u>	<u>920.75</u>	<u>940.55</u>	<u>15,645.00</u>	<u>0.00</u>
Jumlah Besar	<u>15,645.00</u>	<u>14,704.45</u>	<u>19.80</u>	<u>920.75</u>	<u>940.55</u>	<u>15,645.00</u>	<u>0.00</u>



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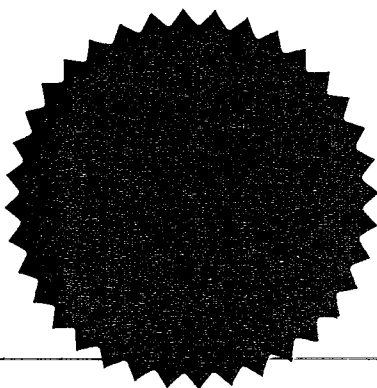
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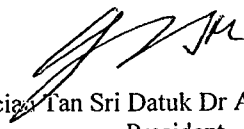
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## Preparation of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) by Modified Mechanical Alloying Technique

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**Abstract.**  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) compounds with a perovskite-type structure have been reported of many researcher that show very high dielectric constant value and temperature independent over a wide temperature range. In this work, the CCTO were prepared by modified mechanical alloying technique. The starting materials of  $\text{Ca}(\text{OH})_2$ ,  $\text{CuO}$  and  $\text{TiO}_2$  powders were weighed according to the stoichiometric ratio and fast ball milling in sealed alumina vial under ambient condition for 5 hours. The mixed powder was submitted to calcination at 600, 700, 800 and 900 °C in air for 12 hours, respectively. The calcined powder was then pressed into a pellet using a stainless steel die set with a diameter of 6 mm and 1 mm in thickness. The prepared pellets were sintered in air at 1050°C and soaking time of 24 hours. Phase analysis was conducted on the calcined powders and sintered pellets by using XRD. The XRD analysis results, shown, that single phase CCTO phase have been successfully synthesized during calcination process at 700-900°C and crystalline structure was improved after sintered at 1050°C for 24 hours. Dielectric constant value of CCTO sintered pellets was obtained up to 11903.

**Keywords:** CCTO, high-dielectric constant, modified mechanical alloying.

### 1. Introduction

The complex perovskite compound  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) has recently attracted considerable attention in view of its anomalously large dielectric response. Low-frequency studies uncovered dielectric constant up to 10,000 for ceramics and 80,000 for single-crystal samples that are nearly constant over a wide temperature range (100-600 K). This unique property make CCTO a promising material for capacitor applications and certainly for microelectronics, microwave devices (cell mobile phones for example) [1, 2]. Moreover, above a critical frequency that range between 10 Hz and 1 MH, dielectric constant value depending on temperature [3]. The highest value of dielectric constant expected obtained during a phase transition as a function of temperature.

With the shrinking of dimensions of the microelectronic devices, high dielectric constant materials have been playing a significant role in microelectronics, since they can be used as important devices such as DRAM based on capacitive elements. Most of the CCTO studies have been performed on bulk materials (ceramics or single crystals) and focused on the identification of the mechanism responsible for unusual CCTO properties [4]. In order to apply CCTO in microelectronic devices and to determine a more fundamental understanding of its properties, will be prepared CCTO thin films by pulsed laser deposition. Lasers can be used to fabricate thin extended films by condensing on a substrate surface the material that is ablated from a target under the action of laser light [5-7]. Recently, ceramic composite of  $\text{BaTiO}_3$ -  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  screen-printed thick films for high dielectric devices application in the medium frequency range have been studied

intensively by Almeida et al. [8]. The composite of high dielectric constant and low loss films are very attractive for use in microwave devices like dielectric resonators and miniaturization of the microelectronic devices.

The unit cell of a cubic perovskite-related material  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is shown in Figure 1. The Ti atoms sit at the center of canted  $\text{TiO}_6$  octahedra (tilt angle is nominally  $141^\circ$ ), which bridging Cu atoms and large Ca atoms sitting at the center and corners of the unit cell [9].

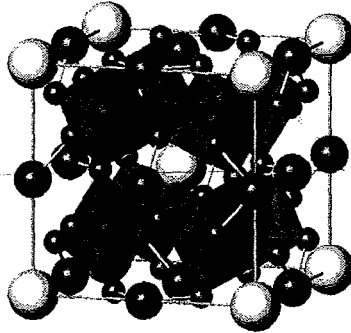


Fig. 1. The unit cell of body-centered cubic  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  [9].

CCTO has been found as a material exhibit a giant dielectric constant with relatively temperature independent over a wide temperature range between 100 and 600 K. However below 100 K its value drops abruptly almost three order of magnitude. Local structural properties of CCTO system as a function of temperature was investigated within a range from 50 K up to room temperature [8]. The temperature dependence of the nearest neighbour Cu-O distance is very flat, supporting the idea that this is bracing the structures. However, an unusual temperature dependence for the atomic displacement parameters of calcium and copper is observed. Temperature dependent modelling, suggests that the Ca atoms become underbonded at low temperature.

Mechanical alloying technique has been used to produce CCTO by using two different experimental procedures [1]. Although this technique is able to produce nanocrystalline powders of CCTO, but this process need a very long milling time up to 100 hours to obtain a single-phase of CCTO formation. To solved this problem, in this work we try to reduced the milling time to 5 hours and then following by calcination process at 600-900 °C to produce a single-phase CCTO formation.

## 2. Experimental

The  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) were prepared by modified mechanical alloying technique. The starting materials of  $\text{Ca}(\text{OH})_2$ , CuO and  $\text{TiO}_2$  powders were weighed according to the stoichiometric ratio and fast ball milling (1500 rpm) in sealed alumina vial under ambient condition for 5 hours. The mixed powder was submitted to calcination at 600, 700, 800 and 900 °C in air for 12 hours respectively. The calcined powder was then pressed into a pellet using a stainless steel die set with a diameter of 6 mm and 1 mm in thickness. The prepared pellets were sintered in air at 1050 °C and soaking time of 24 hours. Phase analysis was conducted on the both calcined powders and sintered pellets by XRD analysis using D8 Bruker diffractometer. Dielectric properties measurement (dielectric constant) were carried out on discs shape samples by using Philips PM6303 LCR meter at 1 kHz frequency in ambient temperature.

### 3. Results and Discussion

Figure 2 shows the XRD analysis results for calcined samples at different temperature of 600 °C, 700 °C, 800 °C and 900 °C by using D8 Bruker diffractometer. The XRD patterns shows that the formation of single-phase CCTO has been formed completely starting at sample calcined 700 °C and the crystalline structure was improved as calcined temperature increasing to 800 °C and 900 °C. All of the peaks detected are corresponded to CCTO (JCPDS File No. 21-0140). It is thus confirmed that calcination temperature of 700 °C has been enough to form CCTO by modified mechanical alloying technique. This calcination temperature is much lower than calcination temperature of CCTO via conventional solid state reaction that is normally in the range of 900-1100 °C [1,8,10-12].

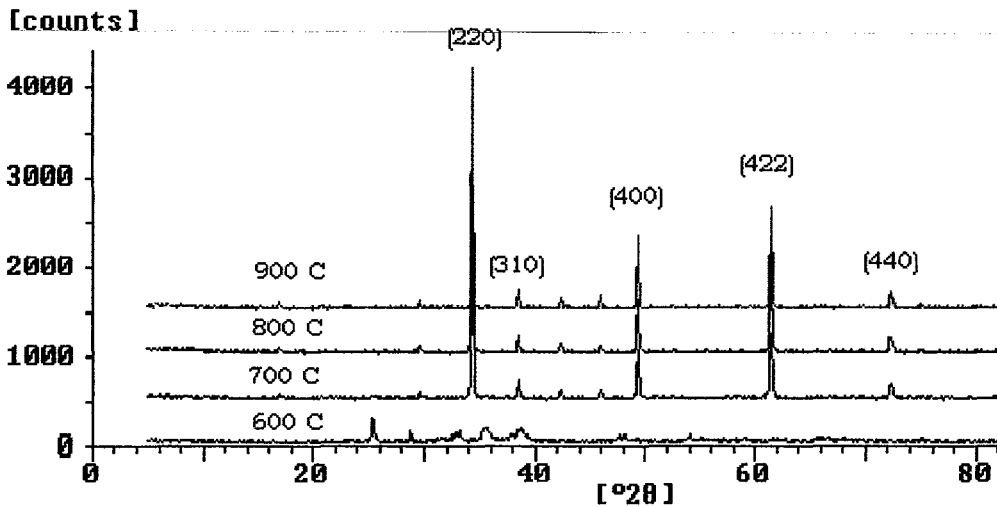


Fig. 2. XRD patterns of the calcined powders at 600-900 °C.

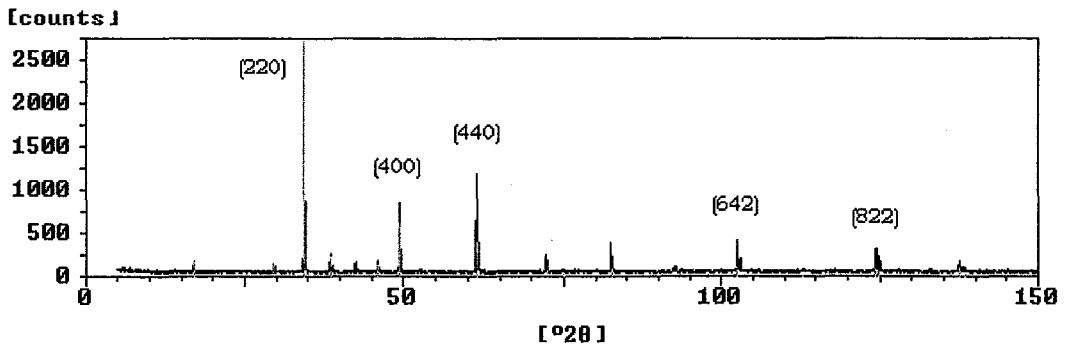


Fig. 3. XRD pattern of sintering pallet at 1050 °C for 24 hours.

The XRD pattern of sintered pellet is similar with those calcined powders indicating that the CCTO formation is stable, see Figure 3. There is no additional major peak were detected that would indicate the formation of secondary phase after the high temperature sintering of 1050 °C.

Figure 4 shows the dielectric constant of pellets with different calcination temperature and sintered at 1050 °C, 24 hours. The dielectric constant of pellets was found to be increasing with the calcined temperature with obtained value up to 11903. This trend is well correlated to the relative density and microstructural of the pellet where the density and grain size had increased with temperature.

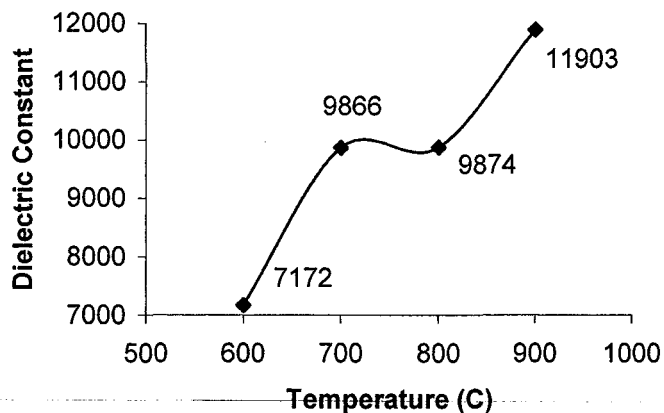


Fig. 4. Dielectric constant value as a function of calcination temperatures.

#### 4. Conclusion

The modified mechanical alloying by using combination of ball milling and solid state reaction method had proven to be another alternative processing method to produce a single-phase CCTO structures.

#### Acknowledgments

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## Microwave Characteristics Of CCTO Dielectric Resonators

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### Abstract

The microwave dielectric properties of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) have been investigated. CCTO was prepared by conventional solid state route.  $\text{CaCO}_3$ ,  $\text{TiO}_2$  and  $\text{CuO}$  powders were weighed according to stoichiometric ratios and mixed thoroughly in a ball mill for an hour. The mixed powder was calcined at 900 °C for 12 hours. The calcined powder was compacted into 5.0 mm diameter and 0.7 mm thick pellet at 300 MPa and sintered in air at 1050 °C for 24 hours. The calcined powder and the pellets were studied using X-Ray Diffraction (XRD) to identify the formation of single phase CCTO. Density and porosity of the sintered samples were measured by the Archimedes method. Dielectric constant ( $\epsilon_r$ ) and quality factor ( $Q \times f$ ) measurements were carried out using RCL meter at room temperature with 1 kHz frequency and network analyzer, respectively. The formation of single phase CCTO was confirmed by XRD analysis for the calcined powder and the sintered pellets. The microwave dielectric properties ( $\epsilon_r = 10\ 175$ ,  $Q \times f = 54\ 400$  (at 16 GHz)) was obtained from CCTO samples.

**Keywords:**  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ , microwave dielectric properties

### Introduction

Ceramic dielectric resonators have been used in place of metallic resonant cavities in RF and microwave circuits for several decades. The important application of dielectric resonators is to provide frequency stabilization of microwave integrated circuits (MIC) oscillators and filters [1]. Due to its desirable properties such as small sizes and low cost, a dielectric resonator not only acts as a frequency determination element but also offers good temperature stability.

Typical applications for these new ceramic dielectric resonators include cellular hand phone (PCS and GSM), satellite television receivers (TVRO and DBS), Global Positioning Systems (GPS), microwave oscillators, filters, speed guns, radar detection, motion sensors and transmitters. One significant advantage of using ceramics dielectric resonators is that the high dielectric constant ( $\epsilon_r$  or  $\kappa$ ) values which the ceramic can afford to reduce size of the circuits approximately equal to the square root of the ceramic's  $\epsilon_r$  value [2].

Nowadays, the highest dielectric constant value in electroceramic materials was obtained in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO). CCTO was discovered to possess one of the largest static dielectric constant ever measured, reaching nearly  $\epsilon_r \sim 80\ 000$  for single crystal samples and 10 000 for bulk material at room temperature. Previously, researchers only focus on its giant dielectric constants properties. They state about the possible applications of this material as a resonators, filters, antennas and etc. [3, 4, 5, 6]. However, there was no study or test was conducted on  $Q \times f$  behaviour of CCTO in order to become a dielectric resonator. In this paper, the  $Q \times f$  of CCTO were studied whether this material is suitable to be used as one of the dielectric resonators existed nowadays. In addition, high dielectric constant value of CCTO will reduce the size of this component.

### Approach and Methods

Sample of CCTO dielectric resonator was synthesized by conventional solid state method from individuals high-purity powders:  $\text{CaCO}_3$  (Aldrich, 99 %),  $\text{TiO}_2$  (Merck, 99 %) and  $\text{CuO}$  (Aldrich, 99 +%). The starting materials were weighed in the appropriate stoichiometric ratios. The mixed powders were ball milled for 1 hour using zirconia balls. The homogenous mixture was then calcined in air at 900 °C for 12 hours. A powder exhibiting free flowing

characteristics was then obtained by sieving the dried calcined powders. The fine powder was pressed into pellets with dimensions of 5 mm diameter and 0.7 mm in thickness under the pressure of 300 MPa. These pellets were sintered in normal atmosphere at 1050 °C for 24 hours. The heating and cooling rate were both set at 5 °C / min. The phase purity, structure and lattice parameters of the calcined powder and sintered samples were identified using an X-Ray Diffraction (XRD) performed on D8 Bruker with a CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Density and porosity of the sintered samples were measured by the Archimedes method. The dielectric constant of CCTO pellets which had been electroded with silver paste were measured using Philips RCL meter PM 6303 at room temperature with 1 kHz frequency. The  $Q \times f$  value was determined by mounting the sample close to a brass microstrip transmission line which both ends were connected to the HP 8720D Network Analyzer.

### Results

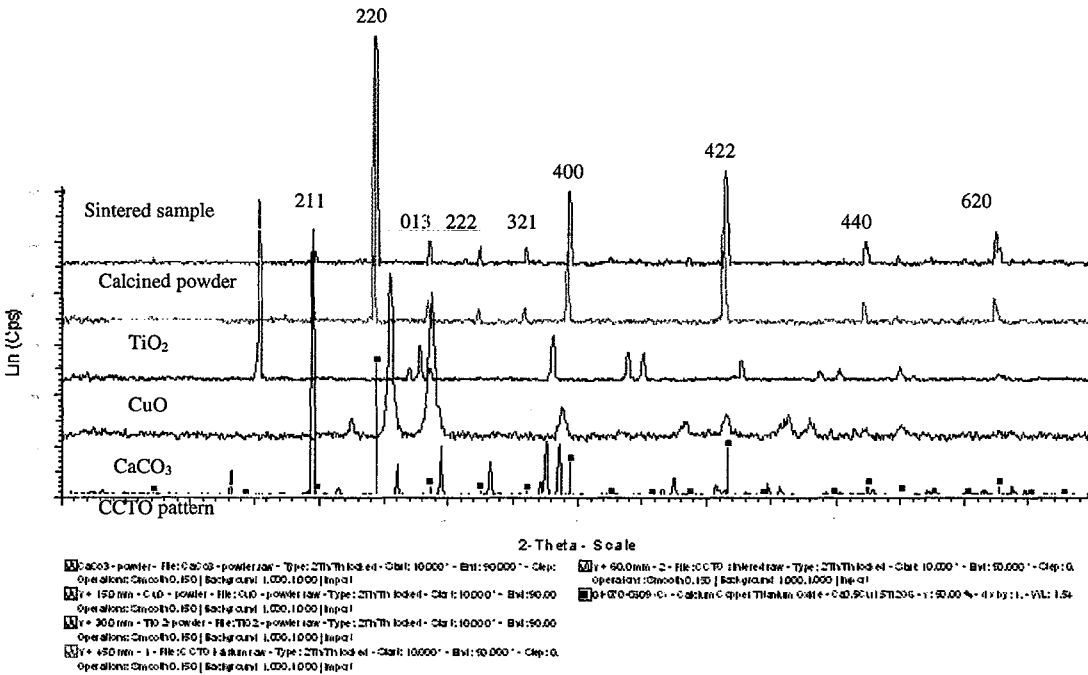


Figure 1 - The XRD result of raw materials, calcined and sintered CCTO

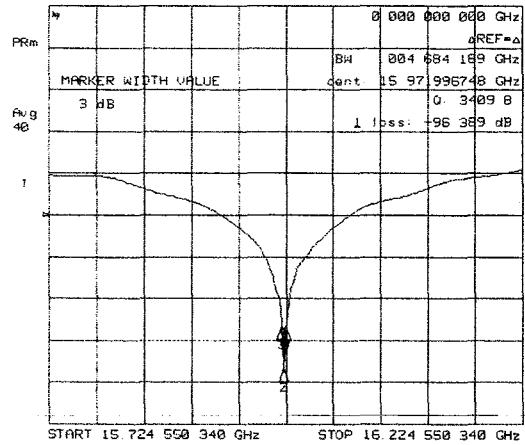


Figure 2 -  $Q \times f$  result from network analyzer

## Discussion

The calcination and sintering parameters were referred to the research before in fabricating CCTO bulk ceramics system [4, 6]. They concluded that single phase CCTO ceramics can be obtained via calcination at 900 °C for 12 hours and sintering at 1050 °C for 24 hours. In this work, the phase identification results were presented in the Figure 1. The result shows the XRD analysis for raw materials, calcined powder and sintered pellets of CCTO. The XRD patterns (ICSD 01-075-2188) show that the compound crystallizes in a body-centered cubic perovskite-related structure (group:  $Im\bar{3}$ ) and the measured lattice parameters ( $a = 7.39100 \text{ \AA}$ ), known as CCTO agreed well with the literature review [6]. The formation of single phase CCTO was identified in both calcined and sintered powders.

The dielectrics constants ( $\epsilon_r$ ) value for the sintered CCTO pellets was 10 175. The  $\epsilon_r$  at this condition was close to the value first reported by Subramanian et. al., 2000 as  $\sim 10\,000$ , and latest reported by Wu et. al., 2005. High dielectric constant material can effectively reduce the size of resonators since that the wavelength ( $\lambda$ ) in the dielectrics is inversely proportional to  $\sqrt{\epsilon_r}$  ( $\lambda = \lambda_0 \sqrt{\epsilon_r}$ ) where  $\lambda_0$  is the wavelength in vacuum [2].

As mentioned before, other researchers were focusing on CCTO's high dielectric constants properties and its phenomena. This paper is highlighting the  $Q \times f$  value for this material to be used as a dielectric resonator. Figure 2 shows the  $Q \times f$  value of the CCTO measured from network analyzer. The  $Q \times f$  value was 54 400 GHz (at 16 GHz) which indicate that CCTO has a very low dielectric loss ( $Q = 3400$ , where  $Q = 1 / \tan \delta$ ). The microwave dielectric loss was mainly caused not only by the lattice vibrational modes, but also by the pores, the grain morphology and other phases existed. However, density also plays an important role in controlling the dielectric loss [7]. CCTO ceramic samples fabricated in this work has a very close bulk density (99 %) compared to the theoretical density. Song et. al., 2004 in their work about  $\text{Sm}(\text{Co}_{1/2}\text{Ti}_{1/2})\text{O}_3$  dielectric resonators claims that  $Q \times f$  values was dominated by the change of density.

## Conclusion

The microwave dielectric properties of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) ceramics have been investigated. The CCTO exhibits a single phase compound with body-centered cubic

structure and a lattice parameter of 7.30100 Å. The microwave dielectric properties ( $\epsilon_r = 10\,175$ ,  $Q \times f = 54\,400$  (at 16 GHz)) was resulted from CCTO samples. For the search of microwave dielectric properties for applications in wireless communication systems, CCTO would be a suitable candidate.

## Acknowledgement

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**Proceeding**

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**The 6<sup>th</sup> National Seminar  
on Neutron and X-Ray Scattering**

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## THE EFFECT OF COMPACTION PRESSURE ON THE CCTO FORMATION AND DIELECTRIC PROPERTIES VIA SOLID STATE TECHNIQUE

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### ABSTRACT

**THE EFFECT OF COMPACTION PRESSURE ON THE CCTO FORMATION AND DIELECTRIC PROPERTIES VIA SOLID STATE TECHNIQUE.** The solid state procedure was used to produce bulk ceramics of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO). Commercial oxides  $\text{CaCO}_3$ ,  $\text{TiO}_2$  and  $\text{CuO}$  were used to prepare CCTO. The carbonate and oxides were weighed according to stoichiometric ratios and mixed thoroughly via ball mill for 1 hour. The mixed powder was calcined at  $900^\circ\text{C}$  for 12 hours. The calcined powders were compacted into 5 mm diameter and 0.5 – 1 mm thick pellet with different compaction pressure (100-500 MPa) and sintered in air at  $1050^\circ\text{C}$  for 24 hours. The calcined powder and the pellets were studied by X-Ray Diffraction (XRD) to identify the formation of single phase CCTO and its structure. SEM was used to measure the particle sizes and morphology observation. The density and porosity of the samples was obtained by Archimedes method. Dielectric measurements were done by using RCL meter at room temperature with 1 kHz frequency. The formation of single phase CCTO was confirmed by XRD analysis for the calcined powder and the sintered pellets. High densification with lowest porosity obtained at 300 MPa compaction pressure. The dielectric constants were fluctuated with different compaction pressure.

**Keywords:** CCTO, Solid state, Dielectric properties, Compaction pressure

### INTRODUCTION

High dielectric constant materials find numerous technological applications. In the case of memory devices based on capacitive components, such as static and dynamic random access memories, the static dielectric constant  $\epsilon_0$  will ultimately decide the level of miniaturization. Search for new high dielectric constant materials with unusual properties is great importance. This has led researcher to take up the challenge to search for new materials or to observe a new properties in known materials. One such material whose properties were studied recently is CCTO. This material belongs to a family of  $\text{ACu}_3\text{Ti}_4\text{O}_{12}$  type and was studied nearly 30 years ago [1].

Recently,  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) was discovered to possess one of the largest static dielectric constant ever measured, reaching nearly  $\epsilon_r \sim 80\,000$  for single crystal samples and 10 000 for bulk material at room temperature [2, 3, 4]. The higher the dielectric constant, the more charge it can store, and the smaller electronic circuits can be designed. In addition, unlike most dielectric materials, CCTO remains its enormously high dielectric constant over a wide range of temperatures, from 100 to 600 K, or  $-173$  to  $327^\circ\text{C}$ , making it ideal for a wide range of applications.

However, the nature of how the CCTO represents such high dielectric constant and how the abrupt changes of dielectric constant occur at 100 and 600 K are still not well understood [5]. Lately, many researcher claims that this behaviour comes from different factor, such as grain boundary, presence of twin boundaries or other planar

defects, displacement of Ti ions and etc. [2, 6]. But the real explanations of the phenomena are still investigated.

In this study, the solid state reaction was chosen though there are a number of preparative methods such as crystallization of solutions, vapour phase transport, mechanical alloying and electrochemical reduction methods. This route was mainly chosen due to its simplicity and suitability to starting materials in order to obtain bulk ceramics and thin film of CCTO [7].

### EXPERIMENT

Single phase powder of CCTO was prepared by solid state technique. The process started by mixing high-purity  $\text{CaCO}_3$  (Aldrich, 99 %),  $\text{TiO}_2$  (Merck, 99 %) and  $\text{CuO}$  (Aldrich, 99 +%) in the appropriate stoichiometric ratios. The mixed powders were ball milled for 1 hour using zirconia balls. A powder exhibiting free flowing characteristics was then obtained by sieving the dried milled powders. The homogenous mixture was then calcined in air at  $900^\circ\text{C}$  for 12 hours. The powder was shaped into 5 mm diameter and 0.5 – 1 mm thick pellet with different compaction pressure (100 – 400 MPa) and sintered in air at  $1050^\circ\text{C}$  for 24 hours. The phase purity, structure and lattice parameters of the samples were determined by X-Ray Diffraction (XRD) performed on D8 Bruker with a  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Scanning electron micrograph (SEM) was obtained on the CCTO powder to measure the particles size and morphology observation. Density and porosity of the sintered samples were measured by the Archimedes method.

The dielectric constant of CCTO pellets which had been electroded with silver paste were measured using Philips RCL meter PM 6303 at room temperature with 1 kHz frequency.

**RESULTS AND DISCUSSIONS**

Figure 1 shows the XRD result for raw materials, calcined powder and sintered pellets of CCTO. XRD patterns (ICSD 01-070-0609) show that the compound crystallizes in a body-centered cubic perovskite-related structure (group: *Im3*) and the measured lattice parameters ( $a = 7.39100 \text{ \AA}$ ), known as CCTO agreed well with the literature review [4]. The formation of single phase CCTO was identified in both calcined and sintered powders. This phenomena shows that the single phase CCTO already can be obtain via calcinations of the

raw materials at 900 °C for 12 hours. All the sintered samples from different compaction pressure show the formation of single phase CCTO, same as XRD results shown in Figure 1.

Figure 2 shows the SEM micrograph of calcined CCTO powder. The micrograph revealed particles in the size range from 110 to 390 nm. It is seen that the CCTO particles were spherical in shape. The similar result was reported by Jha et. al., 2003 that have been studied on polymeric citrate precursor route to the synthesis of the high dielectric constant oxide, CCTO. They were comparing the morphology of the CCTO particles obtained between polymeric citrate precursor and solid state technique. The CCTO obtained from the solid state process give the same morphology, but different sizes (2 – 4  $\mu\text{m}$ ). This is maybe due to the different particles size of raw materials been used.

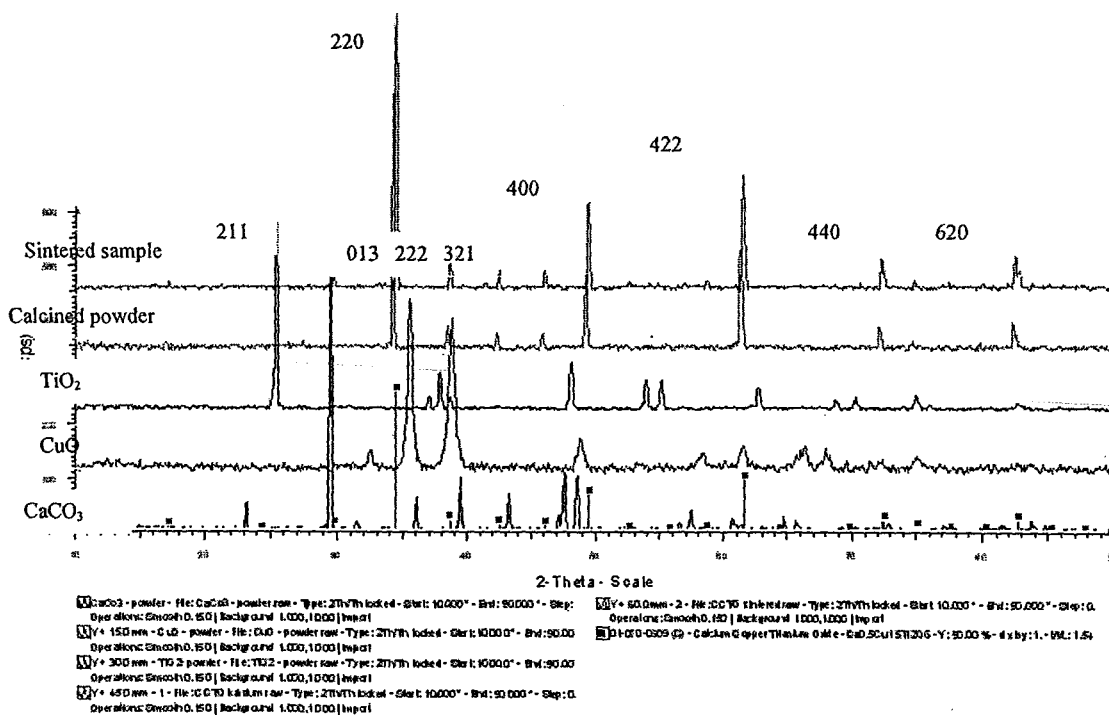


Figure 1. The XRD result of raw materials, calcined and sintered CCTO

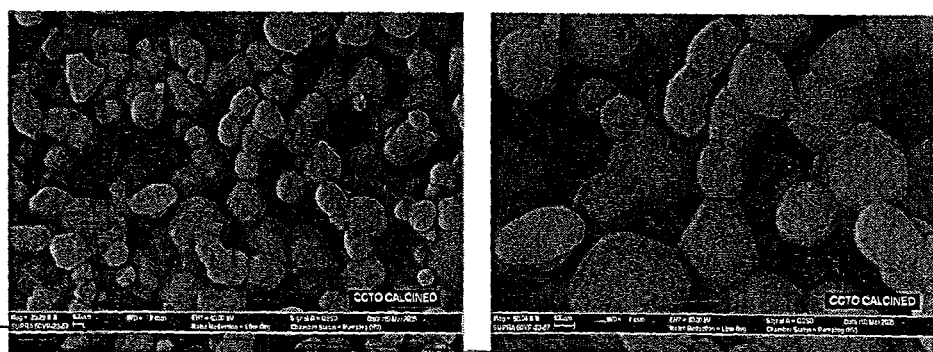


Figure 2. The SEM micrograph of calcined CCTO (a) Mag. 25kx and (b) Mag. 50 kx

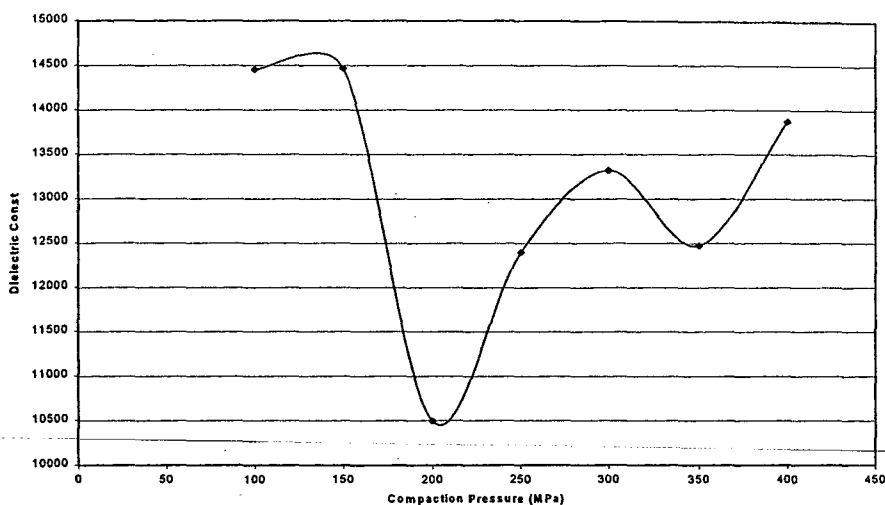


Figure 3. The effect of compaction pressure on dielectric properties.

Figure 3 shows the effect of compaction pressure (MPa) on dielectric constant,  $\epsilon_r$ , measured at room temperature with 1kHz frequency. The dielectric values of CCTO tend to fluctuated with variation of compaction pressure. The  $\epsilon_r$  at compaction pressure of 100 and 150 MPa were high, but the densification of the bulk ceramic was very poor, i.e. less than 90 % compared to theoretical density. The  $\epsilon_r$  was very low at 200 and 250 MPa compaction pressure. The optimum dielectric properties with lowest porosity and bulk density nearest to theoretical density (99 %) were obtained for the sample compacted at 300 MPa. The  $\epsilon_r$  at this condition was 13 320 close to the value first reported by Subramanian et. al., 2000 as ~ 10 000, and latest reported by Wu et. al., 2005 as 12 000. The compaction pressure in fabricating the bulk CCTO did not influence seriously on the dielectric properties, but significant in acquiring the dense with low porosity samples.

## CONCLUSION

The compaction pressure did not give any influence on single phase CCTO formation because all the sintered samples show the single phase CCTO pattern. A CCTO compound with body-centered cubic structure and a lattice parameter of 7.30100 Å was obtained. SEM micrograph shows that the grains were spherical in shape with size range of 110 to 390 nm. Higher compaction pressure increases the density. The highest densification was obtained at 300 MPa compaction pressure. The permittivity of CCTO was fluctuated with different compaction pressure.

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# Microstructure and dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic

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## Abstract

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) was prepared by the solid state technique. The sample was calcined at 900 °C/12 h and sintered at 1050 °C/24 h, then subjected to XRD to ensure CCTO formation. The microstructure was observed by SEM. XRD results identified both samples as single phase CCTO, whereas the microstructure shows abnormal grain growth and large pores. Sintering was studied in the temperature range of 950–1050 °C for 3–12 h. Increasing sintering temperature enhances the density and secondary formation of  $\text{Cu}_2\text{O}$ . A clear grain boundary and dense microstructure were observed. The results show that the sample sintered at 1040 °C/10 h yields a clearly uniform grain size with the highest  $\epsilon_r$  (33,210).

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**Keywords:** Sintering; Microstructure; Dielectric; CCTO

## 1. Introduction

CCTO was discovered to possess the largest  $\epsilon_r$  i.e. ~80,000 for single crystal and 10,000 for bulk material at room temperature [1–4]. The higher the  $\epsilon_r$ , the more charge it can store, and the smaller electronic circuits can be designed. Unlike most dielectric materials, CCTO retains its enormously high  $\epsilon_r$  over a wide range of temperatures (–173 to 327 °C), making it ideal for a wide range of applications. However, the nature of how the CCTO represents such properties is still not well understood [5]. Lately, researchers claim that this behaviour comes from different factors, such as grain boundary, the presence of twin boundaries or other planar defects, displacement of Ti ions, etc. [2,6]. But the real explanations of the phenomena are still investigated.

Four major sintering parameters control the microstructure and properties of CCTO, i.e. temperature, heating rate, duration and atmosphere. It was stated by some researchers [7–9] that

sintering at 1050 °C/24 h in the normal atmosphere will produce good quality single phase CCTO. These earlier studies of CCTO fabrication did not report microstructure development. This paper highlights microstructure development as a function of the sintering parameter. The results show that there was an abnormal grain growth, melting and formation of large pores. Therefore, it is important to investigate the new sintering parameter to ensure that the correct microstructure with high  $\epsilon_r$  will be obtained.

## 2. Experimental procedure

CCTO samples were prepared by solid state method.  $\text{CaCO}_3$  (15.52  $\mu\text{m}$ ) (Aldrich, 99%),  $\text{TiO}_2$  (0.68  $\mu\text{m}$ ) (Merck, 99%) and  $\text{CuO}$  (6.85  $\mu\text{m}$ ) (Aldrich, 99%) were used as starting materials. Stoichiometric ratios of the reagents were mechanically ball milled for 1 h. The powder was calcined in air at 900 °C for 12 h, then subjected to X-ray diffraction (XRD, Bruker D8) phase analysis to ensure the perovskite structure of CCTO had formed. Cylindrical specimens of 5 mm diameter and approximately 0.5–1 mm thick were pressed, then sintered in air at 1050 °C for 24 h, followed by XRD analysis and scanning

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electron microscopy (SEM, Zeiss SUPRA 35VP). Based on this analysis and observation, the sintering parameters then were modified using the temperature range of 950–1050 °C for 3–12 h with a heating rate of 5 °C/min. The microstructures were investigated on the fracture surface of the sintered specimens using SEM. The samples for measuring  $\epsilon_r$  were polished to ensure surface flatness and then painted with silver paste on both surfaces as electrodes. The measurement was done at room temperature by Hewlett–Packard 4912 Impedance Spectroscopy at the frequency range of 1 Hz to 10 GHz.

### 3. Results and discussion

The sintering parameter referred in the literature [7–10] i.e. 1050 °C for 24 h was applied. Single phase CCTO was identified in both calcined and sintered powders. We have tried to keep our experimental condition quite close to those reported for the formation of CCTO, but SEM observation only shows evidence for melting and abnormal grain growth, with large pores (Fig. 1). Fig. 2 shows the XRD analysis for the samples sintered at different temperatures for the same soaking time. The samples sintered at 950–1030 °C show the single phase CCTO, but a minor phase was detected for the sample sintered at 1050 °C. XRD analysis shows the presence of  $\text{Cu}_2\text{O}$ . Theoretically, the  $\text{Cu}^{2+}$  cations are reduced at  $T \approx 1000$  °C into  $\text{Cu}^+$ . The  $\text{Cu}^+$  will reoxidize during the cooling [11]. Subramaniam et al. also reported the existence of impurity  $\text{CuO}$  in their samples of CCTO. An initial assumption made based on XRD analysis was that the samples sintered at 1050 °C/24 h only consist of a CCTO single phase due to undetected  $\text{Cu}_2\text{O}$  glassy phase.

Fig. 3(a) shows the SEM micrographs of CCTO sintered at different temperatures. A porous microstructure with a small grain size is observed in the specimen sintered at 950 °C. Increasing the sintering temperature significantly promotes grain growth and microstructural densification. The grain growth in the sintered specimens sintered above 1030 °C implies an increase in the amount of liquid phase. The 1050 °C for 12 h samples show the liquid phase phenomena. When the soaking time was increased to 24 h, the whole structure melted. A further study was made by sintering the samples at 1040 °C with different soaking times (Fig. 3(b)).

The 3 and 6 h sintered samples show fairly uniform grain sizes with clear grain boundaries. The densest microstructure was obtained

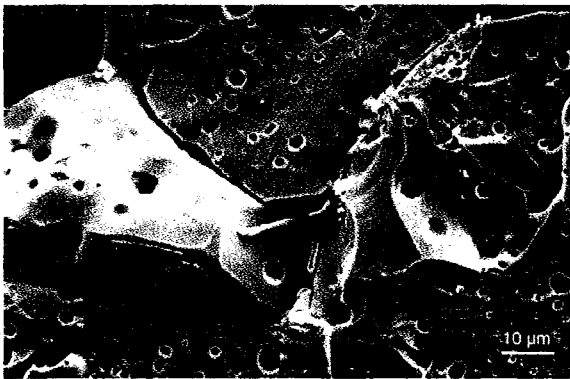


Fig. 1. The microstructure of the melt and abnormal grain growth for the sample sintered at 1050 °C for 24 h (mag: 1000 $\times$ ).

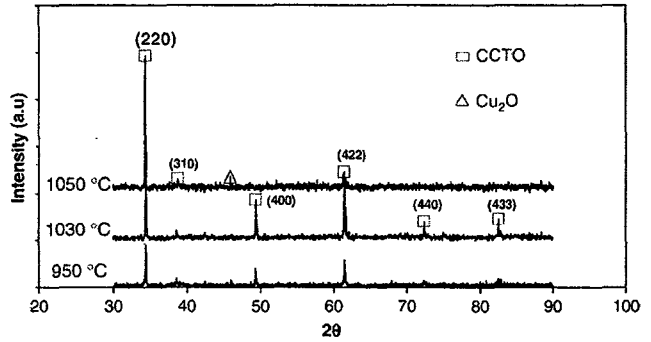


Fig. 2. XRD analysis for the samples sintered at different temperatures for 12 h.

for the sample sintered for 10 h. The grain size is in the range of 1–3  $\mu\text{m}$ . With further sintering to 12 h, the sample began to melt. This may have happened due to the secondary recrystallization and possible vaporization of  $\text{Cu}$  during the very long sintering time. The presence of  $\text{Cu}$  was confirmed by EDX analysis. Fritsh et al. reported that the huge grains observed for the CCTO that contain  $\text{CuO}$  are also probably related to the appearance of a liquid phase that wets the grain during sintering [11]. Small amounts of  $\text{CuO}$  are believed to be responsible for the abnormal grain growth.

The microstructure results are different from those of Jha et al. They claimed that the grains were spherical in shape, with the range size of 2–4  $\mu\text{m}$ . The highest  $\epsilon_r$  they achieved was around 3000, that was much lower than that reported earlier [1]. Meanwhile, the study shows the grains were of square like shape with the average size of 1 to 3  $\mu\text{m}$ . This is similar to recent reports [12,13]. Brize et al. have reported how the grain size affects the  $\epsilon_r$  of CCTO. Their microstructure observation was clearly discussed, but their  $\epsilon_r$  value was lower than that reported earlier. The  $\epsilon_r$  that was obtained from this study was much higher compared to their results [14].

Fig. 4 shows the results of  $\epsilon_r$  and dielectric loss for CCTO samples. For  $\epsilon_r$ , as the frequency increased, each curve presents a plateau followed by a drop of 1 GHz as previously reported [1,13,14]. At 1 kHz, the  $\epsilon_r$  for the samples sintered at 1030 and 1050 °C, were 15,218 and 26,743, respectively (Fig. 4(a)) as reported earlier [11,14,15]. In Fig. 4 (b), at 1 kHz, the  $\epsilon_r$  values for the samples sintered at 1040 °C for 3, 6, 10, and 12, were 1569, 2720, 33,210 and 14,117, respectively. The dielectric loss is around 0.2–1.0, and the value starts to increase at higher frequency. The highest  $\epsilon_r$  value obtained in this study and measured at room temperature was 33,210 i.e. for the sample sintered at 1040 °C for 10 h. Subramaniam et al. first reported that the  $\epsilon_r$  for bulk CCTO at 1 kHz was around 10,000–12,000. The value from our experiment was three times higher than that earlier reported.

### 4. Conclusions

It is crucial to adequately control sintering temperature and times to obtain the desired microstructure and dielectric properties. The sample sintered at 1050 °C for 24 h shows melting and abnormal grain growth. The effects of different sintering conditions on density, phase formation, microstructure and dielectric properties were discussed. Increasing sintering temperature enhances density. A clear grain and dense microstructure were observed for the samples sintered at 1000 and 1030 °C for 12 h, and for the samples sintered at 1040 °C for 3,

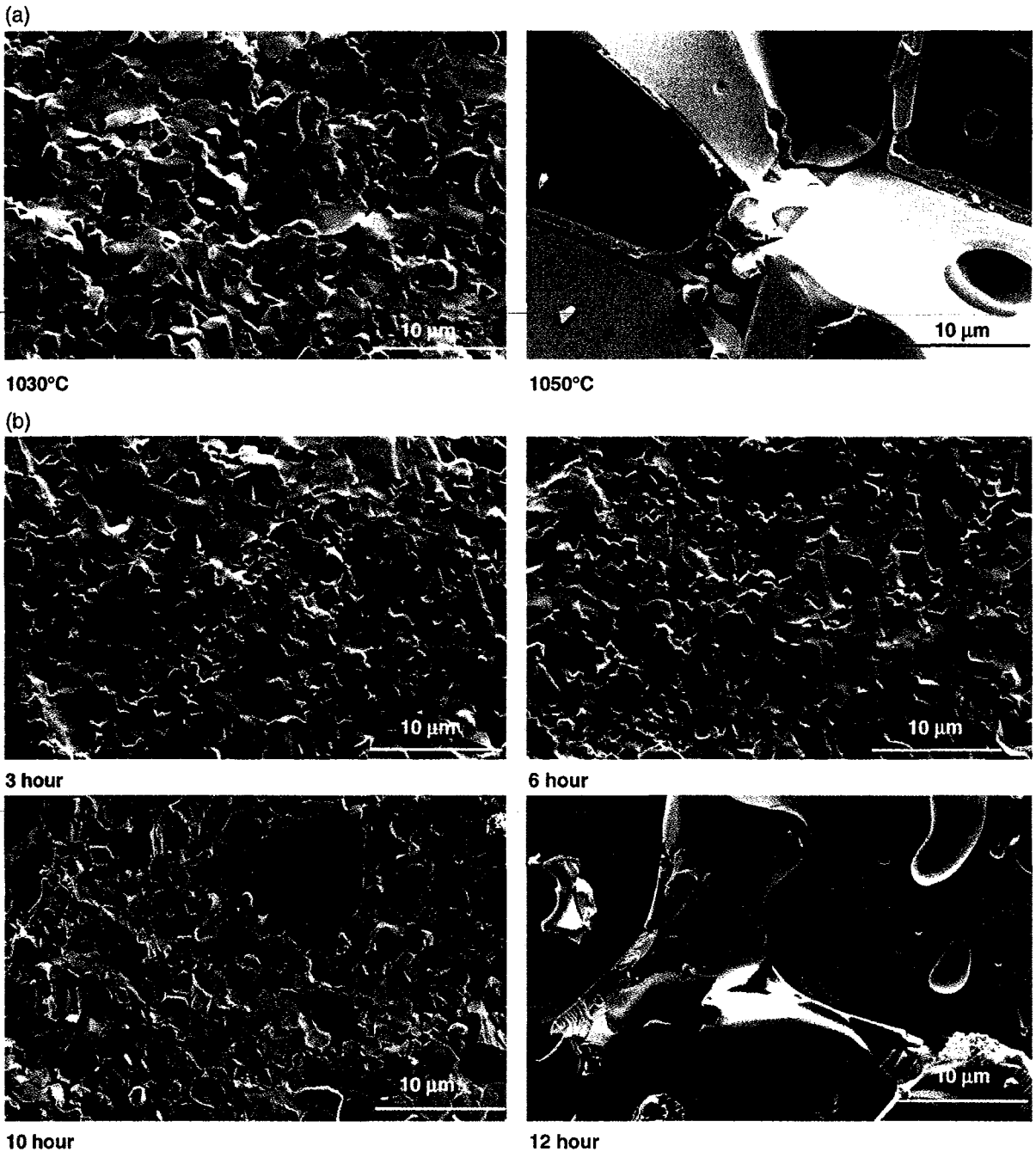


Fig. 3. SEM micrographs of CCTO ceramics sintered (a) at different temperatures for 12 h and (b) at 1040 °C with different sintering times.

6 and 10 h. The melting grains in the sample sintered at 1050 °C for 12 h show the existence of a new phase,  $\text{Cu}_2\text{O}$ . The highest  $\epsilon_r$  (33,210) with clear uniform grain was obtained by the sample sintered at 1040 °C for 10 h.

#### Acknowledgement

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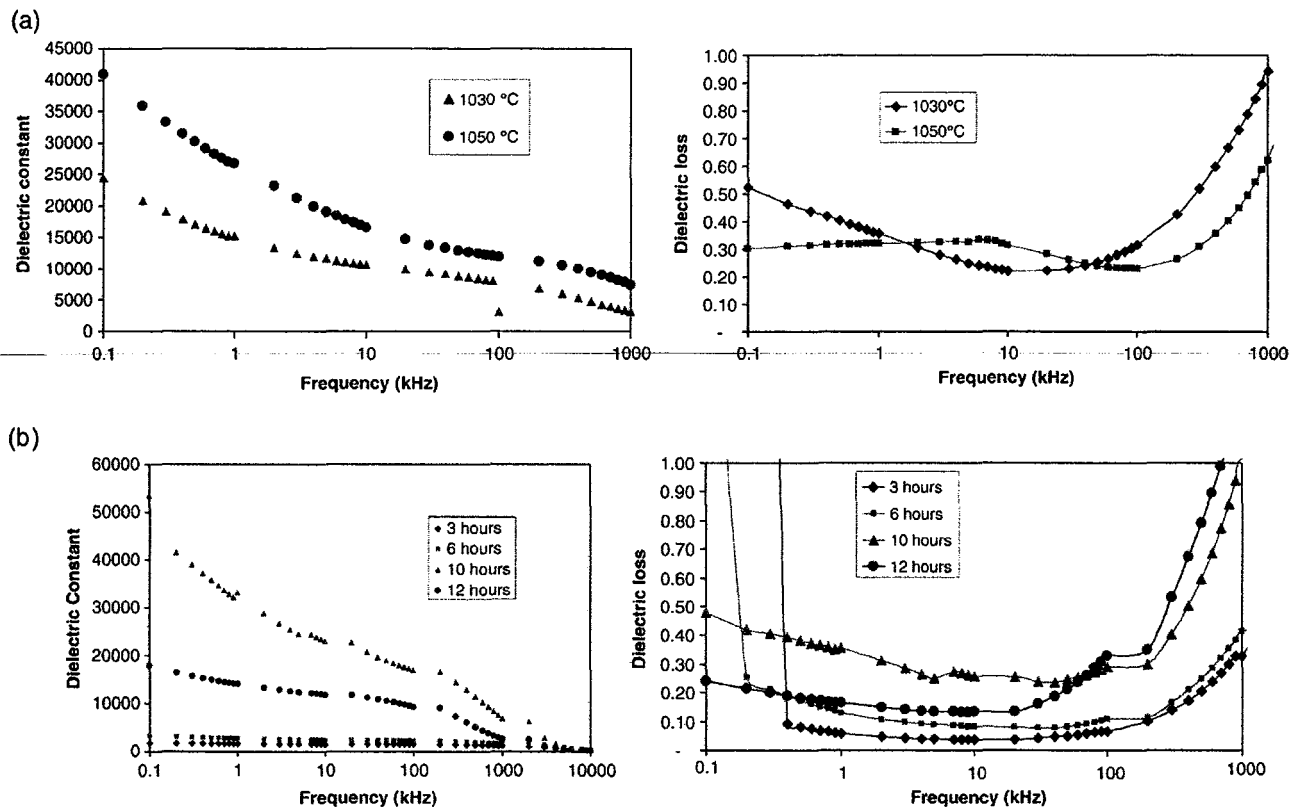


Fig. 4. The  $\epsilon_r$  and dielectric loss value against frequencies for the samples sintered at different (a) temperatures and (b) soaking times.

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## THE EFFECT OF CuO ADDITION IN CCTO ON THE DIELECTRIC PROPERTIES AND MICROSTRUCTURE

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*CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (CCTO) was fabricated from Ca(OH)<sub>2</sub>, TiO<sub>2</sub> and CuO via solid state technique. Raw materials were weighed according to stoichiometric ratios (0-10 mol CuO) and were ball milled for 1 hour. The mixed powder was calcined at 900°C for 12 hours and compacted into 5 mm diameter pellets. The pellets were sintered in atmosphere at 1050°C for 24 hours. The density and porosity of the samples were obtained by Archimedes method. The surface microstructure of the sintered samples was observed through SEM. Dielectric measurements were done by using RCL meter at room temperature at 1 kHz frequency. CuO addition in CCTO system increases the bulk density and subsequently drops the percentage of porosity. Microstructure observation showed grain growth phenomena with CuO addition. The highest dielectric constant, (79018) was obtained in sample with 4 mol of CuO.*

### 1. INTRODUCTION

High dielectric constant oxide materials are important because of their potential impact in microelectronic device applications. Most of the high dielectric constant materials with static dielectric constant greater than 1000 are ferroelectric, such as BaTiO<sub>3</sub>, Pb(Zr,Ti)O<sub>3</sub>, or (Ba, Sr)TiO<sub>3</sub> [1]. The dielectric constant of these materials are highly dependent upon the temperature, which result in instability of the devices with temperature variation. The higher the dielectric constant, the more charge it can store, and the smaller electronic circuits can be designed.

Recently, CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (CCTO) was discovered to possess one of the largest static dielectric constant ever measured, reaching nearly  $\epsilon_r \sim 80\ 000$  for single crystal samples and 10 000 for bulk material at room temperature [2, 3, 4]. In addition, unlike most dielectric materials, CCTO remains its enormously high dielectric constant over a wide range of temperatures, from 100 to 600 K, or -173 to 327 °C, making it ideal for a wide range of applications.

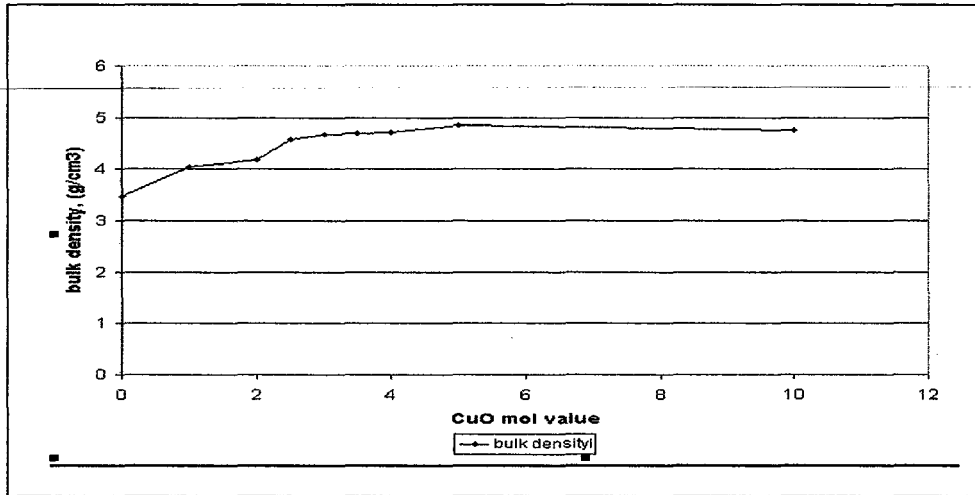
### 2. METHODS & MATERIALS

Single phase powder of CCTO was prepared by solid state technique. The process started by mixing high-purity CaCO<sub>3</sub> (Aldrich, 99 %), TiO<sub>2</sub> (Merck, 99 %) and CuO (Aldrich, 99 +%) in the appropriate stoichiometric ratios. The mixed powders were ball milled for 1 hour using zirconia balls. A powder exhibiting free flowing characteristics was then obtained by sieving the dried milled powders. The homogenous mixture was then calcined in air at 900 °C for 12 hours. The powder was shaped into 5 mm diameter and 0.5 – 1 mm thick pellet with compaction pressure of 300 MPa and sintered in air at 1050 °C for 24 hours. Density and porosity of the sintered samples were measured by the Archimedes method. Scanning electron micrograph (SEM) was obtained on the CCTO powder to measure the particles size and morphology observation. The dielectric constant of CCTO pellets which had been electroded with silver paste were measured using Philips RCL meter PM 6303 at room temperature with 1 kHz frequency.

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### 3. RESULTS & DISCUSSIONS

Figure 1 shows the bulk density result measured by Archimedes method. The result shows that the density rapidly increases at 0 – 2.5 mol CuO addition. It shows a uniform density enhancement for the 3 mol CuO sample up to 5 mol, and no changes after that. The bulk density of the sample increases with increasing CuO addition and this can be related to the density of CuO itself. The CuO addition also reduces the porosity percentage.



**Fig. 1. The bulk density tends to increase with the CuO addition.**

Figure 2 shows the SEM observation for different mol of CuO in CCTO's. The micrograph shows that the grain size increases with CuO addition. The same result also reported by Wang et. al. who were study on effects of CuO on the grain size and electrical properties of SnO<sub>2</sub> – based varistors. They concluded that the grain size increases with CuO addition. Huang et. al. in their research about microwave dielectric properties and microstructures of MgTa<sub>2</sub>O<sub>6</sub> ceramics with CuO addition also reported the same things.

Figure 3 shows the results of dielectric constant with different addition of CuO. The result reveals that the dielectric constant value increases with CuO addition, and obtained the highest value at 4 mol of CuO. But, the value was decreases at 5 mol CuO onwards. The research done before by Bender and Pan conclude that at 1 kHz frequency, the dielectric constant of stoichiometric CCTO obtained was 12000. The value gain in this research was 15221, and it was much higher than experimented before.

If referred to the micrograph, for 2.5 mol up to 4 mol CuO addition, the value of dielectric constant is increases due to the grain enlargement. For 4 mol CuO sample, the grain size is between 50 – 100 μm, and the highest dielectric constant value was obtained. For the 5 mol CuO onwards, the value of dielectric constant was decreases due to extra-large grain size. The dielectric constant for CCTO is relates to grain boundary response. As the grain size getting larger, the volume fraction of grain boundary is reduced and therefore the dielectric constant is small.

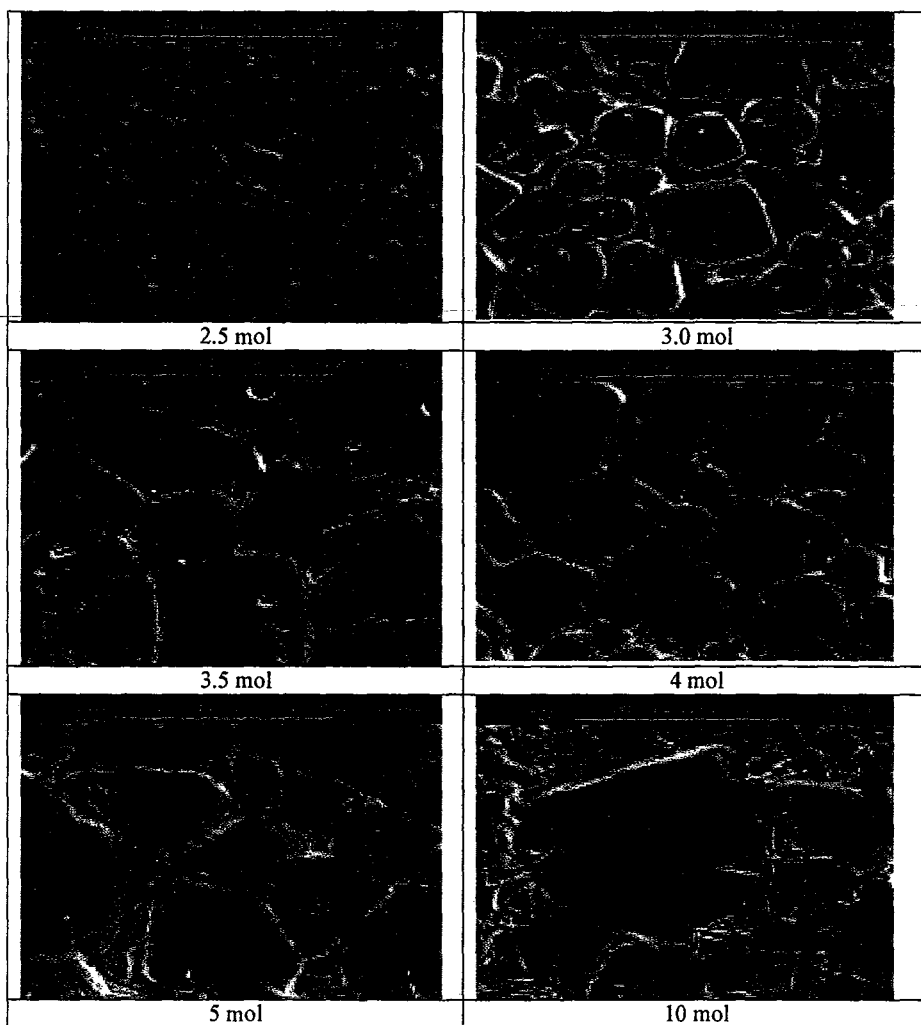


Fig. 2. SEM micrographs for different amount of CCTO. (Mag: 250x)

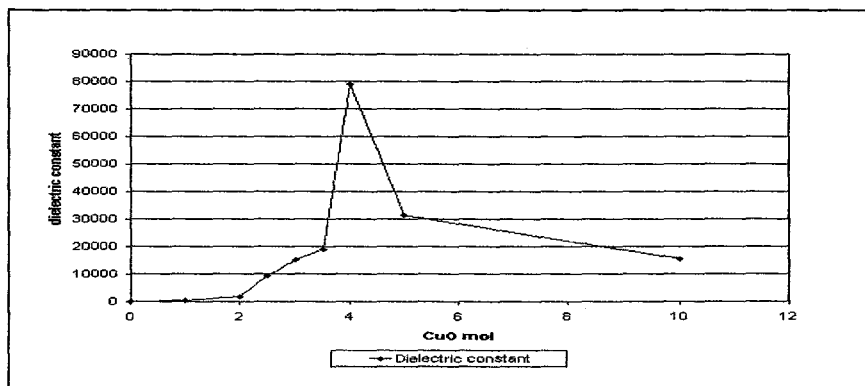


Fig. 3. Result of dielectric constant with different mol of CuO

#### 4. CONCLUSIONS

The CuO addition in CCTO systems improves the bulk density and decreases the porosity. Microstructure observation shows that the grain growth occurs with the increasing percentage of CuO. The dielectric constant increases and obtained the highest value at 4 mol CuO (15221)

#### ACKNOWLEDGEMENTS

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**Proceeding**

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## DIFFERENT SINTERING TIME EFFECT ON THE FORMATION AND DIELECTRIC PROPERTIES OF $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

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### ABSTRACT

**DIFFERENT SINTERING TIME EFFECT ON THE FORMATION AND DIELECTRIC PROPERTIES OF  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ .** The effect of sintering time on the formation and dielectric properties of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) was studied. CCTO was prepared using conventional ceramic solid state reaction processing technique. Commercial carbonate  $\text{CaCO}_3$  and oxides  $\text{TiO}_2$  and  $\text{CuO}$  were weighed stoichiometrically ratios and mixed for 1 hour. The mixed powder was calcined at 900 °C, then was shaped into pellet with compaction pressure of 300 MPa. The pellets were sintered in air at 1050 °C with different sintering time (1-24 hours). The X-Ray Diffraction (XRD) analysis was done to the calcined powder and different duration sintered pellets. The density and porosity of the samples was obtained by Archimedes method. The dielectric properties of the samples were measured by using the RCL meter at 1 kHz frequency. Sintering time have significant effect on the crystallography of CCTO. Pure single phase CCTO was successfully produced for sintering time of 24 hours. Increasing sintering time enhanced the densification and dielectric properties with the best properties achieved at 24 hours sintered sample.

**Keywords:** CCTO, Solid state reaction, Dielectric properties, Sintering time

### INTRODUCTION

High dielectric constant materials are increasingly important for pushing the state of art in semiconductor integrated circuits. They are necessary in applications that require high capacitance values per lateral area. Ceramic materials are also can be used in the microelectronic industries as dielectric substrates, due to their high reliability, high integration potential, good dielectric properties, excellent thermal conductivity and their thermal expansion coefficient close to silicon [1]. It is known that some ceramic compounds with perovskite structures are found to be very interesting dielectric properties. In particular one of the members,  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO), was recently studied to investigate the origin of the so called colossal permittivity, and Chidelli et. al. [2] was reported the dielectric properties result of CCTO for single crystal, powders and also thin films.

The electroceramic compound CCTO has attracted much interest because of its high dielectric constant (up to  $10^5$ ) over a broad temperature range extending from 100 to 600 K and rather wide microwave frequency window [3,4]. This unique property makes CCTO a promising material for microelectronic and microwave device applications.

The dielectric properties of electroceramic materials are depends on the phase transition phenomena, and that is closely related to the crystal structure. On the other hand, the crystal structure is closely dependent on the thermal history and the fabrication method. Therefore, the properties of a certain electroceramic materials will

finally affected by the sintering condition, including sintering temperature and time. In this work, we studied the effect of sintering time on the phase changes and dielectric properties of CCTO.

### EXPERIMENT

Single phase CCTO samples were prepared by a conventional solid state reaction method. High purity  $\text{CaCO}_3$  (Aldrich, 99%),  $\text{TiO}_2$  (Merck, 99%) and  $\text{CuO}$  (Aldrich, 99%) were used as starting materials. A stoichiometric ratio of the reagents were mechanically ball milled for 1 hour using zirconia balls. The powders exhibiting free flowing characteristics were then obtained by sieving the dried milled powders. The mixed powder was calcined in air at 900 °C for 12 hours. Cylindrical shape specimens with 5 mm in diameter and approximately 0.5 - 1 mm thick were then pressed with 300 MPa compaction pressure. The samples were sintered in air at 1050 °C with different sintering time (1, 3, 6, 12, 18 and 24 hours) with a heating rate of 5°C/minutes.

The X-Ray Diffraction (XRD) analysis was done to the calcined powder and different duration sintered pellets by using D8 Bruker diffractometer machine. Density and porosity of the samples were obtained by Archimedes method.

The dielectric properties (dielectric constant) of the sintered pellets were measured by using a Philips PM 6303 RCL meter at 1 kHz frequency in ambient temperature.

## RESULTS AND DISCUSSION

Figure 1 shows the result of powder diffraction data for raw materials ( $\text{CaCO}_3$ ,  $\text{CuO}$ , and  $\text{TiO}_2$ ), calcined and sintered pellet for 24 hours of CCTO recorded by using D8 Bruker diffractometer. The XRD patterns shows that the formation of single-phase structure of CCTO has been formed completely with body-centered cubic structure and a lattice parameter of 7.301 Å. This results

are very close to the data was reported by another researcher [3]. The formation of single phase CCTO was identified in both calcined and sintered powders. This phenomena show that the single phase CCTO already exist via calcination processes of the mixed powders at 900 °C for 12 hours. Sintering process was found to be improving in crystalline structure properties of CCTO compound.

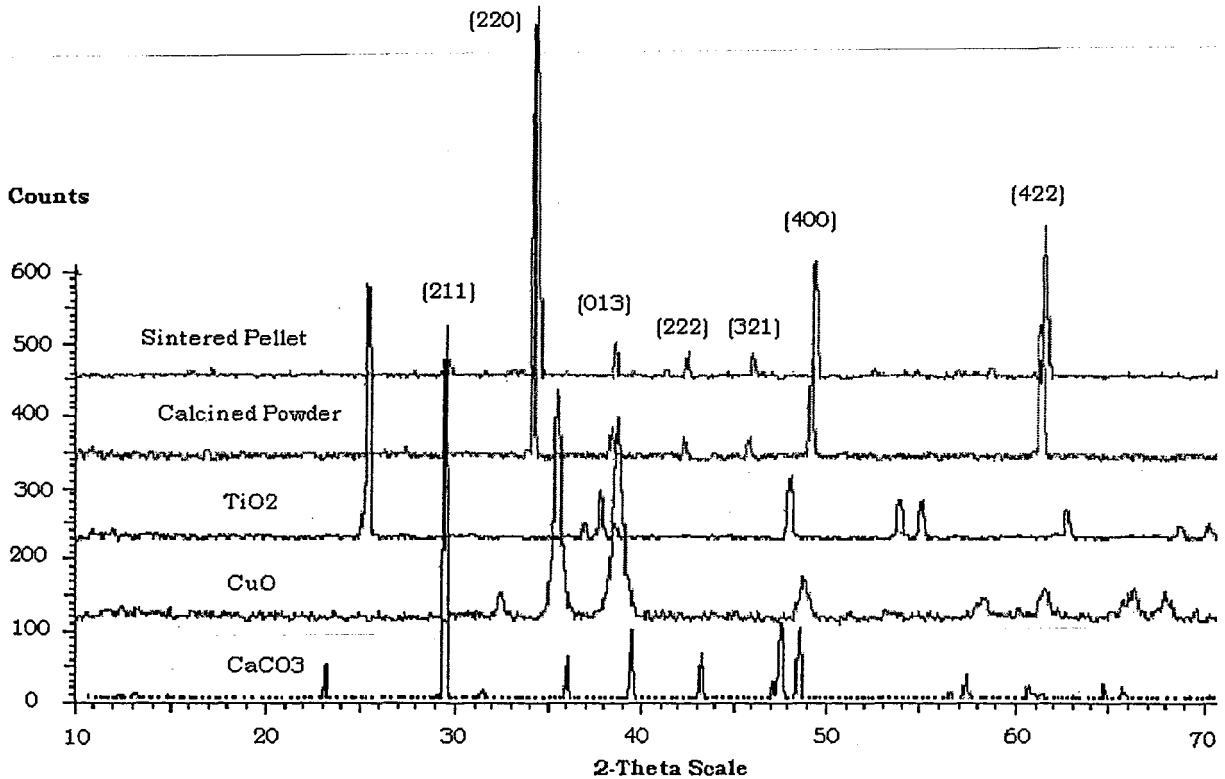


Figure 1. The XRD results for raw materials, calcined powder and sintered pellet of CCTO.

The XRD results in Figure 2 show the formation of phases in the samples at different sintering time. The sintering time have significant effect on the crystallography of CCTO. The sintered samples of 1 and 6 hours were mainly shows crystalline properties of CCTO. On the other hand, a sintered sample of 12 hours shows the existence of  $\text{TiO}_2$  in addition to CCTO phase. This implies that  $\text{TiO}_2$  do exist in the sintered sample at lower sintering time (<12 hours). Unfortunately due to the low degree of crystallinity, it was not observed in the trace.

Further increase sintering time (24 hours) promote the complete reaction within the unreacted  $\text{TiO}_2$  in the

sample. Pure single phase CCTO was successfully produced for sintering time of 24 hours (Figure 1). The density measured by Archimedes method give the results that densification increases as the sintering time increase.

The same trend of results also reported by other researcher that studied on other electroceramic systems [5-8]. The lowest porosity and bulk density nearest to theoretical density (99 %) were obtained for the sample sintered at 24 hours. Sintering temperature, sintering time, heating rate and atmosphere control are the four major sintering parameters to optimize in order to achieve the high density electroceramic material [7].

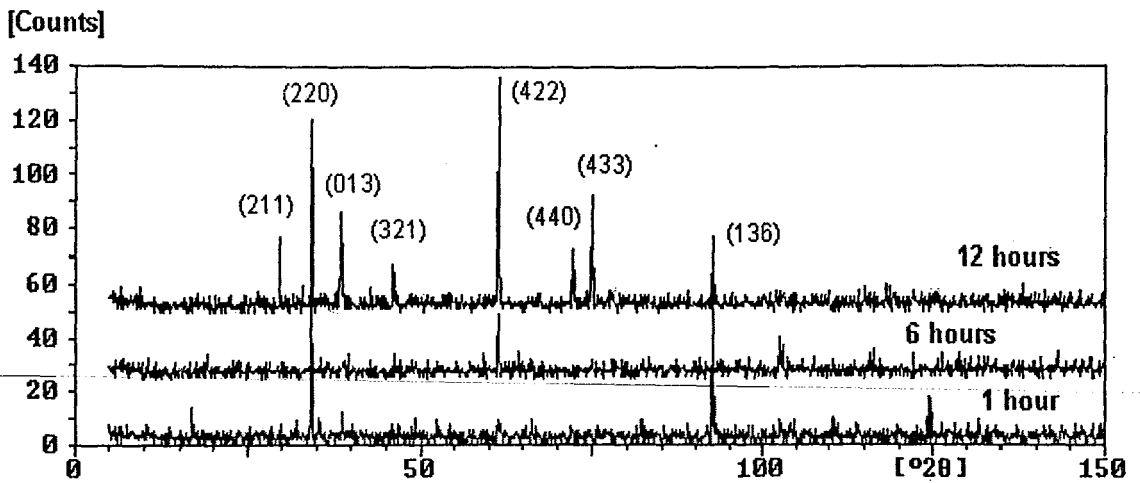


Figure 2. The XRD analysis results of CCTO for different sintering time of 1, 6 and 12 hours.

Figure 3 shows the measured dielectric constant results of CCTO samples with different sintering time of 1, 3, 6, 12, 18, and 24 hours. The dielectric constant values were

increases with sintering time. The highest value of 13320 was obtained for sample with 24 hours sintering time.

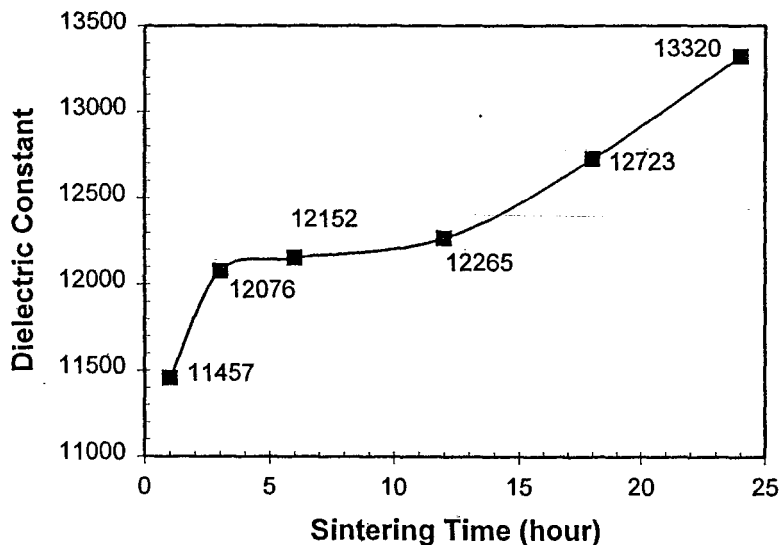


Figure 3. Dielectric constant results for different sintering time of 1, 3, 6, 12, 18, and 24 hours.

Li and Chen [9] was studied the effect of sintering condition on microstructure and microwave dielectric properties of  $\text{Ba}_{6-3x}(\text{Sm}_{1-y}\text{Nd}_y)_{8+2x}\text{Ti}_{18}\text{O}_{54}$  ceramics, and reported that the sintering time has no obvious influence on the dielectric constant. The sintering time was found to be affected of Q-factor and temperature coefficient significantly. In case of the CCTO compounds, there was a raise of dielectric constant with sintering time. The results agree with those observed by Bender and Pan [10]. They claims that the dielectric constant increases with sintering time.

## CONCLUSION

Sintering time have significant effect on the crystallography of CCTO. Pure single phase CCTO was successfully produced for sintering time of 24 hours. A CCTO compound with body-centered cubic structure and a lattice parameter of 7.301 Å was obtained. Increasing sintering time enhanced the densification and dielectric properties. The best performance i.e. relative density (99.7 %) and dielectric constant (10557) was obtained CCTO sample with 24 hours sintering time.

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