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### Abbreviations

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<th>Description</th>
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<tbody>
<tr>
<td>BSE</td>
<td>Backscatter Secondary Electron</td>
</tr>
<tr>
<td>CCTO</td>
<td>Calcium Copper Titanium Oxide</td>
</tr>
<tr>
<td>CCTN</td>
<td>Calcium Copper (Titanium-Niobium) Oxide</td>
</tr>
<tr>
<td>CCTS</td>
<td>Calcium Copper (Titanium-Tin) Oxide</td>
</tr>
<tr>
<td>CN</td>
<td>Coordination Number</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant Phase Element</td>
</tr>
<tr>
<td>DBLC</td>
<td>Double Barrier Layer Capacitance</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersion X-ray Spectroscopy</td>
</tr>
<tr>
<td>PDF</td>
<td>Powder Diffraction File</td>
</tr>
<tr>
<td>FRA</td>
<td>Frequency Response Analyzer</td>
</tr>
<tr>
<td>IBLC</td>
<td>Internal Barrier Layer Capacitor</td>
</tr>
<tr>
<td>ICDD</td>
<td>International Centre for Diffraction Database</td>
</tr>
<tr>
<td>K-K</td>
<td>Kramers-Kronig</td>
</tr>
<tr>
<td>SBLC</td>
<td>Single Barrier Layer Capacitance</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>VDR</td>
<td>Voltage Dependent Resistor</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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Abstract

Three types of Calcium Copper Titanium oxide (CCTO), i.e. pure CCTO, niobium doped CCTO, and tin doped CCTO were obtained by mixed oxide route. The niobium and tin as a dopant were selected with the variation of doping concentration to create the stoichiometric formula $\text{CaCu}_3\text{Ti}_{4-x}\text{M}_x\text{O}_{12}$ ($x = 0.05, 0.10, 0.15, 0.20, \text{and} 0.25$; $\text{M} = \text{Nb, and Sn}$). Three different sintering times were applied for all the samples. X-ray diffraction, scanning electron microscopy, impedance spectroscopy at high and low temperature were used to determine the phases, dielectric constant, dielectric loss, resistivity and capacitance of bulk and grain-boundary, non-linear coefficient of conduction, breakdown voltage-field, barrier height, and microstructural changes of CCTO. The purpose of this research is to investigate and provide the transition of dielectric properties from pure CCTO to non-linear behaviour in niobium and tin doped CCTO. The dielectric properties is represented by grain boundary thickness ($t_{gb}$) and activation energy for electrical conductivity of bulk ($E_{ab}$) and grain boundary ($E_{agb}$). The non-linear behaviours is represented by non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_0$). The relative dielectric constant tends to decrease with increasing the amount of niobium and tin dopant. The activation energy of niobium and tin doped CCTO are in line with barrier height which are associated with conduction processes; the dopants are shown to reduce the conductivity of samples. The barrier height and grain boundary thickness tend to decrease with increasing the amount of niobium and tin dopant. The narrowest grain boundary thickness will increase rapidly the effective dielectric constant which is attributed to the formation of thin insulating boundaries with the conducting grains. The non-linear coefficient of conduction ($\alpha$) of niobium and tin doped CCTO depend on the sintering hold time and the amount of dopant. The maximum value of $\alpha$ of niobium doped CCTO is $\sim 600$ at CCT10N4, and the maximum value of $\alpha$ of tin doped CCTO is $\sim 830$ at CCT15S4. Identically to the $\alpha$ value trend, the barrier height ($\Phi_0$) also varies according to sintering hold time and the amount of dopant, and reaches maximum $\sim 0.180$ eV at CCT05N4 in the range of $\sim 0.173$ to $\sim 0.180$ eV. There is no direct correlation between non-linear coefficient of conduction and barrier height in terms of sintering hold time for niobium and tin doped CCTO. The bulk activation energy of CCTO is in the range of 0.044 and 0.118 eV and the grain boundary activation energy is in the range of 0.389 and 0.706 eV. The large difference between bulk and grain boundary $E_a$ is a strong indicator that different charge transport mechanisms exist for niobium and tin doped CCTO.

The University of Manchester
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Doctor of Philosophy
Bulk and Grain Boundary Electrical Behaviours in Nb and Sn Doped Calcium Copper Titanium Oxide
2014
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To my wine
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1. Introduction

1.1. General Introduction

Calcium Copper Titanium Oxide (CaCu$_3$Ti$_4$O$_{12}$, CCTO) is a ceramic material with high dielectric constant, $\varepsilon$, ($10 - 100,000$) at room temperature [1-3]. High dielectric constant materials have played an important role in microelectronic technology especially as semiconductor components [4]. CCTO has attracted considerable interest over the last 10 years in power electronics and semiconductor technology. Some circuits require non-linear voltage characteristics for surge protectors especially for sensitive microelectronics. The non-linear coefficient of conduction, $\alpha$, values of CCTO ranges from 10 - 900 [5-7], and these values are sufficient for current needs i.e. 40-50 [8-9]. These features have made CCTO a very attractive option as a new material for application in microelectronics such as varistors, capacitors, memory devices and possible further miniaturization of components.

In the 1920's, a sintered semiconducting powder SiC (Thyrite) was developed, which displayed non-linear voltage behaviour with applied current [10]. These devices are known as varistors. Recently, many companies such as EPCOS (now TDK) [11], Littelfuse [12], Tridelta [13], and Vishay [14], produce Metal Oxide Varistors which are manufactured from Zinc Oxide. Zinc Oxide ceramics have dominated the market over 20 years as varistor and reached a $1$ billion industry in 2012 [15], for instance, Tridelta produces ZnO varistors over 1.5 million units per year [13]. More recently, an alternative ceramic material SnO$_2$ was developed to replace ZnO as varistor which has high breakdown voltage (breakdown voltage and non-linear coefficient of conduction are important parameters of varistor [16]). In 1995, Pianaro et. al. investigated SnO$_2$ as a new varistors system, and they found $\alpha$ values reach 40 [17]. Since the year 2000, Subramanian et. al. [18] found that CaCu$_3$Ti$_4$O$_{12}$ have dielectric constant from $10^2$ to about $10^6$. The dielectric properties in CaCu$_3$Ti$_4$O$_{12}$ system are highly-sensitive to processing parameters [18], and in 2004, Chung et. al. studied non-linear behaviour of CaCu$_3$Ti$_4$O$_{12}$ which highest $\alpha$ value reached 900 [7] as a consequence of different processing strategies. Since then CCTO was developed as a potential varistor [19-21].

The non-linear coefficient of conduction ($\alpha$), breakdown voltage-field ($E_b$) and energy
absorption capability are the vital parameters of ceramic as a varistor [22]. The CCTO has a high non-linear coefficient of conduction [7], low breakdown voltage [2-3, 23] and ability to absorb the potentially destructive energy from transient voltage pulse [12]. Despite the many advantages of CCTO as varistor, there are issues that prevent commercial success of CCTO as a varistor material. The issues are with the effect of processing parameters that poorly understood (powder mixing and pressure, sintering temperature) which are dependent on the type of dopant material. The dopant will affect the electrical properties of CCTO which not only the non-linear coefficient of conduction and breakdown voltage but also their dielectric constant [2-3, 23-29]. The dielectric constant depends strongly on the frequency of the alternating electric field. It also depends on the crystal structure and the imperfections or defects of the material. The movement of the atoms by alternating electric field affects the dielectric losses. To decrease the dielectric loss (high dielectric constant associated with low dielectric loss), one option is use dopants [18].

Niobium (Nb) and Tin (Sn) have been found to change the electrical behaviours of CCTO. Both dopants can increase the dielectric constant of CCTO at a low frequency and decrease it at high frequency [2-3, 11]. Internal barrier layer capacitance mechanism has been widely accepted as an explanation for the high dielectric constant observed in CCTO [12]. This mechanism proposes that insulating grain boundaries separating the semiconducting grains give rise to a high dielectric constant.

Since 2006, there have been several investigation of dielectric and non-linear coefficient of conduction of CCTO [24-30] but none of them clearly investigated of the transition and relation from dielectric properties to non-linear conduction behaviours. Also it is unclear whether the non-linear conduction behaviours is directly related to the extrinsic mechanism responsible for high dielectric constant [5, 7, 18-19, 24-30].

1.2. Aims and Objectives

The aim of this project is to investigate the transition from dielectric behaviour in pure Calcium Copper Titanium Oxide to non-linear behaviour with Niobium (Nb) and Tin (Sn) doping. The transition from dielectric to non-linear behaviour will provide insight into the internal
mechanism of the grain boundary and to improve the material design of varistor. The Impedance Spectroscopy, and DC current-voltage measurements were used to obtain electrical properties. X-ray Diffraction (XRD) measurements were carried out on all samples to monitor the phase equilibria and lattice parameter changes associated with adding different levels of dopants and the scanning electron microscope (SEM) was used to observe the grain size and microstructural evolution of samples.
2. Literature Review

This chapter describes the electrical behaviour, and the structure of Calcium Copper Titanium Oxide (CCTO – CaCu$_3$Ti$_4$O$_{12}$) materials being investigated in this study. Also the properties of a varistor based on CCTO are addressed. This review represents a foundation for research carried out in this study.

2.1. Electrical Behaviour of CCTO.

CaCu$_3$Ti$_4$O$_{12}$ (CCTO) is classified as semiconductor behaviour material (inhomogeneous semiconductor [2], p-type semiconductor nature with band gap of 0.28 eV [1, 5], n-type semiconductor [21], semiconducting grains [27-28, 30-31]). As semiconductor material, CaCu$_3$Ti$_4$O$_{12}$ has specific electrical behaviours such as high dielectric constant, low electrical conductivity, small activation energy, and high non-linear coefficient of conduction. Those electrical behaviours are described later. By varying stoichiometry (intrinsic effect), the electrical behaviours of CaCu$_3$Ti$_4$O$_{12}$ can be due to crystallographic defects or electron excitation. On the other hand, the electrical behaviours of CaCu$_3$Ti$_4$O$_{12}$ also depend on the concentration of dopant (extrinsic effect).

The electrical behaviours of CaCu$_3$Ti$_4$O$_{12}$ are due to barrier-layer capacitances that are related to the presence of grain boundaries [31], twin boundaries (or domain boundaries) [4, 32], dislocation network [7] rather than due to an intrinsic contribution. The semi-conductivity of the grains of CaCu$_3$Ti$_4$O$_{12}$ may depend on electron transport based on mixed valence [32] and oxygen loss during ceramic processing in air at elevated temperatures [24].

2.1.1. Dielectric properties of CCTO.

The dielectric properties of CaCu$_3$Ti$_4$O$_{12}$ material were first reported by Subramanian et al. in 2000 [18]. They first reported that large dielectric constants were found in ACu$_3$Ti$_4$O$_{12}$ (where A = Ca, Cd, La, Sm, Dy, Y, Bi, Nd, Gd and Y) type material. CaCu$_3$Ti$_4$O$_{12}$, demonstrates special behaviour, the high dielectric constant (ε) about 12,000 at 1 kHz, and remaining steady over a large temperature range, from 0°C to 200°C [18]. It is generally observed that ceramics
with dielectric constants higher than 1,000 are associated with ferroelectric materials, where the
dielectric constant changes extensively during the ferroelectric phase transition. Therefore, their
application in industry is limited because often it is required that the dielectric constant of the
material is reasonably independent of the temperature.

In the same year, Ramirez et. al. [1] reported that below 100K (-173°C) the dielectric
constant appears to drop suddenly from around 10,000 to as low as 100 at frequency 100 Hz,
although the CCTO maintains a large dielectric constant that varies little in the temperature
range from 100 K to 400 K at the same frequency as is shown in Figure 2.1. The figure shows
the dielectric loss, or tan δ is less than 0.1 when the temperature is higher than 150 K, and a
large peak occurs at around 100 K. Figure 2.1. also shows the frequency dependence of both
dielectric constant and dielectric loss between 100 Hz and 1 MHz.

![Figure 2.1. (a) The temperature-dependence of the dielectric constant (ε) of CCTO, at different frequencies between 100 and 1 MHz. (b) The dielectric loss (tan δ) at the same frequencies (after Ramirez et. al.[1]).](image)

Similar results also are reported by Holmes et.al [4] as the temperature dependence of
the dielectric constant of CaCu$_3$Ti$_4$O$_{12}$, at different frequencies between 20 Hz and 1 MHz, and
the massive reduction below 100K. From optical data on a single crystal of CaCu$_3$Ti$_4$O$_{12}$, they
found that the dielectric constant as a function of frequency displayed a strong temperature
dependence and so the dielectric constant decrease rapidly with decreasing temperature and
frequency.

2.1.1.1. Capacitance of CCTO.

When an electric field, \( E \), is applied across two parallel capacitor plates of area \( A \) and
distance \( h \) from each other (as illustrated in Figure 2.2.a), one plate becomes positive and the
other negative. A dipole is created, as the negatively charged electron cloud is moving relative
to its positively charged core. This means that a surface charge density, \( \sigma = E \varepsilon_0 \), is stored on
each plate. The dielectric constant (permittivity) of a vacuum is a constant of \( \varepsilon_0 = 8.854 \times 10^{-12} \)
F/m and so the total capacitance, \( C_0 \), of the plates in vacuum is given by Equation (1) [33].

\[
C_0 = \frac{A \varepsilon_0}{h} \quad \text{............................................................. (1)}
\]

When a dielectric material (grey) is placed in between the parallel plates, the applied
field causes the material to become polarised. This is illustrated in Figure 2.2.b. The stored
charge (the area under the curve) increases when a piece of dielectric material is inserted
between two plates (conductors) [35-37], as illustrated in Figure 2.2.c. and Figure 2.2.d. The
susceptibility of the material, \( \chi_e \), results in the capacitance of the plates increasing by a factor of
\( (1+\chi_e) \) and thus the absolute dielectric constant, \( \varepsilon \), of the material is defined by Equation (2).

This creates the concept of the relative dielectric constant of the material, \( \varepsilon_r \), otherwise known
as the dielectric constant, which is an intrinsic property. This is defined in Equation (3).

\[
\varepsilon = \varepsilon_0 (1+\chi_e) \quad \text{............................................................. (2)}
\]

\[
\varepsilon_r = (1+\chi_e) = \frac{\varepsilon}{\varepsilon_0} \quad \text{.......................................................... (3)}
\]

The amount of charge that can be stored in a capacitor, \( Q \), is dependent upon the
voltage applied and the capacitance, \( C \). This relationship is shown in Equation (4). Thus,
capacitance \( C \) is defined to be a charge, \( Q \), per unit applied voltage, \( V \) and given in Coulombs
per Volt, or Farad (F).
Figure 2.2. Schematic diagrams showing (a) how charge can store on capacitor plate in vacuum, and (b) how dielectric material in between them can play a role (after Moulson and Herbert [33]) (c) Closing of the circuit causes a transient surge of current to flow through the circuit. Charge stored on the capacitor is equal to the area under the curve. (d) charge stored on the parallel plates that has to be greater than that stored in (c) (after Barsoum [34])

The capacitance itself is dependent upon the relative dielectric constant, $\varepsilon_r$, the area of the parallel plates, $A$, and the thickness of the dielectric material, $t$. The capacitance is defined by Equation (5).

\[
Q = CV \quad \text{........................................................... (4)}
\]

\[
C = \frac{\varepsilon_0 \varepsilon_r A}{t} \quad \text{........................................................... (5)}
\]

Luo et. al. [38] described how the capacitance of CCTO slightly increases with
increasing temperature for various sintering atmospheres from 125 to 300 K, and rapidly increasing temperature from 75 to 100 K (see Figure 2.3.).

![Figure 2.3. Capacitance of CCTO versus temperature (K) curves at dc bias V = 0 at 1 kHz (after Luo et. al. [38]).](image)

The capacitance may be converted to relative dielectric constant per unit length ($\varepsilon_{\text{eff}}'$) using the relation

$$\varepsilon_{\text{eff}}' = \frac{C}{\varepsilon_0} \quad \text{.......................................................... (6)}$$

![Figure 2.4. Capacitance of CCTO versus frequency (a) at different temperature, (b) as function of grain size (after [39]).](image)
West et al. [39] determined low and high frequency plateaux on capacitance data as a function of frequency, that were attributed to grain-boundary and bulk capacitances (Fig. 2.4 (a)). They also described the effect of processing conditions on capacitance as illustrated in Figure 2.4 (b). The capacitance increases as grain size increases (30 μm after 3 h to ~300 μm after 24 h sintering). The change in microstructure could make a variation in oxygen content between grains, or a variation in cation composition between bulk and grain-boundary which change the electrical behaviour of the grain-boundary region.

2.1.1.2. Relaxation Time of CCTO.

The relaxation time (τ) is time needed for the specific polarization mechanism to occur. The relaxation time depends on the frequencies. The electronic polarization only can occur when the electric field oscillates at very high frequencies (for instance light frequencies) and at lower frequencies, the relative displacement of positive and negative ions can occur (ionic polarization). Orientation polarization requires the rotation of a molecule that occurs only if the oscillation is relatively slow (MHz range or slower) [33].

The temperature dependence of the various electric relaxation times in CaCu$_3$Ti$_4$O$_{12}$ is determined by trap state spectroscopy and by dielectric loss function [41]. Figure 2.5. (a) shows the three semicircles region in CCTO, semicircle I is in temperature range over -73°C (200K), semicircle II is in temperature range between -73°C (200K) and -173°C (100K), and semicircle III is in temperature range below -173°C (100K). Figure 2.5.(a) also shows only one semicircle appears in every temperature. The R and C data can be obtained by fitting the semicircles to series of parallel circuits. A curve of ln (τ) versus 1/T with τ(T) = RC can be plotted to reveal activation energies (E) as shown in Figure 2.5.(b). Pre-factor of the relaxation times τ$_0$(T) is a material dependent constant and can be calculated using Equation (7). The pre-factors are 2.45x10$^{-10}$, 3.50x10$^{-13}$ and 3.02x10$^{-9}$ for region I, II, and III, respectively.

\[
\frac{1}{\tau} = \frac{1}{\tau_0} \exp\left(\frac{-E}{k_B T}\right) \tag{7}
\]
2.1.1.3. Dielectric Strength of CCTO.

The dielectric behaviour of CCTO can be described by the Maxwell–Wagner (MW) model [42], expressed as follows:

\[
\varepsilon^* = \varepsilon' + \frac{\varepsilon' - \varepsilon''}{1 + j\omega \tau} - j\sigma / \omega
\]

where \(\varepsilon^*, \varepsilon',\) and \(\varepsilon''\) are the complex, static, and optical dielectric constants, respectively. The parameters of \(\omega, \tau\) and \(\sigma\), are the angular frequency, the relaxation time, and the electric conductivity, respectively. The term complex dielectric constant \(\varepsilon^*\) is similar with the term of relative dielectric constant \(\varepsilon_r\) in this paper.

There are two components of the complex dielectric constant of a material, a real part, \(\varepsilon'\), and imaginary part, \(\varepsilon''\). \(\varepsilon'\) is a measure of how much energy from an external electric field is stored in a material and \(\varepsilon''\) is a measure of how dissipative is to an external electric field [43]. Their relation to the complex dielectric constant is given as Equation (9).

\[
\varepsilon^* = \varepsilon' - j\varepsilon''
\]

In a system with an ideal capacitance (or inductance), the voltage and current of an AC electric field will be 90 degrees out of phase. In reality, this difference is not exactly 90 degrees.
as the current increase after the voltage increases in dielectric materials. The voltage and
current will be in somewhere between 0 (in phase) and 90 degrees (out of phase). If the angle
of lag is defined as $\delta$, then the amount of lag is defined as $\tan \delta$, otherwise known as the
dielectric loss. This is defined by Equation (10). It is the amount of capacitive current that is lost,
or dissipated, as heat [33].

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$ ............................................................. (10)

Table 2-1. shows the dielectric constant and dielectric loss for various CaCu$_3$Ti$_4$O$_{12}$ with
different temperature and hold time sintering. Most of sintering temperature used ~1100°C with
sintering hold time varying between 1 and 32 hours. Huang et al. [45] reported the dielectric
constant ($\varepsilon$) increases and dielectric loss ($\tan \delta$) decreases with increasing sintering hold time.
Their result is not in line to the other workers that found less sintering hold time could have
higher dielectric constant but with higher dielectric loss.

Table 2-1. Dielectric constant and dielectric loss for various CCTO with different temperature
and hold time during sintering at 25°C.

<table>
<thead>
<tr>
<th>Sintering Temp. (°C)</th>
<th>Hold. (hours)</th>
<th>$\varepsilon'$ (1 kHz)</th>
<th>$\tan \delta$ (1 kHz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1060</td>
<td>1</td>
<td>2738</td>
<td>0.139</td>
<td>[45] Huang et.al. (2013)</td>
</tr>
<tr>
<td>1060</td>
<td>3</td>
<td>9426</td>
<td>0.090</td>
<td>[45] Huang et.al. (2013)</td>
</tr>
<tr>
<td>1060</td>
<td>30</td>
<td>30394</td>
<td>0.076</td>
<td>[45] Huang et.al. (2013)</td>
</tr>
<tr>
<td>1100</td>
<td>10</td>
<td>51555</td>
<td>1.000</td>
<td>[26] Cheng et.al. (2012)</td>
</tr>
<tr>
<td>1100</td>
<td>32</td>
<td>14000</td>
<td>15.000</td>
<td>[44] Leret et.al. (2011)</td>
</tr>
<tr>
<td>1040</td>
<td>10</td>
<td>16421</td>
<td>0.040</td>
<td>[27] Sen et.al. (2010)</td>
</tr>
<tr>
<td>1080</td>
<td>3</td>
<td>40000</td>
<td>0.400</td>
<td>[26] Xue et.al. (2009)</td>
</tr>
<tr>
<td>1100</td>
<td>10</td>
<td>13000</td>
<td>0.060</td>
<td>[25] Cai et.al. (2007)</td>
</tr>
<tr>
<td>1100</td>
<td>3</td>
<td>17550</td>
<td>0.070</td>
<td>[24] Lin et.al. (2006)</td>
</tr>
</tbody>
</table>

2.1.2. Conductivity of CCTO.

The conductivity of CaCu$_3$Ti$_4$O$_{12}$ changes from the grain boundary conductivity
relaxation to the bulk conductivity relaxation with increasing frequencies [46]. Figure 2.6 shows
frequency dependent conductivity at different temperatures, increasing frequency shifts the
conductivity from grain-boundary conductivity relaxation to the bulk conductivity relaxation. This
phenomenon indicates the electrical charge carriers in CaCu$_3$Ti$_4$O$_{12}$ are electronic (electrons)
and ionic (oxygen ions and/or vacancies) at high temperatures [46]. The ionic charge does not common occur at high temperature because of the large activation energy required for lattice defect movement.

Li et. al. [47] suggested bulk phase becomes conducting because a tiny amounts of Ti could be on the Cu site in CCTO, as result of reduction of Cu$^{2+}$ to Cu$^{+}$ at high temperature (the reduction of CuO to Cu$_2$O occurs at about 1300 K in air) as shown in Equation (11).

$$\text{Ca}^{2+} (\text{Cu}^{2+}_{1-x} \text{Cu}^{1+}_{x} \text{Ti}^{4+}_{x})_3 \text{Ti}^{4+}_{4} \text{O}_{12}$$ \hspace{1cm} (11)

When temperature decreases, the Cu$^{1+}$ would oxidise to Cu$^{2+}$ giving up an electron to the Ti 3d band according to

$$\text{Ca}^{2+} (\text{Cu}^{2+}_{1-x} \text{Ti}^{4+}_{x})_3 (\text{Ti}^{4+}_{4-6x} \text{Ti}^{3+}_{6x}) \text{O}_{12}$$ \hspace{1cm} (12)

where Ti$^{3+}$ represents electrons in the Ti 3d band. The reduction in the valency of Cu explains that the bulk phase in CCTO becomes conducting and decreases at higher temperatures.

![Graph showing frequency dependent conductivity σ at different temperatures](image)

**Figure 2.6.** Frequency dependent conductivity $\sigma$ at different temperatures [46]

### 2.1.3. Activation energy in CCTO.

Activation energy (for electrical conductivity) can be related directly to grain boundary barrier-layers height. The height depends on occupation of grain boundary states. Grain-boundaries can play a dominant role in activation energy and the barrier height energy can be the dominant impedance of both electron and hole flow (n and p type) [46, 48]. From frequency-
dependent curves, an activation energy can be estimated using Equation (12)

\[ \sigma = \sigma_0 \exp \left( -\frac{E_a}{k_B T} \right) \]  

(13)

where \( k_B \) is Boltzmann's constant (8.6173 x 10^{-5} eV/K) and \( T \) is absolute temperature (K).

Table 2-2. shows the grain and grain boundary activation energy of CaCu_{3}Ti_{4}O_{12} in various sintering temperature and hold time. Both activation energy will represent difference of conductivity and indicate the different conduction mechanisms between grain and grain-boundary. The grains are assumed already highly conductive, while the grain-boundary is highly resistive, the conduction mechanisms will be discussed later in section 2.4.4.

<table>
<thead>
<tr>
<th>Sintering Temp. (°C)</th>
<th>Hold. (hours)</th>
<th>( E_{a \ b} ) (eV)</th>
<th>( E_{a \ gb} ) (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1080</td>
<td>6</td>
<td>0.090</td>
<td>0.430</td>
<td>[48] Yang et.al. (2013)</td>
</tr>
<tr>
<td>1030</td>
<td>2</td>
<td>0.098</td>
<td>0.725</td>
<td>[30] Thongbai et.al. (2012)</td>
</tr>
<tr>
<td>1050</td>
<td>2</td>
<td>0.113</td>
<td>0.676</td>
<td>[30] Thongbai et.al. (2012)</td>
</tr>
<tr>
<td>1070</td>
<td>2</td>
<td>0.119</td>
<td>0.597</td>
<td>[30] Thongbai et.al. (2012)</td>
</tr>
<tr>
<td>1070</td>
<td>6</td>
<td>0.116</td>
<td>0.513</td>
<td>[30] Thongbai et.al. (2012)</td>
</tr>
<tr>
<td>1100</td>
<td>3</td>
<td>0.102</td>
<td>na</td>
<td>[23] Ni et.al. (2010)</td>
</tr>
<tr>
<td>1100</td>
<td>3</td>
<td>0.062</td>
<td>0.662</td>
<td>[31] Adams et.al. (2006)</td>
</tr>
<tr>
<td>1050</td>
<td>24</td>
<td>0.180</td>
<td>na</td>
<td>[42] G-Fritsch et.al. (2006)</td>
</tr>
<tr>
<td>1050</td>
<td>16</td>
<td>0.076</td>
<td>0.762</td>
<td>[49] Capsoni et.al. (2004)</td>
</tr>
</tbody>
</table>

2.1.4. Non-linear behaviour in CCTO.

The current-voltage characteristic of a varistor is non-linear and empirically expressed by the equation

\[ I = kV^\alpha \]  

(14)

where \( k \) is constant and \( \alpha \) is non-linear coefficient of conduction. Besides the high dielectric response, CCTO also exhibit pronounced non-linear characteristic. The electrostatic barrier at the grain boundary is supposed to be reason for the non-linear behaviour [18, 33]. Lin et. al. [24] investigated non-linear electrical behaviours in TiO_{2}-rich of CaCu_{3}Ti_{4}O_{12}, and found the excessive TiO_{2} in the CaCu_{3}Ti_{4}O_{12} can efficiently improve non-linear coefficient of conduction from 5.1 to 7.9 for current density range 0-3.2 mA/cm^{2}. Lin et. al. [24] also expected high...
dielectric properties in their samples due to the internal boundary layer capacitance effect.

Luo et. al. [50] used microcontact measurements to investigate the electrical properties of individual grains and grain-boundaries of CCTO. They supposed that electrons hop between Ti$^{3+}$ and Ti$^{4+}$ as charge carriers, in the CaCu$_3$Ti$_4$O$_{12}$ bulk, while the capacitance decreases from 100 nF to 100 pF using frequencies from 1 Hz to 1 kHz, which is recognized as the low frequency dispersion behaviour. The hopping localized carrier is also reported by Wang et. al. [51] as a part of dielectric constant of CaCu$_3$Ti$_4$O$_{12}$ behaviour. Figure 2.7. shows the I-V characteristic curves of the bulk and individual grain boundaries which exhibit different shapes of curves. The bulk curves are almost linear but the grain boundary curves demonstrate non-ohmic property because the resistance of grain boundary varies with changes in either voltage or current. No sign of domain boundaries with high resistance was observed. The same curve was obtained when the voltage was applied repeatedly, indicating the breakdown voltage of the grain boundary was recoverable. The non-ohmic I-V characteristic showed the existence of the potential barrier at the grain boundaries.

Figure 2.7. The I-V characteristic curves measured (a) within individual grains and (b) across individual grain boundaries. The different curves within one figure were measured at different points under the same measurement condition (after Luo et. al. [50]).

In 2007, Yu et. al. [52] investigated the ferroelectric relaxor behaviours in CaCu$_3$Ti$_4$O$_{12}$ by studying the current density as a function of applied field. They observed a slim I-V loop that is a characteristic of relaxor ferroelectric with a non-linear ferroelectric behaviour and is shown in Figure 2.8.
Figure 2.8. Plot of current density as a function of applied electric field in CCTO ceramics with various grain sizes (15H (15 hours) sintering hold time has larger grain size). Inset is the enlargement of plots of 1H and 3H [52].

The non-linearity in CaCu$_3$Ti$_4$O$_{12}$ is correlated to the microstructures, as grain size decreases (with less sintering hold time), the current density increases. On the other hand, the resistance at grain boundaries decreases significantly with grain size increasing (not for the resistance at grains) [52]. The possibility of decreasing resistance at grain boundary due to the change of oxygen content [39]. This phenomenon correspond with Chung et. al. [7] who have reported the different electrical potential barriers at grain boundaries lead to various non-linearities.

Table 2-3. shows the non-linear coefficient of conduction and breakdown voltage-field for various CaCu$_3$Ti$_4$O$_{12}$ with different temperature and hold time during sintering. The values of non-linear coefficient of conduction seen are smaller than Chung et. al. [7] found so far ($\alpha = 900$). Usually, non-ohmic devices using current density range of 0-10 mA/cm$^2$, but the high current density range was used by Chung et. al. [7] to measure the non-ohmic properties. It is very important to pay attention about the region of current density where the non-linear coefficient of conduction value is calculated. When dealing with non-ohmic properties, higher current density range could increase the non-linear coefficient of conduction by a factor of 10. For instance, Ramirez et. al.[6] found a value of 65 for current density range 1-10 mA/cm$^2$, and in a current density range of 3-30 mA/cm$^2$, it was found a non-linear coefficient of conduction value ~1500.
Table 2-3. Non-linear coefficient of conduction and breakdown voltage-field of CCTO with various sintering temperature and hold time at 25°C.

<table>
<thead>
<tr>
<th>Sintering Temp. (°C)</th>
<th>Hold. (hours)</th>
<th>α</th>
<th>J (mA/cm²)</th>
<th>E_b (V/cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1060</td>
<td>1</td>
<td>5.85</td>
<td>0-2</td>
<td>3270</td>
<td>[45] Huang et.al. (2013)</td>
</tr>
<tr>
<td>1060</td>
<td>3</td>
<td>5.69</td>
<td>0-2</td>
<td>2140</td>
<td>[45] Huang et.al. (2013)</td>
</tr>
<tr>
<td>1060</td>
<td>30</td>
<td>3.81</td>
<td>0-2</td>
<td>550</td>
<td>[45] Huang et.al. (2013)</td>
</tr>
<tr>
<td>1100</td>
<td>10</td>
<td>3.90</td>
<td>0-3</td>
<td>316</td>
<td>[29] Cheng et.al. (2012)</td>
</tr>
<tr>
<td>1060</td>
<td>2</td>
<td>3.40</td>
<td>0-2.25</td>
<td>710</td>
<td>[28] Liu et.al. (2011)</td>
</tr>
<tr>
<td>1040</td>
<td>10</td>
<td>37.57</td>
<td>0-65</td>
<td>442</td>
<td>[27] Sen et.al. (2010)</td>
</tr>
<tr>
<td>1100</td>
<td>3</td>
<td>5.10</td>
<td>0-3.2</td>
<td>480</td>
<td>[24] Lin et.al. (2006)</td>
</tr>
<tr>
<td>1100</td>
<td>3</td>
<td>900</td>
<td>5-100</td>
<td>1300</td>
<td>[7] Chung et.al. (2004)</td>
</tr>
</tbody>
</table>

2.2. The Effect of Additive and Processing Conditions to CCTO Properties.

There are three types of dopant. Acceptor dopant is defined as dopant elements, which have ionic charges lower than the ions they replace. The acceptor dopant is usually applied on the B site of the perovskite structure (ABO₃). Some examples of acceptor dopant elements are Fe, Nb, Sn, Mn and Ce. Second is isovalent dopant which have ionic charges same with the ion it replace. These dopants can be applied on the A or B site of ABO₃ structure. Donor dopants are defined as dopant elements with a higher ionic charge than ionic they replace; La, Cd and Sr are usually used as A site donors in the perovskite structure. Despite of dopant can decrease the dielectric loss that means increase dielectric constant, some dopant also has the disadvantage in a certain amount i.e. increase the breakdown voltage, decrease the non-linear coefficient of conduction [2-3, 23, 25-26].

2.2.1. Structure of CCTO.

In 1967, a group of French researchers, studied ACu₃B₄O₁₂ family, and found the oxygen 2p mediated hybridization among the Cu d-orbitals and the B-site ions is responsible for a variety of electronic properties [18]. Chevanas et al. [53] reported the detailed and more precise structural analysis of CaCu₃Mn₄O₁₂ in 1975. Based on their study, in 1980, Lacroix [54] described the crystallography of CaCu₃Ti₄O₁₂. The CCTO possesses a distorted cubic...
perovskite (ABO₃) structure with the space group Im3 and a lattice parameter of 7.399 Å [54]. Figure 2.9. shows the unit cell structure of CaCu₃Ti₄O₁₂. The Ca²⁺ ions occupy the corners and the centre of the unit cell while Cu²⁺ ions are located on the centres of cell edges and faces. The Ti⁴⁺ ions are surrounded by 6 oxygen ions, forming TiO₆ octahedra which are tilted inward in order to make a square planar arrangement for the nearby Cu²⁺ ions.

CCTO belongs to a family of oxides ACu₃M₄O₁₂ where A is alkali, alkaline or rare earth metal and M is transition metal [55]. The structure of CCTO is refined to space group Im3 and can transition to ferroelectric structure [18], with changes in the bonding of Ti⁴⁺ within its TiO₆ octahedron. When distance of Ti-O becomes larger, the Ti⁴⁺ shifts in the paraelectric state and is displaced from the centre of the octahedron, when perovskite becomes ferroelectric.

Subramanian et. al. [18] noted that the tension of the Ti-O bonds is associated with enhanced polarizability and the high dielectric constant in CaCu₃Ti₄O₁₂. Moreover the inclined TiO₆ octahedra prevent the formation of the ferroelectric state, consider to the Ti⁴⁺ cation is in a site of full cubic symmetry. Although the high dielectric constant in CaCu₃Ti₄O₁₂ can be explained from the structural point of view, there have been many reports that strongly indicate that the other mechanisms also contribute such as grain-boundary layer capacitors [5, 7], and inhomogeneous microstructure [23, 31-32, 50, 52].
2.2.2. The Effect of dopant to electrical properties of CCTO.

Certain dopants, such as Cr\(_2\)O\(_3\), GeO\(_2\), Mg, Zn and S, are reported to increase the dielectric constant (\(\varepsilon\)) and decrease dielectric loss (\(\tan \delta\)). Kwon et. al. [57] found the dielectric constant of CaCu\(_3\)Ti\(_4\)O\(_{12}\) increased up to 17,000 over a wide range of frequency and dielectric loss (\(\tan \delta = 0.049\) between 100 Hz and 1 kHz with 1% Cr\(_2\)O\(_3\) dopant). They suggested this composition for high dielectric constant application considering its temperature independence of the dielectric constant and the bias dependence of capacitance up to 150 V. Amaral et. al. [58] found the dielectric constant increase with 2-10 wt% GeO\(_2\) doped and at a concentration until 6 wt% with sintering temperature 1050°C promotes maximum the increase of sample grain size and increasing dielectric constant up to \(~4,600\) and \(~2,300\) at 100 kHz and 1 MHz, respectively. Dielectric constant increased with increasing Mg-substitution (up to 0.1 mol) was reported by Ni et. al. [59]. They found the dielectric constant increased from \(~32,000\) to \(~125,000\) at frequencies below 100 kHz, they also found increasing substitution Zn from Cu will increase dielectric constant [60] and the dielectric constant around \(~90,000\) for 0.1 mol Zn at 10 kHz.

CaCu\(_3\)Ti\(_4\)O\(_{12}\) that was doped with 0.2 mol Sr decreased dielectric loss within the frequency range between 0.2 and 20 kHz as reported by Li et. al. [61]. On the other hand, adding strontium will improve the sinterability by largely reducing sintering temperature and promoting densification and grain growth during sintering, that is believed to increase the dielectric constant [61]. In 2005, iron was used to decrease dielectric loss by Grubss et. al. [2], they found that increased iron doping makes very low dielectric loss less than 0.01 at a low temperature (below \(~250\) K). Moreover, Mu et. al. [62] reported that resistivity \(\rho\) increases while the dielectric constant decreases in frequency range of 1 kHz to 1 MHz with 0 – 0.2 mol Fe dopant.

There were still contradictory results from the use of niobium doping in CaCu\(_3\)Ti\(_4\)O\(_{12}\), Grubss et. al. [2] found that increased niobium doping lead to lower dielectric constant in the plateau region and to the lower dielectric losses. On the other hand, Liu et. al. [63] reported that increasing niobium doped lead to an increase dielectric constant at low frequencies (40 Hz – 10 kHz) and decrease at high frequencies (10 kHz – 1 MHz), as shown in Figure 2.10. Table 2-5. shows the dielectric constant, dielectric loss, non-linear coefficient of conduction, and electric field breakdown of CaCu\(_3\)Ti\(_4\)O\(_{12}\) with various dopants.
Figure 2.10. Frequency dependence of the dielectric constant and tan δ of CaCu$_3$Ti$_{4-x}$Nb$_x$O$_{12}$ ($x = 0, 0.01, 0.08, 0.2$), measured at room temperature in the frequency range of 40 Hz–110 MHz, (from Liu et. al. [63]).

Table 2-4. Electrical properties of CCTO with various dopants.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dopant</th>
<th>$\varepsilon$ (1 kHz)</th>
<th>$\tan \delta$ (1 kHz)</th>
<th>$\alpha$ (J/mA)</th>
<th>$E_b$ (V/cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCu$<em>3$Ti$</em>{4-x}$Ce$<em>x$O$</em>{12}$</td>
<td>0.05</td>
<td>22628</td>
<td>&lt;1</td>
<td>3 [0-3]</td>
<td>947</td>
<td>[29] Cheng et. al. (2012)</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>916</td>
<td>&lt;1</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>91</td>
<td>6</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>CaCu$<em>3$Ti$</em>{4-x}$Sn$<em>x$O$</em>{12}$</td>
<td>0.05</td>
<td>600000</td>
<td>0.05</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>350000</td>
<td>0.04</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>CaCu$<em>3$Ti$</em>{4-x}$V$<em>x$O$</em>{12}$</td>
<td>0.10</td>
<td>20681</td>
<td>0.06</td>
<td>23.22 [0-65]</td>
<td>185</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>34678</td>
<td>0.08</td>
<td>6.15 [0-65]</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>13074</td>
<td>0.04</td>
<td>1.66 [0-65]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$_{1-3x/2}$Sr$<em>x$Cu$<em>3$Ti$</em>{4}$O$</em>{12}$</td>
<td>0.05</td>
<td>20681</td>
<td>0.06</td>
<td>4.02 [0-15]</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>34678</td>
<td>0.08</td>
<td>3.31 [0-15]</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>13074</td>
<td>0.04</td>
<td>5.02 [0-15]</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>Ca$_{1-3x/2}$La$<em>x$Cu$<em>3$Ti$</em>{4}$O$</em>{12}$</td>
<td>0.025</td>
<td>12840</td>
<td>na</td>
<td>2.8 [0-6]</td>
<td>742</td>
<td>1476</td>
</tr>
<tr>
<td></td>
<td>0.050</td>
<td>8026</td>
<td>na</td>
<td>3.1 [0-6]</td>
<td></td>
<td>71</td>
</tr>
<tr>
<td>Ca$<em>3$Ti$</em>{4-x}$Mn$<em>x$O$</em>{12}$</td>
<td>0.01</td>
<td>~10000</td>
<td>na</td>
<td>3.6 [0-4]</td>
<td>2200</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>~4000</td>
<td>na</td>
<td>2 [0-3]</td>
<td>3080</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>100</td>
<td>na</td>
<td>1 [0-0.025]</td>
<td>3910</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>100</td>
<td>na</td>
<td>1 [0-0.025]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$<em>3$Ti$</em>{4-x}$Nb$<em>x$O$</em>{12}$</td>
<td>0.02</td>
<td>~150000</td>
<td>~0.3</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>~220000</td>
<td>~0.5</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>~420000</td>
<td>~0.2</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>~100000</td>
<td>~0.2</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>~200000</td>
<td>~2.0</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>~1000000</td>
<td>~1.8</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>Ca(Cu$_{1-x}$Mg$<em>x$)$<em>3$Ti$</em>{4}$O$</em>{12}$</td>
<td>0.05</td>
<td>100000</td>
<td>0.70</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>200000</td>
<td>0.30</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>Ca(Cu$_{1-x}$Zn$<em>x$)$<em>3$Ti$</em>{4}$O$</em>{12}$</td>
<td>0.05</td>
<td>~90000</td>
<td>0.08</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>~100000</td>
<td>0.20</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
</tbody>
</table>

Cheng et.al. (2012)
Chen et.al. (2010)
Ni et.al. (2010)
Sen et.al. (2010)
Kue et.al. (2009)
Xue et.al. (2009)
Ni and Chen (2009)
Ni et.al. (2010)
Ni and Chen (2009)
Ni et.al. (2007)
Hai et.al. (2007)
Hong et.al. (2007)
Liu et.al. (2009)
Ni and Chen (2009)
Ni and Chen (2010)
2.2.3. Defect contribution to electrical properties with adding dopant

There are two main defects in chemistry which is intrinsic and extrinsic point defects. Schottky and Frenkel defects are part of intrinsic point defect. Schottky defect consists of charge balancing cation and anion vacancies. Frenkel defect is a charge balancing interstitial and vacancy. Figure 2.11. (a) and (b) show both of intrinsic point defects. Extrinsic point defect will be introduced anion vacancy if cation impurity is introduced into a solid and the dopant does not have the same valence as the cation it is replacing. Three extrinsic point defects are shown in Figure 2.11.(c).

The probable explanation for the stoichiometric changes in CCTO during sintering was first given by Li et al. [65]. They suggested that Cu$^{2+}$ reduces to Cu$^{1+}$ upon heating with the substitution of Ti$^{4+}$ on Cu sites, while the re-oxidation of Cu$^{1+}$ to Cu$^{2+}$ occurs along with the reduction of Ti$^{4+}$ to Ti$^{3+}$ upon cooling. Their experiment did not show an exceptionally high dielectric constant for CCTO. Following this model, there have been reports dealing with the cation stoichiometry correlated with the dielectric responses, microstructures, and processing conditions of CCTO. In 2006, Fang et al. [66] showed that the improvement of grain boundary resistivity is due to the existence of Cu-rich grain boundaries. Using EDS analysis, Fang et. al. [67] also confirmed the presence of Cu-rich grain boundaries as well as Cu-deficient grains in CCTO. Although the copper stoichiometry is related to the very large dielectric constant
response in CCTO, the precise mechanisms remains unresolved at the moment.

On the other hand, in 2007, Capsoni et. al. [49] and Shao et.al [68] studied CuO segregation using the variation in copper content exhibited different aspects from the measured dielectric properties, electrical resistivity, and microstructures, and found that CuO segregation could drop dielectric constant rapidly to around 100 with decreasing temperature or increasing frequency. A similar research performed by Shri Prakash and Varma [69] reported the effects of the segregation of Cu-rich phase on both dielectric properties and microstructures in terms of the sintering temperatures. They found the dielectric constant was not significantly decreased but the grain sizes (50-60 μm) increase with Cu-rich phase segregation at grain boundary.

Schmidt et. al. [70] summarised equation defect mechanisms, solid solutions and possible compensation mechanisms also a further mechanism below. Oxygen loss and the formation of oxygen vacancies (during sintering or sol-gel processing) is represented at Equation (15), which compensation occurs by Ti$^{4+} \rightarrow$ Ti$^{3+}$ reduction.

\[
\begin{align*}
O_2^- + 2Ti^{4+} & \rightarrow V_0^- + 2Ti^{3+} + 1/2O_2 \uparrow : \\
Ca(Cu_3)Ti_{4-v}^{4+}Ti_v^{3+}O_{12}^{-v/2} & \hspace{1cm} \text{(15)}
\end{align*}
\]

Equation (16) represents reduction of Cu$^{2+}$ to Cu$^{+}$ and the Cu sites are partially occupied by Ti$^{4+}$.

Both processes usually take place during heat treatment at elevated temperatures.

\[
\begin{align*}
3Cu^{2+} & \rightarrow 2Cu^{+} + Ti_{Cu}^{4+} + Cu \uparrow : \\
Ca(Cu_3^{3-v}Cu_2^{v}V_0^{v})Ti_{4-v}^{4+}O_{12} & \hspace{1cm} \text{(16)}
\end{align*}
\]

If Equation (16) is cooled by re-oxidation process, the Cu deficiency is compensated for by the partial reduction of Ti$^{4+} \rightarrow$ Ti$^{3+}$ also known as internal redox process represents as Equation (17).

\[
\begin{align*}
Cu^{+} + Ti^{4+} & \rightarrow Cu^{2+} + Ti^{3+} : \\
Ca(Cu_3^{3-v}Ti_0^{v})Ti_{4-2v}^{4+}Ti_{2v}^{3+}O_{12} & \hspace{1cm} \text{(17)}
\end{align*}
\]

The Cu loss is due to Cu segregation and formation of Cu vacancies is represented by Equation (18).

\[
\begin{align*}
3Cu^{2+} & \rightarrow V_{Cu}^{v'} + 2Cu^{3+} + Cu \uparrow : \\
Ca(Cu_3^{3-v}Cu_2^{v}V_0^{v})Ti_4O_{12} & \hspace{1cm} \text{(18)}
\end{align*}
\]

The further mechanisms correspond to excess Cu and compensation occurs by Cu$^{2+}$ occupying
Ti sites and the formation of oxygen vacancies is represented by Equation (19).

\[
\begin{align*}
\text{O}_2^- + \text{Ti}^{4+} & \rightarrow \text{V}^-_{\text{O}} + \text{Cu}^{2+}_{\text{Ti}} + \frac{1}{2}\text{O}_2 \\
\text{Ca} (\text{Cu}^{3+}) \text{Ti}_{4-w}^4 \text{Cu}_w^{2+} \text{O}_{12-w}^{-} & \uparrow \\
& \text{................................................. (19)}
\end{align*}
\]

Some of the possibility of mechanisms above could be occur in the same time, but so far only two of these Equation (16) and (17) are the dominant ones as shown by Li et. al. [65].

The effect of dopant on the electrical properties of CaCu$_3$Ti$_4$O$_{12}$ depends on the stoichiometric changes. The values of dielectric constant, dielectric loss, non-linear coefficient of conduction and also breakdown voltage-field vary from higher to lower. The factors that affected the electrical properties not only depend on the dopant but also it depends on sintering temperature and the atmospheres processing conditions. These will be discussed later in section 2.2.4. Table 2.5. shows the highest dielectric constant (\(\varepsilon\)) and non-linear coefficient of conduction (\(\alpha\)) reach 6.0 \times 10^5 at 1 kHz with 0.05 mol tin dopant [23] and 23.22 at current density range 0 – 65 mA/cm$^2$ with 0.10 mol V dopant [27], respectively. In this case, a correlation between high dielectric constant and non-linear coefficient of conduction does not appear directly.

2.2.4. Electrical properties change relative to sintering time

Ni et. al. [72] suggested that appropriately extending sintering time would benefit the densification and formation of bigger and more uniform grains of CCTO. They found that doubling sintering time, from 3h to 6h, increased dielectric constant from 514 to 12,400. Romero et. al. [73] reported by increasing sintering time (up to 32h) at 1100°C on open air; the dielectric constant of CCTO ceramics increases up to a value of 6\times10^4. This increase of the dielectric constant is accompanied by a thickness reduction of the copper oxide intergranular phase and a Cu enrichment of the CCTO grains.

Kwon and Cann [74] have noted that X-ray diffraction data could explain the secondary phases as a function of sintering time based on the reduction/reoxidation reactions. Grain growth of CaCu$_3$Ti$_4$O$_{12}$ continued from 0.5 to 4h sintering time but after 8h sintering grain growth was limited. These microstructures increase the dielectric constant up to ~90,000 (at 1 kHz) with the dielectric loss 0.3-0.4. That result relevant with investigation by Prakash et. al. [55], the
The dielectric constant of the CCTO ceramic was shown to have strong microstructure dependence in relation to the sintering temperature and duration of sintering. Li et. al. [75] showed that the non-linear coefficient of conduction decreased (from 5.5 to 4.0) with the increased sintering time (from 10 to 20 hours).

Lin et. al. [24] used 3 hours sintering time at 1100°C and found the dielectric constant 1.05 x 10^4 at 10^6 Hz. On the other hand, Cai et. al. [25] and Cheng et. al. [29] found dielectric constant (ε) up to 4x10^4 at 10^6 Hz after sintering for 10h at 1100°C. Leret et. al. [44] used various sintering time 4h, 8h and 16h at 1100°C and found dielectric constant (ε) = 1.1x10^4, 1.2x10^4 and 1.3x10^4 at 10^4 Hz, respectively. The dielectric constant increased as sintering time increased, but the frequency of the maximum dielectric constant did not depend on sintering time. Table 2.6. shows the dielectric constant, dielectric loss and non-linear coefficient of conduction change relative to sintering time.

<table>
<thead>
<tr>
<th>CaCu_{3}Ti_{4}O_{12}</th>
<th>Sintering</th>
<th>Temperature (25-27°C)</th>
<th>Freq. (Hz)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. (C)</td>
<td>Hold. (h)</td>
<td>ε</td>
<td>tan δ</td>
<td></td>
</tr>
<tr>
<td>[24] Lin et.al. (2006)</td>
<td>1100</td>
<td>3</td>
<td>10500</td>
<td>0.07</td>
</tr>
<tr>
<td>[44] Leret et.al. (2011)</td>
<td>1100</td>
<td>4</td>
<td>11000</td>
<td>na</td>
</tr>
<tr>
<td>[44] Leret et.al. (2011)</td>
<td>1100</td>
<td>8</td>
<td>12000</td>
<td>na</td>
</tr>
<tr>
<td>[55] Prakash et.al. (2006)</td>
<td>1100</td>
<td>10</td>
<td>21000</td>
<td>na</td>
</tr>
<tr>
<td>[79] Li et.al. (2010)</td>
<td>1100</td>
<td>10</td>
<td>~4000</td>
<td>0.1</td>
</tr>
<tr>
<td>[29] Cheng et.al. (2012)</td>
<td>1100</td>
<td>10</td>
<td>51555</td>
<td>&lt;1</td>
</tr>
<tr>
<td>[44] Leret et.al. (2011)</td>
<td>1100</td>
<td>16</td>
<td>13000</td>
<td>na</td>
</tr>
<tr>
<td>[75] Li et.al. (2010)</td>
<td>1100</td>
<td>20</td>
<td>~12000</td>
<td>0.09</td>
</tr>
<tr>
<td>[73] Romero et.al. (2010)</td>
<td>1100</td>
<td>32</td>
<td>60000</td>
<td>30</td>
</tr>
<tr>
<td>[74] Kwon &amp; Cann (2009)</td>
<td>1115</td>
<td>2</td>
<td>~30000</td>
<td>0.2</td>
</tr>
<tr>
<td>[74] Kwon &amp; Cann (2009)</td>
<td>1115</td>
<td>4</td>
<td>~70000</td>
<td>0.3</td>
</tr>
<tr>
<td>[74] Kwon &amp; Cann (2009)</td>
<td>1115</td>
<td>8</td>
<td>~90000</td>
<td>0.4</td>
</tr>
<tr>
<td>[72] Ni et.al. (2007)</td>
<td>1120</td>
<td>3</td>
<td>514</td>
<td>2.25</td>
</tr>
<tr>
<td>[72] Ni et.al. (2007)</td>
<td>1120</td>
<td>6</td>
<td>12400</td>
<td>0.87</td>
</tr>
</tbody>
</table>

It has been recognized that non-stoichiometric materials such as CaCu_{3}Ti_{4}O_{12} [65], or containing TiO_{2} become conductive after sintering in reducing conditions [33]. In non-stoichiometric conditions, donor ions will improve the reduction while acceptor ions will impede the process, then, this reduction process during sintering can be significantly modified by composition.
2.3. Impedance Spectroscopy

Impedance spectroscopic measurements normally use two identical electrodes applied to both surfaces of a disk of sample. The common and standard method is to measure impedance directly in the frequency domain by applying a single-frequency voltage to the sample and measuring the phase shift and amplitude [76]. The frequency domain could be several orders of magnitude, typically in this work 5 Hz to 12 MHz. This frequency range is available on most commercial instruments and can achieve a better signal to noise ratio. The other advantage of using wide range of frequencies is that one experiment can detect different processes with different time constants.

2.3.1. Impedance data format

Macdonald and Johnson [76] argued that impedance is a more general concept than resistance because it takes phase differences into account. Electrochemical impedance experimental usually uses excitation of a small amplitude \( V_A \) (Volt) AC voltage signal with applied at frequency \( f \) (Hz). If a small sinusoidal potential \( (V_A \sin (\omega t)) \), and the current signal \( (I(t)) \) is shifted in phase \( (\theta) \) and has a different amplitude \( (I_A) \) across an electrical element with an impedance \( (Z^*) \), then the complex impedance is determined by:

\[
Z^* = \frac{V(t)}{I(t)} = \frac{V_A \sin(\omega t)}{I_A \sin(\omega t + \theta)} \quad \text{................................................ (20)}
\]

where \( V(t) \) is AC voltage signal as a function of time \( t \), and \( \omega \) is radial frequency related to AC frequency \( (= 2\pi f) \). The complex impedance of the system (analogous to Ohm's law) is expressed by

\[
Z^* = Z_A \frac{\sin(\omega t)}{\sin(\omega t + \theta)} \quad \text{................................................ (21)}
\]

where \( Z_A = V_A/I_A \) in term of absolute value of \( Z^* \) \( (Z_A = |Z^*|) \). The impedance also can be represented as a complex number, using Euler's relationship

\[
Z^* = Z_A e^{j\theta} = Z_A (\cos \theta - j \sin \theta) = Z' - jZ'' \quad \text{................................. (22)}
\]

where \( Z' \) is the real part of the complex number and \( Z'' \) is the imaginary part of the complex number, and \( j = \sqrt{-1} = \exp(j\pi/2) \). The plot of \( Z'' \) vs \( Z' \) is called a Nyquist plot where two
rectangular coordinate values are \( Z' = |Z^*| \cos \theta \) and \( Z'' = |Z^*| \sin \theta \), as shown in Figure 2.12.(a) that represents impedance for single parallel R and C circuit. The phase is ratio of the imaginary and real impedance components:

\[
\tan \theta = \frac{Z''}{Z'} \quad \text{or} \quad \theta = \tan^{-1}\left(\frac{Z''}{Z'}\right)
\]

Another plot of the total impedance \( |Z| \) or phase angle \( \theta \) as function of frequency \( \omega \) is called Bode plots (Figure 2.12.(b)). Both the complex impedance plane plot and the Bode plot are used to represent impedance spectroscopy.

![Diagram of impedance plot](image)

Figure 2.12. Nyquist plot of real and imaginary part of impedance, equivalent R|C circuit (a) and Bode plot of phase angle and angular frequency (b).

Equation (22) is modified to express the total, real, imaginary impedance of R|C (parallel R and C circuit) as:

\[
Z^*(\omega) = \frac{R}{1+(\omega RC)^2} - j\frac{\omega R^2 C}{1+(\omega RC)^2}
\]

where the \( Z' \) and \( Z'' \) as shown in Equation (25) and (26), respectively.

\[
Z'(\omega) = R \left( \frac{1}{1+(\omega RC)^2} \right)
\]

\[
Z''(\omega) = \omega \left( \frac{R^2 C}{1+(\omega RC)^2} \right)
\]
and the phase is
\[
\theta = \tan^{-1}(\omega RC) = \tan^{-1}(-\omega \tau) \quad \text{.......................... (27)}
\]
where \(\tau\) is the time constant (relaxation time) of the R|C at the critical frequency \(f_c = 1/(2\pi RC) = f_{\text{max}}\). The frequency at the maxima Bode plot (Figure 2.12.(b)) for R|C is given by
\[
\omega_{\text{max}} = 2\pi f_{\text{max}} = (RC)^{-1} = \tau^{-1} \quad \text{.......................... (28)}
\]
Impedance becomes completely resistive at low-frequencies and becomes completely capacitive at very high-frequencies, and the value of \(R\) is equal to the diameter of the Nyquist plot semi-circle at \(\omega_{\text{max}}\) (Equation (28)) as shown in Figure 2.12.(a).

2.3.1.1. Dielectric constant

The “complex dielectric constant” \(\varepsilon^*\) is analogous to the concept of complex impedance \(Z^*\) as Equation (9) stated \(\varepsilon^* = \varepsilon' - j\varepsilon''\). Based on AC frequency dependence, the complex dielectric constant can written as \(\varepsilon^* = f(\omega)\). Expansion from Equation (9) leads to:
\[
\varepsilon^*(\omega) = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + j\omega\tau} \quad \text{.......................... (29)}
\]
where the \(\varepsilon'(\omega)\) and \(\varepsilon''(\omega)\) as shown in Equation (24) and (25), respectively.
\[
\varepsilon'(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + \omega^2 \tau^2} \quad \text{.......................... (30)}
\]
\[
\varepsilon''(\omega) = \frac{\Delta\varepsilon \omega \tau}{1 + \omega^2 \tau^2} \quad \text{.......................... (31)}
\]

2.3.1.2. Modulus

Another representation of the dielectric properties of analysed media is complex modulus \(M^*\), which is the inverse of complex dielectric constant \(\varepsilon^*\):
\[
M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = M' - jM'' = j\omega\varepsilon_0 Z^*(\omega) \quad \text{.......................... (32)}
\]
where \(\varepsilon_0\) is the dielectric constant of free space, \(8.854 \times 10^{-14}\) F/cm. Expansion from Equation
(25) and (26) leads to:

\[ M'(\omega) = \frac{\varepsilon_0}{C} \frac{j \omega RC}{1 + (\omega RC)^2} \] ................................................ (33)

\[ M''(\omega) = \frac{\varepsilon_0}{C} \frac{\omega^2 R^2}{1 + (\omega RC)^2} \] ................................................ (34)

Morrison et. al. [77] in 2001, used the Debye peak (the peak of the dielectric relaxation curve) in spectroscopy plots of the imaginary components, \(Z''\) and \(M''\) versus \(\log \omega\) to extract \(R\) and \(C\) values. Both of them are independent of geometry of the sample and are intrinsic properties of \(R|C\) element [77]. The magnitudes of Debye peaks scale according to \(R\) for \(Z''\) spectra and \(1/C\) for \(M''\) spectra [77] at the peak maxima are given by

\[ Z''(\omega)_{max} = R/2 \] ..................................................... (35)

\[ M''(\omega)_{max} = \varepsilon_0/2C \] ................................................ (36)

In practice, using Equation (35) and (36), the magnitude of \(R\) and \(C\) can be estimated from \(Z''_{max}\) or \(M''_{max}\). Sinclair and West [78] used combination of impedance and modulus spectroscopy to highlight phenomena between \(Z''\) plot with the largest resistance and \(M''\) plot with the smallest capacitance.

2.3.2. Brick layer model.

In 1976, Beekmans and Heyne (after Bonanos et. al. [79]), proposed a model to describe the electrical properties of a two-phase mixture, has been termed the brick layer model. The model uses the microstructure as an array of cubic grains, separated by flat grain boundaries, as shown in Figure 2.13.(a). \(D\) is the grains side and \(d\) is a thickness of the grain boundaries, where \(d < D\), and so the volume fraction of the grain boundary phase is \(3d/D\) [79].

The current flow is assumed to be one-dimensional, and curvature of the current paths at the corners of the grains is neglected. Figure 2.13.(b) shows two paths that available to the current which are 1) through grains and across grain boundaries (intergranular) or 2) along grain boundaries (intragranular). Depending on the relative magnitudes of conducting, \(\sigma_g\) and \(\sigma_{gb}\) (where the subscript, \(g\) denotes grain (interior) phase, and \(gb\) denotes grain boundary phase) one of the two paths will normally dominate.
2.3.3. Equivalent circuits of impedance plot.

There are three parameters in impedance measurements, i.e. impedance, phase angle, and the frequency. When material is investigated using impedance spectroscopy, the electric field with varying frequency is applied as energy and the electrical response is determined by electrical properties (after Macdonald and Johnson [76]). The microstructure and inhomogeneities of material lead to changes in the electrical properties thus give rise to a different impedance spectrum. The electrical response from grain and grain boundary are reflected in different frequency domains, because both of them commonly have phase differences and time constants. Time constant (τ in second) is equal to the resistance (Ohm) multiplied by the capacitance (F), and in this case is called relaxation time (see section 2.3.1.). These differences also apply at electrode or material interfaces and with different physical processes eg. gas absorption [79]. The Maxwell-Wagner series layer model represents two phases stacked in layers parallel to the electrodes (Figure 2.14.(a)) and every layer is represented by a series equivalent circuit model $R_1|C_1 - R_2|C_2$ (Figure 2.14.(b)).
The series $R|C$ element suitable in the case where a material have electrical response with different of time constants in the wide range of frequencies. This situation should result in the appearance of two semi-circles in Nyquist plot.

The grain and grain-boundary of microstructure contributions, analogous to the Maxwell-Wagner series layer model, is illustrated in Figure 2.15. From this illustration, using electrical components for each of the phenomena for a representative model of the how the material behaves; an equivalent circuit of the material can be derived. This illustration also relates to brick layer model that will be discussed in section 2.3.6.

According to Abrantes et. al. [81], for a two element system the real and imaginary parts of the impedance (given in Equation (25) and (26)) are modified to:
\[
Z'(\omega) = \frac{R_b}{1 + (\omega/\omega_b)^2} + \frac{R_{gb}}{1 + (\omega/\omega_{gb})^2} \quad \cdots \quad (37)
\]

\[
Z''(\omega) = \frac{R_b(\omega/\omega_b)}{1 + (\omega/\omega_b)^2} + \frac{R_{gb}(\omega/\omega_{gb})}{1 + (\omega/\omega_{gb})^2} \quad \cdots \quad (38)
\]

where

\[
\omega = 2\pi f = 1/(RC) \quad \cdots \quad (39)
\]

and subscript b and gb refer to bulk (grain) and grain-boundary, respectively. If the \( \varepsilon_0 \) is substituted with \( C_0/(h/A) \) (Equation (1)), the real and imaginary part of modulus are

\[
M'(\omega) = \frac{j(C_0/C_b)}{1 + (\omega/\omega_b)^2} + \frac{j(C_0/C_{gb})}{1 + (\omega/\omega_{gb})^2} \quad \cdots \quad (40)
\]

\[
M''(\omega) = \frac{(C_0/C_b)(\omega/\omega_b)}{1 + (\omega/\omega_b)^2} + \frac{(C_0/C_{gb})(\omega/\omega_{gb})}{1 + (\omega/\omega_{gb})^2} \quad \cdots \quad (41)
\]

where subscript of 0 represents of vacuum condition (section 2.1.1.1), b is bulk (grain), and gb is grain boundary.

2.3.3.1. Analysis of impedance data.

Abram et. al. [82] suggested two approaches to analyse the impedance spectroscopy data. The first is to assume an equivalent circuit based on visual inspection of the data, impedance \( Z' \) complex plane \( Z'' \) vs. \( Z' \) plot and by a simple hand-fitting procedure calculate the various R and C values. The second is to model the data using various equivalent circuit to extract R and C values, using a quantitative approach, with the final values depending on the quality of agreement between experimental and simulated data. In practice, most samples do not display the ideal Debye-peak behaviour, the arcs are depressed with their centres displaced below the real axis [82]-sometime called “non-Debye” or “Debye-like”-for this reason, it is hard to use hand-fitting procedure to obtain the R and C values. Modelling non-ideal responses and demonstrating a acceptable equivalent circuit to represent the electrical properties is necessary to understanding of electroceramics. Therefore, curve fitting and the testing of various equivalent circuits is essential. Figure 2.16. shows the differences results between two modelling of impedance spectroscopy data of CCTO.
Figure 2.16. Equivalent electrical circuits used to model impedance spectroscopy data.

If \( \omega \to 0 \) and \( \omega \to \infty \), The value of \( Z' (0) = R_b + R_{gb} \), and \( Z' (\infty) = R_b \). Figure 2.17. shows the RC effective circuit, and \( b \) and \( gb \) represent grain and grain boundary, respectively.

\[
Z'(\omega) = \frac{R_b + \frac{1}{R_{gb}} + j \omega C_{gb}}{R_b + \frac{1}{R_{gb}} + j \omega C_{gb}}
\] .......................... (42)

where \( \omega = 2\pi f \) is the angular frequency and \( 0 < \omega < \infty \). \( R_b, R_{gb}, C_b \) and \( C_{gb} \) are the resistance and

Figure 2.17. (a) An equivalent electrical circuit (R|C-R|C) commonly used to model impedance spectroscopy data of electroceramics, and (b) a \( Z^* \) plot for grain and grain boundary (after Abram et. al. [82]).

The complex impedance can be expressed as the following:

\[ Z^*(\omega) = R_b + \left( \frac{1}{R_{gb}} + j \omega C_{gb} \right)^{-1} \] .......................... (42)
capacitance of grain and grain boundary, respectively. The real part of complex impedance spectra was drawn from Equation (42) becomes:

$$Z'(\omega) = R_b + \left(R_{gb}/\left[1 + (\omega C_{gb} R_{gb})^2\right]\right)$$ .............................................. (43)

Each parallel RC element (Figure 2.17.(a)) gives rise to a semicircle or depressed circle from which the component R and C values may be extracted. The magnitude of capacitance (C) is used to interpret the regions of the arc. Irvine et al. [83] gave possible interpretation of capacitance value to phenomenon responsible, as shown in Table 2-7.

The equivalent electrical circuit may be in form of some combination of resistors, capacitors and constant phase elements (CPEs) (section 2.3.4.) connected in series and/or parallel. When there is a single arc seen on the Nyquist plot, starting very close to the origin, for dielectric materials, the electrical contribution is thought to be from the bulk or grain. If there is a second semicircular arc interfering on the right hand side (at lower frequencies), this is generally interpreted as the beginning of grain boundary response [76, 82].

<table>
<thead>
<tr>
<th>Capacitance (F)</th>
<th>Phenomenon Responsible</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-12}$</td>
<td>Bulk</td>
</tr>
<tr>
<td>$10^{-11}$</td>
<td>Minor, Second phase</td>
</tr>
<tr>
<td>$10^{-11} - 10^{-9}$</td>
<td>Grain-boundary</td>
</tr>
<tr>
<td>$10^{-10} - 10^{-9}$</td>
<td>Bulk ferroelectric</td>
</tr>
<tr>
<td>$10^{-9} - 10^{-7}$</td>
<td>Surface layer</td>
</tr>
<tr>
<td>$10^{-7} - 10^{-5}$</td>
<td>Sample-electrode interface</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>Electrochemical reaction</td>
</tr>
</tbody>
</table>

2.3.4. Constant Phase Elements.

In order to account for non-ideal impedance spectroscopy data, constant phase elements (CPEs) are used to replace the capacitor or in addition to resistor-capacitor circuit. The CPE arises because microscopic material properties often have a distribution of values caused by for example electrode inhomogeneity, surface roughness, and electrode porosity, or sometimes containing a large number of surface defects, local charge inhomogeneities, variations in composition or/and stoichiometry [76]. The CPE is an electrical element similar to
capacitance having the property that its phase angle is fixed, but not 90° [84]. A CPE has an impedance \(Z_{\text{CPE}}^*\) defined as

\[
Z_{\text{CPE}}^*(\omega) = \left[\Lambda (j\omega)^n\right]^{-1}
\]

(44)

where \(\Lambda = A/\cos(n\pi/2)\), \(A\) is a constant and \(n\) are constants and \(j = \sqrt{-1}\). The best method of fitting this circuit to the bulk data is to examine spectroscopy plots of the real part of the complex admittance, \(Y^*\). The expression for \(Y^*\) for the circuit shown is:

\[
Y^*(\omega) = R^{-1} + \Lambda \omega^n \cos\left(\frac{n\pi}{2}\right)
\]

(45)

Abram et. al. [82] documented the non-ideal (Debye-like) behaviour of many electroceramics and especially, the bulk component of ionic conductors and can often be successfully modelled using a parallel combination of R, C and CPE components also the \(n\) can be derived from the gradient of curve (see Figure 2.18.).

![Figure 2.18. Schematic plot of log \(Y^*\) against log \(\omega\) illustrating a low frequency plateau and a high frequency dispersion for an electroceramic, (from Abram et. al. [82]).](image)

Abram et. al. [82] illustrated a frequency-independent plateau at low frequencies, using a spectroscopy plot of log \(Y^*\) against log \(\omega\), where \(Y^* \approx R^{-1}\). When log \(Y^*\) increases linearly with log \(\omega\) is called ‘cross-over’ region. This phenomenon happens after the constant line of log \(Y^*\) reaches a point that high frequency spread widely (Figure 2.18). The value of \(n\) gives the gradient of the linear dispersion region, and log \([\Lambda \cos(n\pi/2)]\) is the extrapolated intercept with the log \(Y^*\) axis at \(\omega = 1\) Hz. Non-ideal (Debye-like) behaviour of individual electro-active regions can be modelled by a variety of circuit elements and combinations, such as that shown in Figure 2.18, or by replacing R or C in a parallel RC element with a CPE.
Schmidt et. al. [85] plotted impedance spectroscopy data as negative imaginary against the real part, \(-Z''\) vs \(Z'\), where \(n = 1\) each RC element is represented by a semicircle of radius \(\rho/2\) and maximum at \(\omega_{\text{max}} = \tau^{-1}\). The R|CPE circuit is displayed as a depressed semicircle (see Figure 2.19.) and has specific complex impedance as shown in Equation (46).

\[
Z_{R|\text{CPE}}^* = \frac{\rho_{\text{dc}}}{1 + \rho_{\text{dc}} C_m (j\omega)^n}
\]  

(46)

where \(C_m\) is modified of capacitance with empirical parameter \(n\) in F s\(^{n-1}\) cm\(^{-1}\) and \(\rho_{\text{dc}}\) is dc resistivity in \(\Omega\) cm. Raistrick et. al. [84] also applied combination of \(R_\infty - (R_0 - R_\infty)|\text{CPE}\) to depressed semicircle in any complex-plane as shown in Figure 2.19. The depression of semicircle depends on the CPE parameter \(n\) refers to Figure 2.18 above. When \(R_\infty\) is included (it will be discussed in section 2.3.6.1.), Equation (43) can be rewritten as

\[
Z_{\text{CPE}}'(\omega) = R_\infty + \frac{R_0 - R_\infty}{1 + (\omega CPE (R_0 - R_\infty))^2}
\]  

(47)

Figure 2.19. Compound circuits involving the CPE and their impedance plane plot (after Raistrick et. al. [84]).

2.3.5. Relative Dielectric Constant and Conductivity.

There are four different impedance-admittance (impedance) functions related with impedance spectroscopy and there are many different ways to represent impedance spectra. In the 70’s, Baurle [86] showed the usefulness of the complex admittance approach in solid electrolyte studies, while Macedo et. al. [87] and Ambrus et. al. [88] used modulus plots to analyse conductivity relaxation. In 1974, Armstrong et. al. [89] reinforced the advantage of complex impedance formalisms for analysing impedance data. One year later, Hodge et. al. [90-
91] extended the modulus treatment to study of solid electrolyte systems and showed that a combined analysis using both the complex impedance and the complex modulus formalisms have certain advantages. The complex impedance plot is useful when the relaxation times of various processes differ as a consequence of different capacitive components and the modulus impedance plot is more suitable for a system where relaxation times differ due to different resistive components [92].

Complex dielectric constant $\varepsilon^*$ could be obtained from impedance spectroscopic data. By re-plotted $Z^*$ (impedance) on logarithmic scales or transformed to one of the other three impedance formalisms: admittance, $Y^*$, complex electric modulus, $M^*$ and complex dielectric constant, $\varepsilon^*$, using the equations (after Abram et. al. [82]):

\[
\varepsilon^*(\omega) = \frac{1}{M^*(\omega)} \quad \cdots \quad (48)
\]

\[
M^*(\omega) = j\omega C_0 Z^*(\omega) \quad \cdots \quad (49)
\]

\[
Z^*(\omega) = \frac{1}{Y^*(\omega)} \quad \cdots \quad (50)
\]

\[
\varepsilon^*(\omega) = Y^*(\omega) / j\omega C_0 \quad \cdots \quad (51)
\]

where $C_0$ is the vacuum capacitance that has already mentioned in Equation (1) (section 2.1.1.1.). Due to the different weighting factors inherent in the use of these formalisms, additional insight into the corresponding equivalent circuit can be obtained. Therefore, the correct equivalent circuit must fit to all four formalisms ($Z^*$, $Y^*$, $M^*$, and $\varepsilon^*$).

In 1960, Kingery et. al. [93] described the relationship between conductivity and temperature using an Arrhenius expression, as temperature is raised, the conductivity of a glass rapidly increases and at high temperature range can be expressed as

\[
\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \quad \cdots \quad (52)
\]

where $E_a$ is an experimental activation energy for conductivity, $R$ is gas constant. This activation energy and the temperature dependence of electrical conductivity show a discontinuity at the transformation range corresponding to the freezing of ceramic structure at this temperature. Using modification of the Equation (52) becomes Equation (13), Adam et. al. [31] calculated the...
activation energy of grain ($E_{ag}$) as 0.06(2) eV and 0.66(2) eV for the activation energy of grain-boundary ($E_{agb}$) of CaCu$_3$Ti$_4$O$_{12}$.

### 2.3.6. Internal Barrier Layer Capacitor (IBLC) model

Subramanian et al. [18] observed the barrier layer capacitance effect that possibly comes from the twin boundaries in the several crystals of CaCu$_3$Ti$_4$O$_{12}$. Sebald et. al. [94] demonstrated a colossal dielectric constant ($\varepsilon' \geq 10000$ at 1 kHz) on a variety of different materials (such as CaCu$_3$Ti$_4$O$_{12}$, and the series A$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ with A = Lanthanides), over a broad temperature range and showed the Maxwell-Wagner relaxation process on them. The dielectric constant can be explained by Maxwell-Wagner-type contributions of depletion layers at the interface between sample and their surface contact. Kwon et.al [95] showed that the Maxwell-Wagner polarization can be derived from an internal interface or barrier, and proposed an extrinsic model to explain the high dielectric constant in CaCu$_3$Ti$_4$O$_{12}$.

#### 2.3.6.1. IBLC model on CCTO.

The first evidence of an extrinsic mechanism in CaCu$_3$Ti$_4$O$_{12}$ was reported by Sinclair et. al. [96] in 2002, by using the impedance spectroscopy. Sinclair et. al. [96] used the ideal equivalent circuit consisting two of parallel resistance-capacitor (R|C) elements connected in series (as Irvine et. al. [83] used in 1990) shown in Figure 2.17. The impedance data, represented as the reactant ($Z''$) in the y-axis and the resistance ($Z'$) in the x-axis indicate two semi-circles representing grain and grain boundary responses, respectively. The resistances are obtained from the intercepts on the x-axis while the capacitances can be calculated by using Equation (39) ($\omega_{\text{max}}RC = 1$) [83], where $\omega_{\text{max}} (= 2\pi f)$ is the frequency at the maximum $Z''$ of each semi-circle, equivalent to the reciprocal of the characteristic relaxation time ($\omega = 1/\tau$). Grain and grain boundary resistances can be distinguished by the magnitude of capacitance, bulk effects could to change the magnitude of their impedance response, whereas grain-boundary effects may not [39].
Irvine et. al. [83] used single crystal material (LiTaO\(_3\)) to study the capacitance of grain and found the value as \(\sim 1 \times 10^{-12} \text{ F}\). They continued to investigate the oxide ion conductor Ca\(_{12}\)Al\(_{14}\)O\(_{33}\), then from impedance analysis showed the typically capacitance of grain on the order of \(1 \times 10^{-12} \text{ F} (\sim 1 \text{ pF})\) which is lower than the grain boundary capacitance of \(4 \times 10^{-9} \text{ F} (\sim 4 \text{ nF})\) [67]. The grain and grain boundary resistances from semi-circles also are presented in Figure 2.20.

For the impedance data on CaCu\(_3\)Ti\(_4\)O\(_{12}\) at 27°C obtained by Sinclair et al. [96], there was a small-scale resistance as shown in the inset of Figure 2.21.(a) at low-frequency. This indicates that there could be another semi-circle at high frequency (\(\omega \rightarrow \infty\)) over 10\(^5\) Hz (bulk, or R\(_b\)C\(_b\)). The Figure 2.21.(a) shows only grain boundary circle. When the impedance plot was made below -143°C, however, the new data presented in Figure 2.21.(b) confirmed the presence of a high frequency semi-circle that was attributed to the grain (bulk) resistance and the grain boundary resistance is partially visible.

**Figure 2.20.** Schematic diagram of an equivalent parallel circuit based on the capacitance of bulk and grain-boundary (from Irvine et. al. [83]).
Figure 2.21. The common impedance complex plane plot, $Z^*$ at (a) 27°C, and (b) -169°C, -158°C and -143°C, for CCTO ceramics. The inset in (a) shows an expanded view of the high frequency data close to the origin (after Sinclair et. al. [96]).

2.3.6.2. IBLC phenomenon.

Barium and strontium titanates (BaTiO$_3$, SrTiO$_3$) are good examples of barrier layer capacitors [97]. Under reducing atmospheres (at low temperature regime as below 527°C [97]), this phenomenon (usually occurs at grain boundary [97-98]) can be expressed by the following equation:

$$\text{SrTiO}_3 \rightarrow \text{SrTiO}_{3-x} + \frac{x}{2} \text{O}_2 + 2xe^- \hspace{1cm} \text{(53)}$$

$\text{SrTiO}_{3-x}$ is a non-stoichiometric n-type semiconductor [98]. Due to loss of oxygen, the equation (53) can be rewritten using defect reactions:

$$\text{Sr}_{\text{Sr}}^x + \text{Ti}_{\text{Ti}}^x + 3\text{O}_2 \rightarrow \text{Sr}_{\text{Sr}}^x + \text{Ti}_{\text{Ti}}^x + 2\text{O}_2 + \frac{1}{2} \text{O}_2 \uparrow + V_0 + 2e^- \hspace{1cm} \text{(54)}$$

Equation (53) shows how free electrons, that could increase the conductivity by forming semiconducting grains. Re-oxidation occurs along the grain boundaries resulting in a higher resistivity, due to oxygen rich environment, for instance, when SrTiO$_3$ is annealed in oxygen. The re-oxidation as shown in Equation (55),

$$\text{SrTiO}_{3-x} \rightarrow \text{SrTiO}_3 + \frac{x}{2} \text{O}_2 + 2xe^- \hspace{1cm} \text{(55)}$$
Equation (56) shows the electronic compensation leading to creation of oxygen vacancies and electrons in annealing condition \((T < 527^\circ C)\) [97],

\[
\frac{1}{2}O_2 + V_{O}^x + 2e^- \rightarrow O_{O}^x \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (55)
\]

and Equation (57) shows the ionic compensation leads to formation of oxygen vacancies and reduction of metal ions on their sites.

\[
2M_M^+ + O_{O}^x \Rightarrow V_{O}^- + \frac{1}{2}O_2 + 2M_M^+ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (57)
\]

Waser [97] assumed the oxygen vacancies \(V_{O}^-\) are dominant with an additional contributions of holes at the grain-boundaries and give rise to a depletion of the positively charges. As the result grain-boundaries have highly-resistive than the grains.

### 2.3.6.3. Brick wall model calculations.

Figure 2.22. show a simplified microstructure, based on the simple brick wall model proposed by Beekmans and Heyne (after Bonanos et. al. [79]) (section 2.3.2.), where the grain boundary thickness is much smaller than the grain size. The model is used to verify the enhanced dielectric constant in the barrier layer materials consisting of semiconducting grains and insulating grain boundaries (higher resistivity).
Using a modified version of Equation (9), with $A = t_b \times t_b$ (grain thickness), and $t = t_{gb}$ (grain boundary thickness), the capacitance of a single element can be expressed by:

$$C_i = \varepsilon_0 \varepsilon_t \frac{t^2}{t_{gb}}$$

...(58)

where $\varepsilon_t$ is dielectric constant the material with thickness $t$. When the column of elements is connected in series (i.e. $1/C = 1/C_1 + 1/C_2 + ...$), to find the cumulative capacitance ($C$), Equation (58) becomes

$$\frac{C_i}{n} = \varepsilon_0 \varepsilon_t \frac{t^2}{t_{gb}} \frac{t}{t_b}$$

...(59)

where $n$ is number of elements. The effective dielectric constant of the barrier layer material is calculated by substitute the capacitance per unit area $C/A = \varepsilon_1 \varepsilon_0 t_b/t \ t_{gb}$

$$\varepsilon_{eff} = \frac{\varepsilon_1 \ t_b}{t_{gb}}$$

...(60)

If the ratio of electrical thickness between grain and grain boundary is high, the effective
dielectric constant will very large. For instance, if $t_b = 20 \, \mu m$, $t_{gb} = 0.2 \, \mu m$, $\varepsilon_i = 100$, the effective barrier layer dielectric constant is increased to 10,000. Based on the brick wall model, the giant dielectric constant in CaCu$_3$Ti$_4$O$_{12}$ can be attributed to the formation of thin insulating boundaries with the conducting grains, analogous to the case of a SrTiO$_3$ barrier layer capacitor.

2.3.6.4. Applied IBLC model for CCTO.

Some papers have reported the huge reduction of the dielectric constant in CaCu$_3$Ti$_4$O$_{12}$ at low temperature (below -173°C) [1, 4]. In 2003, Homes et. al. [99] agreed that increasing the Born effective charge per oxygen atom ($Z_o^*$) at lower temperature can initiate electronic localization that increases the insulating region based on the IBLC model.

Single barrier layer capacitance equivalent circuit is well-accepted as IBLC model, consisting of two parallel RC elements connected in series, as shown in Figure 2.18. One parallel RC unit corresponds to the grain or bulk ($R_b$, $C_b$) and the other parallel RC unit corresponds to highly-resistive barrier-layers as grain boundaries ($R_{gb}$, $C_{gb}$). A Maxwell-Wagner relaxation occurs when $R_b C_b \neq R_{gb} C_{gb}$. The values of $R_b$, $C_b$, $R_{gb}$, and $C_{gb}$ can be obtained by an impedance spectrum analysis such as that of Sinclair et. al. [96], in 2002. If impedance analysis indicates that $R_b$ is much smaller than $R_{gb}$, consistent with the IBLC phenomenon. In this case, low-frequency dielectric constant $\varepsilon'$ (see equation (30)) can be obtained using equation:

$$\varepsilon' = \frac{C_{gb}}{C_0} = \varepsilon_{gb} \frac{(GS/t_{gb})}{...........} (61)$$

where $GS$ is the grain size and $t_{gb}$ is the electrical grain boundary thickness. While $\varepsilon_{gb}$ is the dielectric constant of grain boundary.

In 2005, Fang and Liu [32] found two different kinds of barrier layers depending upon the microstructure in CaCu$_3$Ti$_4$O$_{12}$ using SEM and HRTEM. They found internal domains (a group of domains) inside the grains (see Figure 2.23), the domains were observed to be less than 2 $\mu m$ in diameter. Fang and Liu [32] proposed that there are three paths of current flow; the first is across domains-domain boundaries-grain boundaries, the second is along domain boundaries, and the third is along grain boundaries (see inset of Figure 2.23). While the domains were assumed to be conductive, the conductivities of the domain boundary and grain
boundary still need to be established. The resistivity of the grain boundary may be determined by microcracks, mismatch of the lattices, segregation, space charge, or a combination of these factors [33]. The microstructural model for enhancement of the dielectric response of CCTO illustrated in Figure 2.23.(a). The equivalent circuit including these three RC elements is represented in Figure 2.23.(b).

![Schematic illustration of the microstructure of internal domains and equivalent circuit](image)

**Figure 2.23.** (a) Schematic illustration of the microstructure of internal domains, (b) equivalent circuit representing the resistance and capacitance of domain, domain boundary, and grain boundary (after Fang and Liu [32]).

Pan and Bender [100], also in 2005, proposed a simple model with bimodal grain size distribution to describe the dielectric constant of CCTO, based on the concept of barrier layer capacitors. There are two types of cube-shaped grains, the small grains and the large grains, as shown in Figure 2.24. Each grain (containing a conductive core) is treated as a structure by attaching two separate dielectric elements, as illustrated in Figure 2.24.(b). The dielectric elements are a conductive core sandwiched by top and bottom insulating layer and a rectangular wall that surrounds the core. They assumed the thickness of the insulating layer \(d_b/2\) to be independent of the grain size which it will be controlled by the rate of diffusion. Figure 2.24.(c) shows the both equivalent circuit of the dielectric element. Pan and Bender [100] described them as “the bimodal aggregate” or “composite”. Equation (62) shows the dielectric constant of the bimodal material consist of two types of grains are arranged in series electrically, which the electrodes are on the top and bottom as shown in Figure 2.24.(a).
\( \frac{1}{\varepsilon_{\text{serial}}} = \frac{V_L}{\varepsilon_L} + \frac{V_S}{\varepsilon_S} \) \hspace{1cm} (62)

where \( V_L \) is volume fractions of large grains and \( V_S \) is volume fractions of small grains. \( \varepsilon_L \) and \( \varepsilon_S \) are the dielectric constants of the large and small grains bimodal material, respectively.

Figure 2.24. (a) The model is composed of two types of cube-shaped grains. (b) Each grain is constructed by joining two dielectric elements. (c) The equivalent circuit representation of (b) (from Pan and Bender [100]).

The comparison of Pan and Bender's [100] experimental results and the logarithmic model suggests that the barrier layer thickness is approximately 0.05–0.2 μm, when the dielectric constant of the grain boundary insulating layer is assumed as 200. The dielectric constant behaviour of CCTO using the described model is acceptable because these values appear to be of the right order of magnitude when compared with other sources [65, 95-96]. In this case, dielectric constant of the grain boundary plays an important role, the dielectric
constant behaviour of CCTO depends on the value of assumption was taken. The other difficulty of this method is the classification between small and large grains, that the different of small and large grains are not clear enough. The classification of grains size will affect the volume fractions of both of them.

In the same year, Li et. al. [47] used impedance spectroscopy to observe internal barriers in crystals of CaCu$_3$Ti$_4$O$_{12}$. Two different phases was detected, the second phase has higher conductivity, and the conductivity is much less temperature dependent than the first phase. The higher conducting phase was assumed to be the bulk phase, and the less conducting phase the barrier phase (in crystals). Activation energies of is 0.09 eV and 0.24 eV were calculated for bulk and internal barrier conduction, respectively, suggesting that the conductivity of the less conducting phase is the barrier phase (increasing activation energy which decreasing conductivity). Li et. al. [47] argued that the grain-boundary model does not explain the giant dielectric constant in CaCu$_3$Ti$_4$O$_{12}$, instead of insulating barriers model within a crystal and electrode polarization. Despite this, the insulating barriers model has showed the activation energy between the activation energy of bulk ($E_{ab} = 0.06$ eV [99]) and grain-boundary ($E_{agb} = 0.60$ eV [99]), but, Yang et. al. [48] found 0.36 eV for the activation energy of grain-boundary with longer sintering time (32 hours). For this reason, the value is close with Li et. al. [47] mentioned as internal barrier activation energy before, so there is no consensus on which barrier layers play the role.

In 2007, Cao et. al. [101] measured dielectric properties using Double Barrier Layer Capacitance (DBLC) equivalent circuit rather than using single barrier layer capacitance as used by Sinclair et. al. [96]. DBLC is applied when the barriers is not only from the grain boundaries but also from extended defects known as sub-grain (domain walls) inside the grains, as mention by Cao et. al. [101].

Single barrier layer capacitance model succeed in explaining some dielectric properties, but only gives one Maxwell-Wagner relaxation, where some experimental results showed the other relaxation. The DBLC equivalent circuit shows in Figure 2.25. (a) and (b) the arcs were the validity of existing of the DBLC model, where $R_{sg}$, $C_{sg}$, $R_{sgb}$ and $C_{sgb}$ are resistor and capacitor for sub-grain and sub-grain-boundaries, respectively.
Figure 2.25. (a) DBLC equivalent circuit, and (b) Three arcs were shown, manifesting the validity of the DBLC model (after Cao et. al. [101]).

Cao et. al. [101] also described the dielectric constant using this model. At high-frequency (HF) and/or low-temperature (LT), all three capacitors (see Figure 2.25.(a)) is gone through by current, which \( C_{sg} \ll C_{sgb} \ll C_{gb} \), that the result of dielectric constant \( \varepsilon \) is controlled by their sub-grain \( \varepsilon_{sg} \) (\( \varepsilon \approx \varepsilon_{sg} \)) as

\[
\varepsilon \approx \frac{1}{1/\varepsilon_{sg} + 1/\varepsilon_{sgb} + 1/\varepsilon_{gb}} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (63)
\]

At low-frequency (LF) and/or the high-temperature (HT) limit, because the current flow mainly only goes through \( C_{gb} \) (not all capacitors), and affected only the grain boundary determine the dielectric constant: \( \varepsilon \approx \varepsilon_{gb} \). Overall the SBLC is preferred over DBLC because sub-grains rarely appear inside grain and the dielectric constant as result from DBLC is similar with dielectric constant of SLBC with CPE over C.

2.4. Voltage-Dependent-Resistor (Varistor) of CCTO.

A Voltage-dependent-resistor (VDR) is a polycrystalline ceramic solid-state electronic device made of sintered semiconductor powder, which is an electrical insulator at low voltages and becomes a conductor in a high-voltage transient condition [102]. This dual performance is attributed to a non-linearity region (will be discussed in section 2.4.1.).
The function of a varistor is to protect the circuit components which usually operate below the breakdown voltage. If a transient pulse has energy with the potential to damage the circuit, the varistor will protect the circuit by absorbing the energy. Figure 2.26. shows the mechanism of varistor operation that protects an electronic circuit from over-voltage. The high-voltage between electrodes reaches the breakdown voltage during a transient surge and leading to the non-linear behaviour, the varistor becomes highly conductive deflecting the current to ground and keeps the circuit protected.

![Figure 2.26. Principle of over-voltage protection by varistor (from [11]).](image)

The non-linear behaviour emerges from its polycrystalline microstructure whose resistance shows significant dependence on voltage and specifically correlates to processes occurring at the grain/grain boundary. Effect of doping causes the grain interior to be semiconducting while the near grain boundary region becomes highly resistive. Electrostatic potential barriers build up at the grain boundaries due to charges being trapped at interface states [11].

### 2.4.1. Non-linearity behaviours of varistor.

As shown in Figure 2.27., when the curve is in the normal varistor operation region (non-ohmic) of the I and V (current-voltage) plot, the gradient of the curve becomes $1/\alpha$, where $\alpha$ is the non-linear coefficient of conduction. Increases in the value of $\alpha$ (larger working voltage...
range), will increases the ability of the varistor to protect against current surges. A high $\alpha$ implies a better clamp the over-voltage to a level dependent on the design and construction of the device.

![Figure 2.27. Typical varistor V-I curve (after Levine [10] and Clarke [103]).](image)

There are three distinct regions of electrical operation as shown in Figure 2.27. The first region is called the leakage region (Clarke [103] calls pre-switch region), in this area, applies ohmic condition (the ceramic obeys Ohm's law) and grain boundary control the resistivity. The ratio of $V$ and $I$ has a high resistance of $10^9 \, \Omega$ at low current levels (below 0.001 mA). The leakage current is temperature dependent at this region. The second region is the normal varistor region (or switched region [103]), where the gradient of the curve is given by Equation (64), in this condition the resistance decreases rapidly.

\[
I = kV^\alpha \quad \Rightarrow \quad \alpha = \frac{d \ln(I)}{d \ln(V)} \quad \text{.......................... (64)}
\]

The exponent $\alpha$ represents the degree of non-linearity in the resistance characteristic and $k$ is a constant. Alpha ($\alpha$) is a numerical quantity based on this characteristic, determined from the slope of $V$-$I$. The last region is the upturn region (or high-current region [103]), at this region current reached high level, and the resistance will be on the range of 1$\Omega$-10$\Omega$.

The current-voltage relation of a varistor also is given by the equation

\[
J = \left(\frac{E}{C}\right)^\alpha \quad \text{.......................... (65)}
\]
where \( J \) is the current density, \( E \) is the applied field, \( C \) is the proportionality constant, and \( \alpha \) is the non-linear coefficient of conduction.

2.4.2. Barrier height of varistor.

The ZnO is standard material of the varistor ceramic and the theory is well developed [8-16]. The CCTO based varistor is assumed have similar mechanisms with ZnO based varistor. The current-voltage characteristic is controlled by the existence of an electrostatic barrier at the grain-boundaries [103]. The barrier height, \( \Phi_B \), and \( d \) the width of the depletion layer of capacitance energy of grain-boundaries (see Figure 2.28) are given by the relations

\[
\Phi_B (V = 0) = \frac{Q^2}{8 \varepsilon \varepsilon_0 n_0} \quad \text{............................................... (66)}
\]

\[
d = \frac{Q}{2n_0} \approx \left( \frac{\varepsilon \Phi_B n_0}{n_0} \right)^{1/2} \quad \text{............................................... (67)}
\]

where \( Q \) is charge and \( n_0 \) is the carrier concentration in the grains [103]. Both of the barrier height and the width of the depletion layer are illustrated in Figure 2.28.

![Figure 2.28. Formation of a potential barrier at a grain-boundary (after Clarke [103]).](image)

Another important parameter, \( E_b \) breakdown voltage field is taken as the field applied when current flowing through the varistor is 1 mA/cm\(^2\) [33]. Since Schottky-type grain boundary barriers are present in the most varistor material's [8, 10, 17, 22-29, 102], the barrier heights
also are calculated using the equation
\[ J = AT^2 \exp\left(\frac{\beta E_b^{1/2} - \Phi_B}{kT}\right) \] ................................. (68)
where \( J \) is current density, \( A \), equal to \( \frac{4\pi e m k^2}{\hbar^3} \) is Richardson's constant, \( T \) is temperature, \( e \) is electron charge, \( m \) is electron mass, \( k \) is Boltzmann's constant, \( h \) is Plank's constant, \( \Phi_B \) is interface barrier height, and \( \beta \) is constant related to the relationship.

\[ \beta \propto \frac{1}{r \times \omega} \] ................................. (69)
where \( r \) is grain number per unit length and \( \omega \) is the barrier width. The non-linear coefficient of conduction of varistor is controlled by grain-boundary Schottky barrier. The higher barrier height \( (\Phi) \) generates the higher non-linear coefficient of conduction of \( \text{CaCu}_3\text{Ti}_4\text{O}_{12} \) \([19, 21, 24, 32, 45, 47, 99-101]\).

### 2.4.3. Breakdown voltage of varistor.

Henning et. al. \([102]\) and Yu et. al. \([104]\) established that the breakdown voltage of the varistor was related to the grain size of the microstructure of the ceramic. They worked with homogenous microstructure concept with regard to the nature and distribution of phases, the breakdown voltage decreases linearly as the average grain size increases \([102-103]\). Equation (70) shows the relation between breakdown voltage and average grain size:

\[ V_b = \frac{m.d}{G.V_{gb}} \] ................................. (70)
where \( V_b \) is the breakdown voltage, \( d \) the sample thickness or distance between electrodes, \( G \) the average grain size, \( V_{gb} \) the voltage across a single potential barrier or a single grain boundary, and the coefficient \( m \) is actually averaging the potential barrier distribution. The parameter \( m \) is significant evidence for important variations in the performance of individual varistor grain boundaries and includes the inactive grain boundaries that do not have varistor behaviour \([105]\).

Henning et. al. \([102]\) also mentioned that increasing soaking times and higher sintering temperatures lowered the breakdown field \( (E_b = V_b/h, h = \text{thickness}) \), because of the enlargement
of the grains. Huang et. al. [45] also described the breakdown field decrease with the increasing of soaking time; the longer soaking time sintering enlarges the grains.

### 2.4.4. Conduction mechanisms of varistor.

Figure 2.29. shows the conduction mechanisms in varistor element in simplified form of varistor. The grains are assumed already highly conductive, while the intergranular boundary formed from other oxides is highly resistive. The points where grains are adjoining (sintering effect) are called “microvaristors” [11]. The microvaristors could form series or parallel connections in the sintered body and have a high electrical load capacity compared to semiconductors. Each microvaristor is provided with energy absorbers in the form of grains with optimum thermal contact. This allows a high energy absorption that is capable of handling very high surge current.

![Figure 2.29. Conduction mechanism in varistor (after [11]).](image)

The physical dimensions of the varistor will control the electrical properties [11], i.e. thickness, area, and volume. Doubled thickness will produce twice the protection level because the number of microvaristors are arranged in series will increase. Increased area produces higher current handling capability because the number of current paths, that are arranged in parallel will raise. The volume produces the energy absorption capability therefore increasing volume will increase absorbers in the form of grains.
2.4.4.1. Modelling electrical transport in varistor.

The microstructure of varistor is modelled as electrical network of non-linear resistors to represent the current transport. The disorder, refers to the variation from a periodic microstructure, is introduced into the network. Then, the spatial distribution of current flow is determined in response to an applied voltage. Figure 2.30 shows the microstructure as an electric network, where the non-linear resistor is represented by grain-boundary at each two grain junction. An empirical relationship when a current transports across the boundary is given by

\[ I = V \sigma_s + V \frac{\sigma_g}{2} \left[ 1 + \tanh \left( \frac{V - e\Phi_B}{s} \right) \right] \] .............................. (71)

where \( \sigma_s \) is the shunt conductance, describing the leakage current, \( \sigma_g \) is the conductance of the grain which typically larger than \( \sigma_s \), and \( s \) is an additional parameter that is used to adjust the degree of non-linearity of the I-V curve. Because the grain-boundaries are not identical, the shapes of the grains are not same, and the area of grain face could be different, then the characteristic of current-voltage of the varistor would be the result of the summation of these variations.

Figure 2.30. Network of non-linear resistor residing between the nodes (after Clarke [103])

The variable of grain size, the difference of conductance in grains and ohmic proportion of the boundaries are allowed in this model. These simulations have been used to quantify the effect if disorder on the current-voltage characteristic as well as on current localization as a function of applied field [103].
3. Experimental Procedures

3.1. Ceramic Processing of CCTO.

The processing route for CaCu$_3$Ti$_4$O$_{12}$ is shown in Figure 3.1. CaCu$_3$Ti$_4$O$_{12}$ was prepared using the conventional mixed oxide route. Reagent grade calcium carbonate (CaCO$_3$, Alfa Aesar, 99.0%), copper (II) oxide (CuO, Alfa Aesar, ACS, 99.0%) and titanium (IV) oxide (TiO$_2$, Alfa Aesar, Rutile, 99.8%) powders were used.

![Flow diagram of CCTO process](image-url)
Typical impurity levels in the calcium carbonate, copper (II) oxide and titanium (IV) oxide used in this study are shown in Table 3-1.

Table 3-1. Impurities level of CaCO$_3$, CuO, and TiO$_2$ starter powders.

<table>
<thead>
<tr>
<th>Impurity (maximum)</th>
<th>CaCO$_3$ (99.0%)*</th>
<th>CuO (99.0%)*</th>
<th>TiO$_2$ (99.8%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insoluble in dilute hydrochloric acid</td>
<td>0.01%</td>
<td>0.02%</td>
<td>--</td>
</tr>
<tr>
<td>Carbon compounds (as C)</td>
<td>--</td>
<td>0.01%</td>
<td>--</td>
</tr>
<tr>
<td>Chlorine (Cl)</td>
<td>0.001%</td>
<td>0.005%</td>
<td>--</td>
</tr>
<tr>
<td>Nitrogen compounds (as N)</td>
<td>--</td>
<td>0.002%</td>
<td>--</td>
</tr>
<tr>
<td>Fluorine (F)</td>
<td>0.0015%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Sulphate (SO)</td>
<td>0.01%</td>
<td>0.02%</td>
<td>--</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>--</td>
<td>0.01%</td>
<td>--</td>
</tr>
<tr>
<td>NH</td>
<td>0.003%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.003%</td>
<td>0.05%</td>
<td>--</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>0.01%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>0.01%</td>
<td>0.02%</td>
<td>--</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>0.02%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>0.1%</td>
<td>0.05%</td>
<td>--</td>
</tr>
<tr>
<td>Strontium (Sr)</td>
<td>0.1%</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

* Alfa Aesar [106]

3.1.1. Initial processing

Stoichiometric CCTO was prepared using conventional solid state reaction.

\[
\text{CaCO}_3 + 3\text{CuO} + 4\text{TiO}_2 \rightarrow \text{CaCu}_3\text{Ti}_4\text{O}_{12} + \text{CO}_2
\] ............................ (72)

Based on the chemical stoichiometry ratio of Ca:Cu:Ti:O of 1:3:4:12, the weight of each constituent oxide powder was calculated for a batch size of 50 g.

- **Molar mass of CaCO$_3$** = 100.9 g/mol
- **Molar mass of CuO** = 79.55 g/mol
- **Molar mass of TiO$_2$** = 79.87 g/mol

- for a 50 g of batch size:
  - **Weight of CaCO$_3$ required** = 7.604 g
  - **Weight of CuO required** = 18.128 g
  - **Weight of TiO$_2$ required** = 24.268 g

The powders were wet milled using propan-2-ol and a 1:1 zirconia ball-charge ratio using a
vibratory mill for 24 hours and dried at 110°C for 6 hours. The mixed powder was calcined in air at 900°C for 4 hours. If phases other than CCTO were present in the X-ray diffraction spectra of the batch then the powder was remilled and calcined until a single phase material was obtained.

Propan-2-ol was added to form a thick slurry and allow good mixing of the powders. The powder obtained after milling was initially greyish in appearance and changed to dark brown after calcination.

3.1.2. Calcination process

To bring about thermal decomposition, phase transition or removal of a volatile fraction in powder mixture, a thermal treatment called calcination is usually employed prior to sintering. The investigation by Cao et.al [107] showed that the calcination and sintering temperatures which result in high dielectric properties were approximately 850 to 950°C and 1040 to 1120°C respectively. In this study, a calcination temperature of 900°C for 4 hours was chosen (was not a range initially tried). The calcination cycle is shown in Figure 3.2.

Figure 3.2. Schematic diagram of the calcination schedule for CCTO powder

3.1.3. Pressing samples

After a single phase powder was obtained, approximately a mass of 0.5 grams of CaCu$_3$Ti$_4$O$_{12}$ powder was weighed to make a single pellet. The powder was pressed in a 10 mm diameter die at a pressure of 80 MPa. (~ 816 kgf/cm$^2$) for 3 minutes to allow for relaxation of the powder under pressure.
3.1.4. Sintering process

Sintering is used to eliminate porosity and allow grain growth. Densification, typically up to ~93% of the relative density, occurs before separation of the pores [108]. A high density polycrystalline ceramic is essential for better varistor properties [33, 109-111]. The sintering process was intended to give to a structure of conductive grains (most of them are composed of the matrix oxide) surrounded by electrically insulating barriers i.e. a resistive grain boundary region. Due to the strong dependency of the processing conditions on the dielectric properties and microstructures [107], however, the clear mechanism about the stoichiometric changes in CCTO has not been settled yet.

![Diagram schematic of the sintering schedule for CCTO pellet](image)

Kwon and Cann [112] studied about the different sintering temperature effects since the optimum dielectric response was obtained at a sintering temperature of 1100°C and this temperature relevant with the other reports [23-25, 29, 61, 96], all sintering profiles in this study were fixed at this temperature. Sintering was performed at 1100°C for 4, 8, or 12 hours followed by cooling as shown in Figure 3.3. The sintering hold times were not in a range initially tried by Cao et. al. [107]. In this study, different sintering times were used to modify microstructure for better electrical behaviours than recently material.

3.1.5. Adding niobium and tin dopant

Niobium and tin were chosen as dopants to modify the properties of the CCTO. They are expected to substitute for titanium on the B-site because Nb and Sn ions have similar atomic radii to the Ti ion [113]. In the perovskite crystal structure, Ti has a coordination number
of 6 and +4 ionic charge. Based on Shannon's [113] ionic radii, Ti$^{4+}$ with a coordination number of 6 has an ionic radius 60.5 pm, Nb and Sn ions with a coordination number of 6 are Nb$^{5+}$ and Sn$^{4+}$, they have ionic radii 64 pm and 69 pm respectively. It is unlikely that these dopants would occupy the A-site because Cu$^{2+}$ (coordination number = 6) has ionic radius 73 pm, which is bigger than the ionic radius of Nb or Sn. The Nb or Sn ion is suitable for substituting Ti ion by reference to Goldschmidt's rules of substitution which suggest that extensive substitution is possible if the ionic radii differ by less than 15% (Nb has 5.47% and Sn has 12.32% difference). The stoichiometric equation of niobium doped CCTO is shown in equation below;

$$\text{CaCO}_3 + 3\text{CuO} + (4-x)\text{TiO}_2 + \frac{x}{2}\text{Nb}_2\text{O}_5 \rightarrow \text{CaCu}_3\text{Ti}_{4-x}\text{Nb}_x\text{O}_{12} + \text{CO}_2 + \frac{x}{4}\text{O}_2 \quad (73)$$

Niobium has higher oxidation state than titanium, so in the CaCu$_3$Ti$_{4-x}$Nb$_x$O$_{12}$ some charge compensation must occur. Either Cu or Ti must have a lower oxidation state +1 or +3, respectively. This condition is called non-stoichiometry, and it is possible that CaCu$_3$Ti$_{4-x}$Nb$_x$O$_{12}$ will have defects in the crystal structure e.g. extrinsic point defects. The extrinsic point defects can control properties such as the extrinsic conductivity [3, 114] (detail in section 2.2.3.).

The stoichiometric equation of tin doped CCTO has no extra ion charge because tin and titanium have the same +4 charge.

$$\text{CaCO}_3 + 3\text{CuO} + (4-x)\text{TiO}_2 + x\text{SnO}_2 \rightarrow \text{CaCu}_3\text{Ti}_{4-x}\text{Sn}_x\text{O}_{12} + \text{CO}_2 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ ld
Table 3-3. Ratio of initial powder of CCTxS compound.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Molar mass</th>
<th>CCTO (~1.1% imps)</th>
<th>CCT05S (~2.3% imps)</th>
<th>CCT10S (~3.4% imps)</th>
<th>CCT15S (~4.5% imps)</th>
<th>CCT20S (~5.6% imps)</th>
<th>CCT25S (~6.7% imps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>100.09 g/mol</td>
<td>7.604 g</td>
<td>7.563 g</td>
<td>7.523 g</td>
<td>7.483 g</td>
<td>7.444 g</td>
<td>7.405 g</td>
</tr>
<tr>
<td>CuO</td>
<td>79.55 g/mol</td>
<td>18.128 g</td>
<td>18.032 g</td>
<td>17.937 g</td>
<td>17.842 g</td>
<td>17.749 g</td>
<td>17.657 g</td>
</tr>
<tr>
<td>TiO₂</td>
<td>79.87 g/mol</td>
<td>24.268 g</td>
<td>23.838 g</td>
<td>23.412 g</td>
<td>22.990 g</td>
<td>22.573 g</td>
<td>22.160 g</td>
</tr>
<tr>
<td>SnO₂</td>
<td>150.17 g/mol</td>
<td>0 g</td>
<td>0.567 g</td>
<td>1.129 g</td>
<td>1.684 g</td>
<td>2.234 g</td>
<td>2.778 g</td>
</tr>
</tbody>
</table>

Atomic mass Ca = 40.078 g/mol, Ti = 47.867 g/mol, C = 12.011 g/mol, O = 15.999 g/mol, Sn = 118.710 g/mol. Imps. = impurities

For this study, Nb₂O₅ or SnO₂ powders were added to CaCu₃(Ti₄₋ₓMₓ)O₁₂ in concentrations of 0.05, 0.10, 0.15, 0.20 and 0.25 mol. Tables 3-2 and 3-3 show the starting powders used to make 50 g batches of CaCu₃Ti₄₋ₓNbₓO₁₂ and CaCu₃Ti₄₋ₓSnₓO₁₂ respectively. The samples were named CCTₓN or CCTₓS, where N is the niobium, S is tin and x is the amount of dopant in mol%. The overall process flow diagram is shown in Figure 3.4.

Typical impurity levels in the niobium (V) oxide, and tin (IV) oxide used in this study are shown in Table 3-4.

Table 3-4. Impurities level of Nb₂O₅ or SnO₂ powders.

<table>
<thead>
<tr>
<th>Impurity (maximum)</th>
<th>Nb₂O₅ (99.0%)*</th>
<th>SnO₂ (99.0%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insoluble in dilute hydrochloric acid</td>
<td>--</td>
<td>0.02%</td>
</tr>
<tr>
<td>Carbon compounds (as C)</td>
<td>--</td>
<td>0.01%</td>
</tr>
<tr>
<td>Chlorine (Cl)</td>
<td>0.001%</td>
<td>0.005%</td>
</tr>
<tr>
<td>Nitrogen compounds (as N)</td>
<td>--</td>
<td>0.002%</td>
</tr>
<tr>
<td>Fluorine (F)</td>
<td>0.001%</td>
<td>--</td>
</tr>
<tr>
<td>Sulphate (SO)</td>
<td>0.01%</td>
<td>0.02%</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>--</td>
<td>0.01%</td>
</tr>
<tr>
<td>NH</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.003%</td>
<td>0.05%</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>0.01%</td>
<td>--</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>0.02%</td>
<td>0.02%</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>0.01%</td>
<td>--</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>0.1%</td>
<td>0.05%</td>
</tr>
<tr>
<td>Strontium (Sr)</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

* Alfa Aesar [106]
Figure 3.4. Flow diagram of CCTxN or CCTxS process

3.2. Characterisation Techniques

X-ray diffraction measurements were carried out on all samples to monitor the phase
equilibria and lattice parameter changes associated with adding different levels of dopants. Scanning Electron Microscopy was used to observe the grain size and microstructural evolution of samples. Impedance spectroscopy and DC current-voltage measurements were used to obtain electrical properties. Figure 3.5 shows the characterisation methods used on all the composition samples.

3.2.1. Sample preparation

Sintered CaCu$_3$Ti$_4$O$_{12}$, CCTxN, and CCTxS samples were ground to form parallel surfaces. The samples were classified into 2 types: groups according to their surface preparation: surface ground, and polished. The ground samples were used for phase characterisation. The polished samples were used for density measurement and microstructure
Polished samples were also electroded for electrical measurement. Polished samples were accomplished in three stages. Firstly, with a SiC paper grinding using progressively smaller SiC particle size (done to grade P2500) was used followed by diamond polishing to 1 μm and finally using a colloidal silica suspension. Sputtered gold electrodes were deposited on samples for 3 minutes at 1 kV and 40 mA voltage and current, respectively under argon using an Edwards Sputter Coater S150B coating unit.

3.2.2. Measurement of density

The thickness and diameter of polished samples (~1.2 mm thickness by ~ 8 mm diameter) were measured using a micrometer with accuracy of 0.05 mm, and they were measured in 3 different regions. Each composition had 5 samples; the average density of 5 samples was measured to reduce error. Density obtained based on these measurements was used to compare with the theoretical density.

3.2.3. Measurement of phase

X-ray diffraction techniques are used to identify the phases present in powders and sintered ceramics, and to determine lattice parameters. X-rays have wavelengths, \( \lambda \), on the scale of the atomic spacing. When X-rays (generated from a diffractometer) irradiate atoms of the sample, they will be scattered in many directions. Bragg stated an equation to express the diffraction condition.

\[
2d \sin \theta_n = n\lambda \\
\n\text{for} \quad n = 1, 2, 3, \ldots \quad \ldots \quad (75)
\]

A fraction of diffracted X-rays will be deflected with exactly same angle as the incident angle, \( \theta \) (assuming the collision is elastic) (atom P, see Figure 3.6) only if \( \lambda \) complies to Bragg’s law. The distance between parallel atomic planes (A-A’ to B-B’) which have the same h, k, and l Miller indices is called \( d_{hkl} \). Bragg [115] argued, the \( d_{hkl} \) was similar in magnitude to \( \lambda \). He found the angle at which a monochromatic beam of X-rays is reflected by the various faces of the crystal [115]. The intensity of reflected beam depends on the number of scattering of the atom in the planes and their atomic number.
There is a high intensity of diffracted beams at the detector at that point. A detector is placed on the opposite side of the sample, according to record the intensity of the diffracted beams. Figure 3.6. illustrates the angle between the X-ray source producing the incident beams and the plane of the sample surface is $\theta$ and this is the same angle on the other side between the surface of the sample and the detector. The detector will record the intensity of diffracted beam for each $2\theta$ step. From the peak profile, the crystal structure of a material can be calculated.

Fang et. al. [66] and Adams et. al. [114], in 2006, reported that CaCu$_3$Ti$_4$O$_{12-\delta}$ forms a defect structure during reduction and oxidation processes. It is important to investigate the phase equilibria in terms of the evidence of the secondary phases. In order to monitor the phase development, an X-ray diffractometer (Philips X'Pert MPD X-Ray Diffractometer) was utilized for calcined powders and sintered pellets of CaCu$_3$Ti$_4$O$_{12}$ with niobium and tin dopants. XRD was conducted over the range 5-85° 2 theta with a 0.02° step size in an 8 hour continuous scan. The anode was copper which give a X-ray wavelength of ($K\alpha = 1.5406$ Å). In addition, the identity of each peak in the diffraction spectra were searched and verified by the analytical software (X'Pert HighScore Plus).
3.2.4. Measurement of microstructure

The microstructures of the samples were observed by Scanning Electron Microscopy. Two SEM’s were used: Philips XL30 FEG and JEOL JSM 6300. The polished sample was mounted on a stub with an adhesive, a conductive carbon disk and the edge covered by Electrodag paste (conductive silver paint) to improve electrical contact between the sample and machine.

In SEM, from the electron gun (Figure 3.7), an electron beam irradiates the specimen, and various signals are produced by interactions between the incident electrons and the atoms in the specimen. These signals are X-rays, secondary electrons, backscattered electrons, Auger electrons, absorbed electrons, and transmitted electrons [117]. These signals are generated from each irradiated point of the electron beam focused on the specimen surface. Detectors will detect these signals and then convert them into electric signals. Normally, there is amplifier that will used to modify the electric signals, and then send the output to the monitor. The brightness of monitor depends on the modulation of the signals. Both the scanning on the monitor and the electron beam are occurring at the same time, thus each irradiated point on the sample is associated with a pixel on the monitor. The image (morphological or compositional) can be modified with oscillated the signal. The ratio of horizontal size of the display unit to the scan width of the electron probe correlates with the magnification of image [117].

![Figure 3.7: Schematic image enlargement in SEM](image)

Figure 3.7. Schematic image enlargement in SEM [117].
Most the images in this study were taken with an accelerating Voltage (beam voltage) of 8 kV and spot size 3 (basic starting point on Phillips XL30 FEG) to give a good, noise-free image in the vast majority of situations [118]. Backscatter Secondary Electron (BSE) imaging was needed to observe the grains and grain boundaries.

Lineal intercept method was used to measure the average grain size and percentage of small-sized and large-sized grains, also pores were measured using ImageJ software.

3.2.5. Measurement of electrical properties

The coated CaCu$_3$Ti$_4$O$_{12}$ pellets were characterised by using an LF Impedance Analyzer (Model 4192A, Hewlett-Packard) over the frequency range of 5 Hz – 13 MHz to obtain impedance data. The machine was connected to a personal computer with a furnace control program that can be automatically control the furnace temperature from room temperature to 450°C (Carbolite MTF, $T_{\text{max}} = 1000^\circ\text{C}$). A Cryostream unit was used to reduce the sample temperature from room temperature to -175°C. Impedance data was corrected for geometric shape of the sample (thickness/electrode area), the resistance and the inductance. Corrected data was modelled with various equivalent electrical circuits using Zview™ equivalent circuit fitting software (Scribner Associates Inc). Activation energy, capacitance and dielectric constant also can be extracted from impedance data.

Impedance data will be presented in the complex impedance plane format, $Z''$ vs $Z'$. Also in other formats, for instance $Z''$ vs log f or $M''$ vs log f, where $M''$ is the complex electric modulus. $M''$ depend on the angular frequency ($\omega$), empty cell vacuum capacitance ($C_0$) and $Z''$, can be presented as $M'' = j\omega C_0 Z'$, where $j = (-1)^{1/2}$, $\omega = 2\pi f$ and $C_0 = \varepsilon_0 A/h$ (Equation (34) section 2.3.1.2. and Equation (1) section 2.1.1.1.) as shown in Figure 3.8.(b). Normally, in the plot of $Z'$ vs $Z''$, one semicircle contains a single peak, but in some case, with a different plot ($M''$ vs log f) it will display two peaks (Figure 3.8.(b)). The higher and lower frequency peak of $M''$ represents of a bulk and grain boundary component of the specimen, respectively. Irvine et. al. [83] determined the peak of the $Z''_{\text{max}}$ is equal to $R_{gb}/2$ (Equation (35) section 2.3.1.2.) and the $M''$ peak maximum is equal to $\varepsilon_0 /2C$ (Equation (36) section 2.3.1.2.) for that particular element, where smallest capacitance (C) applied.
Figure 3.8. The same impedance data are used in (a) and (b) but are presented in different ways (after Irvine et. al. [83]).

The impedance data were used to calculate the capacitance, \( C \), and dielectric loss, \( \tan \delta \), for the material at each temperature. The capacitance can then be converted to dielectric constant (dielectric constant, \( \varepsilon \)), by use of Equation (5) (section 2.1.1.1.). Where \( \varepsilon_0 \) is the dielectric constant of free space, \( \varepsilon_0 = 8.854187 \times 10^{-12} \) F/m, \( A \) is the surface area of sample (m\(^2\)) and \( t \) is thickness of sample (m) [120].

\[
\varepsilon = \frac{C}{\varepsilon_0 A} \quad \text{.......................................................... (76)}
\]

\( Z \text{view}\) fits the experimental data to a model circuit using an implementation of the Kramers-Kronig (K-K) transform [120]. The Kramers-Kronig theory states that real and complex impedance data should contain equivalent information. The complex values can be calculated from the real values and vice versa. The transformed spectra should be identical to the original spectra. The K-K transform equations are:

\[
Z'(\omega) - Z'(\infty) = \left( \frac{2}{\pi} \right) \int \frac{xZ^2(x) - \omega Z^2(\omega)}{x^2 - \omega^2} \, dx \quad \text{............................................ (77)}
\]

\[
Z^2(\omega) = -\left( \frac{2(\omega)}{\pi} \right) \int \frac{Z'(x)Z'(\omega)}{x^2 - \omega^2} \, dx \quad \text{............................................ (78)}
\]

The integration of a spectrum from zero to infinite frequency, \( \omega = 0 \) to \( \omega = \infty \) was considered by...
this equations. In fact, the experimental data is never available over an infinite frequency range.

Therefore, an approximation must be used at frequencies greater and less than the measured frequencies. This is a crucial limitation of the K-K method. If the wrong approximation is used, the transformation can fail, but there is no way to know that the correct approximation is being used. Zview™ uses a circuit model to calculate impedance data outside the measured frequency range. The circuit model does not have to fit the data in the middle frequencies; it only needs to match the data near the upper and lower frequency limits. Another way is using the Simulation mode and manually to adjusting the R and C values at a high and low frequencies.

The frequency response analyzers (FRA) and furnace control program have option in setting up to an experiment measure. In this case the following were chosen, Impedance – Temperature with temperature start at 25°C, and end at 450°C, with temperature steps of 25°C and hold time at 30 minutes per step, the voltage is set to 500 mV with bias (mean value of voltage waveform between two points) of 0 mV.

For the resistivity data, the current-voltage (I-V) measurements were carried out using a Thurby 1503 digital multimeter with Brandenburg High Voltage Power source-measure unit up to 20 kV. Measurements of I–V characteristics were made on coated samples. The method of measurement by gradually increases the voltage to reach a point of current flow, at which point the machine always shuts off the measurement to avoid heating the sample. The measured current-voltage was plotted on log-log scale so that the non-linear coefficient of conduction, \( \alpha = \frac{d(\ln I)}{d(\ln V)} \) (Equation (64)), which is an exponent in the power law of \( I \propto V^\alpha \) can be derived from the slope of the curve (\( \alpha \)).

The resulting impedance data (\( Z' \) and \( Z'' \)) readings for each frequency is converted into resistivity (\( \rho' \) and \( \rho'' \) respectively) by using Equation (79), and then plotted on a \( \rho''-\rho' \) graph to produce a Cole-Cole semicircular plot. Here \( A \) is the surface area of the sample plates (the surface area of the disc top), and \( t \) is the distance between them.

\[
\rho = \frac{Z' A}{t} = \frac{Z' \pi r^2}{t} = \frac{1}{\sigma} \quad \text{................................................ (79)}
\]

From a semicircular plot, the point at which the semicircle reaches the x-axis (real
resistivity component) on the right hand side defines $\rho_{\text{max}}'$. As resistivity is indirectly proportional to conductivity $\sigma$, the $\sigma_{\text{min}}'$ was found for each temperature by Equation (80).

$$\sigma_{\text{min}}' = \frac{1}{\rho_{\text{max}}'}$$ ........................................................ (80)

$$\frac{1}{\rho} = \frac{1}{\rho_0} e^{-\frac{E_a}{k_B T}}$$ ......................................................... (81)

Equation (81) come from the Equation (13), where conductivity ($\sigma$) is converted to resistivity ($\rho$). Then, finally using the Arrhenius relationship to find the activation energy (Equation (13)), where $E_a$ is the activation energy, $k_B$ is Boltzmann’s constant ($k_B = 1.38065 \times 10^{-23} \text{ J/K}$ or $8.6173 \times 10^{-5} \text{ eV/K}$) and $T$ is an absolute temperature. Using the natural logarithm, the Equation (81) becomes

$$\ln(\rho) = \ln(\rho_0) + \frac{E_a}{k_B T}$$ .............................................................. (82)

A $\ln \rho$ versus $1/T$ graph is plotted in Figure 3.9. A linear relationship is normally observed, where the gradient of the line is $m = E_a/k_B$. As the result, the activation energy is obtained using relation $E_a = m \times (8.6173 \times 10^{-5} \text{ eV})$.[/image]

![Figure 3.9. Activation energy generated from ln ρ versus 1/T plot](image)
4. CaCu$_3$Ti$_{4-x}$M$_x$O$_{12}$ Preparation

In this study, three different composition series were prepared; the first composition is pure CaCu$_3$Ti$_4$O$_{12}$ (CCTO), the second is CaCu$_3$Ti$_{4-x}$Nb$_x$O$_{12}$ (CCTxN), and the last one is CaCu$_3$Ti$_{4-x}$Sn$_x$O$_{12}$ (CCTxS). For CCTxN and CCTxS, there were five different levels of dopant, with $x$ is equal to 5, 10, 15, 20 and 25 mol%. X-ray diffraction measurements were carried out on all samples to monitor the phase equilibria and changes in lattice parameters associated with adding dopants.

The focus of this preparation is to prepare and evaluate the CCTO and CCTO with substitutions that are suitable for use as varistor. Varistor, require high density (less porous), uniform grain size, which will affect the grain boundaries thickness and distribution. The stoichiometric CCTO was prepared using conventional solid state reaction, as shown in Equation (72) and the stoichiometric equation of niobium and tin doped CCTO is shown in Equation (73) and Equation (74), respectively (as described in section 3.1.5). As a varistor material, the CCTO was intended to be n-type conduction mechanisms, as shown in Equation (15) (detail on section 2.2.3.). The other objective is to investigate the effect of sintering time for all of the compositions in terms of the presence of other phase(s), density change, and grain size development of the samples.

4.1. Pure CCTO.

Firstly, each starting powder sample was analysed using X-ray diffraction analysis (X-ray diffraction) at room temperature ($25^\circ$C) to determine the phases present and the structural characteristics of sample. Figure 4.1. shows the x-ray diffraction spectrum of TiO$_2$ powder. XPert HighScore Plus software was used to analyse the pattern, the spectrum matched the spectrum of titania (rutile) with Powder Diffraction File (PDF) number 00-021-1276 for TiO$_2$. 
Figure 4.1. X-ray diffraction pattern of titanium oxide powder.

Figure 4.2. shows the x-ray diffraction spectrum of CaCO$_3$ powder, and matches from the spectrum of calcite, (synthetic) with Powder Diffraction File (PDF) number 04-007-8659 for Ca(CO$_3$).

Figure 4.2. X-ray diffraction pattern of calcium carbonate powder.
The X-ray diffraction spectrum of CuO powder is shown in Figure 4.3, and matches from the spectrum of tenorite, (synthetic) with PDF number 00-048-1548 for CuO.

![X-ray diffraction spectrum of CuO powder](image)

Figure 4.3. X-ray diffraction spectrum of cupric oxide powder.

The SEM micrographs of CaCO$_3$ powder (Figure 4.4), show that the particle size is in the range of 5–30 μm. The powders are polyhedral in shape.

![SEM images of CaCO$_3$ powder](image)

Figure 4.4. SEM images of calcium carbonate powder.

Figure 4.5.(a) and (b) show SEM images of CuO powder. The powder granules are most polyhedral (some are cuboid) in shape. Figure 4.5.(b) shows the SEM image of the cupric oxide in lower magnification than (a), the grain size is in the range of 1 to 5 μm. The titanium
oxide particles are near spherical in shape as shown in Figure 4.6. The particle size is in the range of 0.25 to 1 μm.

Figure 4.5. SEM images of cupric oxide powder

Figure 4.6. SEM images of titanium oxide powder

4.1.1. Single and Double Calcination CCTO.

Powders with different processing conditions were prepared for initial study. These were single calcination (CCTOsc) and double calcination (CCTOdc) powders, both powders pressed into pellets and sintered for 4 hours at 1100°C. Figure 4.7 and 4.8 show the x-ray diffraction spectra from sample CCTOsc and CCTOdc. The X-ray diffraction results indicated that all samples had a typical perovskite CaCu$_3$Ti$_4$O$_{12}$ structure. The information in an X-ray diffraction spectra is a direct result of the size and symmetry of the unit cells, which determine the relative positions of the diffraction peaks. Hence, the size and symmetry of the unit cell from the
positions of the X-ray diffraction peaks were calculated.

The blue strips represent of CaCu$_3$Ti$_4$O$_{12}$ and the green strips fit for Ca(TiO$_3$) as shown in Figure 4.7. The Miller indices of the peaks are shown in the top (beside) of the peak. XPert HighScore Plus software was used to analyse the pattern (after Speakman [121]) and the International Centre for Diffraction Database (ICDD) version PDF4+ was utilised to determine the phases. The main phase was identified as Calcium Copper Titanium Oxide, with Powder Diffraction File (PDF) number 04-010-5727 for both of CCTOsc and CCTOdc. However, there were peaks identified as Calcium Titanate (Ca(TiO$_3$)) in CCTOsc and Tenorite (CuO) in CCTOdc. The intensity ratio of Ca(TiO$_3$) peak at 44.6° (2θ) to the maximum peak at 34.4° (2θ) (ratio to (220) peak) was 0.51%, and 2.16% for CuO peak at 35.6° (2θ).

In Figure 4.7, X-ray diffraction pattern of CCTOsc

In Figure 4.8, the blue strips represent of CaCu$_3$Ti$_4$O$_{12}$ and the green strips fit for CuO. Similar the powders produced with a single calcination step, the Miller indices of the peaks of CCTOdc were shown in the top (beside) of the peak. Presence of CuO phase in CaCu$_3$Ti$_4$O$_{12}$ phase is common. Since Adams et al. [122] reported that a CuO peak (~36.5° (2θ)) was found on the surface of CCTO sample after sintering at a sintering temperature of 1115°C, there might

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*Ellyawan Arbintarso*  Bulk and Grain Boundary Electrical Behaviours in Nb and Sn Doped Calcium Copper Titanium Oxide  96
be a transition temperature where either CuO secondary phase is acceptable depending on sintering temperatures and times.

The Bragg angle, d-spacing and Miller indices (hkl) from CCTOsc and CCTOdc samples are shown at Table 4-1 and 4-2. The indices will be used to calculate the lattice parameters as shown in Table 4-3.

Table 4-1. Peak list of CCTOsc sample.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>17.0500</td>
<td>581.01</td>
<td>0.1800</td>
<td>5.19627</td>
<td>0.85</td>
<td>110</td>
</tr>
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<td>29.6780</td>
<td>1811.42</td>
<td>0.1800</td>
<td>3.00776</td>
<td>2.66</td>
<td>211</td>
</tr>
<tr>
<td>34.3876</td>
<td>68147.38</td>
<td>0.1800</td>
<td>2.60584</td>
<td>100.00</td>
<td>220</td>
</tr>
<tr>
<td>38.5676</td>
<td>4699.30</td>
<td>0.1800</td>
<td>2.33249</td>
<td>6.90</td>
<td>310</td>
</tr>
<tr>
<td>42.4169</td>
<td>8264.45</td>
<td>0.1800</td>
<td>2.12930</td>
<td>12.13</td>
<td>222</td>
</tr>
<tr>
<td>44.6184</td>
<td>350.27</td>
<td>0.2400</td>
<td>2.02922</td>
<td>0.51</td>
<td>Ca(TiO$_3$)</td>
</tr>
<tr>
<td>45.9935</td>
<td>4795.66</td>
<td>0.1800</td>
<td>1.97169</td>
<td>7.04</td>
<td>321</td>
</tr>
<tr>
<td>49.3745</td>
<td>14321.87</td>
<td>0.1800</td>
<td>1.84430</td>
<td>21.02</td>
<td>400</td>
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<tr>
<td>52.5714</td>
<td>1092.75</td>
<td>0.1800</td>
<td>1.73942</td>
<td>1.60</td>
<td>411</td>
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<td>55.6370</td>
<td>480.21</td>
<td>0.1800</td>
<td>1.65062</td>
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<td>420</td>
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<tr>
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<td>0.1800</td>
<td>1.57382</td>
<td>1.45</td>
<td>332</td>
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<tr>
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<td>30148.14</td>
<td>0.1800</td>
<td>1.50755</td>
<td>44.24</td>
<td>422</td>
</tr>
<tr>
<td>64.2330</td>
<td>578.01</td>
<td>0.1200</td>
<td>1.44890</td>
<td>0.85</td>
<td>510</td>
</tr>
<tr>
<td>69.6709</td>
<td>1747.82</td>
<td>0.1800</td>
<td>1.34851</td>
<td>2.56</td>
<td>521</td>
</tr>
<tr>
<td>72.3104</td>
<td>7667.59</td>
<td>0.1800</td>
<td>1.30565</td>
<td>11.25</td>
<td>440</td>
</tr>
<tr>
<td>74.8922</td>
<td>2550.21</td>
<td>0.1800</td>
<td>1.26691</td>
<td>3.74</td>
<td>433</td>
</tr>
<tr>
<td>77.4586</td>
<td>1208.26</td>
<td>0.1800</td>
<td>1.23121</td>
<td>1.77</td>
<td>442</td>
</tr>
<tr>
<td>79.9934</td>
<td>1052.28</td>
<td>0.2400</td>
<td>1.19845</td>
<td>1.54</td>
<td>611</td>
</tr>
<tr>
<td>82.5103</td>
<td>20493.50</td>
<td>0.1800</td>
<td>1.16816</td>
<td>30.07</td>
<td>620</td>
</tr>
</tbody>
</table>

*Pos = Position, FWHM = Full Width at High Maximum, Rel. Int. = Reference Intensity ratio, hkl = Miller indices
Crystal system is cubic, which Im-3 (204) spacegroup, with \(a = 7.3796\) Å. This sample is mostly CaCu\(_3\)Ti\(_4\)O\(_{12}\) (04-010-5727) and the residual phase is Ca(TiO\(_3\)) (01-075-0437) with Reference Intensity ratio 0.51%.

Table 4-2. Peak list of CCTOdc sample.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<td>3.45</td>
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<td>100.00</td>
<td>220</td>
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<tr>
<td>35.6290</td>
<td>535.94</td>
<td>0.1968</td>
<td>2.51993</td>
<td>2.16</td>
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<td>38.5235</td>
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<td>2.33699</td>
<td>9.54</td>
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</tr>
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<td>42.3703</td>
<td>1263.21</td>
<td>0.1476</td>
<td>2.13330</td>
<td>5.09</td>
<td>222</td>
</tr>
<tr>
<td>45.9445</td>
<td>1625.08</td>
<td>0.1968</td>
<td>1.97532</td>
<td>6.54</td>
<td>123</td>
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<tr>
<td>49.3183</td>
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<td>0.1476</td>
<td>1.84780</td>
<td>30.33</td>
<td>400</td>
</tr>
<tr>
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<td>0.1968</td>
<td>1.74243</td>
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<td>1.51026</td>
<td>65.03</td>
<td>422</td>
</tr>
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<td>4739.17</td>
<td>0.1476</td>
<td>1.30795</td>
<td>19.08</td>
<td>440</td>
</tr>
<tr>
<td>74.8281</td>
<td>1034.15</td>
<td>0.1476</td>
<td>1.26889</td>
<td>4.16</td>
<td>433</td>
</tr>
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<td>77.3897</td>
<td>346.77</td>
<td>0.1476</td>
<td>1.23316</td>
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<td>600</td>
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<tr>
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<td>6491.01</td>
<td>0.1800</td>
<td>1.16884</td>
<td>26.14</td>
<td>620</td>
</tr>
</tbody>
</table>

Table 4-3 shows the calculation of lattice parameters based on d-spacing and Miller indices for CCTOsc. This method was also used to calculate the CCTOdc lattice parameters. The lattice parameters of CCTOsc is 7.3796 ± 0.0099 Å and CCTOdc is 7.3798 ± 0.0096 Å. Both of them have similar lattice parameters (errors are 0.134% and 0.130% for CCTOsc and CCTOdc, respectively).

Table 4-3. Lattice list of CCTOsc.

<table>
<thead>
<tr>
<th>d-spacing [Å]</th>
<th>hkl</th>
<th>(h^2+k^2+l^2)</th>
<th>Lattice (a) [Å]</th>
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</tr>
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<td>10</td>
<td>7.3760</td>
</tr>
<tr>
<td>2.12930</td>
<td>222</td>
<td>12</td>
<td>7.3761</td>
</tr>
<tr>
<td>2.02922 202</td>
<td>Ca(TiO(_3))</td>
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<td>14</td>
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<tr>
<td>1.97169</td>
<td>400</td>
<td>16</td>
<td>7.3772</td>
</tr>
<tr>
<td>1.84430</td>
<td>420</td>
<td>20</td>
<td>7.3818</td>
</tr>
<tr>
<td>1.73942</td>
<td>332</td>
<td>22</td>
<td>7.3819</td>
</tr>
<tr>
<td>1.65062</td>
<td>422</td>
<td>24</td>
<td>7.3855</td>
</tr>
<tr>
<td>1.57382</td>
<td>422</td>
<td>24</td>
<td>7.3865</td>
</tr>
<tr>
<td>1.50755</td>
<td>510</td>
<td>26</td>
<td>7.3880</td>
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<tr>
<td>1.44890</td>
<td>521</td>
<td>30</td>
<td>7.3861</td>
</tr>
</tbody>
</table>
1.30565   440   32   7.3859
1.26691   433   34   7.3873
1.23121   442   36   7.3873
1.19845   611   38   7.3877
1.16816   620   40   7.3881

Average: 7.3796
SD       0.0099

The CCTO mixture as interactive mixture (mixture of free-flowing powder with a cohesive powder) shown in Figure 4.9. The interactive units is formed when cohesive particles (small particles – titanium oxide) have to adhered to the free-flowing particles (large particles – calcium carbonate and cupric oxide).

![SEM image of CCTO powders](image)

(a) CCTOsc   (b) CCTOdc

Figure 4.9. SEM image of CCTO powders

The CCTOsc preparation route was chosen in consideration of presence of lower residual phase content (less than 1%) than CCTOdc. Both of them have similar lattice parameters, grain size and shape.

### 4.2. Substitution with Nb (CCTxN)

Nb$_2$O$_5$ powder was added to CaCu$_3$(Ti$_{4-x}$M$_x$)O$_{12}$ in concentrations of 0.05, 0.10, 0.15, 0.20 and 0.25 mol. The aim of this preparation is to substitute Titanium with Niobium (Equation (73)). The X-ray diffraction was used to monitor the phase development and lattice parameter changes associated with adding different levels of dopants. Table 4-4 shows the name of the composition of each sample and the percentage weight of starting powder.
Table 4-4. Name and percentage composition of each powder to synthesis CCTxN.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Sintering Condition</th>
<th>CaCO₃ (wt%)</th>
<th>CuO (wt%)</th>
<th>TiO₂ (wt%)</th>
<th>Nb₂O₅ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05N4</td>
<td>CaCu₃Ti₃.95Nb₀.05O₁₂</td>
<td>1100°C 4 h</td>
<td>15.00</td>
<td>35.75</td>
<td>47.26</td>
<td>1.99</td>
</tr>
<tr>
<td>CCT10N4</td>
<td>CaCu₃Ti₃.90Nb₀.10O₁₂</td>
<td>1100°C 4 h</td>
<td>14.79</td>
<td>35.26</td>
<td>46.02</td>
<td>3.93</td>
</tr>
<tr>
<td>CCT15N4</td>
<td>CaCu₃Ti₃.85Nb₀.15O₁₂</td>
<td>1100°C 4 h</td>
<td>14.59</td>
<td>34.78</td>
<td>44.62</td>
<td>5.81</td>
</tr>
<tr>
<td>CCT20N4</td>
<td>CaCu₃Ti₃.80Nb₀.20O₁₂</td>
<td>1100°C 4 h</td>
<td>14.39</td>
<td>34.32</td>
<td>43.64</td>
<td>7.65</td>
</tr>
<tr>
<td>CCT25N4</td>
<td>CaCu₃Ti₃.85Nb₀.25O₁₂</td>
<td>1100°C 4 h</td>
<td>14.20</td>
<td>33.87</td>
<td>42.50</td>
<td>9.43</td>
</tr>
</tbody>
</table>

Figure 4.10. shows the x-ray diffraction spectrum of Nb₂O₅ powder, and matched from the spectrum as niobium oxide from Powder Diffraction File (PDF) number 00-027-1003 for Nb₂O₅.

Figure 4.11 shows the SEM image of Nb₂O₅ powder. The particles are near spherical in shape. Figure 4.11.(b) shows the SEM image of the Niobium (V) Oxide in lower magnification, the grain size is in the range of 0.2 to 1 μm.
Figure 4.11. SEM image of niobium oxide powder

Figure 4.12. X-ray diffraction spectrum of 0.25 mol Nb doped CCTO at 4 hours sintering hold time

Figure 4.12. shows the X-ray diffraction spectrum from CCT25N4 (0.25 mol Nb doped CCTO at 4 hours sintering hold time) sample which the maximum niobium dopant added has chosen to see if another phase is present. Peaks from niobium oxide (NbO) phase were detected; the NbO peaks at 30.25°, 50.43°, and 59.95° and Relative Intensity ratio of them are 3.03%, 2.28% and 1.94% respectively. Table 4-5 shows the peak list of CCT25N4 sample.
<table>
<thead>
<tr>
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<td>273.72</td>
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</tr>
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<td>111 (NbO)</td>
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<td>49.2061</td>
<td>28739.08</td>
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<tr>
<td>50.4338</td>
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<td>1.80952</td>
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<td>510</td>
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<td>1.28933</td>
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<td>433</td>
</tr>
<tr>
<td>77.3242</td>
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<td>0.3936</td>
<td>1.23404</td>
<td>0.61</td>
<td>442</td>
</tr>
<tr>
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<td>1.20118</td>
<td>0.99</td>
<td>611</td>
</tr>
<tr>
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<td>1.17093</td>
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<td>620</td>
</tr>
<tr>
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<td>0.2400</td>
<td>1.14315</td>
<td>0.73</td>
<td></td>
</tr>
</tbody>
</table>

Crystal system is cubic, which Im-3 (204) spacegroup, with a = 7.3886 Å. This sample is mostly CaCu$_3$Ti$_4$O$_{12}$ (01-072-5884) and the residual phase is NbO (01-084-0455) with Reference Intensity ratio maximum 3.03%.

Figure 4.13. shows the CaCu$_3$Ti$_{4-x}$Nb$_x$O$_{12}$ mixture as an interactive mixture. Its seem all small particles adhered to the large particles. The diffraction spectra for the formulation under
investigation are shown in Figure 4.14. The NbO phase appeared at x = 0.20 and 0.25 mol. The investigation of electrical behaviour was conducted on all compositions to determine the effect of doping of Niobium.

Figure 4.14. shows the diffraction profiles for the formulations of CaCu$_3$Ti$_{4-x}$Nb$_x$O$_{12}$ (0 ≤ x ≤ 0.25) that analysed by X-ray Diffraction in order to know the phase changed with Niobium addition. The pure CaCu$_3$Ti$_4$O$_{12}$ sample shows a second phase CaTiO$_3$ at peak 44.6° (2θ) and disappeared when Niobium was added. In 0.20 mol and 0.25 mol Nb dopant, there were second phases detected, as NbO, with Relative Intensity ratio less than 3%. These all compositions sintered in 1100°C for 4 hours.

Figure 4.14. Diffraction spectra for CCTxN (0 ≤ x ≤ 25) with Miller Indexes.

4.3. Substitution with Sn (CCTxS)

Similar as described in earlier section, SnO$_2$ powders also were added to CaCu$_3$(Ti$_{4-x}$M$_x$)O$_{12}$ in concentrations of 0.05, 0.10, 0.15, 0.20 and 0.25 mol. The aim of this sample preparation is to substitute Titanium with Tin (Equation (74)). Using the same method, X-ray diffraction was used to monitor the phase development and lattice parameter changes associated with adding different levels of dopants. Table 4-6. shows the name and composition
of each sample and the percentage weight of starting powders were used in sample of tin doped CCTO.

Table 4-6. Name and composition of each powder to synthesis CCTxS.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Sintering Condition</th>
<th>CaCO$_3$ (wt%)</th>
<th>CuO (wt%)</th>
<th>TiO$_2$ (wt%)</th>
<th>SnO$_2$ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05S4</td>
<td>CaCu$<em>3$Ti$</em>{3.95}$Sn$<em>{0.05}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>15.13</td>
<td>36.06</td>
<td>47.68</td>
<td>1.13</td>
</tr>
<tr>
<td>CCT10S4</td>
<td>CaCu$<em>3$Ti$</em>{3.90}$Sn$<em>{0.10}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>15.05</td>
<td>35.87</td>
<td>46.82</td>
<td>2.26</td>
</tr>
<tr>
<td>CCT15S4</td>
<td>CaCu$<em>3$Ti$</em>{3.85}$Sn$<em>{0.15}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>14.97</td>
<td>35.68</td>
<td>45.98</td>
<td>3.37</td>
</tr>
<tr>
<td>CCT20S4</td>
<td>CaCu$<em>3$Ti$</em>{3.80}$Sn$<em>{0.20}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>14.89</td>
<td>35.50</td>
<td>45.15</td>
<td>4.46</td>
</tr>
<tr>
<td>CCT25S4</td>
<td>CaCu$<em>3$Ti$</em>{3.85}$Sn$<em>{0.25}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>14.81</td>
<td>35.31</td>
<td>44.32</td>
<td>5.56</td>
</tr>
</tbody>
</table>

XPert HighScore Plus software was used to analyse the pattern of SnO$_2$ powder as shown in Figure 4.15, and matches from the spectrum of Cassiterite with Powder Diffraction File (PDF) number 01-070-4175 for SnO$_2$.

![X-ray diffraction pattern of tin oxide powder.](image)

Figure 4.15. X-ray diffraction pattern of tin oxide powder.

Figure 4.16 shows the SEM image of SnO$_2$ powder. The particles are near spherical in shape. Figure 4.16.(b) shows the SEM image of the tin oxide in lower magnification, and Figure 4.16.(a) shows higher magnification than (b) but it is not clear to see the individual particles of
tin oxide. Approximately, the grain size is less than 0.5 μm.

Figure 4.16. SEM image of tin oxide powder

Figure 4.17. X-ray diffraction spectrum of 0.25 mol Sn doped CCTO at 4 hours sintering hold time.

X-ray diffraction spectrum of CCT25S4 (0.25 mol Sn doped CCTO at 4 hours sintering hold time) sample is shown in Figure 4.17. The CCT25S4 is sample with the maximum tin dopant added that was chosen to see if another phase is present. There was another peak detected as tin oxide (SnO) phase. The SnO peak at 35.73°, and the Relative Intensity ratio is 3.03%. Table 4-7 shows the peak list of CCT25S4 sample.
Table 4-7. Peak list of CCT25S4 sample.

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<tr>
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<td>3.00779</td>
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<td>2.60792</td>
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<tr>
<td>35.7314</td>
<td>514.55</td>
<td>0.5904</td>
<td>2.51294</td>
<td>3.09</td>
<td>310</td>
</tr>
<tr>
<td>38.6907</td>
<td>2038.45</td>
<td>0.5904</td>
<td>2.32728</td>
<td>12.25</td>
<td>310</td>
</tr>
<tr>
<td>42.3804</td>
<td>601.81</td>
<td>1.1808</td>
<td>2.13281</td>
<td>3.62</td>
<td>222</td>
</tr>
<tr>
<td>45.9645</td>
<td>1368.90</td>
<td>0.5904</td>
<td>1.97450</td>
<td>8.22</td>
<td>321</td>
</tr>
<tr>
<td>49.3134</td>
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<td>0.5904</td>
<td>1.84797</td>
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<td>400</td>
</tr>
<tr>
<td>52.5527</td>
<td>388.79</td>
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<td>410</td>
</tr>
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<td>61.4062</td>
<td>8111.25</td>
<td>0.7872</td>
<td>1.50990</td>
<td>48.73</td>
<td>422</td>
</tr>
<tr>
<td>64.1246</td>
<td>155.22</td>
<td>0.5904</td>
<td>1.45229</td>
<td>0.93</td>
<td>510</td>
</tr>
<tr>
<td>66.1853</td>
<td>77.75</td>
<td>0.4920</td>
<td>1.41199</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>68.1800</td>
<td>98.00</td>
<td>0.5904</td>
<td>1.37546</td>
<td>0.59</td>
<td>521</td>
</tr>
<tr>
<td>72.2503</td>
<td>2286.38</td>
<td>0.7872</td>
<td>1.30767</td>
<td>13.74</td>
<td>440</td>
</tr>
<tr>
<td>74.9252</td>
<td>479.99</td>
<td>1.1808</td>
<td>1.26748</td>
<td>2.88</td>
<td>430</td>
</tr>
<tr>
<td>77.3545</td>
<td>282.02</td>
<td>0.5904</td>
<td>1.23363</td>
<td>1.69</td>
<td>442</td>
</tr>
<tr>
<td>79.8853</td>
<td>287.88</td>
<td>0.7200</td>
<td>1.19980</td>
<td>1.73</td>
<td>611</td>
</tr>
</tbody>
</table>

Crystal system is cubic, which Im-3 (204) spacegroup, with a = 7.3832 Å. This sample is mostly CaCu$_3$Ti$_{4-x}$Sn$_x$O$_{12}$ (04-010-5727) and the residual phase is SnO (01-070-4175) with Reference Intensity ratio maximum 3.09%.

![Figure 4.18](image.png)

**Figure 4.18.** SEM image of 0.10 mol Sn doped CCTO 4 hours sintering hold time powders

The CaCu$_3$Ti$_{4-x}$Sn$_x$O$_{12}$ mixture also as interactive mixture is shown in Figure 4.18. Similar to previous mixtures, all small particles (titanium oxide and tin oxide particles) adhered to large particles (calcium carbonate and cupric oxide particles). Figure 4.19 shows the diffraction profiles for the formulation under investigation. The SnO phase appeared at all composition with tin dopant. The investigation of electrical behaviour was conducted on all compositions to determine the effect of tin dopant.
The X-ray Diffraction was used to formulations of CaCu$_3$Ti$_{4-x}$Sn$_x$O$_{12}$ ($0 \leq x \leq 0.25$) in order to know the phase changed with tin addition. Figure 4.19. shows the diffraction profiles for the formulations under investigation. The pure CaCu$_3$Ti$_4$O$_{12}$ sample shows a second phase CaTiO$_3$ at peak 44.6° (2θ) and reduced when tin was added. There were second phases detected, as SnO, in all composition tin dopant. The SnO peak at 35.73°, with Relative Intensity ratio 3.09%. These all compositions were sintered in 1100°C for 4 hours.

In summary, pure CCTO made by the mixed oxide route has CaTiO$_3$ as a secondary phase. The result of single and double calcination were not significantly different. The niobium doped CCTO has NbO as a secondary phase at 0.20 and 0.25 mol niobium dopant. The tin doped CCTO has SnO as secondary phase at all composition.
5. Microstructure and Phase Development

The focus of this section, microstructure and phase development, is to describe the microstructure and phase analysis of three series of samples (pure CaCu$_3$Ti$_4$O$_{12}$, CaCu$_3$Ti$_4$-$_x$Nb$_x$O$_{12}$, and CaCu$_3$Ti$_4$-$_x$Sn$_x$O$_{12}$). The microstructure and phase analysis includes sample and sintering condition, densification data, grain size and their distribution, and phase analysis. Three series of samples were used in this study i.e. CCTOy, CCTxNy and CCTxSy where x is the amount of dopant in mol% and y is sintering hold time in hours. The result of these microstructure and phase development will be used to support the electrical properties discussion in chapter 8.

5.1. Microstructure

5.1.1. Microstructure of CCTO with various sintering hold time

Figures 5.1, 5.2, and 5.3., show micrographs of CCTO4, CCTO8, and CCTO12, respectively. A duplex microstructure consisting of large grains which reach to 50 μm in diameter and isolated regions of small grains is shown in Figure 5.1. and Figure 5.2. The grain size and range of CCTO samples with different sintering hold times are shown in Table 5-1. The fine grain is categorised as small grain size that less than 5 μm, and large grain size is grain equal or more than 5 μm in diameter.
Figure 5.1. SEM image of CCTO at 4 hours sintering hold time with the small grains (inset) spread among the large grains.

Figure 5.2. SEM image of CCTO at 8 hours sintering hold time, the large grains grow bigger and some small grains merged with the large grains.

The Figure 5.1. to 5.3. show the large grains grow more rapidly than the smaller grain as sintering hold time increase. When the sintering time increased up to 8 hours, the microstructure clearly indicates the larger grain's growth (average large grain size increase). Further rise of the sintering time up to 12 hours shows that grain growth continues and reduces the small grain-sized regions. The large grain size was dominant in CCTO12, as shown in
Figure 5.3. The grain with many sides (e.g. when the large grain has more than 6 sides) grows easily in these conditions [93].

A few pores were present in large grains, and either were intragranular and intergranular. The intragranular pores may arise from abnormal grain growth and grain boundaries moving quickly during the sintering process [124]. With increasing sintering hold time, three key changes occur: which is an increase in average (large) grain size (Table 5-1), a change in pore shape and size (decrease average pore size), and decreased porosity (it will be discussed in section 5.3.).

Table 5-1. Grains and pore size of CCTO at various sintering hold time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Small grain Av. Size (μm)</th>
<th>Large grain Av. Size (μm)</th>
<th>Grain Range (μm)</th>
<th>Pore Av. Size (μm)</th>
<th>Range (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCTO4</td>
<td>1.6 ± 0.3</td>
<td>15.8 ± 2.2</td>
<td>0.5-59.7</td>
<td>1.3 ± 0.3</td>
<td>0.5-9.1</td>
</tr>
<tr>
<td>CCTO8</td>
<td>1.5 ± 0.3</td>
<td>18.0 ± 2.7</td>
<td>0.5-49.4</td>
<td>1.3 ± 0.3</td>
<td>0.5-13.7</td>
</tr>
<tr>
<td>CCTO12</td>
<td>na</td>
<td>22.7 ± 5.4</td>
<td>5.0-61.2</td>
<td>0.9 ± 0.5</td>
<td>0.4-17.5</td>
</tr>
</tbody>
</table>

Figure 5.4. shows the grains shape of CCTO are found to be regular and polyhedral type, and the shape of pores are polyhedral type in intergranular and sphere or rod type in intragranular.
Table 5-2. shows the increasing pores distribution with increasing sintering hold time. The shape and size of pore changed during sintering time, which pore size decreases with increases the distribution. The grain size also increases and more uniform with longer sintering hold time. The pores, small and large grains distribution will affected to density of the sample which will discussed in section 5.4.

Table 5-2. Grains and pores distribution of CCTO at various sintering hold time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pores (%)</th>
<th>Grains (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Small (&lt;5μm)</td>
</tr>
<tr>
<td>CCTO4</td>
<td>2.4</td>
<td>3.9</td>
</tr>
<tr>
<td>CCTO8</td>
<td>4.6</td>
<td>1.7</td>
</tr>
<tr>
<td>CCTO12</td>
<td>8.0</td>
<td>na</td>
</tr>
</tbody>
</table>

5.1.2. Microstructure of niobium and tin doped CCTO at 4 hours sintering.

Figure 5.5. to Figure 5.9. show the micrographs of CCTO with various niobium dopant, increasing the amount of dopant reduces average grain and pore size of CCTO. Figure 5.5. shows the SEM image of 0.05 nb doped CCTO at 4 hours sintering hold time (CCT05N4) with small grains dominantly. The pore distribution seems to increase, compared to pure CCTO at 4 hours sintering hold time.
Figure 5.5. SEM image of 0.05 Nb doped CCTO at 4 hours sintering hold time (CCT05N4)

Figure 5.6. shows the SEM image of 0.10 Nb doped CCTO at 4 hours sintering hold time (CCT10N4), similar to CCT05N4, the small grains are dominant. The pore distribution lower than CCT05N4, and there is no existence of large grain.

Figure 5.6. SEM image of 0.10 Nb doped CCTO at 4 hours sintering hold time (CCT10N4).

The SEM image of 0.15 Nb doped CCTO at 4 hours sintering hold time (CCT15N4) is shown in Figure 5.7. The small grains are still dominant. The pore distribution seem lower than CCT10N4.
Figure 5.7. SEM image of 0.15 Nb doped CCTO at 4 hours sintering hold time (CCT15N4).

Figure 5.8. shows the SEM image of 0.20 Nb doped CCTO at 4 hours sintering hold time (CCT20N4). The pore distribution seems similar to CCT15N4, and the small grains are dominant.

Figure 5.8. SEM image of 0.20 Nb doped CCTO at 4 hours sintering hold time (CCT20N4).

The SEM image of 0.25 Nb doped CCTO at 4 hours sintering hold time (CCT25N4) is shown in Figure 5.9. The small grains are still dominant. The pore distribution seem lower than CCT20N4 and the pore is located at conjugate grains.
Figure 5.9. SEM image of 0.25 Nb doped CCTO at 4 hours sintering hold time (CCT25N4).

The niobium dopant shows as an inhibitor to grain growth, which the grain size decreases less than 5 μm in diameter. The large grain size did not appear at all niobium doped CCTO with 4 hours sintering hold time.

Table 5-3. shows grain and pore size of CCTO with various niobium dopant at 4 hours sintering hold time. The small grain and pore size decrease as niobium dopant increase. In general, niobium dopant reduced the grain and pore range size, and increased niobium dopant makes the grain size more uniform (large grain does not appear).

Table 5-3. Grains and pore size of niobium doped CCTO at 4 hours sintering time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Small grain Size (μm)</th>
<th>Large grain Size (μm)</th>
<th>Grain Range (μm)</th>
<th>Pore Size (μm)</th>
<th>Pore Range (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05N4</td>
<td>1.1 ± 0.2</td>
<td>na</td>
<td>0.4-4.4</td>
<td>0.7 ± 1.0</td>
<td>0.0-7.7</td>
</tr>
<tr>
<td>CCT10N4</td>
<td>1.4 ± 0.2</td>
<td>na</td>
<td>0.5-4.2</td>
<td>0.6 ± 0.7</td>
<td>0.0-3.9</td>
</tr>
<tr>
<td>CCT15N4</td>
<td>1.1 ± 0.2</td>
<td>na</td>
<td>0.4-3.2</td>
<td>0.3 ± 0.5</td>
<td>0.0-3.2</td>
</tr>
<tr>
<td>CCT20N4</td>
<td>1.1 ± 0.2</td>
<td>na</td>
<td>0.5-4.2</td>
<td>0.4 ± 0.4</td>
<td>0.0-2.8</td>
</tr>
<tr>
<td>CCT25N4</td>
<td>1.0 ± 0.2</td>
<td>na</td>
<td>0.4-3.9</td>
<td>0.3 ± 0.3</td>
<td>0.0-1.9</td>
</tr>
</tbody>
</table>

Percentage of pore decreases as niobium dopant increases is summarised in Table 5-4. On the other hand, the percentage of grains (small grain-sized) increase from 80 to 96%. The pore distribution and the grain size will affected to the density of samples. The grain growth was inhibited by niobium dopant, the grain size of niobium doped CCTO is smaller than for pure CCTO at 4 hours sintering hold time. The grain shape of niobium doped CCTO was found to be
similar to pure CCTO with the same sintering hold time. Figure 5.5. to Figure 5.9. also show the irregular shape of pore in intergranular, both pore size and their distribution decrease as niobium dopant increases.

Table 5-4. Grains and pore distribution of niobium doped CCTO at 4 hours sintering time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pores (%)</th>
<th>Grains (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Small (&lt;5µm)</td>
</tr>
<tr>
<td>CCT05N4</td>
<td>19.5</td>
<td>80.5</td>
</tr>
<tr>
<td>CCT10N4</td>
<td>9.2</td>
<td>90.8</td>
</tr>
<tr>
<td>CCT15N4</td>
<td>7.4</td>
<td>92.6</td>
</tr>
<tr>
<td>CCT20N4</td>
<td>7.5</td>
<td>92.5</td>
</tr>
<tr>
<td>CCT25N4</td>
<td>4.0</td>
<td>96.0</td>
</tr>
</tbody>
</table>

Micrographs of tin doped CCTO at 4 hours sintering are shown in Figure 5.10. to Figure 5.14. The micrographs show duplex microstructure consisting of large and small grains. Initially, the small amount of tin dopant increased the size of large and small grains compared to pure CCTO then the grains size decrease as the amount of tin dopant increase. The tin dopant did not change the grain shape, the grain is similar to the pure CCTO, which the polyhedral type was dominant in grain shape of tin doped CCTO.

Figure 5.10. SEM image of 0.05 tin doped CCTO at 4 hours sintering hold time (CCT05S4)
Figure 5.11. SEM image of 0.10 tin doped CCTO at 4 hours sintering hold time (CCT10S4).

Figure 5.11 shows the polyhedral pore shape, and dominant position is at intergranular. On the other hand, Figure 5.12., Figure 5.13., and Figure 5.14. show the intragranular pore significantly disappear as the amount of tin dopant increases. Despite the increasing tin dopant also increasing the pore size and pore range, as shown in Table 5-5.

Figure 5.12. SEM image of 0.15 tin doped CCTO at 4 hours sintering hold time (CCT15S4).
Figure 5.13. SEM image of 0.20 tin doped CCTO at 4 hours sintering hold time (CCT20S4).

Figure 5.14. SEM image of 0.25 tin doped CCTO at 4 hours sintering hold time (CCT25S4).

Table 5-5. shows grain and pore size of CCTO with various tin dopant at 4 hours sintering hold time. In general, the small, large grain and pore size tend to decrease as tin dopant increases. The tin dopant reduced the large grain size but did not significantly reduce the small grain size.
Table 5-5. Grains and pore size of niobium doped CCTO at 4 hours sintering time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Small grain</th>
<th>Large grain</th>
<th>Grain</th>
<th>Pore</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Size (μm)</td>
<td>Size (μm)</td>
<td>Range (μm)</td>
<td>Size (μm)</td>
</tr>
<tr>
<td>CCT05S4</td>
<td>3.5 ± 0.7</td>
<td>20.3 ± 3.4</td>
<td>0.5-56.5</td>
<td>0.1 ± 0.1</td>
</tr>
<tr>
<td>CCT10S4</td>
<td>2.9 ± 0.5</td>
<td>7.1 ± 1.0</td>
<td>0.2-29.3</td>
<td>1.1 ± 1.1</td>
</tr>
<tr>
<td>CCT15S4</td>
<td>1.5 ± 0.1</td>
<td>13.1 ± 1.8</td>
<td>0.5-43.5</td>
<td>1.7 ± 1.7</td>
</tr>
<tr>
<td>CCT20S4</td>
<td>2.7 ± 0.4</td>
<td>14.9 ± 1.4</td>
<td>0.5-36.3</td>
<td>1.7 ± 1.6</td>
</tr>
<tr>
<td>CCT25S4</td>
<td>2.4 ± 0.5</td>
<td>12.6 ± 1.6</td>
<td>0.5-40.6</td>
<td>1.2 ± 1.1</td>
</tr>
</tbody>
</table>

In general, the percentage of large grain size increases as tin dopant increases and percentage of pore (pore proportion in relation to a whole microstructure) decreases as tin dopant increases. Table 5-6. shows the percentage of grains and pores of tin doped CCTO at 4 hours sintering hold time. The large grain of tin doped CCTO was dominant compare to pure CCTO, and the percentage of pores was lower than niobium doped CCTO.

Table 5-6. Grains and pores distribution of tin doped CCTO at 4 hours sintering time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pores (%)</th>
<th>Grains (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Small (&lt;5μm)</td>
<td>Large (&gt;5μm)</td>
</tr>
<tr>
<td>CCT05S4</td>
<td>4.0</td>
<td>0.8</td>
</tr>
<tr>
<td>CCT10S4</td>
<td>8.2</td>
<td>6.1</td>
</tr>
<tr>
<td>CCT15S4</td>
<td>4.6</td>
<td>1.3</td>
</tr>
<tr>
<td>CCT20S4</td>
<td>4.7</td>
<td>0.9</td>
</tr>
<tr>
<td>CCT25S4</td>
<td>3.4</td>
<td>1.2</td>
</tr>
</tbody>
</table>

5.1.3. Microstructure of niobium and tin doped CCTO at 8 hours sintering.

Figure 5.15. to Figure 5.19. show the micrograph of CCTO with various niobium dopant at 8 hours sintering. Identically with 4 hours sintering, there is not appearance of large grain size at all samples of niobium doped CCTO with 8 hours sintering hold time. The micrographs show the significant similarity of the shape for all of samples. Figure 5.15. shows the grain shape of initial niobium doped CCTO to be polyhedral type then increases the niobium dopant will changed the grain shape become tetrahedral type (Figure 5.19).
Figure 5.15. SEM image of 0.05 Nb doped CCTO at 8 hours sintering hold time (CCT05N8).

Figure 5.16. SEM image of 0.10 Nb doped CCTO at 8 hours sintering hold time (CCT10N8).
Figure 5.17. SEM image of 0.15 Nb doped CCTO at 8 hours sintering hold time (CCT15N8).

Figure 5.18. SEM image of 0.20 Nb doped CCTO at 8 hours sintering hold time (CCT20N8).
Figure 5.19. SEM image of 0.25 Nb doped CCTO at 8 hours sintering hold time (CCT25N8).

Table 5-7. Grains and pore size of niobium doped CCTO at 8 hours sintering time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Small grain size (μm)</th>
<th>Large grain size (μm)</th>
<th>Grain size range (μm)</th>
<th>Pore size (μm)</th>
<th>Pore size range (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05N8</td>
<td>1.9 ± 0.1</td>
<td>na</td>
<td>0.5-4.5</td>
<td>0.6 ± 0.6</td>
<td>0.0-3.8</td>
</tr>
<tr>
<td>CCT10N8</td>
<td>1.7 ± 0.5</td>
<td>na</td>
<td>0.5-4.1</td>
<td>0.4 ± 0.4</td>
<td>0.0-4.1</td>
</tr>
<tr>
<td>CCT15N8</td>
<td>1.7 ± 0.4</td>
<td>na</td>
<td>0.5-4.9</td>
<td>0.5 ± 0.5</td>
<td>0.0-2.4</td>
</tr>
<tr>
<td>CCT20N8</td>
<td>1.5 ± 0.2</td>
<td>na</td>
<td>0.4-4.9</td>
<td>0.4 ± 0.4</td>
<td>0.0-2.4</td>
</tr>
<tr>
<td>CCT25N8</td>
<td>1.1 ± 0.1</td>
<td>na</td>
<td>0.4-4.9</td>
<td>0.3 ± 0.3</td>
<td>0.0-2.0</td>
</tr>
</tbody>
</table>

The grain size decrease with increased niobium dopant is shown in Table 5-7., similarity with grain size, the pore size and pore range also decreases as the amount of niobium dopant increase. The increasing the amount of niobium dopant does not significantly change the range of grain size. Table 5-8. shows the percentage of pore decreases as the amount of niobium dopant increases. On the other hand, the percentage of small-sized grain increases from around 86 to 97%.

Table 5-8. Grains and pores distribution of niobium doped CCTO at 8 hours sintering time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pores (%)</th>
<th>Grains (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Small (&lt;5μm)</td>
<td>Large (&gt;5μm)</td>
</tr>
<tr>
<td>CCT05N8</td>
<td>13.0</td>
<td>87.0</td>
</tr>
<tr>
<td>CCT10N8</td>
<td>13.3</td>
<td>86.7</td>
</tr>
<tr>
<td>CCT15N8</td>
<td>8.8</td>
<td>91.2</td>
</tr>
<tr>
<td>CCT20N8</td>
<td>5.3</td>
<td>94.7</td>
</tr>
<tr>
<td>CCT25N8</td>
<td>2.8</td>
<td>97.2</td>
</tr>
</tbody>
</table>
The grain size of tin doped CCTO at 8 hours sintering significantly decreases as the amount of dopant increases, as shown in Figure 5.20. to Figure 5.24. The micrographs show a duplex microstructure consisting of large and small grains. In spite of, the small-sized grains of tin doped CCTO at 8 hours sintering hold time bigger than small-sized grains at 4 hours sintering hold time. The tin dopant has not changed the grain shape, the grain shape of tin doped CCTO with 8 hours sintering hold time was identically with pure CCTO and tin doped CCTO with 4 hours sintering hold time samples. The grain shape is polyhedral type for both large and small grains.

Figure 5.20. SEM image of 0.05 Sn doped CCTO at 8 hours sintering hold time (CCT05S8).

Figure 5.21. SEM image of 0.10 Sn doped CCTO at 8 hours sintering hold time (CCT10S8).
Figure 5.20. shows polyhedral pore shape and dominant at intergranular, despite of sphere or rod pore shape at intragranular. The intragranular pore seem to disappear with increasing the amount of tin dopant (compare to Figure 5.22. to Figure 5.24).

Figure 5.22. SEM image of 0.15 Sn doped CCTO at 8 hours sintering hold time (CCT15S8).

Figure 5.23. SEM image of 0.20 Sn doped CCTO at 8 hours sintering hold time (CCT20S8).
Figure 5.24. SEM image of 0.25 Sn doped CCTO at 8 hours sintering hold time (CCT25S8).

Table 5-9. shows the small, large grain size, and pore size of tin doped CCTO at 8 hours sintering hold time. The small grain does not significantly change but the large grain tends to decrease with increasing the amount of tin dopant. The pore size lies between 0.29 and 2.09 μm depending on the amount of tin dopant.

Table 5-9. Grains and pore size of tin doped CCTO at 8 hours sintering time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Small grain</th>
<th>Large grain</th>
<th>Grain</th>
<th>Pore</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Size (μm)</td>
<td>Size (μm)</td>
<td>Range (μm)</td>
<td>Size (μm)</td>
</tr>
<tr>
<td>CCT05S8</td>
<td>4.3 ± 0.4</td>
<td>21.6 ± 3.9</td>
<td>0.6-49.8</td>
<td>2.1 ± 2.4</td>
</tr>
<tr>
<td>CCT10S8</td>
<td>4.0 ± 0.5</td>
<td>12.9 ± 2.3</td>
<td>0.6-38.9</td>
<td>1.3 ± 1.4</td>
</tr>
<tr>
<td>CCT15S8</td>
<td>3.1 ± 0.3</td>
<td>13.8 ± 2.4</td>
<td>0.5-43.6</td>
<td>0.9 ± 1.3</td>
</tr>
<tr>
<td>CCT20S8</td>
<td>4.0 ± 0.7</td>
<td>15.5 ± 2.3</td>
<td>0.5-34.2</td>
<td>1.5 ± 1.8</td>
</tr>
<tr>
<td>CCT25S8</td>
<td>3.5 ± 0.3</td>
<td>13.9 ± 1.8</td>
<td>0.4-39.1</td>
<td>1.8 ± 1.5</td>
</tr>
</tbody>
</table>

In general, the percentage of small and large grain size increases as tin dopant increases and percentage of pore tends to decrease as tin dopant increases. Table 5-10. shows the percentage of grains and pores of tin doped CCTO at 8 hours sintering hold time. The large grain of tin doped CCTO was dominant compared to pure CCTO, but identical with 4 hours sintering hold time. In this case, the longer sintering hold time does not significantly change the percentage of grains. On the other hand, the percentage of pores was lower than niobium doped CCTO at same sintering hold time.
Table 5-10. Grains and pores distribution of tin doped CCTO at 8 hours sintering time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pores (%)</th>
<th>Grains (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Small (&lt;5μm)</td>
<td>Large (&gt;5μm)</td>
</tr>
<tr>
<td>CCT05S8</td>
<td>4.3</td>
<td>0.3</td>
</tr>
<tr>
<td>CCT10S8</td>
<td>5.5</td>
<td>1.9</td>
</tr>
<tr>
<td>CCT15S8</td>
<td>2.7</td>
<td>0.7</td>
</tr>
<tr>
<td>CCT20S8</td>
<td>4.5</td>
<td>1.9</td>
</tr>
<tr>
<td>CCT25S8</td>
<td>2.7</td>
<td>2.0</td>
</tr>
</tbody>
</table>

5.1.4. Microstructure of niobium and tin doped CCTO at 12 hours sintering.

Figure 5.25. to Figure 5.29. show the 12 hour sintering for niobium doped CCTO. The microstructure does not significantly change, the shape and pore distribution are identical.

Figure 5.25. SEM image of 0.05 Nb doped CCTO at 12 hours sintering hold time (CCT05N12).
Figure 5.26. SEM image of 0.10 Nb doped CCTO at 12 hours sintering hold time (CCT10N12).

Figure 5.27. SEM image of 0.15 Nb doped CCTO at 12 hours sintering hold time (CCT15N12).
Figure 5.28. SEM image of 0.20 Nb doped CCTO at 12 hours sintering hold time (CCT20N12).

Figure 5.29. SEM image of 0.25 Nb doped CCTO at 12 hours sintering hold time (CCT25N12).

Figure 5.30. shows grains shape of CCTO with maximum niobium dopant and at longer sintering hold time. The grain shape is found to be regular and polyhedral type, and the pore shape was irregular type at intergranular. The grain size increases and is more uniform with longer sintering hold time. The shape and size of pore also changed during sintering time, which pore size decreases with increases the distribution.
The grain and pore size tends to smaller with increasing the amount of niobium dopant. The pore decreases from 0.49 \( \mu \text{m} \) to 0.19 \( \mu \text{m} \), is shown in Table 5.11. The table also show the range of grain and pore are relatively narrower compare to Table 5.7. (8 hours sintering hold time).

Table 5-11. Grains and pore size of niobium doped CCTO at 12 hours sintering time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Small grain</th>
<th>Large grain</th>
<th>Grain</th>
<th>Pore</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Size (( \mu \text{m} ))</td>
<td>Size (( \mu \text{m} ))</td>
<td>Range (( \mu \text{m} ))</td>
<td>Size (( \mu \text{m} ))</td>
</tr>
<tr>
<td>CCT0.5N12</td>
<td>1.3 ( \pm ) 0.2</td>
<td>na</td>
<td>0.4-3.1</td>
<td>0.5 ( \pm ) 0.5</td>
</tr>
<tr>
<td>CCT1.0N12</td>
<td>1.5 ( \pm ) 0.3</td>
<td>na</td>
<td>0.6-3.9</td>
<td>0.4 ( \pm ) 0.4</td>
</tr>
<tr>
<td>CCT1.5N12</td>
<td>1.4 ( \pm ) 0.4</td>
<td>na</td>
<td>0.5-4.2</td>
<td>0.3 ( \pm ) 0.4</td>
</tr>
<tr>
<td>CCT2.0N12</td>
<td>1.2 ( \pm ) 0.2</td>
<td>na</td>
<td>0.4-4.9</td>
<td>0.2 ( \pm ) 0.2</td>
</tr>
<tr>
<td>CCT2.5N12</td>
<td>1.1 ( \pm ) 0.2</td>
<td>na</td>
<td>0.4-4.9</td>
<td>0.2 ( \pm ) 0.2</td>
</tr>
</tbody>
</table>

Table 5.12. shows the percentage of pore decreases from 18% to 2.4% as the amount of niobium dopant increases. On the other hand, the percentage of small grain increases from 81% to 97%.
In general, added the amount of niobium dopant to CCTO will decrease the grain and pore size. On the other hand, increasing sintering hold time will reduce the pore size but increase the small grain size.

Figure 5.31. to Figure 5.35. show micrographs of tin doped CCTO with 12 hour sintering hold time. The microstructure does not significantly change, the shape and pore distribution are identical. A duplex microstructure consisting of large and small grains was dominantly at all the micrographs. Figure 5.31. shows polyhedral type of pore shape at intergranular, and sphere or rod type of pore shape at intragranular. Figure 5.32. shows the large grains seemly straight, this condition normally happen when secondary recrystallisation occurs in sintering process [93]. Increasing the amount of tin dopant makes the grain size more uniform, the percentage grain size decreases, and grain with diameter around 5 μm was dominant, is shown in Figure 5.33., Figure 5.34, and Figure 5.35.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pores (%)</th>
<th>Grains (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Small (≤5μm)</td>
<td>Large (&gt;5μm)</td>
</tr>
<tr>
<td>CCT05N12</td>
<td>18.1</td>
<td>81.9</td>
</tr>
<tr>
<td>CCT10N12</td>
<td>7.0</td>
<td>93.0</td>
</tr>
<tr>
<td>CCT15N12</td>
<td>5.4</td>
<td>94.6</td>
</tr>
<tr>
<td>CCT20N12</td>
<td>2.9</td>
<td>97.1</td>
</tr>
<tr>
<td>CCT25N12</td>
<td>2.5</td>
<td>97.5</td>
</tr>
</tbody>
</table>

Table 5-12. Grains and pores distribution of niobium doped CCTO at 12 hours sintering time.

Figure 5.31. SEM image of 0.05 Sn doped CCTO at 12 hours sintering hold time (CCT05S12).
Figure 5.32. SEM image of 0.10 Sn doped CCTO at 12 hours sintering hold time (CCT10S12).

Figure 5.33. SEM image of 0.15 Sn doped CCTO at 12 hours sintering hold time (CCT15S12).
Figure 5.34. SEM image of 0.20 Sn doped CCTO at 12 hours sintering hold time (CCT20S12).

Figure 5.35. SEM image of 0.25 Sn doped CCTO at 12 hours sintering hold time (CCT25S12).

Figure 5.36. shows grains shape of CCTO with tin dopant and at longer sintering hold time. The grains and pore shape are found to be regular and polyhedral type, and the pores shape were at intergranular. In lower the amount of tin dopant, the grain size increases and more uniform with longer sintering hold time, but increasing the amount of tin dopant will decrease the grain size with longer sintering hold time. The shape and size of pore also
changed during sintering time, where identically with the grain size.

Figure 5.36. Grain and pore shape of 0.25 mol tin doped CCTO at 12 hours sintering hold time.

The grain and pore size tends to smaller with increasing the amount of tin dopant. The average pore size decreases drastically from 2.71 μm to 0.51 μm, is shown in Table 5.13. Table shows the small, large grain size, and pore size of tin doped CCTO at 12 hours sintering hold time. The grain and pore size are smaller, also the range of grain and pore are relatively narrower compare to Table 5.9. (8 hours sintering hold time).

Table 5-13. Grains and pore size of tin doped CCTO at 12 hours sintering time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Small grain</th>
<th>Large grain</th>
<th>Grain</th>
<th>Pore</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Size (μm)</td>
<td>Size (μm)</td>
<td>Range (μm)</td>
<td>Size (μm)</td>
</tr>
<tr>
<td>CCT05S12</td>
<td>4.2 ± 0.5</td>
<td>24.6 ± 4.7</td>
<td>0.5-70.2</td>
<td>2.7 ± 3.8</td>
</tr>
<tr>
<td>CCT10S12</td>
<td>2.5 ± 0.2</td>
<td>10.2 ± 2.2</td>
<td>0.2-39.7</td>
<td>1.0 ± 1.2</td>
</tr>
<tr>
<td>CCT15S12</td>
<td>4.0 ± 0.6</td>
<td>9.1 ± 1.7</td>
<td>0.1-69.3</td>
<td>1.1 ± 1.0</td>
</tr>
<tr>
<td>CCT20S12</td>
<td>4.4 ± 0.7</td>
<td>8.5 ± 1.1</td>
<td>0.2-30.8</td>
<td>1.0 ± 1.6</td>
</tr>
<tr>
<td>CCT25S12</td>
<td>1.8 ± 0.1</td>
<td>7.7 ± 1.3</td>
<td>0.1-38.5</td>
<td>0.5 ± 0.8</td>
</tr>
</tbody>
</table>

In general, the percentage of small, large grains and pores were not change significantly between 0.15 and 0.25 mol of tin dopant. Table 5-14. shows the percentage of grains and pores of tin doped CCTO at 12 hours sintering hold time. The percentage large grain was dominant identically with 4 and 8 hours sintering hold time. The longer sintering time will change the percentage of grains depend on the amount of tin dopant,
5.2. Grain Size

Figure 5.37. shows the average grain size of CaCu$_3$Ti$_4$O$_{12}$ at various sintering time, in general, longer sintering hold time does not change significantly the average small grain size but increases the average large grain size.

![Average grain size of CCTO at various sintering times.](image)

Figure 5.37. Average grain size of CCTO at various sintering times.

Figure 5.38. shows the average small grain size of niobium doped CCTO at various sintering hold time. In this case, the large grains did not appear with any the amount of niobium dopant. The average small grain size was reached higher for 8 hours sintering hold time, as longer sintering time will decrease the average grain size. The grain size does not change significantly with increasing the amount of niobium dopant.

Table 5-14. Grains and pores distribution of tin doped CCTO at 12 hours sintering time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pores (%)</th>
<th>Grains (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Small (&lt;5μm)</td>
</tr>
<tr>
<td>CCT05S12</td>
<td>5.3</td>
<td>0.5</td>
</tr>
<tr>
<td>CCT10S12</td>
<td>5.5</td>
<td>7.6</td>
</tr>
<tr>
<td>CCT15S12</td>
<td>3.3</td>
<td>5.0</td>
</tr>
<tr>
<td>CCT20S12</td>
<td>6.5</td>
<td>4.1</td>
</tr>
<tr>
<td>CCT25S12</td>
<td>3.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>
Figure 5.38. Average (small) grain size of niobium doped CCTO at various sintering times.

Figure 5.39. shows the average large grain size of tin doped CCTO at various sintering hold time. At 0.05 mol of tin dopant, the large grain was reached highest size and decreased as the amount of tin dopant increased. The average large grain size depends on the amount of tin dopant and sintering hold time. In general, the grain size increased with increase of the sintering time. In this case, average large grain sizes at 12 hours is lower than at 8 hours sintering holding time. The grain range of tin doped CCTO at 12 hours sintering holding time is wider than 8 hours sintering hold time (see Table 5-9 and Table 5-13), for example, in Figure 5.32, the largest grain could be multiplied by a factor of 10. The wider range of grain at 12 hours sintering time will be affected to the average of large grain sized.

Figure 5.39. Average large grain size of tin doped CCTO at various sintering times.

The average small grain size of tin doped CCTO at various sintering hold time is shown in Figure 5.40. The small grain size depends on the amount of tin dopant and sintering hold
time, the grain size lies between 2 and 5 $\mu$m. The small grains at 12 hours sintering hold times, especially at 0.10 and 0.25 mol tin, seem lower than the small grain at 8 sintering hold times. The percentage of small grain is limited to give the perfect calculation, as shown in Figure 5.32 and Figure 5.35, the small grain seems less visible.

![Figure 5.40. Average small grain size of tin doped CCTO at various sintering times.](image)

**5.3. Phase Analysis**

This section describes the analysis of x-ray diffraction patterns and lattice parameters of CaCu$_3$Ti$_4$O$_{12}$ with different sintering hold time and amounts of dopant added. The elements present in the samples were identified using X-ray fluorescence and EDS analysis, and are also presented to support phase analysis.

**5.3.1. Phase of pure CCTO.**

The XRD pattern of CaCu$_3$Ti$_4$O$_{12}$ sintered at 1100°C for 4, 8 and 12 hours is shown in Figure 5.41. It has been found that a sample with 4 hours sintering hold contains CaTiO$_3$. All samples are mostly CaCu$_3$Ti$_4$O$_{12}$ (PDF# 04-010-5727) and the secondary phase is CaTiO$_3$ (PDF# 01-075-0437) with a maximum relative peak height of 0.51 compared to 100 for CCTO as mentioned in Table 4-1. Schmidt et. al. [70] found the CaTiO$_3$ phase in most of their samples, and they reported that there are no observed phases with defect structures or solid solutions between two phases. The secondary phase decreases with increasing sintering hold time.
Figure 5.41. X-ray diffraction spectra of CCTO with different sintering hold time.

Table 5-15. shows XRF data for calcium, copper, titanium and selected elements of pure CCTO with different sintering hold times. The XRF was used to investigate the composition of elements in whole sample. Table 5.15. shows the concentration of copper was higher than as expected (more than 3), so consequently the concentration of calcium and titanium were lower than as expected. The residual concentration of iron and zirconia could be derived from the impurities of starting powder (Table 3-1. section 3.1.) and the effect of using zirconia balls on milling process. The residual concentration was low and tends to lower with increasing sintering hold time. The concentrations of residual elements (Fe or Zr) were less than 0.01 mole (0.13%).

Table 5-15. X-ray fluorescence concentrations for selected elements of pure CCTO

<table>
<thead>
<tr>
<th>Element</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Fe</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCTO4</td>
<td>0.950 ± 0.023</td>
<td>3.140 ± 0.033</td>
<td>3.860 ± 0.041</td>
<td>0.010 ± 0.003</td>
<td>0.002 ± 0.000</td>
</tr>
<tr>
<td>CCTO8</td>
<td>0.960 ± 0.021</td>
<td>3.090 ± 0.036</td>
<td>3.900 ± 0.040</td>
<td>0.010 ± 0.004</td>
<td>0.007 ± 0.002</td>
</tr>
<tr>
<td>CCTO12</td>
<td>0.980 ± 0.024</td>
<td>3.140 ± 0.032</td>
<td>3.880 ± 0.042</td>
<td>0.000 ± 0.000</td>
<td>0.000 ± 0.000</td>
</tr>
</tbody>
</table>
Table 5-16. show EDS data for calcium, copper, titanium and oxygen of pure CCTO with various sintering hold times. The EDS was used to investigate the composition of elements in specific area in microstructure. Table 5.16. shows the ratio of concentration of calcium, copper and titanium less than as expected (Ca:Cu:Ti:O → 1:3:4:12). The data are also lower compared to data in Table 5.15., as EDS used a small area for scanning that only covered a single grain, while the XRF was scanned the whole of the sample surface.

<table>
<thead>
<tr>
<th></th>
<th>Grain</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCTO4</td>
<td>Large</td>
<td>0.945 ± 0.019</td>
<td>2.520 ± 0.102</td>
<td>3.686 ± 0.089</td>
<td>12.850 ± 0.136</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>1.204 ± 0.023</td>
<td>2.837 ± 0.061</td>
<td>3.925 ± 0.033</td>
<td>12.034 ± 0.052</td>
</tr>
<tr>
<td>CCTO8</td>
<td>Large</td>
<td>0.956 ± 0.024</td>
<td>2.952 ± 0.054</td>
<td>3.776 ± 0.102</td>
<td>12.316 ± 0.098</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>0.981 ± 0.068</td>
<td>2.921 ± 0.091</td>
<td>3.897 ± 0.121</td>
<td>12.201 ± 0.113</td>
</tr>
<tr>
<td>CCTO12</td>
<td>Large</td>
<td>0.992 ± 0.046</td>
<td>2.975 ± 0.063</td>
<td>3.969 ± 0.108</td>
<td>12.064 ± 0.127</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
</tbody>
</table>

5.3.2. Phase of CCTxNy

The CaCu$_3$Ti$_{4-x}$Nb$_x$O$_{12}$ (0.05 ≤ x ≤ 0.25) formulations were analysed with laboratory XRD in order to assess how the phase changed with niobium addition and sintering hold time. The major peaks of the X-ray diffraction spectra are identified to be that of CCTO (PDF# 01-072-5884). Figure 5.42. shows X-ray diffraction patterns of six different compositions of niobium doped CCTO at 4 hours sintering hold time. The X-ray diffraction patterns confirm the formation of CCTO compound with small peaks of CaTiO$_3$ or NbO. For niobium doped samples between 0.05 and 0.15 mol, small peaks due to CaTiO$_3$ phase were visible, then the CaTiO$_3$ phase disappeared for niobium dopant of 0.20 and 0.25 mol, as NbO phase emerged.
Figure 5.42. X-ray diffraction spectra of CCTO with different niobium dopant at 4 hours sintering.

The selected elements of niobium doped CCTO with 4 hours sintering are shown in Table 5-17 and Table 5-18. The XRF data show the concentration of niobium was as expected, but the concentration of titanium was lower than as expected. The titanium concentration was not decreasing with increasing niobium concentration, as the result, the relative concentration of copper increases and the relative concentration of calcium decreases. The maximum concentration of residual element (Fe or Zr) was up to 0.016 mole (0.2%), and decreased with increasing concentration of niobium.

<p>| Table 5-17. X-ray fluorescence concentrations for selected elements of CCTxN4. |
|---|---|---|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>mole ratio</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Nb</th>
<th>Fe</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05N4</td>
<td>0.95 ± 0.03</td>
<td>3.11 ± 0.04</td>
<td>3.86 ± 0.03</td>
<td>0.06 ± 0.00</td>
<td>0.01 ± 0.00</td>
<td>0.02 ± 0.01</td>
</tr>
<tr>
<td>CCT10N4</td>
<td>0.94 ± 0.03</td>
<td>3.10 ± 0.04</td>
<td>3.83 ± 0.04</td>
<td>0.10 ± 0.01</td>
<td>0.01 ± 0.00</td>
<td>0.02 ± 0.00</td>
</tr>
<tr>
<td>CCT15N4</td>
<td>0.93 ± 0.03</td>
<td>3.08 ± 0.03</td>
<td>3.82 ± 0.05</td>
<td>0.14 ± 0.01</td>
<td>0.01 ± 0.00</td>
<td>0.02 ± 0.00</td>
</tr>
<tr>
<td>CCT20N4</td>
<td>0.95 ± 0.00</td>
<td>2.96 ± 0.00</td>
<td>3.84 ± 0.00</td>
<td>0.23 ± 0.00</td>
<td>0.01 ± 0.00</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>CCT25N4</td>
<td>0.92 ± 0.00</td>
<td>2.93 ± 0.00</td>
<td>3.86 ± 0.00</td>
<td>0.26 ± 0.00</td>
<td>0.01 ± 0.00</td>
<td>0.01 ± 0.00</td>
</tr>
</tbody>
</table>

Table 5-18. shows the EDS data for calcium, copper, titanium and oxygen of niobium.
doped CCTO with 4 hours sintering hold times. The data are slightly different as compared to data in Table 5.17. The calcium, copper and titanium ratio were slightly lower as niobium dopant increases, as compensation the oxygen ratio was increased.

Table 5-18. Concentrations for selected elements of CCTxN4 by EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Grain</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Nb</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05N4</td>
<td>Large</td>
<td>na</td>
<td>2.91 ± 0.04</td>
<td>3.96 ± 0.02</td>
<td>0.05 ± 0.00</td>
<td>12.07 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>1.01 ± 0.04</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>CCT10N4</td>
<td>Large</td>
<td>na</td>
<td>2.94 ± 0.06</td>
<td>3.91 ± 0.09</td>
<td>0.10 ± 0.02</td>
<td>12.04 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>1.01 ± 0.03</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>CCT15N4</td>
<td>Large</td>
<td>1.00 ± 0.03</td>
<td>2.97 ± 0.10</td>
<td>3.86 ± 0.08</td>
<td>0.16 ± 0.02</td>
<td>12.01 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>0.99 ± 0.05</td>
<td>2.98 ± 0.03</td>
<td>3.79 ± 0.09</td>
<td>0.21 ± 0.02</td>
<td>12.02 ± 0.12</td>
</tr>
<tr>
<td>CCT20N4</td>
<td>Large</td>
<td>na</td>
<td>2.97 ± 0.05</td>
<td>3.76 ± 0.10</td>
<td>0.25 ± 0.02</td>
<td>12.03 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>0.98 ± 0.06</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
</tbody>
</table>

The CaTiO$_3$ as secondary phase still appears at niobium doped between 0.05 and 0.15 mol compositions with 8 hours sintering hold time, is shown in Figure 5.43. At maximum niobium dopant ($x = 0.25$ mol), NbO and Nb$_2$O$_5$ were detected due to the excess of niobium dopant. In this sample, the maximum the amount of niobium dopant without existence of an NbO$_x$ phase is 0.15 mol. This value is less than other reported [3, 63] where they did not detect the NbO$_x$ phase below 0.20 mol of niobium dopant.
Figure 5.43. X-ray diffraction spectra of CCTO with different niobium dopant at 8 hours sintering.

Table 5-19. shows the XRF data of calcium, copper, titanium, and selected elements of niobium doped CCTO with 8 hours sintering. The concentration of niobium and titanium were significant as expected, but the concentration of calcium and copper were lower than as expected. The maximum concentration of residual elements (Fe or Zr) was up to 0.009 mole (0.11%), and lower than value of the 4 hours sintering hold time. The longer sintering time gave a better synthesis of phase.

Table 5-19. X-ray fluorescence concentrations for selected elements of CCTxN8

<table>
<thead>
<tr>
<th>mole ratio</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Nb</th>
<th>Fe</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCuTi$<em>{4}$Nb$</em>{x}$O$_{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT05N8</td>
<td>0.96 ± 0.03</td>
<td>3.00 ± 0.03</td>
<td>3.97 ± 0.04</td>
<td>0.06 ± 0.01</td>
<td>0.01 ± 0.00</td>
<td>0.00 ± 0.00</td>
</tr>
<tr>
<td>CCT10N8</td>
<td>0.94 ± 0.03</td>
<td>2.99 ± 0.03</td>
<td>3.95 ± 0.03</td>
<td>0.01 ± 0.00</td>
<td>0.01 ± 0.00</td>
<td>0.00 ± 0.00</td>
</tr>
<tr>
<td>CCT15N8</td>
<td>0.95 ± 0.00</td>
<td>3.03 ± 0.00</td>
<td>3.86 ± 0.00</td>
<td>0.15 ± 0.00</td>
<td>0.01 ± 0.00</td>
<td>0.00 ± 0.00</td>
</tr>
<tr>
<td>CCT20N8</td>
<td>0.92 ± 0.00</td>
<td>3.00 ± 0.00</td>
<td>3.86 ± 0.00</td>
<td>0.19 ± 0.00</td>
<td>0.01 ± 0.00</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>CCT25N8</td>
<td>0.91 ± 0.00</td>
<td>2.99 ± 0.00</td>
<td>3.80 ± 0.00</td>
<td>0.27 ± 0.00</td>
<td>0.01 ± 0.00</td>
<td>0.01 ± 0.00</td>
</tr>
</tbody>
</table>

Table 5-20. shows the EDS data for calcium, copper, titanium and oxygen of niobium doped CCTO with 8 hours sintering hold times. The data are slightly different as compared to...
data in Table 5.19. The calcium, copper and titanium ratio were slightly lower as niobium dopant increases, as compensation the oxygen ratio was tend to decrease. The ratio of calcium, copper, titanium, and oxygen were better than niobium doped CCTO with 4 hours sintering hold time.

Table 5-20. Concentrations for selected elements of CCTxN8 by EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Grain</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Nb</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05NB</td>
<td>Large</td>
<td>na</td>
<td>1.00 ± 0.02</td>
<td>3.00 ± 0.02</td>
<td>3.92 ± 0.03</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>na</td>
<td>1.00 ± 0.02</td>
<td>3.00 ± 0.02</td>
<td>3.92 ± 0.03</td>
<td>0.05 ± 0.00</td>
</tr>
<tr>
<td>CCT10NB</td>
<td>Large</td>
<td>na</td>
<td>1.00 ± 0.02</td>
<td>na</td>
<td>3.00 ± 0.02</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>na</td>
<td>1.00 ± 0.02</td>
<td>na</td>
<td>3.00 ± 0.02</td>
<td>na</td>
</tr>
<tr>
<td>CCT15NB</td>
<td>Large</td>
<td>na</td>
<td>1.00 ± 0.03</td>
<td>2.99 ± 0.02</td>
<td>3.83 ± 0.09</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>na</td>
<td>1.00 ± 0.03</td>
<td>2.99 ± 0.02</td>
<td>3.83 ± 0.09</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>CCT20NB</td>
<td>Large</td>
<td>na</td>
<td>1.00 ± 0.02</td>
<td>na</td>
<td>3.00 ± 0.01</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>na</td>
<td>1.00 ± 0.02</td>
<td>na</td>
<td>3.00 ± 0.01</td>
<td>na</td>
</tr>
<tr>
<td>CCT25NB</td>
<td>Large</td>
<td>na</td>
<td>1.00 ± 0.01</td>
<td>3.00 ± 0.01</td>
<td>3.72 ± 0.05</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>na</td>
<td>1.00 ± 0.01</td>
<td>3.00 ± 0.01</td>
<td>3.72 ± 0.05</td>
<td>0.26 ± 0.02</td>
</tr>
</tbody>
</table>

Figure 5.44. shows the X-ray diffraction spectra of CCTO with different niobium dopant at 12 hours sintering. The CaTiO₃ as secondary phase also appears at niobium doped CCTO between 0.05 and 0.15 mol compositions. TiO₂ phase appears at CCT05N12, but there is not detected in the other compositions. The presence of TiO₂ phase in the samples could be indicated an incomplete calcination process or poor mixing. NbO phase appears at CTT20N12 and CCT25N12 as due to the excess of niobium dopant.

The selected elements of CCTxN12 are shown in Table 5-21., and Table 5-22. Table 5-21. shows XRF data concentration of calcium was lower than expected, and the concentration of copper varied between 2.930 and 3.136 mole. The concentration of titanium was between 6 and 18% lower than expected. Consequently, decreases in titanium ratio will increase the copper ratio. The maximum concentration of residual element (Fe or Zr) was up to 0.016 mole (0.2%), and similar with 4 hours sintering hold time results.
Figure 5.44. X-ray diffraction spectra of CCTO with different niobium dopant at 12 hours sintering.

Table 5-21. X-ray fluorescence concentrations for selected elements of CCTxN12.

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Nb</th>
<th>Fe</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05N12</td>
<td>0.96±0.00</td>
<td>2.98±0.00</td>
<td>3.95±0.00</td>
<td>0.06±0.00</td>
<td>0.02±0.00</td>
<td>0.00±0.00</td>
</tr>
<tr>
<td>CCT10N12</td>
<td>0.95±0.00</td>
<td>3.09±0.00</td>
<td>3.83±0.00</td>
<td>0.10±0.00</td>
<td>0.01±0.00</td>
<td>0.02±0.00</td>
</tr>
<tr>
<td>CCT15N12</td>
<td>0.96±0.00</td>
<td>3.14±0.00</td>
<td>3.72±0.00</td>
<td>0.15±0.00</td>
<td>0.01±0.00</td>
<td>0.02±0.00</td>
</tr>
<tr>
<td>CCT20N12</td>
<td>0.97±0.00</td>
<td>2.94±0.00</td>
<td>3.85±0.00</td>
<td>0.21±0.00</td>
<td>0.01±0.00</td>
<td>0.01±0.00</td>
</tr>
<tr>
<td>CCT25N12</td>
<td>0.88±0.00</td>
<td>2.93±0.00</td>
<td>3.88±0.00</td>
<td>0.28±0.00</td>
<td>0.01±0.00</td>
<td>0.01±0.00</td>
</tr>
</tbody>
</table>

Table 5-22. shows the EDS data for calcium, copper, titanium and oxygen of niobium doped CCTO with 12 hours sintering hold times. The ratio of element are better as compared to data in Table 5.21. The copper and titanium ratio were not significantly changed as niobium dopant increases. The ratio of calcium, copper, titanium, and oxygen were better than niobium doped CCTO with 8 hours sintering hold time. In this case, longest sintering time the compositions synthesized well developed.
Table 5-22. Concentrations for selected elements of CCTxN12 by EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Grain</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Nb</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05N12</td>
<td>Large</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>12.04 ± 0.04</td>
</tr>
<tr>
<td>Large</td>
<td>Small</td>
<td>0.98 ± 0.02</td>
<td>2.97 ± 0.04</td>
<td>3.96 ± 0.02</td>
<td>0.05 ± 0.00</td>
<td></td>
</tr>
<tr>
<td>CCT10N12</td>
<td>Large</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>12.01 ± 0.03</td>
</tr>
<tr>
<td>Large</td>
<td>Small</td>
<td>0.99 ± 0.01</td>
<td>2.98 ± 0.04</td>
<td>3.91 ± 0.02</td>
<td>0.10 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>CCT15N12</td>
<td>Large</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>12.02 ± 0.02</td>
</tr>
<tr>
<td>Large</td>
<td>Small</td>
<td>0.99 ± 0.01</td>
<td>2.99 ± 0.03</td>
<td>3.86 ± 0.02</td>
<td>0.15 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>CCT20N12</td>
<td>Large</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>12.02 ± 0.02</td>
</tr>
<tr>
<td>Large</td>
<td>Small</td>
<td>0.99 ± 0.01</td>
<td>2.99 ± 0.02</td>
<td>3.80 ± 0.01</td>
<td>0.20 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>CCT25N12</td>
<td>Large</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>12.01 ± 0.02</td>
</tr>
<tr>
<td>Large</td>
<td>Small</td>
<td>0.99 ± 0.02</td>
<td>2.99 ± 0.02</td>
<td>3.73 ± 0.01</td>
<td>0.27 ± 0.03</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.45. to Figure 5.49. show the effect of sintering hold time on the phase of various niobium doped CCTO. Figure 5.45. shows CaTiO$_3$ phase appears at all sintering hold time of CCT05N and TiO$_2$ phase only appears in CCT05N12. The TiO$_2$ phase could arise from an incomplete calcination process, even though, increasing sintering hold time did not reduce the secondary phase of CaTiO$_3$.

![X-ray diffraction spectra of CCT05N with different sintering time](image)

Figure 5.45. X-ray diffraction spectra of CCT05N with different sintering time.

Figure 5.46. shows CaTiO$_3$ phase appears in CCT10N with 8 and 12 hours sintering time and TiO$_2$ phase only appears in CCT10N12. The CaTiO$_3$ phase disappeared with
increasing niobium dopant, but with increasing sintering hold time the secondary phase of CaTiO$_3$ appears again.

Figure 5.47. show spectrum of CCT15N with various sintering hold times. Identically with CCT05N, the CaTiO$_3$ phase appears at all sintering hold time of CCT15N and TiO$_2$ phase only appears in CCT15N12. Again, increasing sintering hold time did not reduce the secondary phase of CaTiO$_3$ in CCT15N spectrum.

Figure 5.46. X-ray diffraction spectra of CCT10N with different sintering time.

Figure 5.47. X-ray diffraction spectra of CCT15N with different sintering time.
Figure 5.48. X-ray diffraction spectra of CCT20N with different sintering time.

Figure 5.48 and 5.49 show spectrum of CCT20N and CCT25N at various sintering hold times, respectively. The CaTiO$_3$ and TiO$_2$ phases disappeared when niobium dopant increased up to 0.25 mol, but the other phases then present were NbO and Nb$_2$O$_5$. Figure 5.48 and 5.49 show the existence of NbO and Nb$_2$O$_5$ phases due to excess of niobium dopant, and again, the increasing sintering hold time did not eliminate the secondary phase in niobium doped between 0.20 and 0.25 mol.
Table 5-23. shows XRF of selected elements of CCT05Ny, CCT10Ny, CCT15Ny, CCT20Ny and CCT25Ny (y = 4, 8 and 12). On the other hand, Table 5-24. shows EDS of selected elements of CCT05Ny, CCT10Ny, CCT15Ny, CCT20Ny and CCT25Ny (y = 4, 8 and 12). In general, the XRF data is slightly different with the EDS data. The XRF data shows the concentration of niobium was seemed as expected, but the concentration of titanium tends to be lower than expected in CCT05Ny, CCT10Ny and CCT15Ny. Consequently, the concentration of calcium was lower than expected and the concentration of copper was also consistently higher than expected. The EDS data shows the concentration of niobium was as expected, and the calcium, copper and titanium ratio still within the range of experimental error in CCT05Ny, CCT10Ny and CCT15Ny.
In CCT20Ny, the XRF data (Table 5.23.) show the concentration of niobium was as expected, but the concentration of titanium was higher than expected. The concentration of calcium and copper were lower than expected. The longer sintering hold time did not significantly affect the ratio of elements. On the other hand, the EDS data (Table 5.24.) show the all concentration of element were at the expected ratios, except at 8 hour sintering hold time the titanium concentration was slightly lower than expected.

Table 5-23. (XRF data) show the concentration of niobium of 0.25 mol niobium doped CCTO at different sintering hold time was higher than expected with longer sintering hold time. The concentration of titanium fluctuated between 3.802 and 3.883 mole, tends to higher than as expected. The concentration of calcium and copper were lower than as expected, less than 0.92 and 2.99, respectively.

Again, the residual concentration of iron and zirconia could be derived from the impurities of starting powder (Table 3-4. section 3.1.5.) and the effect of using zirconia balls on milling process. The longer sintering hold time did not significantly affect the other concentration of elements.
Table 5-24. Concentrations for selected elements of niobium doped CCTO with different sintering hold time by EDS.

<table>
<thead>
<tr>
<th>CCT05N4</th>
<th>Large</th>
<th>Small</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Nb</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.01 ± 0.04</td>
<td>2.91 ± 0.04</td>
<td>3.96 ± 0.02</td>
<td>0.05 ± 0.00</td>
<td>12.07 ± 0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT05N8</td>
<td>Large</td>
<td>Small</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
</tr>
<tr>
<td></td>
<td>1.00 ± 0.02</td>
<td>3.00 ± 0.02</td>
<td>3.92 ± 0.03</td>
<td>0.05 ± 0.00</td>
<td>12.03 ± 0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT05N12</td>
<td>Large</td>
<td>Small</td>
<td>0.98 ± 0.02</td>
<td>2.97 ± 0.04</td>
<td>3.96 ± 0.02</td>
<td>0.05 ± 0.00</td>
<td>12.04 ± 0.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CCT10N4</th>
<th>Large</th>
<th>Small</th>
<th>Na</th>
<th>Na</th>
<th>Na</th>
<th>Na</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.01 ± 0.03</td>
<td>2.94 ± 0.06</td>
<td>3.91 ± 0.09</td>
<td>0.10 ± 0.02</td>
<td>12.04 ± 0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT10N8</td>
<td>Large</td>
<td>Small</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
</tr>
<tr>
<td></td>
<td>1.00 ± 0.02</td>
<td>3.00 ± 0.02</td>
<td>3.88 ± 0.06</td>
<td>0.11 ± 0.01</td>
<td>12.01 ± 0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT10N12</td>
<td>Large</td>
<td>Small</td>
<td>0.99 ± 0.01</td>
<td>2.98 ± 0.04</td>
<td>3.91 ± 0.02</td>
<td>0.10 ± 0.01</td>
<td>12.02 ± 0.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CCT15N4</th>
<th>Large</th>
<th>Small</th>
<th>Na</th>
<th>Na</th>
<th>Na</th>
<th>Na</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.00 ± 0.03</td>
<td>2.97 ± 0.10</td>
<td>3.86 ± 0.08</td>
<td>0.16 ± 0.02</td>
<td>12.01 ± 0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT15N8</td>
<td>Large</td>
<td>Small</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
</tr>
<tr>
<td></td>
<td>1.01 ± 0.03</td>
<td>2.99 ± 0.02</td>
<td>3.83 ± 0.09</td>
<td>0.15 ± 0.01</td>
<td>12.01 ± 0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT15N12</td>
<td>Large</td>
<td>Small</td>
<td>0.99 ± 0.01</td>
<td>2.99 ± 0.03</td>
<td>3.86 ± 0.02</td>
<td>0.15 ± 0.01</td>
<td>12.01 ± 0.03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CCT20N4</th>
<th>Large</th>
<th>Small</th>
<th>Na</th>
<th>Na</th>
<th>Na</th>
<th>Na</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.99 ± 0.05</td>
<td>2.98 ± 0.03</td>
<td>3.79 ± 0.09</td>
<td>0.21 ± 0.02</td>
<td>12.02 ± 0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT20N8</td>
<td>Large</td>
<td>Small</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
</tr>
<tr>
<td></td>
<td>1.00 ± 0.02</td>
<td>3.00 ± 0.01</td>
<td>3.76 ± 0.10</td>
<td>0.22 ± 0.02</td>
<td>12.03 ± 0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT20N12</td>
<td>Large</td>
<td>Small</td>
<td>0.99 ± 0.01</td>
<td>2.99 ± 0.02</td>
<td>3.80 ± 0.01</td>
<td>0.20 ± 0.01</td>
<td>12.02 ± 0.02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CCT25N4</th>
<th>Large</th>
<th>Small</th>
<th>Na</th>
<th>Na</th>
<th>Na</th>
<th>Na</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.98 ± 0.06</td>
<td>2.97 ± 0.05</td>
<td>3.76 ± 0.10</td>
<td>0.25 ± 0.02</td>
<td>12.03 ± 0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT25N8</td>
<td>Large</td>
<td>Small</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
<td>Na</td>
</tr>
<tr>
<td></td>
<td>1.00 ± 0.01</td>
<td>3.00 ± 0.01</td>
<td>3.72 ± 0.05</td>
<td>0.26 ± 0.02</td>
<td>12.02 ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT25N12</td>
<td>Large</td>
<td>Small</td>
<td>0.99 ± 0.02</td>
<td>2.99 ± 0.02</td>
<td>3.73 ± 0.01</td>
<td>0.27 ± 0.03</td>
<td>12.01 ± 0.02</td>
</tr>
</tbody>
</table>

Table 5-25. shows the maximum intensity (relative secondary peak to highest of CCTO peak) of secondary phase on CaCu$_3$Ti$_4$O$_{12}$ with different niobium dopant and sintering hold time, and the maximum the amount of secondary phase is 4%. This table also shows that the secondary phase increases while the sintering hold time increases.
Table 5-25. Maximum intensity of secondary phase compared to CCTO with different niobium dopant and sintering hold time by XRD.

<table>
<thead>
<tr>
<th>Sintering</th>
<th>4 hours</th>
<th>8 hours</th>
<th>12 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaTiO₃</td>
<td>NbO</td>
<td>CaTiO₃</td>
</tr>
<tr>
<td>Residual</td>
<td>0.24%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CCTO</td>
<td>0.90%</td>
<td>-</td>
<td>0.90%</td>
</tr>
<tr>
<td>CCT05N</td>
<td>0.30%</td>
<td>0.20%</td>
<td>0.60%</td>
</tr>
<tr>
<td>CCT10N</td>
<td>0.90%</td>
<td>1.00%</td>
<td>0.70%</td>
</tr>
<tr>
<td>CCT20N</td>
<td>-</td>
<td>1.70%</td>
<td>-</td>
</tr>
<tr>
<td>CCT25N</td>
<td>-</td>
<td>3.01%</td>
<td>-</td>
</tr>
</tbody>
</table>

5.3.3. Phase of CCTₓSᵧ

Figure 5.50., Figure 5.51., and Figure 5.52. show the X-ray diffraction patterns for the Ca₃Ti₄₋ₓSnₓO₁₂ (0.05 < x < 0.25) with 4, 8 and 12 hours sintering hold time, respectively. In the present ceramics, all samples are mostly Ca₃Ti₄O₁₂ (PDF# 04-010-5727) and the residual phase is SnO (PDF# 01-070-4175) with a maximum relative peak height of 3.09 compared to 100 for CCTO peak as mentioned in Table 4-6. The secondary phase SnO was changed to SnO₂ with increasing sintering hold time as shown in Figure 5.52.

Figure 5.50. X-ray diffraction spectra of CCTO with different tin dopant at 4 hours sintering.
Table 5-26. shows the selected elements of tin doped CCTO with 4 hours sintering. The tin concentration was as expected; on the other hand the titanium concentration tends to be lower than expected. The copper concentration was significantly higher than as expected, but the calcium concentration was lower up to 6.5% of expected. The maximum concentration of residual element (Fe or Zr) was up to 0.022 mole (0.274%), and the value of the concentration of residual elements varied with increasing the tin concentration.

Table 5-26. X-ray fluorescence concentrations for selected elements of CCTxS4.

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Sn</th>
<th>Fe</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05S4</td>
<td>0.97 ± 0.01</td>
<td>3.06 ± 0.02</td>
<td>3.91 ± 0.02</td>
<td>0.05 ± 0.01</td>
<td>0.01 ± 0.00</td>
<td>0.00 ± 0.00</td>
</tr>
<tr>
<td>CCT10S4</td>
<td>0.99 ± 0.01</td>
<td>3.09 ± 0.03</td>
<td>3.78 ± 0.04</td>
<td>0.11 ± 0.01</td>
<td>0.01 ± 0.00</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>CCT15S4</td>
<td>0.94 ± 0.02</td>
<td>3.04 ± 0.02</td>
<td>3.84 ± 0.03</td>
<td>0.15 ± 0.03</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>CCT20S4</td>
<td>0.90 ± 0.00</td>
<td>3.10 ± 0.00</td>
<td>3.75 ± 0.00</td>
<td>0.19 ± 0.00</td>
<td>0.01 ± 0.00</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>CCT25S4</td>
<td>0.96 ± 0.00</td>
<td>3.00 ± 0.00</td>
<td>3.77 ± 0.00</td>
<td>0.22 ± 0.00</td>
<td>0.02 ± 0.00</td>
<td>0.02 ± 0.00</td>
</tr>
</tbody>
</table>

Table 5-27. shows the EDS data for calcium, copper, titanium and oxygen of tin doped CCTO with 4 hours sintering hold times. The data are slightly different as compared to data in Table 5.26. The calcium, and copper ratio were slightly lower as tin dopant increases, on the other hand the oxygen ratio remained stable, and the ratio was still acceptable within experiment error. Table 5-27, shows the concentration of element on large and small grains size, there is no significant difference between them.

Table 5-27. Concentrations for selected elements of CCTxS4 by EDS.

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Sn</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05S4</td>
<td>1.00 ± 0.01</td>
<td>2.99 ± 0.03</td>
<td>3.95 ± 0.01</td>
<td>0.05 ± 0.00</td>
<td>12.01 ± 0.06</td>
</tr>
<tr>
<td>Small</td>
<td>1.00 ± 0.02</td>
<td>2.99 ± 0.01</td>
<td>3.95 ± 0.02</td>
<td>0.05 ± 0.00</td>
<td>12.02 ± 0.07</td>
</tr>
<tr>
<td>CCT10S4</td>
<td>1.00 ± 0.01</td>
<td>2.99 ± 0.02</td>
<td>3.90 ± 0.02</td>
<td>0.11 ± 0.01</td>
<td>12.00 ± 0.03</td>
</tr>
<tr>
<td>Small</td>
<td>1.00 ± 0.01</td>
<td>3.00 ± 0.02</td>
<td>3.90 ± 0.01</td>
<td>0.10 ± 0.01</td>
<td>12.01 ± 0.02</td>
</tr>
<tr>
<td>CCT15S4</td>
<td>1.00 ± 0.01</td>
<td>2.99 ± 0.01</td>
<td>3.84 ± 0.02</td>
<td>0.16 ± 0.01</td>
<td>12.01 ± 0.03</td>
</tr>
<tr>
<td>Small</td>
<td>1.00 ± 0.01</td>
<td>2.99 ± 0.03</td>
<td>3.84 ± 0.02</td>
<td>0.16 ± 0.01</td>
<td>12.02 ± 0.04</td>
</tr>
<tr>
<td>CCT20S4</td>
<td>1.00 ± 0.01</td>
<td>3.00 ± 0.03</td>
<td>3.80 ± 0.01</td>
<td>0.21 ± 0.01</td>
<td>12.00 ± 0.03</td>
</tr>
<tr>
<td>Small</td>
<td>0.99 ± 0.02</td>
<td>3.00 ± 0.01</td>
<td>3.80 ± 0.01</td>
<td>0.20 ± 0.01</td>
<td>12.02 ± 0.03</td>
</tr>
<tr>
<td>CCT25S4</td>
<td>1.00 ± 0.01</td>
<td>2.99 ± 0.02</td>
<td>3.75 ± 0.02</td>
<td>0.26 ± 0.00</td>
<td>12.00 ± 0.02</td>
</tr>
<tr>
<td>Small</td>
<td>0.99 ± 0.01</td>
<td>3.00 ± 0.02</td>
<td>3.75 ± 0.02</td>
<td>0.25 ± 0.01</td>
<td>12.01 ± 0.03</td>
</tr>
</tbody>
</table>
Figure 5.51. shows 8 hours sintering hold time of various tin doped CCTO. The SnO phase was detected in all tin doped CCTO, from CCT05S to CCT25S. The concentration of tin was slightly higher than expected, as shown in Table 5-28 and 5-29.

Figure 5.51. X-ray diffraction spectra of CCTO with different tin dopant at 8 hours sintering.

The selected elements of tin doped CCTO with 8 hours sintering by XRF are shown in Table 5-28. The tin concentration was expected, except at CCT20S8, and the titanium concentration also tends to be lower than expected. The calcium concentration was lower up to 8.8% of expected, and the copper concentration was higher up to 2.9% of expected. The maximum concentration of residual elements (Fe or Zr) was up to 0.021 mole (2.6%) at maximum tin dopant.

Table 5-28. X-ray fluorescence concentrations for selected elements of CCTxS8.

<table>
<thead>
<tr>
<th>CaCu$<em>x$Ti$</em>{4-x}$Sn$<em>x$O$</em>{12}$</th>
<th>mole ratio</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Sn</th>
<th>Fe</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05S8</td>
<td></td>
<td>0.97 ± 0.01</td>
<td>3.04 ± 0.03</td>
<td>3.92 ± 0.03</td>
<td>0.06 ± 0.01</td>
<td>0.01 ± 0.00</td>
<td>0.00 ± 0.00</td>
</tr>
<tr>
<td>CCT10S8</td>
<td></td>
<td>1.00 ± 0.01</td>
<td>3.09 ± 0.01</td>
<td>3.80 ± 0.02</td>
<td>0.09 ± 0.03</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>CCT15S8</td>
<td></td>
<td>0.93 ± 0.00</td>
<td>3.03 ± 0.00</td>
<td>3.85 ± 0.00</td>
<td>0.16 ± 0.00</td>
<td>0.01 ± 0.00</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>CCT20S8</td>
<td></td>
<td>0.94 ± 0.00</td>
<td>3.08 ± 0.00</td>
<td>3.75 ± 0.00</td>
<td>0.20 ± 0.00</td>
<td>0.02 ± 0.00</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>CCT25S8</td>
<td></td>
<td>0.91 ± 0.00</td>
<td>3.01 ± 0.00</td>
<td>3.82 ± 0.00</td>
<td>0.22 ± 0.00</td>
<td>0.01 ± 0.00</td>
<td>0.02 ± 0.00</td>
</tr>
</tbody>
</table>
Table 5-29. shows the EDS data for calcium, copper, titanium and oxygen of tin doped CCTO with 8 hours sintering hold times. The data are slightly different as compared to data in Table 5-28. The calcium, copper, and titanium ratio were slightly lower as tin dopant increases, and the oxygen ratio was varied depends on the concentration of tin dopant, but the ratio was still acceptable within experiment error. Table 5-29. shows the concentration of element on large and small grains size of CCTxS8 and there is no significant difference between them.

Table 5-29. Concentrations for selected elements of CCTxS8 by EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Grain</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Sn</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05S8</td>
<td>Large</td>
<td>1.00 ± 0.02</td>
<td>3.00 ± 0.02</td>
<td>3.93 ± 0.02</td>
<td>0.06 ± 0.00</td>
<td>12.01 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>1.00 ± 0.01</td>
<td>3.00 ± 0.02</td>
<td>3.93 ± 0.03</td>
<td>0.06 ± 0.00</td>
<td>12.02 ± 0.07</td>
</tr>
<tr>
<td>CCT10S8</td>
<td>Large</td>
<td>1.00 ± 0.01</td>
<td>2.99 ± 0.02</td>
<td>3.89 ± 0.04</td>
<td>0.12 ± 0.00</td>
<td>12.00 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>0.99 ± 0.01</td>
<td>3.00 ± 0.02</td>
<td>3.89 ± 0.04</td>
<td>0.12 ± 0.00</td>
<td>12.00 ± 0.05</td>
</tr>
<tr>
<td>CCT15S8</td>
<td>Large</td>
<td>0.99 ± 0.02</td>
<td>2.99 ± 0.02</td>
<td>3.84 ± 0.06</td>
<td>0.16 ± 0.01</td>
<td>12.02 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>0.99 ± 0.01</td>
<td>2.99 ± 0.02</td>
<td>3.84 ± 0.06</td>
<td>0.16 ± 0.01</td>
<td>12.02 ± 0.07</td>
</tr>
<tr>
<td>CCT20S8</td>
<td>Large</td>
<td>0.99 ± 0.01</td>
<td>3.00 ± 0.02</td>
<td>3.77 ± 0.06</td>
<td>0.22 ± 0.01</td>
<td>12.02 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>1.00 ± 0.01</td>
<td>3.00 ± 0.02</td>
<td>3.77 ± 0.07</td>
<td>0.22 ± 0.01</td>
<td>12.02 ± 0.08</td>
</tr>
<tr>
<td>CCT25S8</td>
<td>Large</td>
<td>1.00 ± 0.02</td>
<td>2.99 ± 0.02</td>
<td>3.73 ± 0.07</td>
<td>0.27 ± 0.01</td>
<td>12.01 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>1.00 ± 0.02</td>
<td>3.00 ± 0.01</td>
<td>3.73 ± 0.08</td>
<td>0.26 ± 0.01</td>
<td>12.02 ± 0.09</td>
</tr>
</tbody>
</table>

The presence of SnO phase is common on tin doped CCTO, even with short sintering hold time. Consider with other reported, Ni et. al. [23] found the SnO₂ phase after x = 0.20 mol, which using the same temperature as 1100°C but only for 3 hours sintering hold time. In this study, the presence of SnO phase appeared in all tin doped CCTO and became SnO₂ phase with the longest sintering hold time (12 hours). Beside the SnO₂ phase, CuO phase also emerged at 12 hours sintering hold time, due to oxidation reactions of the sample.
Figure 5.52. X-ray diffraction spectra of CCTO with different tin dopant at 12 hours sintering.

Table 5-30. shows XRF data of selected elements of CCTxS12. The tin concentration tends to be higher than expected, consequently the titanium concentration was lower than what it is supposed. The calcium concentration was lower than expected, and the copper concentration tends to be higher than expected. The maximum concentration of residual element (Fe or Zr) was up to 0.020 mole (0.25%), and there was identically with 4 and 8 hours sintering hold time results.

Table 5-30. X-ray fluorescence concentrations for selected elements of CCTxS12.

| CaCu$_{3}$Ti$_{4-x}$Sn$_{x}$O$_{12}$ | mole ratio |
|---|---|---|---|---|---|
| Ca | Cu | Ti | Sn | Fe | Zr |
| CCT05S12 | 0.98 ± 0.00 | 2.99 ± 0.00 | 3.94 ± 0.00 | 0.07 ± 0.00 | 0.01 ± 0.00 | 0.00 ± 0.00 |
| CCT10S12 | 1.00 ± 0.00 | 3.05 ± 0.00 | 3.83 ± 0.00 | 0.10 ± 0.00 | 0.01 ± 0.00 | 0.01 ± 0.00 |
| CCT15S12 | 0.93 ± 0.00 | 3.06 ± 0.00 | 3.80 ± 0.00 | 0.17 ± 0.00 | 0.01 ± 0.00 | 0.01 ± 0.00 |
| CCT20S12 | 0.95 ± 0.00 | 3.11 ± 0.00 | 3.70 ± 0.00 | 0.21 ± 0.00 | 0.01 ± 0.00 | 0.01 ± 0.00 |
| CCT25S12 | 0.92 ± 0.00 | 3.04 ± 0.00 | 3.78 ± 0.00 | 0.24 ± 0.00 | 0.01 ± 0.00 | 0.02 ± 0.00 |

Table 5-31. shows the EDS data for calcium, copper, titanium and oxygen of tin doped CCTO with 12 hours sintering hold times. Again, the data are slightly different as compared to data in Table 5.31 due to the different scanned area of the sample. The calcium, and titanium
ratio were slightly lower as tin dopant increases, but the copper ratio was little bit higher, and the oxygen ratio remained similar for all of tin dopant. The ratio was still acceptable within experiment error. The concentration of element on large and small grains size of CCTxS12 is shown in Table 5-31., and again, there is no significant difference between them.

Table 5-31. Concentrations for selected elements of CCTxS12 by EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Grain</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Sn</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCu₃TixSnO₁₂</td>
<td>mole ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT05S12</td>
<td>Large</td>
<td>0.99 ± 0.02</td>
<td>3.00 ± 0.01</td>
<td>3.94 ± 0.05</td>
<td>0.06 ± 0.00</td>
<td>12.01 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>0.99 ± 0.02</td>
<td>2.99 ± 0.01</td>
<td>3.94 ± 0.04</td>
<td>0.05 ± 0.00</td>
<td>12.02 ± 0.05</td>
</tr>
<tr>
<td>CCT10S12</td>
<td>Large</td>
<td>0.99 ± 0.03</td>
<td>3.00 ± 0.01</td>
<td>3.89 ± 0.05</td>
<td>0.12 ± 0.01</td>
<td>12.01 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>0.99 ± 0.03</td>
<td>3.00 ± 0.01</td>
<td>3.89 ± 0.07</td>
<td>0.12 ± 0.01</td>
<td>12.01 ± 0.05</td>
</tr>
<tr>
<td>CCT15S12</td>
<td>Large</td>
<td>0.98 ± 0.03</td>
<td>3.01 ± 0.02</td>
<td>3.84 ± 0.05</td>
<td>0.16 ± 0.01</td>
<td>12.01 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>0.98 ± 0.03</td>
<td>3.01 ± 0.02</td>
<td>3.84 ± 0.06</td>
<td>0.15 ± 0.01</td>
<td>12.01 ± 0.07</td>
</tr>
<tr>
<td>CCT20S12</td>
<td>Large</td>
<td>0.98 ± 0.03</td>
<td>3.01 ± 0.02</td>
<td>3.78 ± 0.06</td>
<td>0.23 ± 0.01</td>
<td>12.01 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>0.98 ± 0.03</td>
<td>3.01 ± 0.02</td>
<td>3.77 ± 0.07</td>
<td>0.23 ± 0.01</td>
<td>12.01 ± 0.06</td>
</tr>
<tr>
<td>CCT25S12</td>
<td>Large</td>
<td>0.98 ± 0.02</td>
<td>3.01 ± 0.02</td>
<td>3.74 ± 0.07</td>
<td>0.27 ± 0.01</td>
<td>12.01 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>0.98 ± 0.02</td>
<td>3.01 ± 0.02</td>
<td>3.74 ± 0.07</td>
<td>0.27 ± 0.01</td>
<td>12.01 ± 0.07</td>
</tr>
</tbody>
</table>

Figure 5.53. shows that the SnO₂ phase at 12 hours sintering hold time (CCT05S12) replaced the SnO phase at 4 and 8 hours sintering hold time (CCT05S4 and CCT05S8). The presence of SnO₂ phase is due to oxidation reaction with longer sintering hold time.

Figure 5.53. X-ray diffraction spectra of CCT05S with different sintering time.
Figure 5.54. X-ray diffraction spectra of CCT10S with different sintering time.

Figure 5.54. also shows the SnO$_2$ phase at 12 hours sintering hold time (CCT10S12) replaced the SnO phase at 4 hours sintering hold time (CCT10S4). Interestingly, in CCT10S8, there was no indication of secondary phase, but increasing sintering hold time presented SnO$_2$ and CuO phases. The presence of SnO$_2$ and CuO phases was indicated due to oxidation reaction with longer sintering hold time.

Figure 5.55 to Figure 5.57. show the spectrum of CCT15S, CCT20S and CCT25S with various sintering hold time, respectively. The phase was not significantly changed with increasing tin dopant and the secondary phases were identical with lower tin dopant.
Figure 5.55. X-ray diffraction spectra of CCT15S with different sintering time.

Figure 5.56. X-ray diffraction spectra of CCT20S with different sintering time.
Table 5.32. shows the XRF data of selected elements of CCT05S, CCT10S, CCT15S, CCT20S, and CCT25S ($y = 4, 8$ and $12$). The XRF data shows the tin concentration is increased at CCT05S but decreased at CCT10S with increased sintering hold time. The titanium concentration tends to be lower than expected. The calcium concentration was lower and the copper concentration higher than expected.

On the other hand, the XRF data (Table 5.32.) shows the concentration of tin in CCT15S and CCT20S were as expected but the tin concentration was lower than expected in CCT25S. The concentration of titanium tends to be lower than expected. Consequently, the copper concentration consistently higher than expected. The concentration of calcium lower up to 7.7% of expected.

As mentioned in Table 3-4. (section 3.1.5.), the residual concentration of iron and zirconia could originate from the impurities of starting powder and the effect of using zirconia balls on milling process. The longer sintering hold time did not significantly affect the ratio of elements except the ratio of tin.
Table 5-32. X-ray fluorescence concentrations for selected elements of CCTxSy with different sintering time.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Sn</th>
<th>Fe</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05S4</td>
<td>0.97 ± 0.01</td>
<td>3.06 ± 0.02</td>
<td>3.91 ± 0.04</td>
<td>0.05 ± 0.01</td>
<td>0.01 ± 0.00</td>
<td>0.00 ± 0.00</td>
</tr>
<tr>
<td>CCT05S8</td>
<td>0.97 ± 0.01</td>
<td>3.04 ± 0.01</td>
<td>3.92 ± 0.04</td>
<td>0.06 ± 0.00</td>
<td>0.01 ± 0.00</td>
<td>0.00 ± 0.00</td>
</tr>
<tr>
<td>CCT05S12</td>
<td>0.98 ± 0.01</td>
<td>2.99 ± 0.01</td>
<td>3.94 ± 0.01</td>
<td>0.07 ± 0.01</td>
<td>0.01 ± 0.00</td>
<td>0.00 ± 0.00</td>
</tr>
</tbody>
</table>

Table 5-33. shows EDS of selected elements of CCT05Sy, CCT10Sy, CCT15Sy, CCT20Sy and CCT25Sy (y = 4, 8 and 12). In general, the XRF data (Table 5.32.) is slightly different with the EDS data (Table 5.33.) due to different area of scanning. The EDS data (Table 5.33.) shows the concentration of tin was tend to higher than as expected, but the calcium, copper and titanium ratio still on the range of experimental error in CCT05Sy, and CCT10Sy.

On the other hand, the EDS data (Table 5.33.) show the titanium concentration was slightly lower with increasing the concentration of tin dopant between CCT15Sy and CCT25Sy. The other concentrations of elements were in the proper ratio. In general, with lower of the concentration of tin dopant, the titanium is still dominantly on the B site, with increasing the concentration of tin dopant, the concentration of titanium become lower. The data indicated that the titanium was substituted by tin. Table 5-33. also shows the longer sintering hold time did not significantly change the concentration of elements.
Table 5-33. Concentrations for selected elements of CCTxSy with different sintering time by EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Grain</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Sn</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT05S4</td>
<td>Large</td>
<td>1.00 ± 0.01</td>
<td>2.99 ± 0.03</td>
<td>3.95 ± 0.01</td>
<td>0.05 ± 0.00</td>
<td>12.01 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>1.00 ± 0.02</td>
<td>2.99 ± 0.01</td>
<td>3.95 ± 0.02</td>
<td>0.05 ± 0.00</td>
<td>12.02 ± 0.07</td>
</tr>
<tr>
<td>CCT05S8</td>
<td>Large</td>
<td>1.00 ± 0.02</td>
<td>3.00 ± 0.02</td>
<td>3.93 ± 0.02</td>
<td>0.06 ± 0.00</td>
<td>12.01 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>1.00 ± 0.01</td>
<td>3.00 ± 0.02</td>
<td>3.93 ± 0.03</td>
<td>0.06 ± 0.00</td>
<td>12.02 ± 0.07</td>
</tr>
<tr>
<td>CCT05S12</td>
<td>Large</td>
<td>0.99 ± 0.02</td>
<td>3.00 ± 0.01</td>
<td>3.94 ± 0.05</td>
<td>0.06 ± 0.00</td>
<td>12.01 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>0.99 ± 0.02</td>
<td>2.99 ± 0.01</td>
<td>3.94 ± 0.04</td>
<td>0.05 ± 0.00</td>
<td>12.02 ± 0.05</td>
</tr>
</tbody>
</table>

Table 5-34. shows the relative intensity of secondary phase on CaCu$_3$Ti$_4$O$_{12}$ with different tin dopant and sintering hold time, and the maximum of secondary phase is 4.54%.

This table also shows the secondary phase increases while the sintering hold time increases, especially at longer sintering hold time (12 hours).
Table 5-34. Maximum intensity of secondary phase compared to CCTO with different tin dopant and sintering time by XRD.

<table>
<thead>
<tr>
<th>Sintering</th>
<th>4 hours</th>
<th>8 hours</th>
<th>12 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaTiO$_3$</td>
<td>SnO</td>
<td>CaTiO$_3$</td>
</tr>
<tr>
<td>CCTO</td>
<td>0.24%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CCT05S</td>
<td>3.96%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CCT10S</td>
<td>- 4.30%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CCT15S</td>
<td>- 3.30%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CCT20S</td>
<td>- 2.50%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CCT25S</td>
<td>- 3.09%</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

5.3.4. Lattice parameters

Theoretically, niobium substitution will increases the lattice parameters of CCTO, when the niobium ion substitutes the Ti ion during sintering. The increased lattice parameters can be attributed to the ionic radius and valence differences between niobium and Ti ions, $r$(Nb$^{5+}$, CN=6) = 64 pm and $r$(Ti$^{4+}$, CN=6) = 60.5 pm [113], respectively. However, these results show the increasing of lattice parameters only at 12 hours sintering hold time, as shown in Figure 5.58. At 4 and 8 hours sintering hold time, there was not significant increase of lattice parameters with increases in niobium dopant in CCTO.

![Figure 5.58. Lattice parameters of CCTO.](image)

Also shown in Figure 5.58., the lattice parameters increase linearly with increasing tin-
substitution, at longer sintering hold time (8 and 12 hours), but the lattice is not significantly increase at 4 hours sintering hold time. This results are identical with Ni et. al. [23] found which tin-substitution at x = 0, 0.05, 0.1, and 0.2 mol. The increased lattice constant can be attributed to the larger ionic radius of Sn (r(Sn$^{4+}$, CN=6) = 69 pm) compared with that of Ti (r(Ti$^{4+}$, CN=6) = 60.5 pm) [113].

5.4. Densification data

In a previous chapter, two specimens CCTOsc and CCTOdc were prepared for initial study. Table 5-35. shows the actual and theoretical densities, the densities between single and double calcination are identical, and based on the previous results (observed in section 4.1.1.), the single calcination was used to prepare all the CCTO samples in this study.

Table 5-35. Actual and theoretical density of CCTO.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Actual (g/cm$^3$)</th>
<th>Theoretical (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCTOsc</td>
<td>4.80 ± 0.03</td>
<td>5.07 ± 0.01</td>
</tr>
<tr>
<td>CCTOdc</td>
<td>4.81 ± 0.03</td>
<td>5.07 ± 0.01</td>
</tr>
</tbody>
</table>

Figure 5.59. displays both actual and theoretical density of CaCu$_3$Ti$_4$O$_{12}$ for different sintering hold times. The actual density was calculated using the volume (based on the dimension of the sample) and the mass of specimen and the theoretical density was calculated using the volume and mass of the unit cell taken from X-ray diffraction data. The samples show an initial decrease in density with increase in sintering time, the 4 hours sintering is the maximum result at 4.8 g/cm$^3$. The ratio between actual and theoretical densities were shown in percentage of density. The relative density of all samples was more than 90% (95%, 91%, and 92% for CCTO4, CCTO8, and CCTO12, respectively). This result was identical to those Hao and Zhang [123] who found, densities between 91% and 95% using conventional sintering.
Figure 5.59. Actual and theoretical density of CCTO at various sintering time.

Table 5-36. Actual, theoretical density, and porosity of CCTO at various sintering hold time

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Sintering Condition</th>
<th>Actual Density (g/cm$^3$)</th>
<th>Theoretical Density (g/cm$^3$)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCTO4</td>
<td>CaCu$<em>3$TiO$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.80 ± 0.03</td>
<td>5.08 ± 0.00</td>
<td>5</td>
</tr>
<tr>
<td>CCTO8</td>
<td>CaCu$<em>3$TiO$</em>{12}$</td>
<td>1100°C 8 h</td>
<td>4.60 ± 0.03</td>
<td>5.07 ± 0.00</td>
<td>9</td>
</tr>
<tr>
<td>CCTO12</td>
<td>CaCu$<em>3$TiO$</em>{12}$</td>
<td>1100°C 12 h</td>
<td>4.66 ± 0.11</td>
<td>5.06 ± 0.00</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 5-36. shows the actual, theoretical density and porosity of the CCTO with different sintering hold time. The actual density depends on sintering hold time, and the porosity tends to increase as sintering hold time increases. The porosity relates to abnormal grain growth where a few large-sized grain grows rapidly at the expense of smaller grain as shown in Figure 5.1 to 5.3. The abnormal grain growth is accompanied by breakaway of the boundaries from the pores [108]. In CCTO12 (Figure 5.3.), the intragranular pores (trapped inside abnormal grain) are difficult to remove and leading to higher porosity.

Table 5-37. Actual, theoretical, and porosity of CCTxN4.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Sintering Condition</th>
<th>Actual Density (g/cm$^3$)</th>
<th>Theoretical Density (g/cm$^3$)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCTO4</td>
<td>CaCu$<em>3$TiO$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.80 ± 0.03</td>
<td>5.08 ± 0.00</td>
<td>5</td>
</tr>
<tr>
<td>CTO5N4</td>
<td>CaCu$<em>3$Ti$</em>{3.95}$Nb$<em>{0.05}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.25 ± 0.07</td>
<td>5.16 ± 0.02</td>
<td>18</td>
</tr>
<tr>
<td>CTO10N4</td>
<td>CaCu$<em>3$Ti$</em>{3.90}$Nb$<em>{0.10}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.57 ± 0.04</td>
<td>5.23 ± 0.01</td>
<td>17</td>
</tr>
<tr>
<td>CTO15N4</td>
<td>CaCu$<em>3$Ti$</em>{3.85}$Nb$<em>{0.15}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.69 ± 0.02</td>
<td>5.29 ± 0.01</td>
<td>11</td>
</tr>
<tr>
<td>CTO20N4</td>
<td>CaCu$<em>3$Ti$</em>{3.80}$Nb$<em>{0.20}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.75 ± 0.03</td>
<td>5.36 ± 0.01</td>
<td>11</td>
</tr>
<tr>
<td>CTO25N4</td>
<td>CaCu$<em>3$Ti$</em>{3.85}$Nb$<em>{0.25}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.81 ± 0.03</td>
<td>5.44 ± 0.01</td>
<td>12</td>
</tr>
</tbody>
</table>
Table 5-37. and Table 5-38. show the actual and theoretical density of niobium and tin doped CCTO with 4 hours sintering time, respectively. The relative density of niobium doped CCTO was between 82% and 95% and 88% to 90% for tin doped CCTO. The densities were increase with increase in niobium and tin dopant. The maximum density with 4 hours sintering is reached by CCT25S4 sample; at 4.96 g/cm$^3$ (88% density). The porosity of CCT05N4 and CCT10N4 are higher than others, it seem the niobium dopant initiated the interaction between the segregated solute and the grain-boundary. The interaction causes the solute must be carried along with the moving boundary and inhibits the grain growth. As a result, pore size increases as shown in Figure 5.5 and 5.6.

Table 5-38. Actual, theoretical, and porosity of CCTxS4.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Sintering Condition</th>
<th>Actual (g/cm$^3$)</th>
<th>Theoretical (g/cm$^3$)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCT04</td>
<td>CaCu$<em>3$TiO$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.80 ± 0.03</td>
<td>5.08 ± 0.00</td>
<td>5</td>
</tr>
<tr>
<td>CCT05S4</td>
<td>CaCu$<em>3$Ti$</em>{0.95}$Sn$<em>{0.05}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.66 ± 0.05</td>
<td>5.18 ± 0.01</td>
<td>10</td>
</tr>
<tr>
<td>CCT10S4</td>
<td>CaCu$<em>3$Ti$</em>{0.9}$Sn$<em>{0.1}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.76 ± 0.06</td>
<td>5.30 ± 0.01</td>
<td>10</td>
</tr>
<tr>
<td>CCT15S4</td>
<td>CaCu$<em>3$Ti$</em>{0.85}$Sn$<em>{0.15}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.81 ± 0.01</td>
<td>5.42 ± 0.03</td>
<td>11</td>
</tr>
<tr>
<td>CCT20S4</td>
<td>CaCu$<em>3$Ti$</em>{0.8}$Sn$<em>{0.2}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.94 ± 0.03</td>
<td>5.53 ± 0.01</td>
<td>11</td>
</tr>
<tr>
<td>CCT25S4</td>
<td>CaCu$<em>3$Ti$</em>{0.75}$Sn$<em>{0.25}$O$</em>{12}$</td>
<td>1100°C 4 h</td>
<td>4.96 ± 0.00</td>
<td>5.65 ± 0.02</td>
<td>12</td>
</tr>
</tbody>
</table>

The densities of niobium and tin doped CCTO at 8 hours sintering are shown in Table 5-39. and Table 5-40. respectively. The CCT25S8 reached maximum value at 4.98 g/cm$^3$ (89% density). Again, the densities were increased with increase in niobium and tin dopant and there is a significant increasing in density when tin dopant increases, as the tin atom weight (g/mol) is higher than titanium or niobium. The porosity tended to increase as niobium dopant increases, but increasing tin dopant did not significantly increase the porosity. Again, similar to 4 hours sintering in niobium doped CCTO, the niobium as an inhibitor, causes the pore size growth bigger.
Table 5-39. Actual and theoretical density of CCTxN8.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Sintering Condition</th>
<th>Actual (g/cm³)</th>
<th>Theoretical (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCTO8</td>
<td>CaCu₃TiO₁₂</td>
<td>1100°C 8 h</td>
<td>4.60 ± 0.03</td>
<td>5.07 ± 0.00</td>
<td>9</td>
</tr>
<tr>
<td>CCT05N8</td>
<td>CaCu₃Ti₃₅SnO₁₂</td>
<td>1100°C 8 h</td>
<td>4.33 ± 0.03</td>
<td>5.13 ± 0.01</td>
<td>16</td>
</tr>
<tr>
<td>CCT10N8</td>
<td>CaCu₃Ti₃₅Sn₁₀O₁₂</td>
<td>1100°C 8 h</td>
<td>4.61 ± 0.03</td>
<td>5.22 ± 0.01</td>
<td>12</td>
</tr>
<tr>
<td>CCT15N8</td>
<td>CaCu₃Ti₃₅Sn₁₅O₁₂</td>
<td>1100°C 8 h</td>
<td>4.62 ± 0.06</td>
<td>5.27 ± 0.03</td>
<td>12</td>
</tr>
<tr>
<td>CCT20N8</td>
<td>CaCu₃Ti₃₅Sn₂₀O₁₂</td>
<td>1100°C 8 h</td>
<td>4.77 ± 0.03</td>
<td>5.36 ± 0.01</td>
<td>11</td>
</tr>
<tr>
<td>CCT25N8</td>
<td>CaCu₃Ti₃₅Sn₂₅O₁₂</td>
<td>1100°C 8 h</td>
<td>4.83 ± 0.01</td>
<td>5.43 ± 0.01</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 5-40. Actual and theoretical density of CCTxS8.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Sintering Condition</th>
<th>Actual (g/cm³)</th>
<th>Theoretical (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCTO8</td>
<td>CaCu₃TiO₁₂</td>
<td>1100°C 8 h</td>
<td>4.60 ± 0.03</td>
<td>5.07 ± 0.00</td>
<td>9</td>
</tr>
<tr>
<td>CCT05S8</td>
<td>CaCu₃Ti₃₅SnO₁₂</td>
<td>1100°C 8 h</td>
<td>4.74 ± 0.00</td>
<td>5.18 ± 0.01</td>
<td>9</td>
</tr>
<tr>
<td>CCT10S8</td>
<td>CaCu₃Ti₃₅Sn₁₀O₁₂</td>
<td>1100°C 8 h</td>
<td>4.74 ± 0.07</td>
<td>5.27 ± 0.01</td>
<td>10</td>
</tr>
<tr>
<td>CCT15S8</td>
<td>CaCu₃Ti₃₅Sn₁₅O₁₂</td>
<td>1100°C 8 h</td>
<td>4.93 ± 0.00</td>
<td>5.39 ± 0.05</td>
<td>8</td>
</tr>
<tr>
<td>CCT20S8</td>
<td>CaCu₃Ti₃₅Sn₂₀O₁₂</td>
<td>1100°C 8 h</td>
<td>4.95 ± 0.01</td>
<td>5.49 ± 0.01</td>
<td>10</td>
</tr>
<tr>
<td>CCT25S8</td>
<td>CaCu₃Ti₃₅Sn₂₅O₁₂</td>
<td>1100°C 8 h</td>
<td>4.98 ± 0.01</td>
<td>5.59 ± 0.01</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 5-41. and Table 5-42. show the actual, theoretical density and porosity of niobium and tin doped CCTO for 12 hours sintering. Identical with 4 and 8 hour sintering, the density of tin dopant sample is higher than the density of niobium dopant. The relative density range is between 87% and 92%, and maximum average density is 4.84 g/cm³ (CCT25S12). The densities were increased with increases in niobium and tin dopant. The porosity was not significantly increased as niobium dopant increases, but increasing tin dopant was tend to increase the porosity.

Table 5-41. Actual and theoretical density of CCTxN12.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Sintering Condition</th>
<th>Actual (g/cm³)</th>
<th>Theoretical (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCTO12</td>
<td>CaCu₃TiO₁₂</td>
<td>1100°C 12 h</td>
<td>4.66 ± 0.11</td>
<td>5.06 ± 0.00</td>
<td>8</td>
</tr>
<tr>
<td>CCT05N12</td>
<td>CaCu₃Ti₃₅SnO₁₂</td>
<td>1100°C 12 h</td>
<td>4.33 ± 0.01</td>
<td>5.11 ± 0.00</td>
<td>12</td>
</tr>
<tr>
<td>CCT10N12</td>
<td>CaCu₃Ti₃₅Sn₁₀O₁₂</td>
<td>1100°C 12 h</td>
<td>4.61 ± 0.03</td>
<td>5.19 ± 0.00</td>
<td>11</td>
</tr>
<tr>
<td>CCT15N12</td>
<td>CaCu₃Ti₃₅Sn₁₅O₁₂</td>
<td>1100°C 12 h</td>
<td>4.62 ± 0.03</td>
<td>5.26 ± 0.00</td>
<td>10</td>
</tr>
<tr>
<td>CCT20N12</td>
<td>CaCu₃Ti₃₅Sn₂₀O₁₂</td>
<td>1100°C 12 h</td>
<td>4.77 ± 0.01</td>
<td>5.33 ± 0.00</td>
<td>10</td>
</tr>
<tr>
<td>CCT25N12</td>
<td>CaCu₃Ti₃₅Sn₂₅O₁₂</td>
<td>1100°C 12 h</td>
<td>4.83 ± 0.01</td>
<td>5.40 ± 0.00</td>
<td>10</td>
</tr>
</tbody>
</table>
Table 5-42. Actual and theoretical density of CCTxS12.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Sintering Condition</th>
<th>Actual Density (g/cm$^3$)</th>
<th>Theoretical Density (g/cm$^3$)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCTO12</td>
<td>CaCu$<em>3$TiO$</em>{12}$</td>
<td>1100°C 12 h</td>
<td>4.66 ± 0.11</td>
<td>5.06 ± 0.00</td>
<td>8</td>
</tr>
<tr>
<td>CCT05S12</td>
<td>CaCu$<em>3$Ti$</em>{3.95}$Sn$<em>{0.05}$O$</em>{12}$</td>
<td>1100°C 12 h</td>
<td>4.50 ± 0.08</td>
<td>5.15 ± 0.00</td>
<td>13</td>
</tr>
<tr>
<td>CCT10S12</td>
<td>CaCu$<em>3$Ti$</em>{3.90}$Sn$<em>{0.10}$O$</em>{12}$</td>
<td>1100°C 12 h</td>
<td>4.75 ± 0.09</td>
<td>5.26 ± 0.01</td>
<td>10</td>
</tr>
<tr>
<td>CCT15S12</td>
<td>CaCu$<em>3$Ti$</em>{3.85}$Sn$<em>{0.15}$O$</em>{12}$</td>
<td>1100°C 12 h</td>
<td>4.74 ± 0.01</td>
<td>5.35 ± 0.00</td>
<td>11</td>
</tr>
<tr>
<td>CCT20S12</td>
<td>CaCu$<em>3$Ti$</em>{3.80}$Sn$<em>{0.20}$O$</em>{12}$</td>
<td>1100°C 12 h</td>
<td>4.80 ± 0.05</td>
<td>5.47 ± 0.01</td>
<td>12</td>
</tr>
<tr>
<td>CCT25S12</td>
<td>CaCu$<em>3$Ti$</em>{3.85}$Sn$<em>{0.25}$O$</em>{12}$</td>
<td>1100°C 12 h</td>
<td>4.84 ± 0.05</td>
<td>5.58 ± 0.01</td>
<td>13</td>
</tr>
</tbody>
</table>

Figure 5.60 and Figure 5.61 show the actual and theoretical density of niobium and tin doped CCTO at various sintering time. The graph shows the increasing actual densities with increasing the amount of dopant. Longer sintering time resulted in a steady increase in the density of niobium and tin doped CCTO.

The densities of tin doped CCTO (CCTxS) are higher than niobium doped CCTO (CCTxN) because the tin oxide particle is smaller than the niobium oxide particle. The smaller particle will growth rapidly than larger particle, as the smaller particle has a surface energy higher than the large particle. The longer sintering time will affect to the bond grow more rapidly and consequently, the densification becomes evident. The combination of smaller particle size and longer sintering held time is the key of density of tin doped CCTO higher than niobium doped CCTO.
5.5. Summary of observation on microstructure and phase development.

In summary, increasing sintering hold time increased the large grain size and decreased the small grain size, also increased the porosity of CCTO, which will affect to the density. The niobium dopant reduced the grain and pore size, on the other hand, tin dopant reduced the large grain size but did not significantly reduce the small grain size. Sintering hold time could increase or decrease the grain size of niobium and tin doped CCTO depending on the amount of niobium and tin dopant. Increasing sintering hold time also increased the secondary phase of pure CCTO but did not significantly increase the lattice parameters of niobium and tin doped CCTO. The absolute density of pure CCTO increased with increasing sintering hold time, unfortunately also increases the porosity due to the abnormal grain growth. The niobium and tin dopant tend to increase the absolutely density and the porosity of CCTO, but increasing sintering hold time did not significantly change the density of niobium and tin doped CCTO.

Figure 5.61. Theoretical density of CCTxN and CCTxS at various sintering time.

Ellyawan Arbintarso  Bulk and Grain Boundary Electrical Behaviours in Nb and Sn Doped Calcium Copper Titanium Oxide
6. Impedance Spectroscopy of CCTO.

In this chapter, the electrical properties of CaCu$_3$Ti$_4$O$_{12}$ are presented as dielectric constant (ε), dielectric loss (tan δ), capacitance (C), and activation energy (E$_a$). These properties will be used to find the grain-boundary thickness that corresponds to IBLC phenomenon. The frequency range of this work is from 5 Hz to 13 MHz. The work is broken down into two sub-chapters focussing on pure CCTO and CCTO doped with niobium and tin, respectively. The pure CCTO has three different sintering time i.e. 4, 8 and 12 hours sintering hold time, and the niobium and tin doped CCTO only have 4 hours sintering hold time. The composition of pure CCTO (CCTOx) and niobium and tin doped CCTO (CCTxN4 and CCTxS4) were used in this study as described in chapter 4.

6.1. Pure CCTO.

The focus of this section is the electrical properties of pure CCTO with different sintering hold times. Principally using impedance spectroscopy which has been used to calculate resistance (R) and capacitance (C) at grain and grain boundary regions in many electroceramics [31, 33, 35, 37]. Electrical measurements were made on the coated CaCu$_3$Ti$_4$O$_{12}$ pellets described in section 3.2.1. Many researchers interpreted impedance spectrum containing three semicircles in Nyquist plot (Figure 2.5. [41]) or three peaks in Bode plot (M'' versus log f plot) using an ideal equivalent circuit which consists of three parallel RC elements connected in series, correspond to the relaxation behaviour of grains, grain boundaries and electrode. In the initial study with high temperature (from 200°C to 450°C), the impedance spectrum showed only one semicircle (Figure 6.1.a.), so a Cryostream unit was used to reduce the sample temperature from room temperature to -175°C and two imperfect semicircles (only have a small part of curvature that cannot generate a circle) were found at very low temperature (less than -100°C). Figure 6.1.b. shows two very different semicircles, one very small semicircle (a perfect semicircle, the curvature that can generate a circle) and the other is a large semicircle (an imperfect semicircle that cannot generate a circle). The next study of impedance spectroscopy of pure CCTO was repeated with temperature from room
temperature to 450°C, and also found two semicircles in the impedance spectra, one perfect semicircle and one imperfect semicircle. All of impedance data showed two semicircles in Nyquist plot or two peaks in Bode plot and for this reason, two parallel R|CPE elements connected in series were used to fit the impedance data. This circuit showed better fitting than using parallel R|C element (section 2.3.3.1.), because the CPE associated with a distribution of the capacitance that change with frequency as an electrical response from real materials [79].

Figure 6.1. Impedance spectrum of CCTO4 at (a) high temperature and (b) low temperature.

It is not difficult to see that the impedance spectra are rather depressed – the centre of rotation of the semicircle below the real axis [82] - (Figure 6.1.), so it is necessary to use constant phase elements (CPEs), rather than ideal capacitances, in the equivalent circuits [76, 79, 82, 84] (Figure 6.2.).

Figure 6.2. Two R|CPE elements connected in series (R|CPE-R|CPE) as equivalent circuit for CCTO.
6.1.1. Impedance spectroscopy.

Impedance Spectroscopy was used to measure the resistance and capacitance (or CPE) of CCTO as a function of frequency, and then resistance was converted to resistivity ($\rho$) to find the activation energy ($E_a$) using Equation (82) (section 3.2.4.).

$$\ln(\rho) = \ln(\rho_0) + \frac{E_a}{k_B} \left( \frac{1}{T} \right)$$  .............................................. (82)

The activation energy magnitude will help to illustrate of the conduction process in CCTO and the possibility of oxygen vacancies in the system [83]. On the other hand, the CPE was converted to capacitance using Equation (83), for a R|CPE, the real capacitance $C$ can be obtained from CPE value using

$$C = (R^{1-P} \cdot T) \frac{1}{P}$$ ...................................................... (83)

where $T$ is short for CPE-T, a quasi-capacitance as a result of CPE fitting using ZView, and $P$ is short for CPE-P, a depression factor of semicircle in Nyquist plot. If CPE-P equals 1, so CPE-T is equal with capacitance $C$.

The capacitances were used to find the dielectric constant ($\varepsilon$) of bulk and grain boundary using a modification of Equation (76). Based on the brick layer model, Equation (76) was modified to calculate bulk and grain-boundary dielectric constant as

$$\varepsilon_b = \frac{C_b \cdot t_b}{\varepsilon_0 \cdot A}$$ .......................................................... (84)

$$\varepsilon_{gb} = \frac{C_{gb} \cdot t_{gb}}{\varepsilon_0 \cdot A}$$ ........................................................ (85)

Where $A$ is surface area of electrode and the subscript b and gb are short for bulk and grain-boundary, respectively. Both the capacitance and dielectric constant will be used to calculate the grain boundary thickness using Equation (86).

$$\frac{t_{gb}}{t_b} = \frac{C_b}{C_{gb}} \cdot \frac{\varepsilon_{gb}}{\varepsilon_b}$$ .................................................... (86)

By making the assumption $\varepsilon_b = \varepsilon_{gb}$ [79]; the grain-boundary thickness can be calculated using Equation (87), where $t_b$ is bulk thickness equal with average grain size (GS).
Two temperature regions were used in this study; high temperature range is in the range between room temperature and 450°C and low temperature range is in the range from room temperature to -175°C. The Carbolite MTF furnace was used to control temperature at high temperature range and a Cryostream unit was used to control temperature at low temperature range. The high temperature range represented the grain boundary behaviours (resistance and capacitance) and the low temperature range represented the bulk (grain) behaviours. Both the temperature ranges were used in this study, because all impedance data showed two imperfect semicircles, which did not give the bulk and grain boundary behaviours at the same time as shown in Figure 6.3.a. and Figure 6.3.b.

![Figure 6.3. Impedance spectrum of CCTO4 with (a) High Temperature and (b) Low Temperature range.](image)

Frequency range between 5 Hz and 13 MHz was used for all impedance measurements. This frequency range of LF Impedance Analyzer is not wide enough to form two perfect semicircles, as a result, to find the resistance and capacitance of imperfect semicircle, extrapolation was used. Figure 6.1.(a). shows only one perfect semicircle that provided resistance and capacitance of grain-boundary (refer to [83]), and Figure 6.1.(b). also shows only one perfect semicircle that provided resistance and capacitance of bulk (refer to [83]). After it was converted from resistance to resistivity (ρ) and plotted as ln ρ versus 1/T (Kelvin), the
resistivities of grain-boundary and bulk will give an linear equation of activation energy of grain-boundary \((E_{agb})\) and bulk \((E_{ab})\), respectively. Based on the assumption that the activation energy will be same over all the temperature range, the extrapolation of resistance of grain-boundary can be found from high temperature range and the extrapolation of resistance of bulk can be found from low temperature range, as is shown in Figure 6.4. The Zview fitting was used to find the capacitance of imperfect semicircle, based on the extrapolation of resistance and extended the frequency range of fitting. Table 6-1. shows the result of extrapolation of resistance and fitting of capacitance of CCTO4. The extrapolation and fitting result of grain-boundary and bulk are shown in black and green, respectively.

\[ E_a = m \times 8.6173 \times 10^{-5} \text{ eV} \]

Figure 6.4. Extrapolation of resistivities of high and low temperature range of CCTO4 (experimental data are shown in blue and red, and extrapolated data in black and green).
Table 6-1. Extrapolation of resistance and fitting of capacitance of CCTO4.

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<th>$CPE_{T-P}$ (F/Ohm)$^n$</th>
<th>$CPE_{T-P}$ (F)</th>
<th>$R_\infty$ (Ohm)</th>
<th>$CPE_{T-P}$ (F/Ohm)$^n$</th>
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(Experimental data are shown in blue and red, and extrapolated data in green and black).

Impedance spectra were measured for CCTO samples with 8 and 12 hours sintering hold with the same of frequency and temperature range of CCTO4. The resistance and capacitance were analysed with the same steps of CCTO4 analysis. Table 6-2. and Table 6-3. show the result of extrapolation of resistance and fitting of capacitance of CCTO8 and CCTO12, respectively.

Table 6-2. Extrapolation of resistance and fitting of capacitance of CCTO8.

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<th>$CPE_{T-P}$ (F)</th>
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(Experimental data are shown in blue and red, and extrapolated data in green and black).
Table 6-3. Extrapolation of resistance and fitting of capacitance of CCTO12.

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</tbody>
</table>

(Experimental data are shown in blue and red, and extrapolated data in green and black).

6.1.2. Dielectric Constant, Dielectric Loss and Capacitance

There were three threads of investigation. The first investigated the relative dielectric constant per unit length ($\varepsilon_{eff}$), dielectric loss (tan $\delta$) and relative capacitance ($C'$) of pure CCTO at 4 hours sintering hold time and compared it with 8 and 12 hours sintering hold time. The second focussed on an effect of increasing temperature on $\varepsilon_{eff}$, tan $\delta$ and $C'$ all of pure CCTO with various sintering time. The third studied an effect of frequency on the $\varepsilon_{eff}$, tan $\delta$ and $C'$ all of pure CCTO with various sintering time.

The equivalent dielectric constant could be calculated using modified Equation (5) as rewritten in Equation (88) where the equivalent capacitance is $C_{eq} = C_s C_{gb} / (C_b + C_{gb})$.

$$\varepsilon_{eq} = \frac{C_{eq}}{\varepsilon_0} \frac{A}{t} \quad \text{.......................................................... (88)}$$

The equivalent capacitance may be converted to relative dielectric constant per unit length ($\varepsilon_{eff}$) using the modified Equation (6)

$$\varepsilon_{eff} = \frac{C_{eq}}{\varepsilon_0} \quad \text{.......................................................... (89)}$$

Table 6-4. shows the equivalent capacitance and dielectric constant, relative dielectric constant per unit length and grain-boundary thickness of CCTO4.
Table 6-4. The equivalent capacitance and dielectric constant, relative dielectric constant per unit length and grain-boundary thickness of CCTO4

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<th>$C_{gb}$ (F)</th>
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<th>$t_{gb}$ (μm)</th>
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Table 6-5. The equivalent capacitance and dielectric constant, relative dielectric constant per unit length and grain-boundary thickness of CCTO8 and CCTO12 were tabulated in Table 6-5. and Table 6-6., respectively.

Table 6-5. The equivalent capacitance and dielectric constant, relative dielectric constant per unit length and grain-boundary thickness of CCTO8

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Table 6-6. The equivalent capacitance and dielectric constant, relative dielectric constant per unit length and grain-boundary thickness of CCTO12

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<th>$C_{gb}$ (F)</th>
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Figure 6.5. shows the equivalent dielectric constant, relative dielectric constant (short for relative dielectric constant per unit length) and grain-boundary thickness of pure CCTO with different sintering hold times. The Figure 6.5. shows an identically trend of dielectric constant and grain-boundary thickness with increasing temperature. The equivalent and relative dielectric constant increased as temperature rises up on CCTO4 (Figure 6.5.(a)), and reached maximum at -25°C, then decreased as temperature increases. The equivalent and relative dielectric constant of CCTO8 (Figure 6.5.(b)) tended to increase as temperature increases. Identical to CCTO4, the equivalent and relative dielectric constant of CCTO12 (Figure 6.5.(c)) increased from low temperature, and reached maximum at -75°C, then decreased as temperature increases. The grain-boundary thickness of CCTO4 and CCTO12 have the identical behaviours with the equivalent and relative dielectric constant, on the other hand, the grain-boundary thickness of CCTO8 increased as temperature increases.
Many researchers [3, 18-32, 38-39, 133] used the real part of relative dielectric constant per unit length ($\varepsilon_{\text{eff}}$) to see the relationship with temperature at different frequencies. They converted the real part of capacitance ($C'$) of sample into real part of relative dielectric constant per unit length ($\varepsilon_{\text{eff}}$) using Equation (6), where the capacitance was extracted from the imaginary part of modulus ($M''$) (for experimental procedure, see section 3.2.4). The sample dimension (ratio of area and thickness of sample) was taken into account so the relative dielectric constant per unit length of each formulation can be directly compared to those for other samples.

Figure 6.6. shows the real part of relative dielectric constant per unit length ($\varepsilon_{\text{eff}}$) and dielectric loss ($\tan \delta$) of CCTO sintered for 4, 8 and 12 hours are plotted as a function of temperature with varying frequencies. It is clear that the relative dielectric constant per unit length rises with increases in the temperature, and decreases as frequency increases. The dielectric loss also rises with increases in the temperature, and at range between 175°C and 275°C the value rose higher by 10 orders of magnitude than average of dielectric loss in CCTO4 and CCTO12 (Figure 6.6.(a) and (c)), respectively.
Figure 6.6. Real part of relative dielectric constant and dielectric loss of CCTO with (a) 4 hours, (b) 8 hours, and (c) 12 hours sintered hold times at various frequencies.

Figure 6.6. also shows the temperature dependence of relative dielectric constant of CaCu$_3$Ti$_4$O$_{12}$ from -175°C (98K) to 450°C (723K) at frequencies of 1 kHz, 10 kHz, 100 kHz, 1 MHz and 10 MHz, respectively. The values of the relative dielectric constant between 25°C (298K) and 200°C (473K) are almost identical. With further increasing temperature, the relative dielectric constant increases rapidly at low frequency (1-10 kHz). The possible reason of
increasing dielectric constant is a very small amount of Ti may be on the Cu site which at synthesis temperature would be charge compensated by same reduction of Cu$^{2+}$ to Cu$^{1+}$ as suggested by Li et. al. [47].

Figure 6.7. shows real part of relative dielectric constant and dielectric loss of CCTO with different sintering hold times at temperature range between -100°C and 100°C. The temperature range was chosen as represent a transition temperature between low and high temperature ranges.

Figure 6.7. Real part of relative dielectric constant ($\varepsilon_{\text{eff}}'$) and dielectric loss (tan $\delta$) at -100°C to 100°C for (a) CCTO4, (b) CCTO8, and (c) CCTO12.
The $\varepsilon_{\text{eff}}'$ tends to decrease at low-frequency (1 and 10 kHz) and increase at high-frequency (100 kHz to 10 MHz) as temperature increases for all sintering times. On the other hand, $\tan \delta$ increases at low-frequency and decreases at high-frequency as the temperature increases all sintering times. The $\varepsilon_{\text{eff}}'$ decreased as frequency increases for all sintering times and temperature.

Figure 6.8. shows dielectric constant of CCTO curves that it are the typical behaviour of an IBLC structure, where the sharp dielectric constant drop occurs at increased frequency as described by Schmidt et. al [85].

Figure 6.8. Frequency dependence of dielectric constant and loss tangent of CCTO with (a) 4 hours, (b) 8 hours, and (c) 12 hours sintered hold times.
The high frequency dielectric response is dominated by the conducting bulk (grains) and the low frequency response by the insulating grain boundary contribution. These dielectric constant and frequency peaks are comparable to Leret et. al. [44]. Figure 6.8. also shows the decreasing real part of relative dielectric constant with increasing frequency. There is a relaxation peak between 1 and 10 kHz for CCTO4 and CCTO8, and it corresponds to dielectric loss. As seen in Figure 6.8., the dielectric loss (tan δ) was lowest at relaxation peak, and increased as temperature increases. At CCTO12, the relaxation peak range is wider than those with shorter sintering times, between 1 and 100 kHz. At high-frequency, the dielectric loss increases higher than low-frequency for all sintering times. The bulk phases in CCTO become conducting and decrease at high temperature. Decreasing conductivity will increase the dielectric constant.

In order to compare the behaviour between the (real part of relative) dielectric constant and dielectric loss, both $\varepsilon_{\text{eff}}$ and tan δ are replotted from -100°C to 200°C at 1 kHz to 1 MHz in Figure 6.9. In Figure 6.9., there were 2 regions, i.e. at below room temperature – Low Temperature (T < 25°C), the relative dielectric constants decreased as sintering hold times and the frequency increase, and on the other hand, the dielectric loss increased as sintering hold times and the frequency increase. At room temperature or above – High Temperature (T ≥ 25°C), the dielectric constant increased as sintering hold times increase but there was not significant change to dielectric loss. It seem longer sintering hold time increasing conductivity of grain-boundary. On the other hand, increasing the frequency decreased the dielectric constant and dielectric loss for all temperature ranges. In this case, the high frequencies dielectric response dominated by bulk, which more conductive than grain boundary. As result the dielectric constant decreases with increases conductivity.

Figure 6.10. shows frequencies dependence of real part of relative dielectric constant and dielectric loss for specific temperature. Low temperature is represented by -100°C, the transition temperature is represented by 25°C, and the last two temperatures represent high temperature. The relaxation peak of relative dielectric constant shifted to right (higher frequency) as temperature increases. Figure 6.10. also shows the dielectric loss increased as temperature increases at low-frequency but there was not significant change in high-frequency.
Figure 6.9. Real part of relative dielectric constant and dielectric loss of CCTO at various sintering times at (a) 1 kHz, (b) 10 kHz, (c) 100 kHz, and (d) 1 MHz.
Figure 6.10. Frequency dependence of dielectric constant and dielectric loss of CCTO at different sintering times at a) -100°C, b) 25°C, c) 100°C and d) 200°C.
Identical to the relative dielectric constant, there are two regions of relative capacitance ($C'$) as shown in Figure 6.11., below room temperature – Low Temperature ($T < 25^\circ C$), the relative capacitance decreases as sintering hold times increase. In high-frequency, there was another semicircle arc assigned to bulk capacitance ($10^{-12}$ to $10^{-11}$ F refer to West et. al. [39]), as specially in CCTO12, the value decreased lower than CCTO4 and CCTO8.

![Graphs of Capacitance vs. Temperature for CCTO12, CCTO8, and CCTO4 at different frequencies](image)

Figure 6.11. Capacitance of CCTO at various sintering times at (a) 1 kHz, (b) 10 kHz, (c) 100 kHz, (d) 1 MHz, and (e) 10 MHz.

At room temperature or above – High Temperature ($T \geq 25^\circ C$), the relative capacitance...
increases as sintering hold time are extended and decreases as the frequencies increase. Figure 6.11. show the behaviour of relative capacitance to temperatures and frequencies. The relative capacitance was not significant affected by increased frequency at high temperature, but at low temperature, the relative capacitance significant changed with increases frequency. Again, the conductivity of bulk (high-frequency) and grain boundary (low-frequency) play an important role to the capacitance.

The typical ceramic IBLC structure for CCTO ceramic is shown in Figure 6.12, where the sharp relative capacitance drop occurs when the mean electron conduction path permitted by applied alternating voltage signal decrease below the average grain size at increased frequencies [85]. The low-frequency is dominated by the insulating grain boundary and the high-frequency is dominated by conducting bulk. Figure 6.12 does not show the relaxation peak of bulk capacitance, but in high-frequency indicated there will be relaxation peak in extended frequencies. The extrapolation from high temperature data was used to find the bulk capacitance based on the curve of grain boundaries capacitance as mentioned earlier in this chapter.

![Graphs showing frequency dependence of real part of capacitance (C') of CCTO at various sintering times and temperatures: (a) -100°C, (b) -25°C, (c) 25°C, and (d) 100°C.](image)
Figure 6.13. shows both the bulk and grain boundary capacitance of CCTO at various sintering times, based on Table 6-1. to 6-3. The bulk capacitance was significantly changed with increases temperature and longer sintering times, on the other hand, increasing sintering time will increase the grain-boundary capacitance but there was not significant affected by increases temperature. The values of bulk capacitance are higher than the others reported [32, 45, 50-52, 83, 95-96, 99] but the values of grain boundary capacitance are identical to them. The ratio of bulk and grain boundary capacitance multiplied by grain size (Equation (87)) was used to calculate the grain boundary thickness.

Figure 6.13. (a) Bulk and (b) grain boundary capacitance of CCTO at various sintering times.

Figure 6.14. shows the grain boundary thickness of CCTO with different sintering hold time (based on Table 6-4. to 6-6.). The grain boundary thickness depends on the temperature.
and sintering hold time. The correlation between grain-boundary thickness and non-linear coefficient of conduction will be discussed in chapter 8.

Figure 6.14. Grain boundary thickness versus temperature plot of CCTO at various sintering time.

6.1.3. Activation Energy of electrical conductivity of pure CCTO.

The grain boundary and bulk semicircles are not both visible at the same temperature in the $\rho''$ versus $\rho'$ plot. Only at high temperature does the grain boundary semicircle fully develop and the bulk arc is not visible, a non-zero intercept of the data with $\rho'$ axis appears. On the other hand, at low temperature, the bulk semicircle is not fully developed as an arc, and the grain boundary semicircle is only partially visible due to high resistance (Figure 6.3.). Extrapolation of the resistivity of the bulk at low temperature was used to calculate the resistivity of bulk at high temperature, and extrapolation of the resistivity of grain boundary at high temperature was used to calculate the resistivity of grain-boundary at low temperature. Figure 6.15. shows the fitting of the $\rho''$ versus $\rho'$ plot low and high temperature which low temperature represent of bulk arc and high temperature represents grain boundary arc, respectively.
Figure 6.15. Fitting of semicircle of the $\rho''$ versus $\rho'$ plot of CCTO4 at (a) low temperature and (b) high temperature.

Then the Equation (82) was used to calculate the activation energy $E_a$ (eV), by plotted $\ln \rho$ versus $1/T$. Figure 6.16. shows the linear trend and value for grain boundary and bulk activation energy of CCTO4. The linear trends and values for grain boundary and bulk activation energy of CCTO8 and CCTO12 are shown in Figure 6.17 and Figure 6.18 respectively.

Figure 6.16. Bulk and grain boundary activation energy of CCTO4 extracted from linear trend.
Figure 6.17. Bulk and grain boundary activation energy of CCTO8 extracted from linear trend.

Figure 6.18. Bulk and grain boundary activation energy of CCTO12 extracted from linear trend.

Figure 6.19. shows a trend of activation energy of CCTO with different sintering time.

Increased sintering time can decrease the activation energy, these values are comparable with the others reported (Table 2-2.), between 0.06 and 0.18 eV, and from 0.43 to 0.72 eV for bulk and grain boundary, respectively.
6.2. Niobium and tin doped CCTO.

The effect of niobium in CCTO are described in this sub-chapter. The analysis focused on 4 hours sintering time for all concentrations of niobium doped CCTO, and a brief summary effect of sintering hold time to the niobium doped CCTO.

6.2.1. Impedance spectroscopy of CCTxN4.

Figure 6.20. to Figure 6.25. show plots of $\rho'$ versus $\rho''$ for CCT05N4, CCT10N4, CCT15N4, CCT20N4 and CCT25N4 ceramics at different temperatures, respectively. The figures did not show the bulk and grain-boundary behaviours at the same time, so a similar analysis to pure CCTO will be adopted in all niobium doped CCTO samples. The frequency range of LF Impedance Analyzer between 5 Hz and 13 MHz was used for all impedance measurements that is not wide enough to form two perfect semicircles. Figure 6.20.(a). shows only one semicircle at high temperature range and Figure 6.20.(b). also shows only initial semicircle at low temperature range.
Figure 6.20. (a) Impedance complex plane plot $\rho'$ versus $\rho''$ of CCT5N4 and (b) shows an expanded view of the high-frequency data close to the origin.

Figure 6.21. (a) shows only one semicircle in every single temperature and at expanded view Figure 6.21. (b) shows only one semicircle especially at low temperature.

Figure 6.21. (a) Impedance complex plane plot $\rho'$ versus $\rho''$ of CCT10N4 and (b) shows an expanded view of the high-frequency data close to the origin.
Figure 6.22.(a) Impedance complex plane plot $\rho'$ versus $\rho''$ of CCT15N4 and (b) shows an expanded view of the high-frequency data close to the origin.

CCT15N4 only has one semicircle as is shown in Figure 6.22.(a). and Figure 6.22.(b). shows only initial semicircle at high frequency (lower resistivity range).

Figure 6.23. (a) Impedance complex plane plot $\rho'$ versus $\rho''$ of CCT20N4 and (b) shows an expanded view of the high-frequency data close to the origin.

Figure 6.23. and Figure 6.24. show only one semicircle for all temperature. Even though, with an expanded view at high-frequency only initial semicircle was shown in Figure 6.23.(b). and Figure 6.24.(b). for CCT20N4 and CCT25N4, respectively.
Figure 6.24. (a) Impedance complex plane plot $\rho'$ versus $\rho''$ of CCT25N4 and (b) shows an expanded view of the high-frequency data close to the origin.

Table 6-7. to Table 6-11. show the result of extrapolation of resistance and fitting of capacitance of CCT05N4, CCT10N4, CCT15N4, CCT20N4 and CCT25N4, respectively. The extrapolation and fitting result of grain-boundary and bulk are showed in red and blue, respectively.

Table 6-7. Extrapolation of resistance and fitting of capacitance of CCT05N4.

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<th>Temp. (Celsius)</th>
<th>$R_b$ (Ohm)</th>
<th>CPE $\tau_b$ (F/Ohm$^2$)</th>
<th>CPE $\tau_P$ (F/Ohm$^2$)</th>
<th>$C_b$ (F)</th>
<th>$R_p$ (Ohm)</th>
<th>CPE $\tau_b$ (F/Ohm$^2$)</th>
<th>CPE $\tau_P$ (F/Ohm$^2$)</th>
<th>$C_p$ (F)</th>
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(Experimental data are shown in black and extrapolated data in blue and red).
Table 6-8. Extrapolation of resistance and fitting of capacitance of CCT10N4.
Temp.
(Celsius)
-175
-150
-125
-100
-75
-50
-25
0
25
50
100
150
200
250
300
350
400
450

Rb

CPEb-T

(Ohm)
(F/Ohm2)
84051.00 3.87E-14
24224.00 2.79E-15
7492.00 1.15E-14
2309.00 1.09E-13
688.80 2.33E-14
12608.00 9.14E-15
863.64 2.11E-13
617.98 1.37E-13
148.67 1.74E-13
117.48 1.64E-13
80.65 9.32E-14
60.52 5.71E-14
48.25 3.89E-14
40.17 3.10E-14
34.53 1.74E-14
30.42 9.10E-15
27.30 7.08E-15
24.87 3.60E-15

CPEb-P
0.98
0.98
0.98
0.99
0.99
0.99
0.98
0.99
0.98
0.97
0.98
0.98
0.99
0.98
0.98
0.99
0.99
1.00

Cb
(F)
2.53E-14
1.77E-15
6.75E-15
8.24E-14
1.70E-14
7.21E-15
1.27E-13
9.79E-14
1.02E-13
7.17E-14
5.33E-14
3.66E-14
2.69E-14
1.70E-14
1.08E-14
7.49E-15
4.85E-15
3.33E-15

Rgb

CPEgb-T

(Ohm)
(F/Ohm2)
3.54E+26 5.25E-12
1.25E+21 1.38E-11
3.08E+17 1.57E-11
8.36E+14 3.16E-11
1.01E+13 4.14E-11
3.28E+11 6.02E-11
2.13E+10 8.20E-11
2.28E+09 1.07E-10
47906000 1.61E-10
31376000 1.78E-10
14980000 2.70E-10
4101000 5.98E-10
134690 1.08E-09
34520 1.37E-09
12182 2.71E-09
5268 4.30E-09
2653 8.92E-09
1662 1.07E-08

CPEgb-P
0.96
0.98
0.96
0.98
0.97
0.98
0.99
0.99
0.98
0.99
0.99
0.97
0.96
0.99
0.97
0.98
0.97
0.97

Cgb
(F)
1.91E-11
2.44E-11
3.11E-11
3.97E-11
5.07E-11
6.47E-11
8.26E-11
1.05E-10
1.45E-10
1.67E-10
2.51E-10
4.90E-10
7.30E-10
1.21E-09
1.87E-09
3.37E-09
6.26E-09
7.43E-09

(Experimental data are shown in black and extrapolated data in blue and red).

Table 6-9. Extrapolation of resistance and fitting of capacitance of CCT15N4.
Temp.
(Celsius)
-175
-150
-125
-100
-75
-50
-25
0
25
50
100
150
200
250
300
350
400
450

Rb

CPEb-T

(Ohm)
(F/Ohm2)
2381.00 1.81E-12
7290.00 8.34E-15
2602.00 2.77E-14
980.00 2.13E-13
325.00 8.42E-14
4019.00 3.92E-14
94.50 2.10E-12
57.54 2.34E-12
38.08 9.44E-13
26.86 6.04E-13
15.38 3.37E-13
10.05 4.20E-13
7.18 3.45E-13
5.48 2.47E-13
4.38 1.69E-13
3.63 1.22E-13
3.09 6.57E-14
2.69 6.03E-14

CPEb-P
0.97
0.99
0.99
1.00
0.97
0.98
0.98
0.97
0.97
0.98
0.98
0.98
0.98
0.98
0.98
0.98
0.99
0.98

Cb
(F)
9.53E-13
6.28E-15
2.07E-14
2.07E-13
3.84E-14
2.41E-14
1.23E-12
1.12E-12
4.25E-13
3.35E-13
1.82E-13
2.35E-13
1.93E-13
1.33E-13
9.09E-14
6.70E-14
4.57E-14
3.28E-14

Rgb

CPEgb-T

(Ohm)
(F/Ohm2)
4.64E+31 1.31E-12
1.41E+25 6.74E-12
6.81E+20 1.38E-11
5.82E+17 7.57E-13
2.96E+15 2.66E-11
4.92E+13 3.22E-11
1.87E+12 4.44E-11
1.29E+11 5.58E-11
29748000 1.04E-10
9398300 1.34E-10
3454400 3.32E-10
1318300 1.45E-10
639740 2.15E-10
194960 2.18E-10
64306 6.03E-10
23178 8.74E-10
8140 1.78E-09
3151 2.37E-09

CPEgb-P
0.95
0.97
0.97
0.78
0.98
0.97
0.98
0.97
0.99
0.99
0.99
0.98
0.95
0.99
0.96
0.98
0.97
0.98

Cgb
(F)
1.77E-11
2.11E-11
2.50E-11
2.97E-11
3.52E-11
4.18E-11
4.96E-11
5.89E-11
9.64E-11
1.23E-10
3.02E-10
1.20E-10
1.41E-10
1.93E-10
3.82E-10
6.86E-10
1.23E-09
1.83E-09

(Experimental data are shown in black and extrapolated data in blue and red).

Ellyawan Arbintarso Bulk and Grain Boundary Electrical Behaviours in Nb and Sn Doped Calcium Copper Titanium Oxide

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Table 6-10. Extrapolation of resistance and fitting of capacitance of CCT20N4.

<table>
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<th>Temp. (Celsius)</th>
<th>$R_s$ (Ohm)</th>
<th>CPE$_{T}$-T</th>
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<th>$C_p$ (F)</th>
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(Experimental data are shown in black and extrapolated data in blue and red.)

Table 6-11. Extrapolation of resistance and fitting of capacitance of CCT25N4.

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</table>

(Experimental data are shown in black and extrapolated data in blue and red.)

6.2.2. Effects of sintering hold time and adding niobium to impedance spectroscopy.

Firstly CCT15N sample was chosen because this sample is has a maximum level of niobium dopant before the samples has a second phase (NbO$_x$ phase). Figure 6.25. shows the $\rho'$ versus $\rho''$ plot of CCT15N with extended sintering time to 8 and 12 hours. Figure 6.25.(b) and (d) show the expanded view of CCT15N8 and CCT15N12, respectively. The resistivity (the
length of the real part of resistivity - $\rho'$) firstly decreases then increases as sintering hold time increases. At high temperatures, the resistivity fluctuated with longer sintering time, but at low temperatures there was not a significant decrease of the resistivity.

Figure 6.25. Impedance complex plane plot $\rho'$ versus $\rho''$ of CCT15N with (a)-(b) 8 hours and (c)-(d) 12 hours sintering hold time.

Figure 6.26. shows the effect of sintering hold time at specific temperature. The low temperature is represented by -100°C and -75°C and the high temperature is represented by 75°C and 100°C. Figure 6.26.(a) and (b) show the resistivity did not change significantly with increasing temperatures (low temperatures), but Figure 6.26.(c) and (d) show at high temperatures, the resistivity decreases with longer sintering hold time.
Figure 6.26. Effect of sintering hold time to the impedance complex plane at (a) -100°C, (b) -75°C, (c) 75°C and (d) 100°C.

The effect of niobium dopant to CCTO impedance plot is shown in Figure 6.27. and 6.28. that represent the low and high temperature, respectively. Figure 6.27.(a) shows that the frequencies corresponding to the $\rho''$ (= $Z''$.A/t) peak in the impedance spectroscopic plot. The relaxation frequencies of $\rho''$ peaks were assumed between 10 and 100 Hz, while the frequencies at the $M''$ peak were higher than 1 MHz, at low temperature (is represented by -100°C) as is shown in Figure 6.27.(b).
There are three similar aspects among the samples with dopant. The resistance decreased and capacitance increased with increasing temperatures, and the modulus spectra at different temperature were similar, except at when there was high second phase. In this case, the M'' peak depends on the concentration of niobium dopant. The highest M'' peak is CCT20N4 and the lowest M'' peak is CCT05N4. In general, only one relaxation process can be seen in all forms of representations, and the relaxation fluctuated with the concentration of niobium dopant.

Figure 6.28. shows at high temperature (100°C), the frequencies corresponding to the ρ'' peak in the impedance spectroscopic plot fluctuated which depend on the concentration of niobium dopant. The frequencies were between 100 Hz and 100 kHz, while the frequencies at the M'' peak shifted to right with the peak at frequencies higher than 10 MHz (instrument limit), except the CCT20N4.

Figure 6.27. Bode plots of CCTxN4 (a) ρ'' and (b) M'' as a function of log f with different composition at -100°C.
6.3. Tin doped CCTO.

The effect of tin in CCTO are described in this sub-chapter. Identical with niobium doped CCTO, the analysis focused on 4 hours sintering time for all concentrations of tin doped CCTO, and a brief summary effect of sintering hold time to the tin doped CCTO.

6.3.1. Impedance spectroscopy of CCTxS4.

Figure 6.29. to Figure 6.33. show plots of $\rho'$ versus $\rho''$ for CCT05S4, CCT10S4, CCT15S4, CCT20S4 and CCT25S4 ceramics at different temperatures, respectively. There were not significant showed the bulk and grain-boundary behaviours in the same time in those figures, so a similar analysis to pure and niobium doped CCTO will be adopted in all tin doped CCTO samples.
Figure 6.29. (a) Impedance complex plane plot \( \rho' \) versus \( \rho'' \) of CCT5S4 and (b) shows an expanded view of the high-frequency data close to the origin.

Figure 6.30. (a) Impedance complex plane plot \( \rho' \) versus \( \rho'' \) of CCT10S4 and (b) shows an expanded view of the high-frequency data close to the origin.

Figure 6.29. Figure 6.30. and Figure 6.31. show only one semicircle for all temperature. The expanded views at high-frequency show development of semicircle, which increases concentration dopant generates semicircle as seen in Figure 6.29.(b). 6.30.(b). and Figure 6.31. (b). for CCT05S4, CCT10S4 and CCT15S4, respectively. In this case, for instance, resistivity of semicircle (\( \rho'' \)) at low temperature (-100°C) increases with increasing concentration tin dopant.
Figure 6.31. (a) Impedance complex plane plot $\rho'$ versus $\rho''$ of CCT15S4 and (b) shows an expanded view of the high-frequency data close to the origin.

Figure 6.32. (a) Impedance complex plane plot $\rho'$ versus $\rho''$ of CCT20S4 and (b) shows an expanded view of the high-frequency data close to the origin.

At CCT20S4, the resistivity of semicircle ($\rho''$) at low temperature (-100°C) lower than CCT15S4 as is shown in Figure 6.32.(b). On the other hand, at CCT25S4, the resistivity of semicircle ($\rho''$) at low temperature (-100°C) higher than CCT15S4 as is shown in Figure 6.33. (b). It seem, an unexpected result was obtained from CCT20S4 at low temperature between 0 and -100°C (high frequency).
Figure 6.33. (a) Impedance complex plane plot \( \rho' \) versus \( \rho'' \) of CCT25S4 and (b) shows an expanded view of the high-frequency data close to the origin.

Table 6-12. to Table 6-16. show the result of extrapolation of resistance and fitting of capacitance of CCT05S4, CCT10S4, CCT15S4, CCT20S4 and CCT25S4, respectively. The extrapolation and fitting result of grain-boundary and bulk are showed in red and blue, respectively.

Table 6-12. Extrapolation of resistance and fitting of capacitance of CCT05S4.

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<th>( C_b ) (F)</th>
<th>( R_p ) (Ohm)</th>
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(Experimental data are shown in black and extrapolated data in blue and red).
Table 6-13. Extrapolation of resistance and fitting of capacitance of CCT10S4.

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Table 6-14. Extrapolation of resistance and fitting of capacitance of CCT15S4.

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<th>CPE$_{-P}$ (F)</th>
<th>$R_p$ (Ohm)</th>
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(Experimental data are shown in black and extrapolated data in blue and red).
Table 6-15. Extrapolation of resistance and fitting of capacitance of CCT20S4.

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<tr>
<th>Temp. (Celsius)</th>
<th>$R_s$ (Ohm)</th>
<th>CPE$_{s-T}$ (F/Ohm)$^2$</th>
<th>CPE$_s$ (F)</th>
<th>$R_p$ (Ohm)</th>
<th>CPE$_{p-T}$ (F/Ohm)$^2$</th>
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(Experimental data are shown in black and extrapolated data in blue and red).

Table 6-16. Extrapolation of resistance and fitting of capacitance of CCT25S4.

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<th>CPE$_s$ (F)</th>
<th>$R_p$ (Ohm)</th>
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</table>

(Experimental data are shown in black and extrapolated data in blue and red).

6.3.2. Effects of sintering hold time and adding tin dopant to impedance spectroscopy.

The effect of tin dopant to CCTO impedance plot is shown in Figure 6.34. and 6.35. that represent the low and high temperature, respectively. Figure 6.34.(a) shows plot $\rho''$ as a function of frequencies which the $\rho''$ peak did not appear in this plot. The relaxation frequencies of $\rho''$ peaks were assumed between 10 and 100 Hz, while the frequencies at the $M''$ peaks were
higher than 1 MHz, at low temperature (is represented by -100°C) is shown in Figure 6.34.(b).

![Figure 6.34](image1.png)

**Figure 6.34.** Bode plots of CCTxS4 (a) $\rho''$ and (b) $M''$ as a function of log f with different composition at -100°C.

Identical with CCT20N4, unexpected result was found in CCT20S4, the value is lowest than the others. In general, only one relaxation process can be seen in all forms of representations, and the $M''$ increases with increasing concentration dopant.

![Figure 6.35](image2.png)

**Figure 6.35.** Bode plots of CCTxS4 (a) $\rho''$ and (b) $M''$ as a function of log f with different composition at 100°C.

Figure 6.35. shows at high temperature (100°C), the $\rho''$ peak depends on the concentration of tin dopant which the frequencies were between 100 Hz and 100 kHz, except...
CCT10S4 as shown in Figure 6.35.(a). On the other hand, Figure 6.35.(b) shows the frequencies at the M" peaks shifted to right side and were higher than 10 MHz, except the CCT20S4.

6.4. Dielectric Constant, Dielectric Loss and Capacitance of Doped CCTO.

Three threads of investigation also applied to the niobium doped CCTO. The first investigated the relative dielectric constant per unit length ($\varepsilon_{\text{eff}}'$), dielectric loss ($\tan \delta$) and relative capacitance ($C'$) of niobium and tin doped CCTO. The second focussed on effect of increasing temperature on $\varepsilon_{\text{eff}}'$, $\tan \delta$ and $C'$ of niobium and tin doped CCTO. The studied effect of frequencies on $\varepsilon_{\text{eff}}'$, $\tan \delta$ and $C'$ of niobium and tin doped CCTO is the third.

The same dielectric analysis methods of pure CCTO was used to analysis the niobium and tin doped CCTO in 4 hours sintering time. Figure 6.36. shows the equivalent and relative dielectric constant and grain boundary thickness versus temperature of the niobium doped CCTO. The dielectric constant increases when temperature increases from low temperature to room temperature, then decreases as temperature increases from room temperature to high temperature. This phenomenon also behaved toward the grain boundary thickness. Increasing niobium and tin dopant in small amount increase the dielectric constant but in large amount will decrease the dielectric constant as secondary phase emerged. It seems the dopant increases the conductivity of niobium and tin doped CCTO.

In Figure 6.37., the real part of relative dielectric constant of niobium and tin doped CCTO are plotted as a function of temperature at specific frequency. At low frequency (1 kHz), dielectric constant increases when temperature increases, but increasing frequency does not increase the (real part of relative) dielectric constant. The dielectric constant tends to decrease when frequency increases at all temperatures range. The effect of temperature to these results is comparable to Grubbs et. al. [2] that found dielectric constant decreases with decreasing temperature (below -75°C) from 10000 to 100. Figure 6.37 also shows the dielectric constant at temperature transition. At high temperature (above 25°C), the dielectric constant decreases for some large amount dopant, indicates the dopant increase the conductivity of sample.
Figure 6.36. $\varepsilon_{eq}$, $\varepsilon_{eff}$, and $t_{gb}$ of a) CCT05, b) CCT10, c) CCT15, d) CCT20, and e) CCT25.
Figure 6.37. Dielectric constant of CCTxN4 and CCTxS4 at various frequencies.
Figure 6.38. shows the dielectric constant of niobium and tin doped CCTO in specific temperature as a function of frequencies. Most papers reported dielectric constant decreases as frequency increases at room temperature for all niobium doped CCTO (Hong et. al.[3], Liu et. al. [63], Sulaiman et. al.[125]) that comparable to Figure 6.38.(b).

Figure 6.38.(a) shows the real part of relative dielectric constant at -100°C where the relaxation (the peak of dielectric constant) similar to dielectric constant at 25°C but the frequency of relaxation was lower than at 25°C. Figure 6.38.(c) and (d) have similar relaxation behaviour but increasing temperature lead to increases frequency of relaxation. The relaxation shifted from low-frequency to high-frequency with increasing temperature, indicates the change dielectric response from grain boundary to bulk, from less conductive to more conductive.

Dielectric loss of CaCu$_3$Ti$_{4-x}$M$_x$O$_{12}$ with 4 hours sintering hold is shown in Figure 6.38. At low frequency (1 kHz), the dielectric loss reached higher for all samples at low temperature and the dielectric loss decreased with increasing temperature. Figure 6.38. also shows the dielectric loss decreased with increasing frequency. The dielectric loss reached a maximum especially in samples with high residual phase. There is not significant correlation between dielectric constant and dielectric loss in the same range of relaxation frequency. The dielectric constant and dielectric loss depends on concentration of dopant, temperature and frequency.
Figure 6.38. Real part of relative dielectric constant of CCTxN4 and CCTxS4 as a function of frequency (a) -100°C, (b) 25°C, (c) 100°C, and (d) 200°C.
The relative capacitance of sample (C’) of niobium and tin doped CCTO are plotted as a function of temperature at specific frequency is shown in Figure 6.39.

Figure 6.39. C’ of CCTxN4 and CCTxS4 as a function of temperature at specific frequency.

Figure 6.40. and 6.41. show the bulk and grain boundary capacitance of niobium and tin doped CCTO, respectively. The grain boundary capacitance increases as temperature increases for both niobium and tin doped CCTO, but the bulk capacitance depends on temperature and the concentration of dopant.
Figure 6.40. (a) Bulk and (b) grain boundary capacitance of CCTxN4.

Figure 6.41. (a) Bulk and (b) grain boundary capacitance of CCTxS4.

The resulting bulk and grain boundary capacitance were converted to grain boundary thickness by using Equation (61) (see section 2.3.6.3.). The grain boundary thickness of niobium doped CCTO in temperature range between -100°C and 100°C is shown in Figure 6.42. The grain boundary thickness depends on the temperature and concentration of dopant and spreads between 0.01 and 0.001 μm, dominantly.

Figure 6.42. Grain boundary thickness versus temperature plot of CCTxN4.
Figure 6.43. shows the grain boundary thickness of tin doped CCTO in temperature range between -100°C and 100°C. Identical with the niobium doped CCTO, the grain boundary thickness of tin doped CCTO depends on the temperature and concentration of dopant and spreads widely between 0.1 and 0.0001, except for CCT25S4. These grain boundary thickness results will be correlated to non-linear coefficient of conduction results in chapter 7.

Figure 6.43. Grain boundary thickness versus temperature plot of CCTxS4.

6.5. Activation Energy of Doped CCTO.

Table 6-17. shows the activation energy of niobium and tin doped CCTO, and then was described in Figure 6.44 and 6.45. to show a trend of activation energy with adding dopant.

<table>
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<th>Activation Energy (eV)</th>
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<th>Grainboundary</th>
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<td>CCT10N4</td>
<td>0.080 ± 0.0074</td>
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<td>0.075 ± 0.0142</td>
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<td>0.071 ± 0.0025</td>
<td>0.511 ± 0.0326</td>
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</tbody>
</table>

Figure 6.44. shows in general, the activation energy of bulk and grain boundary decreased with increasing the amount of niobium dopant. These results about separate bulk
and grain boundary activation energy for niobium doped CCTO (see Table 2-2 for pure CCTO) have not been previously reported. The activation energies were between 0.06 and 0.10 eV, and from 0.50 to 0.70 eV for bulk and grain boundary, respectively. The low activation energy indicated the bulk has highly conductivity and the high activation energy indicated the grain-boundary has highly resistivity (low conductivity).

![Figure 6.44. Activation Energy as a function of concentration of niobium dopant at 4 hours sintering time.](image)

The activation energy of bulk and grain boundary of tin doped CCTO is shown in Figure 6.45. The bulk activation energy decreased with increasing the amount of tin dopant, but grain boundary activation energy did not decrease with increasing the amount of tin dopant. The result was comparable to Ni et. al. [23] reports; the bulk activation energies were between 0.10 and 0.11 eV for 0.05 and 0.10 mol tin doped CCTO, respectively.

![Figure 6.45. Activation Energy as a function of concentration of tin dopant at 4 hours sintering time.](image)
6.6. Summary of observation on impedance of CCTO.

In summary, the relative dielectric constant per unit length and the dielectric loss of CCTO sintered for 4, 8 and 12 hours increased with increases in the temperature, and decreases as frequency increases. At high temperature range up to 200°C, the values of the relative dielectric constant are almost identical, then with further increasing temperature, the relative dielectric constant increases rapidly at low frequency (1-10 kHz). On the other hand, at low frequency (1 kHz), dielectric constant of niobium and tin doped CCTO increases when temperature increases, but increasing frequency does not increase the (real part of relative) dielectric constant. The dielectric constant tends to decrease when frequency increases at all temperatures range. At high temperature (above 25ºC), the dielectric constant decreases for some large amount dopant, indicating that the dopant increases the conductivity of sample. The relaxation frequency of all the samples shifted to higher values with increasing temperature, indicating that the dielectric response move from grain boundary to bulk, from less conductive to more conductive. The activation energy of bulk and grain boundary decreased with increasing the amount of niobium dopant. The low activation energy indicated the bulk has high conductivity and the high activation energy indicated the grain-boundary has high resistivity (low conductivity). On the other hand, the bulk activation energy decreased with increasing the amount of tin dopant, but grain boundary activation energy did not decrease with increasing the amount of tin dopant. As a result the variation of grain boundary thickness depends on the temperature and sintering hold time.
7. Varistor Properties of CCTO.

In this chapter, the varistor properties of CaCu$_3$Ti$_4$O$_{12}$ are presented as non-linear coefficient of conduction ($\alpha$), barrier height ($\Phi_B$), and breakdowns voltage field ($E_b$). The work is broken down into two sections focusing on pure CCTO and on CCTO doped with niobium and tin, respectively. Three different sintering hold times were applied to both the pure CCTO and the doped CCTO. The composition and microstructure of pure CCTO (CCTOx), niobium doped CCTO (CCTxNy) and tin doped CCTO (CCTxSy) samples were described in chapter 4. Current density in the range of 1 mA/cm$^2$ and 11 mA/cm$^2$ was used to determine non-linear coefficient of conduction for all samples. Sample thickness (t) in the range of 0.1 cm and 0.2 cm and surface area (A) in the range of 0.53 cm$^2$ and 0.60 cm$^2$ were used in this study, and all data presented as current density (J) as function of voltage field (E).

7.1. Pure CCTO.

7.1.1. non-linear coefficient of conduction of pure CCTO.

Three regions of electrical operation was applied in J - E plot i.e. leakage region, normal operation, and upturn region is shown in Figure 7.1. Based on Levine [10], the leakage region applies ohmic condition where the ratio of E and J is high, the normal (varistor) region has a gradient curve which is given by Equation (65), and upturn region where J reaches high level. In this study, current density in the range of 1 mA/cm$^2$ and 11 mA/cm$^2$ was a linear region (normal operation), from which the non-linear coefficient of conduction will be determined using Equation (65), $J = (E/C)^\alpha$. The higher $\alpha$ increases ability of varistor to clamp the over-voltage and protects the electrical circuit from current surges.

Equation (65) was modified to calculate the non-linear coefficient of conduction ($\alpha$) as shown in Equation (86).

$$\alpha = \frac{d \ln(J)}{d \ln(E/C)} \quad .......................... (86)$$

The normal operation for CCTO4 was in the range of 2 mA/cm$^2$ and 10.5 mA/cm$^2$. It was slightly different with CCTO8 that the normal operation was in the range of 1 mA/cm$^2$ and 11 mA/cm$^2$. On the other hand, a normal operation of CCTO12 was in the range of 2 mA/cm$^2$ and...
11 mA/cm². The average sample thickness of CCTO was 0.16 ± 0.05 cm and surface area of CCTO was 0.537 ± 0.007 cm². Figure 7.1, shows plots of J as function of E of CCTO with different sintering hold time, i.e. 4, 8 and 12 hours, respectively.

![Figure 7.1. Current density (J) - voltage field (E) diagram showing the non-linear behaviour of CCTO.](image)

It can be seen that the CCTO4 exhibits the highest breakdown voltage field whilst CCTO8 has the lowest breakdown voltage field. CCTO4 needs higher voltage to become electrically conductive than CCTO8, increases sintering hold time makes the sample more conductive. During the measurement of J with E, a lowest value of non-linear coefficient of conduction was found for CCTO8 (53), compared to CCTO4 (167) and CCTO12 (243) as shown in Figure 7.2.

![Figure 7.2. non-linear coefficient of conduction of CCTO at difference sintering hold time.](image)

In this study, an unexpected result was obtained from CCTO12, since increasing the...
sintering hold time would be expected to decrease the nonlinear coefficient [45]. However, the non-linear coefficient of conduction of CCTO12 is higher than CCTO4 and CCTO8. This trend was drawn and checked on three samples and each with five measurement.

The non-linear coefficient of conduction measured here are ten to forty times higher than many other reported data [24-29, 45] (see Table 2-3) but are lower than Chung et. al. [7] found. Two factors that affect to the non-linear coefficient of conduction are current density range and voltage rate (increasing voltage per second applied when measures the current). For instance, Chung et. al. [7] used high current density range (5-100 mA/cm²) to determine the non-linear coefficient of conduction, and found 900. This result is equal with an value 90 for current density range of 0-10 mA/cm² [128]. Lu et. al. [129] reported that voltage rate significantly decreased the non-linear coefficient of conduction, from 330 to 6.2 as voltage rate increased from 0.1 V/s to 100 V/s. In this study, a slope method was used to determine the non-linear coefficient of conduction as mentioned in Application Note AN9767.1. [12].

7.1.2. Barrier height of pure CCTO.

The effect of grain boundary on the I–V behaviour was described by Zang et. al. [8] using a Schottky barrier relationship. If a Schottky barrier applies at the grain boundary among the grains, based on the ohmic contact region, the relation between electrical current density (J) and the applied electrical field (E) will follow the formula [17]:

\[
\ln \left( \frac{J}{AT^2} \right) = \left( \frac{\beta}{k_B T} \right) E^{1/2} - \frac{\Phi_B}{k_B T} \]

(86)

where \( J \) is current density (mA/cm²), \( A \) is the Richardson constant (120.173 A/cm²K²), \( T \) is the temperature (K), \( \beta \) is a constant related to the potential barrier width, \( k_B \) is the Boltzmann constant (8.617324.10⁻⁵ eV/K), \( E \) is voltage field (kV/cm) and \( \Phi_B \) is the barrier height (eV). The plot of \( \ln(J/AT^2) \) and \( E^{1/2} \) give a linear relationship from which \( \Phi_B \) can be obtained. \( J_0 \) is a datum of \( J \) at upturn region when \( E = 0 \), \( J_0 \) can be obtained by extrapolates the linear curve of \( E - J \) through the y axis (Figure 7.3).
The barrier height can be estimated by fitting the corresponding \( \ln(J_0) \) as function of 1/T curve as shown in Equation (87) and calculated using Equation (88).

\[
\ln J_0 = \ln AT^2 - \frac{\Phi_B}{k_B T} \tag{87}
\]

\[
\Phi_B = k_B T \ln\left(\frac{AT^2}{J_0}\right) \tag{88}
\]

Figure 7.4. shows the barrier height (\( \Phi_B \)) and datum of current density (\( J_0 \)) of CCTO at different sintering hold times. The barrier heights of CCTO12 is higher than the others, as a reason that the non-linear coefficient CCTO12 has high value. This phenomenon is rarely since increasing the sintering hold time would be expected to decrease the barrier height.

**Figure 7.3.** A datum of J at upturn region of E – J plot.

**Figure 7.4.** Barrier height and datum of current density of CCTO at different sintering hold times.
7.1.3. Breakdown voltage field of pure CCTO.

The breakdown voltage field ($E_b$), which determined at the current density of 1 or 2 mA/cm$^2$ based on the normal operation region, is shown in Figure 7.5. Considering the breakdown voltage field as a function of sintering hold time, the $E_b$ value of CCTO12 is different. The breakdown voltage field varies ~1100 V/cm, ~200 V/cm and ~1000 V/cm for the CCTO4, CCTO8 and CCTO12, respectively. In general, it has been reported that longer sintering hold times build lower breakdown voltage field [45, 127], in this study, the CCTO12 was found to have a breakdown voltage field higher than CCTO8. On the other hand the breakdown voltage fields were lower than reported [24-29, 45].

![Figure 7.5. Breakdown voltage field of pure CCTO at difference sintering hold time.](image)

The breakdown voltage field is typically related to grain size. A smaller grain size can effectively increase the breakdown voltage field because the number of grain boundaries per unit thickness of specimen increases which increases the number of barrier layer of capacitance. The breakdown voltage field increases with decreasing grain size consistent with Chung et. al. [7]. In this work, an unexpected result was obtained from the CCTO12. The average large grain size of CCTO12 (22.7 $\mu$m) is larger than CCTO8 (18.0 $\mu$m) and CCTO4 (15.8 $\mu$m) as is presented in Table 5.1. (detail), but the breakdown voltage field of CCTO12 is higher than CCTO8 as shown in Figure 7.6.
Considering the small and large grain in pure CCTO, the CCTO12 was dominant with a large grain size and did not indicate has a small grain size. Clarke [103] argued that the voltage over an individual grain boundary is not linearly dependent on the voltage applied to the whole of varistor. Varistor as a polycrystalline material has a large number of individual boundaries with different characteristics.

7.2. Niobium Doped CCTO.

7.2.1. non-linear coefficient of conduction of niobium doped CCTO.

Current density in the range of 1 mA/cm$^2$ and 11 mA/cm$^2$ was used to determine non-linear coefficient of conduction for all niobium doped CCTO samples. Sample size for individual studies varied, ranging from 0.08 and 0.20 cm, and from 0.52 and 0.58 cm$^2$ for sample thickness and surface area, respectively. The current density - voltage field characteristics of niobium doped CCTO with 4 hours sintering hold time is shown in Figure 7.7. It can be seen that the CCT10N4 exhibits the highest breakdown voltage field whilst CCT25N4 has the lowest breakdown voltage field. The CCT10N4 showed the maximum breakdown voltage field of ~5000 V/cm. The Figure 7.7. shows the breakdown voltage fields of niobium doped CCTO vary depending on the amount of dopant, increases dopant up to 0.10 mol niobium increased breakdown voltage fields then further increases dopant decreased breakdown voltage fields.
Figure 7.7. Current density-voltage field characteristics of niobium doped CCTO with 4 hours sintering hold time.

Figure 7.8. shows the J - E characteristics of niobium doped CCTO with 8 hours sintering hold time. CCT05N8 displays the highest breakdown voltage field whilst CCT25N8 has the lowest breakdown voltage field. The CCT05N8 showed the maximum breakdown voltage field of ~4500 V/cm.

Figure 7.8. Current density-voltage field characteristics of niobium doped CCTO with 8 hours sintering hold time.
The plot of J - E of niobium doped CCTO with 12 hours sintering hold time is shown in Figure 7.9. Identical to 8 hours sintering hold time, CCT05N12 displays the highest breakdown voltage field whilst CCT20N12 has the lowest breakdown voltage field. The CCT05N12 showed the maximum breakdown voltage field of \(~1500\) V/cm. It was a lowest breakdown voltage field result when it compared to breakdown voltage field at 4 and 8 hours sintering hold times.

![Figure 7.9. Current density-voltage field characteristics of niobium doped CCTO with 12 hours sintering hold time.](image)

The non-linear coefficient of conduction of niobium doped CCTO is determined from the current density across the range between 1 and 11 mA/cm\(^2\). The non-linear coefficient of conduction of niobium doped CCTO with different sintering hold times is shown in Figure 7.10. It is found that the non-linear coefficient of conduction of niobium doped CCTO varies with the amount of dopant present. The \(\alpha\) value of 4 hours sintering hold time increases with the amount of dopant increases up to 0.10 mol niobium, then decreases as the amount of dopant increases. Identical to 4 hours sintering hold times, the non-linear coefficient of conduction of 12 hours sintering hold time increases with the amount of dopant increases up to 0.05 mol niobium, then decreases as the amount of dopant increases. On the other hand, 8 hours sintering hold times reached highest value at 0.20 mol niobium and tends to decrease as the amount of dopant increases. It is because the sintering time has different influence on the values of dielectric
constant and nonlinear coefficient of the sintered samples due to the barrier height having a reverse effect on the values of the dielectric constant and non-linear coefficient of conduction [130].

7.2.2. The barrier height of niobium doped CCTO.

Figure 7.11.(a) and (b) show the barrier height (Φ_b) and datum of current density (J_0) of niobium doped CCTO as a function of the amount of dopant, respectively. The barrier height tends to decrease as the amount of dopant increases, while the datum of current density (J_0) tends to increase as the amount of dopant increases. The values of Φ_b vary in range between ~173 and 179 eV, and the values J_0 vary from 10 to ~13 mA/cm² for all niobium doped CCTO and all sintering hold times.

The non-linear coefficient of conduction depends on the the amount of dopant and sintering hold time. These results were higher than other reports as presented in Table 2-5. The maximum value of non-linear coefficient of conduction of niobium doped CCTO was 636 at 0.10 mol niobium doped CCTO at 4 hours sintering hold time. The non-linear coefficient of conduction increased with increasing dopant substitution only at 8 hours sintering hold time as shown in Figure 7.10. These result will be discussed later in chapter 8.
7.2.3. The breakdown voltage field of niobium doped CCTO.

The breakdown voltage field \( (E_b) \) of niobium doped CCTO, was determined at the current density of 1 or 2 mA/cm\(^2\) (depends on the normal operation region), is shown in Figure 7.12. Figure 7.12.(a) shows the breakdown voltage field \( (E_b) \) of niobium doped CCTO as function of the amount of dopant. The \( E_b \) tends to decrease as the amount of dopant increases. Figure 7.12.(b) shows the \( E_b \) of niobium doped CCTO as function of sintering hold time. The \( E_b \) varies dependent on sintering hold time. The breakdown voltage field varies from \( \sim 100 \) to \( \sim 5000 \) V/cm, \( \sim 200 \) to \( \sim 4500 \) V/cm and \( \sim 200 \) to \( \sim 1500 \) V/cm for the 4, 8 and 12 hours sintering hold time, respectively.

Identical with pure of CCTO, the breakdown voltage field niobium doped CCTO are typically related to grain size. The \( E_b \) would be expected to rise up when the grain size decreases, which is similar to other reported [25, 29, 71]. Even though the niobium doped CCTO has dominantly small grain size – less than 2 \( \mu \)m in average (see Figure 5.38) and the grain size decreased as amount of dopant increases that cannot effectively increase the breakdown voltage field. Moulson and Herbert [33] described the intrinsic factor as flaw or structural feature (non uniform grain size) leads to a local intensification of an applied electrical field and reduce the breakdown voltage.
Figure 7.12. Breakdown voltage field of niobium doped CCTO as function of (a) the amount of dopant, (b) sintering hold times.

7.3. Tin Doped CCTO.

7.3.1. non-linear coefficient of conduction of tin doped CCTO.

Similarity with previous study, current density in the range of 1 mA/cm$^2$ and 11 mA/cm$^2$ was used to determine non-linear coefficient of conduction for all tin doped CCTO samples. Sample size for individual studies varied, ranging from 0.09 and 0.20 cm, and from 0.53 and 0.60 cm$^2$ for sample thickness and surface area, respectively. The current density - voltage field characteristics of tin doped CCTO with 4 hours sintering hold time is shown in Figure 7.13. Identical to niobium doped CCTO, the CCT10S4 exhibits the highest breakdown voltage field whilst CCT25S4 has the lowest breakdown voltage field.

The CCT10S4 showed the maximum breakdown voltage field of $\sim$9500 V/cm. Figure 7.13. shows the various breakdown voltage fields of tin doped CCTO will be dependent on the amount of dopant. Again, the breakdown voltage field is the minimum voltage that causes a grain-boundary (as insulator) to become electrically conductive. The higher breakdown voltage field need higher voltage to change grain-boundary more conductive.
Figure 7.13. current density - voltage field characteristics of tin doped CCTO with 4 hours sintering hold time.

Figure 7.14. shows the current density - voltage field plot of tin doped CCTO with 8 hours sintering hold time. In contrast with niobium doped CCTO (Figure 7.8.), CCT10S8 displays the highest breakdown voltage field whilst CCT08 has the lowest breakdown voltage field. The CCT10S8 showed the maximum breakdown voltage field of ~11500 V/cm.

Figure 7.14. Current density-voltage field plot of tin doped CCTO with 8 hours sintering hold time.
The J - E characteristics of tin doped CCTO with 12 hours sintering hold time is shown in Figure 7.15. Identical to niobium doped CCTO, CCT05S12 displays the highest breakdown voltage field whilst CCT25S12 has the lowest breakdown voltage field. The CCT05S12 showed the maximum breakdown voltage field of ~1500 V/cm.

![Figure 7.15. Current density-voltage field characteristics of tin doped CCTO with 12 hours sintering hold time.](image)

Using the same range of niobium doped CCTO, the non-linear coefficient of conduction of tin doped CCTO is also determined from the current density across the range between 1 and 11 mA/cm². The non-linear coefficient of conduction of tin doped CCTO with different sintering hold times is shown in Figure 7.16.

![Diagram showing non-linear coefficient of conduction](image)
The non-linear coefficient of conduction of tin doped CCTO varied with the amount of dopant. The $\alpha$ value of 4 hours sintering hold time increases with the amount of dopant up to 0.15 mol tin, then decreases as the amount of dopant increases. Identical to 4 hours sintering hold times, the non-linear coefficient of conduction of 12 hours sintering hold time increases with the amount of dopant up to 0.10 mol niobium, then decreases as the amount of dopant increases further. On the other hand, 8 hours sintering hold times, $\alpha$ gradually increases and reached highest value at 0.25 mol tin. The non-linear coefficient of conduction depends on the the amount of dopant and sintering hold time. These results were higher than other reports as presented in Table 2-5. The maximum value of non-linear coefficient of conduction of tin doped CCTO was 813 at 0.15 mol tin doped CCTO at 4 hours sintering hold time. This is highest value in this study. The non-linear coefficient of conduction increased with increasing dopant only at 8 hours sintering hold time as shown in Figure 7.16. for tin doped CCTO. These result will be discussed later in chapter 8.

7.3.2. Barrier height of tin doped CCTO.

Figure 7.17.(a) and (b) show the barrier height and $J_0$ of tin doped CCTO as function of dopant, respectively. $\Phi_b$ tends to decrease as the amount of dopant increases, and $J_0$ tends to
increase as the amount of dopant increases. In general, the barrier height of tin doped CCTO is higher than niobium doped CCTO with identical trend of curves.

![Graph of barrier height and current density](image)

Figure 7.17. Barrier height and datum of current density of tin doped CCTO as function of the amount of dopant (a and b) and sintering hold times (c and d).

The values of $\Phi_B$ vary in range between ~173 and 180 eV, and $J_0$ vary from ~9 to ~13 mA/cm$^2$. The range of $\Phi_B$ and $J_0$ are wider than niobium doped CCTO (see Figure 7.11). Figure 7.17. shows the various of $\Phi_B$ and $J_0$ with different sintering hold time.

### 7.3.3. Breakdown voltage field of tin doped CCTO.

The same method of niobium doped CCTO was used to determine breakdown voltage field of tin doped CCTO, which determined at the current density of 1 mA/cm$^2$, are shown in Figure 7.18. The $E_b$ of tin doped CCTO as function of the amount of dopant is shown in Figure 7.18.(a). The breakdown voltage field tends to decrease as the amount of dopant increases only at 12 hours sintering hold time, and the others tend to increase as the amount of dopant increases. Figure 7.18.(b) shows the $E_b$ of tin doped CCTO as function of sintering hold time which shows the 12 hours sintering hold time has lower breakdown voltage field. Even though, the $E_b$ varies in result still depends on sintering hold time. The $E_b$ value varies from ~1100 to ~9200 V/cm, ~200 to ~11100 V/cm and ~100 to ~1200 V/cm for the 4, 8 and 12 hours sintering hold time, respectively.
7.18. Breakdown voltage field of tin doped CCTO as function of (a) the amount of
dopant, (b) sintering hold times.

Identical with niobium doped of CCTO, the breakdown voltage field of tin doped CCTO
are typically related to grain size. Many worker [25, 29, 71] reported that the $E_b$ rises up when
the grain size decreases. The tin doped CCTO has a combination of large and small grain size
which the grain size tends to decrease as the amount of dopant increases (Figure 5.39. and
5.40.). In this work, only results were obtained from the CCTxS4 and CCTxS8 are consistent
with other reported [25, 29, 71] that the breakdown voltage field increases with decreasing grain
size. Both of them show the increasing of breakdown voltage field as the amount of dopant
increases (the average grain size decreases as the amount of dopant increases).

7.4. Summary of observation of varistor properties of CCTO.

In summary of varistor properties of pure CCTO, an unexpected result was obtained
from CCTO12, since increasing the sintering hold time would be expected to decrease the
nonlinear coefficient [45]. However, the non-linear coefficient of conduction, the breakdown
voltage, and barrier height of CCTO12 is higher than CCTO4 and CCTO8. The non-linear
coefficient of conduction depends on the breakdown voltage and barrier height that typically
related to grain sizes. A smaller grain size can effectively increase the breakdown voltage field
because the number of grain boundaries per unit thickness of specimen increases which
increases the number of barrier layer of capacitance.
The non-linear coefficient of conduction of niobium doped CCTO varies with the amount of dopant present and sintering hold time. The dopant and sintering time have different influenced on the values of dielectric constant and nonlinear coefficient of the sintered samples due to the barrier height having a reverse effect on the values of the dielectric constant and non-linear coefficient of conduction. The maximum value of non-linear coefficient of conduction of niobium doped CCTO was 636 at 0.10 mol niobium at 4 hours sintering hold time.

The non-linear coefficient of conduction of tin doped CCTO depends on the the amount of dopant and sintering hold time. Similar to pure and niobium doped CCTO, the dopant and sintering hold time have significantly effect to varistor properties of tin doped CCTO. The maximum value of non-linear coefficient of conduction of tin doped CCTO was 813 at 0.15 mol tin at 4 hours sintering hold time.
8. Relationship Among The Phase Equilibria, Microstructure, and Electrical Properties of Doped CCTO.

8.1. Influence of Sintering Hold Time.

This section focuses on the influence of sintering hold time on the evolution of secondary phase, evolution of microstructure and electrical properties of CCTO. The results are extracted from chapter 4, 5, and 6 to 7 for secondary phase, microstructure, and electrical properties, respectively.


The focus on influence of sintering hold time to the evolution of secondary phase is presented on concentration of selected elements by EDS and XRF. The basic mole ratio of CCTO (CaCu$_3$Ti$_4$O$_{12}$) is 1:3:4:12 for calcium, copper, titanium and oxygen respectively. The basic mole ratio of CCTxM (CaCu$_3$Ti$_{4-x}$M$_x$O$_{12}$) is 1:3:(4-x):x:12 for calcium, copper, titanium, dopant, and oxygen, respectively. The secondary phase was as different mole ratio of element with different sintering hold time were studied.

8.1.1.1. Pure CCTO.

Figure 8.1. shows concentration for selected elements of pure CCTO by EDS with different sintering hold time, which was extracted from Table 5-16. At 4 and 8 hours sintering hold time, there were two type of grain, large and small grains. The mole ratio of the elements at 4 hours sintering is different from the other sintering hold time. There is the presence CaTiO$_3$ as a secondary phase at 4 hours sintering hold time (see Figure 5.41.), then with increasing sintering hold time, the CaTiO$_3$ decreases. The CaTiO$_3$ is common phase in ternary system CuO-TiO$_2$-CaO [131], where CaCu$_3$Ti$_4$O$_{12}$ belongs to them. This result also in line with what Ni et al. [72] reported, where they used 3, 6, and 12 hours sintering hold time. Increasing sintering hold time makes the grain size more uniform and the mole ratio of the elements approach the intended ratio.

Figure 8.2. shows concentration for selected elements of pure CCTO by XRF with
different sintering hold time, which was extracted from Table 5-15. The mole ratio of concentration of copper was higher than basic mole ratio (more than 3), and consequently, the concentration of titanium was lower than 4. Figure 8.2. does not show significant differences in mole ratio over all the sintering hold times. The other is Fe and Zr in all of samples.

Figure 8.1. Concentration for selected elements of pure CCTO by EDS with different sintering hold time. (L = large grain, S = small grain, the error bars are less than 0.14).

Figure 8.2. Concentration for selected elements of pure CCTO by XRF with different sintering hold time (The error bars are less than 0.05).

8.1.1.2. Niobium doped CCTO.

Figure 8.3. shows the concentration for selected elements of CCT05N by EDS with different sintering hold time, which was extracted from Table 5-24. The small grains were dominant in this sample. The mole ratio of copper is less than 3, as consequently, the mole ratio.
of oxygen is more than 12 (Table 5-24.) at 4 hours sintering hold time. The mole ratio of copper increases to close to 3 with increasing sintering hold time. Despite this the CaTiO$_3$ as a secondary phase appears at all sintering hold times (see Figure 5.45), but the mole ratio of calcium did not change significantly.

Figure 8.4. shows concentration for selected elements of CCT05N by XRF with different sintering hold time, which was extracted from Table 5-23. At 4 hours sintering hold time, the mole ratio of concentration of copper was higher than basic mole ratio (more than 3), as consequently, the mole ratio of titanium lower than 3.95 and then both copper and titanium become close to 3 and 3.95, respectively, with increasing sintering hold time.

![CCT05Ny by EDS](image)

Figure 8.3. Concentration for selected elements of CCT05Ny by EDS with different sintering hold time. (L = large grain, S = small grain, the error bars are less than 0.05).

![CCT05Ny by XRF](image)

Figure 8.4. Concentration for selected elements of CCT05Ny by XRF with different sintering hold time (The error bars are less than 0.05).
The concentration for selected elements of CCT10N by EDS with different sintering hold time is shown in Figure 8.5., which was extracted from Table 5-24. Similar to CCT05N, the small grains were dominant in this sample. The mole ratio of copper is less than 3, as consequently, the mole ratio of oxygen is more than 12 (Table 5-24.) at 4 hours sintering hold time. The mole ratio of copper increases close to 3 with increasing sintering hold time. In contrast to CCT05N, the CaTiO$_3$ as a secondary phase appears only at 8 and 12 sintering hold times (see Figure 5.46), even though the mole ratio of calcium did not change significantly.

![CCT10Ny by EDS](image)

**Figure 8.5.** Concentration for selected elements of CCT10Ny by EDS with different sintering hold time. (L = large grain, S = small grain, the error bars are less than 0.09).

![CCT10Ny by XRF](image)

**Figure 8.6.** Concentration for selected elements of CCT10Ny by XRF with different sintering hold time (The error bars are less than 0.05).

The concentration for selected elements of CCT10N by XRF with different sintering hold
time is shown in Figure 8.6., which was extracted from Table 5-23. At 4 and 12 hours sintering hold time, the mole ratio of concentration of copper was higher than basic mole ratio (more than 3), as consequently, the mole ratio of titanium lower than 3.90.

Figure 8.7. shows concentration for selected elements of CCT15N by EDS with different sintering hold time, which was extracted from Table 5-24. Identical to CCT05N and CCT10N trend, the small grains were dominant in this sample. The mole ratio of all elements seems on the intended value, at all sintering hold time. Even though the CaTiO$_3$ as a secondary phase appears at all sintering hold times (see Figure 5.47), the mole ratio of calcium did not change significantly.

![Figure 8.7. Concentration for selected elements of CCT15Ny by EDS with different sintering hold time. (L = large grain, S = small grain, the error bars are less than 0.1).](image)

![Figure 8.8. Concentration for selected elements of CCT15Ny by XRF with different sintering hold time (The error bars are less than 0.05).](image)
Figure 8.8. shows concentration for selected elements of CCT15N by XRF with different sintering hold time, which was extracted from Table 5-23. At 4 and 12 hours sintering hold time, the mole ratio of concentration of copper was higher than basic mole ratio (more than 3), as consequently, the mole ratio of titanium lower than 3.85.

The concentration for selected elements of CCT20N by EDS with different sintering hold time is shown in Figure 8.9., which was extracted from Table 5-24. Similar to CCT15N, the small grains was dominant in this sample and the mole ratio of all elements seems on the intended value, at all sintering hold time. In contrast to previous samples, the NbO and Nb₂O₅ as secondary phases appear at all sintering hold times (see Figure 5.48). The phases appear due to excess of niobium dopant (the mole ratio of niobium higher than 0.20), and increasing sintering hold time did not eliminate the existence of secondary phase of NbO and Nb₂O₅.

![Figure 8.9. Concentration for selected elements of CCT20Ny by EDS with different sintering hold time. (L = large grain, S = small grain, the error bars are less than 0.1).](image)

Figure 8.9. Concentration for selected elements of CCT20Ny by EDS with different sintering hold time. (L = large grain, S = small grain, the error bars are less than 0.1).

The concentration for selected elements of CCT20N by XRF with different sintering hold time is shown in Figure 8.10., which was extracted from Table 5-23. At 4 and 8 hours sintering hold time, the mole ratio of concentration of calcium and copper were lower than basic mole ratio, on the other hand, the mole ratio of titanium higher than 3.80. Increasing sintering hold time, the mole ratio of copper decreases and the mole ratio of calcium increases, and there is no significant change to the mole ratio of titanium.
Figure 8.10. Concentration for selected elements of CCT20Ny by XRF with different sintering hold time (The error bars are less than 0.05).

Figure 8.11. shows concentration for selected elements of CCT25Ny by EDS with different sintering hold time, which was extracted from Table 5-24. The small grains still remain dominant in this sample. Identical to CCT20N trend, the NbO and Nb_2O_5 as secondary phases appear at all sintering hold times (see Figure 5.49). The phases appear due to excess of niobium dopant (the mole ratio of niobium higher than 0.25), and increasing sintering hold time did not eliminate the existence of secondary phase of NbO and Nb_2O_5. As consequently, the mole ratio of copper is a lower than 3 (less 0.03) at 4 hours sintering hold time and the mole ratio of titanium less than 3.75 especially at 8 and 12 hours sintering hold times.

Figure 8.11. Concentration for selected elements of CCT25Ny by EDS with different sintering hold time. (L = large grain, S = small grain, the error bars are less than 0.07).
Figure 8.12. shows concentration for selected elements of CCT25N by XRF with different sintering hold time, which was extracted from Table 5-23. At all sintering hold time, the mole ratio of concentration of niobium was higher than basic mole ratio (more than 0.25), but the mole ratio of titanium higher than 3.75, as consequently, the mole ratio of calcium and copper are lower than their basic mole ratio, 1 and 3, respectively.

![CCT25Ny by XRF](image)

**Figure 8.12.** Concentration for selected elements of CCT25Ny by XRF with different sintering hold time (The error bars are less than 0.05).

In summary, the mole ratio of elements seem on the intended ratio at 12 hours sintering hold time, this indicates, the compositions synthesized were well developed with longest sintering time, despite the presence of CaTiO$_3$ and NbO (and/or Nb$_2$O$_5$) phases in all of the samples.

Table 8-1. shows valencies of niobium doped CCTO with different sintering hold time based on Table 5-24. The oxidation state compensation could potentially rely on mixed valence Ti$^{3+}$/Ti$^{4+}$ or Cu$^{1+}$/Cu$^{2+}$ [70] and possible compensation mechanisms is modified from Equation (15) and (16) as

\[
\begin{align*}
\text{O}_2^2- + 2\text{Ti}^{4+} & \rightarrow \text{V}_0^+ + 2\text{Ti}^{3+} + 1/2\text{O}_2 \uparrow : \\
\text{Ca} (\text{Cu}_3)[\text{Ti}^{4+}_{1-u}\text{Ti}^{3+}_u]_{4-x}\text{Nb}_x\text{O}_{12-u/2} & \hspace{1cm} \text{(89)} \\
3\text{Cu}^{2+} & \rightarrow 2\text{Cu}^{1+} + \text{Ti}^{4+}_{\text{Cu}} + \text{Cu} \uparrow : \\
\text{Ca} (\text{Cu}^{2+}_{1-3v}\text{Cu}^{1+}_{2v}\text{Ti}^{4+}_v)_{3}\text{Ti}_{4-x}\text{Nb}_x\text{O}_{12} & \hspace{1cm} \text{(90)}
\end{align*}
\]

Both Equation (89) and (90) are common phenomenon in perovskite structures and the
processes would likely take place during sintering hold time, which presence of Nb$^+5$ would suppress V$^-2$ [2-3, 21, 57, 63, 68-70, 114]. Both Equations also explain why the mole ratio of titanium and copper vary with sintering hold time. Positive value of oxidation state compensation indicates the requirement for Ti$^{3+}$ or Cu$^{1+}$ present in structure and negative value of oxidation state compensation indicates Cu$^{3+}$ present in structure are shown in Table 8.1.

Table 8.1. Valencies and oxidation state compensation of niobium doped CCTO with different sintering hold time based on Table 5-24.

<table>
<thead>
<tr>
<th>Element</th>
<th>Valency</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Nb</th>
<th>O</th>
<th>Oxidation State</th>
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<td>CCT05N4</td>
<td>+2</td>
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<td>2.91</td>
<td>3.96</td>
<td>0.05</td>
<td>12.07</td>
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<td>CCT10N4</td>
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<td>2.94</td>
<td>3.91</td>
<td>0.10</td>
<td>12.04</td>
<td>-0.05</td>
</tr>
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<td>CCT15N4</td>
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<td>3.86</td>
<td>0.16</td>
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<td>0.15</td>
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<td>0.07</td>
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<td>3.96</td>
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<td>-0.08</td>
</tr>
<tr>
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<td>3.91</td>
<td>0.10</td>
<td>12.02</td>
<td>0.02</td>
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<td>3.73</td>
<td>0.27</td>
<td>12.01</td>
<td>0.24</td>
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</table>

8.1.1.3. Tin doped CCTO.

Figure 8.13. shows concentration for selected elements of CCT05S by EDS with different sintering hold time, which was extracted from Table 5-33. The large grains were dominant in this sample, but the mole ratio of large and small grain is similar. The mole ratio of all elements seems on intended value at all sintering hold times. Despite this, the SnO as a secondary phase appears at 4 and 8 hours sintering hold times (see Figure 5.53), and SnO$_2$ phase replaced the SnO phase with further sintering hold time. The presence of SnO$_2$ phase is due to oxidation reaction with longer sintering hold time [125-126].

Figure 8.14. shows concentration for selected elements of CCT05S by XRF with different sintering hold time, which was extracted from Table 5-32. At 4 hours sintering hold time, the mole ratio of concentration of copper was higher than basic mole ratio (more than 3), as
consequently, the mole ratio of calcium and titanium lower than 1 and 3.95, respectively. Then both the mole ratio of calcium and titanium close to 1 and 3.95, respectively, with increasing sintering hold time.

![CCT05Sy by EDS](image1)

**Figure 8.13.** Concentration for selected elements of CCT05Sy by EDS with different sintering hold time. (L = large grain, S = small grain, the error bars are less than 0.05).

![CCT05Sy by XRF](image2)

**Figure 8.14.** Concentration for selected elements of CCT05Sy by XRF with different sintering hold time (the error bars are less than 0.04).

The concentration for selected elements of CCT10S by EDS with different sintering hold time is shown in Figure 8.15., which was extracted from Table 5-33. Similar to CCT05S, the large grains were dominant in this sample. The mole ratio of all element seems on intended value at all sintering hold times. Despite this, the SnO as a secondary phase appears at 4 hours sintering hold times (see Figure 5.54) and decreases as sintering hold time increases up to 8
hours. Interestingly, SnO$_2$ and CuO phases present at 12 hours sintering hold time. The presence of SnO$_2$ and CuO phases are due to oxidation reaction with longer sintering hold time [125-126, 65-66].

The concentration for selected elements of CCT10S by XRF with different sintering hold time is shown in Figure 8.16., which was extracted from Table 5-32. The mole ratio of concentration of copper was higher than basic mole ratio (more than 3), as consequently, the mole ratio of titanium lower than 3.90 at all sintering hold time.

Figure 8.15. Concentration for selected elements of CCT10Sy by EDS with different sintering hold time. (L = large grain, S = small grain, the error bars are less than 0.07).

![Figure 8.15](image1)

Figure 8.16. Concentration for selected elements of CCT10Sy by XRF with different sintering hold time (the error bars are less than 0.05).

![Figure 8.16](image2)

Figure 8.17. shows concentration for selected elements of CCT15S by EDS with
different sintering hold time, which was extracted from Table 5-33. The large grains were dominant in this sample, but the mole ratio of large and small grain is similar. The mole ratio of all elements seems on intended value at all sintering hold times. Despite this, the SnO as a secondary phase appears at 4 and 8 hours sintering hold times (see Figure 5.55), and SnO\(_2\) phase replaced the SnO phase with further sintering hold time. CuO phase also appears at 12 hours sintering hold time. The presence of SnO\(_2\) and CuO phases are common due to oxidation reaction with longer sintering hold time [125-126, 65-66].

![Figure 8.17. Concentration for selected elements of CCT15Sy by EDS with different sintering hold time. (L = large grain, S = small grain, the error bars are less than 0.07).](image)

![Figure 8.18. Concentration for selected elements of CCT15Sy by XRF with different sintering hold time (the error bars are less than 0.02).](image)

Figure 8.18. shows concentration for selected elements of CCT15S by XRF with
different sintering hold time, which was extracted from Table 5-32. The mole ratio of concentration of copper was higher than basic mole ratio (more than 3), and the mole ratio of calcium and titanium were lower than 1 and 3.85, respectively, at all sintering hold times. The other phase seems increase at all sintering hold times (more than 0.02).

The concentration for selected elements of CCT20S by EDS with different sintering hold time is shown in Figure 8.19., which was extracted from Table 5-33. Similar to CCT15S, the large grains were dominant in this sample. The mole ratio of tin was higher than 0.20 at all sintering hold times, as consequently, the mole ratio of calcium, copper, and titanium were lower than basic mole ratio, 1, 3, and 3.80, respectively. Identical to CCT15S, the SnO as a secondary phase appears at 4 and 8 hours sintering hold times (see Figure 5.56) and the SnO$_2$ and CuO phases present at 12 hours sintering hold time.

Figure 8.19. Concentration for selected elements of CCT20Sy by EDS with different sintering hold time. (L = large grain, S = small grain, the error bars are less than 0.08).

The concentration for selected elements of CCT20S by XRF with different sintering hold time is shown in Figure 8.20., which was extracted from Table 5-32. The mole ratio of concentration of copper was higher than basic mole ratio (more than 3), and as consequently, the mole ratio of calcium and titanium lower than 1 and 3.80, respectively, at all sintering hold times.

Figure 8.21. shows concentration for selected elements of CCT25S by EDS with different sintering hold time, which was extracted from Table 5-33. The large grains were
dominant in this sample, but the mole ratio of large and small grain is similar. The mole ratio of all elements seems on intended value at 4 hours sintering hold times. At 8 and 12 sintering hold times, the mole ratio of tin was higher than 0.25, and as consequently, the mole ratio of calcium, copper and titanium lower than 1, 3 and 3.75, respectively. Identical to CCT15S and CCT20S, the SnO as a secondary phase appears at 4 and 8 hours sintering hold times (see Figure 5.57), and SnO$_2$ phase replaced the SnO phase with further sintering hold time. CuO phase also appears at 12 hours sintering hold time. Again, the presence of SnO$_2$ and CuO phases are due to oxidation reaction with longer sintering hold time [125-126, 65-66].

Figure 8.20. Concentration for selected elements of CCT20Sy by XRF with different sintering hold time (the error bars are less than 0.04).

Figure 8.21. Concentration for selected elements of CCT25Sy by EDS with different sintering hold time. (L = large grain, S = small grain, the error bars are less than 0.08).
Figure 8.22. shows concentration for selected elements of CCT25S by XRF with different sintering hold time, which was extracted from Table 5-32. Despite of the mole ratio of tin less than 0.25, the mole ratio of calcium and titanium were lower than 1 and 3.80, respectively, at all sintering hold times. The other phase seems increase at all sintering hold times (more than 0.02).

In summary, the mole ratio of elements seem on the intended ratio at all sintering hold times. Despite of presence of SnO phase in all of the samples and SnO$_2$ (and/or CuO) phase(s) as effect of longer sintering hold time. In line with what Ni et. al. [23] reported, with 1100°C and 3 hours sintering hold time, there is no secondary phase up to 0.1 mol tin dopant.

Table 8-2. shows valencies and oxidation state compensation of tin doped CCTO with different sintering hold time based on Table 5-33. In contrast to valencies and oxidation state compensation of niobium doped CCTO, the oxidation state compensation is not indicate the oxygen loss or compensates from reduction process. The values are close with the error of measurements.
### Evolution of microstructure.

The focus on evolution of microstructure on term of sintering hold time is presented on density, grains size and pore distribution of pure CCTO, niobium and tin doped CCTO.

#### Pure CCTO.

Figure 8.23. shows density, grains and pores distribution of pure CCTO with different sintering hold times, which was extracted from Table 5-2. The grain was dominated by large grain (see Table 5-1.) and the size increases with increasing sintering hold time (see Figure 5.37) as expected with normal longer sintering processing. This result is in line with what Leret et. al. [44] reported, they found the large grain was dominant and increased as increasing sintering hold time (at 1100°C with 2, 4, 8, 16, and 32 hours sintering hold time). On the other hand, the density was ~4.8 g/cm³, and then tends to decrease as sintering hold time increases.

#### Valencies and oxidation state compensation of tin doped CCTO with different sintering hold time (L = large grain, S = small grain).

<table>
<thead>
<tr>
<th>Element</th>
<th>Valency</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Sn</th>
<th>O</th>
<th>Oxidation State</th>
<th>Element</th>
<th>Valency</th>
<th>Ca</th>
<th>Cu</th>
<th>Ti</th>
<th>Sn</th>
<th>O</th>
<th>Oxidation State</th>
</tr>
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<td>CCT05S4 (L)</td>
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<td>2.99</td>
<td>3.95</td>
<td>0.05</td>
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<td>-0.03</td>
<td>CCT05S8 (L)</td>
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<td>(S)</td>
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<td>3.95</td>
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<td>12.02</td>
<td>-0.07</td>
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<tr>
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<td>3.90</td>
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<td>0.00</td>
<td>CCT10S8 (L)</td>
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<tr>
<td>(S)</td>
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<td>3.90</td>
<td>0.10</td>
<td>12.01</td>
<td>-0.03</td>
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<tr>
<td>CCT15S4 (L)</td>
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<td>-0.02</td>
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<td>3.84</td>
<td>0.16</td>
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<td>(S)</td>
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<td>0.23</td>
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<td>CCT25S12 (L)</td>
<td>0.98</td>
<td>3.01</td>
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<td>(S)</td>
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This phenomenon can be explained with the pores distribution increases as the sintering hold time increases, where this condition as a normal effect of sintering processes for CCTO [20]. There was possibility that the pore network changes shape and breaks up into individual pores with longer sintering hold time.

8.1.2.2. Niobium doped CCTO.

Figure 8.24. shows density, grains and pores distribution of CCT05N with different sintering hold time, which was extracted from Table 5-37, 5-39, 5-41, 5-4, 5-8, and 5-12. The grain was dominated by small grain and the grain size tends to increase with increasing sintering hold time (see Figure 5.38). The density was \( \sim 4.2 \text{ g/cm}^3 \), then increases as sintering hold time increases, reaches \( \sim 4.5 \text{ g/cm}^3 \). The pores distribution tends to decrease as the sintering hold time increases. Interestingly, despite this, the grains and pores distribution were not changed significantly with 12 hours sintering hold time but the density increases at 12 hours sintering hold time.
Figure 8.24. Density, grains and pores distribution of CCT05N with different sintering hold time.

The density, grains and pores distribution of CCT10N with different sintering hold time, which was extracted from Table 5-37, 5-39, 5-41, 5-4, 5-8, and 5-12 are shown in Figure 8.25. The grain was also dominated by small grain and the grain size tends to increase with increasing sintering hold time (see Figure 5.38). The density was ~4.5 g/cm$^3$, then increases as sintering hold time increases, reaches ~4.6 g/cm$^3$. The pores distribution tends to decrease as the sintering hold time increases. Similar to CCT05N, despite this, the grains and pores distribution were not significantly changed with 12 hours sintering hold time but the density increases at 12 hours sintering hold time.

Figure 8.25. Density, grains and pores distribution of CCT10N with different sintering hold time.

Figure 8.25. shows density, grains and pores distribution of CCT15N with different sintering hold time, which was extracted from Table 5-37, 5-39, 5-41, 5-4, 5-8, and 5-12.
Identical to CCT10N, the grain was also dominated by small grain and the grain size tends to increase with increasing sintering hold time (see Figure 5.38). The density was ~4.7 g/cm$^3$, then decreases as 8 hours sintering hold time increases. At further sintering hold time, the density increases and reaches above ~4.7 g/cm$^3$. Identical to CCT10N trend, the grains and pores distribution were not significant change with 12 hours sintering hold time but the density increases at 12 hours sintering hold time.

Figure 8.26. Density, grains and pores distribution of CCT15N with different sintering hold time.

The density, grains and pores distribution of CCT20N with different sintering hold time, which was extracted from Table 5-37, 5-39, 5-41, 5-4, 5-8, and 5-12 are shown in Figure 8.27. Identical to CCT15N, the grain was also dominated by small grain and the grain size tends to increase with increasing sintering hold time (see Figure 5.38). In contrast to CCT15N, the density was ~4.7 g/cm$^3$, increases as sintering hold time increases and reaches ~4.8 g/cm$^3$ at 12 hours sintering hold time. The grains distribution increases and pore distribution decreases with increasing sintering hold time.

Figure 8.28. shows density, grains and pores distribution of CCT25N with different sintering hold time, which was extracted from Table 5-37, 5-39, 5-41, 5-4, 5-8, and 5-12. Similar to CCT20N, the grain was also dominated by small grain but the grain size is not changed significantly with increasing sintering hold time (see Figure 5.38). Identical to CCT20N trend, the density, and grains distribution increases with increasing sintering hold time. On the other hand, the pore distribution decreases with increasing sintering hold time.
In general, increasing sintering hold time reduces the pore size and increases the small grain size of niobium doped CCTO as expected as normal sintering process. The density varies with sintering hold time but tends to increase with increasing sintering hold times. Despite this the grains and pores distribution was not significantly changed but the density increases at longer sintering hold time, it was indicated the sintering hold time well synthesized the sample by decreasing the pore size which it makes more dense the sample. Unfortunately, there is no report that revealed the effect of sintering hold time to microstructure of niobium doped CCTO.

8.1.2.3. Tin doped CCTO.

Figure 8.29. shows density, grains and pores distribution of CCT05S with different
sintering hold time, which was extracted from Table 5-38, 5-40, 5-42, 5-6, 5-10, and 5-14. The grain distribution was dominated by large grains and the grain size tends to increase with increasing sintering hold time (see Figure 5.39 and 5.40). The density was \(\sim 4.6 \text{ g/cm}^3\), then increases to \(\sim 4.7 \text{ g/cm}^3\) as sintering hold time increases, then decreases to \(\sim 4.5 \text{ g/cm}^3\). The grains distribution decreases and the pores distribution increases as the sintering hold time increases. Interestingly, despite the pores distribution decreasing, the density also decreases with 12 hours sintering hold time.

![Figure 8.29](image)

Figure 8.29. Density, grains and pores distribution of CCT05S with different sintering hold time.

The density, grains and pores distribution of CCT10S with different sintering hold time, which was extracted from Table 5-38, 5-40, 5-42, 5-6, 5-10, and 5-14 are shown in Figure 8.30. The grain distribution was dominated by large grains and the grain size tends to increase with increasing sintering hold time (see Figure 5.39 and 5.40). The density tends to decrease as sintering hold time increases. The large grains and the pores distribution tends to decrease as the sintering hold time increases but the small grains distribution tends to increase with increasing sintering hold time.

![Figure 8.31](image)

Figure 8.31. shows density, grains and pores distribution of CCT15S with different sintering hold time, which was extracted from Table 5-38, 5-40, 5-42, 5-6, 5-10, and 5-14. The grain was dominated by large grain and the large grain size tends to decrease with increasing sintering hold time (see Figure 5.39). On the other hand, the small grain tends to increase with increasing sintering hold time (see Figure 5.40).
Identical to CCT05S trend, the density was ~4.8 g/cm$^3$, then increases to ~4.9 g/cm$^3$ as sintering hold time increases, then decreases to ~4.7 g/cm$^3$. The large grains and pores distribution decreases but the small grains distribution increases as the sintering hold time increases. Interestingly, despite the pores distribution decreasing, the density also decreases with 12 hours sintering hold time.

The density, grains and pores distribution of CCT15S with different sintering hold time, which was extracted from Table 5-38, 5-40, 5-42, 5-6, 5-10, and 5-14 are shown in Figure 8.32. Identically to previous samples trend, the grain distribution was dominated by large grains and the large grain size tends to decrease with increasing sintering hold time (see Figure 5.39). On the other hand, the small grain tends to increase with increasing sintering hold time (see Figure 8.33).
5.40). Similar to CCT15S trend, the density was ~4.9 g/cm³, then increases as sintering hold time increases, then decreases to ~4.8 g/cm³ at further sintering hold time. The large grains distribution decreases but the small grains and pores distribution increases as the sintering hold time increases. Despite of the small grains and pores distribution decreases, the density also decreases with 12 hours sintering hold time.

Figure 8.32. Density, grains and pores distribution of CCT20S with different sintering hold time.

Identical to previous samples trend, the grain was dominated by large grain and the large and small grain size tends to decrease with increasing sintering hold time (see Figure 5.39 and 5.40). Identical to CCT20S trend, the density was ~4.9 g/cm³, then increases as sintering hold time increases, then decreases to ~4.8 g/cm³ at further sintering hold time. The large grains distribution decreases but the small grains and pores distribution increases as the sintering hold time increases. Decreasing the large grains distribution significantly decreases the density at 12 hours sintering hold time.
Figure 8.33. Density, grains and pores distribution of CCT25S with different sintering hold time.

In general, increasing sintering hold time reduces the large grains and pore size, but on the other hand, increases the small grain size of tin doped CCTO. The density varies with sintering hold time and the amount of tin dopant which tends to decrease as increasing sintering hold time. Despite the small grains and pores distribution increasing, the density decreases at longest sintering hold time, it was indicated the longest sintering hold time did not produce a uniform sample. Again, there is no report that revealed the effect of sintering hold time to microstructure of tin doped CCTO.

8.1.3. Electrical properties.

In this section, the electrical properties are presented as relative dielectric constant per unit length ($\varepsilon_{er}$), equivalent dielectric constant ($\varepsilon_{eq}$), grain boundary thickness ($t_{gb}$), non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_B$) as a function of sintering hold time.

8.1.3.1. Pure CCTO.

Figure 8.34. to Figure 8.36. show three different characteristic of relative dielectric constant per unit length ($\varepsilon_{er}$), equivalent dielectric constant ($\varepsilon_{eq}$), grain boundary thickness ($t_{gb}$) of pure CCTO as a function of sintering hold time at specific temperatures. Low, transition and high temperatures were represented by -100°C, 25°C and 200°C, respectively.
Figure 8.34. Equivalent and relative dielectric constant ($\varepsilon_{eq}$ and $\varepsilon_{eff}$) and grain boundary thickness of pure CCTO with different sintering hold time at -100°C.

Figure 8.34. shows $\varepsilon_{eq}$, $\varepsilon_{eff}$, and $t_{gb}$ of pure CCTO as a function of sintering hold time at -100°C. The $\varepsilon_{eq}$ increases as increasing sintering hold times, on the other hand, the $\varepsilon_{eff}$, and $t_{gb}$ have identical trend, first the values decrease as increasing sintering hold time then increase at further sintering hold time.

The $\varepsilon_{eff}$, $\varepsilon_{eq}$, and $t_{gb}$ of pure CCTO as a function of sintering hold time at 25°C is shown in Figure 8.35. The $\varepsilon_{eq}$ increases as increasing sintering hold times, but the $\varepsilon_{eff}$, and $t_{gb}$ tend to decrease as increasing sintering hold time.

Figure 8.35. Equivalent and relative dielectric constant ($\varepsilon_{eq}$ and $\varepsilon_{eff}$) and grain boundary thickness of pure CCTO with different sintering hold time at 25°C.

Figure 8.36. shows $\varepsilon_{eff}$, $\varepsilon_{eq}$, and $t_{gb}$ of pure CCTO as a function of sintering hold time at 200°C. The $\varepsilon_{eff}$, the $\varepsilon_{eq}$, and $t_{gb}$ have identical trend, first the values decrease as increasing
sintering hold time then increase at further sintering hold time.

Figure 8.36. Equivalent and relative dielectric constant ($\varepsilon_{eq}$ and $\varepsilon_{eff}$) and grain boundary thickness of pure CCTO with different sintering hold time at 200°C.

Figure 8.37. shows non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_B$) of pure CCTO with different sintering hold time. The value of $\alpha$ at 4 and 12 hours only slightly different, ~200, but the $\alpha$ at 8 hours is lower than both values (~50). Identical to $\alpha$ trend, the $\Phi_B$ at 4 and 12 hours only slightly different, ~0.177 eV, but the $\Phi_B$ at 8 hours is less than ~0.175 eV. Figure 8.37 shows that there is not a direct correlation between non-linear coefficient of conduction and barrier height in term of sintering hold time.

Figure 8.37. non-linear coefficient of conduction and barrier height of pure CCTO with different sintering hold time.

In summary, the $\varepsilon_{eff}$ and $t_{gb}$ of pure CCTO have a similar trend as a function of sintering
hold time. It indicated that grain boundary thickness have correlation with relative dielectric constant per unit length. The dielectric constant reflected the capacitance of sample, as identical, the grain boundary thickness also represented the capacitance behaviours as internal barrier layer capacitor phenomenon [97]. This result is in line with results that Kwon et. al. [95] and Sinclair et. al. [96] reported, where dielectric constant is attributed to the formation of thin insulating boundaries (grain boundary thickness) with the conducting grains. On the other hand, the $\alpha$ and $\Phi_B$ of pure CCTO also have a similar trend as a function of sintering hold time, where both of them tend to increase as increasing sintering hold time. Huang et. al. [45] have already found similar trend to this results, which samples measure at 1, 3 and 30 hours sintering hold time.

8.1.3.2. Niobium doped CCTO.

Figure 8.38. shows non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_B$) of CCT05N with different sintering hold time. The value of $\alpha$ at 4 and 12 hours only slightly different, around 500, but the $\alpha$ at 8 hours is lower than both values (~50). On the other hand, the $\Phi_B$ increases as the sintering hold time increases, from ~0.176 to ~0.178 eV. Figure 8.38 shows that there is not a direct correlation between non-linear coefficient of conduction and barrier height in term of sintering hold time for CCT05N.

The $\alpha$ and $\Phi_B$ of CCT10N with different sintering hold time is shown in Figure 8.39. Identically to CCT05N, the value of $\alpha$ at 8 hours is lower than both the values of $\alpha$ at 4 and 12. Even the value of $\alpha$ at CCT10N is higher than CCT05N. The $\Phi_B$ slightly decreases as the sintering hold time increases, from ~0.176 to ~0.175 eV.
Figure 8.38. non-linear coefficient of conduction and barrier height of CCT05N with different sintering hold time.

Figure 8.39. non-linear coefficient of conduction and barrier height of CCT10N with different sintering hold time.

Figure 8.40. shows the non-linear coefficient of conduction and barrier height of CCT15N with different sintering hold time. In contrast to CCT05N and CCT10N, the non-linear coefficient of conduction of CCT15N is lower than both previously. At 4 hours sintering hold time, the non-linear coefficient of conduction is only ~50 and then increases with increasing sintering hold time and reaches ~300 at 12 hours sintering hold time. On the other hand, identically to CCT10N trend, the $\Phi_B$ slightly decreases as the sintering hold time increases around 0.175 eV.
The non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_B$) of CCT20N with different sintering hold time is shown in Figure 8.41. The value of $\alpha$ is less than 200, and tends to decrease as sintering hold time increases. Similar to $\alpha$ value trend, the $\Phi_B$ slightly decreases as increases the sintering hold time in the range of 0.175 - 0.174 eV.

Figure 8.41. non-linear coefficient of conduction and barrier height of CCT20N with different sintering hold time.

Figure 8.42. shows the $\alpha$ and $\Phi_B$ of CCT25N with different sintering hold time. The value of $\alpha$ is less than 100, and tends to decrease as sintering hold time increases. On the other hand, the $\Phi_B$ slightly increases as the sintering hold time increases from ~0.173 to ~0.175 eV.

Figure 8.42. non-linear coefficient of conduction and barrier height of CCT25N with different sintering hold time.
In summary, the non-linear coefficient of conduction ($\alpha$) of niobium doped CCTO varies on the sintering hold time. The maximum value of $\alpha$ is $\sim600$ at CCT10N with 4 hours sintering hold time, and the value of $\alpha$ also varies according to the amount of niobium dopant. Identical to $\alpha$ value trend, the barrier height ($\Phi_B$) varies according to sintering hold time, and reaches maximum $\sim0.178$ eV at CCT05N with 12 hours sintering time in the range of $\sim0.173$ to $\sim0.178$ eV. The NbO and/or Nb$_2$O$_5$ as secondary phases seem to reduce the non-linear coefficient of conduction of niobium doped CCTO, while increasing the sintering hold time does not reduce the secondary phase(s). There is no paper that reports the effect of sintering hold time to neither non-linear coefficient of conduction nor secondary phase of niobium doped CCTO.

8.1.3.3. Tin doped CCTO.

Figure 8.43. shows non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_B$) of CCT05S with different sintering hold time. The non-linear coefficient of conduction increases as increasing sintering hold time, from $\sim100$ to $\sim300$. On the other hand, the barrier height tends to decrease as sintering hold time increases, from $\sim0.180$ to $\sim0.177$ eV.

The $\alpha$ and $\Phi_B$ of CCT10S with different sintering hold time is shown in Figure 8.44. In contrast to CCT05S, the value of $\alpha$ at 4 hours sintering hold time reaches $\sim400$ (higher than the
α value of CCT05S at all sintering hold time) and then drops to ~100 as sintering hold time increases, then the α increases to ~600 as further increasing sintering hold time. In contrast to α, the Φb drops in the range of ~0.176 to ~0.177 eV (compare to CCT05S), and slightly increases as increases the sintering hold time.

![Graph of CCT05S showing α and Φb vs sintering time](image1)

**Figure 8.43.** non-linear coefficient of conduction and barrier height of CCT05S with different sintering hold time.

![Graph of CCT10S showing α and Φb vs sintering time](image2)

**Figure 8.44.** non-linear coefficient of conduction and barrier height of CCT10S with different sintering hold time.

Figure 8.45. shows the non-linear coefficient of conduction and barrier height of CCT15S with different sintering hold time. In contrast to CCT10S, the non-linear coefficient of conduction of CCT15S at 4 hours sintering hold time is higher than CCT10S, and decreases as sintering hold time increases. At 4 hours sintering hold time, the non-linear coefficient of
conduction reaches ~830. On the other hand, the $\Phi_B$ is lower than CCT10S, the $\Phi_B$ slightly decreases as the sintering hold time increases in the range of ~0.176 to ~0.175 eV.

Figure 8.45. non-linear coefficient of conduction and barrier height of CCT15S with different sintering hold time.

The non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_B$) of CCT20S with different sintering hold time is shown in Figure 8.46. In contrast to CCT15S, the value of $\alpha$ at 4 hours sintering hold time is less than 300, then increases at 8 hours sintering hold time (~450) and tends to decrease as sintering hold time increases. On the other hand, the $\Phi_B$ is lower than CCT15S, and the $\Phi_B$ is slightly not different as the sintering hold time increases in the range of 0.174 - 0.175 eV.

Figure 8.46. non-linear coefficient of conduction and barrier height of CCT20S with different sintering hold time.
Figure 8.47. shows the $\alpha$ and $\Phi_B$ of CCT25S with different sintering hold time. Similar to CCT20S trend, the value of $\alpha$ of CCT25S varies with sintering holding time (reaches maximum ~500 at 8 hours) and it is lower than CCT20S. In contrast to CCT20S, the $\Phi_B$ of CCT25S slightly increases from ~0.173 to ~0.174 eV with increasing the sintering hold time.

![Graph showing $\alpha$ and $\Phi_B$ of CCT25S with sintering time](image)

Figure 8.47. non-linear coefficient of conduction and barrier height of CCT25S with different sintering hold time.

In summary, the non-linear coefficient of conduction ($\alpha$) of tin doped CCTO depends on the sintering hold time. The maximum value of $\alpha$ is ~830 at CCT15S with 4 hours sintering hold time, and the value of $\alpha$ varies according to sintering hold time. Identical to $\alpha$ value trend, the barrier height ($\Phi_B$) also varies according to sintering hold time, and reaches maximum ~0.180 eV at CCT05N with 4 hours sintering time in the range of ~0.173 to ~0.180 eV. There is no paper determining the effect of sintering hold time to neither non-linear coefficient of conduction nor secondary phase of tin doped CCTO.

8.1.4. Discussion in influence of sintering hold time.

The secondary phase (CaTiO$_3$) of pure CCTO only appears at 4 hours sintering hold time, and then increasing sintering hold time decreases the secondary phase. The CaTiO$_3$ also appears up to 0.15 mol niobium doped CCTO at all sintering hold times, and up to 0.05 mol tin doped CCTO, especially at 4 hours sintering hold time. The CaTiO$_3$ phase is common as
secondary phase in pure CCTO, and potentially causing non-stoichiometry in Equation (89) and (90) would be small [131]. The NbO phase appears in CCT20N and CCT25N due to excess of niobium dopant, and Nb$_2$O$_5$ phase appears beside the NbO phase due to oxidation reaction with longer sintering hold time. Hong et. al. [3] and Liu et. al. [63] reported that they observed no secondary phase up to 0.2 mol Nb with 24 and 18 hours sintering hold time at 1100°C, respectively, with a similar conventional solid state reaction method. It is deduced from this point, the longer sintering hold time could reduce the secondary phase. The SnO phase appears in all tin doped CCTO and SnO$_2$ phase replaced SnO phase due to oxidation reaction with longer sintering holding time. In summary, increasing sintering hold time did not reduce the secondary phase of niobium and tin doped CCTO, so far, the effect of sintering hold time on the secondary phases in niobium and tin doped CCTO have not been reported yet.

The large grains and pore size of niobium were reduced with increasing sintering hold time, but on the other hand, the small grain size increases with increasing sintering hold time. The density varies with sintering hold time and the amount of niobium dopant. Despite of the small grains and pores distribution increases, the density tends to decrease at longer sintering hold time, it was indicated the longer sintering hold time did not homogenise the sample. The niobium dopant did not change significantly the microstructure of CCTO with increasing sintering hold time, similar to the secondary phase of CCTO. The tin dopant significantly decreases the microstructure of CCTO with increasing sintering hold time especially the large grain size, even though the secondary phase does not significantly change with increasing sintering hold time. Again, there is no comparable data from the other worker that reveals the effect of sintering hold time on grain size (microstucture) of niobium and tin doped CCTO.

The relative dielectric constant per unit length $\varepsilon_{\text{eff}}$ and grain boundary thickness $t_{gb}$ of pure CCTO have a similar trend as a function of sintering hold time. It indicated that grain boundary thickness have correlation with relative dielectric constant per unit length. On the other hand, the $\alpha$ and $\Phi_b$ of pure CCTO also have a similar trend as a function of sintering hold time. The $\varepsilon_{\text{eff}}$, $t_{gb}$, $\alpha$ and $\Phi_b$ seem not to significantly change with increasing sintering hold time, despite the grain size increases and density tends to decrease with sintering hold time. In contrast with Leret et. al. [44], Kwon and Cann [74], and Kashyap et. al. [133] who reported that
dielectric constant of pure CCTO increases as sintering hold time increases, and Li et. al. [75] reported that non-linear coefficient of conduction of pure CCTO decreases as sintering hold time increases.

The non-linear coefficient of conduction ($\alpha$) of niobium and tin doped CCTO depends on the sintering hold time. The maximum value of $\alpha$ is $\sim 830$ at CCT15S with 4 hours sintering hold time, and the value of $\alpha$ varies according to sintering hold time. Identically to $\alpha$ value trend, the barrier height ($\Phi_B$) also varies according to sintering hold time, and reaches maximum $\sim 0.180$ eV at CCT05N with 4 hours sintering time in the range of $\sim 0.173$ to $\sim 0.180$ eV. There is not a direct correlation between non-linear coefficient of conduction and barrier height in term of sintering hold time for niobium and tin doped CCTO, neither a grain size nor grains distribution. These results are still debatable as there is no paper that has reported the effect of sintering hold time to non-linear coefficient of conduction of niobium and tin doped CCTO.

8.2. Influence of Dopants.

This section focuses on effect of niobium and tin dopant to evolution of secondary phase, evolution of microstructure and electrical properties of CCTO. The results are extracted from chapter 4, 5, and 6 to 7 for secondary phase, microstructure, and electrical properties, respectively.

8.2.1. Evolution of secondary phase.

The focus on evolution of secondary phase on influence of dopant is presented on concentration of selected elements by EDS and XRF. Similar to sintering hold time, the secondary phase was studied in different mole ratio of element with different amount of dopant.

8.2.1.1. Niobium doped CCTO.

Figure 8.48 shows concentration for selected elements of CCTxN4 by EDS as a function of the amount of niobium dopant, which was extracted from Table 5-18. The small grains were dominant in these samples. At pure CCTO, the mole ratio of copper is less than 3,
and then increases close to 3 with increasing the amount of dopant. Despite of the CaTiO$_3$ as a secondary phase appears up to 0.15 mol (see Figure 5.42), but the mole ratio of calcium is not significantly change, the CaTiO$_3$ phase was replaced by NbO and Nb$_2$O$_5$ phases due to excess of niobium dopant at 0.20 and 0.25 mol.

Figure 8.48. Concentration for selected elements of CCTxN4 by EDS with different amount of dopant. (L = large grain, S = small grain, the error bars are less than 0.1).

Figure 8.49. shows concentration for selected elements of CCTxN4 by XRF as a function of the amount of niobium dopant, which was extracted from Table 5-17. The mole ratio of concentration of copper was higher than basic mole ratio (more than 3), and the mole ratio of calcium was lower than 1 at all the amount of niobium dopant.

Figure 8.49. Concentration for selected elements of CCTxN4 by XRF with different amount of dopant (the error bars are less than 0.05).
The concentration for selected elements of CCTxN8 by EDS as a function of the amount of niobium dopant, which was extracted from Table 5-20, is shown in Figure 8.50. The small grains were dominant in all samples. At pure CCTO, the mole ratio of copper is less than 3, and then increases close to 3 with increasing the amount of niobium dopant. The mole ratio of elements seems in intended ratio at all the amount of dopant. Similar to CCTxN4, the CaTiO$_3$ as a secondary phase appears up to 0.15 mol (see Figure 5.43), but the mole ratio of calcium is not significant change. The CaTiO$_3$ phase was replaced by NbO and Nb$_2$O$_5$ phases due to excess of niobium dopant at 0.25 mol.

Figure 8.50. Concentration for selected elements of CCTxN8 by EDS with different amount of dopant. (L = large grain, S = small grain, the error bars are less than 0.1).

The concentration for selected elements of CCTxN8 by XRF as a function of the amount of dopant, which was extracted from Table 5-19, is shown in Figure 8.51. The mole ratio of concentration of copper was higher than basic mole ratio (more than 3), and close to 3 with increasing the amount of niobium dopant. On the other hand, the mole ratio of calcium was lower than 1 at all the amount of dopant.
Figure 8.51. Concentration for selected elements of CCTxN8 by XRF with different amount of dopant (the error bars are less than 0.05).

Figure 8.52. shows concentration for selected elements of CCTxN12 by EDS as a function of the amount of niobium dopant, which was extracted from Table 5-22. The small grains were dominant in all niobium samples. The mole ratio of elements seems in intended ratio at all the amount of dopant. Similar to CCTxN4 and CCTxN8, the CaTiO$_3$ as a secondary phase appears up to 0.15 mol (see Figure 5.44), but again, the mole ratio of calcium is not significant change. The CaTiO$_3$ phase was replaced by NbO phase due to excess of niobium dopant at 0.25 mol.

Figure 8.53. shows concentration for selected elements of CCTxN12 by XRF as a function of the amount of niobium dopant, which was extracted from Table 5-21. The mole ratio of concentration of copper and titanium was not in intended ratio at all the amount of dopant. Despite the mole ratio of calcium was lower than 1 at all the amount of dopant.
In summary, the mole ratio of elements varies with the amount of niobium dopant and sintering holding time. The CaTiO$_3$ as a secondary phase appears up to 0.15 mol and NbO and/or Nb$_2$O$_5$ as secondary phases present in high niobium dopant. In comparison with Hong et. al. [3] and Liu et. al. [63] reported, they observed no secondary phase up to 0.2 mol Nb with 24 and 18 hours sintering hold time at 1100°C, respectively. It means, either CaTiO$_3$ or NbO (and/or Nb$_2$O$_5$) could reduce with longer sintering hold time.
8.2.1.2. Tin doped CCTO.

Figure 8.54. shows concentration for selected elements of CCTxS4 by EDS as a function of the amount of tin dopant, which was extracted from Table 5-27. The large grains were dominant in these samples, but the mole ratio of large and small grain is similar. The mole ratio of all elements seems on intended value at all the amount of dopant. Despite the SnO as a secondary phase appears at all the amount of dopants (see Figure 5.50).

Figure 8.54. Concentration for selected elements of CCTxS4 by EDS with different amount of dopant. (L = large grain, S = small grain, the error bars are less than 0.03).

Figure 8.55. Concentration for selected elements of CCTxS4 by XRF with different amount of dopant (the error bars are less than 0.05).

Figure 8.55. shows concentration for selected elements of CCTxS4 by XRF as a function of the amount of tin dopant, which was extracted from Table 5-26. The mole ratio of concentration of copper was higher than basic mole ratio (more than 3) at all the amount of tin
dopant. The mole ratio of titanium was lower than expected (calculated), as consequently; the mole ratio of calcium varies with increasing the amount of tin dopant.

The concentration for selected elements of CCTxS8 by EDS as a function of the amount of tin dopant, which was extracted from Table 5-29, is shown in Figure 8.56. The large grains still were dominant in these samples, and the mole ratio of large and small grain is also similar. Identically to CCTxS4, the mole ratio of all elements seems as intended value at all the amount of tin dopant. Despite the SnO as a secondary phase appears at all the amount of tin dopant (see Figure 5.51).

![Figure 8.56](image)

Figure 8.56. Concentration for selected elements of CCTxS8 by EDS with different amount of dopant. (L = large grain, S = small grain, the error bars are less than 0.08).

The concentration for selected elements of CCTxS8 by XRF as a function of the amount of tin dopant, which was extracted from Table 5-28, is shown in Figure 8.57. Identically to CCTxS4 trend, the mole ratio of concentration of copper was higher than basic mole ratio (more than 3) at all the amount of tin dopant. The mole ratio of titanium also was lower than expected (calculated), as consequently; the mole ratio of calcium varies with increasing the amount of tin dopant.

![Figure 8.58](image)

Figure 8.58. shows concentration for selected elements of CCTxS12 by EDS as a function of the amount of tin dopant, which was extracted from Table 5-31. The large grains still were dominant in these samples, and there is not a significant difference in the mole ratio of large and small grain. Identically to CCTxS4 and CCTxS8, the mole ratio of all elements seems as the intended value at all the amounts of tin dopant. Despite the SnO₂ as a secondary phase
appears at all the amount of tin dopant and a CuO phase appears from 0.10 to 0.25 mol (see Figure 5.52).

Figure 8.57. Concentration for selected elements of CCTxS8 by XRF with different amount of dopant (the error bars are less than 0.05).

Figure 8.58. Concentration for selected elements of CCTxS12 by EDS with different amount of dopant. (L = large grain, S = small grain, the error bars are less than 0.08).

Figure 8.59. shows concentration for selected elements of CCTxS12 by XRF as a function of the amount of tin dopant, which was extracted from Table 5-30. Identical to CCTxS4 and CCTxS8 trend, the mole ratio of concentration of copper was higher than basic mole ratio (more than 3) at all the amount of tin dopant. The mole ratio of titanium also was lower than expected (calculated), as consequently; the mole ratio of calcium varies with increasing the amount of tin dopant.
Figure 8.59. Concentration for selected elements of CCTxS12 by XRF with different amount of dopant (the error bars are less than 0.05).

In summary, the mole ratio of all elements seem as intended value at all the amount of tin dopant by EDS but vary with increasing the amount of tin dopant by XRF. The SnO as secondary phases is present in all of the samples of CCTxS4 and CCTxS8. SnO$_2$ and/or CuO as secondary phases appear in the sample of CCTxS12. In contrast to Ni et. al. [23] reported, they found no secondary phase up to 0.1 mol tin dopant, with 1100°C and 3 hours sintering hold time. It seems the longer sintering hold time gave more time for the oxidation reaction.

8.2.2. Evolution of microstructure.

The focus on evolution of microstructure on influence of dopant is presented on density, grains size and pores distribution of niobium and tin doped CCTO. The values of them will be analysed as a function of the amount of dopant.

8.2.2.1. Niobium doped CCTO.

Figure 8.60. shows density, grains and pores distribution of CCTxN4 with different amount of dopant, which was extracted from Table 5-37 and Table 5-4. The grain was dominated by small grain (see Table 5-3.) and there is not significant change in size with increasing the amount of dopant (see Figure 5.38). Interestingly, at pure CCTO, the grain was dominated by large grain, and the density was ~4.8 g/cm$^3$, then decreases as niobium dopant
(0.05 mol) added in this system, which the grain was dominated by small grain. The pores
distribution decreases as the amount of niobium dopant increases, as consequently, the density
increases as the amount of niobium dopant increases, and reaches ~4.8 g/cm$^3$ at 0.25 mol
niobium dopant.

Figure 8.60. Density, grains and pores distribution of CCTxN4 with different amount of dopant.

Figure 8.61. shows density, grains and pores distribution of CCTxN8 with different
amount of dopant, which was extracted from Table 5-39 and Table 5-8. The grain was
dominated by small grain (see Table 5-7.) and there is not significant change in size with
increasing the amount of dopant (see Figure 5.38). Interestingly, at pure CCTO, the grain was
dominated by large grain, and the density was ~4.8 g/cm$^3$, then decreases as niobium dopant
(0.05 mol) added in this system, which the grain was dominated by small grain. The pores
distribution decreases as the amount of niobium dopant increases, as consequently, the density
increases as the amount of niobium dopant increases, and reaches ~4.8 g/cm$^3$ at 0.25 mol
niobium dopant.
Figure 8.61. Density, grains and pores distribution of CCTxN8 with different amount of dopant.

Figure 8.62. shows density, grains and pores distribution of CCTxN12 with different amount of dopant, which was extracted from Table 5-41 and Table 5-12. The grain was dominated by small grain (see Table 5-11.) and there is not significant change in size with increasing the amount of dopant (see Figure 5.38). Identical to CCTxN8 trend, at pure CCTO, the grain was dominated by large grain, and the density was $\sim 4.7$ g/cm$^3$, then decreases as niobium dopant (0.05 mol) added in this system, which the grain was dominated by small grain. The pores distribution decreases as the amount of niobium dopant increases, as consequently, the density increases as the amount of niobium dopant increases, and reaches $\sim 4.8$g/cm$^3$ at 0.25 mol niobium dopant.

Figure 8.62. Density, grains and pores distribution of CCTxN12 with different amount of dopant.

In summary, increasing the amount of niobium dopant decreases the grain and pore
size. This result is similar to Hong et. al. [3] and Pereira et. al. [132] reported. Pereira et. al. [132] was agreed that niobium dopant reduces the diffusion coefficient, as consequently, the vacancies as created by niobium are assumed to be bound to the impurity niobium ion and then inhibit the mass transport. The density tends to increase as the amount of niobium dopant increases, and the magnification of density depends on the sintering hold time. The (small) grains distribution increases and the pores distribution decreases with increasing the amount of niobium dopant.

8.2.2.2. Tin doped CCTO.

Figure 8.63. shows density, grains and pores distribution of CCTxS4 with different amount of dopant, which was extracted from Table 5-6. The grain was dominated by large grain (see Table 5-5.) and there is not significant change in size with increasing the amount of tin dopant (see Figure 5.39 and Figure 5.40). Identical to CCTxN4, at pure CCTO, the grain was dominated by large grain, and the density was ~4.8 g/cm³, then decreases as tin dopant (0.05 mol) added in this system. The pores distribution tends to decrease as the amount of tin dopant increases, as consequently, the density increases as the amount of tin dopant increases, and reaches ~4.9 g/cm³ at 0.25 mol tin dopant.

![CCTxS4](image)

**Figure 8.63.** Density, grains and pores distribution of CCTxS4 with different amount of dopant.

Figure 8.64. shows density, grains and pores distribution of CCTxS8 with different amounts of dopant, which was extracted from Table 5-10. The grain distribution was dominated
by large grain (see Table 5-9.) and there is not significant change in size with increasing the amount of tin dopant from 0.10 to 0.25 mol (see Figure 5.39 and Figure 5.40). In contrast to CCTxS4, the density was ~4.6 g/cm$^3$, then increases as the amount of tin dopant increases. Interestingly, the pores distribution is not significantly changed as the amount of tin dopant increases. The density reaches ~5.0 g/cm$^3$ at 0.25 mol tin dopant.

Figure 8.64. Density, grains and pores distribution of CCTxS8 with different amount of dopant.

Figure 8.65. shows density, grains and pores distribution of CCTxS12 with different amount of dopant, which was extracted from Table 5-14. The grain distribution was dominated by large grain (see Table 5-13.) and the size tends to decrease with increasing the amount of tin dopant (see Figure 5.39 and Figure 5.40). In contrast to CCTxS8 but identical to CCTxS4 trend, at pure CCTO, the grain was dominated by large grain, and the density was ~4.6 g/cm$^3$, then decreases as tin dopant (0.05 mol) added in this system. The pores distribution is not significantly changed as the amount of tin dopant increases, but the density increases as the amount of tin dopant increases, and reaches ~4.8 g/cm$^3$ at 0.25 mol tin dopant.
In summary, increasing the amount of tin dopant was decreased the large grain and pore size. Similar to Ni et. Al [23] reported, that the average grain size decreases with increasing the amount of tin dopant up to 0.1 mol, which is from 56 μm to 27 μm. On the other hand, increasing sintering hold time reduces the pore size and increases the small grain size, but recently, the detailed mechanism is not well understood. The density tends to increase as the amount of tin dopant increases, and the magnification of density depends on the sintering hold time. The grains and pores distribution are not significantly changed with increasing the amount of tin dopant.

8.2.3. Electrical properties.

In this section, the electrical properties are presented as relative dielectric constant per unit length ($\varepsilon_{\text{rel}}$), equivalent dielectric constant ($\varepsilon_{\text{eq}}$), grain boundary thickness ($t_{\text{gb}}$), non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_B$) as a function of the amount of dopant.

8.2.3.1. Niobium doped CCTO.

The relative dielectric constant per unit length ($\varepsilon_{\text{rel}}$) of CCTxN4 with different amounts of dopant measured at -100°C, 25°C and 200°C over the frequency range of 5 Hz to 13 MHz are plotted in Figure 8.66.(a). Low, transition and high temperature are represented by -100°C, 25°C
and 200°C, respectively. For niobium doped CCTO samples, relative dielectric constant were much lower than that pure CCTO at selected temperatures. Initially, the relative dielectric constant decreased with additional dopant then increased with increasing the amount of niobium dopant. In general, increasing temperature was decreasing relative dielectric constant ($\varepsilon_{\text{rel}}$).

The grain boundary thickness ($t_{\text{gb}}$) of CCTxN4 with different amount of dopant measured at -100°C, 25°C and 200°C over the frequency range of 5 Hz to 13 MHz are plotted in Figure 8.66.(b). Identical to $\varepsilon_{\text{rel}}$, the $t_{\text{gb}}$ decreased with additional dopant then increased as increasing the amount of niobium dopant. The relative dielectric constant is inversely proportional to the ratio of grain boundary thickness and grain thickness (see Equation (60)).

![Diagram](image_url)

**Figure 8.66.** (a) Relative dielectric constant ($\varepsilon_{\text{rel}}$) and (b) grain boundary thickness ($t_{\text{gb}}$) of CCTxN4 with different amount of dopant.
In this study, the grain thickness niobium doped CCTO increases as the small grain size increases, but the grain boundary thickness also increases with increasing the amount of niobium dopant, as consequently, the relative dielectric constant have similar trend to the grain boundary thickness. In general, increasing temperature was decreasing grain boundary thickness ($t_{gb}$).

Figure 8.67. shows non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_b$) of CCTxN4 with different amount of dopant. The $\alpha$ increases with additional dopant and reaches maximum $\sim$ 630 at 0.10 mol niobium dopant and then drops with increases in the amount of dopant. The $\Phi_b$ decreases as increases with the amount dopant, in the range from 0.177 to $\sim$0.173 eV.

Figure 8.68. shows non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_b$) of niobium doped CCTO with different amounts of dopant at 8 hours sintering hold time. In contrast to CCTxN4, the value of $\alpha$ was lower than 200. In general, the $\alpha$ tends to increase with additional dopant and reaches a maximum $\sim$ 150 at 0.20 mol niobium dopant and then tend to decrease with increasing the amount of dopant. The $\Phi_b$ at 0.05 mol was higher than pure CCTO, then the $\Phi_b$ decreases with increases in the amount dopant, in the range from $\sim$0.177 to $\sim$0.174 eV.

Figure 8.69. shows non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_b$) of...
CCTxN12 with different amount of dopant. The $\alpha$ increases with additional dopant and reaches a maximum $\sim 520$ at 0.05 mol niobium dopant and then decreases with increases in the amount of dopant. The $\Phi_B$ decreases with increases in the amount dopant, in the range from $\sim 0.178$ to $\sim 0.174$ eV.

Figure 8.68. non-linear coefficient of conduction and barrier height of CCTxN8 with different amount of dopant.

Figure 8.69. non-linear coefficient of conduction and barrier height of CCTxN12 with different amount of dopant.

In summary, initially, the relative dielectric constant ($\varepsilon_{\text{rel}}$) and grain boundary thickness ($t_{\text{gb}}$) of niobium doped CCTO decreased with additional dopant, then increased with increasing the amount of niobium dopant. This result is still relevant to Liu et. al. [63] reported, depends on the frequency, the real part of dielectric constant will increase as increasing niobium dopant at low-frequency and will decrease as increasing niobium dopant at high-frequency. In contrast to
the relative dielectric constant, the non-linear coefficient of conduction (\(\alpha\)) of niobium doped CCTO tends to increase with additional dopant, then decreased as increasing the amount of niobium dopant. The barrier height (\(\Phi_B\)) tends to decrease as increases niobium dopant, with the range between \(\sim 0.178\) and \(\sim 0.173\) eV. Unfortunately, there is no paper determining the effect of the amount of niobium dopant to neither non-linear coefficient of conduction nor barrier height of niobium doped CCTO.

8.2.3.2. Tin doped CCTO.

The relative dielectric constant per unit length (\(\varepsilon_{\text{eff}}\)) of CCTxS4 with different amount of dopant measured at -100°C, 25°C and 200°C over the frequency range of 5 Hz to 13 MHz are plotted in Figure 8.70.(a) Similar to CCTxN4, the low, transition and high temperature are represented by -100°C, 25°C and 200°C, respectively.

Identical to CCTxN4, for tin doped CCTO samples, the relative dielectric constants were lower than that pure CCTO at all selected temperatures. The relative dielectric constant decreased with additional dopant then increased as increasing the amount of tin dopant up to 0.20 mol. The relative dielectric constant at 0.25 mol is lower than \(\varepsilon_{\text{eff}}\) at 0.20 mol, but it is not a strong indication that the \(\varepsilon_{\text{eff}}\) will decrease as further tin dopant increases. In contrast to Ni et. al. [23] reported, that dielectric constant decreases with increasing tin substitution. In general, increasing temperature was decreasing relative dielectric constant (\(\varepsilon_{\text{eff}}\)).

The grain boundary thickness (\(t_{gb}\)) of CCTxS4 with different amount of dopant measured at -100°C, 25°C and 200°C over the frequency range of 5 Hz to 13 MHz are plotted in Figure 8.70.(b) Identically to \(\varepsilon_{\text{eff}}\), for tin doped CCTO samples, grain boundary thickness was lower than that pure CCTO at all selected temperatures. The grain boundary thickness decreased with additional dopant then increased with increasing the amount of tin dopant up to 0.20 mol. The grain boundary thickness at 0.25 mol is lower than \(t_{gb}\) at 0.20 mol, but it is not a strong indication that the \(t_{gb}\) will decrease as tin dopant increases. In contrast to niobium doped CCTO, tin doped CCTO was dominant large grain, and the large grain size decrease with increasing the amount of tin dopant. The grain boundary thickness is inversely proportional to the ratio of relative
dielectric constant and grain thickness (see Equation (60)). Decreasing the grain thickness is following by decreasing the grain boundary thickness, as consequently, the relative dielectric constant has a similar trend to grain boundary thickness. In general, increasing temperature was decreasing grain boundary thickness ($t_{gb}$).

![Graph showing relative dielectric constant and grain boundary thickness vs. mol Sn for CCTxS4 at different temperatures.

Figure 8.70. (a) Relative dielectric constant ($\varepsilon_{rel}$) and (b) grain boundary thickness ($t_{gb}$) of CCTxS4 with different amount of dopant.

Figure 8.71. shows non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_B$) of CCTxS4 with different amount of dopant. The $\alpha$ tends to increase with additional dopant (as at 0.05 mol, the $\alpha$ lower than pure CCTO) and reaches maximum ~ 830 at 0.15 mol tin dopant and then decreases with increases the amount of dopant. The $\Phi_B$ at 0.05 mol was higher than pure CCTO, then the $\Phi_B$ decreases as increases the amount dopant, in the range from ~0.177 to
~0.174 eV. The barrier height correlated to conductivity of grain-boundary which the dopant will decreases the conductivity of grain-boundary.

Figure 8.71. non-linear coefficient of conduction and barrier height of CCTxS4 with different amount of dopant.

The $\alpha$ and $\Phi_B$ of tin doped CCTO with different amount of dopant at 8 hours sintering hold time is shown in Figure 8.72. In contrast to CCTxS4, the $\alpha$ was tends to increase with additional dopant and reaches maximum ~500 at 0.25 mol tin dopant, but identically to CCTxS4, the $\Phi_B$ at 0.05 mol was higher than pure CCTO, then the $\Phi_B$ decreases with increases in the amount dopant, in the range from ~0.177 to ~0.174 eV.

Figure 8.72. non-linear coefficient of conduction and barrier height of CCTxS8 with different amount of dopant.
Figure 8.73. shows non-linear coefficient of conduction ($\alpha$) and barrier height ($\Phi_b$) of CCTxS12 with different amount of dopant. The $\alpha$ increases and reaches maximum ~600 at 0.10 mol tin dopant and then decreases with increases the amount of dopant. On the other hand, the $\Phi_b$ decreases with increases in the amount dopant, in the range from ~0.178 to ~0.174 eV.

Figure 8.73. non-linear coefficient of conduction and barrier height of CCTxS12 with different amount of dopant.

In summary, initially, the relative dielectric constant ($\varepsilon_{\text{eff}}$) and grain boundary thickness ($t_{\text{gb}}$) of tin doped CCTO decreased with additional dopant, then increased with increasing the amount of tin dopant up to 0.20 mol. In contrast to the relative dielectric constant, the non-linear coefficient of conduction ($\alpha$) of tin doped CCTO tends to increase with additional dopant, then decreased with increasing the amount of tin dopant. The barrier height ($\Phi_b$) tends to decrease with increases in the amount of tin dopant, with the range between ~0.178 and ~0.174 eV. Again, there is not a report that can be used as comparison.

### 8.2.4. Discussion in influence of adding dopant

The mole ratio of elements varies with the amount of niobium and tin dopant and sintering holding time. The CaTiO$_3$ as a secondary phase appears up to 0.15 mol and NbO and/or Nb$_2$O$_5$ as secondary phases present in high niobium dopant. It seems the secondary phase will be reduced by longer sintering hold time at all the amounts of niobium dopant, based
on Hong et al. [3] and Liu et al. [63] reported. The mole ratio of all elements results correspond to the intended value at all the amount of tin dopant by EDS but vary with increasing the amount of tin dopant by XRF. The SnO as secondary phase is present in all of the samples of CCTxS4 and CCTxS8. SnO$_2$ and/or CuO as secondary phase appear in the sample of CCTxS12. In contrast to niobium doped CCTO, the secondary phase of tin doped CCTO appears at longer sintering holding time, based on Ni et al. [23] reported.

Increasing the amount of niobium and tin dopant decrease the grain and pore size. On the other hand, increasing sintering hold time reduces the pore size and increases the small grain size. The density tends to increase as the amount of niobium and tin dopant increases, and the magnitude of density depends on the sintering hold time. The (small) grains distribution increases and the pores distribution decreases with increasing the amount of niobium dopant. On the other hand, the grains and pores distribution are not significantly changed with increasing the amount of tin dopant.

The relative dielectric constant ($\varepsilon_{\text{rel}}$) and grain boundary thickness ($t_{\text{gb}}$) of niobium and tin doped CCTO decreased with additional dopant, and then increased as increasing the amount of niobium dopant. In contrast to the relative dielectric constant, the non-linear coefficient of conduction ($\alpha$) of niobium and tin doped CCTO tends to increase with additional dopant, and then decreased as increasing the amount of niobium and tin dopant. The barrier height ($\Phi_B$) tends to decrease as increases niobium and tin dopant, with the range between ~0.178 and ~0.173 eV. Unfortunately, there is no report that can be used as comparison the results.

Figure 8.74. shows the activation energy ($E_a$) of bulk and grain boundary (GB) of niobium and tin doped CCTO, which was extracted from Figure 6.44. and 6.45. The bulk activation energy decreases with increasing the amount of dopant and the grain boundary activation energy tends to decrease with increasing the amount of dopant. In contrast to Ni et al. [23] reported that activation energy increases with increasing tin substitution, 0.102, 0.110, and 0.111 eV for 0, 0.05 and 0.10 mol tin dopant, respectively. Their result is similar to bulk activation energy in this study.
Figure 8.74. Activation energy as a function of the amount of niobium and tin dopant at 4 hours sintering hold time.

8.3. Discussion

There are two methods to determine non-linear coefficient of conduction. First, using a slope of a linear curve in plot $\ln J - \ln E$ [12] to determine $\alpha_1$, this method is commonly used in the varistor industry. Second, using a ratio of differential of $\ln J$ and $\ln E$ [10, 50] to determine $\alpha_2$. The two methods are shown in Figure 8.75.

![Figure 8.75. Illustration of two methods were used to determine the non-linear coefficient of conduction.](image)

Equation (91) to (93) determine the $\alpha_1$ using a slope of linear curve in plot of $\ln J - \ln E$. 

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Levine [10] and Clarke [50] determine $\alpha$ using a ratio of $d \ln (J)$ and $d \ln (E)$ is shown in Equation (94), Xue et. al. [26] and Liu et. al. [28] also used similar method but prefer using logarithms equation, $\alpha = \frac{d \log (I)}{d \log (V)}$.

Only a few workers have already mentioned in their paper, what current density range has been used, but not only the current density range will give effect to non-linear coefficient of conduction. A number of points in the current density range will give different value of non-linear coefficient of conduction. Figure 8.76. shows the different results between $\alpha_1$ and $\alpha_2$.
Figure 8.76.(a) and (b) show the different value of $\alpha_1$, and show the same results of $\alpha_2$ in both graphs. Ramirez et. al. [128] reported an $\alpha$ value of 65 for the traditional current density range of 1–10 mA/cm$^2$. However, the $\alpha$ value can reach values 1535 for the current density range of 3–30 mA, was higher than 900 [7]. Both Ramirez et. al. [128] and Chung et. al. [7] did not explain how to determine the non-linear coefficient of conduction and the conditions of current density range.

In this study, a slope method to determine the non-linear coefficient of conduction was used at all samples and the maximum value of $\alpha$ with lowest error of slope is chosen as the final result. The different value of non-linear coefficient of conduction (both $\alpha_1$ and $\alpha_2$) and the current density range of CCTxN4, CCTxN8, and CCTxN12 is shown in Table 8-5., Table 8-6., and Table 8-7. respectively.

Table 8-3. The value of $\alpha_1$ and $\alpha_2$ of CCTxN4 with different current density range.

<table>
<thead>
<tr>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\Delta J$ (mA/cm²)</th>
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<tbody>
<tr>
<td>CCTO4</td>
<td>31</td>
<td>168</td>
</tr>
<tr>
<td>6 28</td>
<td>7.6 – 9.5</td>
<td></td>
</tr>
<tr>
<td>CCT05N4</td>
<td>68</td>
<td>509</td>
</tr>
<tr>
<td>79 175</td>
<td>4.3 – 10.5</td>
<td></td>
</tr>
<tr>
<td>CCT10N4</td>
<td>126</td>
<td>636</td>
</tr>
<tr>
<td>88 576</td>
<td>2.7 – 9.9</td>
<td></td>
</tr>
<tr>
<td>CCT15N4</td>
<td>43</td>
<td>52</td>
</tr>
<tr>
<td>2 2</td>
<td>2.8 – 10.2</td>
<td></td>
</tr>
<tr>
<td>CCT20N4</td>
<td>54</td>
<td>56</td>
</tr>
<tr>
<td>2 2</td>
<td>1.7 – 10.4</td>
<td></td>
</tr>
<tr>
<td>CCT25N4</td>
<td>78</td>
<td>83</td>
</tr>
<tr>
<td>3 3</td>
<td>2.9 – 10.6</td>
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</table>

Table 8-4. The value of $\alpha_1$ and $\alpha_2$ of CCTxN8 with different current density range.

<table>
<thead>
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<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
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<tr>
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<td>41</td>
<td>53</td>
</tr>
<tr>
<td>3 3</td>
<td>2.8 – 11.1</td>
<td></td>
</tr>
<tr>
<td>CCT05N8</td>
<td>17</td>
<td>58</td>
</tr>
<tr>
<td>10 38</td>
<td>4.5 – 9.9</td>
<td></td>
</tr>
<tr>
<td>CCT10N8</td>
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<td>118</td>
</tr>
<tr>
<td>6 10</td>
<td>5.4 – 9.9</td>
<td></td>
</tr>
<tr>
<td>CCT15N8</td>
<td>27</td>
<td>41</td>
</tr>
<tr>
<td>2 2</td>
<td>2.8 – 11.2</td>
<td></td>
</tr>
<tr>
<td>CCT20N8</td>
<td>86</td>
<td>148</td>
</tr>
<tr>
<td>7 10</td>
<td>5.8 – 11.0</td>
<td></td>
</tr>
<tr>
<td>CCT25N8</td>
<td>35</td>
<td>45</td>
</tr>
<tr>
<td>2 2</td>
<td>2.8 – 10.4</td>
<td></td>
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Table 8-5. The value of $\alpha_1$ and $\alpha_2$ of CCTxN12 with different current density range.

<table>
<thead>
<tr>
<th>CCT05N12</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\Delta J$ (mA/cm²)</th>
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<tbody>
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<td>526</td>
<td>31</td>
<td>100</td>
<td>3.6 - 10.7</td>
</tr>
<tr>
<td>505</td>
<td>31</td>
<td>27</td>
<td>5.4 - 10.7</td>
</tr>
<tr>
<td>212</td>
<td>17</td>
<td>27</td>
<td>2.8 - 10.9</td>
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<tr>
<td>315</td>
<td>27</td>
<td>27</td>
<td>2.8 - 11.6</td>
</tr>
</tbody>
</table>

Figure 8.77. shows relative dielectric constant per unit length ($\varepsilon_{eff}$) and non-linear coefficient of conduction ($\alpha$) as a function of the amount of dopant. The relative dielectric constant tends to decrease with increasing the amount of niobium and tin dopant, on the other hand, the non-linear coefficient of conduction increases up to a certain mol of dopant then decreases due to excess of niobium and tin dopant.

![Graph showing relative dielectric constant and non-linear coefficient of conduction vs mol dopant]

Figure 8.77. Relative dielectric constant per unit length ($\varepsilon_{eff}$) and non-linear coefficient of conduction ($\alpha$) as a function of the amount of dopant.

There is no direct relationship between relative dielectric constant and non-linear coefficient of conduction. The dielectric constant was affected by uniformity of grains distribution which come from the sintering behaviour. The secondary phase was assumed not to change, but the grain size and the distribution change that affected the number of grain boundaries and then resulted to grain boundary thickness. The grain boundary thickness was presented the
capacitance between the grains. On the other hand, the non-linear coefficient of conduction is represented by barrier height, which reflected of conductivity of the grains.

Figure 8.78. shows barrier height ($\Phi_B$) and grain boundary thickness ($t_{gb}$) as a function of the amount of dopant. The barrier height and grain boundary thickness tend to decrease as increasing the amount of niobium and tin dopant. Figure 8.78. shows the barrier height in line with grain boundary thickness behaviours. The dopant reduces the energy as present in narrow of grain boundary thickness. The grain boundary thickness is a distance of lattice distortion caused as the grain boundary extends into two neighbouring crystals; it is also have the electrical and physical properties of polycrystalline materials. The narrowest grain boundary thickness will increase rapidly the effective dielectric constant which is attributed to the formation of thin insulating boundaries with the conducting grains.

According to the Figure 8.77. and 8.78., it can be found that the residual impurities come from niobium and tin dopant have a small influence on the barrier height, the barrier height obviously decreases as the amount of dopant increases. Consequently, the dielectric properties tend to decrease too; on the other hand, increasing the sintering hold time could increases the dielectric constant and the non-linear coefficient of conduction of pure CCTO (see sub-chapter 8.1.3). Based on the behaviours of pure CCTO, the decreasing of electrical properties as increasing the amount of dopant could be adjust by sintering hold time.

Figure 8.79. shows barrier height ($\Phi_B$) and activation energy ($E_a$) as a function of the amount of dopant.
amount of dopant (a) CCTxN4 and (b) CCTxS4. The activation energy of CCTxN4 is in line with barrier height which is associated to conduction processes; the niobium dopant is indicated to reduce the conductivity of sample. Similar to CCTxN4, the activation energy of CCTxS4 is in line with barrier height which is associated to conduction processes; the tin dopant also is indicated to reduce the conductivity of sample.

![Graphs of CCTxN4 and CCTxS4](image)

**Figure 8.79.** Barrier height and activation energy as a function of the amount of dopant (a) CCTxN4 and (b) CCTxS4.

Figure 8.79. also shows the large difference displayed in $E_a$ which is a strong indicator that different charge transport mechanisms exist in niobium and tin doped CCTO. In this study, the chemical differences between bulk and grain boundary of pure CCTO and niobium and tin doped CCTO are not well understood, but the valency present, the barrier height and the activation energy show the potential defect mechanisms that are responsible for inducing semiconductivity in the grains. Ni et. al. [23] showed that the behaviours of activation energy
can be considered as the result of modified Ti$^{3+}$/Ti$^{4+}$ and Cu$^+$/Cu$^{2+}$ mixed valence structures. The mixed valence structures were investigated by X-ray photoemission spectroscopy, and they found that decreased concentration of Ti$^{3+}$ and Cu$^+$ ions will lead to less dipoles originating from Ti$^{3+}$/Ti$^{4+}$ and Cu$^+$/Cu$^{2+}$ mixed valence structures, and then will increase the activation energy [23].
9. Conclusion and Suggestion for Further Work.

9.1. Conclusion.

The phase equilibria, microstructures, and the electrical properties of CCTO were investigated in terms of the sintering hold time and dopant. The niobium and tin dopant were added to CaCu$_3$(Ti$_{4-x}$M$_x$)O$_{12}$ in concentrations of 0.05, 0.10, 0.15, 0.20 and 0.25 mol.

The non-linear coefficient of conduction ($\alpha$) of niobium and tin doped CCTO depends on the sintering hold time and the amount of dopant. The maximum value of $\alpha$ of niobium doped CCTO is ~600 at CCT10N with 4 hours sintering hold time, and the maximum value of $\alpha$ of tin doped CCTO is ~830 at CCT15S with 4 hours sintering hold time. Identical to $\alpha$ value trend, the barrier height ($\Phi_B$) also varies according to sintering hold time and the amount of dopant, and reaches maximum ~0.180 eV at CCT05N with 4 hours sintering time in the range of ~0.173 to ~0.180 eV. There is no direct correlation between non-linear coefficient of conduction and barrier height in terms of sintering hold time for niobium and tin doped CCTO.

The relative dielectric constant tends to decrease with increasing the amount of niobium and tin dopant, on the other hand, the non-linear coefficient of conduction increases up to a certain mol dopant then decreases due to excess of niobium and tin dopant. The barrier height and grain boundary thickness tend to decrease with increasing the amount of niobium and tin dopant. The barrier height is in line with grain boundary thickness behaviour. The narrowest grain boundary thickness will increase rapidly the effective dielectric constant which is attributed to the formation of thin insulating boundaries with the conducting grains.

The bulk activation energy of CCTO is in the range of 0.044 and 0.118 eV and the grain boundary activation energy is in the range of 0.389 and 0.706 eV. The large difference between bulk and grain boundary $E_a$ is a strong indicator that different charge transport mechanisms exist on niobium and tin doped CCTO.

9.2. Suggestion for Further Work.

The oxidation state of the metals and the determination of the value of $\delta$ in CaCu$_3$Ti$_{4-x}$O$_{12-\delta}$ may be measured in a number of different ways. Wave length dispersive x-ray spectroscopy
would give greater accuracy in elemental composition of grains. Detailed structural studies using synchrotron x-ray sources or neutrons would allow observation of occupancy levels of both cation and anion sites within the perovskite structure. The neutron data would give better determination of the oxygen position because of the similarity of scattering for all elements, x-ray is in comparison dependent on atomic number.

The oxidation state of the elements within CCTO and its doped variants could also be studied by x-ray photoelectron spectroscopy (XPS). This technique would only give an overall measure of the oxidation state as it measures over a large area of sample (e.g. 5 x 5 mm) and could not therefore show differences between grains as the electron microscopy methods do.

Deep level transient spectroscopy of CCTO will provide details of the trap states in these varistors and their variation with changes in temperature. These trap states can be related to the different types of defects which control overall electrical properties of varistor. The defects include dopant elements, barrier and depleted barrier regions.
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