THE EFFECT OF HEATING AND COOLING SINTERING RATE ON $CaCu_3Ti_4O_{12}$ (CCTO) FORMATION

by

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DECLARATION

I declare that this thesis entitled “The Effect of Heating and Cooling Sintering Rate on $CaCu_3Ti_4O_{12}$ (CCTO) Formation” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ______________________________
Name : ______________________________
Date : ______________________________

ACKNOWLEDGEMENT

This thesis is nearly the end of my long journey in obtaining and fulfill the requirement of my degree in Materials Technology. I have not travelled alone through this journey. There are some people who came by and some who consistently there for me have made this journey easier. With words of encouragement and wisdom, they never failed to guide me into different places and perspectives in search of theories and ideas.

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Thank you.

Munirah

ABSTRACK

CCTO is the dielectric material that possessed giant dielectric constant. The purpose of this study is to investigate the effect of heating and cooling sintering rate on CCTO phase formation, density, microstructures and dielectric properties. The samples were prepared via solid state technique. The raw materials of $CaCO_3$, CuO and TiO_2 based on the calculated stoichiometric ratios were mixed for 24 hours. The powder mixture was calcined at 900 °C for 12 hours. The calcined powder were pressed into pellets and sintered at 1040 °C for 10 hours. Density and porosity were measured using Archimedes Principles, X-Ray Diffraction (XRD) was used to identify phase formation and Scanning Electron Microscope (SEM) was used to observed microstructure of the sintered pellets. The specimens showed the grain size decrease as heating rate increase. Microstructure displayed dense grain formation and hence yielded a high density for SP5. Formation of single phase of CCTO was found in all the sintered pellets. SP3 was identified to have larger and coarser grain when exposed to 3 °C/min of heating rate. In this study, SP5 was found as the optimum pellet that shown a good potential as dielectric material regarding the density and size of microstructure obtained.

ABSTRAK

CCTO adalah bahan dielektrik yang mempunyai pemalar dielektrik yang tinggi. Tujuan kajian ini adalah untuk mengkaji kesan kadar pemanasan dan penyejukan dalam proses pensinteran terhadap pembentukan fasa CCTO, ketumpatan, mikrostruktur dan pemalar dielektrik. Sampel disintesis melalui teknik keadaan pepejal. Bahan mentah $CaCO_3$, CuO dan TiO_2 dicampur berdasarkan nisbah stoikiometri, dikisar selama 24 jam. Campuran serbuk dikalsin pada suhu 900 °C selama 12 jam. Serbuk yang dikalsin ditekan kepada bentuk pelet dan disinter pada suhu 1040 °C selama 10 jam. Ketumpatan dan keliangan ditentukan melalui prinsip Archimedes, Pembelauan sinar-X (XRD) digunakan untuk menetukan fasa pembentukan dan mikroskop imbasan electron (SEM) digunakan untuk memerhatikan mikrostruktur pelet yang disinter. Pelet yang disinter menunjukkan saiz butiran semakin mengecil apabila kadar pemanasan semakin meningkat. Mikrostruktur menunjukkan pembentukan butiran yang padat dan sekaligus menyumbang kepada ketumpatan yang tingi untuk SP5. Pembentukan fasa tunggal CCTO didapati dalam pellet yang disinter. SP3 dikenalpasti mempunyai butiran yang lebih besar dan kasar apabila didedahkan kepada kadar pemanasan 3 °C/min. Dalam kajian ini, SP5 dikenalpasti sebagai pelet yang optimum untuk bahan dieletrik berdasarkan ketumpatan dan saiz mikrostruktur yang diperolehi.

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LIST OF ABBREVIATIONS

CCTO	Calcium copper titanium oxide
$CaCO_3$	Calcium carbonate
CuO	Copper oxide
TiO_2	Titanium oxide
XRD	X-ray diffraction
SEM	Scanning electron microscope

CHAPTER 1

INTRODUCTION

This research is conducted to study about the effect of different heating and cooling rate during the sintering process of Calcium Copper Titanium Oxide (CCTO) formation.

1.1 Background of Study

The increasing development of advanced ceramic materials has already widespreaded and this continue to create many great findings to support the existing technologies. This type of ceramic has unique properties such as electrical, magnetic and optical properties. Sometimes they also appear in combination properties that usually enable them to be exploit into new products. Moreover, advanced ceramics are utilized in device application like electroceramic. Electroceramic can be divided into several classes which are superconductor, semiconductor, piezoelectric, ferroelectric and dielectric.

On top of that, dielectric material getting a high demand in miniaturization of microelectronic device based on its capacitive elements that can store the charge. Dielectric material is a poor conductor of electric current which is no current flow when it is place in electric field. This is due to no free electron moving, make it a good insulator thus suitable for capacitor application.

CCTO has catch great attention of researchers due to their huge dielectric permittivity (ε') that range from 100 000 to near 400 000 that make it be the most potential material for capacitor application (Sulaiman et al, 2013). CCTO is categorised as perovskite structure that has body centred cubic crystal structure.

CCTO can be synthesized in different modes such as sol gel method, precursor oxalate route, chemical layer deposition and solid state reaction. In this study, solid state reaction is adopted for preparation of CCTO. There are a few processes that involved in this route including mixing, calcination, shaping and sintering.

Sintering is the most important step in solid state reaction since it can influence the formation of microstructure (Lutgard and Mohamed, 2003). Solid state sintering is the process whereas the shaped green pellet is heated to a certain range temperature in absence of liquid. It is significant to find the right sintering variables in obtaining the correct microstructure with high dielectric properties.

In this study, the effect of different heating and cooling sintering rate to microstructure and dielectric properties on CCTO formation will be investigated.

1.2 Problem Statement

CCTO has been discovered as a material that exhibits high dielectric constant which is very important in miniaturization of electronic devices. In order to produce CCTO, there are a few routes that can be adopted such as sol gel method, precursor oxalate route, chemical layer deposition and solid state reaction. For this research, solid state is chosen as conventional method in preparation of CCTO. The processes that involve in this technique including mixing, calcination, shaping and sintering. Every single steps in solid state technique will influence the final properties of CCTO. A lot of previous researches were done about temperature and dielectric properties for the sintering. But no research has been report on the effect of different heating and cooling rate during sintering process on CCTO formation.

1.3 Objectives

There are two main objectives to be achieved in this research as stated below:

i. To synthesize pure CCTO

ii. To study the effect of different heating and cooling rate during sintering process on CCTO phase formation, density and microstructure

1.4 Expected outcomes

The information that will be obtained through this study is to produce the single phase CCTO. Other than that, the effect of different heating and cooling rate during CCTO sintering can be understood. The phase composition, microstructure and density will be emphasised during sintering rate.

CHAPTER 2

LITERATURE REVIEW

This part will discuss about previous research that has been done relating to this topic. These include calcium copper titanium oxide (CCTO), solid state reaction, dielectric properties and sintering process.

2.1 Introduction

A lot of study have been carried out on CCTO ceramic regarding the dielectric properties improvement that make it suitable for capacitor application. There are many parameters that have to be considered in synthesizing of CCTO due to the dielectric loss contribution such as temperature and environment. In this paper, the effect of different heating and cooling sintering rate towards microstructure have been highlighted. Before this, there are some previous study that have been carried out by the researchers relating to this topic. Increasing the temperature can improve the density and second phase formation of Cu_2O (Mohamed et al, 2007)

2.2 Electroceramics

Advanced ceramics can be grouped into few types which are insulators, superconductors, high-k dielectric, ferroelectric, magnetic and photonic ceramics. Over passing years and research that have been done, advanced electroceramics have become significant material in the development of new and modern technologies due to its ability to display a rich array of multifunctional properties that give rise to a wide range in electronic applications such as computers and industries such as telecommunications and aerospace. Commonly used electroceramis include barium titanate ($BaTiO_3$), lead titanate ($PbTiO_3$), zinc oxide and lead zirconate-titanate (PZT) [$Pb(Zr, Ti)O_3$] (Callister and Rethwisch, 2011).

2.2.1 Properties of Ceramics

Some advance ceramics are called as electroceramics because of their unique electrical properties such as ferroelectric, piezoelectric, superconductors and dielectric. These properties that appear usually enable them to be exploit into new products and utilized in device application commonly in electronic industry.

Superconductive material is commonly type of electroceramic. Superconductor is a material that conduct electricity with no resistant and carry current without losing any energy. Usually metal is the best superconductor material.

The other significant material is piezoelectric. Piezoelectric material like quartz and lead zirconate ($PbZnO_3$) has complicated crystal structure with low degree of symmetry. By heating or cooling it, the piezoelectric behaviour of polycrysalline sample can be improved (Callister and Rethwisch, 2011). Piezoelectric material commonly used in tranducers and apply in device such as microphones and speakers.

Other than that, this type of electroceramic that having ferroelectric behaviour exhibit spontaneous polarization. barium titanate ($BaTiO_3$) that known as ferroelectric material possess great electric permittivity due to ferroelectric phase transition and their perovskite structure (Callister and Rethwisch, 2000). Figure 2.1 below shows the perovskite structure of $BaTiO_3$.

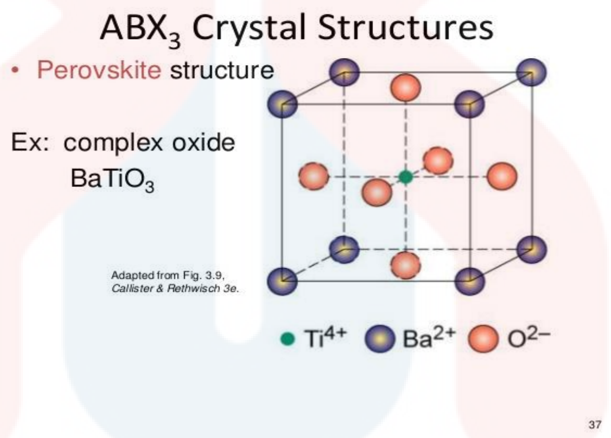


Figure 2.1: Perovskite structure of BaTiO_3 (Callister and Rethwisch, 2000)

In the other hand, dielectric material is a poor conductor of electric current which is no current flow when it is place in dielectric field. This is due to no free electron moving. Thus polarization occurs. Dielectric material attracted much concern due to its ability that can store charge thus make it suitable for capacitor application.

2.3 Dielectric Materials

A dielectric is an electrical insulator that can be polarized only by applying an applied electric field. Electric charges stop flowing through the material but slight shift from their average equilibrium positions causes dielectric polarization whenever a dielectric is placed in the electric field. The term dielectric is used to indicate the energy storing capacity of the material. This type of material usually appears in high mechanical strength and high degree of crystalline structure stability (Callister and Rethwisch, 2011). Usually dielectric material exhibits a great dielectric constant that make them as potential candidate as capacitor application.

Other than PZT, one of the promising of dielectric material that mostly used in microelectronic applications is CCTO. Recently CCTO has captured much interest due to its extraordinarily high dielectric constant (~104) which is and possesses good temperature stability over a temperature range between 100 K and 400 K and practically frequency independent in the frequency range 102 Hz –106 Hz (Chamola et al, 2011)

2.4 Calcium Copper Titanium Oxide (CCTO)

Decreasing the size in microelectronic device seems has been a considerable interest in study of the high dielectric constant materials. The dielectric properties of CCTO material were first reported by Subramanian et al in 2000. $\mathrm{ACu_3Ti_4O_{12}}$ (A=trivalent rare earth or Bi) type materials were discovered exhibit large dielectric constant. $\mathrm{CaCu_3Ti_4O_{12}}$ showed the most great behavior by remaining steady in wide range temperature from 100 K to 400 K and have dielectric constant about 12 000 at 1 kHz. Generally, during ferroelectric transition, some dielectric material having a great change. This property cause the limitation of application in industry since usually it is required for dielectric material is independent of the temperature. Hence, CCTO become significance desire to researchers because its low dependence on temperature.

CCTO has a perovskite structure that has body centered cubic crystal structure with slightly with tilted ($\mathrm{TiO_6}$) octahedra facing each other (Chandra, 2013). Figure 2.2 indicates the structure of CCTO as TiO6 octahedral where Cu atoms are bonded to four oxygen atoms and large Ca atoms without any bond while Figure 2.3 shows a clearer image of the CCTO structure drawn with $\mathrm{TiO_6}$ octahedral, Cu as black spheres, O as white spheres, and Ca at the origin and cube center.

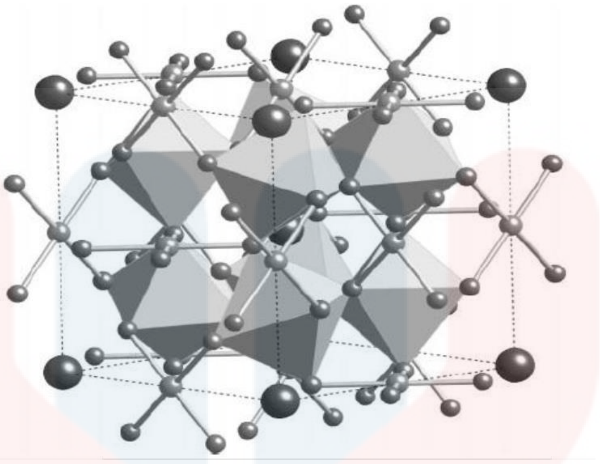


Figure 2.2: The structure of Ca$Cu_3Ti_4O_{12}$ shown as TiO_6 octahedral (Chandra,2013)

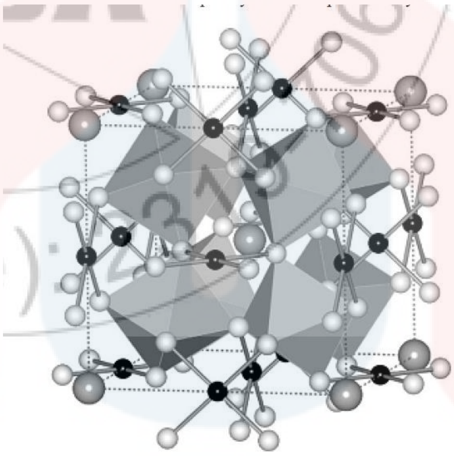


Figure 2.3: The Ca$Cu_3Ti_4O_{12}$ structure drawn with TiO_6 octahedral (Abdelal et al, 2012)

Knowing as a material that display high electric permittivity that make it as the most potential candidate as capacitor, CCTO has been used in wide application such as aircrafts, automobiles and electronic industry.

2.4.1 Dielectric Properties of CCTO

Dielectric material become significant due to the variety of application as an insulator in microelectronic device. The perovskite-based oxide CCTO have been discovered as a great potential candidate in capacitor application due to the giant dielectric permittivity up to 400 K (Chandra, 2013). As the rapid changing in technology, material with high dielectric constant would be good to store charge and offered an opportunity for microelectronic devices miniaturization. However, CCTO can having dielectric loss due to some of parameters such as temperature, environment, thickness (for thin film) and frequencies. Instead this behaviour will turn them into a conductor material that allow the current to flow. According to Li et al (2009), the film with less than 100 nm of dielectrics properties can be affect by the internal layer between metal electrode and CCTO film and by microstructure.

Deep concerning to the dielectric leakage, many researches come out with their study in improving the dielectric properties. Usually substituting and doping are commonly methods to decrease the loss up to present. CCTO ceramics doped with Sr can lower dielectric loss and improve voltage property by decreasing the grain size and increasing the impedance of grain boundary (Mu et al, 2008). Due to the internal boundary layer capacitance effect, Sr-CCTO ceramic display high dielectric properties (Xu et al, 2009). Sulaiman et al (2012) further this investigation by study the effect on grains of Nb-doped CCTO in nanoscale.

2.5 Solid State Reaction

Preparation of CCTO can be carried out in a few different routes such as sol gel method, precursor oxalate route, chemical layer deposition and solid state reaction. In this research, solid state reaction is used to synthesis the CCTO. This is because solid state route offered many advantages to the research outputs such as lower reaction temps, eliminate intermediate impurity phases and produce products with small crystalline structure and high surface area.

This process usually involves mixing, calcine, shaping and sintering. Each step in solid state reaction especially calcination and sintering give influence in controlling the final properties of the ceramics hence contribute to the microstructure formation that enhanced the dielectric properties.

2.5.1 Mixing and Milling

Mixing and milling processes commonly are done simultaneously using ball mill. Both of these processes have their advantages in solid state reaction. Mixing helps to improve the homogeneity in the mixture while milling playing important role in minimizing the primary particle size and achieving particle size distribution.

2.5.2 Calcination

Calcination is the heat treatment process in absence or limited supply of oxygen to solid material to produce thermal decomposition. In calcination, the optimum temperature should be determined in order to gain desired microstructural and dielectric properties (Mohammed et al, 2008). It is stated due to CCTO single phase formed 900 ºC are very appropriate temperature in calcining CCTO. Figure 2.4 shows the SEM micrograph for samples that calcine at 900 ºC.

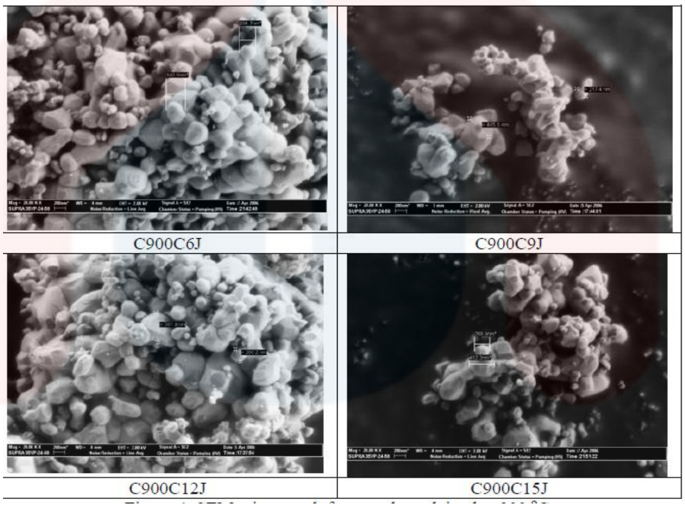


Figure 2.4: SEM micrograph for samples calcined at 900 °C (Mohammed et al, 2008)

2.5.3 Shaping

Shaping or powder pressing are being done after calcination process. Shaping is the process which is powders are compacted into geometric form thus make it a solid part that called pellet or green compact. In this process, it is significant to maintain uniformity of compaction as it can lead to density variation.

2.5.4 Sintering

Sintering is one of the important step in powder densification especially in ceramics production. Sintering is the process of compacting and forming a solid material by giving heat treatment or pressure without melting it. Besides that, the reason of study in sintering become important in order to understand how the processing variables such as temperature, pressure, grain size, particle packing, compaction and atmosphere influence the formation of microstructure (Lutgard and Mohamed, 2003).

2.6 Stages of Sintering

During sintering process, the microstructure of green pellet body that consist discrete particles evolves continuously. Generally, sintering can be divided into 3 stages which are initial, intermediate and final stage.

During the initial stage, small degree of atomic mobility is achieved. If coarsening mechanisms are very active, the amount of densification is small and can be considered quite lower.

Meanwhile, at the intermediate stage, grain growth become significant when the high curvatures of initial stage have been moderate and the microstructure consists of 3D interpenetrating network of solid particles and continuous called channel-like pores. This channel-like pores breakdown into isolated, closed voids which marks the beginning of final stage as sintering proceed. At the final stage, grain growth become more extensive. Figure 2.4 shows the growth of microstructure during the stages of sintering process that begins from loose powder.

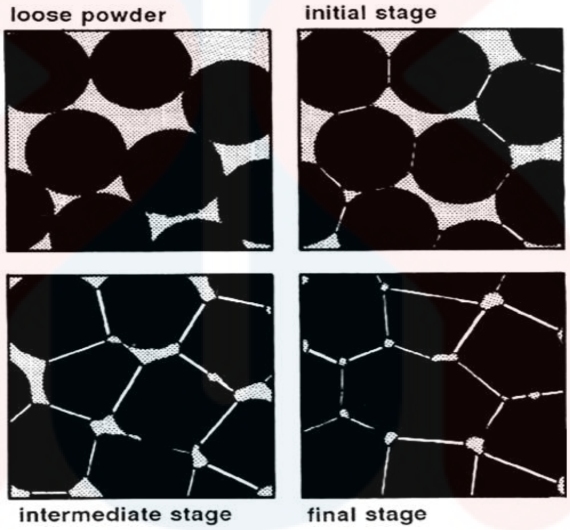


Figure 2.5: Microstructure during the stages of sintering process (Lutgard and Mohamed, 2003)

2.7 Solid State Sintering

In this paper solid state sintering is highlighted as a method since it is used in CCTO formation. Solid state sintering is the method whereas the shaped green body is heated to a certain range of temperature in absence of liquid.

The green pellets are treated to temperature between 70 to 90% of the definite melting point of major constituent during sintering in order to achieve high diffusion rate (Schaffer, 1999). A further research had been done by some researches to discuss more about this. The previous study stated that elimination of residue air gap between the electrodes to the CCTO bulk and improvement in dielectric constant could achieve by heat treatment (Sulaiman et al, 2013). Meanwhile, in the same years, Rainer and Derek (2013) proved that a substantial variation would happen in dielectric constant if the sintering temperature of CCTO ceramic increase from 975 to 1100ºC. Consequently, the temperature of the green pellet should be controlled during sintering rate.

2.8 Effect of Heating Rate on Ceramic Synthesis

In sintering process, heating rate gives a significant result on final properties in ceramics. According to the previous studies that were done, different heating rates give different effect on various ceramics. Mostly, ceramics like $\mathrm{Zr_2Al_3C_4}$ and $\mathrm{ZrB_2}$-based ceramics used spark plasma sintering process since it allows higher heating rate and commonly involves only a very short soaking time. According to Zhang et al (2012), in their study of ternary carbide $\mathrm{Zr_2Al_3C_4}$ through spark plasma sintering stated the loss and aggregation of molten Al can largely effect by heating rate. In their study, the sample was heated to 600 °C at a rate of 200 °C/min, afterwards heated to 700 °C at a heating rate of 50 °C/min for 3 min, and then maintained up to 1800 °C with an average heating rate of 100°C/min. They were reported that the displacement of shrinkage for slow heating rate was significantly higher than the fast heating rate, indicating that the molten Al react incompletely with Zr to form Zr-Al intermetallic compounds, hence, the residual amount of molten Al penetrated into the pores or be squeezed out at low heating rate. So, the fast heating rate can prevent the loss of molten Al.

Meanwhile, another study conducted by Guo et al, (2010) stated that the low heating rate inhibited the densification, maintained the grain size and greatly have decreasing in strength in the $\mathrm{Yb_2O_3}$-doped ceramic, whereas a low heating rate in $\mathrm{Yb_2O_3}$- undoped ceramic promoted densification, induced grain size and slightly increased the strength. They reported that the spark plasma sintered undoped $\mathrm{Zr}B_2$-SiC composites were having an optimum final properties compared to the doped composites. This indicates that dopant also played an important role in obtaining good mechanical properties in ceramics. As a result, obtaining an optimum heating rate is significant in ceramics synthesis.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

Methodology is the most important part in conducting a research as it tells step by step procedure of this study. This part will mainly describe about the procedure and materials used in synthesizing and characterization of CCTO formation by using solid state reaction method. The characterization and comparisons of sintered samples are made in terms of particle size analysis, grain size, morphology, mineralogy and physical properties between composition of different heating sintering rate. In this research, calcium carbonate ($CaCO_3$), copper oxide (CuO) and titanium oxide (TiO_2) is used as raw materials. The summarization of the method in preparation and synthesizing of CCTO is shown in Figure 3.1.

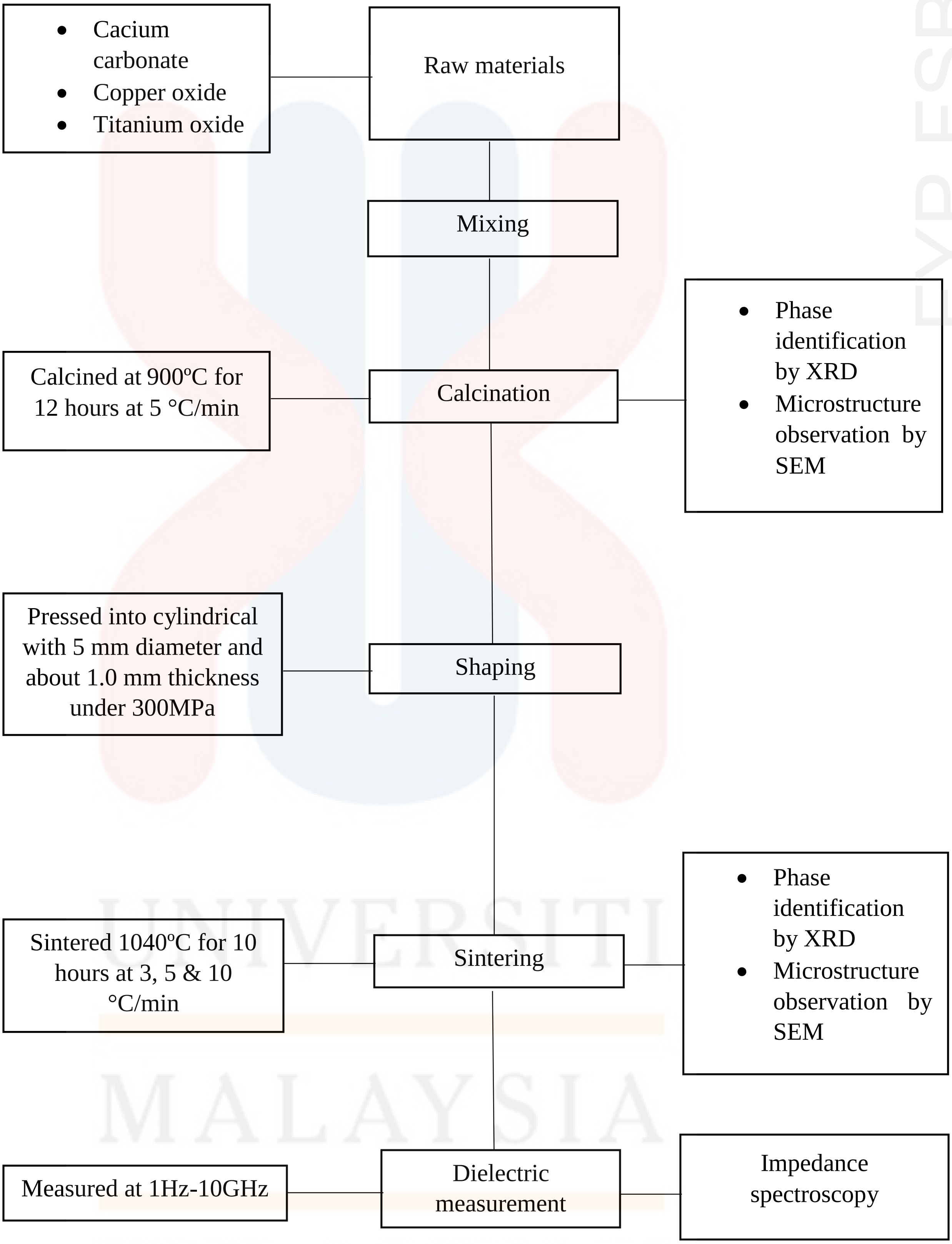


Figure 3.1: Process flow chart

3.2 Preparation of CCTO

In this research, solid state technique is adopted as a method to prepare CCTO that consist a few steps starting from weighing, mixing, calcination, shaping and sintering.

3.2.1 Weighing

As a beginning material, $CaCO_3$, CuO, and TiO_2 with high purity are prepared by weighing according stoichiometric ratio by using high precision balance up to four decimal place in order to get accurate reading. The mass of raw materials needed for calcium carbonate, copper oxide and titanium oxide is based on equation (3.1) show in Table 3.1. Details calculation of the mass for the raw materials is show in appendices.

$$CaCO_3 + 3CuO + 4TiO_2 \rightarrow CaCu_3Ti_4O_{12} + CO_2 \ldots\ldots \text{ Equation (3.1)}$$

Table 3.1: Composition of raw materials used in CCTO preparation

Starting powder	**Formula ratio**	**Relative Molecular Weight (g/mol)**	**Total weight, g (per mol)**	**Weight (g) sample prepared**
$CaCO_3$	1	100.0869	100.0869	8.1471
CuO	3	79.5454	238.6362	19.4250
TiO_2	4	79.8658	319.4632	26.0043
			658.1863	

3.2.2 Mixing and Milling

This process is done by using conventional wet ball milling. Using zirconia balls as grinding media, the raw materials that placed in zirconia jar are mixed and milled simultaneously in ethanol through ball milling process for 24 hours. The ratio of powder to ball is 1:10. After milling process, the mixture was poured into a beaker and then dried in oven for 24 hours.

3.2.3 Calcination

The powder that well mixed and dried are grinded by using mortar and pestle. Then the ground powders are sealed in alumina crucible. After that, the powder is calcined in furnace at 900ºC for 12 hours.

3.2.4 Shaping

The specimens are pressed into cylindrical with 6 mm diameter and about 1 mm thickness under 300 MPa. This process is conducted by using Hand Press Machine.

3.2.5 Sintering

Each pellet then was sintered in air at 1040ºC for 10 hours with heating rate of 3, 5 and 10ºC/minute followed by cooling process in furnace to room temperature. The sintered samples were subjected to X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) for material characterization.

3.3 Characterization of Sample

The characterization of sample is made based on sample density, morphology, mineralogy and dielectric properties.

3.4 Density Measurement

The bulk density of green pellets is measured by using Archimedes technique. Archimedes' principle, principle that states that a body immersed in a fluid is buoyed up by a force equal to the weight of the displaced fluid. The bulk density is referred to the actual density of the sample that consist a big number of imperfections and can be calculated as below:

$$\text{Bulk density} = \frac{M_D}{M_{W-M_S}} \text{ x density of water………Equation (3.2)}$$

$$\text{Porosity} = \frac{M_W - M_D}{M_{W-M_S}} \text{ x 100 \%..................................Equation (3.3)}$$

Where,

M_D= mass of dry sample

M_W= mass of sample in water (saturated)

M_S= mass of sample after vacuum (suspended)

3.5 X-Ray Diffractometer (XRD) Analysis

Recently, XRD is a common method for the study of crystal structures and lattice spacing. XRD is a rapid analytical technique mainly used for phase identification of crystalline material and also can give information on unit cell dimension. The analysed sample must be finely ground, homogenized and average bulk composition is determined. XRD is working based on Bragg's Law ($n\lambda=2d \sin \theta$).

Despite of being one of the non-destructive analysis technique, XRD also can provide information about the presence of element or compounds in the powder mixture. In this research, the phase formation of both calcined and sintered pellets are identified using XRD. Figure 3.2 shows the image of one of the type of XRD machine that usually used.

Figure 3.2: X-Ray Diffraction machine

3.6 Scanning Electron Microscope (SEM)

The SEM as shown in Figure 3.3 is a microscope that uses electrons instead of light to form an image and primarily used for the morphology of the sample surface study and topographical studies where the sample can be examine in three dimension (3D). The SEM has allowed researchers to examine a much wider variety of specimens.

The scanning electron microscope offered many specialities over optical microscopes such as has a greater depth of field, which allows more of a specimen to be in focus at one time. The SEM also has much higher resolution, so closely spaced specimens can be magnified at much higher levels. The user has much more control in the degree of magnification since it uses electromagnets rather than lenses. All of these advantages, as well as the actual strikingly clear images, make the scanning electron microscope one of the most significant instruments in research today.

In this study, the green pellets of CCTO then observed under SEM to determine any changes in sample morphology. The sample is polished first to generate surface flatness.

Figure 3.3: Scanning Electron Microscope

3.7 Dielectric Measurement

Dielectric constant is measured by electroding the sample with the silver paste by using impedance analyzer. The range set from 1 Hz-10 GHz at temperature 25 ºC. The dielectric constant for each sample can be calculated by using formula as follows:

$$\varepsilon = \frac{Ct}{\varepsilon_\circ A} \text{ ……………Equation (3.3)}$$

Where

C = capacitance (F)

t = thickness of sample (m)

A= cross sectional area (m^2)

ε0 = vacuum permittivity constant ~ 8.8543 x 10^{-12} F/m

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter consist the results analysis that was gained from experimental work. In this study, CCTO was synthesized at different heating and cooling sintering rate. Thus, it requires various testing and characterization from raw materials until the sintered pellet. Characterization such as surface morphology, phase identification and density analysis were done in order to get the information about CCTO properties. Previously, the same characterization was done by Warangkanagool (2014) in his study about grain sizes and dielectric properties of CCTO ceramics.

4.2 Raw Materials Characterization

The raw materials were characterized by 2 methods which are using X-Ray Diffraction and Scanning Electron Microscope (SEM). XRD was done to identify the mineralogy of powders and SEM was done to observe the morphology of the powders. This is important to verify the presence of impurity or contamination in the powders so that the pure CCTO can be produced.

4.2.1 Calcium carbonate, $CaCO_3$

a) XRD Analysis

In this study, $CaCO_3$ powder with high purity 99.9 % was used and the powder was white in colour. Figure 4.1 shows the XRD pattern of $CaCO_3$. It shows that the pattern of peaks were similar to ICCD file 00-005-0586 ($CaCO_3$, calcite). It was determined that the crystalline structure of the powder is rhombohedral. Thus, it was indicated that this $CaCO_3$ is single phase and free from contamination.

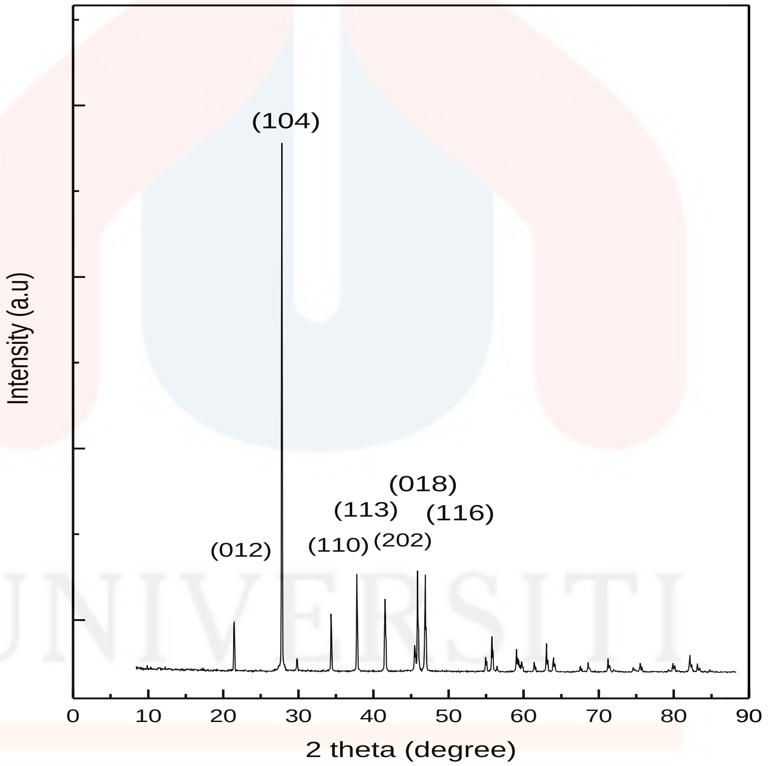


Figure 4.1: XRD pattern for $CaCO_3$ powder (ICCD file: 00-005-0586)

b) SEM Analysis

Figure 4.2 shows the SEM result for $CaCO_3$ powder. From the SEM micrograph, the $CaCO_3$ powder was in a cubic shape. The average of particle size of $CaCO_3$ is 6.55 μm.

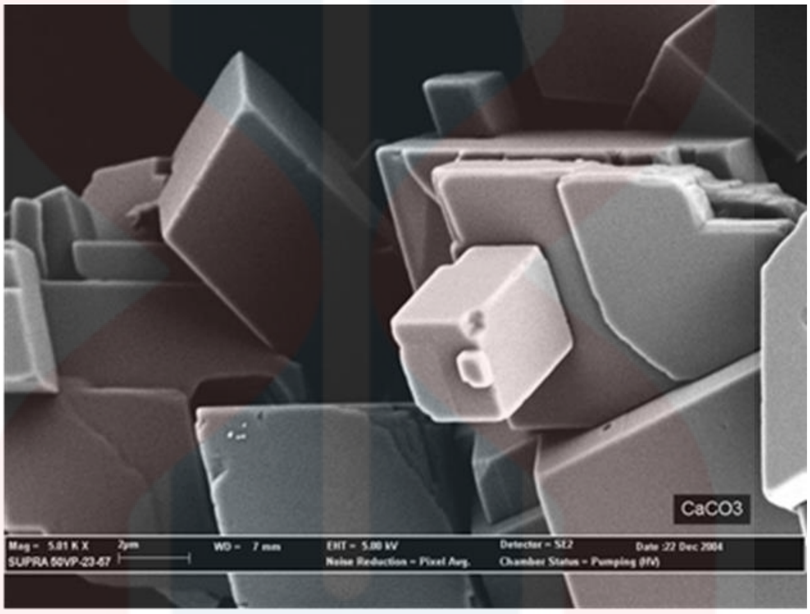


Figure 4.2: SEM micrograph of $CaCO_3$ powder

4.2.2 Copper oxide, CuO

a) XRD Analysis

CuO with 99.9 % purity was used and the colour is in black. Based on the Figure 4.3, the intensity peak of the sample was identified as CuO (tenorite) similar to ICDD file 9014580. It was determined that the crystalline structure of the sample was monoclinic. Hence, it was indicated that CuO was single phase and free from contamination.

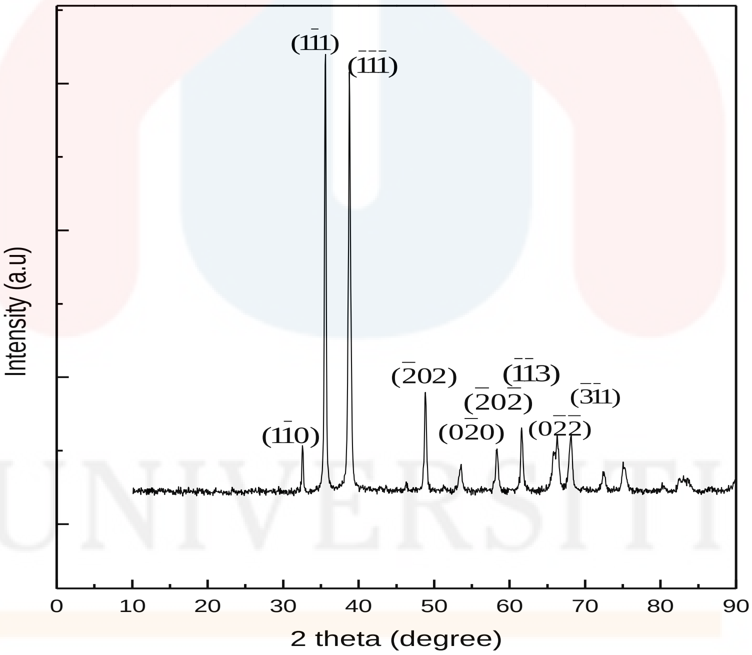


Figure 4.3: XRD pattern for CuO powder (ICCD file: 9014580)

b) SEM Analysis

Figure 4.4 shows the surface morphology of the CuO powder observed by SEM. It was shown that the CuO powder has cylindrical shaped. The average size of CuO powder is 11.01 µm.

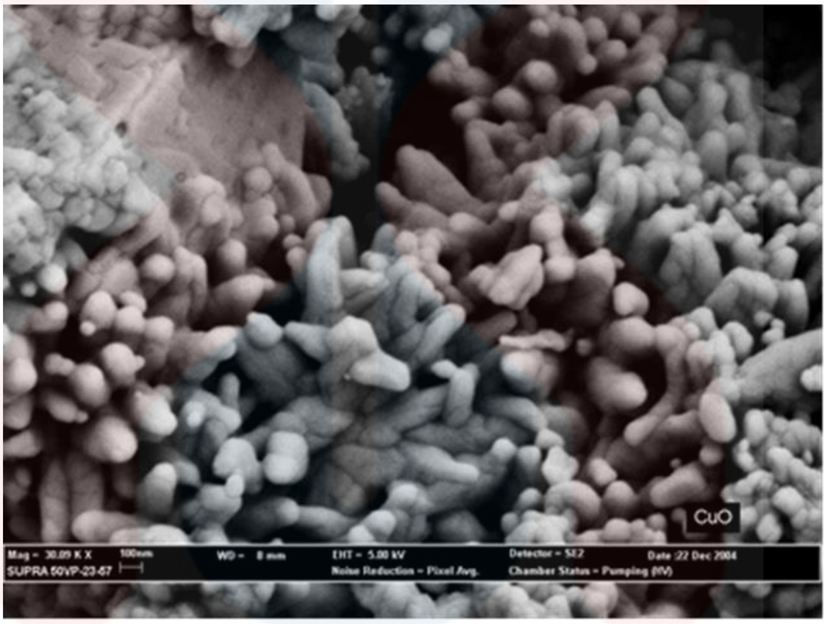


Figure 4.4: SEM micrograph of CuO powder

4.2.3 Titanium dioxide, TiO_2

a) XRD Analysis

TiO_2 with high purity (99.9 %) was used and the colour was white. Figure 4.5 shows the XRD pattern of TiO_2 powders. It shows the pattern of the powder were similar to ICCD file 00-064-0863 (TiO_2, anatase). It was determined that the crystalline structure of the powder was tetragonal. Thus, it was shows that TiO_2 was single phase and free from contamination.

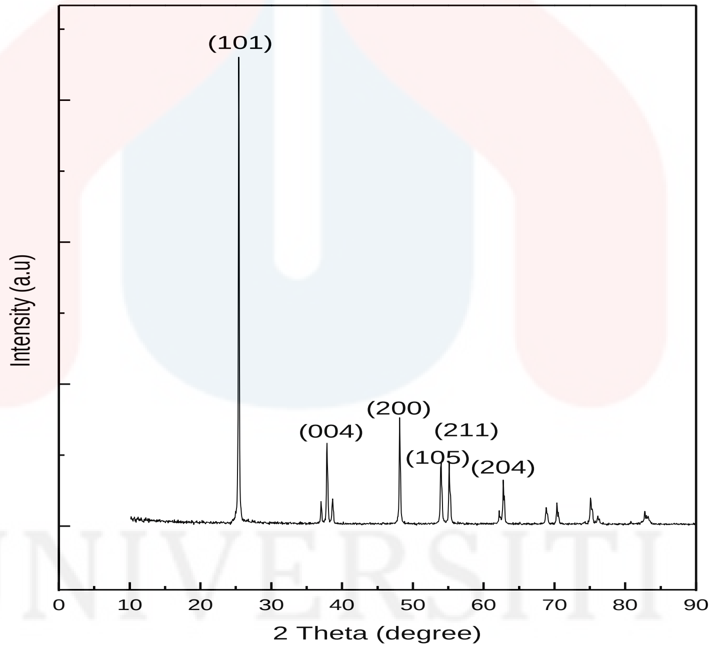


Figure 4.5: XRD pattern for TiO_2 powder (ICCD file: 00-064-0863)

b) SEM Analysis

The surface morphology of TiO_2 powder was shown in Figure 4.6. Observation by the SEM shows that the powder was spherical in shape. The average size of particle of TiO_2 powder is 0.48 µm.

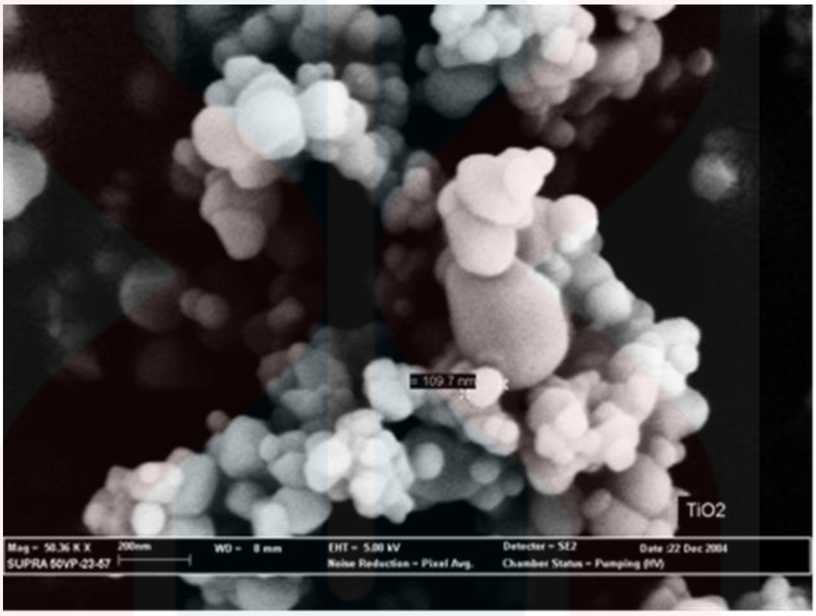


Figure 4.6: SEM micrograph of TiO_2 powder

4.3 Mixed Powder Characterization

In this experimental work, the raw materials were mixed and then milled in ethanol using zirconia ball as media for 24 hours to produce homogenous mixture. The mixture was analysed with XRD and the result obtained was plotted as shown in Figure 4.7. From the XRD result, there are 3 phases that present in mixture powder which were $CaCO_3$, CuO and TiO_2. This indicates there was no reaction occur in the mixing process.

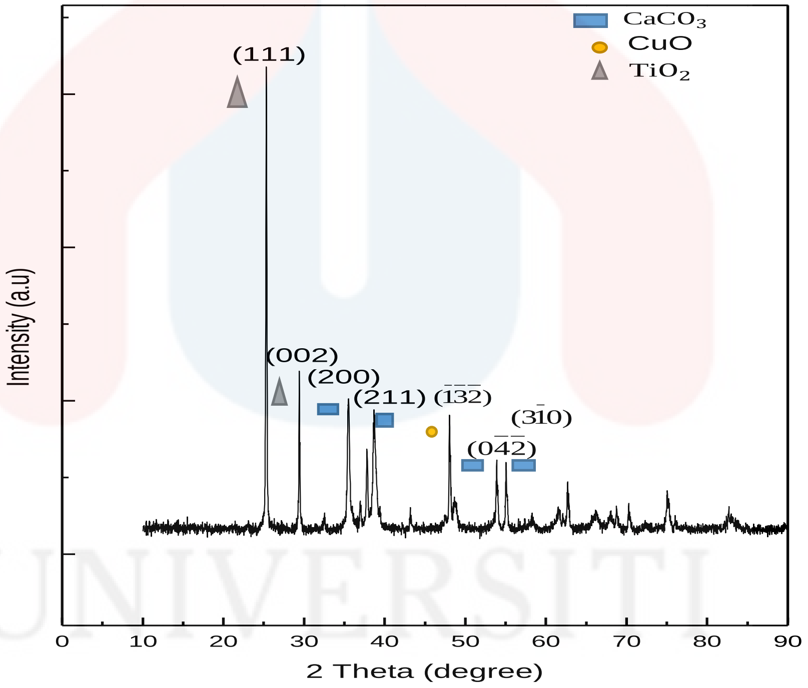


Figure 4.7: XRD pattern for mixed powder

4.4 Calcined Powder Characterization

The mixture was calcined at 900 ºC for 12 hours. In order to obtain the desired microstructural and dielectric constant, the optimum temperature and duration for calcination process must be decided. From the observation, the colour of powder mixture was changed from grey to dark brown after calcined as shown in Figure 4.8. The appropriate temperature in calcine CCTO is 900 ºC due to single phase formed (Mohamed et al, 2008).

Apart from that, (Hutagalung et al, 2007) reported that the complete formation of single phase polycrystalline CCTO occurred starting at 700 °C using modified mechanical alloying process which is much lower compared to other methods. But, for the conventional solid state, most of the researchers report to calcine CCTO powder at 900 °C for 12 hours.

Figure 4.9 shows the XRD pattern of calcined powders that was obtained from XRD analysis. The intensity peak of the sample indicates that the calcined powder is $\mathrm{CaCu_3Ti_4O_{12}}$ which is similar to ICCD file 1001203. The sample is verified to be single phase CCTO. The calcined samples shown that all peaks that closely matched with the standard pattern of CCTO. There were no unreacted raw materials that was detected.

(a) Before (b) After

Figure 4.8: CCTO powder before and after calcination process

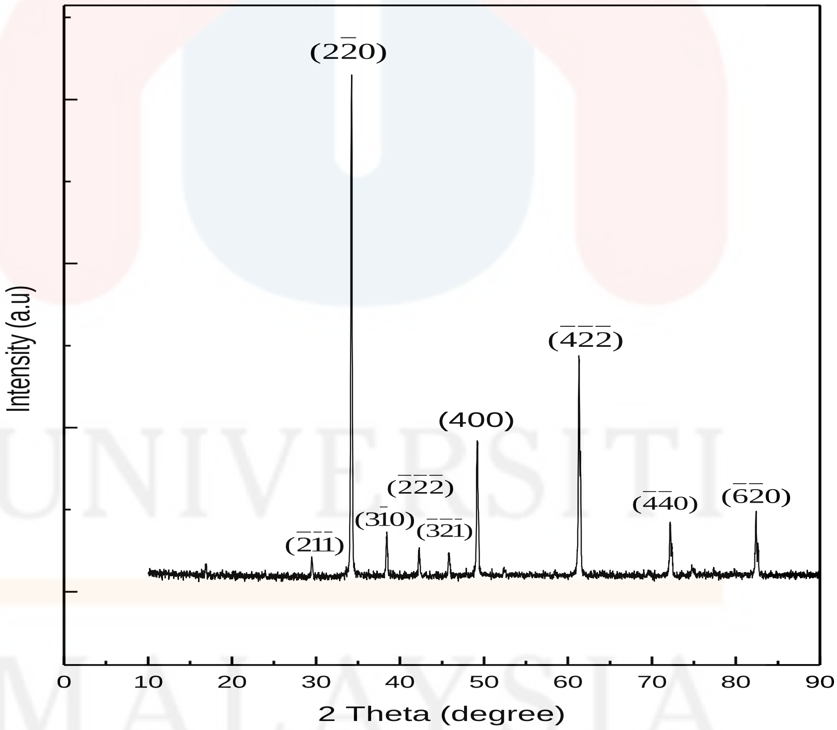


Figure 4.9: XRD pattern for calcined powder

4.5 Sintered Pellet Characterization

After the compaction was done, the pellets were sintered at 1040 ºC at different heating rate which are 3, 5 and 10 ºC/min. The soaking time was 10 hours. There was apparently obvious change occurred in terms of colour of the pellets. All the samples show the black colour was obtained after sintering process. The colour changes of the pellets before and after sintering process was shown in Figure 4.10. Sintered pellets were characterized their properties in a few methods which are by using Archimedes principle for density and porosity analysis, XRD for their phase formation, impedance analyser for dielectric properties and SEM was done for microstructure observation. Table 4.1 shows the sample coding used for sintered pellets in this study.

(a) Before (b) After

Figure 4.10: Observation in colour changes of sintered pellets

Table 4.1: Sample code for sintered pellet

Sample code	Description
SP3	Pellet sintered at 3 °C/min
SP5	Pellet sintered at 5°C/min
SP10	Pellet sintered at 10 °C/min

4.5.1 Density Analysis

Density analysis was carried out to show densification of sintered pellet. Table 4.2 and 4.3 show the bulk density and porosity value of CCTO pellet respectively. The values were taken three times for each sample. The graph of bulk density and porosity against different heating rate was plotted as shown in Figure 4.11.

The density of samples increase as the heating rate was increased from 3 to 5 °C/min but a reduction occurs when the pellets is exposed to 10 °C/min of heating rate. Regarding the microstructure gained, the density of the pellets should tend to decrease when the heating rate increase. This may due to the error occurred during the experimental work. The bubble may not remove properly when exposed in vacuum pump.

According to Lohnert et al (2015), CCTO pellets sintered below 1005 °C exhibit rather poor density, whereas sintering at 1050 and 1100 °C results in high densities of the theoretical value (ρ_{theo}=5.04 g/cm^3). In this research, pellet sintered at 1040 °C by using heating rate 5 °C/min shown quite higher which is 6.498 g/cm^3 compared to theoretical value. Meanwhile, SP3 exhibit the lowest percentage of porosity among the 3 samples.

Table 4.2: Bulk density value of different heating rate on CCTO sample

Sample	Bulk Density (g/cm^3)
SP3	3.432
SP5	6.498
SP10	3.478

Table 4.3: Porosity value of different heating rate on CCTO sample

Sample	Porosity (%)
SP3	13.60
SP5	16.70
SP10	15.80

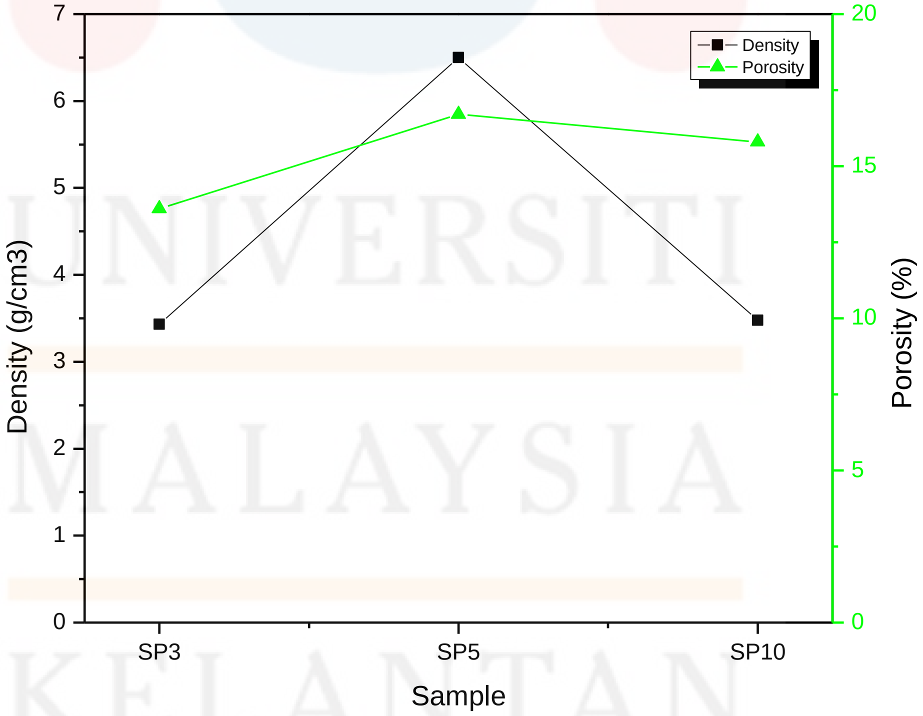


Figure 4.11: Graph of bulk density and porosity against sample

4.5.2 X-Ray Diffraction (XRD) Analysis

Figure 4.12 shows the XRD pattern of 3 different sintered pellets which are SP3, SP5 and SP10 that was obtained from XRD analysis. The intensity peak of the sintered pellets indicates that all the samples is $\mathrm{CaCu_3Ti_4O_{12}}$ (cubic) similar to ICCD file 1008180. All the patterns obtained shown that all peaks that closely matched with the standard pattern of CCTO. The peaks are identified as CCTO with Miller Indices $(\bar{2}\bar{2}0)$, $(3\bar{1}0)$, $(\bar{2}\bar{2}\bar{2})$, $(\bar{3}\bar{2}\bar{1})$, $(\bar{4}00)$, $(\bar{4}\bar{2}\bar{2})$, $(\bar{4}\bar{4}0)$ and $(\bar{6}\bar{2}0)$. The samples are verified to be in single phase.

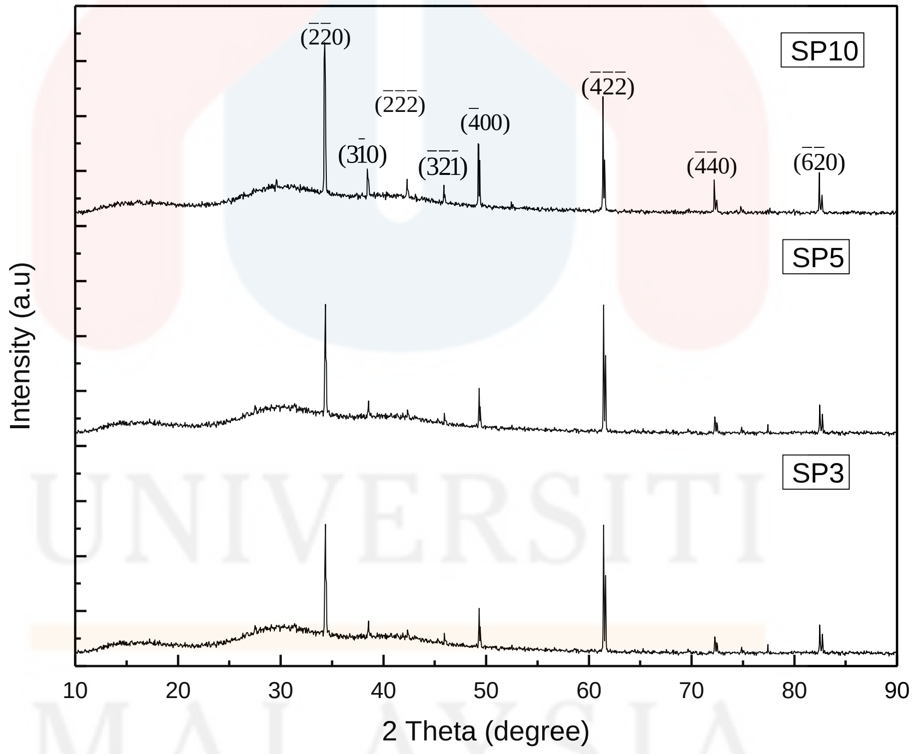


Figure 4.12: XRD pattern for sintered pellets at different heating rate

Figure 4.13 shows the XRD pattern of the phase changes that occurred during CCTO synthesis starting from the raw materials used until the optimum sintered pellet (SP5) that has been obtained. There were slightly changes of peak that can be observed in each process.

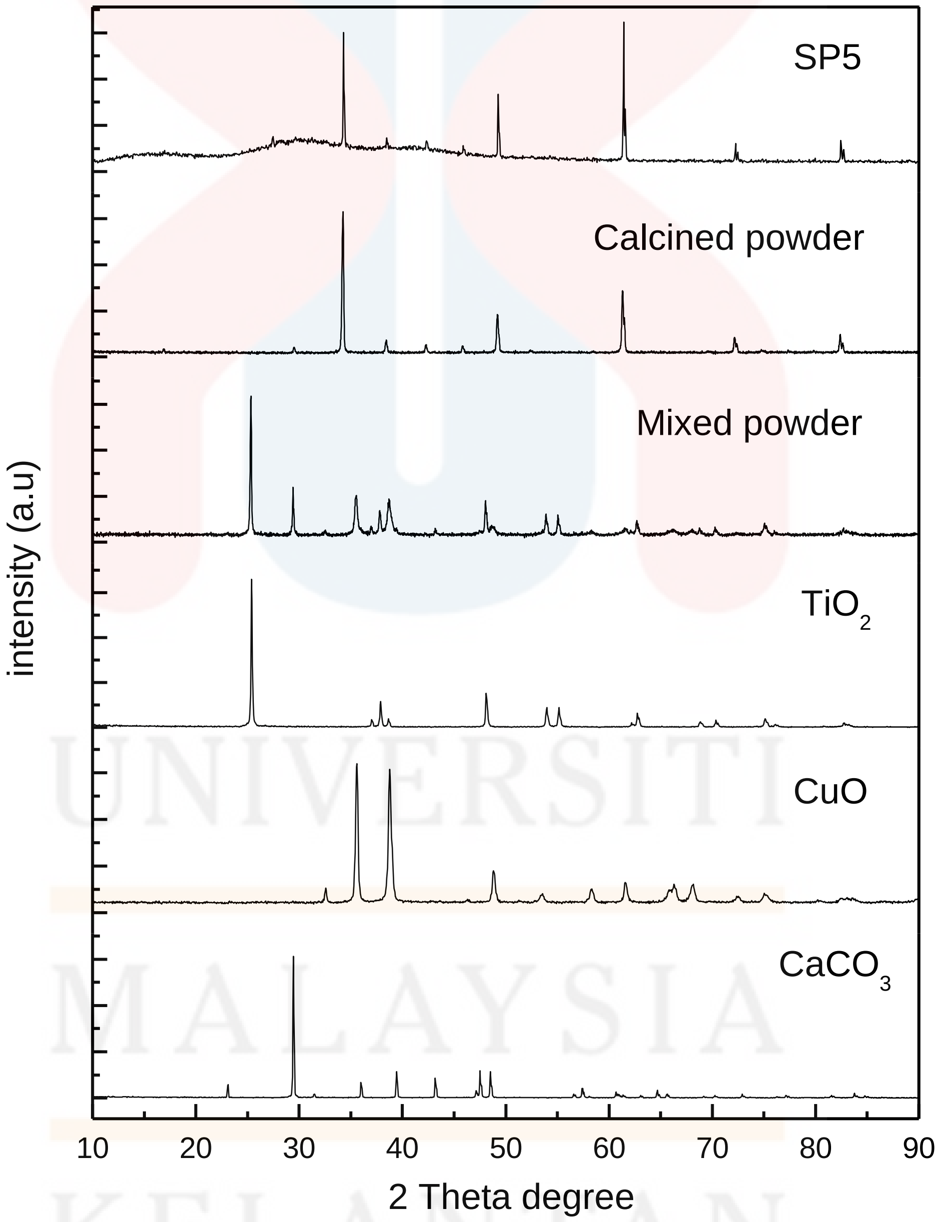
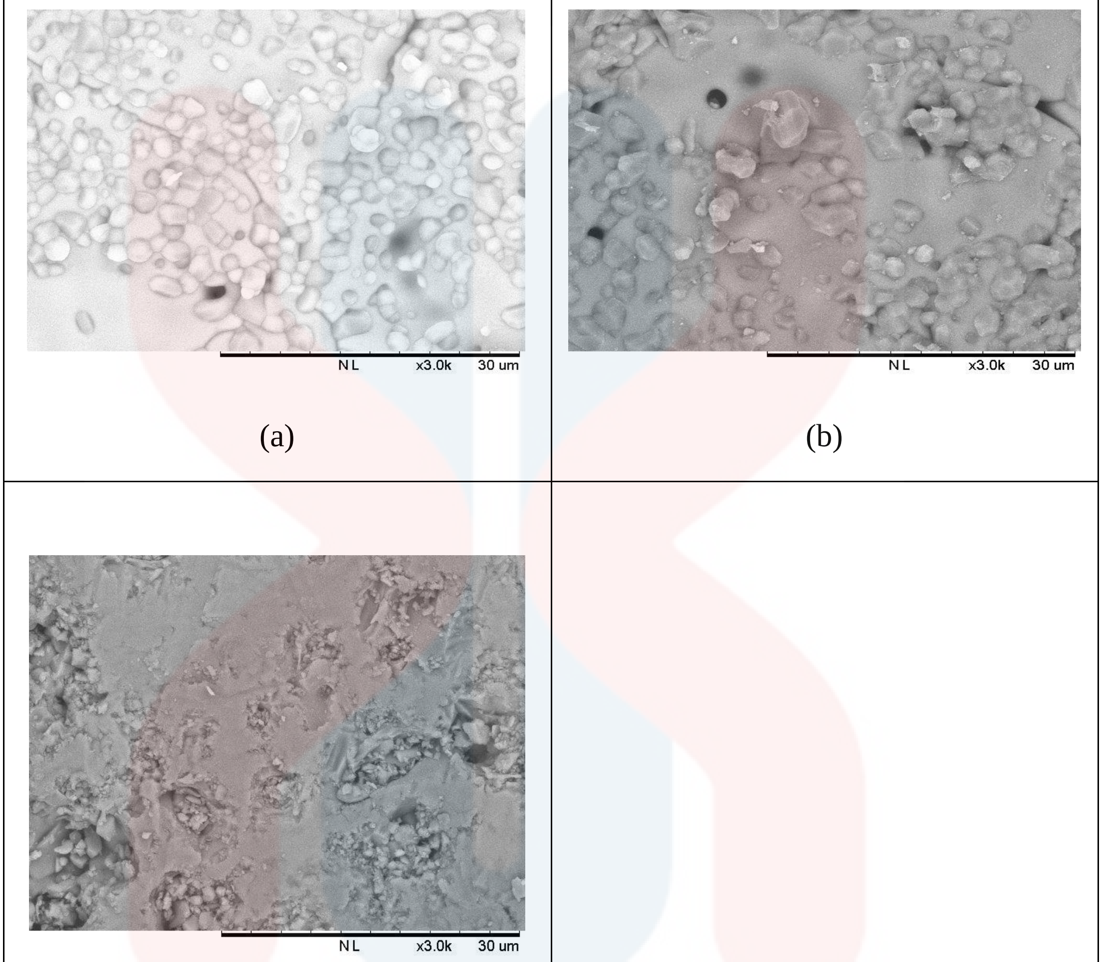


Figure 4.13: Phase changes during CCTO synthesis

4.5.3 Scanning Electron Microscope (SEM) Analysis

Figure 4.14 shows the SEM micrographs for surface morphology of CCTO sintered pellets at 3 different heating rate. Meanwhile, Figure 4.15 shows the observation for cross section for all the sintered pellets. The grain size was decrease as the heating rate became faster. This may due to evaporation occur in grain boundary. Previously, a study done by Kai et al, (2014) reported that CCTO sintered above 1060°C can destroy the grain due to the high temperature. It was also stated that CCTO pellets that sintered below the 1060 °C has larger and more integral grain size. This can contribute high dielectric constant of CCTO.

SP3 was identified to have larger and coarser grain compared to SP5 and SP10. Compared to SP5 and SP10, SP3 also shown uniformity in grain size. It was seen that CCTO particles was in spherical shape for SP3. The same result was obtained by Mohamed et al, (2010) in their research about effect of compaction pressure on CCTO formation and dielectric properties by using sintering temperature at 1050 °C.

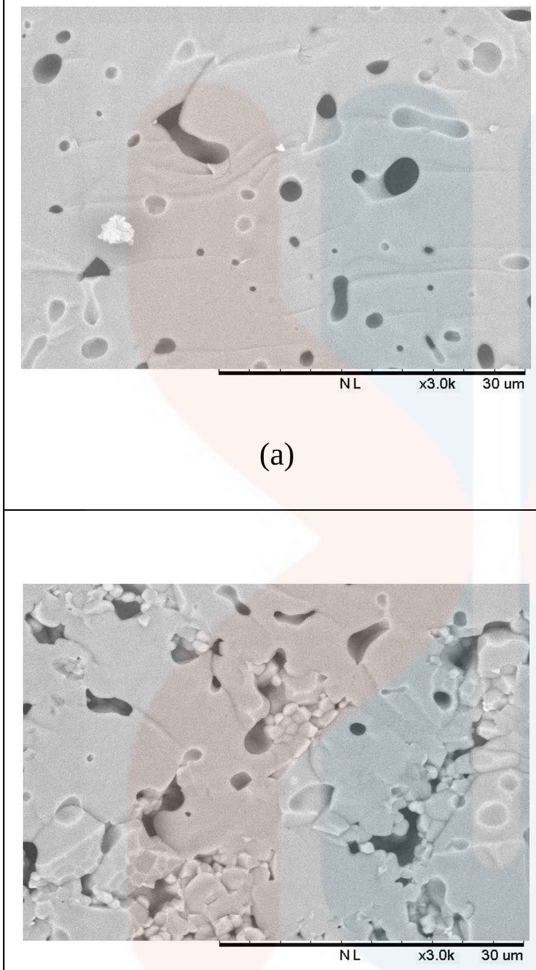


(a)

(b)

(c)

Figure 4.14: SEM micrographs for surface morphology of CCTO sintered pellet at 3000 x for (a) SP3, (b) SP5 and (c) SP10



(a)

(b)

(c)

Figure 4.15: SEM micrographs for cross section of CCTO sintered pellets at 3000 x for (a) SP3, (b) SP5 and (c) SP10

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Based on the results of experiment conducted, it can be concluded that pure CCTO were successfully synthesized via solid state technique. The effect of different heating and cooling sintering rate on CCTO formation was studied.

XRD results of sintered pellets indicates that the SP3, SP5 and SP10 were in cubic structure. All those samples were verified to be in single phase and free from contamination.

SEM results of sintered pellets indicates that the morphology of grains were in spherical shape that was clearly can be seen in SP3. The grain size decrease as the heating rate faster. Microstructure displayed dense grain distribution and yield high density for SP3. It was found SP3 shows the uniformity of grains size among those 3 pellets. However, SP5 was found as the optimum pellet that shown a good potential as dielectric material regarding the density and size of microstructure obtained.

5.2 Recommendations

To optimize the properties of CCTO, a few suggestions for further studies were proposed.

a) Improving the milling method by using planetary milling
b) A further and details study should be done on the effect of heating rate on CCTO formation

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APPENDICES

MASS OF RAW MATERIALS USED

Since total mass needed for CCTO is 50 g, the mole of CCTO prepared is calculated as below:

Mole of $CaCu_3Ti_4O_{12}$ = Mass / Relative Molecular Weight

= 50 / [(40.0780)+(3 x 63.5460)+(4 x 47.8670)+(12 x 15.9994)]

= 50 / 614.1768

= 0.0814 g/mol

By using stoichiometric ratio based on equation 3. 1, mass of raw materials used is calculated as below:

Mass of $CaCO_3$ = Mole of CCTO x Relative Molecular Weight of $CaCO_3$

= 0.0814 x [40.0780 + 12.0107 + (3 x 15.9994)]

= 0.0814 x 100.0869

= 8.1471 g

Mass of CuO = Mole of CCTO x Relative Molecular Weight of CuO

= (3x 0.0814) x (63.5460 + 15.9994)

= 0.2442 x 79.5454

= 19.4250 g

Mass of TiO_2 = Mole of CCTO x Relative Molecular Weight of TiO_2

= (4 x 0.0814) x [(47.8670) + (2 x 15.9994)

= 0.3256 x 79.8658

= 26.0043 g

Mass CO_2 produce = Mole of CCTO x Relative Molecular Weight

= 0.0814 x [12.0107 + (2 x 15.9994)

= 3.5824 g

DENSITY

For SP 3

Sample	M_D (g)	M_W (g)	M_S (g)	Density (g/m^{3})
1	0.076	0.078	0.057	3.613
2	0.075	0.078	0.054	3.119
3	0.078	0.077	0.056	3.565
			Average	3.432

For SP 5

Sample	M_D (g)	M_W (g)	M_S (g)	Density (g/m^{3})
1	0.074	0.075	0.063	6.156
2	0.074	0.075	0.064	6.715
3	0.073	0.077	0.066	6.624
			Average	6.498

For SP 10

Sample	M_D (g)	M_W (g)	M_S (g)	Density (g/m^{3})
1	0.073	0.076	0.055	3.470
2	0.072	0.075	0.056	3.783
3	0.072	0.074	0.056	3.993
			Average	3.748

POROSITY

SP3

Porosity= [(0.078-0.075)/(0.078-0.056)] x 100%

= (0.003/0.022) x 100%

= 0.136

SP5

Porosity= [(0.076-0.074)/(0.076-0.064)] x 100%

= (0.002/0.012) x 100%

= 0.167

SP10

Porosity= [(0.075-0.072)/(0.075-0.056)] x 100%

= (0.003/0.019) x 100%

= 0.158