THE EFFECT OF SINTERING TEMPERATURE AND CLAY ADDITION ON GLASS CERAMIC PRODUCED FROM RECYCLED GLASS FOR STRUCTURAL APPLICATION (CIP METHOD)

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This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) with Honours.

By

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2010

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA MUDA

TAJUK: **The effect of sintering temperature and clay addition on glass ceramic produced from recycled glass for structural application (CIP Method)**

SESI PENGAJIAN: 2009/10 Semester 1

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Author's Name : NUR RIFHAN BINTI ROSLI

Date : 23 MAY 2010

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) with Honours. The member of the supervisory committee is as follow:

……

(DR. JARIAH BINTI MOHAMAD JUOI)

ABSTRACT

The purpose of this project was to determine the effect of sintering temperature and clay addition on glass ceramic produced from recycled glass. In this study, recycled glass of soda lime silica glass is used as main raw materials and ball clays as filler. The scope of this project mainly focused at the effect of sintering temperature and soda lime silica glass to ball clay weight ratio on glass ceramic produce from recycled glass for structural applications. The glass powders are prepared by crushing to a particles size distribution < 75 µm. The SLSG powder are then mixed with the ball clay according to the ratio of SLSG to ball clay of 95:5 wt.%, 90:10 wt.% and 85:15 wt.%. The glass ceramic samples are fabricated using uniaxial pressing and cold isostatic pressing with constant pressure at 40 MPa. The best mixing ratio is 85:15 wt.% ratio of SLSG to ball clay because the presence of ball clay helps the uniformity of the green body. Sintering process is conducted at three different temperatures at 750°C, 850°C and 950°C with 1 h holding time. There are several changes in terms of shape, color and appearance after the sintering process. Physical analyses and mechanical testing of the samples are carried out according to the specific ASTM standard of testing. For physical and mechanical analyses, majority the results showed that the increasing of temperature and percentage of ball clay had significantly increased the porosity and water absorption percentage, bulk density and microhardness properties of the glass ceramic produced. Microstructure analysis showed the surface of glass ceramic samples and phase analysis identified quartz and calcite phases is presence in the sample produced. Temperature 850°C with 85:15 wt.% ratio of SLSG to ball clay is chosen as the optimum parameter to produced new glass ceramic material produced from recycled glass.

ABSTRAK

Tujuan penyelidikan ini adalah untuk mengenal pasti kesan daripada suhu pembakaran dan penambahan tanah liat terhadap penghasilan seramik kaca yang dihasilkan daripada kaca buangan yang boleh dikitar semula. Dalam kajian ini, sisa kaca buangan dari kapur kaca digunakan sebagai bahan utama dan ketulan tanah liat sebagai pengisi. Bidang lapangan kajian ini lebih menitik beratkan kepada kesan suhu pembakaran dan nisbah kapur kaca kepada ketulan tanah liat untuk kegunaan – kegunaan struktur. Kapur kaca akan dihancurkan untuk mendapatkan saiz butiran kaca kurang daripada 75 µm dan kemudian dicampur dengan ketulan tanah liat. Campuran akan dibentuk menggunakan mesin *Uniaxial Pressing* terlebih dahulu sebelum dimasukkan ke dalam mesin c*old isostatic pressing (CIP)* dengan tekanan tetap iaitu sebanyak 40 MPa. Nisbah campuran yang terbaik adalah pada 85:15 wt.% nisbah kapur kaca kepada ketulan tanah liat kerana kehadiran ketualan tanah liat yang membantu kepadatannya. Proses pembakaran akan dilakukan pada tiga suhu yang berbeza iaitu 750°C, 850°C dan 950°C bersama 1 jam waktu perendaman. Terdapat perubahan dari segi bentuk, warna dan penampilan selepas proses tersebut. Analisis fizikal dan mekanikal dilakukan berpandukan piawaian ASTM. Untuk analisis fizikal dan mekanikal, kebanyakkan keputusan menunjukkan apabila meningkatnya suhu dan peratusan ketulan tanah liat, secara tidak langsung sifat-sifat seramik kaca seperti peratus keliangan dan penyerapan air, ketumpatan keseluruhan dan mikro-kekerasan yang dihasilkan meningkat. Analisis mikrostruktur menunjukkan dengan lebih jelas permukaan seramik kaca yang dihasilkan dan fasa yang wujud didalam seramik kaca adalah *quartz* dan *calcite*. Parameter optimum yang dikenal pasti sesuai untuk menghasilkan seramik kaca dari kaca buangan adalah pada suhu 850°C dengan 85:15 wt.% nisbah kapur kaca kepada ketulan tanah liat.

DEDICATION

Dedicated to my father, Rosli Bin Hasan and my mother, Rahmah Binti Nordin
To my supervisor, Dr. Jariah Binti Mohamad Juoi, lecturers and friends for all of their help and friendship.

ACKNOWLEDGEMENT

I would like to convey my thanks to those who have been very helpful in conducting this project for their favorable advice in finding most solution. Thus, I take this golden opportunity to express my millions of gratitude to my supervisor, Dr. Jariah Binti Mohamad Juoi for her kindly advice and guidance during the project; providing tremendous consideration and useful comments and materials to overcome obstacles that I had faced. These thanks also dedicate to Associated Professor Dr Thangaraj Joseph Sahaya Anand and Dr. Azizah Binti Shaaban for their encouragement, fully support, by providing me enormous guidance and idea for my research project. Also, my special thanks to Mrs. Norhafizah Binti Ishak, for your time and co-operation completing my research project. Subsequently to Mr. Mohd Farihan Bin Sabtu and Mohd Azhar Bin Abu Shah and all technicians involved to complete this project. Special thanks to my friends for their help during undertaking this project. Thanks are also extended to FKP lecturers who had provided technical help and assistance throughout the project. Lastly I would like express my gratitude with highly appreciation and dedication to my family who has been the loveliest advisor for their continuous support and inspiration throughout my campus life.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	-	American Standard Testing Material
$CaCO_3$	-	Calcium carbonate
CaO	-	Calcium Oxide
CIP	-	Cold Isostatic Pressing
FA	-	Fine Aggregate
FG	-	Fine Glass
K	-	Kelvin
MHz	-	Mega hertz
MPa	-	Mega pascal
Na_2O	-	Natrium Oxide
PVA	-	Polyvinyl Alcohol
SEM	-	Scanning Electron Microscope
SLSG	-	Soda lime Silica Glass
SiO_2	-	Silicon Oxide
Tg	-	Transition glass temperature
Tm	-	Melting temperature
Wt. %	-	Weight percentage
XRD	-	X-Ray Diffraction
$\alpha\tau$	-	Thermal expansion coefficient
µm	-	micro meter
°C	-	Degree Celsius

CHAPTER 1
INTRODUCTION

1.1 Background of study

Glass ceramic can be defined as a fine-grained crystalline ceramic material that was formed as a glass and subsequently devitrified (Callister W. D., 2005). Nowadays, the used of glass ceramic becomes famous in structural applications as well as in manufacturing industry. The primary advantages of glass ceramic are higher strength, chemical durability, and electrical resistance and can be made with very low thermal expansion coefficients, giving excellent thermal shock resistance (Rahaman M. N., 2003). Throughout its performance, glass ceramic play a vital role in consumer needs or products that exhibits high level of mechanical properties. The main purpose of using recycled glass in glass ceramic is to improve the physical and mechanical properties of existing ceramic materials.

The production of glass ceramic materials made by recycling industrial waste is an innovative development in glass ceramic industry. Many researchers have paid much attention to produce glass, glass ceramic and sintered materials from industrial wastes to make them reasonably safe for the environment (M.Erol *et al*., 2008). For example, many investigations reuse soda lime silicate glass (SLSG) to manufacture glass ceramic products. SLSG is the most common commercial glass and less expensive. Normally, this soda lime glass has composition of 60 wt. % – 75 wt. % silica, 12 wt. % – 18 wt. % soda, and 5 wt. % – 12 wt. % lime. The reuse of the SLSG waste in ceramic system has capable to improve the performance compare to conventional ceramic material, especially in highly demanding the structural applications.

In line with the idea to reuse the SLSG to manufacture glass ceramic products, there have several factors that should be considered in order to make it beneficial. Factors such as particle size distribution and fillers used during powder preparation, processing method and sintering process are among crucial factors that should be properly considered. Physical analyses and mechanical testing for the product should also be considered in order to ensure its quality.

Particle size distribution is important, depending on which consolidation or shaping technique is to be used. Low porosity and fine grain size are beneficial to achieve a glass ceramic with high strength (Richerson D. W., 2005). Thus, fine grained size below than 75 μm is going to be employed in this study. The addition of binder and filler will affect the performances and properties of the new material produce from recycled glass. Various types of binders have been used from previous study by the researchers such as polyvinyl alcohol (PVA), ball clays, quartz-feldsphatic sands and others. These binders and fillers are widely used to provide enough strength in the 'green body' (unfired compact) to permit handling, 'green' machining, or other operations prior to densification (Richerson D. W., 2005). Therefore, the introduction of ball clays as filler has been employed in this study to develop properties which have the precise composition and ratios that give significant affects on some properties.

It is essential to finalize the suitable processing method for this study. In general, pressing method is widely used for forming of ceramic materials. There are various types of pressing techniques such as pressing, slip casting and tape casting. In this study uniaxial pressing and cold isostatic pressing (CIP) is chosen as a method for compaction and shaping of the powder materials into a rigid die body.

Subsequently, rigid die body then has been dried and surface finished (green body) in a furnace to develop the desired microstructure and properties. This stage is called sintering which imply the shrinkage and densification. The performance of the final product will be analyzed in terms of its microstructures, phase's present and physical properties.

In this study, Scanning electron microscope (SEM) and x-ray diffraction (XRD) analysis are use to analyze the microstructure and phases present in the samples produced. Physical analysis and mechanical testing are also conducted in order to analyze the properties of the samples.

1.2 Problem statement

Today in Malaysia, recycled waste such as glasses, papers, plastics and others are not used very constructive. Usually the waste management used landfill method to throw out this disposal. Only certain of that disposal are being used for recycling purpose. Regarding to these, disposal like glasses is reused by crushed into small pieces and melted at high temperature. Then the glass is reformed into desired shape such as bottles and food containers. Recently, glass is choose as an alternative materials in upgrading ceramic into glass ceramic that is useful for various structural applications. Thus is an alternative way in recycling glass waste. Example of glass ceramic used for structural applications are porcelain stoneware tiles which used waste of soda lime float and container glass as raw materials in replacement of sodic feldspar (Matteucci *et al.,* 2002). It is essential and possible to produce a new types of glass ceramic that exhibit the economically and environmentally benefits for this applications. Therefore, it is necessary to characterize and determine the properties for the glass ceramic produce forming. In this work such possibility is investigated, recycled glass is being used to produce glass ceramic because of its potential to improve the general properties of glass ceramics. In this research, new advanced materials are produced to fulfill the requirement as beneficial materials in order to ensure that the glass ceramic available for structural applications, it is being characterize and its physical and mechanical properties is investigated.

1.3 Objectives

The objective of this project is:

i. To study the effects of sintering temperature and clay addition toward glass ceramics produced from recycled glass by using Cold Isostatic Pressing (CIP) Method.
ii. To analyze the physical and mechanical properties of glass ceramics samples produced from recycled glass.
iii. To study the microstructure and phases present in the glass ceramics samples produced from and recycled glass.

1.4 Scope of study

The scope of this project is mainly focus on converting recycling glass into glass ceramic product. This study uses soda lime glass as the raw material. The process started by preparing the soda lime glass powder. The powders of SLSG were prepared by crushing raw materials using hammer. The size of particle then was sieved by using the sieve to determine the average particle size.

Next stage of process involves the mixing the raw materials with filler. The use of filler is to bind the materials together while mixtures. The filler that used in this project is ball clays. The chosen of filler is important to improve the strength of the as-formed product to provide strength for handling (green strength) before the product is densified by firing (Reed J. S., 1995).

The processes then continue with the pressing method to make the compaction on a powders and shaping by confined it in a rigid die or a flexible mold (Reed *et al*., 1995). Firstly, the mixtures are pressed by using uniaxial pressing before do the second compaction by using cold isostatic pressing (CIP) method which also referred as hydrostatic pressing is used. The CIP method is chosen because of its advantage compared to uniaxial pressing has limitations such as the green density of isostatically pressed part is higher and much uniform. Some of the limitations can be

overcome by applying pressure from all direction instead of only one or two directions. Application of pressure from multiple directions achieves greater uniformity of compaction and increased shape capability (Richerson D. W., 2006).

In line with the objectives of this study, the effects of sintering temperature and addition of ball clay are analyzed on the physical and mechanical properties of glass ceramics. Various sintering temperature are used according to the transition glass (Tg) of recycled waste which will result the final product. In this study, there are three sintering temperatures and ratios of SLSG to ball clay are employed.

The samples produced are then analyzed accordance to the appropriate American Standard Testing Material (ASTM) for physical and mechanical properties. ASTM C 373 will be used for physical tests which include porosity, density measurement and water absorption. Morphological and crystallography analysis are observed by using SEM and XRD. The mechanical tests that conducted are microhardness by using Vickers microhardness machine.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

This chapter are discussed the on materials and method which is used in this study. Firstly, this chapter introduce waste glass material and narrows down to type of recycled glass which are used as a raw material. The connection of recycled glass with glass ceramic also will be explained in this chapter. Other than that, the processing of glass ceramic will gives as an image on the method of glass ceramic produced in this study. This chapter end by discussing related research on recycled waste in terms of raw materials, processing and end result focusing on the effects of sintering temperature and clay addition towards glass ceramic produced.

2.2 Recycling Waste

Recycling waste means that fewer new products and consumables need to be produced, saving raw materials and reducing energy consumption. The industrial wastes such as plastics, glasses, papers and others is main disposal which give problems to a country. Year by year the quantity of this disposal increased which is an issue that have received a lot of attention in the society. Malaysians produce over 15,000 tons of rubbish everyday. It is only a matter of time before they run out of space to dispose of them. By recycling, it will reduce waste which in turn reduces the need for landfills and dumpsites (Source: http://www.kpkt.gov.my/kitarsemula - online on 8 October 2009). Figure 2.1 shows the breakdown of solid waste created by Malaysians.

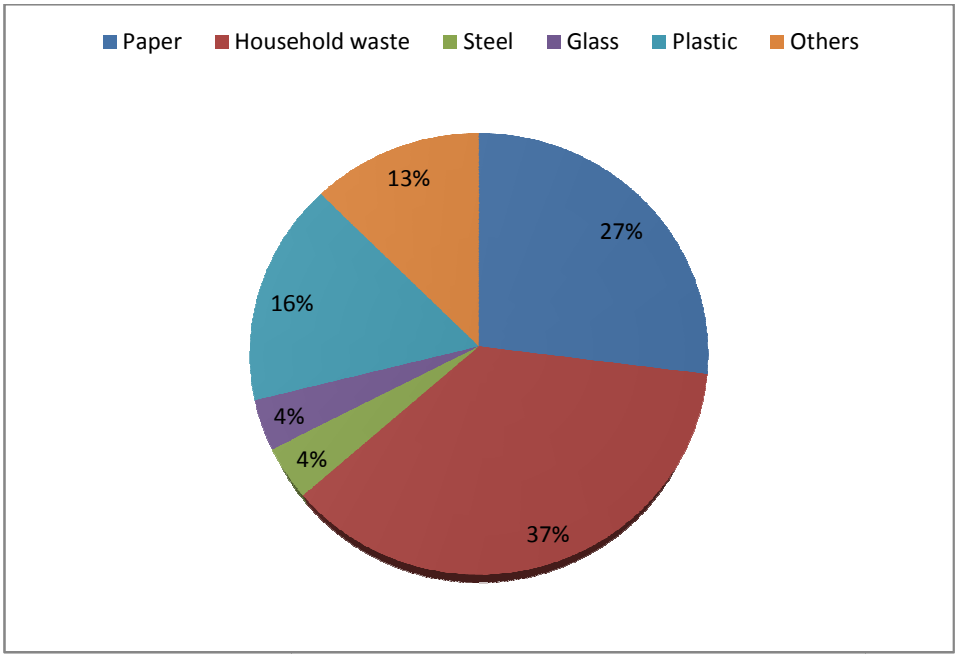


Figure 2.1: Breakdown of solid waste created by Malaysians

(Source: http://www.kpkt.gov.my/kitarsemula - online on 8 October 2009)

2.2.1 Recycling Glass

The amount of waste glass is gradually increased over the recent years due to an ever-growing use of glass product. Most of the waste glasses have been dumped into landfill sites. The landfilling of waste glasses is undesirable because they are not biodegradable, which makes the environment less (Turgut *et al.,* 2009). Therefore a great concern regarding the waste management issues should be taken in order to reduce the wastes by recycling, which give a lot of benefits to the environment and also to the economy.

According to Callister W. D. (2005), the glasses are a familiar group of ceramics. Most ceramic materials fall into an application-classification scheme that include groups of glasses, clay products refractories, abrasives, cements and advanced ceramics. Figure 2.2 presents a classification of ceramic materials on the basic application. Glass is a noncrystalline solid which has a transparent surface that has a mixture of materials such as silica, soda ash and $CaCO_3$ formed by melting at high temperature followed by cooling during which solidification occurs without

crystallization. Glass only has a short-range crystal structure. The bond angles causes the glass structure varies over a range of angles. Glass does not melt at a particular temperature because the variation in bond angles causes the glass structure to soften over arrange of temperatures. The viscosity changes gradually over this range, which allows glass to be formed into a wide variety of products (Haun Labs, 2000). Manufacture products such as sheet glass, bottles, glassware and vacuum tubing in an example of applications of glass.

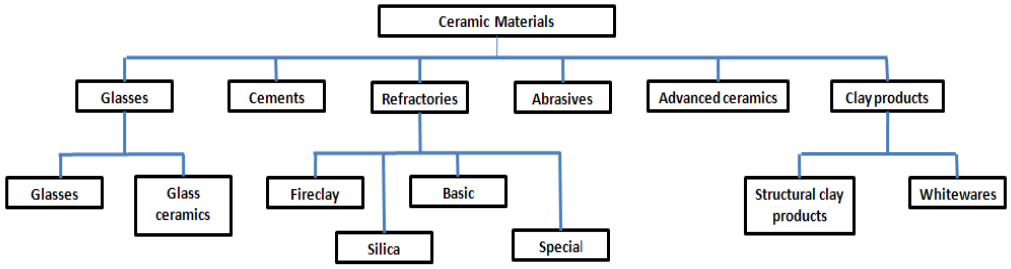


Figure 2.2: Classifications of ceramic materials on the basics application (Callister W. D., 2005)

In ceramic industry, different kinds of wastes have already been recycled. Wasted glasses have a huge potential for using recycled glass in the structural applications. The products such bricks, tiles and concrete is an example of structural product of ceramic materials. The utilization of wasted glasses can be an alternative way to save energy in the production process and to reduce the manufacturing cost (Vorrada *et al.,* 2009). Incorporation of the wasted glasses into a mixture, results in higher density, less water absorption and lower drying shrinkage of the ceramic products. Therefore, soda lime silica glass (SLSG) is chosen as a raw material in this study depending to it appropriate properties such as low melting temperature, easily worked and durable.

2.2.1.1 Raw materials

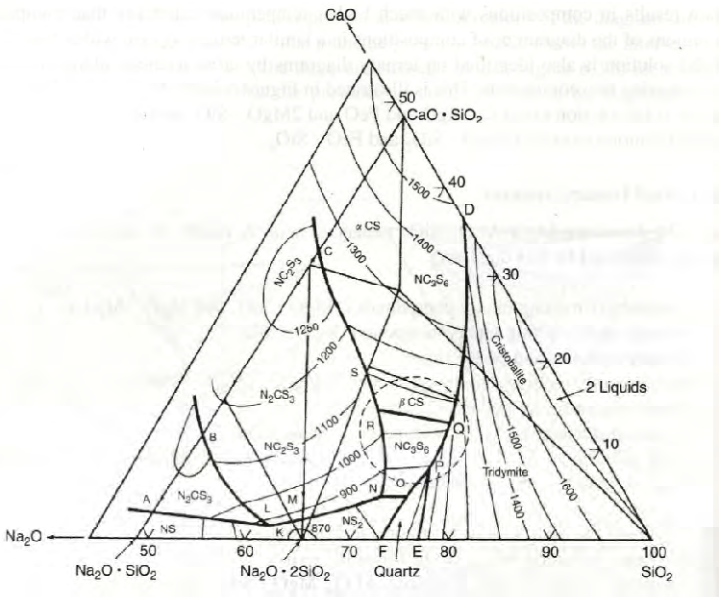
The production of glass ceramic materials made from recycled wastes is a well known technology. Previous researchers have paid much attention to produced glass, glass ceramic and sintered materials from industrial wastes (Erol *et al.,* 2009). The most popular recycled glasses that usually used as raw materials are soda lime float

and food container, structural glass walls, panel glass dismantled cathode ray tubes (CRTs) and white windows glass. Raw material such as SLSG is chosen because it has no significant effect on semi-finished products but it result in firing behavior, increased shrinkage and closed porosity, decreasing open porosity and bulk density and lowering mechanical and tribological performances (Matteucci *et al.,* 2002). Besides to be as a raw material, SLSG also could act as a fluxing agent which resulted in better mechanical characteristics (Vorrada *et al.,* 2009).

In terms of recycled wastes, other than recycled glass, previous study also used industrial wastes such as coal fly ash, mining incinerator residue and lime from fume abatement systems as reagents into stoneware, tiles, bricks and concrete to help lowering firing temperature of glass ceramic products (Vorrada *et al.,* 2009). The influence of adding recycled wastes into glass ceramic products result on the microstructure and mechanical properties in order to obtain new glass ceramic products by powder technology and sintering process (Rozenstrauha *et al.,* 2006). In this study, raw material utilizes is SLSG.

i. Composition and Properties of Soda Lime Silica Glass (SLSG)

SLSG is referred as commercial glass consists mainly of sodium, calcium and silicon oxides (Na_2O, CaO and SiO_2). The minor constituents of SLSG included alumina, magnesia and several other oxides. SLSG has the unique combination of low cost raw material with good glass manufacturing characteristics. SLSG generally fall in a narrow range of compositions along the boundary between (Na_2O – 3CaO – $6SiO_2$) and tridymite (SiO_2) in the Na_2O – CaO – SiO_2 phase diagram. Figure 2.3 shows the phase diagram of Na_2O – CaO – SiO_2. This diagram is of particular importance to glass technology. Most of compositions for window, plate and container glass are located in the circled region of the diagram modified with small additions of other components. Variations from this narrow range can adversely affect various important characteristics, such as the glass melting behavior, crystallization tendency, glass workability and chemical durability (Haun Labs, 2000).



Na_2O – SiO_2 / mass %

Figure 2.3: Phase equilibrium diagram of Na_2O – CaO – SiO_2 (Richerson D. W., 2006)

SLSG can be divided technically into two which is glass used for windows and glass used for container. The composition of this both is fairly similar but slight variations in colorants and the ratios of the constituents can have a significant affect on some properties such as thermal expansion and crystallization behavior. If the recycled glass used is from different sources is combined, these variations can cause problems depending on the processing method used. Processing problem from variations in composition can generally be reduced by using finer glass particles (Haun Labs, 2000). The chemical composition of SLSG is lists shown in Table 2.1

Table 2.1: The variations of chemical composition of Soda Lime Silica Glass (SLSG) (Haun Labs, 2000)

Soda Lime Silica Glass		**(wt. %)**
Silica sand	SiO_2	69 – 74
Lime (calcium oxide)	CaO	5 – 14
Soda	Na_2O	10 – 16
Boron oxide	B_2O_3	-
Potassium oxide	K_2O	-
Magnesia	MgO	0 – 6
Alumina	Al_2O_3	0 – 3
Others		0 – 5

According to Matthias *et al.,* (2008), in contrast to most other materials, glasses do not consist of a geometrically irregular network of crystal but of an irregular network of silicon and oxygen atoms with alkaline parts in between. The composition of chemical gives an important influence on the viscosity, the melting temperature, T_m, and the thermal expansion coefficient, α_τ, of glass. Typical viscosities and physical properties of SLSG is mention in Table 2.2.

Table 2.2: Typical viscosities and physical properties of Soda lime Silica Glass (SLSG) (Matthias *et al.,* 2008)

	Units	**Soda Lime Glass**
Working Point	°C	1040
Softening Point	°C	695 – 730
Annealing Point	°C	514 – 550
Strain Point	°C	470 – 515
Glass Transition Temperature	°C	442 – 592
Thermal Conductivity	W/(m K)	0.94
Specific Heat	J/(kg C)	879
Coefficient of Thermal Expansion	1/C (x10^-6)	8.6
Knoop Hardness	kg/mm^2	565 - 605
Density	kg/cm	2500
Compressive Strength	MPa	
Tensile Strength	MPa	19 - 77
Bending Strength	MPa	41 - 165
Young's Modulus	GPa	70 - 72
Poisson's ratio		0.22
Dielectric Strength	kv/cm	
Dielectric Constant (@1MHz)		7.2 - 7.75
Dielectric Loss Tangent		0.009
Resistivity	ohm/cm	10^{10}
Usable Transmission Range	um	0.50 - 2.7
Refractive Index (@550nm)		1.52

The characteristics of SLSG are low melting temperature, easily worked and durable. In applications, SLSG are widely used as such as bottles. Even though there has various colors of bottles, for this study, transparent SLSG bottles are used as raw material. The comparison between SLSG with other glasses is shown in Table 2.3.

Table 2.3: The comparison between Soda lime Silica Glass (SLSG) with other glasses (Matthias *et al.,* 2008)

Glass	Composition (wt. %)	Properties	Uses
Soda lime silica glass	SiO_2 – 70 NaO_2 – 15 CaO – 10 Others – 4	Low melting point Moldable into shapes Cheap Breakable Can withstand high heat	Glass containers Glass panes Mirrors Lamps and bulbs Plates and bowls Bottles
Lead glass (crystal)	SiO_2 – 70 NaO_2 – 20 PbO – 10	High density and refractive index Glittering surface Soft Low melting point	Containers for drinks and fruit Decorative glass and lamps Crystal glassware Lenses for spectacles
Borosilicate glass (Pyrex)	SiO_2 – 80 B_2O_3 - 13 NaO_2 – 4 Al_2O_3 – 2	Resistant to high heat and chemical reaction Does not break easily Allows infra-red rays but not ultra-violet rays High melting point	Glass apparatus in laboratories Cooking utensils
Fused silicate glass	SiO_2 – 99 B_2O_3 - 1	Expensive Allows ultraviolet light to pass through Difficult to melt or mould into shape	Scientific apparatus like lenses on spectrometer Optical lenses Laboratory apparatus

2.3 Glass Ceramic

Glass ceramic materials are combination of many properties with both glass and more traditional crystalline ceramics. Glass ceramic have no pores between crystals like sintered ceramics. The atomic arrangement of glass is stable at high temperature but not at room temperature. The atoms want to rearrange into a crystalline structure but do not have enough mobility at room temperature (Richerson D. W., 2006). By adding additives when glass is initially formed and by heat treating at a suitable temperature below the melting temperature, the glass can be induced to crystalline. At that temperature, enough energy is present allow the atoms to move. Thus, the atoms in the glass rearrange around the atoms of the nucleating agent to form a polycrystalline ceramic called a glass ceramic.

According to Martin J. W. (2001), properties of glass ceramic can be separate into five properties which thermal, optical, chemical, mechanical and electrical properties. Thermal properties of glass ceramic are not like many other glasses or ceramics. Many commercial glass ceramics capitalize on their superior thermal properties, particularly ultralow thermal expansion together with high thermal stability and thermal shock resistance. In addition, glass ceramic have high temperature resistance and this property depends most on the composition and amount of residual glass in the material. Generally, glass ceramic can operate at temperature of 700 °C to over 1200 °C. For optical properties, glass ceramic may be either transparent or opaque. The chemical durability of glass ceramic is a function of the durability of the crystals and the residual glass. Commonly, highly siliceous glass ceramics with low alkali residual glasses have excellent chemical durability and corrosion resistance. Glass ceramic are brittle materials that exhibit elastic behavior up to the strain that yield breakage a property that is the same as single glass on ceramic. However, in terms of its mechanical properties, glass ceramics show better strength, elasticity, toughness and abrasion resistance than glass. The dielectric properties of glass ceramics strongly depend on the nature of the crystal phase on the amount and composition of the residual glass. Glass ceramics also have high resistivities that can be used as insulators. Nevertheless, most glass ceramics have low dielectric constants, typically between 5 to 8 at 1 MHz and 20 °C.

All commercial as well as most experimental glass ceramic are based on silicate bulk glass compositions. Glass ceramic can be further classified by the composition of their primary crystalline phases, which may consist of silicates, oxides, phosphates, borates or fluorides (Ray *et al.,* 2000). Example of commercial glass ceramics are given in Table 2.4.

Table 2.4: Commercial glass ceramic (Ray *et al.,* 2000)

Commercial Identification	Crystal Phases	Properties	Application
Corning 8603	$Li_2O - 2SiO_2$, SiO_2	Photochemically machinable	Fluid amplifiers, molds for printing printers
Corning 9606	$2MgO - 2Al_2O_3$ - 5 SiO_2, SiO_2, TiO_2	Low expansion, transparent to radar	Radomes
Corning 9608	β – spodumene solid solution, TiO_2	Low expansion, good chemical durability	Household cooking utensils
Corning 9611	α – quartz solid solution	Very high strength	Structural members
Neoceram (Japan)	β – spodumene solid solution	Low expansion	Household cooking ware
Owens-Illinois cervit	β – quartz solid solution	Zero expansion at ambient temperatures	Telescope mirror blanks
Anchor-Hocking Cookware	β – quartz solid solution	Low expansion	Household cooking ware
Corning 0303	$Na_2O - 2Al_2O_3$ - $2SiO_2$, $BaO - 2Al_2O_3$ - $2SiO_2$,	High strength	Tableware and dinnerware
Corning CYKOL and CYKO2	Sodium elobate	High dielectric constant	Miniature capasitors
Corning 9690	β – quartz solid solution	Low expansion	Gas-stove burners
Corning 0333	β – quartz solid solution	High strength, weatherability	Building cladding

Glass ceramics are used in various applications such as dinnerware, telescope mirrors, radomes and semiconductor substrates. This is because ceramic are more economical to produce and they possess special properties that cannot be achieved by other means (Psaras *et al.,* 1987). To obtain desirable properties in those materials, the crystallization process must be control. Most glass ceramic materials formulations contain small amounts of special additives, called nucleating agents,

which initiate the crystallization process and influence the particular mix of phases that develops. Commonly, platinum, TiO_2, ZrO_2 and P_2O_5 in concentration from 0.01 wt. % to 10 wt. % are used nucleating agents as silicate-based glass ceramics. In order to getting good properties of glass ceramic produced from recycled glass, factors such as particle size and processing is a significant with better result in crystal phase and microstructure, physical analysis and mechanical testing.

2.3.1 Particle size

Measurement of particle size distribution is key for characterizing a ceramic powder. Particle size is important depending on which consolidation or shaping technique is to be used. In the previous study, the objective of consolidation step is to achieve maximum particle packing and uniformity, so that minimum shrinkage and retained porosity will result during densification. Turgut *et al.,* (2009) revealed that the replacement fine glass (FG) with fine aggregate (FA) at level of 20 % by weight had a significant effect on properties of glass ceramic samples. Figure 2.4 shows the variation percentage of test results in FG replacement with FA.

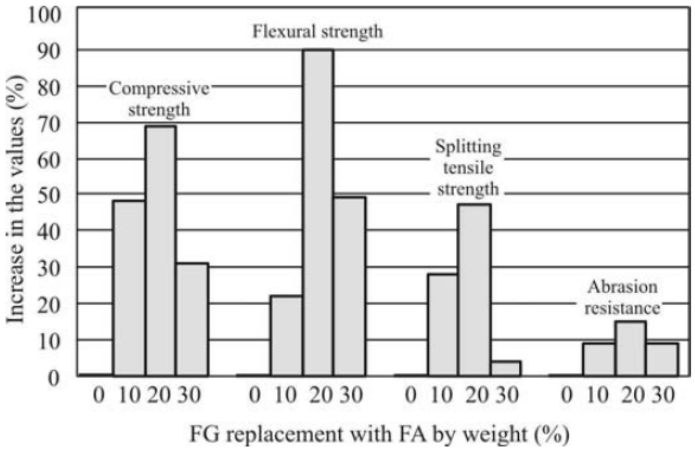


Figure 2.4: The variation (%) of test result in FG replacement with FA (Turgut *et al.,* 2009)

Vorrada *et al.,* (2009) used particle size 18 µm which is 1 mm opening size in generating a powder material and the particle size distribution test was carried out for recycled glass powders using sieve analysis. Besides, coarser powders which below than 88 µm and finer powders which below than 37 µm are used in Bernardo *et al.,*

(2005) study in determined the temperature and time at temperature necessary to achieve sintering.

2.3.2 Processing of Glass Ceramic

The processing of glass ceramic is similar with the processing of ceramics. There are various processing method that are used to produce glass ceramic materials. According to previous study, most of the researchers paid much attention on the sintering behavior of glass ceramic produced. The processing method in Matteucci *et al.,* (2002) started by mixed the soda lime float and food container with glass ceramic product which is porcelain stoneware. The weight percent of recycled glass is 5 wt. % and 10 wt. %. The mixture then continues with normal process and end by sintering process. Differ with Vorrada *et al.,* (2009), which after the mixing process, the mixture will then soaked, stirred and kneaded to formed for 1 day before fired in furnace at temperature 1000 °C – 1200 °C and finished by cooled down at room temperature.

Any other different techniques from Bernardo *et al.,* (2007) study, which the mixture of raw material and mining residue is investigated using X-ray Diffraction (XRD) before treated at 1350 °C for 2 hours until the glass melted and poured on steel plates. The drastic cooling forced the samples into a number of fragments before milled using ball mill and sized to a dimension of 37 µm. Process continues with sintered the samples at 960 °C for 30 minutes and done drying treatment at 120 °C before end out by pressed again at 40 MPa. Techniques from Bernardo *et al.,* (2007) is a fast treatment to the sample product to ensure the mixture of industrial waste has been successfully transformed into dense and strong sintered glass ceramic with short holding times and a very rapid heating.

In order to investigate the influence of the binder on the properties of sintered glass ceramic, Erol *et al.,* (2009) sieved the coal fly ash using 180 µm before humidified at 5 wt. % distilled water without any additives and then cold pressed. To determine the effect of binder toward coal fly ash, polyvinyl alcohol (PVA) were added and cold pressed using 40 tons in a disk shape. Samples were then dried in electric oven at 383

Kelvin (K) for 2 hours. Samples the placed on the alumina bricks and heated at 10 K / min to the maximum nucleation temperature and soaking for 15, 30 and 60 min for crystallization and then were cooled in furnace.

Another different processing technique done by Bernardo *et al.,* (2005) which started the processing with mixed in the proportion panel glass dismantled, lime and residues 28 % - 25 % - 47 % by weight. The mixtures of A, B and C were dry ball milled and sized to grains below than 88 µm for coarse powders and below 37 µm for finer powder. Samples then were gently pressed in rectangular die and sintered in air at the crystallization temperature for 1h to 5h with a heating rate of 10 ℃ min.

The processing by Minoru *et al.,* (2004) begun with weight 30g of each samples and placed in covered alumina crucible. Samples were then heated at 10 K / min to 1400 ℃ in siliconit furnace and then kept the samples at 1450 ℃ for 2h. After refining 1300 ℃ for 1h and the melts were poured onto an iron plate before heat treated at 900 ℃ to 1200 ℃ for 1 to 4 h. This study focused more on the crystalline phase of glass ceramic produced.

Turgut *et al.,* (2009) carried out different technique of processing dry mixed the white windows glass with constant proportions of cement for 1 min and mixed with water for 3 min before poured in molds and force at 17 MPa is applied for 1 min. samples are then removed from molds and cured under the water for 28 days. Then, the samples are dried for 24 h using ventilated oven at 105 ℃ and weight at room temperature.

The last techniques that is similar in this study is the processing by Rozenstrauha *et al.,* (2006) the mixture of raw material and binder were milled using ball mill for 24 h up to an average particle size of 10 µm. the compositions of mixtures were prepared by adding 20 wt. % and 30 wt. % of binders. Other mixtures mixed in dry state were milled using agate mills for 20 min and water were added about 8 wt. % to 12 wt. %. The sintering behavior and thermal changes were determined by differential thermal analysis (DTA) in the temperature range about 20 to 1300 ℃. samples were uniaxially pressed at room temperature using pressures of 50 MPa and

sintered in air with heating rate was 8 ℃ / min between sintering temperature 1000 ℃ and 1120 ℃. The technique used is same which is started with powder preparation, forming and end by sintering differ with other techniques which used different processing even tough the end result of each study is to producing glass ceramic samples from recycled glass.

Processing of glass ceramic usually made in three steps which are forming a powder to desired shape, partially drying and firing at high temperature to produces dense product.

2.3.2.1 Forming

Forming process begins with finely ground powder. Control of particle size and particle size distributions is required to achieve the optimum properties for intended applications. Each application has specific requirements. High strength ceramic require very fine particles which is typically below than 1 μm to achieve a fine grained microstructure with minimum flaw size. Many different powder synthesis and sizing techniques have been developed to achieve the various required distributions. Table 2.5 lists these diverse techniques (Richerson D. W., 2006).

Table 2.5: Major Compaction Techniques Used for Ceramic fabrication (Richerson D. W., 2006)

Technique	Example
Pressing	Uniaxial
	Isostatic
	Hot Pressing
	Hot Isostatic Pressing
Slip Casting	Drain casting
	Solid casting
	Vacuum casting
	Pressure casting
	Centrifugal casting
	Fugitive – mold casting
	Gel casting
	Electrophoretic deposition
Tape Casting	Doctor blade
	Waterfall
Plastic Forming	Extrusion
	Roll forming
	Injection molding
	Compression molding

Then, glass ceramic processing continues with processes to form the ceramic powder into the component shapes. Uniaxial and isostatic pressing, slip casting, extrusion, injection molding, tape forming and green machining are included. Most of the popular techniques in glass ceramic processing are pressing method. Table 2.6 shows techniques powder preparation and sizing used for ceramic fabrication.

Table 2.6: Techniques for Powder preparation and Sizing of Ceramic Fabrication (Richerson D. W., 2006)

Mechanical	Chemical	Miscellaneous
Screening	Precipitation	Calcining
Elutriation	Sol-gel	Fluidinized bedRotary kiln
Air classification	Liquid mix	Combustion synthesis
Ball milling	Decomposition	
Attrition milling	Freeze drying	
Vibratory milling	Hot kerosene drying	
Turbomilling	Plasma	
Fluid energy milling	Laser	
Hammer milling	Hydrothermal	
Roll crushing		

According to Reed J.S. (1995), pressing is the most widely forming process to produced parts. Products produced by pressing include ceramic tile and porcelain products, coarse grained refractories, grinding wheels and structural clay products. Pressing by means of punches in hardened metal dies, commonly called uniaxial pressing, is widely used for pressing parts thicker than 0.5 mm and parts with surface relief in the pressing direction. Isopressing, commonly known as isostatic pressing were used flexible rubber molds. Isostatic pressing is used for producing shapes with relief in two or three dimensions, shapes with one elongated dimension such as rods and tubes, and vey massive product with a thick cross section. Both of uniaxial pressing and isostatic pressing have wet and dry bag. In this study, dry bag isostatic pressing is used in order to produce new type of glass ceramic materials.

i. Uniaxial Pressing Method

In uniaxial pressing, a mold is filled with either dry powder, or a powder and a hard metal punch is driven into the die to form coherent compact. It is important that the unfired or green body has adequate strength for handling before the firing operation, during which organic additives are decomposed. Uniaxial pressing can be reasily automated and is particularly suited for forming components with a simple shape such as flat discs and rings that can be produced to close dimensional tolerances (David S., 1991).

ii. Cold Isostatic Pressing (CIP) Method

There are two kind of isostatic pressing which is wet and dry bag. In both bags, the press mix is placed in an elastomer bag and compacted with hydraulic pressure on the exterior of the bag (King A. G., 2002). In this study, wet bag cold isostatic pressing is used to compact the mixture of raw materials and filler. Dry isostatic pressing was developed to achieve increased production rate and close dimension tolerances. The internal parts of wet bag cold isostatic pressing are shown in Figure 2.5.

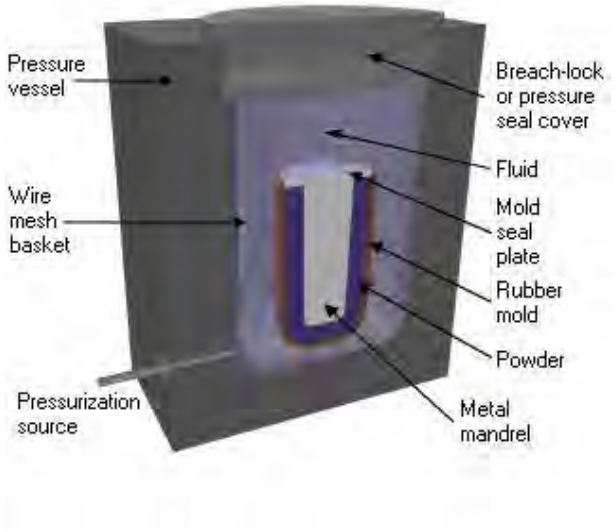


Figure 2.5: Schematic of wet bag Cold Isostatic Pressing
(Source: http://www.designinsite.dk/htmsider/pb1007.htm - online on 5 October 2009)

In isostatic compaction, the defects can be avoided by applies equal pressure from all directions at once. In the wet bag process, the powder is sealed in a flexible container or mold, submerged in the fluid chamber and the pressure applied. Figure 2.6 illustrate the wet bag processing steps.

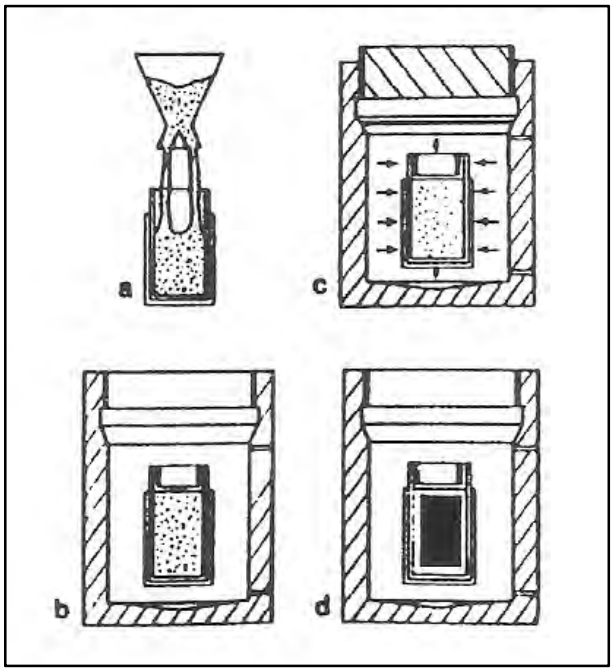


Figure 2.6: The flexible container is (a) filled, (b) submerged, (c) pressed and (d) decompressed before removal (Winter *et al.,* 2005)

2.3.2.2 Densification

Densification is the next stage of glass ceramic processing. Densification is also known as compaction. Ceramic powders are commonly compressed in a die to produce near net shape green bodies prior to final sintering. Density gradients in the resulting compacts may cause distortions in the shape of the parts during sintering processing to obtain the desired final shape (Reed J. S., 1995).

2.3.2.3 Sintering

Sintering maybe considered as a process by which an assembly of particles, compacted under pressure or simply confined in a container, chemically bond themselves into coherent body under the influence of an elevated temperature. The temperature is usually below the melting point of the major constituent (Upadhyaya *et al.,* 1998).

The objectives of sintering is to removed pores at the starting particles, combined with growth together and strong bonding between adjacent particles. Sintering is the

last stage before the end product produced (Richerson D. W., 2006). Table 2.7 represent the stages of sintering while Figure 2.7 shown the changes that occur during sintering. The differences of sintering temperature affect the end properties of the final products.

Table 2.7: Stages of sintering (Richerson D. W., 2006)

Stages of sintering	Changes
1st stage (initial)	Rearrangement
	Neck formation
2nd stage (intermediate)	Neck growth
	Grain growth
	High shrinkage
	Pore phase continuous
3rd stage (final)	Much grain growth
	Discontinuous pore phase
	Grain boundary pores eliminate

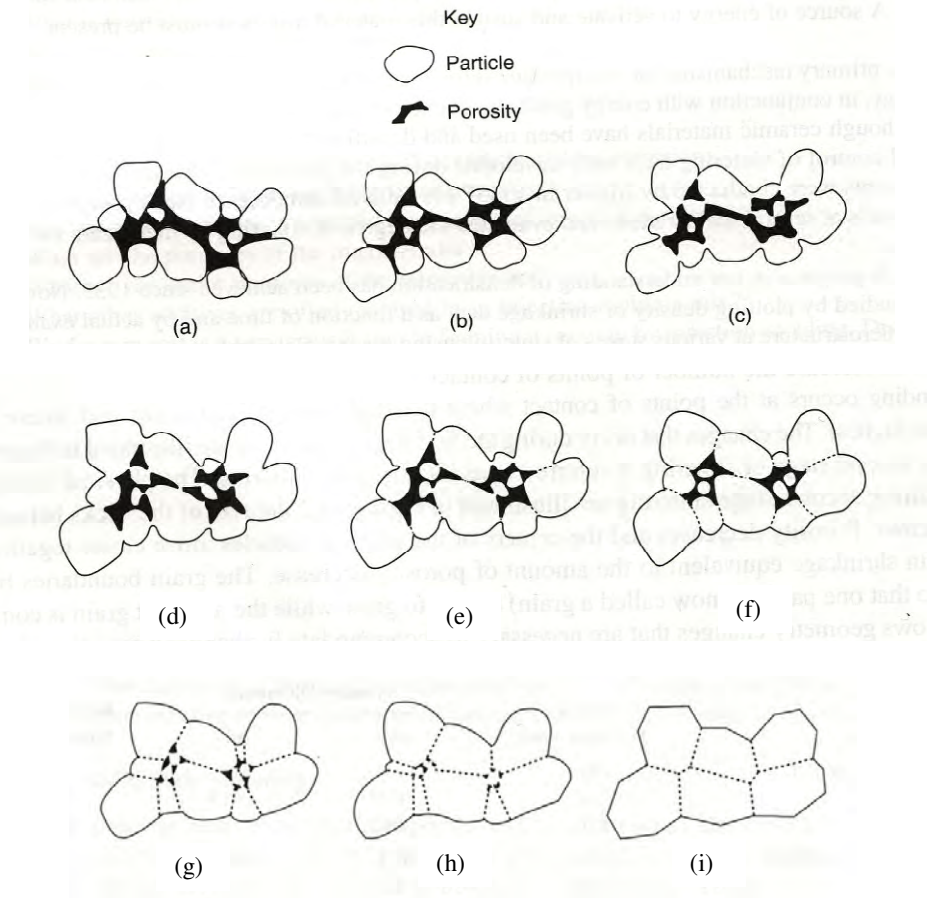


Figure 2.7: Changes that occur during sintering (Richerson D. W., 2006)

i. Solid State Sintering

The sintering process involves heating material formed by the compaction at ambient temperatures of pure fine particles (usually below than 1 μm diameter). At high temperatures, typically from 0.5 to 0.8 of the absolute melting temperature, the particles sinter together. This is a spontaneous process and must thus be accompanied by a decrease in free energy of the sample. The most important driving force for sintering is the reduction in solid/vapor surface area when the individual particles fuse together and the larger particles grow at the expense of smaller ones.

Idealized solid state sintering is of restricted practical use for ceramics in those pure materials and fairly high temperatures are involved. Solid sintering does, however, have important applications, and it is possible to obtain solid material close to theoretical density. The resulting comprises individual crystallites or grains, separated by grain boundaries, and probably residual porosity. The grain size is usually much greater than the original particle size (Davidge R. W., 1979).

ii. Temperature and Time

In sintering process usually the samples will be fired in a variety of kilns and furnaces. From the previous study, sintering temperature and time gives huge effects on performances and properties of glass ceramic produced. In generally, sintering shrinkage increase with the amount of recycled glass, which tends to fasten sintering, as bodies with 10 wt. % waste begin to soft and reduce their shrinkage after sintering at 1180 to 1200 °C (Matteucci *et al.,* 2002). The chemical composition of vitreous phase changes continuously with sintering temperature and time. The presence of recycled wastes contributes to accelerate the sintering kinetics, lowering appreciably the viscosity of the liquid phase (Bernardo *et al.,* 2007). As the sintering temperature was increased, the glass phase became more vitrified. By increasing the sintering temperature, glass particles were eventually fused and bonded with glass ceramic bodies, reducing the total porosity and hence increasing bulk density of the bricks (Vorrada *et al.,* 2009). Sintering temperature and time depending on the glass compositions, impurities, surface area, packing efficiency and crystallization behaviors.

2.3.3 Crystal Phase and Microstructure

The structures of glass ceramic usually investigated using x-ray diffraction (XRD) and scanning electron microscope (SEM). Tanaka *et al.,* (2005) pointed out that wollastonite ($CaO - SiO_2$) and anorhite ($CaO - Al_2O_3$ - SiO2) are prismatic crystal structures that have the suitable properties for construction materials. Bernardo *et al.,* (2007) demonstrates in Figure 2.8 that the crystallization of glass occurred even for a very short holding time of 30 min at 960 °C. Three main crystal phase, consisting wollastonite, pseudo-wollastonite and Na-exchanged anorhite were formed.

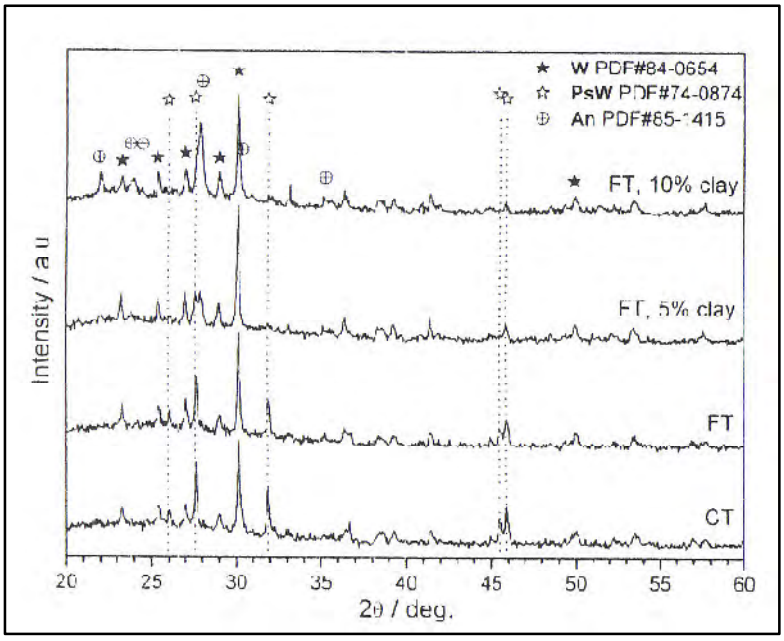


Figure 2.8: XRD spectra of the investigated sintered glass ceramic (Bernardo *et al.,* 2007)

Figure 2.9 shows the SEM images of surface morphology of these glass ceramics at various heat-treatment temperatures (850°C, 900°C, 950°C and 1000°C). A morphological analysis of the specimen heat treated at 850°C and 900°C shows that the well-crystallized whisker-type crystals are partially aggregated in the matrix. However, with an increase of heat-treatment temperature to 950°C and 1000°C a high density of well-crystallized whisker-type crystals is generally aggregated in the matrix which is about 50-70 μ m in size. This is typical of the wollastonite type glass ceramic formed at heat treatment temperature of 1000°C (Park *et al.,* 2007).

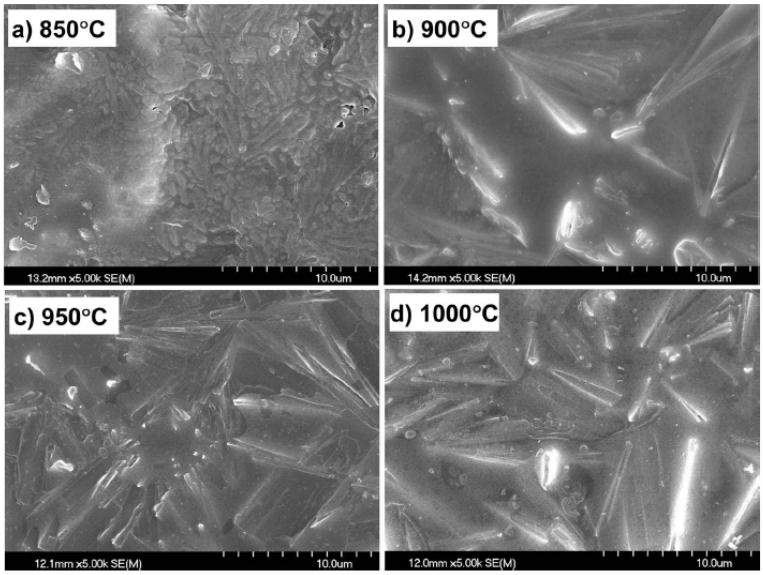


Figure 2.9: SEM images for the glass-ceramics heat-treated at 850 °C - 1000 °C (Park *et al.,* 2007)

For all the processing conditions the microstructure of sintered glass ceramic consist a number of randomly distributed fibrous crystals. The microstructure will change in addition with other binder such as clay to formation of Na-exchanged anorhite, instead of pseudo-wollastonite, leading to improvements in the mechanical properties of glass ceramic produced (Bernardo *et al.,* 2007).

2.3.4 Analyses and Testing

The properties of glass ceramic produced have been determined employing different physical analysis and mechanical testing. For physical analysis that usual done are porosity test, density test and water absorption while for mechanical testing, hardness test, compression test, flexural test and splitting tensile test. Turgut *et al.,* (2009), and Tanaka *et al.,* (2007), conclude that the physical and mechanical test towards properties of glass ceramic samples was relatively better and higher as compared with the standard glass ceramic products. Vorrada *et al.,* (2009) pointed that a large decreased in bulk density, an increase in apparent density and water absorption as low as 2 wt. % to 3 wt. % when bricks containing recycled glass.

In relation to mechanical properties, the strength of glass ceramic samples depends greatly on the amount of wasted glass. The compressive strength, modulus of rupture, hardness gives better result by adding recycled waste into glass ceramic samples. The compressive and modulus of rupture decreased as the recycled wastes increased. The hardness value of glass ceramic samples increased with increase in crystallization degree (Erol *et al.,* 2009).

Final testing of glass ceramic produced will carried out in order to identify the end properties. Commonly, the physical and mechanical testing for glass ceramic produced from recycled glass has improved much better than standard glass ceramic. Testing will be determined in terms of the physical and mechanical properties of glass ceramic samples to ensure samples could be good candidates for industrial use in structural application.

2.3.5 Structural Application and Products

There are only ten percent of the advanced ceramic are used for structural ceramics (Matthias *et al.,* 2008). However, this share is expected to grow. There is a great interest in using glass ceramic in structural application due to high modulus and hardness, low density and resistance to high temperature.

The products of structural application are widely used for building constructions and infrastructures. Tiles, concrete and bricks are an example of structural products. Accordance to previous study, the used of glass recycled as raw material into their glass ceramic products such as clay bricks, concrete blocks and stoneware porcelain tiles is also an example of glass ceramic in structural applications (Matteucci *et al.,* 2002). In addition, glass ceramic produced from wasted materials will provide better in behavior and performances and increase the properties of the products produced.

CHAPTER 3
METHODOLOGY

3.1 Introduction

This chapter explained the component of the processes involved in the whole scope of study. This includes the description of raw material, sample preparation, sample fabrication, physical properties, analyses of microstructure and phase as well as mechanical testing. The raw materials that involved in this study are recycled soda lime silica glass (SLSG) and ball clays as filler. At the beginning, the composition and properties of SLSG are fully characterized. The recycled SLSG and filler are mixed and appropriate compositions between these both were described.

The mixed SLSG and filler are pressed by using uniaxial pressing machine and CIP machine before proceeds with sintering process. At sintering process stage, there have a three different temperature in order to find out the suitable best sintering temperature to the material produced. The effects of this sintering temperature are carried out. Physical study on the glass ceramic produced also had done in order to test the suitability of the glass ceramic to be use in any structural application. Porosity testing, density measurement and water absorption based on ASTM C373 will be conducted. Further studied on the analysis and mechanical testing are proceed after sintering process. In overall, for analysis testing, the microstructure and phase analysis are examined by Scanning electron microscope (SEM) and x-ray diffraction (XRD) analysis.

For mechanical testing, this study carried out two testing towards the glass ceramic produced. Further studied on the mechanical properties of the glass ceramic are

evaluated. In overall, the over view of experimental technique and works is simplified as referred to the flow chart in Figure 3.1.

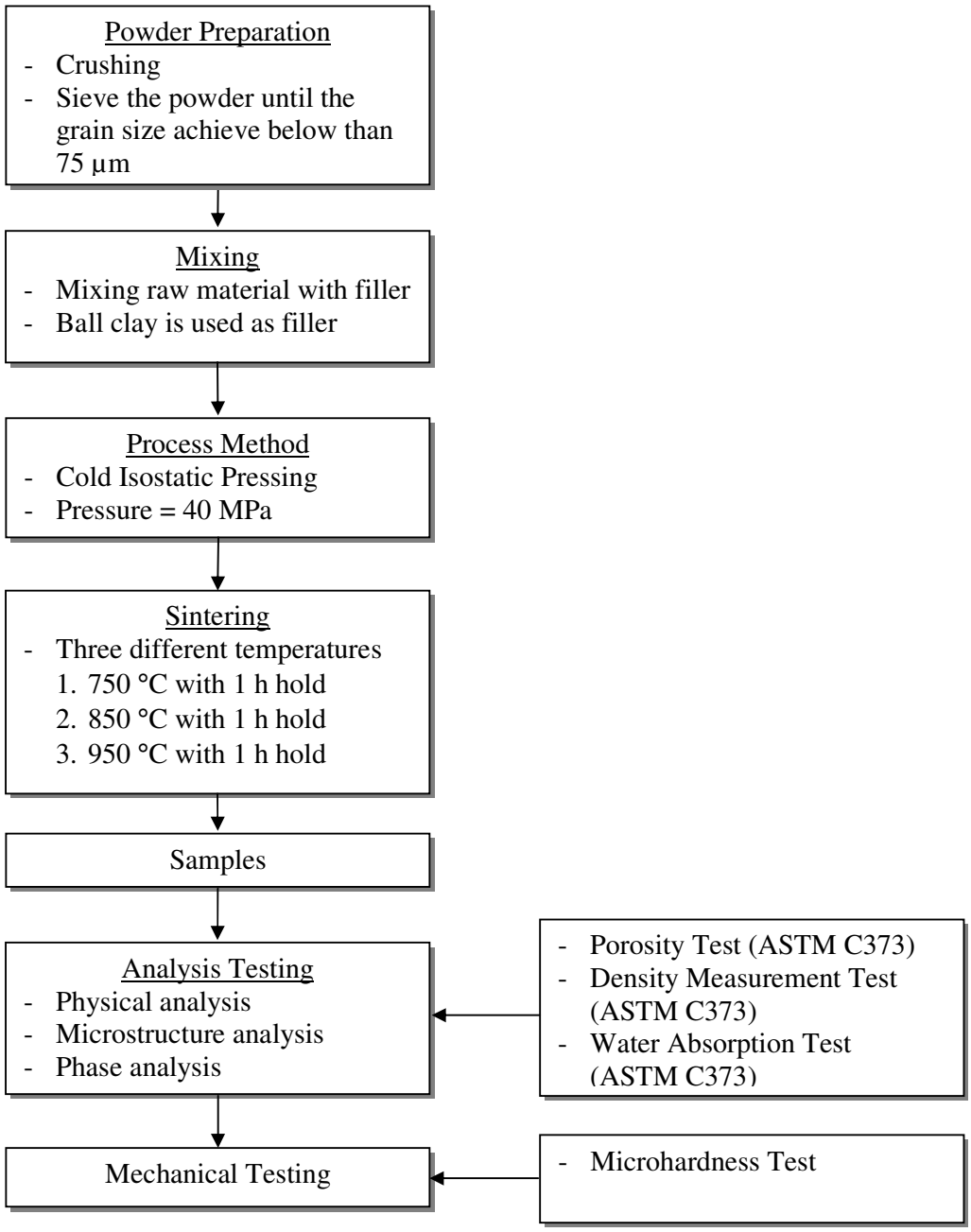


Figure 3.1: Flow chart of methodology

3.2 Materials

The materials employed in this study are recycled soda lime silica glass (SLSG). SLSG will be converted into fine glass particles before mixed with filler. Ball clays are used as filler in this glass ceramic processing.

3.2.1 Soda Lime Silica Glass (SLSG)

Soda lime silica glass (SLSG) obtained from recycled container such as soy bottles, beverages bottles and sauce bottles which is transparent. The SLSG type used was shown in Figure 3.2 and Table 3.1 lists the basic physical properties and relevant ASTM Standard of the SLSG.

Figure 3.2 : Soda Lime Silica Glass (SLSG) containers

Table 3.1: Physical properties and relevant ASTM Standards of Soda Lime Silica Glass (SLSG) (Ray *et al.,* 2000)

Physical properties	Value	Unit	ASTM Standard
Density	2.49	g/cm^3	C373
Porosity	0	%	C373
Hardness	230	kg/mm^2	-
Water absorption			C373

Size of glass particles influences the result of end product. The particles size affects the physical properties of strength, toughness and hardness. Thus, finer glass particles, the properties of end product are much better. In this study, the size of glass particles chosen is < 75 µm. These particles are sieved first using sieve with size of 75 µm.

3.2.2 Ball Clays

Ball clays are an additive that added to provide enough strength after the sintering process to permit handling or other operations prior to densification. The main utility of ball clay is its plasticity and it is mixed with non-plastic or less plastic clays to make them obtain the requisite plasticity. The high plasticity of ball clay is attributed to the fact that it is fine-grained and contains a small amount of montmorillonite. Ball clays are chosen as binder mainly due to its contribution of workability, plasticity and strength to the bodies in drying. Figure 3.3 represent the ball clays filler that are used for this study and Table 3.2 illustrated the ball clays compositions.

Figure 3.3: Ball clays filler

Table 3.2: The variations of chemical composition of ball clays (Worrall W. E., 2006)

Oxide	Range of variation (wt. %)
SiO_2	40 – 60
Al_2O_3	25 - 40
Fe_2O_3	0.25 – 4.0
Na_2O	0 – 0.75
K_2O	0.5 – 4.0

3.3 Samples Preparation

Samples preparation in this study are carried out as show in the experimental flowchart shown in Figure 3.4. It starts with raw material preparation followed by forming, drying and sintering process.

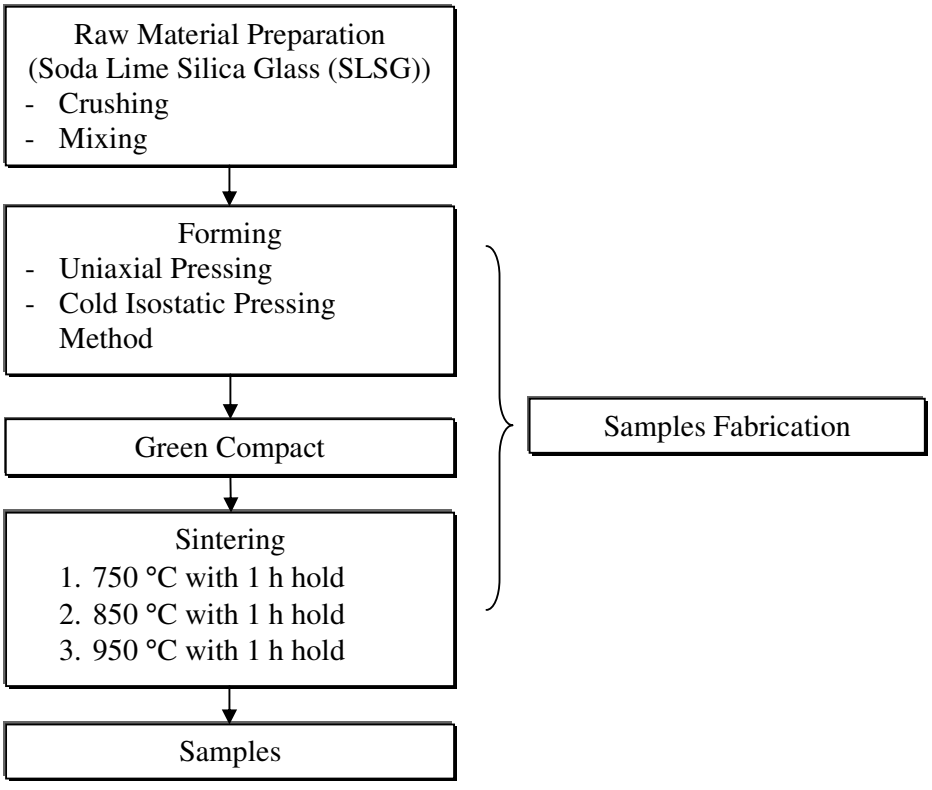


Figure 3.4 : Powder forming technique of Soda Lime Silica Glass (SLSG)

3.3.1 Raw Materials Preparation

3.3.1.1 Crushing

At early stage of raw materials preparation, the raw material which is recycled SLSG were crush manually by using hammer before sieve the SLSG powder < 75 micron by using siever. Same as the ball clay, the powder are sieved to achieve the fineness of < 75 micron. The containers such as bottles are crushed roughly using hammer as depicted in the Figure 3.5.

Figure 3.5: Hammer

3.3.1.2 Mixing of SLSG and ball clay powder

The mixture of raw materials which is recycled SLSG with ball clays filler are mixed into certain ratios. Basically, the amount or ratio of raw material must be higher than filler to ensure that the material produced gives good properties. All the material used for glass ceramic preparations were weighed by using the Top Loading Balances as depicted in Figure 3.6. Ball Clay is mixed with SLSG powder according to ratio during the mixing process. The mixing process were done due to ratio 95 : 5, 90 : 10 and 85 : 15 with the content of SLSG powder are more than ball clay powder. During mixing, SLSG powder and ball clay are mixed according to weight measures based on specific ratio and then added together in a container and shaken for 1 minute to ensure that both powder synonymous. Then, the mixture are weighed to 1 gram of one sample before pressing process started. Weighing process takes about 15 seconds for each sample.

Figure 3.6: Top Loading Balances

3.3.2 Samples Fabrication

3.3.2.1 Forming

The mixed compounded of recycled SLSG with ball clays filler were then compression molded by using Uniaxial Pressing as shown in Figure 3.7 to form the cylindrical shape before do the second compression by using Cold Isostatic Press (CIP) machine model AIP3-12-60CPA as shown in Figure 3.8. The mold size was 10 mm and the pressure is applied to the mold surrounding. End result for this forming process is a green body.

Figure 3.7: Uniaxial Pressing machine

Figure 3.8: Cold Isostatic Press (CIP) Machine AIP3-12-60CPA

Pressing process initiated by enter 1 gram content of mixture powder into the mold and then press with uniaxial pressing machine with pressure of 40 MPa or about 3.5 tonne. This process takes approximately 10 minutes to complete 1 sample of glass ceramic. While pressing, each step is done according to proper procedures to avoid sample broken when released. However, for 100 percent powder SLSG, work emphasis can not be done because the links in the powder are not strong and fragile when removed from the mold. Similarly with the powder which has a ratio of 95: 5, although the ratio is still acceptable but the bonds between the powder of SLSG and

ball clay is not so strong. So, it is not possible if the results produced from the mold are not as beautiful as the sample produced with the ratio of 90: 10 and 85: 15. The sample produced was in pellet shape which is cylindrical shape, the ball clay helps the pellet shaped nicely because the more ratio of ball clay added into the SLSG powder, the pellet shape are more easier to produced. Because there have three different temperatures at the sintering process, in each ratio, 5 samples produce making the total number of samples produced are 45.

For samples that have passed pressing process using uniaxial pressing machine, samples was inserted in the rubber before placed in the CIP machine. Only one sample was added in a rubber. The purpose of sample added in the rubber is to prevent it being contaminated by the liquid when the isostatic pressure was applied to the sample. Pressure used for this process is 40 MPa or 5801 psi. This process takes about 10 seconds to complete pressing of one sample. Basically, after this process the uniformity of the glass ceramic are tougher and not fragile compared to the glass ceramic produced by uniaxial pressing machine.

3.3.3 Sintering Process

The modification of sintering temperature was carried out inclined with the objective of this study. The determination of different sintering temperature is by known the melting point (T_m) and glass transition (T_g) of SLSG. In this study 750 °C, 850 °C and 950 °C are chosen as sintering temperature with 1 h holding time. Table 3.2 simplified the parameters involved in the sintering process.

Table 3.3: Parameters of Sintering Process

Pressure (MPa)	Temperature (°C)	Holding time (h)
40	750	1.0
40	850	1.0
40	950	1.0

Sintering process is done in three different temperatures. For each parameter, a total of 15 samples included in the furnace which 5 sample from each of ratio. While in the furnace, the temperature increase is 2 degree / minute for all three temperatures.

3.4 Analyses

For physical analysis, there are three main analyses which are porosity test, density measurement test and water absorption test. Microstructure analysis is to analyze the microstructure using SEM and the phase analysis is to characterize the crystallographic structure in the sample in the glass ceramic produced by using XRD. 9 samples are provided for each analysis which sample represent for each ratio and temperatures.

3.4.1 Physical analyses

There are three main analyses which are porosity, density measurement and water absorption. 9 sample of glass ceramic produced by according to ASTM C 373. At the beginning of this analysis, all samples are dried in an oven at 150℃ for 15 minutes and then cooled in the dessicator for 15 minutes. Value for dry mass, *D*, obtained by weighted samples using top loading balance to the nearest 0:01 g.

Then, samples are boiled in distilled water for 5 h in immersed condition in the water all the time by using wire to separate the sample from bottom and sides of the beaker as well as each other. After boiled for 5 h, the sample is left soaked in distilled water for 24 h. Value for mass, *S*, glass ceramic samples were weighed after the impregnation process with the mass nearest to 0:01 g. Weighing process performed in a sample loop and tied with wire suspended in the water. Before actually weighing, counterbalance the scale with the wire loop in place and immersed in water to the same depth as is used when the sample are in place.

Next, glass ceramic sample will be wiped with a cotton cloth to remove excess water from the surface and the value for saturated mass, *M*, to the nearest 0:01 g is known. Weighing process must be done quickly to avoid evaporation of water from the

samples. Once completed, the calculation for the amount of apparent porosity, bulk density and water absorption identified with the assumption that 1 cm^3 of water weighs 1g.

3.4.1.1 Porosity

Porosity is main problem that occurred to the ceramic materials. The porosity of glass ceramic produced are tested accordance to ASTM C 373. Other than pores, this testing should able to detected cracks or other voids that might be present in the samples produced. This test carried out three test specimens for each different temperature and ratio of SLSG to ball clay. The percentage apparent porosity are calculated by using the following formula;

$$P\ (\%) = [\ (M - D) / V\ ]\ \times 100 \qquad (3.1)$$

where :

P = percentage of apparent porosity
M = saturated mass
D = dry mass
V = volume

3.4.1.2 Density Measurement

Density measurement test is used to determine the density of glass. The density measurement of glass ceramic produced was known as a bulk density. This test were conducted accordance to ASTM C 373. The bulk density was measure by divided the sample dry mass with exterior volume. The exterior volume determine by saturated mass minus mass after impregnation process. The true density of the samples is identified through this testing. The bulk density, B, of specimens is calculated by divided dry mass, D, with the volume, V as mention in Equation 3.2.

$$B = D / V \qquad (3.2)$$

where :

B = bulk density

3.4.1.3 Water Absorption

This test was carried out inclined with the limitations of samples towards resistance to water absorption. Thus, this study was conducted purposely to determine the water absorption behavior of glass ceramic. This test was performed in accordance to the ASTM C 373 the standard test method for water absorption of ceramic materials. Three specimens also provided for this analysis and the percentage of water absorption will be calculated by using the following formula;

$$A\ (\%) = [\ (M - D)\ /\ D\ ]\ \times 100 \qquad (3.3)$$

where :

A = percentage of water absorption

3.4.2 Microstructure analysis

The microscopy study of glass ceramic produced was measured under the Scanning Electron Microscopy (SEM) EVO 50 (Carl Zeiss SMT, UK) as represent in the Figure 3.9. Analysis was carried out to investigate the microstructural features on the surface of the glass ceramic produced. The surface of glass ceramic sample to be examined is scanned by electron beam and reflected beam of electrode is collected, and then displayed at the same scanning rate on a cathode ray tube which represents the surface features of the glass ceramic produced.

Micrographs will be taken at wide range of magnifications. The resolution that produced from SEM will allow the electron beams to interact with material surface. Thus, the microstructure of the samples will be analyzed. In this analysis, 9 samples for each different temperature and percentages of ball clay will be conducted.

For the preparation, the glass ceramic produced is coated with gold prior to examination. The type of SEM signals used is secondary electron which has interactions between electron beam and atom at or near the surface of the sample. Four magnifications were used 500x, 1000x, 2000x and 3000x at the same area to view the microstructure more clearly.

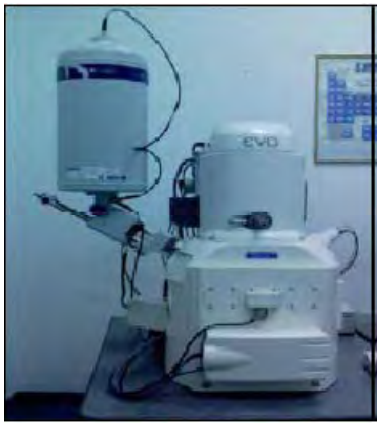


Figure 3.9: Scanning Electron Microscopy (SEM) EVO 50

3.4.3 Phase analysis

X-Ray Diffraction (XRD) is used as equipment for phase identification of a crystalline material and the information on unit cell dimensions are provided. The glass ceramic produced are mounted in the holder of XRD machine as depicted in Figure 3.10 will turn ON. Result for phase study will be analyzed and the analysis result will be displayed in the computer. As referred to SEM analysis, 9 samples for each different temperature and ratio of SLSG to ball clay are performed.

Figure 3.10: X-Ray Diffraction (XRD) Machine

3.5 Mechanical Testing

3.5.1 Microhardness Test

The microhardness test was carried out in this study to identify the hardness of the samples. Basically, this Vickers microhardness testing examines material with a diamond indenter. Hardness of samples affected the behavior and performances of end product. Figure 3.11 represent the Vickers Microhardness HM-200 Series machine that is used in this study. This testing also provided 9 representatives of test samples for each different temperature and ratio of SLSG to ball clay.

Figure 3.11: Microhardness Test Machine

Microhardness test is done to test the ability of glass ceramic produced from penetration on its surface to obtain the hardness value. Samples for microhardness test were mounted in the mixture of epoxy resin and hardener. After that, the samples surface were ground flat by 240 grit abrasive papers. By results obtained from this test, the potential for each sample can be identified through the hardness information, which also influences the mechanical properties of glass ceramic produced. The glass ceramic samples were indent on the sample surface with load 0.5 N.

CHAPTER 4
RESULTS

4.1 Introduction

This chapter covers the observations and results achieved throughout this study. This include observation during sample preparation upon mixing Soda Lime Silica Glass (SLSG) and ball clay, characterization of the glass ceramic produced (microstructure and phase), physical analyses and microhardness test.

4.2 Observation on Sample Produced

During the sample preparation, all the observation is inform clearly starting with powder preparation which include sieving, mixing and weighing process of the mixture powder of SLSG and ball clay. Figure 4.1 shows SLSG particles after the crushing process. Figure 4.2 shows pellets of samples produced after Cold Isostatic Pressing (CIP) the result of powder after pressing process.

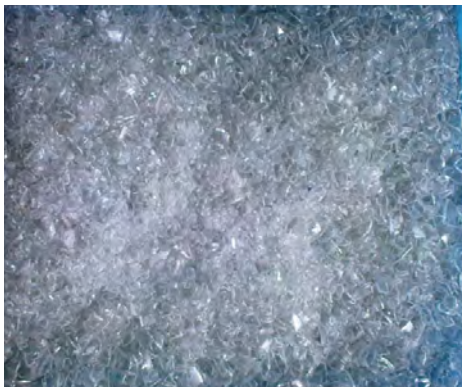


Figure 4.1: Soda Lime Silica Glass (SLSG) particles after crushing process

(a)

(b)

(c)

Figure 4.2: Green pellet of glass ceramic produced at different SLSG to clay weight ratio : (a) 5 wt.% (b) 10 wt.% (c) 15 wt.%

Sample produced from pressing process is in cylindrical shape or pellets form. The surface finish is observed to be affected by the total percentage of ball clay in SLSG powder. The greater percentages of ball clay (5 wt.%, 10 wt.% and 15 wt.%) produced more compact pellet and good surface finish. Figure 4.3 shows a sample produced with a diameter of 10 mm and Table 4.1 shows the result of sample shape for each temperature with different SLSG to ball clay ratio.

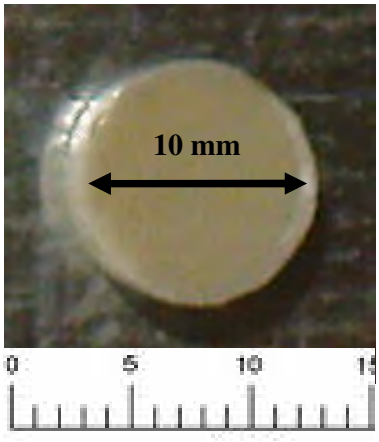


Figure 4.3: Glass ceramic sample with 10 mm diameter

Table 4.1: Glass ceramic samples at different temperature and different SLSG to ball clay weight ratio

Weight ratio SLSG glass to ball clay (wt.%)	**750°C**	**850°C**	**950°C**
95:5			
90:10			
85:15			

Sintering process is done in three different temperatures and different SLSG to ball clay weight ratio. Generally, when the temperature increases, glass ceramic samples are change in terms of color and appearance. The color of brownish samples becomes lighter when the rises of temperature. For the appearance, the glass ceramic samples look glazy and shiny when the temperature increases. For example, at each temperature the colors of samples change from brownish to light brown. This changes of color can seen obviously at 85:15 wt.% of SLSG to ball clay for each temperature. Another observation that can be seen clearly is in term of surface finish for each temperature. At lower temperature 750℃, samples have bad surface finish but at higher temperature give good surface finish. However this trends is not applied to sample produced at 85:15 wt.% ratio of SLSG to ball clay. At this ratio, the glass ceramic samples for each temperature are in good cylindrical shape but at lower temperature there is no glazy and shiny at the surface of samples. This situation can be seen drastically where no glazy surface appear at each ratio at temperature 750℃. The glazing and shining surface happen at the higher temperature.

The effects of ball clay percentage is clearly observed which the changes in terms of shape, color and appearance. The increasing of ball clay percentage gives more good cylindrical shape or pellet, color and surface finish. At 95:5 wt.% ratio of SLSG to ball clay, there is bad cylindrical shape formed for each temperature and this trends also happen at 90:10 wt.% ratio of SLSG to ball clay for temperature 750℃. Also, the samples with ratio 95:5 wt.% ratio of SLSG to ball clay seems like melt at the temperature 950℃ because is so do not form like a pellet. The good cylindrical shape formed obviously at 85:15 wt.% for each temperature which state that the addition of ball clay helps to produce more fine-looking shape for the glass ceramic samples. In terms of color, the color sample becomes more brownish when more ball clay entered which is at ratio 85: 15, wt.% ratio of SLSG to ball clay sample color is darker than the less amount of ball clay percentages. Ratio 95:5 wt.% ratio of SLSG to ball clay give the whiter color although for other two ratio the whiter color change a very light yellow color. Dissimilar with appearance, the surface of the sample ratio 95:5 wt.% ratio of SLSG to ball clay looks glazy, while appearance for the next ratio surface give a little glazy.

Thus at sintering process, when more high temperature is used; it produced the brighter color displays and glazier surface. This proves that the temperature and SLSG to ball clay ratio plays an important role during the sintering process.

4.3 Analyses

Analyses conducted involved physical analysis (porosity, density measurement and water absorption), microstructure analysis and phase analysis.

4.3.1 Physical Analysis

Results of each physical analysis are shown in section 4.3.1.1 (Porosity), section 4.3.1.2 (Bulk Density) and section 4.3.1.3 (Water Absorption).

4.3.1.1 Porosity

Table 4.2 shows the value of porosity at each glass ceramic samples that obtained from the analysis. The porosity of the glass ceramic produced was measured as a percent, in relationship of the volume of the open pores of the samples to its exterior volume.

Table 4.2: The porosity percentage of glass ceramic produced at different temperature and different SLSG to ball clay weight ratio

	Porosity percentage (%)		
Ratio SLSG to Ball Clay Weight Ratio (wt.%)	**750°C**	**850°C**	**950°C**
95:5	1.36	1.68	2.09
90:10	1.10	1.24	1.03
85:15	0.71	0.41	0.40

Figure 4.4 shows the percentage of porosity for glass ceramic samples produced with different SLSG to ball clay weight ratio and sintered at different temperature. From the result obtained the percentage of porosity reduced with the increase of ball clay percentage in the sample. This is observed at all temperatures. The lowest

temperature has low percentage of porosity while the highest temperature has greater percentage of porosity at 95:5 wt% ratio of SLSG to ball clay. The maximum percentage of porosity (2.09 %) and the minimum percentage of porosity (0.40%) occurred at the same temperature 950°C. From the result, the percentage of porosity tends to decrease when the temperature increase. This trend happens at temperature 850°C and 950°C but it is not really applied at temperature 750°C. At that temperature, it has the minimum percentage of porosity occurred at 95:5 wt.% ratio of SLSG to ball clay and maximum percentage of porosity occurred at 85:15 wt.% ratio of SLSG to ball clay.

The percentage of porosity tends to decrease when the ratio of SLSG to ball clay increase. The highest percentage of porosity occurred at 95:5 wt.% ratio of SLSG to ball clay at all temperature but then decrease at 85:15 wt.% ratio of SLSG to ball clay. The total percentage of porosity decreased significantly with 15 wt.% of ball clay.

The optimum parameter that give excellent results for porosity analysis is at 950°C with 85:15 wt.% ratio of SLSG to ball clay.

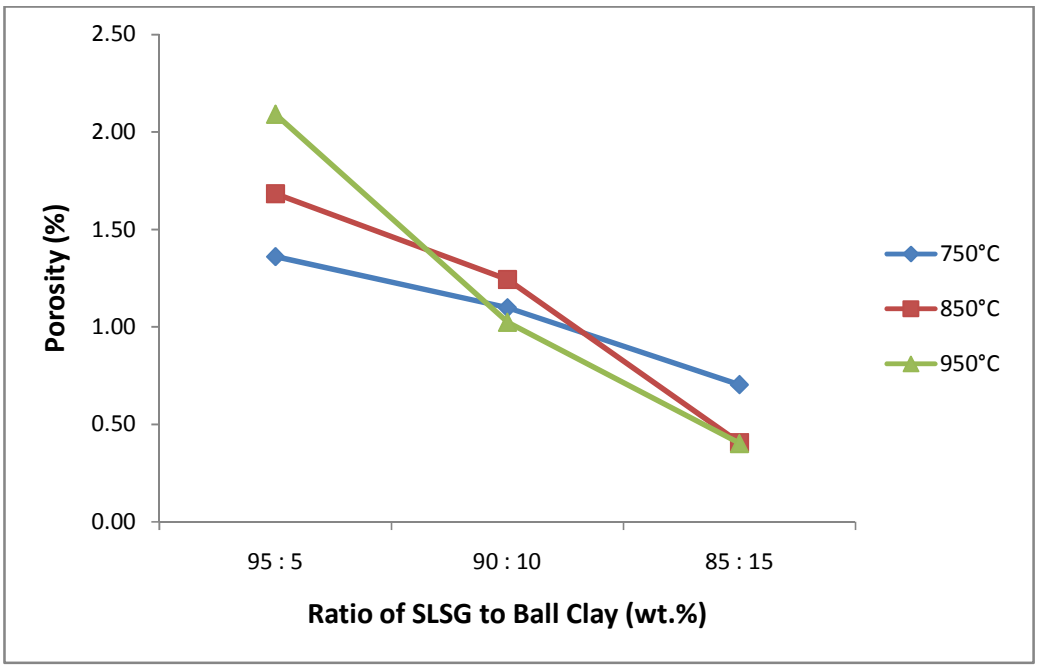


Figure 4.4: Percentage of porosity at different sintering temperature and different SLSG to ball clay weight ratio

4.3.1.2 Bulk Density

Results obtained from density measurement are shown in Table 4.3. Generally, the amount of bulk density tends to increase when the temperature increase. According to Figure 4.5, the trends of all temperature is not consistent because the minimum bulk density (1.71 g/cm^3) happen at temperature 750°C and the maximum bulk density (2.60 g/cm^3) happen at temperature 950°C. This trend is only applicable at 95:5 wt.% and 85:15% wt.% ratio of SLSG to ball clay where the amount of bulk density increasing with the increasing of temperature

With the changes of ball clay, the bulk density tend to decrease when the percentage of ball clay increase. For example, at temperature 950°C the amount of bulk density decrease from 2.60 g/cm^3 at 95:5 wt.% ratio of SLSG to ball clay to 1.99 g/cm^3 at 85:15 wt.% ratio of SLSG to ball clay. This shows that the bulk density is influenced by the sintering temperature and percentages of ball clay, where when the temperature increase, the bulk density will increase and the percentage of ball clay increase, the bulk density is decrease.

Parameter 950°C with 85:15 wt.% ratio of SLSG to ball clay and 850°C with 85:15 wt.% ratio of SLSG to ball clay gives the same result which is 1.99 g/cm^3 and fulfill the general requirement which the sample that have the lowest percentage of porosity and amount of bulk density is still under consideration. This parameter is considered provide the best results for bulk density.

Table 4.3: The bulk density of glass ceramic produced at different sintering temperature and different SLSG to ball clay weight ratio

	Bulk Density (g/cm^3)		
Ratio SLSG to Ball Clay Weight Ratio (wt.%)	**750°C**	**850°C**	**950°C**
95:5 (wt.%)	1.91	1.98	2.60
90:10 (wt.%)	2.33	2.00	2.13
85:15 (wt.%)	1.71	1.99	1.99

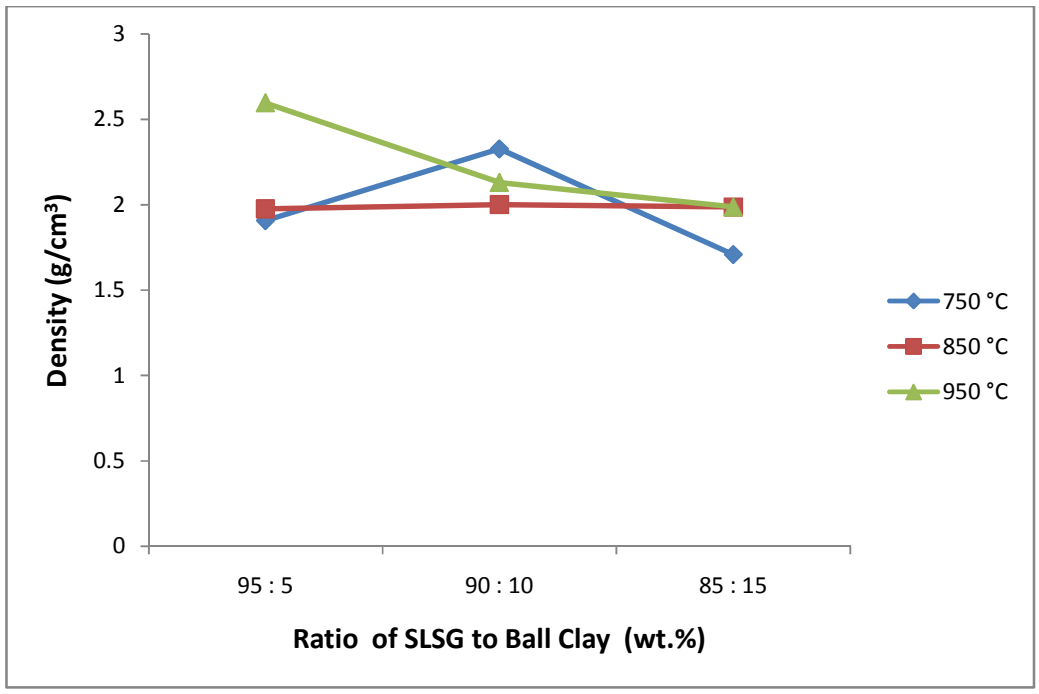


Figure 4.5: Bulk density of glass ceramic produced at different sintering temperature and different SLSG to ball clay weight ratio

4.3.1.3 Water Absorption

Results obtained from water absorption analysis are shown in Table 4.4. Figure 4.6 shows the comparison of percentages of water absorption at each temperature at different ratios. Based from the results, percentages of water absorption decrease when the percentages of ball clay increase. The highest absorption was in ratio 95:5 wt.% ratio of SLSG to ball clay whereas ratio 85:15 wt.% ratio of SLSG to ball clay absorbed the very minimum amount of water at every temperature.

The trend of the graphs shows that at temperature 850°C and 950°C, the percentage of water absorption decrease with an increase of SLSG to ball clay ratio. However, this trend is not applied for temperature 750°C because the percentage of water absorption still at maximum percentage when at the highest percentage of ball clay. The percentage of water absorption is influence by the sintering temperature and

percentage of ball clay. The optimum parameter that give excellent results for water absorption analysis is at 950°C with 85:15 wt.% ratio of SLSG to ball clay.

Table 4.4: The water absorption percentage of glass ceramic produced at different sintering temperature and different SLSG to ball clay weight ratio

	Water Absorption (%)		
Ratio SLSG to Ball Clay Weight Ratio (wt.%)	**750°C**	**850°C**	**950°C**
95:5 (wt.%)	0.71	0.85	0.81
90:10 (wt.%)	0.47	0.62	0.48
85:15 (wt.%)	0.41	0.21	0.20

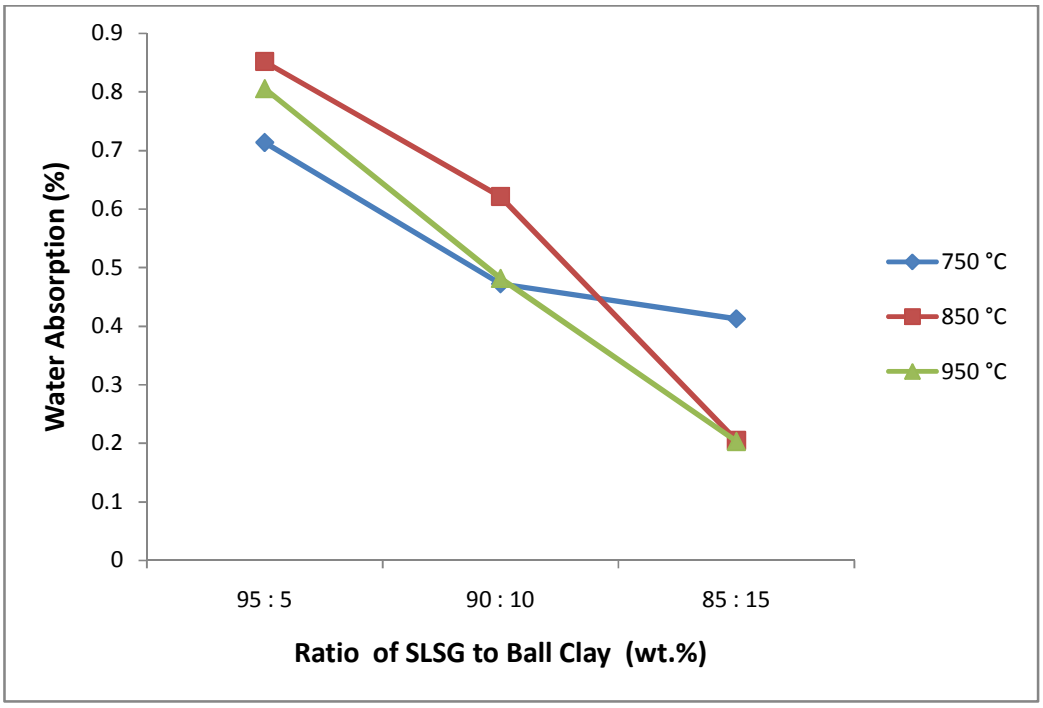


Figure 4.6: Percentages of water absorption towards glass ceramic produced at different sintering temperature and different SLSG to ball clay weight ratio

4.3.2 Microstructure Analysis

Table 4.5–4.7 shows the orientation of glass ceramic produced at each temperature with 95:5, 90:10 and 85:15 wt.% ratio of SLSG to ball clay can be seen clearly and specifically. The SEM micrographs are taken on the surface of glass ceramic produced after the sintering process. At each temperature, micrographs of 95:5 wt.% ratio of SLSG to ball clay gives relatively rough surface compare micrographs for 10 wt.% and 15 wt.% ratio of SLSG to ball clay. Addition of ball clay provides a surface that is more flat and compact. This micrographs show that the temperatures influence the density and strength while the percentages of ball clay influence the uniformity and surface of glass ceramic produced.

Table 4.5: The SEM micrographs for temperature 750°C at different SLSG to ball clay ratio at various magnification

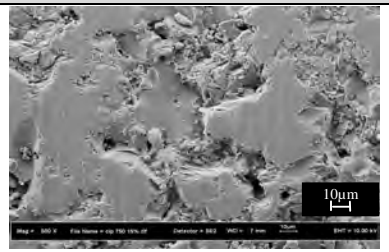
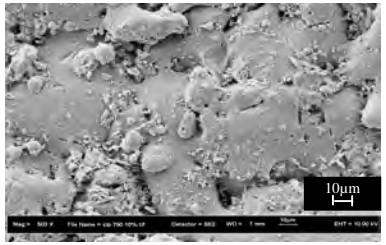
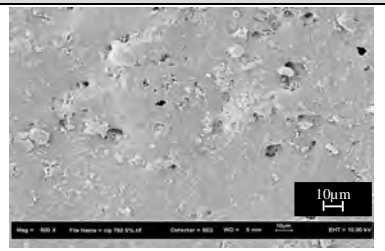
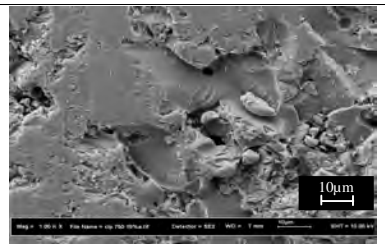
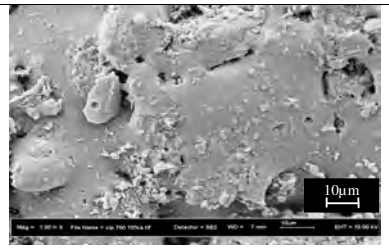
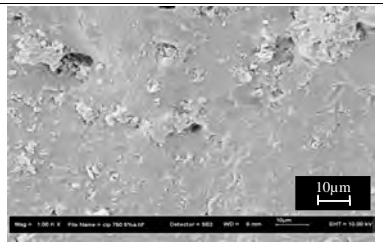
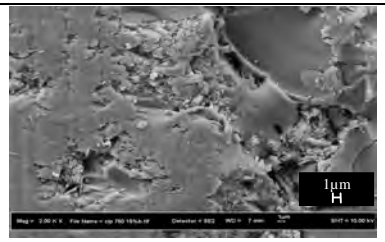
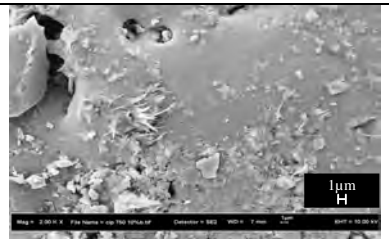
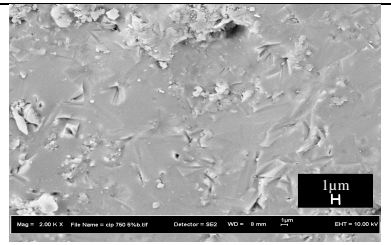
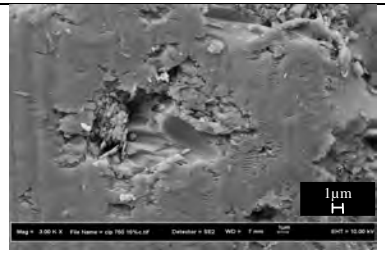
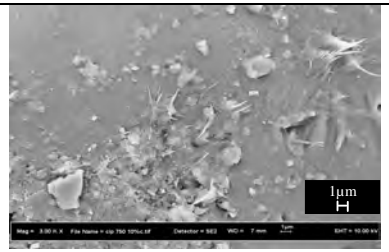
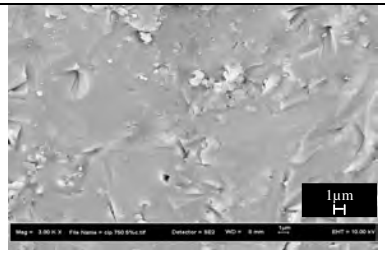
Temperature (°C)	Magnification	95:5 (wt.%)	90:10 (wt.%)	85:15 (wt.%)
750	500x			
	1000x			
	2000x			
	3000x			

Table 4.6: The SEM micrographs for temperature 850°C at different SLSG to ball clay ratio at various magnification

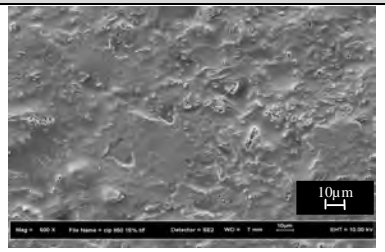
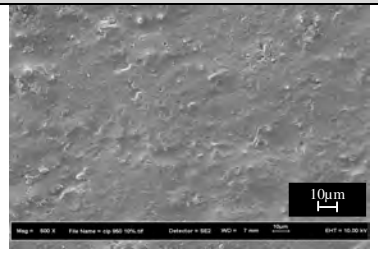
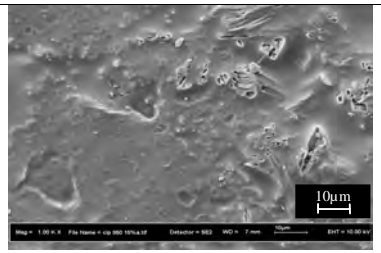
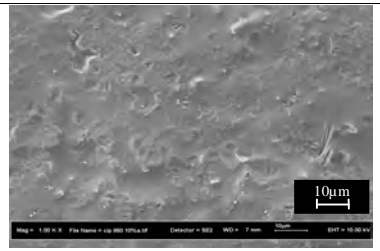
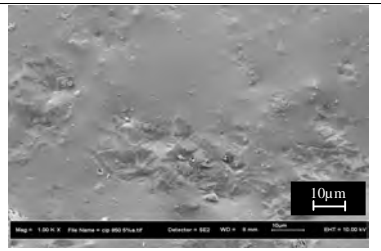
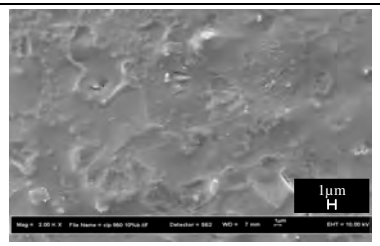
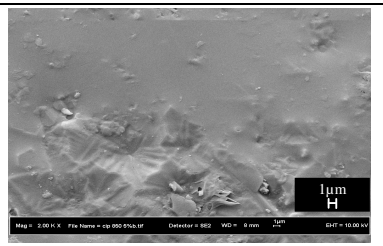
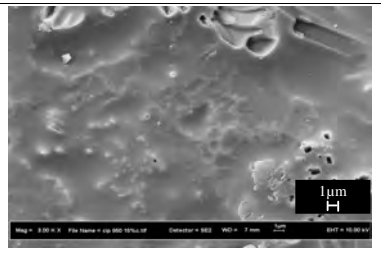
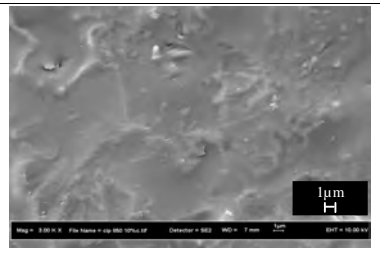
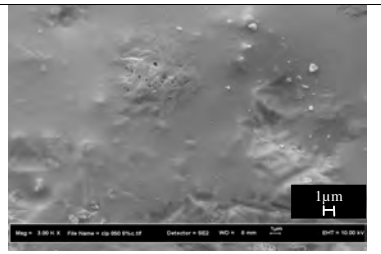
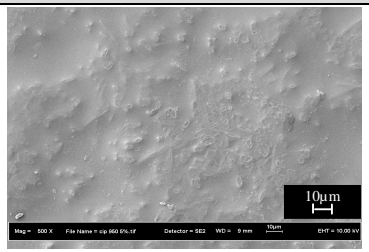
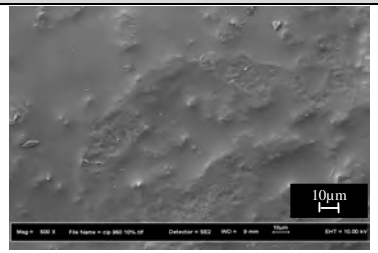
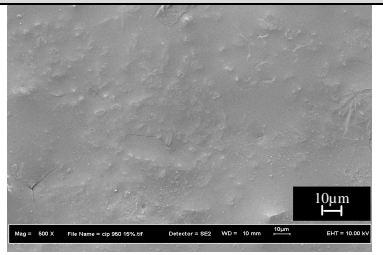
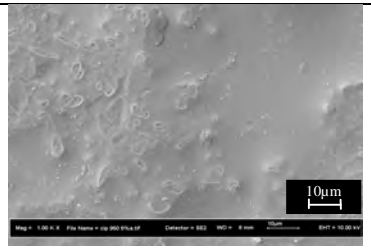
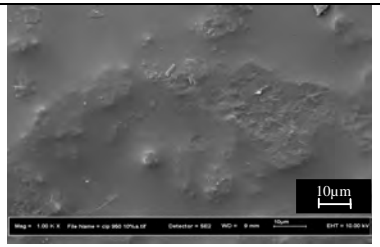
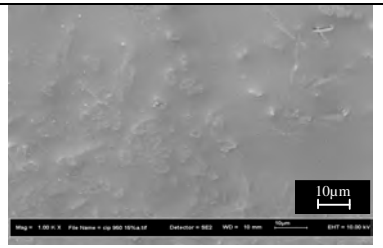
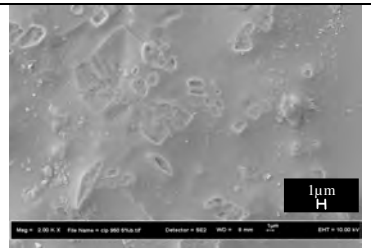
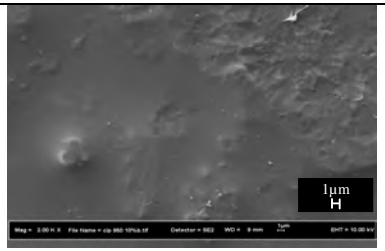
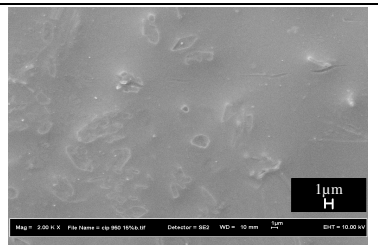
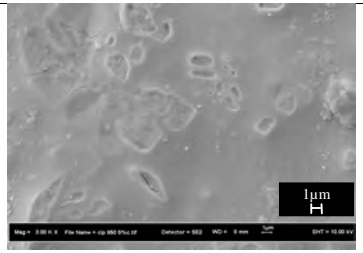
Temperature (°C)	Magnification	95:5 (wt.%)	90:10 (wt.%)	85:15 (wt.%)
850	500x			
	1000x			
	2000x			
	3000x			

Table 4.7: The SEM micrographs for temperature 750°C at different SLSG to ball clay ratio at various magnification

Temperature (°C)	Magnification	95:5 (wt.%)	90:10 (wt.%)	85:15 (wt.%)
950	500x			
	1000x			
	2000x			
	3000x			

4.3.2 Phase Analysis

Phase analysis was established by using XRD to investigate the crystalline phases occurred in the SLSG raw material and ball clay samples. The detector was scanned over a range of 2θ angles from 10° to 90° at a step size of 0.02° and a dwell time of 40.70 s per step. Result obtained for crystallized phases in the glass ceramic samples were identified by comparing the peak positions. Table 4.8 shows the crystal phase identified based on the XRD pattern of the produced samples.

Table 4.8: The crystal phase of XRD pattern of glass ceramic produced from recycled glass

Compound Name	Chemical Formula
Quartz, silicon dioxide	$Si\ O_2$
Calcite	$Ca\ (CO_3)$

In overall, there are only 5 to 6 peaks appear in one samples. By referring to Figure 4.7–4.9 which illustrates the XRD pattern of each sample, it was found that the sample that gives the highest intensity is in a sample with a percentage of 95:5 wt.% ratio of SLSG to ball clay at each temperature. Peak height produced about 1500 cts with position at around 29.24 ° 2Theta.

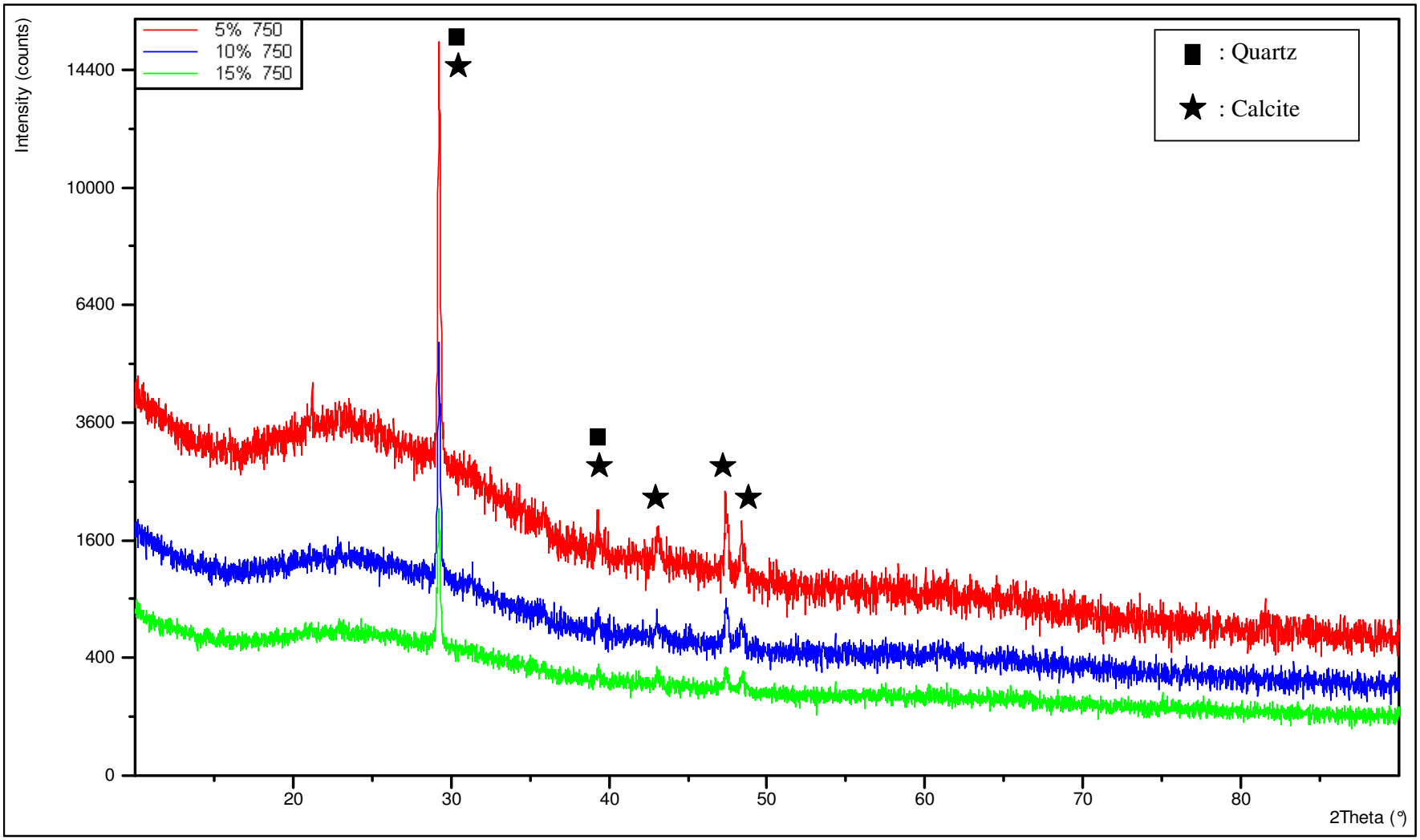


Figure 4.7: XRD patterns of glass ceramic samples at different sintering temperature and different SLSG to ball clay weight ratio at temperature 750°C

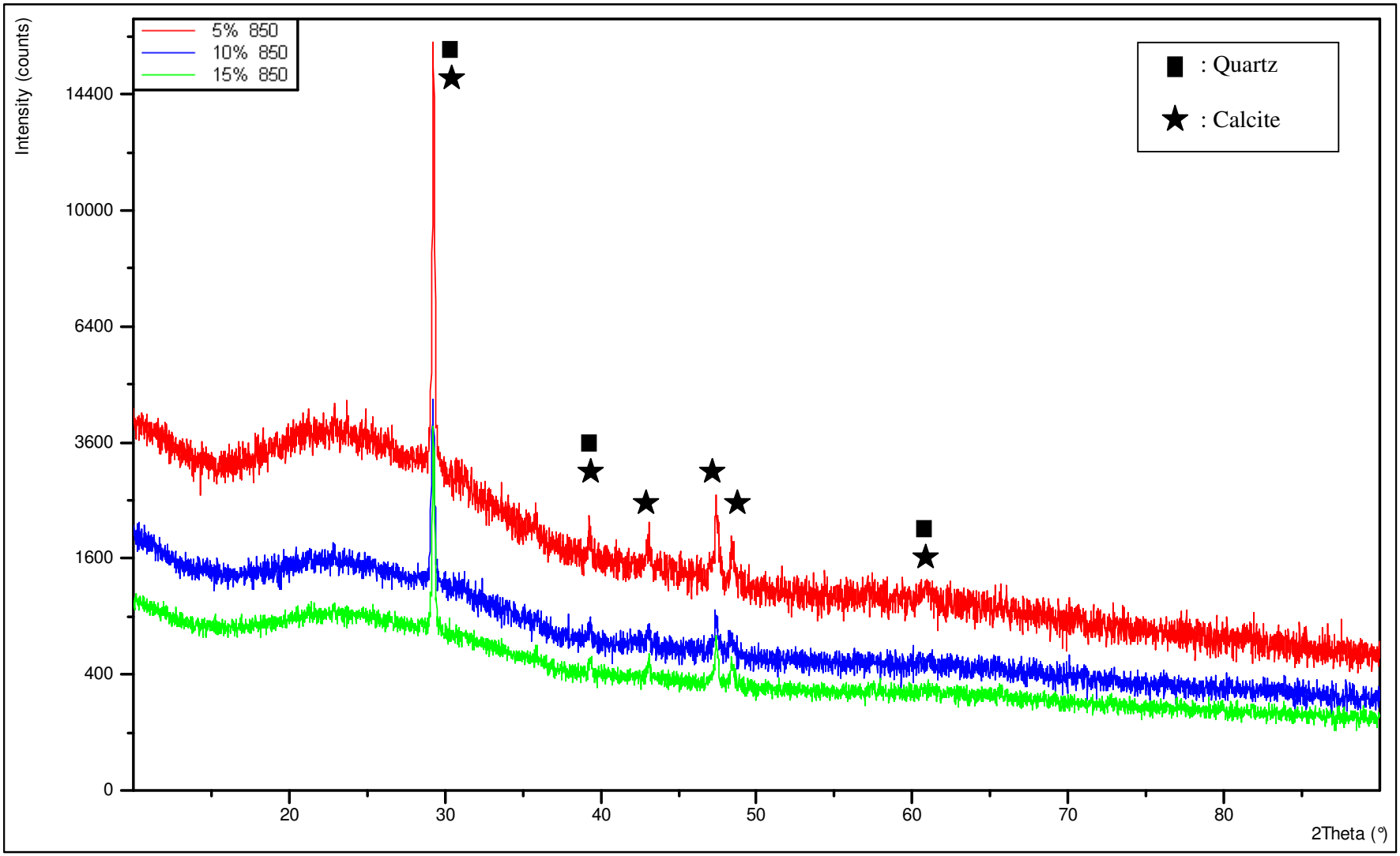


Figure 4.8: XRD patterns of glass ceramic samples at different sintering temperature and different SLSG to ball clay weight ratio at temperature 850°C

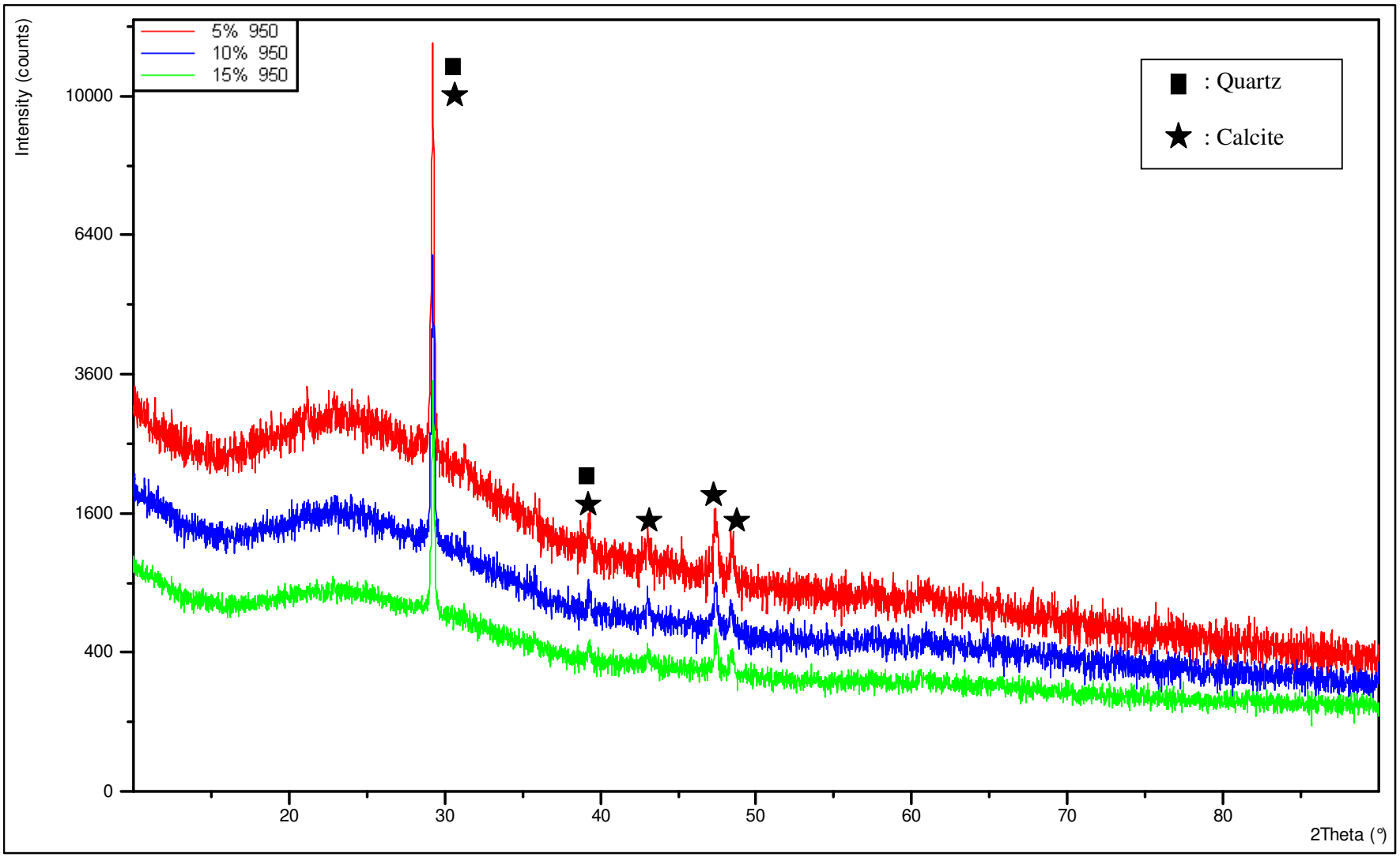


Figure 4.9: XRD patterns of glass ceramic samples at different sintering temperature and different SLSG to ball clay weight ratio at temperature 950°C

4.4 Microhardness

Table 4.9 shows the microhardness of the samples. Based from Figure 4.10, at each temperature, the values of hardness increase when the percentages of ball clay increase. The highest hardness occurs at temperature 850°C and temperature 750°C have the lowest amount of hardness.

Based from the trend obtained from results, it shows that all temperature gives high value of hardness at 85:15 wt.% ratio of SLSG to ball clay. The trend is applicable for all temperature. For example temperature 850°C gives the maximum value for each ratio. Hence, it can be conclude that the increased of percentage of ball clay will increased the hardness of glass ceramic produced.

After analyzed the result of microhardness, parameter 850°C with 85:15 wt.% ratio of SLSG to ball clay provide the maximum value of microhardness and gives the conclusion that this parameter is the optimum parameter that suitable for glass ceramic produced from recycled glass. This chosen is after considering the results of physical and microstructure analysis.

Table 4.9: Microhardness Properties of Glass Ceramic Produced from Recycled Glass at different sintering temperature and different SLSG to ball clay weight ratio

	Microhardness (Hv)		
Ratio SLSG to Ball Clay Weight Ratio (wt.%)	**750°C**	**850°C**	**950°C**
95:5 (wt.%)	449	563	414
90:10 (wt.%)	469	638	462
85:15 (wt.%)	471	658	563

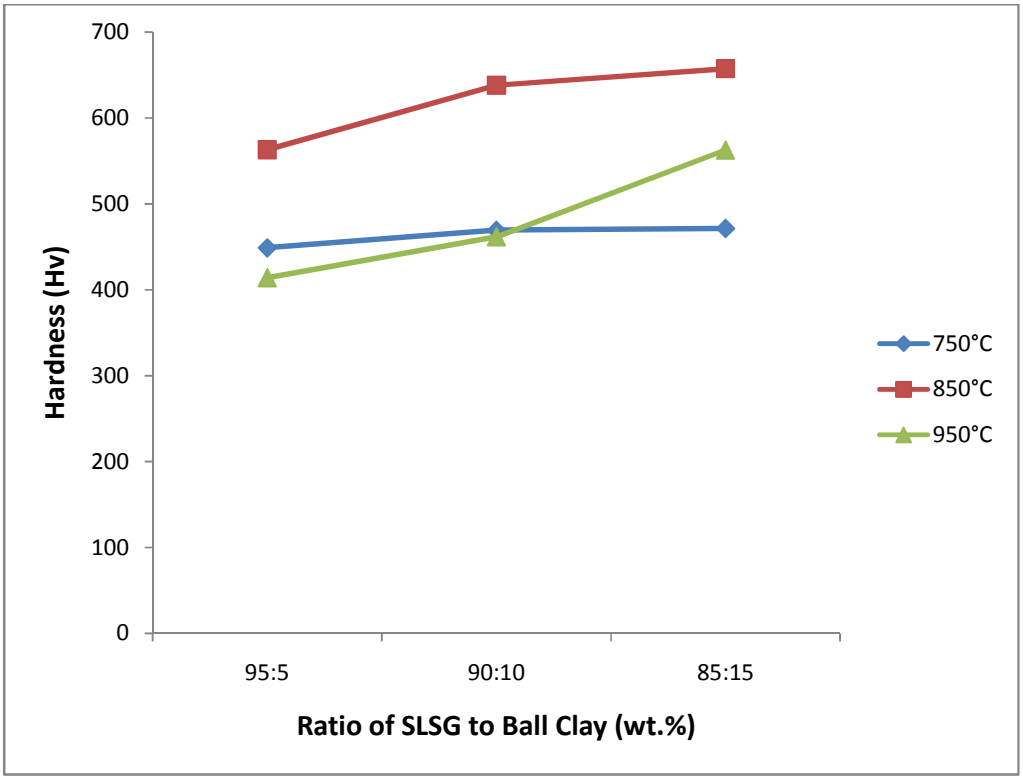


Figure 4.10: Value of microhardness towards glass ceramic produced at different sintering temperature and different SLSG to ball clay weight ratio

CHAPTER 5
DISCUSSION

5.1 Introduction

This chapter discussed the observations and results from all the analyses and mechanical testing done in this study. The discussion consists of the observations during the sample preparations, microstructure analysis and phase analysis towards glass ceramic produced, physical analysis about the physical durability of glass ceramic produced and mechanical testing about mechanical properties of glass ceramic produced.

5.2 Observation on Sample Preparation

Sample preparation is the important process in order to produced glass ceramic samples from recycled glass. The processes involve crushing the SLSG bottles, sieving the powder, mixing the powder, uniaxial and CIP pressing and ends out with sintering process. The samples is pressed into cylindrical shape but for samples produced with 95:5 wt.% ratio of SLSG to ball clay, the surface finish is not good, thus the samples are not in a cylindrical shape. This is due to several factors such as the sintering temperature and time and the percentages of ball clay. At sintering process, the chemical composition of vitreous phase changes continuously with temperature. During sintering, SLSG accelerates the densification process with some positive and negative effects (Matteucci *et al.,* 2002). Addition of ball clay increased the fluidity of glass ceramic produced and excesses of ball clay resulted in the formation of crack in glass ceramic produced. Figure 5.1-5.3 represents the image of glass ceramic sample at each temperature with different ratio. The differences in

terms of shape and the samples occurred due to the different sintering temperature and SLSG to ball clay weight ratio.

5.3 Analyses

In this study, the result from analyses were discussed and compared with the information that gained from literature review.

5.3.1 Physical Properties

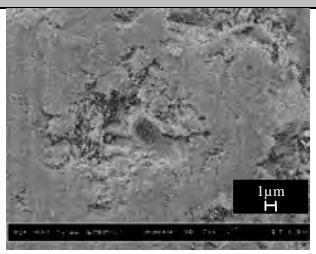
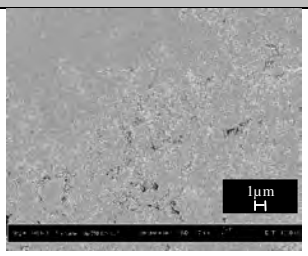
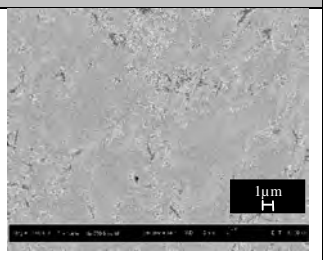
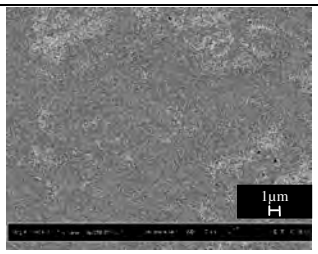
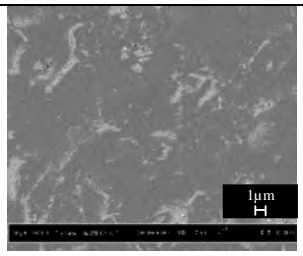
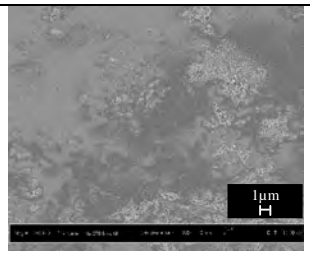
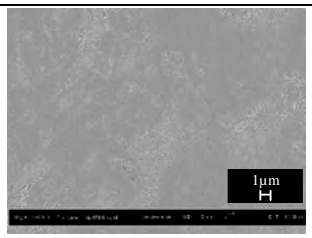
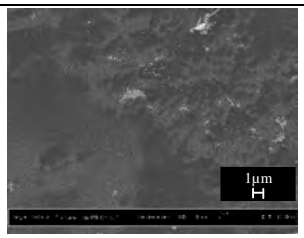
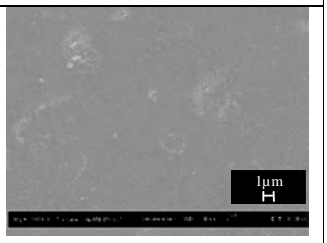
The percentage of porosity tends to decrease when the temperature and percentages of ball clay increase. Bulk density in this study gives the trends that the amount of bulk density increases when the increasing of temperatures happens but the amount of bulk density decrease when the additions of ball clay increase. While for water absorption, the results decrease when temperature and percentages of ball clay increase. The main factors that regulating the physical properties are crystalline phase, crystallization degree, size of the crystallites and homogeneity of crystal size. Fine grained glass ceramic powder also can give better physical properties (Erol *et al.,* 2009).

As reported in physical analysis result, open and closed porosity was observe in glass ceramic sample at temperature 950°C, the samples have the highest porosity value at 95:5 wt.% ratio of SLSG to ball clay and the lowest porosity value at 15 wt.% ratio of SLSG to ball clay in all samples. The density at this temperature for 5 wt.% ratio of SLSG to ball clay also has highest value which is 2.60 g/cm^3 and the lowest value of density happen at temperature 750°C for 15 wt.% ball clay which is 1.71 g/cm^3. Both porosity and water absorption values correlated each other well and decreased with the increase in crystallization degree in all sintered glass ceramic samples (Erol *et al.,* 2009). This can be summarize that the sintered glass ceramic samples have more crystalline sites which decreasing the percentage of porosity.

5.3.2 Microstructure

Table 5.1 shows the SEM micrographs at each temperature and ratio. The micrographs clearly shows that at temperature 750°C, the glass ceramic surface are not flat and smooth compared to the micrographs at temperature 950°C which the surface are more smooth where the occurrence of nucleation and showed crystallization process take place.

Table 5.1: The SEM micrographs at each temperature and ratio at 3000x of magnification

Temperature (°C)	**95:5 (wt.%)**	**90:10 (wt.%)**	**85:15 (wt.%)**
750			
850			
950			

Increased temperature also plays an important function because with high temperature, a high density of well-crystallized whisker-type crystal is generally aggregated in the matrix which are about 5 – 20 µm (Park *et al.,* 2007). Also, the glass composition, sintering time and temperature and addition of filler are important

parameters in the controlling of crystallization behavior of sintered glass ceramic (Erol *et al.,* 2009).

The addition of clay caused a microstructural change (Bernado E., 2005). The glass ceramic samples sintered significantly observed was according to which the ratio of ball clay used. The micrographs of sample with 95:5 wt.% ratio of SLSG to ball clay shows the crystallization process has begun with small cracks and closed porosity formed in the surface. At 15 wt.% ratio of SLSG to ball clay at the same temperature, there are more whisker-type crystal form occurs with more obvious presence of crack and porosity. This shows that increasing percentages ball clay in SLSG powder gives more brittle material. Figure 5.1 – 5.2 shows the micrographs of glass ceramic produced at 950°C with different percentages of ball clay.

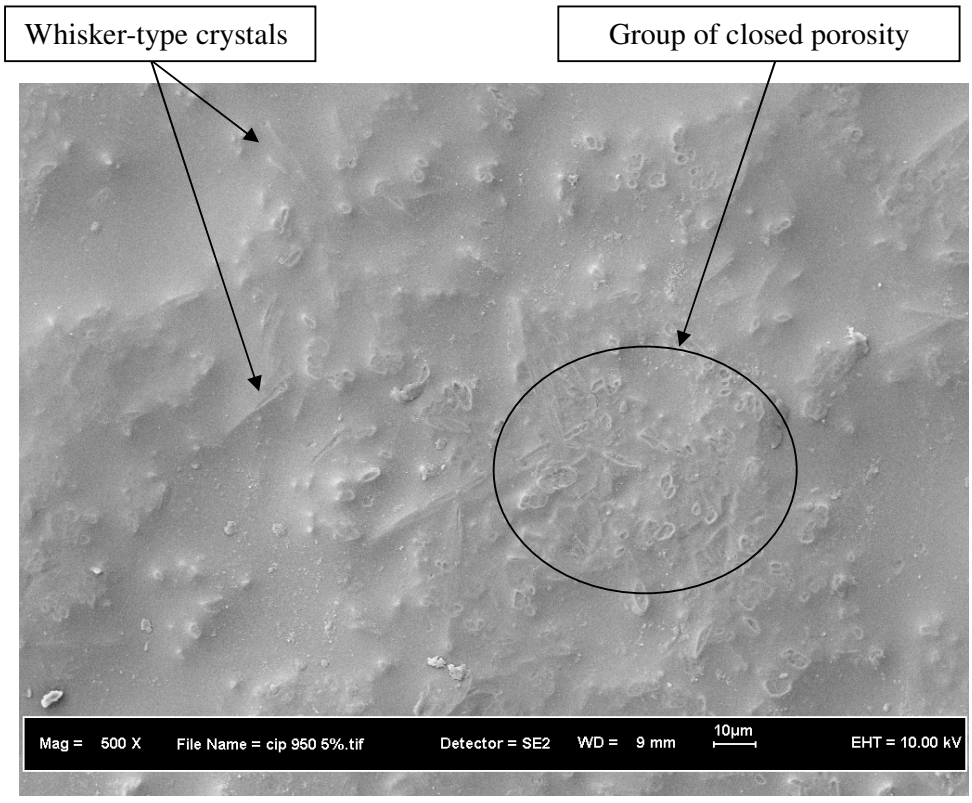


Figure 5.1: The SEM micrographs at temperature 950°C of glass ceramic samples with 5 wt.% of ball clay addition at the 500x of magnification

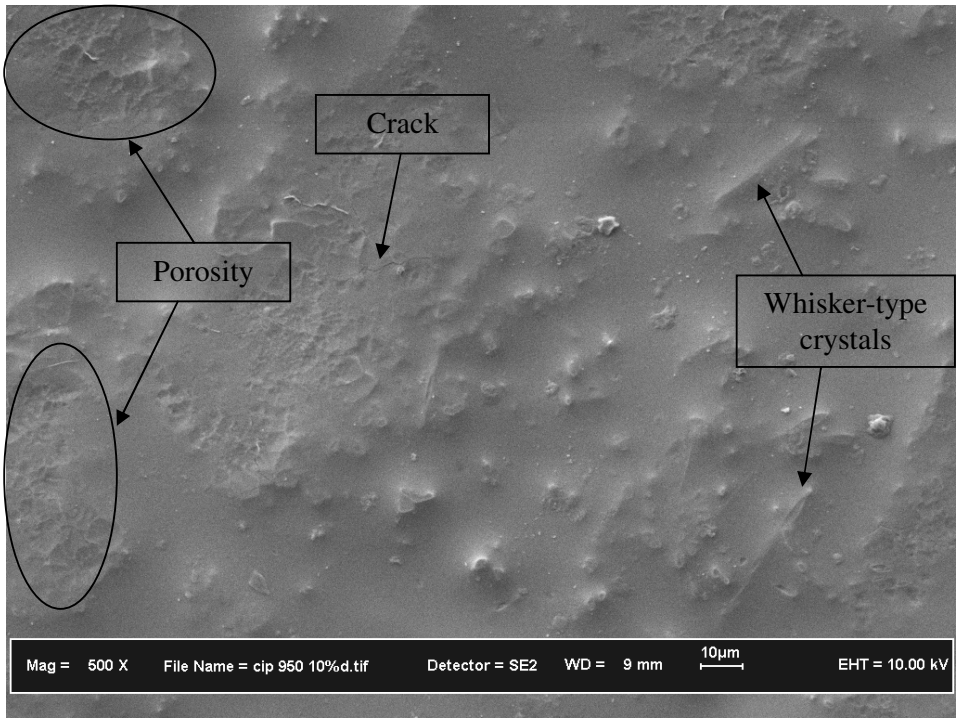


Figure 5.2: The SEM micrographs at temperature 950°C of glass ceramic samples with 10 wt.% of ball clay addition at the 500x of magnification

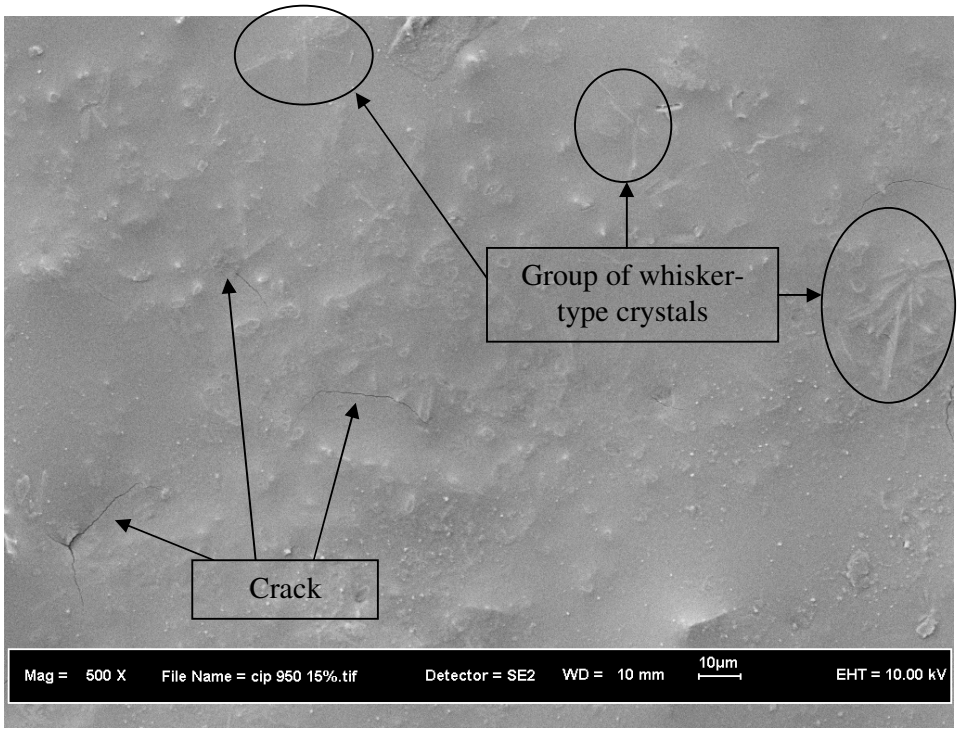


Figure 5.3: The SEM micrographs at temperature 950°C of glass ceramic samples with 15 wt.% of ball clay addition at the 500x of magnification

The presences of open and closed porosity become smaller while the propagation of crack becomes larger when the addition of ball clay increased. This can be proved significantly at 750°C, where there is a large porosity in each ratio. Also, there have an effects of porosity at 15 wt.% ratio of SLSG to ball clay at each temperature. As shown in result, the micrographs at this ratio have good appearance and the presences of porosity are decrease. This can be seen clearly from the result of porosity analysis test which shows that when the addition of ball clay increases, the percentage of porosity decreases.

Other than the addition of ball clay, the cause of this condition is also related to temperature and time for sintering process. Glass phase would be vitrified when sintering temperature increased and glass particles were eventually fused and bonded with glass ceramic bodies, reducing the total porosity and hence increasing bulk density of the glass ceramic samples (Vorrada *et al.,* 2009).

The SEM micrographs at each temperature showed in Figure 5.4 – 5.6 about the open and closed porosity becomes smaller when the temperature increased.

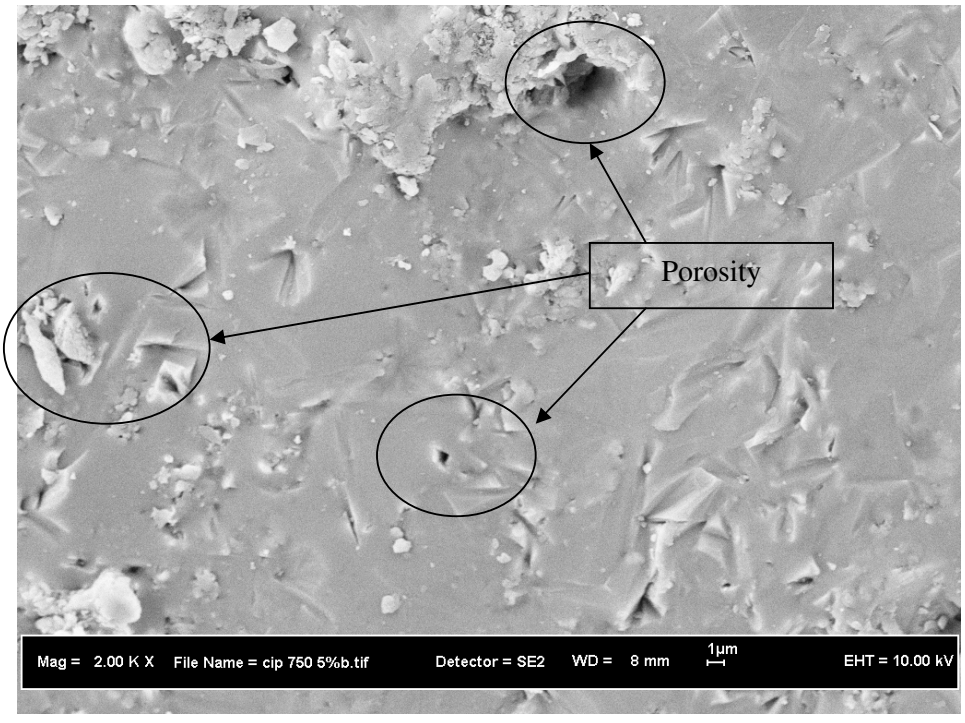


Figure 5.4: The SEM micrographs at temperature 750°C with 13 h sintering time of glass ceramic samples with 15 wt.% of ball clay addition at the 2000x of magnification

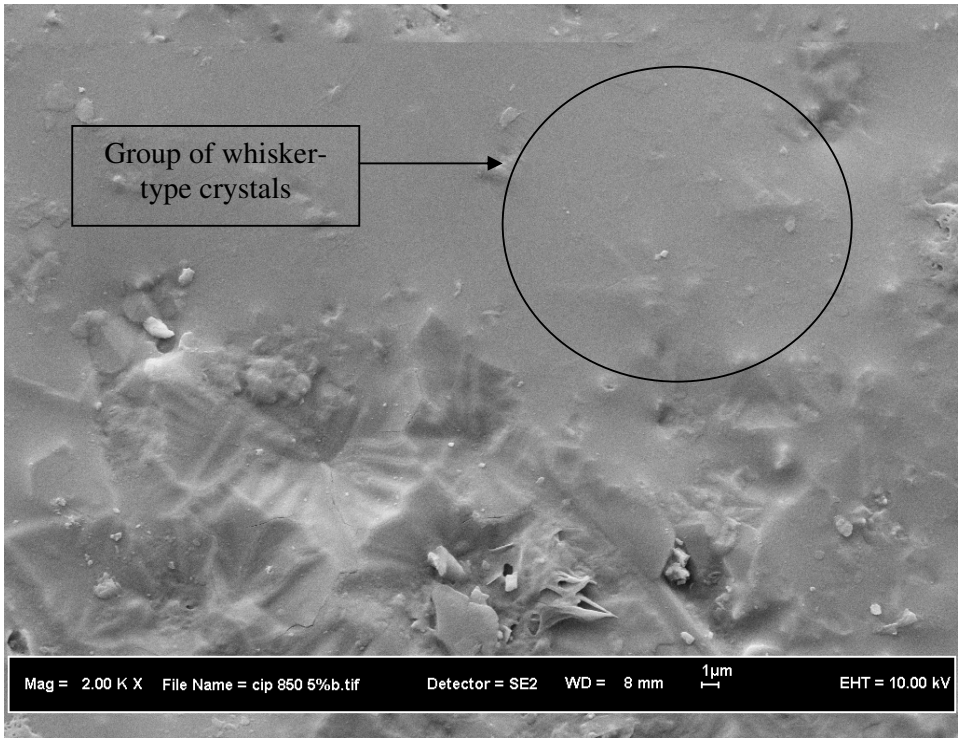


Figure 5.5: The SEM micrographs at temperature 850°C with 15 h sintering time of glass ceramic samples with 15 wt.% of ball clay addition at the 2000x of magnification

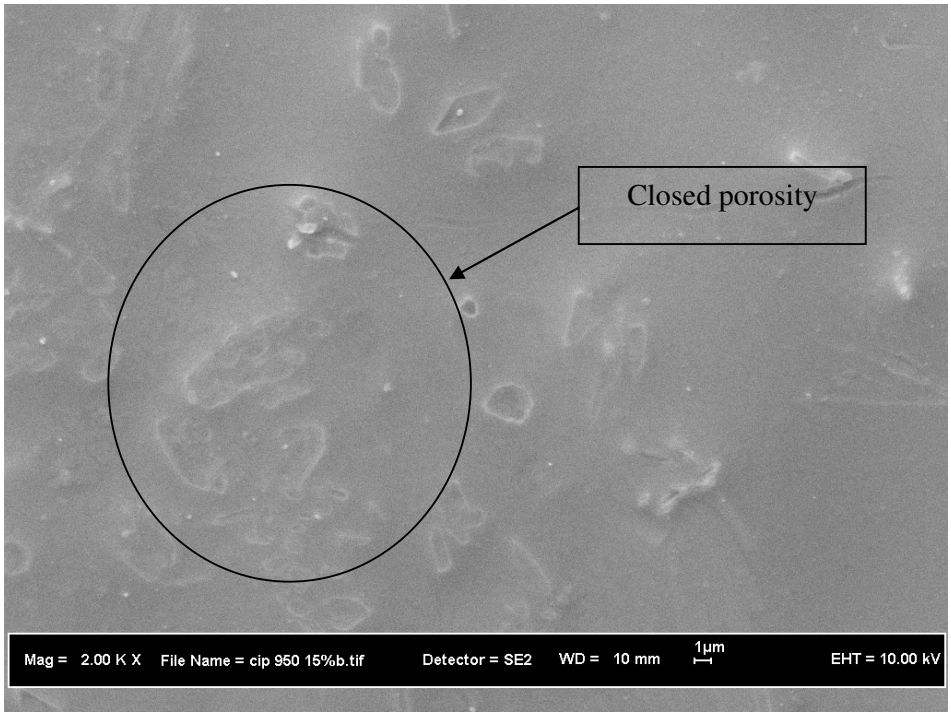


Figure 5.6: The SEM micrographs at temperature 950°C with 17 h sintering time of glass ceramic samples with 15 wt.% of ball clay addition at the 2000x of magnification

5.3.2 Phase

According to the result of XRD analysis, for all materials there are two similar crystalline phases which is quartz (SiO_2) and calcite ($CaCO_3$) have been detected. Quartz crystals are well distributed in the glassy matrix (Rozenstrauha *et al.,* 2006). At surface temperatures and pressures, quartz is the most stable form of silicon dioxide. For calcite crystal, it may occur as fibrous, granular, lamellar, or compact. The crystal for calcite is quite similar with the crystal which presence in this study.

As clearly shown in Figure 41 – 4.2, the peaks at $2\theta = 29°$ and 39° correspond to quartz + calcite while the peaks at $2\theta = 43°$, 47° and 48° correspond to calcite. The entire peak tends to decrease with an increase of sintering temperature and percentages of ball clay.

For the glass ceramic as structural materials it was highly required that Wollastonite and/or Anorhite crystal is precipitated effectively in glasses. However, other crystals were precipitated is a calcite. The reasons for this phenomena is because the addition of ball clay to the SLSG powder is not enough or the mixture of SLSG and ball clay powder must be added with nucleation agent such as iron sulfide (FeS) and anhydrous sodium sulfate (Na_2SO_4) (Tanaka *et al.,* 2005).

The reasons about the absence of Wollastonite and/or Anorhite in glass ceramic produced are related with the preparation during the XRD analysis. The samples used are not in powdered samples but it solid. Therefore, X-rays not travel through many layers of atoms for glass ceramic samples. If the powdered samples are used, the x-rays easily travel into the samples and the required crystal phase will be obtained. To support this statement, the schematic of XRD technique toward powdered samples is illustrates in Figure 5.10. The using of solid samples comes out with the main problem which is undetected of required crystal phase. Thus in order to identified the suitable crystal phase, powdered samples should be used to identify the crystalline phase clearly.

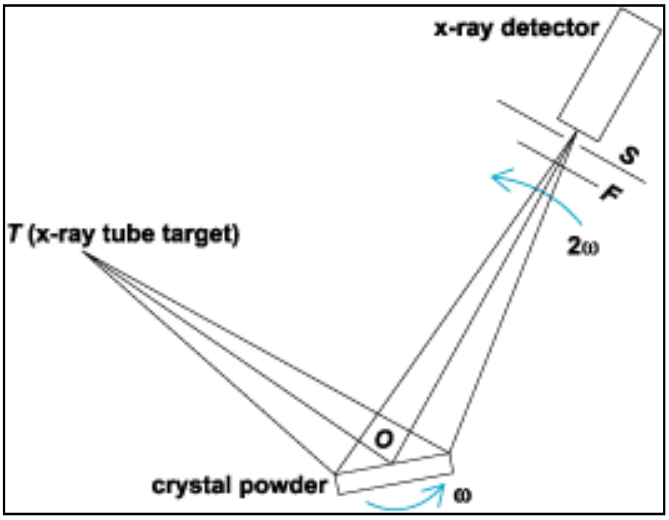


Figure 5.7: The schematic representation of XRD technique towards powdered samples. (Source: http://www.answers.com/topic/x-ray-diffraction-2 - online on 13 April 2010)

5.4 Mechanical Properties

The hardness value increases with the temperature from 750°C to 950°C. As the whisker-type crystal growth at the temperature 850°C and at temperature 950°C the samples becomes brittle and thus lower the microhardness values. As shown in that graph, glass ceramic sample sintered at temperature 850°C with 15 wt.% of ball clay has the maximum value of 658 Hv. The sample that achieve the minimum microhardness value at temperature 950°C with 5 wt.% of ball clay which is 414 Hv. Figure 5.8 illustrates the relationship between microstructure and microhardness of glass ceramic samples. This example is at 850°C because at this temperature shows the maximum value for each weight ratio which is 95:5 wt.%, 10:90 wt.% and 85:5 wt.% ratio of SLSG to ball clay. It is clearly shown that at lower percentage of ball clay, the value of microhardness also have lowest value while at the higher percentage of ball clay, the value of microhardness are at the maximum value. For the lowest value of microhardness, the micrographs obviously shows that there have a lot of open porosity while at the higher value of microhardness there have a very small open porosity occurred. The samples that have the lowest presences of porosity give the higher value of microhardness.

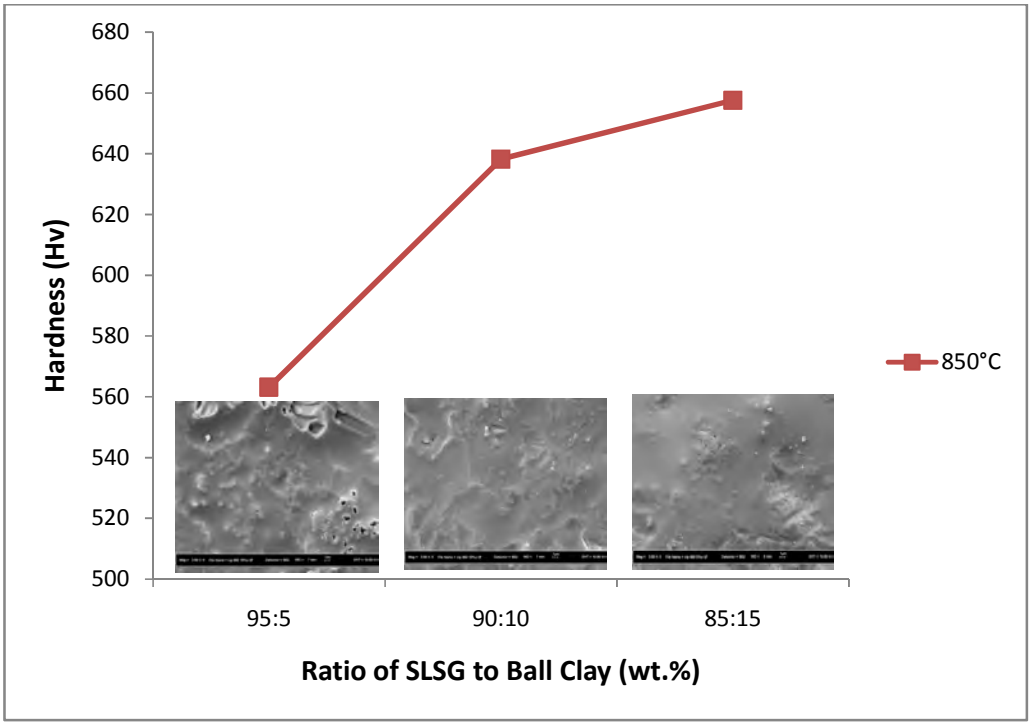


Figure 5.8: Value of microhardness towards glass ceramic produced at different sintering temperature and different weight ratio

In this study, the development of whisker-type crystal influence to the mechanical properties of glass ceramic produced. Other than that, the crystal phase also influence to the microhardness values which the presence of Wollastonite and/or Anorhite structure is needed to upgrade the strength of the samples produced.

CHAPTER 6
CONCLUSION AND RECOMMENDATION

6.1 Conclusion

At the end of this study, the following discussion can be drawn:

- Soda Lime Silica Glass (SLSG) with the addition of ball clay as a filler at a various weight ratio successfully produced a new material of glass ceramic produced from recycled glass. Preparation of glass ceramic by using Cold Isostatic Pressing (CIP) method is the suitable method in order to produce more compact and uniform glass ceramic materials.

- The glass ceramic produced from the sintering process provide a various changes in term of color, shape and appearance. The best result happen at 850°C and 950°C with 85:15 wt.% ratio of SLSG to ball clay because the cylindrical shape are compact and flat. This result is different at 750°C with 95:5 wt.% ratio of SLSG to ball clay that gives the worst result in term of color and appearance.

- The effects of sintering temperature and weight ratio of SLSG to ball clay produced a different physical, microstructure, phase and mechanical properties. The optimum parameter that have the excellent results in this study where at 850°C with 85:15 wt.% ratio of SLSG to ball clay.

- Generally, the physical properties which include the porosity and water absorption had increased with the increasing of temperature and SLSG to ball clay weight ratio. The bulk density had increased with the increasing of

temperature but had decreased with the increasing of SLSG to ball clay weight ratio.

- The observations on microstructure gives a lot of information about surface of glass ceramic produced to identify the existence of a positive effect in terms of crystal growth and the negative effects terms of open and closed porosity and cracks.

- The investigation on crystalline phases that occurred in glass ceramic samples had not successful because there is no existence of Wolastonite and/or Anorhite crystal that suitable for structural applications. However, quartz and calcite crystal is a proper crystal is in the glass ceramic produced.

- Through the study, the trends microhardness for all temperature had increased with the increasing of temperature and SLSG to ball clay weight ratio. The microhardness value is related with the microstructure that presences in glass ceramic produced.

- Sintering temperature plays an important role during this study because the glass ceramic produced give various results of physical and mechanical properties. The appropriate temperature for this study is at 850°C because at this temperature had the best result of physical and mechanical properties.

- The addition of ball clay provides a very uniform and good surface finish when the amount of ball clay had increased. 95:5 wt.% ratio of SLSG to ball clay produced a very bad surface finish while at 85:15 wt.% ratio of SLSG to ball clay produced a very good surface finish.

- Overall, the sintering temperature and addition of ball clay provide different effects on each of the samples, but most result, in the event of increasing temperatures, the values such as the porosity, density measurement and water absorption will decrease.

6.2 Recommendation

In order to further increase the development of glass ceramic produced from recycled glass study, the recommendation and suggestion for future works and improvement are listed as follows:

- The optimum parameter is happen at 850°C with 85:15 wt.% ratio of SLSG to ball clay, therefore further research should be investigated with the range 10 wt.% to 15 wt.% ratio of SLSG to ball clay. In terms of temperature, the research should be investigated with temperature 850°C.

- The preparation before microhardness test should be done according to the right procedure to ensure the surface of glass ceramic is smooth to get the best indentation of Vickers microhardness.

- The SEM micrograph should be done in back-scattered mode to clearly observe the micrograph produce from recycled glass.

- The XRD samples must be in powder to easily identify the crystalline phases that presences in the glass ceramic produced.

- Further study should be characterized the mixture of SLSG and ball clay because the characterization is influence the properties of glass ceramic produced.

- The comparison of results between uniaxial pressing method and CIP method should be further investigate in order to identify the best method to produce glass ceramic produced from recycled glass.

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APPENDIX A

GANTT CHART FOR PSM 1

PSM 1 Duration / activities			W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15	W16	W17	W18	W19	W20	W21
PSM Briefing		Sch																					
		Act																					
INFORMATION SEARCHING	i) Abstract / Background	Sch																					
		Act																					
	ii) Problem Statement	Sch																					
		Act																					
	iii) Objective	Sch																					
		Act																					
	iv) Scope	Sch																					
		Act																					
	v) Literature Review	Sch																					
		Act																					
METHODOLOGY	i) Raw material, equipment method	Sch																					
		Act																					
	ii) Characterization, mechanical testing	Sch																					
		Act																					
REPORT WRITING	i) Draft 1	Sch																					
		Act																					
	ii) Draft correction	Sch																					
		Act																					
	iii) Final submition	Sch																					
		Act																					
PRESENTATION	i) Slide preparation	Sch																					
		Act																					
	ii) Presentation	Sch																					
		Act																					

APPENDIX B

GANTT CHART FOR PSM 2

PSM 2 Duration / activities			W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15	W16	W17	W18	W19	W20
PSM Briefing		Sch																				
		Act																				
Powder Preparation	i) Crushing Bottles	Sch																				
		Act																				
	ii) Mixing Process	Sch																				
		Act																				
	iii) Pressing Process	Sch																				
		Act																				
	iv) Sintering Process	Sch																				
		Act																				
Analysis & Mechanical Testing	i) Microstructure Analysis	Sch																				
		Act																				
	ii) Phase Analysis	Sch																				
		Act																				
	iii) Physical Analysis	Sch																				
		Act																				
	i) Microhardness Test	Sch																				
		Act																				
Report Writing	i) Draft 1	Sch																				
		Act																				
	ii) Draft correction	Sch																				
		Act																				
	iii) Final submission	Sch																				
		Act																				
Presentation	i) Slide preparation	Sch																				
		Act																				
	ii) Presentation	Sch																				
		Act																				

APPENDIX C

	Temperature (°C)	Ratio (wt %)		
		95:5	90:10	85:15
W (g)	750	0.840	0.846	0.969
	850	0.821	0.965	0.976
	950	0.744	1.038	0.983
D (g)	750	0.841	0.847	0.970
	850	0.822	0.966	0.977
	950	0.745	1.039	0.985
S (g)	750	0.406	0.487	0.406
	850	0.413	0.489	0.487
	950	0.464	0.556	0.491
M (g)	750	0.847	0.851	0.974
	850	0.829	0.972	0.979
	950	0.751	1.044	0.987
V (cm^3)	750	0.441	0.364	0.568
	850	0.416	0.483	0.492
	950	0.287	0.488	0.496

The data information while porosity, density measurement and water absorption analysis