UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERISATION OF ALUMINO-SILICATE-FLUORIDE BASED GLASS CERAMICS FROM CLAM SHELL AND SODA LIME SILICA GLASS WASTE

NADIA ASYIKIN BINTI ABDUL RAHMAN

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By

NADIA ASYIKIN BINTI ABDUL RAHMAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

November 2019

DEDICATION

To my beloved husband Mohd Zaky bin Nordin
For his unconditional love and support

To my son Muhammad Arish Iman
For making my life complete

To siblings and family
For their love and care

To all my very wonderful friends
For making my life full of joy and happiness

To all my lecturers
For helping me a lot throughout this journey

Without all of them, this success would not be mine
Thank you all

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman : Associate Professor Khamirul Amin bin Matori, PhD
Faculty : Science

The design of bioactive glass materials which is strictly related to glass technology is one of the main achievements in glass production. The attention towards the preparation of glass and glass-ceramics materials for applications in dentistry has increased. The $CaO\text{-}SiO_2\text{-}CaF_2\text{-}P_2O_5\text{-}Al_2O_3$ glass system has been studied by other researchers where the material produced has high mechanical strength as compared to other bioactive glass and glass-ceramics. Although this glass and glass-ceramics are well established for dental application, its effect on using waste materials such as clam shell (CS) and soda lime silica (SLS) glass for use in the dental field has not been extensively studied. Thus, in this study, Alumino-Silicate-Fluoride (ASF) glass and glass-ceramics were fabricated and synthesised using CS and SLS glass as a source of CaO and SiO_2, respectively. A series of ASF glass samples were prepared by using the conventional melt-quench technique. The thermal, chemical, physical, structural and mechanical properties of precursor glass and glass-ceramics were measured by differential scanning calorimetry (DSC), x-ray fluorescence (XRF), energy-dispersive x-ray (EDX), average density, molar volume, linear shrinkage, x-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR) and Vickers hardness (H_v) measurement. The density of the un-sintered pellets was found to increase with increasing of CS powder in the glass samples. Moreover, the density and linear shrinkage of glass-ceramic samples also increased with the increasing of sintering temperature. However, these measurements have slightly decreased at 1100 ℃ and 1200 ℃. The introduction of $CaO\text{-}SiO_2\text{-}CaF_2\text{-}P_2O_5\text{-}Al_2O_3$ containing materials, as well as the specific regime of sintering of the glass, gave glass-ceramics materials with crystalline phases of the hexagonal $Ca_5(PO_4)_3F$ (fluorapatite), orthorhombic $Al_5SiO_{9.5}$ (mullite) and anorthic ($Ca(Al_2Si_2O_8)$) (anorthite) crystals. The average calculated crystallite size of fluorapatite obtained from XRD was found to be in the range 16-53 nm. The formation of needle-like microstructure, which is known as fluorapatite, was observed in FESEM micrograph. The appearance of P−O and Si−O−Al bands detected from FTIR measurements indicate that the formation of apatite and mullite crystal phases. The H_v of the glass-ceramic have the same trends as the density of the pellets. The results obtained shows that there was a slight decrease in both measurements at 1100 ℃ and 1200 ℃, due to porosity formation and decomposition of fluorapatite phase into mullite and anorthite phase. As a result, the optimum density and H_v were in a range of 2.651-2.810 g/cm^3 and 4.75-6.14 GPa, respectively, at 1000 ℃. Overall results promoted the ASF glass and glass-ceramics samples produced from waste materials as a high potential candidate for dental applications since both fluorapatite and mullite phases are likely to result in the development of glass-ceramics with high mechanical strength.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN PENCIRIAN KACA-SERAMIK BERASASKAN ALUMINO-SILIKAT-FLORIDA DARI KULIT KERANG DAN SISA KACA SILIKA

Oleh

NADIA ASYIKIN BINTI ABDUL RAHMAN

November 2019

Pengerusi : Profesor Madya Khamirul Amin bin Matori, PhD
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Reka bentuk bahan kaca bioaktif yang sangat berkait rapat dengan teknologi kaca merupakan salah satu pencapaian utama dalam penghasilan kaca. Baru-baru ini, perhatian terhadap penyediaan bahan kaca dan kaca-seramik untuk aplikasi dalam pergigian telah meningkat. Oleh itu, penyelidikan khusus tentang sifat fizikal, struktur dan mekanikal kaca dan kaca-seramik adalah penting untuk aplikasi tersebut. Sistem kaca CaO-SiO_2-CaF_2-P_2O_5-Al_2O_3 telah dikaji oleh penyelidik lain di mana bahan yang dihasilkan mempunyai kekuatan mekanikal yang tinggi berbanding kaca dan kaca-seramik bioaktif yang lain. Walaupun kaca dan kaca-seramik ini telah dibuat untuk aplikasi pergigian, kesannya terhadap bahan terbuang seperti kulit kerang dan sisa kaca silika untuk digunakan dalam bidang pergigian tidak lagi dikaji secara meluas. Oleh itu, dalam kajian ini, kaca dan kaca-seramik Alumino-Silika-Florida (ASF) telah direka dan disintesis dengan menggunakan kulit kerang dan sisa kaca silika sebagai sumber CaO dan SiO_2. Satu siri kaca ASF telah disediakan dengan menggunakan teknik lindapan leburan. Sifat-sifat terma, kimia, fizikal, struktur dan mekanik dari kaca prekursor dan kaca-seramik diukur dengan *DSC*, *XRF*, *EDX*, purata ketumpatan, isipadu molar, pengukuran pengecutan linear, *XRD*, *FESEM*, *FTIR* dan pengukuran kekerasan *Vickers* (H_v). Ketumpatan pelet yang tidak disinter didapati meningkat dengan peningkatan kandungan serbuk kulit kerang dalam sampel kaca. Tambahan pula, ketumpatan dan pengecutan linier sampel kaca-seramik turut meningkat dengan peningkatan suhu sintering. Walau bagaimanapun, pengukuran ini sedikit menurun pada suhu 1100 ℃ dan 1200 ℃. Pengenalan bahan yang mengandungi CaO-SiO_2-CaF_2-P_2O_5-Al_2O_3, serta rejim suhu sintering tertentu bagi kaca, menunjukkan kaca-seramik mengandungi fasa kristal seperti $Ca_5(PO_4)_3F$ (*fluorapatite*), $Al_5SiO_{9.5}$ (*mullite*) dan ($Ca(Al_2Si_2O_8)$) (*anorthite*). Purata saiz kristal *fluorapatite* yang diperolehi daripada XRD adalah dalam julat 16-53 nm. Pembentukan struktur mikro seperti jarum, yang dikenali sebagai *fluorapatite*, diperhatikan dalam mikrograf *FESEM*.

Kemunculan dan penghasilan ikatan P–O dan Si–O–Al yang dikesan dari pengukuran *FTIR* menunjukkan bahawa pembentukan fasa kristal *apatite* dan *mullite*. Kekerasan *Vickers* kaca-seramik mempunyai hala yang sama seperti ketumpatan pelet. Keputusan yang diperoleh daripada kedua-dua pengukuran menunjukkan sedikit berkurangan pada 1100 ℃ dan 1200 ℃, kerana pembentukan porositi dan penguraian fasa *fluorapatite* menjadi fasa *mullite* dan *anorthite*. Akibatnya, ketumpatan serta H_v optimum masing-masing berada dalam lingkungan 2.651-2.810 g/cm^3 dan 4.75-6.14 GPa, pada suhu 1000 ℃. Hasil keseluruhan dapatan menunjukkan kaca dan kaca-seramik ASF yang dihasilkan daripada bahan terbuang adalah sebagai material yang berpotensi tinggi untuk aplikasi pergigian kerana fasa *fluorapatite* dan *mullite* berkemungkinan akan menghasilkan kaca-seramik dengan kekuatan mekanikal yang tinggi.

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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Name of Member of Supervisory Committee: Dr. Mohd Hafiz bin Mohd Zaid

Signature: ______________________________

Name of Member of Supervisory Committee: Dr. Norhazlin binti Zainuddin

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LIST OF ABBREVIATIONS

CS	Clam shell
SLS	Soda lime silica glass
Al_2O_3	Aluminium oxide
CaF_2	Calcium fluoride
P_2O_5	Phosphorus pentoxide
CaO	Calcium oxide (lime)
SiO_2	Silicon dioxide
$CaCO_3$	Calcium carbonate
Na_2O	Sodium oxide
Sc_2O_3	Scandium (III) oxide
SO_3	Sulfur trioxide
Fe_2O_3	Ferric oxide
K_2O	Potassium oxide
ZrO_2	Zirconium dioxide
Cr_2O_3	Chromium (III) oxide
ZnO	Zinc oxide
SrO	Strontium oxide
CuO	Copper oxide
Ho_2O_3	Holmium (III) oxide
XRF	X-ray fluorescent
EDX	Energy dispersive x-ray
XRD	X-ray diffraction
FESEM	Field emission scanning electron microscopy

FTIR	Fourier transform infrared spectroscopy
DSC	Differential scanning calorimetry
n	Integer
λ	Wavelength
d	Distance between the lattice planes
θ	Angle between the incident and lattice plane
ρ	Density
m	Mass
M_v	Molar volume
V	Volume
M	Molecular weight
D_i	Initial diameter
D_f	Final diameter

CHAPTER 1

INTRODUCTION

1.1 Research background

Glass-ceramics materials are composed of more than one crystal or known as solid polycrystalline, which were prepared by appropriate sintering process of glass (McMillan, 1964). The process of producing the glass-ceramics includes the formation of glass and further sintering process (Höland and Beall, 2019). The glass sample had nucleated and crystallised with numerous kinds of crystal phase after it was sintered at certain temperatures. Besides, the essential parameters in the sintering process are duration and temperature, which lead to the highest nucleation rate and the growth of the crystal, in order to achieve the useful features of glass-ceramics (Valderrama et al., 2019). The changes in composition and further sintering process can customise the broad-ranging properties of glass-ceramics such as non-appearance of porosity, fine-grain, reproducible and uniform microstructure (Partridge et al., 1989; Parsell, 1993). Therefore, these glass-ceramics materials become more attractive and useful in well-established applications.

Furthermore, the possibility of the utilisation of usual glass-forming methods, such as casting, blowing, rolling and pressing earlier than crystallisation during sintering process (McMillan, 1964; Strnad, 1986) allows industrialists to manufacture delicate and multi-shape parts. Further interest in glass-ceramics has been developed because of their superior mechanical, thermal, biological, chemical and dielectric properties. The applications of glass-ceramics such as magnetic heat-resistant windows, nosecones of rockets, memory disk substrates, telescope mirror blanks, liquid crystal displays, biomaterials and household crockery are successfully used (Beall, 1993; Hench and Wilson, 1995; Sukumaran and Bharadwaj, 2006). Figure 1.1 shows the classification and applications of synthetic biomaterial.

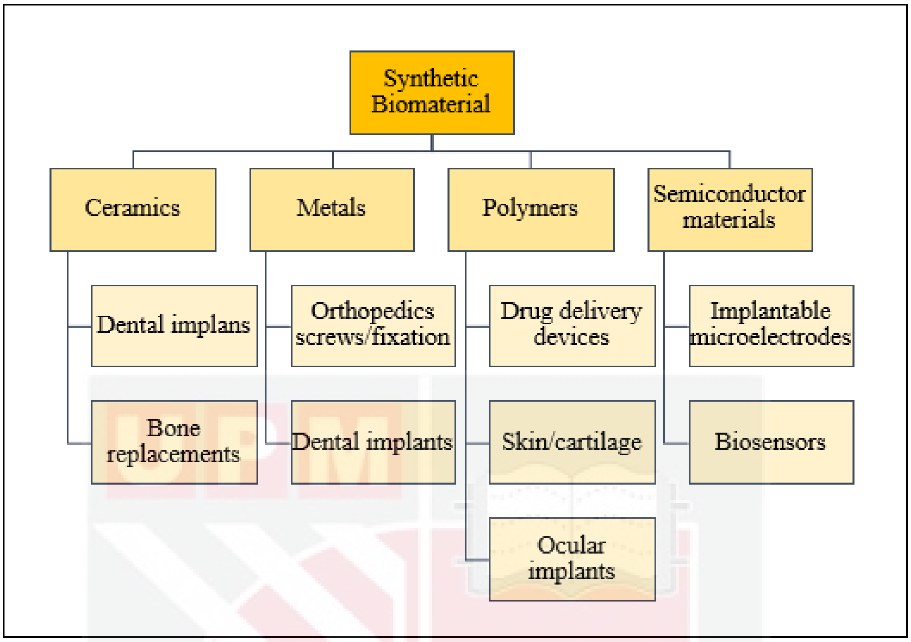

Figure 1.1: Classification and applications of biomaterials (El-Meliegy and Noort, 2012)

Due to the biocompatibility of the material with living tissues, glass-ceramics have created attention in the biomedical applications, specifically in the dental repair, replacement, as well as restoration of human bone. (Vaverka and Hrabalek, 2002; Sukumaran and Bharadwaj, 2006; Dias et al., 2007). Bioactive glass-ceramics are usually made up of specific compositions, where bioactivity is commonly defined as the ability to elicit a favourable cellular response (Yamamuro et al., 1998; Chen et al., 2006). Therefore, glass-ceramics are considered as the appropriate materials for reconstruction as well as restoration of damaged or diseased of the hard tissues of the body. Several commercial commerce names such as Ceravital®, Bioverit®, and Dicor®, are the product of glass-ceramics that have been marketed earlier (Dubok, 2000; Peitl et al., 2001). But, most bioactive glass-ceramics have similar compositions to those of Bioglass® 45S5 (Peitl et al., 2001).

The glass-ceramics containing both phases of fluorapatite ($Ca_5(PO_4)_3F$) and mullite ($Al_5SiO_{9.5}$) crystals as the major crystal phases in the CaO-SiO_2-CaF_2-P_2O_5-Al_2O_3 glass medium have received considerable importance in dental applications, especially for the dental cement purposes. Previously, Hill et al. (1991) have made a SiO_2-CaO-P_2O_5-Al_2O_3-CaF_2 based glass-ceramics and utilised it for ionomer glass purposes. Meanwhile, Lukacs et al. (1993) reported that the glass compositions studied by Hill et al. (1991) have shown high mechanical strength and also fracture toughness when converted to ceramic.

These materials must exhibit high strength, wear-resistance, hard-wearing in the oral environs, and have the look of natural tooth structure (Höland et al., 2006).

Biomaterials are used to interact with a biological system that helps in terms of body functioning (O'Brien, 2011). The prefix bio in biomaterial means that it is biocompatible where biocompatibility refers to the ability to respond to the host in a specific application without any harm (Chen et al., 2014). The biomaterial is categorised into two mechanisms that are bioglass and bioceramics material (Patel et al., 2019). Bioactive glass, also known as bioglass, is a type of bioactive material which was discovered as the first human-made material that consistently bonds to live tissues which is also known as bioactive material. In 1969, Larry Hench and colleagues discovered the first bioglass at the University of Florida when an interfacial bond with host tissue was seen after implantation of this first material (Hench, 2013). Bioglass is an amorphous silicate-based material, where it is suitable for the human body and is able to form new bone growth and bond to the bone. The finding by Hench et al. (1971) that some SiO_2-CaO-Na_2O-P_2O_5 glass samples have aroused much interest in the development of bioglass and bioglass-ceramics with the formation of no fibrous tissue on contact with living tissue, but rather bond chemically to it, especially that used in the medical field.

Meanwhile, bioceramics are biomaterial that is in the form of an amorphous or crystalline solid produced by sintering inorganic raw material that can be used to repair the skeletal system that consists of bones, joints and teeth (Khang et al., 2008). Bioceramics are made by controlling the crystallisation of a glass, where the sintering process can convert its amorphous structure into the crystalline structure for mechanical strength improvement. The bioglass composition and the crystal phase play an important part to determine the biological response of bioceramics. Bioceramics will interact with the natural environment when placed inside the human body and triggers new bone formation.

In this study, the Alumino-Silicate-Fluoride (ASF) based glass-ceramics composition is used in the production of glass and glass-ceramics for dental applications such as glass ionomer cement (GIC), as well as glass-ceramics ionomer cement (GCIC). The major components of this dental cement consist of CaO, SiO_2, CaF_2, P_2O_5 and Al_2O_3. Besides, most of the food wastes contain valuable minerals that could serve as raw materials for the fabrication of glass, glass-ceramics and ceramics (Cornejo et al.; 2014). From the previous research, clam shell (CS) is composed of more than 98 wt.% of $CaCO_3$ and the remainder is organic matter and another compound (Rashidi et al., 2011; Buasri et al., 2013). Besides, soda lime silica (SLS) glass is the most common made glass composed of silica in range of 70.9 to 80.0 wt.% which can act as silicate precursor source (Bateni et al., 2014). SLS glass is made from a composition of SiO_2, CaO, Na_2O and Na_2CO_3, which its major application is widely used in the production of bottles, jars, drinking glasses and window glass (Stevenson, 2012). Therefore, in this study, CS and SLS glass were chosen as the raw materials for the ASF glass-ceramics due to its high purity of CaO and SiO_2, respectively.

In the composition of glass-ceramics, fluoride from CaF_2 plays an essential part in determining the properties and features of glass. CaF_2 is a white insoluble solid which is an inorganic compound. CaF_2 has a structure of fluorite type cubic based on XRD analysis by Al-Ajely et al. (2018). The CaF_2 is known to have calcium ion (Ca^{2+}) and fluoride ion (F^-) which these ions characterise the properties of its compound. The CaF_2 was explicitly used for characterising glass-ceramics behaviour as CaF_2 that can affect the properties of glass ceramic material which will contribute to its application in dental and medical courses. Yon et al. (2019) state that fluoride is known to perform an essential role as a species which fight dental caries in the mouth. Fluoride ions may influence glass ceramic bioactivity since they enhance the rate of decomposition of hydroxyapatite (Featherstone, 1999). In the making of GIC, fluoride took place as a vital component of the glass as it is a substance that lowers the melting point (Nicholson and Czarnecka, 2016).

1.2 Problem statement

Many dental materials consist of CaO, SiO_2, Na_2O, CaF_2, Al_2O_3 and P_2O_5 are in form of glass, ceramics or composite. The compound in bioactive glasses are in amorphous structure. Dental ceramics which consist of particular crystalline phases contributed useful properties to dental application. For example, fluorapatite phase behave as human teeth but it has higher stability and mechanical strength. Hence, the crystalline phase transformation in the glass-ceramics upon sintering process became an important field to be studied.

Recently, the use of waste materials to synthesis glass-ceramics was received encourage response from many researchers across the world. This idea gives an innovation to produce a new valuable product from the waste materials. Besides that, these waste materials also can be recycled, then change it into more valuable things and keep environment safely. In previous report, glass-ceramics was synthesised by using waste materials such as sea shell (Santhosh and Prabu 2013), eggshell (Dávila et al. 2007), animal bones (Sobczak et al. 2009), shell of garden snail (Singh 2012), and fruit waste extract (Wu et al. 2013). These materials consist of high source of calcium that can be act as calcium precursor which is suitable to produce glass-ceramics which is suitable for dental. CaO can be obtained by calcined the $CaCO_3$ at 900 ℃ for 4 hours (Khiri et al., 2016). Menwhile, SiO_2 can be derived by using waste materials such as SLS glass bottle (Ibrahim et al., 2018) white rice husk ash (Lee et al., 2017), and coconut husk ash (Anuar et al., 2018). Based on previous research, the percentage of $CaCO_3$ in CS and SiO_2 in SLS glass are usually ~98% (Awang-Hazmi et al., 2007; Kamba et al., 2013; Mustaffa et al., 2015; Khiri et al., 2016), and ~70% (Stevenson, 2012) respectively, which is comparable to the pure substance. Besides, pure SiO_2 is expensive, especially for industrial use because of the high quantity needed for a particular product. Therefore, CS and SLS glass were recycled to get a large amount of pure substance, and thus, it can reduce the cost of fabrication.

The researches regarding the synthesising ASF based glass-ceramics from the execution of waste material are still genuinely new and limited in industrial research. Even though this type of glass-ceramics is well recognised for the dental field, its effect on CS and SLS glass for use in the dental applications have not been extensively studied. Therefore, a new improvement is needed in terms of different composition of waste material in order to study the effectiveness of ASF based glass-ceramics properties. By using the waste product as a substance to synthesis the glass-ceramics instead of commercial substance is a solution in reducing costs material in biomaterial research.

Bioactive glass has excellent bioactive properties, but the major disadvantages are low mechanical strength, as well as low fracture toughness. By developing the bioactive glass-ceramics, it can improve the mechanical performance and become more useful especially in biomedical applications. Fluorapatite ($Ca_5(PO_4)_3F$) based glass-ceramics have higher potential for application in numerous dental and medical biomaterials due to the antibacterial effect of its F^- ions (Hill et al., 2006). Furthermore, the combination of fluorapatite and mullite ($Al_5SiO_{9.5}$) phases is expected to result in the development of glass-ceramics with high mechanical strength and excellent bioactive properties (Fathi and Johnson, 2016). Thus, the primary purpose of this project is to turn CS and SLS glass into a valued product and then determine the physical, structural and mechanical properties of the glass-ceramics when CS and SLS glass were used as part of the elements of the glass composition.

For that reasons, a comprehensive study of the crystallisation, properties and effect of sintering on ASF based glass which derived from CS-SLS-CaF_2-P_2O_5-Al_2O_3 glass system are carried out, and the results of this research are expected to find potential application for the dental cement purposes.

1.3 Significant of study

Today, many countries are having a difficulty to dispose solid wastes from industries. These countries have limited landfill sites to dump these solid wastes. Recycling of waste materials such as CS and SLS glass were reported by other researchers to reduce solids wastes. This study focused on the phase transformation of CS-SLS-CaF_2-P_2O_5-Al_2O_3 glass-ceramics by using waste materials. This research is an early study of preparation of bioactive glass-ceramics in dentistry by using waste materials. Hence, it is an initiation to the manufacture of glass-ceramics from solid wastes for dental applications.

The phase transformations of $CS\text{-}SLS\text{-}CaF_2\text{-}P_2O_5\text{-}Al_2O_3$ glass-ceramics from waste materials are important to dental applications. The glass with amorphous phase is useful as bioglass and GIC. The glass-ceramics with particular crystalline phase are useful in dental crown. Sintering process can transform a glass into glass-ceramics through several crystalline transformations with different crystallinity occurred in glass-ceramics. Besides, this study also concerned on effects of the presence of CaO from calcined CS, in the phase transformations of the glass-ceramics. The crystalline phases are expected to provide significant useful physical and mechanical properties for dental applications.

1.4 Research objective

The main objective of this study is to develop and improve ASF based glass-ceramics derived from $CS\text{-}SLS\text{-}CaF_2\text{-}P_2O_5\text{-}Al_2O_3$ glass system. This study involved the design of suitable glass compositions, conventional melt-quenching technique, development of the sintering process, and a series of fundamental studies of the crystallisation process.

From the problem statements stated above, the objectives for this study were:

1) To utilise the uses of CS and SLS glass for making ASF based glass and glass-ceramics.
2) To investigate the effect of different ratio of CS and SLS glass to the formation of ASF based glass and glass-ceramics.
3) To study the effect of sintering temperature on the physical, structural and mechanical properties of ASF based glass-ceramics.

1.5 Scope of the study

In order to achieve the objectives of the study, the scopes of the study as follow:

1) A series of precursor glass based on the stoichiometric equation of $[xCS\cdot(45\text{-}x)SLS\cdot15CaF_2\cdot20P_2O_5\cdot20Al_2O_3]$ where x = 5, 10, 15 and 20 (wt.%), has been prepared using CS, SLS glass, CaF_2, P_2O_5, and Al_2O_3 powder by conventional melt-quench method.
2) The chemical composition of the precursor $CS\text{-}SLS\text{-}CaF_2\text{-}P_2O_5\text{-}Al_2O_3$ glass system has been measured using XRF and EDX spectroscopy in order to confirm the elements and percentage of chemical elements in the waste materials and glass samples respectively.
3) The glass transition temperature (T_g) and glass crystallisation temperature (T_c) have been measured using DSC spectroscopy.

4) ASF glass-ceramics samples were derived from CS-SLS-CaF_2-P_2O_5-Al_2O_3 glass system by an appropriate crystallisation process.
5) The physical, structural and mechanical properties of ASF based glass-ceramics have been analysed using Archimedes method, molar volume, linear shrinkage, XRD, FESEM, FTIR, Vickers hardness analysis.

1.6 Outline of thesis

Chapter 1 gave an introduction to the waste product and ASF based glass-ceramics. Besides, the significant of the research, problem statement along with the objectives of this research are briefly explained in this part. The theory of glass, glass-ceramics, as well as previous works, including past and current, has been carried out by other researchers were covered in Chapter 2. Chapter 3 discussed the method used in preparing the samples starting from the raw material until the measurement to determine the physical, structural and mechanical properties of the ASF glass and glass-ceramics samples.

Meanwhile, Chapter 4 revealed the findings and results obtained from various measurements and was discussed in detailed. The results concerning the effect of CS powder addition in the glass system, as well as the progression of sintering temperatures towards the physical, structural and mechanical properties of the glass-ceramics was depicted. Finally, the conclusion had been made based on the results obtained, and some suggestions and recommendations for the upcoming works were presented in Chapter 5.

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