DEVELOPMENT OF GLASS CERAMICS USING KAOLIN PROCESSING WASTE, SODALIME AND BOROSILICATE GLASS WASTES

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TITLE PAGE

DEVELOPMENT OF GLASS CERAMICS USING KAOLIN PROCESSING WASTE, SODALIME AND BOROSILICATE GLASS WASTES

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A THESIS SUBMITTED TO THE SCHOOL OF POST GRADUATE STUDIES, AHMADUBELLOUNIVERSITY, ZARIA IN PARTIAL FULFILMENT OF THE REQUIREMENTSFOR THE AWARD OF DOCTOR OF PHILOSOPHY DEGREE IN GLASS TECHNOLOGY.

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DECLARATION

I declare that the work in this thesis entitled.,'**Development of Glass Ceramics Using Kaolin Processing Waste, Soda Lime and Borosilicate Glass Wastes**'has been carried out by me in the Department of Industrial Design,Faculty of Environmental Design, Ahmadu Bello University, Zaria, under the supervision of **Dr.E.A Ali, Dr. A.D Garkida** and **Professor S.P.Ejeh**. The information derived from literature has been duly acknowledged in the text and the list of references provided.No part of this dissertation was previously presented for another degree or Diploma at any University.

Hauwa Isa _____ _____

Name of Student Signature Date

CERTIFICATION

This thesisentitled DEVELOPMENT OF GLASS CERAMICS USING KAOLIN PROCESSING WASTE SODALIME AND BOROSILICATE GLASS WASTESby Hauwa ISA meets the regulations governing the award of the degree of Doctor of Philosophy of the Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This thesis is dedicated to my late brother Dr. ISA Umar Faruq of blessed memories. May his gentle soul rest in perfect peace. Amin.

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In the name of Allah the Beneficent, the Merciful. All thanks be to Allah, who taught man what he knew not and gave him the knowledge of interpretation. I once again thank Allah for giving me the health, courage, knowledge and the ability to successfully complete this research work through His guidance and mercy.

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ABSTRACT

The utilisation of waste materials to producea useful product is highly encouraged to avoid its disposal on land fields so as to safeguard the environment. Kaolin waste, soda lime and borosilicate glass wastes were used to develop glass ceramic. The oxides content of the raw materials were determined using the X-Ray Florescence machine while the moisture content and loss on ignition were determined by the weight loss method and the following results were obtained; SiO_2 80.50% for borosilicate 77.63% in soda lime and 46.80% in kaolin, Fe_2O_3 content in borosilicate was O.22%, 0.30%in soda lime and 0.01% in kaolin .V_2O_5 was found in kaolin and soda lime glass wastes and B_2O_3 only in borosilicate glasswaste.CaO content of 7.46% in soda lime with value less than 1.0% in kaolin and borosilicate. Loss on ignition of 10.13% was found in kaolin, 0.30% in soda lime and 1.34% in borosilicateAl_2O_3 content of kaolin is 31.41%, 0.60% in soda lime and 0.52% in borosilicate, the MgO content of 0.20% in kaolin, 2.63% soda lime and 0.03% in borosilicate waste glass. Particle sizes of 90 µm, 125 µm and 250 µm of the waste glasses were used to formulate batches. which were compressed into pellet shape of 20mm in diameter with a thickness of 5mm.Hydraulic pressing machine at a pressure of 10metric tones using the polyvinyl chlorine (PVC) organic binder was used to produce pellets.Then sintered at 750c°, 850°c and 950°c in a furnace at a heating rate of 5^0C /min with residence time of one hour and cooled gradually. The composition containing kaolin, soda lime, borosilicate with 90µm particle size sintered at 950°Cgave the highest shrinkage in diameter with value of 17.36% and a batch containing kaolin, borosilicate and Na_2SO_4 with 250 µm particle size sintered at 750°C gave average of 0.94% in diameter. The physical properties of porosity, water absorption and bulk density were measured at all sintered temperatures for all the batches. The highest bulk density was found to be 2.54g /cm^3 in the batch $K_5B_5SL_{9o}$ with 90 µm particle size at 850°C sintering temperature.The least bulk density is 1.34g/cm^3 and the highest porosity of 26.84% were observed in batch K_{15} B_5 SL_{8o} with 250µm particle size at 750°C.The least value of 0.68% in batch K_{1o} B_{85} NS_5 with 125µm particle size at 950°C.The highest value of 18.02% water absorption was recorded for batch K_5 B_5 SL_{8o} with 250µm at 750°C with the least value of 0.34% at 950°C .The highest hardness value was recorded for batch K_5B_{95} NS_o with 90µm particle size at 950°Cwas81.5 Nm^2 Rock well superficial scale and the least value of 70.5Nm^2 was found in batches $K_{10}B_{85}$ NS_5 with 125 µm particle size and $K_{10}B_5$ SL_{85} with 125µm particle size sintered at 950° C. The most acid resistance batch was K_{15} $B_{8o}NS_5$ with 250µm sintered at 750°C, 850°C and 950°C. The least acid resistance batch was K_{1o} B_{85} NS_5 with 7.85% loss sintered at 950°C with 125 µm. The most alkali resistance batch was found to be K_5 B_5 SL_{9o} with 90 µm particle size with value of 0.35% sintered at 850 °C and 950°C and the least alkali resistance batch was observed in K_5 B_{95} NS_0 with 90 µm particle size with value of 8.87% sintered at 850°C. The X-Ray Diffraction (XRD) result for batch K_5 B_5 SL_{9o} with 90 µm particle size showed thatCrystallisation occurs at 750°C and for batch K_5 $B_{95}NS_0$ of same particle size, amorphous peaks were observed at the same sintering temperature. Scanning Electron Microscopy (SEM) appearance of a square pillar like crystals for batches K_{15} B_{80} NS_5 at 125 µm and 250 µm sintered at 850°C and 950°C revealed sharp XRD peaks which correspond to that of diopside crystalline phase (CaO .MgO.Al_2O-SiO_8) .The SEM appearance of feathery crystals for batches $K_5B_5SL_{90}$ with 90 µm sintered at 850^0C, K_{10} $B_5SL_{85}$with 125 µm sintered at 850°C and 950°Cindicated an anorthite(CaO .$Al_2O_3SiO_8$) crystal phase.. The results obtained in this study showed that the glass ceramic developed can be used as lining for materials in construction and communication, heat and wear-resistance appliances for thermo-chemical, biomedical and ceramic coatings.

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CHAPTER ONE

INTRODUCTION

1.1 Background

Glass ceramics are fine grain polycrystalline ceramic materials obtained through the controlled Crystallisation of suitable glass compositions and different heat treatments (Callister, 2005).Considerable research work has been devoted to the recovery and safe, use of waste residuesfrom industries and domestic uses. The wastes from industry contain a high concentration of toxic substances, heavy metals, organic substances and soluble salts. Waste processing resulting in reduction of the noxious and toxic substance occupies a central place for environmental preservation. Recycling methods and technologies with minimum quantity of energy and time are designed for the protection of the environment against pollution by toxic elements produced by industrial chemical waste (Sheppard, 1990).The development of new glass ceramics is particularly relevant due to the possibilities of recycling large amounts of waste materials by incorporating them into the glass ceramics formulations. This trend is in line with one of the most important concerns of the present to ensure the quality of life of future generations by the minimization of the consumption of traditional raw – materials (Menezes *et al.,* 2002 and Andreola *et al.,* 2002).

The production of glass ceramic materials made by recycling industrial waste is an innovative development in theglass ceramic industry. Many researchers have paid much attention to the production of glassceramic and sintered materials from industrial wastes to make them reasonably safe for the environment .The insertion of waste materials into the productive cycle might represent an alternative option which is interesting from both environmental and economic perspective (Sanchez*et al.,* 2006).

The primary advantages of glass ceramics materials are higher strength, chemical durability and electrical resistance which can be made with very low thermal expansion coefficients, giving excellent thermal shock resistance (Rahaman, 2003). They are attractive materials used in various applications and are commercially important due to their unique properties. These properties make them superior to the parent glass, making them suitable for the construction, mechanical and chemical industries around the world (Romualdo*et al.,* 2008).

There has been considerable research on the production of glass -ceramics from a variety of silicate wastes in the last few decades. The development of glass ceramics involved intensive heat treatment technologies that have been widely used for the treatment of several silicate wastes usually processed to form glass ceramic products. These wastes, coming from numerous sources can be considered raw-materials (Rawlings et *al.* 2006).

Kaolin being an important raw material for various industries, such as the ceramic, rubber, plastic,and paint, chemicals, cement and paper industries generateslarge amount of wastes because the part used for the industries is small compared to the waste being generated. A lot of studies have indicated the viability of using the kaolin processing wastes as alternative raw materials for the production of ceramic bricks and glass ceramic materials which shows better chemical and mechanical performance (Erol*et al.*, 2008). The reuse of the glass waste in ceramic system is capable of improving the performance of both chemical and mechanical properties compared to conventional ceramic material, especially in highly demanding structural applications (Romualdo et *al.,* 2009).

Several factors such as particle size distribution, and binders for holding the powder together during pellets formation and sintering process are to be considered to ensure quality of glass ceramics manufactured from waste silicates.

The present study concentrates on the preparation of glass ceramics using kaolin processing waste, borosilicate and soda lime waste glass.The developed glass ceramics were subjected to physical, chemicaland mechanical tests. Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) analysis were used to analyze the microstructure and crystal phases present in the samples produced. The properties achieved would determine the potential applications of the product.

1.2 Statement of Problem

Nigeria has abundant mineral deposits, and kaolin is one of the raw – material that is important in various industries for different kinds of production.It isestimated that over 70 percent of the wastes coming from mining and beneficiation is discharged into streams, rivers or dumped in open air sites. These are inorganic wastes that contain heavy metals such as lead, chromium and other toxic elements.Kaolin waste aggravating problem is that it is not exploited, and its powdery nature leads to its inhalation which causes lungs and skin diseases. So its disposal is a serious threat to humans (Luisa et *al.*, 2002).

Today in Nigeria, wastes such as glasses, papers, plastics and others are not adequately utilised but are usually disposed in landfills. These cause damage to the environment through air, soil and water contamination which are potentially harmful to plants, animals and human.

Disposal of waste glass(borosilicate glasses) obtained from scientific laboratories and glasses used for containers, furniture in our homes as table tops and window glasses (soda lime glasses) are dumped on landfills which litters around or buried in the soil and being non-biodegradable cause contamination and pollution of the environment.

1.3 Aim and Objectives of the Study

The aim of this study is to develop and characterize a glass ceramic product using kaolin processing waste, borosilicate and soda lime wastes glass with the following objectives;

i. To determine the chemical oxides composition of waste kaolin , borosilicate and sodalime glass waste

ii. To formulate batch compositions of three different proportions considering the particle sizes of the waste glasses, with some batches containing sodium sulphate to study the effect of soda lime glass waste

iii. To determine the effect of sintering temperatures on the properties of the produced glass ceramics.

iv To determine the physical, chemical and mechanical properties of the glass ceramic

vTo analyse the crystalline phases present in glass ceramics as well as their microstructure.

1.4 Justification

Glass ceramics arecategory of glasses used for high technology and special applications such as building materials, cooking ceramics, machinable ceramics,optical materials and bio-active glass ceramics in addition to their common uses in domestic appliances. They are mostly produced using numerous silicate based wastes from processing industries such as coal combustion ash, slag from steel production, sugar cane baggase, fly ash, bottom ash, pulp paper waste ashes,and filter dust from blast furnace slag and mud from hydrometallurgy plant. All these ashes are by products of the incineration process which

releases toxic particles and gaseous emissions to the atmosphere leading to pollution and contamination causing health hazards.

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.. The application of glass ceramics is gaining strength in all fields of science and technology such as in medical (dental and orthopedic), electrical and architectural field.This makes it necessary for researchers to intensify their activities in this growing field of material sciences.

1.5 Significance

The significance of this study is to develop glass ceramic from wastes other than incinerated by products which are of great concern on the enormous quantity of wastes generated by the numerous industrial sectors which have been the sources of environmental contamination and pollution in Nigeria. Using recycled materials will ultimately reduce the environmental contamination.

Mining and beneficiation processes are good examples of waste generation, these waste materials have traditionally been discarded in landfills and often dumped directly into the ecosystems without adequate treatment. These waste products often contain heavy metals that lead to environmental contamination and pollution causing major health hazards such as cancer, brain and nerve damage, birth defects, lung injury and respiratory problems (Luisa et *al*.,2002)

Recycling and utilization of glass and kaolin wastes will reduce its disposal in landfills which invariably sanitize the environment, making it clean and safe from the effects of contamination and pollution. Currently over 4.2 million glass waste is generated from household and industrial wastes and collected for recycling worldwide, this saved over 1.34million tonnes of carbon dioxide from being released to the environment (Luisa *et al*.,2002;Oluseyi *et al.,* 2013).

Economically, the use of these wastes will minimize the consumption of natural raw materials, reduce production cost, save energy, reduce importation, promote industrial development and provide employment in Nigeria.

1.6 Scope and Delimitation of the Study

This study is delimited to the development of glass ceramic using waste kaolin obtained from kaolin mining and processing plant in Kaloma, Alkaleri- Bauchi State. The borosilicate glass wastes from the Science Laboratories in NuhuBamalli Polytechnic, Zaria and soda lime glass wastes from postconsumer white bottles and broken window glasses in SabonGari Zaria. The particle sizes investigatedwere 90μm, 125μm and 250μm. The waste materials were mixed with poly vinyl chloride (PVC) as binder, then pressed by uniaxial pressing at 10 metric tonnes, and sintered at temperatures of 750^{o}C, 850^{o}Cand 950^{o}C.

Physical, chemical, mechanical, scanning electron microscopy and x-ray diffractrometry characterizations of the properties of the glass ceramic products were determined using ASTM standard methods.

CHAPTER TWO

LITERATURE REVIEW

2.1Glass Ceramics

Glass ceramics are derived from the controlled Crystallisation of glasses to give materials consisting of one or more crystal phases and some residual glass depending on the starting composition, grain size and the heat treatment given (McMillan, 1979). During the Crystallisation process, molecular rearrangement occur to produce the appropriate crystalline phases that are sometimes metastable polymorphs, which under further heat treatment can transform to the thermodynamically more stable crystal phases (Strnad, 1986).

Control of the nucleation and Crystallisation stages is the most critical aspect in the glass ceramic process. In addition to structural factors, the devitrification of a glass depends on the thermodynamic and kinetic behavior, which will determine the most adequate thermal cycle to obtain the final glass ceramic material. The preparation of a satisfactory glass ceramic depends on crystallizing the glass composition under strictly controlled conditions to provide the desired closely interlocking, microcrystalline structures (James*et al.*, 1993).

Natural glass ceramic, such as some types of obsidian, always have existed. Synthetic glass ceramic were accidently discovered in 1953. Stookey of the corning glass laboratories in the United States discovered glass ceramic accidentally in an attempt to heat a photosensitive glass to a temperature beyond its normal melting temperature .The glass instead of melting, turned into an opaque, polycrystalline material with properties superior to those of the original glass (Stookey, 2000).

2.2 Waste Generation

The industrial revolution changed the world; it generated great humanity progress, and industrialization is accompanied by the generation of wastes which could be negative to the natural environment (Gungor and Gupta, 1999).

The current state of manufacturing processes consumes enormous tones of different forms of natural resources, energy and water (Gungor and Gupta, 1999). Recent report had shown that six percent of the 2million tonnes of waste generated in 2013was glass. The huge amount of waste generated is still far from being used in its totality as a product or byproduct, making technological alternatives needed in order to reduce its possible environmental impact.The major potential impacts of its disposal on terrestrial ecosystems include leaching of potentially toxic substances into soils and ground water(Numerow, 1983).

The environmental concerns and economic relatives provide an incentive to develop new solid state waste management technologies. These reduce disposal costs and other harmful effects. However, the main concern in the use of waste as secondary raw material in the formulation of glass-ceramic product is its immobilization inside the ceramic body after transformations have occurred during the process. Glass ceramic products could be considered interesting in the immobilization of hazardous wastes because they are able to retain heavy metals in their structure with a significant reduction of volume. The positive aspects of waste inertization technology in glass ceramic product are flexibility, since various types of waste such as sediments and ashes can sometimes be used without preliminary preparations (Zimmer and Bergmann, 2007).

Waste materials like fly ash generated from coal and oil-fired electric power stations, fly ash from power plants, urban solid waste incinerators, granulated blast furnace slag, steel industry

dust and sewage sludge from water purification have been used to manufacture glass ceramic materials (Erol *et al.,* 2008).

Heavy metal contamination is also a concern in land disposal, and costs may prohibit their method of disposal. Another alternative route of glass ceramic production is the utilization of incinerated byproducts. Incineration is perceived as a viable disposal option, in some instances, incineration may provide the most cost effective and environmentally acceptable option due to increasingly stringent constraints on alternative routes of disposal (Charles, 2001).

2.3 Waste Recycling

Recycling of waste is capable of exploiting and developing new marketable products aimed at limiting the wastes generated from municipalities which are mainly incinerated leading to environmental pollution. The recycling of the raw materials reduces energy consumption and save ecological destruction thus, minimizing the use of virgin raw material (Luisa*et al.*, 2002). The industrial wastes such as plastics, glasses, papers and others are mainly disposed which constitutes problems to a country. Year by year the quantity of this disposal increases, which is an issue that have received a lot of attention in the society. By recycling, it will reduce waste which will in turn reduce the need for landfills and dumpsite, thereby make the environment clean and free from hazards of pollution and contamination.Silicate residues are significant group of materials when considering the recycling and reuse of industrial wastes (Baccacciniand Rees, 2002).It follows that for efficient use of the world's resources, recycling and reuse of waste is necessary for environmental safeguard (Rees,2003).

2.4 Glass Recycling

The importance of glass in improving the quality of life of man is continuously increasing.This will invariably results to an increase in the generation of waste due to an ever growing use of glass products for containers and in architectural buildings. The landfilling of waste glasses is undesirable because they are not biodegradable (Turgut and Yahlizade, 2009).

Waste reduction can be by recycling waste products and its utilization to manufacture new products, which give a lot of benefits to the environment and also to the economy (Callister, 2005).

Glass is a non-crystalline solid which has a transparent surface that has a mixture of materials such as silica, (S_iO_2), soda ash (Na_2CO_3) and limestone ($CaCO_3$) formed by melting at high temperature followed by cooling during which solidification occurs without Crystallisation . Glass has a short-range ordered crystal structure.The bond angle causes the glass structure to vary 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 range of temperatures. The viscosity changes gradually over this range, which allows glass to be formed into a wide variety of products (Martin, 2007).

The utilization of waste glasses can be an alternative way to save energy in the production process and reduce manufacturing cost. Incorporation of the wasted glass into a ceramic mixture, results in higher density, less water absorption and lower drying shrinkage (Vorrada *et al.,* 2009).

2.5 Borosilicate Glass

Borosilicate glass is an amorphous material formed by melting silica sand (S_1O_2) together with the oxides of elements such as boron, sodium and smaller amount of aluminum. They are also characterized by relatively low alkali and consequently good chemical durability and high thermal resistivity. They are good for the chemical industry, laboratory apparatus/wares and for high intensity lighting applications and as glass fibres for textiles. In some homes, they are used as oven wares and other heat resisting wares better known as pyrex in the consumer market (Budd, 1971)(Appendix I).

2.6 Borosilicate Glass Waste

Borosilicate glass wastes are mostly generated from scientific laboratory wares and chemical processing industries. The waste has a relatively low melting temperature of 1050 to 1150^{o}C with an acceptable high waste solubility, leach resistance and radiation stability.

Due to its amorphous nature, borosilicate glass can accommodate a wide range of waste composition while providing good product and processing characteristics (Johnson and Marples, 1979).

Thus, a large variety of nuclear waste compositions exist and there is a great deal of flexibility for formulating glasses from these wastes In most countries, high level of radioactive wastes have been incorporated into borosilicate or phosphate waste forms for many years and vitrification is established (Ojovan and Lee, 2005).

2.7 Soda Lime Silica Glass

Soda lime silica glasses are used extensively as commercial glass. It comprises mainly of sodium, calcium, and silicon oxides (Na_2O, CaO and S_1O_2). Other minor constituents are alumina, magnesia and several other oxides. The glass has unique combination of low cost raw materials with good manufacturing characteristics. Sodalime glass generally fall in a narrow range of compositions along the boundary between (Na_2 – CaO-$6S_1O_2$) variation from this narrow range can adversely affect some important characteristics, such as the glass melting behavior, Crystallisation tendency, glass workability and chemical durability (Haun Labs, 2000).

Sodalime can be divided technically into two,those used for windows and those used for containers. The composition of both is fairly similar but slight variations in colorants and the ratios of the constituents can have significant effect on some properties such as thermal expansion and Crystallisation behavior (Appendix II).

In contrast to other materials, glasses do not consist of a geometrical regular network of crystal but of an irregular network of silicon and oxygen atoms with alkali parts in between. The chemical composition gives an important influence on the viscosity, melting temperature and the thermal expansion coefficient of the glass (Marthias*et al.*, 2008).

2.8 Soda Lime Silica Waste Glass

The main sources of sodalime waste glass arise from its popular usage for containers and in architectural buildings. Waste is generated from containers and panels from dismantled buildings which is a cheap and readily available source of waste (Vorrada*et al.*, 2012) (AppendixIII).

2.9. Kaolin

Kaolin is a mineral belonging to the group of aluminum silicates. It is commonly referred to as "China clay" because it was first discovered at Kao – Lin, in china. The term kaolin is used to describe a group of relatively common clay minerals dominated by kaolinite and derived primarily from the alteration of alkali feldspar and micas (Smoot, 1963).

Kaolin are used in a multiplicity of industries because of its unique physical and chemical properties such as natural whiteness, fine particle size, softness and non-abrasiveness, low exchange capacity and chemical inertness over a relatively wide pH range. Some of the important physical constants of kaolin are: Specific gravity- 2.60, Index of refraction – 156, hardness 2 (Mohrs Scale) fusion temperature 1850^{o}C and dry brightness of 78 – 92 percent.The ultimate chemical composition of a typical kaolin specimen is shown in (Appendix IV).

Individual kaolin varies in many physical aspects, which in turn influence their end use. The particular commercial interest is the degree of crystallinity which influences the brightness, whiteness, opacity, gloss, film strength and viscosity. These properties makes it an important material for many industrial processes like the paper, ceramic paint, rubber, plastic and glass manufacture (Ahuwan,1997).

2.10 Kaolin Deposit in Nigeria

Nigeria has an estimated reserve of about two billion metric tonnes of kaolin deposit scattered in different parts of the country. Researchers have worked extensively on different fields due to the importance of this raw-material for economic and technological development of Nigeria (Abdulsalam and Abdulkarim 2012). The deposit in Kankara and Bauchi have shown its suitability as ceramic raw materials in Nigeria and can also be used in the development of glass ceramics (Aliet *al.*, 2008).

The bulk of the kaolinite –clay deposits in the country are either sedimentary or residual in origin and are usually associated with granitic rocks. The occurrences of kaolin have been recorded in different parts of the country and specific abundant deposits have been identified in parts of Enugu, Anambra, Kaduna, Katsina, Plateau, Ondo, Ogun, Oyo, Bauchi ,Borno Benue Ekiti and Nassarawa states out of the large deposits, only about 800 million tons of proven deposits have been quantified from the different reserves (RMRDC, 2010).A large proportion of the kaolin deposits in Nigeria are won manually with unsophisticated implements such as shovel and diggers. Field studies are required for reserve evaluation and documentation, quarry characteristics and mining design. The major problems in quarrying of kaolin include caving in of holes, influx of ground water particularly in the rainy season and presence of impurities such as quartz, feldspar, tourmaline, muscovite etc which are derived from the parent rock (RMRDC, 2012) (Appendix V).

2.11 Kaolin Processing Waste

The crude kaolin mining and processing to produce highly refined kaolin with controlled properties for industrial applications generates large amount of waste. The kaolin industry which processes primary kaolin were basically two different methods to remove the major impurities, the dry and wet process. The dry method involves the separation of the sand from the ore, which represents about 70 percent of the total waste produced. The wet method is the mud – like sludge which consists of wet sieving to separate the finer fraction, hence purifying the kaolin. Thewastegeneratedconsist of kaolinite ($Al_2Si_2O_5(OH)_4$), mica ($KAl_2(Si_3Al)O_{10}(OH,F)_2$ and quartz (SiO_2)which are major raw – materials for glass ceramic production (Chen and Tuan, 2001).

2.12 Glass Ceramics Products

Glass ceramic are poly-crystalline materials obtained through controlled Crystallisation (devitrification) of selected glass compositions. The decided compositions and its heating treatments have been studied in respect to producing glass ceramics (Strnad, 1986).

The established compositions and uses of glass ceramics are extensive and include the low thermal expansion, high thermal shock resistance and chemically durable, Li_2O-Al_2O_3 SiO_2 compositions which are based on β-quartz or β-sodumene solid solution used in both transparent and opaque cookware range tops, heat-resistant windows and telescope mirror blanks. Other notable glass ceramics are the photo machinable lithium silicates, high strength alumino silicate, mechanically machinable mica based materials and a variety of compositions withproperties such as hardness ,wear resistance, resistance to chemical oxidation, superior optical and electrical properties (James, 1995).

2.13 Nucleation and Crystallisation

The transformation of glass to form-glass ceramic is called Crystallisation . This transformation consists of two parts, called nucleation and growth. Nucleation is the key part in controlling the Crystallisation where crystalline glass phases occur.There are two types of nucleation; the first is the volume nucleation, which is a common technique used for both homogeneous and heterogeneous nucleation. The second is surface nucleation, which makes it difficult to control the Crystallisation . The nucleation process mostly ends with an undesired microstructure setting the characteristics of glass ceramics. In some parent glass compositions, nucleating agents are needed; these agents can be either metallic or non-metallic due to envisaged characteristics of the glass ceramics (Partridge, 1994).

The growth part takes place after obtaining a nucleus matching desired characteristics, the transformation in growth parts is movement of atoms and molecules from the glass across the glass-crystal interface and into the crystal, this process is temperature depending treatment to the growth of the grains (Rawlings*et al.*, 2006).

2.14 Glass Ceramic Process Route

The secret to making glass ceramic is control, selection of exact temperature, compositions and grain size distribution which are all important parameters in the process routes (Donald, 1977).

The processing of glass ceramic is similar with the processing of ceramics. In the preparation of glass ceramics, the mixture of materials that will form the desired composition is melted at a temperature generally in the range of 1000 – 1700^{o}C. A homogeneous quality glass when produced will be reduced to glasspowders, which will be subjected to controlled heat treatment which converts the glass to glass – ceramics (Partridge, 1994) as shown in the (Figure. 2.1).

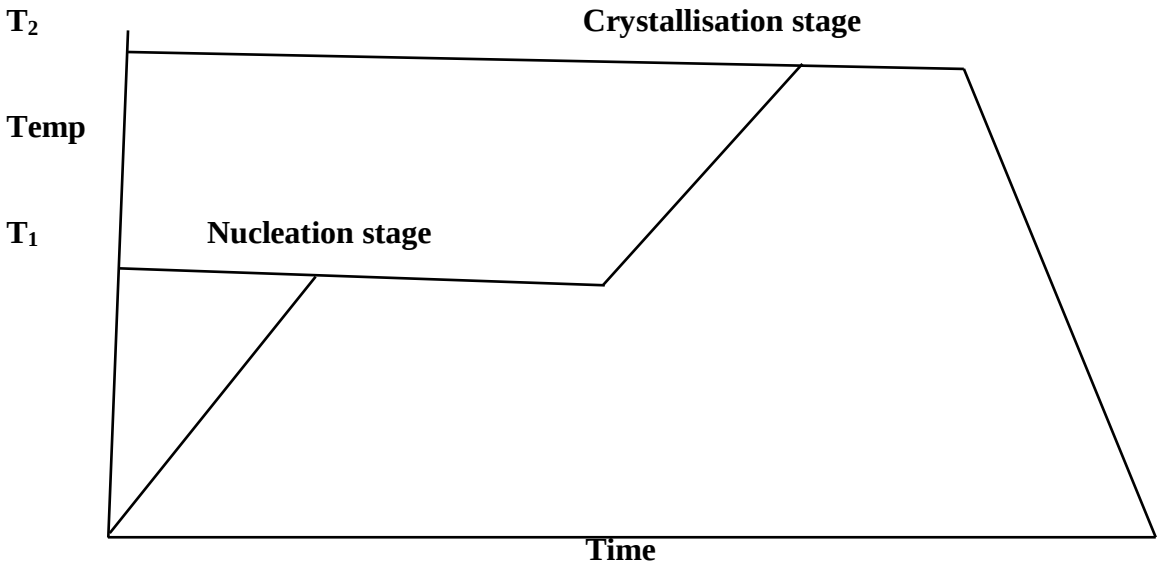


Figure 2.1 Schematic Two Stage Heat Treatment Schedule for the Production of Glass

Source: Rawlings, 2006

In the first stage, the object is reheated at a rate of 2-5^{o}C min^{-1} from ambient up to the nucleation temperature (T_1) and maintained for a given time. The optimum nucleation temperature generally corresponds to a viscosity in the range of 10^{11} – 10^{12}dpa. At the end of the nucleation stage, the temperature further increased at a rate less than 5^{o}Cmin^{-1} to the optimum growth temperature (T_2). This is for the maximum development of the crystalline phase without deformation of the material by viscous flow. After holding at temperature for the required time, the crystallized object can be rapidly cooled to ambient temperature without the need for further annealing. The periods during which the temperature is maintained for nucleation and Crystallisation are selected according to the chemical composition and the properties required of the final product. The heat treatment is designed so that the microstructure of the resultant material has one or more crystal phases existing together with residual glassy phase. The phases produced are influenced by both the major and minor constituents in the composition of the materials. The phase compositions may also be affected by the glasses, particularly for glasses of high silica contents (Partridge, 1994).

Nucleating agents promote volume nucleation and glass ceramic formation, their roles are to increase nucleation of a stable or metastable phase by increasing the bulk energy change to decrease the crystal liquid interfacial energy per unit area .Nucleating agents for oxides glasses are commonly TiO_2, ZrO_2, P_2O_5 and fluorides and water for non-oxide glasses. Nucleation through nucleating agents, are referred to as internal or bulk nucleation (Romero*et al.*, 2000).

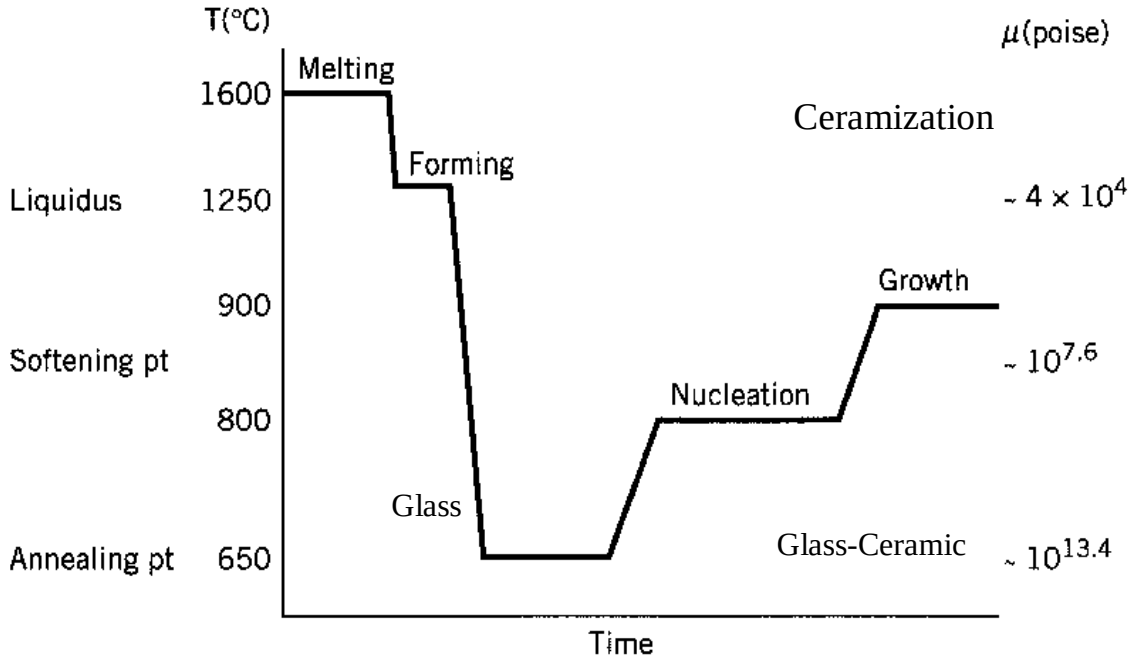


Fig. 2.2: Typical Processing Cycle for Li_2O-Al_2O_3-Si_2O Glass ceramics.

Source: Romero*et al.*, 2000).

2.15 Devitrification

Devitrification is aprocess by which glassy substances change their structure into that of crystalline solids. Most glasses are silicates in which the atomic structure does not have the repetitive arrangement required for the formation of crystals. Any form of devitrification in a glass structure will produce one degree or another of opacity. Large crystals are more prone to making the glass opaque, while small crystals evenly scattered throughout the structure have less of an impact on the optical qualities of the finished product (Ali*et al*, 2008).

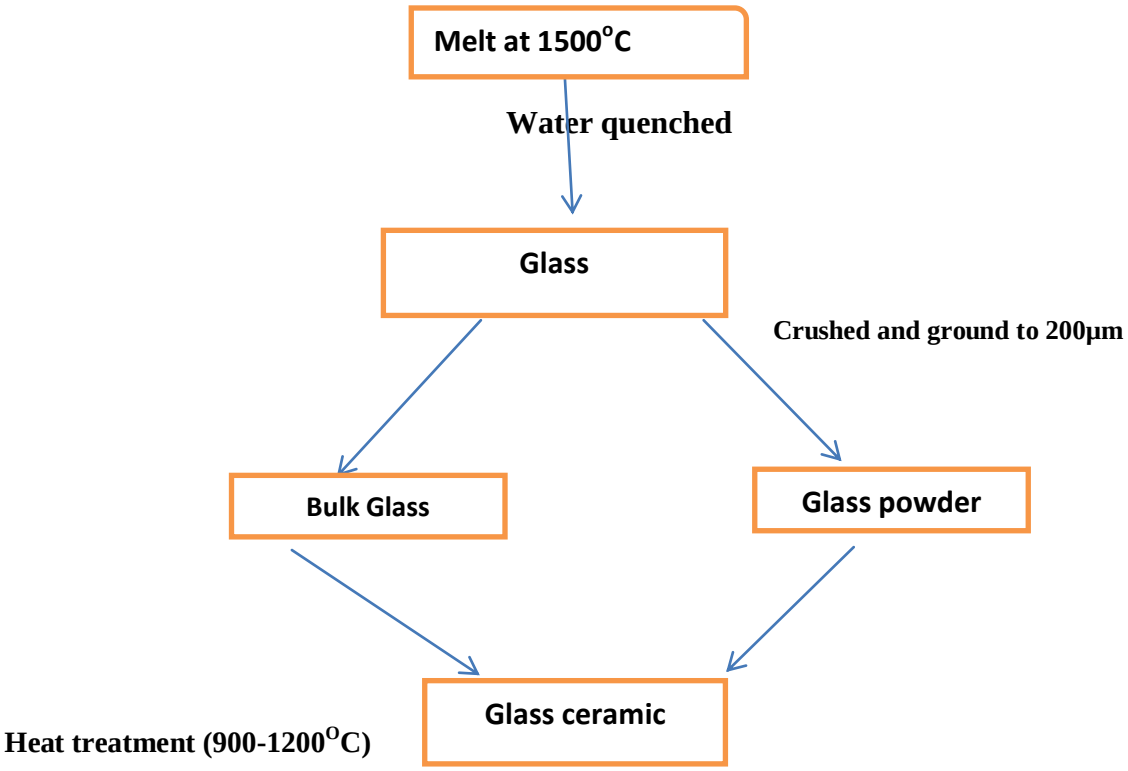


Figure 2.3: Flow Chart for Devitrification Process

Source: Mathumathi, 2000

2.16 Glass-Ceramics Composition Systems

Proper selection of compositions and the heat treatment process design produce the micro structure of the resultant material in which one or more crystal phases exist together with a residual glassy phase. The phases produced are influenced not only by the major constituents in the compositions of the material but also the minor constituents that can also have a profound effect (Partridge, 1994).

(a) Li_2O-Al_2O_3-SiO_2: This glass ceramic composition system has various crystal phases which are metastable and can break into other phases at a temperature of 900^oC. It has low thermal expansion usually, approaching zero near ambient temperature, which is derived from β-quartz or β-spodumene solid solution crystal phase. Little percentage of nucleating agents in the compositions (0-2mol %) renders the material transparent due to the fine scale of the crystal distribution of less than 50nm. The fine crystal size and the low birefringence inherent in β-quartz results in minimal light scattering which is achieved when the particle size is the same with that of the wavelength of the ambient light which bounces off and scatter, resulting to cloudiness. The degree of opacity is determined by the population of the particles, which can be adjusted by controlling the size and concentration of the crystal, this is done precisely by controlling the heat treatment cycle.This system yields products for applications such as for cookware, telescope, mirror blanks, woodstove, windows and infra-red transmitting range tops which are obtained from the combined effect of transparency, low thermal expansion, optical polishability and strength greater than glass (Macmillan, 1979).

(b) MgO-Al_2O_3-S_iO_2: This glass ceramic is based on corderite crystal phase together with otherphases like the quartz, crystobalite, enstatite and forsterite. They are characterized by highstrength, excellent dielectric properties, high thermal stability and shock resistance.

The coefficient of thermal expansion measured within the range of 0 -700^{o}C is 45 x 10^{-7o} and the fracture toughness is 2.2Mpa. $m^{½}$ and thermal conductivity of 0.0038.j/s.cm.^{o}C.Its major areas of applications are in missile radomes (Macmillan, 1979).

(c) S_iO_2-Al_2O_3-Na_2O-T_iO_2: This glass ceramic are the fine grained nepheline based on soda nepheline ($NaAlSiO_4$). This group is ordinarily expected to have high thermal expansion coefficient reflecting the property of the major crystalline phase which is structurally related to silica polymorph tridymite. The addition of barium oxide in the composition promotes secondary aluminosilicate phase known as celsian ($BaAl_2S_1O_8$). This glass ceramic has an improved thermal shock resistance and a lower thermal expansion coefficient compared to nepheline.The upper Crystallisation temperature of nepheline glass ceramic is 1100^{o}C, the major area of application is where toughness and durability are of primary concern due to the high extravagance in terms of use (Macmillan, 1979).

Typical examples of the composition and the principal crystal phases that develop in a number of glass ceramic forming systems are given in (Appendix VI).

2.17 Glass Ceramic Production Methods

Glass ceramic articles may be produced by three routes namely:

i. Heat treatment of solid glass, known as conventional or traditional route.
ii. Control cooling of a molten glass, known as petrurgic method.
iii. Sintering and Crystallisation of glass powders

2.17.1 Conventional Method

In this method, glass is devitrified by a two stage heat treatment. The first stage is a low temperature heat treatment at a temperature that gives a high nucleation rate, thus forming a

high density of nuclei throughout the interior of the glass, this is important as it leads to desirable microstructure consisting of a large number of small crystals. The second stage is a higher temperature required to produce the growth of a nuclei at a reasonable rate. Glass production and the subsequent heat treatment are in general, energy intensive and therefore expensive (Atkinson and McMillan, 1977).

2.17.2 Petrurgic Method

This method leads to the development of certain glass ceramic by a controlled, usually very slow cooling of the parent glass from the molten state without a hold at an intermediate temperature. In this method, both nucleation and Crystallisation can take place during the cooling, this is more economical than the conventional method (Romero*etal.*, 2000).

2.17.3 Powder Sintering Method

The shaping by cold compacting of powder followed by a high heat treatment to sinter the compact is a common route for the fabrication of ceramics and it has also been employed for glass ceramics production (Hing*et al.*,1977). There are limitations on the size and shape of component that may be cold compacted and also the cost of producing the powders, this method is only used if an obvious benefits is identified. In most cases there is little advantage in compacting and sintering a glass ceramic powder because a high sintering temperature is required and the properties of the final product do not differ significantly from those produced by other routes. The economic advantage of this method is the powders are densified at relatively low temperatures by exploiting a viscous flow sintering mechanism to obtain the required glass ceramic microstructure in that both the densification and Crystallisation may take place during a single sintering step. The powder technology route is suitable for the

production of a range of advanced materials, including glass ceramic with specified porosities and glass ceramic matrix composites (Rawlings *et al.,* 2006).

2.17.4 Uniaxial Pressing Technique

In uniaxial pressing, a required mold is filled with dry powder, and a hard metal puncher 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 by the use of organic additives which will decompose. Uniaxial pressing can be easily automated and is particularly suited for forming components with a simple shape such as flat disc and rings that can be produced to close dimensional tolerance (Davies*et al*, 1970).

2.18 Particle Size

Particle size distribution is a major aspect for the characterization of a glass ceramic powder. It is important depending on which consolidation or shaping technique will be used. Studies have shown that the objective of consolidation step is to achieve maximum particle packing and uniformity, so that minimum shrinkage and retained porosity will be achieved during densification. Thereplacement of fine glass powder with fine aggregate also has significant effect on the properties of glass ceramic samples (Nur,2010). Particle size distribution test was conducted on recycled glass powders using sieve analysis, with coarse powders below 88μm and finer powders below 37μm to determine the temperature and time necessary to achieve sintering.Itwas observed that lower particle size require less time to achieve sintering (Bernardo, 2005).

2.19 Forming

Articles of many shapes can in principle be made by rolling, casting, pressing, blowing, and drawing or by any other glass processing method that already exist or may be invented. Forming process begins with finely ground powder with control of particle size distribution which is required to achieve optimum properties for intended application. High strength ceramic require very fine particles which is typical for the achievement of fine grained microstructure with minimum flaw size. Many different powder synthesis and sizing techniques have been developed to achieve the various required distributions. The most popular technique used in glass ceramic processing is the pressing method of either uniaxial isostatic or hot isostatic pressing (Richerson, 2006).

Products produced by pressing include ceramic titles and porcelain products, coarse grained refractories, grinding wheels and structural clay product. Pressing by means of punches in hardened metal dies, commonly called uniaxial pressing, is widely used for pressing parts thicker than 0.5mm and parts with surface relief in the pressing direction. Isopressing, commonly known as isostatic pressing are used on flexible rubber molds to produce shapes with relief in two or three dimensions, shapes with one elongated dimension such as rods and tubes, and very massive product with thick cross section (Nur,2010).

2.20 Densification

Densification is a glass ceramic process also known as compaction. Ceramic powders are commonly compressed in a die to produce net shape green bodies prior to final sintering. Density gradient in the resulting compacts may cause distortion in the shape during sintering to obtain the desired final shape (Reed, 1995).

2.21 Sintering

Sintering commonly refers to processes which involve assembly of particles, compacted under pressure, chemically bonded into coherent body under the influence of an elevated temperature. The temperature is usually below the melting point of the major constituents .Sintering process has been an important operation in the fabrication of various materials into useful articles (Gaillard *et al* 2004). The objectives of sintering are to remove pores at the starting particles, combined with growth and strong bonding between adjacent particles. Sintering is the last stage before the end product achieved and the differences in the sintering temperature affect the properties of the final products (Richerson, 2006).

2.21.1 Solid State Sintering

Solid state sintering is achieved through changes in particle shape without the presence of liquid. The sintering process involves heating material formed by the compaction at ambient temperatures of pure fine particles. This is a spontaneous process and must be accompanied by a decrease in free energy of the sample. The most important driving force for sintering is the reduction in solid or vapour surface area when the individual particles fused together and the larger particles at the expense of smaller ones. Solid state sintering is of restricted practical use for ceramic materials and fairly high temperatures are involved (Davies et al, 1970).

2.21.2 Sintering Mechanism

Sintering occurs by atomic diffusion processes that are stimulated by high temperature. This phenomenon causes substantial particle re-arrangement and consolidation especially in loosely packed bodies (Yan, 1991).

During sintering, the atoms in the powder particles diffuse across the boundaries of the particles, fusing the particles together and creating one solid piece. Sintering phenomenon involves fusion of particles, volume reduction, decrease in porosity and increase in grain size. Amorphous materials sinter by one or more mechanisms occurring singly or in parallel depending on the materials system and the sintering conditions. The mechanism include: Surface diffusion of atoms, evaporation or condensation of atoms, grain boundary diffusion and plastic deformation (Rahaman,2003). In general bulk transport mechanisms such as volume diffusion, grain boundary diffusion, plastic flow and viscous flow result in shrinkage or densification while surface transport does not. However, surface transport is important in inter-particle neck growth and the sintering of some covalent solids and low –stability ceramics. The entire sintering process is generally considered to occur in three stages as indicate in(Appendix VII).

There is no clear cut distinction between the stages since the processes that are associated with each stage tend to overlap each other. The initial stage is characterized by particles rearrangement, formation and growth of neck by diffusion (lattice or grain boundary), vapour transport, plastic flow or viscous flow. Intermediate stage is considered to begin when the pores have attained their equilibrium shapes as dictated by surface and interfacial energies. In the final stage, isolated pores are eliminated and there is grain growth (Nur, 2010).

The driving force for all these mechanisms is the tendency for the material to reduce its chemical potential or energy and this is accomplished by material transport from regions of high chemical potential to region of low chemical potential (Okuyama, 2006).

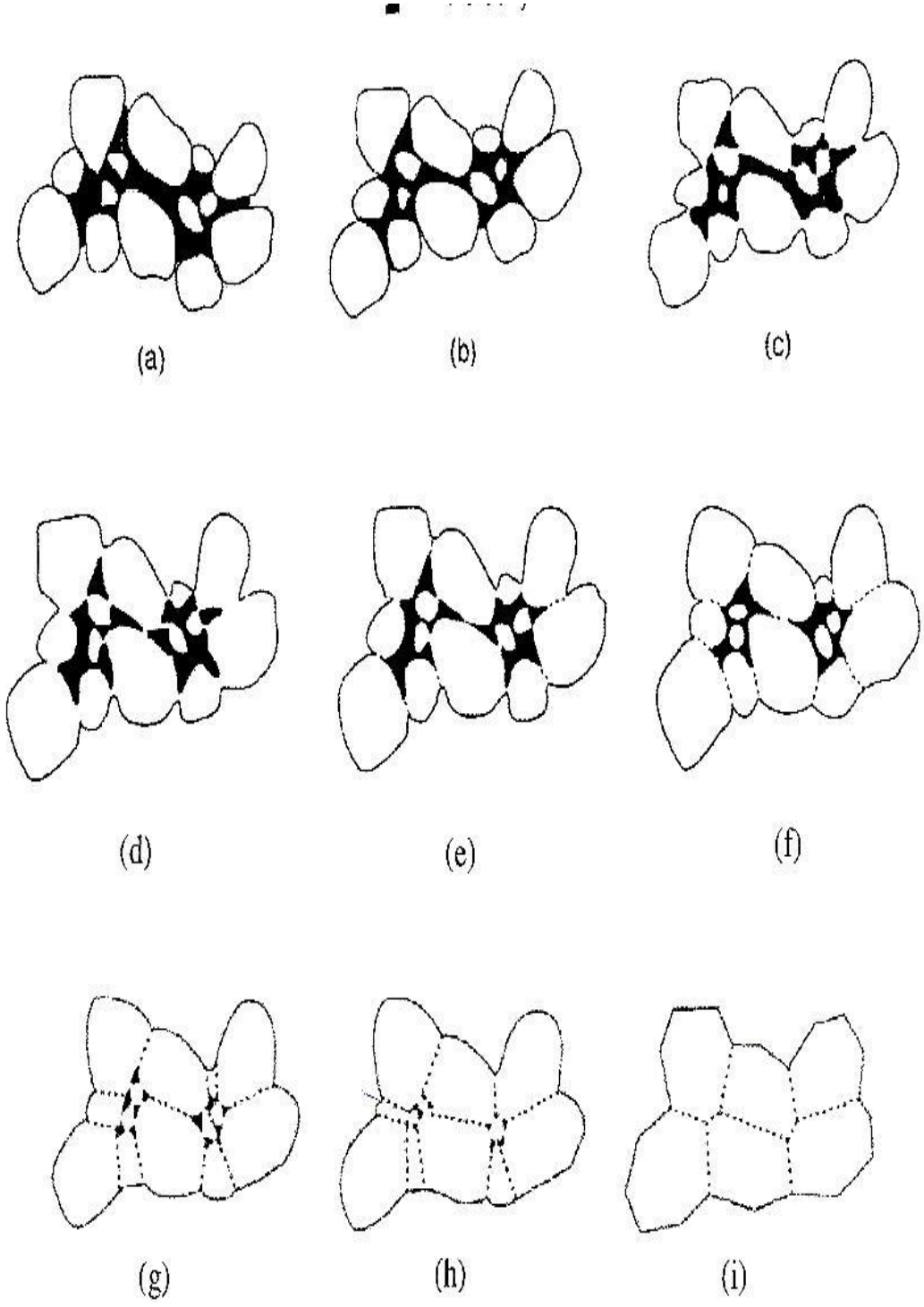


Fig. 2.4: Changes that occur during Sintering

Source: (Richerson, 2006).

2.23 Types of Glass Ceramics

Glass ceramics are classified by the composition of their primary crystalline phases, which may consist of silicates, oxides, phosphates, borates or fluorides (Ray *et al.*, 2000). Glass ceramics for domestic or technical use are made from pure materials. They are generally white and grouped according to their major components like Li, Mg, B, Ba. In other to vary the final properties of these products, T_1O_2 or P_2O_5 is used as a nucleating agent. All commercial as well as most experimental glass ceramics are based on silicate bulk glass compositions.

2.23.1 Commercial Glass Ceramics

The first commercially viable glass ceramic was developed in the aerospace industry in the late 1950s as radomes to protect radar equipment in the nosecones of aircraft and rockets. Glass ceramics used in this application must exhibit challenging combination of properties to withstand critical conditions resulting from rain erosion and atmospheric re-entry; homogeneity, low dielectric constant; low coefficient of thermal expansion; low dielectric loss, high mechanical strength, and high abrasion resistance. No glass, metal or crystal can simultaneously meet all these relevant specifications. A range of commercially successful glass-ceramic for consumer applications include famous brands of low expansion products that are resistant to thermal shock, corning ware and vision – a transparent glass- ceramics. These products rely on their relatively high toughness compared with glasses, appealing aesthetics and very low thermal expansion coefficient(Holland and Beall, 2010).

The most important system commercially is the Li_2O-Al_2O_3-SiO_2 system with additional components such as CaO,MgO,ZnO, BaO, P_2O_5, Na_2O and K_2O. Fining agents include AS_2O_5 and SnO_2.ZrO_2 in combinations with T_1O_2 are the most commonly used nucleating agents. The main crystalline phase is a β-Quartz solid solution, which is highly anistropic and has an overall

negative thermal expansion coefficient. Li_2O-Al_2O_3-SiO_2 glass-ceramics can sustain repeated and quick temperature changes of 800^oC to 1000^oC (McMillan, 1979 and Strnad, 1986) (AppendixVIII).

2.23.2 Machinable Glass Ceramics

Machinable glass ceramics such as Macor, Dicor, vitronit and photored are some brands which rely on mica crystals, in their microstructure. Their high thermal expansion, coefficient readily matches most metals and sealing glasses. They exhibit zero porosity and in general are excellent insulators at high voltages, different frequencies and high temperatures. Typical Macor applications include insulators and support for vacuum environment feed-troughs, spacers' headers and windows for microware tube devices, sample holders for microscope, aerospace components, welding nozzles, fixtures and medical equipment (Holland and Beall, 2010).

2.23.3 Dental Glass Ceramics

Biocompatible glass ceramics are used in dental restorations; they have superior aesthetics with low thermal conductivity which makes them comfortable in the mouth. Lithium disilicate glass ceramic are ideal for fabricating single tooth restoration, this glass ceramic produces high aesthetic results and its hardness is similar to that of natural teeth and it is stronger than other dental ceramics. The material can either be pressed or machined to the desired shape in the dental laboratory because of its high strength and toughness. This glass ceramic possess true-to-natural looking light transmission versatile applications and a comprehensive spectrum of indications (Edgar, 2010).

2.23.4 Bioactive Glass Ceramics

This glass ceramics have been used as granular fillers, artificial vertebrae, scaffolds, iliac spacers, spinous spacers, intervertebral spacers, middle ear implants and as other types of small-bone replacements. Numerous clinical trials have shown intergrowth between this glass ceramic and human bone (Kokubo, 2008; Hench*et al.*, 2010).

A new glass ceramic based on Na-Ca-Si-β-O system that has a young's modulus closer to that of cortical bone with much higher bioactivity desired for several application but with some compositional modifications and greater than 99.5 percent crystallinity has been developed (Roriz*et al.*, 2010 and Edgar, 2010).

Another interesting class of bioactive glass ceramics is heat generating bioactive or biocompatible glass ceramics intended for use for hyper thermic treatment of tumors. Glass plates of $CaO\text{-}SiO_2\text{-}Fe_2O_3\text{-}B_2O_3P_2O_5$ were ceramized, the resulting glass-ceramic containing magnetite and wollastonite crystals showed high-saturation magnetization This glass-ceramic formed a calcium and phosphorus rich layer on its surface and tightly bonded with bone within some weeks of implantation (Koichiro*et al.*,1991).

2.23.5 Electrically Conducting and Insulating Glass Ceramic

Electrically insulating materials, such as spinel-enstatite canasite and lithium disilicate glass ceramics as well as glass ceramic substrates are used in magnetic media disks for hard disks drive. These materials offer the key properties necessary for higher density, smaller and thinner drive designs. These glass ceramics also have high toughness, provide low surface roughness and good flatness ultralow glide heights and excellent shock resistance (Holland and Beall, 2010).

2.23.6 Transparent Glass Ceramics

Transparent glass ceramics based on fluoride, chalcogenide and oxyfluoride dope with rare-earth ions have been successfully used for wavelength up-conversion devices for europium-doped wave guide amplifiers. Transport mullite, spinal, willemite, ghanite and gelenite-based glass ceramics doped with transition metal ions have been developed for use in tunable and infrared lasers, solar collectors and high temperature lamp applications The vast majority of existing transparent glass-ceramics rely on crystal size less than about 200 nanometers and havesmall or moderate crystallized fractions of 1 – 70 percent (Edgar, 2010).

2.23.7Glass – Ceramic Armor

Ceramic material are used particularly in armors for which low weight is important, bullet-vests and armor for automobiles, aircraft and helicopters especially in cockpits or seats and for protection of functionally important parts. The first and still used ceramic armor materials consist of high modulus and high Al_2O_3, although its density is quite high of about $4g/cm^3$ (Edgar, 2010).

Most glass-ceramics have lower hardness and young's modulus than the above-described ceramics, but have the great advantage of low density and much lower cost. Moreover, glass ceramics can be transparent to visible light. Alstom's Transarm, a transparent glass ceramic armor is based on lithium disilicate. It originally was developed for protective visor for bomb disposal work. Another example is Schott's Resistant, arange of low-expansion glass-ceramics that can be opaque or transparent and are intended for substrate for vehicular and personal armor systems (Edgar, 2010).

2.24 Properties of Glass ceramics

Glass ceramic materials are considered as non-porous, consisting of fine crystals uniformly distributed throughout a residual glass phase. It contain arbitrarily oriented crystals, their properties are independent of direction. The extremely fine and uniform crystal structure, even distribution throughout the bulk of the material, and the absence of pores are important characteristics in the structure of the glass ceramic (Strnad, 1986).

The properties depend primarily on the physicochemical properties of the main crystalline phase and the size of the crystal, residual glass, the amount and morphology of the glass phase present in the total bulk material and the interface formed between the crystalline and glass phase (McMillan, 1979).

2.24.1 Mechanical Properties

Mechanical properties such as strength, elasticity, hardness, and abrasion resistance are influenced by particle size, and volume fraction of the crystalline phase.Increased strength over the parent glass is a result of fine grain and uniform microstructure, the tensile strength of the glass ceramic system and also the heat treatment employed. The system containing MgO have greater strength as the main crystalline phase is the corderite. Generally, the strength of a glass ceramic material is high compared with ordinary glass and with other types of ceramics (Strnad, 1986). The young's modulus and bending strength of glass ceramic materials compared with other materialsare shown on (Appendices IX and X).

2.24.2 Density

The densities of glass and glass ceramics are often different, and volume change usually occurs during heat treatment. Oxides such as BaO, and PbO tend to confer high densities upon glasses

and results to glass-ceramics with high densities. Similarly glass ceramics having lithium as a major constituent have low densities while increase in the proportion of MgO, CaO, ZnO, BaO or PbO at the expense of Al_2O_3 or S_1O_2 in glass-ceramics systems leads to higher densities (Strnad, 1986).

2.24.3 Thermal Properties

The thermal expansion coefficients of glass ceramic are different from that of glass. This is as a result of the formed crystal phase present, which is selectively controlled by a suitable heat treatment process. Glass ceramics are very strong with good resistance to thermal shock; the thermal conductivity of the glassceramic material is an important value to be employed as heat conductors or as insulators. The thermal conductivity can be controlled positively or negatively with a range of stability from about 400^{o}C to 1,450^{o}C with low conductivity. Glass ceramics have higher thermal conductivity values than glass but lower than ceramics made from pure oxides (Mathumathi, 2000).

2.24.4 Optical Properties

The important property is radiation transmission, some glass ceramics are transparent, but they are mostly opaque. The passage of light is affected primarily by the crystal size. The major factor affecting the passage of light is the optical anisotropy and the difference in refractive index between the glass and crystalline phases (Edgar, 2010).

2.24.5 Electrical Properties

The electrical conductance of glass ceramic is dependent on the presence of mobile species, primarily alkali metal ions increases with increasing content of these ions. The electrical

resistivity also decreases with increasing temperature, but can be increased by having non – alkali glass ceramic materials based on S_1O_2-Al_2O_3-ZnO with the addition of B_2O_3, BaO and CaO (Strnad, 1986).

2.24.6 Dielectric Properties

The dielectric breakdown strength becomes important when the glass ceramic materials are to be used at a high voltage gradient like insulators or condensers. The main factors affecting these values are very high homogeneous, free grain structure and non-porous nature of the glass ceramic material (Figure 2.5).

The ferroelectric properties permit electrical control of double refraction or scattering, useful in telecommunications for switches or for spectral filters. If the glass phase contains the oxides of the transition metals or rare earths, then the system can contain crystalline phase of magnetic ferrites, garnets or magnetic plumbites and the glass ceramic material can be used in high frequency technology, provided it has a high electrical resistance (Mathumathi, 2000).

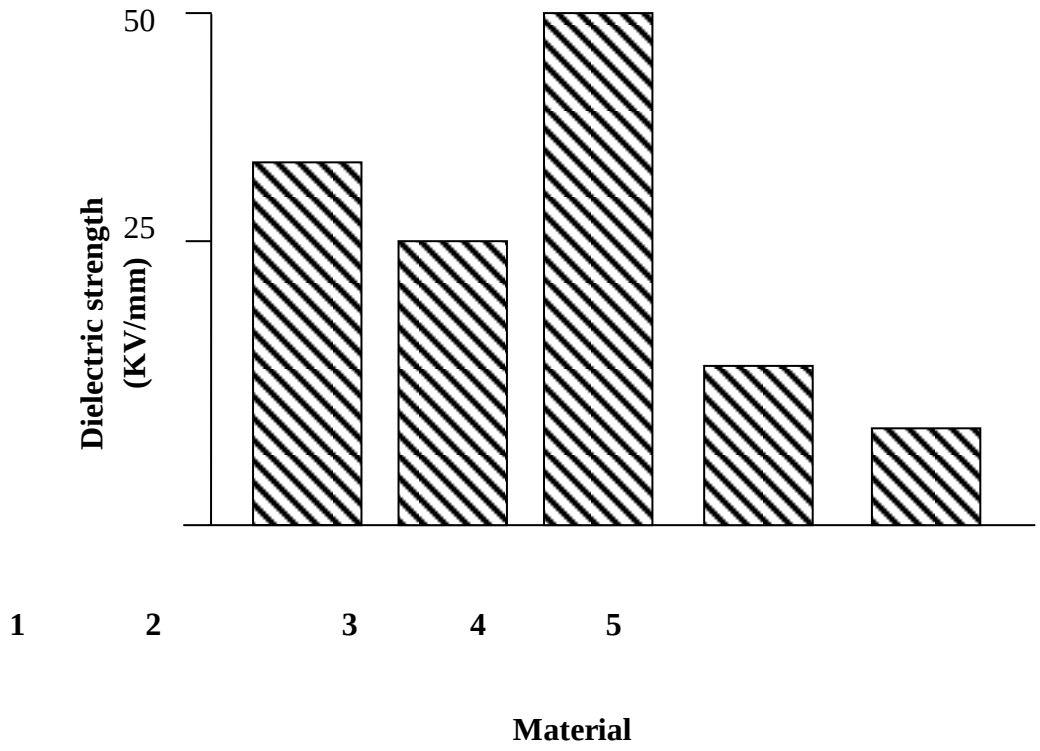


Figure2.5: Dielectric Strength of Materials

Source: Strnad, 1986.

Key:

1 – Glass, 2 – Ceramics; 3 – Glass ceramics

4 – Acrylates; 5 – Nylon

2.24.7 Chemical Properties

The chemical stability and durability of glass ceramics is affected by the composition of the crystalline phase, the composition and amount of residual glass phase and its morphology. The achievement of higher chemical durability in glass ceramic require the volume of residual glass phase to be small for the chemical composition of the phase to favour good stability. The chemical composition of the residual phase is affected by the heat treatment process and also by the initial glass composition. A silica – rich glass phase containing Al_2O_3 and ZnO with alkali-earth oxides favours attainment of good chemical durability (Strnad, 1986).

2.25 Applications of Glass Ceramics

Glass ceramics materials used in various application possess excellent combined properties that cannot be achieved by other means, due to their manufacturing methods (McMillan, 1979;Psarsa*et al.*, 1987).

The transparent low expansion glass ceramics have improved optical properties, greater thermal stability and strength than the parent glass, these are capable of being shaped by fast and flexible glass forming process with wide applications for industrial usages, such as fire screens for heating equipment, heat resisting security windows, hosting medium for transition metals, heat resisting panels for furnaces, heat – resistant and high pressure transparent containers and block gauges for calibration of high precision instruments (Wada and Kawamura, 1981).

The white opaque glass ceramic has excellent thermal shock resistance because of its low expansion coefficient ($11x10^{-7o}C$) about one – third of ordinary heat resistance glasses and also of its high endurance with maximum service temperature of 1100^oC. This excels the transparent in mechanical properties, such as bending and impact strength for use as ordinary cooking ware, trays and shelves for microwave oven because it has fairly low electrical loss at

the frequency of 2.45$GH^{\cdot}_{2}$ specified for the microwave ovens Glass ceramics for structural applications are widely used for construction (Matteucci *et al.*,2002). The commercial application of sintered glass ceramics includes: devitrify frit solder glasses for sealing television tubes, co-fired multilayer substrate for electronic packaging, marble like floor and wall tiles and some bioactive glassceramics (Pascual *et al.*,2005).

Glass ceramic fordental application is as result of properties such as high strength, toughness, transparency, biocompatibility, chemical durability and relatively low hardness (Edgar, 2010).

2.26 Production of Glass Ceramics from Wastes Materials

The rapid increase in municipal and industrial growth and the generation of buildup solid wastes has necessitated finding new methods of disposing these wastes (Numerow, 1983). Silicate residues are significant group of materials when considering the recycling and reuse of industrial wastes such as coal power station ash, bottom – ash and fly – ash from waste incinerators, slag from steel production and glass cullet and combustion dusts (Boccacciniand Rees, 2002).

The differing compositions and morphology of these wastes necessitate the employment of specific processing routes and conditions that would result in glass ceramics with range of microstructures and properties (Rawlings*et al.*, 2006).

Initial composition and the heat treatment conditions are the most important parameters that affect the kind of crystalline phases that occur in the glass ceramics and the final properties of the material. The glass ceramic is heated to the maximum nucleation temperature and held for a sufficient time for stable nuclei formation, following nucleationthe temperature is raised to the Crystallisation temperature and held at that temperature for a selected period of time where the crystal growth occurs. The nucleation and Crystallisation of glasses are important in

understanding the stability of glasses in practical application and in preparing glass ceramics with desired microstructures and properties (Ray*et al.,* 1991).

Glass ceramics based on wastes can have different applications, such as architectural and anti-corrosive equipment, heat and sound insulation material, if porous, floor and roofs in industrial and public buildings, interior facing of containers for the chemical industry and as road surfacing material. Glass ceramics prepared form kaolin refining waste and silica sand was found to show excellent mechanical and chemical durability (Kharter, 2002).

Glass matrix composites intended for the immobilization of nuclear waste have been manufactured, where two different matrices, a borosilicate glass and a lead silicate glass were proposed for encapsulating lanthanum and gadolinium zirconate having pyrochlore crystalline structure. The fabrication of the composites involved powder mixing followed by cold pressing and pressureless sintering at relatively low temperatures (<620^{o}C) which resulted to relatively high densification even with substantial loading of pyrochlore phase (40 Vol%). The absence of micro cracks due to close matching of thermal expansion coefficients of the composite constituents together with the strong pyrochlore particle and glass matrix interfacial bonding, the composites showed good mechanical properties (Boccaccini*et al.,* 2004).

The densification and Crystallisation of a glass ceramic containing B_2O_5,SiO_2,P_2O_5 and SrO were investigated and the major crystalline phase sintered below 1000^{o}C.It was found that its electrical properties such as the dielectric constant, the resistance and also voltage were satisfactory (Chen and Jin, 2004).

Fly ash and glass wastes using a specific particle size and heat treatment was used to develop glass ceramic at sintering temperature of 700 – 930^{o}C. The mechanical, thermal and chemical properties of the material, measured and analyzed showed good properties which were influenced by the grain – sizes of the glass waste and the fly ash (Karamanov*et al.,* 2003).

Bottom ash and glass waste coming from municipal solid waste incineration and community glass recycling program and industrial waste are particularly suitable to be subjected to Devitrification process, leading to the production of alkaline silicate colored glasses with good chemical properties capable of being transformed into surface nucleated basaltic glass – ceramics. This material was investigated using DTA, SEM and XRD. The results show good chemical durability both in alkali and water (Luisa*et al.,* 2002).

$CaO\text{-}MgO\text{-}Al_2O_3$: glass ceramic composition prepared from a mixture of waste generated from refining of kaolin clay and dolomite in a mass ratio of 65/35 and 75/25 were melted at 1350^oC and quenched in water to obtain glasses which were used to prepare glass ceramics. Crystallisation of the parent glass occurred above 900^oC producing diopside ($CaMgSi_2O_6$) and the mechanical properties, chemical durability and thermal expansion coefficient of the glass ceramic were investigated and found to be excellent for application as building materials and ceramic tiles (Kiyoshi *et al.,* 2004).

Glass ceramics prepared from mixture of wastes generated from refining of silica and kaolin clay and paper sludge ash in a mass ratio of 55/45, melted at 1400^oC was quenched in water to obtain glasses used to prepare glass ceramics. Crystallisation of the parent glass occurred above 950^oC producing Quartz solid solution at 1000^oC and cristobalite at 1100^oC as major crystalline phases. The product showed excellent bending strength ranging from 63 to 66MPa and Vickers micro hardness values from 6.0 to 6.4 GPa. The average coefficient of thermal expansion ranges from $6.3x10^{-6}/^oC$ to $8.1x10^{-6}/^oC$. Chemical durability is good in alkali but poor in acid solution. It showed better performance than commercial glass ceramics prepared solely from wastes as starting materials (Tomohiro *et al.*, 2006).

Crystallisation capability of parent glass produced form mixture of coal ash and sodalime glass waste was investigated using differential thermal analysis (DTA), X –ray diffraction (XRD)

and scanning electron microscopy (SEM). Different glass particle size distributionswere considered in the range of 20 - 50μm. The Crystallisation phases formed as confirmed by XRD analysis are pyroxenes, diopside, augite and plagioclase (Francis *et al.,* 2004).

Panel glass from dismantled cathode ray tubes, mining residues form feldspar excavation and lime from fume apartment systems of the glass industry have been employed as raw-materials for several glass composition. The prepared glasses were grounded into fine powders and subjected to sintering treatment at low temperatures of 880 – 930^{o}C, with concurrent Crystallisation, sintered glass ceramic was obtained. The mechanical properties, such as bending strength and aesthetic appearance of the material together with the simplicity of the manufacturing method are promising for application in the building industry (Bernardo *et al.,* 2007).

Glass wastes showed efficient fluxing agent when used as an additive in glass ceramic composition. It accelerates the densification process with some positive effects during firing. The use of small amounts of glass powders in addition to feldspar showed good results of mechanical and technological properties that represents the reliability of the product (Luz and Ribeiro, 2007).

Glass ceramics developed from zinc hydrometallurgy waste and glass cullets exhibit high density and strength depending on the amount of cullet present. The strength of the glass slightly increase as the content of the glass cullet decreases (Hanpongpun*et al.,* 2007).

Sintering process was employed to produce glass ceramic using coal bottom ash and soda lime glass culets using 100, 70, 50 and 30wt% bottom ash, the particle size was same for all the formulations. The mixtures containing 50wt% bottom ash had its particle size distribution changed. The samples formed by dry pressing and fired at 950, 1050 and 1150^{o}C were evaluated for linear shrinkage, water absorption, scanning electron microscopy and mechanical

strength. It was observed that the linear shrinkage increases with increasing firing temperature and that the finer powdered particles influence on water absorption and mechanical resistance of the ceramic bodies fired at 1050 and 950^{o}C was not significant (Daniela and Carlos, 2007).

The effect of TV and PC Cathode tube and screen glass additions of 5wt% and 10wt% to a porcelain stone ware body, in replacement of feldspar, were evaluated by stimulating the tile making process. The presence of glass allows preservation of good technological and mechanical properties, complying with the latest requirement of industrial practice. The presence of 5wt% of the cathode glass tube brought about lowering of the maximum densification temperature and also the activation energy (Romualdo*et al.*,2007).

Glass ceramics produced from coal fly ashes by mean of controlled nucleation and Crystallisation were analyzed on the basis of DTA, SEM and XRD, the results revealed that the main crystalline phases were diopside and aluminum augite and the microstructural observation clearly indicated that the Crystallisation volume increased when the length of thermal treatment time increased and the glass ceramic samples produced from industrial waste have high density micro hardness values with negligible porosityand water absorption. The glass ceramics also showed resistance to alkali solution in contrast to acid solutions which make them attractive for industrial use in the construction, tiling and cladding application (Erol*et al.*, 2007).

The mixture of raw materials and mining residue was investigated using XRD before treatment at 1350^{o}C for 2 hours. The glass melted was and subjected to drastic cooling which forced the samples into a number of fragments before milling to a dimension of 37μm and pressed at 40Mpa. The process continued with sintering at 960^{o}C for 30 minutes. Fast treatment of mixture of industrial waste has been successfully transformed into dense and strong sintered glass ceramic with short holding times and a very rapid heating (Bernardo *et al.*, 2007).

The influence of binder on the properties of sintered glass ceramic was investigated and determined by using sieved coal fly ash of 180μm grain size which was humidified with 5wt% distilled water without any additives and cold pressed. Other samples were prepared using the coal fly ash addition of polyvinyl alcohol (PVA) were added and were cold pressed using 40 tons in a die shape,dried in electric oven at 383K for 2 hours and placed on alumina bricks and heated at 10K/min nucleation temperature and soaking for 15, 30, 60 minutes for Crystallisation and cooled to produce a glass ceramic (Erol*et al.*, 2009).

Kaolin processing waste was characterized for its stability as an alternative ceramic raw material for the production of porous technical ceramic bodies. The waste was physically and chemically tested, and evaluated for its suitability. Several formulations were prepared and sintered at different temperatures. The sintered samples were tested to determine their porosity, water absorption, fire shrinkage and mechanical strength, the results indicated that the waste consisted of quartz, kaolinite and mica and the ceramic formulation with 66% of waste can be used to produce ceramic with porosities higher than 40% and strength of 70MPa (Romualdo*et al.*, 2008).

Glass ceramics were synthesized from fly-ash of a thermal power plant and waste glass cullet as starting materials. The SEM and XRD analysis revealed that glass ceramics heated at 950^{o}C and 1000^{o}C exhibited favourable improvements in chemical durability, since their crystalline phases maintained the amount of alkali ions such as sodium ions and showed smaller calcium ions variation between, before and after acid immersions. The compressive strength and bending strength of the material was good regardless of whether before or after immersion in acid solution. The comprehensive strengths were 236.4- 279.7 MPa (before immersion) and 192.1 – 248.6 MPa (after immersion) and the bending strengths were 72.8 -94.9 MPa (before immersion) and 55.3 – 72.6 MPa (after immersion) as the heat treatment temperature increased

from 850^{o}C – 1000^{o}C. This showed mechanical properties strong enough for practical usage (Soon-Do and Yeon-Hum, 2008).

Furnace slag waste mixed with 5-10wt% potash feldspar powder was mixed and milled. The blended powders were uniaxially pressed in a steel die at room temperature using hydraulic pressure of 40-60 MPa without binder. The samples formed were sintered in air at temperature of 720-760^{o}C and Crystallisation temperature of 800-900^{o}C with firing rate of 2-5^{o}C/min followed by high temperature heat treatment of 1200^{o}C. The blended powders were examined for density, chemical and mechanical properties which proved to be excellent (Chen*et al.*, 2009).

Kaolin processing waste was used for the production of ceramic tile and dense mullite bodies,several formulations were prepared and sintered at different temperatures. The sintered samples were characterized to determine the porosity, water absorption, firing shrinkage and mechanical strength, the results showed that the ceramic tile formulation of up to 60% of waste could be used for the production of tiles with low water absorption (0.5%) and low sintering temperature of 1150^{o}C. Mullite formulation with more than 40% of kaolin waste could be used in the production of bodies with high strength of about 75 MPa which can be used as refractory materials (Romualdo *et al.*, 2009).

Low cost homogeneous single phase growth ofmullite was obtained by directly mixing alumina and coal ash and heated to a high plasma temperatures produced by TAP touch of low power (10kw). Equal weight percentages of alumina and coal ash are necessary for a complete homogenous and single phase growth of mullite, which occurs at 920^{o}C. The weight percentage of alumina and coal ash, in addition to mullite phase, Quartz is formed. The problems encountered in the conventional sintering method in the form of low bulk, grain boundary diffusion of Mullite and very long processing time are eliminated in TAP plasma process. Low

cost raw materials are used hence cost of production of mullite is reduced compared to conventional sintering method (Suriyanarayanan*et al.,* 2009).

Boric and phosphorus oxide (B_2O_3& P_2O_5) were used to determine the effect of sintering process in glass ceramics development. The sintering process occurs at 800-1000^oC for 6 hours, the sintering and Crystallisation behavior were examined by XRD and SEM. The rate of shrinkage was high with 2% B_2O_3 and P_2O_5 and low with 5% P_2O_5, minor addition of P_2O_5 and B_2O_3 shows good sintering behavior (Wu *et al.,* 2010).

Cement Kiln waste was successfully used for making glass ceramics material with valuable properties that can be used for different purposes such as floor, wall tiles and sewage pipes. Cement dust that exceed 70wt% of the glass ceramic batch possess high hardness indicating high abrasion resistance which make them suitable for many applications under aggressive mechanical conditions (Khater, 2010).

Glass ceramics manufacturing have been considered as a very effective method of utilization of industrial wastes. Crystallisation of sintered glass ceramics prepared from vitrified mixtures in the range of 68-80% Kaolin, Al_2O_3 and T_1O_2 was investigated. Initially, the parent glass was prepared and the product obtained was heat treated at 1000^oC. The Crystallisation behavior was studied by x-ray diffraction and scanning electron microscopy. The examined microstructure was in accordance with surface nucleation which leads to good mechanical properties (Mihailova*et al.,* 2011).

Organic waste obtained from sugar cane bagasse ash was used to produce glass ceramic material. The major component of the ash as analyzed is SiO_2 and among the minor components are some minerals which serves as the fluxing agents which shows the potentials of transforming silicate based residues into glass ceramic products of great utility (Teixeira*et al.,* 2011).

Solar panel waste glass was recycled and converted into a new glass ceramic material. The crystallized phases were corderite and anorthite. The material was heated to 600^{o}C and 850^{o}C, the hardness and Crystallisation of the glass ceramic decreases, the density, hardness and flexural strength were strongly correlated with each other and increase with degree of Crystallisation with the sintered samples in accordance with the type of crystalline phases (Lin and Cheng, 2011).

Fly ash and waste glass were used to produce glass ceramics at the optimal sintering temperature of 1000^{o}C with 1 hour isothermal time and heating rate of 10^{o}C/min. The composite was produced with the addition of 40%wt waste glass and fly ash. It showed density of 2.180kg/cm^{3} and increased bending strength from 9.93±3 to 63.18±4, MPa and E-modulus from 4.23±2 to 30.55±3GPa, porosity of the composite was 14.32±2% and linear shrinkage of 15.77±2%. The chemical and physical properties of the dense material make them suitable for a wide range of applications in the building industry (Biljana, 2011).

Granite waste was modified with dolomite, limestone and aluminum oxides to form batch constituents of 52wt%. The batches were melted and subjected to heat treatment to induce Crystallisation at 1000^{o}C for 3 hours. It was found from the resulting glass ceramic material that increasing the contents of MgO and CaO in the batch resulted to increasing bulk Crystallisation. The obtained glass ceramic material possessed very high hardness indicating high abrasion resistance, making them suitable for many applications under aggressive mechanical conditions (Gamal, 2012).

Glass ceramic with electrical insulation properties were produced by conventional melt-quenching techniques, using 5wt% of T_1O_2 as nucleating agent. The physical and electrical properties of all the specimens were investigated.It was observed thatdielectric strength increases with increase in sintering temperature (Shukur *et al.*, 2012).

Glass ceramics produced from alkali lead glass composites by simple addition of different alkali oxides percentages produce microscopically homogeneous ceramic material which has specific applications in electrical equipment and dental prostheses (Shukur*et al.,* 2012).

The effect of borosilicate glass waste addition on the sintering and properties of porcelain bodies was studied between 1000^{o}C- 1300^{o}C in air on a selected porcelain composition consisting of 50% kaolin, 25% potassium – feldspar and 25% Quartz. The sintering activation energy of this composition was calculated as 166kJ/mol, indicating that the starting temperature for sintering was reduced by the additional fluxing oxides such as B_2O_3 and Na_2O which eased the verification by reducing the viscosity of the liquid phase during sintering (Cagatay*et al.,* 2012).

The sintering behavior and dielectric properties of glass ceramic composites using lead borosilicate glass was studied with T_lO_2 and Al_2O_3 based glass ceramic composite by a liquid phase sintering with a deformation temperature of about 627^{o}C. There was no Crystallisation in the T_lO_2 and lead borosilicate glass composite but the Crystallisation of the anorthite-type phase occurred in the Al_2O_3 and lead borosilicate glass composite. The dielectric constant of the T_lO_2 composite was about 30 implying that it is suitable as filters while the dielectric constant of Al_2O_3 composites was about 10 and can be useful for application as substrate (Kwan *et al.,* 2010).

The effect of sintering temperature and clay addition towards glass ceramic produced from recycled glass by using pressing method was studied by the varying the sintering temperature at 750^{o}C, 850^{o}C and 950^{o}C. The recycled glass powder was mixed with clays in the percent ratio of 95:05, 90:10 and 85:15. The green article was uniaxially pressed, the microstructure and phase present in the glass ceramic was analyzed using SEM and XRD. The physical and mechanical properties such as porosity, density measurement and water absorption test and the

micro hardness were determined. The results indicated that 10wt% of clay addition and sintering temperature of 850^{o}C, glass ceramic produced has good temperature suitable physical and mechanical properties (Nur, 2010).

Great concerns regarding the increasing amount of industrial wastes have received a lot of attention on the disposal modalities which pose high demand on the safety of the environment. Efforts have been made to replace the traditional natural raw materials with cheap readily available wastes (Vorrada *et al.*, 2012).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Raw Materials

The materials used in this study are kaolin waste obtained from Kaloma town in Bauchi State, sodalime glass waste from the post-consumer container glass wares and broken window glasses; while the borosilicate glass wastes was from the Science Laboratories in Zaria,Kaduna State.

The kaolin waste was obtained from the Kaloma processing factory in Alkaleri local government of Bauchi state which processes primary kaolin and the waste obtained was the product of the first processing step of separating sand from the ore which represents about 70% of the total waste generated.

The soda lime glass waste are the white post-consumer container glasses such as the beverages, soft drink, medicine bottles and broken window glasses were hand-picked from the dumpsites and set up collection points in Sabon-Gari and Samaru Area in Zaria. The broken laboratory glass wastes (Pyrex) was collected from laboratories in NuhuBamalli Polytechnic Zaria (AppendicesXI,XII,XIII,XIV,XV and XVI).

3.2Sample Treatment and Laboratory Analysis

3.2.1. Beneficiation

The waste glass samples of sodalime and borosilicate were at the initial stage, sorted out by picking manually to separate the white containers from the coloured. The labels, metal, wood, plastic rims and covers were then removed and the waste glasses were washed with cold water

to clear away the dusty particles, furthermore the waste were rinsed with dilute hydrochloric acidto remove other forms of impurities and contaminants due to prolonged exposure to humid or smoggy atmosphere as a result of reaction with substances like carbon (IV) oxide and other substances in the air. These wastes were further soaked and rinsed in distilled water, and air dried in the laboratory at room temperature for 3 hours.

3.2.2 Sample Preparation

I. **Crushing**

The clean waste glasses were roughly crushed manually using hammer to break and reduce the sizes and were packed in plastic containers and labeled prior to pulverization.

II. **Pulverization and Sieving**

The prepared crushed samples were further crushed and pulverized sieved using 174, 120, 60 meshes to produce 90µm, 125µm, 250µm particle sizes respectively.While the kaolin waste was used as collected after removal of the foreign materials.

The particle sizes are important for the shaping technique used to achieve maximum particle packing and uniformity so that minimum shrinkage will result during densification (Nur, 2010).

3.3X-Ray Fluorescence Analysis

The chemical analysis of the kaolin and glass wastes was conducted at the Nigerian Geological Survey Agency, National Geosciences Research Laboratory (NGRL) Kaduna. Standard analytical procedure was carried out with the mini pal 4 X-Ray Fluorescence, non-destructive machine, to determine the elemental and oxide contents andloss on ignition of the samples based on the work of Ben Dor and Banin(1999).

3.4Determination of Moisture Content of Kaolin

This was conducted using the ASTM (373) standard procedures and calculated using equation 3.1. The waste samplewas weighed initially and dried in an oven at 110^{o}C for 2hours to a constant weight. It was then allowed to cool and weighed again; the total moisture content was calculated as percentage of the initial weight.

$$\text{Percentage moisture content} = \frac{\text{Initial weight— final weight}}{\text{Initial weight}} \times 100 \quad \text{... ... ... (eq 3.1)}$$

3.5 Batch Formulation

The batches were formulated based on the work conducted by Francis *et al*, 2002 Gorokhovsky*et al*, 2001 and Nur , 2010 where various compositions of glass wastes were utilized to form glass ceramics using sintering method.The formulated batchesare shown in Tables 3.1and 3.2.

Table 3.1 Kaolin, Borosilicate Glass Wastes and Sodium Sulphate Batch Compositions

Grain Size (µm)	Composition wt /%		(Na_2SO_4) wt /%	Temperature °C
	Kaolin	Borosilicate		
$K_5B_{95}NS_0$ (90 µm)	5	95	0	750 , 850, 950
$K_{10}B_{85}NS_5$(125 µm)	10	85	5	750 , 850, 950
$K_{15}S_{80}NS_5$(250 µm)	15	80	5	750 , 850, 950

Table 3.2 Kaolin, Soda Lime and Borosilicate Glass Wastes Batch Compositions

Sample	Composition wt /%		Borosilicate	Temperature °C
	Kaolin	Soda Lime		
$K_5B_5SL_{90}$(90 µm)	5	90	5	750 , 850, 950
$K_{10}B_5SL_{85}$(125 µm)	10	85	5	750 , 850, 950
$K_{15}B_5SL_{80}$(250 µm)	15	80	5	750 , 850, 950

3.6 Pellet Formation

Powdered samples of kaolin, glass wastes and Na_2SO_4 were weighed according to the specified ratios on a digital balance. The powdered samples were mixed with 5wt% Polyvinylchloride as organic binder prepared by dissolving in Tween 80 and allowed to drybefore grinding using mortar and pestle.The powdered material was molded into compacted die shapes of 20mm diameter and thickness of 5mm pellet (20mm x 5mm), compressed using uniaxial hydraulic pressing machine at a pressure of 10metric tones, to produce the pellets of 30g each (Plate I).

3.7 Sintering

The pellets were arranged on an unglazed ceramic slab of 18cm x 8cm (Plate II).The pellets were each sintered at 750°C, 850°C and 950°C temperatures in an electric furnace

(NORTHERM)at heating rate of 5°C per minutes and was held for a residence period of one hour and cooled gradually in the furnace.(Mihailova*et al.*, 2011; Bernardo *et al.*, 2007).

The temperature range was adopted based on the report that binder burnt out occurred within the range of 400-770°C (Chung-Lun *et al.*,.2003) as such a temperature of 750^{o}C was used as the least sintering temperature for this study.



Plate I:Uniaxial Hydraulic Pressing Machine.



PlateII:Pellets Placed in a Furnace Prior to Heating.

3.8 Determination of Percentage Firing Shrinkage

The pellets diameter were measured using digitalverniercaliper before and after sintering at the various temperatures and the average percentage firing shrinkagewas calculated as follows **(**ASTM C373-88).

$$\% \text{ firing shrinkage} = \frac{\text{Initial diameter— final diameter}}{\text{Initial diameter}} \times 100 \ldots\ldots\ldots\ldots \text{eq 3.2}$$

3.9Measurement of Bulk Density, Apparent Density and Percentage Porosity

The sintered pellets were dried at 110°C for 24hrs in an oven to ensure total water loss. The weights were recorded as dried weights. Each pellet was in turn immersed in beaker of water and the soaked weight was measured and recorded. The suspended weight of each pellet was measured so as to determine its density using Archimedes' principle (Plate III).The respective bulk density, percentage porosity and apparent density were calculated using the following formulae (ASTM C373-88):

Bulk density=D/ (W-S) g/cm^3……..... (eq 3.3)

Apparent Density=D/(D-S) g/cm^3 ……(eq 3.4).

Percentage porosity (W-D)/(W-S)X100……(eq 3.5)

Where; D= weight of fired pellet;S= Weight of fired pellet suspended in water; W= Weight of soaked pellet suspended in air.



Plate III:Experimental Set up for Determination of Density by Archimedes' Principles.

3.10. Water Absorption

The sintered pellets were dried to a constant weight and cooled to room temperature, and then weighed. The pellets were immersed in distilled water and boiled for 2hours and allowed to remain immersed for 24hours. It was removed and excess water dried from the surfaces with damp cloth and weighed again. The water absorption was calculated using the formula.

% water absorption=$(W_s-W_d)/W_d X100$……(eq 3.6).

Where; W_d=dried weight of the pellet, W_s=soaked weight of the pellet(ASTM C373-88).

3.11 Hardness Test

The sintered pellets were subjected to hardness test using Durometer Shore A(Francisco Munoz Ires .C.B. Model; 5019 Serial number; 01554) ASTM D2240 ISO 7619 (Plate VI) The results were converted to Shore D using conversion chart which was finally converted to Rockwell superficialhardness values(Hardness Conversion ASTM140-07).



Plate IV:Durometer for Hardness Testing.

3.12 X-ray Diffraction Studies

The X-ray Diffraction Studiesof each batch was carriedout at National Steel Raw Materials Exploration Agency, (NSRMEA). Malali Kaduna using Schmaltz machine model XRD 6000 automated with Ni-Filtered Cu Kαradiation operating at 40.0(kV) and 30.0(mA) with a graphite monochromator (λ=1.5418).

3.13 Scanning Electron Microscopy Studies

The Scanning Electron Microscopy of the developed glass ceramics was conducted at Department of Chemical Engineering Multi user Laboratory Ahmadu Bello University,Zaria usingSEM machine.

3.14 Chemical Durability Test

The samples were weighed using digital balance,then immersed separately in 120ml 0.1M HCl and 0.1MNaOH and placed on a waterbath, heated to 90°C for one hour. The samples were then removed, mopped with clean dried cloth and heated in an oven at 120°C. Each sample was allowed to dry and weighed again. The percentage lost in weight was calculatedusing equation 3.7 below (Romero*et al*,.2000).

$$\text{Percentage weight loss} = \frac{\text{initial weight-final weight in acid/base}}{\text{Initial weight}} \times 100 \quad \ldots\ldots\ldots \text{Eq 3.7}$$

The data is presented in Tables 3.3 and 3.4.

Table 3.3. Determination of Chemical Resistance of the Formulated Sintered Batch Compositions in 0.IM HCl (Acid)

Composition	Initial Weight(g) in HCl(0.1M)			Final Weight(g) in HCl(0.1M)		
	750°C	**850°C**	**950°C**	**750°C**	**850°C**	**950°C**
$K_5B_{95}NS_0$ (90 µm)	2.84	2.71	2.91	2.82	2.69	2.82
$K_{10}B_{85}NS_5$(125 µm)	2.70	2.83	2.93	2.67	2.69	2.70
$K_{15}B_{80}NS_5$(250 µm)	2.72	2.74	2,80	2.71	2.73	2.79
$K_5B_5SL_{90}$(90 µm)	2.76	2.82	2.87	2.73	2.75	2,84
$K_{10}B_5SL_{85}$(125 µm)	2.43	2.90	2.84	2.42	2.83	2.79
$K_{15}B_5SL_{80}$(250 µm)	2.83	2.86	2.84	2.75	2.67	2.80

Table 3.4:Determination of Chemical Resistance of the Formulated Sintered Batch Compositions in 0.IM NaOH (Alkali)

Composition	Initial Weight(g) in NaOH (0.1M)			Final Weight(g) in NaOH (0.1M)		
	750°C	**850°C**	**950°C**	**750°C**	**850°C**	**950°C**
$K_5B_{95}NS_0$ (90 µm)	2.86	2.93	2.90	2.84	2.67	2.89
$K_{10}B_{85}NS_5$(125 µm)	2.81	2.85	2.81	2.72	2.81	2.79
$K_{15}B_{80}NS_5$(250 µm)	2.86	2.79	2,83	2.74	2.75	2.81
$K_5B_5SL_{90}$(90 µm)	2.69	2.87	2.89	2.65	2.86	2.88
$K_{10}B_5SL_{85}$(125 µm)	2.79	2.87	2.91	2.72	2.73	2.80
$K_{15}B_5SL_{80}$(250 µm)	2.74	2.69	2.79	2.72	2.60	2.76

CHAPTER FOUR

RESULTS

4.1 Sample Collection

The samples collected for kaolin, borosilicate and sodalime glass wastes are shown in (AppendicesXI,XII,XIII,XIV,XV and XVI).

4.2.Pulverised and Sieved Samples

Theprepared samples of borosilicate and sodalime glass wastes were pulverised and sieved to 90µm,125µm and 250µm particle sizes were placed in labelled plastic containers prior to use.

4.3. Moisture Content and Loss on Ignition

The value of 14.82 % moisture content for kaolin and loss on ignition of 10.13%, 1.34% and 0.30% for kaolin, borosilicate and the soda lime wastes glasses respectively were recorded.

4.4 Oxides Analysis

Kaolin, borosilicate and sodalime waste glasses oxides content were analyzed by X-ray fluorescence method.The results are presented in Table 4.1.

Table 4.1: The Results of X-ray Fluorescence Analysis for Kaolin, Soda Lime and BorosilicateGlass Waste

S/N	Oxides	% Kaolin	%Soda lime	%Borosilicate
1	SiO_2	46..80	77.63	80.50
2	Al_2O_3	39.41	0.64	0.52
3	K_2O	0.49	0.29	0.80
4	CaO	0.34	7.46	0,31
5	TiO_2	1.50	0.09	0.07
6	V_2O_5	0.15	0.02	-
7	Cr_2O_3	0.03	0.05	0.02
8	MnO	0.03	0.04	0.03
9	Fe_2O_3	0.01	0.30	0.22
10	B_2O_3	-	-	11.24
11	MgO	0.25	2.63	0.03
12	BaO	-	-	0.06
13	Na_2O	0.50	10.75	4.76
14	LOI	10.13	0.30	1.34

4.5 Pellets Formation

The pulverized sieved samples of kaolin, glass wastes and $NaSO_4$ were weighed according to the specifiedratios on digital balance. The powdered mixtures were mixed with 5wt% Polyvinyl chloride (PVC) binder which provided enough strength and stabilityto prevent the green body from breaking (Plate V).

4.6 Sintering

Sintered glass ceramics were developed from borosilicate and sodalime wastes glass in combination with various composition of waste kaolin (Tables 3.1and 3.2). All the composition formed at 90μm, 125μm and 250μm particle sizes were subjected to sintering temperatures of 750^{o}C, 850^{o}C and 950^{o}C at a sintering rate of 5^{o}C/min with residence time of one hour (Plate VI).



Plate V: Sampleof Prepared Pellets before Sintering.



Plate VI: Sample of Prepared Pellets after Sintering.

4.7. Shrinkage

The shrinkage of the glass ceramic produced is temperature dependent .The sintered glass ceramics developed in this study clearly demonstrated this assertion(Appendix XVII, Figures 4.1 and 4.2).

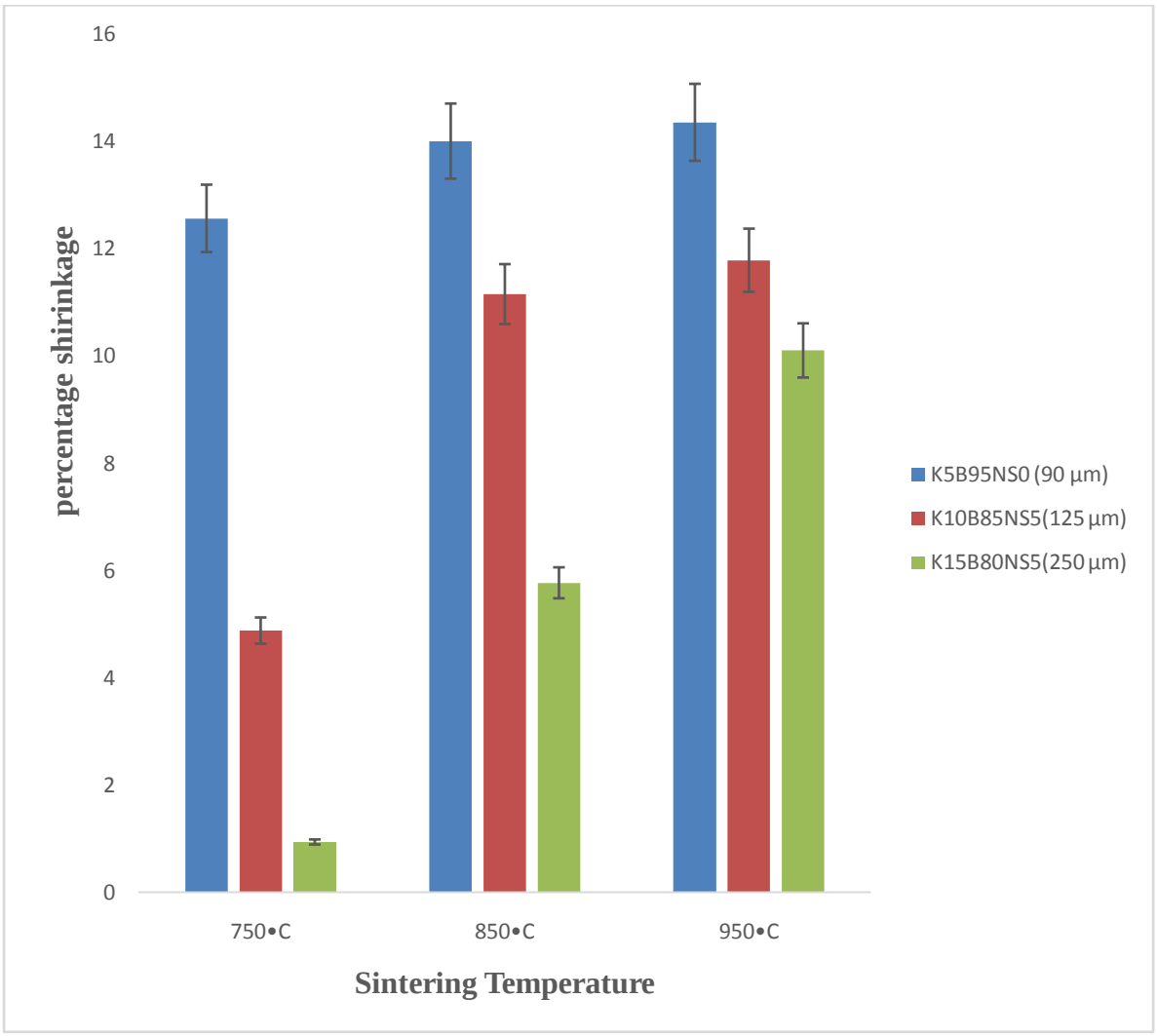


Figure 4.1: Percentage Firing Shrinkage at Various Sintering Temperatures of Batches of Different Grain Sizes Containing Kaolin, Borosilicate Glass Waste and Sodium Sulphate

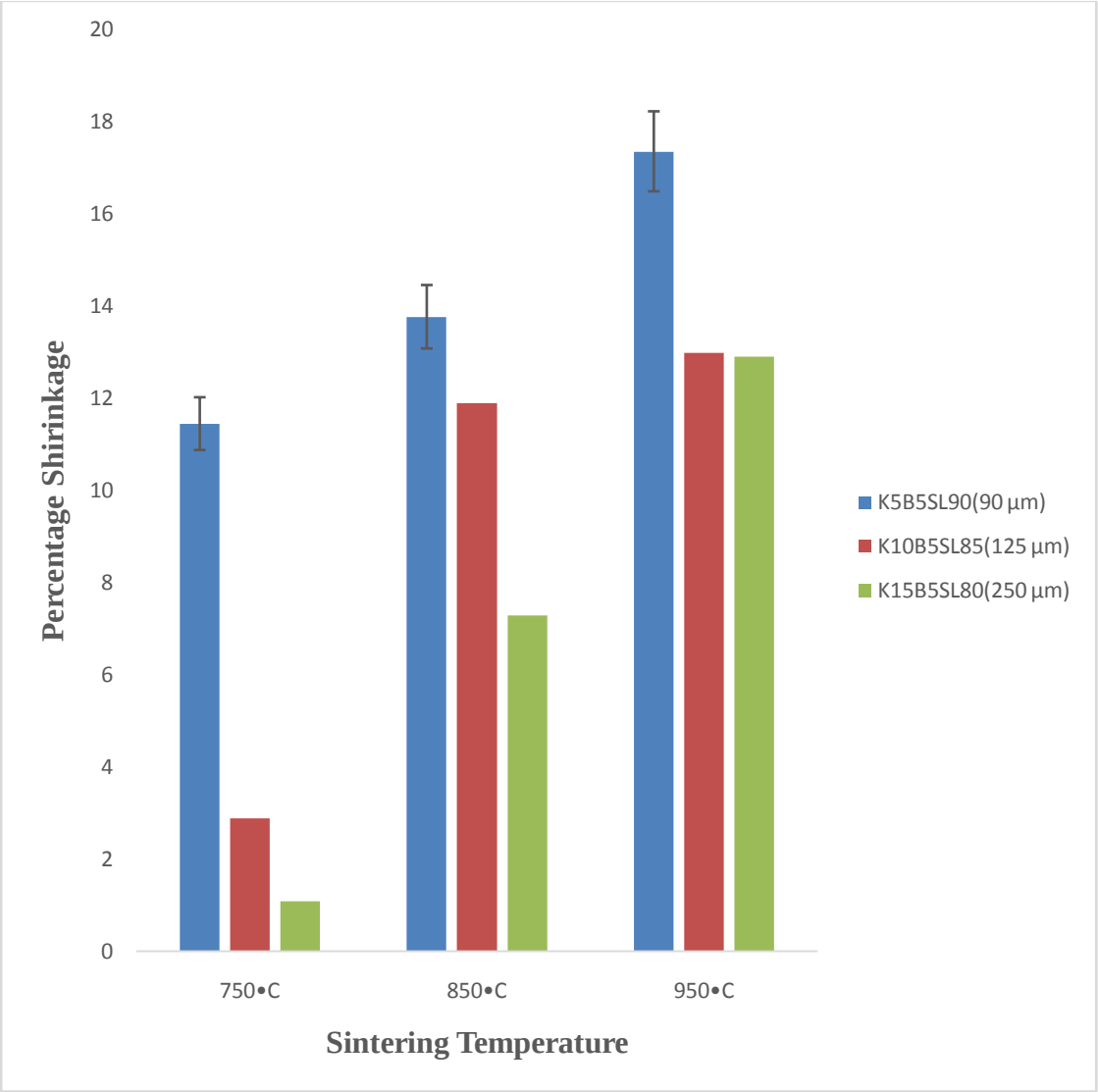


Figure 4.2:Percentage Firing Shrinkage at Various Sintering Temperatures of Batchesof Different Grain Sizes Containing Kaolin, Borosilicate and Soda Lime Glass Wastes

Compositions containing soda lime, kaolin and borosilicate have high shrinkage due to the sintering aids of soda lime and borosilicate compared to that of sodium sulphate

4.8 Water absorption, Percentage Porosity, Bulk and Apparent Densities

The results of the effects on change in compositions with sintering temperatures on water absorption,percentage porosity, bulk and apparent densities at 750^{o}C, 850^{o}C and 950^{o}C (AppendicesXVIII,XIX and XX).

4.8.1 Water Absorption

The trend of water absorption of the sintered batch compositions containing sodium sulphate and those containing soda lime in which both served as sintering aid, showed an increase with increasing particle size at all sintering temperatures and decrease with increasing sintering temperatures. The observed trend is clearly indicated in (Figures 4.3 and 4.4).

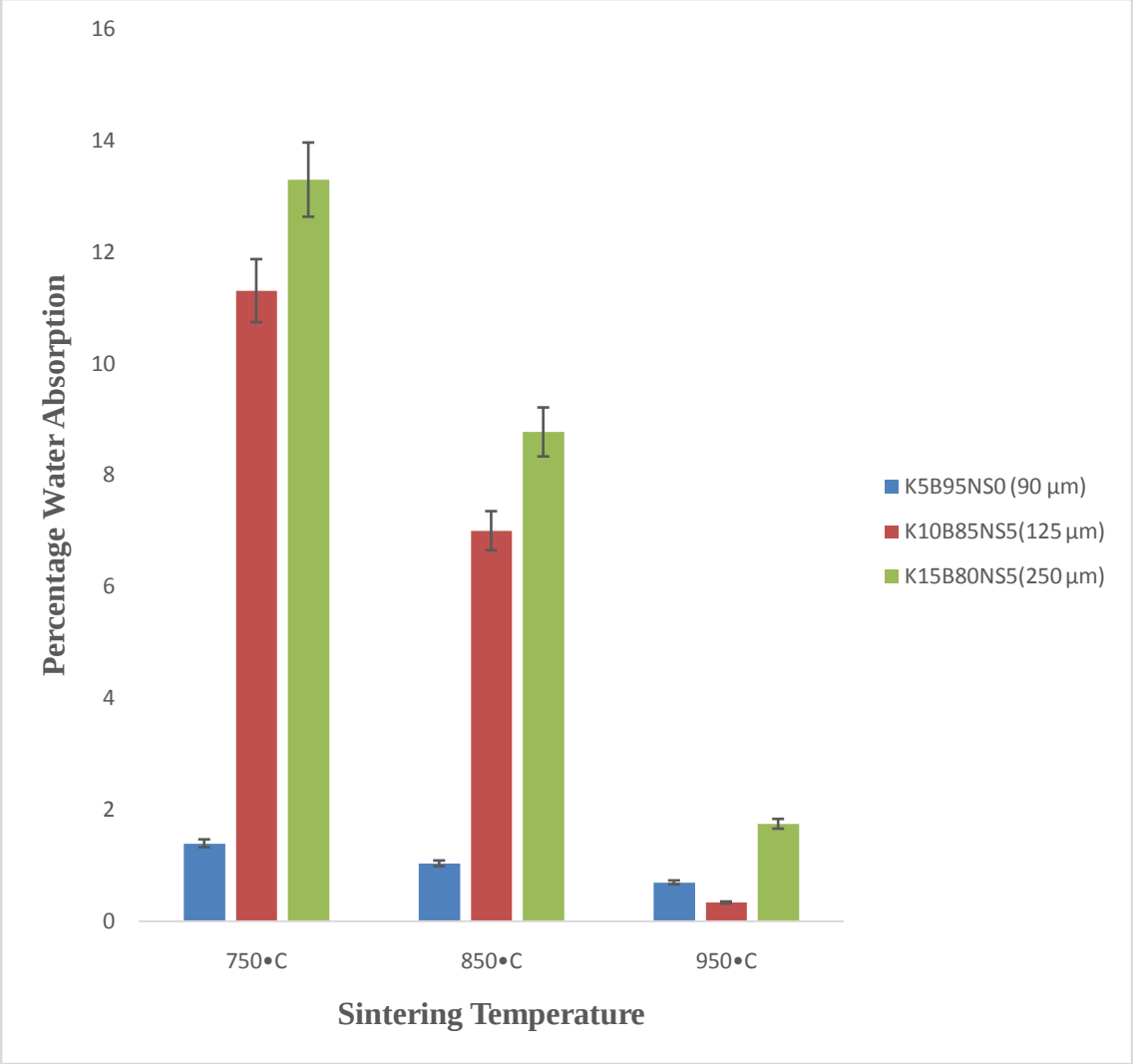


Figure 4.3:Percentage Water Absorption at Various Sintering Temperatures of Batches Containing Kaolin, Borosilicate Glass Waste and SodiumSulphate

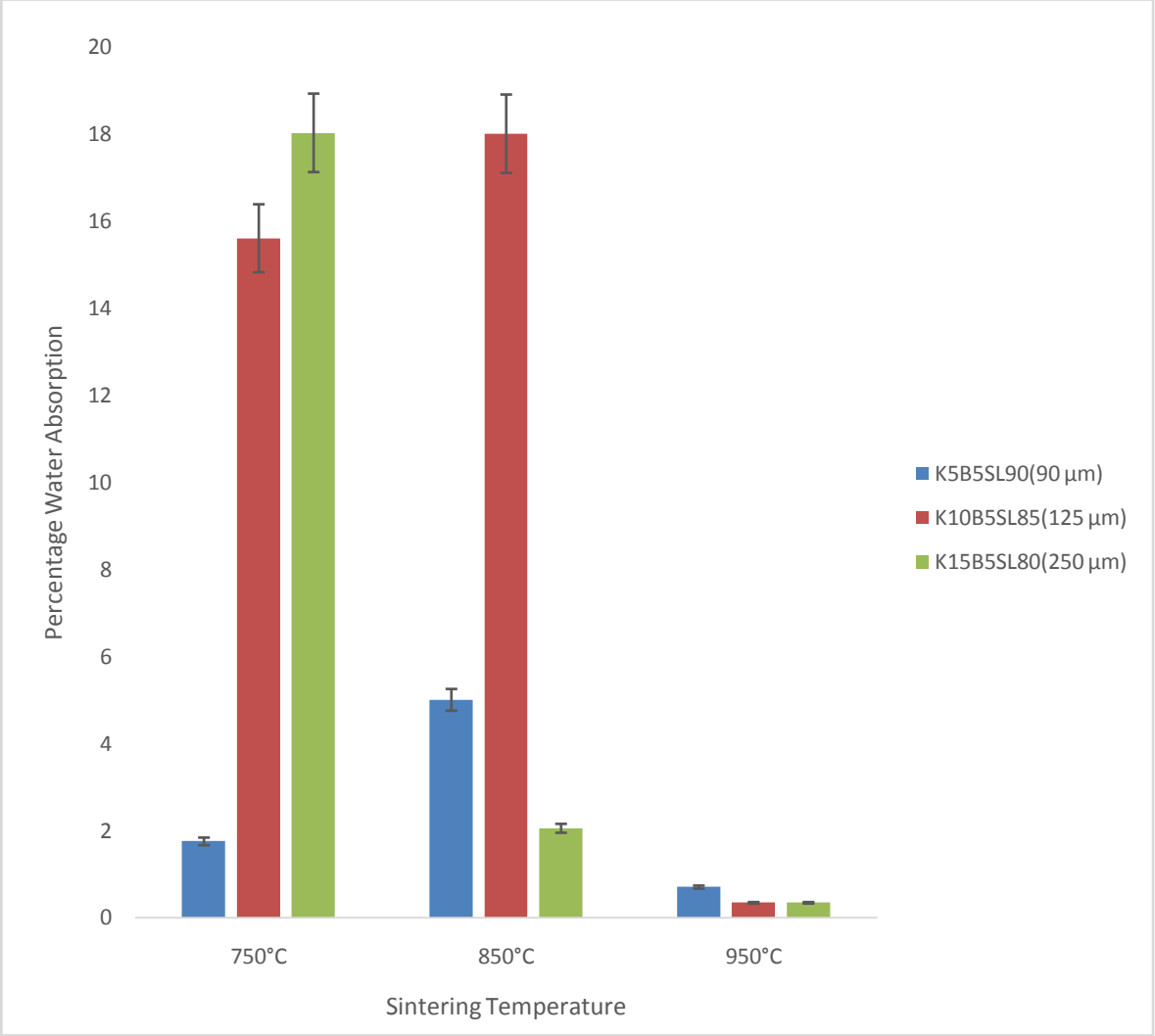


Figure 4.4:Percentage Water Absorption at Various Sintering Temperatures of Batches Containing Kaolin, Soda Lime and Borosilicate Glass Wastes

4.8.2 Porosity

The porosity generally decreases with the increase in sintering temperature and increase with increase in particle size in all the sintered batch compositions.

The highest value of porosity observed was 26.84% in batch composition of $K_{15}B_5SL_{80}$ with 250μm grain size at 750^oC sintering temperature (Figure4.6)and the lowest obtained is 0.68% in batch composition of $K_{10}B_{85}NS_5$ at 125μm grain size at 950^oC sintering temperature (Figure4.5).

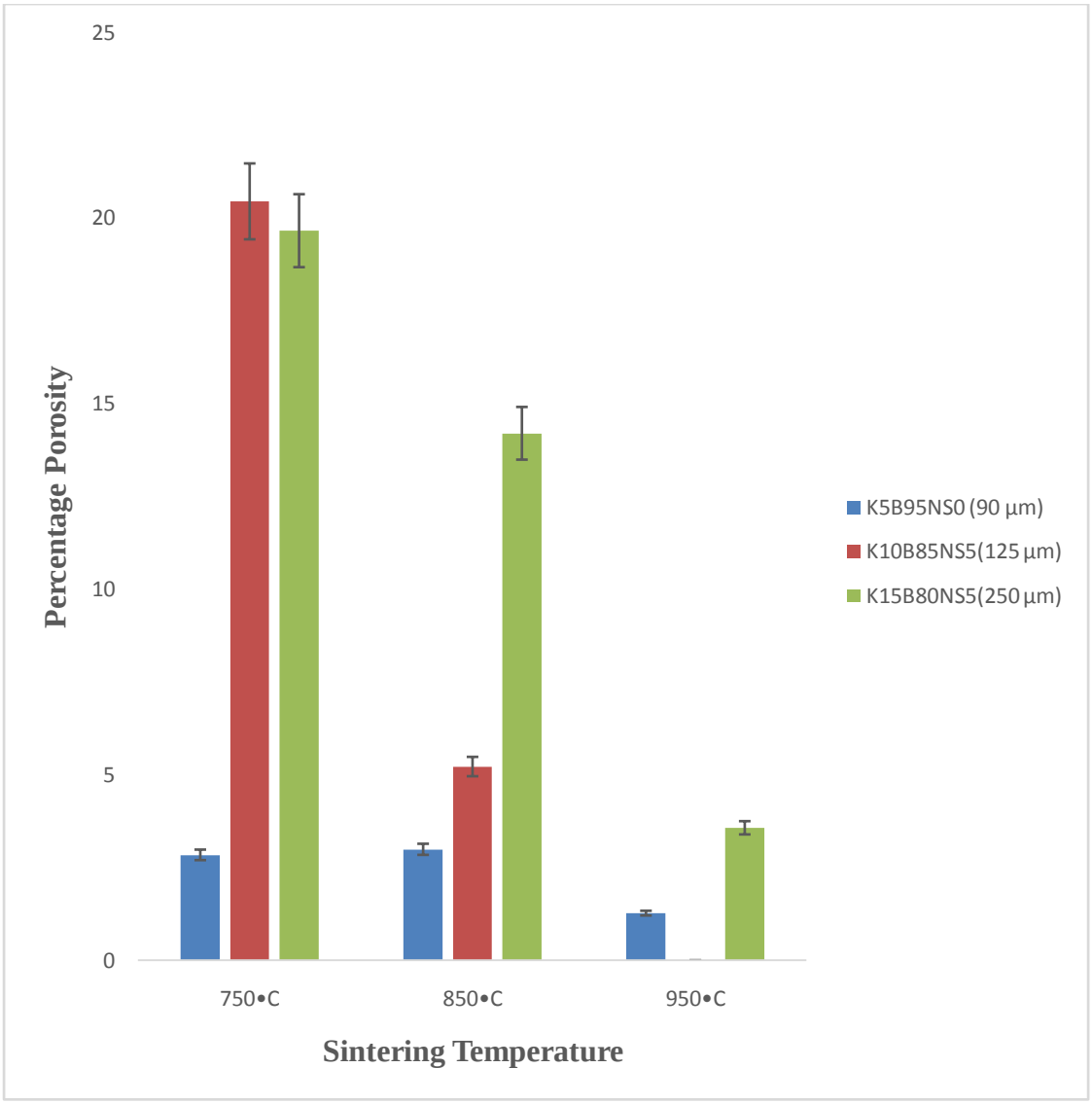


Figure 4.5: Percentage Porosity at Various Sintering Temperatures of Batches Containing Kaolin, Borosilicate Glass Waste and Sodium Sulphate

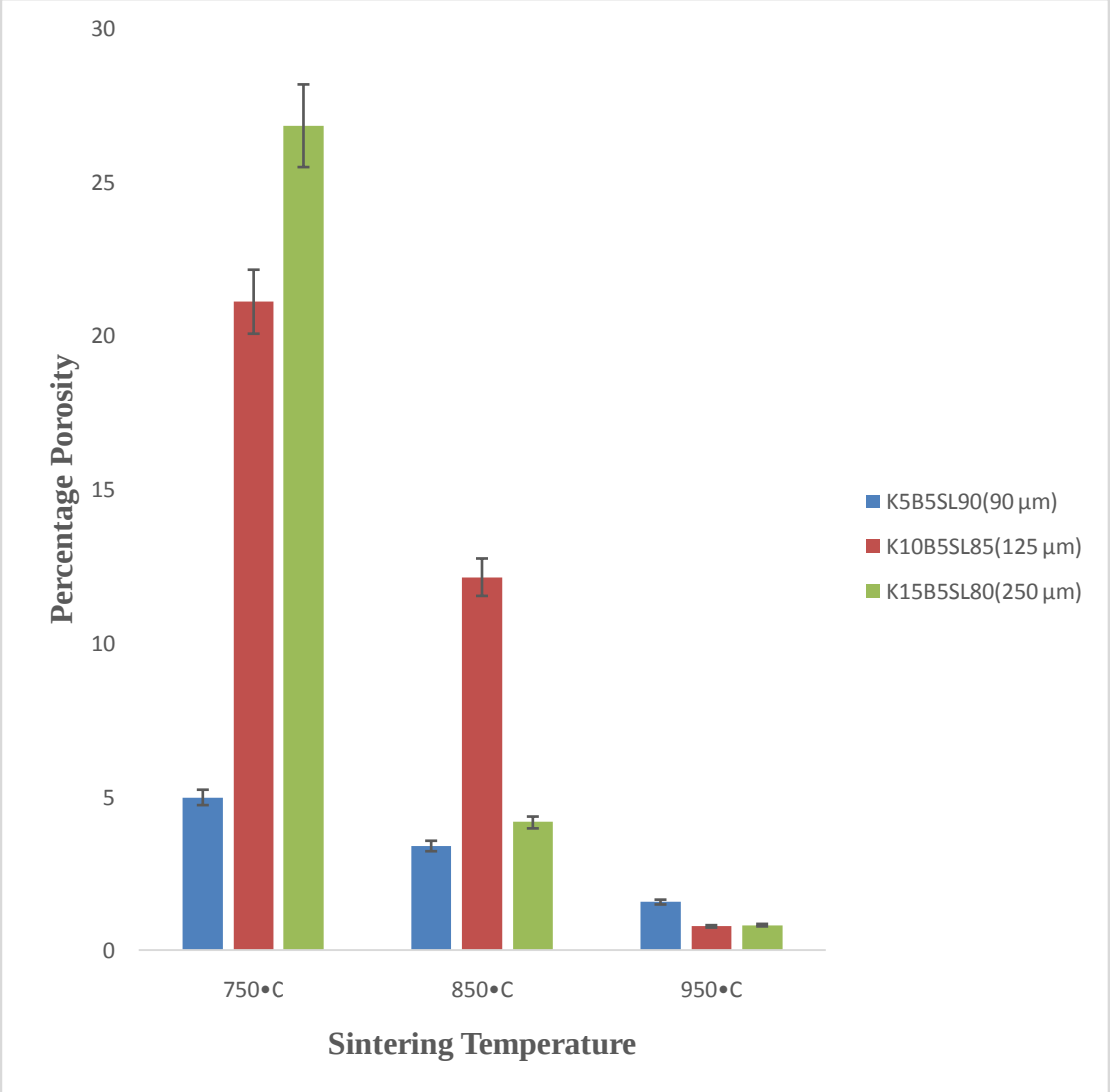


Figure 4.6: Percentage Porosity at Various Sintering Temperatures of Batches Containing Kaolin, Borosilicate and Soda Lime Glass Wastes

4.8.3 Bulk and Apparent Densities

The bulk density increases for a given composition with increasing sintering temperatures and decrease with increase in the particle grain sizes.

In case of the compositions containing kaolin, borosilicate waste glasses, with the Na_2SO_4 serving as sintering aid, high density was observed for batch K_{10} $B_{85}NS_5$ with 125µm particle size which had a bulk density of 2.14g/cm^3 at 850°C (Figures 4.7 and 4.8).

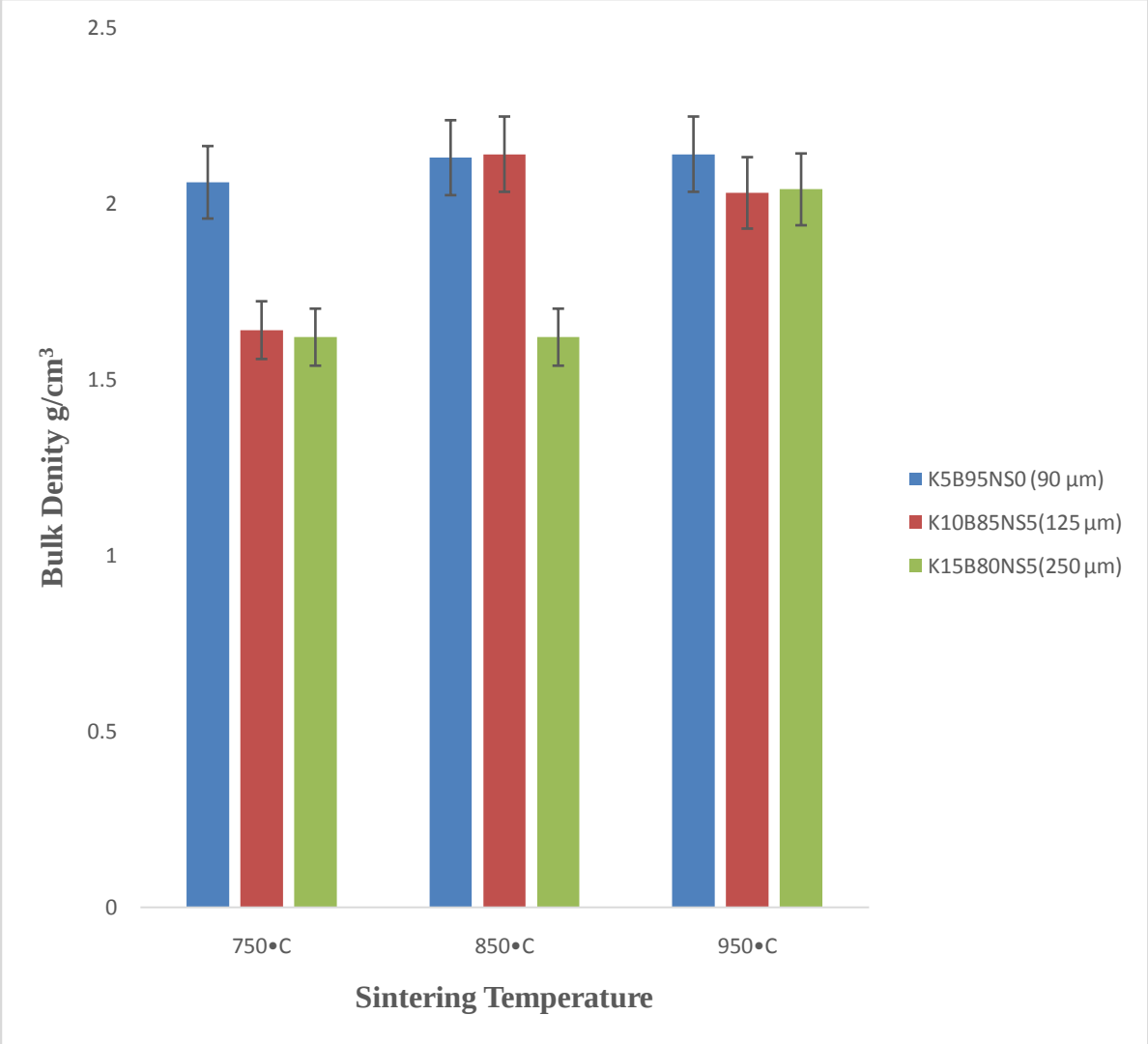


Figure 4.7: BulkDensities at Various Sintering Temperatures of Batches Containing Kaolin, Borosilicate and Sodium Sulphate

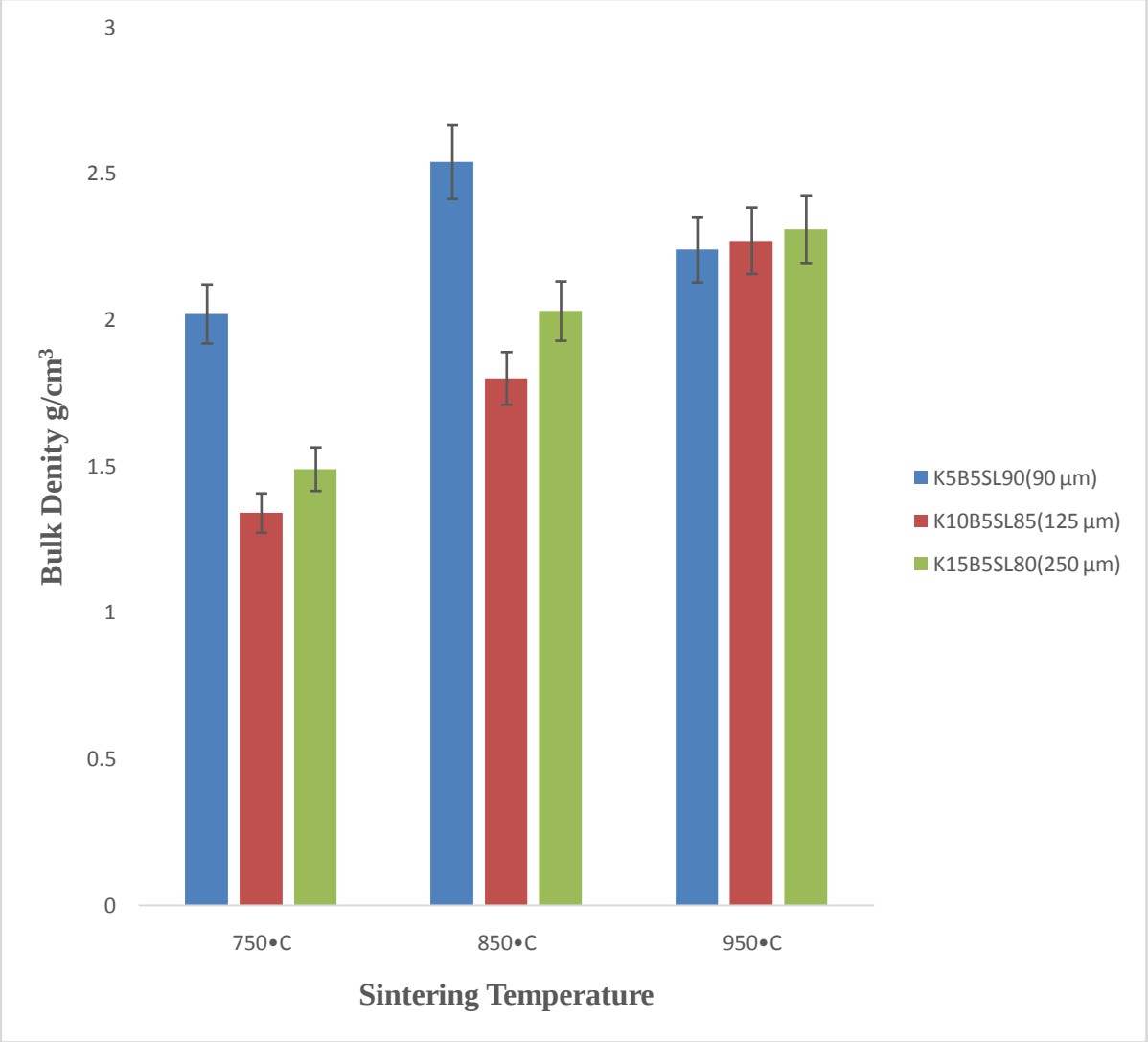


Figure 4.8:Bulk densities at various Sintering Temperatures of Batches Containing Kaolin, Soda lime and Borosilicate Glass Wastes

In compositions containing kaolin, borosilicate, and soda lime at 90µm particle sizes, the bulk density of 2.54g/cm^3 at 850^{o}C and the density decreased to 2.24g/cm^3 at 950^{o}Csintering temperature.The least value of 1.34g/cm^3 in composition containing kaolin , borosilicate and soda lime waste with125µm at 750^{o}Cwas observed. The composition containing $K_5B_5SL_{90}$ with 90µm grain size at 750^{o}C sintering temperature has a value of density 2.02g/cm^3 but greatly increased to 2.54g/cm^3 at 850^{o}C (Figure 4.8).

The apparent densities for all the batch compositions in this study have no definite pattern at all sintering temperatures. The highest value of 2.65g/cm^3 was observed in the batch $K_5B_5SL_{90}$ with 90µm at 850•C, the least value of 1.65g/cm^{3}was recorded for the composition $K_{10}B_5SL_{85}$ with 125µm at 950•C (Figure 4.9). The compositions containing sodium sulphate was found to have low apparent densities at all sintering temperatures compared to the batches containing soda lime as sintering aid(Figures 4.9 and4.10).

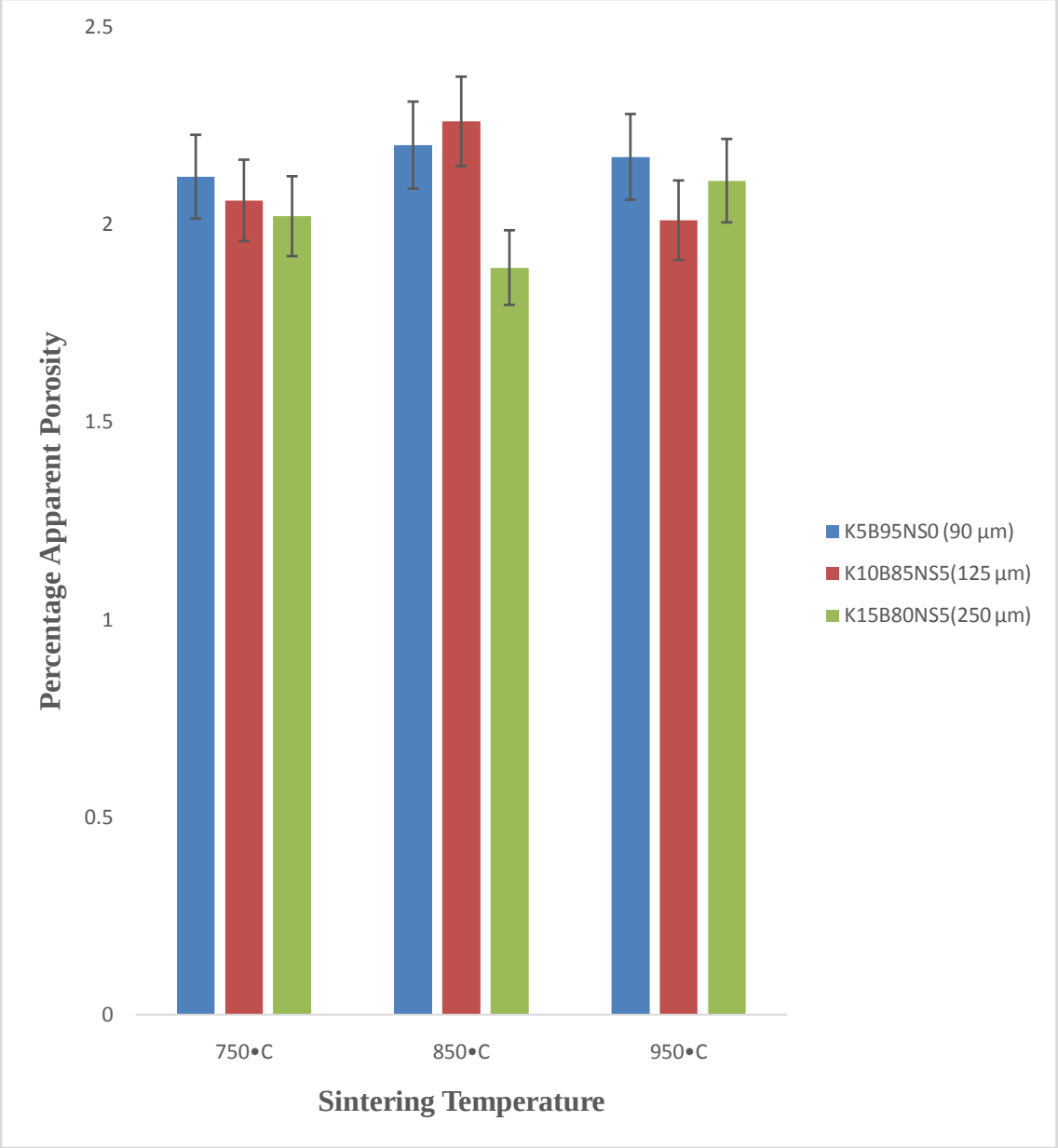


Figure 4.9: Apparent Density at Various Sintering Temperatures of Batches Containing Kaolin, Borosilicate Glass Waste and Sodium Sulphate

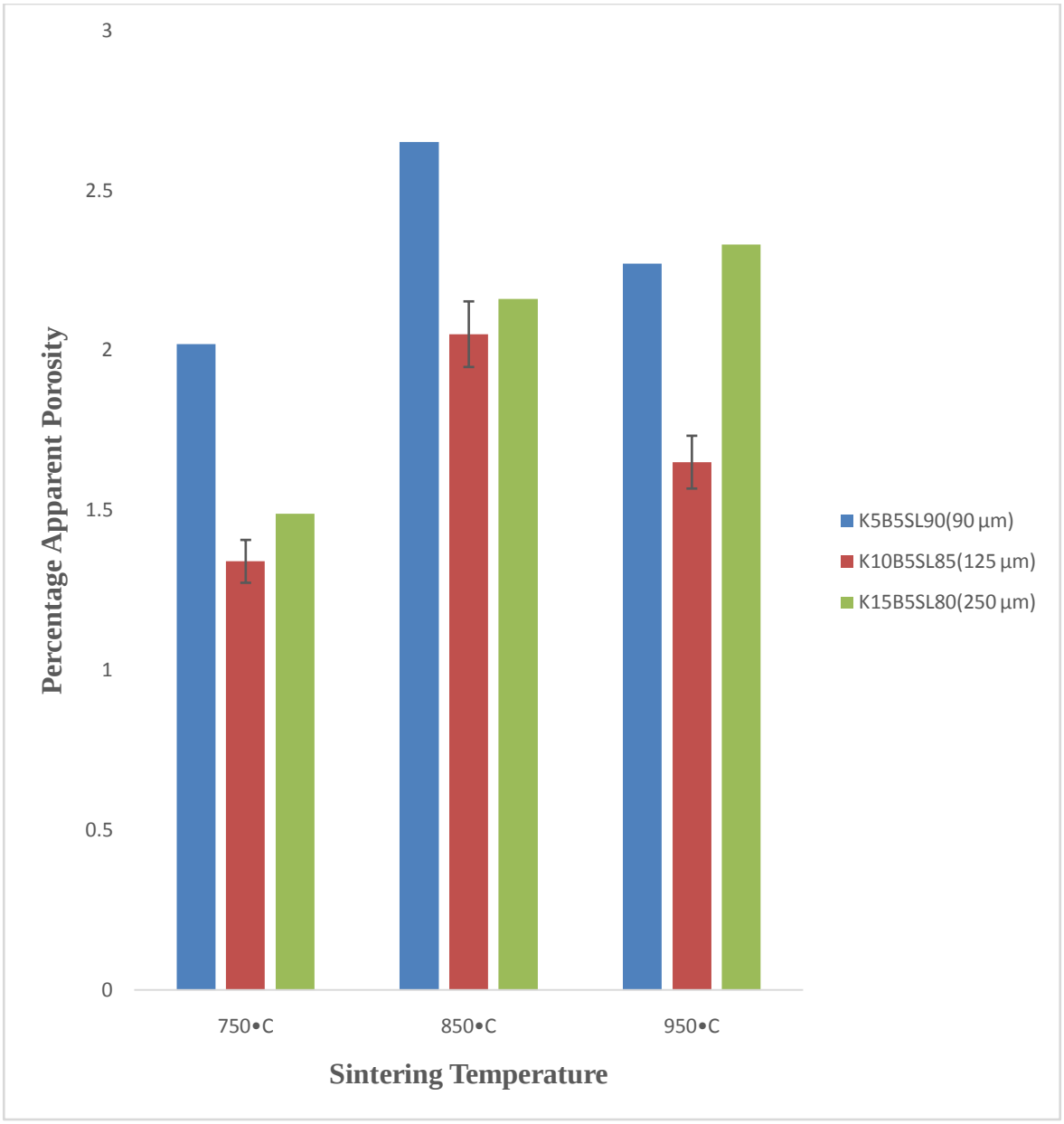


Figure 4.10:Apparent Density at Various Sintering Temperatures of Batches Containing Kaolin, Borosilicate and Soda Lime Glass Wastes

4.9 Hardness

The batch composition $K_5B_{95}NS_o$ with 90µm grain size at 950°C sintering temperature was found to have high value of Rockwell superficial hardness of 81.5N/m^2(Appendix XXI) This showed that it is best sintered composition among all the batches formed.There is a trend in the hardness increase with increase in sintering temperature (Figures 4.11 and 4.12).

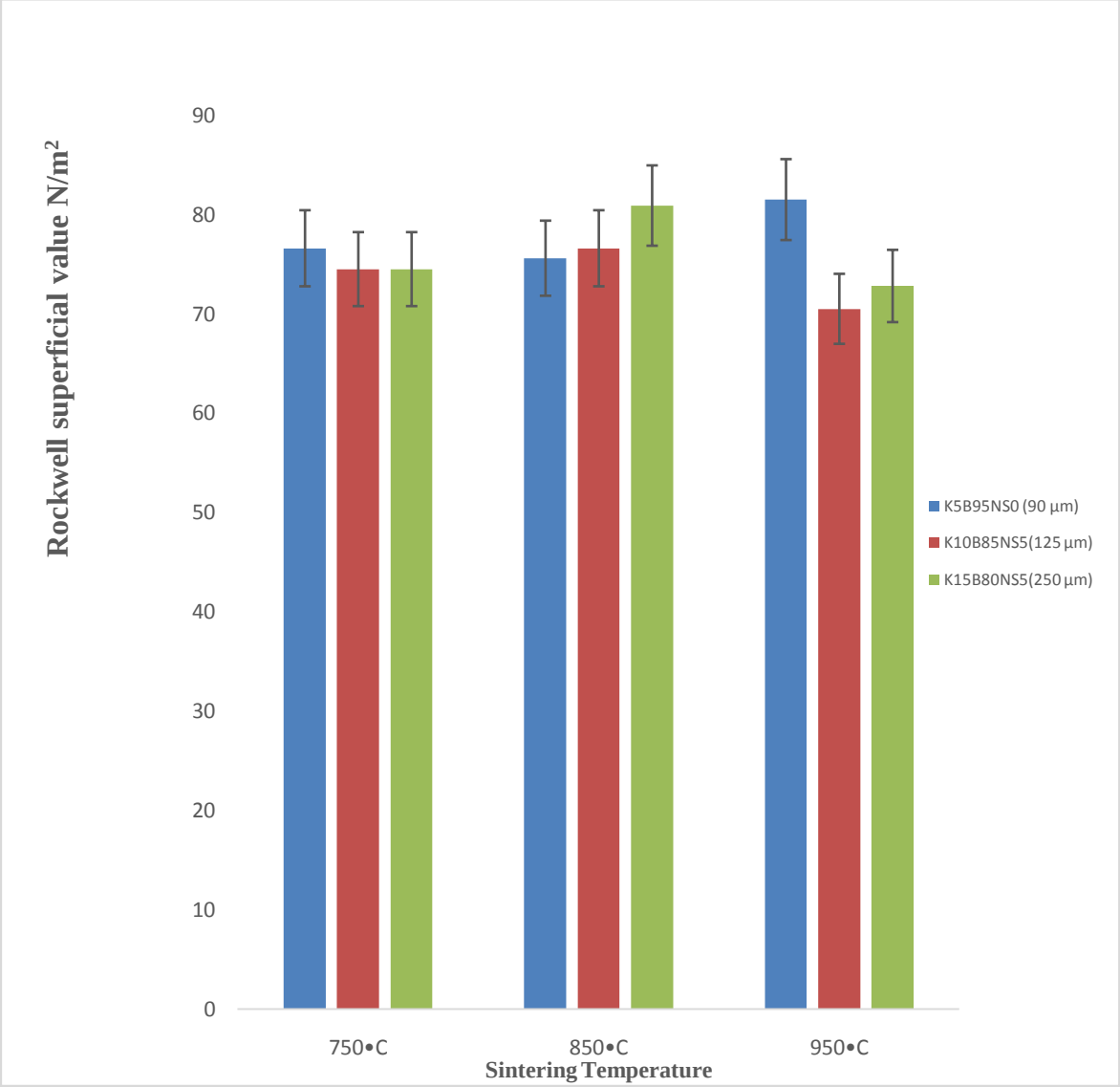


Figure4.11:Rockwell Superficial Hardness (N/m^2) at Various Sintering Temperaturesof Batches of Different Grain Sizes Containing Kaolin, Borosilicate Glass Waste and Sodium Sulphate

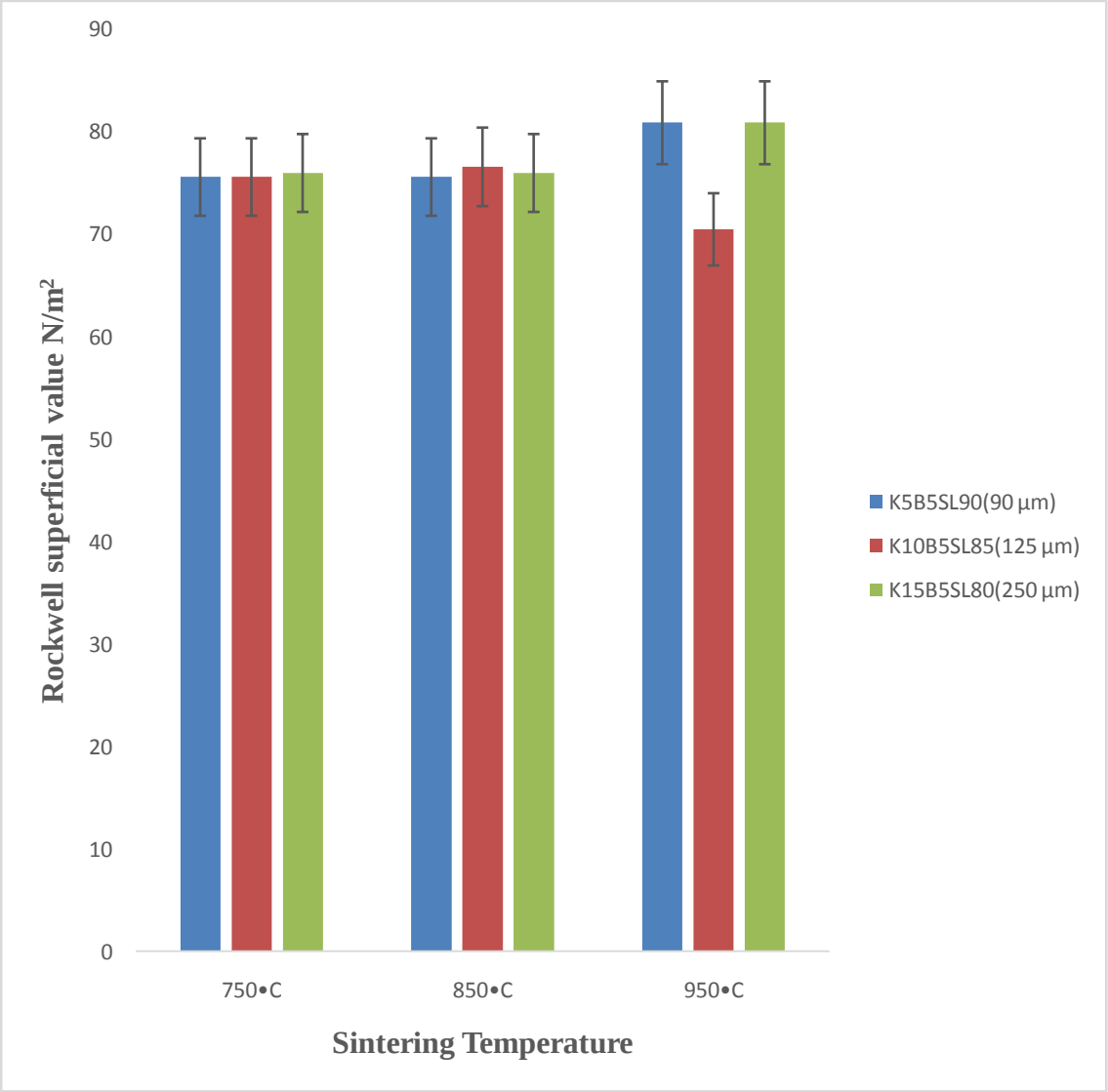


Figure 4.12:Rockwell Superficial Hardness (N/m^2) at Various Sintering Temperatures of Batches Containing Kaolin, Borosilicate and SodaLime Glass Waste

4.10 Chemical Durability

In compositions containing Na_2SO_4 at 90um and 125um grain sizes, there is a decrease in chemical durability in acid with increase sintering temperature. Two compositions also showed a sharp increase in acid resistance from the value of 7.85% weight loss at 125μm to 0.36% and 4.95% to 0.36% at 250μm at 850•C and 950•C respectively (Table4.2).

Batch $K_{15}B_{80}NS_5$particle size of 250μm showed high acid resistance at all sintering temperatures. Batch $K_5B_5SL_{90}$with particle size 90μm sintered at 850^0C and 950^0C have more alkaline resistance. All other compositions showed different kind of variation in both acid and alkaline. This indicated that acid and alkaline resistance depend on the formulated composition.

Table 4.2: Percentage weight Loss in 0.1M HCl and 0.1M NaOH

Composition	% Weight loss in HCl (0.1M)			% Weight loss in NaOH (0.1M)		
	750°C	850°C	950°C	750°C	850°C	950°C
$K_5B_{95}NS_0$ (90 µm)	0.70	0.74	3.09	0.70	8.87	0.70
$K_{10}B_{85}NS_5$(125 µm)	1.11	4.95	7.85	3.20	1.40	1.07
$K_{15}B_{80}NS_5$(250 µm)	0.36	0.36	0.36	4.20	1.43	0.71
$K_5B_5SL_{90}$(90 µm)	1.09	2.48	1.05	1.49	0.35	0.35
$K_{10}B_5SL_{85}$(125 µm)	0.41	2.41	1.76	2.51	4.88	3.78
$K_{15}B_5SL_{80}$(250 µm)	2.83	6.64	1.41	0.73	3.34	1.10

For batches containing soda lime, $K_5B_5SL_{90}$90um grain size a value of 1.05% weight lossin acid was observed at 950^0C which is the lowest among all the compositions showing high acid resistance (Table.4.2).

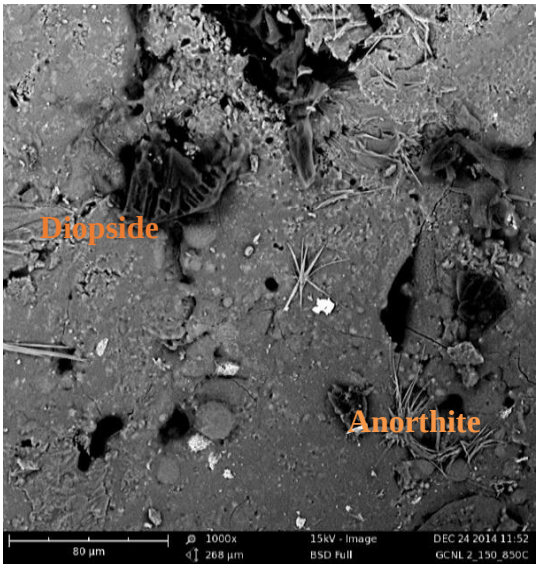
The values observed for alkali resistance in all the compositions were found to be lower than that of the acid at higher sintering temperatures.Compositions containing soda lime glass waste are more durable than those containingNa_2SO_4 at all particle sizes and sintering temperatures with few exceptions as indicated in (Table 4.2).

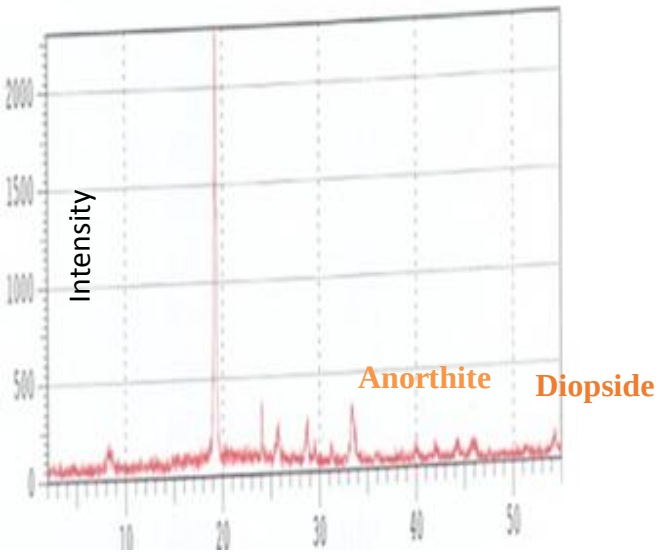
4.11 Scanning Electron Microscopy and X-ray Diffraction

The formation of crystal system in batch compositionK_{10} B_5 SL_{85} with125µm at850 °C was observed as indicated by SEM in (Plate VIIa).

The XRD pattern of the batch K_5 B_5 SL_{90} of particle size 90 µm revealed the formation of crystals even at a low sintering temperature of 750^oC, this showed that Crystallisation was achieved which was observed by the sharp peak intensity of the XRD (Plate VIIIb).

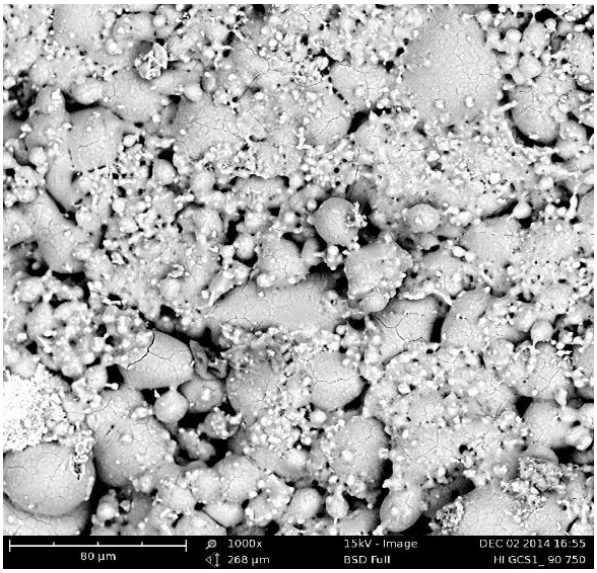
The XRD result for the batch $K_5B_{95}NS_0$ of the same particle size showed mixture of amorphous and sharp peaks at the same sintering temperature (Plate IX).The crystallisation of the batches occurs at slow heating rate of 5°C/minute which indicated bulk crystallisation.



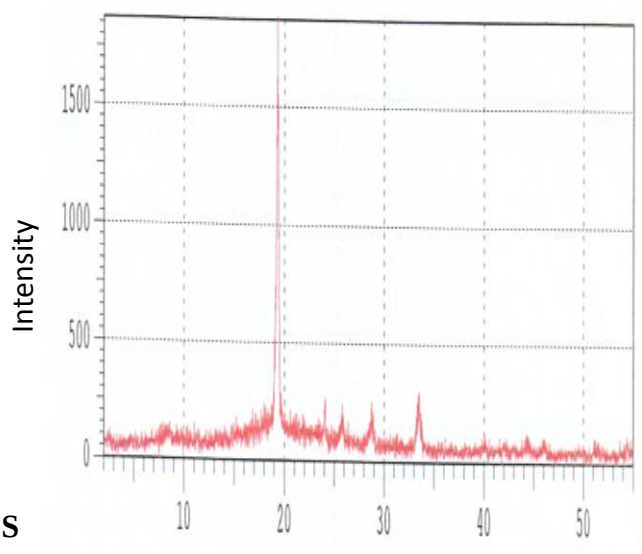


(a) **SEM Magnification x1000** (b) XRD**Degree**

Plates VII: SEMand XRD of the Glass CeramicK_{10} B_5 SL_{85}125µmSintered at 850 °C

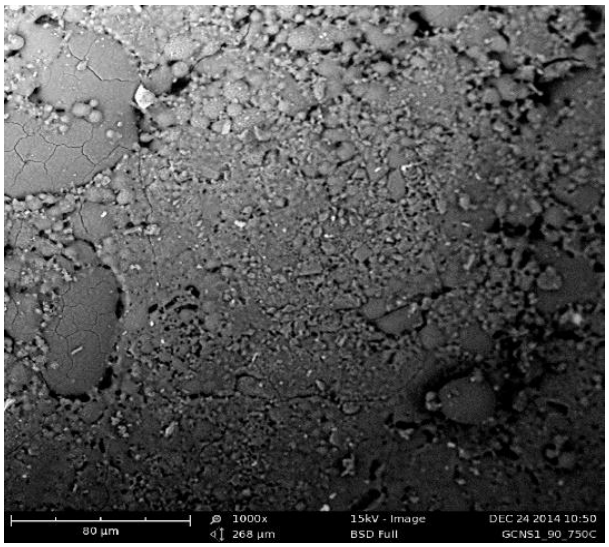


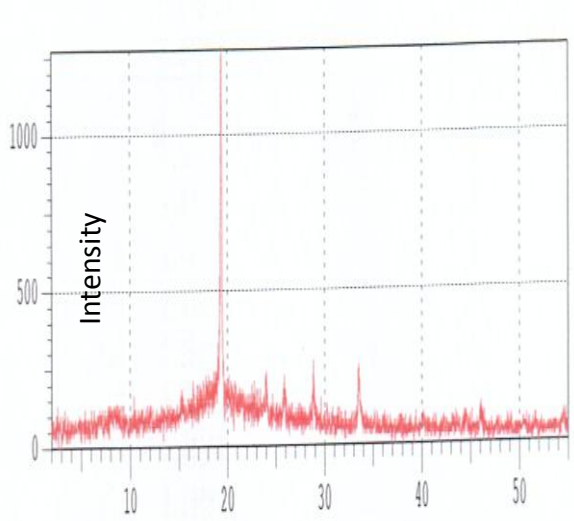
(a) S



EM Magnification x1000 **(b) XRD** **Degree**

Plates VIII: SEM and XRD of the Glass Ceramic K_5 B_5 SL_{90}90µmSintered at 750 °C

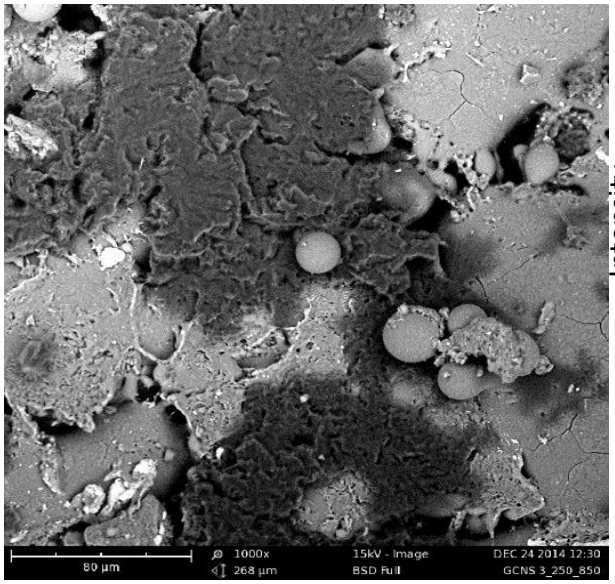


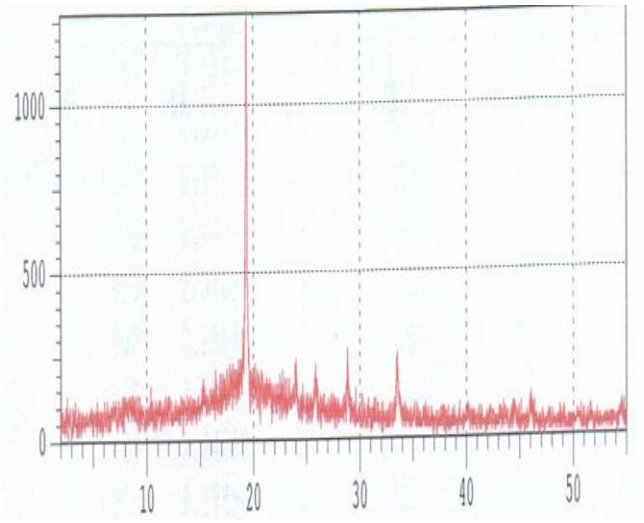


(a) **SEM Magnification x1000** (b) **XRD Degree**

Plates IX: Microstructures and XRD of the Glass Ceramic$K_5B_{95}NS_0$ 90µmSintered at 750 °C

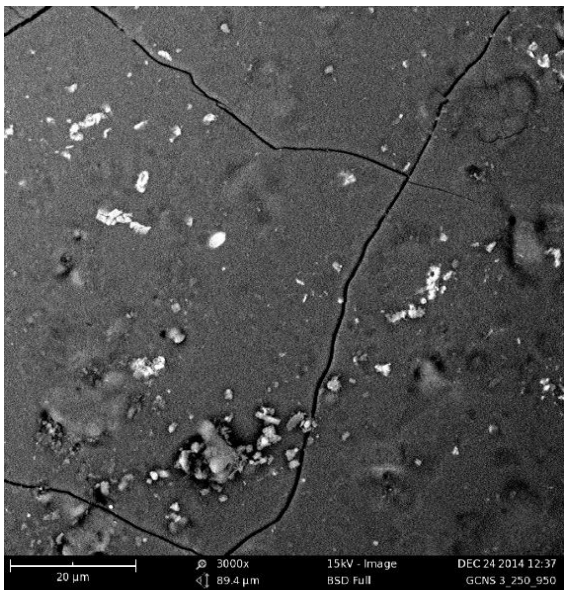
The XRD pattern of the batches sintered at 850^{o}C and 950^{o}C revealed amorphous portion with intensity peaks that correspond to that of diopside(Plates Xb and XI b).

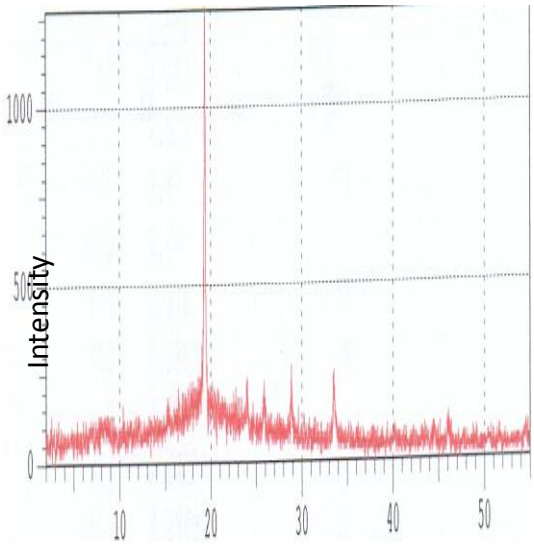




(a) **SEM Magnification x1000** **(b) XRD** **Degree**

Plates X:Microstructures and XRD of the Glass Ceramic $K_{15}B_{80}NS_5$250µmSintered at 850°C



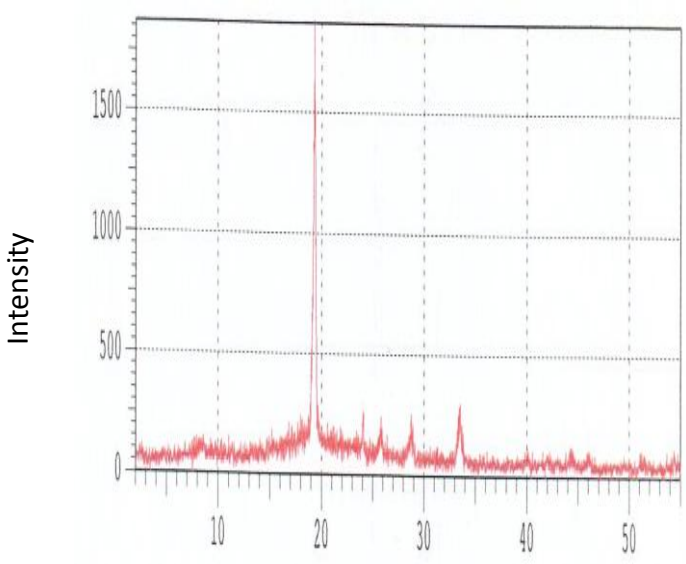


(a) SEM Magnification x1000 **(b) XRD** **Degree**

Plates XI: Microstructures and XRD of the Glass Ceramic $K_{15}B_{80}NS_5$250µm Sintered at 950°C

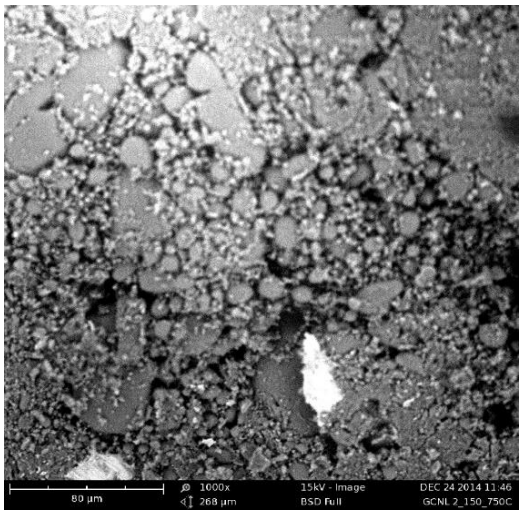
The result of the XRD Pattern of all the batches developed at 750^{o}C in this study with the exception of batches 90µm $K_5B_5SL_{90}$ and $K_5B_{95}NS_0$with 90µm(PlatesVIIIb and IXb)produced amorphous patterns(Plates XIIa, XIIIa, XIVa, XVa, XVIa and XVIIa).



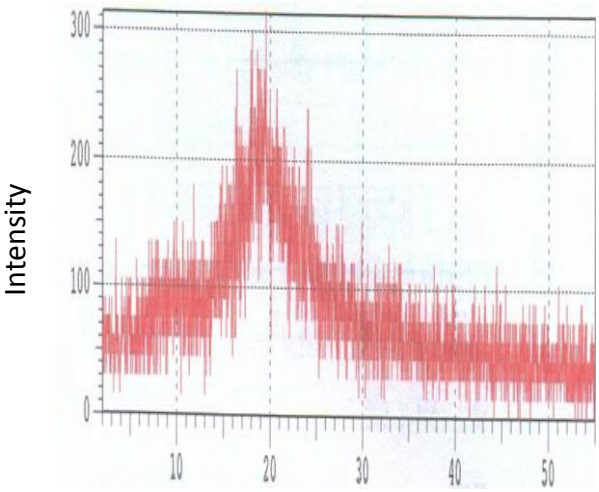


(a) SEM Magnification x1000 **(b) XRD Degree**

Plates XII: SEMand XRD of the Glass Ceramic K_5 B_5SL_{90}90µmSintered at 750°C

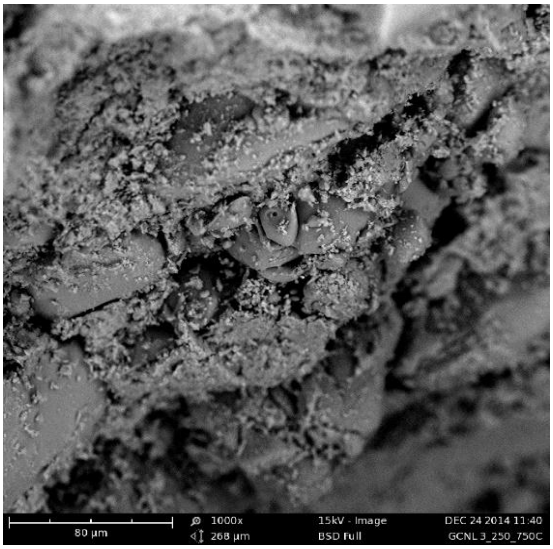


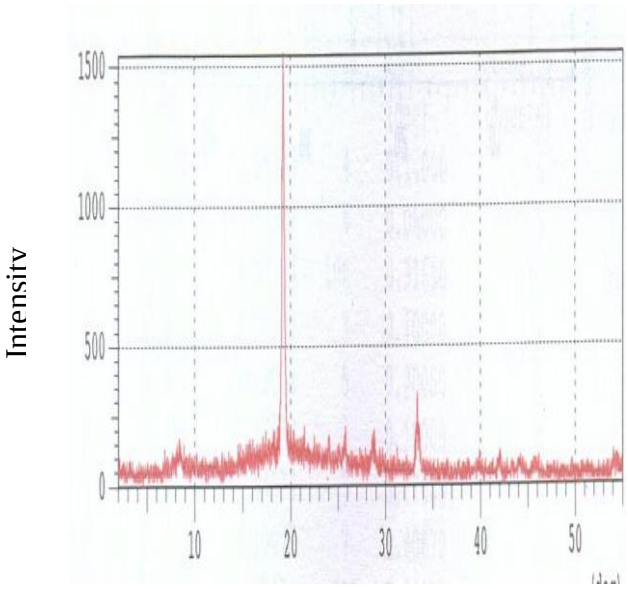
(a) SEM Magnification x1000



(b) XRD Degree

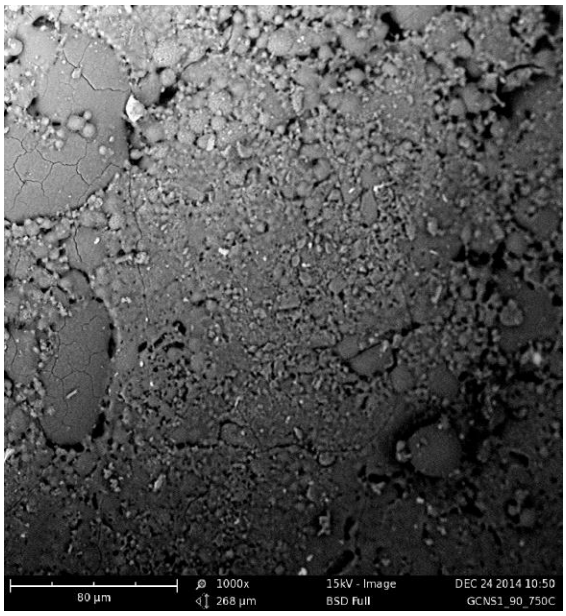
Plates XIII: SEMand XRD of the Glass Ceramic K_5 B_5SL_{90}125µmSintered at 750°C

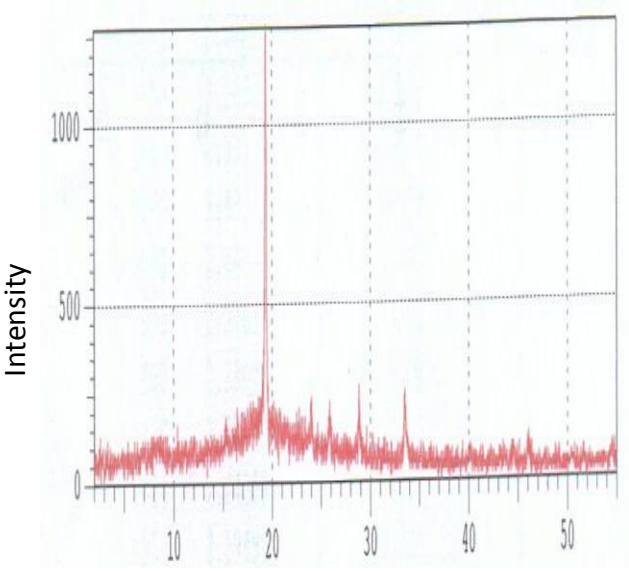




(a) SEM Magnification x1000 **(b) XRD** **Degree**

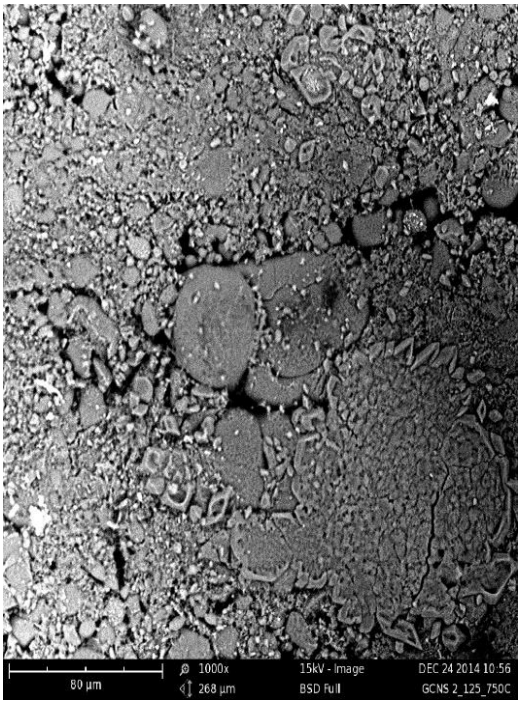
Plates XIV: SEMand XRD of the Glass Ceramic K_5 B_5SL_{90}250µmSintered at 750°C

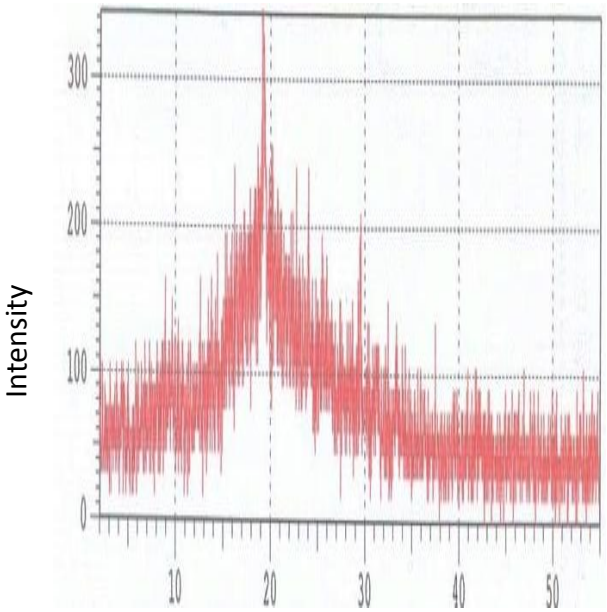




(a) SEM Magnification x1000 **(b) XRD** **Degree**

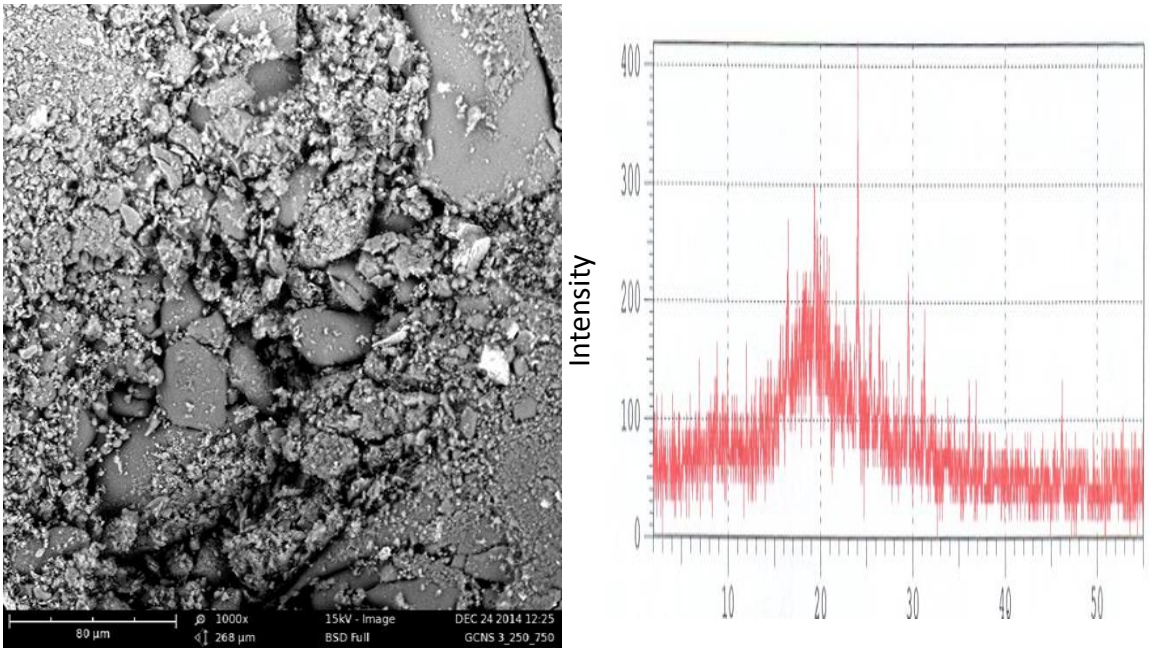
Plates XV: SEMand XRD of the Glass Ceramic $K_5B_{95}NS_0$ 90µmSintered at 750°C





(a) SEM Magnification x1000 **(b) XRD** **Degree**

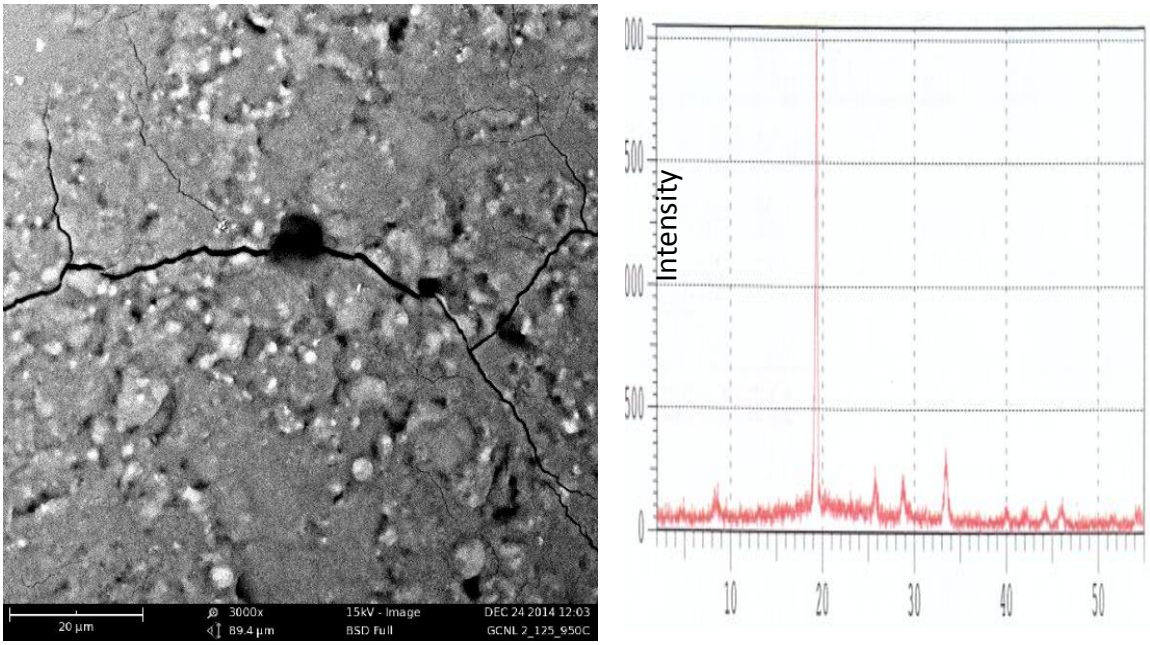
Plates XVI: SEMand XRD of the Glass Ceramic $K_5B_{95}NS_0$ 125µmSintered at 750°C



(a)SEM Magnification X1000(b) XRD Degree

Plates XVII: SEMand XRD of the Glass Ceramic $K_5B_{95}NS_0$ 250µmSintered at 750°C

Increasing the temperature to 850^0Cand 950^0C indicates high degree of densification and appearance of crystalline phases as shown in SEM images (Plate VIII, XI and XII). Square pillar–like crystals and typical layer of feathery structures were observed in batchesK_{10} B_5 SL_{85} 125µm at 850 °C and 950°C (Plates VIIa and XVIIIa)respectively.



(a) SEM Magnification x1000 **(b) XRD** **Degree**

Plates XVIII: SEMand XRD of the Glass Ceramic K_{10} B_5 SL_{85}125µmSintered at 950°

CHAPTER FIVE

DISCUSSION

The utilization and reuse of waste materials to develop valuable products have been used intensively based on their silicate and other oxide compositions.

Kaolin, soda lime and borosilicate glass wastes were used as primary raw-material with the addition of 5wt% sodium sulphate (Na_2SO_4) as sintering aid in this study with varying compositions as reported in the work of Gorokhvosky *et al.*, (2001). The use of glass wastes from a mixture of panel glass waste and Cathode Ray Tubes (CRT) in combination with mining residues from feldspar excavation and lime from basement system of glass industries to produce a glass ceramic was also reported by Bernardo*et al*(2005).

5.1 Moisture Content and Loss on Ignition

Moisture content and loss on ignition of the kaolin and waste glasses used to produce glass ceramics were found to be within the range of 10-30% as reported byMathumathi (2000). Romuoldo et al, 2007 developed a glass ceramic with 6.75% moisture content of fly and bottom ash wastes, so the value of 14.82% for moisture content and loss on ignition for the waste glasses and kaolin obtained in this study are within the range ofreported literature.

5.2 Oxides Analysis

The x-ray fluorescence analysis of the waste materials showed that borosilicate waste glass contain the highest $SiO_2$with 80.50%, soda lime waste glass with 77.63% and kaolin waste has the lowest of 46.80%. The SiO_2 content of container and laboratory glasses as reported by Samuel(1974) were 77.80% and 80.60% respectively. The chemical oxides compositions obtained by XRF of container and window waste glasses were similar to the work reported by

Coasta*et al*,(2009) and other oxides percentages (Table 4.1)are within the range of the literature values (Madhusudan, 2014).

5.3 Particle Size Effect

Sintering is the most commonly used method to fabricate glass ceramics products. A glass ceramic with homogeneous and dense surface produce crystalline phases which lead to development of glass ceramics of high strength used for structural application sintered at 750^{o}C, 850^{o}C and 950^{o}C with holding time of one hour (NurRiftan*et al.,* 2011). Glass ceramic batches with particle size of 90μm sintered more than the compositions with 125μm and 250μm. This is as a result of greater surface area of smaller particles andincrease in particle to particle contact for compositions with particle sizeof 90μm compared to 125μm and 250μm as shown in (Figures 4.1and 4.2) which revealed highest percentage shrinkage for compositions with 90μm particle sizes at all sintering temperatures compared to other compositions of higher particles size. Similar observation was reported by Hwang *et al.*,(2006)and Chinnam, (2014).

5.3.1 Shrinkage

Glass ceramic body made from a mixture of bottom ash and waste soda lime glasses sintered at 950^{o}C showed higher shrinkage and low water absorption (Daniela and Carlos, 2007). In this study the waste glasses and sodium sulphate were used as sintering aid.

In all the batches formulated there was decreased in percentage shrinkage with increase in particle size. The highest percentage shrinked batch is $K_5B_5SL_{90}$ 90μm particle size at 950^{o}C was 17.36%. This revealed the high sintering aid of soda lime glass waste compared to sodium sulphate. The least shrinkage value of 0.94% was found in batch containing 15wt% kaolin 80wt% borosilicate and 5wt% sodium sulphate with 250μm particle size at 750^{0}C. This is attributed to larger particle size, higher percentage kaolin and decrease in percentage

composition of borosilicate glass waste as sintering aid. The result of higher shrinkage for the batches with 125μm and 250μm particle sizes at 950^0C revealed the roles of high temperature and sintering aid of sodium sulphate and soda lime waste glasses (Appendix XII, Figures 4.1and 4.2)This have effect on the gradual decrease of viscosity as reported by Salwaand Abeer(2012).

5.3.2. Water Absorption

The trend of water absorption of the sintered batchescontaining sodium sulphate and those containing soda lime in which both served as sintering aids, showed an increase with increasing particle size at all sintering temperatures and decrease with increasing sintering temperatures. The observed trend is clearly indicated in (Figures 4.3 and 4.4).This phenomenon is as a result of the porous nature of the compositions due to higher particle size and increase in sintering process at a higher temperature.

The highest value of water absorption observed in batches $K_{15}B_5SL_{80}$ with 250μm particle size at 750°C is 18.02% and value of 18.00% in batch$K_{10}B_5SL_{85}$with 250μm at 850°C. The least value of 0.34% was observed on three different sintered samples of composition $K_{10}B_{85}NS_5$ and $K_{10}B_5SL_{85}$ with 125μm particle sizes and $K_{15}B_5SL_{80}$ with 250μm particle sizes at 950°C sintering temperature. This observationwas due to the influence of compositions and the sintering aid effect of both the sodalime and sodium sulphate which outweighed that of larger particles.

5.3.4 Porosity

The highest value of porosity observed was 26.84% in batch composition of $K_{15}B_5SL_{80}$ with 250μm particle size at 750°C sintering temperature (Figure 4.6)and the lowest obtained was 0.68% in batch composition of $K_{10}B_{85}NS_5$ at 125μm particle size at 950°C sintering

temperature (Figure4.5). This supports the work of (Costa *et al.*,2009) in which the porosity decreases with the increase in sintering temperature and increase with increase withparticle size in all the sintered batch compositions as observed in this study.

5.3.5 Bulk and Apparent Densities

The bulk density increases for a given batch with increasing the particle sizes.In this study, the variations in particle size, the batch constituents and the sintering temperatures play important role in the variation of both bulk and apparent densities.

In case of batch $K_{10}B_{85}NS_5$ with 125µm particle size which had a bulk density of 2.14g/cm^3 at 850^{0}C was supported bythe sintering aid of sodium sulphate despite the high particle sizes. The value of 2.13g/cm^3 bulk density was recorded for batch $K_5B_{95}NS_0$ 90µmat 850^{o}C(Figures 4.7 and 4.8.) This was due to non-addition of sodium sulphate in the batch.

In batch $K_5B_5SL_{90}$ at 90µm particle size, the bulk density of 2.54g/cm^{3}was observed at 850^{o}C and the density decreased to 2.24g/cm^3 at 950^{o}Csintering temperature.This is as a result of crystal growth at a temperature lower than 950^{o}C which usually decreases densification (Chung–Lun*et al.,* 2003). The least value of 1.34g/cm^3 in batch$K_5B_5SL_{90}$with125µm at 750^{o}C clearly manifest the effect of high particle sizes (NurRiftan, 2011).

The batch $K_5B_5SL_{90}$ with 90µm particle size at 750^{o}C sintering temperature has a value of density 2.02g/cm^3 but greatly increased to 2.54g/cm^3 at 850^{o}C (Fig 4.8) This showed high specific surface energy and particle – particle contact for lower particle size (Chinnam, 2014).

The highest apparent density of 2.65g/cm^3 was observed for batch $K_5B_5SL_{90}$ with 90µm at 850^{0}C, the least value of 1.65g/cm^{3}recorded for the batch $K_{10}B_5SL_{85}$ with 125µm at 950^{0}C(Figure 4.9) demonstrated the influence of higher particle size despite the higher sintering temperature.

5.3.6 Hardness

For a given batch the type ofparticle size have effect on the hardness of the glass ceramic formed particle size affect densification during the sintering process by decreasing or increasing it depending on the size of the particles.Hardness in glass ceramic is the extent of sintering and densification which is particle size dependent (Kothiyal, 2004). This is shown in case of batch $K_5B_{95}NS_0$90µm that contained only kaolin and borosilicate at 950˚Cwith hardness of 81.5N/m^2which is the highest value observed in this study. There is a trend in the hardness decrease with increase in particle size observed in this study(Figures 4.11 and 4.1).

5.4 Composition Effect

5.4.1 Shrinkage

The type of compositions played a great role in the variation of percentage shrinkage (Daniela and Carlos, 2007) In this study the waste glasses and sodium sulphate were used as sintering aid.The batch containing 5wt% kaolin 90wt%soda lime and 5wt%borosilicate showed the highest percentage shrinkage of 17.36% with 90µm particle size at 950˚C. The least shrinkage value of 0.94% was found in batch containing 15wt% kaolin 80wt% borosilicate and 5wt% sodium sulphate with 250µm particle size at 750˚C. This is attributed to larger particle size, higher percentage kaolin and decrease in percentage composition of borosilicate glass waste as sintering aid. The result of higher shrinkage for the batches with 125µm and 250µm particle sizes at 950˚C revealed the role of high temperature and sintering aid of sodium sulphate and soda lime waste glasses (Appendix XII,Figures 4.1and 4.2).Which have effect on the gradual decrease of viscosity as reported by Salwaand Abeer(2012).

5.4.2. Water Absorption

The trend of water absorption of the sintered batch compositions containing sodium sulphate and those containing soda lime in which both served as sintering aid, showed an increase with increasing particle size at all sintering temperatures and decrease with increasing sintering temperatures. The observed trend is clearly indicated in (Figures 4.3 and 4.4).This phenomenon is as a result of the porous nature of the compositions in sintering process at a higher temperature.

The highest value of water absorption observed in batch composition $K_{15}B_5SL_{80}$ with 250μm particle size at 750^{o}C is 18.02% and value of 18.00% in composition $K_{10}B_5SL_{85}$with 250μm at 850^{o}C. The least value of 0.34% was observed in three different sintered samples of composition $K_{10}B_{85}NS_5$ and $K_{10}B_5SL_{85}$ with 125μm particle sizes and $K_{15}B_5SL_{80}$ with 250μm particle sizes at 950^{o}C sintering temperature. The exceptional higher percentage of water absorption for $K_{10}B_5SL_{85}$ with 125μm at 850^{o}C was due to higher percentage kaolin in the batch, which lowers the sinteringprocess (Costa *et al.*,2009).Compositions containing soda lime, kaolin and borosilicate have high shrinkage due to the sintering effect of soda lime and borosilicate compared to that of sodium sulphate. The higher densification in the batch containing soda lime allows presence of smaller pores compared to the composition containing sodium sulphate and borosilicate which allows the presence of the higher pores hence higher water absorption.

5.4.3 Porosity

The observed decrease in porosity depends on the type of composition. It was reported that the sintering aid of waste glasses are higher than that of fresh raw-materials (Costa *et al.*,2009). The observed decrease in porosity in composition containing sodium sulphate in batch

$K_{10}B_{85}NS_5$with 125µmat 950^{o}Cwas as a result of viscous flow which is commonly observed in glass ceramics sintered at low temperatures (Boccaccini *et al.*, 1997).

The highest value of porosity observed was 26.84% in batch composition of $K_{15}B_5SL_{80}$ with 250µm particle size at 750^{o}C sintering temperature (Figure4.6)and the lowest obtained was 0.68% in batch composition $K_{10}B_{85}NS_5$with 125µm particle size at 950^{o}C sintering temperature (Figure4.5).

5.4.4 Bulk and Apparent Densities

In this study, the variations in composition of the batch constituents and the sintering temperatures play important role in the variation of both bulk and apparent densities.

In case of the compositions containing kaolin, borosilicate waste glasses, with the Na_2SO_4 serving as sintering aid, high density was observed for batch $K_{10}\ B_{85}NS_5$ with 125µm particle size which had a bulk density of 2.14g/cm^3 at 850•C.The high bulk density supported the sintering aid of Na_2SO_4. The value for the bulk densityrecorded for the batch with no sodium sulphate is 2.13g/cm$^{3.}$at850•C. (Figures 4.7 and 4.8).

In compositions containing 5wt % kaolin, 5wt % borosilicate, and 90wt % soda lime at 90µm particle sizes, the bulk density of 2.54g/cm^3 at 850^{o}C and the density decreased to 2.24g/cm^3 at 950^{o}Csintering temperature.This is as a result of crystal growth at a temperature lower than 950^{o}C which usually decrease densification (Chung–Lun*et al.*, 2003). The least value of 1.34g/cm^3 in composition containing kaolin, borosilicate and soda lime waste with125µm at 750^{o}Cwas observed.

The increase in kaolin content in a given batch increases the presence of $Al^{3+,}$ which is known to reduce the Na+ in the composition, thus give rise to increasing density (Bahman and Behzad , 2012;Behzad and Gholam,2013).

The apparent densities for all the batch compositions in this study have no definite pattern at various sintering temperatures considered. The highest value of 2.65g/cm^3 was observed in the batch $K_5B_5SL_{90}$ with 90µm at 850•C, the least value of 1.65g/cm^{3}was recorded for the composition $K_{10}B_5SL_{85}$ with 125µm at 950•C (Figure 4.9). The compositions containing sodium sulphate was found to have low apparent densities at the various sintering temperatures compared to the batches containing soda lime as sintering aids (Figures 4.9 and4.10). The density variations revealed to a certain extent the degree of Crystallisation in the glass ceramics developed (Gutzow 1979; Gutzow and Shmeltzer, 1995).

5.4.5 Hardness

The batch composition $K_5B_{95}NS_o$ with 90µm particle size at 950^{o}C sintering temperature was found to have high value of Rockwell superficial hardness of 81.5N/m^2(Appendix XIII). This showed that it is the best sintered composition among all the batches formed. The type of composition and sintering aidenhanced densification during the sintering process play a significant role in the values of the hardness of the developed glass ceramics.Hardness in glass ceramic is the extent of sintering and densificationwhich is composition dependent (Kothiyal, 2004). This is shown in case of composition that contained only kaolin and borosilicate at 950•C (Figures 4.11 and 4.1**).**

5.5 Sintering Temperature Effect

5.5.1 Shrinkage

The shrinkage of the glass ceramic produced is temperature dependent.The sintered glass ceramics developed in this study clearly demonstrated this assertion(Appendix XII).Glass ceramic body made from a mixture of bottom ash and waste soda lime glasses sintered at 950^{o}C showed higher shrinkage, (Daniela and Carlos, 2007).The batch containing 5wt% kaolin

90wt%soda lime and 5wt%borosilicate ($K_5B_5SL_{90}$)showed the highest percentage shrinkage of 17.36% sintered at 950•C.The least shrinkage value of 0.94% was found in batch ($K_{15}B_{80}NS_5$)sintered at 750•C. The result of higher shrinkage for the batches with 125μm and 250μm particle sizes at 950•C revealed the roleincrease in temperature (Appendix XII, Figures 4.1and 4.2).The work of Hwang *et al.*, 2007confirmed this trend.

5.5.2 Water Absorption

The trend of decrease in water absorption with increasing sintering temperatures and increase with decreasing sintering temperatures is clearly indicated in (Figures 4.3 and 4.4). This phenomenon is as a result of the porous nature of the compositions at lower sintering temperature and densified with increase in sintering process at a higher temperature. The highest value of water absorption observed in batch composition $K_{15}B_5SL_{80}$ at 750^{o}Cwith 250μm was 18.02% and value of 18.00% in composition $K_{10}B_5SL_{85}$with 250μm at 850^{o}C. The least value of 0.34% was observed on three different sintered samples of batches $K_{10}B_{85}NS_5$ and $K_{10}B_5SL_{85}$ with 125μm particle size and $K_{15}B_5SL_{80}$ with 250μm particle size at 950^{o}C sintering temperature. The exceptional higher percentage of water absorption for $K_{10}B_5SL_{85}$ with 125μm at 850^{o}C was due to higher percentage kaolin in the batchwhich lowers the sinteringprocess (Costa *et al.*, 2009).

5.5.3 Porosity

The porosity decreases with the increase in sintering temperature. The highest value of porosity observed was 26.84% in batch $K_{15}B_5SL_{80}$ with 250μm sintered at 750^{o}C and the lowest obtained is 0.68% in batch $K_{10}B_{85}NS_5$with 125μm sintered at 950^{o}C sintering temperature(Figures 4. 4 and4.5).

The observed decrease in porosity in batch $K_{10}B_{85}NS_5$with 125µmat 950^{o}Cwas as a result of viscous flow which is commonly observed in glass ceramics sintered at low temperature (Boccaccini *et al*., 1997).

5.5.4 Bulk and Apparent Densities

The sintering temperatures play important role in the variation of both bulk and apparent densities. The bulk density increases for a given composition with increasing sintering temperatures and decrease with decrease in the sintering temperatures.

The batch $K_{10}B_{85}NS_5$ had a bulk density of 2.14g/cm^3 at 850•C and batch $K_5B_5SL_{90}$ sintered at 850^{o}C with the bulk densityof 2.54g/cm^{3}and decreased to 2.24g/cm^3 at 950^{o}Csintering temperature .This is as a result of crystal growth at a temperature lower than 950^{o}C which usually decreases densification (Chung –Lun*et al.*, 2003). The least value of 1.34g/cm^{3}for composition containing kaolin, borosilicate and soda lime waste with125µm at 750^{o}Cwas observed. This is in line with the low sintering temperature effect on bulk density (NurRiftan, 2011).

The composition containing $K_5B_5SL_{90}$ with 90µm particle size at 750^{o}C sintering temperature has a value of density 2.02g/cm^3 but greatly increased to 2.54g/cm^3 at 850^{o}C (Figure 4.8).This supported the observed effect of increase in density with increase in sintering temperature.(Chinnam, 2014).

The highest value for the apparent density was 2.65g/cm^3 in the batch $K_5B_5SL_{90}$ with 90µm sintered at 850•C, the least value of 1.65g/cm^{3}was recorded for the batch $K_{10}B_5SL_{85}$sintered at 950•C (Figure 4.9). The compositions containing sodium sulphate was found to have low apparent densities at various sintering temperatures compared to the batches containing soda

lime as sintering aids (Figures 4.9 and4.10).This showed that the nature of batch constituents have effect on the apparent density regardless of the sintering temperature.

5.5.5 Hardness

Hardness in glass ceramic is the extent of sintering and densificationwhich is composition dependent (Kothiyal, 2004).The highest value of Rockwell superficial hardness of 81.5N/m^2 was observed for the batch $K_5B_{95}NS_o$ with 90µm sintered at 950^{o}C (Appendix XIII)This showed that it is the best sintered composition among all the batches formed. Batches $K_{10}B_{85}NS_5$ and $K_{10}B_5SL_{85}$with 125µm sintered at 950^{o}C recorded the least value ofRockwell superficial hardness of 70.5N/m^2.This was due to the onset of crystallisation which lowers hardness of glass ceramic (Figures 4.11 and 4.12**).**

5.6. Chemical Durability

In the batch compositions $K_5B_{95}NS_0$with 90µm and $K_{10}B_{85}NS_5$with 125µm particle sizes, there is decrease in chemical durability in acid with increase sintering temperature .Two compositions also showed a sharp increase in acid resistance from the value of 7.85% weight loss with 125µm to 0.36% and 4.95% to 0.36% with 250µm at 850˚C and 950˚C respectively (Table4.2).This is comparable to the work of Leroy*et al*(2001) for glass ceramic developed from silicate containing coal ash.

The batches $K_{10}B_{85}NS_5$ with particle size 125µm sintered at 950˚C and $K_5B_{95}NS_0$ with particle size 90µm sintered at 850^{o}C showed less resistance to acid and alkali respectively. Batch $K_{15}B_{80}NS_5$ particle size of 250 µm showed high acid resistance at all sintering temperatures. Batch $K_5B_5SL_{90}$with particle size 90µm sintered at 850˚C and 950˚C have more alkaline resistance. All other compositions showed different kind of variation in both acid and alkaline. This indicated that acid and alkaline resistance depend on the formulated compositions.

Batches containing soda lime, $K_5B_5SL_{90}$ 90µm particle size a value of 1.05% weight loss in acid was observed for the product sintered at 950•C which is the lowest among all the compositions showing high acid resistance (Table4.2).

The values observed for alkali resistance in all the compositions were found to be lower than that of the acid at higher sintering temperatures .This indicated that the developed glass ceramics are more alkali resistant. This clearly supported the assertion that alkali metal ions are much more stable in crystalline phase than in the residual glass phase during the action of leaching solution in the glass ceramics material (Chinnam, 2011).

Compositions containing soda lime glass waste are more durable than those containingNa_2SO_4 at all particle sizes and sintering temperatures with few exceptions as indicated in (Table 4.2).

5.7 Scanning Electron Microscopy and X-ray Diffraction

The initial compositions and heat treatment are the most important parameters that affect the kind of crystalline phases and the final properties of the glass ceramic which may fulfill many applications (Erol*et al.*, 2007).

It was reported that Crystallisation ability of glass ceramics increases with the addition of nucleating agent such as TiO_2 Park and Bary(1981).The oxides analysis of all the wastes in this study were found to contain significant amount of TiO_2(Table 4.1). The Crystallisation process in glass ceramics is known to be connected with the nature and properties of its oxide compositions.A glass-ceramics developed from blast furnace slag in the presence of 3 -5% TiO_2 attained surface Crystallisation at 950•C(Ovecoglu, 1998).

The presence of crystals at a temperature lower than 900^{o}C was observed for anorthite based glass ceramics because of the presence of TiO_2 which act as nucleating agent to reduce the Crystallisation temperature. The anorthite crystal were observed to grow with the forms of

feathery spherical particles, having a tendency to coalescence into huge domain (chung-lun*et al.*,2002) this clearly supports the formation of an anorthite crystal system in the batch compositionK_{10} B_5 SL_{85}. 125µm 850 °C as indicated by SEM in (Plate VIIa).

The XRD performed on various heat treated or sintered compositions of a glass ceramics showed slight variations as a result of changes in the wastes compositions of the pellets produced (Marghussian and Niaki, 1995).The XRD pattern of the batch $K_5B_5SL_{90}$ of particle size 90µmrevealed the formation of crystals even at a low sintering temperature of 750^oC, this showed that Crystallisation was achieved which was observed by the sharp peak intensity of the XRD (Plate VIIIb).The XRD result for the batch $K_5B_{95}NS_0$ of the same particle size showed amorphous peaks at the same sintering temperature(Plate IXb). The crystal formation in case of batch K_5 B_5 SL_{90} of particle size 90µmwas as a result of sintering aidof the soda lime waste glass. The crystallisation of the batches occured at slow heating rate of 5°C/minute which indicated bulk crystallisation as reported by Karamanov*et al.*,(2003).

The angle of diffraction observed at higher temperature and low particle size, correspond to that of anorthite crystalline phase (CaO. Al_2O_3. SiO_8) (Plate VIIb). Considering the oxide compositions, anorthite phase occurs when the amount of CaO is minimumand SiO_2 maximum. Increase in quantity of kaolin results in high content of SiO_2.The batches that contains higher percentage of kaolin give rise to more SiO_2 with low CaO.This favoured the formation of anorthite (Sa'ad and Hussein, 2005).

The formulated batch compositions showed that all the XRD of batches with lower CaO and high SiO_2 revealed the peaks corresponding to that of anorthite.This resembles the XRD pattern of batch $K_{10}B_5$ SL_{85} with125µm at 850°C(Plate VIIb).The XRD pattern of a crystalline phase depend on the sintering temperature, for the anorthite crystalline system it appears at a relatively high temperature compared to diopside. The XRD pattern of the batches sintered at

850^{o}C and 950^{o}C revealed amorphous portion with intensity peaks that correspond to that of diopside(Plates Xb and XI b).

The cracks observed on the SEM(Plates XIa and XIIa) were due different thermal expansion coefficient of the amorphous and crystalline phases which supported the porosity nature of the batch in which the variation of porosity decreases with increase in sintering temperatures.The result of the XRD pattern of all the batches developed at 750^{o}C in this study with the exception of batches 90µm $K_5B_5SL_{90}$ and $K_5B_{95}NS_0$with 90µm(PlatesVIIIb and IXb)produced amorphous patterns.The XRD pattern of a glass ceramic developed from dried drill cuttings in the presence of sodium and calcium oxides at a sintering temperature of 750^{o}C and 800^{o}C revealed amorphous peaks (Zaid, 2008; Abbe *et al,* 2009). The SEM of the batches sintered at 750^{o}C results in partial sintering which is the stage of a well-defined grain boundaries formation (Plates XIIa, XIIIa, XIVa, XVa, XVIa and XVIIa).

Increasing the temperature to 850˚Cand 950˚C brings about high degree of densification and appearance of crystalline phases are as shown in SEM images (Plate VIII, XI and XII).This observation is supported by the work of Roether*et al.*, (2010).

Glass ceramics developed from fly ash produced two crystalline phases; anorthite and diopside at 1050^{o}C but the anorthitebased is produced more at 1150^{o}C (Young *et al,*.(2003). This shows that anorthite and diopside can coexist in a given glass ceramics system, diopside appears as square pillar – like crystals while anorthite appears as typical layer of feathery structures, this was observed inthe batches, K_{10} B_5 SL_{85} 125µm at 850°C and 950°C(Plates VIIa and XVIIa) .The XRD and SEM are similar to the work of Young*et al.*, (2003). The presence of Cr_2O_3 in a given batch composition is known to serves as nucleating agent in the formation of diopside crystalline phase (Karamanov*et al.*, 2004). This supports the formation of the two crystalline

phases suggested for the batches in which crystallisation was observed to occurred at 850^{o}C and 950^{o}C sintering temperatures (Plates VIIIb and XIIIb) respectively.

Anorthite based glass ceramics are low-temperature sintered material, with low-dielectric properties sintered at a temperature equal to or less than 950°C (Chung-lun*et al.,* 2003). Studies conducted by Marques*et al.,*(2006) showed that anorthite based glass ceramic predominantly crystallized between temperatures 850 °C and 950°C with diopside detected within the same range in compositions rich in magnesium oxide. This clearly showed that the developed glass ceramic in this study is of anorthite diopside crystalline systems as indicated by the sintering temperatures and oxide compositions.

The results of physical properties and chemical resistance of some of the batches showed resistance to both acid and alkali with particular high resistance to alkali onbatch $K_5B_5SL_{90}$ with 90µm sintered at 850˚C.The research conducted in this study showed that the developed glass ceramics of batch compositions $K_5B_5SL_{90}$ with 90 µm, $K_{10}B_5SL_{85}$ with125µm and $K_{15}B_{80}NS_5$ with 250 µm sintered at 850˚C and 950˚C are of anorthite diopside as revealed by their physical and mechanical properties, the XRD and SEM of the batches as supported by the literature in previous works. The glass ceramic developed can be used as lining materials for constructions and communications, also for heat and ware resistance appliances, thermochemical, biomedical and ceramics coatings.

The anorthite can be used for lining of materials used for communication and the diopsidecrystalline phase in materials where high heat resistance is required, as well as in wear resistance thermo-chemical, biomedical and ceramic coatings.

CHAPTER SIX

SUMMARY, CONCLUSION AND RECOMMENDATIONS

6.1.Summary

Glass ceramics were developed using kaolin, Sodalime and borosilicate waste. The method of sintering was adopted using temperatures of 750•C, 850•C and 950•C with heating rate of 5^0C/min and residence time of one hour. The physical,chemical and mechanical properties of the glass ceramics were analyzed. The Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) analysis of the developed glass ceramics particularly the batches that gave anorthite crystalline phasesconform to that of glass ceramics.

The chemical behavior of some of the batches showed resistance to both acid and alkali with particular high resistance to alkali sintered at 850•C. The properties of the glass ceramics developed in this study are of anorthite- diopside based. The anorthite can be used for lining of materials used for communication and the diopside crystalline phase in materials where high heat resistance is required, as well as in wear resistance thermochemical, biomedical and ceramic coatings.

6.2Conclusion

Inconclusion, the waste materials used contain oxides that provide ambient condition for the development of the glass ceramics. Various batches were formulated with varying composition and particle sizes and were sintered at different temperatures.The properties of the developed glass ceramics were observed to be particle size, composition and temperature dependent in which the variations determine the physical, chemical and mechanical properties of the glass ceramics.

The scanning electron microscopy and the x-ray diffraction patterns of the batches showed the presence of the crystalline and amorphous structures of anorthite and diopside phases

Based on the determined physical, chemical and mechanical properties of the developed glass ceramics particularlyfor batches $K_5B_5SL_{90}$ with 90 µm, $K_{10}B_5SL_{85}$ with125µm and $K_{15}B_{80}NS_5$with 250 µm sintered at 850^{0}C and 950 ^{0}C ,the crystalline phases and morphology revealed by XRD and SEM in this study, the glass ceramic are of anorthite- diopside which provide qualities that can be used as lining materials for construction and communication, also as for heat and wear-resistance appliance for thermochemical, biomedical and ceramics coatings.

6.3Recommendations

1. The composition for a given grain size be varied, to ascertain the effect of composition at a given sintering temperature.
2. The residence time for the batches produced may be varied from one, two and three hours to observe the improvement of the Crystallisation pattern and hence possible appreciable properties of the developed glass ceramics.
3. Detail test on the mechanical properties such as flexural and bend strengths, young modulus and electrical properties such as conductivity and dielectric constant be conducted to determine more applications of the glass ceramics
4. Diopside crystalline phases observed in some of the batches can be made highly bioactive by in cooperating some oxides that will develop a good material for producing artificial teeth.
5. The outcome of the research have shown that utilizing these wastes to produce useful products is feasible, so there is the need for the government to put this finding into a large scale to commercialize the research for the establishment of industries for glass ceramic development which will provide employment, reduce importation of such items, enhance the economy and sanitize the environment.

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Appendix I

Chemical Composition of Borosilicate Glass

Raw Materials	Oxide	% Composition
Silica sand	SiO_2	65 – 85
Soda ash	Na_2O	3 – 9
Lime	CaO	0 – 2.5
Barite	B_2O_3	8 – 15
Alumina	Al_2O_3	1 – 5
Potash	K_2O	0 – 2

Source: (Haun Labs, 2000).

Appendix II

Chemical Composition of Soda Lime Glass

Raw Material	Oxide	% Composition
Silica sand	S_iO_2	69 – 74
Lime	CaO	5 – 14
Soda	Na_2O	10 – 16
Magnesia	MgO	0 – 6
Alumina	Al_2O_3	0 – 3
Others		0 – 5

Source: Haun Labs, 2000

Appendix III

The Comparison between Borosilicate Glass and Soda Lime Glass

S/N	Glass	% Oxide Composition	Properties	Uses
1	Borosilicate glass (pyrex)	SiO_2 – 80 B_2O_3 – 13 Na_2O – 4 Al_2O_3 – 2	High melting Point, Resistant to high heat and chemical reaction. Allow infra-red rays but not ultraviolet rays Does not break easily and are expensive.	For Lab. Apparatus cooking utensils
2	Sodalime glass	SiO_2 – 70 Na_2O – 15 CaO – 10 Others – 4	Low melting point moldable into shapes Break easily, cannot withstand high heating cheap to obtain	Containers, panels mirrors, bulbs , lamps plates and bottles

Source: Mathias *et al.,* 2008

Appendix IV

Typical Chemical Composition of Kaolin Specimen

Oxide	% Composition
S_1O_2	46.60
Al_2O_3	38.30
T_1O_2	0.1
Fe_2O_3	0.4
CaO	0.3
MgO	0.3
Na_2O	0.3
K_2O	0.7
LoI	13.0

Source: Hamer, 1975

Appendix V

Location of Kaolin Deposits in Nigeria

S/N	State	Location	Estimated Reserve
1	C/Rivers	Ala, Babuege, Betikwe, Mba, Babuabong	-
2	Akwa-Ibom	Ibiaku, Ntok, Okpo, Mbiafun, Ikot, Ekwere	-
3	Abia	Umuahia, Ikwuano, IsiukwuatoNnochi	Small scale exploration
4	Enugu	UzoUwami, Nsukka South, Udi River Orgi, Enugu.	Small Scale exploration
5	Imo	Ehime, Mbano, Ahiazu, Mbaise, Orlu, Ngor-Okpalla, Okigwe, Oru	Small scale mining
6	Benue	Apa, Ogbadibo, Okpokwu, Vandikya	-
7	Anambra	Ozubulu, Ukpor, Ekwusigo, Nnewi Ihiala, Njikola, Aguata, Anambra	Partial exploration
8	Ondo	Obusoro, Ifora, Ewideaya, Okitipupa, Omifun-fun	Partial exploration
9	Ekiti	Usan-Ekiti, Omi-Alafia, IkereEkiti	-
10	Nasarawa	Awe, Keffi	45,000 metric tonne
11	Ogun	Ibese, Bamoje, Onibode Abeokuta	Partial exploration

12	Kogi	Agbaja	-
13	Niger	Lavung, gbako, pategi, Kpaki	-
14	Kaduna	Kachia, Mararaban- Rido	5.5 million tonnes partial exploration
15	Plateau	Nahuta, Barikin-LadiMangu, Kanam	20 million tonnes commercial exploration
16	Bauchi	Alkaleri, Ganjuwa, DarazoMissau, Kirfi, Dambua	20 million tones commercial exploration
17	Yobe	Fika (Turmi)	-
18	Borno	Maiduguri, Biu, Dambua	-
19	Edo	All parts of the state	Large and yet to be exploited
20	Delta	Anoicha, Ndokwu	Large and yet to be exploited
21	Osun	Irewole, Ile-Ife, Ede	Partial exploitation
22	Katsina	Kankara, Dutsen-Ma, SafanaBatsari, Ingawa, Musawa, Malumfashi	20 million tonnes
23	Kano	Rano,Bichi,Tsanyawa, DawakinTofaGwarzo	-

24	Kebbi	Danko, Zuru, Gira, Dakin Gari, Illo, Kaoje	-
25	Oyo	Tede, Ado-Awaye	Exploitation by local potters
26	FCT	Kwali, Dongara	-

Source:RMRDC, 2010.

Appendix VI

Typical Crystal Phases Developed in Glass – Ceramic

S/N	Glass Ceramic System	Crystal Phase
i	$Li_2O – Al_2O_3$-SiO_2 (low Al_2O_3)	Quartz, crystobalite, Lithium disilicate Lithium metasilicate
ii	Li_2O- Al_2O_3-SiO_2(High Al_2O_3)	Beta spodumene, Beta eucryptite
iii	$Li_2O – MgO – SiO_2$	Quartz, crystobalite, Enstatite Lithium disilicate, forsterite Lithium metasilicate.
iv	MgO-AI_2O_3 –SiO_2	Quartz, Cristobalite, Corderite Enstatite, Forsterite
v	ZnO-Al_2O_3- SiO_2	Quartz, Cristobalite, Gahnite, Willemite

Source: Mathumathi, 2000.

Appendix VII

Stages of Sintering

Stages of Sintering	Changes
1st stage (initial)	Rearrangement and 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 eliminated

Source: Richerson,2006

Appendix VIII

Commercial Glass Ceramics

Commercial Identification	Crystal Phases	Properties	Application
C8603	$L_{12}O$-$2SiO_2$,S_1O_2	Photochemicallymachinable	Fluid amplifiers, mold for printing
C9608	2MgO-$2Al_2O_3$ $5SiO_2$, S_1O_2,T_1O_2	Low expansion, good transparent rader	Radomes
C9608	B-spodumene, solid solution, T_1O_2	Low expansion, good chemical durability	Household cooking utensils
C9611	α- quartz solid solution	Very high strength	Structural members
Neoceramic	β-spodumene solid solution	Low expansion	Household cooking wares

Owns illions	β-quartz solid solution	Zero expansion at ambient temperature	Telescope mirror blanks
A-H cookware	β-quartz solid solution	Low expansion	Household cook ware
C303	Na_2O-$2A_2O_3$-$2S_1O_2$,Bao-$2Al_2O_3$-$2SiO_2$	High strength	Table ware and dinner war
C9690	B quartz solid solution	Low expansion	Gas stove burners
C0333 β-quartz solid solution		High strength, weather-ability	Building cladding
C-CYKOL and CYKO2	Sodium elobate	High dielectric constant	Miniature capacitors

Source:Richerson,2006

Appendix IX

Young Modulus of Glass Ceramic Materials Compared with other Materials

Material	**Young's Modulus ($Mpa.10^{-4}$)**	**Material**	**Young's Modulus ($Mpa\text{-}10^{-4}$)**
Glass–ceramic	8 – 14	Steatite low – loss ceramics	7.0
Fused Quartz	7.4	Electroporcelain	6.7
Sodium-Calcium Glass	7.0	Sintered MgO	21.0
Borosilicate Glass	6.6	Marble	2.7 – 8.2
Ceramics (high Al_2O_3)	28 – 35	Granite	4.2 – 6.0
Sintered Al_2O_3	37.4		

Source: Strnad, 1986.

Appendix X

Bending strength of Glass ceramics Compared with other Materials

Material	Bending strength (MPa)
Glass	55 – 70
Glass ceramics	70 – 350
Glass ceramic with modified surface	Upto 1400
Electropocelain (glazed)	86 – 140
Ceramics (high Al_2O_3)	212 – 353
Cast iron	140 – 320
Steel	300 – 1400

Source: Strnad, 1986.

Appendix XI



Sample of Kaolin Waste

Appendix XII



Sample of Borosilicate Glass Wastes

Appendix XIII



Sample of Soda Lime (Post-Consumer) Glass Wastes

Appendix XIV



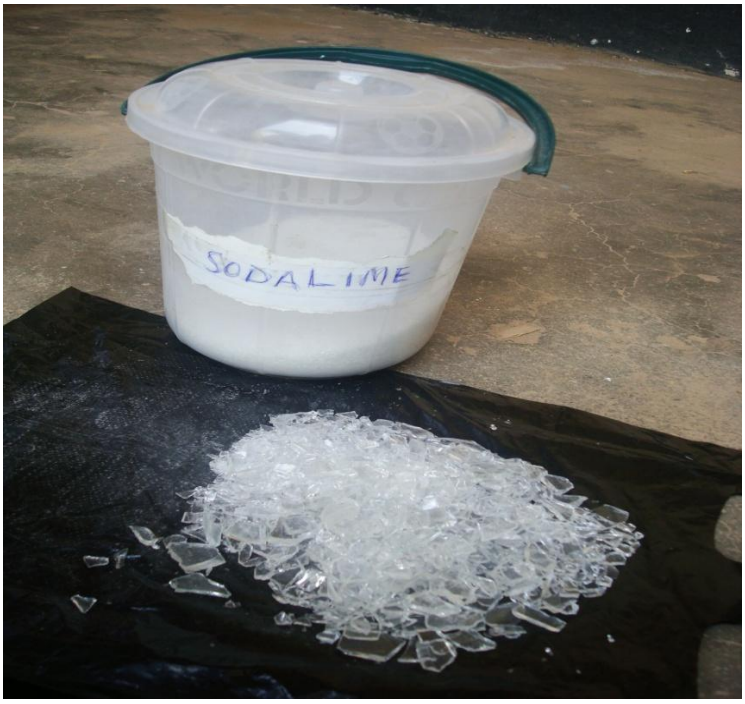
Sample of Soda Lime (Window) Glass Wastes

Appendix XV



Sample of Crushed Borosilicate Glass Wastes

Appendix XVI



Sampleof Crushed Soda Lime Glass Wastes

Appendix XVII

Percentage Shrinkage of Batch Compositions Formulated at Various Sintering Temperatures

Composition	Percentage Shrinkage at Various Sintering Temperature		
	750˚C	850˚C	950˚C
$K_5B_{95}NS_0$ (90 µm)	12.56	14.00	14.35
$K_{10}B_{85}NS_5$(125 µm)	4.88	11.15	11.78
$K_{15}B_{80}NS_5$(250 µm)	0.94	5.77	10.10
$K_5B_5SL_{90}$(90 µm)	11.45	13.77	17.36
$K_{10}B_5SL_{85}$(125 µm)	2.89	11.90	12.99

$K_{15}B_5SL_{80}$(250 µm)	1.09	7.29	12.91

Appendix XVIII

Bulk and Apparent Densities, Percentage Porosity and Water Absorptions at 750°C

composition	Fired weight (g)	Suspended weight (g)	Soaked weight (g)	%water absorption	% porosity	Apparent density g/cm^3	Bulk density g/cm^3	Temperature °C
$K_5B_{95}NS_0$ (90 µm)	2.90	1.53	2.94	1.40	2.84	2.12	2.06	750
$K_{10}B_{85}NS_5$(125 µm)	2.92	1.49	3.25	11.30	20.45	2.06	1.64	750
$K_{15}B_{80}NS_5$(250 µm)	2.89	1.46	3.24	13.29	19.66	2.02	1.62	750
$K_5B_5SL_{90}$(90 µm)	2.83	1.50	2.90	1.75	5.00	2.13	2.02	750
$K_{10}B_5SL_{85}$(125 µm)	2.44	1.02	2.82	15.60	21.11	1.72	1.34	750
$K_{15}B_5SL_{80}$(250 µm)	2.83	1.44	3.34	18.02	26.84	2.04	1.49	750

Appendix XIX

Bulk and Apparent Densities, Percentage Porosity and Water Absorptions at 850°C

composition	Fired weight (g)	Suspended weight (g)	Soaked weight (g)	%water absorption	% porosity	Apparent density g/cm^3	Bulk density g/cm^3	Temperature °C
$K_5B_{95}NS_0$ (90 µm)	2.86	1.56	2.90	1.04	2.99	2.20	2.13	850
$K_{10}B_{85}NS_5$(125 µm)	2.87	1.60	2.94	7.00	5.22	2.26	2.14	850
$K_{15}B_{80}NS_5$(250 µm)	2.85	1.34	3.10	8.77	14.20	1.89	1.62	850
K_5B_5 SL_{90}(90 µm)	2.89	1.80	2.94	5.00	3.39	2.65	2.54	850
$K_{10}B_5SL_{85}$(125 µm)	2.67	1.37	2.85	18.00	12.15	2.05	1.80	850
$K_{15}B_5SL_{80}$(250 µm)	2.92	1.54	2.98	2.05	4.17	2.16	2.03	850

Appendix XX

Bulk and Apparent Densities, Percentage Porosity and Water Absorptions at 950°C

composition	Fired weight (g)	Suspended weight (g)	Soaked weight (g)	%water absorption	% porosity	Apparent density g/cm^3	Bulk density g/cm^3	Temperature °C
$K_5B_{95}NS_0$(90 µm)	2.93	1.58	2.95	0.70	1.27	2.17	2.14	950
$K_{10}B_{85}NS_5$(125 µm)	2.94	1.49	2.95	0.34	0..68	2.01	2.03	950
$K_{15}B_{80}NS_5$(250 µm)	2.85	1.50	2.90	1.75	3.57	2.11	2.04	950
$K_5B_5SL_{90}$(90 µm)	2.84	1.59	2.86	0.70	1.57	2.27	2.24	950
$K_{10}B_5SL_{85}$(125 µm)	2.91	1.65	2.92	0.34	0.78	1.65	2.27	950
$K_{15}B_5SL_{80}$(250 µm)	2.84	1.62	2.85	0.34	0.82	2.33	2.31	950

Appendix XXI

Hardness of Developed Glass

S/N	Composition	Temperature °C	Shore A	Shore D	Rockwell superficial value N/m^2
1	$K_5B_{95}NS_0$ (90µm)	750	95.00	46	76.6
2	$K_{10}B_{85}NS_5$(125µm)	750	92.00	41	74.5
3	$K_{15}B_{80}NS_5$(250µm)	750	92.34	41	74.5
4	$K_5B_5SL_{90}$ (90µm)	750	93.34	43	75.6
5	$K_{10}B_5SL_{85}$(125µm)	750	93.34	43	75.6
6	$K_{15}B_5SL_{80}$(250µm)	750	94.3	45	76.0
7	$K_5B_{95}NS_0$ (90µm)	850	93.00	43	75.6
8	$K_{10}B_{85}NS_5$(125µm)	850	95.34	46	76.6
9	$K_{15}B_{80}NS_5$(250µm)	850	97.00	55	80.9
10	$K_5B_5SL_{90}$ (90µm)	850	93.34	43	75.6
11	$K_{10}B_5SL_{85}$ (125µm)	850	95.00	46	76.6
12	$K_{15}B_5SL_{80}$(250µm)	850	94.34	45	76.0
13	$K_5B_{95}NS_0$ (90µm)	950	97.67	56	81.5
14	$K_{10}B_{85}NS_5$(125µm)	950	89.34	35	70.5
15	$K_{15}B_{80}NS_5$(250µm)	950	90.34	39	72.8
16	$K_5B_5SL_{90}$ (90µm)	950	96.67	55	80.9
17	$K_{10}B_5SL_{85}$(125µm)	950	90.34	39	70.5
18	$K_{15}B_5SL_{80}$ (250µm)	950	89.67	55	80.9