SOL-GEL SYNTHESIS OF SILICA FROM RICE HUSK ASH FOR GLASS CERAMICS PRODUCTION

BY

SAMUEL ADE GIDEON, B.Sc. (ABU) 2010
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DEPARTMENT OF INDUSTRIAL DESIGN,
FACULTY OF ENVIROMENTAL DESIGN,
AHMADU BELLO UNIVERSITY ZARIA,
NIGERIA

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ABSTRACT

This study is an experimental research on the possible use of rice husk ash silica for the Production of glass ceramics utilising the abundant agricultural waste. Rice husk was pre-treated, carbonised to drive out volatile matter and ash at 700^oC. The brown ash (BA) obtained was characterised by X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) to determine the chemical composition and to know the crystal phases present in the ash. The XRF result contained 79.98% SiO_2 and the rest 20.02% included 1.80% P_2O_3, 0.42% Na_2O, 1.54% CaO, 0.05% BaO, 0.11% TiO_2. XRD result of the RHA showed a broad peak zone centred near $2\theta=22.2^o$ signifying the amorphous nature of silica. A solution of the ash was prepared with Sodium hydroxide, titre against a solution of Calcium trioxonitrate(iv) tetrahydrate and Trioxonitrate (v) acid, after some minutes the gel was formed and dried to powder. Fourteen samples were compacted and sintered at 700^oC. The products were characterised by XRD, Scanning Electron Microscopy (SEM) and the physicochemical properties were tested. The XRD Pattern of the product showed the presence of sodium calcium silicate phase ($Na_4Ca_4SiO_6O_{18}$) combeite which belong to the bioactive ceramics family. The SEM showed a circular morphology of glass ceramics in glassy matrix with Energy Dispersive X-ray analysis (EDS) elemental spectra showing Si, Ca, P and Na. Physicochemical test also showed the material having 0.2% water absorption below the convectional range of between 5-10% making it better by being less porous and good resistance to alkali attack than acid attack. Above all, a glass ceramics product has been produced highlighting the importance of utilising an agricultural waste RHA in the glass and glass ceramics industry for production. It also, goes to show that RHA is an alternative raw material to silica sand. The sol-gel route employed proves that it is a high energy saving technique when compared with the conventional methods and powder processing through sinter-crystallisation.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the Study

Rice is a major crop grown in some states in Nigeria. After rice grain milling, rice husks remain as an agricultural waste material. Many people have tried to use this waste to produce useful materials such as silica, silicon carbide, silicon nitride or silicon for solar cells (Yalcin and Sevinc, 2001). Rice husk is one of the largest readily available but most unutilised biomass resources and has long been an ideal fuel for electricity generation (kumar and Venugopal, 2013).

Numerous silicate based wastes, such as coal ash, slag from steel production, fly ash and filter dusts from waste incinerators, mud from metal hydrometallurgy, different types of sludge as well as glass cullet or mixtures of them have been considered for the production of glass ceramics (Rawlings *et al*., 2009).

Rice husk (RH) is one of the by-products obtained during milling of rice. It is reported that approximately 0.23 tonnes of rice husk is formed from every tonne of rice produced (Jain *et al.*, 1996). Global production of rice, the majority of which is grown in Asia, is approximately 550 million tonnes per year. The milling of rice generates a waste material, the husk surrounding the rice grain. This is generated at a rate of about 20% of the weight of the product rice, or some 110 million tonnes per year globally. The husk in turn contains between 15 and 20% of mineral matter the majority of which is amorphous silica (Groszek and Laughin, 2015).

In Nigeria, rice production is reported as 4.7 million tonnes in the year 2013 by the (FAOSTAT in GEOHIVE, 2015), the National Rice Development Strategy produce; in 2010 put national paddy production in 2007 at 3.4 million tonnes and a projection of 13.27 million tonnes for 2018 (Adesina, 2014). Three types of rice are cultivated in Nigeria. These are the African rice, *Oryza glaberrima*; Asian rice, *Oryza sativa*; and the recently introduced, West African Rice Development Association (WARDA) hybrid rice, New Rice for Africa (NERICA) available only to farmers under WARDA's programme. The major rice type grown in Nigeria is the Asian rice *Oryza sativa* (Longtau, 2003). There are varieties of the rice the grown in various geo-location of Nigeria which include: Upland, Hydromorphic, Rain fed Lowland, Irrigated Lowland, Deep Inland Water and Mangrove Swamp. Rice cultivated in Kujama in Chikun Local government area of Kaduna state is classified under the rain fed lowland rice.

Burning rice husk as fuel to generate energy, results in the waste product, rice husk ash (RHA). RHA is rich in silica (about 60%) and can be an economically viable raw material for production of silica gels and powders (Chakraverty and Kaleemullah, 1991; Kamath and Proctor, 1998). RHA has been evaluated and use as an adsorbent of minor vegetable oil components (Proctor *et al.*, 1995, Proctor and Palaniappan, 1990). Although various uses for rice husk and RHA have been suggested in literatures, their disposal or utilisation remains a major concern. Soluble silicates produced from silica are widely used in the glass, ceramics, cement as a major component, in pharmaceuticals, cosmetics and detergents industries as a bonding and adhesive agents. (Laxamana, 1982, Anon., 1997). Rice husk is sometimes used as a fuel for parboiling paddy in the rice mills and to power steam engines. The partially burnt rice husk in turn contributes to environmental pollution. It would be beneficial to the environment to recycle the waste to produce eco-material having high end value (Pijarn *et al.*, 2010).

One of the most recent products of glass is the glass ceramics. Glass ceramics are fine-grained polycrystalline materials formed when glasses of suitable compositions are heat treated and thus undergo controlled crystallisation to the lower energy, crystalline state (McMillan, 1979; Hölland and Beall, 2002). The concern of the glass and glass ceramics industries is the availability of raw materials at an affordable price and the production of glass and glass ceramics by low energy consumption production processes.

1.2 Statement of the Problem

The production of glass ceramics depends on the availability of raw materials and requires high temperatures. These raw materials are usually imported, therefore, the inadequacy of the materials pose a problem to the glass and glass ceramics manufacturing industries, that rice husks being produced in abundance; though, an unutilised biomass posing environmental pollution and the difficulty in their use will be a good source of material for glass ceramics production in the country. Sol-gel synthesis of RHA for glass ceramics requires lesser temperature consumption hence, will be a better method of producing glass ceramics through sinter-crystallisation of powders. Therefore, the problem of the study is to utilise the abundant biomass (RHA) as raw materials for glass and glass ceramics production. This process would reduce the cost of production in addition to preventing the environmental pollution associated with the husk disposal.

1.3 Aim of the Study

The aim of the research study is to produce glass ceramics using rice husk ash by sol-gel process.

1.4 Objectives of the Study

The objectives of the study are to:

i. analyse the chemical composition and crystal phases of the rice husks ash.
ii. prepare the gel solution from rice husk ash.
iii. prepare powder of the gel after drying and sinter the powder to form glass ceramics.
iv. characterise the product by XRD, SEM and Test the physicochemical properties of the glass ceramics.

1.5 Research Questions

i. Has RHA a suitable composition for glass ceramics production?
ii. Will the RHA be soluble in solution preparation?
iii. Will the solution prepared form gel?
iv. Can the gel be converted into powder after drying?
v. Can the powder sinter-crystallise to form the glass ceramics?
vi. Do the physical and chemical properties conform to standard?

1.6 Basic Assumptions

The basic assumptions made were:

i. That the RHA will be a suitable composition.
ii. That the RHA will form a soluble solution.

iii. That the solution will form gel.

iv. That the powder obtained will sinter-crystallise to form glass ceramics.

v. That the properties of the ceramics would conform to standard.

1.7 Justification of the Study

Although various uses for rice husk and rice husk ash have been recommended in literatures, their disposal or utilisation remains a major concern. Soluble silicates produced from silica are widely used in the glass, ceramics, cement as a major component, in pharmaceuticals, cosmetics, and detergents industries as a bonding and adhesive agents (Laxamana, 1982; Anon., 1997). Rice husks ash is rich in silica (about 60%) and can be an economically feasible raw material for production of silica gels and powders (Chakraverty and Kaleemullah, 1991; Kamath and Proctor, 1998). RHA has been evaluated as an adsorbent of minor vegetable oil components (Proctor *et al*., 1995; Proctor and Palaniappan, 1990). Rice husk ash has high content of silica and being readily available, with an estimated 3.4 million tonne of rice produce yearly in Nigeria (Adesina, 2014), used as a substitute for the relatively expensive raw material employed in glass manufacturing without compromising the quality.

1.8 Scope of the Study

The research will utilise the abundant biomass (rice husk) from Kujama (Chikun L.G.A in Kaduna states) to produce the ash, which will be analysed, processed with Sodium hydroxide, Calcium trioxonitrate (iv) tetrahydarate, Trioxonitrate (v) acid to form glass ceramics pieces which will be characterised and tested for their physical and chemical properties.

1.9 Significance of the Study

The production of glass and glass ceramics depends on high temperature and the importation of some raw materials for the production of glasses and glass ceramics. Due to these facts there is a need to utilise the available biomass, rice husk for the production of glasses and glass ceramics using the non-conventional methods of production to reduce energy cost and dependence on importation of these raw materials for the production of glass ceramics. This study proposes a reduction in agricultural waste rice husk ash, reduction in cost of procuring and processing raw materials, reduction in energy consumption, production of high purity end product with high homogeneity, less contamination and the utilisation of the end product for useful applications that will enhance the technological advancement of the society and knowledge.

1.10 Limitation of the Study

The limitation of the study was lack of standard and well equipped laboratory where the research work can be carried out completely without the researcher moving from one laboratory to another.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

Glass ceramics are fine-grained polycrystalline materials formed when glasses of suitable compositions are heat treated and thus undergo controlled crystallisation to the lower energy, crystalline state (McMillan, 1979; Hölland and Beall, 2002). Glass-ceramics are ceramics materials formed through the controlled nucleation and crystallisation of glass. Glasses are melted, fabricated to shape and thermally converted to a predominantly crystalline ceramics. The basis of controlled internal crystallisation lies in efficient nucleation, which allows the development of fine, randomly oriented grains generally without voids, micro cracks, or other porosity (Chan, 2003).

Only specific glass compositions are suitable for glass ceramics; some glasses are too stable and difficult to crystallise, (such as ordinary window glass) whereas, on the other hand, some crystallise too readily in an uncontrollable manner resulting in undesirable microstructures. Secondly, the heat treatment is critical to the attainment of an acceptable and reproducible product.

2.2 A New Field of Technology

Glass ceramics are ceramics materials formed through the controlled nucleation and crystallisation of glass. Glasses are melted, fabricated to shape and thermally converted to a predominantly crystalline ceramics. The basis of controlled internal crystallisation lies in efficient nucleation, which allows the development of fine, randomly oriented grains generally without voids, micro cracks, or other porosity properties.

Beall (2002) observed that a dense ceramic made via the crystallisation of glass objects would be highly desirable. The invention of glass ceramics took place in the mid - 1950s by the famous glass chemist and inventor, S.D Stookey. It is useful to examine the sequence of events leading to the discovery of these materials (Figure 2.1) (Cahn, 2003).

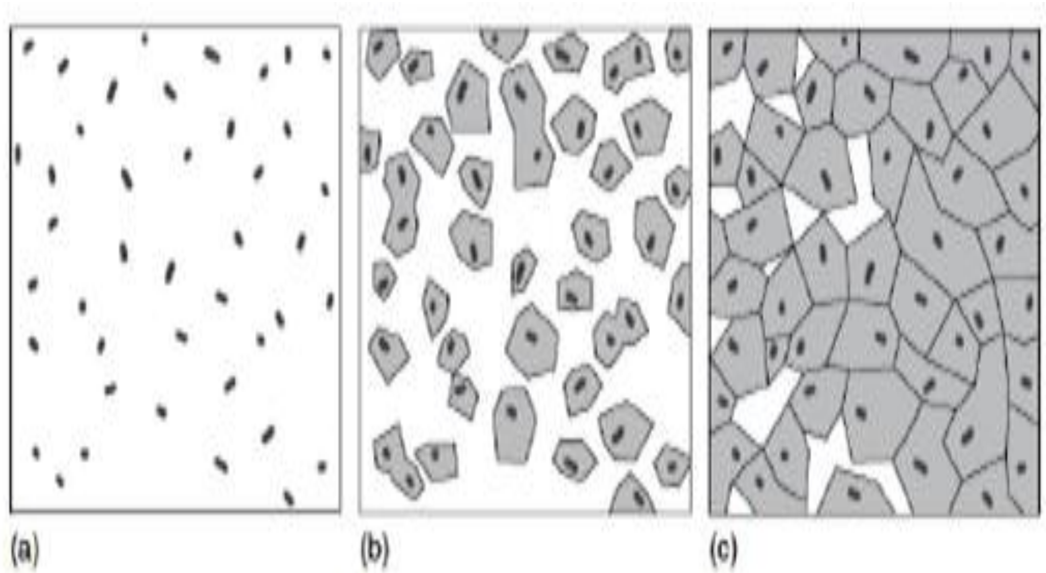

Figure 2.1 From Glass to Glass Ceramics (Source: Beall, 2002).

(a) Nuclei Formation (b) Crystal Growth on Nuclei and (c) Glass Ceramics Microstructure.

Stookey at the time was not primarily interested in ceramics. He was preoccupied in precipitating silver particles in glass in order to achieve a permanent photographic image. He was studying as host glasses lithium silicate compositions because he found he could chemically precipitate silver in alkali silicate glasses and those containing lithium had the best chemical durability. In order to develop the silver particles, he normally heated glasses previously exposed to ultraviolet light just above their glass transition temperature at around 450°C. One night, the furnace accidentally overheated to 850°C and on observation of the thermal recorder, he expected to find a melted pool of glass. Surprisingly, he observed a white material that had not changed shape. He immediately recognised it as a ceramics, evidently produced without distortion from the original glass article. A second unexpected event then occurred. He dropped the sample accidentally and it sounded more like metal than glass. He then realised that the ceramics he had produced had unusual strength (Cahn, 2003).

2.3 The Scientific Importance of Glass Ceramics

Glass ceramics fall under the category of glasses valued for high technology and specialty application, in addition to their common uses in domestic appliances. Specialty glasses differ from traditional glasses in the contents of specific additives, or may be of entirely different compositions. Novel processes have been exploited in developing many of these compositions (Beall, 2002).

2.3.1 Dental Applications

Glass ceramics can be used for artificial tooth, the cores can be made strong and sometimes opaque while the veneer is translucent and aesthetic, yet they are made of the same glass ceramics (Clark and Anusavice, 1991).

2.3.2 Bearings

Glass can also be used for their mechanical superior properties and their ability to take on smooth surfaces coupled with good abrasion resistance. These bearings are resistant to corrosive liquids such as seawater (Sibold, 1991).

2.3.3 Electrical Insulators

The high surface and volume resistivity of glass ceramics makes them useful as electrical insulators especially as high voltage carriers.

2.3.4 Heat Exchangers

Since glass ceramics can be made to have high thermal and chemical stability, they offer great possibilities for use as heat exchangers in regenerators. They can be made to have zero or negative expansion coefficient and as such can stand temperature changes without failure (Richlen and Parks, 1991).

2.3.5 Medical (Bio-ceramics)

The biological and medical application of glass ceramics include uses such as: orthopaedic joint replacement, prosthesis, bone implants and tooth implant (Hench, 1991).

2.3.6 Aerospace

The application of glass ceramics in aerospace includes uses as: space shuttle tiles, thermal barriers, high temperature glass windows and fuel cells (Levine and Herbell, 1991).

2.3.7 Automotive

In the automotive industries glass ceramics has such uses as: catalytic converters, ceramics filters, airbag sensors, ceramic rotors, valves, spark plugs, pressure sensors, thermostats, vibration sensors, oxygen sensors, safety glass windshields and piston rings (Costin, 1991).

2.4 Crystallisation and Devitrification

The crystallisation and devitrification of glass to form a glass ceramics is a heterogeneous transformation and as such consists of two stages, namely a nucleation stage and a growth stage. In the nucleation stage small, stable volumes of the product (crystalline) phase are formed, usually at preferred sites in the parent glass. The preferred sites are interfaces within the parent glass or the free surface. The latter is usually undesirable as the resulting glass ceramics microstructure often consists of large oriented crystals that are detrimental to mechanical properties. However, in a few instances an oriented structure is beneficial, e.g. glass ceramics for piezoelectric and pyroelectric devices (Sigaev *et al*., 1997) and machinable glass ceramics. In most cases internal nucleation, also known as bulk nucleation is required and the parent glass composition is chosen to contain species that enhance this form of nucleation. These species are termed nucleating agents and may be metallic (e.g., Au, Ag, Pt, and Pd) or non-metallic (e.g., TiO_2, P_2O_5 and fluorides) (Rawlings and Boccaccini, 2009).

2.5 The Glassy State

Glassy or non-crystalline materials do not solidify in the same sense as do those that are crystalline. Upon cooling, a glass becomes more and more viscous in a continuous manner with decreasing temperature; there is no definite temperature at which the liquid transforms to a solid as with crystalline materials. In fact, one of the distinctions between crystalline and non crystalline materials lies in the dependence of specific volume (or volume per unit mass, the reciprocal of density) on temperature, as illustrated in Figure 2.2

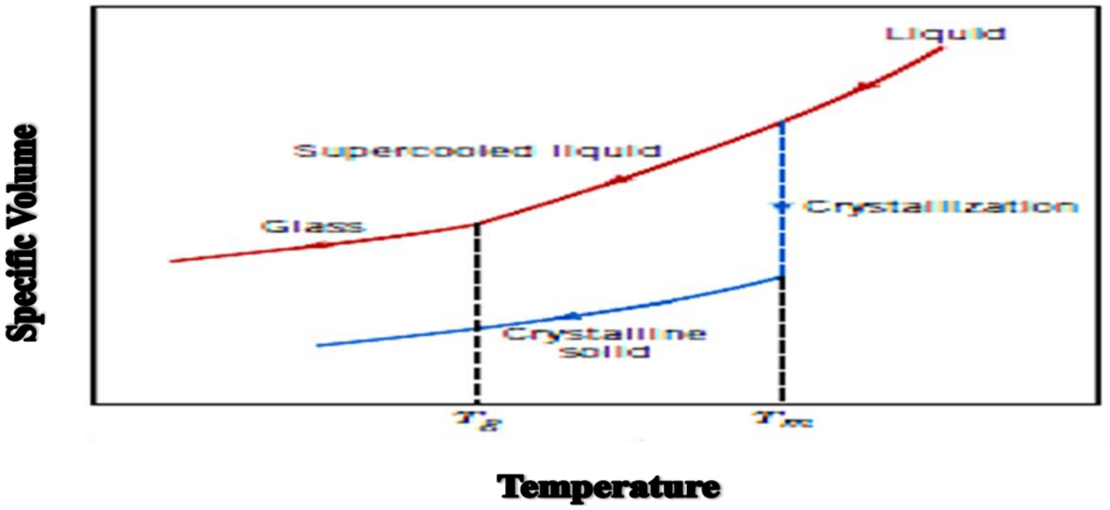

Figure 2.2 Contrast of Specific Volume against Temperature Behaviour of Crystalline and Non-Crystalline Materials (Source: Calister and Rethwisch, 2010).

Crystalline Materials solidify at the Melting Temperature *Tm*. Characteristic of the Non-crystalline state is the Glass Transition Temperature *Tg.*

For crystalline materials, there is a discontinuous decrease in volume at the melting temperature *Tm*. However, for glassy materials, volume decreases continuously with temperature reduction; a slight decrease in slope of the curve occurs at what is called the glass transition temperature or fictive temperature, *Tg*. Below this temperature, the material is considered to be a glass; above it is first a super cooled liquid and finally a liquid (Calister and Rethwisch, 2010).

2.6 Nucleation and Types of Nucleating Catalyst

The presence of nuclei in the melt once equilibrium is attained is the prerequisite to the formation of optically visible crystals. Nuclei are crystals of particulate sizes, which ideally should be close to the atomic dimension (Moody, 1971 Ali 2008). Nucleation can be homogenous or heterogeneous. Homogenous nucleation is as a result of molecular fluctuations in the melt which result in the formation of unstable, intermediary states called embryos. The embryos having attained the minimum critical size are capable of developing spontaneous particles into gross particles of the stable phase called nuclei. The formation of an embryo, its transformation into a stable nucleus as well as its growth rate is a subject of such factors as viscosity, super saturation and temperature (Ali, 2008).

Composition of homogenous nuclei is the same as that of the crystals that grow on them but compositions of heterogeneous nuclei on the other hand varies radically from the surrounding glass composition. Heterogeneous nucleation is similar to the existence of dust particles as a precondition for the condensation of dew in the atmosphere. Nucleation is not always due to high surface energy volume ratio required in forming the critical size and also due to the difficulty of excluding foreign nuclei from the melt. These extraneous materials includes refractory material fragments, vessels walls and the nucleating agents which are deliberately added to precipitate into tiny nuclei that are precursor to the formation of the major crystalline phase in glass. Nucleating agents promote volume nucleation and glass ceramics formation. Nucleating agents for oxide glasses are commonly TiO_2, ZrO_2, P_2O_5 and fluorides and water for non-oxide glasses. These species are termed nucleating agents and may be metallic (e.g., Au, Ag, Pt, and Pd) or non-metallic (e.g., TiO_2, P_2O_5 and fluorides) (Rawlings and Boccaccini, 2009).

2.7 Selection of Glass Type

Through proper selection of composition, there are six composition system commonly listed by most authors and their whole range of different types of crystals can be precipitated so that properties are channelled to their different end demand. In a similar vein, all sort of starting raw materials have been converted to glass ceramics from fly ash through cullet to virgin materials (Rawlings and Boccaccini, 2009).

The six common compositions are: li_2O-Al_2O-SiO_2 with exceptional low coefficient of thermal expansion, 2MgO-Al_2O-SiO_2- cordierite glass ceramics with good mechanical, thermal and dielectric properties, LiO_2-SiO_2 with photochemical etching capabilities, nephline glass ceramics with high mechanical strength attained through compression glazing, machinable flouromica glass ceramics and CaO-MgO-Al_2O-SiO_2 which is an expensive variety from natural minerals and the blast furnace slag (Ali, 2008).

2.7.1 LiO_2-Al_2O_3-SiO_2

The major property of this glass ceramics is low coefficient of expansion usually approaching zero near ambient temperature. A feature derived from β-quartz or β-spodumene solid solution crystal phase, which though metastable breakdown to other phases at about 900^{O}C. The nucleating agents for this group of glass ceramics are TiO_2 and ZnO_2 for most commercial compositions.

2.7.2 MgO-Al_2O_3-SiO_2

Cordierite based glass ceramics this category of glass ceramics based on the cordierite also called indialite, has remarkable strength, excellent dielectric properties, high thermal stability and shock resistance the major area of application is missiles randomes. They are nucleated by titania with cordierite, the major crystalline phase mixed with cristobalite, rutile, magnesium, dititania, and minor isolated glass grain boundary nodes. The coefficient of thermal expansion measured within the range of 0-700^{O}C is 45×10^{-7} $^{O}C^{-1}$ (Ali, 2008).

2.7.3 Photosensitive Lithium Silicate Glass Ceramics

They are result of homogenous nucleation of metal particles, catalysed by photoelectron produce by the action of radiation in special composition containing small amount of gold or silver ions. These glasses also contain cerium oxide added as an optical sensitizer such that ultraviolet radiation converts the Ce^{3+} to Ce^{4+} ions. The photoelectrons ejected in the process are then captured by gold or silver ions to convert to their metallic equivalences. On reheating, the metals nuclei grow to crystal of colloidal dimension, which manifest as colour or an opaque appearance. The operating temperature for this glass ceramics is 500^{o}C and the heat treatment is carried out at 610^{o}C.

2.7.4 Glazed Nepheline Glass Ceramic

The fine grained nepheline glass ceramics based on soda Nepheline ($NaAlSiO_4$), are based on SiO_2- NaO-TiO_2 composition. The titania content promotes opacity in addition to functioning as the nucleating agent. These glass ceramics are ordinarily expected to have high thermal expansion coefficient reflecting the properties of the major crystalline phase, Nepheline that is structurally related to the silica polymorph tridymite.

2.7.5 Glass Ceramics Based on Blast Furnace Slag

It is based on NaO-CaO-MgO-Al_2O-SiO_2 and called minelite is characterise by high resistance and good chemical durability. The glass from this composition is melted at 1450^{O}C, cooled and subsequently heat treated to a temperature of about 1000^{O}C to allow for the development of internal nuclei site between 850 and 1000^{O}C. The alumino-silicate residual glass, grey in colour remains in the product. Slag based glass ceramics are widely used in Eastern Europe, especially Hungary and Russia, as wall cladding to serve housing need of low income earners. Although the composition is designed to allow crystallisation at a particular stage, premature devitrification during shaping operations cannot be ruled out calling for modification of compositions to forestall such shortcoming.

2.7.6 Machinable-Flouromica Glass Ceramics Material

They are based on flouromica nucleated crystal phases, their machinability even by convectional metal tools arises from the randomly oriented fine grained mica crystal with a microstructure allowing crack to readily propagate between flexural flakes but either arrest fractures and causes the deflection or branching of cracks propagation across layers. Macor has a composition based on a magnesium flouro-alumino-silicate glass. Localised damages due to the dislodging of tiny polyhedral of glass are sometimes experienced.

2.8 The Glass Ceramics Process

The process of making glass ceramics include:

1. Glass is made with the special addition of a special raw material as a nucleating agent to the raw ingredients of the glass batch. The nucleating agent forms microscopic particles called nuclei.

2. The formed glass is heated again. Crystals will grow on the nuclei.

3. The resultant material is the glass ceramics, whose properties are different from the original glass.

The secret to making a glass ceramics is control of the heat treatment to allow for nucleation and crystal growth. Scientists select the exact temperatures and ingredients needed to make crystals grow in the glass. When enough crystals have formed, the glass becomes a new material (Ali, 2008).

Bulk glass ceramics processing is the most common method of glass ceramics manufacture where components are melted and fabricated to shape while in the glassy state. Most forming methods may be employed including rolling, pressing, casting and blowing, spinning. The article is then crystallised using a heat treatment designed for that material. This method is known as *ceramming*. Because crystallisation occurs at a high viscosity, article shapes are typically preserved with little or no shrinkage or deformation during the ceramming.

Powdered glass ceramics processing is the manufacture of glass ceramics from powdered glass using conventional ceramics processes e.g. extrusion, spraying, or slip casting which has extended the realm of useful glass ceramics composition by taking advantage of the surface crystallisation. In these materials, the crystal phases nucleate and grow from sites on the surface of glass grains. The glass undergoes viscous sintering just before the crystallisation process is completed. The final crystalline microstructure is essentially the same as that produced from the bulk process. Glass ceramics frits for example are applied like glass frits and then crystallised during the soldering process.

2.9 Raw Material to the Forming Process

The high point of achieving success in glass ceramics processing is the proper and suitable selection of raw material and the successful introduction of ingredient not used previously as glass raw materials. It was a major success owing to Stookey and his colleagues at Corning Glasswork, United States (Macmillan, 1964 in Ali, 2008). After the selection of materials then the melting process as reported by (Gunther, 1959 in Ali, 2012), is the most difficult stage of the production chain in part because once started cannot be reversed. Process monitoring and control involving regimes of temperature and furnace atmosphere is adhered to while the melt is in progress to ensure melt to melt reproducibility of the desired physical conditions. Conversion to polycrystalline material called the ceramming process is preceded by heat treatment that involves holding the glass at a temperature that would allow nucleation of the crystal. Crystal grow, the longer it is held at these temperature and will lead to a strong glass ceramics depending on the crystal growth and distribution. Then, the Glass forming process and equipment, depend on the form of product required by the customer and vary from plant to plant. The forming process could be either carried out on casting tables or through the use of relatively small, slow presses, as used in preparing glass gobs. These presses are designed to suit specific needs of the glass manufacturer (Ali, 2012).

2.10 Conversion of a Glass to a Micro Crystalline Ceramics

2.10.1 Conventional Method (Two-Stage)

The conventional method for producing a glass ceramics is to crystallise a glass by a two-stage heat treatment (Figure 2.3b). The first stage is a low temperature heat treatment at a temperature that gives a high nucleation rate around T_N in Figure 2.3a thus, forming a high density of nuclei throughout the interior of the glass. A high density of nuclei is important as it leads to a desirable microstructure consisting of a large number of small crystals. The second stage is a higher temperature heat treatment at around temperature T_G to produce growth of the nuclei at a reasonable rate.

The parent glass may be shaped prior to crystallisation employing any of the well established, traditional glass shaping methods such as casting and forming or more special methods such as extrusion. Glass production and the subsequent heat treatments are in general energy intensive and therefore expensive.

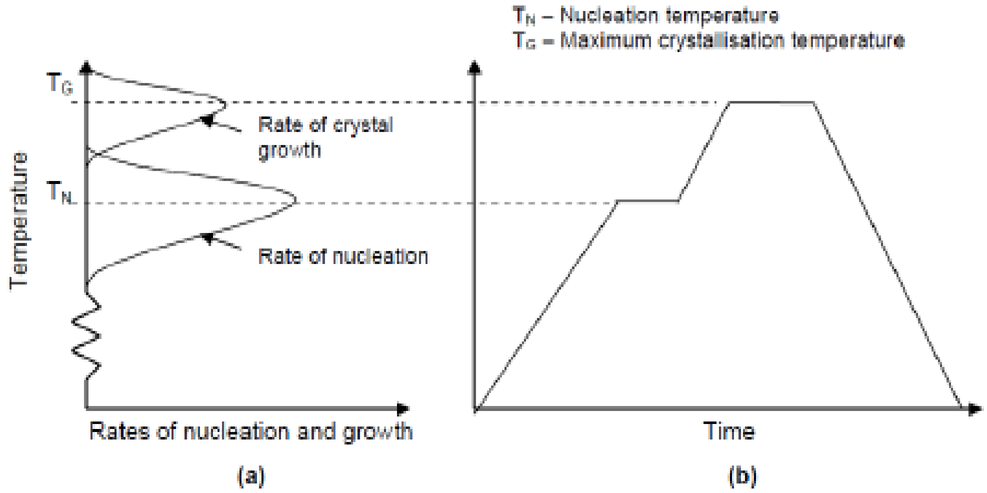

Figure 2.3: Crystallisation of a Glass to Form a Glass Ceramics (Source: Rawlings and Boccaccini, 2009).

(a) Temperature Dependence of the Nucleation and Growth Rates with Negligible Overlap (b) Two-Stage Heat Treatment.

2.10.2 Modified Conventional Method (Single-Stage)

The reason for the two-stage heat treatment of the glass is a consequence of the limited overlap between the nucleation and growth rate curves (Figure 2.4a). If there is extensive overlap of the rate curves then nucleation and growth can take place during a single-stage heat treatment at temperature T_{NG} as indicated in Figure 2.4. The rate curves, particularly the nucleation rate curve, is sensitive to composition and hence by optimising the glass composition it is in some cases, possible to obtain the necessary overlap. By careful choice of nucleating agents, this was first achieved for the glass ceramics system known as “Silceram” (Rawlings, 1997).

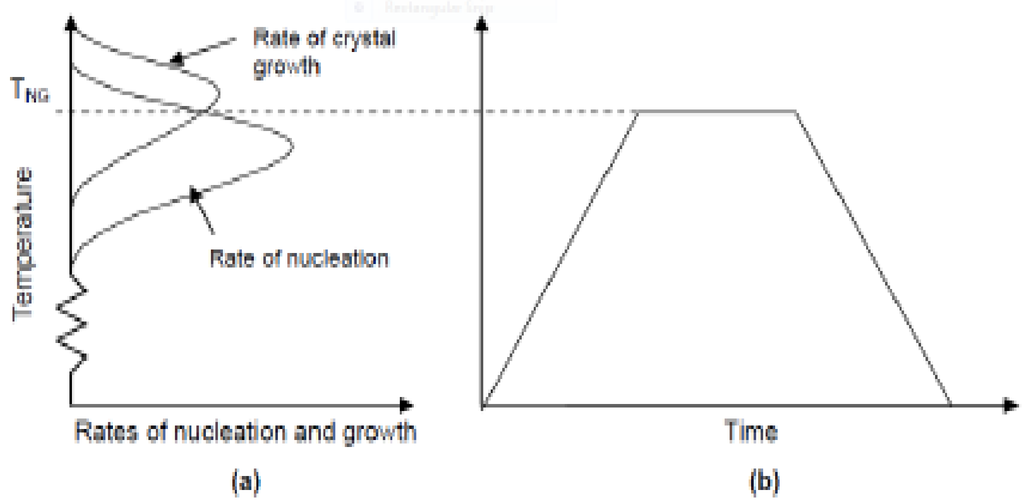

Figure 2.4 Crystallisation of a Glass to Form a Glass Ceramics by a Single-Stage Heat Treatment (Source: Rawlings and Boccaccini, 2009).

(A) Temperature Dependence of the Nucleation and Growth Rates with Significant Overlap (B) Single-Stage Heat Treatment.

2.10.3 Petrurgic Method

It was found with "Silceram" that it made little difference whether the glass was heated up to T_{NG} from room temperature or the molten glass was cooled to T_{NG} (Rawlings, 1997). This led to the development of the production of certain glass ceramics by a controlled, usually very slow cooling of the parent glass from the molten state without a hold at an intermediate temperature. With this method, referred to in literature as the petrurgic method, both nucleation and crystal growth can take place during the cooling. Both the modified conventional (single-stage) and the petrurgic methods are more economical than the conventional method (two-stage) (Rawlings and Boccaccini, 2009).

2.10.4 Powder Methods

The shaping by cold compacting of powder followed by a high temperature heat treatment to sinter the compact is a common route for the fabrication of ceramics and it has been employed for glass ceramics production. As there are limitations on the size and shape of components that may be cold compacted and also cost in producing a powder, this method is only used if an obvious benefit is identified.

In most cases there is little advantage in compacting and sintering a glass ceramics powder because a high sintering temperature is required and the properties of the final product do not differ significantly from those of glass ceramics produced by the other routes. It is more attractive to sinter a parent glass powder, which sinters by a viscous flow mechanism at lower temperatures (Scherer, 1977).

It is important to consider the rates of viscous flow sintering and crystallisation and the interaction of these processes. If crystallisation is too rapid the resulting high degree of crystallinity will hinder the low temperature sintering leading to an unacceptable amount of porosity (Rawlings and Boccaccini, 2009).

On the other hand, if sintering is fully completed before crystallisation, then the final product is unlikely to differ significantly from those fabricated by other methods. With appropriate rates it is possible in some cases to fabricate a dense glass ceramics by a sintering process in which both densification and crystallisation take place simultaneously at the same temperature. Optimisation of composition and sintering temperature can lead to different microstructures and even different crystalline phases, compared to those from the conventional method with different properties of the product. Pressure assisted densification methods such as hot pressing and Hot Isostatic pressing have also been successfully applied for production of glass ceramics from powders. Although these methods give improved products exhibiting near full densification, they are more expensive than cold pressing and sintering and thus, unlikely to be employed for processing wastes into monolithic glass ceramics (Rawling Ibid).

Powder technology facilitates the production of dispersion reinforced glass ceramics matrix composites (Boccaccini and Rawlings, 2009). Fabrication of these particle reinforced composites involves intimately mixing the powdered parent glass with the reinforcement in the required proportions. The mixture is then shaped, sintered and crystallised. Hard and rigid inclusions used as reinforcement hinder the sintering process. The production of continuous fibre reinforced glass ceramics is more complex and requires dedicated apparatus (Boccaccini, 2001). For both particulate and fibre-reinforced glass ceramics the densification is usually carried out by hot pressing and a final heat treatment is required to achieve crystallisation of the glass matrix.

2.11 The Properties of Glass Ceramics

Glass ceramics have been shown to feature favourable thermal, chemical, biological and dielectric properties, generally superior to metals and organic polymers in these areas. Moreover, glass ceramics also demonstrate considerable advantages over inorganic materials, such as glasses and ceramics. The large variety of compositions and the possibility of developing special microstructures should be noted in particular. It goes without saying that these advantageous properties assure the favourable characteristics of the glass ceramics end products.

2.11.1 Optical Properties

Since glass ceramics are non porous and usually contain a glass phase, they demonstrate a high level of translucency and in some cases even high transparency. Furthermore, it is also possible to produce very opaque glass ceramics, depending on the type of crystal and the microstructure of the material. Glass ceramics can be produced in virtually every colour. In addition, photo induced processes may be used to produce glass ceramics and to shape high precision and patterned end products. Fluorescence, both visible and infrared and opalescence in glass ceramics are also important optical characteristics.

2.11.2 Chemical Properties

Chemical properties ranging from reabsorb ability to chemical durability, can be controlled according to the nature of the crystal, the glass phase or the nature of the interface between the crystal and the glass phase. As a result, reabsorb able or chemically durable glass ceramics can be produced. The microstructure in particular also permits the combination of reabsorb ability of one phase and chemical durability of the other phase (Smallman and Bishop, 1991).

2.11.3 Mechanical Properties

Although the highest flexural strength values measured for metal alloys have not yet been achieved in glass ceramics, it has been possible to achieve flexural strengths of up to 500 MPa. The toughness of glass ceramics has also been considerably increased over the years. As a result, toughness constant (*K*IC) values of more than 3MPa have been reached (Ali, 2008). No other material demonstrates these properties together with translucency and allows itself to be pressed or cast, without shrinking or pores developing, as in the case of monolithic glass ceramics. The fact that glass ceramics can be produced as machinable materials represents an additional advantage. In other words, by first processing the glass melt, a primary shape is given to the material. Next, the glass ceramic is provided with a relatively simple final shape by drilling, milling, grinding, or sawing. Furthermore, the surface characteristics of glass ceramics, for example, roughness, polish ability, lustre, or abrasion behaviour, can also be controlled.

2.11.4 Electrical and Magnetic Properties

Glass ceramics with special electrical or magnetic properties can also be produced. The electrical properties are particularly important if the material is used for isolators in the electronics or micro electronics industries. It must also be noted that useful composites can be formed by combining glass ceramics with other materials, for example, metal. In addition, glass ceramics demonstrating high ion conductivity and even superconductivity have been developed. Furthermore, magnetic properties in glass ceramics were produced similarly to those in sintered ceramics. These materials are processed according to methods involving primary shaping of the base glasses followed by thermal treatment for crystallisation (Hölland and Beall, 2002).

2.11.5 Thermal Properties

A particular advantage in the production of glass ceramics is that products demonstrating almost zero shrinkage can be produced. These specific materials are produced on a large scale for industrial, technological, and domestic applications (e.g., kitchenware) (Ashby and Jones, 1999).

2.12 The Future of Glass Ceramics

An impressive variety of glass ceramics has been developed during the past six decades. Yet, many others with unusual and unforeseen properties and applications are likely to be discovered in the future. Glass ceramics possess many favourable features.

i. Composition: Compositions can, in principle be vitrified by combining and varying by 1 mole percent of most elements of the periodic table, which could then be crystallised to form a glass ceramics.

ii. Forming: Articles of any shape can, in principle be made by rolling, casting, pressing, blowing, drawing or by any other glass processing method that already exists or may be invented.

iii. Thermal treatment: Crystallisation is induced on the cooling path, in one step or multiple steps.

iv. Microstructure: Articles can be engineered from nano grains, micro grains or macro grains; low or high crystallinity; zero, low or high porosity; one or multiple crystal phases; random or aligned crystals and surface induced or internal crystallisation.

v. Thermal properties: Thermal expansion can be controlled to be negative, zero or highly positive; stability can range from about 400°C to 1450°C; and low thermal conductivity is common.

vi. Mechanical properties: Some articles have much higher strength and toughness than glasses, but the limits are far from being reached, possibility to be further strengthened by fibre addition, chemical and thermal methods.

vii. Chemical properties: Articles are reabsorb able or highly durable.

viii. Biological properties: Articles are biocompatible (inert) or bioactive.

ix. Electrical and magnetic properties: Articles have low or high dielectric constant and loss, high breakdown voltage, ionic conducting or insulating, superconducting, piezoelectric and ferromagnetic properties.

x. Optical properties: Articles can be translucent or opaque, opalescent, fluorescent, coloured and photo induction nucleation are possible (Zanotto, 2010).

From several thousand patents, only a few dozen glass ceramics products have reached the market. However, most of them or their modernised versions remain there and some have sold millions. Much is already known about glass ceramic technology, but many challenges in glass ceramics research and development are ahead. They include the search for new compositions, other and more potent nucleating agents and new or improved crystallisation processes. A deeper understanding and control of photo-thermal induced nucleation associated or not with chemical etching; the development of harder, stiffer, stronger and tougher glass ceramics and glass ceramics with increased transparency or conductivity are also timely.

A wide range of potential properties of glass ceramics is possible because of the ability to design their composition, thermal treatment and resulting microstructure. This combined with the flexibility of high speed hot glass forming will ensure continued growth of glass ceramic technology. As in their unexpected discovery, luck based on systematic exploratory research, solid understanding of glass structure, relaxation, crystallisation and properties, as well as knowledge of the vast literature and deductive reasoning, may allow other great inventions to bear fruit. From their glorious past, starting with their accidental discovery, to their very successful commercial products as well as their impressive range of properties and their exciting potential applications, glass ceramics have indeed a bright future (Zanotto, 2010).

2.13 Sol-Gel Processing

Sol-Gel is the chemical synthesis of oxide involving hydrolysable alkoxides that undergo transition. Sol-gel processing has been used to prepare glasses, glass ceramics and ceramics, either amorphous or crystalline material giving result depending on the composition, the precursor, the handling, and heat treatments. These factors lead to either a powder or powder free process. A powder process refers to any process that uses discrete particles which in this case are generated from a sol-gel process. A powder free process does not involve particles, starting from hydrolysable alkoxides, a powder free process would generate a porous preform of a glass ceramics or glass in the desired shape by linking molecules together (Reed, 1991). One of the significant advantages of the sol-gel method is the ability to synthesize silicate glasses at low sintering temperature enabling the preparation of glass ceramics with special compositions which are not possible to be obtained by melting (Saravanapavan and Hench, 2001).

2.14 Glass Ceramics Production by Synthesis of Silica from Rice Husk

In recent years glass ceramics has been produced by synthesis of materials from corn cob ash, combination of metal and non metals had been investigated by sol-gel to produce ceramics.

2.14.1 Collection and Pre-treatment

A sample of green rice husk was boiled with water, washed, dried and then fired at various temperatures in an atmosphere of air to obtain the ash (Hanafi and Abo-El

Enein, 1980). The rice husk sample is from the Extension Centre of ASTRA (Centre for the Application of Science and Technology to Rural Areas). The sample of fumed silica is Santocel silica aerogel from M/s Monsanto Co., U.S.A. Husk is washed well with distilled water to remove adhering soil and clay. It is first dried at ambient temperature and later at about 353 K in an air oven. Dried husk is powdered to 80 mesh size and the powder was employed in thermal study (James and subbaRao, 1986).

Dry raw Rice Husks (RRH) was sieved to eliminate residual rice and clay particles and was subjected to acid treatment. A 200 g sample of RRH was fed into 3 N HCl solution in deionised water, and boiled for 1h. After thorough washing with deionised water, the RRH were filtered and dried in an oven at 110^{o}C (Jones 1953 in Krishnarao *et al.*, 2001).

The rice husks were supplied from the Trakya Region (Turkey). They were washed with water to remove dirt and other contaminants present in them and then dried in an oven dried (Model FN 400, Nuve) at about 110^{o}C for 24 h. The washed and dried rice husks were subjected to different types of chemical treatment. Acid leaching was performed by reflux boiling in 3% (v/v) HCl and 10%(v/v) H_2SO_4 for 2 h, at a ratio of 50 g husk/l. Alkaline leaching used a 3% (v/v) NaOH solution for 24 h at room temperature (approx. 25^{O}C), at a ratio of 50 g husk/l. After leaching, the husk was thoroughly washed with distilled water and then dried in an air oven at110^{o}C (Yalcin and Sevinc, 2001). Rice husk (RH) was collected from a rice mill in Rourkela, India. The RH was separated from rice grain by air blowing and washed with tap water several times till all the blackish impurity floating on water was completely removed. The rice husk was then dried at 110^{O}C for 8 h (Kumar, 2009).

The RH was separated from rice grain by air blowing and washed with tap water several times until all the impurities were completely removed. Then the water cleaned husk was treated with acid, i.e. acid leaching, for 1h. Acid leached husk was cleaned repeatedly with hot distilled water to remove the acid portion which had adhered to the surface of the husk. Finally, the husk was dried overnight in oven at 110^{o}C (Warjri, 2010).

Separation of rice husk from residue of rice grains and impurities like sand, clay is the initial pre treatment after sourcing most rice husk then, water washing to remove more of the impurities which were preceded by either acid treatment or drying at 110^{O}C.

2.14.2 Ashing of Husk

The temperatures used were 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300 and 1400°C and the resultant rice husk ash silica's are designated as RH 500, RH 600, RH 700, RH 800, RH 900, RH 1000, RH 1100, RH 1200,RH 1300, and RH 1400, respectively. At each firing temperature, the ash was soaked for a period of 3 h and then quenched in air (Hanafi and Abo-El-Enein, 1980).

The burning of RH in air always leads to the formation of silica ash varying in colour from grey to black and of inorganic impurities along with unburned carbon. An attempt to remove the unburned carbon by further heating to higher temperatures (>700^{o}C) leads to the crystallisation of amorphous silica to cristobalite and tridymite. (Jones 1953 in Krishnarao *et al.,* 2001). The cleaned husks were then burned inside a muffle furnace (Model FN 100, Nuve). Four different methods were applied.

First, incineration took place in a porcelain crucible for 4h in static air. Alternatively, incineration was performed in a stainless steel tubular reactor which was 160 mm in length and 70 mm in diameter under flowing argon (1.5 l/min, for 3h) and then flowing oxygen (1.0 1/min for 1h). This reactor was placed horizontal inside the muffle furnace. Third, incineration took place in the same reactor under flowing air (3 l/min, for 3h). And last, the husks were burned in the same reactor under flowing oxygen (1.0 l/min, for 2h). They also have shown that, by mineral acid leaching, silica of >99% purity can be obtained by burning rice husks at 600^{o}C under inert atmosphere (Real *et al.,* in Yalcin and Sevinc, 2001).

The dried husk was burnt at 700°C for 6h for complete combustion by which all volatile material is removed and ash was obtained (Kumar, 2009). The dried husk was burnt at 700°C for 6h for complete combustion by which all volatile material is removed and ash was obtained (Warjri, 2010).

RHA can be obtained by burning rice husk in electric furnace at 600^{o}C for 4 hours (Rao *et al*., 2005 in Prasad and Pandey, 2012). Another study reported (Bhattachrya and Wu, 1986 in Prasad and Pandey, 2012) that burning of RH (−10 mm) in a fluidized bed of fine sand (0.5mm diameter) with cross section of 380×406 mm and total height of 4.8 m. The bed temperature is maintained at 923–1173 K, fluidizing velocity is kept 0.4–2.2 m/s, bed depth is 30–60 cm and excess air levels of 30–95%. A proto type incinerator was designed with special features to burn rice husk (Prasad and Pandey, 2012).
The reviews above show various techniques use in processing, treatment and preparing rice husk into ash. The study undertaking will ash the rice husk to obtain ash by burning

at a temperature of $700^{o}c$ in an electric furnace which falls within range in most literatures for ash rice husk.

2.14.3 Synthesis of Silica from Husk

The composition of gel powder to be synthesised was taken as SiO_2- 50mol%, Na_2O-25mol%, CaO-25mol%. RHA was taken as source of silica whereas NaOH and $Ca(NO_3)_2.4H_2O$ were the sources of Na_2O and CaO respectively. RHS – 2.5 gm, NaOH—1.6634 gm, $Ca(NO_3)_2.4H_2O$ – 4.9198 gm, HNO_3 (conc)—95 ml.

First of all, 2.5 gm of RHS was taken and corresponding amount of NaOH and $Ca(NO_3)_2.4H_2O$ were obtained. Estimated NaOH and $Ca(NO_3)_2.4H_2O$ were dissolved in 20 ml and 30 ml of deionised water in beaker which gave clear solutions. NaOH solution was warmed RHA was added into it in warm condition only and volume was made 60 ml by adding water. The boiling was continued for 1 hr while volume was maintained up to 60 ml mark of beaker regularly at around time interval of 15 min. After 1 hr of boiling, RHA dissolved completely. Then this solution was filtered and we obtained 50 ml of Sodium silicate solution.

Estimated amount of $Ca(NO_3)_2.4H_2O$ solution was prepared by dissolving it in 30 ml of deionised water. Then 15 ml of HNO_3 (conc.) was added in $Ca(NO_3)_2.4H_2O$ solution, which was kept in stirring condition, followed by addition of Sodium silicate solution drop wise very slowly. At intervals, HNO_3 (conc.) was added for neutralisation and to avoid precipitation. When concentration of HNO_3 was high in solution, its fume were rising up and some reaction occurred with Sodium silicate solution drop falling from burette. From earlier trial it was observed that just before precipitation, the stirring sound changed suddenly. So, in final gel powder preparation it was completely avoided by adding HNO_3 at proper interval. Initially, addition rate of Sodium silicate solution was 5 ml per min. At the end when 7-8 ml of Sodium silicate solution was left in beaker, rapid addition was made. By the time gelation start, it took 45 min for completion after complete addition of Sodium silicate solution. Then it was left for 3 days at $70^{O}C$ for ageing so that glass network formation is optimised. Then it was dried at $150^{o}C$ for 2 days (Kumar, 2009).

The composition of gel powder to be synthesised was taken as SiO_2- 50mol%, Na_2O-25mol%, CaO-25mol%. RHS was taken as source of silica whereas NaOH and $Ca(NO_3)_2.4H_2O$ were the sources of Na_2O and CaO respectively. 100 ml of water was taken in a beaker and NaOH pellets weighing 3.326g was added to it. 5g of white ash powder (WAP) was added to the solution and the resulting solution was kept in boiling condition for 1hr. 100 ml of Na_2SiO_3 solution was then prepared. 9.84g of $Ca(NO_3)_2.4H_2O$ was taken in 150 ml of $HNO_{3\ (conc.)}$ and a clear solution was prepared. The Na_2SiO_3 solution was then added dropwise into the $Ca(NO_3)_2$ solution. Turbidity appeared in the solution. After leaving the solution for 30 minutes the gelling process was complete (Warjri, 2010).

Rice husk ash has been synthesised to obtained glass ceramics powder the research study will adopt the synthesis process in making glass then sintering of glass powder to glass ceramics piece from waste rice husk as a substitute to the costly, unavailable raw materials, and high energy processing processes.

2.14.4 Drying

Drying is the removal of liquid in the porous material by means of its transport and evaporation into a surrounding unsaturated gas or in some cases a desiccating liquid. It is important before firing in processing bulk raw material, products formed by plastic forming and casting, decorations and coating on surfaces. Drying must be carefully controlled, because stress produced by differential shrinkage or gas pressure may cause defects in the final product (Reed, 1991). The various methods of drying gels includes: aerogel, xerogel, sonogel, cryogel and vapour gel.

2.14.4.1 *Aerogel*

This method of drying is to place in an autoclave and remove the liquid by hypercritical evacuation. These gels are called aerogel. According to (Frickel, 1986 in schnieder, 1991) aerogel are processed by increasing the pressure above the critical point to by-pass the liquid vapour interface and then vent out the vapour leaving a network of about 95% porosity. The pore size may be bimodal. This network must be de-aired before the pores closed during firing.

2.14.4.2 *Xerogel*

This method involves the natural evaporation of the solvent and water to the atmosphere while the liquid is evaporating, the gel structure is collapsing on itself. The gels obtained this way are called xerogels. (Zarxycki *et al*., 1984 in schnieder, 1991) stated that xerogel may have pores as small as 20nm. Large stresses develop when the liquid is removed from the capillaries which lead to shrinkage.

2.14.4.3 *Sonogel*

Another method as reported by (Flemings and Flemings, 1988 in schnieder, 1991) is to subject them to ultrasound in the 20Hz range. Gels obtained are called Sonogels.

2.14.4.4 *Cryogel*

A similar method to xerogel in that the liquid phase is absent, is to prepare aqueous hydro gel that are dried in a freeze drying apparatus by subliming the water at a pressure below the triple point so only ice and water vapour are present. Normally, a pressure of about 130pa and (10-30 torr) is used, drying time may exceed 24 hr. gels obtained are called cryogels (pajouk *et al*., 1990 in schnieder, 1991).

2.14.4.5 *Vapour gel*

A rapid formation of gel involves injecting a steady stream of liquid $SiCl_4$ or SiCl vapour acidified water, along with other organo metallic such as $Gecl_4$, while stirring. The gelling is almost instantaneous. This method allows higher incorporation of GeO_2 into gel. The gel obtained is called xerogel (Flemings ibid).

Drying techniques from various authors have been reviewed showing drying based on equipment and sometimes addition of some compounds to aid the drying. In this research work the xerogel process will be used to dry the gel to powder by allowing the evaporation of the liquid phase.

2.14.4.6 *Sintering/Densification*

Sintering is a process used to create objects from powders. It is based on atomic diffusion. Diffusion occurs in any material above absolute zero but it occurs much faster at higher temperatures. In most sintering processes, the powdered material is held in a mould and then heated to a temperature below the melting point. The atoms in the powder particles diffuse across the boundaries of the particles, fusing the particles together and creating one solid piece. Because sintering temperature does not have to reach the melting point of the material, sintering is often chosen as a shaping process for materials with extremely high melting points such as tungsten and molybdenum. Sintering is traditionally used for manufacturing ceramics objects but finds application in almost all fields of industry.

Most ceramics forming process starts with a powder and consists of compaction of powder into porous shape which is usually to achieve a high degree of particle packing and a high degree of homogeneity. Close packing reduce the amount of porosity which must be removed during densification and so reduce the total shrinkage of the particles during densification. Close packing helps densification. Homogeneous powder packing reduces the possibility of distortion or micro structural in-homogeneity during sintering. A variety of parameters must be controlled to achieve optimum particle packing, these include particle size, particle size distribution, and degree of dispersion (Shroup, 1991).

2.14.4.7 *Characterisation of Rice Husk Ash, Gels, and Glass Ceramics*

Scanning electron micrograph (SEM) of prepared aero-gel indicates that the aero-gel was a porous material with a continuous meshwork structure. In the SEM photo, the white parts are the bulges in the surface of the aero-gel, while the black parts are pores in the aero-gel (Qi and Tao 2005). After calcination of this sample at 700^{o}C for 6h, Crystallite size of ash was found to be smaller than that in case of rice husk as peak in XRD pattern of ash is broader than in the rice husk. The temperature so chosen is as because calcining at temperature below it, volatile materials do not go off completely. Calcination at temperature above it causes silica to react with other constituent decreasing percentage yield. Since percentage of silica, which is amorphous in nature, is increased, this caused the broadening of peak in rice husk ash (Kumar, 2009).

The XRD patterns of 700 and 800ºC heat treated gel powders, which shows the presence of sodium calcium silicate phase ($Na_6Ca_3Si_6O_{18}$) (JCPDS NO. 79-1089).The pattern shows an amorphous halo region in the range between 20-35º (2θ) including crystalline phases in 700^{o}C calcined BGC powder. This halo region disappeared in 800^{o}C calcined powder. Amorphous halo zone was speculated due to the presence of silica in the glassy matrix. Crystalline peaks were developed due to the decomposition of nitrates mainly along with calcium, sodium and silica. After heat treatment with higher temperature this halo region disappeared due to the growth phenomena of crystalline phases (Warjri, 2010).

The microstructure of aero-gels can be determined by high resolution scanning electron microscopy (SEM) (Moner-Girona *et al.*, in Prasad and Pandey, 2012). Characterisations by Scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX) etc., suggest that silica is present all over, but is concentrated on protuberances and hairs (trichomes) on the outer epidermis, adjacent to the rice kernel (Sharma *et al.*, 1984; Ding, 1999; Krishnarao and Godkhindi, 1992 in Prasad and Pandey, 2012). The result obtained by characterisation of reviews show presence of structure, pores, crystals, presence of silica. This study will conduct XRF, XRD of the rice husk ash then XRD, EDS and SEM of the glass ceramics piece to check their conformity with the reviews.

2.15 Products Produced by Ceramics Powder Processing

2.15.1 Electronics

Substrates, chip carrier, electronic packaging, capacitors, inductors, resistors, electrical insulation, transducers, servisors, electrodes, igniters, motor magnets, spark plug insulators.

2.15.2 Advance Structural Ceramics

Cutting tools, ware-resistant inserts, engine component, resistant coating, dental and orthopaedic prostheses, high efficiency lamps.

2.15.3 Chemical Processing Component

Ion exchange media, emission control components, catalyst support, liquid and gas filters.

2.15.4 Refractory Structures

Refractory lining in furnaces, thermal insulations, kiln furniture, recuperators, regenerators, crucibles, metal processing materials, filters, mould, heating elements.

2.15.5 Construction Materials

Tiles, structural clay products, Cements, concrete.

2.15.6 Institutional and Domestic Products

Cookware, Hotel china and dinnerware, Bathroom fixture, Decorative fixture and household items.

Table 2.1 Classifications of Ceramics by Function

Functions	Class Nominal	Composition
Electrical	Insulation	α-Al_20_3, MgO, porcelain
	Ferroelectrics	$BaTiO_3$, $SrTiO_3$
	Piezoelectric	PbZr, TiO_3
	Fast ion exchange	β-Al_2O_3, doped ZrO_2
	Superconductors	$Ba_2YCu_3O_7$
Magnetic	Soft ferrite	Mn, Zn, Fe_2O_4
	Hard ferrite	$BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$
Nuclear	Fuel	UO_2, UO-PuO_2
	Cladding /shielding	SiC, B_4C
Optical	Transparent envelop	α-Al_2O_3, $MgAl_2O_4$
	Light memory	doped PbZr, TiO_3
	Colours	doped $ZrSiO_4$, doped ZrO_2, doped Al_2O_3
Mechanical	Structural refractory	α-Al_20_3, MgO, SiC, Si_3N_4, $Al_6Si_2O_{13}$
	Wear resistance	α-Al_20_3, ZrO_2, SiC, Si_3N_4, toughened Al_2O_3
	Cutting	α-$Al_20_3ZrO_2$, TiC, Si_3N_4, SIALON
	Abrasive	α-Al_20_3, SiC, toughened Al_2O_3, SIALON
	Construction	Al_2O_3-SiO_2, CaO-Al_2O_3-SiO_2, procelian
Thermal	Insulation	α-Al_20_3, ZrO_2, $Al_6Si_2O_{13}$, SiO_2
	Radiator	ZrO_2, TiO_2
Chemical	Gas sensor	ZnO, ZrO, SnO_2, Fe_2O_3
	Catalyst carrier	$Mg_2Al_4Si_5O_{18}$, Al_2O_3
	Electrode	TiO_2, TiB_2, SnO_2, ZnO
	Filters	SiO_2, α-Al_20_3
	Coatings	NaO-CaO-Al2O3-SiO2
Biological	Structural prostheses	α-Al_20_3, porcelain
	Cements	$CaHPO_4.2H_2O$
Aesthetics	Pottery, Art ware, Tile, Concrete White ware, Porcelain, White ware, CaO-SiO_2-H_2O	

*white ware is a family of porous-dense materials with a glassy matrix usually containing Al_2O_3, SiO_2, K_2O and Na_2O. Porcelain is a type of white ware that is nonporous, hard and translucent. SIALON is a solid solution phase with the nominal composition $Si_4Al_2N_6O_2$ toughened $Al_2O_3$is a two-phase material containing a minor amount of doped or undoped ZrO_2.

(Source: Reed,1989).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

The materials used for this work include (Rice Husk) sourced from Kujama (Chikun Local Government Kaduna State), Trioxonitrate (v) acid HNO_3 $_{(Conc.)}$, Sodium hydroxide $(NaOH)_{(S)}$, Calcium trioxonitrate (iv)tetrahydrate $[Ca(NO_3)_2.4H_2O]_{(aq)}$ and Hydrochloric acid (HCl) $_{(conc.)}$.

3.2 Methodology

3.2.1 Preparation of Silica from Rice Husk

Rice husk (RH) was collected from Kujama Rice Mill Chikun Local Government, Kaduna State. The RH was separated from remaining rice grain and unwanted materials washed with tap water several times till all the impurity that float on water were completely removed. It was then dried at 110^{o}C for 2 h. in an electric furnace (Gemco Son-Holland Type CFR 40/90/40, power 20KW, volt 4153 Ph, NR 91.442, frequency 50Hz). It was then combusted in a perforated metal container in open air to burn out volatile materials before ash at 700°C for 2h. Fig. 3.1 shows the flow chart for the preparation of the rice husk ash.

Plate I, Rice Husk

Plate II, Researcher pre-treating RHA

Plate III, Kiln Dried RHA

Plate IV, Carbonisation of Dried RHA

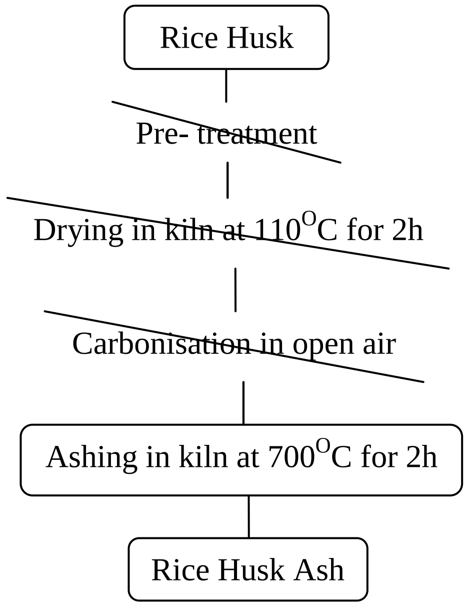

Figure 3.1 Flow Chart of RHA

3.2.2 Characterisation of Rice Husk Ash

3.2.2.1 Chemical Analysis

Elemental content of RHA, were determined by X-ray fluorescence (EDXRF, Midi pal 4). XRF spectroscopy is widely used for the semi-qualitative and quantitative elemental analysis of samples. XRF has the advantage of generally being non-destructive, multi elemental detection, fast analysis and cost effective. The main disadvantage is that analyses are generally restricted to elements with atomic number greater than 9.

The principle of X-ray fluorescence is as follows; the sample excited by X-rays emits a short wavelength radiation (fluorescence), characteristic of each alloying element. A parallel beam of the secondary radiation is directed by means of a collimator onto the analysing crystal; it is separated according to wavelengths and then reflected into a radiation detector mounted on a high precision goniometer. The angular position of crystal and goniometer is a function of the wavelength and allows the identification of the element in the matrix.

3.2.2.2 Phase Analysis

RHA powder was analysed for crystalline phase contents by X-ray powder diffraction performed with a Pananlytical Diffractometer (Model: Empyrean). Powder sample were pack on a sample stage so that it can be irradiated by the X-ray. To detect the diffracted X-rays, an electronic detector is placed on the other side of the sample from the X-ray tube and rotated through different Bragg's angles. The goniometer keeps track of the angle (θ), and the detector records the detected X-rays in units of counts/sec and sends this information to the computer. The operating parameters were; 40kV and 35mA with the Cu target, a step size of 0.02 (degree) with continuous scanning. X-ray intensity (counts/sec) was plotted against the angle two-theta (2θ). The angle (2θ) for each diffraction peak was then converted to d-spacing, using the Bragg equation. Both the XRF and XRD were carried out at the Nigerian Geological Survey Agency; National Geosciences Research Laboratory (NGRL), Kaduna.

3.2.3 Preparation of Glass Gel Powder

3.2.3.1 Synthesis of Silica from Rice Husk Ash (RHA)

RHA - 40g, $NaOH_{(s)}$ - 16.68g, $Ca(NO_3)_2.4H_2O_{(aq)}$ - 49.2g, $HNO_{3\,(conc.)}$ - 600 ml

Initially, 40g of RHA were taken and corresponding amount of $NaOH_{(s)}$ and $Ca(NO_3)_2.4H_2O_{(aq)}$ were obtained. $NaOH_{(s)}$ and $Ca(NO_3)_2.4H_2O_{(aq)}$ were dissolved in 200 ml and 10 ml of distilled water in different beaker which formed clear solutions. NaOH solution was warmed RHA was added into it in warm condition and volume was made 400 ml by adding water. The boiling was continued for 1 hr while volume was maintained up to 400 ml mark of beaker regularly at around time interval of 5 min. After 1 hour of boiling, RHA was dissolved in the solution of NaOH $_{(aq)}$, then the solution was filtered and 300 ml of Sodium silicate solution ($Na_2SiO_{3(aq)}$) was obtained According to Nayak, (2010) $Ca(NO_3)_2.4H_2O$ solution was prepared by dissolving it in 10 ml of distilled water. Then 600 ml of HNO_3 $_{(conc.)}$ was added in $Ca(NO_3)_2.4H_2O$ a solution was prepared, then titration of Sodium silicate solution drop wise very slowly into the Calcium trioxonitrate(iv)tetrahydrate and Trioxonitrate (V) acid. Immediately turbidity appeared in the solution titration was stopped and kept within 40 min gel was formed which has the solute glass phase and the liquid solvent phase. The gel formed was left for 3 days at room temperature for proper network formation. Then it was dried on a hotplate by evaporation to obtain xerogel powder. The synthesis of silica from RHA, preparation of solution, gel and drying to powder were carried out at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria.

Plate V, Boiling solution of RHA + $NaOH_{(aq)}$

Plate VI, Solution of $Ca(NO_3)_{2(aq)}$ + $HNO_{3(conc)}$

Plate VII, Researcher Titrating $Na_2SiO_{3(aq)}$ against $Ca(NO_3)_{2(aq)} + HNO_{3(conc)}$

Plate VIII, Turbidity indicate formation of gel

Plate IX, Drying gel

3.3 Compaction

The powder was then compacted at 150 Psi forming the green body in (30×10×5) mm mould according to (Reed, 1989). The green glass powder after compaction was measuring (28×9×5) mm then, fired at 700^{o}C in an electric furnace. The compaction was conducted at the Metallurgical Engineering Department Laboratory of Ahmadu Bello University, Zaria.

Plate X, Compaction of glass powder

3.4 Sintering

The samples were heated in a closed electrical furnace (Gemco Son-Holland) to a temperature of 700^{o}C for densification and sinter crystallisation of the glass compact this is as reported (Reed, 1989) that glass particle sinter at or below the transition temperature of the glass depending on the composition in this case Soda lime silicate glass. The sample was then allowed to cool to room temperature in the furnace before removal.

3.5 Microstructure and EDS Analysis

Microstructure of the Glass Ceramics specimen was analysed by a Scanning Electron Microscope (SEM, Model: Phenom prox manufactured by Phenom World, Eindhoven Ltd., Holland). Elemental analysis was carried out by Energy Dispersive X-ray spectroscopy analysis; (EDAX or EDS, Phenom Prox Instrument). In SEM, a hot tungsten filament electron gun under vacuum emits electrons which pass through a series of electromagnetic lenses. The sample is then bombarded with a fine beam of electrons having acceleration potentials range from 1-40 KV. A part of the beam is reflected as back scattered electrons (BSE) along with low energy secondary electron emission (SE), cathode luminescence, X-ray excitation and electron transmission also took place. Images formed from the (SE) beam were studied in the extrinsic mode of SEM. The emitted secondary electrons are detected and displayed on a scanning TV display. EDS technique was used to identify the elemental composition of the specimen the EDS analysis system works as an integrated feature of an electron microscope.

During SEM scanning, the specimen is bombarded with an electron beam. The bombarding electrons collide with the electrons of the specimen atoms, knocking some of them off, thus, transferring some of its energy by emitting an X-ray. By measuring the amounts of energy present in the X-rays being released by a specimen, the identity of the atom from which the X-ray is emitted can be established. The output EDS spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to an individual element. The concentration of the element in the specimen is indicated by the high intensity of the peak in a spectrum. Fig. 3.2 shows a flow chart of the synthesis of glass ceramics from rice husk to characterisation of the formed piece. The scanning Electron Microscopy was carried out at the chemical Engineering Department of Ahmadu Bello University, Zaria.

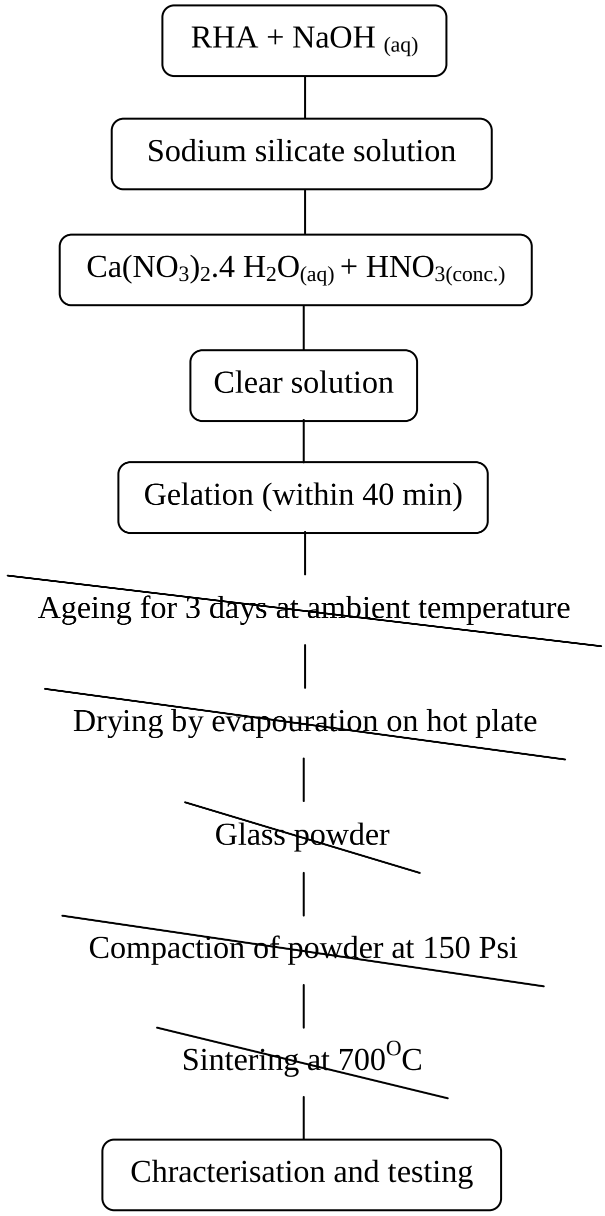

Figure 3.2 Flow Chart for Synthesis of RHA Silica for Glass Ceramics

3.6 Physical and Chemical Properties Test

3.6.1 Physical Properties

Percentage Water Absorption, measured using ASTM C-373 which is a measure to determine the quantity of water which a glass ceramics can absorb under particular conditions express as a percentage in weight of the dry sample weight. This percentage indicates whether, a material is impervious, vitreous, semi-vitreous or non-vitreous. The sample after firing was soaked in distilled water at room temperature for a period of 24 hours; the weight was then taken before and after soaking in water. The water absorption was determined as percentage water absorption of the sample using.

Water absorption % (W) = $\frac{(W_s - W_d)}{(Wd)} \times 100$

Where:

Ws-weight of block waterlogged weight on air

Wd-weight of block weight after sintering.

3.6.2 Firing Shrinkage

The firing shrinkage, measured according to ASTM C-326 Which is a measure to determine the percentage decrease in the dimension of the unfired compacted glass powder and fired compact. The samples were compacted by pressing, the green glass compact length were measured using vernier calliper before and after it were fired at 700^{O}C in an electrical furnace. Percentage shrinkage was calculated as shown below.

$S_i = \frac{(L_p - L_f)}{(L_p)} \times 100$

Where:

S_i= percentage Shrinkage after firing

L_p = Green Body Length of sample

L_f =length of fired sample

3.6.3 Resistance to Chemical Attack

The chemical resistances of the glass ceramics to acidic and alkaline substance were tested using ASTM C-650 to determine the resistances of glass ceramics to attack by continuous contact with chemicals for 24 hours, rinsing the surface and then examining the surface for visible changes and colour variation. The samples were tested in a 10% solution of $HCl_{(aq)}$ acid for their resistance to acid attack for 24 hours. Similarly, a sample was also tested with 10% solution of $NaOH_{(aq)}$ for 24 hours. The samples were removed from the solution rinsed, dried and examined for changes in colour, texture and weight. The physicochemical properties tests were carried out at the Department of Chemical Engineering, Ahmadu Bello University, Zaria.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Preparation and Characterisation of Amorphous Silica Precursor (RHA)

The amorphous silica powder was prepared using rice husk. It was brown ash in colour (BA). BA was prepared by burning husk at $700^{O}C$ for 2 hour after pre-treatment, carbonisation and ash. This rice husk silica precursor was characterised by XRF analysis and XRDS analysis as shown in table 4.1 and figure 4.1.

Plate XI, Rice Husk Ash obtained

Table 4.1 Showing Result of XRF of RHA

OXIDES	% CONTENT
SiO_2	79.98
P_2O_5	1.80
SO_3	0.26
Na_2O	0.42
K_2O	0.302
CaO	1.54
MgO	0.74
TiO_2	0.11
V_2O_5	0.01
Cr_2O_3	0.014
MnO	0.17
Fe_2O	4.43
ZnO	9.85
CuO	0.017
BaO	0.05
EU_2O_3	0.089

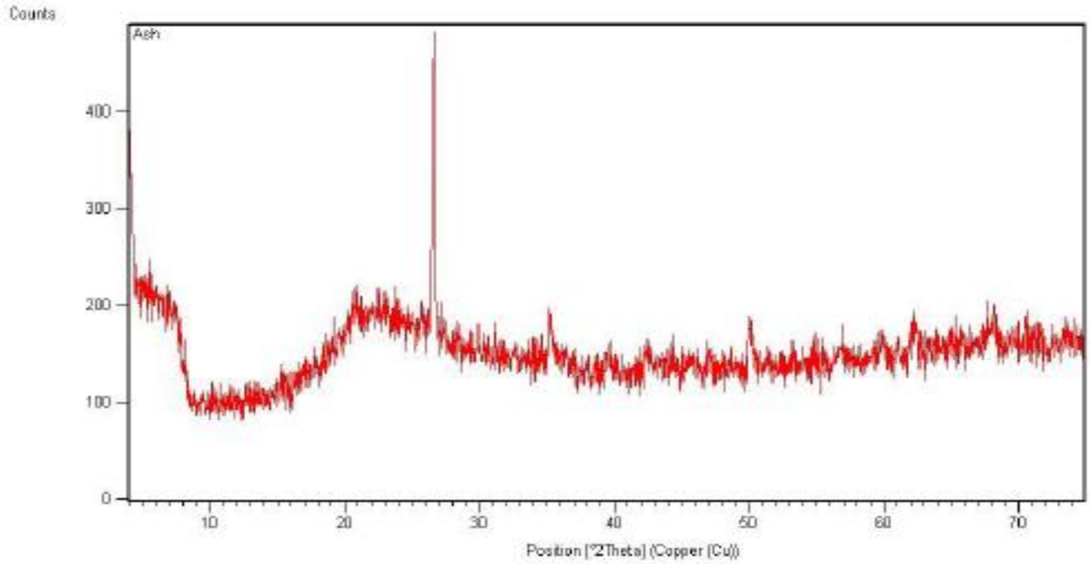

Figure 4.1 Result of XRD pattern of RHA.

The chemical analysis XRF of the RHA contains 79.98% SiO_2 and the rest 20.02% in which 1.80% P_2O_3, 0.42% Na_2O, 1.54% CaO, 0.05% BaO, 0.11% TiO_2 which are major and minor glass formers. Figure 4.1 shows the X-ray diffraction patterns of RHA. It showed a broad peak zone centred near $2\theta=22^o$, signifying the amorphous nature of silica based materials. A sharp crystalline peak in raw husks at $2\theta=26.86^o$ was due to the presence of impurities sand particles as the peak was identified to match with quartz or due to the transformation of the silica to any of it crystalline phase tridymite or crystobalite.

4.2 Sol Gel Synthesis of RHA

It was observed that RHA was soluble when mixed with $NaOH_{(s)}$ solution that was prepared giving a solution of sodium silicate. Then, solution of Calcium trioxonitrate (iv)tetrahydrate and Trioxonitrate (v) acid prepared, it was a clear solution. Solution of sodium silicate was titre against Calcium trioxonitrate (iv)tetrahydrate and Trioxonitrate (v) acid immediately turbidity appeared it lead to the formation of gel within 40 min.

Drying the gel after it was left for three days to age resulted in powder obtained called xerogel gel from the process of drying, the powder was white with some shinny speck visible when view through it is also white in colour. Then, compacted into the green bodies using the mould the powder was compacted easily and was also released without much effort and the compact was sintered successfully to glass ceramics resulting in a grey colour piece on the one side and the other had some whitish colouration after cooling. Plates, below shows solution prepared, gel formed, powder formed, green bodies formed by compaction and the sintered pieces.

Plate XII, Filtered $Na_2SiO_{2(aq)}$

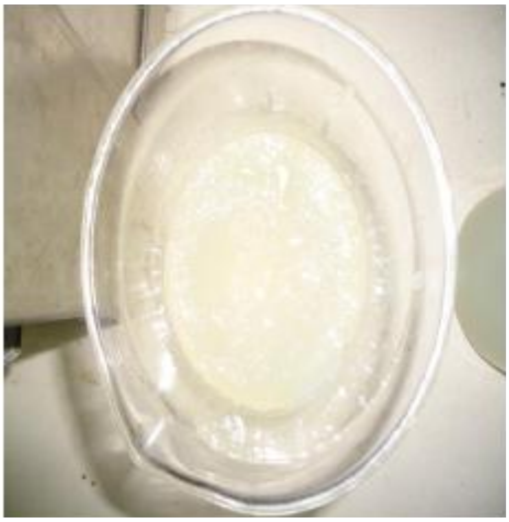

Plate XIII, Gel Formed

Plate XIV, Glass Powder Formed

Plate XV, Sample of Green Body Compact

Plate XVI, Glass Ceramics piece

4.3 Phase Analysis of Glass Ceramics

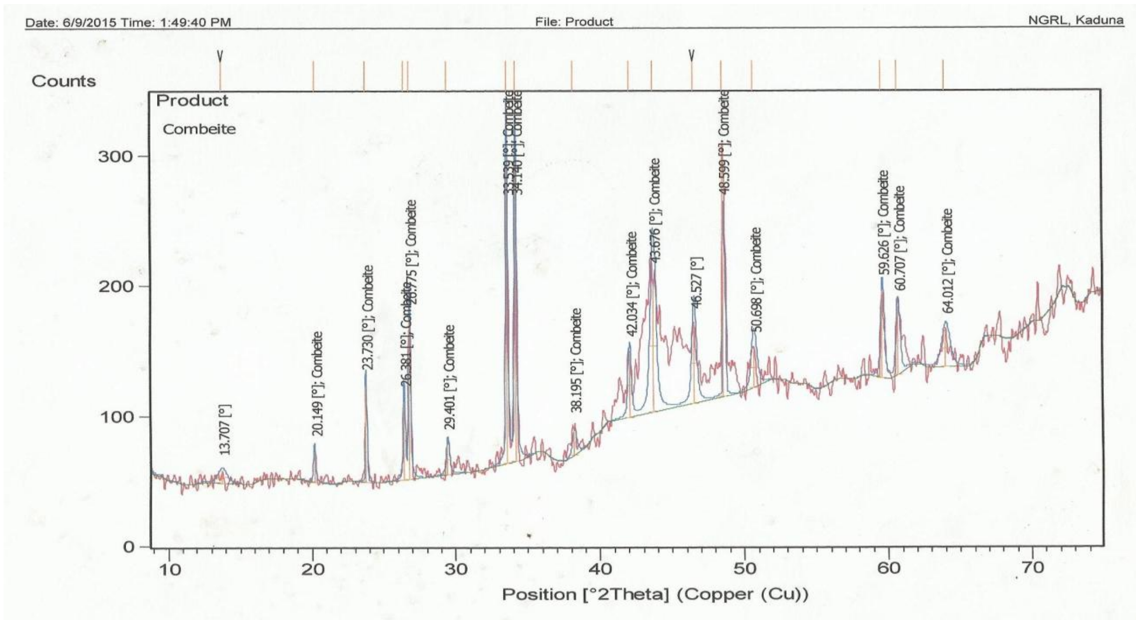

Figure 4.2 XRD Pattern of Sintered Glass Powder Forming the Product.

Figure 4.2 shows XRD patterns of 700^{o}C sintered glass powder compact, shows the presence of sodium calcium silicate phase ($Na_4Ca_4Si_6O_{18}$) combeite at 2θ =33.5-34.1 being the highest peaks a bioactive ceramics glass family as reported by Warji (2010).

4.4 Scanning Electron Microscopy of Glass Ceramics

Figure 4.4 shows a circular morphology of glass ceramics is due to the precipitation of ceramics in glassy matrix. So, the grains and clusters shown by this surface are attributed to the formation of phosphate phases. Similar changes in apatite morphologies have been reported for sol-gel derived glasses and glass ceramics (Nayak, 2010). The glass ceramics specimen with a circular structured morphology with EDS elemental spectra showing Si, Ca, P and Na.

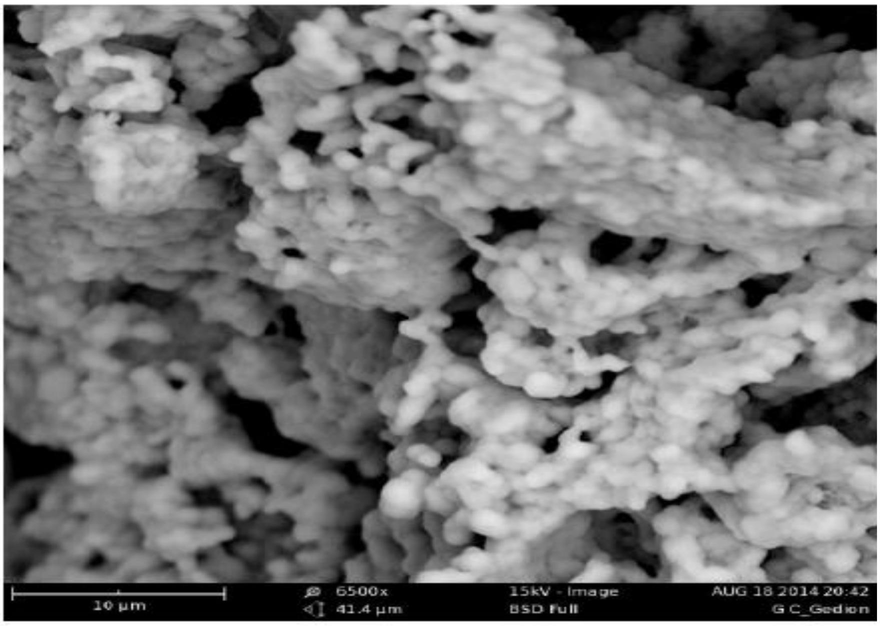

Plate XVII, SEM of the Sintered Glass Product Magnified at 6500×

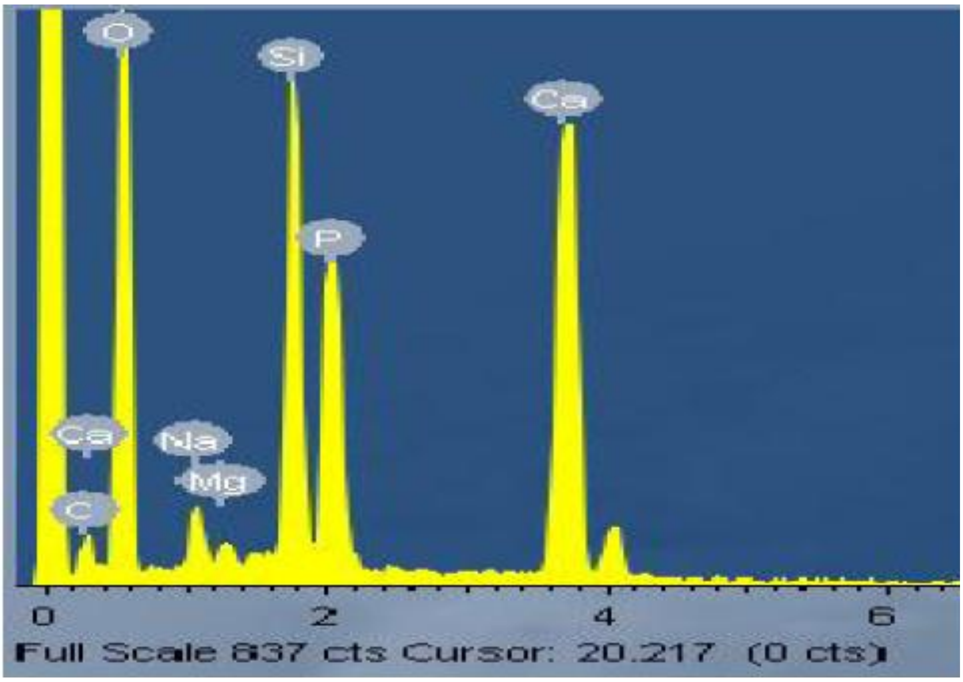

Plate XVIII, EDS of the Sintered Glass Product

4.5 Physical and Chemical Test

Table 4.2 Results of Water absorption, Acid resistance and Alkali resistance.

S/NO	Test	Dry Weight before test	Weight after test	Difference before and after test
1	Water absorption	0.4444	0.5525	-0.1085
2	Acid resistance with 10% $HCl_{(aq)}$	0.5673	0.5126	0.0547
3	Alkali resistance test with 10% $NaOH_{(aq)}$	0.4970	0.4692	0.0278

The table 4.2 above shows result of water absorption, physical and chemical test carried out at the Department of Chemical Engineering, Faculty of Engineering Ahmadu Bello University, Zaria.

4.5.1 Percentage Water Absorption

Absorption % (W) $=\frac{(0.5525-0.4444)}{(0.4444)} \times 100 = \frac{0.1085}{0.4444} = 0.2441\%$

Table 4.2 above shows the result of the percentage water absorption. Evaluation of the properties has a direct link with the characteristics of the glass ceramics product. Although, the expected result is 100% impermeability (0% water absorption), the measurement is found to be 0.2441% for this product. However, it is possible to attain 0% water absorption, for maximum dielectric gain provided that more compaction is applied before sintering. Although, the porosity level of the product is quite low when compared on the same scale with convectional ceramics where the lowest level of porosity is normally between 5 to 10 % as posited by Ali (2008).

4.5.2 Firing Shrinkage

$S_i = \frac{(28-25)}{28} \times 100 = 0.1071429 \times 100 = 10.714\%$

The shrinkage in size is as a result of the sintering and densifications, compaction pressure applied which resulted in volume reduction, and the loss of water due to the firing temperature which is above the point where water phase can exist. There will be less decrease in volume as a result of densification if the pressure applied during compaction is increased as a result of close particle package. Although, the results indicate a good percentage shrinkage.

4.5.3 Resistance to Chemical Attack

The samples were tested and the following observations were made.

4.5.3.1 Alkali Test:

The result shows no colour change for alkali attack. No change in texture. There is a negligible (0.0278) amount of weight change.

4.5.3.2 Acid Test:

For the acid attack there was colour change from gray to white, no change in texture and there was a change in weight (0.0547).

The product having been tested shows more resistance to alkaline medium than acidic medium due to the level at which it worn out showing a difference in weight and colour change from gray to white in acid medium. It can be concluded at this stage that the material may be more suitable for application in condition more prone to basic than acidic solutions.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the results and discussion of the study, the following conclusion can be drawn:

1. By analysing the RHA it was found that it contains compounds such as 79.98% SiO_2 and the rest 20.02% which includes1.80% P_2O_3, 0.42% Na_2O, 1.54% CaO, 0.05% BaO, 0.11% TiO_2 that can be used for glass and glass ceramics formulation and production.

2. It was also found that a solution can be prepared with the ash, gel the same solution with a solution of Calcium trioxonitrate(iv)tetrahydrate and Trioxonitrate(v) acid.

3. The sinter crystallisation of the powder obtained from drying of the gel was also possible, specimens were sintered at a temperature of $700^{o}C$.

4. The sintered powder mainly contains combeite ($Na_6Ca_3Si_6O_{18}$) crystalline phase dispersed in amorphous glass matrix from the result of its characterisation by XRD and Scanning Electron Microscope (SEM).

5. The presence of crystalline phases confirmed by XRD and the morphology shown by SEM confirm both crystalline and amorphous phases as seen in the microscopy identify the material as that of glass ceramics.

The outcome has been found to be good energy and time saving method of glass ceramics production. This method has no regards to the composition of the starting raw materials, with a promising future in Nigeria especially with respect to agricultural waste materials in glass ceramics production with advantage of promoting safe environment. This has shown that the unutilised abundant and growing biomass RHA that is an environmental problem in terms of pollution and disposal can be used to produce glass ceramics. This research will contribute to other research to be carried out on glass ceramics, to knowledge of the advantage of using agricultural waste to the raw materials imported and advantage of using a low energy consuming process. Finally, it can be concluded that rice husk ash may be a low cost raw material for the preparation of glass ceramics materials through simple sol-gel route.

5.2 Recommendations

1. To improve the amount of silica in the ash further pre-treatment by washing and acid leaching should be carried out.

2. Further research should be carried out on other agricultural waste to ascertain their suitability for glass and glass ceramics development.

3. Compaction test should be carried out varying the pressure to determine the best compaction pressure with good result of water absorption and firing shrinkage.

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Appendix I

Firing shrinkage table

Green body length of sample	28 mm	28 mm	28 mm	28 mm	28 mm
Length of fired sample	25 mm	24 mm	24 mm	27 mm	25 mm

L_p – Green body sample length – 28 mm

Average L_f – length of five fired samples $= \frac{(25+24+24+27+25)mm}{5} = \frac{125\ mm}{5} = 25\ mm$