# DEVELOPMENT OF LOW TEMPERATURE GLASS CERAMIC FROM LOCAL RAW MATERIALS

**By**


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**A DISSERTATION SUBMITTED TO THE POSTGRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY IN INDUSTRIAL DESIGN (GLASS TECHNOLOGY)**


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## DECEMBER, 2008

**DECLARATION**

I declare that the work in the dissertation titled 'Development of Low Temperature Glass Ceramic from Local Raw Materials' has been performed by me in the Department of Industrial Design under the supervision of Dr. A. S. Ahmed, Prof. A. M. Ahuwan and Dr. G. Ndukwe.

The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of the dissertation was previously presented for another degree or diploma at any university.

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## CERTIFICATION

This dissertation titled 'DEVELOPMENT OF LOW TEMPERATURE GLASS CERAMIC FROM LOCAL RAW MATERIALS' by Ali, Edwin Adoyi meets the regulations governing the award of the degree of Doctor of Philosophy of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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**ABSTRACT**

Glass ceramics, a new family of polycrystalline materials produced by the controlled crystallization of glass has many uses cutting across all spheres of life from domestic appliances through medical devices to space exploration. The production process, just like that of other pyrotechnic products, takes a high toll on energy demand as a high temperature process. The best example can be drawn from the US economy where the annual energy bill for the glass industry as a multibillion-dollar industry is put at more than 1.3 billion USD.

In the present study, an attempt is made to find alternative route for ceramic glass production in the Nigeria that is cost effective in terms of energy input. In the process, a novel route outside the

two usual routes employed in glass ceramic production was adopted in fabricating a product which when subjected to some physical tests showed every attribute of glass ceramics. Although the process, which involved the sintering crystallization of glass and crystalline composites, has no preference to any particular glass composition or crystalline material, a low melting glass composition was used in the experiment to situate the process within the many limitations of the experiment. In this case an ophthalmic glass composition was selected, partially melted at 1200$^{o}$C, fritted and remixed with a fresh batch and sintered at 1000$^{o}$C. The percentage water absorption, porosity bulk density and specific gravity were evaluated using by the Archimedes' Principle (ASTM C373). The evaluation of these properties has a direct bearing to the ultimate characteristics of the glass-ceramic product.

The values obtained were 0.176 % for water absorption, 0.268% for porosity, 1.528 for specific gravity and 1.53gcm$^{-3}$ for density. The density is indicative of a lightweight material relative to the properties of the derivative materials. The XRD analysis shows the main crystalline phase in the material to be cristobalite and nephline. Optical microscopy obtained confirmed the presence of crystalline phases in a glassy matrix, which is conclusive of the fact that the product is indeed glass ceramic.

With further improvement the product of the experiment is a candidate for application as an electronic spacer as a lightweight material. However if substitute can be found for the Pb content, which is considered a toxic substance, its future use will extend to utility objects.

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To my father,
**Peter Abugwu Ali (Arih)**
*For his courage and vision in investing in the education of his children and relations, female and male at a time when the import of Western education was not within grips*

## DEFINITION OF SPECIAL TERMS

**Arrhenius type dependency:** Tendency of most materials increase in rates of reaction with increasing temperature

**Cristobalite** A silicate mineral that is a high-temperature form of quartz; stable above 1470°C; crystallizes in the tetragonal system at low temperatures and the isometric system at high temperatures.

**Heat treatment:** A procedure of heating and cooling a material without melting.

**Lever rule:** A method of determining the molar ratio or percentage content of the components of a binary system.

**Liquidus Temperature:** As used in glass melting refers to the temperature at which no single phase is thermodynamically stable

**Metastable equilibrium:** A state of pseudo-equilibrium having higher free energy than the true equilibrium state.

**Non-stoichiometry:** Refers to materials with no fixed chemical composition

**Phase:** Homogenous physical state mechanically separable but not necessarily continuous

**Phase Diagram:** A graphical representation of the equilibrium relationships between phases (such as vapor-liquid, liquid-solid) of a chemical compound, mixture of compounds, or solution.

**Phase rule:** A relationship used to determine the number of state variables *F*, usually chosen from among temperature, pressure, and species compositions in each phase, which must be specified to fix the thermodynamic state of a system in equilibrium.

**Periodicity:** The quality or state of being periodic; recurrence at regular intervals.

**Rayleigh scattering:** The elastic scattering of light or other electromagnetic radiation by particles much smaller than the wavelength of the light, prominent in gases but can occur when light travels in transparent solids and liquids

**Refractory:** One of a number of ceramic materials used in high-temperature structures usually in the upwards of means above about1000°C

**Sintering:** Adherence of particles to one another, prior to melting.

**Thermodynamics:** Characteristic of or resulting from the conversion of heat into other forms of energy.

**Supercooling:** Cooling of a substance below the temperature at which a change of state would ordinarily take place without such a change of state occurring, for example, the cooling of a liquid below its freezing point without freezing taking place; this results in a metastable state.

# Chapter 1

## INTRODUCTION

### 1.1 BACKGROUND

Glass ceramics, a family of polycrystalline materials prepared by the controlled crystallization of glasses, constitute an essential part of modern living. From their simplest use as cookware, through critical but still familiar uses in dental restoration to the even more critical use as missile radomes, they are yet to find complete replacements in the face of stiff competition from synthetic products such as plastics and other lightweight materials, in a world increasingly moving away from reliance on naturally sourced materials. The several advantages offered by glass over other materials, which has served to reinforce its competitiveness over a long period of use spanning several centuries, include exceptional chemical durability, multi-faceted optical properties and complete recycling capability in an era of heightened environmental consciousness.

Although glass ceramics, like conventional ceramics, contain a substantial refractory crystalline component, the difference between the two classes of materials stems from the fact that a glass ceramic starts out as a pure glass in which finely dispersed crystalline structures are made to "grow" within the glass matrix by a process of controlled crystallization. The presence of the so called ‘home groomed’ microstructure, in addition to enhancing the strength of the glass, increases its flexibility, with the consequential minimal presence of the severe microcracks that act as stress concentrators in the event of brittle failure but also simultaneously preventing the deterioration of less severe flaws thus acting as crack inhibitors.

Due to the fact that the size and distribution of the crystalline substructure within the glass can be accurately controlled, the resulting crystals confer on the end product various characteristics such as lack of porosity and extremely low coefficient of thermal expansion which can all be precisely controlled to suit specific applications but often the crystal chemistry is much different from that of the original or residual glass.

That Science is at odds in finding complete substitutes to glass products generally, notwithstanding the long history of use, spanning several millennia, is a factor attributable to what Rao (1981) describes as the twin freedom enjoyed by materials in the glassy state vis-à-vis "freedom from the restraints of periodicity and freedom from the requirements of stoichiometry". This peculiar nature of glassy materials has generated a lot of research interest in Glass Science especially since the early 60s referred to, in the annals of history, as "the Golden Age of Glass Science" (Doremus, 1983). Professor N. F. Molt earned the Nobel Prize "for having done so much to transfer glass science from the archives to the forefront of solid state" (Rao, 1981). This acknowledgement serves as a pointer to the flurry of activities in present day glass research.

As a non-stoichiometric substance, a single glass composition can accommodate as many as 60 elements at once. Michael Faraday, long ago, in recognition of the special attributes of glass, preferred to call it a "solution' rather than a compound (Doremus, 1983). This position, largely, holds sway to the present day. New glass forming systems are being developed everyday. Thus the same glass, which can be made stronger than steel as symbolized by fibreglasses valued as structural reinforcers, can by way of alteration of composition be made to dissolve in water as typified by sodium silicate composition (water glass). Again as illustrated by the $Li_2O$-$Al_2O$-$SiO_2$ family of compositions, by way of modification of composition, glass can be made to have negative or zero expansion coefficients within some ranges of temperature.

In spite of the usefulness of glass ceramics as a modern material, there is no form of productive activity in Nigeria relating to glass ceramics or record of any research effort directed at its development by the dozen or so research institutes in the country that engage in industry related activities as an extension of their mandates. It is therefore reasonable to state that any research

directed at an important branch of glass usage such as glass ceramics, especially in a country with huge potentials for industrial growth as Nigeria, cannot be in any way exhaustive, at least not at this stage of her development.

An attempt will be made in this study to explore the possibility of production of glass ceramics from local raw materials with particular reference to low energy input varieties. The energy dimension is chosen as the focus of study, partly as a response to the unsteady global energy situation and also because Nigeria's precarious energy infrastructure calls for steps, in her path of industrial take off, with inbuilt guarantee of sustainability.

## 1.2 DEFINITION OF GLASS

The versatility of glass has infused some dynamism into the term "glass" to the extent that numerous definitions have been proposed for it over its many years of history. The one most frequently quoted definition of glass proposed in 1945 by the American Society for Testing and Materials (ASTM) refers to it as an inorganic product of fusion which has cooled to rigid condition without crystallizing (Rawson, 1980). Although this "traditional" definition accommodates the majority of glasses, which are usually inorganic with one known mode of production materials, i.e. cooling to rigidity from the melt, it is considered too restrictive in the sense that it cannot account for organic polymers and other materials with glassy structures made by methods other than cooling from the melt. For instance amorphous thin glassy coatings made by sputtering directly from the vapour state have every claim to being called glasses just as sodium silicate glass can be made by two methods, one by cooling from the melt and the other by preparing an aqueous solution of sodium silicate and evaporating to dryness.

These changes in the material world prompted a committee of the US National Research Council

to come up a broader definition in 1976 without recourse to mode of production or constituent materials. The broader outlook refers to glass as "an x-ray amorphous solid, which exhibits the glass transition, that being defined as that sudden change in the derivative thermodynamic properties from crystal-like to liquid-like values". Its rigidity must approach that of an ideal elastic solid i.e. it should be at least $10^{13.7}$ Pa s on the viscosity scale and when examined by x-ray diffraction it should have the structural attribute of liquids, which is a short range order. Critics of the newer definition rest their case on the fact that only a few materials referred to as "borderline cases" do not fit into the ASTM definition which they regard as the classical definition of glass.

### 1.3 THE PROBLEM OF THIS STUDY

According to Hoover (1964), an important consideration in the location of industries is the disposition of a country's mineral and energy resources. Nigeria on this basis has all it takes to become an industrial nation. Available statistics based on studies carried out by the relevant agency, the Raw Materials Research and Development Council (RMRDC), shows that the raw materials for glass making exist in great abundance in the country (RMRDC, 1997). The existence of commercially exploitable deposits hosted by rock of the basement complex around Egbe, Udiaraku, Okene and Lokoja has been reported (RMDC, 2003). A number of other deposits located in Kenyi/Madakiya in Kaduna State and Gworza in Borno State have been covered in isolated studies with sketchy details regarding their glass forming ability (Malgwi, 1989; Jekada, 1997). These findings are in agreement with the assertion of Pincus (1967) to the effect that glass raw materials are among the cheapest and most abundant of all industrial raw materials the world over.

While the raw material need of the glass industry can be said to be met with some degree of

certainty, the same assertion cannot be made for the energy requirement not withstanding the fact that Nigeria is the world's sixth largest producer of fossil fuels. The country's weak energy infrastructure remains the stumbling block to the maximum utilization of the country vast oil and gas resources. Apart from the fact that Nigeria is a net importer of refined petroleum products, long queue of vehicles are not uncommon sights at gasoline stations due to poor storage facilities. The matter is made worse by the fact that regions of petroleum resources have remained the hotbed of global sociopolitical instability against the mounting energy cost of global output of glass products the use of fossil fuels. Electricity power generation required for glass melting is also in short supply in the country.

According to the US Department of Energy (2000), the total energy bill of the glass industry is more than $1.3 billion. Representing an important segment of the country's economy the industry engages more than 150, 000 people in skilled jobs and generating more than 21 million tonnes of consumer products each year at an estimated value of $22 billion.

The approach to be adopted in tackling the energy issue in glass production as the problem of this study is to explore ways of producing glass ceramics with low energy input.

## 1.3 RESEARCH QUESTIONS

I. What would be the economic implications of such an approach?

II. How would it fit into the Nigerian situation of the weak energy infrastructure of the country?

III. How would it contribute to solving the global energy crises?

### 1.4 OBJECTIVES OF THE STUDY

The precise objectives are to:

I. Identify a source of raw material suitable for glass ceramic production in Nigeria.

II. Carry out chemical analysis on samples of the raw material to ascertain the chemical constituents.

III. Identify the appropriate glass formula with the least energy input.

IV. Explore the most appropriate route for conversion of the raw material into glass ceramic with respect to the energy demand of the product.

V. Test-melting the batch.

VI. Characterize the product of the experiment as the basis for further development.

### 1.5 JUSTIFICATION.

Glass ceramics fall under the category of glasses valued for high technology and specialty applications, 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 also been exploited in developing many of these compositions.

According to a report by Business Communications Company, Incorporated (BCC), (www.bccresearch.com), the North American market for advanced and specialty glasses reached $2.3 billion in 2002 and with a projected growth rate of 7.8% would reach $3.3 billion by 2007.

The global market was estimated at $8.5 billion in 2002, and at an expected growth rate of 8.3% would reach $12.6 billion by 2007.

The largest market for advanced and specialty glasses according to the report are concentrated in electronics displays, which include liquid crystal displays (LCDs) and gas and vacuum discharge displays. This market in North America was worth approximately $1.3 billion in 2002 and was expected to have reached almost $2 billion by the year 2007. The global market was expected to grow from $4.8 billion in 2002 to $7.8 billion in 2007.

Over 60% of the total market according to the survey is for electronic applications. The combined electronics segment market for North America was put at $1.4 billion in 2002 and was expected to increase to $2.2 billion by 2007. The medical/dental market is expected to witness a relatively strong growth, as demand for dental aesthetics increases and new products find their ways to the market. The applications that would fuel this growth include glass-ceramic crowns and DNA microanalysis. On the whole, the demand for advanced glasses is expected to maintain the growth level as new applications in these various segments come on the market.

In the aspect of global competition, North America is in the lead in several areas, since the US glass company, Corning Inc. has the largest market share in these areas. Japan follows closely behind in the two market segments, for the reason that a number of Japanese companies are also major producers of specialty glasses. In the same manner the German multinational, Schott Glas AG, makes Europe another strong competitor, as a major player in most EU countries.

Glass ceramics manufacture holds great potential for employment generation in a country like Nigeria as it is becoming increasingly evident that no country can afford to insulate itself from the effects of the global marketplace. Glass demand, as stated by Limbs (2002), remains strong and growing, exceeding worldwide gross domestic product, and will continue to grow with the focus of growth shifting to Asia, especially China as her rising economic fortune is raising a new crop of consumer population. For instance, the Chinese share of global demand for glass, which reached 4 billion square meters in 2003, was put at 30 percent while the overall annual increase in global demand for glass products between 1990 to 2003 was put at 4 percent per year, is 1.2 percent higher than the worldwide average GDP of 2.8 percent a year, within that same period.

Judging from the experience of India and China, Nigeria's huge population translates into a considerable consumer market for any local industry that specializes in glass ceramics products. This market potential is further boosted by the realizable dream of a common market within the West African sub region under the aegis of West African Economic Community (ECOWAS). According to a report in the UNIDO Quarterly, Africa has a high potential for investment in untapped human and natural resources (Punch, February 9, 2000). The report states that many investors are discovering that Africa provides high returns from carefully selected investments even in conflict-infested regions. The same report adds that Africa enjoys many advantages in the global market place and this includes the benefits of locating projects on the continent to supply the U. S., Europe and Japan. Furthermore, a joint poll by the United Nations Conference on Trade and Development (UNCTAD) and the International Chamber of Commerce (IICC) released in Bangkok in February 2000 placed Nigeria top among four countries on the continent that would likely benefit from increased transnational activities in the next five years. (Punch, February 18, 2000).

The glass ceramics industry is certain to benefit from the attendant capital inflow to Africa by virtue of the groundwork being laid by this study. It is therefore timely to embark on a study that will develop the basis for glass ceramics manufacture in Nigeria and the present study is set to establish that framework.

## 1.6 SIGNIFICANCE OF THE STUDY

The significance of this study hinges on the attempt to improve the economic situation in Nigeria via the production of low energy input glass ceramics. Although energy costs in the glass industry according to the US based Manufacturing Energy Consumption Survey (MECS), do not vary substantially across glass sectors as a cost item, it does account for 6-12% of total production costs (Dohn, 2000). The same survey revealed that in the United States, the glass industry consumed 206 trillion B.T.U. of energy worth about $1.4 billion on energy in 1998. About 8% of the energy supply came from fossil fuels. Apart from its being physically limited, the use of fossil fuels constitutes a threat to our health and environment. In addition to its contribution to global warming, burning fossil fuel releases chemicals and particulates that can cause cancer, brain and nerve damage, birth defects, lung injury, and respiratory problems to mention a few.

Those that might question the relevance of a research directed at energy reduction at this stage in our national life, given that Nigeria, a major exporter (sixth largest in the world) will for a long time to come have enough petroleum oil to satisfy local consumption, must take a cue from the transformations that turned the United States into a modern industrial nation. In 1950, the U.S. was producing half the world's oil but fifty years on, the country no longer produce half her own oil need. Moreover, the world's burgeoning population has other uses for petroleum products that extend to fertilizer such that it is feared that demands will outstrip production unless some

alternative is found for petroleum fuels.

### 1.7.0 LIMITATIONS OF THE STUDY

This form of research should ideally attract funding from government or the business community. The financial constraint has undoubtedly placed a heavy limitation on the outcome of this highly practical work.

Another limitation placed on this study is the vast size of the country and the lack of updated geological information regarding the country's mineral resources. The only mineral map currently in use in the country dates as far back as the early 60s. This weak database of the country's mineral resources is most likely to affect the outcome of this and related studies.

Another obvious impediment in the way of a successful completion of the work is the level of infrastructure needed to sustain the work. The researcher is unaware of any assembly of laboratory facility needed to carry this work to a successful end. This situation calls for improvisations that may have compromised the standard of the outcome.

### 1.8 SCOPE

Within the scope of this study, local raw materials has a restricted meaning limited to quartz, quartzite or glass sand because glass ceramics as other raw materials used in the experiment as a control measure are in analytical grades. More so because glass ceramics as value added products require the use of analytical grades of other raw materials/chemicals as supplements to silica as the main raw material.

The laboratory aspect of the present work was limited in scope to the sequence of procedures followed in converting the raw batch to a molten glass and annealing it to the required

specification in physical characteristics. The work stops at any form of operation carried out on the products of the experiment to transform them into testable samples but not beyond that.

# Chapter 2

# 2 LITERATURE REVIEW

## 2.1 DEVELOPMENT OF GLASS CERAMICS

The development of glass ceramics has a conflicting beginning but there is a convergence of views centering on the fact that it was discovered accidentally. While Moody (1971) stated that it came about as a result of a furnace fault, Macmillan (1964) in his own account gave credit to S. D. Stookey of the Corning Glass Laboratories in the United States, who discovered it accidentally in an attempt to heat a photosensitive glass to a temperature beyond its normal melting temperature. Stookey found out that the glass, instead of melting, turned into an opaque, polycrystalline material with derivative properties superior to those of the original glass. Unlike traditional ceramics, where most of the crystalline materials are introduced at the stage of preparation, the crystalline phase in glass ceramics is produced by the growth of the crystals in a homogenous glass melt.

Crystallization itself is not a new phenomenon in glass production and when encountered in standard glass production it is viewed as a defect called devitrification. However, the roots of glass ceramics can be linked to the works of Rémur, the 16$^{th}$ French chemist who earned the reputation of preparing opal glasses from photosensitive glass melts. The problem with Rémur's opal glasses was his inability to control the degree of opacity. The opacity of glass ceramics, unlike that of Rémur's opal glasses, can be adjusted by controlling the size and concentration of the crystals, and this can be done precisely by controlling the firing cycle. Tiny crystals scattered throughout the glass body produce opacity in the same way as tiny water droplets suspended in the air produce fog.

## 2.2 GLASS FORMATION VERSUS CRYSTALLIZATION

Most elements and compounds exhibit Arrhenuis type dependency in the sense that an increase in temperature or decrease in activation energy increases their rates of reaction. On cooling these materials crystallize at or a little below their freezing points. There are however a few other materials which rather than follow the path of crystallization, transform into glasses on cooling. The uniqueness of the latter category, chief among them, silica ($SiO_2$), lies in their ability to form highly viscous melts. The viscosity of $SiO_2$ at the melting point of cristabolite is $10^7$ Pa s implying that silica melts could be 10 billion times as "thick" as water when measured on the same scale! Rawson (1980), argued that the high viscosity of glassformers at their melting points constituted a barrier in the process of crystallization as "the atoms or molecules are not easily moved, relative to one another by applied forces". The process of crystallization itself involves structural changes in the form of rearrangement of atoms relative to one another in a long-range pattern. Figure 2.1, which is perhaps the most used diagram in glass technology best, illustrates the difference between glassy materials and crystalline solids at their formation stages.

From the volume-temperature diagram in Figure 2.1, the melting temperature or the freezing point (Tf) in a reversed order is marked by a sudden decrease in volume. No such discontinuous change is experienced if the melt follows the path of supercooling along be. The decease in volume on cooling can be attributed partly to the decreasing amplitude of atomic vibrations, and partly to changes in the structure of the melt making it more compact as the temperature drops. At temperatures near Tf, these structural changes occur at such a speed that they will appear to occur instantaneously with any slight change in the temperature of the material.

As the viscosity increases with falling temperature, the tempo of these changes slows down until the viscosity becomes so high that no such changes are possible any longer. The consequence is a decrease in slope at the point e along the path of supercooling. Further fall in temperature beyond Tg is due almost entirely to the decreasing amplitude of vibration, which is a characteristic, exhibited by all elastic solids.

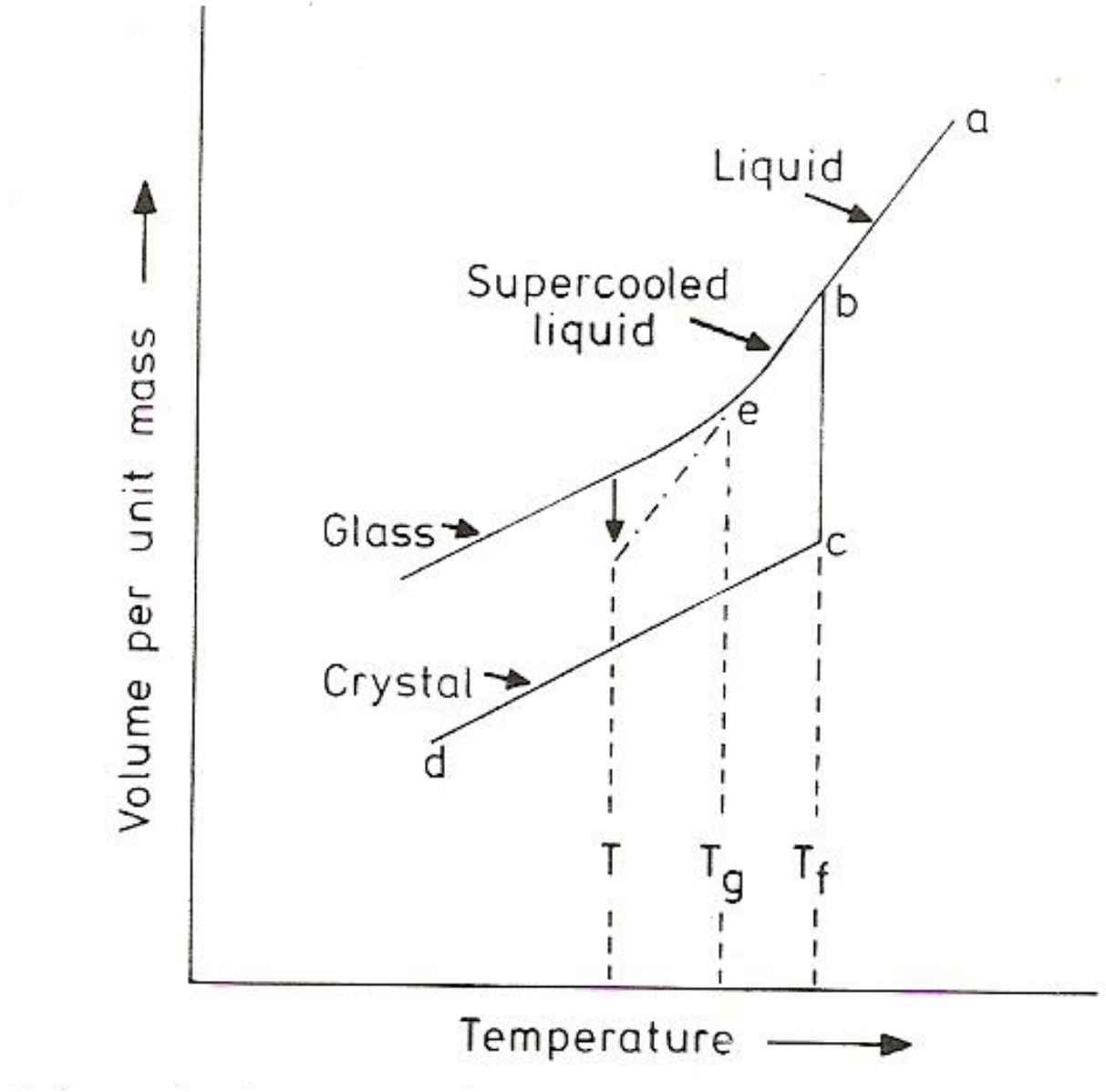



***Fig. 2.1. Relation between the Glassy, Liquid and Solid States***

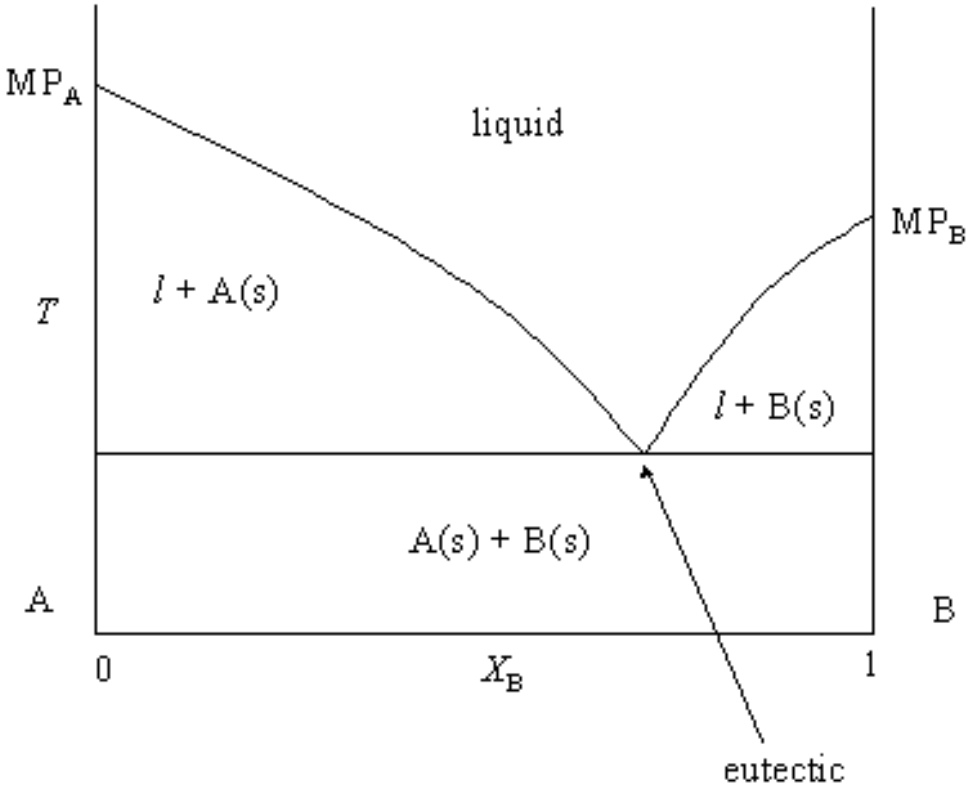
The temperature at which the change in slope occurs is this called the glass transformation or transition temperature (Tg). Rawson (1980) insists that it is only at Tg and below that “it is correct to describe the material as glass’. It is ‘safer’ to use the term transformation range in place of transformation point since the temperature at which the change occurs rather than being a fixed quantity is found to decrease as the rate of cooling is decreased. In that case, if the glass is held at T a little below Tg, its volume deceases slowly until it reaches a point on the dash-dot line, an extrapolation of the contraction curve of the supercooled liquid. It should be noted that the rate of change of volume decreases as the equilibrium configuration of glass (dash-dot line) is approached. The equilibrium configuration has a lower free energy than other liquid-like structures at that temperature but not the lowest free energy at that point, as that would be its crystalline equivalence. Glass in general is said to be in a state of metastable equilibrium.

## 2.2 DEVITRIFICATION

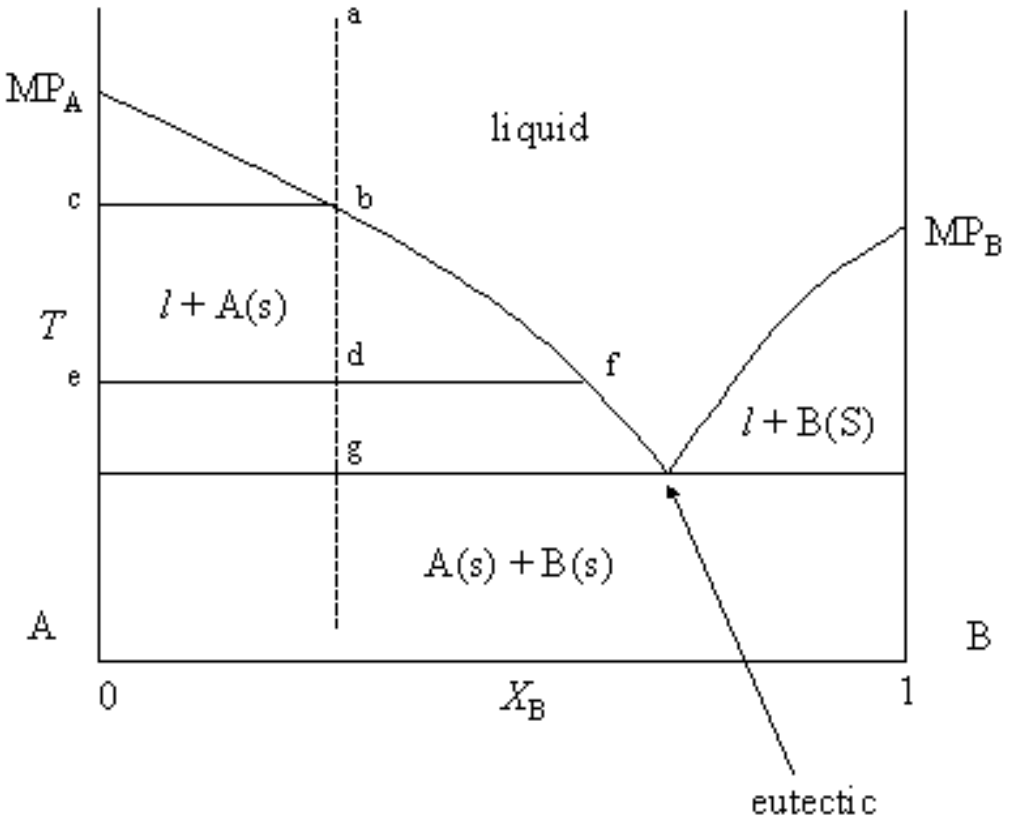
It is clear from the preceding that glass melts will crystallize if given sufficient time at or a little below liquidus temperature. The condition is that the temperature should be high enough to permit structural rearrangement at an appreciable rate. Under this condition, the time taken for crystals to appear in the melt, even for a single component system could stretch from a few minutes to several hours depending on composition. In a melt of two or more components, depending on how rigorous the mixing process is done, crystallization may occur in the form of a mixture of phases.

If the cooling process in Fig. 1 proceeds along route bc the system will eventually reach a temperature where one or both of the components will freeze. In a phase diagram of temperature versus mole fractions involving substances "A" and "B", (Fig.2.2a), the freezing point of the solution (the liquidus temperature) decreases as the composition is varied away from either pure

A or pure B. If point "a." along the dash-dot line is chosen as the starting point in the liquid region in Fig. 2.2b and the system cooled at a constant composition and pressure not much change is experienced.




***Figures 2.2 a: Plot of Temperature against Molar Fractions of Two Component***




***Figures 2.2 b: Plot of Temperature against Molar Fractions of Two Component System***

From point a to point b, the melt is merely losing heat. At point b, however, some pure component A begins to crystallize out. On crossing the curved line at point b marks a two-phase region. The two phases are pure component A and the liquid mixture. The two different compositions can be tracked by the tie-line running from point b to point c using the so-called level rule. Where the tie-line intersects the closed curve at b indicates the composition of the liquid phase. In the diagram the other end of the tie-line intersect the edge of the diagram at pure solid A (point c). As the cooling continues, the tie-lines continues to track the composition of the liquid and solid phases such that by the time, point d is reached, the left end of the tie-line (point e) still tracks the pure solid A while the right end of the tie-line tracks the liquid composition at point f. It should be

observed that the liquid at point f is much richer in component B for the fact that the process removes component A from the solution by crystallizing it out. The lever rule can be used to calculate the mole fraction of each component in a mixture comprising solid A + liquid. In essence, the relative lengths of the tie line give the proportions of the phases present. The length of the tie-line which is furthest from the phase of interest is corresponds to the amount of the phase present. For example, on the diagram shown in Fig 2.2, the percentage of A present can be calculated from line *ef*:

Fraction of A = (34.5 - 23.7) / (34.5 - 5.2) = 0.3686
Thus, percentage of A = 0.3686 x 100 = 36.86%
and, as the A and the liquid make up 100% of the composition:
Percentage of liquid = 100 - 36.86 = 63.14%

The liquid is said to reach the eutectic composition on reaching point g at which the temperature and liquid composition of both pure solid A and pure solid B will crystallize out together. In the diagram, crystals of the two substances will be interspersed among each other. The interspersing could as well be achieved at the microscopic level to an extent that the crystals making up the mixture may appear homogeneous to the naked eye. The morphology of the mixture of the two different crystals can be easily revealed under a microscopic examination. Further extraction of heat from the mixture makes the system will remain at the eutectic temperature until all of the remaining liquid solidifies.

As the temperature decreases below point g the system crosses over into another two phase region where no single phase is thermodynamically stable. This time the two phases in equilibrium are pure solid A and pure solid B. Tie-lines in this region run from the pure A side to the pure B side and since this is a two-component system, the variance is given on the basis of the phase rule by *v*

$= 2 + c - p = 4 - p$ where $c$ is the number of components and $p$ the number of phases present at equilibrium. One of the degrees of freedom contributing to the variance is pressure, but because pressure is constant in this diagram, the pressure variable is regarded as being plotted perpendicular to the plane of the paper. It is usual to define the "reduced variance," $v'$, as just the variance in the plane of the diagram. That is, the reduced variance is the phase rule variance minus the pressure variable. The reduced variance in a two-component phase diagram is given by $v' = 3 - p$ which in this case is 2 in the liquid region. (Temperature and composition can be altered arbitrarily) In the two-phase regions, like the A(s) + liquid, or B(s) + liquid, regions the reduced variance is 1. In these regions a change in the temperature of the composition will result in a corresponding change in the liquid phase. However the composition of the solid phase will remain constant in these cases for the simple reason that the solid phase is either pure A or pure B.

### 2.2.1 Solid/Solid Solubility

There are situations when cooling a material from the melt to its "freezing point" rather than crystallizing out as pure components yields a solid solution. Figure 2.3 displays the region labeled α(s) as a solid solution of B in A in which case, component A would be regarded as the solvent and B the solute. It is equally correct to refer to this phase as "impure A" just like the region labeled β(s) is a solid solution of A in B could also be regarded as impure B.

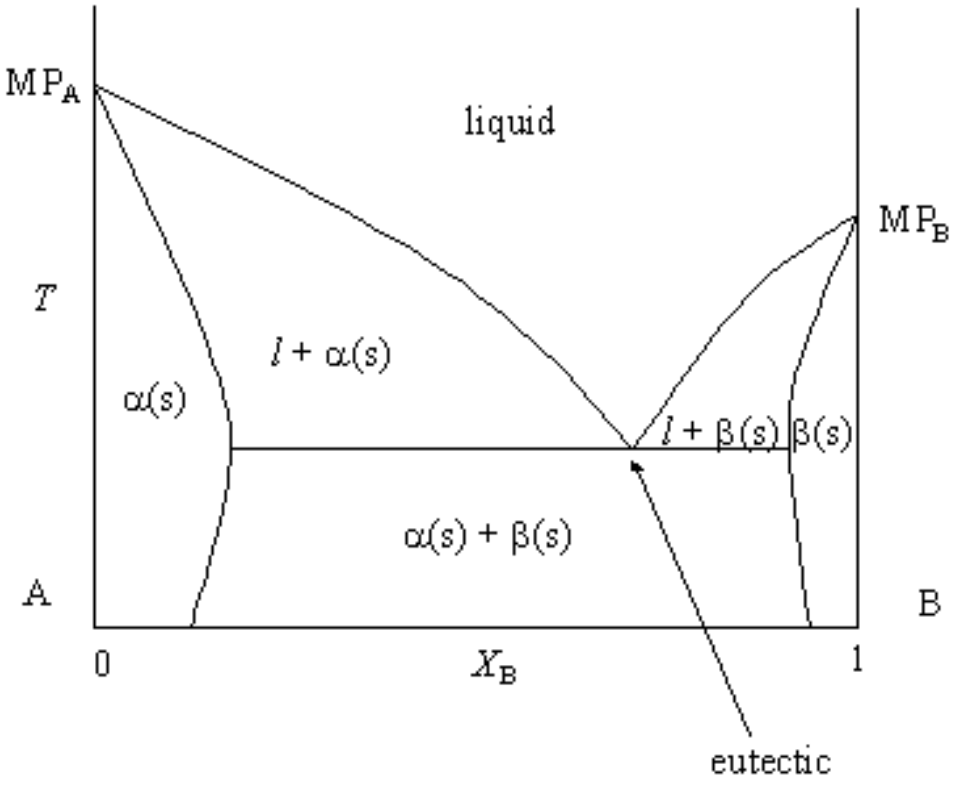



***Fig.2. 3: Temperature vs. Molar Fraction showing solid/solid mixture***

Going by the phase rule, the reduced variance in the solid solution areas labeled α(s) and β(s) is 2 because the regions are one-phase regions. The reduced variance in the other regions is the same as in the phase diagram with no solid-solid solubility. On this diagram it is easier to see why the reduced variance is 1 in the region labeled α(s) + β(s). The composition of the two solid solution phases in the coexistence region changes slightly as the temperature is changed.

Silver and copper form solid-solid solutions similar to the above diagram where the solid-solid solubility of one component in the other is not very large.

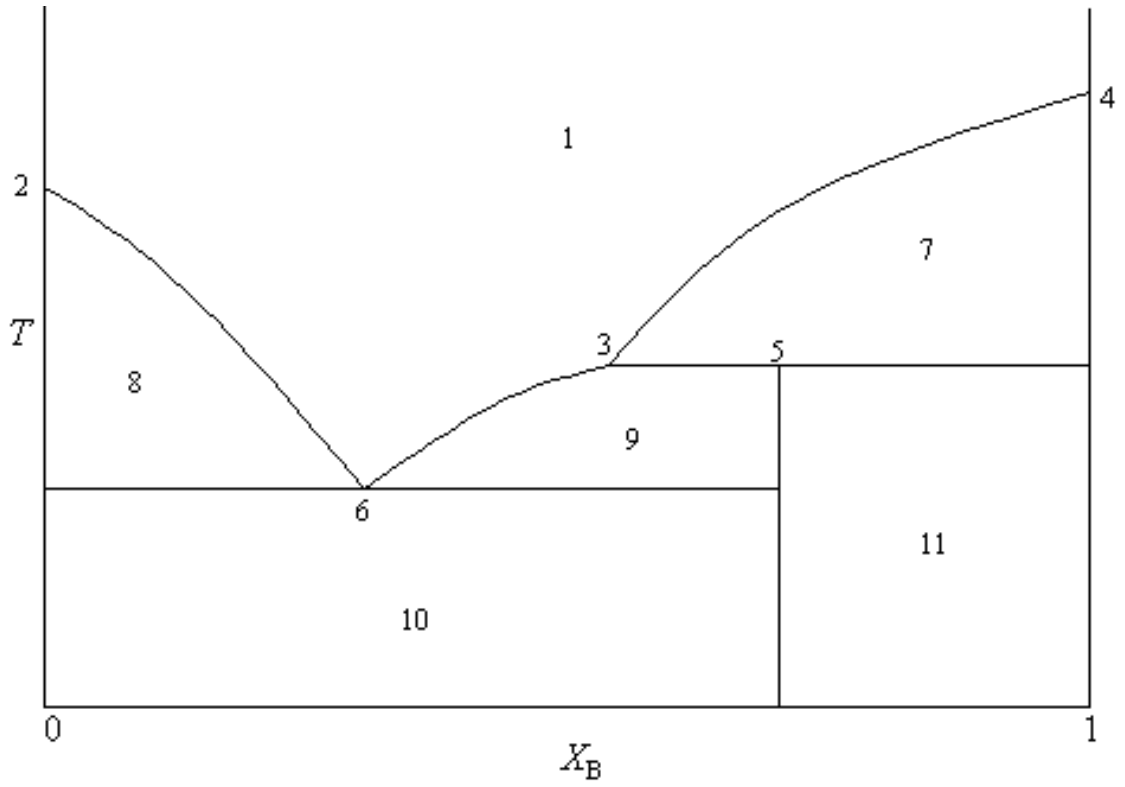



***Fig. 2. 4: Incongruent Melting Point (melting with decomposition)***

This phase diagram in Figure 2.4 shows an incongruent melting point. The vertical line at point 5 represents formation of a compound. It looks like the composition of the compound is $X_B = 2/3$, from which we conclude using the previous arguments,

$$X_B = \frac{2}{3} = \frac{n_B}{n_A + n_B} = \frac{2}{1+2},$$

so that the compound is $AB_2$. Point 5 is the melting point of $AB_2$, but notice that melting $AB_2$ does not give liquid of the same composition. Rather, melting of $AB_2$ gives liquid with the composition at point 3 and pure B(s). So the compound, $AB_2$, melts and decomposes at the same time. An analysis of the points and regions is:

1= liquid

2 = MP of A

3 = the peritectic point ( eutectic of $AB_2$ and B)

4 = MP of B

5 = the incongruent melting point of $AB_2$

6 = eutectic of A and $AB_2$

7 = liquid + B(s)

8 = A(s) and liquid

9 = liquid and $AB_2$(s)

10 = A(s) + $AB_2$(s)

11 = $AB_2$(s) + B(s)

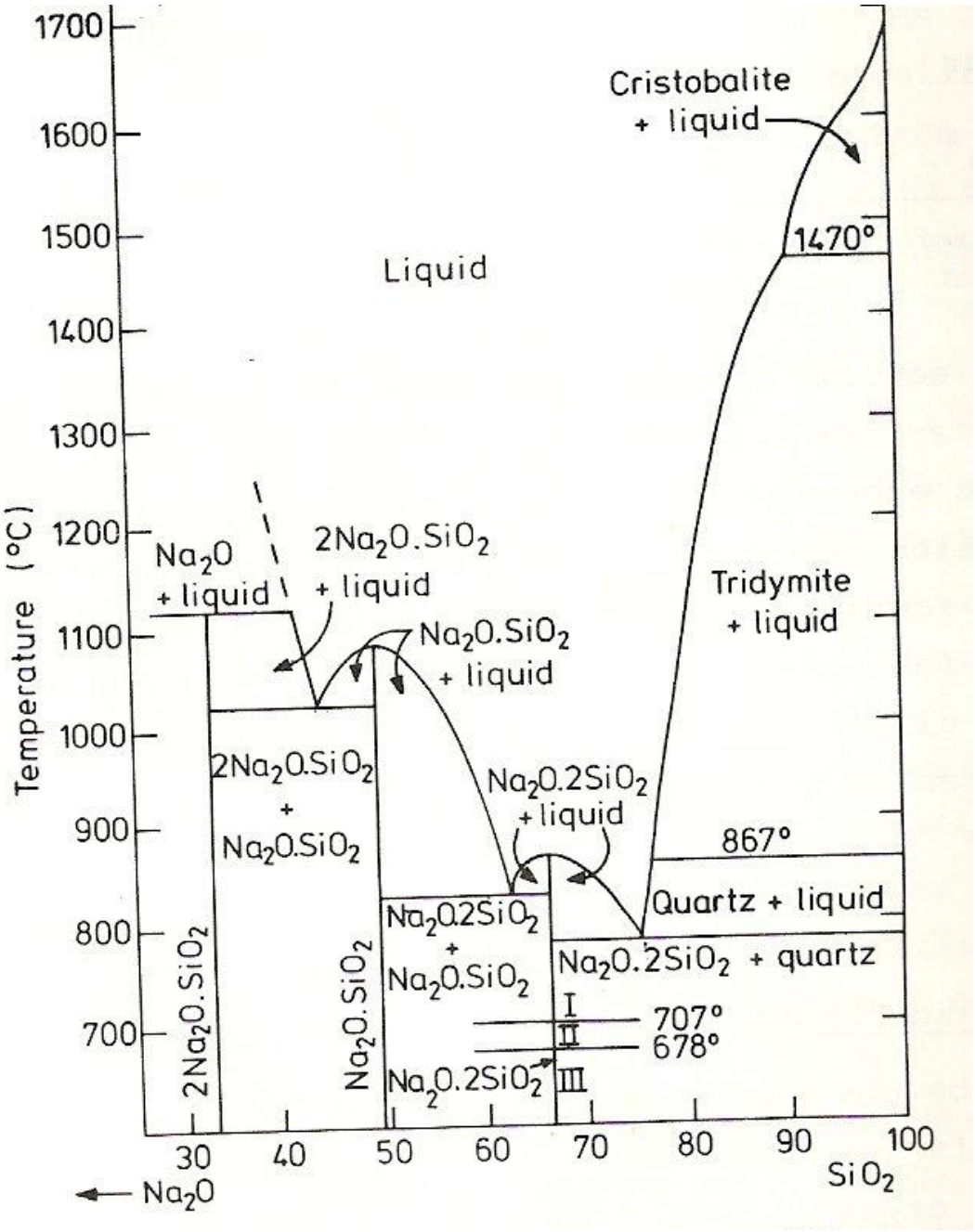



***Fig.2.5: Phase Diagram of the $Na_2O$-$SiO_2$ (Two-component) System***

The various crystalline forms of the binary system of $Na_2SiO_2$ are indicated in Fig. 2.5. Note the eutectic point at a temperature of about 780$^oC$ and the composition is $Na_2O.2SiO_2$. The peritectic

point, the eutectic of the combination of $Na_2O.2SiO_2$ and quartz as shown in the diagram occurs at 867$^oC$.

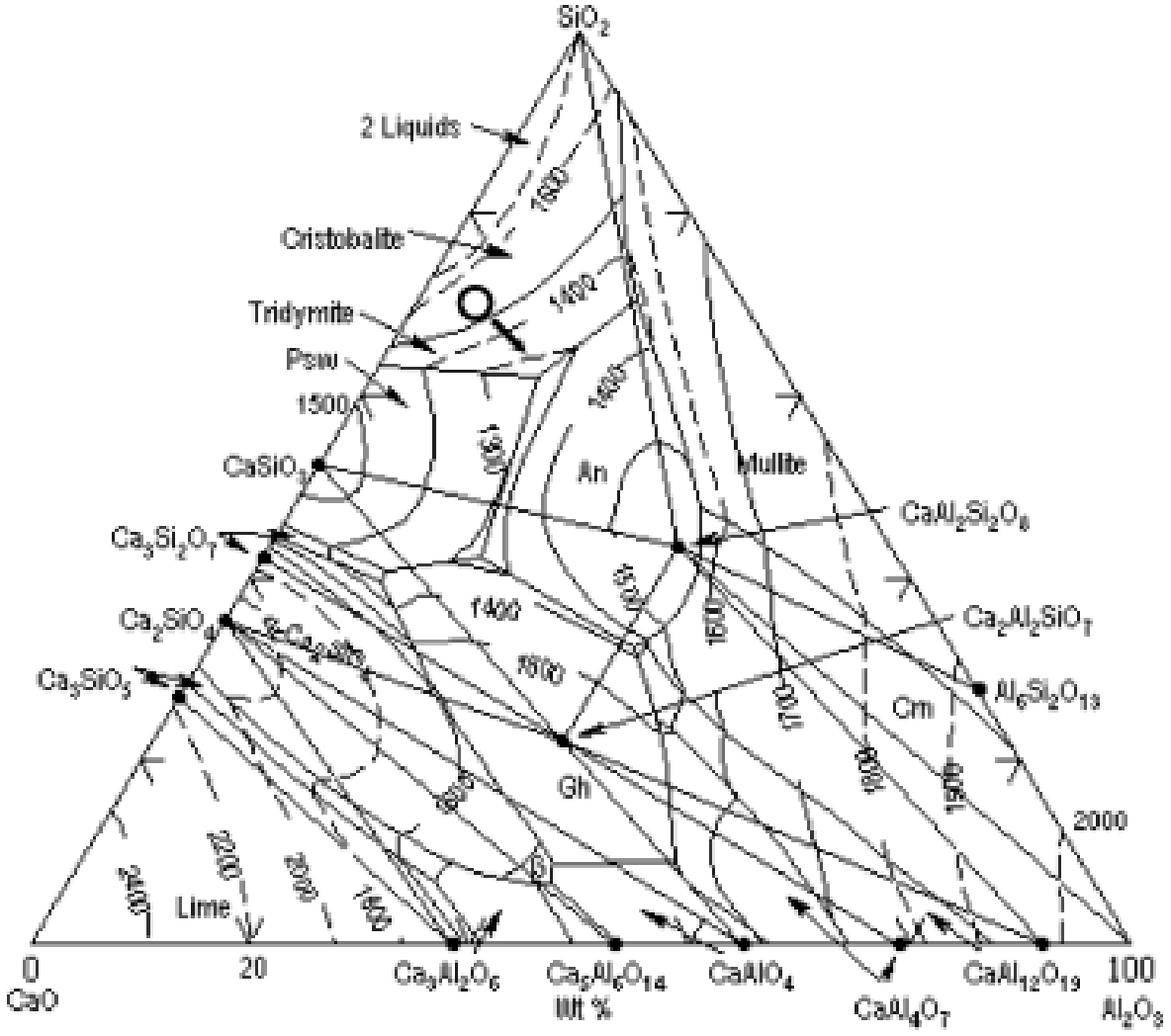



***Fig. 2.6: Ternary phase diagram of SiO2–Al2O3–CaO System***

Phase diagrams, of a much more complicated form than the examples sited in this presentation (Fig.2.5) are used in the study of equilibrium conditions in fields such as metallurgy, materials science, geology and geophysics, planetary science and the more practically useful ones as presented in Fig. 2.6 extend beyond two components systems. The ternary eutectic occurs at 1300$^oC$. The thermal maxima arrived at by extrapolation as indicated by the dash-dot lines is

2400$^{o}$C.The diagrams, as products of experimental observations, are obtained from a set of cooling curves.

### 2.2.2 Nucleation and crystal growth

The existence of nuclei in the melt, once equilibrium is attained, is the prerequisite to the formation of optically visible crystals. Nuclear are crystals of particulate sizes, which, ideally should be close to atomic dimensions (Moody, 1971). Nucleation can be homogenous or heterogeneous.

Homogenous nucleation arises from molecular fluctuations in the melt resulting in the formation of unstable, intermediary states called embryos. The embryos having attained the minimum critical sizes are capable of developing spontaneously 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, supersaturation, and temperature. Furthermore, the kinetics of nucleation and crystal growth generally depends on the thermodynamic driving force and heterogenous inclusions in the melt.

The composition of homogenous nuclei is the same as that of the crystals that grow on them but the composition of heterogeneous nuclei on the other hand, varies radically from the surrounding glass composition. Heterogenous nucleation is analogous to the existence dust particles as precondition for condensation of dews in the atmosphere. Nucleation is however seldom homogenous partly due to the high surface energy to volume ratio required in forming the critical size and also due to the difficulty of excluding foreign nuclei from the melt. These extraneous materials include fragments of refractories, vessel walls and the so called nucleating agents which are deliberately added to precipitate into tiny nuclei that are the precursors to the formation of the

major crystalline phases in the glass. As shown in Figure 2.7, the optimal condition for nucleation and crystal growth generally, do not overlap.

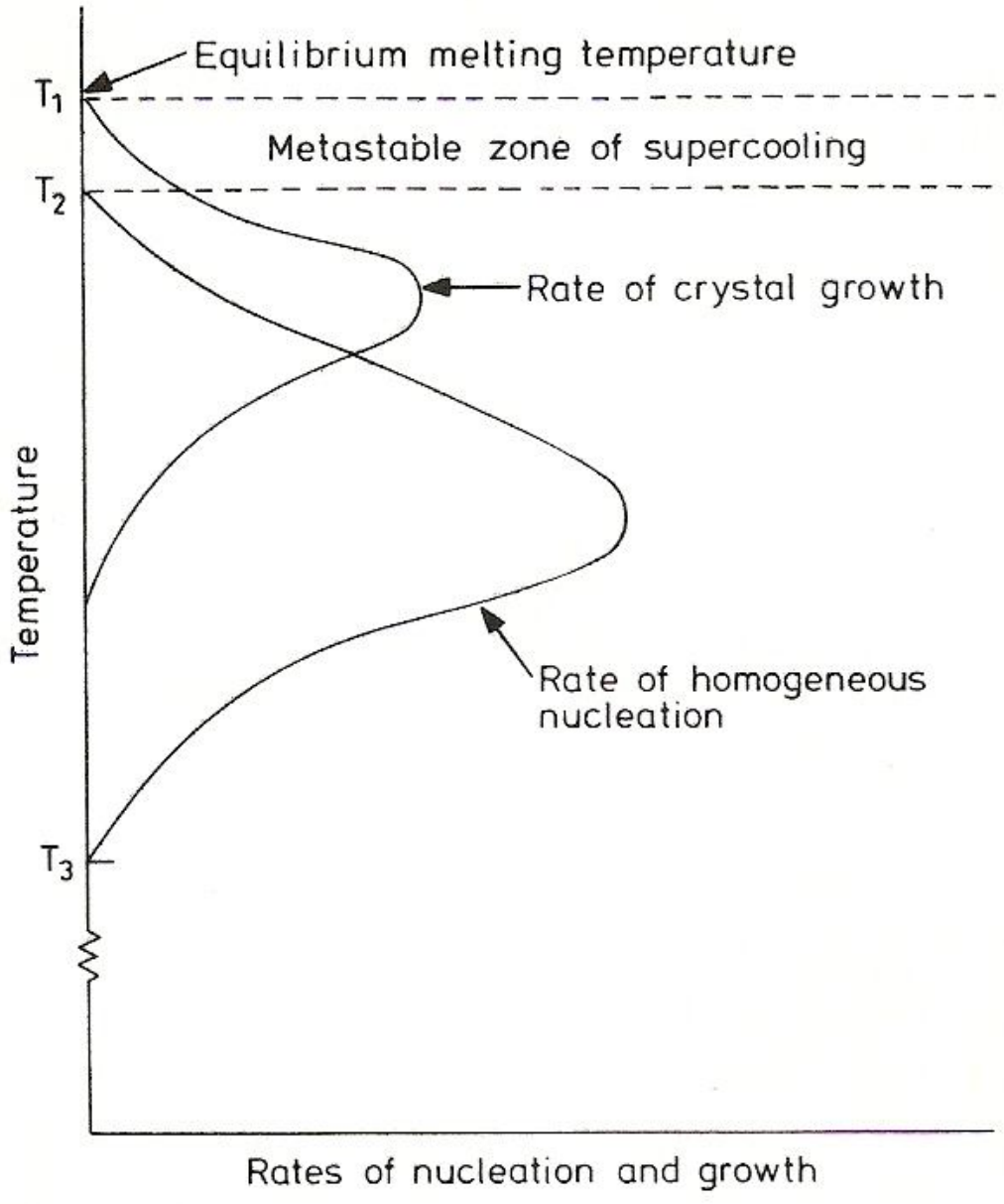



***Fig. 2.7 . Rates of nucleation and crystal growth vs. temperature***

Nucleating agents promote volume nucleation and glass ceramic formation. Their possible roles according to Weinberg (1992), are to increase nucleation of a stable or metastable phase by increasing the bulk energy change or to decrease the crystal liquid interfacial energy per unit area ($\sigma$). Nucleating agents for oxide glasses are commonly $TiO_2$, $ZrO_2$, $P_2O_5$ and fluorides and water for non-oxide glasses.

## 2.3 GLASS CERAMICS COMPOSITION SYSTEMS

Although there are six composition systems frequently listed by most authors, through proper selection of composition, a whole range of different types of crystals can be precipitated so that the properties are tailor made to their different end use demands. Similarly, all sorts of starting materials have been converted to glass ceramics from fly ash through cullet to virgin materials. The six common types are namely: $Li_2O$-$Al_2O_3$-$SiO_2$ with exceptionally low coefficient of thermal expansion, $2MgO$-$Al_2O_3$-$SiO_2$ – cordierite glass ceramics with good mechanical, thermal and dielectric properties, $Li_2O$-$SiO_2$ with photochemical etching capability, nephline glass ceramics with high mechanical strength attained though compression glazing, machinable flouromica glass ceramics and $CaO$-$MgO$-$Al_2O_3$-$SiO_2$ which is an inexpensive variety prepared from natural minerals and blast furnace slag. Table 1 is a display of the common glass ceramic types and their nucleating agents.

### 2.3.1 Glass Ceramic Types and Nucleating Agents.

**$Li_2O$-$Al_2O_3$-$SiO_2$ based Glass Ceramic:** The major characteristic of this glass ceramic type is its low thermal expansion coefficient usually approaching zero near ambient temperature. This feature is derived from either β-quartz or β-spodumene solid solution crystal phase, which though metastable can breakdown to other phases at a temperature of about $900^oC$. This particular kind of

**Table 1: Glass Ceramic Composition system and the dominant crystalline phases**

| System | Nucleating Agent | Crystal Phase | Application |
|---|---|---|---|
| $Li_2O$-$Al_2O_3$-$SiO_2$ $Al_2O_3$ > 10% | $TiO_2$ $TiO_2$+$P_2O_5$+Zr $O_2$ | B-spodumene, B-eucyptite | Cooking ware; heat exchanger; telescope mirrors |
| 2MgO-$Al_2O_3$-$SiO_2$ $Al_2O_3$ < 10% | $TiO_2$ | Cordierite, cristobalite | Missile radomes |
| $Li_2O$-$SiO_2$ | $P_2O_5$ Cu, Ag, Au | Lithium Disilicate Lithium Meta-silicate | Glass ceramic/metal seals, photochemical machining |
| $Na_2O$-BaO-$Al_2O_3$-$SiO_2$ | $TiO_2$ | Nephline, hexacelsian | Tableware |
| F-$Al_2O_3$-$SiO_2$ | $H_2O$, F | Fluorine-phlogopite | Machinable dental decoration |
| $Na_2O$-CaO-MgO-$Al_2O3$-$SiO_2$ | $P_2O_5$ | Diopside | Tiles, wall claddings |

*Source:* Macmillan, 1964

glass ceramics has stable crystal phases of the general formula ($Li_2$, R) $O.Al_2O_3.nSiO_2$ where N varies from 1 to 10 and R is a divalent ion normally $Mg^{2+}$ or $Zn^{2+}$. In commercial compositions N is usually in the range of 4 to 7. By substituting MgO and ZnO for $Li_2O$, $AlPO_4$ for $SiO_2$, batch cost can be reduced in addition to lowering liquidus temperature to enhance stability. The nucleating agents for this group of glass ceramics are $TiO_2$ and $ZnO_2$ for most commercial compositions. About 2 mol% of nucleating agents render the material transparent because of the fine scale of the crystal distribution, usually less than 50 nm in crystal size. It is the fine crystal size and the low birefringence inherent in B-quartz that results in minimal light scattering.

If opacity is the intended result the particles must be at least the size of the wavelength of the ambient light so that the light waves will bounce off them and scatter, producing cloudiness, with the degree of opacity determined by the population of the particles. On the other hand, if the particles are smaller than the wavelength of the ambient light, then Rayleigh scattering comes into effect making the glass remaining transparent. Rayleigh scattering, which is the elastic scattering of light or electromagnetic radiation by particles less small than the wavelength of the light, is the cause of the blue hue of the daytime and the reddening of the sun at sunset. Thus the opacity of the glass ceramics can be adjusted by controlling the size and concentration of the crystals, and this can be done precisely by controlling the heat treatment cycle. If the index of refraction of both the crystals and the glass medium are the same, then light will not reflect off the crystals, and the glass remains transparent no matter how dense the concentration of crystals, or how large they grow. Diffusion of light can take place only if the refractive indices of the crystals and the glass are substantially different. The greater the difference, the greater the reflection and refraction, and the more opaque the glass will appear.

Applications such as cookware, telescope mirror blanks, woodstove windows and infrared transmitting range tops are obtained from the combined effect of transparency, low thermal expansion, optical polishabilty and strength greater than that of the parent glass. The liquidus temperature is 1230 $^{o}$C corresponding approximately to $10^5$ poise. Crystallization is achieved commercially close to 800$^{o}$C roughly 100$^{o}$C below liquidus. The coefficient of thermal expansion is less than $10^{-7o}C^{-1}$ (0 – 500$^{o}$C). This confers on the product, exceptional thermal shock reesisitance.

This system yields opaque glass ceramics at what is considered, a relatively high temperature (1000 – 1200$^{o}$C) involving the development of the stable crystalline assemblage which as usual includes β-spodumene in solid solution of the main phase. The transformation from β-quartz to β-spodumene solid solution occurs between 900 and 1000$^{o}$C. This irreversible change is accompanied by grain size increase in the region of five to 10 fold.

**$MgO$-$Al_2O_3$-$SiO_2$ Cordierite Based Glass Ceramics:** This category of glass ceramic based on cordierite, also called indialite, has remarkable strength, excellent dielectric properties, high thermal stability and shock resistance. Its major area of application is missile radomes. They are nucleated by titatania with cordierite, the major crystalline phase mixed with cristabolite, rutile, magnesium dititanate and minor isolated glass grain boundary nodes. The coefficient of thermal expansion measured within the range of 0 to 700$^{o}$C is 45 X $10^{-7o}C^{-1}$. The fracture toughness is 2.2 MPa.$m^{1/2}$ and the thermal conductivity is 0.0038 J/s.cm.$^{o}$C. Knoop's hardness is 700 and the dielectric constant and loss at 6 Hz is 5.5 and 0.0003 respectively. It is usually difficult to relieve the stresses generated in the course of the densification that accompanies the phase transformation from glass to metastable crystalline assemblage, occurring at a temperature of about 1010$^{o}$C, followed in turn by volume expansion in the process of cordierite formation above

this temperature. The heat treatment schedule should therefore be carried out in such a way as to minimize extreme changes in density by allowing enough plasticity to avoid cracks and undue stresses.

The liquidus temperature is about 1350$^{o}$C, which is close to ternary eutectic of $MgO$-$Al_2O_3SiO_2$. The limited plasticity in turn restricts the forming process to spinning or casting. Fortunately, the radome shape conforms to centrifugal casting.

**Photosensitive Lithium Silicate Glass Ceramics:** As one of the earliest glass ceramic products to assume commercial significance, photosensitive glass ceramics are the result of homogenous nucleation of metal particles, catalyzed by photoelectrons produced by action of radiation in special compositions containing small amounts 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 metal nuclei grow to crystals of colloidal dimensions, which manifest as colour or an opaque appearance. A photograph can be developed on the dendritic form of crystalline lithium metasilicate, a far more stable phase than the parent glass. The selectively exposed potion of the metastable crystal, when etched out in HCl and heat treated to a region above the temperature of formation of the metastable phase, yields the stable lithium disilicate phase.

This chemically machined glass ceramic (marketed under the Corning code 8603) is strong, tough and faithfully replicates the original glass. The nucleation temperature for this glass ceramic is 510$^{o}$C and the heat treatment is carried out at 610$^{o}$C. The etched glass ceramic has to be exposed and reheated at 810$^{o}$C, above the metastable stage, for two hours for it to develop to the stable disilicate form.

**Glazed Nepheline Glass Ceramics:** The fine grained nepheline glass ceramics based on soda nepheline ($NaAlSiO_4$), are based on $SiO_2$-$Al_2O_3$-$Na_2O$-$TiO_2$ compositions. 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 property of the major crystalline phase, nepheline that is structurally related to the silica polymorph tridymite. Barium oxide is added to promote a secondary aluminosilicate phase called celsian ($BaAl_2SiO_8$) or barium feldspar. The resulting glass ceramic has an improved thermal shock resistance and a lower thermal expansion coefficient compared to nepheline. Barium oxide also promotes lower liquidus temperature thus allowing the glass to attain the viscosity suitable for forming at the forming stage of the pressed ware which serves as the major area of application of this glass ceramic type.

In order to meet the high surface finish demanded by quality tableware, a glaze that matures at temperatures at which the glass will not deform under its own weight is normally applied. The glaze initially used was a lead-lime-alkali-aluminosilicate but the use of the lead component is no longer in vogue due to an increasing concern for the environment. This glaze has a thermal expansion coefficient of 65 X $10^{-7o}C^{-1}$, some 30 points lower than that of the glass ceramic body (95 X $10^{-7o}C^{-1}$ (0 – 300$^oC$)). The expansion differential between the glass ceramic body and the glaze creates residual compressive stresses on the surface, thus increasing the flexural strength of the glazed body. The upper crystallization temperature of nepheline glass ceramics is 1100$^oC$. Marketed by Corning under the band name, “Pryocerams”, the major area of application is in the institutional segment (hotels and restaurants) where toughness and durability are of primary concern due to the high extravagance in terms of use.

**Machinable Fluormica Glass-Ceramic Materials:** Machinable glass-ceramics based on fluoromica nucleated crystal phases developed in the early 1970s by Corning Inc. in the USA, has been in the market for about two decades under the band name, “Macor”. Their machinability even by conventional metal tools arises from the randomly orientated fine-grained mica crystals with a "house of cards" microstructure allowing cracks to readily propagate between the flexural flakes but either arrests fractures or cause the deflection or branching of crack propagation across the layers. At that time of its introduction, CAD-CAM technology systems, though available, were too expensive to deploy in the machining process. Macor has a composition based on a magnesium-fluoro-alumino-silicate glass. Localized damages due to the dislodging of tiny polyhedra of glass are sometimes experienced.

Due to falling costs, CAD-CAM machining is an increasingly used technology. In addition to machinability, Macor is now a commercially important machinable ceramic and is used in many advanced applications like, electrical vacuum feedthroughs, microwave tube windows, sample holders for field ion microscopes, seismograph bobbins, gamma ray telescope frames, precision electrical insulators, in optoelectronics and in over 200 parts of space shuttles. Macor glass ceramics posses attractive properties such as high dielectric strength (40 kV/nm) and very low helium permeability which make them good materials for high vacuum applications.

Another brand of fluormica glass ceramics with improved chemical durability and high translucency, marketed as Dicor, is based on tetrasilicic mica ($KMg_{2.5}Si_4O_{10}F_2$) as opposed to Macor which is based on fluorine-phlogopite ($KMg_3AlSi_3O_{10}F_2$) phase. Dicor is transparent in the parent glass state but the translucency that occurs during the heat treatment stage is achieved by the rough matching of the indices of refraction of both the glass and the fine gained microstructure (approximately 1 μm). In dental applications, Cerium oxide is added to give Dicor

the semblance of the fluorescent character of natural teeth such that the appearances coupled with hardness makes the product useful for the restoration process.

**Glass ceramics based on Blast furnace Slag:** This glass ceramic, based on $Na_2O$-CaO-MgO-$Al_2O_3$-$SiO_2$ and called minelite, is characterized by high wear resistance and good chemical durability. The glass from this composition is melted at 1450$^oC$, cooled and subsequently heat treated to a temperature of about 1000$^oC$ to allow for the development of internal nuclei based on manganese sulphide. Diopside, the major crystalline phase develops on the sulphide site between 850 and 1000$^oC$. 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 claddings to serve the housing needs of low income earners. Although the composition is designed to allow crystallization at a particular stage, premature devitrification during shaping operations cannot be ruled out, calling for modification of composition to forestall such shortcomings.

### 2.4.0 GLASS AND GLASS-CERAMIC MATRIX COMPOSITES

Advanced composite materials with improved mechanical properties can be fabricated by reinforcing glass and glass-ceramic matrices with ceramic or metallic fibres. Although these composites were originally developed as model systems for laboratory-scale experiments, their remarkable thermo-mechanical properties have made them candidate for a variety of technical applications. Relatively limited manufacturing of engineering components and structures having complex geometry and large dimensions using glass ceramic composites has been carried out to date. The application of electrophoretic deposition techniques in order to manufacture

three-dimensional components, e.g. tubes, represents a considerable improvement in process development geared towards exploiting the high technological potential of these materials.

## 2.5 PROPERTIES OF GLASS-CERAMIC MATERIALS.

The characteristics of glass-ceramic materials depend on the properties of both the finely separated crystalline phase and the residual glass phase, the combination of which makes up the glass-ceramic material. The kind of crystalline phase and thus the final properties of the glass-ceramic material can be controlled by appropriate choice of glass composition and by its heat treatment. The crystals formed within the glass lend the finished body various characteristics such as greater thermal expansion and elasticity, which can be precisely controlled to suit the appropriate area of application.

Glass ceramics are nevertheless a form of glass by implication, when bonded directly to tooth structure, their chemical inertness helps to improve the strength of the restoration and prevention of tooth decay. The size and distribution of the crystalline substructure within the glass can be precisely controlled in such a way that an almost unlimited number of types of glass-ceramic material can be prepared with various combinations of properties, many of which are reflected in their numerous applications. The extremely fine grain structure is by and large responsible for its mechanical strength as a highly valuable property. The average size of the microstructure is for transparent glass ceramics is less than 50 nm and closer to 1 micron for opaque even though it is not uncommon to find size range between 20 and 30 micron. The fineness of the gain size will be better appreciated when contrasted with conventional ceramics of size range between 10 and 20 micron with some particles extending to 40 microns. The degree of fineness normally does not

permit the use of optical microscope in its examination and electron microscopy is normally required.

The random orientation of the crystals is a direct result of precipitation from a homogenous liquid which takes place in an atmosphere devoid of stresses that would have interfered with crystal alignment. By implication, the properties of glass ceramics are independent of the direction in which they are measured and where some of the crystals manifest different properties in different crystallographic directions (i.e. anisotropic behavior) they are averaged out over some characteristic volume.

The residual glass may differ in composition from the parent glass specifically as a result of incongruent crystallization. Although it is possible to achieve 100% impermeability in conventional ceramics, the total absence of porosity is unheard of. The lowest level of porosity is normally put between 5 and 10%. In feldspathic porcelain used as electrical insulators, the percentage of closed pores is estimated to be 10%. Glass ceramics are entirely free of all form of porosity on condition that the original glass is free from trapped gas bubbles. Porosity does not develop during the conversion to polycrystalline solid from glass because only a relatively small volume change is experienced in the process and where such a change occurs, it is not because of the creation of voids but rather as a creation of crystals of lower density. It should also be noted that the liquid nature of the residual glass does not allow for the formation of voids during crystallization.

The absence of pores helps to reduce internal surfaces that could serve as sources of crack yielding flaws. Its absence also serves the purpose of enhanced mechanical strength as the presence of pores increases the valuable cross-section of the material that contributes negatively

to the mechanical strength of the material. Where pores are present, they sometimes become advantageous in reducing electrical conductivity which is desirable in some applications. Generally, all glass ceramic properties stand out from those of conventional ceramics. In specific terms, the nature and proportion of the crystalline phases present are extremely important in determining the individual characteristic of the glass ceramic.

## 2.6 APPLICATIONS OF GLASS CERAMICS

### 2.6.1 Dental Applications

The production of glass-ceramic materials is a field of material technology that requires special manufacturing processes suited to their end use requirements. In the case of artificial teeth, the cores can be made strong and sometimes opaque while the veneer is translucent and aesthetic, yet they are made out of the same glass ceramic. This guarantees the best integration of the two components with the best combination of strength and esthetics for the finished crown. These internally grown crystals are much more attuned with the existing glass chemistry and their complete incorporation into the glass allows for much better translucency than the older aluminous core crowns.

### 2.6.2 As Bearings

Glass ceramics can be used as bearings, due to their ability to take on smooth surfaces coupled with high mechanical strength including good abrasion resistance. Glass ceramics can be polished to surface finishes of 1 – 2 micron-inches compared to the best conventional ceramics, (alumino-ceramic) with surface finishes of 8 – 9 micro-inches. These bearings are resistant to corrosive liquids such as sea water. Their high abrasion resistance implies less use of lubricants compared to metals where they are applied. This becomes a big advantage where constant

lubrication is made difficult due to inaccessibility and in turn leads to lower maintenance costs. Since glass ceramic bearings serve their best purpose where operating conditions are stringent, the forms of lubricant often used are liquids and gas films. The various types of bearings, that can be fashioned from glass ceramics includes ball, roller and joiner bearings often using techniques that permit metal shafts to be housed in glass ceramics.

### 2.6.3 Cookware

The largest application of glass ceramics is as domestic appliances, especially cookware. The chief requirement is good thermal shock resistance due to the temperature fluctuations encountered between intervals of heat application and removal. With thermal coefficient of less than 15 X $10^{-7o}C^{-1}$ coupled with high mechanical strength, glass ceramic forms the ideal material for this application. The mechanical strength of glass ceramics is higher that that of borosilicate heat resisting glass such that accidental breakages are minimized when used as substitutes for borosilicate glass.

Since mechanical strength does not depend on the surface compressive forces unlike tempered glass, catastrophic failures due to accidental overheating of ware are eliminated. The high abrasive resistance and extremely smooth surfaces renders it very hygienic and easily cleaned. It is superior to glazed ware as cracking or crazing are rare occurrences in glass ceramics. Crazing which occurs under prolonged use is virtually eliminated. One other advantage over conventional ceramics is that high speed production of ware can be carried out without having to go though the glazing process.

### 2.6.4 Heat exchangers

Since glass ceramics can be made to have high thermal and chemical durability, they offer great possibilities for use as heat exchangers in regenerators. The regenerator glass ceramic is first made into powdered glass frits before it is turned into a honey comb in order to maximize heat transfer from hot exhaust gasses to the incoming air required for combustion. They can be made to have zero or negative expansion coefficient and as such can survive temperature changes without failure.

### 2.6. 5 Neutron Absorbing Materials

Glass ceramics can be used as neutron absorbing media for reactor control rods. A number of standard materials, including boron containing steel rods, have been used with boron as the absorbing medium. The disadvantage of use of boron-containing materials is the limited proportion of boron that can be incorporated into the steel rod without a corresponding increase in the surface area and by increasing the surface area of the steel rods to accommodate more boron renders the rods too heavy and bulky to handle. On the other hand, if a glass ceramic substitute is used, a high concentration of boron as well as other oxides with high neutron capture cross-sections can incorporated into the parent glass with ease as part of the glass structure.

Glasses containing these materials are notably low in refractoriness but when converted to glass polycrystalline solids, they dramatically increase this attribute.

### 2.6.6 As Sealing and Bonding Medium or Thermosetting Elements

Prior to the application of glass ceramics as a joining medium, joints between glass or ceramic and metals or between two glass parts such as the face plate and cone of a cathode ray tube, were made by fusing the glass locally and then allowed to flow and seal the joints. The disadvantage of

this method is that the joints cannot withstand temperatures beyond the level tolerated by the sealing glass. There is also the risk of losing dimensional accuracy due to the softening of the glass. Even when a solder glass is used as the sealing medium, the problem of withstanding high temperature conditions still persists but when devitrified into glass ceramics, the possibility of the joints withstanding high temperature conditions increases tremendously.

### 2.6.7 Electrical Insulators

The high surface and volume resistivity of glass ceramics particularly alkali free varieties, makes them useful as electrical insulators, especially as high voltage carriers.

## 2.7 STAGES IN THE GLASS CERAMIC PROCESS

The glass ceramic process goes through a number of stages, namely,

1) The selection of raw materials
2) the melting of a homogenous glass
3) the forming process
4) the final stage which is the conversion into polycrystalline solid often called the ceramming process. The size of the crystals, as well at the number and rate of growth is determined by the time and temperature of the heat treatment.

### 2.7.1 Raw Material Selection and Processing

The key to the successes recorded in making available a suitable selection of glass ceramics was the introduction of elements not used previously as glass ingredients. The major advance was recorded especially in the course of the work by Stookey and his colleagues at Corning Glassworks in the United State (Macmillan, 1964). The raw materials used to introduce the oxides commonly introduce more than one type of oxide for each raw material. The restriction is that any

such raw material must retain those constituents required in the glass composition. Sometimes it may be desirable to retain non-oxides as well, especially the halides in the case of photosensitive glasses. The most prevalent of impurities not required in most glass compositions is iron, which gives the glass a greenish tinge and interferes with light transmission in the medium. The intended use of the glass determines the level of tolerance of such impurities, with optical glasses being the most demanding. The selection of composition should be so as to ensure a high rate of internal rather than surface nucleation and to prohibit deformation of the wares dung heat treatment. If the rate of growth of crystals is too high, strains developed in the uncrystallized glass cannot be relieved at a rate that will eliminate cracking. Again, materials in which the crystal growth rate is too high do not develop the kind of microstructure necessary for achieving high mechanical strength owing to the coarsening process that occurs at the late stage of the heat treatment.

**Quartz/Silica Sand**: Silica ($SiO_2$), comprising 12% of the earth's crust is one of the most widely available minerals second in abundance only to feldspar. Petrological forms of $SiO_2$ include quartz, tridymite, crystabolite and hydrous silica minerals. Quartz, which is by far the commonest variety occurring as a rock-forming mineral, has many industrial uses. High purity quartz ($SiO_2$ 99.5, $Cr_2O_3$ 0.008, $Fe_2O_3$ 0.0001) is the major raw material for the manufacture of high premium grade glass and chemical ware. The greatly increased cost involvement is justified by the enhanced properties of the final product. It occurs in almost all types of rocks (igneous, sedimentary and metamorphic) but most commercially exploitable deposits exist either as pure sedimentary sandstones or metamorphic quartzite. These deposit modifications are the direct result of the weathering and subsequent accumulation and solidification of quartz as a highly resistant mineral (7 on Moh's Scale). As seen from the typical analysis on Table 2.2 the composition the percentage content of $SiO_2$ is usually very high (approaching 100%). The analysis shows the presence of other

oxides ascribed to fluid inclusions within the quartz grains.

**Table 2.2. Chemical Analysis of Quartz Samples (wt.%)**

| | $Li_2O$ | $Na_2O$ | $K_2O$ | $Al_2O_3$ | $Fe_2O_3$ | $MnO_2$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|
| Colourless | 0.0005 | 0.0004 | 0.0002 | 0.0008 | 0.0000 | 0.00002 | 0.0001 |
| Smokey | 0.0004 | 0.0000 | 0.0000 | 0.0008 | 0.0005 | 0.00002 | 0.0002 |
| Rose | 0.0008 | 0.0011 | 0.0001 | 0.0001 | 0.0003 | 0.00005 | 0.0015 |
| Amethyst | - | - | - | 0.0004 | 0.0216 | 0.00000 | 0.0004 |

*Source:* Deer et al (1992)

In the course of weathering, quartz as a highly resistant mineral (7 on Moh's Scale) accumulates in sediments and in the solidification that ensues, transforms into such significant deposit modifications like quartzite and sandstones.

Glass sand is prepared as grains from any of these forms – sandy deposits, sandstones, quartzite and quartz pebbles or vein quartz. Although the prescribed granularity going by British Standard Specification (BS) is 0.1 to 0.6mm, Franče (1980) recommends a lower limit of 0.06 just as Simmingsköld (1997) recommends that components above 0.4 mm should not be more than 2% of the entire range while grains less than 0.2mm in diameter should be less than 1% of the range. In practice, individual manufacturers set their own granularity and purity specifications as part of their trade secrets. The same manufacturers usually control their sand mines and treatment plants and all deliveries are routinely analyzed to ensure compliance with set standards.

Scholes (1974) and Franče (1980) recommend various methods for processing quartz dependent on scale of production, beginning at the quarry site and terminating at the point of the batching

process. The general requirement is that the sand ought to be free of clay minerals and similar impurities. Organic matter should be sieved away and magnetic particles removed by the use of a magnetic separator after the drying of the sand. Most of the deposits in Nigeria are quantifiable in several millions of tons although records of estimates of individual deposits are still lacking (RMRDC, 2003).

### 2.7.2 Melting and Forming.

The melting process according to Gunther (1959), is the most difficult stage of the production chain in part because when once started cannot be reversed. Fortunately efficient devices already exist for dealing with this situation. The range of glass and batch compositions and conditions of melting have given rise to the variety of melting units found presently in the market. The second step is the shaping of the molten glass into the appropriate forms by casting, pressing, blowing, etc.

Process monitoring and control involving a strict regime of temperature and furnace atmosphere is adhered to while a melt is in progress to ensure melt-to-melt reproducibility of the desired physical conditions. Although Deeg (1986) asserts that it is still possible to effect batch corrections to alter some properties especially the refractive index if need be, during the production process. The composition and thermal history are the two usual variables manipulated to achieve that objective.

Glass-forming processes and equipment, depending on the form of supply required by the customer, 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, also used for preparing glass gobs. The presses are designed to suit the specific needs of the glass manufacturer. The strips can be

extruded or continuously cast in inclined channels. Pressings for small orders could be hand made from cut and tumbled blanks of a given volume. In some cases, experimental work is required to determine the compatibility of a new forming mechanism with individual glasses as well as already-installed melters and annealers. Mold materials include stainless steels and beryllium bronze or graphite-based materials.

### 2.7.3 Conversion into polycrystalline solid

There are two parts to the ceramming process: crystal nucleation and crystal growth. Each process happens because the glass body is held at a specific temperature for a specific length of time. The heat treatment itself is a two stage process. The preparation of a homogenous glass is typically made from any of the six glass composition already noted in (Table 2.1). The object of the heat treatment process is to produce a microcrystalline structure with properties that are superior to the original glass. The process is done in two phases. The first phase takes the form of either raising or lowering the glass temperature to the nucleation temperature where it is held for between one to two hours. This temperature according to Doyle (1979) corresponds to a viscosity of between $10^{11}$ and $10^{12}$ and as a rough guide it is given as Mg + 50 where Mg corresponds with the glass transition temperature (Tg) of the parent glass.

After allowing enough time for a large number of crystals to be created at the nucleation temperature the temperature, is then raised to the upper crystallization temperature for the nuclei to grow to a level that will promote the interlocking of resulting crystals.

**Crystal nucleation:** Crystals have a tendency to develop in a mixture of glass when it is held at a specific temperature called the crystal nucleation temperature. This means that when held at the crystal nucleation temperature, multiple seed crystals begin to grow throughout the glass body. The longer the glass is held at this temperature, the more seed crystals will form. Ideally, a

glass ceramic will be strongest when there are a very large number of small crystals distributed evenly throughout its mass. Once a seed crystal forms, it will also begin growing larger at this temperature, but quite slowly. If the temperature of the glass body is held at the crystal nucleation temperature for a very long time, a very large number of crystals of widely varying size will form. The earliest to nucleate will be the largest while the crystals that have recently just begun to grow will be the smallest.

**Crystal growth:** In order to better control the aesthetics of the finished product, the ideal glass ceramic will have crystals of a small, relatively uniform size. 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. Thus it is of benefit to hold the temperature at the point of maximum seeding for a finite length of time in order to allow numerous tiny seed crystals to nucleate, and then to stop the nucleation process and encourage the ones that have already formed to grow to suitable size. In some cases, the ideal temperature range for crystal seeding in glass bodies is different than the ideal temperature range for the crystal growth, so it is possible to control both phases separately and precisely. The temperature of the melt is brought to the nucleation temperature and held there for long enough to allow large numbers of seed crystals to form. Then the temperature is raised to the temperature where nucleation halts and growth of the existing crystals is accelerated. It is held there for the time required to grow the crystals to the ideal size, and then the temperature is lowered fairly rapidly to the annealing temperature (near Tg, the temperature where the glass is nearly hard, but the

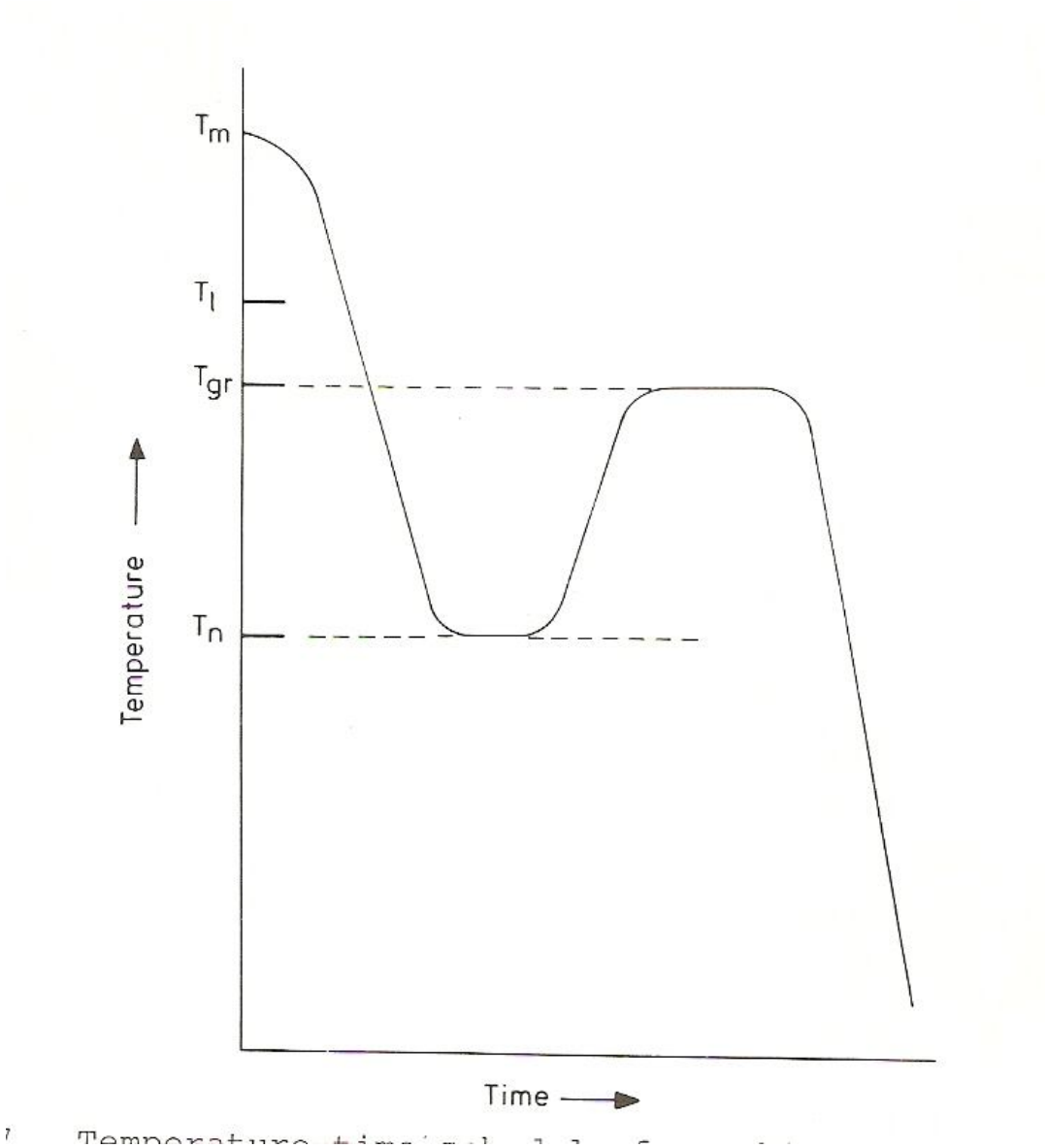



***Figure 2.8. Time temperature schedule in the heat treatment process.***

molecules in the residual glass are still mobile enough to move about in the matrix relieving stresses) and finally harden into the finished product. The two stage process is illustrated in commercial glass ceramic production is illustrated in Fig. 2.8.

## 2.8. ANNEALING

Temperature gradients resulting from different parts of a piece of glass cooling by different amounts lead to stresses in the glass. Such stresses, some temporary, others permanent and residual, develop in the course of manufacture of all glass products. Such stresses are the causes of unpredictable failure in service performance of the glass item and as such have to be eliminated through a systematic cooling process called annealing. Mass-produced items are annealed in continuous lehrs, which are usually tunnel-like air-circulating electric furnaces but in low output productions the same process is carried out in electric ovens designed for that purpose. Each case, especially as it relates to optical and glass ceramics, requires precise temperature control and strict adherence to pre-established annealing schedule. The schematic diagram in Figure 2.9 is illustrative of a typical annealing process.

The first step (Zone A) is to bring the glass to a uniform temperature from either a higher or lower temperature point, such that stresses already present can be released within minutes.

Time taken for the temperature equalization depends on the rate of heat transfer from the surrounding air in the furnace to the glass surface and the thermal conductivity of the glass. Once uniformity of temperature is attained, some additional time is allowed for stress decay

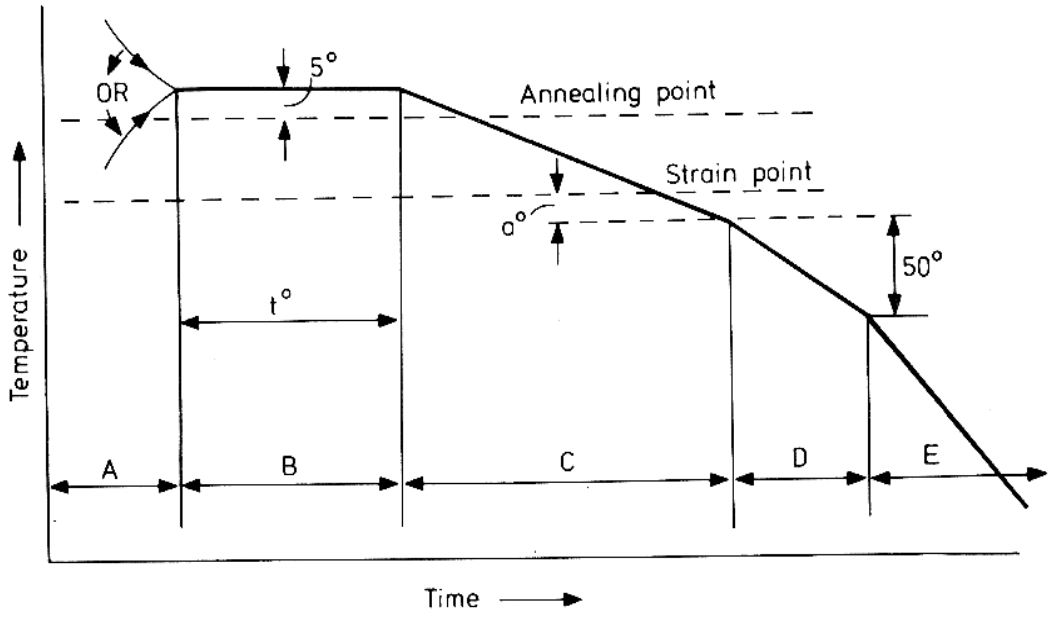



***Figure 2.9. Temperature – time schedule for annealing of commercial glassware.***

by viscous flow at a temperature usually $5^{o}$C above the annealing point temperature with the limit set by the ability of the glassware to withstand deformity under its own weight (Zone B). The glass is now cooled slowly at a rate that will not permit the reestablishment of temporary stresses except of course the permanent stresses manifested in the form of tensile stresses in the surface areas balanced by compressive stresses in the central layers (Zone C). As the cooling process continues, a temperature corresponding to the strain point on the viscosity scale is reached when the glass is effectively a solid ($10^{14.5}$ Poise). As the glass continues to cool, no stresses will be reintroduced, provided every part of the glass continues to lose heat at the same rate (Zone D). Once the glass has been cooled below the strain point (Zone E) the rate of cooling can then be increased to a level that will permit the attainment of room temperature within the shortest time possible (Zone E). Factors that influence the annealing process include the glass thickness and composition.

The Quality Assurance (QA) or visual inspection unit of the R & D department have precision laboratories equipped with optical and electron microscopes as part of an array of instruments used to provide rapid, reproducible and automated means of periodic characterization of raw materials and quantitative evaluation of quality of the final product. Precision annealing schedules have been developed not only for every glass but also for different-volume articles of the same glass. With annealing rates in the order of a few degrees per hour or less, and considering the low thermal diffusivity of glass, it is hardly surprising that massive pieces of optical glass are annealed for several months.

The optical method of stress analysis known as photoelasticity has been available for many years. This method has been used very effectively in the evaluation of the stresses occurring in structures of varying complexity, together with their components, when subjected to specified loading conditions. The photoelastic technique requires materials that are both transparent and birefringent. However glasses by their isotropic nature are not birefringent but could exhibit birefringent when under non-uniform mechanical loads. The photoelastic technique can be used to determine the stress level in glass. It is therefore necessary to quantify these stresses for proper process control to be exercised.

Very often production is a matter of routine and there is no reason to assume anything, other than the expected stress distribution, to be present in the glass products being manufactured. However some routine quantitative analysis of the stress level is carried out as part of the specifications from the customer. If, however, there are production problems leading to undesirable stress distributions, photoelasticity can readily be used to gather detailed information about the stresses produced. This obviously requires a more extensive analysis and a greater understanding of the

techniques available.

## 2.9 ESTABLISHED ROUTES FOR GLASS CERAMIC PRODUCTION

There are three identifiable routes for developing crystals in glass. The two usual routes, according to Zhang and Gao (2008), are controlled crystallization of bulk glass articles and sintering crystallization of glass powder compacts. The common ground shared by the two methods is that all the crystalline phases are precipitated from the parent glass but the difference however lies in their crystallization mechanism which for the former is by volume crystallization and the latter by surface crystallization.

The third method described by the same workers, simple and cost effective, takes the form of sintering a mixture of glass and crystalline powders at elevated temperatures. The route has "the most important advantage of direct introduction of having the crystalline phase in the glass ceramics introduced either directly or by reaction at the glass crystal interface. This route has no limitations as to type of glass or crystalline material used in the mixture since it does not require any form of direct precipitation in the melt. The only condition is that the desired crystalline phase should not be dissolved in the matrix glass. The same procedure was adopted in the present experiment as a response to the research questions posited in this study.

In the case under reference, fluoramphibole glass–ceramics, usually fabricated by controlled crystallization of bulk fluosilicate glass, was replaced by fluormica. Under normal conditions, fluoramphibole is first precipitated from the parent glass after the nucleating treatment, and then allowed to react with the glassy matrix to form fluoramphibole during the crystallizing process. However, Zhang and Gao (2008) produced fluoramphibole glass ceramics by the simple

and cost effective process of direct reaction between fluormica and soda-lime glass powders obtained from recycled window glass. As acknowledged by the authors, there are few reports concerning this novel route in the literature, implying that the method is still at the experimental stage. Their results further showed that the complete densification temperature for specimens was as low as 900°C and that sufficient crystallization was achieved by subsequently raising the firing temperature to 950°C.

In an earlier experiment reported by Cheon-Young et al (2002) a low-temperature (900°C) densifiable anorthite glass-ceramic without either lead or alkali oxide was successfully fabricated by reducing the particle size of glass powders to the submicrometer scale. In the said work, attention was focused on the effects of the nucleating agent ($TiO_2$) and the sintering aid ($B_2O_3$) on microwave dielectric characteristics. The influence of crystallinity on the permittivity and dielectric quality factor were also investigated. In addition, the crystallization process was controlled by modifying the firing temperature to evaluate the relationship between crystallinity and microwave dielectric prop.

The purpose of the present work is to demonstrate the new preparation method for its energy efficiency and consequent cost effectiveness. The series of procedures and outcome of the experiment within the limits of this study are presented under Methodology and the ensuing analysis of the results.

**2.10 GLASS SAND DEPOSITS IN NIGERIA**

There are very few reported sources of glass sand deposits in Nigeria, possibly because of the short history of glass manufacture in the country (RMRDC, 2003). Glass production began in Nigeria only in 1962 with the establishment of the West African Glass Industry (WAGI) in Port

Harcourt. The works so far carried out only serves the purpose of the utility glasses to the exclusion of the glass ceramic industry. Table 2.3 is a presentation of a relatively recent survey of glass

***Table 2.3: Glass Sand Deposits in Nigeria***

| Deposit | Coarse Fraction | Ideal Fraction | Fine Fraction | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO |
|---|---|---|---|---|---|---|---|---|
| Igbokoda | 29 | 65 | 6 | 99.97 | 0.09 | 0.06 | 0.01 | 0.01 |
| Badagri | 32 | 63 | 5 | 99.8 | 0.09 | 0.04 | 0.15 | 0.03 |
| Makun Omi | 18 | 80 | 2 | 99.3 | 0.40 | 0.06 | 0.00 | 0.01 |
| Ughelli | 18 | 97 | 3 | 98.1 | 1.40 | 0.09 | 0.28 | 0.10 |
| Agbarho | 15 | 81 | 4 | 96.7 | 1.70 | 0.22 | 0.12 | 0.22 |
| Amadi Creek | 23 | 76 | 1 | 98.1 | 1.30 | 0.30 | 0.35 | 0.11 |
| Calabar River | 50 | 50 | - | 97.1 | 2.00 | 0.20 | 0.40 | 0.15 |

*Source: RMRDC (2003)*

sand deposits in Nigeria. Two of the listed deposits (Igbokoda and Badagri) appear fit for optical use but the inhibiting factor remains the high content of $Fe_2O_3$. The Igbokoda deposit already serves its purpose as a raw material source for Oluwa Sheet Glass Company (RMRDC, 2003). This calls for more exploratory works on sources of high grade sand for use in local optical glass manufacture.

The Zangon Daji deposit is a segment of the Lokoja geological formation which is perhaps, one of the most studied of the Nigerian portion of the Pan African pegmatites on account of its high mineralization (RMRDC, 2003; Ali and Ogedengbe, 2005). The pegmatites form straight or curved ridges with comparatively poorly exposed gneiss such that quantifying the underlying rock is made relatively difficult. Although a number of Ceramic industries including the Royal Ceramic Industries Suleija, have found the deposit of value in glaze formulation, no available chemical data exists to show their suitability for use for higher grade glass manufacture.

# Chapter 3

# 3 METHODOLOGY

## 3.1 THE SILICA SOURCE

Based on information obtained from published monographs of the Raw Materials Research and Development Council reinforced by data obtained from the Nigerian Mining Corporation, the statutory bodies responsible for mining activities in documentation and practical involvement respectively, the Zangon Daji Quartzite was used as the silica source. There is no data available with regards to its chemical composition. It therefore became imperative to first find out the chemical composition to ascertain its usefulness for glass production.

## 3.2 FIELD SAMPLING.

Since sampling, according to Potts (1992), is not an exact science the formats of Scholes (1974) and Fraňce (1980) had to be adopted in a selective sampling procedure that involved first chipping off a boulder weighing about 1 kg and then crushing to fist sizes before subjecting a sub sample to chemical analysis.

## 3.3 CHEMICAL ANALYSIS

The chemical analysis conducted at the Geochemical Laboratories, Earth & Planetary Sciences, McGill University Montreal, Canada used the X-Ray Fluorescence Analytical Procedure to determine the elemental content of the silica source. The procedure is as contained in Appendix I

## 3.4 RAW MATERIAL PROCESSING AND PARTICLE CHARACTERIZATION

The pebbles now reduced to fist sizes were calcined for 7 hours in an electric furnace at a temperature of 500$^{o}$C following the Franče (1980) prescription. They were next reduced to the required particle size (between 0.6 and 0.06mm) (BS 2975) by ball milling. The grains were washed to remove discrete particles of iron, organic materials and other adhering fine particles. The sand was dried for final screening by magnetic separation and stored in a covered specimen bottle. The ground sample was leached in $H_2SO_4$ acid to get rid of $Fe_2O_3$. The leaching acid was then neutralized by $Ca(OH)_2$ and the sample washed again with water to remove all traces of acid. It was then washed manually five times by attrition with distilled water.

Under the standard specification, glass sands as the major raw material are put in three categories on the basis of contents of $SiO_2$ and the deleterious oxides. For sand meant for the highest grade glasses (optical category), grade A, the silica content should not be less than 99.5% while the tolerant level of the following impurities, $Fe_2O_3$, $TiO_2$ and $Cr_2O_3$ are limited to 80, 300, and 2ppm respectively (Doyle, 1994). Sand used in glass manufacture consists essentially of quartz grains restricted to a given size range. Under the British Standard Specification (BS 2975) the particle size requirement is such that 80% should fall between 420 microns (36 BS mesh) and 150 microns (16 BS mesh). There should be no grain coarser than 1000 microns (16 BS mesh) and those coarser than 600 microns (25 BS mesh) should not be more than 2%. In the smaller particle range, not more than 5% should be finer than 125 microns (120 BS mesh)

The melting process is dependent upon the physical properties of the sand grains in terms of size and size distribution. The particle size defines the time and temperature required to attain melting. A direct relationship also exists between particle size and the pores existing in the batch. Large

particles tend to pack inefficiently, leading to large pore sizes. These pores are found to remain during sintering, thus leading to inhomogeneous conditions. Packing can be improved by reducing the particle size and the presence of large agglomerates must be avoided, as agglomerated grains tend to create stones in the final product.

## 3.5 CHOICE OF GLASS COMPOSITION

The five batches *(Fig. 3.1)* isolated, all flint, for testmelting range from glass numbers 24 to 28 they were each put in a ceramic crucible and fired for six hours at a temperature of 1200$^{o}$C at the Industrial Development Centre, Zaria. The purpose was to determine the sample with the highest shrinkage value as candidate for use for the production of the glass ceramic.

Glass number 28 was selected as the base composition among a set of five ophthalmic compositions on the basis recording the highest sintering value as signified by volume change in the selection process. The chemical composition was $SiO_2$ 34%, PbO 18%, BaO 14%, CaO 6%, $Na_2O$ 8% and $As_2O_3$ 10%. The crystalline phase was introduced by Zangon Daji quartzite, which also doubled as the silica source with the following composition $SiO_2$ 71.91%, $Al_2O_3$ 15.27% MgO 39%, CaO 1.34%, $Na_2O$ 4.81%, $K_2O$ 4.24%. The oxides were introduced as analytical grades in their stiochiometric equivalence.

***Table 3.1: Some Ophthalmic Glass Compositions***

| Glass Numbers | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Ophthalmic Crown | | | | | | Ophthalmic Flint | | | | |
| | **19** | **20** | **21** | **22** | **23** | **24** | **25** | **26** | **27** | **28** |
| $P_2O_5$ | | | | | 20 | | | | | |
| $SiO_2$ | 67 | 68 | 70 | 56 | 21 | 47 | 48 | 45 | 39 | 34 |
| $TiO_2$ | *t* | *t* | 1 | | *t* | 3 | 4 | 1 | 4 | 7 |
| $ZrO_2$ | | | | 2 | 2 | 2 | | 1 | 6 | 5 |
| $B_2O_3$ | | | | 16 | 12 | 5 | 4 | | 2 | 6 |
| $A1_2O_3$ | 2 | 2 | | 9 | 22 | 1 | | 1 | | |
| MgO | *t* | | | | *t* | | | | | |
| CaO | 9 | 9 | 6 | | 3 | 4 | 6 | | 6 | 8 |
| SrO | | | | | | | *t* | | | *t* |
| BaO | | | | 7 | 9 | 22 | 13 | | 19 | 14 |
| ZnO | 2 | 3 | 5 | | | 2 | | | | |
| PbO | | | | 6 | | | 14 | 40 | 16 | 18 |
| $Li_2O$ | | | | 3 | *t* | | | | | |
| $Na_2O$ | 7 | 8 | 9 | 2 | 2 | 6 | 7 | 3 | 6 | 8 |
| $K_2O$ | 11 | 9 | 8 | | 7 | 7 | 2 | 8 | 1 | *t* |

*Source: Deeg (1986).*

## 3.6 BATCHING AND MELTING

The ingredients constituting the batch were weighed in plastic containers and blended in a mortar into a homogenous mix of 400 g total weight and melted at 1280$^{o}$C. The batch was divided into two equal parts, one part for development into the base glass and the other kept as stock for introduction of the crystalline phase. The first part was then put into the furnace and heated to a temperature of 1280$^{o}$C at the rate of 2$^{o}$ per minute and the soaking time was one hour. The temperature limit was defined by the operating condition and the other parameters by convention. The resulting partial glass melt was cooled overnight, crushed, ball milled and sieved to yield a

powder <100μm (130 mesh) <150μm (100 mesh) for use as the base glass. The second batch was then blended with the powder glass and the mixture sintered for 2 hours at 1100$^{o}$C to obtain the glass ceramics.

## 3.7 PRODUCT CHARACTERIZATION

The percentage porosity, percentage water absorption, bulk density and specific gravity of the sample were determined using the Archimedes method (ASTM C-373) at the Soil Science Department, Faculty of Agriculture Ahmadu Bello University, Zaria and obtained from the average value of three specimens. The procedure is as contained in Appendix II

The crystalline phases were identified at the Centre for Energy Research and Technology, Obafemi Awolowo University Ile-Ife via X-ray diffraction analysis with CuKα radiation generated at 40 kV and 30 mA, in $10^{o}<2\theta<75^{o}$ range at scan speed of $2^{o}$ 2 θ /minute.

The optical microscopy of the crystal structure in the absence of a scanning electron microscopy was carried out at the Geology Department, Ahmadu Bello University, Zaria. The flowchart of the entire processes under Methodology is presented in Figure 3.1

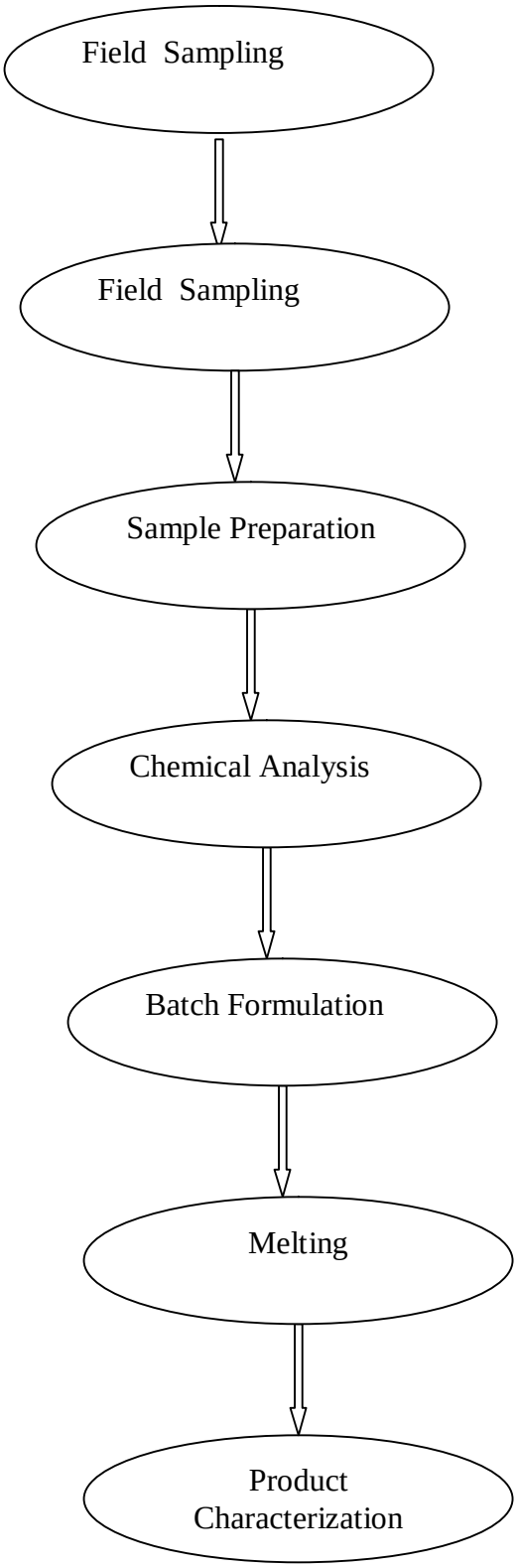



*Figure 3.1: The Process chart*

## Chapter 4

# 4.0 RESULTS AND ANALYSIS

## 4.1 CHEMICAL ANALYSIS

Tables 4.1 (a and b) show the contents in percentage of oxides, which must follow a specified standard against the actual contents as revealed by the chemical analysis. The figures determine the extent of beneficiation the material must be subjected to bring it to acceptable standard. The results are expressed as weight percent for the major elements and the trace elements (Ba to Zn) as mg/kg. The total iron present has been recalculated as $Fe_2O_3$

***Table 4.1 (a): Chemical Analysis of Major Elements expressed as oxide percent***

| **Sample** | **$SiO_2$** | **$TiO_2$** | **$Al_2O_3$** | **$Fe_2O_3$** | **MnO** | **MgO** | **CaO** | **$Na_2O$** | **$K_2O$** | **$P_2O_5$** |
|---|---|---|---|---|---|---|---|---|---|---|
| ED-1 | 71.91 | 0.156 | 15.27 | 1.02 | 0.038 | 0.39 | 1.34 | 4.81 | 4.24 | 0.053 |
| Detection Limits(mg/kg): | 60 | 35 | 120 | 30 | 30 | 95 | 15 | 75 | 25 | 35 |

.

***Table 4.1 (b): Chemical Analysis of Trace Elements in mg/kg***

| **Sample** | **Ba** | **Ce** | **Co** | **Cr** | **Cu** | **Ni** | **V** | **Zn** | **LOI** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|
| **ED-1** | **1525** | **56** | **94** | **24** | **3** | **12** | **14** | **<d/l** | **0.45** | **99.85** |
| **Detection Limits(mg/kg):** | **17** | **15** | **10** | **15** | **2** | **3** | **10** | **2** | **100** | |

In cases where most of the iron was originally in the ferrous state (usually the case with unaltered rocks) a higher total is the result. Analyses were done on fused beads prepared from ignited samples. The detection limits are based on three times the background sigma values.

## 4.2 CHOICE OF GLASS COMPOSITION

The basis for glass number 28 having the lowest shrinkage value. The shrinkage is a stage that precedes melting so if a composition attains shrinkage before others it can as well be used as an index of lower melting composition. At 45% $SiO_2$ content (the lowest among the five candidates) the corresponding influence on the glass structure is a reduced melting temperature given that the higher the silica content, the higher the melting point. The complementary role played by $B_2O_3$ as a low melting glass former increases the range of glass formation of $SiO_2$ which under normal conditions loses its glass forming ability at less than 50% content (Rawson, 1980). PbO and BaO play interchangeable roles in the glass structure in promoting low viscous melts at relatively low temperatures and their combined content at 32% is in line with experimental observations that the glass would have the lowest melting temperature.

## 4.3 BATCHING AND MELTING

The product of the melting process was in an opaque hard crystalline material, which proved in subsequent tests to be glass ceramic. The object also showed a glossy outlook in addition to the colour manifestation as a further indication of its true nature as a glass ceramic.

## 4.4. PRODUCT CHARACTERIZATION

### 4.4.1 Water absorption, porosity and specific gravity

Table 4.1 is the display of the results of the percentage water absorption, porosity and specific gravity tests. Evaluation of these properties has a direct bearing with the ultimate characteristics of the glass-ceramic product. Although the anticipated result is 100% impermeability (0% water absorption), the measurement recorded 0.176 % for this product.

**Table 4.1. Some evaluated properties of the product**

| **Property** | **Determined Value** | | | | | |
|---|---|---|---|---|---|---|
| | Formula | Specimen 1 | Specimen 2 | Specimen 3 | Mean Value | Standard Value |
| Suspended mass (S) g | measured | 3.346 | 4.121 | 6.125 | 4.531 | NA |
| Saturated mass (M) g | measured | 8.976 | 13.395 | 17.421 | 13.264 | NA |
| Dry mass (D) g | measured | 8.960 | 13.371 | 17.390 | 13.241 | NA |
| Exterior volume (V) cm^3 | M-S | 5.630 | 9.274 | 11.296 | 8.723 | NA |
| Open pores (Vop) cm^3 | M-D | 0.016 | 0.024 | 0.031 | 0.023 | 0.000 |
| Closed pores (Vip) cm^3 | D-S | 5.614 | 9.251 | 11.265 | 8.710 | 0.000 |
| Apparent porosity (P) % | [(M-D) /V]×100 | 0.277 | 0.255 | 0.270 | 0.267 | 0.000 |
| Water absorption (A) % | [(M-D)/D]×100 | 0.174 | 0.177 | 0.175 | 0.176 | 0.000 |
| App sp. gravity (T) gcm^3 | D/(D-S) | 1.596 | 1.445 | 1.544 | 1.528 | 1.500 |
| Bulk density (B) gcm^3 | D/V | 1.591 | 1.442 | 1.539 | 1.516 | 1.500 |

The recorded apparent porosity for the product of this experiment is 0.267%. Although it is possible to attain 0% porosity for maximum dielectric gain provided that a densification process is carried out on the specimen prior to sintering, that first step was not achievable under the condition. However the porosity level of the product is quite low when placed on the same scale with conventional ceramics where the lowest level of porosity is normally put between 5 and 10%. In feldspathic porcelain used as electrical insulators, the percentage of closed pores is estimated to be 10%. It should be noted that the presence of pores in glass-ceramics would induce a larger loss mechanical and thus degrade the dielectric properties.

Glass ceramics should be entirely free of all forms of porosity provided that the original glass is free from trapped gas bubbles. Porosity does not develop during the conversion to polycrystalline solid from glass because only a relatively small volume change occurs during crystallization.

This product with a density of about 1.53 $gcm^{-3}$ compared to the average density of glass (density, 2.41 $gcm^{-3}$) and sintered alumina (density, 2.78 $gcm^{-3}$) can be considered a light weight material and in applications where density is the critical requirement, the ceramic glass premix could be compacted prior to sintering.

### 4.4.2 X-Ray Analysis and Optical Microscopy

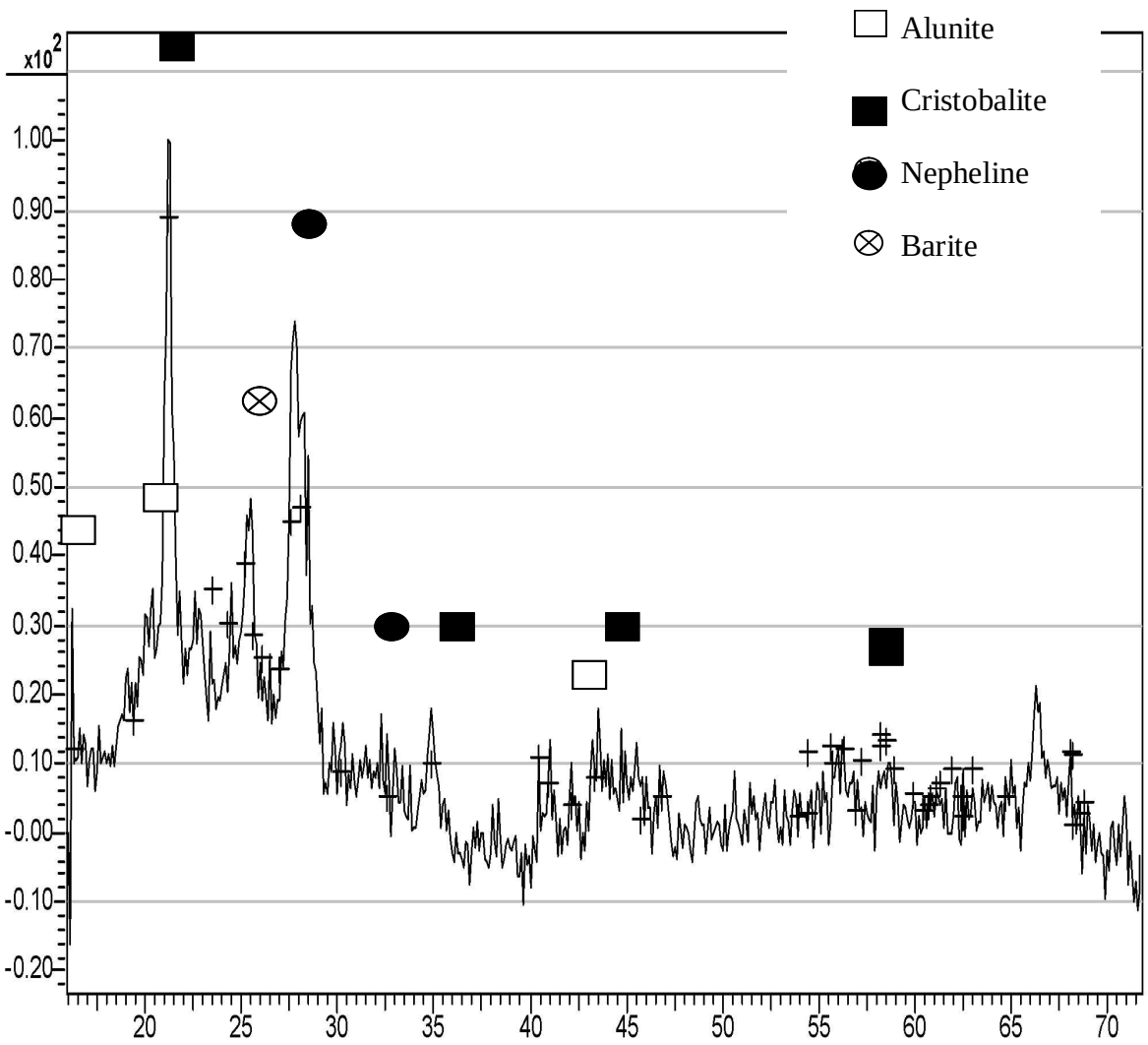
XRD results (Fig. 4.1) shows a preponderance of crystalline varieties in agreement with previous works by Cheon-Young Park, Soon-Do Yoon and Yeon-Hum Yun (2002), asserting that glass ceramics comprises almost always a multiplicity of crystalline phases embedded in a glassy matrix. The most significant mineral identified using peak intensity as a measure of fractional volume is high cristobalite (hexagonal) at $2\theta$ = 21.41, 41.61 and 43.72 in order of decreasing intensity. The next major mineral forming the major crystalline phase is nepheline at $2\theta$= 27.27,

21.20 and 34.91 in the same order of peak intensity.

It is possible that the use of a ceramic crucible instead of a platinum crucible may have contributed to the multiplicity of mineral phase in the product, many of which are difficult to identify. The extraneous materials that likely contributed to increasing the variety of crystalline phases in the glass matrix came about as a result of interface reactions between thee container and the contents. The use of a platinum crucible which would have given the experiment some level of control over extraneous matter which ordinarily should not be found within the system as part of the expected mineral assemblage. However the lack of a platinum crucible falls within the limitation of this experiment.

The relative peak intensity as a function of heat treatment in XRD patterns can be used to evaluate the degree of crystallization. It also reveals that the peak intensity increases with temperature, indicating the enhancement of crystallinity. See Appendix III for the data obtained from the XRD analysis.

Each of the three dominant crystalline phases occupy a fraction of the total volume, and the volume fractions of the amorphous, and crystallized phases are identifiable in a micrograph as two distinct categories vis-à-vis glass and ceramic (Plate I A - D). The low magnification of the optical microscopy relative to scanning microscopy makes the interpretation a tedious procedure often requiring the services of trained personnel to interpret the morphological properties of the crystalline phase. Such professionals can identify the various crystalline phases present as well as their sizes and approximate abundance. Nevertheless the polyhedral shapes of the crystalline phase against the amorphous background can be easily recognized in the micrographs.


Alunite
Cristobalite
Nepheline
Barite
x10^2
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
-0.00
-0.10
-0.20
20
25
30
35
40
45
50
55
60
65
70

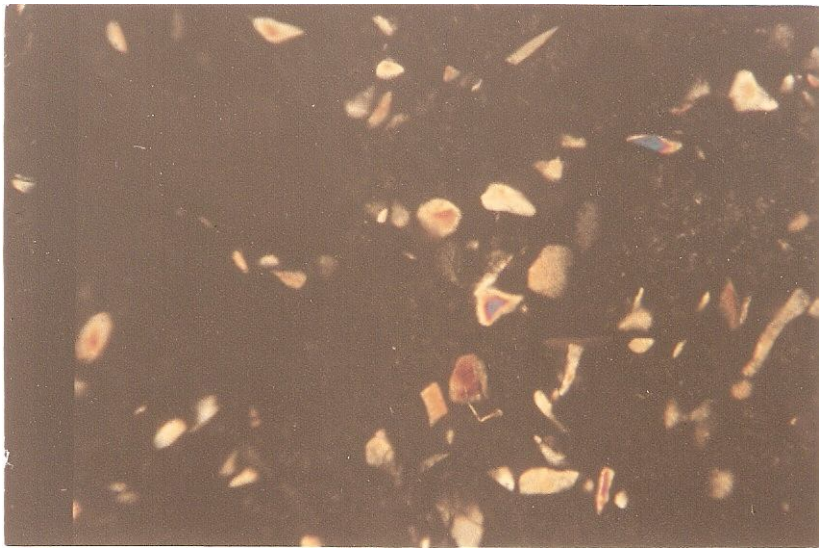


***Plate I Optical Micrograph of the Sample in XPL Section A***

***Plate I Optical Micrograph of the Sample in XPL, Section B***

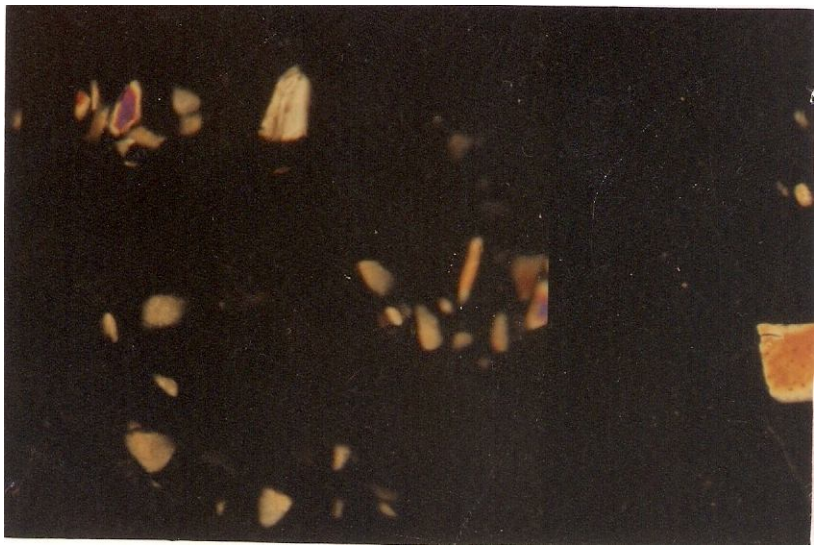


***Plate I Optical Micrograph of the Sample in XPL, Section C,***

***Plate I Optical Micrograph of the Sample in XPL, Section D,***

## 4.5 COST ANALYSIS

The breakdown of the project cost, which like any prototype development is still at the incubation stage, is as follows:

1. Data gathering involving two several visits to the Raw Materials Research and Development Council Head office Abuja and one trip to the Jos Head office of Nigerian Mining Company - - - - - -N15,000
2. Field Sampling (Three visits to the site) at Zangon Daji including fuelling and Care of Geologist and field staff of Nigerian Mining Company - 106,000
3. Purchase of Chemicals and reagents - - - - - - 75,000
4. Processing of raw material and chemicals - - - - - 36,000
5. Product Characterization including a visit to OAU Ile-Ife - - - 102,300
6. Total - - - - - - - - - -N336,300

# Chapter 5

# 5 SUMMARY, CONCLUSION AND RECOMMENDATION

## 5.1.0 SUMMARY

This project demonstrated that a glass-ceramic could be produced at a temperature of less than 1000°C via a novel route that involves a sintering crystallization of a composite of a solid crystalline phase and an amorphous phase. The outcome is a tremendous saving in cost of energy. This method, which has no regard to the composition of the starting materials, has a promising future especially with regards to glass waste reuse with the attendant advantage of promotion of a safe environment.

The preference given to ophthalmic glass composition as the composition of choice notwithstanding the fact that any other composition would have been adequate as a starting material was to maintain the experimental conditions within the operating environment at a maximum temperature of 1200$^{o}$C. The presence of crystalline phases was confirmed by XRD and the amorphous phase was shown by optical microscopy. The coexistence of both crystalline and amorphous phases as seen in the micrograph confirms the material's identity as that of a glass ceramic.

## 5.2 CONCLUSION

Notwithstanding the fact that success was recorded in fabricating a low temperature glass ceramic product as witnessed in this experiment, any hope of an immediate market launch of the product by way of patenting is too ambitious for two reasons. In the first place reliability which is the most fundamental concern encountered in any application of materials property data would require some tests for validity. What constitutes reliable data, however, depends on the purpose

of the data set and how it will be used. To establish a degree of reliability in the context of "purpose" and "use" requires both quantitative and non-quantitative criteria. Details of material composition, chemical phase, microstructure, and methodology, in particular, all play critical roles in assessing reliability. Consequently, the American based National Institute of Standards and Technology (NIST) recommends the use of a data quality indicator called the "data evaluation level" as a protocol for determining its value.

In essence, a data evaluation level summarizes the status of the evaluation process that has been applied to the set of data at the base of which are two counterbalancing mandates: (1) ensure the reliability of the data; and (2) do not reject data without cause (Munro, 2003). In the NIST protocol, there are seven classes of accepted data listed as follows:

(a) Certified data are standard reference values, usually established by recognized national standards laboratories

(b) Validated data values confirmed or supported by means of correlations and model calculations.

(c) Qualified data, the broadest category of data which must satisfy at least the minimum acceptance criteria. Such data are generally compatible with other related values in the database

(d) Commercial data is the manufacturer's data

(e) Typical data usually values or ranges of values derived from surveys or broad reviews

(f) Research indicates the preliminary values obtained from work in progress.

(g) Unevaluated are all other accepted data commonly, the measurement method is unknown or described insufficiently but, useful supplementary data.

These set criteria explain why the design of a glass composition of technological significance follows an arduous routine with a gestation period stretching several years (Rawson, 1980). In the same vain, this research effort as successful as it is marks the beginning of a new effort geared towards transforming the product of this experiment into a material of technological significance.

## 5.3 RECOMMENDATIONS

In the light of the conclusion arrived reached at the end of this research, the following recommendation are made with regards to the direction of efforts to enable the product of the experiment assume technological significance.

(a) The characterization should be expanded to include such properties as the dialectic and mechanical strength of the material under study. Such properties which could not be determined under the limitations of this research are vital for determining the area of product application.

(b) Studies should be carried out determine chemical parameters like level of volatility of constituent materials as well as effect of variation of composition on the general properties of the material for ease of product reproducibility and improvement of its vital properties.

(c) Government through agencies like the Engineering Materials Institute and RMRDC should pick interest in the development of this material in view its potential as a material that is capable of bringing in high return on investment.

**REFERENCES**


Ali E. A. and Ogedenge J. (2004), Chemical Analysis of Okehe Quartzite and the Determination of its Suitability for Glassmaking Journal of Science Lab Tech. Vol. 1 pp. 34 – 39

Brill, Thomas (1980) Light, it's Interaction with Art and Antiquity, Plenum Press, New York.

Chung-Lun L et al (2002) Low-Temperature Sintering and Microwave Dielectric Properties of Anorthite-Based Glass-Ceramics *J. Am. Ceram. Soc., 85 [9] 2230 –35*

Clark-Monks, C. and Parker, J. M. (1980) Stones and Cord in Glass Society of Glass Technology, Sheffield England.

Deeg, E. W. (1986). Advances in Ceramics: Optical and Glass Ceramics, American Ceramic Society, Vol. 18.

Deer, W. A., Howie R. A. and Zussman J. (1992), An Introduction to Rock Forming Minerals. Longmans Scientific and Technical Publications, Essex, England.

Dinger D. R. (2005), Characterization Techniques for Ceramists, Morris Publishing, Kearney, USA.

Doremus, Robert H. (1973), Glass Science, John Wiley and Sons, New York

Doyle, P. J. (1979), Glassmaking Today Portcullis Press Ltd (Copyright Holders), R.A.N. Publishers Marietta, India

Encyclopedia Britannica (2003), Deluxe Edition, CD – ROM.

Encyclopedia Britannica Vol. 13, pg. 947-952: Vol. 15, pg.386-38 William Benton, Publisher, London, 1968.

Fraňce J. (1980), Silica Raw Materials for Refractories, Ceramics, Glass and Building Materials.

UNIDO-Czechoslovakia Joint Programme for International Development, Prague.

Hans-Georg Kapitaz (1996), Digital Innovation in Microscopy. Zeiss Information with Jena Vol. 5 No. 7, pg. 4 – 7 Jena

Hoover, M. E. (1963), The Location of Economics Activity. McGraw–Hill, New York

Isa H., Ali E. A. and Abede A. A. (2001) High Refractive Index Production from Local Raw Materials, *Journal of Chemical Society of Nigeria,* Vol. 26 pg. 36 - 39

Jekada, Julius Z. (1997), The Exploration of Madakiya Quartz and the Determination of its Suitability for optical Glass Production. Unpublished B.Sc. Thesis, Ahmadu Bello University, Zaria

Mahmoud K. H (2008) Optical Study of Lithium–Bismuth–Borate Glasses *Int. J. Appl. Ceram. Technol., 1 – 7,* American Ceramic Society, Westerville Ohio

Malgwi, Yamta (1989) The Exploration of Gworza Quartz and the Determination of its Suitability for Optical Glass Production Unpublished B.Sc. Thesis Ahmadu Bello University, Zaria

Munro R. G. (2003), Data Evaluation Theory and Practice for Materials Properties, NIST SP 960-11, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Parsons, C.J. (1973), Thesis and Project Work – A Guide to Research and Writing. George Allen and Unwin Ltd, London.

Pincus Alexus and Davies David (1983), Raw Materials in the Glass Industry, Ashley Publishing New York. Part I pp. 15 1- 254

Potts, P. J. (1992), A Handbook of Silicate Rock Analysis. Blackie & Sons, London.

Rao, K. J. Currents Trend in glass Research *Current Science*, September 20, 1981 Vol. II No. 18 Pg 789 – 794. Delhi

Rauscher M. and Roosen A (2007). Influence of Low-Temperature Co-Fired Ceramics Green Tape Characteristics on Shrinkage Behavior *Int. J. of Appl. Ceram. Technol., 4 [5] 387 – 397* American Ceramic Society, Westerville Ohio

Rawson, H. (1986). Properties and Applications of Glass, Elsevier Scientific Publishing Company, Amsterdam.

Scholes, Samuel R. (1974), Modern Glass Practice, Sterling Publishing, New York

RMRDC (1997), Raw Material Sourcing for Manufacturing in Nigeria. Mufadenic Press, Lagos

Simmingsköld, Bo (1997), Raw Materials for Glass Melting. Society of Glass Technology, Sheffield England.

Sydenham, P.H. (1983). Practical Fundamentals in: Handbook of Measurement Science Vol. 2, John Wiley and Sons, New York

Watson, Janet (1979). Introducing Geology Series No. 4: Rocks and Mineral George Allen and Unwin, London

150 Years of Innovation in Optics, Innovation: Zeiss Information and Jena Review, Vol. 1, 1996

***www. Umr.edu/-brow/PPF-Glassmaking.pdf***

***www. Vision 2020. Optical Glass. Ophthalmic Glass. Fiber Optics: Executive Summary***

***(www.bccresearch.com)*** *RGB-094N Advanced Glasses and Glass* ***Ceramics: Materials, Processing, New Developments,***

***http://www.eia.doe.gov/emeu/mecs/iab98/glass/expenditures.html***

Riley Dohn (2000) Infinite Energy Magazine Issue #34 November-December, pasted on ***www.infinite-energy.com/iemagazine/issue34/comingenergycrisis.htm***