

**DEVELOPMENT AND EVALUATION OF THE  
OPTICAL PROPERTIES OF OPTICAL GLASS  
PRODUCED FROM OTAMIRI SILICA SAND**

**BY**

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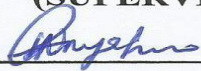
# CERTIFICATION

This is to certify that this work titled “**Development and Evaluation of Optical Properties of Optical Glass produced from Otamiri Silica Sand**” was carried out by **VICTOR T.D. AMAAKAVEN**, with Registration Number: **20114774028**, in partial fulfillment of the requirements for the award of Master of Engineering (M. Eng) Degree in Materials and Metallurgical Engineering, Federal University of Technology, Owerri, Imo State.



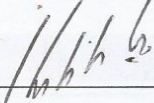
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## **DEDICATION**

This work is dedicated to the Almighty God

And to

My Parents, Dr. Fabian Amaakaven and Late Mrs. Esther Amaakaven.

Your love and care reared the seed of fruition to full brew.

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## ABSTRACT

*This work investigates the optical properties of glass prepared using Otamiri Silica sand mixed with analytical grade oxides as a function of their composition. Three batches were prepared with Phosphorus as the main variable of the  $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3\text{-CaO-ZnO}$  glass system. The glass was melted in a ceramic crucible with a lid and the glasses melted after two hours of firing in a monolithic charcoal furnace. The effect of varying  $\text{SiO}_2$  and  $\text{P}_2\text{O}_5$  on optical properties was determined using a SHIMADZU3600 spectrophotometer by determining the absorption, transmission and reflection spectra. The samples were subjected to X-ray diffraction and were confirmed to be glass from the diffuse pattern. The spectrophotometric results showed that the sample 1 glass absorbed 28% of the light and sample 2 showed peak absorption at 55% with different spectra in shape having multiple absorption centres possibly due to contamination of the glass by the crucible. The optical band gap energy was also determined from the optical band gap energy of the glass as determined by the SHIMADZU3600 spectrophotometer and found to be 2.2eV and 1.9eV for sample 1 and 2 respectively. The refractive indices of the samples were determined from the optical band gap energy of the glass as determined by the SHIMADZU3600 spectrophotometer using four different formulas and was found to range from 2.601 to 2.94 for the two samples. The refractive indices increased with increasing % $\text{P}_2\text{O}_5$  in composition in all the methods used. The refractive indices calculated using the relations all gave similar results for samples 1 and 2. Sample 3 however had a very poor chemical durability as shown by its reaction with atmospheric moisture forming a thick white crust. This was found to be due to the absence of CaO and ZnO in its composition. It is clear therefore that the glass made in this work upon further studies and research has great potential as a candidate for light scattering device and for lighting across large surface areas.*

**Key Words:** *Glass properties, refractive index, optical band gap energy, absorption, transmittance, reflectance, X-ray diffractometer, spectrophotometer.*

# CHAPTER ONE

## 1.0 INTRODUCTION

### 1.1 Background Information

The use of any engineering material for whatever purpose is dependent on its inherent properties. Glass by far is no exception and it is among a long list of other engineering materials in which their properties can be tailored to suit particular applications. Glass is used primary because of its transparency and interaction with light; both in the visible region and other regions of the electromagnetic spectrum.

The hallmark of all optical applications is in the material's characterization optically. For various optical purposes, the optical properties of glasses are determined using various instruments depending on the property sought. The spectrophotometer is used to determine the regions which a glass transmits, reflects or absorbs radiation. Thus, a material's absorption spectrum gives information on which frequencies are absorbed and to what degree they are absorbed and this in turn is the principal criteria for their specific application.

Lim, et al, (2014) stated that the properties of glasses have well been studied by many researchers due to their easy preparation, good strength and excellent

isotropic behaviour. However, the development and utilization of glasses for most imaging applications and many other applications in the field of optics and optoelectronics have emerged specifically due to purposeful research that has been carried out and is still being carried out. This has made glass a material of choice in many applications which have matured, others growing and yet others just now emerging. Mohd et al. (2012) pointed out that oxide glasses are among the few solids that transmit light in the visible region of the spectrum and form the various types of glass that have been studied over the years. In their work, they further state that phosphate and silicate glasses are the two most important oxide glasses that have been used extensively for lasers and as fibre amplifiers. Their optical properties are important in many applications including components for laser technology, optical sensors, radiation sensors, optical radiation windows and optical shielding instruments, optic fibres, optical amplifiers in telecommunication fibre networks, semiconductors and other photonic glass applications. Studies into glass properties include the exploration of the local environment of structural modifiers like zinc, barium, rare earth and transition metals incorporated to the host material such as borate, silicate, phosphate or germanium through the use spectroscopic instruments like the UV-VIS-IR spectrophotometer, fourier transform spectroscopy, nuclear magnetic resonance and luminescent spectroscopy.

Among these glasses, borate glass is commonly known for its high thermal stability, low melting point, variable coordination numbers and good solubility of modifier ions. However, pure borate glass is hygroscopic and sensitive to its surrounding atmosphere. The glass easily becomes unstable due to its ability of absorbing water especially in moisturized environments.

Phosphate glasses on the other hand are also good optical glasses save for the fact that they too are hygroscopic. According to Harper (2001), pureborosilicate crown glasses and special fluoro-phosphate glasses have been applied to lens systems operating at wavelengths longer than 300 nm of which only high-purity fused silica is capable of meeting all lens design needs at shorter wavelengths, specifically 248 nm and 193 nm. This makes silica glass transparent throughout the entire range of the visible spectrum, plus the near infrared (IR) and much of the ultraviolet (UV) spectral regions. It is to this effect that these modifiers are added to silica thus creating non-bridging oxygen atoms that contain unpaired valence electrons that create electron energy states or levels within the insulator's band gap, thereby causing the absorption of light at a wavelength corresponding to the energy needed to excite these electrons into the conduction band and the effect of this is that the modifier ion causes a shift in the absorption edge to longer wavelengths. This makes the silica glass commercially feasible to

produce and avails the glass the required optical properties suitable for particular applications.

Fluoro-phosphate and phosphate glasses with good chemical durability have a wide transmission range. This is because of their low electron-phonon coupling strength which makes phosphate glass a promising material for IR-to-VIS up conversion lasers (Ebendorff-Heidepriem et al, 2013).

Additions of oxides like transition metal oxides which act as coloring agents, rare earth metals and other modifying elements to the glass have been found to modify glass optical properties. For example other oxides such as alumina additions in a Zinc-phosphate glass reduces dissolution rates in water by 4 orders of magnitude and increases the glass transition temperatures. Furthermore, hydrofluoric acid-resistant glasses have been made from zinc-alumino-phosphate glasses. Erbium, a rare earth metal is used in the form of a trivalent ion  $\text{Er}^{3+}$  and is known to be a laser-active dopant in silicate and phosphate glasses. Consequently, Dorosz, (2008) has stated that with the absence of rare earth metals, an alternative for applications within mid-infrared range of up to 5  $\mu\text{m}$  may be the glasses of low  $\text{SiO}_2$  content modified by the elements that either combine with the dopant ions or cause non-bridge oxygen to appear in the rigid silicate structure. Such properties are manifested in particular by oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{BaO}$ .

ZnO has been studied as a thermoelectric material due to its wide band gap, good chemical stability at high temperatures and environmental friendliness. Structurally ZnO is an RO-type modifier oxide similar in behaviour to PbO, whereby at high concentrations it acts more as a network former than a modifier. Gautam, et al, (2012) in their work submitted that the network forming characteristics of  $B_2O_3$  and  $SiO_4$  is affected with the addition of some metal cation<sup>+</sup> additives such as Pb, Zn, Cd,  $TeO_2$ ,  $Bi_2O_3$ , MgO, CaO, SrO, and BaO as glass modifiers and are optimistic materials for probable applications in the fields of optical communications and others.

Furthermore, according to Abdel-Baki and El-Diasty, ternary phosphate glass system required for infrared photonic devices are currently being researched to be applied in telecommunication systems with absorption edge around 1550 nm and thus the effect of replacing  $Na_2O$  with ZnO. It is on this premise that this work is tailored towards the use of non-transition metal modifiers in glass for optical applications. The optical properties of glass are a reflection of the ability of the glass to interact with the electromagnetic spectrum uniquely in the form of light.

The inclusion of these optically active ions amplifies the optical and photonic properties of the glass and in other cases, the glass acts as a perfect host for these optically active ions in applications over a wide range of wavelengths.

Material composition is one of the chief dependent variables which affect optical properties. Properties such as absorption, transmission and reflectance are paramount in characterizing glass for advanced optical applications.

This study focuses on the evaluation of the optical absorption, transmission, and band gap characteristics of the glass in the UV-VIS-IR regions of the electromagnetic spectrum. The glass made from Otamiri silica sand mixed with varying amounts of phosphorus pentoxide ( $P_2O_5$ ) and other fluxing agents which are important in the enhancement of its commercial viability and hence its characterization will be a pointer toward the kind of application suited for this kind of glass.

## **1.2 Problem Statement**

The production of glasses generally is one that requires a large amount of energy. Glasses are also numerous and each depending on its properties, suits a particular application. Therefore the study of the optical characteristics are of great importance. However:

- a.** Despite the abundance of sand and other raw materials for glass making in Nigeria, thorough studies have not been carried out on their optical characteristics.

- b. There is also need for studies in the development of low temperature melting optical glass from these sand deposits that could absorb optical band wavelengths within the neighborhood of fibre optics applications or other light transmitting or scattering applications which will promote local content development and utilization for economic development.
- c. The lack of information on optical glasses produced in Nigeria has also prompted this study.

### **1.3 Objectives**

- To produce glass through melt quenching using Otamiri sand and other oxides.
- To fabricate through melting, a  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-CaO-P}_2\text{O}_5\text{-Na}_2\text{O-ZnO}$  glass using Otamiri sand ( $\text{SiO}_2$ ) as the glass former.
- To determine the absorption, reflectance and optical band gap energy of the glass.
- To contribute to knowledge on the optical characteristics of Otamiri sand as a glass former.

### **1.4 Justification**

Studies of the optical properties has for decades been under taken with the aim of matching properties with function and application. With the dynamic nature

of glass compositions, glass can be prepared and properties determined and matched with application.

This study involves the fabrication of optical glass using Otamiri sand as the major network former. The study has the potential of utilizing Otamiri sand for production of glasses for optical applications in Nigeria. The study will also provide additional information on the optical characteristics of glass made from Otamiri sand.

### **1.5 Scope of the Study**

The scope of materials for this study is limited to sand samples obtained from the banks of Otamiri River, Imo State and other minor glass making oxides of analytical grade obtained from the open market in South East Nigeria.

Also the scope of the test for the study is limited to the determination of the Absorption, Reflection and band gap characteristics of the glass.

## **Chapter Two**

### **2.0 Literature Review**

#### **Preamble**

The use of different optical glasses for different applications are based on their compositions. The components so used will determine their behaviour with light. Phosphorus based glasses offer good light transmission. It is worthy of note that the dynamic nature of glass compositions in the area of variable weight percentage of components, standard processing and a proper technique for testing are ingenious and critical in achieving credible results of properties desired.

#### **2.1 Optical Materials**

Optical materials are a group of materials which are not only transparent to light but also have good transmission due to their unique interaction with the electromagnetic spectrum in the ultraviolet, visible and near infrared regions. These interesting materials include: single crystals, polycrystalline materials, some plastics and notably Glass. (McGraw-Hill Encyclopedia of Science and Technology online 2014).

These materials function in ways such as to control or influence the path of electromagnetic radiation. The region in which these individual materials are

useful in applications is dependent on their inherent macroscopic properties such as chemical composition and material structure. The electromagnetic spectrum is the distribution of radiations according to energy, frequency of radiation and wavelength. (mse-web, 2006).

An optical material especially not silica glass, if exposed to high energy rays of the EM spectrum may lose part or all of their optical properties as a result of the short wavelength radiation which is capable of distortions in the material's structure permanently. However, these materials are fabricated into optical elements such as lenses, mirrors, prisms, polarizers, etc. that interact with radiations in one way or another both in the visible, ultraviolet or infrared spectral regions. Their unique interaction with 'light' has been their "selling point" in terms of functionality.

### **2.1.1 Plastics**

Optical plastics are used in small fractions of optical systems as compared to glasses and crystals. The largest application of plastics is in ophthalmic lenses, however others include low end camera lenses, microscopes and binocular lenses. (Paquin1999). Plastics are generally divided into two broad groups; thermosetting and thermoplastics, however, the most widely used optical plastics are specifically

known as Polymethylmethacrylate (PPMA). Their properties include low cost, easy mouldability, machinability and polishability and they have a good combination of macroscopic optical properties. Another optical plastic is polystyrene which when combined with acrylic can be a good achromatic lens.

### **2.1.2 Crystals and Semiconductors**

According to Paquin (1999), optical crystals and ceramics are widely used in optical systems and include both synthetic and naturally occurring materials. These crystals could be single or polycrystalline. They are basically used in infrared applications but some other crystals also have good transmission from the ultraviolet to the far-infrared wavelength region and these crystals include sapphire,  $\text{CaF}_2$  and  $\text{LiF}$ . Crystal quartz which occurs naturally, can also be made synthetically and is another useful crystal used in UV prisms, infrared windows and infrared applications in wavelength regions of up to of  $4\mu\text{m}$ .

### **2.1.3 Glass**

According to Varshneya and Mauro (2010), a glass is formed by imposing a kinetic constraint on a viscous liquid, thus reducing the temperature such that the dynamics occur on a much longer time scale than needed for equilibration on a typical laboratory time scale. However, as defined by the ASTM, glass is an

inorganic product of fusion which has been cooled to a rigid condition without crystallizing.

According to Zachariasen, glass is a substance which can form extended three-dimensional networks lacking periodicity with an energy content comparable with that of the corresponding crystal network. In essence, the density and the mechanical properties of glass are solid-like; however, the atoms form a continuous random network such that the unit cell is infinitely large, containing an infinite number of atoms. A definition of glass put forward by Harper, (2001) is that it is a solid with a liquid-like structure.

Glass formation is possible, in principle, for a system of any composition provided that it contains sufficient of the component called 'network former'. Thus, a wide variety of multi-component glasses can be prepared to attain the desired properties by adjusting the chemical composition. Glass can be inorganic or organic, there are however other processes which could be used to achieve a product which is non-crystalline and they include vapour deposition, precipitation of silica and sol-gel processing. Glass therefore can be said to be a phenomenon rather than a material because all glasses are amorphous but not all amorphous materials are glasses. It is now standard practice to classify glasses using different criteria. The distinction from an amorphous solid from a glass is that there exist a

smooth transition of a glass to a molten liquid on heating while amorphous solids appear to crystallize before transformation to the liquid state. Glass can then be primarily classified by their different methods of production which include;

1. Glass by Melt-quenching technique.
2. Glass by Chemical Vapor Deposition.
3. Glass by Sol-gel process.

#### **2.1.3.1 Glass by Melt-quenching Technique**

This process is the most popular. It is one in which a collection of variable amounts of the raw materials in their oxide forms are fused into a viscous liquid subsequent conditioning of the melt to viscosities suitable for forming and then forming it into the shape of choice through different processes such as casting, blowing, centrifugal casting, drawing, floating and rolling. This method is the oldest method of glass making and is still very useful today and according to several authors, it still accounts for more than 90% of total tonnage of glass produced globally. Table 2.1 shows different glass types and applications with their corresponding compositions primarily from the melt quenching process or technique.

Table 2.1 Chemical composition of some industrial glasses made by melt-quenching technique. Adapted from Yamane and Asahara(2004.)

Glass type	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	PbO	Other
Sheet glass by float Method	72.6	1.8	-	7.9	3.8	12.2	-	0.7	
Container glass	72.8	1.6	-	11.3		13.8	-	0.5	
Crystal glass	56.9	-	-	-	-	2.8	13.6	26.0	0.3
Optical glass SF6	26.9	-	-	-	-	0.5	1.0	71.3	0.3
Optical glass BK7	66	-	12.4	-	-	8	12	-	1.6
TV panel glass	63.8	1.3	9.4	2.9	2.2	7.2	8.8	2.8	1.6
			(SrO)		(BaO)				

### 2.1.3.2 Glass by chemical vapour deposition

The production of glass by chemical vapor deposition is a process based on thermally activating a homogeneous metal halide vapor activated in an oxygen plasma phase via an oxy-hydrogen flame within a temperature neighborhood of

about 2000<sup>0</sup>C. The process is however not commercially viable and hence only used on a laboratory scale. (Industrial Materials for the Future. 2002)

### **2.1.3.3 Glass by sol-gel process.**

Vitreous silica can be manufactured by the sol–gel. According to Shackelford &Doremus (2008), the sol-gel process is carried out through the destabilization of colloidal sols or by the hydrolysis of metal organic compounds. This second method is the most common technique because it yields a silica–alcohol–water gel which is subsequently dried and fused to produce silica glass a glass made of SiO<sub>2</sub> alone. The manufacture of three dimensional articles by this method is limited due to the difficulty in drying porous gels without large shrinkage and cracking and also the associated high costs of the raw materials used in this process which make them uneconomically feasible for large scale production. This product finds application as silica gel which is used as a drying agent and as supports for chromatography and catalysis.

## **2.2 Optical Glass**

Optical glasses are the first of what was referred to as “high tech” materials. Boyd and McDowell (1986). Consequent on this, Saxena et al (1991) concludes that optical glasses are a vital and strategic material for defense, scientific research,

surveys in industry and scientific education. These materials are so important that without it various instruments like periscopes, gun sights, microscopes, telescopes and a host of other scientific instruments would not exist and that their value lie in their exacting functions and the technological perfection required for their production.

Glass is almost the ideal material for use in the visible and near infrared spectral regions. It is stable, readily fabricated, homogeneous, clear and economically available in a fairly wide range of characteristics. Smith (2000).

Smith points out further that optical glass has been playing a vital role in shaping science and engineering. Today, only a handful of countries produce optical glass and have made their technology a well-guarded secret. The total volume of optical glass produced today represents just a fraction of a percent of the total tonnage of glass produced globally. The manufacture of optical glass is based upon continuous research into the properties, effects of composition upon density, refractive index, melting properties, durability, freedom from colour, and devitrification tendencies studied on a small scale, and the results translated into terms suitable for works practice. Peddle (1922).

The features which are characteristic of these optical properties and which also make them special include high degree of bulk homogeneity, transparency and Melt-to-Melt Reproducibility. Glass properties are dependent on these features and hence, Tropsch, et al, (1995) states that the nature of anisotropy in glasses varies from sample to sample though in some cases negligible.

### **2.2.1 Bulk Homogeneity**

Homogeneity of glass can be said to be a state or form which is physically and chemically uniform throughout the whole volume of the glass which will enable a uniformity of measurable properties. According to Reitmayer & Schuster. (1972), Homogeneity of glasses depends on three factors which include mixing and melting process, density variation due to imbalances thermodynamically and thermal strains instituted by steep temperature gradients during annealing. Fluctuations of the chemical composition during the melting process caused by surface evaporation of specific components and also reactions between part of the melt and the mould wall material reduces homogeneity.

### **2.2.2 Chemical Durability**

According to Hoya (2004).The resistivity of glass to the reactions of leaching and disintegration is directly related to the intrinsic chemical durability of glass to moisture. Boyd & McDowell (1986) have inferred that the ability of a component of glass to withstand minimum resident chemical degradation which may be atmospheric is referred to as chemical durability.

The chemical durability is the most sought after non-optical property of glasses generally. For many applications of glass, the chemical durability is perfectly adequate but it can be seen in some cases that some glass compositions are not completely resistant to atmospheric attack. The resistivity of glass to reactions of leaching and disintegration is directly related to the intrinsic chemical durability of glass to water.

### **2.2.3 Melt-to-Melt Reproducibility**

Smith (2000), asserts that the characteristics of optical glass vary somewhat from melt to melt because of variations in composition and processing and also due to variations in annealing procedures. However, it is necessary as a requirement that glasses with the same composition are required to have similar properties even if melted in quick succession. This is achieved through standard raw material handling, melt processing and annealing procedures which assures uniformity of properties to a very high degree.

#### **2.2.4 Interdependence of Glass Composition, Structure, and Properties**

The atomic arrangements in glass are more or less random. Hence, the physical properties of glass are, in general, isotropic like those of liquids. Viscosity of glasses increases with an increased network connectivity. Thus, the tetrahedrally coordinated  $\text{SiO}_2$  glass has the highest viscosity at any temperature among commercial glasses of practical interest while the triangularly connected  $\text{B}_2\text{O}_3$  glass has the lowest. Conversion of triangular boron to tetrahedral boron increases connectivity, and as such raises the viscosity. The non-bridging oxygen in glasses increases fluidity and their increase generally raises the thermal expansion coefficient due to an increase in the average atomic separation between the non-bridging oxygen and the network former.

Harper, (2001) has revealed that the additive rule accounts for the interdependence of composition on properties such that each component in the glass batch contributes to a particular property of the glass an amount proportional to its molar or weight fraction in the glass. The particular property is then a linear sum of the additivity factors multiplied by the molar or weight fraction. Properties such as density, refractive index, elastic moduli, and to some extent, thermal expansion and viscosity are a few of those properties where the additivity factor lends considerable application.

### **2.3 Phosphate Glasses as Optical Materials**

Phosphate glasses are a class of glass composed of metaphosphates. They are highly resistant to hydrofluoric acids. They also are a perfect host for rare-earth ion for solid state lasers and nuclear waste immobilization. (Wikipedia). Alkali containing phosphate glasses are a good host for optically active rare earth metals and transition metals because of their high solubility in these glasses. Prakash et al (2011). Furthermore, Prakash et al concludes that oxide glasses, such as borate, silicate, tellurite and phosphate glasses, have proved to be the appropriate host materials for the development of optoelectronic components. Among the oxide glass hosts, phosphate glasses have attracted much attention due to their high transparency, thermal stability, good rare earth ion solubility, easy preparation in large scale, shaping and cost effective properties. Phosphates glasses generally have an absorption peak within the neighborhood of 880 nm and 1500nm. Rai et al. (2014).

### **2.4 Optical Properties of Phosphate Glass**

For a material to be useful as an optical material, Smith (2000) asserts that the substance must meet certain basic requirements the first being that the material should be able to accept a smooth polish, be mechanically and chemically stable, have a homogeneous index of refraction, be free of foreign inclusions, and of

course transmit, reflect or generally interact with radiant energy in the wavelength region in which it is to be used.

The phenomenon of glass optical properties is governed by the bandgap associated with the glass which refers to the energy gap between the conduction and valence band. Oxide glasses generally are transparent to wavelengths in the visible and near infrared regions due to their wide band gap.

Yamane & Asahara (2004), states also that the primary requirements for an optical glass are high purity and high homogeneity to allow the propagation of a light beam with minimum optical loss.

Accordingly Smith, (2000) points out that the two characteristics of an optical material which are of primary interest to the optical engineer are its transmission and its index of refraction, both of which vary with wavelength.

However Schott (2002) asserts that refractive index and hence dispersion which is a variation of index of refraction with wavelength and Abbe number are also among the most important optical properties an optical engineer or instrument maker seeks for when designing an optical instrument with the basic principle of linear propagation of light.

Broadly, the optical properties are grouped into linear and nonlinear optical properties. These represent the behaviour of a material linearly or nonlinearly with the interaction of light under the influence of either an electric or magnetic field.

#### **2.4.1 Linear and Nonlinear Optical Properties of Glass**

Reshak, (2007) states that linear and nonlinear optics covers a variety of phenomena involving the interaction of light with matter with a constantly growing application of optics in technologies such as telecommunication, medicine, etc. while, Träger (2007), has stated that the linear polarization of light governs linear-optical phenomena such that it corresponds to the regime where the optical properties of a particular medium are independent of the field intensity (electric or magnetic). Currently, investigations have been directed towards the largest possible non-linearities for optical signal processing, this means that the optical glasses with high refractive indices and high dispersions are the best suited type of materials for these applications. Furthermore, a host of different glass systems are being investigated by many scholars with the aim of increasing their optical nonlinearities by introducing a variety of modifiers into the glass network with the greatest effects recorded with the use of transition metals or rare earth metals with characteristic large ionic radii.

Yamane &Asahara (2004), has stated that the relationship between the linear and the nonlinear refractive indices is cation-dependent. Consequently Reshak (2007) further explains that the various ways in which light interacts with matter are of immense practical interest e.g. absorption, transmission, reflection, scattering or emission stating that these properties are energy dependent.

#### **2.4.2 Non-linear Optical Properties**

Nonlinear optics describes the behaviour of light in a nonlinear media in which the dielectric polarization responds nonlinearly to the electric field of the radiation. This phenomenon is observed at very high intensities of radiation, also, when a uniaxial stress is applied to a specimen of glass of known refractive index, there is always a change in refractive index due to the applied stress.

Reshak (2007) has pointed out that the applications of nonlinear optics (NLO) range from basic research to spectroscopy, telecommunications and astronomy. Rawson, (1980) has also stated that the study of the alternating current (A.C.) electrical properties of a glass and the study of optical properties at even longer wavelengths and the resultant behaviour regarded as nonlinear optical properties of the glass. Almeida, (2005), further affirms that an optical non-linearity is a deviation from the linear relationship between a material's

polarization response and the electric component of an applied electromagnetic field. Optical nonlinear glass materials may be divided into two main categories of resonant and non-resonant types.

### 2.4.2.1 Non-resonant Nonlinear Optical Properties

Non-resonant nonlinear optical glasses include high refractive index, high dispersion glasses like heavy flint optical glasses, or heavy metal oxide glasses, or chalcogenide glasses. Huang (2005) states that chalcogenide glasses have the highest level of nonlinearity among optical glasses, consequently, Dimitrov & Sakka (1996) have affirmed that materials with

Table 2.2 The chemical composition, experimental optical bandgap ( $E_g$ ) and calculated ( $E_{g,calc}$ ) optical band gap values of some glasses. Adapted from Ticha and Tichy (2011).

	Chemical composition			$E_g$ [eV]	$E_{g, calc.}$ [eV]
	(PbO)	(ZnO)	(P <sub>2</sub> O <sub>5</sub> )		
1.	30	10	60	4.98	5.34
2	35	10	55	4.96	5.13
3	40	10	50	4.93	4.92
4	45	10	45	4.82	4.69

5	50	10	40	4.7	4.48
6	55	10	35	4.6	4.27
7	50	50	-	4.91	4.86
8	50	5	45	4.71	4.67
9	50	15	35	4.6	4.29

high nonlinear refractive index are found to possess a high linear refractive index and a small energy gap, which has been attributed to the increase in the oxides metallicity. On this basis, it is suggested that materials containing PbO, TiO<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub>, CdO, Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, and CeO<sub>2</sub>, as well as TeO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, Bi<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>, WO<sub>3</sub>, MnO, Fe<sub>2</sub>O<sub>3</sub>, CoO, and NiO in appropriate amounts would be promising materials for nonlinear optics not necessarily transitional or rare earth metals.

#### **2.4.2.1.1 Refractive index**

Refractive index is the most significant optical property of glass, because this index shows interactions between light and a transparent glass material. Though the refractive index of opaque and translucent materials is also possible. High refractive index enhances or affects the emission property or optical non-

linearity of a material, thus this feature is very important for the advanced optical telecommunication, in semiconductors, insulators, oxides, halides and processing devices. (Singh and Karmakar 2001).

Optical glasses especially lenses are characterized or graded by their linear refractive index, dispersion and Abbe number. The linear index of refraction however is characterized in the middle of the visible region of the spectrum which falls between 587.56nm as stated by MellesGroit (2009). This refractive index is an important property in optics and photonics as well. The criteria for use of a glass as a light transmitting device is that it should have a high index of refraction and must transmit light from the UV through the far infrared regions of the electromagnetic spectrum. This in photonics, determines other material and field dependent properties which are non-linear in nature.

According to Sathish and Eraiah (2012), refractive index can also be calculated using the relation proposed by Dimitrov&Sakka (1996).

$$(n^2-1/n^2+2) = 1 - \frac{\sqrt{E_g}}{20} \dots\dots\dots (1)$$

where  $n$  and  $E_g$  are refractive index and energy gap respectively.

Ravindra et al (as cited in Salem, 2003, p 288) proposed a linear relation governing the variation of the optical refractive index  $n$  with the energy gap  $E_g$  to be

$$n = 4.08 - 0.62E_g \dots\dots\dots (2)$$

Table 2.3 shows the values based on experimental data of energy gap to evaluate the refractive indices of various semiconductors, insulators, oxides and halides for entire range of energy gap using the equation below where  $E_g$  is the optical bandgap energy.

$$n = \sqrt{\frac{12.417}{E_g - 0.365}} \dots\dots\dots (3)$$

Table 2.3 Refractive Index of different materials

Materials	Expt. Energy Gap <sup>23</sup> (eV)	Exp. <sup>23</sup>	Authors	Moss	Ravindra	Reddy	Ananiet	Herveet	Reddy
			Cal. Eq. (8)	<i>et al</i>	<i>et al</i>	<i>et al</i>	<i>al</i>	<i>al</i>	<i>et al</i>
Refractive Index ( <i>n</i> )									
GeTe	0.10 <sup>#</sup>	6.000 <sup>#</sup>	7.0724	5.5518	4.0220	NA	7.9062	4.0123	
InSb	0.17,0.235* <sup>§</sup>	5.130	5.3697	4.7931	3.9724	NA	6.1911	3.9283	3.93
PbSe	0.278	4.590	5.0866	4.2543	3.9042	NA	5.7776	3.8189	
PbTe	0.311	5.350	4.9060	4.1509	3.8856	NA	5.6433	3.7902	
InAs	0.354,0.417* <sup>§</sup>	4.100	4.4634	4.0305	3.8608	NA	5.3777	3.7527	3.76
Ge	0.664	4.052	3.8419	3.3892	3.6376	4.5651	4.0955	3.4491	
GaSb	0.726,0.812* <sup>§</sup>	3.820	3.6006	3.2909	3.5818	4.3144	3.9185	3.3816	3.38

Adapted from Kumar & Singh (2010)

### 2.4.2.1.2 Transmittance

Transmittance is a property or ability of electromagnetic radiation to pass through a transparent or partly transparent material with low or no loss in its intensity. Jacobs & Kildiff (1994), defines transmittance as the percentage of an incident ray remaining after passing through a material. Transmittance is divided

into external and internal transmittance. Transmittance is important in optics and optoelectronics.

MellesGroit, (2009) states that external transmittance is the single-pass irradiance transmittance of an optical element. While internal transmittance is the single-pass irradiance transmittance in the absence of any surface reflection losses and this is actually the transmittance of the material. The light transmission of optical glasses is frequently given in terms of the internal transmission  $T_i$  after correction for reflective losses  $R$ ,

$$\text{that is, } T_i = T/R \dots \dots \dots (4)$$

The deviation of  $T_i$  from 100% is a measure of absorption due to impurities and scattering due to defects. The transmission of light through a glass is a key factor in many applications of optical glass. Optical fibres utilize the property of transmission to transmit data. In optical communications for example, the fibres consists of two important sections with different attributes. The attributes notably are that light rays be solely confined to it and secondly, that long-distance transmission occur with minimum loss in light intensity. The sections of the optical fiber waveguide include an active inner cylindrical fiber core which is covered and surrounded by another glass cladding whose respective indices of refraction are  $n_f$

and  $n_c$ , where ( $n_f$ ) refractive index of fibre is higher than ( $n_c$ ) the refractive index of the cladding glass. Whereas the cladding is most often silica while the core is most often doped which normally will raise the refractive index. (Optical properties of materials. n.d).

#### **2.4.2.1.3 Transparency**

Transparency which is the inverse of absorption is one of the most important properties of glass for its application. Light travels through oxide glasses essentially unimpeded because the energy of the light is ineffective in exciting structural vibrations or causing changes in electronic energy states within the glass, either of which would result in the light being absorbed. The high transparency to visible light is one of the most important properties of oxide glasses generally. This property has made glass a key material in a majority of optical instruments. In principle, a glass is transparent to radiation in the wavelength regions where the intrinsic absorption does not occur. Between two intrinsic absorption edges that could be determined by band-gap energy and the vibration energy of its constituents. Oxide glasses and fluoride systems having a wide gap between conduction and valence bands are transparent to visible radiation and near infrared region, however, the chalcogenide systems have narrower band gaps and appear

translucent in the visible region but are actually transparent in the near and far infrared regions of the electromagnetic spectrum.

#### **2.4.2.1.4 Dispersion**

According to Träger (2007). The refractive index of a medium to a great extent depends on the wavelength of the light being transmitted. This relationship between refractive index and wavelength is known as dispersion, meaning different wavelengths of radiation will be modulated differently by the same glass material. Each wavelength of light will be refracted differently meaning it has a close relationship with index of refraction. The principle of dispersion is that white light is dispersed into its principal visible components through a glass prism or refracting medium in accordance with Snell's law. The same authors continues further that in normal dispersion, the index increases for shorter wavelengths of radiation. Normal dispersion is valid only far away from absorption bands

#### **2.4.2.1.5 Transmission and Absorption**

A material's absorption spectrum gives information on which frequencies are absorbed and to what degree they are absorbed and this depends on the structure of the material at atomic scale. Dresselhaus, (2001) asserts that the measurement of the absorption of light is one of the most important techniques to determine optical

characteristics in solids. Absorption in the transparent region, away from the electronic and vibrational resonances, is governed by impurities and defects. The level of absorption in glass is highly dependent on the purity of the starting materials, conditions of manufacture, and subsequent machining and polishing (Tropf et al, 1995).

Accordingly, Smith (2010) asserts that Absorption in glass results in a decrease in intensity of transmitted radiation through the glass material. This is evident as in the use of coloured glass containers to shield radiation or light sensitive chemicals or medicine. The decrease is not accounted for partly due to reflection losses mostly at the surface and internal scattering. Furthermore Smith continues that absorption is not uniform across all wavelengths of interest which fall within a range of between 200–2000nm and covers the UV–VIS–IR region.

Tropf et al, (1995), has stated that glasses are typically transparent from the near UV to the near IR. The intrinsic absorption is dominated by electronic transitions in the UV–VIS range, while in the IR it is dominated by molecular vibrations. In absorption measurements, the impurity level or active centers are observed as peaks.

#### **2.4.2.2 Absorption Spectroscopy**

The amount of light transmitted through a solid material, solution or suspension may be diminished by the absorption of light by the colored compounds or by the scattering of light rays by particulate matter. An instrument that measures the amount or intensity of light passing through a sample is called a spectrophotometer. Absorption spectroscopy has many uses. It can be used to study pH, Nutrient analysis, Organic compound analysis, Metals analysis (complexes), gas analysis by infrared spectroscopy, Pharmaceutical Industry analysis of drugs and in optical characterization of crystals, semiconductors, insulators and glasses for optical applications. The main requirement is that light be absorbed or scattered by some substance in the sample under investigation and inferences made based on the amount of wavelengths absorbed, reflected or transmitted.

#### **2.4.2.3 Resonant Nonlinear Optical Properties**

Resonant Nonlinear optical glasses include semiconductor or metal particle doped glasses. The study of nonlinear optical properties has opened new fields of study. Reshak, (2007), explained that an understanding of both the linear and nonlinear optical properties of a solid requires a detailed understanding of quantum mechanics as to how electrons move in these materials. This is an important emerging area which is to be explored. These nonlinear properties possessed by doped glasses are now being utilized in applications such as LASER glass and

optical communications, by splitting of energy levels which is caused by electron-electron and electron-host interaction.

Tropf et al, (1995), also explains that dielectric constant and refractive index are functions of frequency and hence wavelength. The frequency or wavelength variation of refractive index linearly is well known to be dispersion and is an important property in the transmission of information if in a nonlinear media, via pulse spreading. Nonlinear optical properties are derived from the change in refractive index with other properties such as temperature (thermo-optic coefficient), stress or strain (piezo-optic or elasto-optic coefficients), or applied field (electro-optic or piezo-electric) coefficients.

Birefringence is a phenomenon in which the index of refraction of an optical material varies in the direction it is measured; which means that it is a property of having two indices of refraction concurrently relative to the direction of measurement.

## **2.5 Optical Band gap**

The energy band gap is defined as the separation between the maximum energy in the valence band and the minimum energy in the conduction band and is represented in literature as  $E_g$ . It can also be defined as the energy range in a solid

be it a semiconductor or an insulator where no electron state can exist. It refers to the energy difference in electron volts between the top of the valence band and the bottom of the conduction band. It is a major factor determining the electrical conductivity of insulators which generally have a wider band gap and also in semiconductors with relatively smaller band gaps. According to Harper, (2001), oxide glasses can be considered to be wide-band-gap insulators. Silica glass, for example, has an energy band gap of about 8.5 eV, which means that the energy difference for electrons between the highest occupied bonding orbital and the first unoccupied nonbonding orbital is about 8.5 eV. The photon energy 8.5 eV corresponds to a wavelength of about 145 nm.

The optical band gap determines what proportion of the electromagnetic spectrum is absorbed and is otherwise referred to as the threshold for photons to be absorbed. Optical band gap is related to the refractive index of a material as proposed in the literature by different authors like Kumar & Singh (2010), Dimitrov&Sakka (1996) and Ravindra et al (1979).

The Kumar & Singh relation:  $n = KE_g^c$  .....(5)

Where K and C are constants 3.3368 and -0.32234 respectively and n is refractive index.

## 2.6 Optically Active Ions

The ability of a substance to rotate a plane polarized light is called optical activity Senese (2010). Furthermore, any ion which absorbs optical radiation in the visible region of the spectrum is termed optically active. It is a popular process known as 'doping' to incorporate optically or electrically active ions in glass to achieve certain field dependent optical properties. Some of such optically active ions are  $Y^{3+}$ ,  $Fe^{2+}$  and other rare earth metals.  $Fe^{2+}$  and  $Fe^{3+}$  which are dreaded impurities in optical glass manufacture should be avoided especially for optics and some other applications which are not meant to absorb infrared bands.

The presence of optically active ions brings about a phenomenon of ionic absorption in glass. This is as a result of the optically active metallic impurities possessing at least the d-orbital. This particular group of metals are the transition-metals and rare-earth metals which also have the f-orbital that modify the network structure. These structural modifications are often a function of coordination number of the modifying ion within the ligand complex. This optically active ions absorb radiations of the Ultraviolet and far infrared bands. Materials most suited for doping are those that have high mass density, contain atoms with high atomic number, large ionic polarizability and a large degree of covalent bonding, they include  $TaO_2$ ,  $SrO_2$ ,  $La_2O_3$  e.t.c.

## 2.7 The Optical Glass Process

The different stages in optical glass production if properly executed play an important role in achieving glass of optical quality, but most importantly, the quality of raw materials is the first step towards achieving optical quality glass. Optical glass process also entails the basic glass making steps but the only differences relate to purity of raw materials, homogenizing during melting and annealing in which standards have to be raised.

Mellor, (1958), states that the art of making optical glass consists of melting a set of desired pre-weighed raw materials together to form a molten mass sufficiently fluid enough to be readily and thoroughly stirred to achieve uniformity or homogeneity. Almost the entire process is centered on procedures designed to ensure that the glass is perfectly homogeneous, free from bubbles and surface flaws during casting, and of exactly the desired optical properties, only so can the desired optical behaviour be achieved.

The properties sought after are controlled by the inclusion of a wide range of compounds and oxides which either opacifies or interacts with light uniquely. These oxides include; Tin oxide, Fluorites, Zirconia, Titania, Zinc oxide, cryolite, Lead antimonite, and Phosphates of Sodium and Calcium. In practice it calls for

the highest degree of control and skill. Chemical purity of the raw materials, especially freedom from traces of iron and titanium and these are essential if the glass is to be colourless and highly transparent.

### **2.7.1 Characterization of Glass for Optical Applications**

Glasses to be analysed for optical characteristics are usually made into standard glass slides of dimension 75 x 25 x 1mm. The optical characteristics include the determination of the light absorption, light transmission and light reflectance spectra of the glass using a spectrophotometer. All measurements are carried out at room temperature within a range of wavelengths.

The wavelength range often covers the Ultraviolet, visible optical region and the infrared regions of the electromagnetic spectra. The UV, visible and near infrared region cover a range between 200-1100 nm. The spectrophotometer is designed to measure the amount of light absorbed, reflected and transmitted by a material. This involves directing a radiation across the glass sample and recording how much light has been transmitted and at what wavelength it was transmitted using a detector.

### **2.7.2 Raw material requirement for optical glass manufacture**

Raw materials for glass manufacture must meet a set of criteria so as to ensure quality standards. These raw materials are sand or quartz of high quality and purity, which must be free from iron, which imparts colour. The glass industry in Nigeria is relatively undeveloped despite the availability of glass sand which is the most important raw materials for the manufacture of glass as well as the abundance of other raw materials. Ofulume&Amadi (2011). Much is not known about the Nigerian optical glass industry and neither is there much to talk of about the industry in terms of output and specific products and grade of glass produced.

It has been stated by McLaws, (1971)that the requirements of Sands for Glass should contain a minimum of between 95-98%  $\text{SiO}_2$ , while  $\text{Fe}_2\text{O}_3$  should not exceed 0.02% for optical glass. The grain size of the sand is also very important. As a requirement, BSS 2975 (1958), stipulates the granularity as follows: 80% of the particles should be less than 420 microns (36 BS mesh) but greater than 150 microns (16 BS mesh), 2% should be less than 600 microns (25 BS mesh) and 5% should be less than 125 microns (120 BS mesh) these grain sizes have been found to facilitate easy and better melting. Excessive fine sands should be avoided as they carry impurities the most and cause inclusions and bubbles. Table 2.2 below shows the grain size distribution of Otamiri sand from four different locations showing percentage of sand passing through different standard mesh sizes.

Table 2.4 showing the grain size distribution of Otamiri sand.

Sample number	Percentage passing (mm)/Mesh size					
	2	1	0.425	0.125	0.075	0.063
1	93.82	78.07	36.87	0.70	0.15	0.08
2	92.33	81.48	43.75	1.24	0.95	0.06
3	87.35	69.92	29.74	0.85	0.53	0.09

From table 2.5 below, the chemical composition of Otamiri sand has an SiO<sub>2</sub> content of well above 95% indicates that the sand is suitable for optical glass manufacture.

Table 2.5 chemical composition of Otamiri sand as adapted from Ushie, et al (2005).

S/no	Al	Ca	Fe	K	Mg	Na	Cr	SiO <sub>2</sub>
1	0.00126	0.000003	0.0017	0.0002	0.0001	0.005	0.000024	99.1
2	0.0062	0.000001	0.0039	0.00025	0.0001	0.025	0.000022	99.3
3	0.0015	0.000002	0.0017	0.00025	0.0001	0.01	0.000032	99.5
4	0.0103	0.000002	0.0032	0.00042	0.0002	0.038	0.000026	99.0
Mean	0.0048	0.000002	0.0026	0.00028	0.00013	0.02	0.000026	99.2

Having visited Glassforce, Aba and Sunglass, Kaduna that both produce container glasses of different color, their optical properties are of minimal interest hence they use decolorizers. The methods used by many glass manufacturers in Nigeria for impurities removal from the sand include gravity processing, spirals and hydro-cyclones to wash off these impurities which are mainly organic matter. Depending on the level of impurities in the sand, washing may however be done in stages.

### **2.7.3 Glass batch factors responsible for errors in the glass process**

For raw materials which occur in combination of more than one oxide, batch weight/percentage calculations are very essential to ensure that all oxides are added in their right proportions to ensure predetermined properties such as melting temperature, colour intensity and annealing range temperature.

Koreyo&Odewale (2005) state that these factors must be critically considered for an accurate calculation of glass batch weights and glass composition. These factors and sources of error should be prevented.

#### **2.7.3.1 The Variation in Raw Materials**

Raw materials used for glass melting vary in composition since they are procured from various sources. Moreover, there may be an accumulation of moisture in transit or during storage of these raw materials from a given source.

Dampness in sand is at once indicated by clinging of grains, so that the presence of moisture as little as 0.2% is noticeable. If the sand is actually wet, it must be tested for loss on ignition, and a correction factor applied. (Scholes 1974).

### **2.7.3.2 Solution of Refractories**

Proportion of oxides in glass batch being melted could increase as a result of the clay or refractory walls dissolving into the molten glass. This corrosive action introduces alumina ( $\text{Al}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ ) into the molten glass. Small percentages of Zirconia may also come from modern tank blocks refractories.

### **2.7.3.3 Dusting Losses**

The character of raw materials, most of which contain fine particles capable of being carried by air, gives rise to their escape as dust during the mixing operation. The transportation and charging of the batch also causes dust. When carbon dioxide is evolved during the decomposition of dolomitic lime, lime dust may be observed to be projected from the batch. The loss as a result of dusting is not economically serious, but significant enough to affect the accuracy of calculations and also of minor or trace raw materials. Koreyo&Odewale (2005).

### **2.7.3.4 Volatilization of Raw Materials (Oxides)**

Effects of volatilization in compositions of soda-lime-silicate glasses are less compared to those compositions of Technical, Borosilicate and lead glasses as a result of evaporation of boric oxide and lead oxide and halides from these glasses.

Scholes (1974). Further explains that definite data are lacking for boric oxide, which is one the most volatile of the glass forming oxides. Boric oxide ( $B_2O_3$ ) is especially volatile with steam such that losses occur as boric acid decomposes in the early stages of melting in batches containing this constituent.

#### **2.7.4. Melting**

The response of a glass batch to heating is determined by the batch makeup and this in turn determines the rate of melting. Hrma, et al. (2010). Glass melting processes vary widely with respect to the kind of product being manufactured. A major step in melting is the conversion of batch to molten liquid containing a large fraction of undissolved sand and gaseous inclusions. The most important parameter of this conversion being heat transfer as earlier stated.

The quality of all glass made, largely depends on five processes that take place in the course of melting, which include: dissolution of batch aggregates, Fining, Homogenization, Refining and Thermal conditioning. These processes depend on furnace temperatures, velocities of the melt (flow patterns), and the chemistry of the glass and resident time distributions during the melting process. Huisman, (2005).

Hrma, et al. (2010), explains that the type of batch materials and the size of silica grains determines how much primary foaming occurs during melting. Small

quartz grains, 5 $\mu$ m in size, causes extensive foaming because their major portions dissolve at temperatures below 800°C, contributing to the formation of viscous glass-forming melt that traps evolving batch gases. Melting of glass on a laboratory scale is done in crucibles that have a small melt surface area relative to melt volume and in order to reduce the effect of evaporative losses and since many of the oxides are volatile and have very high vapour pressures, continuous evaporation could reduce the foaming of the melt. Epstein and Sheik-Mansoor (2009).

Melt quenching of glass as earlier explained has a wider utilization in making commercial glasses for a wide range of applications. It has been explained by Smith, (2000), that the starting point for quantity production of glass optics is more often a rough moulded glass formed after the melting process referred to as a blank or one that has been pressed. This could be got through remelting of glass rods to the molten state and casting while for large scale production heating a mixture of carefully weighed raw materials to molten state and pouring it into the desired mould to take its shape. Fischer, et al. (2008) also, states that the procedures for optical glass manufacture after quality of raw materials have been ascertained and chemical composition determined for raw materials include:

1. Batch weighing and mixing in the powder form.

2. Melting in a furnace or crucible
3. Stirring while melting for homogenizing.
4. Casting into blank mould.
5. Annealing of the glass using time-temperature schedules.

In the case where blanks are made, they are often cast larger than the desired size required of the element to allow for grinding. Furthermore, Smith, advocates that for prisms slides and other blocks, the blank could be made large enough to allow removal of about 2 mm on each surface.

#### **2.7.4.1. Furnace atmospheres in optical glass melting**

Melting atmospheres are controlled to achieve a particular red-ox state which is paramount in determining the oxidation states of the oxides which translates into the colour of the glass. Lee, (2012), Explains that the intensity and type of colour in glass is caused by the oxidation state of the colouring ion and primarily its characteristic colour. The addition of oxides such as iron, chromite, sodium sulphate and charcoal promotes oxidation. A reducing furnace environment is however most suitable for optical glass melting. Which limit instances of colour formation which could trigger ionic absorption.

### **2.8 Glass Property Dependence on Composition**

Tropf, et al (1995), points out that high material quality and uniformity of processing is required to avoid impurity absorption, refractive index non-uniformity, voids, cracks, and bubbles and defects. Practical manufacturing techniques limit the size of optics of a given material. Purity of starting materials is a prime factor in determining the quality of the final product.

Glasses have no fixed stoichiometry, and as such, by varying the chemical composition of a glass its properties could also be varied in one way or another and this greatly affects the glass transition temperature. The amount in composition of any of these oxides and compounds have an effect on the properties ranging from melting temperature range, annealing temperature range, coefficient of thermal expansion, and thermal shock resistance, viscosity at a given temperature, glass-forming-ability of the melt, refractive index, colour, transparency and opacity.

The amount of  $\text{Fe}^{2+}$  in a glass composition is considered to be an impurity and which is above the tolerable standards will give the glass a greenish tint or Colour and is however considered a defect in optical glass.

### **2.8.1 Opacifiers**

In the case of opacity, opacifiers are included in the batch to render the bulk medium opaque. When in glass, they are undissolved in the glass and are dispersed in the bulk glass which scatter light. This phenomenon makes the determination of refractive index impossible by normal methods but the refractive index can only be

determined by the Kramers-Kronig (KK) analysis of reflectance data with moderate accuracy and also by other mathematical expressions.

However, the refractive index and energy gap of semiconductors and amorphous represent two fundamental physical aspects that characterize their optical and electronic properties and are affected not only by opacifying minerals or oxides but also other structural network modifiers which have a direct effect on the electronic properties and as such affecting optical properties.. Major opacifying minerals include fluorides of aluminum, calcium, barium and magnesium, calcium phosphate, titanium oxide and zinc oxide.

## **2.9 Casting requirements**

Casting is a manufacturing process by which a liquid material capable of solidifying with the manipulation of its thermodynamic properties is poured into a mould, which contains a hollow cavity of the desired shape, and then allowed to solidify. The solidified part is also known as a cast or casting and is removed or released out of the mould to complete the process. Casting materials are usually glasses of different kinds, molten metals into ingots, clay slips and various other cold setting materials that cure after mixing two or more components together which include epoxy, concrete and plaster of Paris. The requirements for casting of

glass in a mould is the same for casting high temperature liquids like metals, the mould should be heat resistant, and heat conducting to enable quick setting of the material once filled with molten glass, the glass allowed to solidify in the mould, and then the mould inverted and with the part simply falling out.

## **2.10 Annealing of Optical Glass**

If a freshly made glass object is cooled rapidly to room temperature, it may be strained and could may break easily or crack due to uneven cooling rate. Annealing of glass is a time and temperature sensitive process and when glass is annealed using a typical annealing lehr the stresses are relieved during the cooling process. Rao, (1952)., explains that the outer portions of a block of hot glass become rigid faster than the inner section, thereby introducing outer layer compression stresses with corresponding inner tensile forces. Owing to the poor thermal conductivity of the glass part, these stresses can be quite large and pose serious optical defects. This can be brought to coherent normalcy only through a good and efficient heat treatment process otherwise referred to as annealing.

The first objective while carrying out annealing is to raise the glass part temperature to its annealing point which is the temperature at which internal stresses in the glass are potentially relieved through internal viscous flow. This assures the whole section is in a uniform state of expansion, but not too high as to

cause the glass to fall under its own weight, slump or deform. The second objective is to control the cooling rate of the glass to avoid creating a large variations in temperature through the thickness of the glass. As the glass cools, molecular realignment also occurs at a diminishing rate. Eventually the glass reaches a point where the significant contraction is complete. This is described as the lower annealing point or strain point. Once the cooling rate to this temperature is controlled the actual annealing process is complete.

## **2.11 Grinding and polishing**

Grinding is paramount where surfaces must be mirror smooth and must fit into components. This is done on pre-cast glass blocks which must be shaped and surface-polished. The surface of the glass blank after annealing is further refined by a set of grinding and polishing operations, performed with loose abrasive in a water slurry in most cases peat is used and cast iron grinding tools. The objective of polishing is to produce regular transparent surfaces on a piece of glass or other clear substances. The surfaces are usually required to be flat or spherical, although occasionally slight departures from these shapes are needed in order to obtain some optical advantages not otherwise attainable. The process is divided into two: Grinding and Polishing. Twyman, (1945).

In grinding, powders with loose abrasive grains delivered in some type of oil or water-based vehicle are used in loose form over a variety of grain size ranges in levelling out asperities. Both cases require powders but the difference is in character of the material on which grinding occurs and the material itself. The process uses emery backed by a hard surface like glass while grinding and the powder is embedded in a comparatively yielding substances. The overall activity in grinding is to remove asperities and to achieve a uniform flat surface by the use of gritty powders with the application of proportional force in a process that may be referred to as mechanical comminution. While polishing also utilizes powders but the main aim is to achieve better surface finish which will not affect the direction of light as it comes in contact with material and also offer better protection as it removes some of the cracks from the surface.

## **2.12 Optical glass defects and methods of their identification**

Optical defects are described as the defects which affect the definition of images and paths of rays formed by lenses, prisms and other optical media. (Clark-monks & Parker 1980). Inclusions in glass have been both a scourge and a fascination to the glass maker for centuries.

Twyman, (1945) asserts that these defects are equally important in optical testing and application as they have adverse effects on the optical piece. In

conducting the tests, it is standard practice to ensure that the tests which must be carried out on the piece should not only be those simulating in-service operations but also others more severe than those to which the optical part will be engaged in and this is carried out also to ascertain the level of other defects that may be and their origin. Clark-monks & Parker have also stated that these defects are classified into groups based on their intensity and degree.

### **2.12.1 Stones**

Clark-monks & Parker, (1980) explain that stones usually refer to any crystalline inclusion present in the glass. The normal method of identifying them and their sources is to study their component minerals and the nature of their assemblage. The study of their components is rarely successful one method is to use the strain viewer which only shows the presence of an inclusion. In this case the strain viewer utilizes a differential in thermal expansion coefficient due to an inhomogeneity surrounded within the bulk glass and shown as a strain in the localized region. The degree of the stress will be dependent on the nature of inclusion.

### **2.12.2 Cord**

This according to Clark-monks & Parker, (1980), is a part of a glass which differs in composition from the surrounding matrix. This tends to produce a change in refractive index which enables it to be spotted and spoils the appearance of the

article. This can also result to a surface disturbance due to a varying temperature-viscosity of the region of the defect. Some other defects often look like cords but are due to defects in the forming operation but could be corrected by fine annealing. The basic approach which is used in identifying cords is through chemical analysis but most importantly, strict control of operating conditions and quality control information such as batch analysis and glass density are vital as this could be caused by batch weighing errors, segregation due to over mixing, incorrect batch chemistry, and may be averted through spending considerable time in analysis. Siliceous cords may also appear due to evaporation of batch constituents such as Alkalis and boric oxide in borosilicate melts.

### **2.13 Prisms and Slides as optical components**

Although prisms are commonly known as light reflecting and refracting glass pieces, a prism technically constitutes any three-dimensional shape with two faces of the same size and shape and parallelogram sides.

A glass slide is a flat rectangular piece of glass unto which a prepared sample may be viewed through an optical characterizing instrument. There are

various uses for prisms and slides, though the use of light reflecting and refracting prisms relate almost exclusively to optical imaging. In a general sense, prisms are involved in various fields, including scientific experiments, photography, architecture and other sophisticated optical systems. They are cut and ground to specific tolerances and exact angles. Many prism designs can perform more than one function. Basically, for any optical material to be tested of its index of refraction, it must be made into a prism shape if a spectrometer is to be used in determine the index of refraction. However the instruments used to determine index of refraction include: Abbe refractometer and a spectrometer.

The minimum angle of deviation method is one of the methods used and it is also a very accurate and commonly used method.

In the case of optically characterizing a material, the material is either made into a glass slide or is deposited on a glass slide and analysed using a spectrophotometer to determine the absorption, transmission and reflectance at different wavelengths.

## **2.14 The Spectrophotometer**

Ultraviolet and visible spectrophotometers have been in general use for the last 35 years. Over this period, they have become the most important analytical instrument in the modern day laboratory. In many applications other techniques could be employed but none rivals the UV-Visible spectrophotometry for its

simplicity, versatility, speed, accuracy and cost-effectiveness. A spectrophotometer however, is an instrument designed to measure the amount of light absorbed by a material. Various types are in use today and are utilized to characterize optical materials while others analyze solutions to determine concentration.

### **2.15 Summary**

This chapter has talked about the theory behind the work, the techniques involved and the process of fabrication and characterization and brings to bear the understanding of the subject matter, particularly referring to phosphate glasses as optical materials of choice in devices for telecommunication applications and other optical applications. The next chapter will talk about the methodology used in order to achieve the objectives of the work.

## Chapter Three

### 3.0 Materials, Apparatus and Experimental Procedure

This chapter seeks to describe the process of melting a glass batch and of fabricating a glass slide from scratch, through melting quenching method, then casting it in a machined graphite mould.

### 3.1 Materials

The materials and equipment include the glass batch ingredients and others like:

- a. Quartz sand from the Ihiagwa axis of the Otamiri River.
- b. Analytical grade Borax.
- c. Analytical grade  $P_2O_5$
- d. Analytical grade Soda ash.
- e. Analytical grade  $CaCO_3$
- g. Graphite block for mould making
- f. Vandeikya clay (kaolin) for ceramic crucible production.
- g. Grog for ceramic crucible production.
- h. Plaster of Paris (P.O.P)
- i. Deflocculant for slip production.
- j. a furnace

k. a pair of thongs

l. abrasive paper for grinding

m. glass polishing machine

### **3.2 Apparatus**

- a. Ceramic drying cabinet.
- b. Ceramic kiln.
- c. Spectrophotometer
- d. furnace
- e. Strain viewer
- f. Electronic weighing balance.
- g. Ceramic crucible.

### **3.3 Description of the study area and the Otamiri sand**

The study area covers the banks of the Otamiri River in Ihiagwa along the Nekede - Ihiagwa – Obinze road in Imo State Nigeria. It is bounded by longitudes  $6^{\circ} 58'E$  and  $7^{\circ} 04E$  and latitudes  $5^{\circ} 23'N$  and  $5^{\circ} 30'N$ . The area is currently the major source of building sand and gravel as it is mined on daily basis. The Otamiri

river runs from Egbu where it has its major base or source through to Nekede, Ihiagwa, Eziobodo, Olokwu, Umuisi, Mgbirichi, Umuagwo and finally to Ozuzu in Etche town of Rivers State of Nigeria.

The silica sand is whitish in colour which signifies presence of only little amounts of iron impurities in the sand which is another form of examining the raw material physically.

### **3.4 Research Design**

1. Raw material sourcing which includes buying of analytical grade oxides.
2. Sand sample acquisition from Otamiri river banks.
3. Washing and drying of the sand samples.
4. Sieving of the sand sample using standard sieves to obtain the optimum grain size to melt faster with minimum defects.
5. Weighing and mixing of the batch components which include sand and the oxides.

6. Production of ceramic crucible for glass melting.
7. Mixing, charging and melting of the mixed batch.
8. Preparation of graphite mould and casting.
9. Annealing of the glass pieces.
10. Preparation of samples and examination using a strain viewer.
11. Grinding and polishing of the samples
12. Testing of the glass pieces to determine the optical characteristics which include reflection, absorption, transmission spectra and band gap energy.
13. Determination of refractive indices of the samples from different expressions proposed by different authors.

### **3.5 Experimental procedure**

#### **3.5.1 Raw material acquisition**

The borax, phosphorous, barium, potassium, lime, soda ash and zinc oxide were purchased from the chemicals and reagent vendors in the form of analytical grade oxides. Representative sand samples were collected from a location in

Ihiagwa in Imo State, southeast Nigeria. The sand sample was washed thoroughly to remove loose impurities and other unwanted constituents such as organic matter. Washing continued until relatively clear water was achieved indicating the removal of a significant amount of the organic matter and after washing, the sand sample was dried under ambient conditions and in a drying cabinet to remove moisture. An amount of the sand was weighed out and poured into a set of mesh.

The grain size used in this study was that remaining on mesh 44 corresponding to 0.425mm and a portion remaining on mesh 72 corresponding to 0.25mm. This was done to ensure easy melting of the sand. The total mixing ratio for the two grain sizes was 3:1. The sand was then coned and quartered for even mixing. One portion was then used from which the required amount was weighed out according to the compositions of the batches in table 3.1.

### **3.5.2 Ceramic crucible production**

In making the crucible, a plaster of Paris model was cast and shaped using a porter's lathe to the desired shape. A 2-piece mould was made using the P.O.P model. The mould was then allowed to dry and harden.

In preparing the clay for actual crucible production, the chemical composition of the clay was determined using XRDF at Center for Energy Research (CERT) Zaria. A representative clay sample was taken from the source in Vandeikya Local

Government area of Benue State. The clay dug out was then dried, crushed, sieved and mixed with grog of the same clay in a 1:1 ratio. The grog had been sieved using a mesh 150 corresponding to 0.11mm and only those passing were used.

The clay was mixed thoroughly and a casting slip was prepared from the clay-grog mixture. Casting was done by coupling the P.O.P mould parts and pouring the slip into it. The mould normally would absorb the moisture from the slip and once the required wall thickness was achieved, the slip was poured out and allowed to get detached from the walls of the mould. In this case, a thickness of 150mm was achieved in four minutes after the slip was poured into the p.o.p. mould. The cast crucibles were then allowed to dry under normal atmospheric conditions for 4 days and the green piece was fettled to remove rough edges and excess material.

The pieces were then dried inside a ceramic drying cabinet at 110<sup>0</sup>C for 6hrs. During the bisque firing, the crucible was pre-heated at 750<sup>0</sup>C for 6hrs and rapid firing followed for 8hrs at 1250<sup>0</sup>C. The crucible now a refractory material is suitable for fusing glass at temperatures within the neighborhood of 900<sup>0</sup>C to 1150<sup>0</sup>C.

### **3.5.3 Graphite mould fabrication**

Graphite was chosen because of its many qualities that make it an ideal mould material. The good properties of graphite at high temperatures, low

coefficient of expansion, non-wettability and non-rusting nature were some of the characteristics that made it the choice. The ease of machining graphite which allows for extremely smooth milled surfaces which in turn eliminates the need for much post-milling processing (polishing) was also another key factor in its choice as a mould material.

During the mould production process, a graphite block was marked showing the cavities to be chopped off using a drilling machine. The hollow cavity was then polished to attain a smooth surface using sand paper of 150, 76 and 60  $\mu\text{m}$ .



Plate 3.1 machined Graphite block.

### **3.5.4 Mixing, Melting and casting of the glass**

The individual batch components which consisted of sand, soda ash, Boron oxide, calcium carbonate, zinc oxide and phosphorous pentoxide in their proportions as shown in a Table 3.1 below were weighed using an electronic

weighing balance of 0.0001g accuracy and then mixed thoroughly in glazed porcelain mortar to ensure proper mixing and also to kick start the process of realizing a homogeneous glass melt.

Table 3.1 showing the compositions of the glasses produced

Batch#	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	B <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	ZnO
1	30	15	20	7.5	30	2.5
2	20	20	20	7.5	30	2.5
3	30	10	25	-	35	-

The mixture was then charged into a ceramic crucible with lid and subsequently heated inside a monolithic solid fuel fired furnace. Firing was carried out slowly to preheat the crucible for 30 minutes in order not to introduce thermal stresses that could cause thermal shock and after which rapid firing was carried out by increasing the voltage of the blower. After firing for another 50 minutes, the batch became molten and a time of 30 minutes was allowed for a reduced viscosity of the melt to enable good flow and mould filling properties during casting of the glass samples.



Plate 3.2 picture of furnace before firing



Plate 3.3 monolithic charcoal furnace firing the glass batch with air supply by a DC powered electronic blower constructed for this work.



Plate 3.4 firing in progress of the glass in a ceramic crucible with lid.



Plate 3.5 after about 2hour of firing crucible is opened showing molten glass.

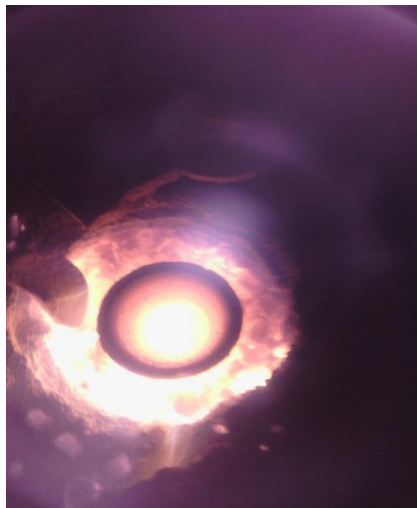


Plate 3.6 firing in progress during the evening hours for sample 2



Plate 3.7 firing of the second sample in progress.

### 3.5.5 Mould preparation for casting

The mould was cleaned to remove dust and other materials which may act as nucleating agents that may cause devitrification of the glass. This was followed by preheating the mould to about 450<sup>0</sup>C this enabled mould filling of the melt inside the cavity.

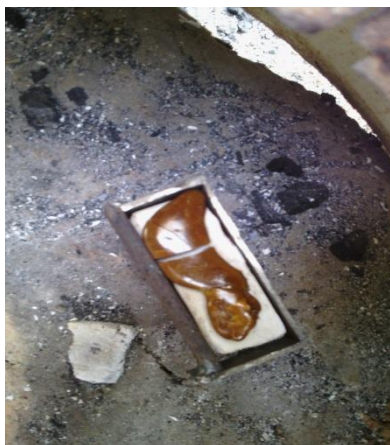


Plate 3.8 another sample contaminated by an iron thong used to open the crucible lid



**Plate3.9** casting of glass slide



**Plate3.10** showing Sample 3 after three days of casting with a heavy white crust on its surface due to atmospheric weathering

### **3.5.6 Annealing of the glass slides and slabs**

The standard process of annealing generally follows that a freshly formed glass is heat treated also referred to as annealing. This is carried out through the gradual heating of the glass to a temperature corresponding the annealing point where thermal stress is relieved. The viscosity corresponding to this is  $10^{12}$ Pa.s in

this work, after casting, a ceramic test kiln was used to anneal the glass at a temperature of 490<sup>0</sup>C for thirty minutes and allowed for uniform distribution of heat and then subsequently allowed to cool to room temperature.



**Plate 3.11**electric test kiln used for annealing

### **3.5.10 Preparation of samples for testing and examination using a strain viewer**

Having annealed the samples, the glass was then examined using a strain viewer. This ensured that there were no stresses that could interfere with the tests to be carried out. The strain viewer was powered and the articles viewed through the viewer. The presence of any available stresses or crack was not detected or noticed by way of colour variations along the samples. This showed that sample A and B were not hygroscopic and could be analysed.

### **3.5.11Grinding and polishing of the samples**

The cast samples from which the slide was obtained were ground where necessary and polished so as to reduce to the barest minimum the phenomenon of light scattering on the surface due to rough or uneven surfaces. Throughout the process of grinding, grit paper of different sizes which included 60,200, 400 and 800 was used. During grinding care was taken not to break the samples. While polishing, an ECOMET polishing machine was used while the powder used was  $\text{Al}_2\text{O}_3$ .

### **3.6 Determination of absorption, transmission and reflection spectra of the glass**

In determining the absorption, transmission and reflection spectra of the glass, a UV36000 Shimadzu UV-VIS-NIR spectrophotometer equipment was used. The glass piece used was ground and polished to a dimension of 75 x 25 x 1mm. The samples were placed on the sample holder and the sample compartment closed and the light source switched on causing the radiation to be focused on the glass. The amount of light transmitted, reflected and absorbed through the glass was recorded by the detector and represented graphically showing the amount of light absorption with respect to wavelength.

The same Shimadzu 3600 spectrophotometer was also used to determine the optical band gap energy of the glass. The refractive index of the glass was then

determined using the relation involving the optical band gap energy and refractive index by Dimitrov and Sakka (1996).

$$\left(\frac{n^2-1}{n^2+2}\right) = 1 - \frac{\sqrt{E_g}}{20}$$

### 3.7 Experimental Setup

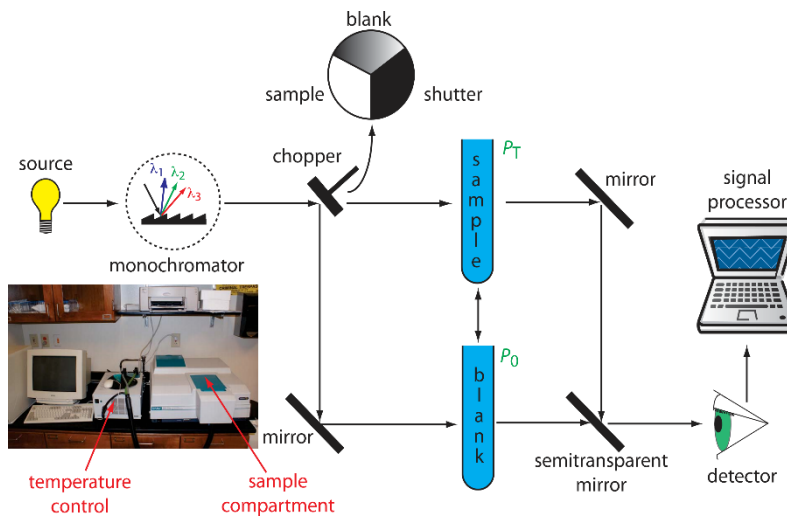


Fig. 3.1 Schematic diagram of a scanning, double-beam spectrophotometer.

In the setup above, a chopper directs the source's radiation, using a transparent window to pass radiation to the sample and a mirror to reflect radiation to the blank. The chopper's opaque surface serves as a shutter, which allows for a constant adjustment of the spectrophotometer's 0% transmission. A scanning monochromator allows for the automated recording of spectra.

## Chapter Four

### 4.0 Results and Discussion

#### 4.1 X-ray diffraction results of clay used for glass melting crucible

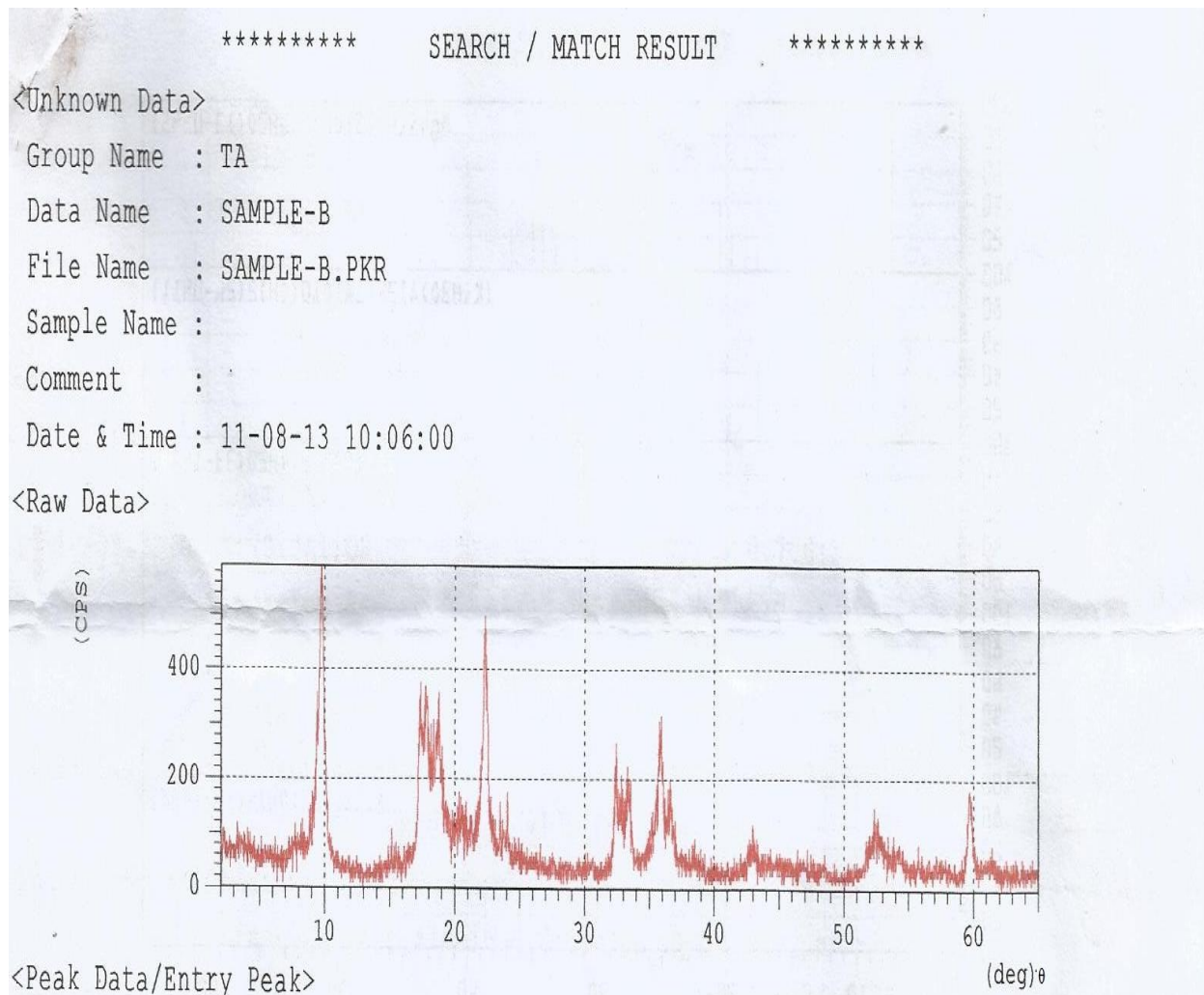


Fig. 4.1 X-ray diffractogram of Vandekya clay used as crucible material

## 4.2 X-Ray Diffraction results of the glass samples

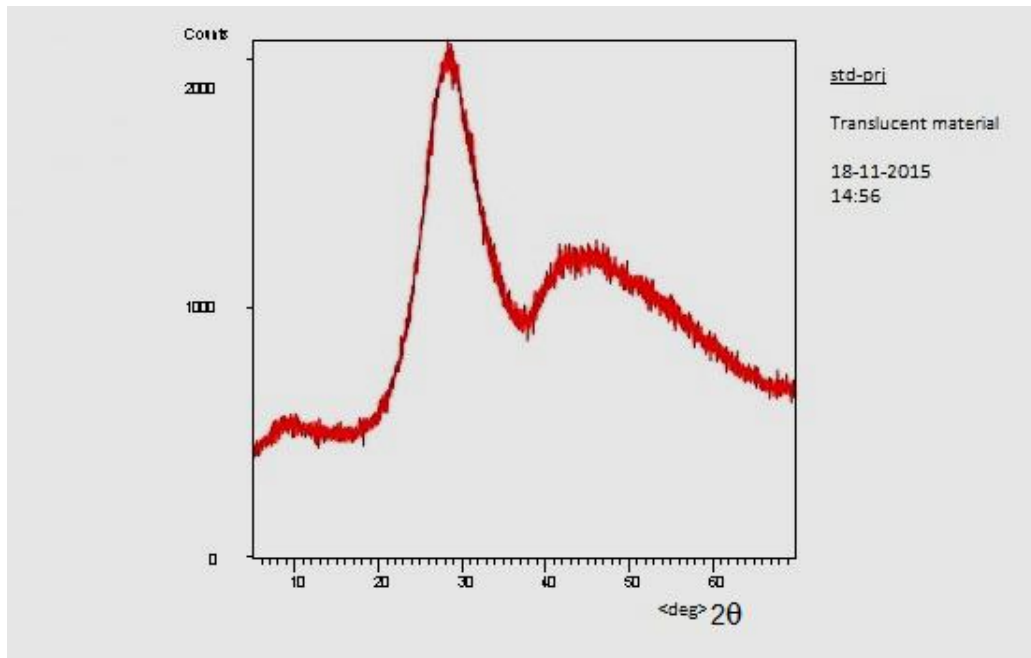
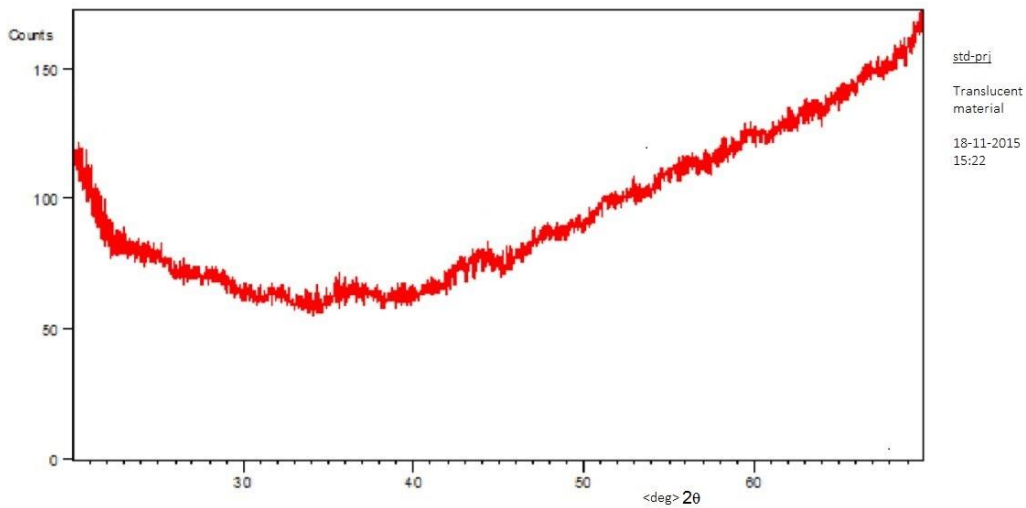


Fig. 4.2 XRD patterns of sample 1

Fig. 4.2 above shows the XRD patterns of the glass sample 1. It reveals a diffuse scattering at different angles of  $2\theta$  which is characteristic of an amorphous material.



### **Fig 4.3 XRD patterns of sample 2**

Fig. 4.3 above also shows the XRD pattern of sample 2. This also reveals a broad diffuse scattering without defined peaks which is also characteristic of an amorphous material.

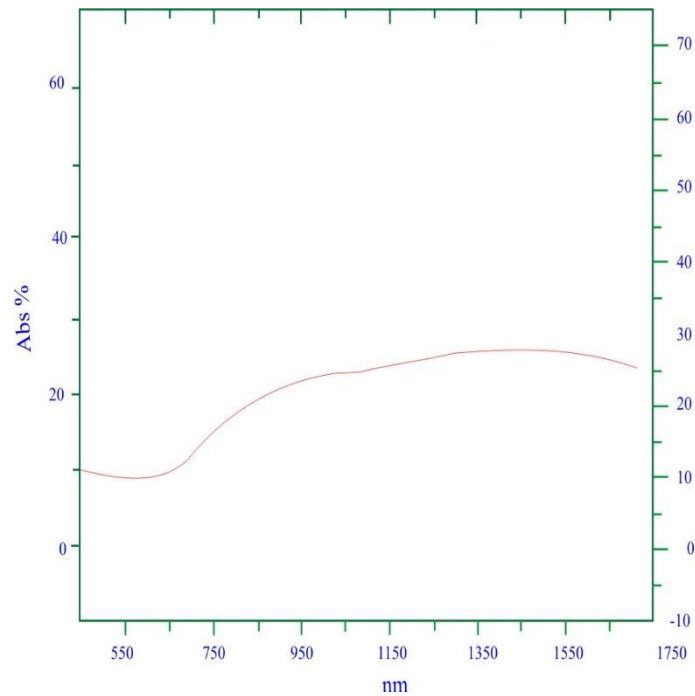
### **4.3 Spectrophotometric results**

Optical absorption in UV, visible and near Infrared regions of the spectrum was carried out on samples with a thickness of 1mm. The different spectra of the glasses were taken using a Shimadzu 3600 UV-VIS-NIR scanning spectrophotometer at room temperature and from the results there showed peak absorption of 28% for sample 1 and 58% for sample 2 though sample 2 had multiple peaks. The results obtained from the analysis are shown in Fig. 4.4 and Fig. 4.5

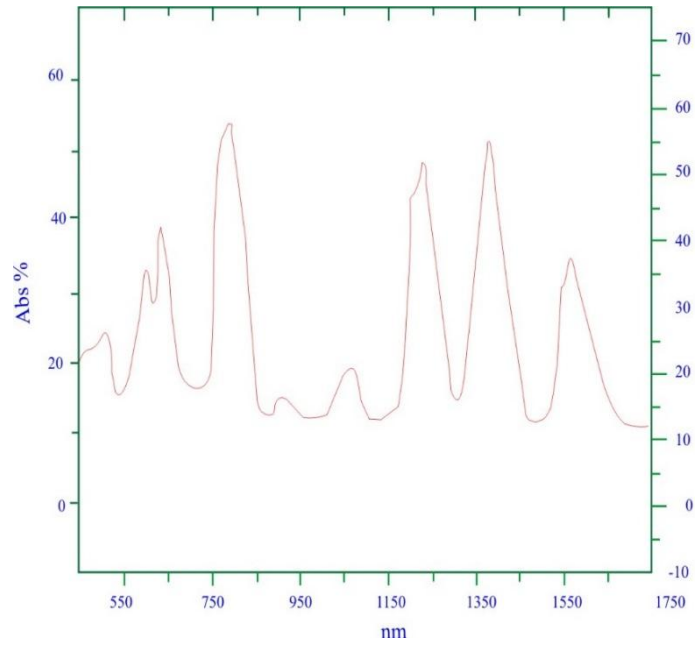
#### **4.3.1 Absorption**

The optical absorption spectra provides very useful information for the investigation of optically induced transitions and an insight into the optical energy gap and the band structures of crystalline, non-crystalline materials and semi-conductors. With the absence of a sharp absorption edge on the spectral properties of sample 1, it corresponds to the characteristics of the glassy state. Hence sample 1 is glass and therefore an optical glass.

The absorption characteristics of sample 1 show a peak at 28% adsorption at a wavelength of 1450nm which falls within the telecommunication windows in which the presence of hydrogen and hydroxide ions within the glass causes an increase in attenuation. While its lowest absorption was recorded at a wavelength of 610nm. From the result this glass will be most suitable for optical applications operating at wavelengths in the region of its peak absorption of 1430nm and 1470nm which falls between the s-band and c-band of the optical communications windows.



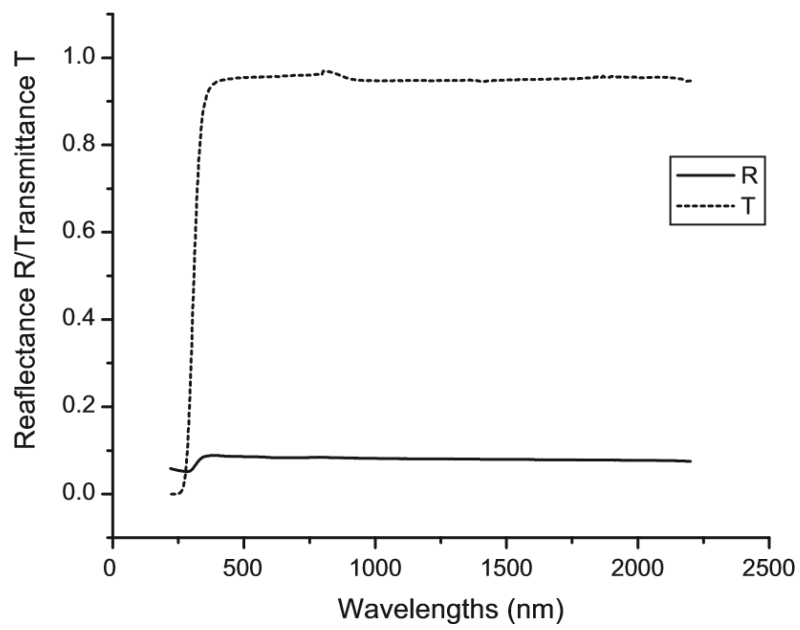
**Fig. 4.4** Absorption spectra of sample 1



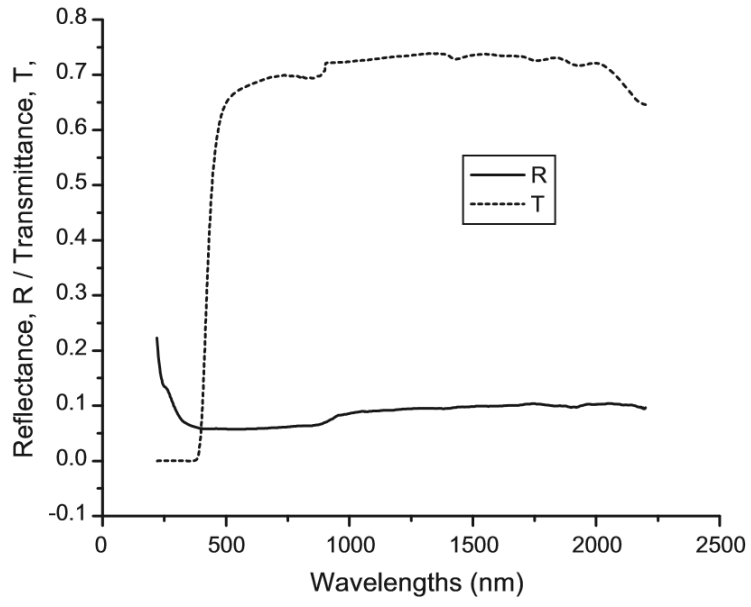
**Fig 4.5** Absorption spectra of sample 2.

For sample 2, the spectra shows an absorption peak at about 58%. This could be beneficial because glasses with high absorption are good in attenuating lasers and other light sources where the power cannot be adjusted or reduced.

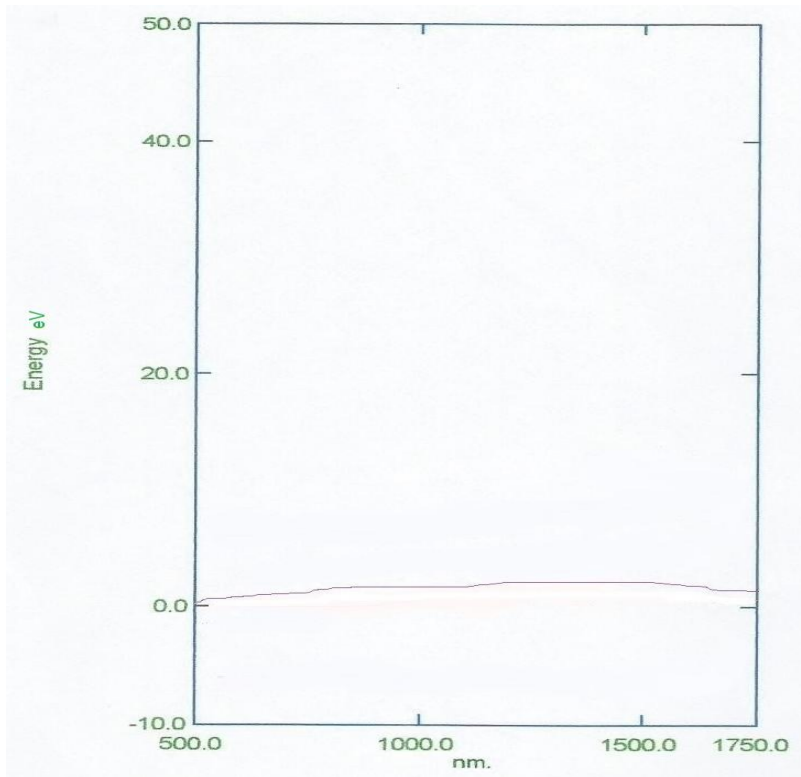
#### 4.4 Transmission



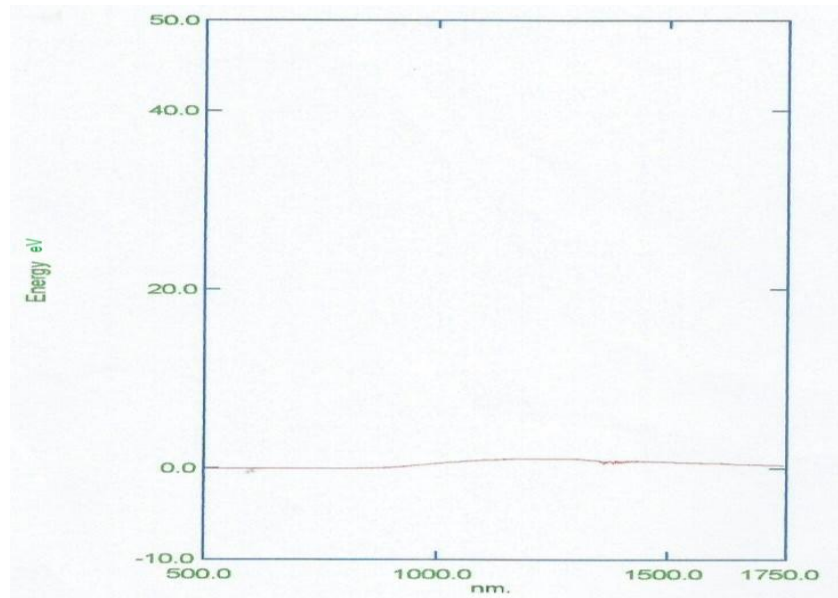
**Fig.4.6** Transmission and reflection spectra of sample1



**Fig4.7** Transmission and reflection spectra of sample 2



**Fig. 4.8** Energy gap plot of sample 1



**Fig. 4.9** Energy gap plot of sample 2

From the optical band gap of the two glass samples determined, the optical band gap of sample 1 from the plot was found to be 2.2 eV while that of sample 2 was found to be 1.9 eV. This decrease in the optical band gap energy of the two glasses sample 1 and sample 2, could be as a result of an increase in  $\text{SiO}_2$  content or a decrease in  $\text{P}_2\text{O}_5$  content in sample 1. While a decrease in the optical band gap in sample 2 could be as a result of a decrease in the  $\text{SiO}_2$  content of the sample. However, sample 3 would have confirmed either of these possibilities if it had sufficient chemical durability.

Following the determination of the optical band gap energies of the samples, the refractive indices of the two samples was then calculated using four different

relationships proposed in the literature by the authors Kumar & Singh (2010), Dimitrov&Sakka (1996) and Ravindra et al (1979).

Table 4.1 Calculated refractive indices of samples 1 and 2 using the relationships proposed by Kumar & Singh, (2010), Reedy et al, (2008),Dimitrov&Sakka (1996) and Ravindra et al (1979).

Refractive index relation	Kumar&Singh (2010)	Dimitrov&Sakka (1996)	Ravindra et al (1979)	Reedy et al (1998)	Optical band gap energy
Mathematical relations	$n=KE_g^c$	$(n^2-1/n^2+2) = 1 \frac{\sqrt{E_g}}{20}$	$n=4.08-0.62E_g$	$n = \sqrt{\frac{12.417}{E_g-0.365}}$	
Sample 1	2.611	2.65	2.716	2.601	2.2eV
Sample 2	2.737	2.78	2.94	2.84	1.9eV

From the table of results of the optical bandgap and calculated refractive indices of the glass samples, it is clear that composition affects the refractive index of a base glass as shown in the variation of the optical bandgap energy 'E<sub>g</sub>' and refractive index 'n' of sample 1 and sample 2 across all the expressions used in the calculations of refractive index. These values are fairly in agreement with proposed

models for calculating refractive indices of materials in the form of semiconductors, oxides, halides and non-transparent glasses.

## Chapter Five

### 5.0 CONCLUSION, RECOMMENDATIONS AND CONTRIBUTION TO KNOWLEDGE

#### 5.1 Conclusion

In this study, on the Development and evaluation of the optical properties of glass produced using Otamiri sand such as absorption, transmission and reflection of glass prepared using Otamiri silica sand, three glass samples were successfully prepared using the melt quenching technique. The results can be summarized as follows:

1. The glass so produced was translucent in the case of sample 1, opaque in the case of sample 2 and transparent in that of sample 3. However, sample three had insufficient chemical durability and as such had a thick white crust covering it and optically characterizing it would be unproductive. The white crust could be as a result of the reaction of the glass sample with atmospheric moisture.
2. There showed in sample 2, multiple absorption peaks could possibly be due to multiple absorption centers in the glass matrix.
3. A combination of three glass forming oxides was used as batch material to determine its optical characteristics as substitute for rare earth metals and sample 1 showed good absorption between 1430 and 1470 nm which is in the infrared region.

4. The energy gap of the samples was found to be 2.2eV for sample 1 and 1.9eV for sample 2, which was then used to calculate the refractive index for both samples using different relations.

## **5.2 Recommendations**

From the findings made in this work, it has been observed that the refractive index which is a paramount optical property in the design of optical instruments can be enhanced through the incorporation of optically active ions to modify the structure of the network former. It is therefore recommended that in order to ensure acceptable results, a close control of the melting conditions which include furnace atmospheres (either reducing or oxidizing) which affect the glass redox of the various oxides in the batch makeup can be improved upon.

It is also recommended that better crucible materials be used with minimal contamination. Contamination of the glass with undesired oxides affect glass forming ability, favors devitrification and reduces absorption characteristics which is a deviation from the basic characteristics of optical glass.

### **5.3 Contribution to knowledge**

The refractive indices calculated is in fair agreement with other expressions used in determining the refractive index of some semiconducting materials.

The Otamiri sand has a potential for applications particularly in illumination of large surface areas in light scattering devices and which can have applications in the fields of light emitting diodes (LED) and also the Otamiri sand contains a low and acceptable level of iron impurity therefore can be useful in the production of glass for optical applications.

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