GLASSES AND GLASS CERAMICS AS BIOMATERIALS

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Submitted By

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CERTIFICATE

This is to certify that the Seminar report entitled ***"Glasses and glass ceramics for biomedical applications"*** *submitted by Mr. Sachin Tyagi in the final fulfillment of the requirement for the award of the degree of M. Tech in Materials Science and Engineering from the School of Physics and Materials Science, Thapar Institute of Engineering and Technology (Deemed University), Patiala, is record of candidate's own work carried out by him under my supervision and guidance. The matter embodied in this report has not been submitted in part or full to any other university or institute for the award of any degree.*

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Abstract

Glasses are playing a very vital role in the progress of society. It finds application not only in the domestic front as well as in the field such as telecommunication, architecture, automation etc. Recently a new class of glasses is being developed i.e. bioactive glasses and glass ceramics. Glass ceramics can have superior properties such as high mechanical strength and impact resistance as compared to their counterpart. Now-a-days glasses are being used as a bone substitute as they have tendency to form the direct bond with the living tissue after implanting in the human body. In the near future these glasses will be widely used in dental prosthetic, orthopedics and also as a filler material in bone defects

In the present study silica based glasses of different composition have been synthesized by taking appropriate proportion (mol%) of each oxide constituents. The quenched samples were characterized by using the various techniques viz X-Ray diffraction, UV – Visible spectroscopy, weight measurement in SBF solution, density measurement. Amorphous nature of all the as cast samples is confirmed by X-Ray diffraction and band gap is calculated by UV-visible spectroscopy. All the samples were dipped in simulated body fluid (SBF) solution and their change in density, weight, pH of solution and band gap are also examined. The formation of hydroxyapatite layer on the glass sample surface is also analyzed by X-ray diffraction, weight (loss/ gaining) of glass samples, change in pH of solution, change in band gap of sample before and after dipping.

Accomplished with the blessings of

Lord Shiva

&

Dedicated to

My Beloved Parents

Sh. N. S. Tyagi & Smt. Yashoda Tyagi

Chapter- 1

INTRODUCTION

1.1 Introduction to Glasses

1.2 Introduction to Glass and Glass ceramics as Biomaterials

1.3 Applications of Bioglasses

CHAPTER1. INTRODUCTION

1.1 Historical Background

No one is certain where, when or how glass originated. It may have appeared first in the Middle Eastern regions such as Egypt and Mesopotamia around 3000 to 2000 B.C although there are hints of gazing on pottery as early as 8000 B.C. Egyptian craftsmen developed a method for producing glass vessels around 1500 B.C. About 2000 years ago, Syrian craftsmen invented glassblowing, a skill adopted by the Romans, who carried it with them as they swept through Western Europe on their conquest. The rise of Venice to prominence in the 13th century, Venice becomes the center of glassmaking in the western word. As the industrial revolution gathered momentum, new manufacturing technologies enabled the production of scientific glass instruments, bottles, windowpanes, and many other items.

Historically [1], glass has been used in five different ways, which varied depending on the locality. Glass beads, counters, toys, and jewelry are produced almost universally throughout Eurasia before 1850, with glass becoming substitute for precious stones. The great developers of glass vessels, vases, and containers were the Italians, Romans and later the Venetians. The use of glass vessels was largely restricted to the western part of Eurasia until the 1850s with little evidence of use in India, China, and Japan.

Another important use of glass was for making window. Until the 20th century, window glass was found manly in the western regions of Eurasia (principally north of the Alps), appearing rarely in China, Japan, and India. Another application of glass depended on its reflective capacity when silvered produced by the Venetians in the 16th century, the use of glass mirrors spread throughout the whole of western Europe but appeared rarely if at all in Islamic civilizations or in India, China or Japan. A final critical application of glass was in the production of lenses and prisms. This led to the manufacture of spectacle to improve human sight; eyeglasses first appeared in Europe during the 13th and 14th centuries. All Eurasia Civilizations probably knew the concept of glass, discovered by the Chinese in the 12th century. Yet only in Western Europe did the practice of making lenses. This coincides precisely with the surge in interest in optics and mathematic during medieval time, which fed into other branches of learning, including architecture and painting.

The reasons for the different uses of glass in different parts of the world may be largely accidental, reflecting variations in climate, drinking habits, availability of pottery, political events and many other characteristics. Intention, planning individual psychology individual psychology¸ Superior intellect or better resources seems to have little to do with it yet these accidents instigated the move of western European societies around the knowledge innovation-quantification triangle. Improvements in glassmaking and the production of more sophisticated glass instruments yielded more accurate information about the natural and physical worlds, which fed back into refinements in glass manufacture and, hence, in glass quality.

1.2 Glasses

All glasses found to share two common characteristics. First, no glass has a long range, periodic atomic arrangement. Even more importantly, every glass exhibits time-dependent glass transformation behavior. This behavior occurs over a temperature range known as the glass transformation region. A glass can thus be defined as "an amorphous solid completely lacking in long range, periodic atomic structure, and exhibiting a region of glass transformation behavior." Any material, inorganic, organic, or metallic, formed by any technique, which exhibits glass transformation behavior is a glass.

1.3 Enthalpy-Temperature Diagram

We have established that any material, which exhibits glass transformation behavior, is a glass. What, then, is glass transformation behavior? We traditionally discuss glass transformation behavior on the basis of either enthalpy or volume versus temperature diagrams, such as that shown in figure: 1.1 since enthalpy and volume behave in a similar fashion, the choice of the ordinate is somewhat arbitrary. In either case, we can envision a small volume of a liquid at a temperature well above the melting temperature of that substance. As we cool the liquid, the atomic structure of the melt will gradually change and will be characteristic of the exact temperature at which the melt is held. Cooling to any temperature below the melting temperature of the crystal would normally result in the conversion of the material to the crystalline state, with the formation of a long range, periodic atomic arrangement. If this occurs, the enthalpy will decrease abruptly to the value appropriate for the crystal. Continued cooling of the crystal will result in a further decrease in enthalpy due to the heat capacity of the crystal.

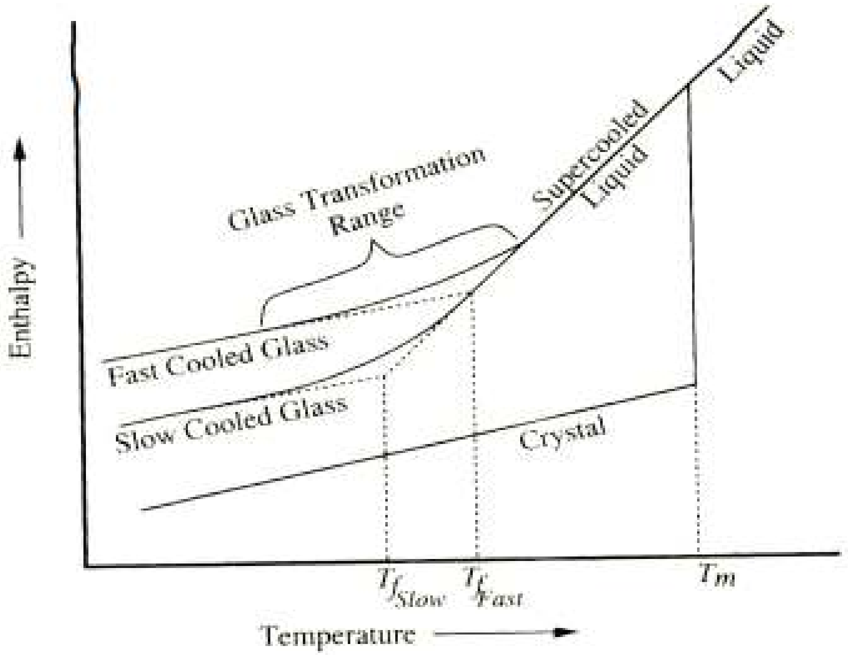

Figure: 1.1 Effect of temperature on the enthalpy of a glass forming melts

If the liquid can be cooled below the melting temperature of the crystal without crystallization, a super cooled liquid is obtained. The structure of the liquid continues to rearrange as the temperature decreases, but there is no abrupt decrease in enthalpy due to discontinuous structural rearrangement. As the liquid is cooled further, the viscosity increases. This increase in viscosity eventually becomes so great that the atoms can no longer completely rearrange to the equilibrium liquid structure, during the time allowed by the experiment. The structure begins to lag behind that which would be present if sufficient time were allowed to reach equilibrium. The enthalpy begins to deviate from the equilibrium line, following a curve of gradually decreasing slope, until it eventually becomes determined by the heat capacity of the frozen liquid, i.e., the viscosity becomes so great that the structure of the liquid becomes fixed and is no longer temperature-dependent. The temperature region lying between the limits where the enthalpy is that of the equilibrium liquid and that of the frozen solid is known as the glass transformation region. The frozen liquid is called glass or supercooled liquid.

Since the temperature where the enthalpy departs from the equilibrium the viscosity of the liquid controls curve. i.e., by kinetic factors, use of a slower cooling rate will allow the enthalpy to follow the equilibrium curve to a lower temperature. The glass transformation region will shift to lower temperatures and the formation of a completely frozen liquid, or glass, will not occur until a lower temperature. The glass obtained will have a lower enthalpy than that obtained using a faster cooling rate. The atomic arrangement will be that characteristic of the equilibrium liquid at a lower temperature than that of the more rapidly cooled glass.

As indicated above, the glass transformation occurs over a range of temperatures and cannot be characterized by any single temperature. It is, however, convenient to be able to use just such a single temperature as an indication of the onset of the glass transformation region during heating of a glass. This temperature, which is termed either the glass transformation temperature, or the glass transition temperature, (Tg), is rather vaguely defined by changes in either thermal analysis curves or thermal expansion curves. The values obtained from these two methods, while similar, are not identical. The value obtained for T is also a function of the heating rate used to produce these curves. Since Tg is a function of both the experimental method used for the measurement and the heating rate used in that measurement, it cannot be considered to be a true property of the glass. However, Tg is a useful indicator of the approximate temperature where the super cooled liquid converts to a solid on cooling, or, conversely, of which the solid begins to behave as a viscoelastic solid on heating.

1.4 CONSTITUENTS OF GLASSES

In general, glasses are either produced from high quality, chemically pure components, or from a mixture of far less pure minerals. Regardless of the source of the components used to produce a specific glass, the batch materials can be divided into five categories on the basis of their role in the process are:

1) Glass former
2) Flux
3) Property modifier
4) Colorant
5) Fining agent.

The same compound may be classed into different categories when used for different purposes. Alumina, for example, serves as a glass former in aluminate glasses [2], but is considered a property modifier in most silicate glasses [2].

The most essential component of any glass batch is always the glass former. Every glass contains one or more components which serve is the primary source of the structure. While these components are commonly designated as glass formers, they are also called net work formers, or glass forming oxides in many oxide glasses. The identity of these components usually serves as the basis for the generic name used for the glass. If most of the glass former present in a specific sample is silica, for example, that glass is called a silicate. If a significant amount if boric oxide is also present, in addition to silica, the sample is termed borosilicate glass.

The primary glass formers in commercial oxide glasses are silica (SiO_4, boric oxide (B_2O_3). and phosphoric oxide (P_20_5), which all readily form single component glasses. A large number of other compounds may act as glassformers under certain circumstances, including GeO,Bi_2O_3, As_2O_3, Sb_2O_3 TeO_2, Al_2O_3, Ga_2O_3, and V_2O_5.

Adding certain other materials can do the alteration in the properties of glass forming material which are Known as property modifier such as alkaline earth and Transitional metal oxide, and most importantly Alumina oxide.

Colorants are used to control the color of the final glass. In most cases, colorants are oxides of either the 3d transition metals or the 4f rare earths elements. Uranium oxides were once used as colorants, but their radioactivity obviously reduces their desirability for most applications. Gold and silver are also used to produce colors by formation of colloids in glasses. Colorants are only used if control of the color of the glass is desired, and are usually present in small quantities. Iron oxides, which are common impurities in the sands used to produce commercial silicate glasses, act as unintentional colorants in many products. When colorants are used to counteract the effect of other colorants to produce a slightly gray glass, they are referred to as decolorants.

Finally, fining agents are added to glass forming batches to promote the removal of bubbles from the melt. Fining agents include the arsenic and antimony oxides, potassium and sodium nitrates, NaCl, fluorides such as CaF_2, NaF, and Na_3AlF_6, and a number of sulfates. These materials are usually present in very small quantities (< 1 wt%), and are usually treated as if they have only minor effects on the properties of commercial glasses, which would be prohibitively expensive to produce without the aid of fining agents in reducing the content of unwanted bubbles in the final product.

1.5 Glass structure and its determination

The most useful experimental techniques for studying the structure of glasses are X-Ray diffraction, neutron diffraction, infrared and Raman spectroscopy. Techniques such as nuclear magnetic resonance, X-ray photoelectron spectroscopy or electron spectroscopy for chemical analysis and X- ray absorption fine structure with longer wavelength X-ray are useful for special structural studies, especially to determine the coordination numbers of atoms in glasses.

The most important constituent of glasses are silicates. The building blocks of all silicates both crystalline and amorphous are the rigid silicon oxygen tetrahedron. In silicates glasses silicon oxygen bonds in three-dimensional network link these tetrahedral. The network can be partially broken up by other oxides like alkali and alkaline earth oxides, which are called network modifiers

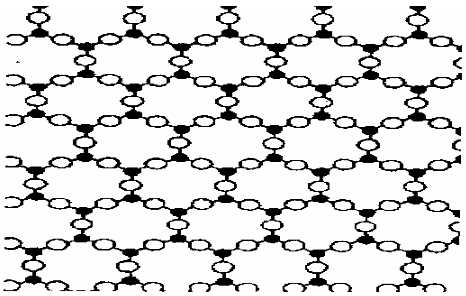

Figure. 1.2 Molecular arrangement in a crystal

From the detailed study of X-ray diffraction study of pure amorphous silica, [2] have concluded that its structure could be described as a random network. In this model the rigid silicon oxygen tetrahedral are linked into a three dimensional network; randomness results from a distribution of silicon-oxygen-silicon bond angles around an average value of 144°.The distribution of angles around the maximum is rather narrow compared to a completely random distribution of bond angles from 90° to 180°. Thus the structure of amorphous silica is quite uniform at atomic distances, although there is no order beyond several layers of tetrahedral.

In silica glasses containing alkali and alkaline earth oxides, these cations apparently are not randomly distributed throughout the glass; their average separation less than from a uniform distribution. It is possible that alkali ions form in sheets, as they in certain crystalline alkali silicates. This intermediate range structure has been emphasized in recent studies of multicomponent silicates glasses and other compositions such as sulfides and selenides.

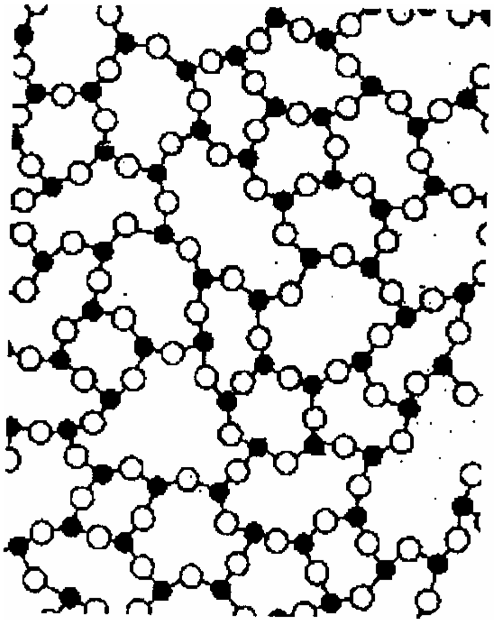

Figure.1.3 Molecular arrangement in a glass

The structure of glassy metals with no more than a few percent of impurities can be described as a dense random packing of hard spheres. The packing fraction is 0.637, compared with 0.74 for close packing of spheres of the same size in a crystalline structure, such as face-centered cubic and close-packed hexagonal. This model fits the radial distribution from scattering experiments.

The structures of amorphous alloys of compounds M_4X, in which M is a transition or noble metal and X a nonmetal, have been extensively studied. The best model seems to be slightly distorted dense random packing of hard spheres for the M atoms, with the X atoms located interstitially in polyhedral in the structure.

The structure of zirconium fluoride glasses is of special interest because it is quite different from that of silicate glass-forming. Coordination numbers of 7 and 8 for zirconium atoms have been deduced from X-ray radial distribution functions and molecular-dynamics calculations, and several different structures have been proposed for these glasses.

1.6 classification of Glasses

Depending upon chemical composition, a large number of glasses with different chemical and physical properties can be prepared. Chemical composition is chosen depending upon the required application of prepared glass. Oxide glasses have considerable potential advantages over non-oxide materials because non-oxides readily react with water and atmospheric oxygen to form oxides. On the basis of chemical compositions, glasses can be divided into following categories:

1.6.1 Silicate Glasses

Most of the commercially made glasses are based on silica (SiO_2). Besides silica, glasses also contain other oxides like CaO, Na_2O, K_2O and Al_2O_3, which influence their properties. Among various types of silicates glasses vitreous silica is the most refractory glass in commercial use. It has high chemical resistance to corrosion, a very low electrical conductivity, a near zero coefficient of thermal expansion and good ultra violet (UV) transparency on the other side, It has high cost of manufacture and uses are limited to astronomical mirrors, optical fibers and crucibles for melting. Soda-lime glasses are the most common form of commercial silicate glass and least expensive. These usually contain 60 – 70% silica (SiO_2), 12 – 18% soda (Na_2O) and 5 – 10% lime (CaO). Soda-lime glasses are mainly use for windows because they transmit a high percentage of visible light. They are also used as glass containers as they are virtually inert hence can't contaminate the inside components. The main disadvantage of these glasses is that they have high value of thermal expansion. Soda-lime silicate glasses have received lots of attention for medical application as bioactive glasses.

Small amount of alkali added to silica and boron make a family of borosilicate glasses having low thermal expansion and high resistance to chemical attack. They are mainly used in pipelines, light bulbs, sealed-beam headlights, laboratory and cooking. The silicate glasses containing PbO and SiO_2 as the principal components with small amount of soda are termed as lead silicate glasses. These glasses are utilized in microelectronics for their high degree of brilliance, large working range and high electrical resistivity. Aluminosilicate glasses contain an average of 20% Al_2O_3 in addition to other oxides like magnesium oxide, boric oxide, calcium oxide and soda. Their softening point is higher (915^0C) than other oxide glasses so they are used in high temperature applications. Compared to borosilicate, alumonosilicates are more difficult to fabricate due to high melting point of constituents. They are also used in applications, where chemical resistance is important. These glasses are very expensive. A major commercial use of this system is high efficiency lamps inside an automobile halogen headlamp where the glass can be sealed directly to molybdenum electrical leads.

1.6.2 Halide Glasses

Halide glasses are based entirely on heavy metal inorganic fluorides. The most studied chemical composition is the "ZBLA" glass which comprises 57ZrE. $36BaF_2$. 4 LaF_3 $3AIF_3$ (mol %). These glasses are used in mid-IR transmitting short-haul sensors but these glasses are extremely prone to crystallization.

1.6.3 Chalcogenide Glasses

These glasses are obtained by melting group VI elements with one or more group V and IV elements. Compositions modified by adding halogens are called "chalcohalides". These glasses show semi conducting behavior, photoconductivity and IR transmitting properties.

The photoconductivity is utilized for photocopying. Chalcogenides are more resistive to water attack then halides. Thus, it may be used as mid-IR sensor.

1.6.4 Metallic Glasses

Metallic glasses are non crystalline materials composed of either pure metals or combination of metal and metalloids. These glasses have electrical, optical and magnetic properties like metals. Glasses are made in the form of thin tapes or fibers using very high speed quenching techniques and are used inside thermonuclear reactors because of their amorphous nature makes them less susceptible to radiation damage.

1.6.5 Phosphate Glasses

Phosphate glass has been researched for over one hundred and fifty years [3], however, despite P_2O_5 being one of the four classic Zachariasen glass forming oxides (along with SiO_2, GeO_2 an B_2O_3), the nature of the glass, its applications, research and development have been limited due to its hygroscopic nature. It was not until the addition of at least 30 mol. % of metal Oxides was found to improve the durability of the glass significantly and its possible applications were actively pursued after that .

These glasses have a very high transmission in the ultraviolet region, low thermo-optical coefficient and large emission compared to silicate glasses [4]. So, these are suitable materials for high power laser. Phosphate glasses are also attractive as glass-metal seals due to their low melting temperature, low viscosity and high thermal expansion coefficients. The lack of durability of some phosphate glasses was utilized to find elemental deficiencies in cattle and sheep [5,6].

1.6.6 Borate Glasses

In borate systems, melts of composition that are rich in B_2O_3 show a high viscosity and a marked tendency to glass formation. It allows the preparation of glasses that may posses interesting physical properties for optical applications. Addition of heavy metal oxides (HMO) increase density of glass system and finds applications in scintillator materials for high energy particle and medical imaging, poled second order nonlinear optoelectronics such as laser host fibers for communication and photonic switches, third order harmonic light generation and glazes. Recent researches [7,8] have demonstrated that silica free alkali-calcium borate glasses also exhibit bioactive behavior, and it can be used as a possible alternative for some of biomedical applications.

1.7 Properties of Glasses

The special properties of glasses are related to their liquid like structure. The property of transparency is a character of liquids than that of solid state. Glasses are isotropic and lack internal grain boundaries or structural elements lying in specific orientations. Some of the special properties of glasses are listed as follows:

1.7.1 Optical Properties

The major technological developments that have added to the comfort of living are glass lenses as an aid to failing vision, glass windows to bring daylight into housing structure while providing protection from the harsh elements of nature, glass in the light bulb to provide light in dark and glass fibers for enhanced communication. The glass fiber communication is based upon the refractive index, optical dispersion and transmission properties in infrared region of spectrum. Silicate glasses have relatively small index of refraction due to absence of non-bridging oxygen atoms. In case of alkali silicate glasses, non-bridging oxygen ions with higher polarizability are present, which result an increase in the index of refraction with rising alkali content. An increase in the refractive index has also been observed with increase in the composition of the oxides like CaO, MgO, ZnO, PbO and B_2O_3. Besides composition, the refractive index of a glass also depends upon the rate of cooling. A glass cooled at higher rate will have high index of refraction than a well-annealed glass at room temperature.

1.7.2 Physical Properties.

Density of a glass is a strong function of its composition and most important measure of a glass. It also stands on its own as an intrinsic property capable of casting light on short range structure. The addition of network modifier component increases the density as the network modifier ions attempt to occupy the interstices within the network. The addition of alkalis to SiO_2 results in an increase in density.

1.7.3 Electrical Properties

Electrical properties of glasses are most important to be studied for their applications in electrical and electronic industries. A substance is said to be electrically conducting when free electrons or ions within it make the flow of current possible. This property is characterized by the parameter called electrical conductivity, which is reciprocal of resistivity. The electrical conductivity of a glass changes due to the presence of network modifiers. Glass, which does not contain any modifier posses a very less conductivity as compared to the crystalline counterpart. Vitreous silica and pure B_2O_3 glasses fall under this category. The strength of the bond of the ions in the network and their size influence the electrical properties. On the basis of electrical properties [2], glasses can be categorized as follows:

(i) Glasses with very small conductivity (high resistivity).
(ii) Glass with very high ionic conductivity and low electronic conductivity.
(iii) Glasses with electronic conductivity only.

Glasses with very high resistivity are generally used as an insulator. The glasses of this type are free from network modifiers. Glasses having high ionic conductivity can be prepared by the use of network modifiers, which generally have a small ion radius. The composition of the glass also plays an important role for such type of glasses. When the oxygen ions are replaced by sulphide ions, then the prepared glass contains open structure and hence an improvement in the ionic conductivity are obtained by the proper choice of the elements and are called semi-conducting glasses. They contain large amount of transition elements that can occur in several valences like Fe, Co, Mn, V etc. For example V can occur as V^{5+} ion as well as V^{4+} ion. The electronic conductivity is obtained by the transition of an electron from V^{4+} ion to an adjacent V^{5+} ion. Besides these glasses. Chalcogenide glasses also show semi-conducting properties than mainly contain elements like S, Se and Te.

1.7.4 Mechanical Properties

Glasses are brittle materials as a result fracture behavior is usually determined by environmental factors and not by the inherent strength of the bonds forming the vitreous network. The fracture strength of glasses varies with prior surface treatment, chemical environment and inherent stress etc. The glasses are also quit susceptible to failure due to thermal shock. Other mechanical properties of glasses are inherent to the material. The elastic modulus is determined by the individual bounds in the material and by the structure of the network. The hardness of glasses is a function of the strength of individual bonds and density of packing of the atoms in the localized structure.

1.7.5 Thermal Properties

The expansion and the contraction due to thermal energy is an important consideration for product design. When a glass is heated it expands. If the temperature over the body of glass is equal everywhere and body is not restrained then there will be no development of stress in the body. On the other hand if there is non uniform heating of the body, then the different layers of glass will attempt to expand differently and consequently stress develop. The magnitude of stress so generated is related to thermal expansion. Thermal expansion of glasses with few exceptions increases with increase in temperature. Vitreous silica display negative thermal expansion coefficient over a temperature range of 227-727°C. The negative thermal expansion coefficients are believed to result from the ability of the network to absorb lattice expansions through bending of bonds into empty interstices of the structure. The addition of alkali to silica network breaks up the oxygen bridges, resulting in monotonically increasing thermal expansion coefficient. Addition of modifier ions to glass network prevents bond bending and hence increase thermal expansion coefficient. The large thermal expansion coefficient of vitreous boric oxide is due to two dimensional nature of the structure of glass and weak bonding in there dimensions. Addition of alkali oxides to borate network shows borate anomaly.

1.7.6 Chemical Properties

Glass is much more resistant to corrosion than other materials, so much so that it is easy to think of it as corrosion-proof. Glass windows after several years of exposure to sunlight and atmosphere remain clear and apparently unaffected. Glass bottles hold wide range of liquids that would dissolve other materials. In the laboratory, reactions are carried out in glass beakers and flasks without damage to the beaker or contamination of the solution reacting.

But, in spite of these indications that glass is indestructible by chemical attack, under certain conditions it will corrode, even dissolves. In these cases, it is important to choose the right type of glass, since some are more corrosion resistant than others. Only a few chemical aggressively attack glass, i.e. hydrofluoric acid, concentrated phosphoric acid (when hot, or when contains fluorides), hot concentrated alkali solutions and superheated water. Hydrofluoric acid is the most powerful of this group; it attacks any type of silicate glass. Other acids attack only slightly; the degree of attack can be measured in laboratory tests but such corrosion is rarely significant for acids other than hydrofluoric and phosphoric.

Acids and alkali solution attack glass in different way. Alkali attack the silica directly while acids attack the alkali in the glass. Corrosion by water is similar to acid corrosion in that alkali is removed from the glass surface. Water corrosion acts at a much slower rate. At high temperatures, however, water corrosion can be become significant. Many factors influence the rate of corrosion and no laboratory test is capable of predicting behavior under all conditions. Corrosion plays an important role in characterizing the glasses as it helps in determining the bioactive properties of the glasses.

The properties of glass can be varied and regulated over an extensive range by modifying the composition, production techniques or both. In any glass the mechanical, chemical, optical, and thermal properties cannot occur separately. Instead, any glass represents a combination of properties. Selecting an individual glass for an application, it is its initial constituents that it important. Usually, one property cannot be changed without causing a change in the other properties. It is the art of the glass scientist to produce the most favorable combination of properties.

1.7.7 Viscosity

The kinetic model of glass formation indicates that the temperature dependence of the viscosity plays a major role in determining the ease of glass formation for any melt. Glasses are most easily formed if either (a) the viscosity is very high at the melting temperature of the crystalline phase which would form melt or (b) the viscosity increases very rapidly with decreasing temperature. In either case, crystallization is impeded by the kinetic barrier to atomic arrangement which results from a high viscosity. Viscosity is also very important in determining the melting condition to form a bubble-free, homogenous melt, the temperature of annealing to remove internal stress and the temperature range used to form commercial products. The range of the viscosity is very wide and it is not possible to make measurements over the whole range by any one method. At transition temperature (T_g) the viscosity of the glass melt is high as 10^{23} Poise. Viscosity of a glass is affected due to the presence of a modifier. The polarizability or ionic field strength of a modifier affects the viscosity of a glass at high temperature. Low field strength modifiers decrease the viscosity. At low temperature, the coordination number of a modifier also affects the viscosity.

1.8 Glass and glass ceramics as a biomaterials

Hench et al.[9] discovered that bone can bond chemically to certain glass compositions. This group of glasses had become known as bioactive glasses based on the following definition [10]: "A bioactive materials is one that elicits a specific biological response at the interface of the material which results in formation of a bond between the tissues and material". Bioactive glasses have numerous applications in the repair and reconstruction of diseased and damaged tissue, especially hard tissue (bone). One aspect that makes bioactive glasses different from other bioactive ceramics and glass ceramics is the possibility of controlling a range of chemical properties and rate of bonding to tissue. The most reactive glass compositions develop a stable, bonded interface with soft tissues [11]. It is possible to design glasses with properties specific to a particular clinical application. This is also possible with some glass-ceramics, but their heterogeneous macrostructure restricts their versatility

1.8.1 Types of Biomaterial-Tissue Interface

The ideal goal of surgery is to restore the structure and function of the body to its natural state [12]. Bone is a unique tissue which can heal itself without scarring, a process referred to as regeneration. Developers of new materials for bone regeneration applications are faced with the challenge of utilizing this feature.

Even a single material implanted in the living tissues is inert; all materials elicit a response from the host tissue. The response occurs at the tissue-implant interface and depends upon many factors [13], listed in Table 1.1. There are four general types of implant-tissue responses, as summarized in Table 1.2.

It is critical that any implant material avoid a toxic response that kills cells in the surrounding tissues. Released chemicals can migrate within tissue fluids and cause systemic damage to the patient. One of the interests in glass / ceramic implant is their lack of toxicity and corrosion resistive ness.

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Table 1.1 factors affecting implant-tissue interface response

Tissue side	Implant side
Type of Tissue	Composition of Implant
Health of Tissue	Phases in Implant
Age of Tissue	Phase Boundaries
Blood Circulation in Tissue	Surface Morphology
Blood Circulation at interface	Surface Porosity
Motion at Interface	Chemical Reaction
Closeness of Fit	Closeness of Fit
Mechanical Load	Mechanical Load

Table 1.2 Consequences of implant-tissue interaction.

Implant-Tissue reaction	Consequence
Toxic	Tissue dies
Biologically nearly inert	Tissue forms a non-adherent fibrous capsule around implant
Bioactive	Tissue forms and interfacial bound with the implant
Dissolution of implant	Tissue replaces implant

The most common response of tissue to an implant is formation of a non-adherent fibrous capsule. The fibrous tissue is formed in order to "wall of" or isolate the implant from the host. It is a protective mechanism and with time can lead to complete encapsulation of an implant within the fibrous layer. Metals and most polymers produce this type of interfacial response.

Biologically inactive, chemical inertness of alumina or Zirconia, results in a very thin fibrous layer under optimal conditions. More chemically reactive metallic implants elicit thicker interfacial layers. However, it is important to remember that the thickness of an interfacial fibrous layer also depends upon motion and fit at the interface, as well as the other factors indicated in Table 1.1.

The third type of interfacial response, indicated in Table 1.2, is due to bond forms across the interface between implant and the tissue. This is termed as "bioactive" interface. The interfacial bond prevents motion between the two materials and mimics the type of interface that is formed when natural tissue repair themselves. This type of interface requires the material to have a controlled rate of chemical reactivity. An important characteristic of a bioactive interface is that it changes with time, as do natural tissues, which are in a state of dynamic equilibrium.

When the rate of change of a bioactive interface is sufficiently rapid the material "dissolves" or "resorbs" and is replaced by the surrounding tissues. Thus, resorbable biomaterials must be of a composition that can be degraded chemically by body fluids or digested easily by macrophages. The degradation products must be chemical compounds that are not toxic and can be easily disposed of without damage to cells.

1.8.2 Mechanism of Bioactive Bonding

When a bioactive material is implanted in the body, a series of biophysical and biochemical reactions occur at the implant-tissue interface. These reactions eventually result in mechanical strong chemical interfacial bonding [13,14]. This attachment is called "Bioactive Fixation". Hence et al. [9] reported that certain compositions of silicate glasses can form a bond with bone tissue. Research has shown that these bioactive glasses can also bond with certain types of connective tissue through attachment of collagen to the glass surface. The basis of the bone bonding property of bioactive glasses is chemical reactivity of the glass in body fluids, the surface chemical reactions result in the formation of a hydroxycarbonate apatite (HCA) layer to which bone can bond. Bonding occurs due to a sequence of reactions. On immersion of a bioactive glass in an aqueous solution, three general processes occur:

(i) Leaching
(ii) Dissolution
(iii) Precipitation

Leaching is characterized by release, usually by cation exchange with H^+ or H_3O^+ ions, of alkali or alkaline earth elements. Ion exchange is easy because these cations are not part of the glass network, they modify the network by forming non-bridging oxygen bounds. The release of network-modifying ions is rapid for glasses in the bioactive compositional region. This ion exchange process leads to an increase in interfacial pH (>7.4).

Network dissolution occurs concurrently by breaking of –Si-O-Si-O-Si- bonds through the action of hydroxy1 (OH) ions, Breakdown of the network occurs locally and release silica into solution in the form of silica acid [$Si(OH)_4$]. The rate of dissolution of silica depends very much on glass composition. The dissolution rate decreases greatly for the composition of >60% SiO_2 because of the larger number of bridging oxygen bonds in the glass structure. The hydrated silica (SiOH) formed on the glass surface by these reactions undergoes rearrangement by polycondensation of neighboring silanols, resulting in silica-rich gel layer.

In the precipitation reaction, calcium and phosphate ions released from the glass together with those from solution form a calicia-phophate-rich (CaP) layer on the surface. When formed in vitro, the CaP layer is mainly located on the top of the silica gel, whereas in vivo it is formed within the gel layer. The calcium phosphate phase that accumulates in the gel surface is initially amorphous (a-CaP). It later crystallizers to a hydroxycarbonate apatite (HCA) structure by incorporating carbonate anions from the solution within the a-CaP phase. The mechanism of nucleation and growth of the HCA layer appears to be the same in vitro and in vivo and is accelerated by the presence of hydrate silica.

All these process can be summarized by five reaction stages.

Stage 1: Leaching and formation of silanols (SiOH).

Stage 2: Loss of soluble Silica and formaton of silanols.

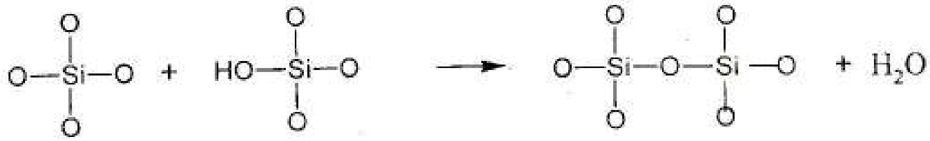
Stage 3: Polycondensation of silanols to form hydrated silica gel.

Stage 4: Formaton of an amorphous calcium phosphate layer.

State 5: Crystallization of a hydroxycarbonate apatite layer.

Table 1.4 summarizes these five reaction stages in detail.

Table 1.3 Reaction stages of a bioactive glass implant

Stage	Reactions
1.	Rapid exchange of Na^+ or K^+ with H^+ or H_3O^+ from solution: $Si\text{-}O\text{-}Na^+ + OH^-$ □ $Si\text{-}OH^+$ Na^+ (solution) + OH^-. This stage is usually controlled by diffusion and exhibits a $t^{-1/2}$ dependence.
2.	Loss of soluble silica in the form of $Si(OH)_4$ to the solution, resulting from breaking of Si-O-Si bonds and formation of Si-OH (silanols) at the glass solution interface: Si-O-Si + H_2O □ Si – OH + OH – Si This stage is usually controlled by interfacial reaction and exhibits a $t^{1.0}$ dependence.
3.	Condensation and repolymerization of a SiO_2-rich layer on the surface depleted in alkalis and alkaline-earth cations: 
4.	Migration of Ca^{2+} and PO_4^{3-} groups to the surface through the SiO_2-rich layer forming a $CaO\text{-}P_2O_5$-rich film on top of the SiO_2 rich layer, followed by growth of the amorphous $CaO\text{-}P_2O_5$-rich film by incorporation of soluble calcium and phosphates from solution.
5.	Crystallization of the amorphous $CaO\text{-}P_2O_5$ film by incorporation of OH^-, CO_3^{2-} or F^- anions from solution to form a mixed hydroxyl, carbonate, fluorapatite layer.

1.8.3 Types of Bioactive Glasses

The bioactive glasses are broadly divided in two classes: Class A and Class B[15].

1.8.3.1 Class A bioglasses

These are materials, which are osteoproductive in nature. They can bond to both soft and hard tissues. They release Si ions in the form of silicic acid, which provides a silica gel layer, which further enhances the precipitation of amorphous CaP layer and also rapidly crystallizes HCA layer. Generally HCA layer is formed within 1-10 hours for this type of materials. Bioglass 45S5 ® (45 wt. % SiO_2, 24.5 wt. % CaO, 24.5 wt. % Na_2O and 6.0 wt. % P_2O_5) is a class A bioactive glass.

1.8.3.2 Class B bioglasses

These are the materials, which are osteoconductive in nature. They don't produce silica gel layer and they only bond to hard tissues. In this type of glasses HCA layer is formed within 24 hours to several days.

1.9 Other Important bioactive materials

The wide diversity of materials currently used in medicine is testimony to the number of advances that have occurred over the past fifty years. Biomaterials can be classified in four categories, namely metals, ceramics, polymers and natural materials (of both plant and animal origin). In addition to this, two classes of materials may be combined to form a composite, which is a fifth class of biomaterials.

1.9.1 Metals

Currently there are three metals used for fixation devices: stainless steel (3.16L), cobalt chromium alloy and titanium, which is either commercially pure of alloyed with vanadium, aluminum and/or niobium. Of these, titanium and its alloys are the most popular for craniofacial use because of its high strength and reduced artifacts on CT and MR imaging [16,17]. Permanent metal fixation implants leave a residual implant within the body, which may cause secondary problems. Metal implants may cause stress shielding and subsequent bone weakening in load bearing applications; implants may be palpable and cause tissue irritation and pain, necessitating their removal. There are also concerns of implant migration and interference with diagnostic and therapeutic applications of radiation [12]. Metallic implants are often darker than the surrounding tissue and may cause discoloration, also, due to the rigidity of metals, it is often difficult to match the implant to the contours of the underlying bone. This may result in implant edges that are visible through the skin [18]. The application of metallic implants close to the skin may result in temperature effects. During cold weather the implant may be cooled sufficiently to cause pain or discomfort [19]. Observations of malignancy in association with metal fixation devices are rare, with only 20 cases reported in the literature [20], with latencies between 1-30 years. Only one was reported to occur above the neck. This implies that the local risk of cancer is low with metallic implants. However, it has been found that there is a significant increase in the risk of systematic tumors, e.g. lymphatic, in patients who have undergone total hip replacement [21]. It should be noted that there are other factors associated with arthritic disease which may have contributed. The release of metal ions from implants via corrosion has raised concerns over system toxicity. The accumulation of ions can result in local fibroblastic tissue reaction which has been implicated in implant failure of maxillofacial plates [22].

1.9.2 Polymers

There are many different polymers that have been used in maxillofacial surgery, however, only the most popular will be considered here. Cancer associated with a polymer implant is very rare. Even a single case is not reported in association with a polymer craniofacial implant [20].

1.9.2.1 Polyethylene

This is normally used in its ultra high molecular weight form as the low friction acetabulum cup part of total hip replacement. It also make as a porous implant. Medpor, which allows the in growth of both soft tissue and bone, which makes the implant very difficult to remove. It has been used in orbital fracture repair and in the management of cosmetic and post traumatic facial deformities [20].

1.9.2.2 Polytetrafluoroethylene (PTEF)

Proplast is a porous composite of PTFE and carbon fibers. It has been used since 1960 as filler in non-load bearing applications because of its porous surface and consequential ingrowth of fibrous tissue. Proplast has been used for malar, chin, nasal and orbital floor implants with acceptable complication rates. When it was used as an interpositional disc implant within the temporomandibular joint, complication rates rose to well above acceptable limits. Nearly all implants fractured under the load of the joint. Additionally, the Proplast particulates caused a vigorous foreign body reaction and subsequent erosion of the joint .

1.9.2.3 Polymethylmethacrylate (PMMA)

This is commonly used as cement, formed by mixing powdered polymer with liquid monomer. The resultant chemical reaction is exothermic, and toxicity has been associated with the unreacted monomer (Rubin and Yaremchuk, 1997). The hardened methylmethacrylate is brittle and prone to fracture. Hard tissue replacement (HTR), is a porous composite of PMMA and polyhydroxylmethacrylate. It has a calcium hydroxide coating which is through to impart a negative surface charge to encourage bony in-growth [23]. Methylmetharcylate has been shown experimentally to cause vasodilatation. After insertion of hip prostheses with freshly mixed MMA cement into the femur, patients have suffered acute hypotension that can progress to cardiovascular collapse and death [24,25,26].

1.9.3 Composite Materials

Composite materials allow the use of two materials which individually, would be unsuitable for the desired application. This allows the combination of polymers with insufficient mechanical properties with ceramics and glasses of low fracture toughness to produce a material which possesses the best of both materials. Composite used within medicine can be broadly cast into two classes: particulate reinforced or fiber reinforced. Particulate reinforcement is easier to produce as the composites are isotropic; hence may be prepared in-situ, however, this leads to lower mechanical properties. Fiber reinforced composites are anisotropic, as is bone, and possess superior mechanical properties to their particulate analogures.

1.9.4 Bioresorbable Materials

Due to their nature, restorable material are usually utilized in short term non load bearing applications such as sutures and drug delivery devices, however, applications for medium term such as fracture fixation are being considered as new, novel materials are researched. As discussed previously, metallic implants are the material of choice to stabilize fractures, but they may exhibit complications such as stress shielding, migration, tissue irritation and pain. These complications may require secondary surgery to remove the implant. It presents the patient with prolonged trauma and recovery time, whilst adding to the cost of surgery and requiring more theatre time. Resorbable materials offer a potential solution to these problems, by eliminating the need for follow up surgery to remove the implant. Stress shielding is eliminated as a gradual loss of material, and hence material properties, exposes the immature bone to gradually increasing levels of stress, aiding remodeling. This will clearly be beneficial to medicine as patient trauma, surgical time and related costs are all reduced. Ideally, a resorbable polymer should server its temporary need, be metabolically eliminated completely by the body within an acceptable time period, without eliciting an adverse physiological response [20]. The current market for resorbable biomaterials is dominated by poly-lactic acid (PLA), and polyglycolic acid (PGA), or co-polymers of these materials. PGA is not used on its own due to its fast resorption rates. The low mechanical properties of PLA and PLA/PGA copolymers have limited their use in low load bearing applications. The relatively fast degradation of these polymers may lead to the build up of degradation products, which leads to a decrease in pH and possible aseptic foreign body reactions [20]. Applications within craniomaxillofacial surgery include: plates, screws and mesh panels.

1.9.5 Ceramics

1.9.5.1 Alumina

Extensive research on Al_2O_3 was done during the 1950s and 1960s. it was used as a coating for the articulating surface in total hip replacement as it has very favorable wear and corrosion properties as well as good biocompatibility. However, its use was discontinued after complaints of post-operative pain.

1.9.5.2 Hydroxyapatite

The hydroxyapatite (HAp) $Ca_{10}(PO4)_6(OH)_2$ is a well known as a valuable material for bone substitution. It is one of a few bioactive implantation materials capable of creating a direct bond with bone tissue. The most common form of hydroxyapatite is hexagonal and the crystal structure has been described in the space group $P6_3/m$ with lattice parameters a=b=9.422A° and c=6.883A° [27].

1.10 Clinic Application For Bioglasses

Biomaterials science involves both biology and material science & engineering. It has developed into an important division of the biomedical field. It has been reported that certain compositions of silicate glasses are bioactive [9]. The main clinical use of bioactive glasses has been in the area of bone grafting in the oral cavity and as a glass ceramic for orthopedic use. There has also a significant amount of work on the development of bioactive glass bone cement.

Successful tooth root implants were achieved in baboons using bulk Bioglass ® [28]. In 1973, a surface-active glass ceramic of lower bioactivity was first developed and tested in Germany for maxillofacial applications and as an ossicular chain prosthesis, FDA approval for sales of middle ear prosthesis devices was given in 1982 [29-31].

Soft-tissue bonding to Bioglass ® was demonstrated and after establishment of biocompatibility in vivo and in vitro by Wilson et al. [11] and successful comparison with a wide range of alternative materials in the middle ear by Merwin et al. [32], the FDA gave approval, which allowed sales of Bioglass ® middle ear prosthesesin1984.

The first successful use of 45S5 bioglass ® was a replacement for the ossicles in the middle ear, as a treatment for the conductive hearing loss which develops when sound waves impinging on the tympanic membrane do not reach the oval window in the inner ear. Conduction loss in the middle ear can result from trauma, chronic infection or be due to congenital abnormality. Replacement of one or more of the ossicles can restore the continuity of the conducting system. Inditially, polymers, both porous and solid, and metals of various types are used. These materials engender a fibrous tissue reaction which effectively holds the implant in place. Scar tissue around an implant however will dampen, rather than transfer sound waves and implants which promote scar tissue become gradually less efficient. The major mode of failure is extrusion through the tympanic membrane. When metals or plastic implants are in continuous contact with soft tissue of the ear drum they wear through and are lost through the hole. The two problems, immobilization by a means other than fibrous tissue and prevention of extrusion, are solved by the special properties of 45S5 Bioglass ® which bonds to both hard and soft tissue.

Beginning in 1985, bioactive glasses have been used in a number of clinical applications, and their use has increased steadily over the recent years [33-36]. Research has shown that these bioactive glasses can also bond with certain types of connective tissue through attachment of collagen to the glass surface [15]. These bioglasses have as bone graft substitutes, in dentistry, as drug delivery vehicle, macroporus scaffolds and in molecular tailoring.

Clinical trials of Bioglass® tooth root implants for maintenance of the alveolar ridge of edentulous patients were completed [37]. Preclinical testing in monkeys of Bioglass ® powder for periodontal testing in dogs of bulk Bioglass® for facial augmentation was completed by Wilson et al. [11].

In oral surgery (dentistry), two main uses are reported. Dental pins are devices which are drilled into the mandible and are used to hold prosthetic teeth in place. These are usually made from bioactive materials such as low silica glass. A large number of dental filers are also used, cone-shaped devices made from 45S5 Bioglass® has been used to fill the defect in the jaw which is created when a tooth is removed. Removal of one or more teeth produces changes in the jaw bone which are followed by gradual bone loss so that the normal shape of the bone which supports healthy teeth changes to narrow "knife edge" ridge with reduced height which cannot comfortably support dentures. Without some means of preventing this bone loss, denture wearers are often destined to suffer increasing discomfort from ill-fitting dentures and in many cases may eventually become unable to wear dentures at all. These devices have now been in use for almost a decade and those made from bioactive glass have proven to be more successful than others, which have been tried.

There have been a number of recently published clinical studies on bone grafting in the oral environment [38-40]. These clinical studies have compared the amount of bone fill of the bioactive glasses in periodontal defects to standard clinical practice of debridement and found significantly more bone formation.

In Finland an innovative use of solid, cast bioactive glass implants has been used in the treatment of facial injuries in which the bone which supports the eye is damaged. Another use, in ENT surgery at present, but with the potential for much wider applications, is that of providing a soft tissue seal for an implant which passes through the skin. Electrodes, which are an essential part of an extracochlear implant developed at the University of London to treat profound deafness, must be connected both to the cochlea (or inner ear) and to the complex electronics on the outside. Any material which passes through the skin and subcutaneous tissues without an effective seal can provide a channel along with bacteria, which are always present on the skin, can move to cause infection. This is any case dangerous in any position close to brain because of potentially fatal meningitis. The anchors which contain the electrodes in this implant are coated with 45S5 Bioglass ® and are implanted in the cranium. The implant is placed so that part is in bone where the Bioglass provides a bond to immobilize it. The par which passes through the skin bonds to the soft tissues and provides the essential seal. The soft tissue bond is protected from damage due to movement, by the bone bond and relatively thin layer of soft tissue overlaying it. Such implants have been in place for several years with no significant problems. Another application which is being developed using 45S5 Bioglass ® particulate is for the treatment of patients with paralysis of one of the vocal cords.

According to a report published in "The glass researcher" by inventor of Bioglass, trademarked 45S5 bioglass ® is a miracle material [41], it has saved more than 2,000,000 human teeth and repaired numerous bony defects in the jaw, head and cranium in the past 16 years. More than 800,000 units of Bioglass ®, marketed as Perioglass ® by US Biomaterials Corp., are estimated to have been sold since 1986. Approvals by regulatory bodies for use of bioactive glasses in orthopedics have recently been achieved and the bioactive glasses are used in a variety of applications where large bone defects are present, such as in revision surgery for total hip replacements and in spinal repair. Their clinical performance is an improvement over previously used bioinert implants or Class B, osteoconductive implants.

1.10.1 Latest Developments

From the advances in related medical technologies, bioactive material appear to be entering a new stage of development in which they will have to be skillfully designed to exhibit a variety of new functions. Recently, research at Imperial College, London, conducted in Dr. Hench'lab in collaboration with Prof. Julia Polak of the Faculty of Medical Science, has shown that the unique biological behavior of bioactive glasses is due to activation of seven families of genes that are present in bone growing cells (osteoblasts).

The genes are activated to produce various proteins that serve as growth factors and enhance the proliferation of new osteoblasts. An important aspect of this discovery is that the biological control is due to the controlled release of critical concentrations of soluble silica and calcinations from the bioactive glasses. In other words, the bioactive glasses serve as a controlled release system as well as a biologically active substrate for anchoring and growth of new cells. This discovery provides a conceptual base for new cell-based medical therapies. Two alternative cellular-based methods can be used to repair diseased, damaged or aged tissues:

(i) in situ stimulation of tissue regeneration

(ii) in vitro growth of tissues followed by in vivo transplantation.

Both methods are enhanced by use of bioactive materials that release biologically active molecules at controlled rates.

Binary gel-glasses are being designed to stimulate specific responses at the molecular level. Molecular modifications of S70C30 are expected to elicit specific interactions with cell integrins and thereby direct cell proliferation, differential, and extracelluar matrix production and organization. Macro porous foams of this composition are being designed to activate genes that stimulate regeneration of living tissues whilst reducing the possibility of infection after surgery.

Bioactive glasses and newly developed bioactive gel-glasses made from the SiO_2-CaO-P_2O_5 and SiO_2-CaO system can be used as controlled release systems and bioactive, resorbable scaffolds. Bioactive foams made from the gel-glass systems are especially attractive for these new applications because they are hierarchical materials that provide interconnected porosities of 100-500 micrometers to produce the 3-D architecture required for stable cell-cell interactions and maintenance of an intercellular blood supply.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

This chapter presents a review of the literature, beginning with the evolution of bioactive glasses and glass ceramics implant and work performed on bioactive glasses and glass ceramics by various researche groups.

2.2 Evolution and Growth of Bioactive Ceramics

Bioactive ceramics include bioactive glasses, bioactive glass-ceramics, and dense hydroxyapatite (HA) ceramics. A characteristic common to these materials is that they bond to bone with no fibrous tissue at the interface. Since the 1970's, when it was first realized that the special properties of ceramic materials could be exploited to provide better materials for certain implant applications, the field has expanded enormously.

The first bioactive material reported, Bioglass® 45S5, was four-component silica glass (45 wt % SiO_2, 24.5 wt. % CaO, 24.5 wt. % Na_2O and 6 wt. P_2O_5). The low silica content and the presence of sodium ions in the glass result in very rapid ion exchange with the proton and hydronium ions of physiological solutions [10].

The ion exchange creates and alkaline pH (>7) at the implant interface with the body fluid leading to the nucleation and crystallization of a carbonate apatite layer that is equivalent chemically and structurally to the biological bone mineral [15].

Until the late 1980s, the rapid rate of hydroxyl carbonate apatite (HCA) formation exhibited by the Bioglass® was attributed to the presence of Na_2O and other alkali and alkaline earth ions in the glass composition [10] Addition of other multivalent ions such as aluminum or boron stabilized the glass structure (by eliminating non bridging oxygens) but served to retard the rate of HCA formation [10] It is now widely accepted that increasing silica content in glass decrease the rate of dissolution. This is due to reduction in the number of network modifier ions present in the glass structure, which serve to disrupt the network resulting in faster network breakdown.

Hench et al. [9] have revealed that for melt-derived bioactive glasses, three key compositional features to these glasses that distinguish them from traditional Na_2O-CaO-SiO_2 glasses and make them highly reactive when exposed to an aqueous medium are:

(i) Less than 60 mol. % silica.

(ii) High-Na_2O and high-CaO content,

(iii) High-CaO/P_2O_5.

Glasses with substantially lower molar ratio of Ca to P (in the form of CaO and P_2O_5) do not bond to bone [42]. However, substitutions in the 45S5 formula of 5 to 15 wt. % B_2O_3 for SiO_2 or 12.5 wt. % CaF_2 for CaO or crystallizing the various bioactive glass compositions to form glass ceramics has no measurer able effect on the ability of the materials to form a bone bond [42].

The compositional dependence (in weigh percent) of bone bonding and soft tissue bonding for the Na_2O-CaO-P_2O_5-P_2O_5-SiO_2 glasses is illustrated in fig. 2.1. All glasses contain a constant 6 wt. % of P_2O_5. Composition in the middle of the diagram (region A) forms a bond with bond. Consequently, region A is termed the bioactive-bone-bonding a boundary. Silica glasses within region B (such as window, bottle, or microscope slide glasses) behave as type 1 nearly cannot make the deals and illicit a fibrous capsule at the implant-tissue interface. Glasses within region C are resorbable and disappear within 10 to 30 days of implantation. Glasses within region D are not technically possible and therefore have not been tested as implants [15].

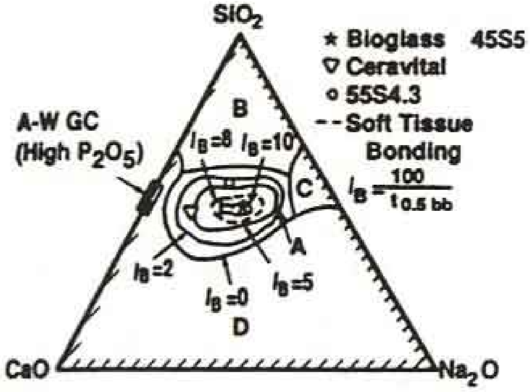


Figure 2.1 Compositional dependence (in weight percent) of bone bonding and soft tissue bonding of bioactive glasses and glass-ceramics.All compositions in region A have a constant 6% of P_2O_5. A/W glass-ceramics has a higher P_2O_5 content. Region E (soft-tissue bonding) is inside the dashed line. [(*) 45S5 Bioglass®, 55S4.3 Bioglass®.

Ebisawa et at. [43] has studied the compositional dependence of bioactivity of P_2O_5 and Na_2O free CaO-SiO_2 glasses through invitro studies. The surface structural changes have been investigated by soaking the glasses in the simulating body fluid (SBF) and also observed their effects on adding a third component. The observed results indicate that P_2O_5 free CaO-SiO_2 glass bonds to the living bone. In addition, an increase in bioactivity with addition of

Na_2O and P_2O_5 content, and a decrease in the same with the addition of MgO, B_2O_3, CaF_2, and Fe_2O_3 contents have been revealed.It has been also demonstrated that CaO-SiO_2 based glasses, without phosphate, formed an apatite layer on their surface when exposed for 2 to 30 days in simulating body fluid [44]. Work carried out by Locker et al. [45] determined the effect of substituting sodium oxide for calcium oxide on some glass properties. CaO-SiO_2 glasses are bioactive both in vitro and in vivo [46]. Previously, it was found that P_2O_5-free Na_2O-SiO_2 glasses formed an apatite layer on their surface when exposed to aqueous solution containing calcium and phosphate ions [47] . Recently, it has been demonstrated that glasses containing primarily SiO_2 with only 10 mol% of CaO and P_2O_5 and no Na_2O formed apatite layers in a tris buffer solution [48]. Earlier, Walker [49] demonstrated that even nearly pure SiO_2 eventually formed a bone bond if the surface had a very high surface area, > 400 m^2/gm. Unfortunately; the interface was not analyzed for the presence of an interfacial apatite layer which could have been nucleated on the surface by hydroxylation and /or dissolution of soluble SiO_2.

The bioactivity of the glasses has been analyzed by creating a micro roughness on their surfaces [50] . Three bioactive glasses namely 13-93, 1-98 and 3-98 with different compositions (SiO_2-Na_2O-K_2O-MgO-P_2O_5-B_2O_3) are studied. These glasses are flame-sprayed into micro spheres to form porous bioactive glasses. Different acid etching techniques have been employed to create the micro rough surfaces. Atomic force microscopy (AFM) and BEI-SE have been used to characterize the surface roughness of etched samples. Its is inferred from the observed result that the chemical etching of a bioactive glass surface doesn't interfere with the formation of the characteristic surface reactions and the same has been confirmed by soaking the etched and control glass in a SBF and hydrochloric acid.

Attempts has been made to study the bioactivity of CaO-SiO_2 by adding third component such as Na_2O, MgO, B_2O_3, P_2O_5, CaF_2. After soaking the bioactive glasses in SBF for 8-25 weeks, the implantation has been observed after 8 weeks. Its is inferred that the glasses containing B_2O_3, P_2O_5 and F have good compatibility and hence, bonded tightly with bone, while Fe_2O_3 containing glass has no compatibility with bone even after 25 weeks [51].

The effect of substitution of Y_2O_3 for CaO on the bioactivity of 2.5CaO.2SiO_2 glasses is studied. Their study shows that high values of Y_2O_3 negatively influenced bioactivity, i.e. the tendency to form a calcium phosphate layer reduces when greater the amount of CaO is substituted. However, more Y_2O_3 can be substituted without inhibiting the reaction with SBF, than in the case of CaO poorer series (2-x) CaO.x/3Y_2O_3. 2SiO_2

Filqueiras et al. [52] reported that the substitution of CaO by MgO had little effect on bone bonding, while additions of 1-1.5 wt. % AI_2O_3 prevented it. West and Hench [53] working with molecular orbital models, proposed that only a special type of silanol groups (trigonal siloxane rings) would be able to induce apatite nucleation. It is also suggested that only a certain type of structural unit of silanol groups is effective for apatite nucleation.

The first materials incorporating magnesium oxide were Ceravital® glasses and the resulting glass-ceramic materials The base Ceravital® glasses contain (wt. %) 40-50 SiO_2, 10-15 P_2O_5, 5-10 Na_2O, 0.5-3.0 K_2O and 2.5-5 MgO. From the set of cervical materials, glasses and glass ceramics KG Cera (2.9 wt. % MgO) and Mina (5 wt. % MgO) were derived. Ohtsuki et al. [54] have reported an intimate contact between living tissues and these materials.

Vogel and Holand [55] developed the Bioverit family of glass ceramic in which MgO content is in the range 6-28 mol. %. These glass-ceramics have apatite, mica and/or cordierite phases in their structure. The authors have reported a direct intergrowth between the materials and the living tissues. The role of magnesium oxide in glasses and glass-ceramics of the system $CaO\text{-}P_2O_5\text{-}SiO_2\text{-}MgO$ (AI_2O_3) in a pseudo-extracelluar fluid is investigated. They found that ability to form the apatite layer in glass-ceramics decreases with increasing MgO content, so that glass-ceramics with more than 8 wt. % MgO did not form such layer.

Kokubo et al.[56] worked with glasses of $SiO_2\text{-}CaO\text{-}P_2O_5\text{-}MgO$ system and developed the A-W.G glass containing (wt. %) 4.6 Mg, 44.7 CaO, 34 SiO_2, 16.2 P_2O_5 and CaF_2. An apatite-and wollastonite containing glass ceramic (A-w.GC) was obtained by crystallization of a glass powder compact. They also developed the A.GC and A-W-CP.GC glass ceramics, the first being rich in apatite and the second in apatite, wollastonite and tri-calcium phosphate. When in contact with simulated body fluid (SBF) these materials developed an HCA layer with compositional and structural characteristics similar to the one developed on the Bioglass® surface. He also proposed a mechanism to explain the bioactive of these materials based on the ceramic leaching with Ca^{2+} and Si^{4+} dissolution and increase in local fluid supersaturation with respect to apatite, followed by nucleation of apatite on sites of material provided by the dissolution of silicate ions.

Ohtsuki et al. [46] working with $CaO\text{-}SiO_2\text{-}P_2O_5$ glasses, showed that no bioactive $CaO\text{-}P_2O_5$ composition increases the degree of supersaturating more than the bioactive $CaO\text{-}SiO_2$ glass, concluding that degree of supersaturating must not glass. A non-bioactive alumina-containing glass-ceramic A-W (AI) developed an apatite rich layer when immersed in a synthetic fluid with calcium and silicate ions added simultaneously, which means that soluble silicate, ions play an important role in silicla layer formation. However, a silica layer was not detected on the A-W.GC surface tested in SBF solution. The bioactivity of glass ceramics have been discussed on the basis of surface chemical studies of glass ceramics [57] The observed result shows that apatite phase present in the glass ceramic does not play an important role in forming the chemical bond to bone. However, a Ca-P rich layer formed on the surface of the glass-ceramic in the body environment plays the essential role in forming the chemical bond of glass-ceramic to bone. Further, it is concluded that various kinds of bioactive materials with different function can be designed using glasses and glass ceramics.

Roman et al [58] have been studied the bioactive of CaO-SiO_2-P_2O_5-MgO-CaF_2 (G 13) glass by inducing the bioactivity in a non-bioactive ceramic GC13, chemically treated with 1ml HCI for different time period through invitro studies. The observed results show that the etching time influences the kinetics of growth of the apatite-like layer in SBF. Further, the microstructural and morphological fluctuations associated with presence of the hydroxyapatite crystal favour the more bioactive behaviour of GC13 ceramics etched for 1 min. invitro. A new composition of bioactive glass-ceramic CaO-MgO-SiO_2-P_2O_5 has developed by Liu et al. The invitro studies have been carried and the formation of an apatite layer on the glass ceramic surface has been analyzed using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) studies. It has been observed that glass ceramic has a flexural strength and fracture toughness and also exhibits a high bioactivity. The above glass ceramics are utilized in load bearing medical applications.

Oliiverira et al. [59] have prepared the glass and glass ceramic of MgO-CaO- P_2O_5-SiO_2 glass for different compositions. The Ca/P rich layer has been identified as hydroxyapatite on both samples after immersion in SBF for different time periods but the precipitated film on glassy sample was weakly bonded and the glass ceramic was strongly adherent. These microstructural characteristic has been observed through SEM studies. Although, the glass ceramic has higher chemical and mechanical stability, these glasses are expected to be capable of bone boding with bone which results in good bioactivity.

Lin et al. [60] have studied the structure and elastic properties of two bioactive glasses of compositions $Na_2CaSi_2O_6$(45S5.2) and $Na_2CaSi_3O_8$ (55S4.1) employing Raman and Brillouin scattering techniques. It has been observed that the annealed 45S5.2 glass has more Q^2 and O^6, but less Q^3 species than 55S4.1 glass due to its low (Si^{4+}+P^5/(Na^++Ca^2) ratio. The Brillouin scattering measurements of the annealed glasses indicate that 45S5.2 glass is higher in elasticity that 55S4.1 glass due to more modifiers in 45S5.2 glass. It has been concluded that from structure and elasticity of the 45S5.2 glass, it can be used as a substitute for bone than its parent glass.

Serra et al. [61] studied the bonding configuration of bioactive silica based glasses and identified the silicon-oxygen groups by combining two spectroscopic techniques; X-ray Photoelectron Spectroscopy (XPS) and infrared spectroscopy (IR).

Peitl et al. [62] have shown that crystallization of Bioglass^R 45S5 did not inhibit HCA formation in an invitro test with SBF-K9, even with a fully crystallized glass-cereamic. The onset time for HCA layer formation did decrease with increased crystallinity in his study. They concluded a fact that crystallization did not affect significantly the kinetic reactions in $1.5Na_2O$-$1.5CaO$=$3Sio_2$ containing 0,2,4, 6, wt. % P_2O_5 glasses. This system of glasses was shown to be highly bioactive as these show bioactivity even in the absence of phosphorous than other commercial bioactive glass-ceramics. They have revealed the in vitro bioactivity of partially crystallized 45S5 BG® as a function of time through in situ observation using AFM. The thermal treatments have been carried out to obtain a material that is less resorbable, still bioactive and stiffer than standard BG®. This crystallized BG® is more suitable than those of hydroxyapatite C faces and can be used as filler for polymeric matrix bioactive composites.

Itala et al. [50] have characterized the in vitro surface reactions of micro roughened bioactive glasses employing a novel chemical etching method. The prepared porous bioactive glasses are immersed in SBF for several hours and the formation of reaction layers have been analyzed by SEM and Energy Dispersive X-ray analysis (EDX) studies. It has been concluded that microroughening significantly accelerated the early formation of surface reaction on bioactive glasses and has a positive effect on cell attachment.

The in vitro studies of bioactive glass tapes have been carried in SBF. The characterization studies such as FTIR, XRD, SEM and EDAX are used to characterize the effects of sintering at various temperature on the tape cast bioactive glass ceramic in SBF. It has been revealed that well established crystalline hydroxyapatite layer is formed after immersion in SBF from 20-24 h on tape cast sintered (TCS) bioactive glass ceramics, which is sintered at 1273 K.

Kim and Jee [63] have studied the dependence of hydroxyapatite forming behaviour with respect to the crystalline phases in the alumina coated bioactive glasses. When bioactive glazed alumina reacts in the SBF, it is inferred that no silica Rich layer has been found in crystallized bioactive glazed alumina, while Si-rich layer has been formed on the bioactive bulk glass.

Glass ceramics containing magnetic phase with glass matrix, could be used as thermoseed for hyperthermia treatment of cancer [64] This magnetic phase is exposed to alternating magnetic field, by which heat is generated due to hystersis loss. This hyperthermia treatment is considered to be an effective treatment for cancer without side effects and this process can be repeated many times after implanting a bioactive and biocompatible ceramic in to the body. A glass ceramic with lithium ferrite ($LiFe_5O_8$) and magnetite (Fe_3O_4) in an Al_2O_3-SiO_2-P_2O_5 glassy matrix could be used as a thermoseed for hyperthermia treatment of caner.

Singh and Bahadur [65] have also reported the synthesis and characterization of structural and magnetic properties of different compositions of glass and glass ceramics in SiO_2-Na_2O-CaO-P_2O_5-B_2O_3-Fe_2O_3 systems.

Phosphate based glass materials have potential for use as biomaterials, because their chemical composition is close to bone. Franks et al. [66] have prepared phosphate based glasses in the system CaO-Na_2O-P_2O_5 and hence, studied the thermal parameters with differential thermal analysis. Further the precipitation phases are identified by XRD and it is evident that one phase nucleates via bulk nucleation, while the second nucleates via surface mechanism by grinding the samples to different particle sizes. Systematic study of same system of glasses has been done with an attempt to correlate whether the fibers could be produced with the glass cross-link density, network connectivity and chain length.

Glasses with P_2O_5-Na_2O-CaO-TiO_2 contents with fixed P_2O_5 (45 wt. %) and CaO (24 wt. %) have been prepared employing the normal melting and annealing technique [67]. Measurements such as ultrasonic velocity, attenuation, solubility and pH have been carried out in all the glasses. It has been noticed that the measured ultrasonic parameters show interesting observation by exhibiting an abnormal behavior (minimum) at 0.5 wt. % of TiO_2, beyond which an increase in the trend of variation with increase in TiO_2 content. Further, the maximum pH values and Ca^{2+} ion release have been observed for TiO_2 free and with the low content of TiO_2 (< 1.0 wt. %).

Kasuga [68] has reported the calcium phosphate glass based materials in the pyrophosphate region. Bone like apatite the surface of the glasses, when it is soaked in simulating body fluid at 1310K. It has been observed that –$Ca_2P_2O_7$ crystal formed in the glass-ceramics plays an important role in the mach inability in addition to the apatite formation ability in SBF. They studied in situ thermal and structural characterization of bioactive calcium phosphate glass ceramics with addition of TiO_2 and MgO oxides. The heat treatments at different temperatures from 954 to 998 K lead to the confirmation of the precipitation of crystalline phases in the glassy matrix. The heat treatments at different temperatures lead the varied biocompatibility of the glasses.

In early 1990s, sol-gel processing was introduced for the synthesis of bioactive glasses [69]. The sol-gel route allows glasses of higher purity and homogeneity to be obtained at temperatures notably lower than those required to obtain glasses by the melting method. These bioactive glasses have higher bioactivity and resorbability in vitro, which have application as bone graft material.

Various research groups used sol-gel route for preparation of bioactive glasses not only in the ternary SiO_2-CaO-P_2O_5 system but also in the quaternary SiO_2-CaO-P_2O_5-Mg system and binary SiO_2-CaO system for biomedical applications. In vitro studies have shown that nucleation and crystallization rates of hydroxycarbonate apatite (HCA) depend on many factors including the sol-gel glass composition.

CHAPTER 3 EXPERIMENTAL DETAILS

3.1 Introduction

In this chapter, the design and working of experimental setup used for characterization and preparation of silica based glasses have been described. In addition, the detailed measurement techniques and procedure employed for in vitro bioactivity testing, solibility, density, X- ray diffraction (XRD), Band gap measurement by UV-Visible Spectroscopy and sample preparation procedure are given in details.

3.2 Sample Preparation

Silica based glasses with chemical composition as shown in Table 3.1 were prepared by using melt quenching technique. All the chemical used were of analytical reagent grade the weight of various oxide were calculated according to formula

$$W_a = \frac{X_a Z_a}{\sum_{i=1}^{n} X_i Z_i}$$

Here W_a = weight fraction

X_a = mole fraction

Z_a = molecular weight of oxide.

Table 3.1Glass composition (mol %) with their label

Sample Label	SiO_2	Al_2O_3	SrO	B_2O_3	Na_2O	MgO	P_2O_5	CaO
SS1	40	10	30	20	-	-	-	-
SS2	40	10	-	20	-			30
SS3	60	5	-	-	30	5	-	-
SS4	65	5	-	-	25	5	-	-
SS5	65	-	-	-	25	5	5	

.

The amounts of oxides were weighed by using digital electronic balance. The chemical were then mixed in a pestle mortal. The mixed powder of these samples were placed in recrystallized alumina crucible and melted in an atomized Molybdenum Disilicide ($MoSi_2$) electric resistance furnace. The powder of the samples were initially kept at 1000^0C for 1 hour for calcination to occur and release of water from the starting materials then they were reheated at 1550^0C and kept at this temperature for half an hour in order to achieve the homogeneity. The schedule for sample melting is shown in figure 3.1. The melt was poured either in graphite mold or on the flat copper plate and quenched by other copper plate in air to obtain flakes. All the samples were prepared using the route described above. The detail as of the sample preparation and other relevant information about preparation and characterization are summarized in the flow chart

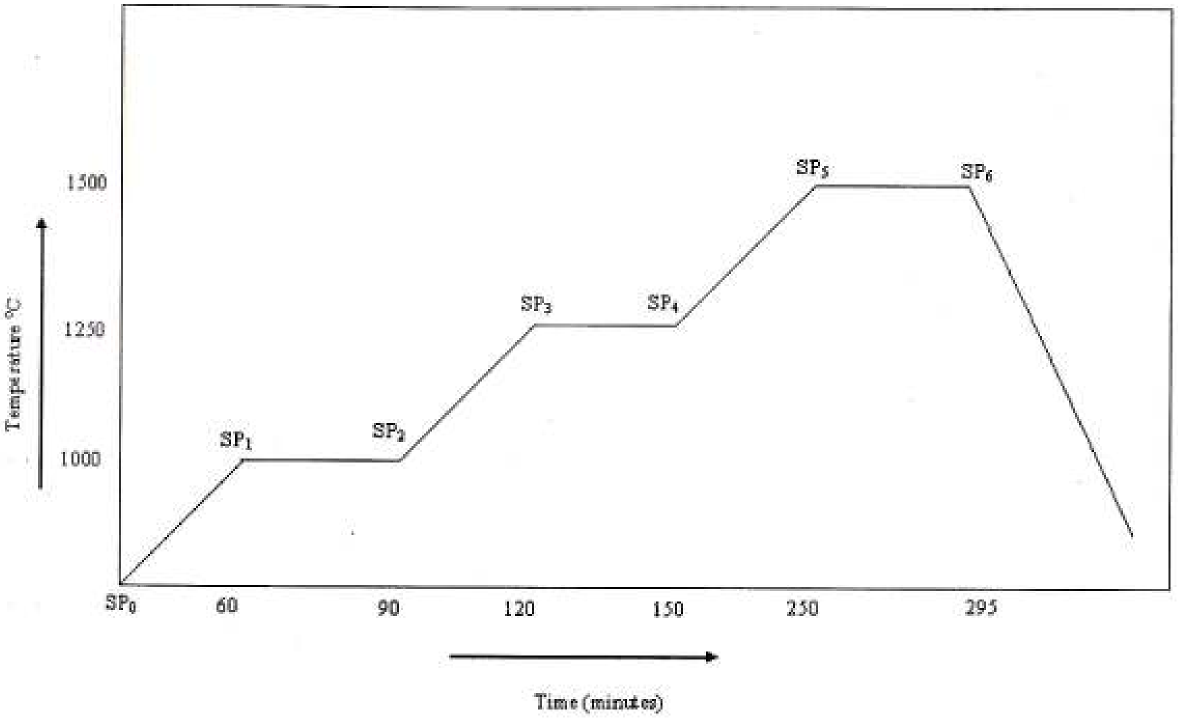
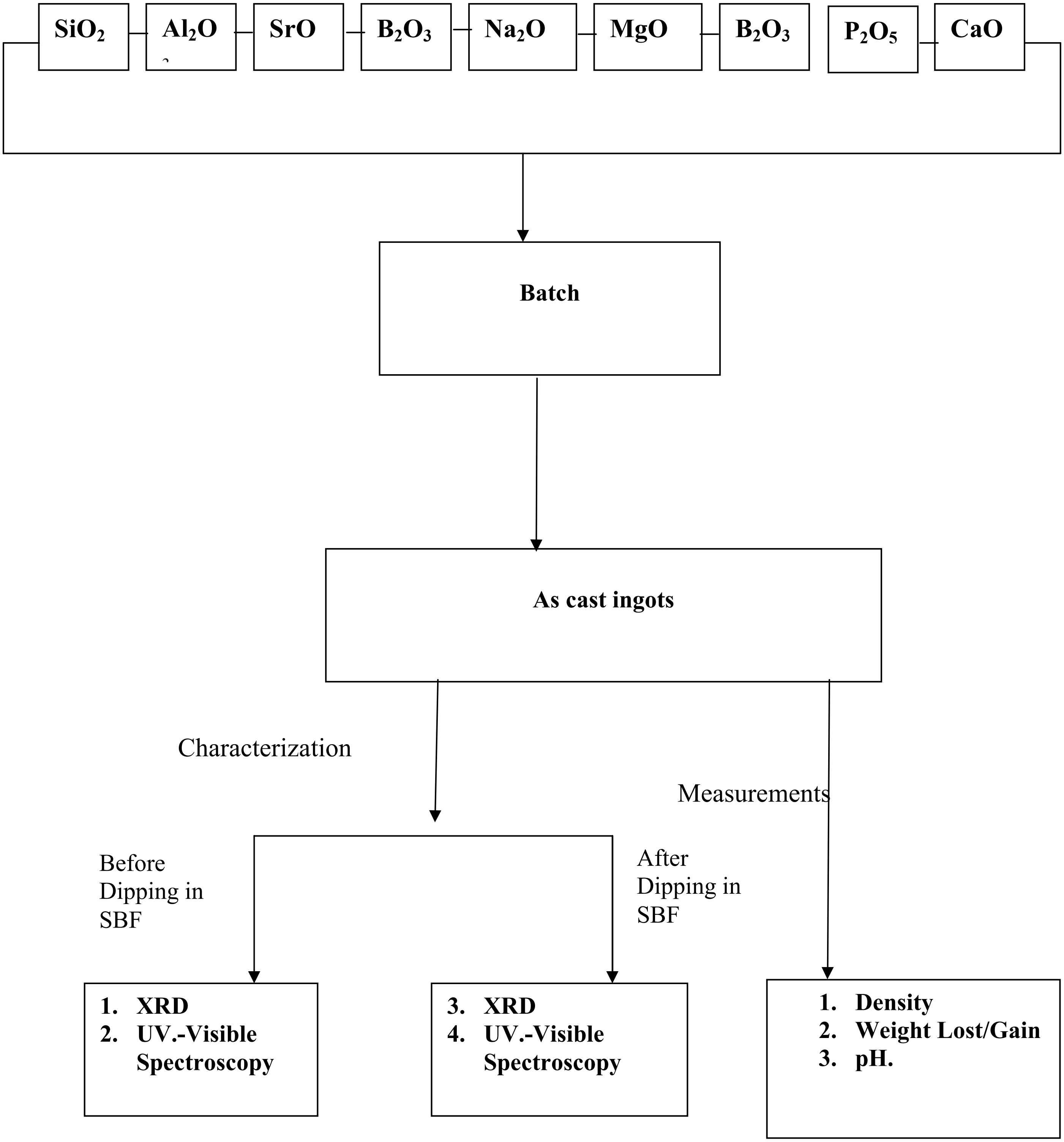


Fig 3.1. Typical schedule followed for the melting of the glass samples.

FLOW CHART


SiO₂
Al₂O₃
SrO
B₂O₃
Na₂O
MgO
B₂O₃
P₂O₅
CaO
Batch
As cast ingots
Characterization
Measurements
Before Dipping in SBF
After Dipping in SBF
1. XRD
2. UV.-Visible Spectroscopy
3. XRD
4. UV.-Visible Spectroscopy
1. Density
2. Weight Lost/Gain
3. pH.

Typical flow chart showing the path followed for the preparation, Characterization and Measurements of glass Samples.

3.3 In Vitro Bioactivity Analysis

There is a well-established relationship between the ability of a given material to form bonds with living tissues and its ability to grow an apatite-like layer when soaked in fluids mimicking human plasma, and so in vitro assay are popular tool in the study of bioactivity of new synthetic/processed implant materials. The in vitro testing minimizes the use of animals, a worthy goal, but is also required by most regulatory agencies in the device approval process for clinical application. In vitro testing also provides useful insights as to whether a device needs further evaluation in expensive in vivo experimental models.

In present research simulated body fluid (SBF) proposed by Kokubo et al. [44] has been used. SBF is an, aqueous solution with an ionic composition that closely resembles that of human plasma, buffered to physiological pH (7.25-7.40) at 37° C with a mixture of HCI/tris (hydroxymethyl) aminomethan. The ionic concentrations of SBF and human blood plasma are given in Table 3.2 for comparison. Since this fluid contains ca^{2+} and $HPO^{2-}{}_4$ ions, it can be used to assess the in vitro bioactivity of a wide range of materials.

An SBF-K9 solution was prepared by mixing sodium chloride, sodium bicarbonate, potassium chloride, calcium chloride, dibasic potassium phosphate and magnesium chloride in deionised water, according to the method proposed by Kokubo

. **Table 3.2 Ion concentrations of the SBF and Human Blood Plasma**

Ion	Simulated Body Fluid	Human Blood Plasma
Na^{+}	142.0	142.0
K^{+}	5.0	5.0
Mg^{2+}`	1.5	1.5
Ca^{2+}	2.5	2.5
Cl^{-}	147.8	103.0
HCO_3	4.2	27.0
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5

3.3.1 Standard operating procedure for preparing simulated body fluid (SBF#9)

i) Wash all beakers, bottles and wares with 1 N HCO, neutral detergent, ion exchanged water and then dry them.

ii) Put 500 ml of ion exchanged water and a stirring bar into an 800 ml beaker and cover the beaker with a watch glass.

iii) Stir the water with a magnetic stirrer. Add the reagents given in Table 3.3 into the water one by one in the order given in the table but only after each reagent has dissolved. After adding each reagent, use a small amount of ion-exchanged water to wash the weighing boat using a wash bottle and pour into the beaker. Be sure the entire reagent has been transferred to the solution.

iv) Set a warm water bath and place the beaker into it. Adjust the temperature of the solution in the beaker to 36.5^{o}C and adjust the pH of the solution to 7.25 with 1 N-HCl while stirring the solution (usually 4 to 5 ml of 1 N-HCl would be needed if everything was right).

Table 3.3 Required Chemicals for SBF Preparation

Order	**Ion**	**Amount (g.dm^{-3})**
1	NaCl	7.996

2	NaHCO$_3$	0.350
3	KCl	0.224
4	K2HPO$_4$.3H$_2$O	0.228
5	MgCl$_2$.6h$_2$O	0..305
6	1N-HCl aqueous solution	≈35 ml
7	CaCl$_2$-2H$_2$O	0.368
8	Na$_2$SO$_4$	0.071
9	Tris (hydroxymethyl) amino Methane (CH$_2$OH)$_3$CNH$_2$	6.057
10	1N-HCl aquesous solution	≈10 ml

v) Rinse the pH electrode using ion exchange water from a washing bottle to the solution when removing the electrode from the solution.

vi) Transfer the solution from the beaker to a 1-litre volumetric glass flask. Rinse the beaker with ion exchanged water to the solution in the flask. Allow the solution to cool.

vii) Bring the total volume of the solution to one litre by adding ion-exchanged water and shake the flask at room temperature to mix well.

viii) Transfer the solution from the flask to a one litre polyethylene bottle and store the solution in a refrigerator at 5-10^{o}C (If any precipitates are found in the solution during storage do not use this solution or bottle again).

Samples were polished with 600 grit polishing paper, washed ultrasonically in acetone for five minutes and were placed in polyethylene bottles which contain SBF for time periods ranging from 2 weeks to 4 weeks. To homigenise our studies, to avoid effects due to volumetric differences, the relationship between the geometrical area of the glass samples and the volume of the solutions was maintained as 0.075 cm $^{-1}$ in all the cases. After the assays, pieces were washed with water and acetone and dried in air. Microorganism contamination of samples is avoided by performing all manipulations inside the incubator.

3.4 Density

The density of glasses was obtained from Archimedes' principle using water as buoyant. The density was determined employing the following relation:

$$\rho=\frac{W_a}{W_a-W_b}\times\rho_b$$

Where W_a is the weight in air, W_b is the weight in buoyant and ρ_b the density of buoyant. All the weight measurements have been made using a digital balance. The experiment was repeated 3 tikes to get an accurate value in density.

3.5 X-Ray Diffraction Study

In order to confirm the amorphous nature of the glass sample & to find the change in its nature after dipping in SBF solution, X-ray diffraction study had been made on each glass sample using Rigaku Model Geiger diffractogram with the CuKα radiation (λ= 1.5418 A^o) obtained from copper target using an in built Ni filter. The 20 values for XRD patterns were generally taken in the range of 5^o to 100^o for most of the samples at a scan speed of 5 degree per minute. The inter planar spacing (d) values of samples were calculated using the Bragg's law.

$$2\ \mathrm{d}\sin\theta = n\ \lambda$$

Where λ is the wavelength of incident X-ray, d is the interplanar distance and 0 is diffraction angle. The XRD patterns were identified using powder Diffractions files (PFD). The geometric representation of Bragg's law is given in figure 3.3

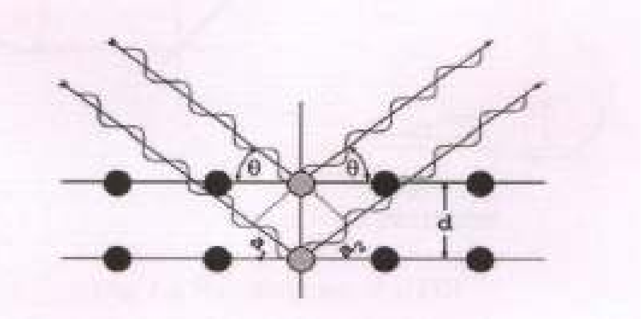


Figure 3.3 Geometric derivation of Bragg's law: constructive interference occurs when the delay between the waves scattered from adjacent lattice planes given by a_1+a_2 is an integer multiple of the wavelength λ .

3.6 U V- Visible Spectroscopy

The Ultraviolet and Visible spectroscopy is a reliable and accurate analytical laboratory assessment procedure that allow for analysis of a substance. Specifically Ultraviolet and Visible spectroscopy measures the absorption, transmission and emission of ultraviolet and visible light wavelength by matter. Ultraviolet and visible light comprise only a small portion of the wide ranging electromagnetic radiation spectrum. Although lower in frequency and therefore lower in energy than cosmic, gamma or x rays ultraviolet and visible light are of a higher frequency and therefore of higher energy, than infrared, microwave and radio waves.

The ultraviolet band of the electromagnetic spectrum is further separated into three region termed UV-A, UV-B, and UV-C. Although not all the scientist agree on the exact subdivisions of these wave length, UV-A is generally considered to be light with wavelength between 320-400 nm; UV-B wavelength are generally considered to be those between 290-320 nm and UV-C wavelength usually fall between 200-290 nm.

In the practical sense, spectroscopy measures the absorption, emission or scattering of electromagnetic radiations by atoms or molecules. By such measurements, the type of atom or molecule present in a sample as well as measure of their concentration or abundance can be made to an astonishing degree of accuracy.

In the present study we are calculating the band gap of given glass samples to know the effect of deposition of hydroxyl apatite layer on the energy band of glass samples.

3.6.1 Direct and indirect band gap

When the material absorbs a photon of incident light, an electron is excited from lower to upper energy level or state. This transition of electron can be direct (without phonon assisted mechanism) or can be indirect (in which the interacted with a phonon takes place).

In a direct transition, an electron gives off the energy difference, E_{gg}, as a photon of light and fall from the conduction band to an empty state in the valance band. In indirect transition, if an electron in the conduction band cannot migrate directly to the valence band, but must undergo a momentum change as well as change in its energy. This difference between direct and indirect band structure is very important for deciding that which material can be used in a device according to the requirement of light output.

3.6.2 Determination of Energy Band Gap (E_g)

Absorption spectra is a power tool, which is used for measuring the energy band gap (E_g) of a polycrystalline material. This method is applicable for a large range of band gap i.e. narrow band gap to wide band gap material.

In this mechanism photon of selected wavelength is incident on the sample and the relative transmission of the various photons are observed.

Let a photon beam intensity I_0 (photon/cm^2 sec) is incident the sample of thickness t and the intensity of light transmitted is I_t then.

$$I_t = I_0 e^{-\alpha t}$$

Where α is absorption coefficient with unit cm^{-1}. This coefficient varies with photon wavelength and also with material to material.

Discriminating between direct and indirect transition is possible on the basis of the dependence of adsorption coefficient on photon energy. They various type of transition gives rise to different frequency dependence absorption coefficient near the fundamental absorption edge.

For direct transition, we have

$$\alpha\, hv = A\, (hv - E_g)^n$$

Where hv = photon energy

E_g = band gap

α = Absorption coefficient

N = 1/2 for the allowed transitions

The indirect transitions give rise to relation.

$$\alpha\, hv = A\, (hv - E'_g)^n$$

Where $E'_g = E_g \pm hv_{pn}$ (v_{pm} is frequency of photon)

n' = 2 provides the allowed transitions

In case of direct band gap the allowed transitions are given by using the equ.

$$\alpha hv = A(hv - E'_g)^{1/2}$$

A plot of $(\alpha\, hv)^2$ vs photon energy (hv), when extrapolated to zero absorption provides the value of energy gap.

3.7 Solubility Measurements

3.7.1 Weight loss measurement

The solubility of glasses was evaluated by the measurement of weight loss in simulating body fluid (SBF) at 37° C in the incubator. Solubility can directly be correlated to glass corrosion. Samples were polished with 600 grit polishing paper, washed ultrasonically in acetone for a minute and were placed in polyethylene bottles which contain SBF. At various points of time, the samples were removed and excess moisture was removed with tissue and weighted. The percentage change in weight loss can be directly correlated to glass corrosion or solubility in SBF. The amount of weight loss was evaluated using the following relation:

Weight loss (mg/g) = $(W_0 - W_t)/W_0$

Where W_0 is the initial weight of the specimen and W_t the weight at each period of time. The measurements were carried out in triplicate.

3.7.2 pH measurement

At the time of solubility measurements, the pH of the solution was also measured as a function of time employing a pH meter with accuracy of 0.01. The calibration of the electrode against buffer solution was performed at an interval of 75 h.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Density and Weight loss measurements

Density is a useful tool in revealing the degree of change in structure with composition of glasses. The variation of density of before and after dipping samples as a function of composition shown in figure 4.1.

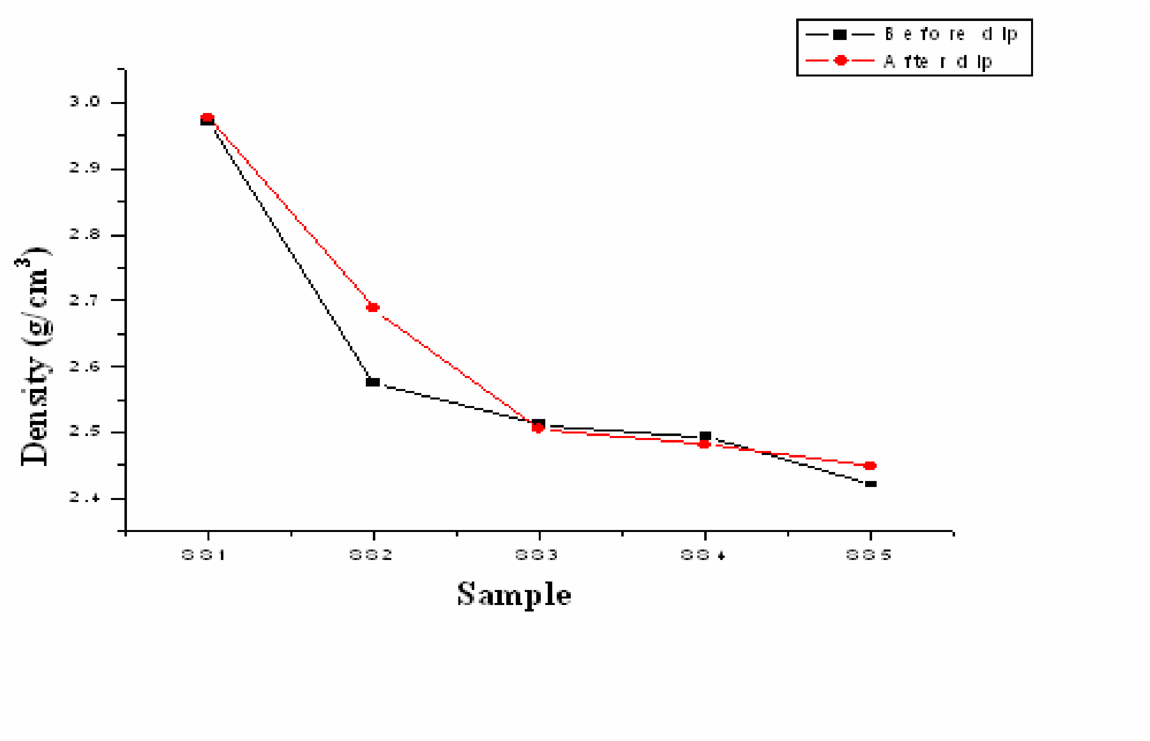


Figure: 4.1 Variation of density of glasses before and after dipping as function of composition

Sample SS2 where SrO is replaced by CaO, the density decrease .However, the field strength of Sr^{2+} is less than Ca^{2+}.But at the same time, the atomic mass of Ca is less as compared to Sr so the decrement in density of SS2 sample as compared to SS1can be explained on the basis of atomic mass difference in both the cations.After dipping in SBF solution, the density is not changed in sample SS1 which is the manifestation of the durability of the particular sample. On the other hand, sample SS2 show the increasing trend as shown in figure 4.1.It is clearly indicate that SrO sample is more durable than CaO based sample. Further verification of this hypothesis, weight measurement as a function of dipping time are also taken for each sample.SS2 sample indicate the weight loss during dipping

Sample SS3 and SS4 could not show appreciable change in their densities after dipping in SBF solution. SS3 sample exhibit higher density than SS4 sample. Interestingly, sample SS3, having higher contents of network modifier (Na_2O) at the cost of SiO_2 (network former).In general, network former decreases the density and glass transition temperature. This anomaly in density measurement might be attributed due to slight change in processing conditions. Sample SS5 where Al_2O_3 was replaced by P_2O_5, the density decreases, however, P_2O_5 treated as network former [65] and Al_2O_3 considered to work as network modifier. Many reports have been appeared in literature on the role of Al_2O_3 in glasses that is less than 5% Al_2O_3 could be worked as a network former because it coordinates as tetrahedrally [65]

In all the samples, sample SS2 and SS5 exhibit higher density than virgin counterpart of these samples. In weight measurement, both the samples shows weight loss as compared to other three samples as shown in figure 4.2.In both the samples Ca^{2+} and P^{5+} leached out from the samples and formed the layer on the surface of the samples. This layer might be denser than the layer formed on the surface of SS1,SS3 and SS4 samples.. Interestingly, Ca^{2+} and P^{5+} are very important constituents of Hydroxyapatite layer. To get insight of mechanism of layer formation, weight loss and pH with dipping time were observed in all the samples. The weight loss (mg/g) and pH value are shown graphically in the figure 4.1 and figure 4.2 respectively

Sample weight measurement provides better idea of sample dissolution. It is clear that sample SS2 and sample SS5 experience weight loss in some stages of dipping. On the other hand, remaining samples could not show the weight loss after immersion in SBF solution. Basically resorption or biodegradation of a material in vivo is a very complex process that is reaction take place between physiochemical (guest) and biological mechanism (host) .Therefore it is not exclusively controlled by its physiochemical properties such as solubility in SBF solution [70].

In the present study, some samples show weight loss and some are gaining weight. sample SS5 is less durable exhibited higher weight loss as shown in figure 4.2 .Some earlier researches have been reported whenever phosphate added in glass composition, glass samples exhibit less durability [71]

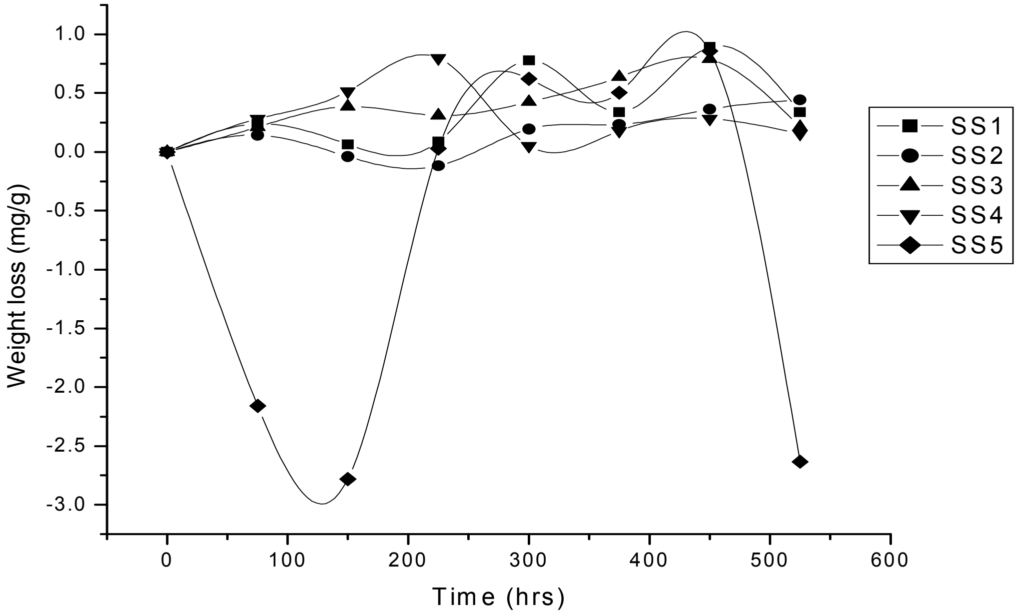


Figure4.2 weight loss/gain as a function of time

4.2 pH Measurement

variation of pH of the SBF solution after samples immersion as a function of time is shown in figure 4.3. The change in pH of the solution also provides a better idea of sample dissolution.

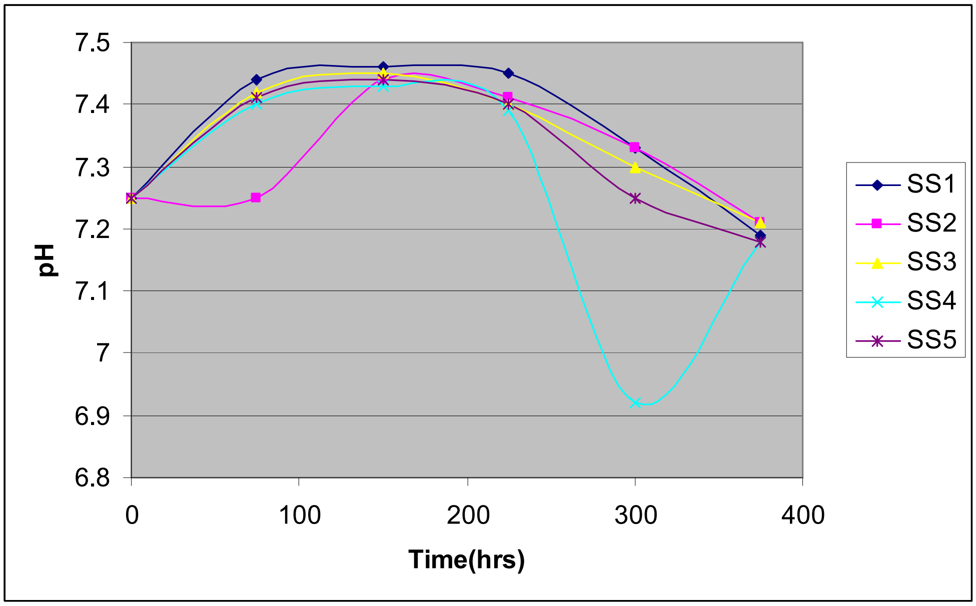


Figure 4.3 Variation of pH of SBF with time.

All samples show small change in pH ie7.25 to 7.45 in 15 days. Data obtained suggests that species such as H^+, H_3O^+ and OH^- from the solution attack the glass network and are exchanged with Na^+ and Ca^{2+} ions from the glass network. Leaching of alkali and alkaline ions form glass to solution leads to the increase of pH. The less durable glasses tend to leach more alkali, causing pH to increase as compare to more durable glass. In the later stage of the pH measurement, the pH value decrease due to formation of Hydroxyapatite layer on the surface of the samples.

4.3 XRD Analysis

The XRD spectra from all as prepared silica based glasses (SS1, SS2, SS3, SS4 and SS5) possessed the characteristic 'amorphous hump'. A typical X-ray diffraction of SS1 sample is given in figure 4.4. The absence of sharp peaks and presence of broad humps confirms amorphous nature of glasses.

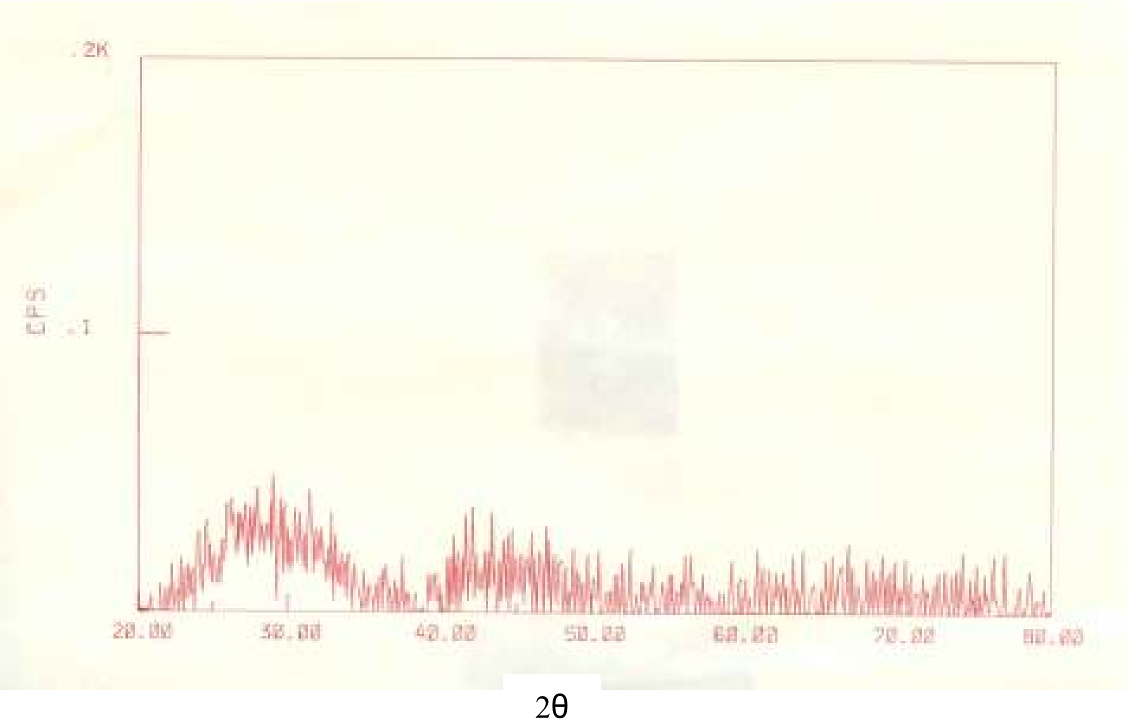


Figure4.4 XRD Diffractogram for sample SS1

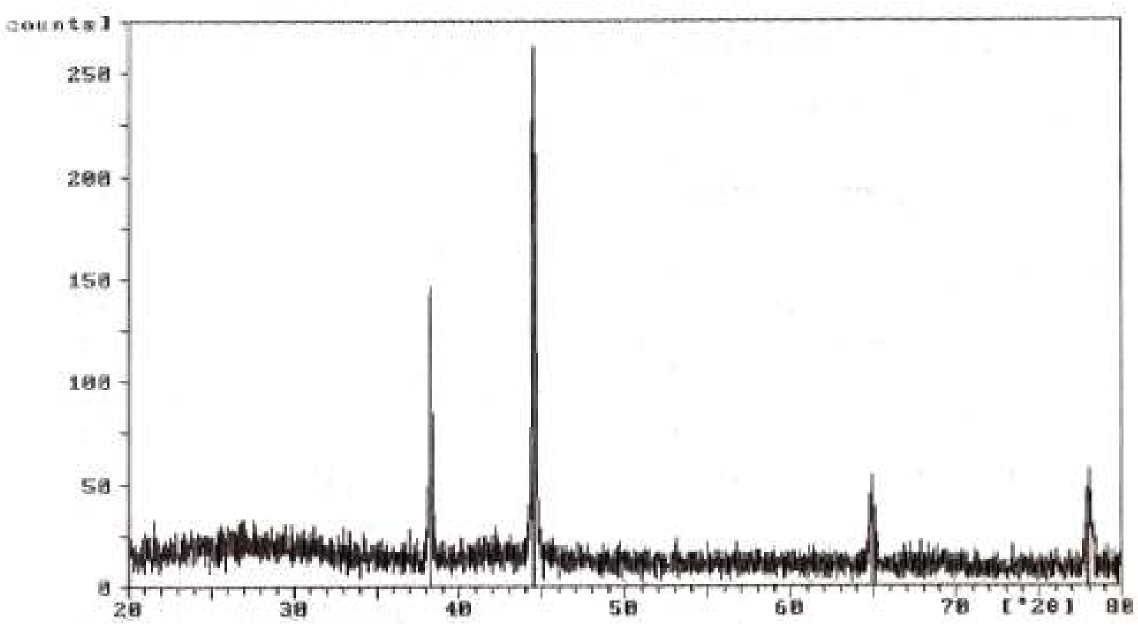


Figure4.4 XRD Diffractogram for sample SS1

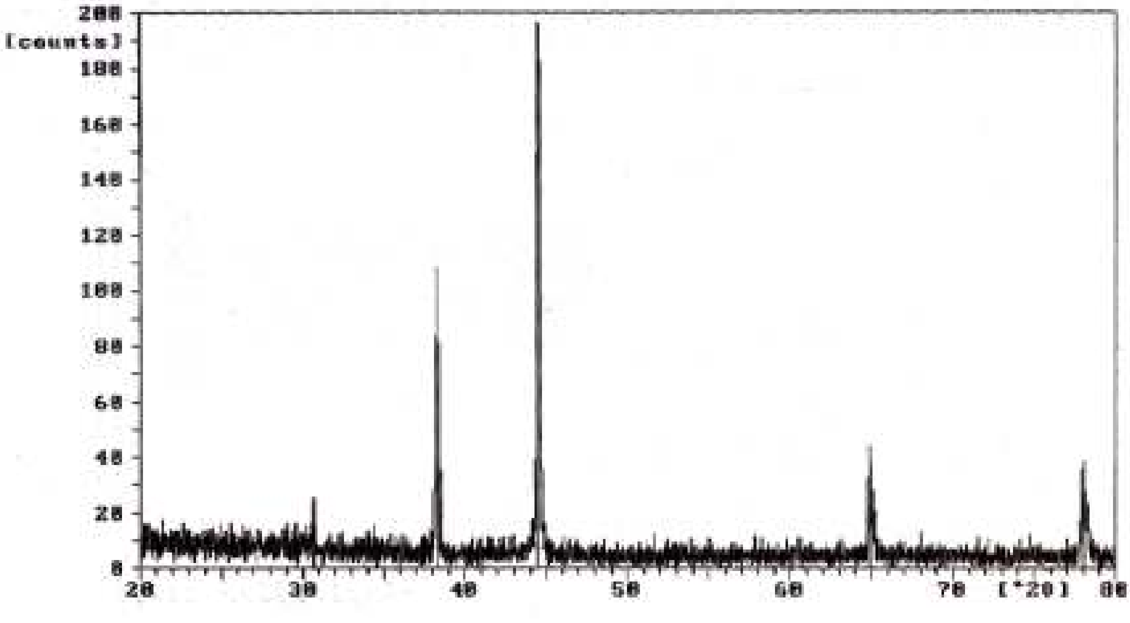
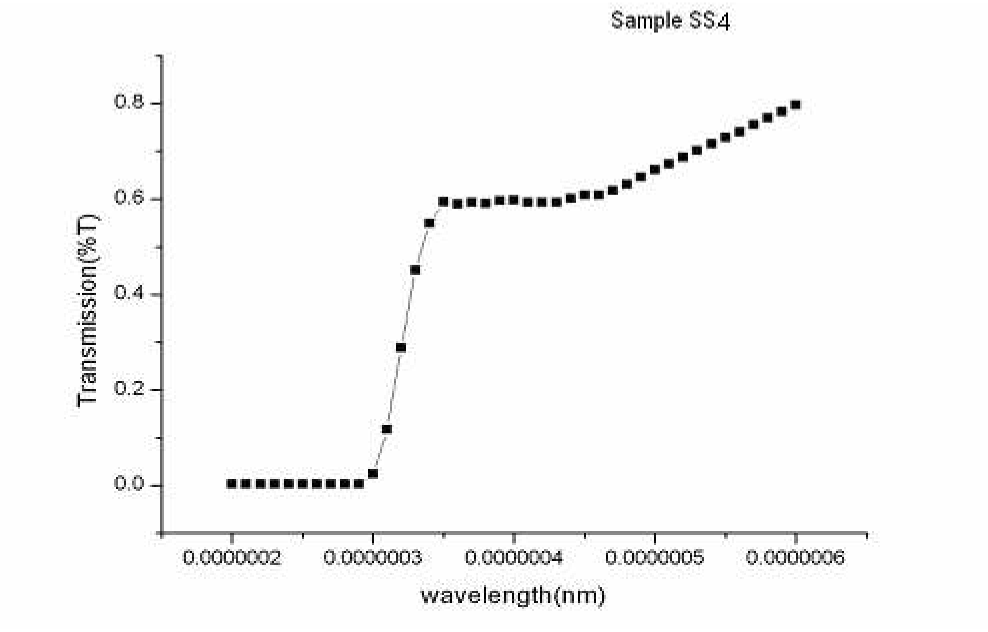


Figure 4.5 XRD Diffractogram for sample SS4

As the sample dipped in the SBF solution some chemical reaction take place between the constituents of glasses and the ions presents in SBF solution with time. These chemical reactions result in the formation of crystalline layer on the surface of all the glass samples as shown in figure 4.2 and 4.3 for sample SS1and SS4 respectively. The compositions of all the glass samples are different. In present study, however, after dipping these samples in SBF solution, XRD patterns of these samples exhibit similar pattern except sample SS4.In this particular sample a extra peak observed at 30.5°. The crystalline phases in above mentioned samples could be indexed with $Ca_{10}(PO_4)_6(OH)_2$ (JCPDS card no 74-0566). A typical XRD pattern of SS1 and SS4 samples are given in figure 4.4 and figure 4.5 respectively .This behavior of the present samples clearly indicated that the hydroxyapatite layer formation depends on the reactions between SBF and glasses as indicated in density,pH and weight loss measurement. Based on these measurements, it is very difficult to conclude that leaching from samples play important role to form hydroxyapatite layer

4.4 Energy Band Gap

The optical band gap were determined by transmission spectra. A typicall graph between percentage transmission versus wavelength for the sample SS4 are shown in figure 4.6



ss3

Fig.4.6 Transmission spectra as a function of wavelength of sample SS4

The band gap of (before and after dipping) samples are calculated using UV-Visible Spectroscopy. These results give further insight of the layer formation. In other words, if a layer is forming on the surface of the sample after dipping due to the reaction between SBF solution and glass samples then , the band gap must be changed. Firstly, the transmission absorption coefficients(α) and energy ($h\nu$) were calculated to use the transmission spectra of the samples. These values are plotted as $h\nu$ versus $(\alpha h\nu)^2$ Now these graphs are used to calculate the band gap of the samples .

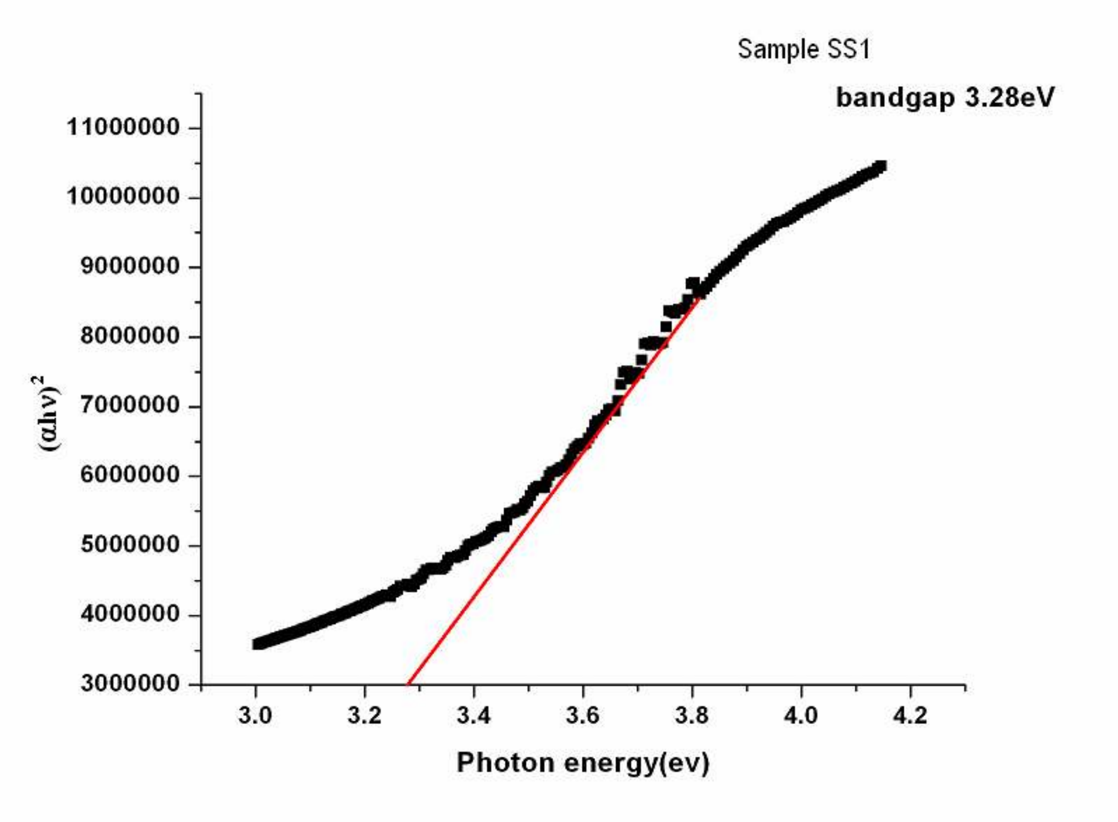


Figure 4.7

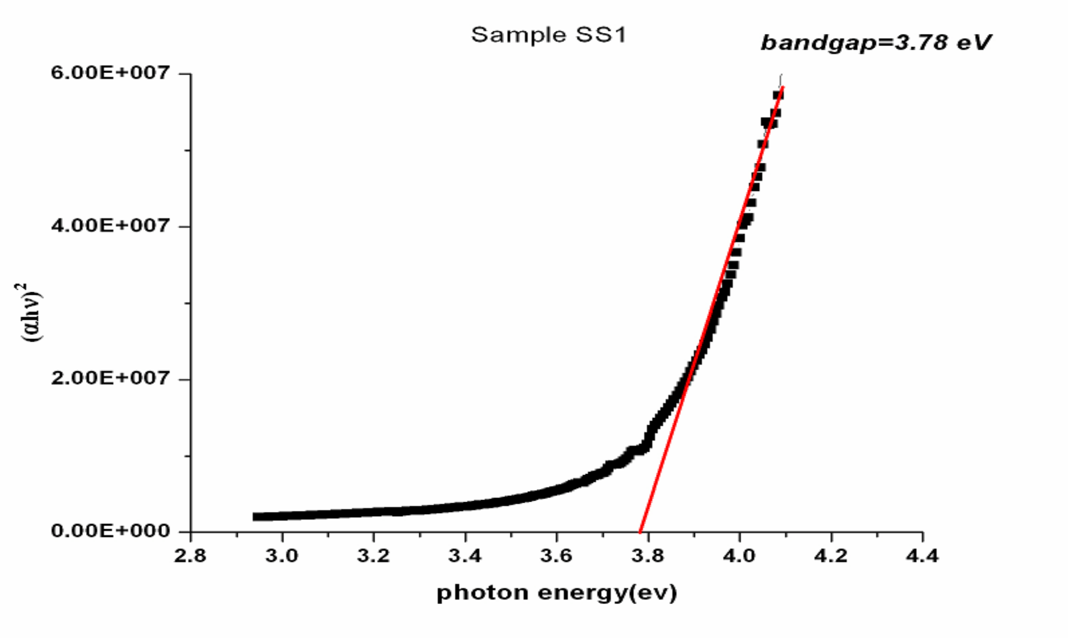


Figure 4.8

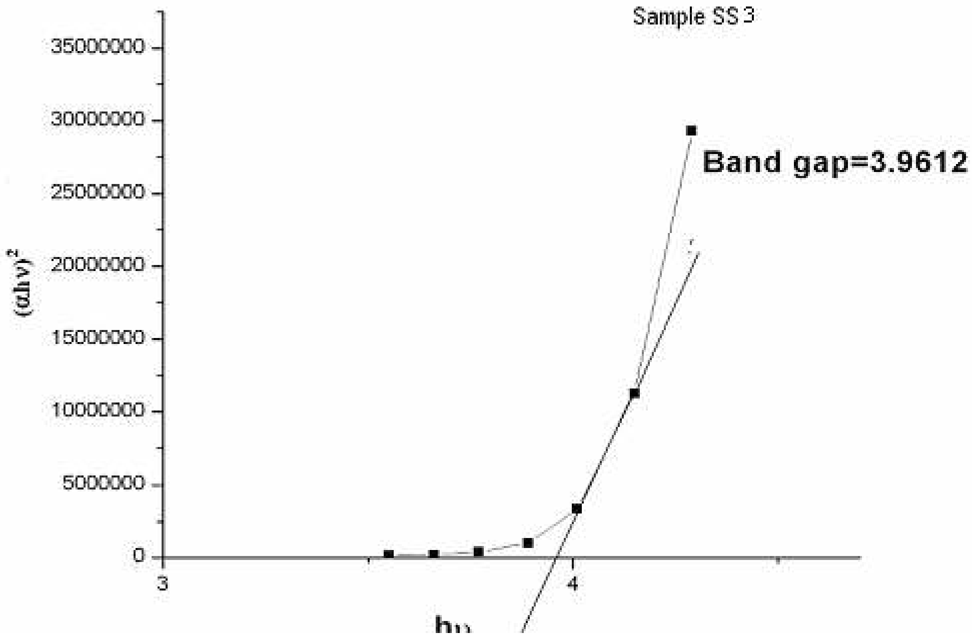


Figure 4.9

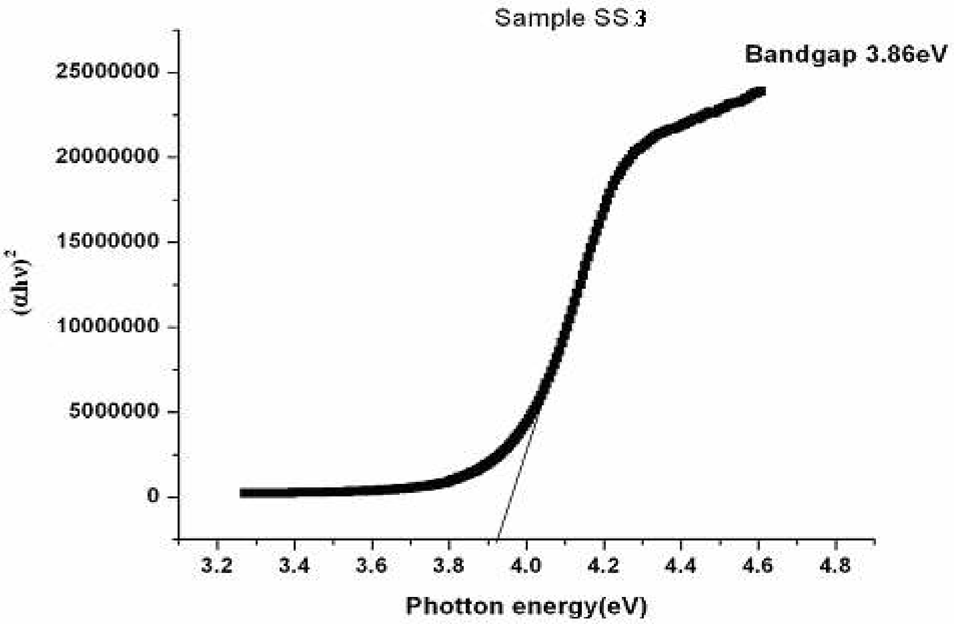


Figure 4.10

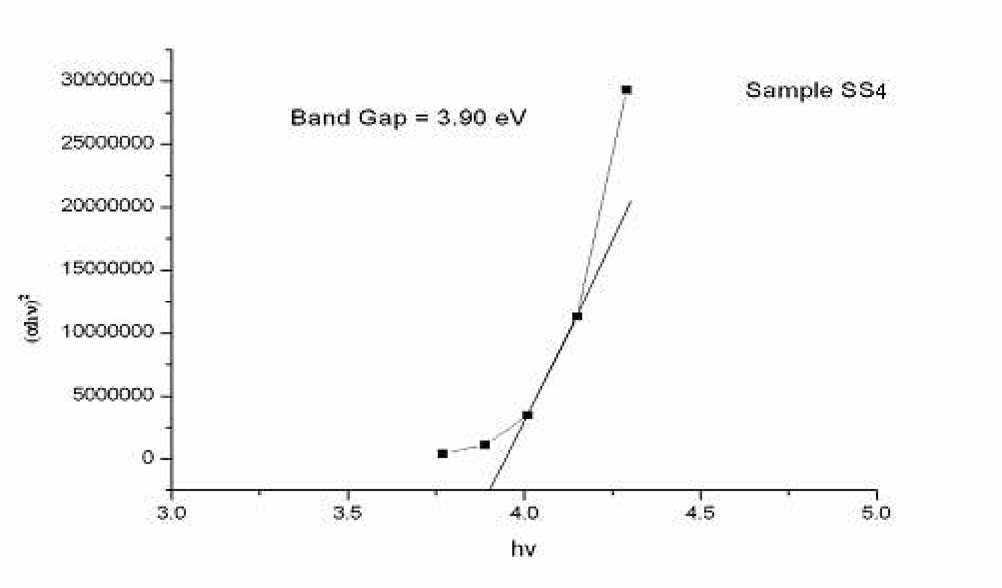


Figure 4.11

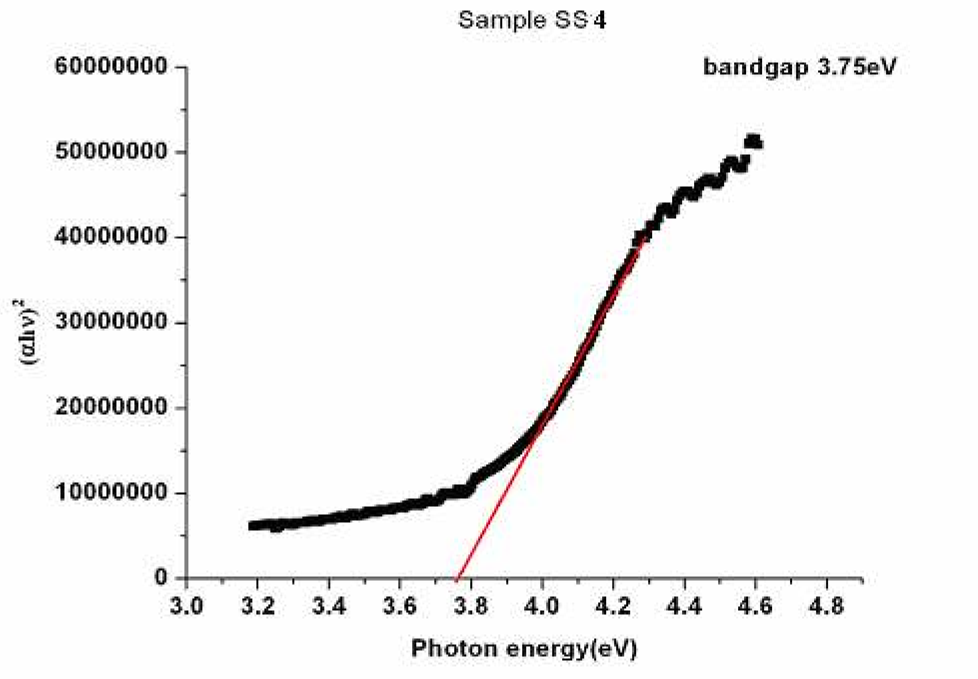


Figure 4.12

Table 4.1 showing the variation of band gap before and after dipping in SBF solution

Sample Label	Band gap before dipping in SBF (eV)	Band gap after dipping in SBF (eV)
SS1	3.28	3.78
SS3	3.96	3.86
SS4	3.90	3.75

. In case of sample SS1 the value of band gap increases after dipping. On the other hand the band gap of SS3 and SS4 exhibits reverse trend than SS1 sample. In both the samples (SS1andSS2), Na_2O was used as a constituent of glasses. It means Na_2O is playing very crucial role in changing the band gap as well as density of these samples as indicated in figure 4.1.

It may be noted that SrO (SS1) and Na_2O (SS3 and SS4)are working as a network modifier in these samples. Obviously Sr-O bond is more stronger tha Na-O bond , hence bond length of Na-O is larger than Sr-O bond. This may increase the volume of the system , hence the density decrease as shown in figure 4.1. Therefore, the band gap in SS3 and SS4 is larger thanSS1 sample. Comparing sample SS3 and SS4, the density of SS4 sample is less as compared to SS3, However the band gap of SS3 is more as compared toSS4 sample. The composition of both the samples exhibit only 5% Na_2O less at the cost of SiO_2. This anomaly in band gap measurement might be attributed due to a little variation in processing conditions. After dipping these samples in SBF solution, the density of SS1 sample increases while for SS3 and SS4 samples, it decreases. Accordingly, the band gaps of the samples are changed. Band gap in amorphous solids, proposed by Molt and Davis, can be explained as the width of the localized states near the mobility edge which in turn depends on the degree of disorder and defects present in amorphous structure.

CHAPTER 5 CONCLUSIONS AND FUTURE SCOPE

All the virgin samples are amorphous in nature as confirmed by X-rays diffraction. A layer is formed after immersion in SBF solution ,in all the samples, which is also confirmed by X-rays Diffractogram. There might be a possibility that hydroxyapatite layer is formed along with some other phase such as $CaSiO_3$. However the formation of hydroxyapatite layer is a very complex process which further depends upon many factors such as initial glass constituents, processing conditions and dipping durations.

SrO based sample (SS1) is most durable as compared to other samples. The least durable sample is SS5 in which Al_2O_3 is replaced by P_2O_5. Based on our study and findings CaO and P_2O_5 based samples are more likely to form a hydroxyapatite layer. The pH measurements clearly indicate that some reactions were taking place between the SBF solution and glasses irrespective to the leaching of glasses whether it is taking place or not.

SrO based sample exhibit higher density and lower band gap as compared to other samples which can be explained on the basis of electronic density. In case of SS3 and SS4 samples the density is lower as compared to SS1.After dipping in SBF solution, the density increases in SS1 sample and result in increase in band gap. However in case of samples SS3 and SS4, the density decreases after dipping in SBF solution, the band gap also decreases.

In order to understand the durability, mechanism of hydroxyapatite layer formation requires further study on the present samples. The change in band gaps after immersion in SBF solution is new findings. Therefore, to confirm these results more structural and microstructural study is required which can be done by SEM and FTIR.

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