GLASS AND GLASS SEALANTS AS BIOCERAMICS

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Dedicated to my loving parents

CERTIFICATE

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ABSTRACT

The optimization of bioactive glasses requires a proper understanding of chemical, physical mechanical and biological properties. The formation of a hydroxyapatite layer on silica based bioactive glasses has already been investigated by many researchers. In the present investigation, calcium based glasses of different composition have been synthesized by taking appropriate proportion of each oxide composition. The samples are charatererized by using the various techniques viz, X-ray diffraction (XRD), UV-Visible spectroscopy, and FT-IR, density and solubility measurements. The entire samples were dipped in simulated body fluid (SBF) solution for different time duration. Sample AS1 and AS3 show the formation of hydroxyapatite layer. On the other hand, samples AS2 and AS4 were not formed the hydroxyapatite layer. Apart from this, AS1 and AS3 samples also exhibit higher durability as compared to other two samples (AS2 and AS4).

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CHAPTER 1

INTRODUCTION

1 Historical Background

Anyone who has looked at the long-term history of human civilizations over the last 50,000 years will notice that one of the most significant transformations took place during the period 1200 to 1850. This transformation affected two of the most important human capacities: the way in which we think and our sense of sight. Natural glass has existed since the beginning of time, formed when certain types of rocks melt as a result of high-temperature phenomena such as volcanic eruptions, lightning strikes or the impact of meteorites, and then cool and solidify rapidly. Stone-age man is believed to have used cutting tools made of obsidian (a natural glass of volcanic origin also known as hyalopsite, Iceland agate, or mountain mahogany) and tektites (naturally-formed glasses of extraterrestrial or other origin, also referred to as obsidianites)[1].

Glass beads, seals, and architectural decorations date from around 2500 BC. Glass was also discovered by Native Americans during the same time period. The earliest known beads from Egypt were made during the New Kingdom around 1500 BC and were produced in a variety of colors. The Egyptians also created the first colored glass rods which they used to create colorful beads and decorations. They also worked with cast glass, which was produced by pouring molten glass into a mold, much like iron and the more modern crucible steel [2]. By the 5th century BC this technology had spread to Greece and beyond. In the first century BC there were many glass centre located around the Mediterranean. Around this time, at the eastern end of the Mediterranean, glass blowing, both free-blowing and mould-blowing, was discovered. The 11th century saw the emergence in Germany of new ways of making sheet glass by blowing spheres. The spheres were swung out to form cylinders and then cut while still hot, after which the sheets were flattened. This technique was perfected in 13th century in Venice. Until the 12th century, stained glass, glass with metallic and other impurities for coloring, was not widely used.

Around 1688, a process for casting glass was developed, which led to its becoming a much more commonly used material. The invention of the glass pressing machine in 1827 allowed the mass production of inexpensive glass products. The cylinder method of creating flat

glass was used in the United States of America for the first time in the 1820s. It was used to commercially produce windows. This and other types of hand-blown sheet glass was replaced in the 20th century by rolled plate glass, and then again in the 1960s by float glass, at first in the UK and then elsewhere[3].

1.1 Glasses:

Glass is a non-crystalline material that can maintain indefinitely, if left undisturbed, its overall form and amorphous microstructure at a temperature below its glass transition temperature. Glass synthesis is achieved by quenching a glass - forming liquid through its glass transition temperature sufficiently fast to avoid the formation of a regular crystal lattice, producing an amorphous solid. Amorphous solids may also be formed by methods other than melt quenching, such as vapour deposition or the sol-gel method. Silica glass may be produced by using sand as a raw material (or "quartz sand") that contains almost 100 % crystalline silica in the form of quartz. The most common method for glass pane production is using molten tin, where the molten glass floats on top of the perfectly flat molten tin, thus giving it the name "float glass". The refractive, reflective and transmission properties of glass make specific chemical compositions suitable for technological applications such as optics and optoelectronics. The manipulation of heated glass enables it to be shaped into different forms and the incorporation of additives at the manufacturing stage produces different colors which enable glass to be used as an art [3].

So a glass may 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 exhibit glass transformation behavior is a glass.To better understand how bioactive glasses work when put in contact with body fluids, a few concepts concerning glass structure and glass surface will be given in the following sections:

1.2 Glass structure:

There are many possible definitions of glassy phase. An interesting one is that glass is a solid material with a structure similar to a liquid. This somehow reflects the practical operations necessary to obtain a glass: a glass is formed when a liquid is overcooled, in absence of enough sites of nucleation. The resulting solid structure is not completely organized, on the contrary of the crystalline structure typical of all other solids. For this reason, glass structure is called

amorphous (without a definite shape). Most of glasses are silica-based. In a crystalline solid made of silica (e.g. quartz), SiO_4 tetrahedral are organized in a well-defined network. In amorphous silica, SiO_4 tetrahedral are still linked

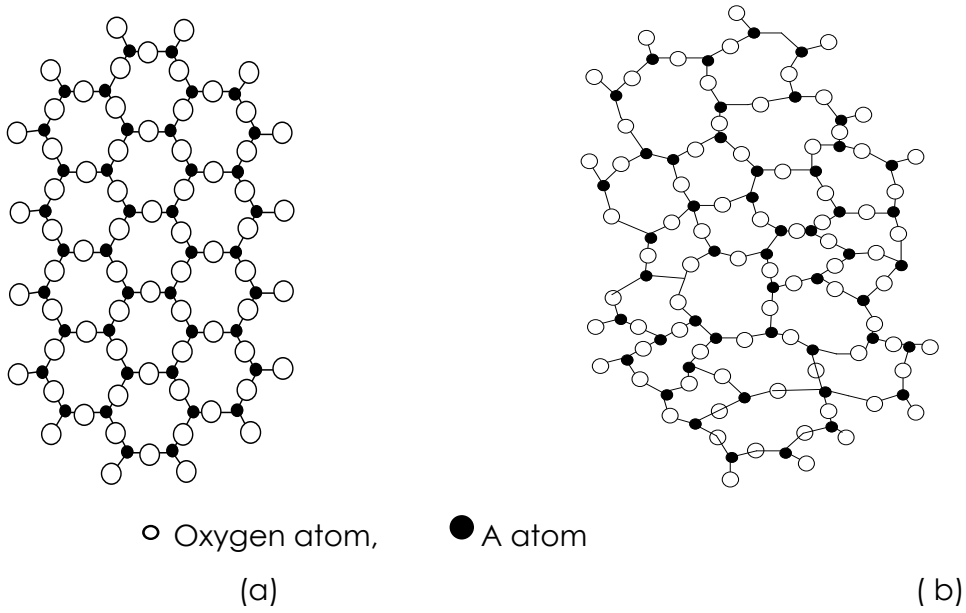

Fig. 1.1 Atomic arrangement of A_2O_3 in (a) crystalline form (b) glassy form

together, but the angle between them is not constant, and the resulting structure is not organized SiO_2 is called glass former, since glass structure is mostly kept together by SiO_4 tetrahedral. Other oxides can be used as glass formers, such as B_2O_3 or P_2O_5. Alkaline and alkaline-earth oxides are added to glass as glass modifiers, in that they interrupt the network created by the glass former the resulting structure is called random network, and was at first hypothesized by Zachariasen in 1932 [4].

1.2.1 Glass Transition:

Glasses are amorphous substances which undergo the glass transition. The most striking feature of the glass transition is the abrupt change in the properties of a liquid, such as the thermal expansion coefficient (a) and heat capacity **(cp),** as it is cooled through the range of temperature where its viscosity approaches 10" Pa.s. In that range the characteristic time for structural relaxation is of the order of a few rninutes, so the effects of structural reorganization are easily detected by human observers.

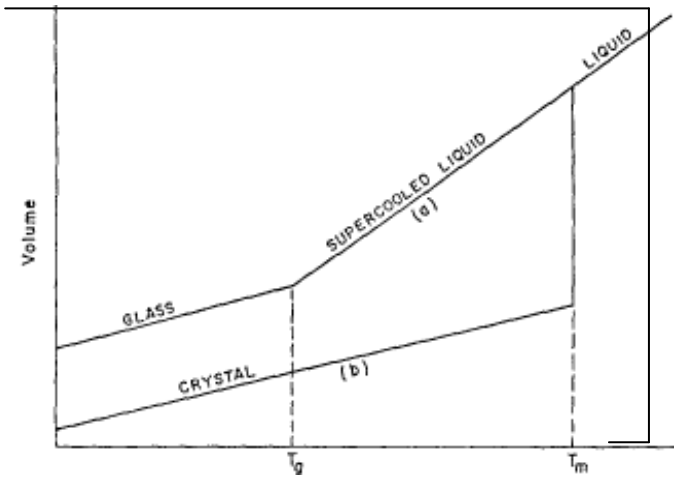

Fig. 1.2 Plot of volume vs. temperature of (a) glass (b) crystal

If the liquid is cooled slowly (path b) it may crystallize at the melting point, T_g. If the cooling rate is fast enough to avoid crystal nucleation and growth, a super cooled liquid would be produced (path a). As the temperature drops, the time required to establish the equilibrium configuration of the liquid increases, and eventually the structural change cannot keep pace with the rate of cooling. At that point a transition temperature, T_m, is reached below which the atoms are frozen into fixed positions (only thermal vibrations remain) and a glass is formed. Thus, glass formation from the liquid state is feasible if path (a) is followed.

1.3Fabrication techniques of glasses:

1.3.1 sol-gel technique:

The Sol-Gel process allows synthesizing ceramic materials of high purity and homogeneity by means of preparation techniques different from the traditional process of fusion of oxides. This process occurs in liquid solution of organ metallic precursors (tetramethylorthosilicate(TMOS), tetraethylorthosilicate(TEOS), Zr(IV)-Propoxide, Ti(IV)-Butoxide, etc.), which, by means of hydrolysis and condensation reactions, lead to the formation of a new phase (SOL).

M-O-R + H_2O ⟶ M-OH + R-OH (hydrolysis)

(1)

M-OH + HO-M ⟶ M-O-M + H_2O (watercondensation)

(2)

M-O-R + HO-M ⟶ M-O-M + R-OH (alcohol condensation)

(M = Si, Zr, Ti) (3)

The sol is made of solid particles of a diameter of few hundred of nm suspended in a liquid phase. Then the particles condense in a new phase (gel) in which a solid macromolecule is immersed in a liquid phase (solvent). Drying the gel by means of low temperature treatments (25-100ºC), it is possible to obtain porous solid matrices (XEROGELs). The fundamental property of the sol gel process is that it is possible to generate ceramic material at a temperature close to room temperature. Therefore such a procedure opened the possibility of incorporating in these glasses soft dopants, such as fluorescent dye molecules and organic chromospheres [5].

13.2 Pressing technique: pressing is used in the fabrication of relatively thick-walled pieces. The glass piece is formed by the pressure application in the graphite coated cast iron mold having the desired shape; the mold is ordinary heated to ensure an even surface. The pressing technique is better than powder technique. The pressing pars encapsulated in the glass to excrude glass into body to form a glass crystalline composite

may be useful in some cases. The capabilities of size, shape and tolerance reflect advantages that may be achievable in a number of cases of applying glass forming techniques [6].

13.3 Blowing technique: The transformation of raw materials into glass takes place around 2400°F (1315°C); the glass emits enough heat to appear almost white hot, the glass is then left to "fine out" (allowing the bubbles to rise out of the mass), and then the working temperature is reduced in the furnace to around 2000°F (1100°C). At this stage, the glass appears to be a bright orange color. Though most glassblowing is done between

1600°F - 1900°F (870°C - 1040°C), "Soda-lime" glass remains somewhat plastic and workable as low as 1350°F (730°C). Annealing is usually done between 800°F - 900°F (430°C -

480°C).Glassblowing involves three furnaces. The first, which contains a crucible of molten glass, is simply referred to as "the furnace." The second is called the "Glory Hole", and is used to reheat a piece in between steps of working with it. The final furnace is called the "lehr" or "annealer", and is used to slowly cool the glass, over a period of a few hours to a few days, depending on the size of the pieces. This keeps the glass from cracking due to thermal stress. [6].

1.3.4 Glass Fiber Spinning

The interaction between multiple fibers and air flows within the quench box of glass fiber spinning process is a very difficult phenomenon to analyze from a theoretical perspective. In the process, continuous strands of fibers are drawn by extruding molten polymers through spinneret nozzles. The fibers are formed by the balance of the tension from a winder and gravity. Fiber attenuation and interaction with quenching air flows characterizes this process. Quenching air flow pattern and fiber temperature are significantly altered by the entrainment of air due to the drag induced by fiber motion

1.4 Properties of glasses

The special properties of glasses are related to 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 lying in specific orientation [4].

1.4.1 Physical properties:

Density of the glass is his strong function of its composition and most important measure of the glass. It also stands on its own as an intrinsic property 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.

1.4.2 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 glasses are also susceptible to failure due to thermal shock. The fracture strength of the glasses varies with prior surface treatment, inherent stress etc. Other mechanical properties of glasses are inherent to the material. The hardness of glasses is a

function of the strength of individual bonds and density of packing of the atoms in the localized structure [4]

1.4.3 Thermal properties:

The contraction and expansion due to thermal energy is the important factor.

When a glass is heated it expands and if the temperature over the body is uniform and body is not restrained then there will be no stress formation in the body. If there is non-uniform heating of the body, then different layers of glasses will attempt to expand differently and stress develop. The magnitude of glass generated is related to thermal expansion. Thermal expansion of glasses increases with increasing temperature.

1.4.4 Electrical properties:

The electrical conductivity of glasses changes due to the presence of network modifiers. Glass which does not contain any modifier possesses a very less conductivity as compared to crystalline counterpart. The strength of bond of the ions in the network and their size influence the electrical properties. On the basis of electrical properties glasses can be categorized as follows:

1. Glasses with very small conductivity (high resistivity).
2. Glasses with high ionic conductivity and low electronic conductivity.
3. Glasses with electronic conductivity only.

1.4.5 Chemical properties:

Glass is more corrosion resistant than any other materials. Glass is indestructible by chemical attack, under certain conditions it will corrode, even dissolves... Acid and alkali solution attack glass in different way. Alkali attacks the silica directly whereas acids attack the alkali in the glass. Corrosion by water is similar to acid corrosion in alkali is removed from the glass surface. The properties of glass can be varied and regulated over an extensive range by modifying the composition, production techniques or both. In any glass mechanical, chemical, thermal properties cannot be occur separately.

1.5 Applications of glasses:

1.5.1 Toughened glass :

For many applications such as buildings requiring large spans of glass, toughened glass is the only acceptable alternative. These glasses have exceptional strengths compared to standard annealed float glasses. These improved properties are a result of the stress profile that is induced in the glass by the toughening heat treatment process. When performed correctly, the glass surface is in compression, while the centre is in tension. This stress profile in the glass is successful as most failures start at the surface from tensile loads as shown in fig 1.3. In toughened glass, the applied tensile load must overcome the compressive stress at the surface before the surface can go into tension and fail.

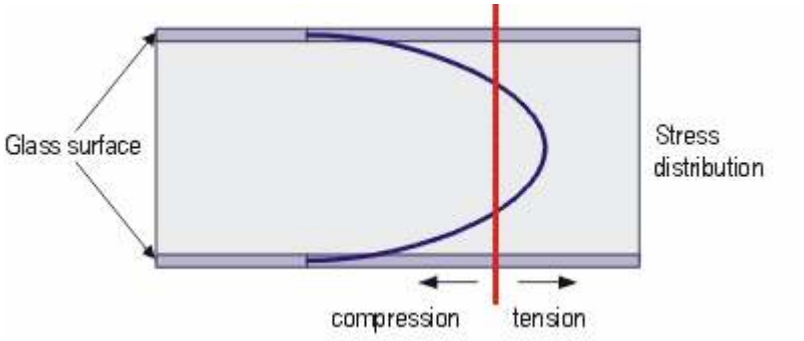

Fig 1.3 Schematic representation of the stress profile in toughened glass

The heat treatment process involves heating annealed (stress free) glass up to a temperature between its glass transition temperature and its softening point and then rapidly cooling the surface. This is usually achieved using air jets. This process freezes the surface, while the interior may still be molten and consequently there is a temperature differential across the thickness of the glass. The hotter core section then contracts at a faster rate compared to the outside until an isothermal state is reached. Initially the rapid cooling of the surface tends to induce a tensile stress in the surface. This is reversed in the latter stages of cooling, resulting in compressive stresses in the surface. Nevertheless, evacuated glazing is still as insulative as much thicker conventional double glazing and

tends to be stronger, since the two constituent glass sheets are pressed together by the atmosphere, and hence react practically as one thick sheet to bending forces. Evacuated glazing also offers very good sound insulation in comparison with other popular types of window glazing [3].

1.5.2 Chemically strengthened glass:

When broken it still shatters in long pointed splinters similar to float (annealed) glass. For this reason, it is not considered a safety glass and must be laminated if a safety glass is required. Chemically strengthened glass is typically six to eight times the strength of annealed glass. The glass is chemically strengthened by submersing the glass in a bath containing a potassium salt at 450°C. This causes sodium ions in the glass surface to be replaced by potassium ions from the bath solution Chemical strengthening results in a strengthening similar to toughened glass, however the process does not use extreme variations of temperature and therefore chemically strengthened glass has little or no bow or warp, optical distortion or strain pattern. This differs from toughened glass, in which slender pieces can often be significantly bowed. Chemically strengthened glass was used on some fighter aircraft canopies

1.5.3 Evacuated glazing:

Another recent innovation for insulated glazing is evacuated glass, which as yet is produced commercially only in Japan and China. The extreme thinness of evacuated glazing offers many new architectural possibilities, particularly in building conservation and historicist architecture, where evacuated glazing can replace traditional (much less energy-efficient) single glazing. An evacuated glazing unit is made by sealing the edges of two glass sheets, typically by using a solder glass, and evacuating the space inside with a vacuum pump.

CHAPTER 2

BIOCERAMICS

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Bio-ceramics are "those engineered materials that are inorganic and nonmetallic and find their applications in the field of medicine." So the class of ceramics used for repair and replacement of diseased and damaged parts of the musculoskeletal system are referred to as bio-ceramics. These bio-ceramics are also called ceramics biomaterials.

Bio-ceramics can have structural functions as joint or tissue replacements, can be used as coatings to improve the biocompatibility of metal implants, and can function as resorbable lattices which provide temporary structures and a framework that is dissolved, replaced as the body rebuilds tissue. Some ceramics even feature drug-delivery capability.

2.1 Types of bio-ceramics:

2.1.1 Inert bio-ceramics:

Bioinert materials do not release any toxic material but also do not show positive interaction with living tissue. As a response of the body to these materials usually a non-adherent capsule of connective tissue is formed around the bioinert material that in the case of bone remodelling manifests itself by a shape-mediated contact osteogenesis. Through the bone-materials interface only compressive forces will be transmitted (bony on-growth). Typical bioinert materials are titanium and its alloys, ceramics such as alumina, zirconia and titania, and some polymers, as well as carbon.

2.1.2 Bioactive materials*:*

Bioactive materials show a positive interaction with living tissue that includes also differentiation of immature cells towards bone cells. In contrast to bioinert materials there is chemical bonding to the bone along the interface, thought to be triggered by the adsorption of bone growth-mediating proteins at the biomaterials surface. These are durable materials that can

bind chemically with the surrounding bones and in some cases even with soft tissue. The material is ideal as bone cement filler and coating due to its biological activity.

2.1.3 Biodegradable materials:

These materials degrade on implantation to the body. This is Desirable is that the material degrades at the same rate at which the host tissue regenerates. Almost all Biodegradable ceramics are variations of calcium phosphate. The benefit of calcium phosphate biomaterials is that the human body can readily assimilate the dissolution products. The material can for example be used for bone repair. The bone grows into the material and replaces it, which makes the bone full functionally again [7].

Fig. 2.1 shows the bioactivity spectrum for various bio ceramics implants. The first figure shows over which time scale the interactions, if any, between the implant and the tissue take place. The second figure shows the time dependence of formation of bone bonding at an implant interface for the different groups of materials (resorbable, bioactive and inert) [8].

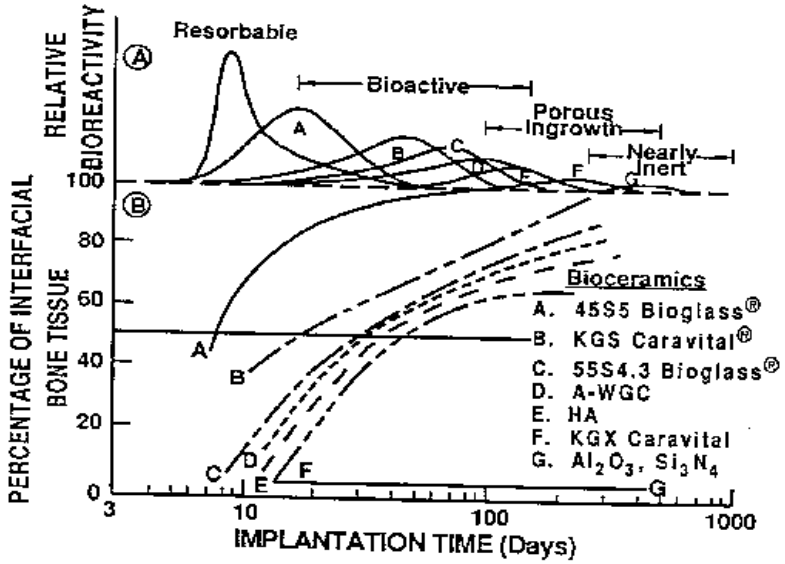

Fig. 2.1. Bioactivity spectrum for various bio ceramics implants.

2.2 Bio ceramics and their properties:

- Connective tissue cells, such as bone and cartilage cells,

Large response to injury

Low replication rate

- Bioceramics are often osteoconductive and have good strength
- Biocompatible Less stress shielding
- No disease transmission
- Unlimited material supply

2.3 Classification of bio ceramics:

Materials that can be classified as bioceramics with their activities are given in table 2.1

Table 2.1: Ceramics used in biomedical applications

Ceramics	Chemical formula	Comment
Alumina	Al_2O_3	Bioinert
Zirconia	ZrO_2	Bioinert
Pyrolytic carbon		Bioinert
Bioglass	$Na_2OCaOP_2O_3SiO$	Bioactive
Tricalcium phosphate	$Ca_3(PO_4)_2$	Biodegradable

2.3.1 Alumina:

The properties and required purity of alumina used in biomedical applications. The new ISO norm deviates from the existing norm in that much lower average grain size is specified with a concurrent increase in the flexural strength to beyond 450 MPa. This can be achieved by grain boundary engineering based on the suppression of grain growth at the high sintering temperature required by addition of minor amounts of magnesium oxide in the range of a few tenth of a percent. Alumina has Smaller the grain size and porosity, higher the strength; E=380 GPa (stress shielding may be a problem)

Alumina has

High hardness

Low friction

Friction: surface finish of <0.02 um

Low wear

Wear: no wear particles generated

Corrosion resistance

Its ability to be polished to a high surface finish makes it an ideal candidate for this wear application, where it operates against materials such as ultra high molecular weight polyethylene [7].

The properties of Al_2O_3 are summarized in table 2.2

Table2.2: Properties of alumina ceramics

Properties	**Alumina**
Density (g/cm^3)	>3.94
Avg. grain size(μm)	<4.5
Compressive strength(GPa)	n.s.
Tensile strength(MPa)	n.s.
Flexure strength(MPa)	>450

2.3.2 Zirconia:

As zirconia is produced from naturally occurring zirconium silicate (zircon, $ZrSiO_4$) or baddeleyite (monoclinic β-ZrO_2) trace amounts of uranium and thorium replacing the isovalent zirconium ion in the crystal lattice may remain in the processed material making it slightly radioactive. This indeed was a major concern that in the past had hampered the development of otherwise mechanically superior zirconia ceramics for biomedical applications. Zirconia is known for their general chemical inertness and hardness as shown in table 2.3.

These properties are exploited for implant purposes, where it is used as an articulating surface in hip and knee joints.

Table 2.3. Mechanical properties of commercially available zirconia

Property	Range of value
Density [g/cm³]	6.05 – 6.09
Zirconia content [%]	95 – 97
Yttria content [%]	3 – 5
Average grain size [µm]	0.2 – 0.4
E modulus [GPa]	150 – 210
Compressive strength [MPa]	> 2000
Tensile strength [MPa]	> 650
Flexural strength [MPa]	900 – 1300

2.3.3 Calcium phosphate:

Family of minerals having a calcium ion (Ca^{2+}), and an orthophosphate (PO_4^{3-}), metaphosphates or pyrophosphates ($P_2O_7^{4-}$), and sometimes hydrogen or hydroxide ions. Stability of calcium phosphate phases depends on temperature and water presence in processing and in the environment.There are several calcium phosphate ceramics that are considered biocompatible. Of these, most are resorbable and will dissolve when exposed to physiological environments. Some of these materials include, in order of solubility:

Tetracalcium Phosphate ($Ca_4P_2O_9$) > Amorphous calcium Phosphate > alpha-Tricalcium Phosphate ($Ca_3(PO_4)_2$) > beta-Tricalcium Phosphate ($Ca_3(PO_4)$ 2) >> Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$)

Unlike the other calcium phosphates, hydroxyapatite does not break down under physiological conditions. In fact, it is thermodynamically stable at physiological pH and actively takes part in bone bonding, forming strong chemical bonds with surrounding bone. This property has been exploited for rapid bone repair after major trauma or surgery. While its mechanical properties have been found to be unsuitable for load-bearing applications such as orthopedics, it

is used as a coating on materials such as titanium and titanium alloys, where it can contribute its 'bioactive' properties, while the metallic component bears the load [7].

2.3.4 Glass ceramics:

The bioactive glasses can be employed to repair and to rebuild damaged tissues, particularly hard tissues. One point that differentiates them from other bioactive ceramics or glass-ceramic is the possibility to tailor a great chemical range of properties and of linking speed to the tissues. Therefore is it possible to design glasses with tailored property for a specific clinical application. The bioactive glasses can be produced with the conventional technologies of the glass industry, but it is necessary to verify the purity of the raw materials, to avoid the contamination by impurity and the loss of volatile elements, like Na_2O or P_2O_5. The different phases of production, so like the choice of the raw materials, influence the final features of the piece. The bioactive glasses are soft glasses and therefore the final shape can be easily given with conventional tools [9].

The base components are usually SiO_2, Na_2O, CaO, and P_2O_5.

Glass ceramics were the first biomaterials to display bioactivity (bone system):

- Capable of direct chemical bonding with the host tissue
- Stimulatory effects on bone-building cells

The main advantage of the bioactive glasses is the high superficial speed reaction that brings to rapid connections to the tissues. The greater disadvantages are the not optimal mechanical property and the meagre break resistance. The out-bending-tensile rigidity of the greater part of the bioactive glasses varied between 40 and 60 MPa, and they are not therefore useable for loading applications [7].

2.3.5 Pyrolytic carbon:

Pyrolytic carbon is commonly used in artificial heart valves and has been the most popular material for this application for the last 30 years. Properties that make this material suitable for this application include good strength, wear, resistance and durability, and most

importantly, thromboresistance, or the ability to resist blood clotting. Pyrolytic carbon is also used for small orthopaedic joints such as fingers and spinal inserts.

2.3.6 Hydoxyapatite:

Another bioceramic coating that has been reached a significant level of clinical applications are the use of hydroxyapatite, as a coating on porous metal surface for fixation of orthopedic prosthesis. This approach combines methods of fixation and originates from the observations ducheyne and collogues in 1983 that hydroxyapatite powder in the pores of porous, coated-metal implant could significantly affect the rate and vitality of bone in the growth of bone. There is sustainable enhancement of the early stage interfacial bond strength of implants with hydroxyapatite coating when compared with porous metals without coating. Long term animal studies and clinical trials of load bearing dental and orthopedic prosthesis suggest that some hydroxyapatite coating may degrade and comes off with time depending upon crystallity of hydroxyapatite layer Hench et al [9].

2.4 Glass and glass ceramics as biomaterials:

Hench et al. [10] discovered that bone can bond chemically to certain glass composition. This group of glasses is known as bioactive glasses. So bioactive glasses are “Bioactive refers to a material, which upon being placed within the human body interacts with the surrounding bone and in some cases, even soft tissue. This occurs through a time – dependent kinetic modification of the surface, triggered by their implantation within the living bone.” The bioactive glasses can be employed to repair and to rebuild damaged tissues, particularly hard tissues. One point that differentiates them from other bioactive ceramics or glass-ceramic is the possibility to tailor a great chemical range of properties
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Table 2.4 Composition of common bioactive glasses

Component	**45S5 Bio glass**	**45S5.4F Bio glass**	**52S4.6 Bio glass**	**52S4.3 Bio glass**	**A/W Glass-ceramic**	**MB Glass-ceramic**
SiO_2	45	45	52	55	34.2	19-52
P_2O_5	6	6	6	6	16.3	4-24
CaO	24.5	14.7	21	19.5	44.9	9-3
CaF_2		9.8			0.5	
MgO					4.6	5-15
Na_2O	24.5	24.5	21	19.5		3-5
Al_2O_3						12-33
B_2O_3			15			

2.5 Types of bioactive glasses

Bioactive glasses are broadly divided in two glasses: class A and class B

2.5.1 Class 'A' bio glasses:

These materials are osteoproductive in nature. These can bond to soft and hard tissues. They releases silica ions in the form of silicic acid, provides a silica gel layer, which further enhances the precipitation of amorphous CaP layer and rapidly crystallizes hydroxyapatite layer. Generally hydroxyapatite layer is formed within 1-10 hours for this type of materials. Bioglasses 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 glasses.

2.5.2 Class B bio glasses:

These materials are osteoconductive in nature. They don't produce silica gel layer and they only bond to hard tissues. In his type of glasses hydroxyapatite layer is formed within 24 hours to several days [13].

2.6 Bioactive glasses

The most studied of these is the Bioglass® 45S5. The abbreviation indicates that it contains 45 % in weight of SiO_2 (oxide creator) and the molar rate between Ca and P is of 5:1. Glasses with significantly lower molar rate (in the form of CaO and P_2O_5) don't generate connections with the bone [11]. A lot of glasses were studied in this four components system with a constant content of P_2O_5 of 6%. The results are summarised in the diagram of figure 2.2.

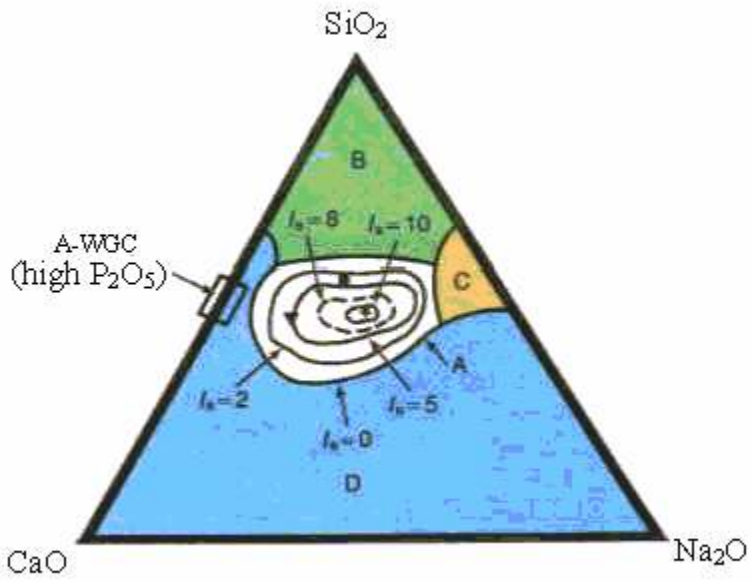


Fig. 2.2. Ternary diagram

In the diagram were indicated the lines of iso-bioactivity. The level of bioactivity is defined like $I_b = 100/t_{0.5bb}$, where $t_{0.5bb}$ is the necessary time to bind at the bone more of 50% of the surface. The bioactive glasses are in zone A and they bind with the bone. Into the sketched line ($I_b > 8$), the glasses bind also with the soft tissues, while moving from the centre decrease I_b, and therefore the speed of reaction decreases. In the zone B they behave like almost inert, while the

glasses in the region C are reabsorb in a time included between 10 - 30 days. The compounds in the zone D did not result technically interesting, and therefore were not implanted. An indicator of very high bioactivity brings to a wide connection zone, but also to a low sheer resistance. So the optimal compound is chosen in function of the necessity to have rapid connections, or high sheer resistance.

A partial substitution of CaO with CaF_2 doesn't changes significantly the behaviour of the linkage-disintegration and changes the boundary between the zone A and C. Also the substitution of CaO with MgO or of Na_2O with K_2O does not influence the connection on the bone. The addition of Al_2O_3 is useful to monitor the duration of the glass surface and the features of forging and of merger, but can forbid the connection with the bone. The percentage of alumina tolerated varied between 1% and 1.5%. It can surpass these values if the glass has a high reactivity (bioactivity). Increasing the amount of Al_2O_3, the dimension of the limit zone of connection with the bone (zone A) decreases.

The role of the phosphate is interesting: at first it is believed that it was necessary to make a glass bioactive, then it was demonstrated that also glasses without phosphate, or glass-ceramics in which P_2O_5 is bound in a phase of insoluble apatite and it is relatively stable, have bioactive behaviour.

The main advantage of the bioactive glasses is the high superficial speed reaction that brings to rapid connections to the tissues. The greater disadvantages are the not optimal mechanical property and the meagre break resistance. The out-bending-tensile rigidity of the greater part of the bioactive glasses varied between 40 and 60 MPa, and they are not therefore useable for loading applications. The elastic modulus is in order of 30-35 GPa, and it is very similar to that of the cortical bone. The low resistance does not hinder the use of the bioactive glasses like covering, where the limiting factor is the resistance of the interface between the metal and the covering, so like it is not hinder the use in low load or loaded in compression implantations, in shape of dust, or like bioactive phase in composites.The unique surface reactivity of bioactive glasses has been described extensively. Figure 6 summarizes the various reactions that transpire at the bioactive glass—tissue surface, with stages 1 through 5 occurring ostensibly in sequence [11].

Stage (1) is the loss of sodium ions (Na^+) from the surface of the glass via ion exchange with hydrogen (H^+ or H_3O^+). This reaction occurs very rapidly, within minutes of material exposure to

bodily fluids, and creates a dealkalinization of the surface layer with a net negative surface charge. This stage is usually controlled by diffusion and exhibits a $t^{-1/2}$ dependence.

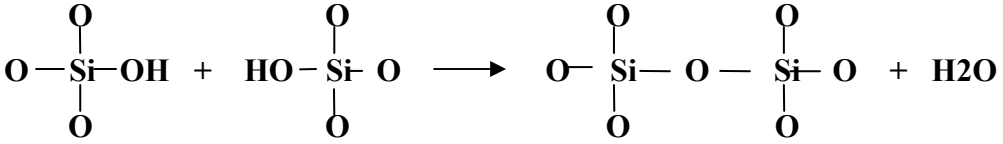
$$Si\text{-}O\text{-}Na^{+} + H^{+} + OH^{-} \longrightarrow Si\text{-}OH\text{-} + Na^{+}(solution) + OH^{-} \quad (4)$$

Stage (2) Loss of soluble silica in 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.

$$Si\text{-}O\text{-}Si + H_2O \longrightarrow Si - OH + OH\text{-}Si \quad (5)$$

This stage is usually controlled by interfacial reaction and exhibits a $t^{1.0}$ dependence. Hench has proposed that the loss of soluble silica from the surface of bioactive glasses might be at least partially responsible for stimulating the proliferation of bone-forming cells in the area of the glass surface.

Stage (3) Condensation and repolymerization of a SiO_2-rich layer on the surface depleted in alkalis and alkaline earth cations.



(6)

Stage (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.

Stage (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, fluoroapatite layer.

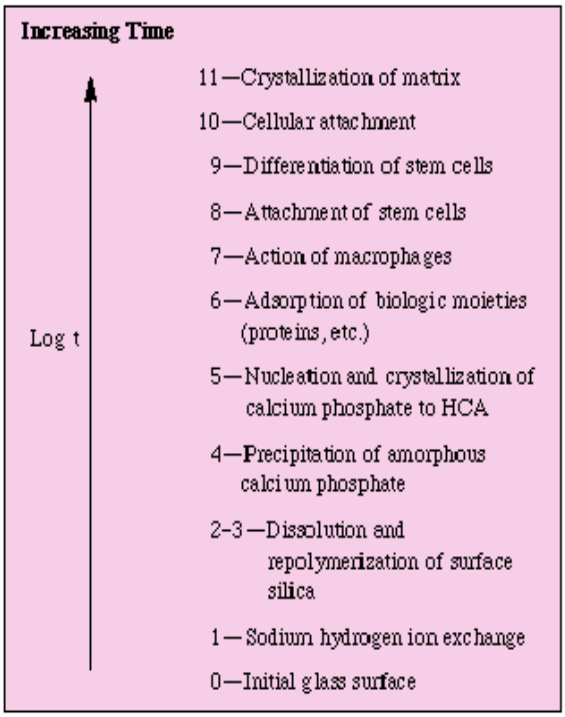


Fig. 2.3. Sequence of interfacial reactions involved in forming a bond between bone and bioactive glasses

2.7 Clinical uses of biomaterials:

An overview of areas where bioceramics can be used:

2.7.1 Osteoporosis:

Osteoporosis is characterized by loss of bone density that can lead to debilitating fractures of the hip and spine. The disease usually strikes postmenopausal women, age 50 to 70, as a result of decreased estrogen and progestin levels. The disease also can occur later in life in women and, as a result of testosterone imbalance, in men. Orthovita produces two biomaterials Vitagel™ Surgical Hemostat and Vitoss™ Scaffold. Vitagel, composed of thrombin, is a product that assists the body in blood clotting when all conventional methods fail. Vitoss is intended to be gently packed into bony voids or gaps of the skeletal system (i.e., the extremities, spine and pelvis) [12].

2.7.2 Hip replacement:

The common reason for hip replacement surgery is the wearing down of the hip joint, resulting from osteoarthritis. Other conditions include: rheumatoid arthritis (a chronic inflammatory disease that causes joint pain, stiffness, and swelling), avascular necrosis (loss of bone caused by insufficient blood supply), injury, and bone tumors. System incorporates the proven performance of alumina-on-alumina ceramic bearing couples and the advantageous history of the hemispherical porous cup. Its use can be in either cemented or non-cemented hip arthroplasty.

2.7.3 Scaffolds for bone tissue engineering:

Bioceramics calcium phosphate cement has attracted much attention in medicine and dentistry because of its excellent biocompatibility and bone-replacing behavior over long periods. The 3D dicalcium phosphate dihydrate cement (DCPD) is proposed for potential guided bone tissue regeneration. The DCPD porous scaffolds were fabricated with a specific design of macropores with chosen size and interconnectivity by indirect solid freeform fabrication (ISFF). Calcium phosphate cement (CPC) has been widely evaluated in medicine and dentistry trials because of its excellent biocompatibility and bone-replacement behavior over long periods. Furthermore, the CPC can be cured at physiology temperature which is clinically desired [14].

2.7.4 Facial Skeleton deformities:

The removal of certain deformities of facial bones is a prerequisite to a restoration of function, stability, and appearance. Synthetic bone substitutes are beneficial in cases where other operative technique would represent an inadequate burden for a patient. A result is achieved in onesurgical intervention with low costs and low demands on technical equipment. Biocompatible nonresorbable glass-ceramics based on oxyfluoroapatite and wollastonite presenting osteoconductivity permits osteointegration

2.7.5 In Situ treatment of Cancer by radiotherapy and hyperthermia:

One of the most common approaches in cancer treatment is the removal of the diseased parts, however unfortunately recovery or return of full function is seldom achieved. Non-invasive treatment techniques where only the cancer cells are destroyed were introduced in mid 80's. In 1987, microspheres of $17Y_2O_3$-$19Al_2O_3$-$64SiO_2$ (mol wt%) glass, 20-30 μm in diameter were shown to be effective for in situ radiotherapy of liver cancer.

2.7.6 Silicate cement

Silicates constitute the first dental cement to use glass as its component. The cement powder is a glass consisting silica, alumina and fluoride compounds. The liquid, on the other hand, is an aqueous solution of phosphoric acid with buffer salts. The cement powder and liquid are mixed together resulting in an acid-base reaction. Fluoride ions are leached out from the set cement, which is responsible for the anti-cryogenic property exhibited.

2.7.7 Glass ionomer cement (GIC)

Glass ionomer cement represents a logical step in the evolution of therapeutic cements. They constitute an improved version of the silicate cement, in which the liquid is replaced by carboxylic acids with glass remaining as the powder. It is the most popular
dental cement that is used in various aspects. The highlight of this material is demonstrated by its superior biocompatibility and anti-cariogenic property.

Modifications of glass ionomer cement include the high density Glass ionomers, packable ionomers for use in Atraumatic Restorative Treatment (ART). Resin modified Glass ionomer cements incorporate resins in their powder component for better strength.

CHAPTER 3

LITERATURE REVIEW

Bio ceramics have proven to be attractive materials for repairing and replacing body parts due to their biocompatibility. In many applications bio ceramics are used in the form of bulk materials of a specific shape. However in loading bearing applications their inherent brittleness requires them to be used as a coating material on a tougher substrate. Hydroxyapatite (HA) is a bio ceramic that has a composition similar to that of bone. As well as improving biocompatibility, it encourages the ingrowth of bone and thus can be used as a method of fixation for implants such as total hip replacements and dental implants

Over the last several decades, bio-ceramics have helped improve the quality of life for millions of people. These specially designed materials—polycrystalline aluminum oxide, hydroxyapatite (a mineral of calcium phosphate that is also the major component of vertebrate bone), partially stabilized zirconium oxide, bioactive glass or glass-ceramics, and polyethylene-hydroxyapatite composites—have been successfully used for the repair, reconstruction, and replacement of diseased or damaged parts of the body, especially bone. For instance, aluminum oxide has been used in orthopedic surgery for more than 20 years as the joint surface in total hip prostheses because of its exceptionally low coefficient of friction and minimal wear rates. In this chapter the advancement in the field of bioceramic glasses are summarized.

Hench and Wilson et al. [15] have reported the first bioactive material reported bioglass 45S5, contained a 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 results in very rapid ion exchange with the proton and hydronium ion in physiological solution. The evaluation of bioceramics with reference are given in table 3.1

Table 3.1 Evolution of bioactive glass and glass ceramic implants

Year	Event	Reference
1969	Evidence of bone bonding to bioactive glass and glass ceramics(45S5bioglass)	Hench et al.,1970
1973	Mechanism of bone-bioactive glass identified	Hench and Paschall, 1973
1973	Bone bonding of bioactive glass ceramic in Europe	Bromer et al.,1975
1975	Successful load bearing orthopaedic prostheses in monkey using 45S5 Bioglass	Piotrowski et al.,1975
1976	Compositional profile of bioactive glass bone measurement	Clark et al.,1976
1976	Successful bonding of bioactive glass dental implant	Stanley et al.,1976
1980	Comparative histology of implants variable bioactivity	Gross and strunz,1980
1981	Clinical use of bioactive glass ceramics in middle ear prostheses	Reck,1981
1981	Structultral analysis of bioactive glass ceramic and bone	Gross et al.,1981
1982	High strength bioactive implant(A/Wglass-ceramic)and prostheses	Kokubo et al.,1982
1983	Machinable bioactive glass ceramic	Hohland et al.,1983
1984	FDA approval of bioactive glass as middle ear prostheses	Hohland et al,1984

Chia-Hao et. al. [16] studied that Polymer, ceramic and metal is widely applied in orthopedic and dental materials. However, most metal including titanium, titanium alloy and 316L stainless

steel do not posses bioactivities to bond with bone tissue. For improving this weakness, we incubated titanium wire and 316L stainless steel fiber into the simulated body fluid (SBF) after alkaline and thermal treatments to form a bone-like apatite layer on it. With the reaction, the coating was formed on the surface of metal and it can induce apatite nucleus appear on the surface. The surface appearance was observed and the chemical constitution of bone-like apatite was examined. As the result show, when the titanium wire and 316L stainless steel fiber treated with 5 M NaOH aqueous solution, subsequently heated at 400 °C and soaked into SBF at a temperature of 80 °C increase the possibility of nucleation of considerable quantities of bone-like hydroxyapatite. They also found the main components of both the HA structures were Ca and P, and the percentage Ca/P were 1.69 and 1.1, which is similar to that of a natural bone.

V. Rajendran et. al. [17] made the bioactive glass of composition $53SiO_2–6Na_2O–22CaO–11K_2O–5MgO–2P_2O_5–1B_2O_3$ (1–98) has been prepared using the melt method. The ultrasonic velocities, attenuation and elastic properties measurements have been made operated at a fundamental frequency of 5MHz at room temperature on bioactive glass 1–98 before and after different thermal treatment conditions. Thermal treatments of bioactive glasses lead to changes in elastic properties of bioactive glass. Furthermore, a long-term thermal treatment at higher temperatures also seemed to cause such changes to the glass surface that the formation of Ca,P-layer was inhibited during a 48 h immersion in simulated body fluid (SBF).

Ohtsuki et. al. [18] working with $CaO-SiO_2-P_2O_5$ glasses, showed that no bioactive $CaO-P_2O_5$ composition increases the degree of supersaturating more than the bioactive $CaOSiO_2$ 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 39 soluble silicates, 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 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.

K. El-Egili et. al. [19] analyzed Infrared spectra of $Na_2O–B_2O_3–SiO_2$ and $Al_2O_3–Na_2O–B_2O_3–SiO_2$ glasses (with intermediate SiO_2 contents) have been to calculate the fraction N4 of four coordinated borons. A reasonable agreement between the N4 values calculated from IR spectra and those determined from NMR spectroscopy (or using literature models) could be attained under certain condition. It has been proposed that the absorption bands in the region 1000–1120 cm_1 arise from contributions of SiO_2 and B_2O_3 vibrations the contribution of an oxide is proportional to its concentration. Heat treatment of $Na_2O–B_2O_3–SiO_2$ glasses does not change the value of N4 and this indicates that the structure of alkali borate phase is the same in the glass obtained from melt and in the heat-treated one.

Peitl et. al. [20] have shown that crystallization of Bioglass® 45S5 did not inhibit HCA formation in an invitro test with SBF-K_9 even with a fully crystallized glass-ceramic. The onset time for HCA layer formation did decrease with increased crystalline 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.

Roman et. al. [21] studied the influence of the phosphorus on the crystallization and bioactivityof glass-ceramics obtained from sol–gel glasses. For this purpose two sol–gel glasses with a similar composition but one of them containing P_2O_5 (70% SiO_2; 30% CaO and 70% SiO_2; 26% CaO; 4% P_2O_5, mol %) were prepared. Pieces of these glasses were treated at temperatures ranging between 700ºC and 1400ºC for 3 h. The obtained materials were characterized by XRD, FTIR, SEM-EDS and the biaxial flexural strength was determined in samples heated at 1100ºC. In

addition, an in vitro bioactivity study in simulated body fluid (SBF) was carried out. The results showed that phosphorus plays an important role in the crystallization of the glasses: it induced the crystallization of calcium phosphate phases, the stabilization of the wollastonite phase at high temperature as well as the crystallization of SiO_2 phases at low temperatures. Moreover, the presence of phosphorus produced a heterogeneous distribution of defects in the pieces and, therefore, the flexural strength of samples containing this element decreased. Finally, glass-ceramics obtained from glasses containing phosphorus showed the fastest formation rate of the apatite layer when soaked in SBF.

Renlong Xin et. al. [22] Formation of calcium phosphate (Ca-P) on various Bioceramic surfaces in simulated body fluid (SBF) and in rabbit muscle sites was investigated. The Bioceramics were sintered porous solids, including bioglass, glass-ceramic hydroxyapatite, a-tricalcium phosphate and b-tricalcium phosphate. The ability of inducing Ca-P formation was compared among the Bioceramics. The Ca-P crystal structures were identified using single-crystal diffraction patterns in transmission electron microscopy. The examination results show that ability of inducing Ca-P formation in SBF was similar among Bioceramics, but considerably varied among Bioceramics in vivo. Sintered b-tricalcium phosphate exhibited a poor ability of inducing Ca-P formation both in vitro and in vivo. Octacalcium phosphate (OCP) formed on the surfaces of bioglass, A-W, hydroxyapatite and a-tricalcium phosphate in vitro and in vivo.

Kasuga et. al. [23] studied that Calcium phosphate glass-based materials in the pyrophosphate region are briefly reviewed. Calcium pyrophosphate glasses can be prepared by including a small amount of TiO_2 ($\leqslant$10 mol %). Bonelike apatite forms on some of the glasses in simulated body fluid. By heating powder-compacts of the glasses, they are crystallized and subsequently are sintered, resulting in fabrication of high-strength glass-ceramics with machinability; they are easier to be machined using conventional tools in comparison with conventional calcium phosphate ceramics. β-$Ca_2P_2O_7$ crystal formed in the glass-ceramics plays an important role in the machinability. Their apatite-forming ability in simulated body fluid is drastically enhanced after autoclaving in distilled water. The glass-ceramics can be easily coated on a new β-type titanium alloy using a conventional glazing technique.

Kim Y et. al. [24] studied that alumina was coated with bioactive glass which is known to show a bonding behavior to living tissue. Another glass also coated between alumina and bioactive glass to compensate their differences in thermal expansion. After coating the alumina with bioactive glass, it reacted in simulated body fluids to investigate the formation of hydroxyapatite. The bioactive-glazed layer crystallized into α-wollastonite and β-wollastonite crystalline phases when the glaze was fired at 1200 °C and 1100 °C, respectively. When the samples reacted in SBF α-wollastonite easily leached out of the surface and hydroxyapatite formed on the leached site. The leaching rate of α-wollastonite was faster than that of β-wollastonite, and the hydroxyapatite-forming rate was also faster in the sample containing α-wollastonite than in the other sample. No silica-rich layer was found underneath the newly developed hydroxyapatite.

V. Simon et. al. [25]The in vitro behavior of xAg_2O $(100 - x)[50P_2O_5 \cdot 30CaO \cdot 20Na_2O]$ glasses ($0.14 \leqslant x \leqslant 20$ mol%) is investigated in simulated body fluid (SBF) mainly with respect to bioactivity and silver ions release. In order to estimate the biodegradability and bioactivity, the samples were soaked in SBF, which has almost equal ions concentration to those of human blood plasma, and kept at 37 °C for fixed periods of time up to 18 days. After the fixed periods of time analyses were performed on the SBF solutions. Calcium and silver ions concentration of SBF after different soaking times of the glass samples were primarily examined. Conductivity data support the assumption that the released silver ions are reduced in SBF and their release is obstructed by growth of the bioactive layer on the glass surface. X-ray diffraction and infrared analysis attest the development on glass surface of a hydroxyapatite type layer.

Oliveira, et. al. [26] studied glass of nominal composition (wt %) 17.25 MgO-52.75 3CaO.P, 0,-30 $SiO_2$and a glass-ceramic obtained from it showed surface modifications when immersed in and a cellular medium having a composition similar to that of human blood plasma. A (Ca, P)-rich layer, with an approximate, CalP atomic ratio of 1.7, identified as hydroxyapatite, developed on both samples. The precipitated film on the glassy sample was weakly bonded, whereas that formed on the glass-ceramic was strongly adherent. The apatite precipitated during the in virro tests on both samples grew as a needle-like structure with crystals about 150-200 nm long and 50-70 nm thick, as measured on specimens soaked for 1 month in the simulated body fluid

(SBF). The presence of calcium and phosphate ions in the SBF contributed to the precipitation of the (Ca, P)-rich layers on both specimens.

Rapacz et. al. [27] has reported the Performance of hydroxyapatite material in a living body depends on a number of factors. Stability of hydroxyapatite structure, which is influenced by both, preparation conditions of the starting precursor powders and fabrication method of the implant materials, is an important one. Inappropriate preparation conditions of synthesis, calcination of powder and sintering of formed samples result in dehydroxylation and even in decomposition of HAp which lead to the change in the physicochemical properties of implants.In the work samples of hydroxyapatite ceramics have been obtained by two methods, i.e. by hot pressing and by pressureless sintering in the temperature range of 1150–1300 8C. The materials prepared have been studied using FTIR and XRD in order to identify the dehydroxylation processes and the possible hydroxyapatite decomposition during thermal treatment. The usefulness of both methods in identification of thermal stability of hydroxyapatite was confirmed.

In early 1990s, sol-gel processing was introduced for the synthesis of bioactive Glasses. 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.

In the recent time borate glasses have fetched lots of attention for the medical applications. Brown et al, Day et.al, Rehman et.al.[28] have demonstrated that silica free borate glasses also exhibit bioactive behavior and have been shown to convert to calcium phosphate at a remarkable rapid rate.

3.1 MECHANICAL PROPERTIES OF BIOGLASSES

The new generation biomaterials with new compositions and their applications have been highlighted by many reachers in view of their potential biomedical applications. A review on the materials such as phosphate based compositions, sol-gel derived materials, matrices in composites, packing and scaling and high strength high toughness and machinable materials and their applications in implants.

Hench and Anderson et. al. [5] devoted his review to the use of bioceramics as implants to repair of the body. The achievements of the use of clinical applications which require match of Mechanical behavior of implants with the tissue to be replaced has been revealed. The development of biomaterials for dentistry is concentrated on fulfilling the expectation regarding the strength, shade, translucency, chemical resistance and wear of the material. The fracture behavior of binary of CaO-MgO phosphate glasses has been studied by ashizuka by measuring the fracture toughness and determining the resulting fracture fracture surface energy. The fracture toughness and fracture surface energy of binary glasses decreases with increase in CaO or MgO content, even an increasing trend in elastic module was noticed.

Kokubo et. al. [16] showed the mechanical strength of A-W glass –ceramics is superior to that of cortical bone. The mechanical properties of some of the bioceramic glasses are given in table 3.2

Rajendran et. al. [17] has studied elastic properties of bioactive glasses in SiO_2-Na_2O-CaO-P_2O_5 system. They concluded that the strength of the network containing up to SiO_2 equal to 45 wt% further additions of SiO_2 contents leads to softening network.

Table3.2. Mechanical properties of some clinically used biomaterials

Name	Young's modulus	Compressive strength	Hardness	Fracture toughness	references
Al_2O_3	*380*	4000	2000-3000	5-6	Thamaiselvi (2004)
ZrO_3	*150-200*	2000	1000-3000	4-12	Thamaiselvi (2004)
Bioactive HAP	*73-117*	600	350	<1	Thamaiselvi (2004)
Bioglass®	*75*	1000	Na	0.7	Hench (1982)
Bone	*3-30*	130-180	Na	na	Thamaiselvi (2004)
Porcelain	*Na*	Na	Na	na	Abe (1990)
Bioverit 1	*70-88*	500	5000	1.2-2.1	Holand (1993)
Bioverit 2	*70*	450	8000	1.2-1.8	Holand (1993)
Bioverit 3	*45*	Na	na	0.6	Holand (1993)
AW glass ceramic®	*118*	1080	680	2	Thamaiselvi (2004)

CHAPTER 4

EXPERIMENTAL DETAILS

4. Introduction

In this chapter procedure applied during the experiment is presented. The detailed measurement techniques and procedure employed for vitro bioactivity testing, density, X-ray diffraction (XRD), band gap measurement of samples by UV-Visible Spectroscopy and Fourier transform infrared spectroscopy (FT-IR) are given in detail.

4.1 Sample preparation:

For the present study silica rich glasses were selected. The compositions of glasses with their label are given in table 1.

Table 4.1. Glass composition (mol %) with their label

Sample Label	SiO_2	CaO	B_2O_3	Y_2O_3	Al_2O_3	Cr_2O_3	La_2O_3
AS1	40	30	20	10			
AS2	40	30	20		10		
AS3	40	30	20			10	
AS4	40	30	20				10

All these glass samples were taken and cut one by one in the rectangular shapes by diamond cutter. Then grinding and polishing of these samples was done on emery paper and after then these samples were cleaned by ultrasonic washing in ultrasonic bath cleaner. After that density of these samples were found by Archimedes principle. Then XRD of all these glass samples were taken o conform he glassy nature of samples. Then the 1000 ml simulated body fluid (SBF) solution was prepared by taking all the chemicals in the proper proportions. During the preparation of simulated body fluid (SBF) solution the pH was maintained~ 7 to 7.5. This solution was preparing by maintain temperature at 37°C and put this solution at the cool place for 1 day. Then these samples were immersed in simulated body fluid (SBF) solution for 17 days.

During this period we check out the pH of the samples after small interval of time and after removal the samples from simulated body fluid (SBF) solution again density of these

samples is find out and get the relevant information and done XRD of all these samples. Than again all these samples were again immersed in simulated body fluid (SBF) solution for 8 days. During this duration the pH of all these samples were taken. After 8 days all the samples were taken out from simulated body fluid (SBF) solution and density of samples were measured using Archimedes principle. After than all characterizations of these samples like XRD, UV-Visible, FT-IR were done.

The steps for the formation of hydroxyapatite layer are

1. Exchange of Na. for H. $=H^3O$. at the glass surface - pH increase.
2. Break up of silicate network - silanol groups.
3. Condensation and polymerization of silanols - silica gel layer.
4. Migration of Ca, P to surface - Ca, P-rich layer.
5. Crystallization of calcium phosphate - hydroxyapatite

4.2 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 fluid similar to 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 applications. In vitro testing also provides useful insights as to whether a device needs further evaluation inexpensive in vivo experimental models.

In present research simulated body fluid (SBF) proposed by Kokubo has been used. simulated body fluid (SBF) is an aqueous solution with an ionic composition that closely resembles to human plasma, buffered to physiological pH (7.25-7.40) at 37°C with a mixture of HCl/ tris (hydroxymethyl) amino methane. The ionic concentration of simulated body fluid (SBF) and human plasma are given below in table 4.2. Since this fluid contains Ca^{2+} and HPO_4^{2-} ions, it can be used to assess the in vitro bioactivity of a wide range of materials.

An SBF-K_9 solution was prepared by mixing sodium chloride, sodium bicarbonate, potassium chloride, calcium chloride, dibasic potassium phosphate and magnesium chloride in deionised water, according to method proposed by Kokubo et al. [31].

Table 4.2. Ion concentrations of SBF and Human Plasma

Ions	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^{2-}_4	1.0	1.0
SO^{2-}_4	0.5	0.5

4.3 Standard operating procedure for preparing Simulated Body Fluid

Simulated body fluid (SBF) is a metastable solution containing calcium and phosphate ions already supersaturated with respect to the apatite. Therefore simulated body fluid (SBF) is prepared as follows:

(a) Cleaning

- Clean all the bottles including flasks, beakers etc. with dilute hydrochloric acid solution, sterilizing agent and ultra-pure water in this order.
- Immerse all the bottles etc. in dilute hydrochloric acid solution for several hours. Remove the bottles from the solution and wash with tap water well.
- Immerse the bottles etc. in sterilizing liquid for overnight. Remove them from the liquid, and washed with ultra-pure water well.

(b) Dissolution of chemicals

- Put 750 ml (=cm^3) of ultra-pure water into a 1000 ml beaker (polyethylene beaker is preferred). Stir the water and keep its temperature at 36.5^oC with magnetic stir

with heater. The beaker is preferred to be placed in clean bench, to avoid dusts.

- Add each chemical given in Table 4.3 into the water until 8, one by one in the order given in Table 4.3, after each reagent was completely dissolved. Weigh a chemical with weighing bottle. Add it in the water.

- Addition of reagent 9 should be little by little with less than about 1g, in order to avoid local increase in pH of the solution.

(c) Adjustment of pH

- Calibrate the pH meter with fresh standard buffer solution.
- After 9 on the order in Table 4.3, check the temperature of the solution in the beaker, and place the electrode of pH meter in the solution. Measure its pH while the temperature is at 36.5^{o}C. At this point, pH of the solution is approximately 7.5 Titrate 1kmol/dm^{3}-HCl solution with pipette to adjust the pH at 7.25 (or 7.40).
- After the adjustment of pH, transfer the solution from the beaker to a glass volumetric flask of 1000 ml. Wash the inside of the beaker with ultra-pure water several times and add the solution to the flask.
- Add ultra pure water to the solution, adjusting the total volume of the solution to 1000 ml, and the shake the flask well.

(d) Storage

- Rinse a polyethylene (or polystyrene) bottle of 1000 ml with a bit of the prepared solution, simulated body fluid (SBF), at least three times. Transfer the solution from the flask to the polyethylene bottle.
- Store the bottle in a refrigerator at 5-10^{o}C.

Stability of the solution obtained must be examined. Put 50 ml of the solution in a polystyrene bottle and place it in incubator at 36.5^{o}C. After 2-3 days, check whether the solution has any precipitation or not. If any precipitation would be found, do not use the solution. Bottles in which precipitation occur must not be used for any further experiments, because some calcium phosphates would be adhered on their walls inside. A precipitation of calcium phosphate

especially such as hydroxyapatite easily induces further formation of hydroxyapatite in the solution, since the simulated body fluid (SBF) is already supersaturated.

Table 4.3. Reagents for preparation of simulated body fluid (SBF)

Order	**Ions**	**Amount(g/dm^3)**
1	NaCl	7.996
2	$NaHCO_3$	0.350
3	KCl	0.224
4	$K_2HPO_4.3H_2O$	0.228
5	$MgCl_2.6H_2O$	0.305
6	1N-HCl aqueous solution	35 ml
7	$CaCl_2.H_2O$	0.368
8	Na_2SO_4	0.071
9	$(CH_2OH)_3CNH_2$	6.057
10	1N-HCl, aqueous solution	10ml

4.4 Density

Density of all glass samples were found out from Archimedes principle using water buoyant. The density was determined from the following relation:

$$\rho = W_a/W_a\text{-}W_b \times \rho_b \quad (7)$$

Where W_a is the weight in air, W_b is the weight in buoyant and ρ_b is the density of buoyant. All the weight in measurement has been made using a digital balance. The experiment was repeated for three times for accurate values

Archimedes' principle, principle that states that a body immersed in a fluid is buoyed up by a force equal to the weight of the displaced fluid. The principle applies to both floating and submerged bodies and to all fluids, i.e., liquids and gases.

4.5 X- Ray Diffraction (XRD):

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of bulk materials as well as thin films. These techniques are based on observing the

scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. To confirm the amorphous nature of glass samples and to find out the change in samples after dipping in SBF solution, XRD has been made of all samples with CuK α (1.54A°) radiation.

4.6 UV-Visible Spectroscopy

Ultraviolet-visible spectroscopy (UV/ VIS) involves the spectroscopy of photons in the UV-visible region. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions (Fig 4.2).

This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

Fig 4.2 Diagram of UV Spectrometer

UV-visible spectroscopy is the reliable and accurate procedure for analysis of samples. UV measures the absorption, transmission and emission of ultraviolet and visible wavelength by matter. UV Spectroscopy measures absorption and transmission of electromagnetic radiations by atoms or molecules. Here we are calculating the band gap of the samples to know the effect of hydroxyl apatite layer on the energy band of without soaked and soaked samples. If some modification on the surface of the samples were happened in soaked sample, it can be verified by UV-Vis spectroscopy.

4.7 Band gap

The band gap, also called an energy gap is a region where a particle or quasiparticle is forbidden from propagating. For insulators and semiconductors, the band gap generally refers to the energy difference between the top of the valence band and the bottom of the conduction band. The transition of electron can be direct or can be indirect.

Direct band gap means that the minimum energy of the conduction band lies directly above the maximum energy of the valence band in momentum space. In a direct band gap semiconductor, electrons at the conduction-band minimum can combine directly with holes at the valence band maximum, while conserving momentum. The energy of the recombination across the band gap will be emitted in the form of a photon of light**.**

Indirect band gap is a band gap in which the minimum energy in the conduction band is shifted by a k-vector relative to the valence band. The k-vector difference represents a difference in momentum. In indirect band gap semiconductors such as crystalline silicon, the momentum of the conduction band minimum and valence band maximum are not the same, so a direct transition across the band gap does not conserve momentum and is forbidden. Recombination occurs with the mediation of a third body, such as a phonon or a crystallographic defect, which allows for conservation of momentum.

4.8 Determination of Energy Band gap (E_g)

Absorption is the powerful tool for measuring the band gap of the glass samples. Let the photon beam intensity I_o is incident the sample of the thickness t and intensity of light transmitted is I_t, then

$$\mathbf{I_t = I_o e^{-\alpha t}} \qquad (8)$$

α = absorption coefficient

This varies with photon wavelength and also with material to material.

For direct transition

$$\mathbf{\alpha h\nu = A(h\nu - E_g)^n} \qquad (9)$$

Eg = photon energy

α=Absorption coefficient

n= ½ for allowed transitions

For indirect transitions

$$\alpha h\nu = A(h\nu - E'_g)^n \quad (10)$$

Here n= 2 for allowed transitions

So the graph plot of αhν vs. $(\alpha h\nu)^2$, gives the value of energy band gap.

4.9 Fourier transform infrared spectrometer (FT-IR)

FT-IR is an effective analytical tool for identification of unknowns, sample screening and profiling samples. FT-IR absorption spectra were recorded at room temperature in the 400–4000 cm^{-1} range using a spectrometer of type Shimadzu (Japan) FT-IR-8700. The spectra obtained were used to analyze the structure of glasses before and after exposure to the SBF. Before soaking in simulated body fluid (SBF), 4.0 mg of each powdered sample was mixed with 200 mg of KBr in an agate mortar and then pressed to a pressure of 100 kg/cm^2 and the resulting pellets of 13 mm diameter were used for recording the absorption spectra. The FT-IR analysis after exposure to simulated body fluid (SBF) has been performed on 13 mm diameter pellets prepared by mixing about 4 mg of materials scraped from the glass surface with KBr. For each sample, the spectrum represents an average of 20 scans, which were normalized to the spectrum of the blank KBr pellet. FT-IR using the KBr technique was fruitfully performed to study the structure-composition relation in various glasses and glass –ceramics.

Fourier transform spectroscopy is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation as shown in fig. 4.3. FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting Spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same Infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. FTI-R is used to analysis the bonding of the samples [28].

FT-IR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitative some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier transform infrared spectroscopy (FTI-R) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. FT-IR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FT-IR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum [28].

The change occurs in the samples before and after dipping in the simulated body fluid (SBF) solution can be measured using FT-IR method. Fourier transform infrared spectroscopy (FT-IR) studies reveal the existence of phosphate, carbonate and hydroxyl groups, suggesting that HA coatings are carbonated. FT-IR were measured and compared for some selected bioactive glasses before and after immersion in various solutions to follow up formation of silanol group. Formation of HCA layer is confirmed by bands assigned on the basis of published data (table 4.4).

Table 4.4 FTIR band assignment

Wave number (cm^{-1})	Vibrational mode
1350-1080	P=O stretch
890-800	C-O stretch
610-600	P-O bend/crystal
560-550	P-O bend/ glass
530-515	P-O bend /crystal
1415-1465	C-O stretch
1045,1025	P-Stretch
960	P-Stretch

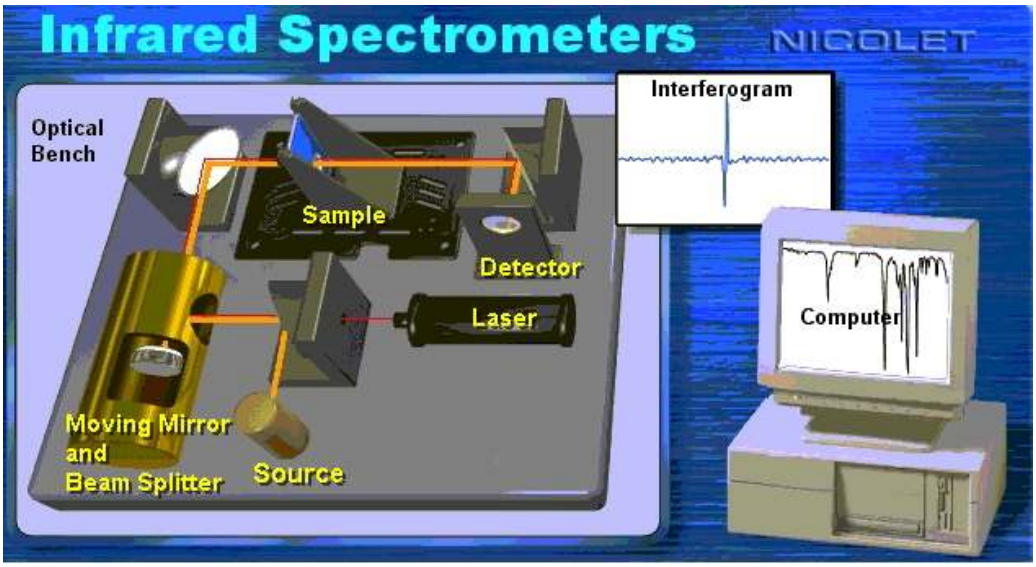


Fig 4.4 Diagram of FT-IR

CHAPTER 5

RESULTS AND DISSCUSION

CHAPTER 5

RESULT AND DISSCUSSION

5.1 Density measurement:

The density measurement is very useful tool in showing the degree of change in the structure with composition of the glass and glass ceramics [Feller et.al.][32] [Dowied et.al.] [33]. The variations of density before and after soaking in simulated body fluid are given in table 5.1.

Table5.1 Variation in density before and after dipping on SBF solution

Sample	Density before dipping in SBF solution	Density after dipping in SBF solution	% change in density
AS1	3.93	4.01	2.0
AS2	2.27	1.30	-42.73
AS3	3.32	3.66	10.24
AS4	2.53	1.21	-52.17

The AS1 sample exhibit higher density than any other studied samples. The increase in the value of density for glasses AS1 and AS3 as compared to glass AS2 and AS4 might be due to the fact that the addition of (Y_2O_3) and (Cr_2O_3) have strong glass network than other two samples. This can also be explained on the basis of the glass transition temperature. AS1 and AS3 samples show higher glass transition temperature as reported unpublished work [K. Singh et.al] [33]. Interestingly, lower T_g samples could not show the formation of hydroxyapatite layer (fig. 5.3 and fig. 5.4). Moreover, the samples also show the decreasing trend in density and dissolution in simulated body fluid (SBF) solution.

5.2 Weight –loss measurements:

The percentage weight loss of the entire prepared samples immersed in simulated body fluid at room temperature is given in table 5.2. Sample weight measurement provides a good estimation of dissolution. It is clearly evident from the table 5.2 that all the samples show a weight loss > 10% in 25 days. Thus these glasses offer a good range of degradable glasses. Percentage weight loss is highest for AS2 sample and least durable glass exhibits highest weight loss.

Table 5.2 Percentage weight loss of the samples after dipping in SBF solution

Sample	Weight of samples before dipping in SBF solution	Weight of samples after dipping in SBF solution	Weight loss (%)
AS1	2.16	1.92	11.17
AS2	2.18	1.07	50.45
AS3	1.72	1.62	17.2
AS4	2.34	1.23	47.4

The most durable glass exhibits least weight loss. In the present study AS2 is the least durable and AS1 is the most durable glass among all four studied glasses. Addition of Cr_2O_3 to glass serves to increase its durability as compared to AS4 (La_2O_3) glass. The durability sequence are observed in the studied samples as AS1 > AS3 > AS4 > AS3. This result is in agreement with the density measurement as shown in table 5.1. resorption or biodegradation of materials in vivo is very complex process that is reaction takes place between physiochemical (quest) and biological (host). Therefore it is not exclusively controlled by its physiochemical properties, such as degradation of glasses in simulated body fluid (SBF) solution [13].

5.3 X –ray diffraction (XRD) Analysis:

The XRD pattern from all as prepared silica based glasses (AS1, AS2, AS3 and AS4) possessed the charterstic hump. The hump in XRD pattern confirms the "amorphous" nature of the sample as shown in fig.5.1. As the samples dipped in the simulated body fluid solution, some chemical reaction takes place between the constituents of glasses and ions present in the simulated body fluid (SBF) solution with time. These chemical reactions results in the formation of crystalline layer on the surface of AS1 and AS3 samples as shown in fig. 5.1 and 5.2. On the other hand sample AS2 and AS4 could not form any hydroxyapatite layer on shown in fig. 5.3 and 5.4 respectively. In case of AS1 and AS4 samples, the crystalline phases could be indexed as $Ca_{10}(PO_4)_6(OH)_2$ (JCPDF card no74-0565) and $Ca_{3.29}P_{2.4720}18H_{17.94}$ (JCPDF card no 83-1888) respectively. Interestingly, those samples showed higher dissolution rate could not form the hydroxyapatite layer even after 25 days soaking. This behavior of the present samples indicated that the hydroxyapatite layer formation depends on the reaction between simulated body fluid (SBF) and glasses as indicated in density, weight loss measurement. Based on these measurements, the formation of hydroxyapatite layer purely depends on the affinity of various

ions of simulated body fluid (SBF) solutions and initial ingredient of glasses. However, it is very difficult to conclude that higher leaching from samples (AS2 and AS4) play important role to form hydroxyapatite layer.

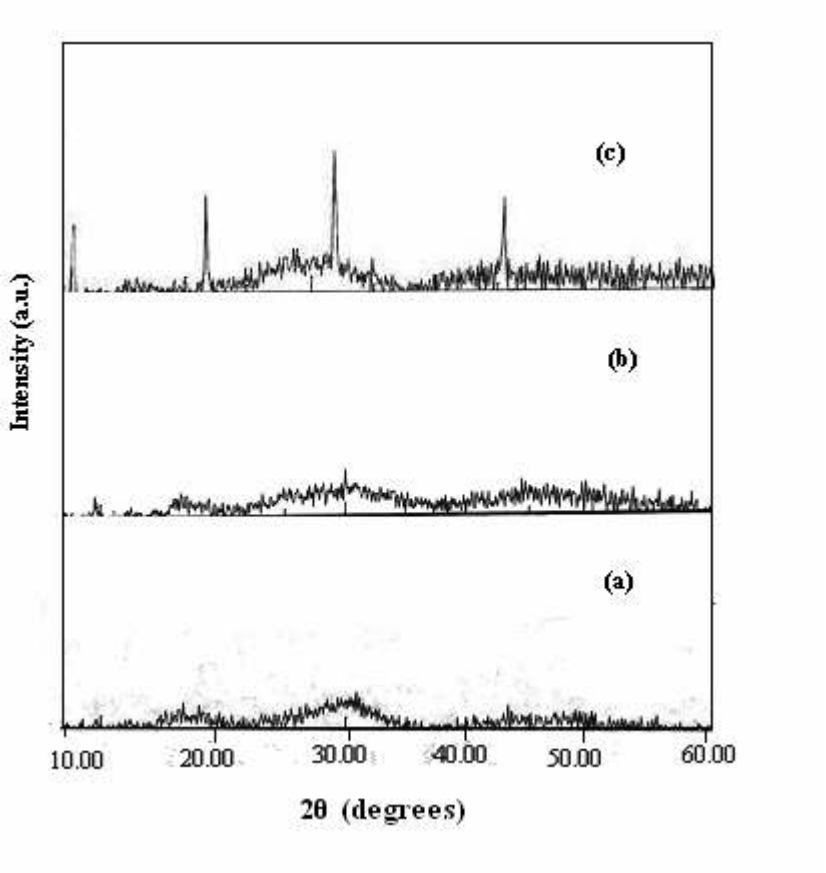


Fig 5.1. XRD diffractogram for sample AS1
(a) 0 hr (b) 400 hrs (c) 600 hrs

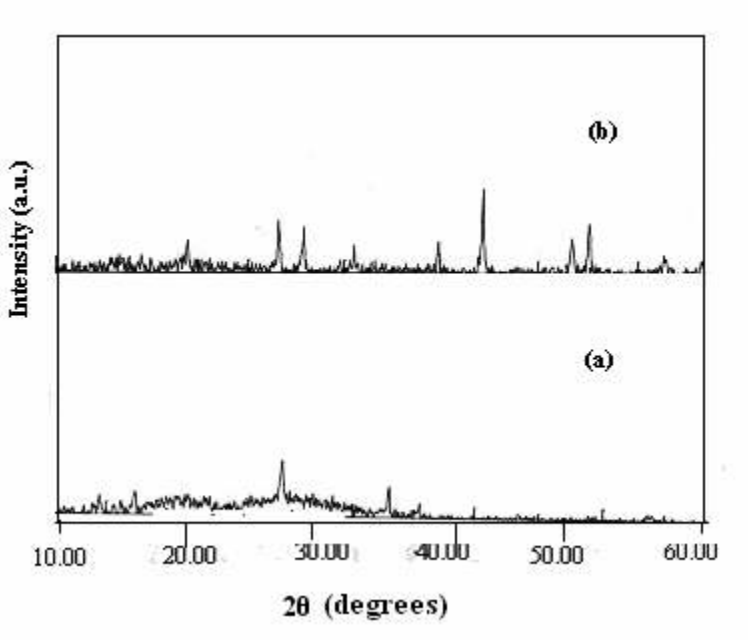


Fig 5.2. XRD diffractogram for sample AS3

(a) 400hrs (b) 600hrs

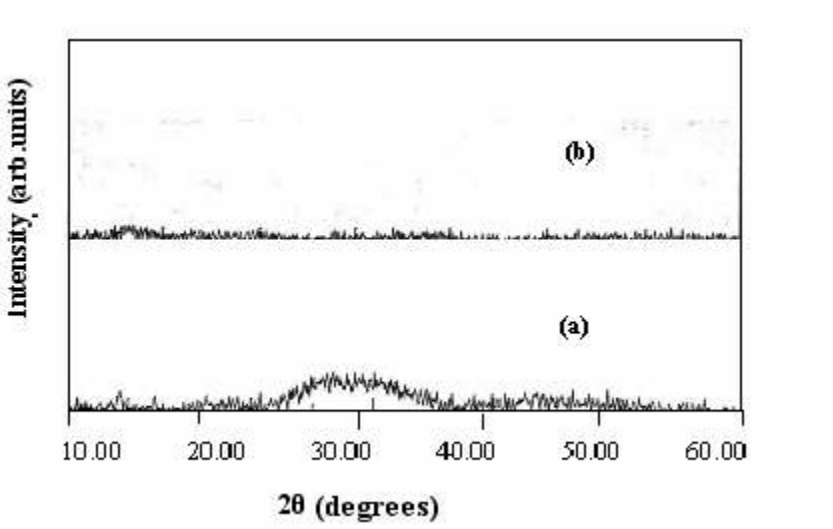


Fig. 5.3. XRD diffractogram for sample AS2

(a) 400hrs (b) 600hrs

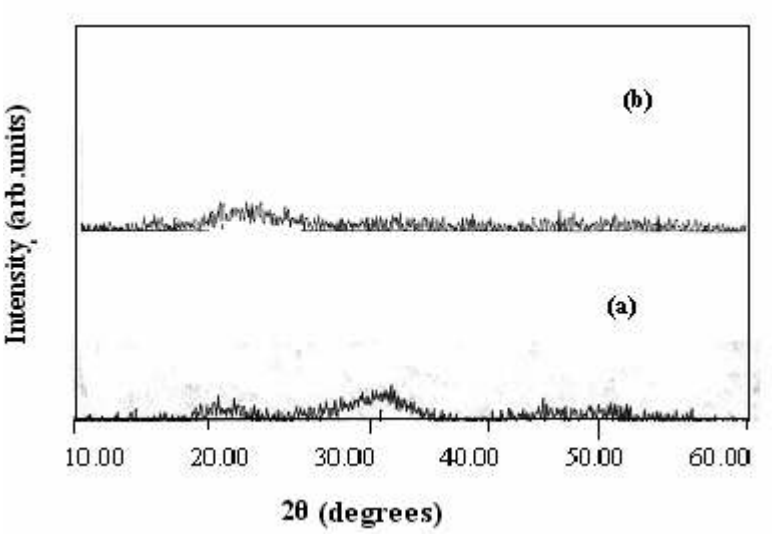


Fig. 5.4. XRD diffractogram for sample AS4

(a) 400 hrs (b) 600hrs

5.4 Band gap measurement

The band gap of all samples, before and after dipping in simulated body fluid (SBF) solution is calculated by UV-Spectroscopy. These results will give the information about the formation of hydroxyapatite layer. If the hydroxyapatite layer is formed then there must be change in the band gap of samples. The transmission absorption coefficient and energy were calculated to use the transmission spectra of the samples. These values are plotted as hν and $(\alpha h\nu)^2$ and these graphs are used to calculate the band gap of the samples.

TABLE 5.3 Variation of band gap before and after dipping in SBF solution

Sample	Band gap before dipping in SBF solution (eV)	Band gap after dipping 25 days in SBF solution(eV)
AS1	2.7	2.4
AS2	2.0	2.5
AS3	2.5	2.3
AS4	2.3	2.8

The band gaps of samples AS1and AS3 decrease after soaking samples in simulated body fluid (SBF) solution 25 days. Whereas, in case of samples AS2 and AS4 the band gap increases after dipping in simulated body fluid (SBF) solution. From comparing these results with XRD results this can be seen that those samples (AS1 and AS3) form the hydroxyapatite layer shows the

decreasing trend in band gap. The formation of crystalline hydroxyapatite layer (AS1 and AS3) samples reduces the porosity and increases the ordering which lead to decrease the band gap. On the other hand the band gap of AS2 and AS4 exhibits the reverse trend than AS1 and AS3 samples. As shown in table 5.1 and 5.2, those samples shows higher weight loss could not form the apatite layer. The density of AS2 and AS4 samples decreases after dipping in simulated body fluid (SBF) solution. It indicates that these samples became more porous due to higher rate of leaching. This leads more amorphization in these samples. Therefore, the band gap in AS2 and AS4 samples increases after immersing in simulated body fluid (SBF) solution.

Band gap in amorphous solids 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. The band gap of samples before and after dipping in simulated body fluid (SBF) solution is shown in figures 5.5. to 5.12 for AS1, AS2,AS3 and AS4 samples.

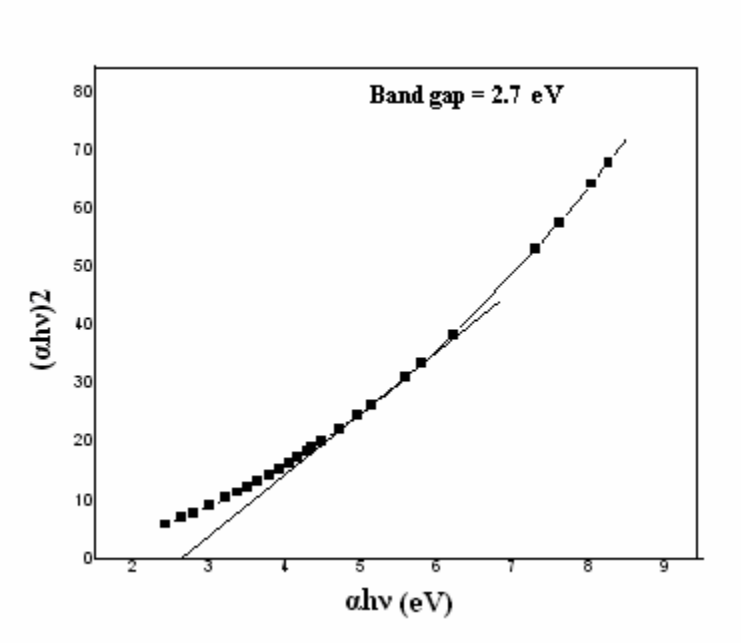


Fig. 5.5 Sample AS1 before dipping in solution

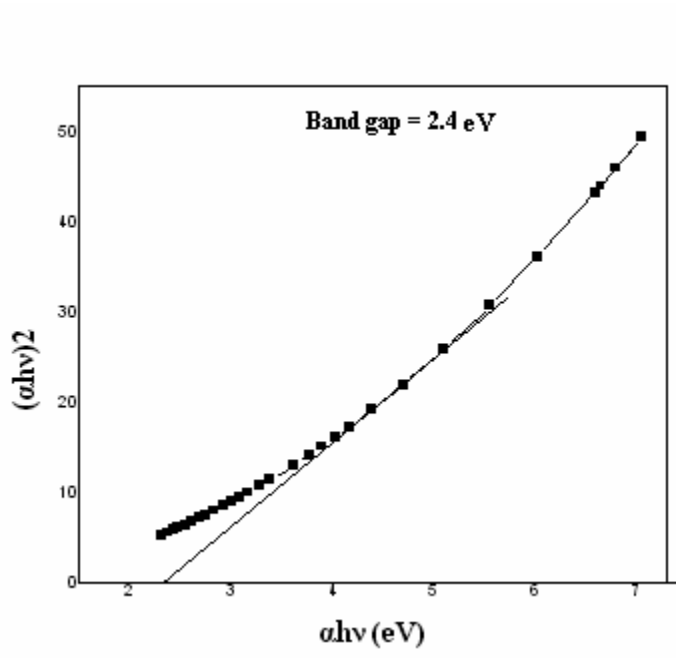


Fig 5.6 Sample AS1 after dipping 600hrs in SBF solution

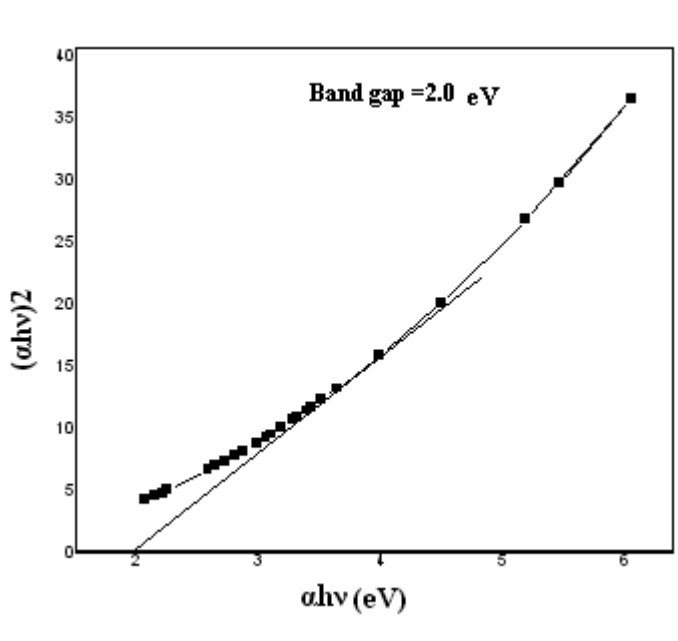


Fig 5.7 Sample AS2 before dipping in SBF solution

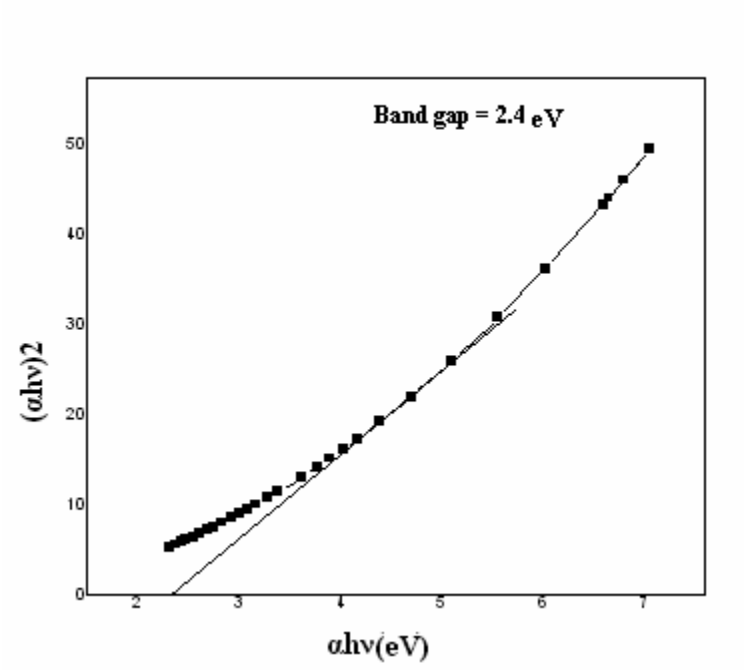


Fig 5.8 Sample AS2 after dipping 600 hrs in SBF solution

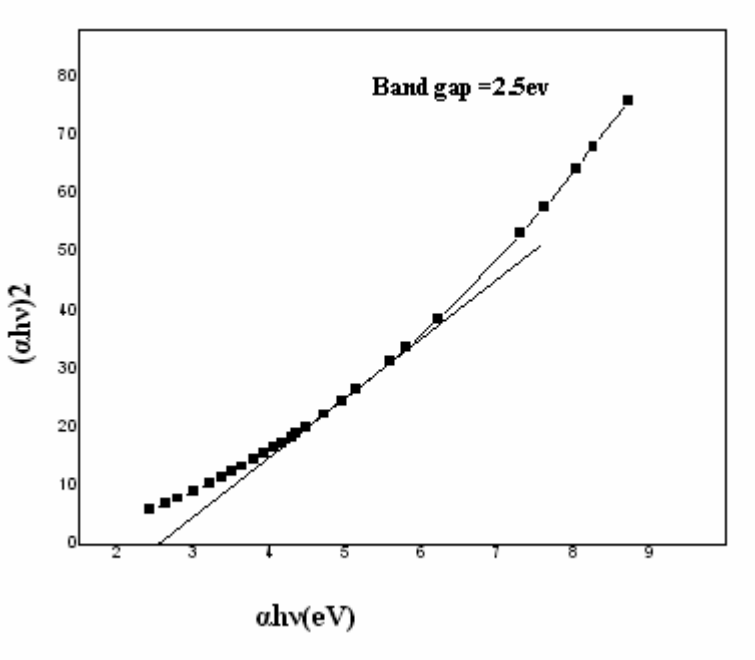


Fig 5.9 Sample AS3 before dipping in SBF solution

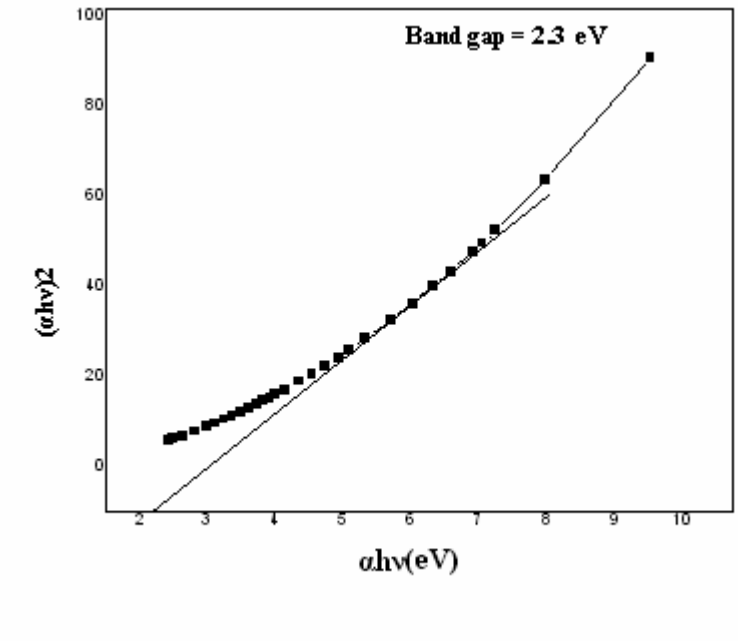


Fig 5.10 Sample AS3 after dipping 600 hrs in SBF solution

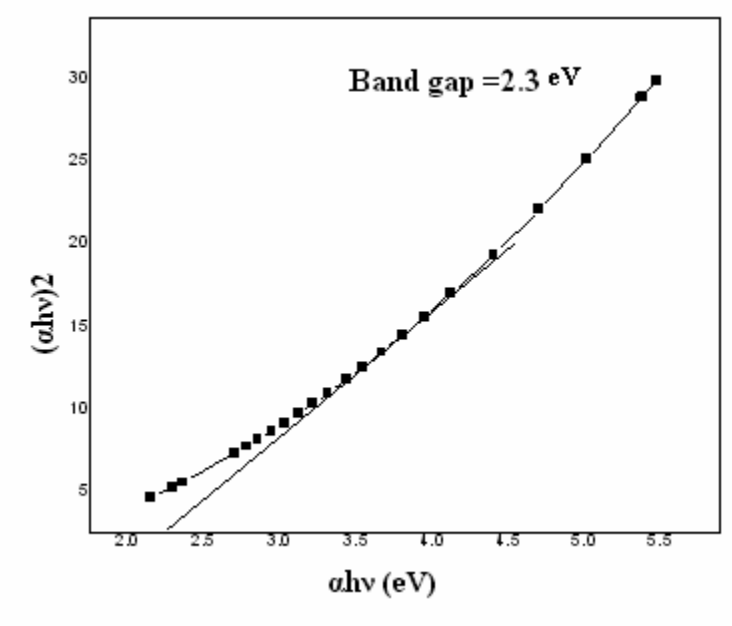


Fig 5.11 Sample AS4 before dipping in SBF solution

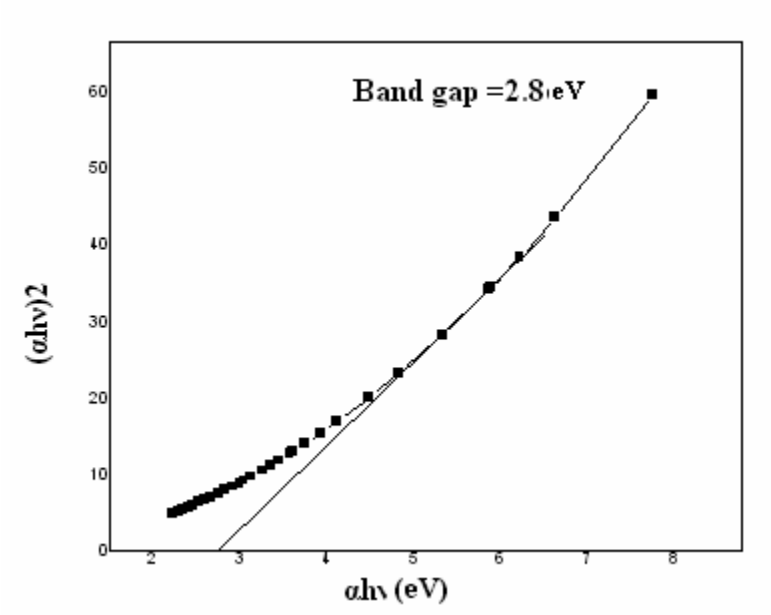


Fig 5.12 Sample AS4 after dipping 600 hrs in SBF solution

5.5 Evaluation of bioactivity using FTI-R Spectra

The bioglass–ceramic absorption spectra show well defined transmission bands characteristic of the Si–O–Si stretching and bending modes which are associated with the crystalline phases of the samples. The observed limited changes in the transmission spectra of bioglass–ceramics samples relative to the parent amorphous bioglass samples are restricted to the region between 700 and 400 cm^{-1}. All the bioglass–ceramics samples show new absorption bands in this region at (650–619 cm^{-1}) and (580–570 cm^{-1}) which can be attributed to the vibrational modes of the formed precipitated phases of calcium sodium silicate and this is verified by Elbattal et.al [29]. The weak reflection at 1620 cm^{-1} can be assigned to the molecular water. The broad band centered at 3438 cm^{-1} can be assigned to hydroxyl group (–OH) or silanol group (SiO–H).

In order to investigate the formation of the hydroxyapatite layer on the surface of the samples, FT-IR analysis of the glass samples before and after dipping in the SBF solution was done. The glass sample AS1 after dipping in simulated body fluid (SBF) solution shows the broad hump ~3500 cm^{-1} due to the OH^- group. On the other hand there is no peak at that region in sample AS1 before dipping in simulated body fluid (SBF) solution. Presence of water bands after soaking in simulated body fluid (SBF) solution ensure the ion exchange process between hydronium ions from solution and ions from the surface of the glass sample. Peaks ~ 1500 cm^{-1} and ~ 1000 cm^{-1} is due to the CO_3^{2-} and PO_4^{2-} ions, respectively in soaked samples as shown in figure 5.13. There is another peak ~ 700 cm^{-1} which again shows the presence of OH^- ions. These results clearly indicate formation of the hydroxyapatite layer in sample AS1 after dipping in the simulated body fluid (SBF) solution. Similar results were obtained and reported by Torre et.al. [28].

The pronounced hydroxyl band formed~ 3500, 627 and 700 cm^{-1} are typical of hydroxyapatite with crystallinity and at 1000 shows the PO_4^{2-} ions. These bands are typical of carbonate occupying OH^{-1} and $PO4^{3-}$ sites in hydroxyapatie hexagonal structure and suggest the formation of carbonated hydroxyapatite coatings in AS1 sample.

In sample AS3 there is change in the peak at ~3500 cm^{-1} before and after dipping in solution as shown in fig 5.14. After dipping in SBF solution sample shows the broad hump ~3500 cm^{-1} which is due to the OH^- group as explained earlier and also the peak formation ~

1500 cm^{-1} after dipping in solution is due to the CO_3^{2-} ions. Peak also formed at ~ 1000 cm^{-1} after dipping in the solution shows the presence of PO_4^{2-} ions. Thus the simultaneous presence of the above bands and decrease of intensity of $B0_3$ units (~709 cm^{-1}) confirms the formation of CaP hydroxyapatie layer. Oliveira et. al [35].

In FT-IR spectra of AS2 and AS4 samples could no show the appreciable change in peaks before and after dipping. The dissolution rate of glasses in SBF was fast. However in sample AS2 there was no change in the peak which was ~ at 3500 cm^{-1} whereas in sample AS4 there was very little change in that peak as shown in figures 5.15 and 5.16. Apart from this sample AS4 also show a single peak at~ 700cm^{-1}. It might be possible an amorphous apatite layer formation. Brown et.al. [36].

This result can further be supported by X-ray diffraction pattern (fig.5.4 (b)). Obtained from studied glass in SBF solution.

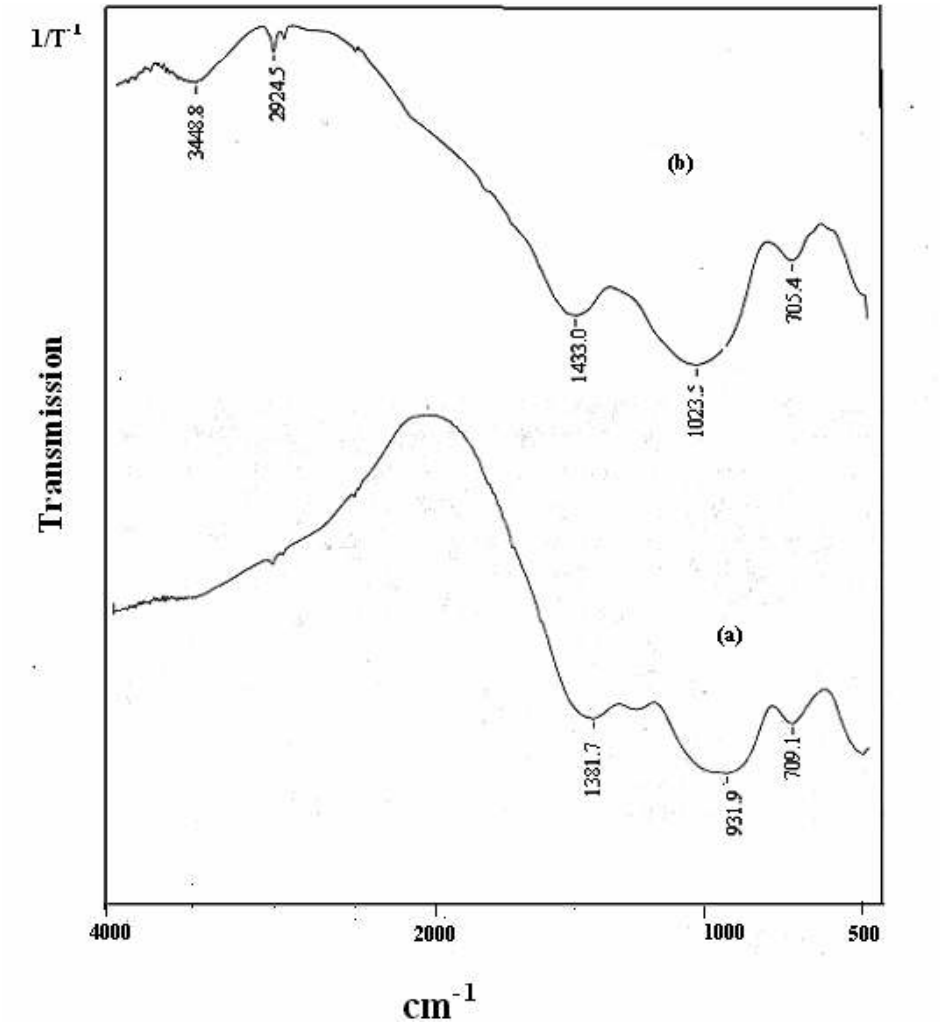


Fig. 5.13 FTIR Spectra showing change in sample AS1 (a) 0 hr (b) 600hrs

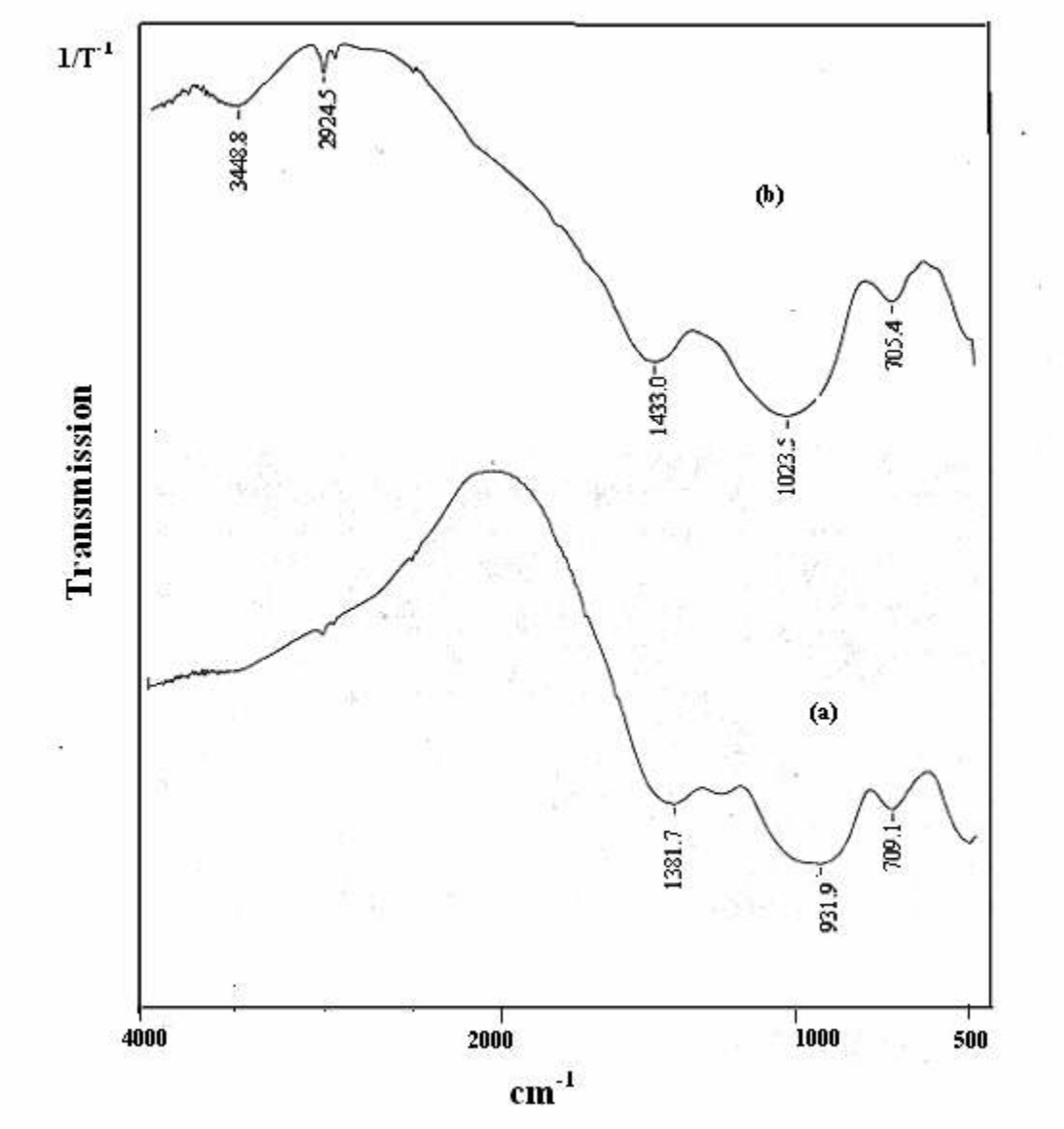


Fig. 5.14 FTIR Spectra shows sample AS3 (a) 0 hr (b) 600 hrs

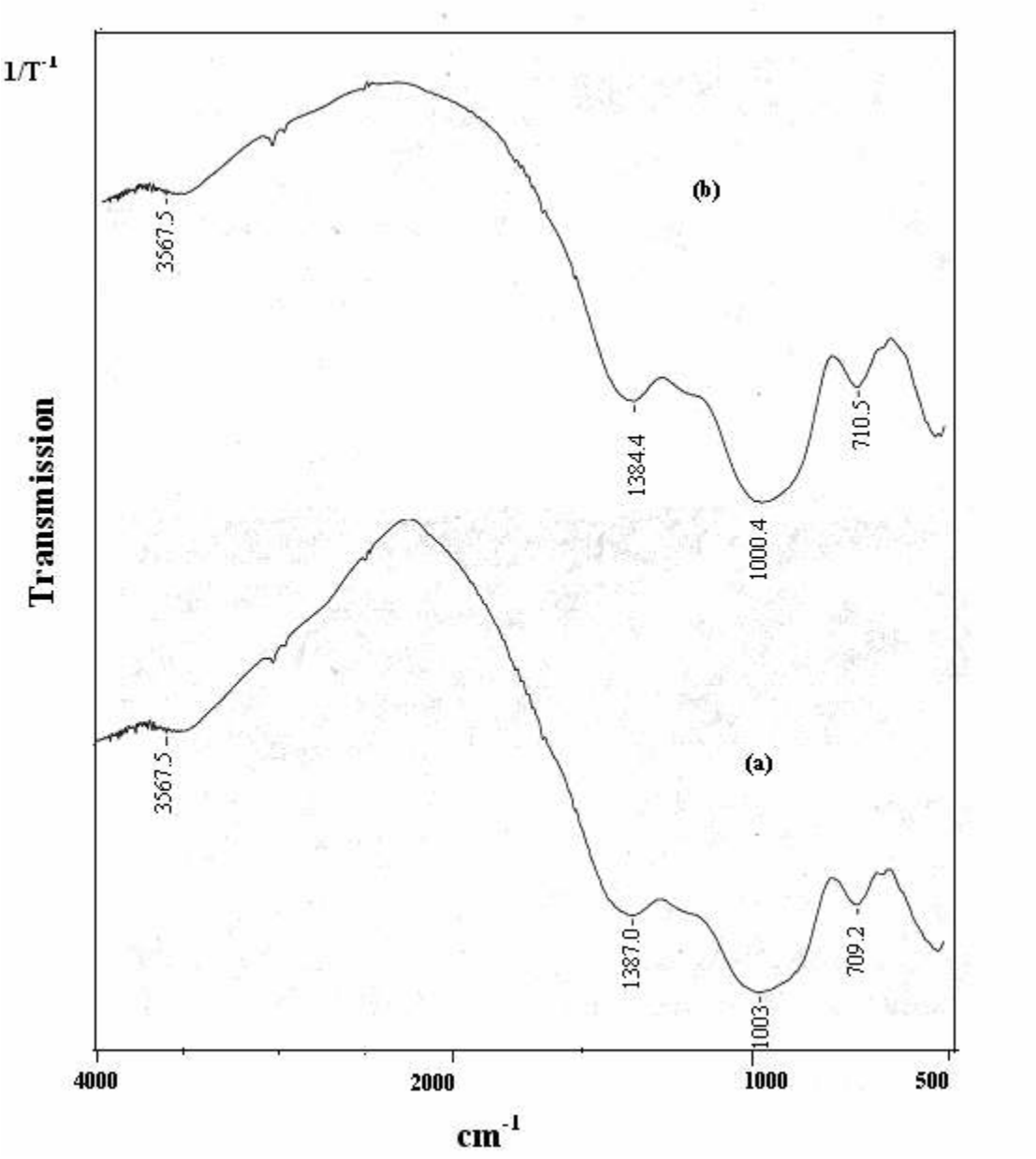


Fig. 5.15 FTIR Spectra of sample AS2 (a) 0 hr (b) 600 hrs

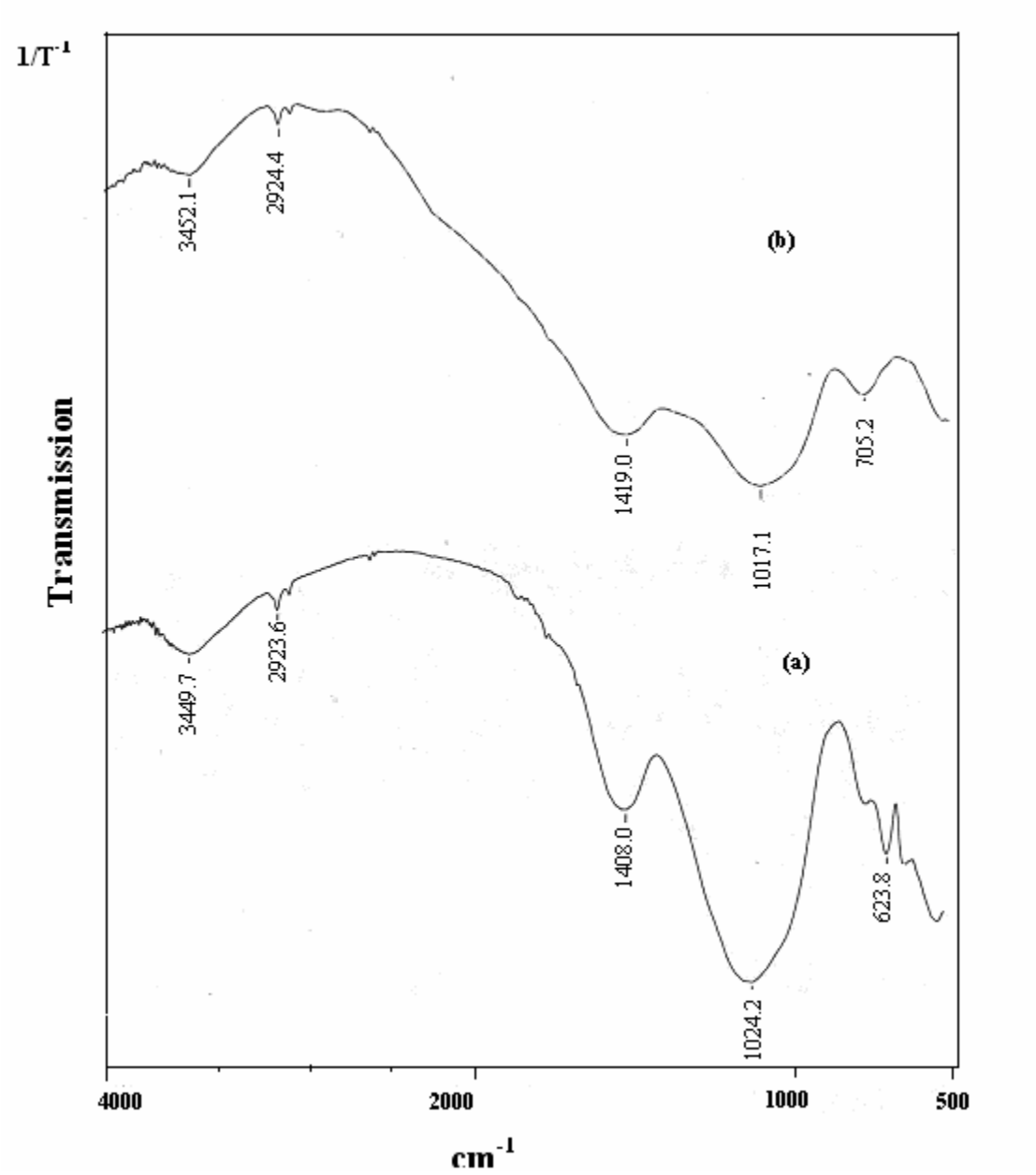


Fig. 5.16 FTIR Spectra of sample AS4 (a) 0 hr (b) 600 hrs

CHAPER 6

CONCLUSIONS AND FUTURE SCOPE

CHAPTER 6

CONCLUSIONS AND FUTURE SCOPE

In present investigation, four SiO_2 –CaO rich glass samples were selected to check their bioactivity. These samples were cauterized using XRD, FT-IR, UV-Vis spectroscopy, density and solubility measurement. It is concluded from invitro analysis that calcium-containing bioglass reacts with solution and the reaction product is hydroxyapatite layer (AS1andAS3). These glasses are referred as the bioactive. All the glass samples initially taken are amorphous in nature as confirmed from the XRD. In these samples a layer named hydroxyapatite was formed after dipping in SBF solution for 25 days, which was also confirmed from XRD. However the formation of this layer depends upon many factors such as formation of silanol group, dipping conditions, initial ingredient of glass and time period for which samples are dipped.

Further the UV-spectroscopy confirmed the hydroxyapatie layer in AS1andAS3 samples. There was some change in the band gap before and after dipping in the SBF solution. FTIR analysis further confirmed the functional groups present in the samples AS1 and AS3 which were due to the hydroxyapatite layer. Whereas, there was no formation of this layer in AS2 and AS4.

In order to understand more about the durability and functionality of hydroxyapatite layer there is need to study more about it. However SEM coupled with EDX will prove to be a very handy tool which will provide more insight into the morphology of hydroxyapatite layer. After from this sample AS1and AS3 will be investigated for longer duration of soaking. So that the growth rate of hydroxyapatite layer will be calculated.

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