

Bioactive glass/glass ceramics for dental applications

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1.1 Introduction

Humans have known about glasses since 5000 BC, when 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) were used for making weapons. With the passage of time, there was a transformation in techniques for obtaining glass and the applicability of glasses. Table 1.1 summarizes the key advancements in glass history along with their time, domain, and types. The forefathers of modern glass research were the German scientist Otto Schott (1851–1935) and Ernst Abbe (1840–1905), a professor at the University of Jena and joint owner of the Carl Zeiss firm. The tailoring of glass compositions according to scientific need began at very large scale after the pioneer work of these two scientists.

The 20th century led to some new technological developments of synthesizing glasses by tailoring their compositions according to the scientific/technical need. On the basis of their compositions, glasses are categorized into three main families, which include (i) organic glasses, (ii) inorganic glasses, and (iii) metallic glasses. These three categories are further divided into subcategories as shown in Fig. 1.1. Metallic glasses are solid metallic materials with a disordered atomic-scale structure. Unlike common glasses, which are typically electrical insulators, metallic glasses have good electrical conductivity. Organic glasses are transparent thermoplastics often used in sheet form as a lightweight or shatter-resistant alternative to glass, for example, poly-methyl methacrylate (PMMA). The inorganic glasses include oxides, nonoxides and hybrid glasses. The hybrid glasses are generally a mixed with compositions of oxide and nonoxides in different proportions. The oxide glasses primarily include borate, silicate, and phosphate glasses, but other glasses like bismuthate, germinate, and their combinations such as borosilicate, etc., also lie in the family of oxide glasses. The nonoxide glasses include halide, nitride, and carbide glasses. The third category is hybrid glasses, which include oxyhalide, oxynitride, and oxycarbide glasses.

Different glass applications have been discovered by scientists over the years, but the use of glasses in biomedical applications was not even a hope before the discovery of bioglass by Hench in the late 1960s [1]. Hench unlocked the path to a new era of bioactivity between artificial materials and bones. Before this discovery, body parts

Table 1.1 Development in glasses over the years

Year	Glass type	Use	Domain
~5000 BC	Obsidian/tektites	Weapons	Syria
~3500 BC	Non-transparent beads	Ceramic glazes	Egypt/Mesopotamia
~1500 BC	Core-dipped glass	Decoration	Egypt
~20 BC	Blown glass	Hollow glass items	Syria
~100 AD	Clear glass	Windows	Rome/France/ Germany
~1000 AD	Potash glass	Decoration/ containers	Europe
~1100 AD	Sheet glass	Luxurious buildings	Germany
~1270 AD	Quartz glass	Crystal ornaments	Italy/Syria/Europe
~1650 AD	Lead crystal	Engraved crafts	England
~1690 AD	Plate glass	Mirrors	France
~1900 AD	Glass industries	Scientific/ technological	Germany
~1910 AD	Bottle blowing	Container glass	America
~1917 AD	Flat glass	Civil engineering	Belgium/France/ America

were replaced by some metallic or metal composite materials through the inactivity between artificial and actual bone. The discovery of bioactive glass was not accidental, but it was called miraculous by Hench himself. This all started with a conversation between Hench and an Army colonel who was coming back from Vietnam with his injured soldiers. As a renowned scientific personality, Prof. Hench was challenged by the colonel to “make a material that will survive exposure to human body.” This prompted Prof. Hench to focus his research on investigating radiation’s effects on glass. Inspired by the colonel’s proposal, Prof. Hench applied for funding to an Army medical agency. This turned out to be a miraculous moment, as nobody could imagine that a person without a medical degree could obtain such funding, and Hench’s journey started. He began with a phase diagram of $\text{Na}_2\text{O}-\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$, and it was miraculous that the first composition he selected (45S5.0) exhibited great bone-bonding ability compared to other compositions (45S2.0, 45S1.8, 55S5.0, and 55S2.0) in this phase diagram. The study produced many observations, including the formation of a hydroxyapatite-like structure after heat treatment without the presence of any hydroxyl groups. In-vitro analysis in the body’s serum-like liquid revealed the formation of a layered structure on the glass surface, inspiring hope that there might exist some bioactivity yet to be confirmed through in vivo analysis. Infected rat femur was then bonded with 45S5.0A (as quenched), 45S5.0B (heat-treated between 400°C and 500°C, i.e., partially crystallized with the presence of some polycrystalline phases), and 45S5.0C (heat-treated between 600°C and 1000°C, i.e., fully crystallized) and kept for 6 weeks. A fine amount of bonding was observed in 45S5.0A and 45S5.0B (most), but not with 45S5.0C. The strength was then tested, and it was observed that milling, and cutting with diamond and carbide was not enough to separate the bonding

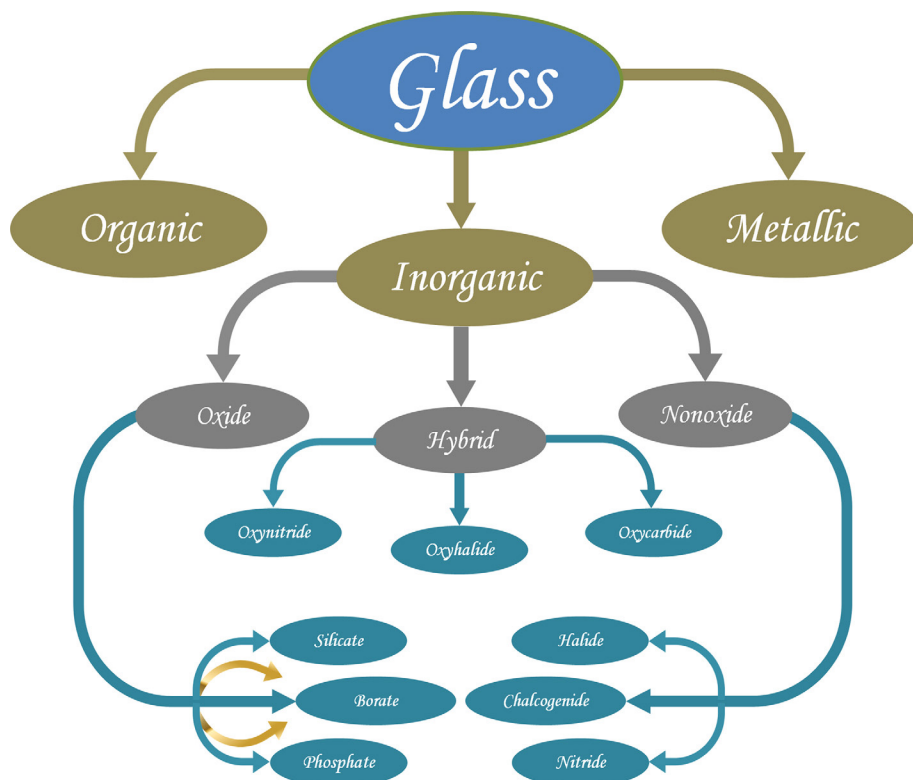


Fig. 1.1 Glasses and their types based on chemical composition.

between glass/glass ceramic and bone, confirming a remarkable degree of bioactivity in this glass/glass ceramic substance. The presence of hydroxyapatite, however, was not confirmed through selected area electron diffraction due to the amount of material used. The curiosity now centered around knowing the bonding mechanism of bioglass with bone, which could only be discerned after sequential study of the events taking place during the bonding process. Investigation revealed that development of an alkaline pH implant surface (making it alkaline) and surface-active Ca and P sites were the main factors controlling bone bonding with glass [2,3]. The bonding process starts with exchange of Na^+ and Ca^{2+} ions from the glass with H^+ and H_3O^+ ions from the body fluid. This process is followed by dissolution and repolymerization of silica; formation of amorphous calcium phosphate precipitates and its nucleation; crystallization of calcium phosphate with HCA (hydroxycarbonate apatite), biological protein adsorption; macrophase action; attachment and differentiation of stem cells; cellular attachment, and finally, matrix crystallization [4,5]. Hench and others [4,6–11] kept investigating the surface reactivity of bioactive glasses. Meanwhile, experiments focused on the application of these bonding concepts in various animal models toward the creation of bone bridges, corneal implants, and bioglass-ceramic enamel-based fixation of prostheses. The 45S5 Bioglass (US Biomaterials Corp., Alachua, FL, United

States) was first used in ear reconstruction for remediation of hearing impairment in mice and rabbits [12–16]. The studies were very successful in achieving complete repair of the ear bone and opened the field for applications of bioglass in living beings.

The successful use of bioactive glasses in dental restorations (i.e., replacing the incisal/dental portion of the tooth to acquire its original shape) requires durability in the oral environment, strength, wear resistance, and similarity with the natural tooth structure [17]. The use of bioactive glasses in dentistry started with Prof. Hench's development of lithium disilicate glass ceramics to be used for dental restorations [18, 19]. Bioglass was exploited as a bioactive aid in ERMIs (Endosseus Ridge Maintenance Implants) in 1986 [20, 21]. The quest was to discover dental materials based on bioactive glasses for use as inlays, crowns, bridges, dental posts with abutments, fillers, and veneers [22–30]. Some common glass compositions used for various dental applications are listed in Table 1.2 [17]. As can be seen, a lot has changed over time to facilitate novel compositions for dentistry. These discoveries provide solutions that yield materials for temporary dressings, restorations, root canal treatment, impressions, prosthetic aids, etc. However small it may be, the decay of bioactive implants/restorations nevertheless occurred after several years. Therefore, some self-healing materials had to be discovered to accelerate the research hunt. This advancement was achieved by Prof. Jones and his fellow Imperial researchers through mixing silica bioglass with polycaprolactone to fabricate a flexible and durable glass material. This new bioglass material “mimics the shock-absorbing and load-bearing qualities of real

Table 1.2 Common bioglass compositions for dentistry

Sr. no.	Prime crystal phase	Product name	Use	References
1.	Mica	DICOR MGC	Crowns, inlays	[31–33]
2.	Leucite	IPS EMPRESS	Crowns, inlays, veneers	[34–36]
3.	Leucite	PRO CAD	Crowns, inlays, veneers	[37–39]
4.	Leucite, fluoroapatite	IPS d.SIGN	Crowns, bridges	[40–42]
5.	Lithium zirconium silicate	IPS EMPRESS 2	Abutments	[43–45]
6.	Lithium disilicate	IPS EMPRESS Cosmo	Crowns, bridges	[46–48]
7.	Lithium silicate	IPS e.max CAD	Crowns, inlays, veneers, bridges	[49–51]
8.	Fluoroapatite	IPS eris	Crystallization on lithium disilicate glass ceramic	[52–54]
9.	Fluoroapatite	IPS e.max Ceram	Sintering on IPS e.max CAD	[55–57]
10.	Fluoroapatite	IPS e.max Zirpress	Viscous flow on ZrO ₂	[58–60]

Modified from W. Holand, V. Rheinberger, E. Apel, C. Hoen, M. Holand, A. Dommann, M. Obrecht, C. Mauth, U. Graf-Hausner, Clinical applications of glass ceramics in dentistry, *J. Mater. Sci. Mater. Med.* 17 (2006) 1037–1042.

cartilage,” according to a press release by Imperial [61]. A set of videos, available on YouTube, clearly shows the material’s bounciness and the self-healing process in real time and under computer-simulation [62–64]. Bioactive glass in dental fillers is much better at reducing bacteria than its ceramic counterparts [65, 66]. This chapter focuses on discussing glass synthesis methodologies, along with their contributions in the field of dentistry.

1.2 About glass

These materials can be categorized as either amorphous or crystalline, the basic difference between which pertains to their structure. Amorphous solids are characterized by an irregular (or short-range ordered) arrangement of atoms, while crystalline solids consist of a periodic array (long-range ordered arrangement) of atoms. However, amorphous solids, if bonded through covalent bonds, have a tendency to reach medium-range ordered arrangement ($\sim 20\text{\AA}$). The crystalline materials have a regular arrangement of atoms, but in the case of polycrystalline materials, the periodicity of the structure is interrupted after a particular region. The region up to which a single-ordered arrangement is followed is called the grain boundary. When the size of the grain boundary is compatible with the size of the ordered unit, materials are classified as noncrystalline materials. The positions of the atoms are disordered, and long-range order is absent. However, the short-range order of noncrystalline materials is preserved in a way similar to their crystalline counterparts. The bond lengths and bond angles fluctuate around respective average values corresponding to those found in ordered crystals. The particle positions are totally uncorrelated, and the system has complete disorder.

One way to obtain solids with desired compositions is to cool down the melts of the appropriate components. However, the nature of the product obtained by cooling down the melt is strongly related to the cooling rate. A simplified approach for understanding the dependence of solidification on cooling rate is shown in Fig. 1.2. From this figure, it is clearly observed that the liquid follows two paths toward the solidification process, and each path is characterized by a particular rate of cooling. The cooling rate is a totally material-dependent parameter, and some substances avoid crystallization at lower cooling rates. Such solids are said to have good glass-forming ability. The straight line in the slow cooling path is characterized by a period (however small it may be) during which the temperature of material remains constant, and it is this isotherm along which the complete liquid-to-solid transition takes place, leading to the formation of crystalline solids.

A more scientific look at the process of cooling of melt and the dependence of enthalpy/volume on temperature to yield crystalline or glassy solids is shown in Fig. 1.3. This figure shows that slower cooling provides sufficient time for the crystallization to occur, whereas rapid cooling below the melting temperature (T_m) leads to the formation of an amorphous state without providing sufficient time for a regular crystal lattice to form. Cooling of the melt to any temperature below T_m of the crystal usually leads to conversion of the material to the crystalline state through long-range ordered

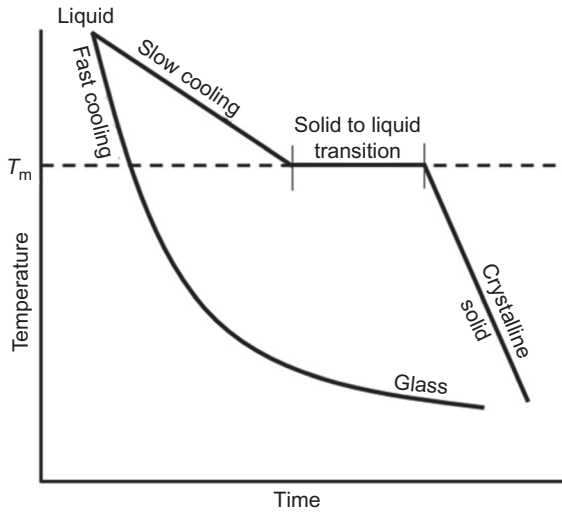


Fig. 1.2 Liquid to solid conversion (dependence on cooling rate).

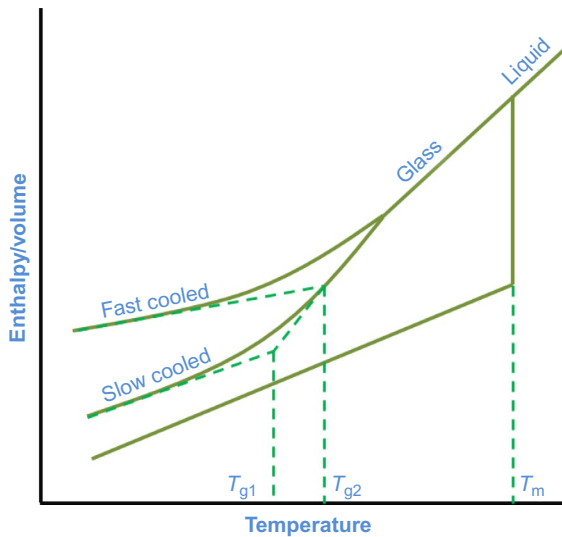


Fig. 1.3 Temperature dependence of enthalpy/volume of glass-forming melt.

structural rearrangements. In such conditions, enthalpy decreases gradually to a value appropriate for the crystal. Further cooling of the crystal will result in decrease of enthalpy. If the liquid can be cooled below the melting temperature of the crystal without crystallization, a super-cooled liquid can be obtained. The structure of the liquid continues to rearrange as the temperature decreases, but there is absence of abrupt change in enthalpy values. With further cooling of the liquid, viscosity increases, eventually becoming high enough that it prevents the atoms to completely rearrange to

the equilibrium liquid structure. The resultant structure becomes fixed and no longer depends upon temperature. The enthalpy values begin to deviate from the equilibrium line, following a curve of gradually decreasing slope. The temperature region lying between the enthalpy limits of equilibrium liquid and frozen solid is known as the glass transformation region, and the frozen liquid is glass. The temperature at which enthalpy departs from the equilibrium curve is controlled by the viscosity of the liquid, and use of a slower cooling rate will allow enthalpy to follow the equilibrium curve up to a lower temperature; in such a case, glass formation will not occur. Glass transformation usually occurs over a temperature range.

If we extrapolate the glass and super-cooled liquid lines, they intersect at a temperature defined as the fictive temperature. The structure of the glass is considered to be that of the equilibrium liquid at the fictive temperature. Although the fictive temperature concept is not a completely satisfactory method for characterizing the thermal behavior of glasses, it provides a useful parameter for discussing the effect of cooling rate changes on glass structure and properties. It is easy to estimate a single temperature as an indication of the onset of the glass transformation region during the heating of glass. This temperature, which is also called the glass transformation temperature, is rather vaguely defined by changes in either thermal analysis curve or thermal expansion curves (usually, there is a difference between the transition temperatures obtained from the thermal analysis and expansion curves). The glass transition temperature (T_g) can be a useful indicator of the approximate temperature at which the super-cooled liquid converts to a solid upon cooling or at which the solid begins to behave as a viscoelastic solid on heating. The dependence of T_g on the heating rate and the applied characterization techniques means that T_g cannot be considered a true property of glassy materials, but the transition temperature can be used to estimate the temperature at which the super-cooled liquid starts solidifying. In other words, it helps in approximating the temperature at which a solid becomes a viscoelastic solid and resists allowing the atoms to rearrange themselves. It is generally thought that the glass transition temperature, as determined by thermal measurement, is a point at which the viscosity of the solid changes at its maximum rate, and the material (glassy materials, in this case) becomes soft.

As glasses have many different characteristics, it is important to agree upon a definition of glass. Different definitions have been used over the years for glass, but each one has led to some misconceptions. In this section, some of these definitions will be reviewed, and critiques of each definition will be discussed to explore the limitations of each particular definition. In the renowned book on glass, *The Glassy State*, Tammann [67] states that, "In the glassy state, there are solid, uncrystallized materials." This definition is, however, extremely generalized and puts all noncrystalline materials into the glassy state category. According to this definition, silica gel would also be placed into the glass category, which is not the case. Another definition proposed by Tammann in the same book said, "Glass is a frozen supercooled liquid." Again, this definition provides no clear, concise picture of the glassy state of a material, as glasses are solid materials and not liquids. Definitions proposed in this era, however, were not constrained to the composition of glasses. In 1945, the American Society for Testing and Materials (ASTM) offered the following definition [68]: "Glass is an inorganic product of fusion

which has been cooled to a rigid condition without crystallizing.” This definition limits the glass synthesis method to just melt-quenching despite the existence of other synthesis routes for amorphous materials (like glass), including sol-gel processing, chemical vapor deposition, neutron bombardment, etc. Glass is also not limited to inorganic compositions, and other glasses like organic glasses, metallic glasses, etc., exist and can be synthesized. Jones [69] said, “A glass is a material formed by cooling from the normal liquid state, which has shown no discontinuous change at any temperature range, but has become more or less rigid through a progressive increase in its viscosity.” This definition also only takes the melting process into consideration.

Critiquing the available definitions of glass, Scholze [70] considered its physicochemical aspects and defined it, saying “In physico-chemical sense, a glass is a frozen-in under cooled liquid.” However, this definition requires clarification of whether glass is a liquid or solid. Although glasses have structures similar to liquids, glasses are very hard and brittle and can’t be considered liquids. Doremus [71] said, “A glass is an amorphous solid.” If this definition is considered standard, then materials like wood, cement, thin-film oxides, etc., would also be categorized as glasses, but none of these materials are identified with the existence of glass transition. Shelby [72] defined glass, saying it was, “an amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region of glass transformation behavior. Any material, organic, inorganic, or metallic formed by one of the stated processes which shows glass transition behavior can be categorized as glass.” The definition proposed by Shelby overcomes the shortcomings in all previous definitions to a great extent, but it lacks the inclusion of the word “vitreous.” In a letter communicated to the Society of Glass Science and Technology, Prof. Adrian Wright [73] questioned the ASTM definition of glass by debating the basic idea on which the definition was founded. He justified this by considering the facts that glasses don’t form as a result of fusion, but through a complete chemical process in which the carbonates of glass network modifiers and the acids of glass formers react chemically to extract the excess water and carbon dioxide content from the melts of the starting batch mixtures. Prof. Wright corrected the proposed ASTM definition of glass by saying, “A glass is an inorganic material that has been quenched from the liquid to a rigid state without crystallizing.” Prof. Wright also invited the entire glass scientific community to challenge the definition he proposed and debate the questions he posed regarding the ASTM definition of glass. From the concepts, theories, and definitions of glass discussed earlier, a common definition of glass can be obtained: *A glass is an amorphous solid (organic, inorganic, or metallic) which lacks in long-range order (similar to that of liquids) and exhibits a region of glass transition.*

Although humans had known about glasses for ages, advances in modern glasses (which also includes glasses other than silica and silicates) came no earlier than 1932, when Zachariassen [74] advanced understanding of the disordered arrangements in glassy oxides. Zachariassen’s work created a field of research focused on understanding glass’s structure and paved the way for many researchers to propose theories about glass structure. This includes the work done by Sun et al. [75,76], Stanworth [77,78], Smekel [79], Rawson [80], Greaves [81,82], Krogh-Moe [83–85], etc. These theories helped to tailor glasses according to our needs. Today, thousands of books are available

regarding the structure, properties, processing, and applications of glasses. Millions of scientific reports can be found relating to the different aspects of glasses. Glasses have become indispensable. From domestic and luxury items (like container glass, decorative glass, mirror glass, vehicle glass, window glass, etc.) to scientific items (like lenses in telescopes and microscopes, flat panel displays, optical wave guides, nuclear waste processors, thin-film deposition bases, bioactive body parts, etc.), today, glasses are all around us. Glass can be obtained through a number of synthesis strategies, as explained in the next section.

1.3 Glass synthesis methods

Depending upon the required physical, chemical, and biological properties, numerous routes can be employed for glass synthesis. Route selection also depends upon the production amount and compositional constituents required. All these techniques have their own implications regarding practicability and deployment. Some popular glass synthesis techniques of glass are explained in the following sections.

1.3.1 *Sol-gel synthesis*

In glass sol-gel synthesis, first, a sol consisting of colloids dispersed in a liquid medium is formed. The method of sol preparation depends upon the material. The most widely used method is hydrolysis and polycondensation of silicon alkoxide with alkoxides of modifiers like Ti, Al, Zr, Ge, etc. Another way involves dispersion of particles of sub-micron size (obtained by flame hydrolysis of SiCl_4) in chloroform using *n*-propanol as the dispersing agent. Coagulation of the colloids, while they are standing in a mold or on a substrate (used as coating film), results in the conversion of sol into gel. The obtained gel is dried and sintered into a pore-free dense glass or glass film. The sintering is usually done at a temperature which is slightly above the glass transition temperature. The disadvantage of sol-gel synthesis is that the shrinkage of the wet gel produces fractures in the prepared glass. Other problems are the preferential precipitation of a particular oxide during sol formation for multicomponent glasses made from alkoxide precursors, and the heterogeneous precipitation of metal salts on the surface during the drying of a gel which was made using aqueous solutions of metal salts as the source of alkali, alkaline-earth oxides, etc. Although the sol-gel process has some disadvantages, this process has been extensively applied for synthesis of bioactive glasses [86–88]. This is because it works at relatively lower temperatures. The creation of the latest category of mesoporous bioactive glass (MBG) was possible only because of its sol-gel synthesis roots [89–95].

1.3.2 *Chemical vapor deposition*

This method is based on the thermally activated, homogeneous oxidation or hydrolysis of an initial metal halide vapor (or mixture of metal halides) to form particulate glass material, followed by viscous sintering of the soot into solid, inclusion-free, glass

bodies. The oxidation or hydrolysis reaction is usually activated by either oxygen plasma or oxy-hydrogen flame. In the hydrolysis of halides by oxygen plasma, an oxide, along with the halogen gas (generally chlorine), is released as byproduct, but in hydrolysis using oxy-hydrogen flame, the byproduct formed with oxide is HCl. The difference in both hydrolysis techniques is the level of OH contained in the glass, which is 1000 times more while using oxy-hydrogen flame for hydrolysis. The disadvantage of the CVD method is that it imposes restrictions on the preparation of glasses containing alkali, alkaline earth, and rare earth metals. The CVD process is extensively used to synthesize glasses and glassy alloys [96–100].

1.3.3 Melt-quench technique

The melt-quench technique is the earliest known technique for preparation of glasses with acceptable size. Even today, more than 99% of the practical glasses are synthesized via the melt-quench technique. The melt quench technique is based on the fusion of crystalline raw materials (oxides, acids, or carbonates) into a viscous liquid, followed by the casting of melt through rapid quenching. The melt quench technique has certain advantages over the other techniques:

- (i) It is the easiest of the known synthesis techniques.
- (ii) It offers high flexibility in the geometrical shape of glass.
- (iii) It offers ease in obtaining large materials in comparison with a single crystal.
- (iv) It is highly flexible regarding composition due to the nonstoichiometry in batch calculation.
- (v) The doping of active ions (rare earths and transition metals) is very easy.
- (vi) Prepared glass is free from fracture and strains.

The above-mentioned advantages have led to the increased popularity of the melt-quench technique, and it has been extensively used to synthesize oxide/oxyhalide glasses [101–115].

1.4 Glasses/glass ceramics for dentistry

The bioactive structures of glasses/glass ceramics have not only been scientifically investigated for dental use, but are actually being applied in a variety of dental materials. Similar to other bones, the alveolar bone can also suffer loss which must be healed or repaired using active biological replacements. Therefore, scientists are motivated to discover various permutations and combinations of glass compositions so that these can be used in dentistry. Scientific investigations searched for a glass composition which could be combined with anti-osteoporotic drugs to accelerate the process of apatite formation and thereby enhance the bioactivity of the glass structure. Bioactive glasses combined with bisphosphonates are reported to be beneficial as a filling material for surgical repair of bone defects [116]. In the following sections, the eligibility of bioactive dental materials, along with some popular dental glass ceramics, will be discussed.

1.4.1 Eligibility for dental materials

In the field of dentistry, there are certain oral body parts which can be repaired with bioactive glass ceramics. These materials include inlays, onlays, crowns, bridges, veneers, or abutments for implant therapy. But there are certain conditions imposed on bioactive materials which they must meet in order to act as successful bioactive materials. These conditions are:

1. Excellent matching of the appearance of the natural tooth in terms of translucency, opalescence, and fluorescence.
2. Maintaining chemical durability after implantation so that the treatment can last as long as possible (including decay resistance, body fluid stability, etc.).
3. Matching the abrasive wear behavior of real teeth so that the patient can feel as natural as possible.
4. Maintaining an excellent toughness and flexural strength (even higher than that of natural teeth) so that adequate functionality can be obtained for bridges and abutments during high load bearing.
5. Radioactivity concentration less than 1.0 Bq/g of U^{238} .
6. An optimum level of flexural toughness, microhardness, and refractive index.
7. Machinability, for convenient handling and proper treatment (i.e., available in paste, powder, solid, or solution form).
8. Exhibiting excellent thermal stability, such as thermal expansion, thermal stress, thermal indentation etc., after implantation.

Materials which satisfy these conditions can be engineered in accordance with the medical treatment so that the patient can be successfully treated.

1.4.2 Glass/glass-ceramic-based dental materials

There is a large family of glass-ceramic-based dental materials, but most of them are derived from the popular basic industrial bioglasses. The following subsection will deal with some common dental materials:

1.4.2.1 Mica-based glass ceramics

The first glass ceramic developed for dental restorations was DICOR (Corning Inc./Dentsply Int., United States), which was based on mica crystals grown in a glass matrix [117]. The process included precipitation of tetrasilicic mica ($KMg_{2.5}Si_4O_{10}F_2$) crystals via controlled crystallization in the SiO_2 - MgO - K_2O - F glass system. This ceramic was derived from the popular BIOVERT glass family whereby a phase-separated crystal phase was grown inside the glass system. The family included BIOVERT II, in which mica was the main crystal phase along with some secondary crystals like cordierite [118–122]. Clinical tests with inlays and crowns derived from DICOR were performed, and it was found that the replacements displayed strong similarity with the appearance of natural teeth. The molding capacity and flexural strength (150 MPa) were quite fine, and the conversion to glass ceramic required some heat treatment. This category of dental ceramics was the flagship of machinable glass

ceramics (MGC) [123]. Time and again, the compositions, conditions, and processing methodologies have been tuned to obtain further improvements in the performance of these glass ceramics [39, 124–126].

1.4.2.2 *Leucite-based glass ceramics*

Leucite-based glass ceramics are extensively used as dental ceramics because of their better thermal expansion [127–130]. Leucite-based glass ceramic systems (also called feldspar glass ceramics) are fabricated from materials containing silica or quartz embedded with different amounts of alumina. The naturally occurring feldspars, that is, aluminosilicates containing potassium and sodium (or synthetic aluminosilicates), are usually modified through different routes to obtain dental glass ceramics [131, 132]. The primary function of leucite crystal is to increase flexural strength through thermal expansion as it is known for its higher thermal expansion co-efficient. The leucite-based glass ceramics (IPS Empress flagship) are highly pressed to contain higher amounts (~35 vol%) of leucite crystals [133]. For obtaining materials with enhanced performance, leucite crystals are added to aluminum oxide and subsequently heat pressed [134, 135]. The ability of feldspar to form leucite can also be exploited to develop porcelains for bonding metals. Further development in leucite-based ceramics led to the development of glass ceramics with much finer leucite crystals (10–20 μm) which were found to be very suitable for use as veneer porcelains in restorations assisted by metal ceramics [136–139].

1.4.2.3 *Lithium disilicate-based glass ceramics*

Lithium disilicate glass ceramics (LDGC) are aesthetic dental materials derived from $\text{SiO}_2\text{-Li}_2\text{O-Al}_2\text{O}_3\text{-K}_2\text{O-ZrO}_2\text{-P}_2\text{O}_5$ glass systems via solid-state reaction route [140–143]. LDGCs are known for their high strength and they are the earliest known system for dental restorations [18, 19, 144–147]. The constituents of LDGC include ~70% of lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$) crystals having a needle-like structure embedded in a matrix containing mainly SiO_2 , Li_2O , Al_2O_3 , K_2O , P_2O_5 and other oxide substitutes [148–150]. The dimensions of $\text{Li}_2\text{Si}_2\text{O}_5$ crystals reinforced in the glassy matrix are of the order of a few microns, and the structure is of interlocking type providing high strength (360–400 MPa) [151–159]. The chemical durability, aesthetic nature, and enhanced translucency make LDGCs excellent materials for use in dental implants [160, 161]. Compared to the typical yttria-stabilized polycrystals, although the strength of LDGCs is lower, their translucency and color matching with natural teeth is excellent [50, 162–166]. This has led to the exploitation of LDGCs in ceramic restoration for inlays, onlays, veneers, and anterior/posterior crowns. Moreover, the survival rates of monolithic LDGCs are excellent, as 97.4% can survive up to 5 years posttreatment and 94.8% survive up to 8 years posttreatment [167]. The success rates are also quite excellent as these figures show: 91.1% after 5 years, and 69.8% after 10 years [168, 169]. Recent developments in LDGCs focus on improving their mechanical strength and wear resistance by tailoring their compositions, processing methods, heat treatment modifications, synthesis control, etc. [170–176].

1.4.2.4 Fluorapatite-based glass ceramics

Fluoride is believed to be an efficient material for preventing dental cavities through inhibition of enamel and dentine demineralization [177, 178]. These also assist in the process of bacterial enzyme inhibition. When incorporated into bioactive glass systems, fluorides result in the formation of fluorapatite in body fluid/physiological solution, and fluorapatite is relatively more acidic than HCA (hydroxycarbonated apatite, i.e., a prime dental component). Moreover, fluorides have the advantage of increasing bone density and preventing fracture, making the fluoride-based implants an effective material for osteoporosis patients [179–183]. The ability of fluorapatite-based glass ceramics to exhibit osseointegration and osteoconduction makes them potential materials for exploitation in dental/orthopedic caries [184–188]. Studies show that the fluorapatite crystallization process is strongly dependent upon the amount of phosphate in the glass matrix, and the low content of phosphate (<1.1 mol%) is not enough to support crystallization even after extensive heat treatments [182, 189, 190]. The omnipresence of fluorapatite in human bones hints at the possibility of significant improvement in the biological behavior of glass ceramics containing fluorine. Therefore, study has been devoted to develop these crystals, and earlier studies resulted in the formation of a particle-like morphology, unlike the needle-like structure found in human bones [191–198]. The fluorapatite crystals ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) with needle-like morphology grown in glass ceramics have the potential to generate a light-scattering effect, which makes the biomaterial's translucency extremely similar to that of natural teeth [28, 199]. However, sometimes this may lead to a loss in bioactive properties, requiring more scientific exploration for successful implementation of fluorapatite-based glass ceramics.

1.4.3 Treating hypersensitivity using bioactive glass/glass-ceramic: NovaMin

Hypersensitivity is a form of tooth pain which is directly related to thermal, chemical, or tactile sensitiveness of the tooth [200–202]. Tooth pain can be found in about 57% of the general population in extreme cases, and hypersensitivity makes up about 98% of the cases of tooth pain according to some dental survey reports [203–205]. Hypersensitivity is treated using many over-the-counter (OTC) products such as desensitizing pastes/gels/toothpastes, rinses, atraumatic tooth brushing, dentine bonding agents (DBA), glass-ionomer cements (GIC), or other alternate restorations [206]. Glass-ceramic materials can be embedded in any of these OTC treatments, for example, using basic glass-ceramic materials such as 45S5 Bioglass as already discussed. This glass ceramic is processed to obtain a very fine powder composed of particles in the micrometer range and commercialized by NovaMin. A toothpaste named Sensodyne (NovaMin) is the OTC product recommended by most of the dentists around the world [206]. The basic glass-ceramic system used for hypersensitivity treatment is an inorganic composition of calcium sodium phosphosilicate (CSPS). CSPS particles are observed to exhibit excellent response toward reducing tooth sensitivity through physically occluding dentin tubules. Using CSPS materials in periodontal treatments (PerioGlas) to cure hypersensitivity in teeth has been hugely successful as its surface

exhibits a strong attraction to collagen. Because collagen forms almost half of the dentin, tubules can be physically filled with ease by CSPS materials. Moreover, it is believed that CSPS releases ions that react with the surface to form HCA, providing fast and continual relief of tooth sensitivity [207, 208].

1.5 Conclusions and future scope

This chapter has reviewed bioactive glass/glass ceramics for use as dental materials. Glass ceramics are potential candidates for inlays, onlays, crowns, bridges, etc., and can be actively used for treatment of dental ovules, hypersensitivity, cavity protection, dental implantations, etc. The categories of bioactive materials applicable to dentistry include those which are mica-based, lithium disilicate-based, leucite-based and fluorapatite-based glass-ceramics, and these are obtained through the growth of crystalline phase which is primarily responsible for their bioactivity. Each category of these glass-ceramics is already commercialized and sold under various banners, but as we know, science is a synonym for advancement. Therefore, efforts have always been devoted toward the improvement of already-known materials and methods. Such is the case with bioactive glass/glass ceramics in dentistry. Scientists have tried to improve the materials through compositional shuffling (the compositional flexibility of glasses is a key factor determining the application of a particular glass/glass ceramic, as almost all elements of the periodic table can be successfully incorporated in glasses), postproduction thermal, chemical, radiation, or physical treatments, functionalization with other products, and embedding materials which can enhance a particular property. The research hunt is always on, and the future scope is open to develop materials or to modify already-known materials so that 100% success/survival rates can be obtained, and the reach of these materials can be extended to each corner of the world in an affordable manner.

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