Some Types of Glass-Ceramic Materials and their Applications

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ABSTRACT

Synthesis of glass-ceramics with tailored properties for diverse uses has always been a challenge for scientist, a wide range of glass-ceramics was developed through combinations of different parent glass compositions, along with, permutation of temperature, and time during the heat-treatment stage. Controlled crystallization of glasses produces uniform reproducible fine-grain pores free, microstructures. Reinforcing glass-ceramics and creating variable composites are conducted for obtaining the desired properties. Several articles and books have been published discussing glass-ceramic production, properties and applications. In this review article, a comprehensive study was made regarding the effect of different synthesis protocols on the obtained glass-ceramic's properties.

Keywords: *glass-ceramic, properties, synthesis, reinforced glass ceramics, composites*

INTRODUCTION

The first glass-ceramic capable of being produced industrially was discovered in the 1950s by Stookey, 1960 [1] he was able to control the devitrification of glass by adding the nucleating agent TiO2.

Several researches on sintered glass-ceramics were published after Stookey's discovery of the controlled nucleation and crystallization of glass-ceramics [2][3].

However, as noted by McMillan [4], the sinter-crystallization was used even at the end of the nineteenth century. Glass-ceramic technology is based on controlled crystal nucleation and growth in certain glass compositions, and has several advantages over conventional powder processed ceramics, such as very low or null porosity, as well as uniformity and reproducibility of microstructure.

The crystalline phases precipitated in some glass-ceramics have, for instance, low thermal expansion coefficients coupled with high thermal and chemical stability, high mechanical strength and optical transparency [3].

The Advanced ceramics industry supports many industries, including, Aerospace, Automotive, Communication Computers, Medical, and Military, with products as wide ranging as fuel cells through to safety glass and sup conductors. In the past decade, the use of glass-ceramics has expanded in four major categories namely; electronics, medicine and dentistry, optical materials and in severe thermal mechanical environments.

As for electronics, glass-ceramics have found major application in microelectronic packing, where as in medicine and dentistry, bio glass-ceramics have found wide use as implants.

In bone and in dental prostheses, as regards optical materials, the dimensional stability, lumine scence, or photosensitive characteristics of glass-ceramics can be exploited in a variety of new applications.

Whereas tough, fibrous glass-ceramics have been developed for severe thermal mechanical environments. Figure 1 illustrates the steps of glass-ceramics manufacturing process.

Glass-ceramics demonstrating particularly favorable properties were developed on the basis of two key advantages; the variation of the chemical composition and of the microstructure [3].

These properties are briefly outlined and listed in Tables 1 and 2.
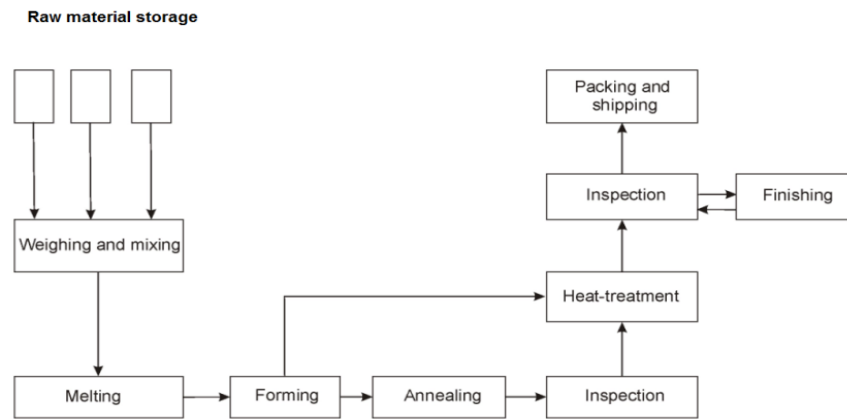
Figure1. *The glass-ceramic manufacturing process*

Table1. *Particularly Favorable Properties of glass-ceramics*

Thermal properties	Expansion can be controlled as desired, depending on the temperature, with zero or even negative expansion being coefficients of thermal expansion possible High-temperature stability
Optical properties	Transparency or translucency or opacity, Photo-induction is possible, Pigmentation, Opalescence, fluorescence.
Chemical properties	Durability, Biocompatibility, Bioactivity
Mechanical Properties	Machinability, High strength and toughness.
Electrical and magnetic properties	Isolation capabilities (low dielectric constant and loss, high resistivity and breakdown voltage), Ion conductivity and superconductivity, Ferromagnetism

Table2. *Particularly favorable combinations of properties of glass-ceramics (selection)*

Mechanical property (machinability) + thermal properties (temperature resistance).
Thermal property (zero expansion + temperature resistance) + chemical durability.
Mechanical property (strength) + optical property (translucency) + Favorable processing properties.
Strength + translucency + biological properties + favorable processing properties.

GLASS-CERAMIC CONCEPTS

Two significant factors play the main role in the production of fine-grained polycrystalline glass ceramics. First, the compositions of the glass utilized, as some glasses are difficult to crystallize, such as ordinary window glass, whereas others suffer uncontrolled crystallization resulting in undesirable microstructures.

Secondly, the heat treatment is critical to the attainment of an acceptable and reproducible product. As will be discussed later, a range of generic heat treatments procedures are used each of which has to be carefully developed and modified for a specific glass composition [3, 4]

The glass crystallization or devitrification, process of glass represents one of the important steps in glass ceramic preparation. This heterogeneous transformation consists of two stages; the nucleation stage and the growth stage.

In the nucleation stage, small crystalline phases are formed at interfaces within the parent glass or the free surface. If nucleation is formed at the free surface, the resulting microstructure will have large oriented crystals that are disadvantageous to mechanical properties but advantageous for piezoelectric and pyroelectric devices [5] and machinable glass-ceramics[6]. However, for internal nucleation -also referred to as bulk nucleation- to occur, the chosen parent glass composition should contain species to enhance the internal nucleation.

After formation of the stable nucleus, the crystals start to grow. The difference in volume or chemical free energy, ΔGv, between the glass and crystalline states force atoms/molecules to move from the glass, across the glass-crystal interface, and into the crystal.

The transport of atom/molecules across the interface is thermally activated with an associated activation energy ΔGa. Models, involving the terms ΔGv and ΔGa, have been developed for the temperature Dependence of the growth rate and the form of the resulting curve is given in Figure 2(a).
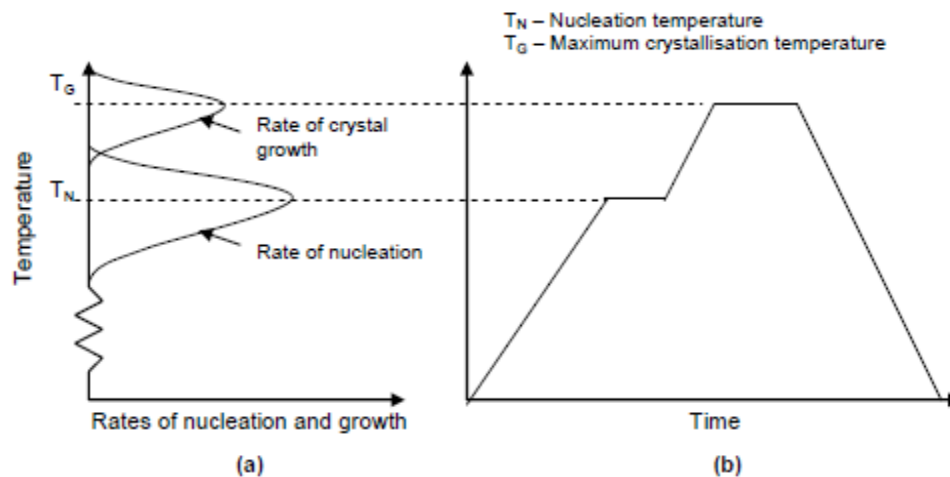
Figure2. *Crystallization of a glass to form a glass-ceramic. (a) Insignificant overlap between nucleation and growth rates (b) double-stage heat treatment.*

TECHNOLOGIES OF GLASS - CERAMIC PREPARATION

Conventional Method (Two-Stage)

Devitrification of glass by two-stage heat treatment is the conventional method for producing a glass-ceramic (Figure2 (b). The first stage is a low temperature heat treatment at a temperature that gives a high nucleation rate (around TN in Figure 2a) thus forming a high density of nuclei throughout the interior of the glass.

A high density of nuclei is important as it leads to a desirable microstructure consisting of a large number of small crystals. The second stage is a higher temperature heat treatment at around temperature TG to produce growth of the nuclei at a reasonable rate.

Modified Conventional Method (Single-Stage)

The double-stage heat treatment of glass in the conventional method is due to the limited overlap between the nucleation and growth rate curves (Figure 2 (a). If there is extensive overlap of the rate curves then nucleation and growth can take place during a single-stage heat treatment at temperature TNG as indicated in Figure 3. The rate curves, particularly the nucleation rate curve, is sensitive to composition, hence by optimizing the glass composition and the included nucleating agents it is, in some cases, possible to obtain the necessary overlap. The pioneer glass-ceramic system utilized this method is known as "Silceram"[7], as will be explained in the next section.
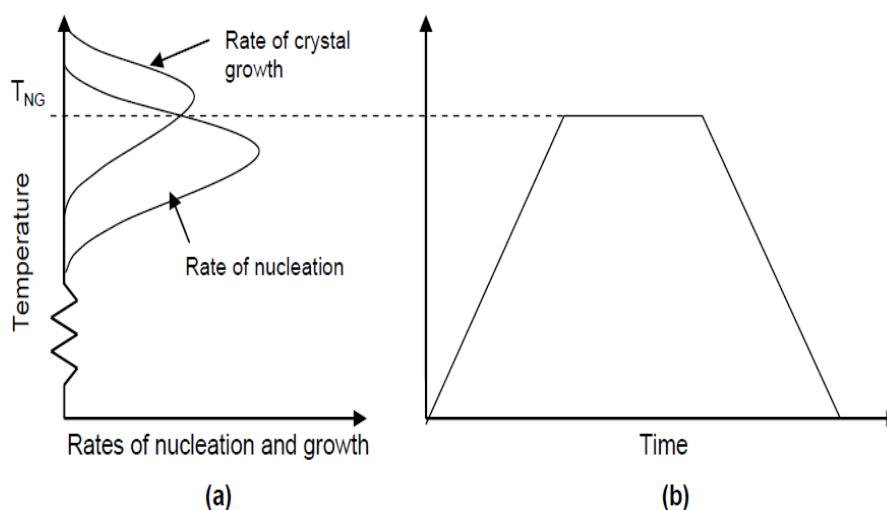

Figure3. *Crystallization of a glass to form a glass-ceramic by a single-stage heat treatment. (a) Temperature dependence of the nucleation and growth rates with significant overlap (b) single-stage heat treatment.*

Petrurgic Method

It was found with "Silceram" that it made little difference whether the glass was heated up to TNG from room temperature or the molten glass was cooled to TNG [7]. This directed scientist to produce certain glass-ceramics by a controlled, very slow cooling of the parent glass from the molten state directly without a hold at an intermediate temperature.

With this method, referred to in the recent literature as the Petrurgic method [8], both nucleation and crystal growth can take place during the cooling. Both the modified conventional (single-stage) and the Petrurgic methods are more economical that the conventional method (two-stage).

Powder Methods

High temperature heat treatment (sintering) of cold-compacted powder is the common method for the fabrication of ceramics and it has been likewise used for glass-ceramic manufacture [9, 10]. As there are limitations on the size and shape of components that may be cold compacted, and also a cost in producing a powder, this method is only used if an obvious benefit is identified.

In most cases there is little advantage in compacting and sintering a glass-ceramic powder because a high sintering temperature is required and the resulted glass-ceramics do not have significant better properties than those manufacturing by other techniques.

It is more attractive to sinter a parent glass powder, which sinters by a viscous flow mechanism at lower temperatures [11]. It is important to consider the rates of viscous flow sintering and crystallization and the interaction of these processes.

If crystallization is too rapid the resulting high degree of crystallinity will hinder the low temperature sintering leading to an unacceptable amount of porosity [12].

Sol-Gel Precursor Glass

So far only glasses produced from the molten state have been considered but in the last decades there has been considerable interest in using sol-gel and colloidal techniques to obtain the precursor glass in either powder or bulk form [13]. Glass-ceramics produced by all the previous routes could be produced by sol-gel technique except that; they can't be manufactured from waste materials.

DEVELOPMENT OF GLASS CERAMICS COMPOSITIONS

In recent years, new compositions, processing methods and applications have begun to emerge. There are six basic composition systems which commercial glass-ceramics of economic importance are made: (1) $Li_2O-Al^2O^3-SiO_2$, glass-ceramics of very low thermal expansion coefficient; (2) $MgO-Al_2O_3-SiO_2$ cordierite glass-ceramics of good mechanical, thermal, and dielectric properties; (3) Li_2O-SiO_2 glass-ceramics with photochemical etching capability; (4) $Na_2O-Al_2O_3-SiO_2$, nepheline glass-ceramics with high mechanical strength from compression glazing; (5) $K_2O-MgO-Al_2O_3-SiO_2-F$, machinablefluormica glass-ceramics; and (6) $CaO-MgO-Al_2O_3-SiO_2$, inexpensive glass-ceramics from natural materials and slag[14].The following sections present details of some of the above mentioned systems.

Glass-Ceramics Based on $Li_2O-Al_2O_3-Sio_2$

Glass-ceramics in the $Li_2O-AL_2O_3-SiO_2$ system have great commercial value because of their very low thermal expansion and excellent chemical durability[15]. These glass ceramics are based on either β-quartz or β-spodumene solid solution crystal phases.The wide compositional range of these solid solutions allows one to tailor an essentially monophase composition with only minor nucleant phases and residual glass.

B-Quartz Solid Solution

In the Li aluminosilicate system, a hexagonal phase with β-quartz structure is known for compositions ranging from near SiO_2 to $LiAlSiO_4$. In other words, the β -quartz solid solution can be described as $Li_2O.Al_2O_3.nSi O_2$, where n ranges from 2 to 10. Over most of this range, β-quartz is actually a metastable phase. The Li-rich end member, $LiAlSiO_4$ (β - eucryptite), has an ordered arrangement of AI and Si, resulting in a doubling of its c axis, but is otherwise structurally identical to the intermediate members of this series; compositions with n ≥ 4 have disordered Si/AI distributions and are truly iso structural with β-$SiO2$.β-quartz glass-ceramics are made by crystallizing TiO_2-or TiO_2+ZrO_2-nucleated Li aluminosilicate glasses at 850-900°C[16]. Despite the metastability of β-quartz, these glass-ceramics persist indefinitely and can survive repeated thermal cycling provided that a maximum temperature of about 900°C is not exceeded. If heated about 900°C, β-quartz will

transform to β-spodumene. Table 3 lists the compositions of three commercial β-quartz glass-ceramics from different manufactures and their areas of application [17].

Table3. *Commercial glass-ceramics based on β-quartz solid solution (Wt.%)*

		Vision Corning	ZERODUR* Schott	Narumi* Nippon Electric
SiO_2		68.8	55.5	65.1
Al_2O_3		19.2	25.3	22.6
Li_2O		2.7	3.7	4.2
MgO	x1	1.8	1	0.5
ZnO		1	1.4	
P_2O_5			7.9	1.2
F				0.1
Na_2O		0.2	0.5	0.6
K_2O	gl	0.1		0.3
BaO		0.8		
TiO_2	n	2.7	2.3	2
ZrO_2		1.8	1.9	2.3
As_2O_3	f	0.8	0.5	1.1
Fe_2O_3	c	0.1	0.03	0.03
CoO		50 ppm		
Cr_2O_3		50 ppm		
		Transparent cookware	Telescope mirrors	Range tops, Stove windows

*As analyzed at Corning Glass Works, x1, oxides concentrated in crystal; gl, oxides concentrated in glass, n, nucleating-agent oxides, f, fixing-agent oxide; c, colorant oxides.

B-Spodumene (Keatite) Solid Solution

β-spodumene is a tetragonal phase that is isostructural with keatite which, like β-quartz, is a polymorph of SiO_2. β-spodumene is therefore characterized by the same stoichiometry as β-quartz, although the compositional range of the solid solution is more restricted, with *n* ranging from 4 to 10. β-spodumene glass-ceramics can be made from the same glasses that yield (β - quartz glass-ceramics simply by altering the heat treatment: β-quartz glass-ceramics are formed by crystallizing at or below 900°C, whereas β-spodumene glass-ceramic are obtained from heat treatment at temperatures in excess of 1000°C [18].

Table 4 lists the composition of two commercial β-spodumene glass-ceramics, one used for cookware and one for ceramic regenerators in turbine engines [19]showed that the Li F addition increased from 0 to 5% in the Li_2O-Al_2O_3-SiO_2 system decreased the thermal expansion coefficient from 8.3 x 10^{-7} to 5×10^{-7} /°C (25°C to 900°C). Table4. Composition of transparent glass-ceramics based on β-spodumene Solid Solution (Wt.%) [17]

Table4. *Commercial glass-ceramics based on β-spodumene solid solution*

		CORNING WARE			CERCOR Corning
		(Wt. %)	(mol %)	(Wt. %)	(mol%)
SiO_2		69.7	73.6	72.5	75.9
Al_2O_3		17.8	11	22.5	13.6
Li_2O	x1	2.8	5.9	5	10.5
MgO		2.6	4.1		
ZnO		1	0.8		
Na_2O	gl	0.4	0.4		
K_2O		0.2	0.1		

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TiO$_2$	n	4.7	3.7		
ZrO$_2$		0.1	0.1		
Fe$_2$O$_3$	c	0.1	0.1		
As$_2$O$_3$	f	0.6	0.2		
		Cookware, hot plates		Heat exchangers, regenerators	

in crystal; gl, oxides concentrated in glass, n, nucleating-agent oxides, f, fixing-agent oxide; c, colorant oxides.

Mgo-Al$_2$O$_3$-Sio$_2$ Glass-Ceramics Based on Cordierite

Glass-ceramics of the magnesia-alumina-silica type are of importance because they combine good electrical insulation characteristics with high mechanical strength and medium to low thermal expansion coefficients. These desirable properties arise largely as a result of the presence of alpha-cordierite (2MgO. 2Al2O3 .5SiO2) as a principal phase in glass-ceramics of this type. This crystal appears upon heat-treatment of compositions throughout the whole glass-forming region. Other phases which may be present include cristobalite in the high silica compositions and clino-enstatite (MgO.SiO$_2$) or forsterite- (2MgO.SiO$_2$) for compositions having high magnesium oxide contents.

The advantages of the hexagonal form of the cordierite based glass-ceramics are their high strength, excellent dielectric properties, good thermal stability, and thermal shock resistance. The commercial composition is the - missile nose cones -standard glass-ceramic nucleated with titanium, its major constituent is cordierite (Mg2AL4Si5O18) with some "Mg-beryl" solid solution (Table5).

Table5. *Commercial Cordierite Glass-Ceramics [17]*

Composition		wt.%	mol%		Phases
SiO$_2$		56.1	58.1		
Al$_2$O$_3$	x1	19.8	12.1		Cordierite
MgO		14.7	22.6		Cristobalite
					Rutile
CaO		0.1	0.1		
TiO$_2$	n	8.9	6.9		Mg-dititanate
As$_2$O$_3$	f	0.3	0.1		
Fe$_2$O$_3$		0.1	0.1		
		Use: Radomes			

Nano-Crystalline Microstructures

Glass-ceramics with crystallites' size less than 100 nm are called nano-crystals. The development of glass-ceramics based on such small crystallites was one of the earliest examples of nanotechnology [20], a term now applied in the fabrication of carbon nanotubes, sintered ceramics, sol-gel glass, etc. the volume percent of nano-crystals in glass-ceramics vary from very few volume percent to more than 90 vol. %.Usually, the nano crystals are surrounded by glass matrix. To achieve such a fine microstructure, the nucleation rate must be very high, but the secondary crystal growth must be suppressed.

SYNTHESIS OF FUNCTIONAL GLASS-CERAMICS

Bioactive Glass-Ceramics

The concept of bioactive material is midway between those of inert material and resorbable material. Although a number of definitions of bioactivity have been reported, one by Hench [21]is especially simple: the property of an implanted material that allows it to bond to living tissue.

It has been reported [22]that, bioactive ceramics, glasses and glass-ceramics, are able to form a biologically active carbohydro xyapatite layer directly with bone, this layer is chemically and structurally correspondent to the mineral phase of bone, thus provides a strong interfacial bonding. Bioactive glasses and glass-ceramics have been developed in response to the need to suppress interfacial mobility in implanted bioinert ceramics.

Thus, in 1967, Hench proposed, to the US Army Medical Research and Development Command, to conduct research with a view to change the chemical composition of glasses, in order to enable their interaction with the physiological system and provide chemical bonding between

living tissue and the implant surface. This away, in 1971, Hench et al. [23]showed, for the first time, that a material made by the man could bond to bone through stimulating positive biological reactions at the material/tissue interface.[24]. The invention, named BioglassR, was the first bioactive glass material ever developed.

According to Hench and Wilson [25], bioactive materials include hydroxyapatite (HA) ceramics, glasses, glass ceramics and surface-active composite materials.

Bioactive Glass-Ceramic Compositions

Most biomedical glass-ceramics are based on compositions similar to those of Hench's bioactive glasses (BioglassR)[26], however, all of them have very low   contents in alkali oxides. Table 6 summarizes the properties of bioactive glass ceramics used in the clinical field as compared to those of BioglassR 45S5.

Ceravital®

The earliest glass-ceramic material of clinical use was developed by Bromer and Pfeil in 1973 [27]and named CeravitalR. This designation, however, includes a wide range of glass-ceramic compositions. Originally, CeravitalR was believed to possess extraordinary properties as a replacement material even for bone in loaded zones and teeth.

However, as can be seen from Table 6, their mechanical properties, even for the optimum compositions, they are below the 160 MPa of the human cortical bone and are similar to those of sintered dense hydroxyapatite (115 MPa).Also, long-term in vivo tests questioned the stability of these materials. However, subsequently Gross et al. [28]developed improved compositions, the solubility of which was reduced by using various metals as nucleating agents. The bioactivity of CeravitalR is roughly one-half that of BioglassR 45S5 (5.6 versus 12.5). At present, CeravitalR implants are exclusively used to replace the ossicular chain in the middle ear, where loads are minimal and the mechanical properties of this material are thus more than adequate.

Cerabone® A/W

One of the glass-ceramics of more clinical success, be probably the denominated A/W, which is constituted by two crystalline phases: oxyfluorapatito$Ca10$ $(PO_4)6(O,F_2)$ and wollast onite (β- $CaSiO_3$) and a residual vitreous phase. This was originally developed by Kokubo et al.[29]and is commercially available under the trade name CeraboneR A/W.

Its composition is shown in the Table 6.After some failed attempts of producing a glass-ceramic of the $Ca_3(PO_4)_2$- SiO_3-$MgCa(SiO_3)_2$ system, starting from a monolithic glass or even powdered glass, the glass-ceramic A/W was obtained by adding a small amount of CaF_2 to the original composition.

Glass ground to an average particle size of 5 μm was isostatically pressed at 200 MPa in the desired shapes and thoroughly densified at ca. 830 oC, which resulted in the precipitation of oxyfluorapatite and β- wollastonite at 870 and 900 oC, respectively. The end-product was thus a glass-ceramic with a very fine microstructure free of cracks and pores.

The special microstructure of this glass-ceramic endows it with the best mechanical properties among all the materials shown on Table 6; thus, it's of (220 MPa) is nearly twice that of dense hydroxyapatite (115 MPa) and exceeds that of human cortical bone (160 MPa). In addition, its tenacity is ca. 2.0 MPaAm–1/2 and its Vickers hardness about 680 HV[30].

Table6. *Composition and selected properties of glass-ceramics with clinical applications as compared to those of Bioglass 45S5*

Compound(wt.%)	Bioglass45S5	Ceravital*	Cerabone A/W	Ilmaplant *	Bioverit*
Na_2O	24.5	5-10	0	4.6	3-8
K_2O	0	0.5-3.0	0	0.2	0
MgO	0	2.5-5	4.6	2.8	2-21
CaO	24.5	30-35	44.7	31.9	10-34
Al_2O_3	0	0	0	0	8-15
SiO_2	45.0	40-50	34.0	44.3	19-54
P_2O_5	6.0	10-50	6.2	11.2	2-10
CaF_2	0	0	0.5	5.0	3-23
Phases	Glass	Apatite +Glass	Apatite +β-wollast. + Glass	Apatite + β-wollast. + Glass	Apatite + Flogopite + Glass
Flexural Strength of	42	100 – 150	220	170	100 – 160

(MPa					
CompressiveStrength (Mpa)	n.d	500	1060	n.d	500
Young's Modulus(GPa	35	n.d	117	n.d	70 - 88

n.d = not determined

Equally that in the bioactive glasses, an appetite layer is formed on the surface of the glass-ceramic A/W in simulated body fluid and it is also attributed to this layer the capacity of joint to bony tissue. Due to the chemical and structural characteristics of this CHA, similar to the bony tissue, it is of expecting that, in the interface with the bone, proliferate the osteoblasts preferably to the fibroblasts.

However, unlike bioactive glasses, no amorphous silica layer between the carbohydro xyapatite (CHA) and the A/W glass-ceramics has been observed not even by high resolution electron microscopy. In any case, Kokubo and coworkers believe that silanol groups formed at the glass ceramic surface are those responsible for the formation of the CHA layer as they provide the favorable sites required for its nucleation and growth.

Their hypothesis relies on the following mechanism for the formation of the CHA layer on A/W glass-ceramics: dissolution of calcium ions from the glass-ceramic surface increases the ionic activity product of apatite in the simulated body fluid, while hydrated silica at the glass-ceramic surface provides favorable sites for CHA nucleation.

Imaplant-L1®

Berger et al. [31] developed this implant, which consists of apatite/wollastonite glass-ceramic. As can be seen from Table III, it differs from A/W glass-ceramics in its alkali contents; increased proportions of CaF2, SiO2 and P2O5; and decreased content in CaO. Because of its low mechanical bending strength (see Table 6), its use is restricted to maxillofacial implants.

Bioverit®

In 1983, Holland et al.[32], of the University of Jena, developed a new series of bioactive glass-ceramics, which they called BioveritR I (Table 6). BioveritR glass-ceramics can be readily machined with standard tools and even retouched in the operating theatre.

These materials are obtained from a silicate-phosphate glass of complex composition in the SiO_2-Al2O$_3$-MgO-Na$_2$O-K$_2$O-F-CaO-P$_2$O$_5$ system. The procedure involves generating phase separation in the glass, through controlled nucleation and subsequent growth of the crystal phases, by thermal treatment at 610 and 1050oC.

The resulting product consists of residual glass plus a mixture of apatite crystals (1-2 μm in size) and a fluoroflogopite-like mica (Na/KMg3[AlSi3O10F2]) which facilitates machining of the material.

Subsequently, the same authors developed another family of also readily machined glass-ceramics, which they called BioveritR II. As can be seen from Table 7 , the new materials contained very little P2O5 relative to BioveritR I. Like its predecessor, BioveritR II contains fluoroflogopite-like mica, (whose crystals present a curved morphology that are not encountered in nature), in addition to other crystalline compounds, specially prominent among of cordierite ($Mg_2[Si_5Al_4O_4]$).

Finally, Vogel and Holland[33]developed a further family of glass-ceramics named BioveritR III (see Table 7) from a phosphate glass containing no silica. To this end, they used an inverted phosphate glass in the P_2O_5-Al_2O_3-CaO-Na$_2$O system, consisting of mono- and diphosphate structural units and doped it with Fe_2O_3 or ZrO_2. The end product consisted of residual glass in addition to apatite, berlinite ($AlPO_4$) and complex structures of phosphates of the varulite-like type (Na-Ca-Fe phosphate).

The contents in crystalline phases and vitreous matrix in BioveritR glass-ceramics can be modified with a view to modulating their physical properties and bioactivity by changing the ingredient contents within the composition ranges shown in Tables 6 and 7. Thus, translucence in these materials is a function of the proportion of crystal phases, whereas machinability depends on their mica content (e.g. BioveritR II is easier to machine than is BioveritR I). In addition, the material color can be modified by addition of small amounts of oxides such as NiO, Cr_2O_3, MnO_2, FeO, Fe_2O_3, etc.

By the mid-1990s, more than one thousand bone replacement implants had been successfully fitted in various biomedical fields including orthopedic surgery (e.g. acetabular reconstruction, vertebral replacement, tibial head osteoplastic,

joint plastic surgery) and head and neck surgery (middle ear implants, orbital base repair, cranial base reconstruction, rhinoplasty, etc.).

Bioactive Glass Coatings and Composites

As noted earlier, the greatest constraint on a wider use of bioactive glasses and glass-ceramics is derived from their relatively poor mechanical properties, especially in zones under mechanical loads. This shortcoming has been circumvented by using various methods to increase the strength of these glass materials and facilitate their use as implants. One solution to the problem is using bioactive glasses as a coating for materials with a high mechanical strength. This method has been used with a number of substrates, including dense alumina [34], various types of stainless steel [35], cobalt-chromium alloys [36]and titanium alloys[37, 38]. This last alloy is especially attractive on account of its high strength, low elasticity modulus and good biocompatibility.

The methods used to prepare the coatings range from immersion in the molten glass or in a solution, suspension or gel (dip coating); electrophoresis from a solution or suspension (the metal to be coated acting as an electrode), biomimetic coating growth or flame or plasma spraying. Plasma spraying is the method of choice when depositing a bioactive glass onto a metal substrate.

Table7. *Composition and selected properties of the Bioverit types II and III*

Compound	Bioverit文II(wt.%)	Bioverit文III(wt.%)
SiO_2	43 – 50	---
Al_2O_3	26 – 30	6 – 18
MgO	11 – 15	---
Na_2O/K_2O	7 – 10.5	11 – 18
F	3.3 – 4.8	---
Cl	0.01 – 0.6	---
CaO	0.1 – 3	13 – 19
P_2O_5	0.1 – 5	45 – 55
$(MeO/Me_2O_5/MeO_2)*$	---	1.5 - 10
Density (gr/cm3)	2,5	2.7 – 2.9
Coefficient of Expansion (K-1)	7.5 – 12 · 10-6	14 – 18 · 10-6
Flexural strength (MPa)	90 – 140	60 – 90
Toughness (KIC) (MPa · m.)	1.2 – 1.8	0.6
Young's Modulus (GPa)	70	45
Compressive strength (MPa)	450	---
Vickers hardness (HV 10)	up to 8000	---
Hydrolytic Class (DIN 12111)	1 - 2	2 – 3
Roughness(after polishing) (μm)	0.1	---

* (MnO, CoO, NiO, FeO, Fe_2O_3, Cr_2O_3, ZrO)

Another application of bioactive glasses is in the production of composites, being reinforced the bioactive glass with a second phase. The materials thus obtained include "biofibre glass" and alumina, organic polymers or metal fibers. The former has fallen short of the original expectations as it seemingly releases large amounts of alumina powder that are detrimental to tissues. The materials reinforced with metal fibers are those with the strongest potential. In fact, metal fibers strengthen bioactive glasses and improve their deformability. The most widely used procedure for producing these materials is hot pressing [39].

Scaffolds for Bone Tissue Engineering

Macro porous bioactive Glass-ceramic scaffolds was developed for tissue engineering via polyurethane sponge template. The starting glass (CEL2) belongs to the system SiO_2-P_2O_5-CaO-MgO-Na_2O-K_2O and has been synthesized by a conventional melting-quenching route. Slurry of CEL2 powder, polyvinyl alcohol and water has been prepared in order to coat, by impregnation, the polymeric template. An optimized thermal treatment was then used to remove the sponge and to sinter the glass powders, leading to a glass-ceramic replica of the template. Morphological observations, image analyses, mechanical tests and in vitro tests showed that the obtained devices are good candidates as scaffolds for bone-tissue engineering, in terms of pore-size distribution, pore interconnection, surface roughness, and both bioactivity and biocompatibility. In particular, a human osteoblast cell line (MG-63) seeded onto the scaffold after a standardized preconditioning route in simulated body fluid

showed a high degree of cell proliferation and a good ability to produce calcium nodules. The obtained results were enhanced by the addition of bone morphogenetic proteins after cell seeding [40].

Glass-Ceramics for Dental Hypersensitivity Treatment

Dentin hypersensitivity is a common dental pain arises when subjecting tooth to thermal, chemical or tactile stimuli, it occurs due to loss of minerals from tooth, attempts to replace these minerals was investigated. bioactive glasses was first used as a dental hypersensitivity treatment in SensodyneVR toothpaste containing BioglassVR 45S5 particulate named Nova Min VR was in 2004.

Bioactive glass-ceramics as BiosilicateVR was also introduced, its composition[23, 24] $23.75Na_2O–23.75CaO–48.5SiO_2-4P_2O_5$ (wt %). its microstructure can be engineered to be composed of one or two crystalline phases through controlled double-stage heat treatments, these two phases are: a sodium-calcium silicate phase ($Na_2CaSi_2O_6$) or both and sodium-calcium phosphate ($NaCaPO_4$).[41]

Infiltrated Ceramic Composites for Dental Prostheses

In the last years, many bioceramics and processing methods for all-ceramic prosthesis have been developed, because these materials can result in dental restorations with improved biocompatibility, chemical stability, and aesthetic qualities compared to metals and polymers restorations. The market of dental bioceramics is growing rapidly in Brazil and abroad. Despite the recent developments, bioceramics used as core materials still need to be improved in relation to their optical characteristics as well as to their mechanical properties.

The aim of this project is to develop a new method of preparation of ceramic composites infiltrated with glass with improved optical transmission and high mechanical properties for use in dental prostheses. A new method for the production of cores of ceramic-glass composites is proposed, in which the infiltration of the glass in the partially sintered perform is conducted under pressure. This method is a hybrid technique between the systems In-Ceram Vita Zahnfabrik) and Empress (Ivoclar). Using this method, it is expected to develop translucent composites by decreasing the porosity and matching the optical characteristics of the phases present in the microstructure to minimize the light scattering. To achieve this objective, the targets are: 1) develop glasses with high refraction indexes, comparable to those of the reinforcing ceramic phases; 2) develop ceramic composites infiltrated with glass under pressure; 3) study and understand the optical phenomena of light scattering of the new composites using the Kubelka-Munk model; and 4) characterize the mechanical properties of composites [42].

A recent study revealed comparable properties of mica glass ceramics containing 20 wt.% YSZ. particular, to the commercially available IPS emax Press and IPS emax CAD as regards mechanical and chemical durability. [43]

Transparent Glass-Ceramics

Some successful and many trial optical applications have been proposed for transparent glass-ceramics: cookware (Vision) that allows continuous visualization and monitoring of the cooking process); fireplace protection; transparent eyeshields; transportation windows; substrates for LCD screens; ring laser gyroscopes; rockets' fronts; fiber grating athermalization; precision photolithography; printed optical circuits.

As for telescope mirrors (Zerodur), the telescope's optical components should resist distortions caused by temperature fluctuations. Therefore, they utilize glass-ceramics with zero expansion.

Wavelength up-conversion devices for europium-doped waveguide amplifiers uses fluoride, chalcogenide and oxyfluoride-based transparent glass-ceramics, doped with rare-earth ions. Transparent mullite, spinel, willemite, gahnite and gelenite based glass-ceramics doped with transition-metal ions have been developed for use in tunable and infrared lasers, solar collector and high-temperature lamp applications. Glass-ceramics that exhibit second harmonic generation and material with high kerr constant for electroopical devices have been developed as well. The combination of several properties is the hallmark for their success [42].Other optically active applications include luminescent glass-ceramics for solar concentrators, up-conversion and amplification devices; illumination devices using IR; heat-resistant materials that absorb UV, reflect IR and are transparent to visible light; materials that absorb UV and fluoresce in red/IR; substrates for arrayed waveguide grating; solid-state lighting – white light; and laser pumps.

To be transparent in the visible range, a glass-ceramics must have one or a combination of the following characteristics: the crystal size must be much less than the wavelength of visible light (i.e., less than 200 nanometers); and the birefringence must be very low or there must be negligible difference between the refractive indexes of the residual glass matrix and the crystals.

This is the case in most existing transparent glass-ceramics, as they have crystals size less than 200 nanometers and a crystallized fraction of only 1 to 70 percent. However, an interesting new discovery was recently reported by [44]. They developed a large grain (about 10-50 micrometer), highly crystalline (97 percent) and transparent glass-ceramic.

New Types of Glass-Ceramic Glazes

For many years, ceramists have known that certain glaze compositions are susceptible to large visible crystallization effects when they are applied as coatings on decorative ceramic ware[45]. Likewise, formerly, glass beads used to have opaque or opalescent heterogeneity colors and natural stones appearances due to crystallization in either the bulk or surface.[46]. Both controlled nucleation and crystallization of glasses have been widely developed since the 1960s, due to the wide interest in the production and commercial exploitation of glass ceramic products in domestic and technological applications [2].

Not much investigation, however, has been devoted to the production of glass-ceramics in thin layers, although surface crystallization phenomena in glasses have been investigated [47]. Yet, these studies considered surface crystallization a consequence of defects in glasses or a transitional stage during formation of bulk crystallization of glass-ceramics.

In recent years, there has been a growing interest in ceramic glazes and frits for developing new glaze compositions that can be crystallized in order to improve the mechanical and chemical properties of fast-fired glazed tiles. Nucleation and crystallization of thin layers of certain glasses covering ceramic substrates (glazes) to obtain high-performance glass-ceramic coatings[48], are scientific and technological challenges due to the difficulties of controlling crystal growth homogeneously. Several parent glasses from a wide range of compositions in the $CaO–MgO–Al_2O_3–SiO_2$ system, the $Li_2O–ZnO/BaO–Al_2O_3–SiO_2$

system, and the G–C commercial systems based on spodumene, cordierite, nepheline, and leucite were melted and water quenched to obtain powdered glasses (or frits). The glasses/frits obtained were subsequently applied to stoneware tiles , as is usual in the production of ceramic pavements.

An industrial fast firing to 1100°C for 30 min. was used, during which the (nucleation 1 growth) stages were accomplished in the thin layer of glassy coating (approx. 0.3 mm). In some cases, a complementary (nucleation 1 growth) thermal treatment was carried out, in order to recrystallize the residual glassy phase remaining after the fast-firing cycle.

In these cases, the temperature used for the additional thermal treatment was that of the main DTA exothermic crystallization peak (DTA conditions: heating rate of 10°C/min. and cooling rate of 30°C/min.). The final result was tiles with glass-ceramic glazes containing several volume percent of crystals.[49]

The feldspar composition produced a very stable glass with respect to nucleation and crystallization, whereas the cordierite glass showed two exothermic peaks at 800 and 920°C due to the precipitation of α- and β-cordierite phases.

The difficulty of crystallization made it necessary to introduce some nucleating agents[50] into several of the glassy compositions considered here, mainly in the case of the most thermally stable glassy frits. Table 8 gives the glass systems investigated, together with the crystalline phases precipitated after fast thermal treatment at 1000°C for 30 min. As can be seen in Figure 4, the crystallization microstructure of the surface of these glass-ceramic glazes is different depending on the crystalline phase and composition of the original glassy matrix. SEM observation of the microstructure of the cross section of the glaze/substrate interface revealed many bubbles indicating high volume of crystallization exists and coarse crystallization in some thin layer glazes.

Therefore, in those cases where there was a high tendency to crystallize, it was necessary to dilute the original frits with some commercial boro-zinc silicate frits, which likewise were phase separated [50]. This enabled the crystallization process to be better controlled, as can be observed in the SEM micrograph shown in Figure 5.

Table8. *Glass Frits and Crystalline Phases Obtained After Blade Deposition and Fast Firing Over Ceramic Substrates of Earthenware Tiles*

| Composition system	Main crystal phase	Microstructure
Li_2O-CaO-MgO-Al_2O_3-SiO_2	Spodumene cordierite diopside diopside 1 anorthite	rounded crystallites dot crystals square/rounded crystals elongated and prismatic crystals
G-C commercial systems	Cordierite spodumene	grained crystals prismatic crystals
Li_2O-ZnO/BaO-Al_2O_3-SiO_2	nepheline/celsian	needle crystals
Li_2O-K_2O-Al_2O_3-SiO_2	leucite	as whiskers 1-2 mm crystals
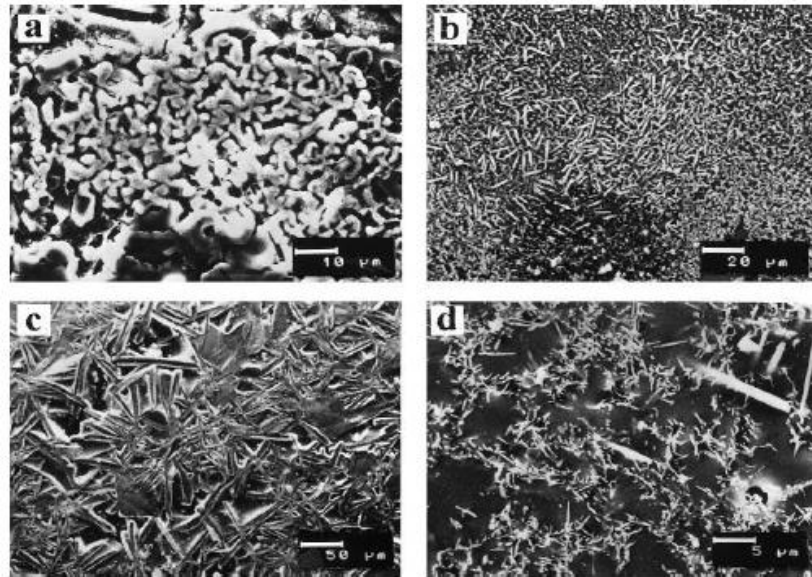
Figure4. *SEM micrographs from glass-ceramics glazes of (a) spodumene, (b) cordierite, (c) nepheline, and (d) leucite.*
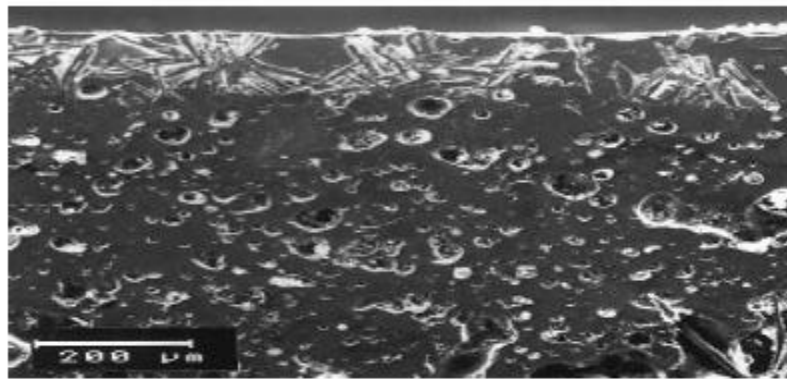

Figure5. *SEM micrograph obtained from a perpendicular cross section of the nepheline glass-ceramic glaze diluted with a commercial frit.*

This dilution advances the abrasion and hardness of the glaze surface through permitting a reticular crystalline microstructure embedded in the original residual glassy phase to be attained. In the case of the spodumene glaze, the dilution allowed the precipitation of crystals between the cracks produced by the different expansion coefficient of the spodumene glassy matrix and the solvent frit (Fig. 5). This type of nucleation of crystals associated with the cracks and interfaces agrees well with the models of surface nucleation recently developed by Schmelzer et al. [47]. Contrary to bulk glasses crystallization mechanisms and comparable to sintered powdered glasses, this case has three different nucleating interfaces; viz., air/surface of glaze, substrate/glaze interface, and frit/frit interface. A wide range of crystallization microstructures has been achieved by this processing, depending on the original glass

composition. However, the very short time for the growth step makes it difficult to obtain high percentages of volume crystallization. Crystals ranging in size from less than 1 mm to elongated crystallites larger than 20 mm precipitated in the glassy matrix of the coating were obtained.
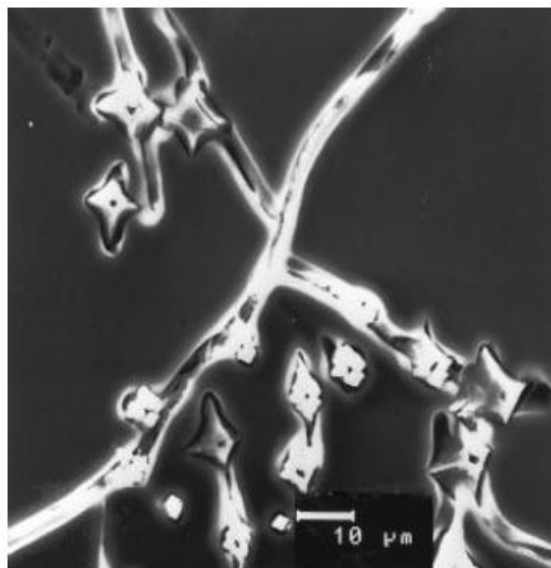

Figure6. *Nucleation of spodumene star crystals, or incipient dendrites, in the S2 glaze composition.*

Glass Ceramics for Nuclear Waste Immobilization

Glass-ceramic waste form has been development to immobilize fission-product generated by the uranium extraction separations process. The glass ceramics were slow-cooled and characterized in terms of phase assemblage and preliminary irradiation stability. The phases identified in these glass ceramics were oxyapatite, powellite, cerianite, and lanthanide – borosilicate.[51]

Glass-Ceramic Armor

Some patents have been filed and others have been granted for inventions related to armor material for the protection of people or equipment against high speed projectiles or fragments. Ceramic material is used particularly in armors for which low weight is important: bullet-proof vests; and armor for automobiles, aircraft and helicopters, especially in cockpits or seats and for protection of functionally important parts. Hard, high modulus Al2O3, despite its high density (~ 4 gm / cm3)remains the gold standard ceramic armor material. Other very hard, but less dense materials, such as SiC and B4C, can be produced only at very high temperatures by costly manufacturing processes and are, hence expensive.

Inexpensive Glass-Ceramics Based On Slag

The principal proposed usage for basalt and slag derived glass ceramics is in the form tiles and pipes for the conveyance or storage of abrasive materials (e.g. coal) where the glass ceramics are much more resistant to abrasion than alternative metals and out in the UK and the USA[52] a great deal of development and use has been undertaken in Russia [53]. It is an indication of its value that it is claimed that this application may represent the greatest use of glass ceramics worldwide.

Table9. *Commercial glass-ceramic materials and their applications*

Basic Chemical System	Unique properties	Product
$Li_2O - SiO_2$	Photosensitivity and differential solubility of phases leads to ability to form intricate patterns	Substrates; fine-mesh screens; fluidic devices; printing-plate molds; spacers
$Li_2O-Al_2O_3- SiO_2$	Low expansion, thermal shock resistance	Cookware; burner covers; preheaters; mirror substrates; low expansion housing; valve parts
$MgO - Al_2O_3 - SiO_2$	High strength, good dielectric properties	Radomes; antenna windows
$K_2O - MgO - Al_2O_3 - B_2O_3 - SiO_2 - F$	Machinable	Pacemater parts; welder's fixture holder; welding nozzles; circuit bases
$CaO - MgO\ Fe_2O_3 - Al_2O_3SiO_2$	Abrasion resistance	Industrial floor coverings, wall facings; abrasion resistant linings; high temperature insulators
$CaO - ZnO - Al_2O_3 - SiO_2$	Abrasion resistance	Floor coverings; wall facings; counter tops
$B_2O_3 - Al_2O_3 - SiO_2$	Selective-ion evaporation at elevated temperatures	Semiconductor doping sources
$P_2O_5 - Al_2O_3 - SiO_2$	Elevated temperatures	
$Na_2O - Al_2O_3 - SiO_2$	Good strength	Dinnerware
$Li_2O - CeO_2 - Al_2O_3 -$	Chemical durability; mechanical toughness	Coatings for chemical reactor

Some Types of Glass-Ceramic Materials and their Applications

SiO_2		accessories
$BaO - Al_2O_3 - SiO_2$	Specific expansion coefficient	Alloy bonding
$Li_2O - BaO - SiO_2$	Dielectric properties	Insulators in devices

CONCLUSIONS

- Glass-ceramic technology is based on controlled crystal nucleation and growth in certain glass compositions.

- Technologies of glass-ceramic preparation include:

Conventional Method (Two-Stage)

Modified Conventional Method (Single-Stage)

Petrurgic Method

Powder Methods

Sol-Gel Precursor Glass

- The basic composition systems which are used for production of commercial glass-ceramics can be grouped in the following systems:

(1) $Li_2O-Al_2O_3-SiO_2$ (2) $MgO-Al_2O_3-$ (3) Li_2O-SiO_2; (4) $Na_2O-AI_2O_3-SiO_2$, (5) $K_2O-MgO-AI_2O_3-SiO_2-F$, (6) $CaO-MgO-AI_2O_3-SiO_2$, (7) $BaO-AI_2O_3-SiO_2$.

- Glass-ceramics have different functions and uses in many fields and applications.

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