A bright future for glass-ceramics

From their glorious past, starting with their accidental discovery, to successful commercial products, the impressive range of properties and exciting potential applications of glass-ceramics indeed ensure a bright future!

by Edgar Dutra Zanotto

(Credit: Schott North America.)

Glass-ceramics were discovered – somewhat accidently – in 1953. Since then, many exciting papers have been published and patents granted related to glass-ceramics by research institutes, universities and companies worldwide.

Glass-ceramics (also known as vitrocerams, pyrocerams, vitrocerâmicos, vitroceramiques and sittals) are produced by controlled crystallization of certain glasses – generally induced by nucleating additives. This is in contrast with spontaneous surface crystallization, which is normally not wanted in glass manufacturing. They always contain a residual glassy phase and one or more embedded crystalline phases. The crystallinity varies between 0.5 and 99.5 percent, most frequently between 30 and 70 percent. Controlled ceramization yields an array of materials with interesting, sometimes unusual, combinations of properties.

Unlike sintered ceramics, glass-ceramics are inherently free from porosity. However, in some cases, bubbles or pores develop during the latter stages of crystallization. Glass-ceramics have, in principle, several advantages.

- They can be mass produced by any glass-forming technique.
- It is possible to design their nanostructure or microstructure for a given application.
- They have zero or very low porosity.
- It is possible for them to combine a variety of desired properties.

One example of the fourth advantage is combining very low thermal expansion coefficient with transparency in the visible wavelength range for cooking ware. Another is combining very high strength and toughness with translucency, biocompatibility, chemical durability and relatively low hardness for dental applications.

Glass-ceramics are normally produced in two steps. First, a glass is formed by a standard glass-manufacturing process. Second, the glass article is shaped, cooled and reheated above its glass transition temperature. The second step is sometimes repeated as a third step. In these heat treatments, the article partly crystallizes in the interior. In most cases, nucleating agents (e.g., noble metals, fluorides, ZrO_2, TiO_2, P_2O_5, Cr_2O_3 or Fe_2O_3) are added to the base glass composition to boost the nucleation process.

A less frequently used method is to induce and control internal crystallization during the cooling path of a molten viscous liquid. This process is used sometimes to form relatively coarse-grained glass-ceramics from waste materials to be used in the construction industry.

Glass-ceramics also can be produced by concurrent sinter-crystallization of glass-particle compacts. In this case, crystallization starts at glass–particle interfaces. A main advantage of the sinter-crystallization process is that nucleating agents are not necessary, because the particle surfaces provide nucleation sites. A disadvantage of this method is 0.5 to 3.0 percent residual porosity. However, this can be sometimes minimized or even eliminated by hot-pressing techniques. The sintering route also is attractive to produce glass-ceramics from reluctant glass-forming compositions, which could be made as a "frit," molded and sinter-crystallized. Commercial applications of sintered glass-ceramics include devitrifying frit solder glasses for sealing TV tubes, cofired multilayer substrates for electronic packaging, marblelike floor and wall tile (Neopariés and similar brands) and some bioactive glass-ceramics. References 1–6 provide a list of recent articles and reviews on the fundamentals of the sinter-crystallization process.

Fig. 1. Standing, from left to right, TC-7 members Ralf Muller, Guenter VoelKsch, Linda Pinckney, Edgar Zanotto, Wolfgang Pannhorst, Takayuki Komatsu, Miguel Prado, Michael Budd, Joachim Deubener, Wolfram Hoeland and Ian Donald. Sitting are distinguished guests George Beall and Donald Stookey. Picture taken in Jackson Hole, Wyo., September 2006.

Patents and papers

An idea of the scientific and commercial importance of glass-ceramics comes from a search on *Free-patents Online*, which comprises granted patents or applications in the United States, Europe and Japan. About 2,400 granted or filed U.S. patents appear with the keywords "glass ceramic" in the abstract. There also are about 1,500 European and 2,700 Japanese patents. There is some overlap in these numbers, because the same patent is often deposited in different countries.

A similar search for published papers in the Scopus database with the same keywords yields about 10,000 articles. These are very impressive numbers for such a narrow field within all the numerous materials classes and types. This suggests that plenty is already known about glass-ceramics technology. A similar search in Scopus indicates that, since 1960, the most prolific companies in glass-ceramics research are Corning Inc. (114 articles), Schott Glaswerke (69), IBM (65), Nippon Electric Glass Co. (30), Ivoclar Vivadent AG (29), NEC Corp. (24), Aerospace Corp. (20) and Toyota TI (18).

There are far too many papers and patents to be cited in this short "insight" article. Thus, we will direct the interested reader to a limited number of key books and papers, including some of our own. The fundamentals behind the understanding and control of glass crystallization concern the mechanisms, thermodynamics and kinetics of crystal nucleation, growth and overall crystallization. Several groups have focused on such studies during the past century. Interested readers are invited to check References 7–9 for reviews on the basics of internal and surface nucleation in glasses. Readers are referred to classical textbooks in References 10–12 and review articles in References 13–16 for more detailed information on glass-ceramics.

Discovery of glass-ceramics

Natural glass-ceramics, such as some types of obsidian, "always" have existed. Synthetic glass-ceramics were serendipitously discovered in 1953. Stanley Donald Stookey, then a young researcher at Corning Glass Works, meant to anneal a piece of a lithium disilicate glass with precipitated silver particles (meant to form a permanent photographic image) in a furnace at 600°C. He accidentally overheated the glass to about 900°C. "Damm it, I've ruined a furnace!" Stookey thought. Instead of a melted pool of glass, the astonished Stookey observed a white material that had not changed shape.

He then accidentally dropped the piece on the floor, but it did not shatter, contrary to what might normally have been expected from a piece of glass! He was surprised by the unusual toughness of that material. Stookey had accidentally created the first glass-ceramic, denominated Fotoceram.[17]

In their book, Volfram Hoeland and George Beall mention that "knowledge of the literature, good observation skills and deductive reasoning were clearly evident in allowing the chance events to bear fruit." This glass-ceramic was later known also as Pyroceram. This first synthetic glass-ceramic eventually led to the development of CorningWare in 1957.[17] It also influenced the development of Vision, a transparent cookware. CorningWare entered the consumer marketplace in 1958 and became a multimillion dollar product.

The scientific and commercial importance of glass-ceramics was recognized by the International Commission on Glass, which established TC-7, the "Nucleation, Crystallization and Glass-Ceramic Committee" (www.icg.group.shef.ac.uk/tc7.html) about three decades ago. Figure 1 shows some past and present TC-7 members and guests.

Commercial glass-ceramic products

The first commercially viable glass-ceramic was developed in the aerospace industry in the late 1950s as radomes to protect radar equipment in the nosecones of aircraft and rockets. Glass-ceramics used in these applications must exhibit a challenging combination of properties to withstand critical conditions resulting from rain erosion and atmospheric reentry: homogeneity; low dielectric constant; low coefficient of thermal expansion; low dielectric loss; high mechanical strength; and high abrasion resistance. Glass-ceramics now are used in nosecones of high-performance aircraft and missiles. No glass, metal or single crystal can simultaneously meet all of these relevant specifications.[10]

Another class of traditional, but still modern and very interesting glass-ceramics, is represented by Corning's Fotoceram (also invented by Stookey) and Schott's Foturan. These glass-ceramics can be patterned by ultraviolet light and selectively crystallized by thermal treatments. The crystallized regions then are completely dissolved by acid etching. The patterned glass can be used as-is or can be heated once more to form polycrystalline glass-ceramic plates that have high-precision holes, channels or any desired intricate pattern. The products are used in electronics, chemistry, acoustics, optics, mechanics and biology in applications that include microchannels in optical fibers, ink-jet printer heads, substrates for pressure sensors and acoustic systems in head-phones.[10–12]


Fig. 2 Glass-ceramic teeth.

Consumer products

Corning, Schott, St. Gobain, Nippon, Ohara, Ivoclar and few others presently produce commercial glass-ceramics for consumer and specialized markets. We could not confirm whether Fuji Photo, Japan; Pittsburg Plate Glass, U.S.; NGK Insulators, Japan; Sklo Union, Czech Republic; CBP Engineering, U.K.; International Ceramics, U.K.; and Konstantinovskii, Russia; remain active in the glass-ceramic business.[11]

A range of commercially successful glass-ceramics for consumer applications include famous brands of low-expansion products that are resistant to thermal shock: CorningWare; and Vision – a transparent glass-ceramic. Cooktop plates, such as Schott's Ceran, Eurokera's Kerablack and Nippon Electric Glass' Neoceram also are available. These products rely on their relatively high toughness (compared with glasses), appealing aesthetics and very low thermal expansion coefficient.

The most important system commercially is the $Li_2O–Al_2O_3–SiO_2$ (LAS) system with additional components, such as CaO, MgO, ZnO, BaO, P_2O_5, Na_2O and K_2O. Fining agents include As_2O_5 and SnO_2. ZrO_2 in combinations with TiO_2 are the most commonly used nucleation agents. The main crystalline phase is a β-quartz solid solution, which is highly anisotropic and has an overall negative TCE. LAS glass-ceramics can sustain repeated and quick temperature changes of 800°C to 1000°C. The dominant crystalline phase of these glass-ceramics, β-quartz solid solution, has a strong negative CTE.

Keatite solid solution (β-spodumene) also has a negative CTE, higher than β-quartz solid solution. The negative CTE of the crystal phase contrasts with the positive CTE of the residual glass. Adjusting the proportion of these phases offers a wide range of possible CTEs in the finished composite. For most current applications, a low or zero CTE is desired. A negative CTE also is possible. At a certain point, generally between 60 and 75 percent crystallinity, the overall negative expansion of the crystal phase(s) and the positive expansion of the residual glass phase cancel each other. Thus, the glass-ceramic as a whole has a TCE that is very close to zero. But such a balance is not straightforward, because the relative stiffness of the glass and crystal phases also is important.

Glass-ceramics also can be adjusted to match the CTE of the material to which they will be bonded. LAS glass-ceramics were originally developed for use in mirrors and mirror mounts of astronomical telescopes. They now have become known and have entered the domestic market through their use in cooktops, cookware and bakeware as well as high-performance reflectors for digital projectors. Other well-known brands of these low-expansion glass-ceramics are Ceran, Kerablack and Neoceram (cooktops); and Robax, Keralite and Neoceram (stoves and fireplaces). Nippon Electric Glass's related

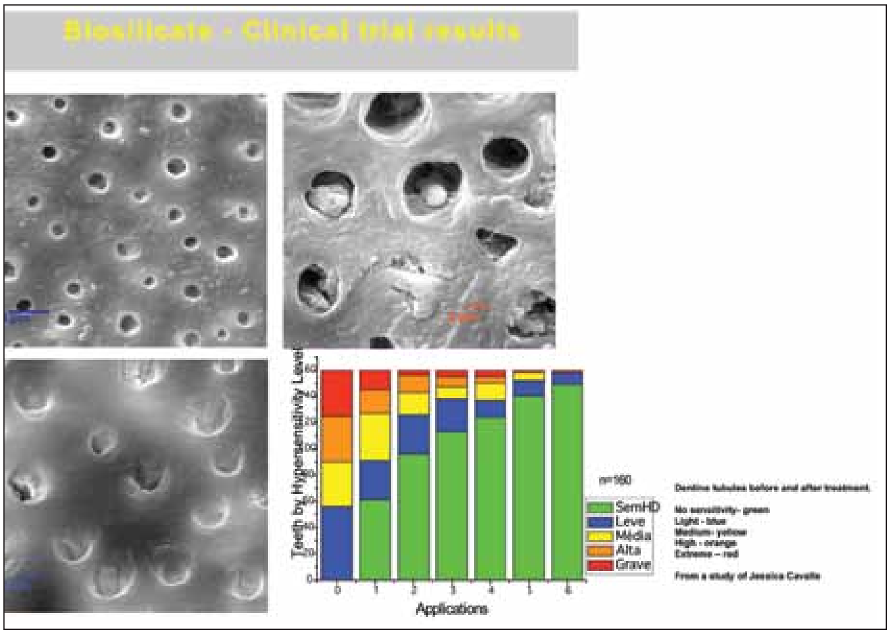

Fig. 3. Micrographs of open and partially blocked dentin tubules by Biosilicate glass-cermic powder. RHS – results of a clinical study of dentin sensitivity level of 160 teeth: Initial and after 1 to 6 applications of Biosilicate. (Reprinted from a research report for Vitrovita – Glass-Ceramic Innovation Institute.)

products in this area include Firelite fire-rated glass. The same class of material was also used until the late 1990s as CorningWare dishes, which could be taken from the freezer directly to the oven with no risk of thermal shock damage. These low-CTE glass-ceramics are the most successful commercial glass-ceramics thus far developed.[10–12]

Thermal uses of glass-ceramics

Another particularly important material is Zerodur, a semitransparent, nonporous glass-ceramic made by Schott. Zerodur has an extremely low CTE ($0.00 \pm 0.02 \times 10^{-6}$/K between 0°C and 50°C), which can even become zero or slightly negative in some temperature ranges. Another unique characteristic of this glass-ceramic is its exceptionally good homogeneity. Even in large material blocks, it is almost impossible to measure the fluctuations in mechanical and thermal properties. Its good transparency in the range 400 to 2,300 nanometers allows a verification of internal quality. Therefore, it can be ensured that neither bubbles nor inclusions go undetected.

Because of its unique properties, Zerodur is a preferred material for lightweight honeycomb mirror mounts made for satellite mirrors. Other typical applications include precision optics, mirror substrates for large astronomical telescopes, mirror substrates for X-ray telescopes, optical elements for comet probes, ring laser gyroscopes and standards for precision measurement technology. Other great low-CTE glass-ceramics success stories are Ceran panels for cooktops and Robax for fireplaces and stoves.[10–12,14]

Another relevant thermal property of glass-ceramics is their limiting use temperature. Because of their residual glass phase, most glass-ceramics flow and deform at relatively low temperatures, typically below about 700°C. However, some notable exceptions exist. An example is a celsian glass-ceramic in the $SrO–BaO–Al_2O_3–SiO_2$ system, which has use temperatures as high as 1,450°C and CTEs that match silicon, SiC and Si_3N_4. This material is meltable at commercial temperatures (1,650°C).[18]

Machinable glass-ceramics

Macor, Dicor, Vitronit, Photoveel and other brands of machinable glass-ceramics rely on mica crystals in their microstructure. Their high CTE readily matches most metals and sealing glasses. They exhibit zero porosity and, in general, are excellent insulators at high voltages, various frequencies and high temperatures. When properly baked out, machinable glass-ceramics will not outgas under vacuum environments. They can be machined to complicated shapes and precision parts with ordinary metalworking tools, quickly and inexpensively.

Machinable glass-ceramics require no postfiring after machining. This means that specifications can be met without having to resort to costly machining with diamond tools. Typical Macor applications include insulators and supports for vacuum environment feed-troughs; spacers, headers and windows for microwave tube devices; sample holders for microscopes; aerospace components; welding nozzles; fixtures; and medical equipment. Some dental and some bioactive glass-ceramics also are machinable using modern CAD–CAM techniques.[10–12]

Construction materials

Several authors, especially in the United Kingdom, Eastern Europe, Cuba, Italy and Brazil have developed many glass-ceramics made from a wide variety of waste materials, such incinerator ashes, blast furnaces slags, steel slags and sugar-cane ashes. Their composition and predominant crystal phases vary widely. These low-cost, dark-colored (because of the high level of transition elements in wastes) materials are generally strong, hard and chemically resistant. Their intended use is for abrasion and chemically resistant parts or floor and wall tile used in chemical, mechanical and other heavy-duty industries or construction.

A high-end-use construction and architecture glass-ceramic is Neopariés, which was pioneered by Nippon Electric Glass about 20 years ago and continues to be used. This glass-ceramic is one of the few commercial products made by sintering, and its main crystal phase is wollastonite (calcium metasilicate). Neopariés is a pore-free, partially crystallized material with a soft rich appearance similar to marble and granite. However, it has none of the maintenance problems of natural stone and is an attractive material for exterior and interior building walls and table tops.

Because of the growing concern

about sustainability and exhausting reserves of natural stones, the use of glass-ceramics as a construction material deserves much attention. References 11 and 19–21 discuss these uses further.

High-strength glass-ceramics

The average fracture strength ($S_f \approx$ 100–250 MPa) and toughness ($K_{Ic} \approx$ 1–2.5 MPa·m$^{1/2}$) of most glass-ceramics are generally higher than those of commercial glasses ($S_f \approx$ 50–70 MPa; K_{Ic} $\approx$ 0.7 MPa·m$^{1/2}$). Glass-ceramics with especially high strength and toughness have been reported by George Beall and colleagues[10] for canasite glass-ceramic ($S_f \approx$ 300 MPa; $K_{Ic} \approx$ 5 MPa.m1/2). Somewhat smaller but still impressive values of strength and toughness ($S_f \approx$ 350–400 MPa; $K_{Ic} \approx$ 2.3–2.9 MPa·m$^{1/2}$) have been reported for the lithium disilicate IPS e.max Press developed by Wolfram Hoeland and other Ivoclar researchers.[10] The common feature of these glass-ceramics is their lath-shaped crystals that lead to crack deflection and toughening.

Other successful strategies to increase strength and toughness include fiber reinforcement, chemical strengthening by ion-exchange methods and development of a thin surface layer with a lower thermal expansion than the interior to induce a compressive surface layer. All these concepts have been demonstrated for a few glass-ceramic compositions. However, they are far from being fully explored, and, thus, there is much scope for further research. Another important aspect that needs further study is effect of the type (compressive versus tensile) and magnitude of the internal residual stresses that are always present and are maximum at the crystal–glass interfaces. Values of 0.1 to 1.0 gigapascals have been reported in some glass-ceramics. These stresses certainly affect the overall mechanical performance of the material. A few papers have dealt with residual stresses in glass-ceramics, including References 16 and 22–24.

Dental glass-ceramics

All-ceramic dental restorations are attractive to dentists and patients, because they are biocompatible, have superior aesthetics and their low thermal conductivity makes them comfortable in the mouth. Moreover, the material is extremely durable, and it is relatively easy to manufacture to customized units. All-ceramic restorations can be used to cover even dark tooth cores (e.g., if the tooth is severely discolored or a titanium abutment is used).

Current lithium disilicate glass-ceramics – e.g., Ivoclar's IPS e.max – are ideal for fabricating single-tooth restorations (Fig. 2). This innovative glass-ceramic produces highly esthetic results. Its hardness is similar to that of natural teeth, and it is two to three times stronger than other dental glass-ceramics. The material can be either pressed or machined to the desired shape in the dental laboratory. Because of its high strength (S_f $\approx$ 360–400 MPa) and toughness ($K_{Ic} \approx$ 2.3–2.9 MPa·m$^{1/2}$(single-edge V-notched beam)), restorations fabricated with this material can be cemented by various techniques. These glass-ceramics possess true-to-nature shade behavior, natural-looking esthetics, natural-looking light transmission, versatile applications and a comprehensive spectrum of indications.

Bioactive glass-ceramics

Bioactive glass-ceramics form in-situ a biologically active layer of hydroxycarbonate apatite (the mineral phase of bone and teeth) that bonds to bone and teeth and sometimes even to soft tissue. Moreover, load-bearing applications require excellent mechanical properties. Many products have reached commercial success: Cerabone A-W (apatite–wollastonite), Ceravital (apatite–devitrite), Bioverit I (mica–apatite), Bioverit II (mica) and Ilmaplant L1 and AP40. They have been used as granular fillers, artificial vertebrae, scaffolds, iliac spacers, spinous spacers, intervertebral spacers, middle-ear implants and as other types of small-bone replacements. Some of their interesting properties are listed in Table I.

Table I. Relevant properties of bioactive glass-ceramics

	Glass-ceramic		
Property	**Cerabone**	**Bioverit I**	**Highly bioactive glass ceramic**
Bioactivity class	B†	B†	A‡
Machinability	Low	Good	Fair
Density (g/cm^3)	3.1	2.8	2.6
Three-point flexural strength (MPa)	215	140–180	210
Young's modulus (GPa)	120	70–90	70
Vickers hardness (HV)	680	500	600
Toughness (MPa·m$^{1/2}$)	2.0	1.2–2.1	0.95
Slow crack growth index	33		

†Biomaterial class B bonds only to bone. ‡Biomaterial class A bonds to hard (bone) and soft (cartilage) tissues.

Cerabone – developed by Tadashi Kokubo and produced by Nippon Electric Glass Co. Ltd. – is probably the most widely used bioactive glass-ceramic for bone replacement. Numerous clinical trials have shown intergrowth between this glass-ceramic and human bone. Tadashi informed us in 2009 that about 50,000 successful implants already have been made using Cerabone. Bioverits are machineable glass-ceramics that are very useful, because they can be easily modified during clinical procedures. Bioverit II is especially good in this respect.[10,11,25–27]

A different type of highly bioactive glass-ceramic was developed by Peitl et al.[28] in 1995. This is a low-density glass-ceramic in the Na-Ca-Si-P-O system that has a Young's modulus closer to that of cortical bone and much higher bioactivity than previous bioactive glass-ceramics. This particular combination of properties is desired for several applications. This glass-ceramic is about 30 to 50 percent crystalline, and its main phase is $Na_2O{\cdot}2CaO{\cdot}3SiO_2$. The first clinical trials for middle-ear bone replacements in 30 patients yielded very positive results. Table I summaries the main properties of some bioactive glass-ceramics.

A new glass-ceramic based on the same Na-Ca-Si-P-O system (Biosilicate) but with some compositional modifications and greater than 99.5 percent crystallinity recently was developed by Zanotto and colleagues.[29–32] This glass-ceramic is as bioactive as the "gold standard" bioglass 45S5 invented by Larry

Fig. 4. From left to right: parent glass, glass-ceramic with 97 percent crystallinity and glass-ceramic with 50 percent crystallinity. Grain size is about 20 micrometers.

Hench. Clinical tests of treatment with Biosilicate powder for dentin hypersensitivity in 160 sensitive teeth conducted by dentist Jessica Cavalle are shown in Fig. 3. After the first treatment, one-third of the teeth lost their sensitivity. After six applications of Biosilicate powder, 94 percent of the teeth were cured. This powdered glass-ceramic also can be useful for making small sintered bones and bioactive scaffolds, such as those shown in the studies of Enrica Verné[33] and Aldo Boccaccini[34] and their colleagues.

Another interesting class of bioactive glass-ceramics is heat-generating bioactive or biocompatible glass-ceramics intended for use for hyperthermic treatment of tumors. For instance, in one study by Koichiro et al.,[35] glass plates of the chemical composition $CaO–SiO_2–Fe_2O_3–B_2O_3–P_2O_5$ were ceramized. The resulting glass-ceramic containing magnetite and wollastonite crystals showed high-saturation magnetization. This glass-ceramic formed a calcium- and phosphorous-rich layer on its surface and tightly bonded with bone within about eight weeks of implantation. The parent glass did not form the calcium- and phosphorous-rich layer and did bond with bone at 25 weeks. Under an external magnetic field, granules of this glass-ceramic filled in rabbit tibias heated surrounding bone to more than 42°C and maintained this temperature for 30 minutes.[35] Since then, this promising route for tumor treatment has been followed by several authors. Several other compositions have been and are presently being tested in various laboratories.

Electrically conducting and insulating glass-ceramics

Electrically insulating materials, such as spinel–enstatite, canasite and lithium disilicate glass-ceramics (made by Corning) as well as TS-10 glass-ceramic substrates (made by Ohara) are used in magnetic media disks for hard disk drives. These materials offer the key properties necessary for today's higher areal density, smaller, thinner drive designs. These glass-ceramics have high toughness, provide low surface roughness and good flatness, ultralow glide heights and excellent shock resistance.[10]

On the other hand, lithium-ion-conducting glass-ceramics are promising solid electrolytes for lithium batteries. Sufficiently high conductivity at ambient temperature (10^{-3} $(\Omega\cdot cm)^{-1}$) has been demonstrated when precursor glasses crystallize in the highly conductive nanoscale application specific integrated circuit structure. Systems derived from the $LiTi_2(PO_4)_3$ composition have been extensively studied. In fact, partial substitution of Ti^{4+} by a trivalent cation, M^{3+}, such as Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Y^{3+}, La^{3+}, Cr^{3+} or Fe^{3+}, generates a deficiency in positive charges, which is compensated by additional Li^+ ions, leading to the $Li_{1+x}M_xTi_{2-x}(PO_4)_3$ system.

Some authors claim that the main advantage of obtaining such materials by the glass-ceramic route would be a decreased porosity if compared with ceramic materials obtained by the classical sintering route. However, one feature that has been scarcely explored, is that, if the parent glass presents internal nucleation, one may easily and effectively control, for instance by double-heat treatments, the microstructure of the glass-ceramic to further increase its conductivity.[36]

Solid oxide fuel cells are ceramic solid-state energy conversion devices that produce electricity by electrochemically combining fuel (e.g., hydrogen gas or natural gas) and oxidant (e.g., air) gases across an ionic conducting oxide at operating temperatures of about 800°C. The planar SOFC configuration provides a simple manufacturing process and high current densities, but it requires hermetic sealing to prevent fuel–oxidant mixing and to electrically insulate the stack.

A suitable sealing material must meet several criteria: chemical stability at 800°C under oxidizing and reducing wet atmospheres (air, hydrogen gas); electrically insulating; chemical compatibility (i.e., must not poison other cell components); ability to form a seal at about 900°C that results in a hermetic bond with high strength; CTE of 10–12 ppm/K; and long-term reliability during high-temperature operation and during thermal cycles to room temperature. In the scientific literature phosphosilicate, boron-free alkaline-earth silicates and borosilicate glass-ceramics, for instance $SrO–La_2O_3–Al_2O_3–B_2O_3–SiO_2$, have been suggested for SOFC sealing applications.[37] Several research groups in the world are attempting to develop such materials.

Some groups have experimentally demonstrated the possibility of producing glass fibers of the famous BISCO ($Bi_2Sr_2CaCu_2O_8$) system – which are not superconducting – and then crystallizing them to produce glass-ceramic superconductors.[38]

Last, but not least, several glass-ceramics-containing piezoelectric and ferroelectric phases have been studied. These areas for glass-ceramics applications have not yet been fully explored.

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 armors for visors or vehicle windows; substrates for LCD devices; ring laser gyroscopes; missile noses; fiber grating athermalization; precision photolithography; printed optical circuits; and small or very large telescope mirrors (Zerodur). In this last example, the telescope's optical components are required to overcome distortions caused by temperature fluctuations. Therefore, glass-ceramics with zero expansion are highly suitable.

The keen interest in glass-ceramics for optical applications is caused by their advantages over glasses, single-crystals and sintered transparent ceramics. Unlike glasses, glass-ceramics demonstrate properties similar to those of single crystals. In contrast with single crystals or sintered ceramics, glass-ceramics can be made in intricate shapes and sizes by fast and cost-efficient glass-manufacturing processes.

Transparent glass-ceramics based on fluoride, chalcogenide and oxyfluoride doped with rare-earth ions have been successfully used for wavelength up-conversion devices for europium-doped waveguide amplifiers. Transparent mullite-, spinel-, willemite-, ghanite- and gelenite-based glass-ceramics doped with transition-metal ions have been developed for use in tunable and infrared lasers, solar collectors and high-temperature lamp applications. Glass-ceramics that exhibit second harmonic generation and materials with high Kerr constant for electrooptical devices have been developed as well. The combination of several properties is the hallmark for their success.[39]

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. Ohara's WMS-15 glass-ceramic substrates, a commercially available product, have improved transmittance and exceptionally low surface roughness values. They enable manufacturers to produce leading-edge dense wavelength division multiplexer and gain-flattening filters. The WMS substrates facilitate the production of special filters.[10,11]

One interesting case of optical application is the photothermal refractive glass-ceramic produced by photothermo-induced crystallization. PTR glass, invented by Stookey, is an iron bromine sodium zinc aluminosilicate glass doped with silver, cerium, tin or antimony that can be locally crystallized by UV exposure in selected regions followed by heat-treatment above its glass transition temperature.

However, PTR glass-ceramic has reached the consumer market during the past 15 years thanks to the development of Bragg gratings and other types of volume holograms for laser devices (narrow-band spectral and angular filters, laser beam deflectors, splitters and attenuators). Leon Glebov and his team at the College of Optics and Photonics (CREOL), University of Central Florida, have been responsible for this development. At least two companies produce such Bragg gratings. This glass-ceramic is interesting because of the low amount of its crystal phase, less than 1 percent of nanosized NaF, and the intricate photothermal crystallization mechanism of PTR glass is yet scarcely known![40–41]

To be transparent in the visible range, a glass-ceramic 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. The vast majority of existing transparent glass-ceramics relies on crystal size less than about 200 nanometers and has a small or moderate crystallized fraction of 1 to 70 percent. However, an interesting new discovery was recently reported by Berthier da Cunha and colleagues.[42,43] They developed a large-grain (about 10–50 micrometer), highly crystalline (97 percent) and transparent glass-ceramic, as shown in Fig. 4.

Mark Davis[16] mentions in his 2008 review paper that "many of the exotic optical features now demonstrated in glass-ceramics (e.g., SHG, lasing, electrooptical effect) have not yet been made into a commercial product."

Glass-ceramic armor

Some patents have been filed and others have been granted for inventions related to armor materials for the protection of people or equipment against high-speed projectiles or fragments. Ceramic materials are 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. The first and still-used ceramic armor materials consist of high-modulus and hard Al_2O_3, although its density is quite high, about 4 grams per cubic centimeter. Other very hard, but less dense materials, such as SiC and B_4C, can be produced only at very high temperatures by costly manufacturing processes and are, hence, expensive.

Most glass-ceramics have lower hardness and Young's modulus than the above-described ceramics, but have the great advantage of low density and much lower cost. Moreover, glass-ceramics can be transparent to visible light. Alstom's Transarm, a transparent glass-ceramic armor is based on lithium disilicate. It originally was developed for protective visors for bomb disposal work. Another example is Schott's Resistan, a range of low-expansion glass-ceramics that can be opaque or transparent and are intended for substrates for vehicular and personal armor systems.

Little has been published and patented on this particular use of glass-ceramics, compared with other applications, because of the sensitive nature of this military-related research. For more information the reader is referred to patents granted to Michael Budd and colleagues.

Concluding remarks

An impressive variety of glass-ceramics has been developed during the past six decades. Yet, many others with unusual and unforeseen properties and applications are likely to be discovered in the future.

Glass-ceramics possess many favorable features.

- Composition: 10^{52} compositions can, in principle, be vitrified by combining and varying by 1 mole percent of all the 80 "friendly" elements of the periodical table, which could then be crystallized to form a glass-ceramic.[44]
- Forming: Articles of any shape can, in principle, be made by rolling, casting, pressing, blowing, drawing or by any other glass-processing method that already exists or may be invented.
- Thermal treatment: Crystallization is induced on the cooling path, in one step or multiple steps.
- Microstructure: Articles can be engineered from nanograins, micrograins or macrograins; low or high crystallinity; zero, low or high porosity; one or multiple crystal phases; random or aligned crystals; and surface-induced or internal crystallization.
- Thermal properties: Thermal expansion can be controlled – negative, zero or highly positive; stability can range from about 400°C to 1,450°C; and low thermal conductivity is common.
- Mechanical properties: Articles have much higher strength and toughness than glasses, but the limits are far from being reached, possibility to be further strengthened by fiber addition, chemical and thermal methods. They are hard, some are machinable.
- Chemical properties: Articles are resorbable or highly durable.
- Biological properties: Articles are biocompatible (inert) or bioactive.
- Electrical and magnetic properties: Articles have low or high dielectric constant and loss, high breakdown voltage, ionic conducting or insulating, superconducting, piezoelectric and ferromagnetic properties.
- Optical properties: Articles are translucent or opaque, opalescent, fluorescent, and colored and photo-induction nucleations are possible.

Mark Davis mentions in his review article, that "… as George Beall pointed out to me some years ago, although the number of glass-ceramics in total that [make it] into commercialization is quite small, once they do make it, they exist as a viable product typically for decades." This is certainly true: From several thousand patents, only a few dozen glass-ceramics products have reached the market. However, most of them – or their updated versions – remain there, and some have sold millions!

Much is already known about glass-ceramic technology, but many challenges in glass-ceramic research and development are ahead. They include the search for new compositions (and there are many alternatives to explore), other and more potent nucleating agents, and new or improved crystallization processes. Challenges include microwave heating, biomimetic microstructures, textured crystallization demonstrated by Christian Russel of the OSI in Jena and laser crystallization demonstrated by Taka Komatsu of Tohoku University in Japan. A deeper understanding and control of photothermal-induced nucleation associated or not with chemical etching; the development of harder, stiffer, stronger and tougher glass-ceramics; and glass-ceramics with increased transparency or conductivity are also timely.

A wide range of potential properties of glass-ceramics is possible because of the ability to design their composition, thermal treatment and resulting microstructure. This, combined with the flexibility of high-speed hot-glass forming will ensure continued growth of glass-ceramic technology. As in their serendipitous discovery, "luck" based on systematic exploratory research, solid understanding of glass structure, relaxation, crystallization and properties, as well as knowledge of the vast literature and deductive reasoning, may allow other great inventions to bear fruit. From their glorious past, starting with their accidental discovery, to their very successful commercial products as well as their impressive range of properties listed above (and not listed) and their exciting potential applications, glass-ceramics have indeed a bright future! ■

Editor's note

All of the glass-ceramic products cited in this article have registered trademarks held by the companies that produced them.

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Acknowledgments

I am indebted to Donald Stookey for discovering glass-ceramics! I also deeply thank my former and present TC-7 colleagues and friends – from whom I learned much about the intricacies of glass crystallization, properties and applications of glass-ceramics during the past three decades: Peter James, Mike Weinberg, Stvan Szabo (all deceased), Tadaski Kobubo, Klaus Heide, Wolfgang Pannhorst, Linda Pinckney, Ian Donald, Guenter Volsksh, Taka Komatsu, Akihiko Sakamoto, Michael Budd, Maria Pascual, Miguel Prado, Vlad Fokin, Jeri Sestak, Mark Davis, Gilles Querel, Jojo Deubener, Ralf Mueller, Falk Gabel and Robert Hill.

Thanks also to Christian Ruessel for hosting several dozen internship students from LaMaV at the famous Otto-Schott Institute in Jena. To Leon Glebov, Larissa Glebova, Julien Lumeau, Vlad Fokin, Gui Parent and all the members of the photothermo-induced nucleation research team. To Larry Hench, Oscar Peitl, Murilo Crovacce, Renato Siqueira, Alex Fraga, Marina Ismael and Bruno Poletto – LaMaV's bio glass-ceramics team. To Miguel Prado, Ralf Muller, Catia Fredericci, Edu Ferreira, Anne Barbosa, Vivi Oliveira and Rapha (Bode) Reis – the sinter-crystallization team of LaMaV. To Ana Rodrigues, JL and their students – the ionic conducting glass-ceramics team of LaMaV. To Vlad Fokin, Juern Schmelzer, Dick Brow, Joe Zwanziger, Aldo Boccacini, Alicia Duran, M.J. Pascual, Marcio Nascimento, Mariana Villas Boas, Daniel Cassar, Leo Gallo, Tiago Mosca, Diogo Alves and all past collaborators on fundamental studies on nucleation and crystallization. To Gui Parente, Michael Budd, Mark Davis and George Beall for their valuable critical review of this manuscript. Finally, I thank the Brazilian funding agencies Capes, CNPq and Fapesp for continuously supporting the vitreous materials research group of UFSCar during the past 34 years.

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