GLASS-CERAMICS

1. Introduction

Glass-ceramics are polycrystalline materials formed by the controlled crystallization of glass. Most commercial glass-ceramic products are formed by highly automated glass-forming processes and converted to a crystalline product by the proper heat treatment. Glass-ceramics can also be prepared via powder processing methods in which glass frits are sintered and crystallized. The range of potential glass-ceramic compositions is therefore extremely broad, requiring only the ability to form a glass and control its crystallization.

Glass-ceramics can provide significant advantages over conventional glass or ceramic materials, by combining the ease and flexibility of forming and inspection of glass with improved and often unique physical properties in the glass-ceramic. They possess highly uniform microstructures, with crystal sizes on the order of 10 μm or less; this homogeneity ensures that their physical properties are highly reproducible.

Unlike conventional ceramic materials, glass-ceramics are fully densified with zero porosity. They generally are at least 50% crystalline by volume and often are >90% crystalline. Other types of glass-based materials that possess low amounts of crystallinity, such as opals and ruby glasses, are classified as glasses and are discussed elsewhere (see Glass).

Glassmakers have traditionally aimed to formulate highly stable glass compositions that are resistant to devitrification in order to minimize the crystal growth rate in the working range. However, it was reasoned that carefully controlled crystallization might provide glass with greatly improved mechanical properties. In an early attempt (1) to crystallize soda-lime glasses, only surface crystallization similar to that observed in ice was achieved, wherein the crystals grow in a columnar fashion from the surfaces, resulting in deformation and poor strength.

The development of the principles of nucleation and growth early in the twentieth century (2) ultimately led to the discovery that certain nucleating agents can induce a glass to crystallize with a fine-grained, highly uniform microstructure that offers unique physical properties (3). The first commercial glass-ceramic products were missile nose cones and cookware.

More than \$500 million in glass-ceramic products are sold yearly worldwide. These range from transparent, zero-expansion materials with excellent optical properties and thermal shock resistance to jade-like highly crystalline materials with excellent strength and toughness. The highest volume is in stovetops and stove windows, cookware and tableware, and architectural cladding. Glass-ceramics are also referred to as Pyrocerams, vitrocerams, devitrocerams, sitalls, slagceramics, melt-formed ceramics, and devitrifying frits.

2. Processing

Glass-ceramic articles can be fabricated by means of either bulk or powder processing methods. Both methods begin with melting a glass of the desired composition.

2.1. Bulk Glass-Ceramic Processing.

In this most common method of glass-ceramic manufacture, articles are melted and fabricated to shape in the glass state. Most forming methods may be employed, including rolling, pressing, spinning, casting, and blowing. The article is then crystallized using a heat treatment designed for that material. This process, known as ceramming, typically consists of a low temperature hold to induce nucleation, followed by one or more higher temperature holds to promote crystallization and growth of the primary phase. Because crystallization occurs at high viscosity, article shapes are typically preserved with little or no shrinkage (1–3%) or deformation during the ceramming.

Nucleation and Crystallization. Nucleation commonly begins with phase separation, whereby an amorphous, homogeneous glass unmixes into two immiscible phases of different compositions. Although some glass compositions are self-nucleating, more commonly certain nucleating agents are added to the batch to promote phase separation and internal nucleation. These melt homogeneously into the glass, but promote very fine-scale phase separation on reheating. The dispersed phase, which can be a metal, titanate, zirconate, phosphate, sulfide, or halide, is structurally incompatible with the host glass and is normally highly unstable as a glass. It therefore precipitates tiny crystalline nuclei on heating at temperatures ~30–100°C above the annealing point of the host glass. These crystals serve as the sites for subsequent nucleation of the primary crystalline phases.

Nucleation is followed by one or more higher temperature treatments to promote crystallization and development of the desired microstructure. During

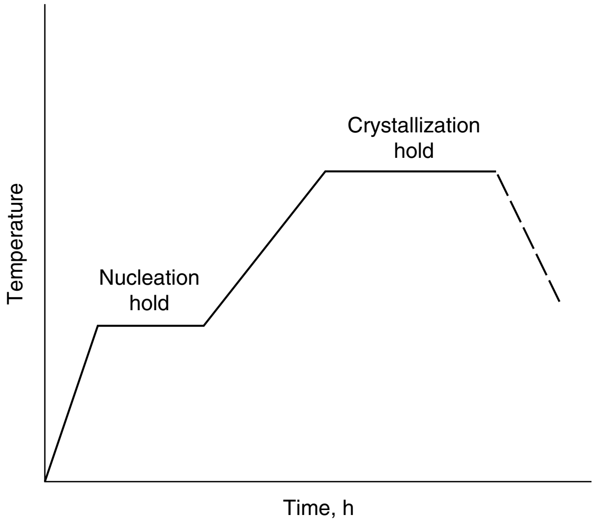

Fig. 1. Heat treatment cycle for a glass-ceramic material.

this stage of the heat treatment, typically at 750–1150°C, the primary crystalline phases nucleate and grow on these nuclei until they impinge on neighboring crystals. Given a high nucleation density, the resulting microstructure is highly uniform, consisting of fine-grained, randomly oriented crystals in a matrix of minor residual glass. Depending on composition and heat treatment, crystal size ranges from <0.1 μm to >10 μm.

A typical heat treatment cycle, as illustrated in Figure 1, comprises both nucleation and crystallization temperature holds, but some glass-ceramics are designed to nucleate and/or crystallize during the ramp itself, eliminating the need for multiple holds.

2.2. Powder Glass-Ceramic Processing. The manufacture of glass-ceramics from powdered glass, using conventional ceramic processes such as spraying, slip-casting, or extrusion, extends the range of possible glass-ceramic compositions by taking advantage of surface crystallization. In these materials, the surfaces of the glass grains serve as the nucleating sites for the crystal phases. The glass composition and processing conditions are chosen such that the glass softens prior to crystallization and undergoes viscous sintering to full density just before the crystallization process is completed. Given these conditions, the final crystalline microstructure is essentially the same as that produced from the bulk process.

The precursor glass powders may be produced by various methods, the simplest being the milling of quenched glass to an average particle size of 3–15 μm. Sol-gel processes, in which highly uniform, ultrafine amorphous particles are grown in a chemical solution, may be preferable for certain applications.

Such so-called devitrifying frits are employed extensively as sealing frits for bonding glasses, ceramics, and metals. Other applications include cofired multilayer substrates for electronic packaging (4), matrices for fiber-reinforced composite materials (5), refractory cements and corrosion-resistant coatings, honeycomb structures in heat exchangers, and bone and dental implants and prostheses. These products take advantage of the complete densification, thermal stability, and wide range of physical properties possible in glass-ceramic systems, and provide a number of advantages over conventional glass frits. Products incorporating glass-ceramic seals, eg, can be reheated to their soldering temperature without deformation.

2.3. Secondary Processing (Strengthening).

Because their polycrystalline microstructures provide resistance to crack propagation, glass-ceramics possess mechanical strength inherently superior to that of glass. This strength may be augmented by a number of techniques that impart a thin surface compressive stress to the body. These techniques induce a differential surface volume or expansion mismatch by means of ion-exchange, differential densification during crystallization, or by employing a lower expansion surface glaze.

3. Design

There are three key variables in the design of a glass-ceramic: the glass composition, the glass-ceramic phase assemblage, and the nature of the crystalline microstructure.

The glass composition controls much of the workability of the material, including glass viscosity as well as the effectiveness of nucleation and rapidity of crystallization. A glass-ceramic base glass must meet the seemingly contradictory requirements of resistance to uncontrolled devitrification during melting and forming, while simultaneously being amenable to high nucleation density and homogeneous crystallization during subsequent heat treatment.

The glass-ceramic phase assemblage, ie, the types of crystals and the proportion of crystals to glass, is responsible for many of the physical and chemical properties, such as thermal and electrical characteristics, chemical durability, elastic modulus, and hardness. In many cases these properties are additive; eg, a phase assemblage comprising high and low expansion crystals has a bulk thermal expansion proportional to the amounts of each of these crystals.

Finally, the nature of the crystalline microstructure, ie, crystal size and morphology and the textural relationship among the crystals and glass, is the key to many mechanical and optical properties, including transparency/opacity, strength and fracture toughness, and machinability. These microstructures can be quite complex and often are distinct from conventional ceramic microstructures (6).

4. Properties

Given the three key structural variables discussed under design, glass-ceramics can be engineered to provide a broad range of physical properties.

4.1. Thermal Properties.

Many commercial glass-ceramics have capitalized on their superior thermal properties, particularly low or zero thermal expansion coupled with high thermal stability and thermal shock resistance: Properties that are not readily achievable in glasses or ceramics. Linear thermal expansion coefficients ranging from -75 to $200 \times 10^{-7}/°\mathrm{C}$ can be obtained. Near-zero expansion materials are used in applications such as telescope mirror blanks, cookware, and stove cooktops, while high expansion frits are used for sealing metals. Recently, glass-ceramics with strongly negative thermal expansion were developed as substrates for the athermalization of fiber Bragg gratings, devices important in a variety of telecommunications applications (7).

Glass-ceramics have high temperature resistance intermediate between that of glass and of ceramics; this property depends most on the composition and amount of the residual glass in the material. Generally, glass-ceramics can operate for extended periods at temperatures of 700 to $>1200°\mathrm{C}$. Thermal conductivities of glass-ceramics are similar to those of glass and much lower than those of conventional oxide ceramics, ranging from 0.5 to 5.5 $\mathrm{W/(m \cdot K)}$.

4.2. Mechanical Properties. Like glass and ceramics, glass-ceramics are brittle materials that exhibit elastic behavior up to the strain that yields breakage. Because of the nature of the crystalline microstructure, however, strength, elasticity, toughness (resistance to fracture propagation), and abrasion resistance are higher in glass-ceramics than in glass. The modulus of elasticity ranges from 80 to 140 GPa ($12–20 \times 10^6$ psi) in glass-ceramics, compared to $\sim$70 GPa (10^7 psi) in glass. Abraded modulus of rupture values in glass-ceramics range from 50 to 300 MPa (7250–43,500 psi), compared with 40–70 MPa (5800–10,000 psi) in glass. Strengths can be increased further by employing a compressive layer. Fracture toughness values range from 1.5 to 5.0 $\mathrm{MPa}\sqrt{\mathrm{m}}$ in glass-ceramics, compared with $<1.5\ \mathrm{MPa}\sqrt{\mathrm{m}}$ in glass. Knoop hardness (qv) values of up to 900 can be obtained in glass-ceramics containing particularly hard crystals such as sapphirine.

4.3. Optical Properties. Glass-ceramics may be either opaque or transparent. The degree of transparency is a function of crystal size and birefringence, and of the difference in refractive index between the crystals and the residual glass (8,9). When the crystals are much smaller than the wavelength of light, as in some mullite and spinel glass-ceramics, or when the crystals have low birefringence and the index of refraction is closely matched, as in some Mg-stuffed β-quartz glass-ceramics, excellent transparency can be achieved.

Certain glass-ceramic materials also exhibit potentially useful electro-optic effects. These materials include glasses with microcrystallites of Cd-sulfoselenides, which show a strong nonlinear response to an electric field (9,10), as well as glass-ceramics based on ferroelectric crystals such as niobates, titanates, zirconates, and germanates, (11–14). Such crystals permit electric control of scattering and other optical properties. Ferroelectric glass-ceramics have potential use as optical modulators, switches, and filters.

4.4. Chemical Properties. The chemical durability is a function of the durability of the crystals and the residual glass. Generally, highly siliceous glass-ceramics with low alkali residual glasses, such as glass-ceramics based on β-quartz and β-spodumene, have excellent chemical durability and corrosion resistance similar to that obtained in borosilicate glasses.

4.5. Electrical Properties. The dielectric properties of glass-ceramics strongly depend on the nature of the crystal phase and on the amount and composition of the residual glass. In general, glass-ceramics have such high resistivities that they are used as insulators. Even in relatively high alkali glass-ceramics, alkali migration is limited, particularly at low temperatures, because the ions are either incorporated in the crystal phase or they reside in isolated pockets of residual glass. Loss factors are low, typically 0.01–0.02 at 1 MHz and 20°C. The fine-grained, homogeneous, nonporous nature of glass-ceramics also gives them high dielectric breakthrough strengths, especially compared with ceramics, allowing them to be used as high voltage insulators or condensers.

Most glass-ceramics have low dielectric constants, typically 6–7 at 1 MHz and 20°C. Glass-ceramics comprised primarily of network formers can have dielectric constants as low as 4, with even lower values ($K < 3$) possible in microporous glass-ceramics (15). On the other hand, very high dielectric constants (>1000) can be obtained from relatively depolymerized glasses with crystals of high dielectric constant, such as lead or alkaline-earth titanate (11–16).

5. Glass-Ceramic Families

All commercial as well as most experimental glass-ceramics are based on silicate bulk glass compositions. Glass-ceramics can be further classified by the composition of their primary crystalline phases, which may consist of silicates, oxides, phosphates, or borates.

5.1. Glass-Ceramics Based on Silicate Crystals. The principal commercial glass-ceramics fall into this category. These can be grouped by composition, simple silicates, fluorosilicates, and aluminosilicates, and by the crystal structures of these phases.

Simple silicates and fluorosilicates are composed primarily of alkali and alkaline-earth silicate or fluorosilicate crystals, whose crystal structures are based on single or multiple chains of silica tetrahedra or on two-dimensional (2D) hexagonal arrays (layers) of silica and alumina tetrahedra. Their crystal morphologies tend to reflect the anisotropy of their structures, with chain silicates typically occurring as blades or rods, and layer silicates occurring as plates. With the exception of the lithium silicate glass-ceramics, these materials are valued most for their mechanical properties.

Simple Silicates. The most important simple silicate glass-ceramics are based on lithium metasilicate [10102-24-6], Li_2SiO_3; lithium disilicate [13568-46-2], $Li_2Si_2O_5$; enstatite [14681-78-8], $MgSiO_3$; diopside [14483-19-3], $CaMgSi_2O_6$; and wollastonite [14567-57-2], $CaSiO_3$. A number of silicate glass-ceramic compositions are given in Table 1.

There are four groups of commercially important lithium silicate glass-ceramics, three of which are nucleated with P_2O_5. The first comprises strong, fine-grained materials based on a microstructure of lithium disilicate crystals with dispersed nodules of quartz or cristobalite crystals (17). Several companies have introduced these finely textured glass-ceramics for use as magnetic disk substrates for portable computer hard drives. More recently, internally nucleated lithium disilicate glass-ceramics in the $SiO_2{-}Li_2O{-}K_2O{-}ZnO{-}P_2O_5$ system with high mechanical strength and excellent chemical durability have been developed for use as dental overlays, crowns, and bridges (18). The third group

Table 1. **Silicate Glass-Ceramic Compositions, Wt%**

			Slagsitalls[a,b]	
Oxide	Fotoform/Fotoceram[c], [d]Corning 8603	Enstatite Corning[e]	Slagsitallwhite	Minelbite Gray
SiO_2	79.6	58.0	55.5	60.9
Li_2O	9.3	0.9		
MgO		25.0	2.2	5.7
CaO			24.8	9.0
Al_2O_3	4.0	5.4	8.3	14.2
Na_2O	1.6		5.4	3.2
K_2O	4.1		0.6	1.9
ZnO			1.4	
MnO			0.9	2.0
Fe_2O_3			0.3	2.5
crystal phases	lithium metasilicate lithium disilicate	enstatite β-spodumene tetragonal zirconia	wollastonite	diopside
abraded MOR,[f], [g]MPa			65–100	80–120

[a] White is from Russia, gray is from Hungary. White has 0.4 and gray has 0.6 wt% S.

[b] Used as cladding and in industrial products.

[c] Also Ag, 0.11; Au, 0.001; $CweO_2$, 0.014; SnO_2; 0.003; and Sb_2O_3, 0.4.

[d] Commercial applications include substrates, fluidic devices, fine mesh screens, and magnetic head pads.

[e] Also ZrO_2, 10.7.

[f] MOR = modulus of rupture.

[g] To convert MPa to psi, multiply by 145.

comprises high expansion lithium disilicate glass-ceramics that match the thermal expansion of several nickel-based superalloys and are used in a variety of high strength hermetic seals, connectors, and feedthroughs (19).

The fourth group is nucleated with colloidal silver, which in turn is photosensitively nucleated. By suitably masking the glass and then irradiating with ultraviolet (uv) light, it is possible to nucleate and crystallize only selected areas. Although this process can be used to make decorative products, an even more interesting group of products takes advantage of the large difference in chemical durability between the crystals and the residual glass. The crystallized portion consists of dendritic lithium metasilicate crystals, which are much more soluble in hydrofluoric acid than is the glass. These crystals can thus be etched away, leaving the uncrystallized portion intact. The resulting photoetched glass can then be flood-exposed to uv rays and heat-treated at higher temperature, producing the stable lithium disilicate phase. The resulting glass-ceramic is strong [~140 MPa (20,000 psi)], tough, and faithfully replicates the original photoetched pattern. These chemically machined materials have been used as fluidic devices, cellular display screens, lens arrays, magnetic recording head pads, and charged plates for ink jet printing.

Fig. 2. Replica electron micrograph of the fracture surface of enstatite–β-spodumene–zirconia glass-ceramic, showing twinning in the enstatite grains (white bar = 1μm).

No commercial applications have yet been found for glass-ceramics based on the chain silicate enstatite, $MgSiO_3$, but these materials are interesting because the phase undergoes a martensitic transformation on cooling. This in turn provides an additional toughening mechanism as fracture energy is absorbed by fine lamellar twinning (Fig. 2). Highly crystalline, fine-grained enstatite glass-ceramics can be produced in the $SiO_2-MgO-ZrO_2$ and $SiO_2-MgO-Al_2O_3-Li_2O-ZrO_2$ systems (20). Fracture toughness values as high as 5 $MPa\sqrt{m}$ and use temperatures approaching 1525°C can be obtained in these materials.

Blast furnace slags, with added sand and clay, have been used in Eastern Europe for >25 years to manufacture inexpensive nonalkaline glass-ceramics called slagsitall (21). The primary crystalline phases are wollastonite ($CaSiO_3$) and diopside ($CaMgSi_2O_6$) in a matrix of aluminosilicate glass. Metal sulfide particles serve as nucleating agents. The chief attributes of these materials are high hardness, good-to-excellent wear and corrosion resistance, and low cost. The relatively high residual glass levels of these materials (typically >30%), coupled with comparatively equiaxial (less rod-shaped) crystals, confers only moderately high mechanical strengths of ~100 MPa (14,500 psi). Slagsitall materials have found wide use in the construction, chemical, and petrochemical industries. Applications include abrasion- and chemical-resistant floor and wall tiles, industrial machinery parts, chimneys, plungers, parts for chemical pumps and reactors, grinding media, and coatings for electrolysis baths. These materials presently constitute the largest volume applications for crystallized glass.

More recently, attractive translucent architectural panels of wollastonite glass-ceramics have been manufactured by Nippon Electric Glass and sold under the trade name Neopariés. A sintered glass-ceramic with $\sim$40% crystallinity, this material can be manufactured in flat or bent shapes by molding during heat treatment. It has a texture similar to that of marble, but with greater strength and durability than granite or marble. Neopariés is used as a construction material for flooring and exterior and interior cladding.

Fluorosilicates. Compared to the simple silicates, these crystals have more complex chain and sheet structures. Examples from nature include hydrous micas and amphiboles, including hornblende and nephrite jade. In glass-ceramics, fluorine replaces the hydroxyl ion; fluorine is much easier to incorporate in glass and also makes the crystals more refractory. Four commercial fluorosilicate glass-ceramic compositions and their properties are listed in Table 2.

Sheet Fluorosilicates. Machinable glass-ceramics based on sheet silicates of the fluorine–mica family have unique microstructures composed of interlocked platy mica crystals. Because micas can be easily delaminated along their

Table 2. **Fluorosilicate Glass-Ceramic Compositions and Properties**

Components, wt %	Macor (Corning 9658)	Dicor (Dentsply)	Pyroceram (Corning)	Code 9634 (Corning)
SiO_2	47.2	56–64	67.3	54–62
Al_2O_3	16.7	0–2	1.8	1–4
B_2O_3	8.5			
MgO	14.5	15–20	14.3	0–2
CaO			4.7	17–25
Na_2O			3.0	6–10
K_2O	9.5	12–18	4.8	6–12
Li_2O			0.8	
BaO			0.3	
F	6.3	4–9	3.5	4–8
P_2O_5			1.0	
ZrO_2		0–5		
CeO_2		0.05		
crystal phases	F-phlogopite	tetrasilicic fluormica	F–K–richterite cristobalite	canasite
abraded MOR,[a] MPa[b]	100	$\sim$150	150–200	250–300
fracture toughness,			3.2	4–5
Young's modulus, GPa[b]	65		95	80
hardness, KNH_{100}[c]	250	$\sim$360		500
coefficient of thermal expansion	12.9×10^{-6} (25–600°C)	7.2×10^{-6} (25–600°C)	11.5×10^{-6} (0–300°C)	12.5×10^{-6} (0–300°C)
commercial applications	machinable components	dental restorations	tableware	rigid disk substrates

[a] MOR = modulus of rupture.

[b] To convert MPa to psi, multiply by 145.

[c] Knoop hardness (qv).

cleavage planes, fractures propagate readily along these planes but not along other crystallographic planes. The random intersections of the crystals in the glass-ceramic, therefore, cause crack branching, deflection, and blunting, thereby arresting crack growth, which provides the material with high intrinsic mechanical strength, but, in addition, the combination of ease of fracture initiation with almost immediate fracture arrest enables these glass-ceramics to be readily machined.

The commercial glass-ceramic Macor (Corning Code 9658), based on a fluorophlogopite [12003-38-2], $KMg_3AlSi_3O_{10}F_2$, mica, is capable of being machined to high tolerance (±0.01 mm) by conventional high speed metal-working tools. By suitably tailoring, its composition and nucleation temperature, relatively large mica crystals with high 2D aspect ratios are produced, enhancing the inherent machinability of the material. This "house-of-cards" microstructure is illustrated in Figure 3. In addition to precision machinability, Macor glass-ceramic has high dielectric strength, very low helium permeation rates, and is unaffected by radiation or oxygen–acetylene flames. The glass-ceramic has been employed in a wide variety of applications including high vacuum components and hermetic joints, precision dielectric insulators and components, seismograph bobbins, sample holders for field ion microscopes, boundary retainers for the space shuttle, and gamma-ray telescope frames.

Another machinable glass-ceramic, Dicor, was used for many years in dental restorations. Based on a tetrasilicic fluormica, $KMg_{2.5}Si_4O_{10}F_2$, this material

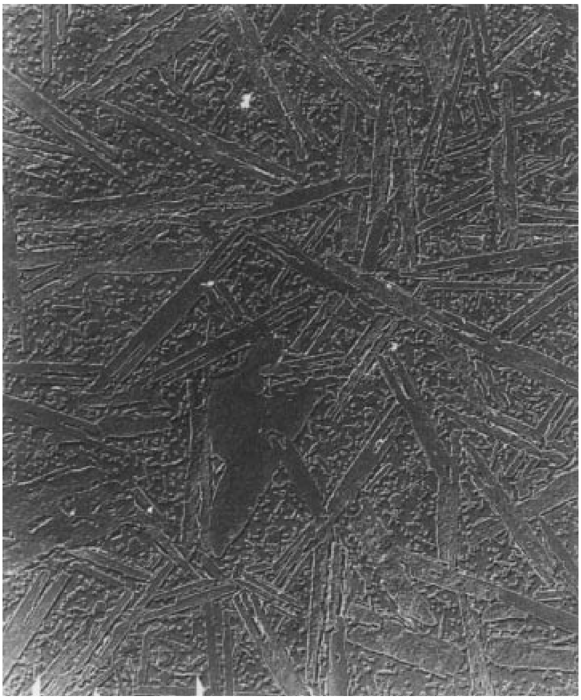

Fig. 3. Replica electron micrograph showing "house-of-cards" microstructure in a machinable fluormica glass-ceramic (white bar = 10 μm).

had higher strength (150 MPa) and improved chemical durability over that of Macor as well as a hardness and translucency closely matching natural tooth enamel.

In recent years, the inherent strength and machinability of mica-based materials have extended the growing field of biomaterials. Biomaterials for bone implants are biocompatible (well tolerated by the body) and may even offer bioactivity—the ability to bond with the hard tissue (bones) of the body. Several strong, machinable, and biocompatible mica—and mica/fluorapatite glass-ceramics have been widely studied as bone implants.(22) The mica phase imparts strength and machinability to the material while the fluorapatite confers bioactivity.

Chain Fluorosilicates. Interlocking blade- or rod-like crystals can serve as important strengthening or toughening agents, much as fiber glass is used to reinforce polymer matrices. Naturally occurring, massive aggregates of chain silicate amphibole crystals, such as nephrite jade, are well known for their durability and high resistance to impact and abrasion. Glass-ceramics with microstructures of randomly oriented, highly anisotropic chain silicate crystals generally provide superior strength and toughness, for in order for a fracture to propagate through the material it generally will be deflected and blunted as it follows a tortuous path around or through cleavage planes of each crystal. Indeed, glass-ceramics based on chain silicate crystals have the highest toughness and body strength of any glass-ceramics (20).

Fig. 4. Fracture surface (replica micrograph) of fluorcanasite glass-ceramic showing interlocking blade-shaped crystals and effects of cleavage splintering (white bar = 1 μm).

Glass-ceramics based on the amphibole potassium fluorrichterite ($KNaCaMg_5Si_8O_{22}F_2$) have a microstructure consisting of tightly interlocked, fine-grained, rod-shaped amphibole crystals in a matrix of minor cristobalite, mica, and residual glass. The flexural strength of these materials can be further enhanced by employing a compressive glaze. Richterite glass-ceramics have good chemical durability, are usable in microwave ovens, and, when glazed, resemble bone china in their gloss and translucency. These glass-ceramics have been manufactured for use as high performance institutional tableware and as mugs and cups for the Corelle line.

An even stronger and tougher microstructure of interpenetrating acicular crystals, as shown in Figure 4, is obtained in glass-ceramics based on fluorcanasite (K_{2-3} $Na_{4-3}Ca_5Si_{12}O_{30}F_4$) crystals. Cleavage splintering and high thermal expansion anisotropy augment the intrinsic high fracture toughness of the chain silicate microstructure. Highly crystalline canasite glass-ceramics have flexural strengths up to 300 MPa (43,500 psi) and fracture toughness of 5 $MPa\sqrt{m}$.

Aluminosilicates. These silicates consist of frameworks of silica and alumina tetrahedra linked at all corners to form three-dimensional (3D) networks; familiar examples are the common rock-forming minerals quartz and feldspar. Framework silicates generally form blocky crystals, more isotropic in nature than the crystals discussed previously. The nature of their tetrahedral linkages often results in low thermal expansion coefficients.

Commercial glass-ceramics based on framework structures comprise compositions from the $Li_2O-Al_2O_3-SiO_2$ (LAS) and the $MgO-Al_2O_3-SiO_2$ (MAS) systems. The most important, and among the most widespread commercially, are glass-ceramics based on β-spodumene, cordierite, and the various structural derivatives of high (β-) quartz. These silicates are important because they possess very low bulk thermal expansion characteristics, with the consequent benefits of exceptional thermal stability and thermal shock resistance. Thus materials based on these crystals can suffer large thermal upshock or downshock without experiencing strain that can lead to rupture, a critical property in products like missile nose cones and cookware. Representative aluminosilicate glass-ceramic compositions are given in Table 3.

Glass-ceramics in the LAS system have great commercial value for their very low thermal expansion and excellent chemical durability. These glass-ceramics are based on essentially monophase assemblages of either β-quartz or β-spodumene (keatite) solid solution, with only minor residual glass or accessory phases. Partial substitution of MgO and ZnO for Li_2O improves the working characteristics of the glass while lowering the materials cost. Figure 5 illustrates the range of thermal expansion coefficients of some β-quartz glass-ceramics, compared with those of fused silica and borosilicate glassware (23).

Glass-ceramics containing β-quartz or β-spodumene can be made from glass of the same composition by modifying its heat treatment: β-quartz is formed by ceramming at or below 900°C, and β-spodumene by ceramming $>1000°C$.

β-Quartz Solid Solution. A mixture of ZrO_2 and TiO_2 produces highly efficient nucleation of β-quartz [14808-60-7], resulting in very small (<100 nm) crystals. This fine crystal size, coupled with low birefringence in the β-quartz phase and closely matched refractive indexes in the crystals and residual glass, results in a transparent yet highly crystalline body, as illustrated in

Table 3. **Aluminosilicate Glass-Ceramic Compositions,[a] Wt%**

Components	Visions[b]	Zerodur[c]	Ceran[c]	Neoceram[d]	Corningware 9608[e]	Code 9606[bf]
SiO_2	68.8	55.5	63.4	65.1	69.7	56.1
Al_2O_3	19.2	25.3	22.7	22.6	17.8	19.8
Li_2O	2.7	3.7	3.3	4.2	2.8	
MgO	1.8	1.0		0.5	2.6	14.7
ZnO	1.0	1.4	1.3		1.0	
CaO						0.1
BaO	0.8		2.2			
P_2O_5		7.9		1.2		
Na_2O	0.2	0.5	0.7	0.6	0.4	
K_2O	0.1			0.3	0.2	
F				0.1		
Fe_2O_3	0.1	0.03		0.03	0.1	0.1
TiO_2	2.7	2.3	2.7	2.0	4.7	8.9
ZrO_2	1.8	1.9	1.5	2.3	0.1	
As_2O_3	0.8	0.5		1.1	0.6	0.3

[a] Crystal phase is β-quartz $ZrTiO_4$ unless otherwise noted.

[b] Corning.

[c] Schott.

[d] NEG.

[e] Crystal phase is β-spodumene rutile.

[f] Crystal phase is cordierite, rutile, and $MgTi_2O_5$.

Figure 6. An important commercial application for low CTE β-quartz glass-ceramics is the smooth, radiant cooktop for electric stoves. In this case, the glass-ceramic typically is doped with 0.1% V_2O_5 in order to render the material black in appearance. The vanadium does, however, allow transmission in the red and near-infrared (ir) where the tungsten halogen lamp and other resistive elements radiate energy. In addition to cooktops, the combination of near-zero thermal expansion behavior with transparency, optical polishability, excellent chemical durability, and strength greater than that of glass, makes-these glass-ceramics highly suitable for use as telescope mirror blanks (eg, Zerodur) (24), thermally stable platforms, ring laser gyroscopes, woodstove windows (eg, Neoceram), firedoors, and transparent cookware (eg, Visions).

β-Spodumene Solid Solution. Opaque, low expansion glass-ceramics are obtained by ceramming these LAS materials at temperatures >1000°C. The β-quartz to β-spodumene [1302-37-0] transformation takes place between 900 and 1000°C and is accompanied by a 5- to 10-fold increase in grain size (to 1–2 μm). When TiO_2 is used as the nucleating agent, rutile development accompanies the silicate phase transformation. The combination of larger grain size with the high refractive index and birefringence of rutile gives the glass-ceramic a high degree of opacity. Secondary grain growth is sluggish, giving these materials excellent high temperature dimensional stability. Because of their larger grain size, these glass-ceramics are stronger than those based on β-quartz, and they are also amenable to additional surface strengthening

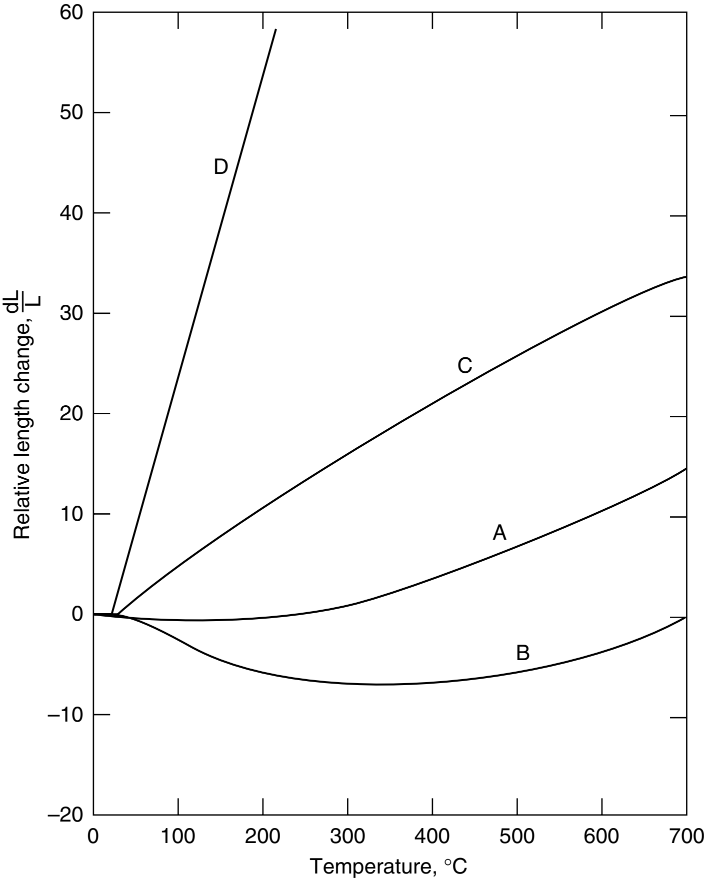

Fig. 5. Relative change in length with temperature of β-quartz glass-ceramics designed for A, precision optics and B, cooktop panels. Curves for C, fused silica glass and D, borosilicate laboratory glassware, are given for comparison (23).

techniques. β-spodumene glass-ceramics, such as Corningware 9608, have found wide utilization as cookware, architectural sheet, and industrial products.

Recently, N.E.G. introduced a durable, scratch-resistant ferrule for optical connectors that is made by redrawing a cerammed preform of LAS glass-ceramic. The cerammed preform contains ~50 wt% β-spodumene solid solution in a glassy matrix and can be redrawn into micro-capillaries with submicron accuracy.

Cordierite Glass-Ceramics. These glass-ceramics in the MAS system combine high strength and good thermal stability and shock resistance with excellent dielectric properties at microwave frequencies. Corning Incorporated produces a silica-rich, cordierite-based glass-ceramic with a complex phase assemblage that includes the high expansion cristobalite phase. The surface of the glass-ceramic can be selectively leached to provide an abrasion resistant layer (~0.38 mm thick) that inhibits flaw initiation and increases the strength

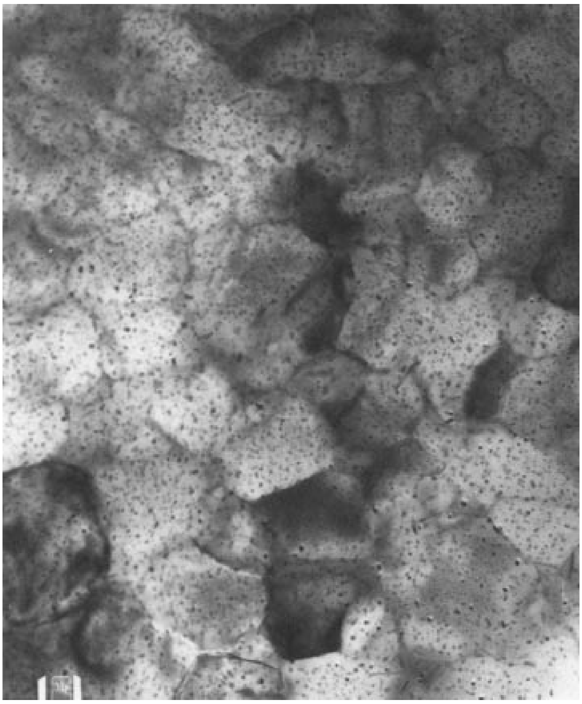

Fig. 6. Microstructure of transparent β-quartz solid solution glass-ceramic as revealed by transmission electron microscopy (white bar = 0.1 μm).

from 120 to 240 MPa (17,400–34,800 psi). This material, with its high transparency to radar, is the standard glass-ceramic used for missile radomes (Code 9606).

More recently, sintered glass-ceramics of cordierite [12182-53-5] (with minor clinoenstatite) have been developed by IBM for use as high performance multilayer ceramic packaging (25). These higher magnesia cordierite compositions provide a number of advantages over conventional alumina packaging: lower dielectric constant and thermal expansion, superior dimensional control, and low coprocessing temperatures compatible with copper. Small additions of B_2O_3 and P_2O_5 enhance sintering and densification prior to crystallization; the higher MgO levels aid sintering and can be adjusted to provide a thermal expansion match for either silicon or GaAs.

Other Aluminosilicates. Transparent mullite glass-ceramics can be produced from modified binary $Al_2O_3{-}SiO_2$ glasses (26). In these materials, the bulk glass phase separates into tiny alumina-rich droplets in a siliceous matrix. Further heat treatment causes these droplets to crystallize to mullite spherulites <0.1 μm in size. When doped with ions such as Cr^{3+}, transparent mullite glass-ceramics can be made to absorb broadly in the visible while fluorescing in the near-ir (27), thereby making them potentially useful for luminescent solar collectors.

Powder-sintered glass-ceramics based on the high expansion aluminosilicate phase leucite ($KAlSi_2O_6$) have found commercial success as dental restorative products (28).

5.2. Glass-Ceramics Based on Nonsilicate Crystals.

Oxides. Although not widespread commercially, glass-ceramics consisting of various oxide crystals in a matrix of siliceous residual glass offer properties not available with more common silicate crystals. In particular, glass-ceramics based on spinels and perovskites can be quite refractory and can yield useful optical and electrical properties.

Spinels have cubic crystal structures, with the general chemical formula AB_2O_4, where A is a tetrahedrally coordinated, typically divalent metal such as Mg, Zn, Fe, or Mn, and B is an octahedrally coordinated, usually trivalent metal such as Al, Fe, or Cr. Glass-ceramics based on spinel compositions ranging from gahnite ($ZnAl_2\,O_4$) toward spinel ($MgAl_2O_4$) can be crystallized from glasses in the system $ZnO{-}MgO{-}Al_2O_3{-}SiO_2$, with ZrO_2 or TiO_2 as a nucleating agent (29). These glass-ceramics can be made highly transparent, with spinel crystals on the order of 10–50 nm. The phase assemblage consists of spinel solid solution crystals dispersed throughout a continuous siliceous glass. Possible applications for transparent spinel glass-ceramics include high temperature lamp envelopes, solar collector panels, and liquid crystal display screens. Recently, non-alkali, nanocrystalline glass-ceramics based on Mg-rich spinel and enstatite ($MgSiO_3$) crystals were developed for potential use as magnetic disk substrates in computer hard drives (30). These materials have high elastic modulus (>140 GPa) and can be polished to an average roughness of 0.5–1.0 nm.

Perovskites have the chemical formula ABO_3, where A is an 8–12 coordinated cation such as an alkali or alkaline earth, and B is a small, octahedrally coordinated high valence metal such as Ti, Zr, Nb, or Ta. Glass-ceramics based on perovskite crystals are characterized by their unusual dielectric and electro-optic properties. Examples include highly crystalline niobate glass-ceramics that exhibit nonlinear optical properties as well as titanate and niobate glass-ceramics with very high dielectric constants.

Phosphates. Many phosphates claim unique material advantages over silicates that make them worth the higher material costs for certain applications. Glass-ceramics containing the calcium orthophosphate apatite, eg, have demonstrated good biocompatibility and, in some cases bioactivity, making them useful as bone implants and prostheses. Mixed phosphate–silicate glass-ceramics based on fluorapatite and wollastonite, fabricated via powder processing techniqies, are bioactive and possess good flexural strength of up to 200 MPa. The aforementioned combination of fluorapatite with phlogopite mica provide bioactivity as well as machinability. Cast glass-ceramics with microstructures comprising interlocking needles of fluorapatite and mullite provide high fracture toughness, with K_{Ic} values $>3\ \mathrm{MPa}\sqrt{\mathrm{m}}$. (31–33).

More recently, a novel class of bulk microporous glass-ceramics based on skeletons of titanium phosphate crystals has been developed, including several materials that offer catalytic and bacteriostatic activity. Potential applications include supports for enzyme immobilization and ion exchange media. Related lithium ion conductive glass-ceramics, based on $LiTi_2(PO_4)_3$ solid solutions in which Ti^{4+} ions are partially replaced by Al^{3+} and Ga^{3+} ions, have been proposed for use as solid electrolytes and gas sensors. A number of other phosphate-based glass-ceramic systems have been investigated, including fine-grained glass-ceramics based on crystals isostructural with NZP [$NaZr_2(PO_4)_3$], which offer a wide range in thermal expansion, with coefficients ranging from -20 to 60×10^{-7}/°C (34,35).

Glass-ceramics containing BPO_4 can be obtained by heat treating $B_2O_3-P_2O_5-SiO_2$ glasses having molar ratios between 1:1:1 and 1:1:3 (36). This phase is isostructural with β-cristobalite, a high temperature polymorph of silica. The material can be opaque or transparent depending on the crystallite size. Crystallization of the BPO_4 phase produces a threefold increase in chemical durability over that of the bulk glass, as the residual glass becomes more and more siliceous and depleted in B_2O_3 and P_2O_5. These glass-ceramics also have exceptional dielectric properties, with dc resistivity of 10^{16} at 250°C, a loss tangent $<10^{-3}$ above 1 kHz and below 200°C, and dielectric constants of 3.8–4.5.

Heat treatment of related glasses melted under reducing conditions can yield a unique microfoamed material, or "gas-ceramic" (37). These materials consist of a matrix of BPO_4 glass-ceramic filled with uniformly dispersed 1–10 μm hydrogen-filled bubbles. The hydrogen evolves on ceramming, most likely due to a redox reaction involving phosphite and hydroxyl ions. These materials can have densities as low as 0.5 g/cm^3 and dielectric constants as low as 2.

Fluorides and Borates. Transparent oxyfluoride glass-ceramics, consisting of fluoride nanocrystals dispersed throughout a continuous silicate or aluminosilicate glass, have been shown to combine the optical advantages of rare-earth-doped fluoride crystals with the ease of forming and handling of conventional oxide glasses. Transparent glass-ceramics based on submicron, spherical crystallintes of β-BaB_2O_4 (BBO) in a glass of the same composition have demonstrated second harmonic generation to uv wavelengths; such materials offer promise as potential optical components. Other aluminoborate glass-ceramics may be useful as low-expansion sealing frits (38,39).

6. New and Potential Applications

Although glass-ceramics have been employed for many years as cookware and dinnerware, as cladding and other architectural materials, and in a wide range of industrial components, their future roles are likely to involve entirely new technologies. Glass-ceramics will find numerous applications in the rapidly growing field of optoelectronics. Zero-expansion β-quartz glass-ceramics are used for ring laser gyroscopes, which require a transparent medium of critical dimensional stability. The investigation of unusual optical properties in transparent crystalline materials is still at the early stages of research, but these materials show great promise for applications ranging from optical switches to tunable lasers. The potential coupling of nonlinear optical properties, lasing capability, or luminescence with thermal and dimensional stability promises to yield unique combinations of properties not available in glass or ceramics.

Glass-ceramics will also play a role in the burgeoning field of information storage (qv) and display. Several glass-ceramics have been developed for use as disk substrates in hard disk drives; these are thinner, flatter, and more rugged than traditional aluminum alloy substrates, and their precise, uniform surfaces permit higher data storage capacity and improved reliability. Glass-ceramics have also been used for the read/write heads used in disk drives.

Other glass-ceramics may find potential use in liquid crystal and electroluminescent displays.

Finally, glass-ceramics will play a key role in the growing arsenal of advanced materials, both alone and in combinations with other materials. For example, glass-ceramic composites incorporating ceramic fibers yield high temperature strengths superior to metal alloys, and also exhibit gradual failure behavior similar to that of metals and plastics, as opposed to the normal catastrophic behavior common to brittle ceramics (see COMPOSITE MATERIALS, CERAMIC-MATRIX). Low dielectric constant glass-ceramics are projected as the best candidates for high performance multilayer packaging materials. Other potential products include superconducting glass-ceramics, new types of bioceramics for bone implants and prostheses, durable glass-ceramics for waste disposal, and refractory, corrosion-resistant glass-ceramic coatings for superalloys.

BIBLIOGRAPHY

"Slagceram" in *ECT* 2nd ed., Suppl. Vol., pp. 876–889, by S. Klemantaski, British Steel Corp. (Corporate Laboratories); "Glass-Ceramics" in*ECT* 3rd ed., Vol. 11, pp. 881–893, by D. R. Stewart, Owens-Illinois; "Glass-Ceramics" in *ECT* 4th ed., Vol. 12, pp. 627–644, by Linda R. Pinckney; "Glass-Ceramics" in *ECT* (online), posting date: December 4, 2000, by Linda R. Pinckney, Corning Inc.

CITED PUBLICATIONS

1. A. Reaumur, *Mem. Acad. Sci.*, 370 (1739).
2. G. Tammann, *The States of Aggregation*, D. Van Nostrand Co., New York, 1925.
3. S. D. Stookey, *Ind. Eng. Chem.* **51**, 805 (1959).
4. G. Partridge, C. A. Elyard, and M. I. Budd, in M. H. Lewis, ed., *Glasses and Glass-Ceramics*, Chapman and Hall, London, 1989, pp. 226–271.
5. K. M. Prewo, J. J. Brennan, and G. K. Layden, *Am. Ceram. Soc. Bull.* **65**, 305 (1986).
6. G. H. Beall, *Annu. Rev. Mater. Sci.* **22**, 91 (1992).
7. G. H. Beall, *Glastech. Ber. Glass Sci. Technol.* **73 C1**, 3 (2000).
8. G. H. Beall and D. A. Duke, *J. Mater. Sci.* **4**, 340 (1969).
9. G. Partridge and S. V. Phillips, *Glass Technology* **32**, 82 (1991).
10. N. F. Borrelli and co-workers, *J. Appl. Phys.* **61**, 5399 (1987).
11. N. F. Borrelli, *J. Appl. Phys.* **38**, 4243 (1967).
12. A. Herczog, *J. Am. Ceram. Soc.* **47**, 107 (1964).
13. N. F. Borrelli and M. M. Layton, *J. Non-Cryst. Solids* **6**, 197 (1971).
14. M. Todorovi and Lj. Radonji, *Ceram. Intern.* **23**, 55 (1997).
15. J. F. MacDowell and G. H. Beall, *Ceram. Trans.* **15**, 259 (1990).
16. M. Sadhukhan and co-workers, *J. Appl. Phys.* **85**, 3477 (1999).
17. U.S. Pat. 6,120,922 (Sep. 19, 2000) N. Goto.
18. U.S. Pat. 5,968,856 (Oct. 19, 1999) M. Schweiger and co-workers (to Ivoclar AG).
19. T. J. Headley and R. E. Loehman, *J. Am. Ceram. Soc.* **67**, 620 (1984).
20. G. H. Beall, *J. Non-Cryst. Solids* **129**, 163 (1991).
21. A. I. Berezhnoi, *Glass-Ceramics and Photo-Sitalls*, Plenum Press, New York, 1970.
22. W. Höland and co-workers, *J. Non-Cryst. Solids* **129**, 152 (1991).
23. H. Scheidler and E. Rodek, *Am. Ceram. Soc. Bull.* **68**, 1926 (1989).

24. J. Petzoldt and W. Pannhorst, *J. Non-Cryst. Solids* **129**, 191 (1991).
25. R. R. Tummala, *J. Am. Ceram. Soc.* **74**, 895 (1991).
26. J. F. MacDowell and G. H. Beall, *J. Am. Ceram. Soc.* **52**, 17 (1969).
27. L. J. Andrews and co-workers, *J. Lumin.* **36**, 65 (1986).
28. W. Höland and co-workers, *J. Non-Cryst. Solids* **180**, 292 (1995).
29. L. R. Pinckney, *J. Non-Cryst. Solids* **255**, 171 (1999).
30. L. R. Pinckney and G. H. Beall, *J. Non-Cryst. Solids* **219**, 219 (1997).
31. L. L. Hench, *J. Am. Ceram. Soc.* **74**, 1487 (1991).
32. T. Kokubo and co-workers, *J. Mater. Sci.* **21**, 536 (1986).
33. R. Hill and D. Wood, *J. Mater. Sci. Mater. Medicine* **6**, 311 (1995).
34. H. Hosono and Y. Abe, *J. Non-Cryst. Solids* **190**, 185 (1995).
35. B. G. Aitken, *15th Int. Cong. Glass* **3a**, 96 (1989).
36. J. F. MacDowell, *15th Int. Cong. Glass* **3a**, 90 (1989).
37. U.S. Pat. 4,666,867 (May 19, 1987), G. H. Beall and J. F. MacDowell (to Corning Glass Works).
38. Y.-H. Kao and co-workers, *J. Non-Cryst. Solids* **167**, 247 (1994).
39. J. F. MacDowell, *J. Am. Ceram. Soc.* **73**, 2287 (1990).

GENERAL REFERENCES

P. W. McMillan, *Glass-Ceramics*, 2nd ed., Academic Press, Inc., New York, 1979.

R. Morrell, *Handbook of Properties of Technical and Engineering Ceramics, Part 1: An Introduction for the Engineer and Designer*, HMSO, London, 1985.

Z. Strnad, *Glass-Ceramic Materials, Glass Science and Technology*, Vol. **8**, Elsevier, Amsterdam, 1986.

W. Vogel, *Chemistry of Glass*, The American Ceramic Society, Columbus, Ohio, 1985.

M. H. Lewis, ed., *Glasses and Glass-Ceramics*, Chapman and Hall, London, 1989.

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