

Transparent Glass-Ceramics

G. H. BEALL, D. A. DUKE

Research & Development Laboratories, Corning Glass Works, Corning, NY 14830, USA

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Glass-ceramic materials may transmit visible light if either of the following conditions are operative: (i) the crystallites of all species are much smaller than the wavelength of visible light, or (ii) the optical anisotropy (birefringence) within the crystals and refractive index difference between crystals and glass are very small. These conditions are achieved in several aluminosilicate glass-ceramic systems. Solid solutions (ss) of β -quartz, spinel, and mullite are the major crystalline phases in these transparent glass-ceramics.

The transparent β -quartz solid solution glass-ceramics can be divided into three areas: ultra-low expansion materials, refractory and colourless materials, and high electrical resistivity—low dielectric loss materials. These three material groups, though chemically distinct, are all characterised by high crystallinity, thermal shock resistance, excellent chemical durability, and susceptibility to mechanical strengthening by ion-exchange techniques.

The transparent spinel and mullite glass-ceramics contain considerable glassy phase, but nevertheless are characterised by excellent transparency, even after thermal exposure for long periods above 1000° C.

1. Introduction

Stookey originally reported that certain glasses, when crystallised by a simple heat treatment, form very fine-grained, transparent materials [1]. Polycrystalline materials formed in this manner have several distinct advantages over glasses. One of the most important is their capacity for extremely low thermal expansion. Essentially zero or even negative expansion coefficients are fairly common over various temperature ranges with substances whose chemical composition and crystalline structure are appropriate.

High strength is another property which glass-ceramic materials often possess. Many transparent glass-ceramics, though not appreciably stronger than their parent glasses, can be strengthened by an ion exchange process in which the crystalline structure at the surface of the body is modified to produce a compressive layer [2].

Thermal stability is a third property in which transparent glass-ceramics generally show improvement over glasses. The devitrification process always produces an assemblage of phases of greater thermodynamic stability than the

original glass. In addition, a composite material almost entirely composed of crystals does not flow significantly until the solidus temperature of the assemblage is reached. This temperature is considerably higher than the softening point of a glass of similar bulk composition.

The advantage of transparent and translucent glass-ceramics over polycrystalline light-transmitting substances formed by conventional ceramic processes lies in the capacity and diversity of glass-forming processes. It is also easier to achieve transparency in a polycrystalline article through controlled nucleation and growth of minute crystals in glass than by any other ceramic process.

Potential applications for transparent crystalline materials capable of being shaped by the glass-forming process are numerous. Thermal and mechanical shock-resistance are important requirements for consumer and laboratory ware, and thermal stability is a major requirement for high temperature lamp applications. In addition, the extremely low thermal expansions of certain transparent glass-ceramics in combination with the ability of these very fine-grained materials to

take an optical polish, permits their use in reflective optic applications.

2. Theory

2.1. Light Scattering: Requirements for Transparency in an Inhomogeneous Medium

There are two distinct ways in which light energy can be attenuated or removed by a medium. One of these, atomic absorption, converts light energy into heat in the medium. The other, light scattering, involves the absorption and simultaneous re-radiation of energy by atomic, molecular, or ionic species.

The scattering phenomenon is essentially due to the radiation of secondary waves caused by oscillating dipoles induced in heterogeneities in the medium through which the light is passing. A light wave is constituted by electric and magnetic vibrations in planes perpendicular to the direction of wave propagation. When an aggregate of atoms or ions such as the molecules in a gas or a small crystallite in a glass are subjected to an external electric field, dipoles which are induced by the field are formed in each element of volume. When the electric field is due to an electromagnetic wave, the induced dipoles themselves become radiators of electromagnetic waves and scattered light results.

The dependence of small particle scattering on the wavelength of light was first investigated by Rayleigh [3]. He considered an incident electromagnetic wave to be monochromatic and linearly polarised with the electric vector along the x -axis and the direction of propagation in the z -direction. The field at a scattering particle was therefore given by

$$\begin{aligned} E_x &= e^{-j\omega t}, \\ E_y &= 0, \\ E_z &= 0. \end{aligned} \quad (1)$$

Rayleigh assumed the scattering particle was small in comparison to the wavelength of light. The result was that the net scattered wave caused by the sinusoidal oscillations at frequency ω of each of its elastically bound electrons was just that which would be radiated by a single dipole oscillator with some specific dipole moment.

The scattering cross-section for these particles as given by Rayleigh is

$$\sigma_s = 8/3\pi \left(\frac{2\pi}{\lambda}\right)^4 |\beta|^2, \quad (2)$$

where λ is the wavelength and β is the polaris-

ability of the scattering material. Assuming independent spherical particles, $|\beta|^2$ is given by

$$|\beta|^2 = \alpha^6 \left| \frac{M^2 - 1}{M^2 + 2} \right|^2, \quad (3)$$

where α is the radius of the particle and M the ratio of the refractive index of the particle to that of the surrounding medium. The angular intensive distribution of scattered light can therefore be written as

$$I(\theta) = \left(\frac{1 + \cos^2\theta}{r^2} \right) \frac{8\pi^4}{\lambda^4} \alpha^6 \left| \frac{M^2 - 1}{M^2 + 2} \right|^2 I_0. \quad (4)$$

I is the specific intensity, θ the scattering angle, r the distance from the scattering centre, and I_0 the intensity of the incident beam.

It can be seen that the magnitude of Rayleigh (small particle) scattering is inversely dependent upon the fourth power of the wavelength. Thus, this form of scattering is characterised by a sharp scattering of blue and ultraviolet light with a minimum of scattering in the longer wavelengths. The two criteria for complete transparency of a light transmitting material from equation (4) are seen to be twofold, either sufficient in themselves: (i) $\alpha \ll \lambda$, where the particles are very much smaller than the wavelength of light, or (ii) $M \cong 1$, where the refractive indices of the particles and surrounding medium approach equality. In addition, as a general condition for transparency, even in a homogeneous medium, absorption effects should be minimised.

The more general scattering problem, that of an isolated sphere of any diameter in an electromagnetic field of any character, has been investigated by Mie [4]. This theory finds major application where the simpler Rayleigh theory breaks down, i.e. where the size of the scattering particle is about the same size or larger than the wavelength of the incident radiation.

Although the scattering cross-section and angular scattering function cannot be simply expressed in this more general case, the important parameters remain, the size of the particles relative to the wavelength of light, and the refractive index ratio of the particles and the surrounding environment. For complete transparency in an assemblage of Mie scatterers ($2\alpha \cong \lambda$), the refractive index of the particles must approach that of the surrounding medium. Optical absorption, of course, must also be minimised.

2.2. The Choice of a Glass-Ceramic System

From the standpoint of light-scattering theory, it is clear that two possibilities exist for producing a transparent crystal-glass system. In one case, the dispersed crystalline phases must be sufficiently small in size that they produce no effective scattering, even at the shorter wavelengths of the visible spectrum. In the other case, complete optical isotropy must be achieved within the composite material, i.e. the refractive index difference between all crystalline and amorphous phases must be minimised, and the birefringence within any single crystalline phase must be small.

In choosing a glass-ceramic system for transparency, the above requirements must be combined with the desired physical characteristics which are defined by the application. A degree of compositional flexibility is generally desired in order to minimise the grain size or to match the refractive index of an optically isotropic crystalline phase to that of the residual glass, and still produce such desired physical properties as low thermal expansion and high mechanical strength.

One system of glasses with this flexibility contains the basic oxides SiO_2 - Al_2O_3 - Li_2O - MgO - ZnO plus the nucleating oxides ZrO_2 and/or TiO_2 . These materials can be crystallised almost completely to series of solid solution (ss) phases based upon the structure of the high temperature silica polymorph β -quartz.

Other systems which produce transparent glass-ceramics are the SiO_2 - Al_2O_3 and SiO_2 - Al_2O_3 - ZnO - ZrO_2 systems. In these, the high-index phases mullite and spinel are the major crystalline precipitates. Because of their extremely fine grain size, excellent transparency can be achieved in these glass-ceramics, despite a large proportion of low-index siliceous residual glass.

2.3. Solid Solution in the β -Quartz Structure

Buerger [5] first recognised that certain aluminosilicate crystals composed of three-dimensional, tetrahedral networks of SiO_4 and AlO_4 are similar in structure to crystalline forms of pure silica. These aluminosilicates are termed stuffed derivatives, because they may be thought of as produced from a silica polymorph by network replacement of Si^{4+} by Al^{3+} , accompanied by a filling of structural vacancies by larger cations. The crystal β -eucryptite, LiAlSiO_4 , which is structurally similar to β -quartz, is such a stuffed derivative. Roy [6] first described a complete series of ss between β -eucryptite and silica. Schreyer and Schairer [7] found an analagous

series along the binary join SiO_2 - MgAl_2O_4 . These ss series were discovered through heat treatment of glasses, and it was recognised that these phases, though persistent, were metastable rather than stable. Evidently, monovalent Li^+ , divalent Mg^{2+} , and to a smaller extent divalent Zn^{2+} ions [8] can fill the interstitial vacancies in the β -quartz structure when Al^{3+} replaces Si^{4+} .

The ss limits of ionic substitution in the stuffed β -quartz phase and the effects of this substitution upon thermal expansion have been discussed by Beall *et al* [8].

3. Experimental

In order to investigate transparent glass-ceramics based upon β -quartz ss, glasses within the system SiO_2 - LiAlO_2 - MgAl_2O_4 - ZnAl_2O_4 were investigated. ZrO_2 , TiO_2 , and combinations of these oxides were added to the glasses in amounts appropriate to promote phase separation, nucleation, and fine-grained crystallisation upon heat treatment. Further oxide substitutions were made in these glasses where it was suspected that additional β -quartz ss could be achieved. Thus the components $\text{Zn}(\text{Al}_2\text{O}_4)$, $\text{Al}(\text{AlO}_2)_3$, Li_2ZnO_2 , and LiBeO_2 were used to investigate the potential substitution of Zn^{2+} and Be^{2+} in network positions.

In the case of mullite and spinel glass-ceramics, the systems SiO_2 - Al_2O_3 and SiO_2 - Al_2O_3 - ZnO - MgO were investigated. While the former system required no additional nucleating agent, the latter system was found to require ZrO_2 or TiO_2 to produce fine-grained internal crystallisation. The best transparency and colour was produced using zirconia. In all cases, the starting materials were homogeneous glasses melted from standard batch materials of greater than 99.6% purity. These glasses were melted using platinum or silica crucibles in electric furnaces at temperatures of about 1650° C. They were drawn into cane approximately 5 mm in diameter, which was subsequently cut into 10 cm lengths.

The cane was crystallised by heat treatments in electrically heated furnaces. In some cases, the resulting crystalline rods were then placed in chemically pure, molten alkali salt baths for the purpose of strengthening. Two bath compositions were used: one of composition 52% KCl -48% K_2SO_4 , was contained in a VYCOR® brand crucible, and the other, of composition 90% Li_2SO_4 -10% K_2SO_4 , was contained in a stainless steel crucible. These salt baths were kept in a molten condition in a Kanthal-wound

furnace.

Both salt treated and untreated glass-ceramic rods were then given a tumble abrasion treatment for 15 min in a half-gallon ball mill with 30-grit SiC. Modulus of rupture measurements were made on a Tinius-Olsen testing machine using an 8.9 cm span and a 1.9 cm spaced, double, central knife edge. These strength measurements showed good precision and reproducibility.

Routine thermal expansion measurements were made on 10 cm glass-ceramic rods. The average linear expansion coefficient from 0 to 300°C was measured using the method described in ASTM designation: C 337-57. Continuous thermal expansion curves from 0 to 650°C and from 0 to 1000°C were also obtained using a fused-silica dilatometer.

Crystalline phases were studied by conventional X-ray diffraction techniques. The replica electron microscopic method was used to study nucleation and growth phenomena in several glass-ceramic compositions.

4. Results and Discussion

4.1. Composition

4.1.1. Stuffed β -Quartz Glass-Ceramics

There are three major composition areas where transparent, stuffed β -quartz glass-ceramics with unique properties were formed. These areas can be classified as follows: (i) ultra-low expansion glass-ceramics; (ii) colourless and refractory glass-ceramics; (iii) non-alkali glass-ceramics.

The transparent, ultra-low expansion glass-ceramics constitute a group of materials which have thermal expansion coefficients ($\Delta L/L$) of approximately $0 \times 10^{-7}/^\circ\text{C}$ over considerable temperature intervals. These compositions fall in the basic system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Li}_2\text{O}$ with combinations of TiO_2 and ZrO_2 required as nucleation agents. The best compositions were found in the range: SiO_2 68 to 76%, Al_2O_3 17 to 24%, Li_2O 2.5 to 5%, MgO 0 to 3%, ZnO 0 to 4%, excess nucleation agents, TiO_2 1.5 to 4% and ZrO_2 0 to 3%. These glasses characteristically crystallised to stuffed β -quartz glass-ceramics at relatively low temperatures in the range from 700 to 850°C. In this form, they were found to be metastable and transformed to β -spodumene ss glass-ceramics when heat treated at higher temperatures.

The colourless and refractory transparent glass-ceramic composition area was found in the basic system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-Li}_2\text{O}$ with ZrO_2

used as the nucleation agent. When crystallised according to specific stepwise heat treatments, these glass-ceramics were found to be colourless, to have little or no haze, and to have low thermal expansions in the range 10 to $20 \times 10^{-7}/^\circ\text{C}$. The best compositions were located in the range SiO_2 68 to 76%, Al_2O_3 17 to 22%, MgO 2.5 to 7%, Li_2O 1.5 to 3%, ZnO 0 to 3%, and excess nucleating agent ZrO_2 3 to 6%. These materials are evidently the most stable of all the stuffed β -quartz glass-ceramics. Even when heated for long periods at temperatures just below the point of softening or first melting, they did not normally break down to other phases.

The transparent non-alkali stuffed β -quartz composition area was found in the basic system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-ZnO}$, with ZrO_2 as the nucleation agent. These glass-ceramics represent some of the lowest expansion, non-alkali glass-ceramics. Linear thermal expansion coefficients range from 11 to $30 \times 10^{-7}/^\circ\text{C}$. The best compositions were located in the range SiO_2 64 to 75%, Al_2O_3 16 to 25%, MgO 3 to 10%, ZnO 0 to 7%, and excess nucleation agent ZrO_2 3 to 10%. Examples of these compositions are listed in table I.

4.1.2. Spinel Glass-Ceramics

The spinel mineral group encompasses a large number of aluminates, gallates, ferrites, titanates, and solid solutions of these groups. The general chemical formula is AB_2O_4 , where A is a tetrahedrally co-ordinated ion, generally divalent, and B is an octahedrally co-ordinated ion, generally trivalent. None of these minerals, when melted and cooled, forms a glass. It is possible, however, to precipitate many of these phases from a glass containing largely silica and a considerable percentage of spinel chemical components. Zirconium oxide is the most effective nucleating agent for spinel precipitation, particularly in cases where a very small crystallite size is required to afford transparency to the resulting glass-ceramic.

The best transparent spinel glass-ceramics can be formed from glasses in the following composition range: SiO_2 65 to 75%, Al_2O_3 15 to 25%, ZnO 4 to 15%, and MgO 0 to 6%, to which is added 5 to 10% ZrO_2 as a nucleation agent. Less than 10% of an oxide of a large alkaline cation (e.g. K_2O , Cs_2O) may be added to prevent devitrification of the residual siliceous glass to cristobalite. Examples of some of the compositions of these glasses and typical heat treatments

required to transform them to transparent spinel glass-ceramics are listed in table I.

4.1.3. Mullite Glass-Ceramics

Simple binary glasses in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system can be heat treated to form glass-ceramics composed of finely divided mullite in a siliceous glassy matrix [9]. With many of these compositions, the mullite can be precipitated so finely as to produce a transparent glass-ceramic. The best compositions fall in the range SiO_2 60 to 90%, Al_2O_3 10 to 40%. Oxides such as BaO , Na_2O , K_2O , Rb_2O , and Cs_2O can be added to prevent the siliceous residual glass from devitrifying to cristobalite. Examples of some of these glasses and the heat treatment required to produce transparent mullite glass-ceramics are also listed in table I.

4.2. Nucleation and Crystallisation

4.2.1. Ultra-Low Expansion Stuffed β -Quartz Glass-Ceramics

The sequence of nucleation and crystallisation of lithium-stuffed β -quartz glass-ceramics has been described briefly by Beall *et al*[8], and in more detail by Duke and Chase [10]. Among transparent glass-ceramics of this type, for example composition 1, table I, the initial nucleation event was generally an amorphous phase separation. With this composition, the liquid-liquid separation was observed to take place between 700 and 750° C. Figs. 1 and 2 are replica electron micrographs

showing the appearance of this glass before and after the phase separation. It is believed that this process represents a tendency for the high-valence transition oxides, TiO_2 and ZrO_2 , to separate from the basic tetrahedral aluminosilicate network, thus forming an oxide polyhedral structure of higher cation co-ordination.

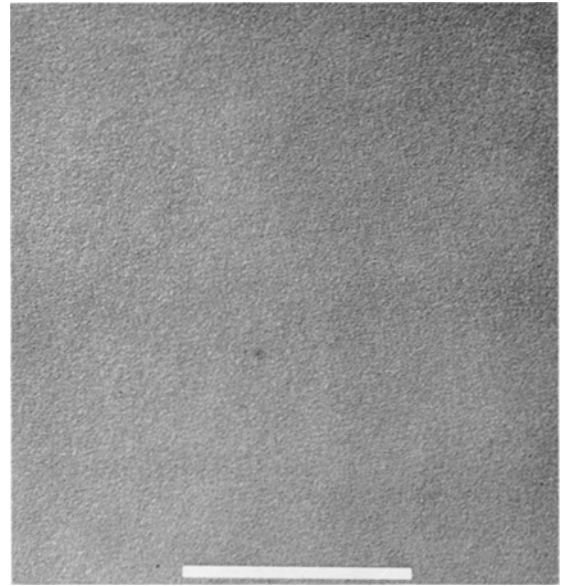


Figure 1 Electron micrograph of glass of composition 1 as formed (white bar = 1 μm).

TABLE I Compositions and critical data for selected transparent glass-ceramics

	1	2	3	4	5	6	7	8
SiO_2	65	74	65	74	70	70	77	50
Al_2O_3	23.0	19.5	25	16.5	19	17	23	40
MgO	1.8	4.5	10	3.5	5	—	—	—
Li_2O	3.8	2	—	—	—	—	—	—
ZnO	1.5	—	—	6	6	13	—	—
BaO	—	—	—	—	—	—	—	10
Excess ZrO_2	2.0	4	10	4	8	6	—	—
Excess TiO_2	2.0	—	—	—	—	—	—	—
Excess As_2O_5	0.9	0.5	—	1.0	—	—	—	—
Excess Cs_2O	—	—	—	—	—	4	—	—
Heat treatment	Variable	780-4 830-4 910-4	800-4 960-4	750-4 860-4	800-4 950-4	800-4 1000-4	1000-10	1000-10
Thermal expansion coefficient (0 to 300° C)	0-5	15.5	31.0	15.0	33.0	32.1	16.1	36.5
Crystal phases	β -quartz ss $\text{ZrO}_2\text{-TiO}_2$ ss	β -quartz ss tetragonal ZrO_2	β -quartz ss tetragonal ZrO_2	β -quartz ss tetragonal ZrO_2	spinel ss tetragonal ZrO_2	gahnite tetragonal ZrO_2	mullite	mullite

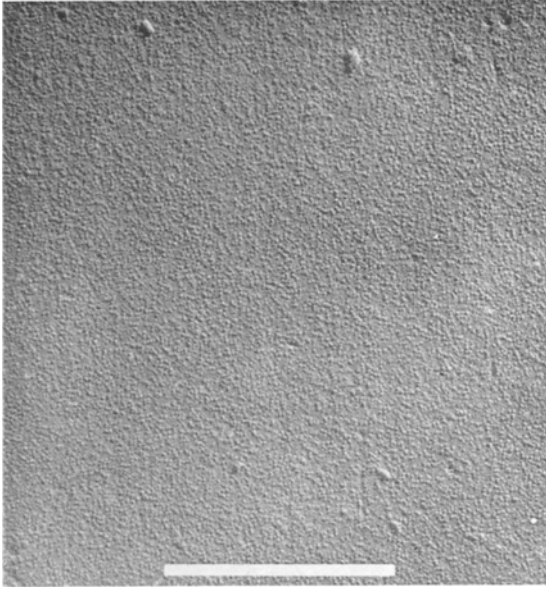


Figure 2 Electron micrograph of phase separated glass of composition 1 after heat treatment at 750° C (white bar = 1 μm).

Subsequent crystallisation of this more unstable, amorphous, oxide-rich phase to either cubic zirconia ss or a titanate ss phase occurs below 800° C. These randomly dispersed oxide crystals catalysed the heterogeneous nucleation of the aluminosilicate phase β -quartz ss in the bulk glass. At higher temperatures, the β -quartz ss transformed into β -spodumene ss. This transformation was sometimes accompanied by the exsolution of minor phases such as magnesium and zinc spinels.

This crystallisation sequence expressed itself in visual changes in the appearance of the material. The initial glasses were pale amber in colour, but upon heat treatment became darker, possibly due to the increased absorption of the oxide-rich member of the phase separated glass. Further heating resulted in the development of slight haze due to scattering caused by the differences in the indices of refraction of the glass and the β -quartz ss which was starting to crystallise. Large local stresses were created by the density and thermal expansion differences between the stuffed β -quartz crystals and still viscous ($\sim 10^{11}$ poises) glass. In some cases, micro-cracking and surface crazing resulted from these stresses. This was particularly noticeable in large pieces of glass where either thermal or composition gradients were present during processing.

Upon further heating beyond this critical stage, the haze tended to diminish, producing a highly crystalline, amber, transparent glass-ceramic. Fig. 3 shows the appearance of this material in an electron micrograph. The average grain size of the stuffed β -quartz crystallites can be seen to be about 0.1 μm. It is likely that the transparency is the result of the small grain size, the diameter of the crystals being significantly smaller than the wavelength of visible light.



Figure 3 Electron micrograph of fully developed ultra-low expansion transparent glass-ceramic of composition 1 (white bar = 1 μm).

If heated further, the β -quartz ss transformed to the tetragonal crystal β -spodumene ss. This increased the haze and resulted finally in an opaque body with a crystal size of about 0.5 μm. The opaque material remained stable until heated to the softening temperature, generally well above 1100° C.

It should be noted that the original crystallisation of the major portion of the glass to β -quartz ss was accompanied by energy release in the form of heat. From differential thermal analyses, this heat of crystallisation was estimated by Duke and Chase [10] to be 60 to 70 cal/gm. Assuming a specific heat of 0.3 cal/gm/°C, a temperature increase of over 200° C might be expected from instantaneous crystallisation. Although this great increase was never observed,

temperature rises of from 50 to 100° C were noted during the crystallisation of the interior portions of large blocks of glass, thus presenting some difficulty in controlling heating schedules and preventing undesirable gradients.

In addition, with most lithium-rich aluminosilicate glass-ceramic compositions, the β -quartz ss phase is metastable and somewhat transitory. Therefore, these materials cannot be heat treated very far above the crystallisation temperature, lest they undergo phase transformation. Whereas a transparent β -quartz glass-ceramic of this type may be stable indefinitely at 800° C, it may transform to β -spodumene ss in a matter of 10 h at 850° C [10]. A typical time-temperature stability diagram for glass, β -quartz ss glass-ceramic, and β -spodumene ss glass-ceramic is shown in fig. 4. Such a plot could be used to set limits upon both processing and use temperatures for transparent, ultra-low expansion β -quartz ss glass-ceramics.

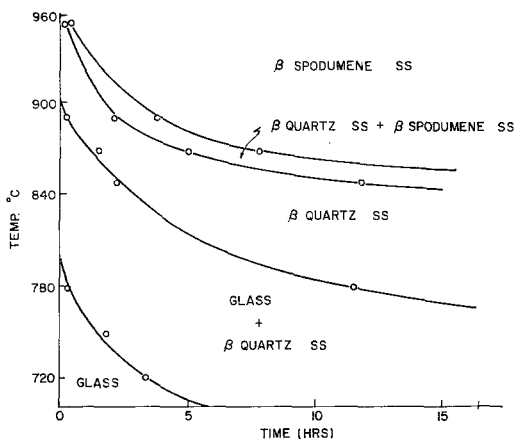


Figure 4 Time-temperature metastable phase diagram for glass-ceramic composition 1.

4.2.2. Colourless and Refractory Stuffed β -Quartz Compositions

The sequence of crystallisation of transparent and colourless β -quartz ss glass-ceramics in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-Li}_2\text{O-ZrO}_2$ system was found to involve a three-step heat treatment in order to assure maximum transparency. The first hold, normally from 2 to 6 h in length, was the nucleation hold, generally at a temperature of about 800° C. During this hold, the first crystalline phase, tetragonal zirconia, precipitated. The zirconia formed very minute crystals, which, judging from X-ray diffraction peak broadening,

were less than 500 Å in diameter. X-ray analysis showed that this phase is slightly tetragonal but almost cubic (c/a ratio = 1.06) [11].

An attempt was made to extract chemically the cubic zirconia nuclei from a sample of transparent glass-ceramic composition 2, table I. This crystallised material was etched in hydrofluoric acid, and an insoluble zirconia-rich residue of about 1/2% by weight of the original material was obtained. Spectrographic analysis showed considerable alumina and magnesia to be present along with the major oxide zirconia. It is likely that these oxides are present in ss in the crystalline pseudo-cubic zirconia phase.

Neilson [12] has studied the nucleation by zirconia of a glass of composition $\text{MgO:Al}_2\text{O}_3\text{:SiO}_2 = 1:1:3$, which, although lower in silica and free of lithium, falls in the same general system as composition 2, table I. He concluded by means of a low-angle X-ray scattering study that the initial process leading to nucleation at 850° C was a glass-in-glass separation of a phase enriched in zirconia. During this early phase separation process, he reported that the zirconia-rich regions increased in density and zirconia content, but did not grow in size. When the zirconia content in these regions became critical, crystallisation began. The crystallites, reported to be tetragonal zirconia, were believed to form in each enriched region at more than one site within the region. Each group of crystallites then collectively grew as a single particle by a process which was described as diffusion-controlled.

It is interesting to note that when a sample of glass (e.g. composition 2, table I) was removed after the nucleation hold, it was still transparent, although the colour may have changed from the original pale green colour to a more colourless shade.

The second hold, referred to as the development hold, generally occurred between 800 and 900° C for a period of from 1 to 4 h. If a sample were cooled after this treatment, it was noticeably hazy, and X-ray diffraction analysis showed it to be partially crystalline with considerable β -quartz ss having formed. This hold was necessary to achieve minimum haze in the final material. Presumably, at the relatively low temperature of this hold, the major silicate crystal, β -quartz ss, was forming upon the zirconia nuclei. The rate of this heterogeneous nucleation of β -quartz upon the zirconia was great compared to the growth rate of the quartz. If the temperature was raised, the growth rate increased with respect to

the rate of nucleation, and there was less efficient use of the zirconia nuclei. A coarser-grained body then resulted with a consequent increase in scattering and haze.

The final hold, or growth hold, normally took place between 880 and 1000° C for a period of from 2 to 4 h. This hold assured a highly crystalline final product, with the chemical composition of the major silicate phase being very close to that of the parent glass. The grain size of the final product tended to vary from about 0.1 μm to about 0.25 μm . Fig. 5 is an electron micrograph of composition 2, table I, in the fully developed glass-ceramic condition.



Figure 5 Electron micrograph of fully developed refractory and transparent glass-ceramic of composition 2. (white bar = 1 μm)

It should be noted that heat treatments in excess of 1100° C for significant periods of time ($\frac{1}{2}$ h or more) produced an opaque material from any of these transparent β -quartz glass-ceramics. This was primarily due to grain growth, both of the major silicate phase and the tetragonal zirconia. Phase transformations, however, were not uncommon, particularly in the case of the tetragonal zirconia, which was observed to convert to the monoclinic form, baddeleyite, at temperatures much in excess of 1100° C. In addition, those compositions containing more

than 2.5% Li_2O by weight generally were converted largely to β -spodumene ss above about 950° C. In most compositions in this area, however, the β -quartz ss persisted even to the melting temperature. It is interesting to note that these are the most stable of the β -quartz compositions, with the exception of those low-silica phases around the eucryptite ($\text{Li}_2\text{O}:\text{Al}_2\text{O}_3:2\text{SiO}_2$) stoichiometry.

4.2.3. Non-Alkali Stuffed β -Quartz Compositions

In the base system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-ZnO}$ with ZrO_2 as the nucleation agent, transparent to translucent glass-ceramics were produced with average crystal sizes much larger than those required for transparency in the lithium-containing systems. This is believed due to the very low birefringence of magnesium-stuffed β -quartz crystals within the silica range of 64 to 72% SiO_2 . Schreyer and Schairer [7] showed that the birefringence of β -quartz ss between cordierite and silica is minimised at approximately 70 wt % SiO_2 , where the mineral changes from optically positive as in pure quartz, to optically negative. Evidently the behaviour of ZnO in substituting for MgO does not alter the birefringence significantly, because transparent materials could be produced with significant substitution of ZnO for MgO despite large crystal sizes in the glass-ceramic material. Compositions 3 and 4 in table I were crystallised to transparent β -quartz glass-ceramics with average crystal sizes of 1 μm and 10 μm , respectively. Clearly the lack of optical scattering in these materials must be due to the isotropic nature of the β -quartz ss which composed these glass-ceramics. These non-alkali β -quartz ss materials must be crystallised according to a two-hold treatment. Typically, a glass such as composition 3, table I, was heated at 800° C for 4 h to produce phase separation and crystallisation of tetragonal zirconia. This was followed by a heat treatment at 900° C to produce the stuffed β -quartz ss upon the zirconia nuclei. Crystallisation of the same glass at 900° C without a nucleation hold tended to produce significant amounts of another metastable phase resembling petalite in structure [13]. Heat treatments significantly above 900° C (e.g. at 1000° C) invariably resulted in the breakdown of the β -quartz ss and the production of siliceous quartz and spinel. Therefore, like the lithium-rich β -quartz ss, the non-alkali solid solutions were unstable at high temperatures.

4.2.4. Spinel Glass-Ceramics

The sequence of nucleation and crystallisation in spinel glass-ceramic compositions appears relatively simple. As in the case of the non-alkali β -quartz ss glass-ceramics, which are similar chemically but contain a higher MgO/ZnO ratio and less ZrO_2 (table I), the first step is an amorphous phase separation, which can be induced at temperatures above the annealing point of the glass, generally around $800^\circ C$.

The initial crystalline precipitate is invariably tetragonal zirconia, which begins to form after a few hours at the phase separation temperature. With an increase in temperature to about $900^\circ C$, spinel begins to crystallise, presumably upon the zirconia nuclei. The spinel is generally gahnite ($ZnAl_2O_4$) or a spinel ss - $(Zn, Mg)Al_2O_4$ - close to the gahnite composition. The spinel crystallites are very fine-grained, and judging from X-ray diffraction line broadening, are initially less than 500 \AA in diameter. Further heating at temperatures considerably above $1000^\circ C$ may cause secondary grain growth, which can produce light scattering and resulting haze.

Cristobalite may form through devitrification of the residual siliceous glass, if the glass-ceramic is held at temperatures above $1000^\circ C$ for several hours. If cristobalite forms, it is invariably nucleated at the air-glass-ceramic interface and not inside the glass-ceramic. This surface crystallisation can be suppressed by the addition of alkaline oxides to the batch; particularly effective is Cs_2O . Composition 6, table I, containing Cs_2O , will not surface-crystallise to cristobalite for many hours, even at temperatures approaching $1200^\circ C$.

4.2.5. Mullite Glass-Ceramics

The sequence of nucleation and crystallisation of mullite glass-ceramics in the $SiO_2-Al_2O_3$ and $SiO_2-Al_2O_3-BaO$ systems has recently been described by MacDowell and Beall [9]. These authors describe the spontaneous amorphous phase separation which takes place in binary alumina-silica glasses between about 7 and 55 mole% alumina. The composition of the aluminous phase, usually the dispersed phase in the area of stable glass formation, is very close to mullite. A photomicrograph of a phase separated, quenched binary glass of composition 7, table I, is shown in fig. 6. This phase separation is the essential cause of nucleation of finely divided mullite upon reheating these glasses above $1000^\circ C$.

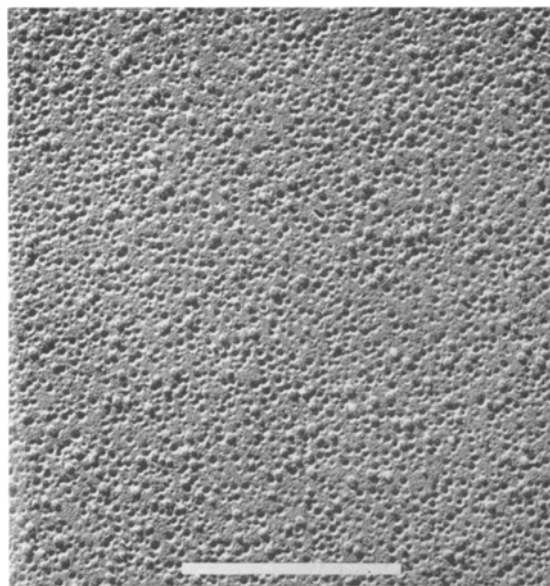


Figure 6 Electron micrograph of phase-separated binary alumino-silicate glass of composition 7 (white bar = $1 \mu m$).

The prevention of devitrification of the residual siliceous glass of mullite glass-ceramics, as in the case of the transparent spinel materials, rests with the stabilisation of this glass through additions of such oxides as BaO , K_2O , and Cs_2O . These oxides form very stable alumino-silicate glasses which are resistant to cristobalite formation. However, they must be added in small amounts (less than 10 mole%), since they also suppress the basic phase separation of aluminous and siliceous amorphous components.

Fig. 7 is a photomicrograph of a transparent mullite glass-ceramic of composition 8, table I. Heat treatment for long periods of time at $1200^\circ C$ and above, will produce secondary grain growth and opacification in this composition. The mullite crystal size must be held below $0.25 \mu m$ for good transparency.

4.3. Properties and Uses

4.3.1. Ultra-Low Expansion Stuffed β -Quartz Glass-Ceramics

The ultra-low thermal expansion of the lithium-stuffed β -quartz glass-ceramics is their most unique property. Since these materials are very highly crystalline, the bulk thermal expansion characteristics resemble those of the β -quartz ss crystals, which are a strong function of chemical

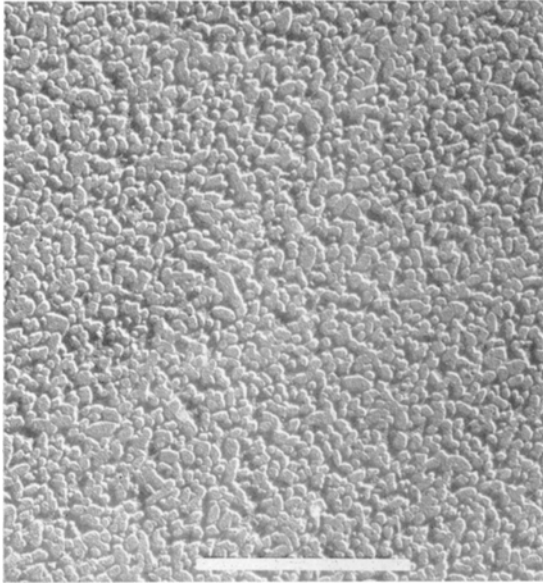


Figure 7 Electron micrograph of transparent mullite glass-ceramic formed by heat treatment of composition 8 at 1150°C for 8 h (white bar = 1 μm).

composition. The small amount of residual glass present does not greatly affect the bulk expansion because it is highly siliceous and has, therefore, like the β-quartz ss crystals, a very low thermal expansion.

It was possible, by manipulating the composition variables, to produce several glass-ceramics with expansion curves very near zero. Fig. 8 shows the expansion curve of a glass-ceramic of this type, Corning's Code 9623 glass-ceramic, over the temperature range -200 to +200°C.

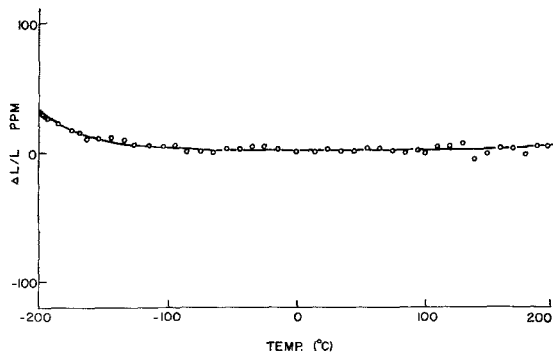


Figure 8 Expansion curve of Corning Code 9623 glass-ceramic, a composition closely related to composition 1, table I.

The very fine-grained nature of the transparent glass-ceramics in the ultra-low expansion area is also an important property. This fine crystal size allows these materials to take a very fine polish similar to that possible with glasses. Since glass-ceramics, as the name implies, are polyphase crystalline assemblages with significant residual glass, polishing problems could arise due to differential hardness between the phases. It was found that when the grain size was kept smaller than the wavelength of visible light, an optical finish could be obtained with no evidence of relief polishing [10].

These two unique properties, ultra-low thermal expansion and polishability equal to glass, allow these transparent glass-ceramics to be used as mirror blank materials [10]. Their transparent nature allows inspection of the mirror blank for residual stress and quality.

4.3.2. Colourless and Refractory Stuffed β-Quartz Glass-Ceramics

The physical properties of the magnesium-lithium-stuffed transparent β-quartz glass-ceramic area are also unique, particularly in terms of the combination of low thermal expansion, excellent chemical durability, and excellent transparency over all visible light wavelengths. Thermal expansions measured from 0 to 750°C ranged from 0 to 20 × 10⁻⁷/°C, but the best materials from the standpoint of colour and haze fell in the 12 to 15 × 10⁻⁷/°C range. The chemical durability of these transparent glass-ceramics is excellent. Composition 2, table I, for example, showed the following weight loss data: (i) in 5% HCl solution at 95°C for 21 h, 0.01 mg/cm²; (ii) in 5% NaOH at 95°C for 6 h, 0.56 mg/cm²; (iii) in 50% Na₂CO₃ at 95°C for 6 h, 0.01 mg/cm². This compares to figures of 0.01, 0.61, and 0.02 mg/cm² in the original glass, also very durable. The comparable figures for the standard borosilicate laboratory glassware composition, Corning Code 7740, are 0.005, 1.05, and 0.12 mg/cm². This indicates that the clear glass-ceramic is considerably more resistant to alkali attack than standard laboratory borosilicate glass.

Transmittance in these transparent crystalline materials varies with composition and heat treatment. As an example of the degree that can be achieved, consider composition 2, table I. When crystallised according to a three-step heating schedule of 4 h, at temperatures of 780, 830 and 920°C, this glass formed a colourless,

highly crystalline material with an average crystal size of about $0.2 \mu\text{m}$ (fig. 5). The transmittance through a polished plate 3 mm in thickness is illustrated in fig. 9. The combination of low thermal expansion, good chemical durability, good transparency, and lack of colour would allow these transparent glass-ceramics to be considered for such applications as laboratory glassware and consumer ware. The thermal stability of these materials, often in excess of 900°C , allows their consideration for such refractory uses as high temperature lamp envelopes and oven windows.

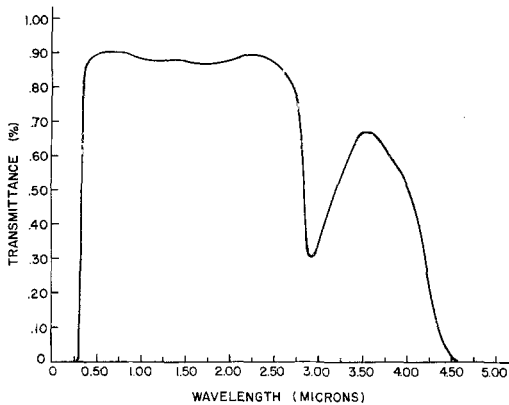


Figure 9 Transmission curve for 3 mm thick polished plate of glass-ceramic composition 2.

4.3.3. Non-Alkali-Stuffed β -Quartz Glass-Ceramics

Magnesium-zinc-stuffed β -quartz glass-ceramics have slightly higher thermal expansions than those containing lithium. Typical linear coefficients from 0 to 300°C fall within the range of 14 to $35 \times 10^{-7}/^\circ\text{C}$. Among the lowest expansion materials in this area is composition 3, table I. Colour and haze in these transparent materials is also inferior to that which can be achieved in both the ultra-low expansion and refractory colourless composition areas. This is partly due to the fact that it is more difficult to produce very fine-grained materials in the non-alkaline area. Chemical durability, however, remains excellent in this area, and this, combined with the high temperature resistivity characteristics and generally superior dielectric properties, allows the consideration of these materials for a wide range of high temperature applications where low electrical losses are required.

4.3.4. Spinel and Mullite Glass-Ceramics

The properties of transparent spinel and mullite glass-ceramics are generally not as unique as those of the β -quartz ss glass-ceramics. The thermal expansion characteristics more closely resemble those of borosilicate glass than of fused silica. Average thermal expansion coefficients from 0 to 300°C generally range from 15 to $40 \times 10^{-7}/^\circ\text{C}$ for both groups. The reasons for these moderate thermal expansions are twofold. First, the residual siliceous glass, while it generally forms a continuous network and is the major phase, is not pure silica. It contains some alumina and, in most compositions, also some modifying cations; therefore, its thermal expansion is higher than that of fused silica. Secondly, there is a contribution of the crystallites to the bulk thermal expansion of these materials. Mullite, gahnite, and tetragonal zirconia all have thermal expansions in the moderate (30 to $70 \times 10^{-7}/^\circ\text{C}$) range. Hence, these glass-ceramics are not ultra-low expansion materials, but they do fall in the moderately low expansion range.

The viscosity/temperature characteristics of spinel and mullite glass-ceramics, because they are largely amorphous, more closely resemble glasses than glass-ceramics. Considerable deformation occurs with increasing temperature. Applications requiring high temperature rigidity are, therefore, ruled out.

The most unique feature of these materials is their high temperature transparency. Many spinel and mullite compositions, including compositions 6 and 8 (table I), remain transparent when heated at temperatures in excess of 1000°C for over 100 h. High temperature lamp applications may therefore be considered.

4.4 Strengthening of β -Quartz Solid Solution Glass-Ceramics by Ion Exchange

The base abraded modulus of rupture of the zirconia-nucleated, transparent, stuffed β -quartz glass-ceramics averages about 8000 psi. Some compositions are slightly stronger, with abraded strengths up to 12000 psi. It is clear, however, that in order to produce a material significantly stronger than glass, a method of external strengthening is required. This technique is through surface ion exchange.

The method of chemically strengthening glass-ceramics composed predominantly of β -quartz ss has been discussed by Duke *et al* [2] and by Beall *et al* [8]. It was found possible to strengthen most

stuffed β -quartz glass-ceramics which contain significant lithium oxide (greater than 1% by weight) by an alkali ion-exchange reaction, resulting in surface compression produced by a "crowding" mechanism. Typical abraded strengths range around 50 000 psi. This reaction is carried on by immersing the glass-ceramic in a mixed 52% KCl - 48% K_2SO_4 salt bath. The most favourable temperature range is normally between 700 and 800° C for periods of time of several hours. The ion-exchange reaction involves the replacement of small Li^+ cations in the β -quartz structure by larger K^+ ions.

Similarly, magnesium-bearing transparent β -quartz glass-ceramics can be strengthened in suitable lithium salt baths. Optimum strengths are obtained at temperatures of 800 to 900° C after several hours treatment. The most convenient molten salt base is Li_2SO_4 . Typical strengths vary from 35 000 to 60 000 psi. This ion-exchange reaction involves the replacement of Mg^{2+} cations in the β -quartz structure by two Li^+ ions. Compression results from two mechanisms: (i) "crowding" by the two-for-one ion replacement, and (ii) stress development through differential expansion between the essentially zero expansion lithium-stuffed quartz surface and the higher expansion interior.

Abraded modulus of rupture values for typical transparent β -quartz ss glass-ceramics before and after ion exchange are given in table II.

5. Conclusions

Transparent glass-ceramic materials can be formed through simple heat treatment of various alumino-silicate glasses in the systems SiO_2 - Al_2O_3 -BaO, SiO_2 - Al_2O_3 , SiO_2 - Al_2O_3 - Li_2O - TiO_2 - ZrO_2 , SiO_2 - Al_2O_3 - MgO - ZrO_2 , and SiO_2 - Al_2O_3 - ZnO - ZrO_2 . Through consideration of crystalline phases which characterise these glass-ceramics, they can be classified into three groups:

stuffed β -quartz glass-ceramics, spinel glass-ceramics, and mullite glass-ceramics.

Phase separation constitutes the first event in the formation of these crystalline materials from glass. The precipitation of finely divided zirconia or titanate nuclei precedes the crystallisation of β -quartz or spinel ss; but, in the case of mullite, direct precipitation of silicate crystallites from the phase-separated glass occurs.

Transparency is generally due to the extremely fine crystallite size (much smaller than the wavelength of visible light) of these glass-ceramics. This is true in the case of the spinel, mullite, and many of the stuffed β -quartz materials. In the case of certain β -quartz ss materials where the major phase attains crystal sizes approaching 1 μm , the optical isotropy of the stuffed β -quartz is a critical factor allowing transparency.

The stuffed β -quartz materials are the most unique by virtue of their very low thermal expansion behaviour and their susceptibility to chemical strengthening by ion-exchange techniques. They can be made to have virtually zero expansion over significant temperature ranges, can be made refractory, or can be made with very high electrical resistivities and low dielectric losses. The spinel and mullite glass-ceramics contain considerable glass and show a gradual softening with temperature, but may remain transparent for long periods, even when held at temperatures in excess of 1000° C.

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TABLE II Chemical strengthening of transparent β -quartz ss glass-ceramics

Composition no.	Initial average modulus of rupture	Salt bath	Temp. (° C)	Time (h)	Exchange mechanism	Average* abraded modulus of rupture after exchange
2	9000 psi	90% Li_2SO_4 -10% K_2SO_4	850	4	$2Li^+ \rightleftharpoons Mg^{2+}$	45 000 psi
2	9000	52% KCl-48% K_2SO_4	780	4	$K^+ \rightleftharpoons Li^+$	45 000
3	12 000	90% Li_2SO_4 -10% K_2SO_4	850	8	$2Li^+ \rightleftharpoons Mg^{2+}$	60 000
4	10 000	90% Li_2SO_4 -10% K_2SO_4	850	8	$2Li^+ \rightleftharpoons Mg^{2+}$	25 000

*Standard deviation = $\pm 10\%$

References

1. S. D. STOOKEY, *Glastech. Ber.* (Fifth International Congress on Glass. Verlag der Deutschen Glastechnischen Gesellschaft, Frankfurt am Main, 1959) pp. V/1-8.
2. D. A. DUKE, G. H. BEALL, J. F. MACDOWELL, and B. R. KARSTETTER, "Chemical Strengthening of Glass-Ceramics" (XXXVIth International Congress on Industrial Chemistry, Brussels, Belgium, September 1966).
3. LORD RAYLEIGH, *Phil. Mag.* **4** XLI (1871) 274, 447; XLVII (1899) 375.
4. GUSTAV MIE, *Ann. Physik* **25** (1908) 377.
5. M. J. BUERGER, *Amer. Min.* **39** (1954) 600.
6. R. ROY, in "Symposium on Nucleation and Crystallization of Glasses and Melts", edited by M. K. Reser, G. Smith, and H. Insley (The American Ceramic Society Inc, Columbus, Ohio, 1962) p. 39.
7. S. SCHREYER and J. F. SCHAIRER, *Z. Krist.* **116** (1961) 60.
8. G. H. BEALL, B. R. KARSTETTER, and H. L. RITTLER, *J. Amer. Ceram. Soc.* **50** (1967) 181.
9. J. F. MACDOWELL and G. H. BEALL, "Immiscibility and Crystallization in the Al_2O_3 - SiO_2 System", to be published in the *J. Amer. Ceram. Soc.*
10. D. A. DUKE and G. A. CHASE, *Applied Optics* **7** (1968) 813.
11. D. L. EVANS, personal communication.
12. G. F. NEILSON, JR., "Small-Angle X-ray Scattering Study of Nucleation and Devitrification in a Glass-Ceramic Material" (Paper presented at the Pittsburgh Diffraction Conference, 1966).
13. S. B. HOLMQUIST, *Z. Krist.* **118** (1963) 477.