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Glass-ceramics - Vitrocéramique - Glaskeramik

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NEW LITHIUM DISILICATE GLASS-CERAMICS

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ABSTRACT

Glass-ceramics containing 40 to 90 wt % lithium disilicate, $\text{Li}_2\text{Si}_2\text{O}_5$, have been produced that exhibit: 1) abraded MOR values of 20-35 Ksi, 2) toughness of 2-5 $\text{MPa m}^{1/2}$, 3) good chemical durability, 4) translucency, 5) glossy cerammed surfaces, and 6) low densification upon ceramming. In order to achieve these properties, a high degree of control of microstructure is required. This is attained through the incorporation of stable accessory glasses of novel compositions, which results in the stabilization of the bulk glass, allowing microstructural control of the crystalline phases.

INTRODUCTION

Glass-ceramics based on lithium silicates have been known for several decades. Corning Inc.'s product Fotoform[®] consists of 40 wt% lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$). General Electric has marketed an electrically insulating glass-ceramic, RE-X[®], based on phosphate nucleation of lithium disilicate; Pfaudler has produced a $\text{Li}_2\text{Si}_2\text{O}_5$ -based glass-ceramic enamel for steel (1).

Lithium disilicate, by virtue of its ease of crystallization, has been widely used to study crystallization rates (2,3,4) and structure (5,6) with high strengths reported (7,8). Ease of crystallization of lithium silicates is responsible for large grain sizes that create difficulties in reproducing results: glasses based on lithium silicates are very unstable, hampering the critical control of microstructure. Studies have commonly been carried out on compositions close to stoichiometric $\text{Li}_2\text{Si}_2\text{O}_5$. In order to stabilize glasses in the binary SiO_2 - Li_2O system, an excess of silica needs to be incorporated, which results in unwanted high levels of cristobalite.

Novel glasses designed to stabilize high levels of lithium disilicate are discussed here. Several compositional areas have been developed that result in stable glasses, and allow controlled crystallization. The resultant glass-ceramics exhibit high strength (20-40 Ksi) that is reproducible, as well as a host of other properties that make them suitable for a variety of applications.

EXPERIMENTAL

Glasses were melted as 1000 g. batches at 1450°C overnight, and cast into two 12x12 cm patties, which were allowed to cool down before annealing at 450°C. Cooling down before annealing prevents the development of haze that is otherwise commonly observed in these glasses.

COMPOSITION OF ACCESSORY COMPONENT

The glass compositions discussed here can be described as mixtures of three components: lithium disilicate, a nucleating agent, and an accessory component. The compositional areas of the accessory components were selected because they form glasses that are slow to crystallize, thus improving the glass stability of the system. Typical bulk compositions, in wt %, are presented in Table I.

1 - Chkalovite component \pm excess

silica - Residual glasses based on chkalovite, $\text{Na}_2\text{O} \cdot \text{ZnO} \cdot 2\text{SiO}_2$, were incorporated at 10 to 20 wt % levels. Extending this compositional field, glass-ceramics in which the residual glass can be described as $\text{R}_2\text{O} \cdot \text{ZnO} \cdot x\text{SiO}_2$, where R is Na or K, and x ranges from 2 to 10, were investigated.

2 - *Potassium feldspar component* - Residual glass with the composition of potassium feldspar, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, was incorporated at levels between 10 and 20 wt %.

3 - *RO-aluminosilicate \pm excess silica* - Accessory glasses based on alkaline earth aluminosilicates ($\text{R}_n\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$, where R can be Ca, Ba, or Sr, and x = 2, 6) were incorporated at 30 to 50 wt % levels. In addition, for some of these compositions, an extra 10 wt % SiO_2 was incorporated, resulting in the lowest levels of lithium disilicate studied: 50 and 60 wt %.

GLASS PROPERTIES

1 - *Viscosity* - The systems defined above result in soft glasses, with viscosity curves comparable to that of soda lime glass. Fig. 1 shows curves for three different compositions. It can be observed that, as a result of addition of 10 wt % SiO_2 to the chkalovite component, the glass viscosity is raised by 100-200°C. Liquidus temperatures for the compositions discussed here are close to 1050°C. The low viscosity and liquidus simplified delivery and forming of these glasses, and allows diverse forming techniques.

Systems with chkalovite residual glasses have strain and anneal points around 405 and 435°C, respectively, and are lower by approximately 20°C than those of other systems (Table II).

TABLE I
Compositions of representative lithium disilicate glass-ceramics

| GLASS | A | B | C | D | E | F |
|-------------------------|------|------|------|------|------|------|
| SiO_2 | 69.3 | 76.3 | 75.3 | 74.2 | 68.6 | 71.8 |
| ZrO_2 | - | - | - | - | 2.01 | 2.4 |
| Al_2O_3 | - | - | - | 3.54 | 8.56 | 8.95 |
| ZnO | 5.28 | 2.92 | 1.9 | - | - | - |
| CaO | - | - | - | - | 1.01 | 3.83 |
| Li_2O | 15.4 | 13.4 | 17.4 | 15.4 | 11.2 | 10.7 |
| K_2O | 6.05 | 3.38 | 2.2 | 3.25 | - | - |
| P_2O_5 | 3.84 | 3.84 | 2.90 | 3.37 | 4.18 | 4.37 |

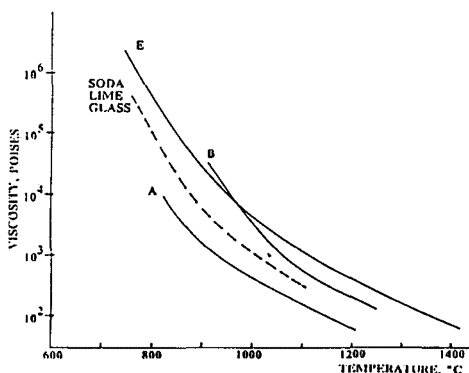


Fig. 1 - Viscosity curves for compositions A, B and E compared to a soda lime glass.

2 - *Expansion* - The studied glasses exhibit moderate thermal expansion, with coefficients near 100×10^{-7} (Table II).

3 - *Density* - Density values for these glasses are close to 2.4 g/cc (Table II).

TABLE II
Physical properties of lithium disilicate glasses and glass-ceramics

| GLASS | Anneal Pt., °C | Strain Pt., °C | CTE*E-7 | | Density, g/cc | |
|-------|-------------------|-------------------|---------|--------|---------------|--------|
| | | | Glass | Gl-Cer | Glass | Gl-Cer |
| A. | 431 | 401 | 112 | 127 | 2.44 | 2.50 |
| B | 453 | 426 | 97 | 111 | 2.38 | 2.49 |
| C | 440 | 410 | 109 | 101 | 2.37 | 2.45 |
| D | 452 | 423 | 100 | 78 | 2.35 | |
| E | 495 | 462 | | 50 | 2.44 | 2.48 |
| F | | | | 51 | | 2.46 |

CERAMMING SCHEDULE

For compositions with chkalovite residual glass, nucleation around 500°C and crystallization near 800°C result in glass-ceramics with well-developed microstructures and good mechanical properties. Heating ramps to and between hold temperatures are generally 300°C/min. The schedule that optimizes strength consists of a nucleation event at 480°C, with crystallization at 850°C. Nucleation can be as short as 30 minutes at 480°C, but 60 minutes is preferred; a crystallization hold of 1 hr at 850°C yields good strengths, but 2 hrs usually improves mechanical properties. With potassium feldspar as the residual glass, both nucleation and crystallization are optimized at higher temperatures: 650°C and 950°C, respectively.

PROPERTIES OF GLASS-CERAMICS

1 - *Phase assemblage* - Glass-ceramics with residual glass compositions based on K-feldspar or K-chkalovite have simple mineral assemblages dominated by lithium disilicate, with minor α -quartz \pm cristobalite and residual glass. The crystallization sequence is straightforward, with lithium phosphate as the presumed species that nucleates lithium metasilicate. This precursor lithium silicate first appears below 580°C, and is shortly followed by the disilicate phase around 600°C.

For systems with Ca-Al silicate residual glasses, the final assemblage consists not only of lithium disilicate + cristobalite + residual glass, but also of wollastonite (CaSiO_3), and β -spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$) as well. Furthermore, the final assemblage has a higher percentage of crystallinity in these systems than in those with K-based residual glasses.

2 - *Microstructure* - Control of microstructure proved to be difficult with noble metals as nucleating agent. As in previous work (10), P_2O_5 (3.5 to 4.5 wt %) was added as a nucleating agent in an attempt to develop a microstructure of interlocking crystals that might be controllable through heat treatments. The microstructure consists of well-cleaved crystals in interlocking aggregates with grain size varying as a function of crystallization temperature (Fig. 2). The cleavage results in step-like fracture surfaces. In contrast to other textures described for chain silicates (e.g., canasite, jade) (11), the crystals are tabular rather than prismatic. The interlocking nature of the texture, together with the step-like mode of fracturing are characteristic of glass-ceramic systems with excellent mechanical properties.

3 - *Expansion* - The highest expansion is observed for compositions with chkalovite residual glass, e.g., Glass A, with a coefficient (20-300°C) of 126×10^{-7} (Table II).

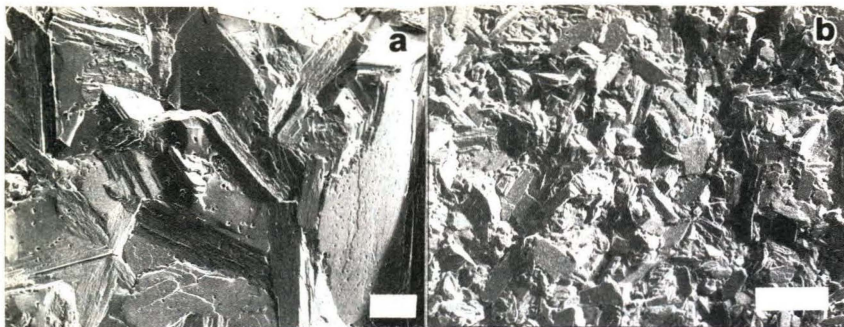


Fig. 2 - Replica TEM micrographs of fractured surfaces of lithium disilicate glass-ceramics. Scale bar = 1 micrometer. a) Composition A cerammed at a maximum temperature of 800°C/4 hr. Interlocking tabular crystals show well developed step-like fracture mode imparted by the well defined cleavage. b) The same composition cerammed at a maximum temperature of 750°C/4 hrs. Note the different grain size relative to a).

Addition of excess silica to this composition lowers the expansion to the 110-100 *E-7 range (Glasses B&C). Intermediate expansions are observed for compositions with K-feldspar residual glasses, such as Glass D, with a coefficient of 78*E-7.

The lowest expansion has been observed for systems with Ca-Al silicate accessory component. Thus, compositions E and F have coefficients of 50*E-7. This extreme lowering of the expansion is due to the presence of β -spodumene.

4 - Density - For most glass-ceramic studies, the density lies in a narrow range, from 2.45 to 2.50 g/cc (Table II). The densification upon ceramming is low, ranging from 2.5 - 4.6%.

5 - Mechanical Properties - Excellent mechanical properties are key attributes of lithium disilicate glass-ceramics. Throughout the residual glass compositional field based on chkalovite, moduli of rupture (MOR) measured on abraded bars between 25 and 34 Ksi were achieved (Table III), and toughnesses (K_{IC}, chevron notch technique) between 2 and 3.6 MPa m^{1/2}. Both strength and toughness improved with higher levels of lithium disilicate (c.f., Glass A vs. C, Table III). In

addition, replacement of Zn by Mg in the residual glass results in a further improvement of mechanical properties. With the addition of SiO₂, strength is somewhat lowered, with MOR values ranging from 22 to 28 Ksi (Table III).

Potassium feldspar residual glass yields the optimum combination of strength and toughness for a given level of lithium disilicate: at 80 wt % lithium disilicate, Glass D has a strength of 31.4 Ksi and a toughness of 3.3 MPa m^{1/2}.

TABLE III
Mechanical properties of lithium disilicate glass-ceramics

| GLASS | Strength, Ksi | Toughness MPa m ^{1/2} |
|-------|------------------|-----------------------------------|
| A | 28.5 | 2.83 |
| B | 27.6 | 2.29 |
| C | 33.9 | 3.0 |
| D | 31.4 | 3.3 |
| E | 22.1 | |

With levels of lithium disilicate between 50 and 60 wt %, compositions with Ca-Al silicate residual glass naturally display poorer mechanical properties relative to other lithium disilicate systems. However, on a more absolute scale, with strengths of 20-22 Ksi and K_{IC} values around 2 MPa m^{1/2}, these glass-ceramics are certainly not "weak materials".

6 - Gloss - Most lithium disilicate systems studied so far develop glossy surfaces during ceramming. The "self-glazing" effect is controlled by the ceramming schedule. In compositions with chkalovite or K-feldspar residual glasses, gloss appears to be strongly dependent on the maximum ceramming temperature, and is optimized between 650 and 850°C. In addition to this variable, gloss in systems with Ca-Al silicate residual glass is also strongly dependent on the length of nucleation hold. Excellent gloss has been routinely achieved in composition E when the nucleation event exceeds 3 hrs.

For most compositions studied, the origin of gloss lies in the formation of a glassy layer that diffuses to exterior surfaces during ceramming. If surface nucleation is not completely suppressed, protrusion of crystals through this glassy layer results in dull surfaces. As observed for systems with Ca-Al silicate residual glass, a long nucleation hold guarantees the dominance of body nucleation and minimizes surface nucleation, thus enhancing gloss. Higher levels of nucleating agent should accomplish a similar effect.

CONCLUSIONS

In lithium disilicate glass-ceramics investigated to date, a range of compositions has been found that exhibit desirable properties, and which can be broadly defined by the following limits: Li₂O 8-17 wt %, Si₂O 65-80 wt %, K₂O 3-7 wt %, Na₂O 2-5 wt %, ZnO 2.5-6 wt %, Al₂O₃ 0-10 wt %, CaO 0-5 wt %, MgO 0-1 wt %, ZrO₂ 0-2.5 wt %, P₂O₅ 1-5 wt %.

The precursor glasses have low viscosities, and are amenable to a variety of forming techniques. Their low delivery temperature (1100-1250°C) offers another processing advantage.

The glass-ceramics all share common properties such as excellent strength and toughness, self-glazing and controllable translucency. Some physical properties, such as gloss, translucency, and expansion, are a function of the composition of the accessory glass, whereas mechanical properties, while affected by the composition of the accessory component, are more strongly influenced by the amount of lithium disilicate in the system.

The excellent mechanical properties of lithium disilicate glass-ceramics are the result of interlocking tabular crystals with a well-developed cleavage that results in step-like fracture surfaces. This mode of fracture is an effective energy-absorbing mechanism which effectively arrests fracture propagation. The high toughness observed attests to this.

Residual glass compositions based on K-feldspar have yielded optimum combinations of strength and toughness. At 80 wt % lithium disilicate, strengths of 30-35 Ksi and toughness values of 3.3 MPa m^{1/2} have been reached.

Optimum gloss and opacity have been obtained in systems with Ca-Al-silicate accessory glass, at levels of 50 wt % lithium disilicate. This system also yields the highest degree of crystallinity of the accessory components. One of the accessory phases present, β -spodumene, contributes to lowering the expansion of this system to 50 *E-7, the lowest value observed. Expansion coefficients for the other systems range from 80 *E-7, for those with K-feldspar accessory component to 100-120 *E-7 for those with K-chkalovite.

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