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DESIGN OF ENERGY AND ENVIRONMENTALLY FRIENDLY FIBERGLASS  
COMPOSITIONS DERIVED FROM THE QUATERNARY  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$  PHASE  
DIAGRAM – PART I: STRUCTURES, PROPERTIES AND CRYSTALLIZATION  
POTENTIAL OF EUTECTIC AND SELECTED MULTI-OXIDE E-GLASS COMPOSITIONS

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ABSTRACT

Incumbent E-Glass fibers contain 6.0-10.0%  $\text{B}_2\text{O}_3$  and 0.5-1.0% fluorine. Emissions of  $\text{B}_2\text{O}_3$  and fluorine from commercial furnaces were recently identified as environmental hazards. First-generation boron- and fluorine-free E-glass compositions have high fiber forming temperatures and require more energy in production. Second-generation boron- and fluorine-free E-glass compositions and third-generation fluorine-free E-glass compositions were developed, which contain low levels of  $\text{B}_2\text{O}_3$  and/or  $\text{Li}_2\text{O}$ , and have 26 to 65°C lower fiber-forming temperatures, respectively, than optimum first generation boron-and fluorine-free E- glass.

INTRODUCTION

Incumbent E-glass compositions have a low viscosity, since they contain 6-10% boron and 0.5-1.0% fluorine, i.e., ingredients, which are known to act as fluxes [1].

Table I. Incumbent ASTM E-glass Compositions Containing 6-10% Boron and  $\leq 1\%$  Fluorine

| Composition                        | Quaternary [1] | Ternary [1] | ASTM E-Glass [2] |
|------------------------------------|----------------|-------------|------------------|
| $\text{SiO}_2$ , weight %          | 54.0           | 53.27       | 52 to 62         |
| $\text{Al}_2\text{O}_3$ , weight % | 14.0           | 13.98       | 12 to 16         |
| $\text{CaO}$ , weight %            | 17.5           | 23.53       | 16 to 25         |
| $\text{MgO}$ , weight %            | 4.5            | 0.61        | 0 to 5           |
| $\text{TiO}_2$ , weight %          | -              | 0.51        | 0 to 1.5         |
| $\text{Fe}_2\text{O}_3$ , weight % | -              | 0.36        | 0.05 to 0.8      |
| $\text{K}_2\text{O}$ , weight %    | -              | 0.10        | Total alkali     |
| $\text{Na}_2\text{O}$ , weight %   | -              | 0.93        | metal oxide:     |
| $\text{Li}_2\text{O}$ , wt.%       | -              | -           | from 0 to 2      |
| $\text{B}_2\text{O}_3$ , weight %  | 10.0           | 6.00        | 0 to 10          |
| F, weight %                        | -              | 0.48        | 0 to 1.0         |
| Log3 Forming T, °C                 | 1200           | 1174        | -                |
| Liquidus T, °C                     | 1120           | 1068        | -                |
| Delta ( $\Delta$ ) T, °C           | 80             | 106         | -                |

The first incumbent high-boron E-glass composition [1] shown in Table I was based on the quaternary  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$  phase diagram. Dolomite ( $\text{MgO}$ ) was deliberately added to the commercial composition. The second high-boron E-glass is based on the ternary  $\text{SiO}_2\text{-}$

Al<sub>2</sub>O<sub>3</sub>-CaO phase diagram. Thus, dolomite (MgO) was not added [1] but small amounts of MgO (~0.5%) are almost always introduced in a commercial batch as tramp material (impurity).

Both compositions have a low “log3” fiber forming temperature and a high difference (delta) between log3 forming and liquidus temperature. The so-called log3 forming temperature is a reference temperature for comparing all fiberglass melts at the same viscosity of 1000 poise. The liquidus temperature is the temperature at which solid (crystals) and liquid (melt) form an equilibrium state. The melt must be crystallization resistant in a continuous process, i.e., have a delta of at least 55-65°C between the log3 forming and liquidus temperature. A higher delta temperature keeps the log3 forming temperature unnecessarily high. A lower delta temperature might cause incipient crystallization of the melt in a stationary section of the furnace.

Depending on furnace design, the conventional environmental control systems, which have been used in the past, may remove boron emissions resulting from E-glass compositions with up to 2% B<sub>2</sub>O<sub>3</sub>, but they do not remove emissions of fluorine in any amount. Thus, E-glass compositions with little or no-boron, but essentially fluorine free, which meet the ASTM E-glass specifications [2], are required to replace the incumbent high boron, high-fluorine E-glass.

#### FIRST-GENERATION ENVIRONMENTALLY FRIENDLY E-GLASS

Boron and fluorine, when removed from the melt, as required for environmentally friendly glass fibers, will increase the melt viscosity and log3 fiber forming temperature. Thus the process energy required, another environmental concern, will increase dramatically and must, in turn, be reduced by goal-oriented compositional design studies.

Table II. Ternary and Quaternary First-Generation Boron- and Fluorine-Free E-Glass Variants

| Examples                                  | <i>Ternary Eutectic</i> | Ex. 1 | <i>Quaternary Eutectic</i> | Ex. 1 | Ex. 2 |
|-------------------------------------------|-------------------------|-------|----------------------------|-------|-------|
| SiO <sub>2</sub> , weight %               | 62.10                   | 60.00 | 60.00                      | 60.10 | 59.30 |
| Al <sub>2</sub> O <sub>3</sub> , weight % | 14.60                   | 15.00 | 15.00                      | 12.99 | 12.10 |
| CaO, weight %                             | 23.30                   | 25.00 | 20.00                      | 22.13 | 22.60 |
| MgO, weight %                             | -                       | -     | 5.00                       | 3.11  | 3.40  |
| TiO <sub>2</sub> , weight %               | -                       | -     | -                          | 0.55  | 1.50  |
| Fe <sub>2</sub> O <sub>3</sub> , weight % | -                       | -     | -                          | 0.25  | 0.20  |
| K <sub>2</sub> O, weight %                | -                       | -     | -                          | 0.14  | Trace |
| Na <sub>2</sub> O, weight %               | -                       | -     | -                          | 0.63  | 0.90  |
| Li <sub>2</sub> O, weight %               | -                       | -     | -                          | -     | -     |
| B <sub>2</sub> O <sub>3</sub> , weight %  | -                       | -     | -                          | -     | -     |
| F, weight %                               | -                       | -     | -                          | 0.04  | -     |
| SiO <sub>2</sub> /RO Ratio                | 2.67                    | 2.40  | 2.40                       | 2.37  | 2.28  |
| Log3 Forming T, °C                        | 1335                    | 1294  | 1299                       | 1259  | 1258  |
| Liquidus T, °C                            | 1217                    | 1235  | 1225                       | 1174  | 1185  |
| Delta (Δ) T, °C                           | 118                     | 59    | 74                         | 85    | 73    |
| ASTM E-Glass                              | -                       | +     | +                          | +     | +     |
| References                                | [5]                     | [5]   | [11]                       | [4]   | [3]   |

Five boron- and fluorine-free environmentally friendly compositions were known [1] [3] [4] [5] [11]. The ternary eutectic SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO composition (Table II, Example 1) has the

highest log3 forming temperature and is not an E-glass by ASTM specifications [2]. A near-eutectic  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  composition (Example 2) was developed by trend line design [5]. It is an E-glass by ASTM specifications [2] and has a 41°C lower temperature at a melt viscosity of 1000 poise (or log3 fiber forming temperature) than the eutectic composition (Example 1). Despite the dramatic reduction of the forming temperature, the melt viscosity and the energy demand remain very high.

Example 3 is a quaternary eutectic  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$  E-glass [11]. Replacement of 5% CaO (Example 2) with 5%MgO raises, both the forming and the liquidus temperature and therefore does not reduce the energy demand. The other first-generation boron-free E-glass compositions (Examples 4 and 5) are also derived from the quaternary  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$  phase diagram. Both contain ~0.5% MgO from tramp in the ingredients and  $\leq 3\%$  MgO from dolomite that is deliberately added.

Example 4 was reported in 1985 [3]. It additionally contains ~0.5%  $\text{TiO}_2$  from tramp (impurities) and ~1% rutile (pure  $\text{TiO}_2$ ) that is added to the batch. Example 5 was reported in 1996 [4]. It contains only ~0.5%  $\text{TiO}_2$  from tramp with no rutile added. Examples 4 and 5 have lower, but still high forming temperatures (1259 and 1258°C) and high delta temperatures (73 and 85°C). Their energy demand in commercial use is considered to be as high. The examples in Table I therefore served as starting point for the design of new generations of environmentally friendly E-glass compositions.

## SECOND-GENERATION ENVIRONMENTALLY FRIENDLY E-GLASS

### Design Considerations

A pure  $\text{SiO}_2$  melt has a very high melt viscosity and a very low crystallization potential. A pure  $\text{Al}_2\text{O}_3$ , MgO or CaO melt has a very low melt viscosity and a very high crystallization potential as evidenced by a sharp melting point. By combining  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , CaO and MgO at a given weight ratio, each oxide makes its unique contribution.

In a boron-free or low-boron E-glass composition, the melt viscosity that depends on the level of  $\text{SiO}_2$ , is lower than that of pure  $\text{SiO}_2$ , but higher than that of pure CaO, MgO, or  $\text{Al}_2\text{O}_3$ . The crystallization potential that depends on the level of CaO, MgO, and  $\text{Al}_2\text{O}_3$ , is lower than that of the pure ingredients. The effect of  $\text{Al}_2\text{O}_3$  is variable [6]. Modulus, morphology and melt temperature of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  containing fibers [13] rise with increasing  $\text{Al}_2\text{O}_3$  content from borosilicate E-glass (14%  $\text{Al}_2\text{O}_3$ , 79 GPa, 1174°C) to single crystal sapphire fibers (100%  $\text{Al}_2\text{O}_3$ , 410 GPa, 2000°C). Only low levels of  $\text{Al}_2\text{O}_3$  (<16%) yield crystallization resistant glass fibers.

According to prior references [5] [6], a high  $\text{SiO}_2$  content (and therefore low RO content) will translate into a high log3 forming temperature and a low liquidus temperature, and therefore into a high delta between forming and liquidus temperature. Conversely, a high RO content (therefore low  $\text{SiO}_2$  content) will translate into a low log3 forming temperature and a high liquidus temperature and into a low delta between forming and liquidus temperature.

First-generation boron-free E-glass compositions have a low liquidus temperature, a high log3 forming temperature and a relatively high delta between forming and liquidus temperature. Compositional design is best started at the eutectic, the lowest liquidus temperature of a given

system. Thus, the MgO level of a typical boron-free E-glass composition was varied from 3.4% to 1.5% [7]. The lowest liquidus temperature (figure 1) is obtained near 2.5% MgO [7].

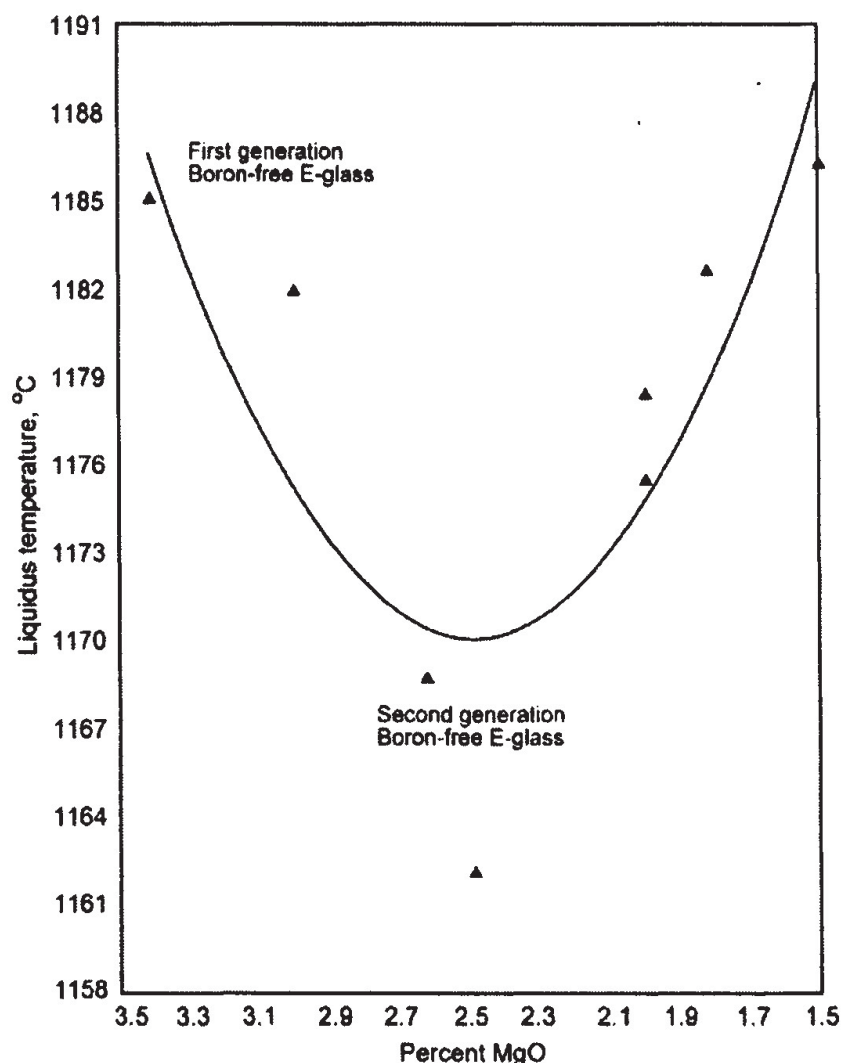


Figure 1. Eutectic with Regard to MgO for Second Generation Boron- and Fluorine-Free E-Glass

Having thus identified the approximate eutectic of the of first generation multi-oxide E-glass composition to be at or near 2.5% MgO, it was then necessary to determine how far the forming temperature of this eutectic can be reduced the without creating a composition that would have an unacceptably low delta temperature, i.e., an unacceptably high crystallization potential.

#### Trend Line Design

Brückner et al. [12] used a compositional design method that relies on a generic understanding of the contributions of each oxide. Aubourg and Wolf [13] additionally used "linear and complex regressions" in the design of experiments. The trend line design of

experiments, a new design tool, takes these known methodologies [12][13] another step forward [5] by applying the conceptual understanding of the contributions of each oxide. Thus, it is an exploratory method aimed at discovering the path, with a limited number of trend-setting compositions, from a known composition with known properties to a goal composition with design-required properties. It not a statistical method, but can it can be augmented at each step in the design process, preferable near the goal composition, with statistical methods.

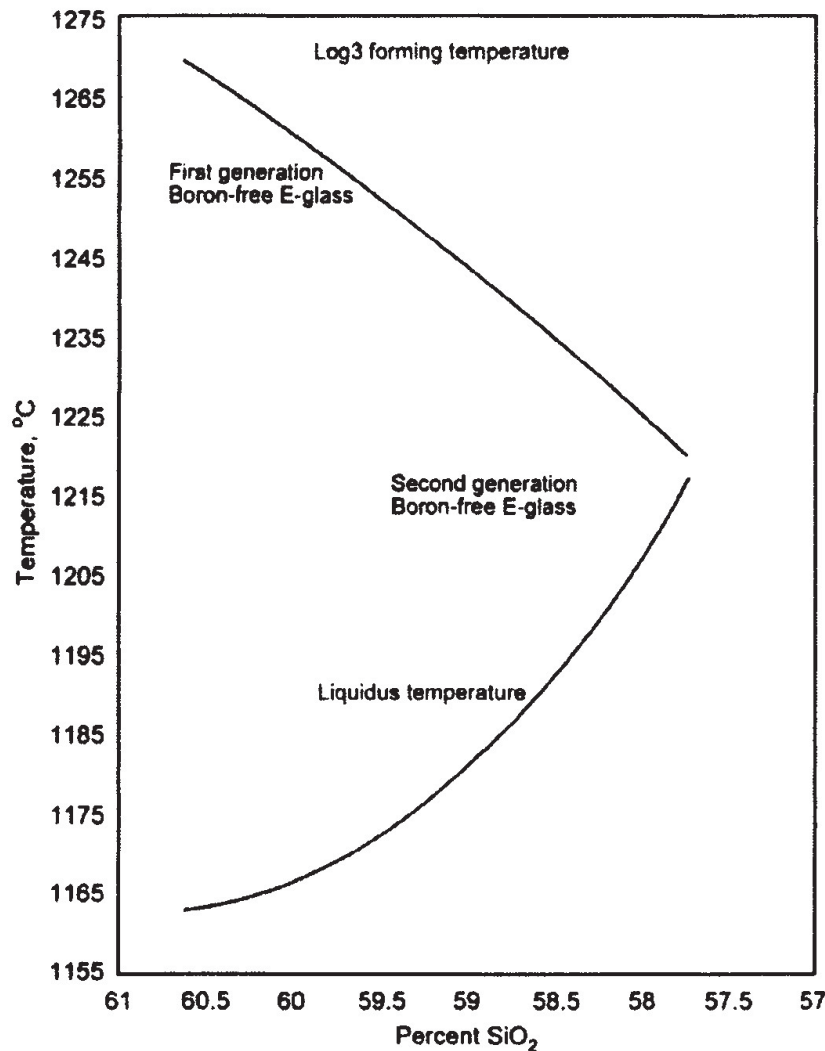


Figure 2. Trend Lines (%SiO<sub>2</sub> versus Melt Properties) for Second Generation Boron- and Fluorine-Free E-Glass Compositions

First-generation boron-free E-glass compositions have a high forming temperature a low liquidus temperature, and a high delta between forming and liquidus temperature. The goal of the design process was to identify a composition that has (1) the lowest possible log3 fiber

forming temperature with a given set of ingredients and (2) a delta between forming and liquidus temperature of 55-65°C to be crystallization resistant.

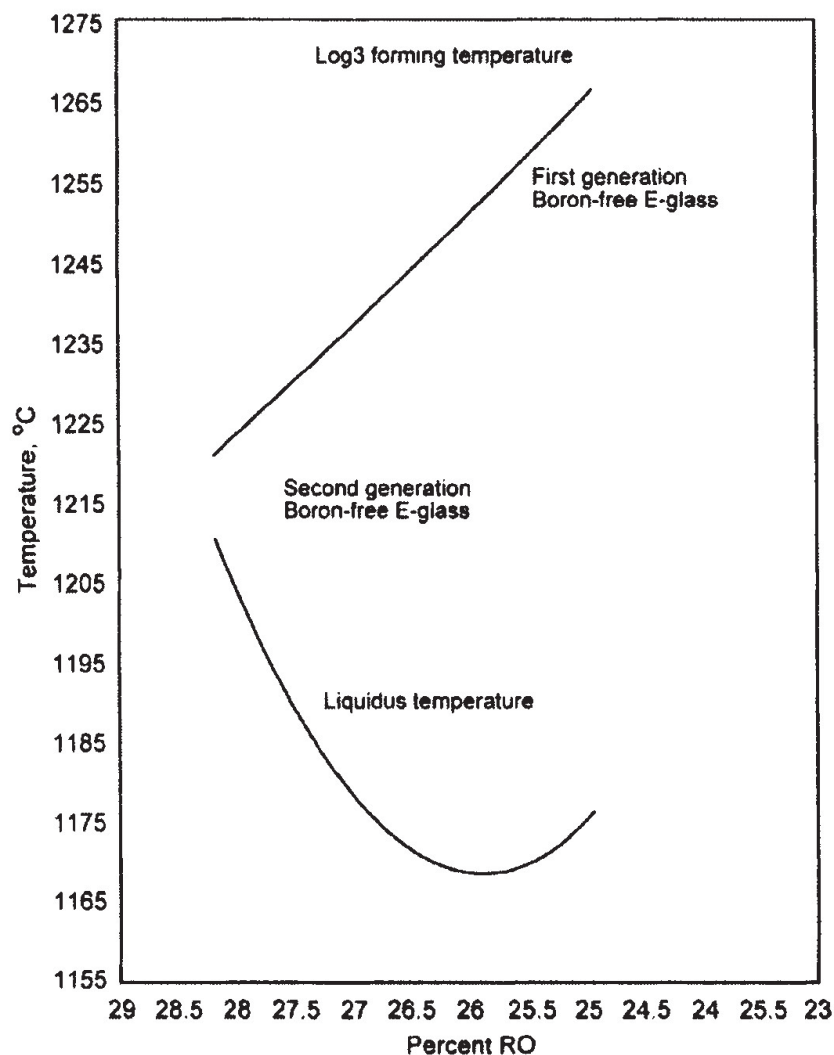


Figure 3. Trend Lines (%RO versus Melt Properties) for Second Generation Boron- and Fluorine-Free E-Glass Compositions

The new compositional design tool is best employed in an early research phase before the relatively large number of experiments becomes available that would be required to conduct their meaningful statistical evaluation. The trend lines needed for the design of second-generation boron- and fluorine free E-glass compositions were therefore stepwise developed from the starting composition toward the goal composition to show the effect of reducing percent  $\text{SiO}_2$  (Figure 2), increasing percent RO (Figure 3), reducing the ratio of  $\text{SiO}_2/\text{RO}$  (Figure 4) on forming, liquidus and (implicitly) delta temperature. The trend lines for other compositional parameters ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2+\text{Al}_2\text{O}_3$ ) were also developed but are not shown here. Once

a narrow range of near-goal compositions has been developed by this method with relatively few experiments, a statistical study might be appropriate to fine-tune the results. Percent  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaO}$ , and the  $\text{SiO}_2/\text{CaO}$  ratio of any composition are codependent. Log3 forming, liquidus and delta temperature of any composition are also codependent.

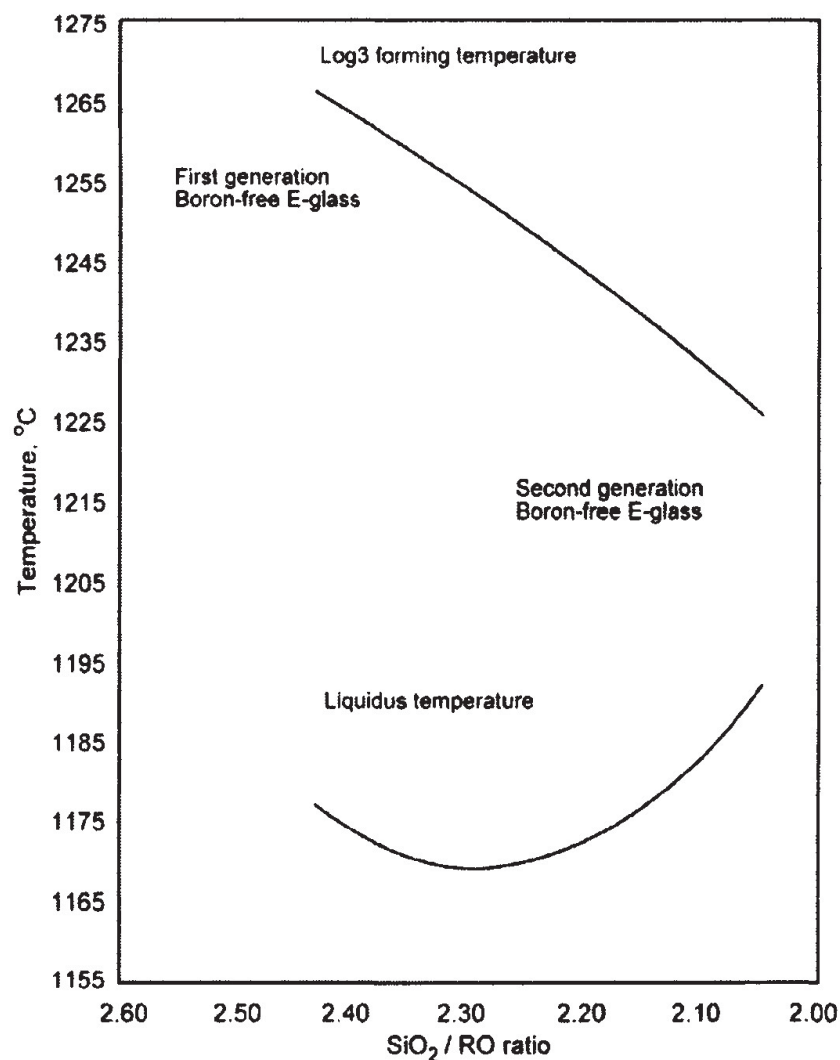


Figure 4. Trend Lines ( $\text{SiO}_2/\text{RO}$  Ratio versus Melt Properties) for Second Generation Boron- and Fluorine-Free E-Glass Compositions

Compositional design methods, which treat compositional inputs and performance outputs as independent variables, are not suitable as a design or analytical tool. In summary, successive generations of environmentally friendly E-glass compositions were designed by this method, each offering a lower melt viscosity or fiber forming temperature and require less process energy than the previous generation, although some may cause an increase of the materials cost.

## Analysis of the Results

Figure 2 shows the changes in log3 forming temperature (i.e., melt viscosity at 1000 poise) and liquidus temperature resulting from a stepwise reduction of the SiO<sub>2</sub> level at 12–14% Al<sub>2</sub>O<sub>3</sub> for a series of carefully designed compositions, starting with of the SiO<sub>2</sub> level of a first-generation boron- and fluorine-free E-glass control. Figure 3 reflects the concurrent increase of the RO level, as the forming and delta temperature drops, and as the liquidus temperature rises. Figure 4 shows the decrease of the SiO<sub>2</sub>/RO ratio.

The starting composition in Figures 2, 3 and 4 had a high SiO<sub>2</sub> level, SiO<sub>2</sub>/RO ratio, forming temperature and delta temperature, as well as a low RO level. It was highly crystallization resistant. The very final composition in the completed trend line had design a very low SiO<sub>2</sub> level, SiO<sub>2</sub>/RO ratio, and forming temperature and liquidus temperature, as well as a very high RO level. As a result it had a substantially lower delta temperature than required for a melt to be crystallization resistant in a continuous commercial furnace. In fact its delta temperature approached 0°C near a log3 forming temperature (or viscosity of 1000 poise) of 1215°C.

Table III. Design of New Second-Generation Boron- and Fluorine-Free E-Glass Compositions

| Compositions                         | Containing 1.10% TiO <sub>2</sub> |       |        |       |       | Containing 0.55% TiO <sub>2</sub> |       |       |
|--------------------------------------|-----------------------------------|-------|--------|-------|-------|-----------------------------------|-------|-------|
| Examples [9]                         | Control                           | Ex. 6 | Ex. 2* | 5     | Ex. 1 | Control                           | Ex. H | Ex. I |
| SiO <sub>2</sub> , wt%               | 59.30                             | 59.05 | 57.45  | 57.95 | 57.75 | 60.10                             | 57.60 | 58.18 |
| Al <sub>2</sub> O <sub>3</sub> , wt% | 12.10                             | 12.20 | 13.40  | 13.20 | 13.20 | 12.99                             | 13.55 | 13.68 |
| CaO, wt%                             | 22.60                             | 23.95 | 24.35  | 24.05 | 24.25 | 22.13                             | 24.50 | 23.75 |
| MgO, wt%                             | 3.40                              | 2.55  | 2.55   | 2.55  | 2.55  | 3.11                              | 2.55  | 2.55  |
| TiO <sub>2</sub> , wt%               | 1.50                              | 1.10  | 1.10   | 1.10  | 1.10  | 0.55                              | 0.55  | 0.55  |
| Fe <sub>2</sub> O <sub>3</sub> , wt% | 0.20                              | 0.25  | 0.25   | 0.25  | 0.25  | 0.25                              | 0.35  | 0.35  |
| Na <sub>2</sub> O, wt%               | 0.90                              | 0.90  | 0.90   | 0.90  | 0.90  | 0.63                              | 0.90  | 0.91  |
| B <sub>2</sub> O <sub>3</sub> , wt%  | -                                 | -     | -      | -     | -     | -                                 | -     | -     |
| F, wt%                               | -                                 | -     | -      | -     | -     | 0.04                              | -     | -     |
| SiO <sub>2</sub> /RO                 | 2.28                              | 2.23  | 2.14   | 2.18  | 2.15  | 2.37                              | 2.13  | 2.20  |
| Log3 FT, °C                          | 1258                              | 1239  | 1238   | 1235  | 1232  | 1259                              | 1240  | 1238  |
| LT, °C                               | 1185                              | 1181  | 1165   | 1164  | 1166  | 1174                              | 1185  | 1183  |
| ΔT, °C                               | 73                                | 58    | 73     | 71    | 66    | 85                                | 55    | 55    |
| References                           | [3]                               | [9]   | [9]    | [9]   | [9]   | [4]                               | [9]   | [9]   |

\* Average of five samples

Several second-generation boron- and fluorine-free E-glass compositions were identified from these trend lines (Tables III) having the lowest forming temperature for this compositional variant and a goal delta temperature of 55–65°C as required for a crystallization resistant melt.

In general, Table III confirms that the lowest log3 forming temperature of second-generation boron- and fluorine-free E-glass compositions with a delta temperature of 55–75°C range from 1232 to 1238°C. These compositions have a SiO<sub>2</sub>/RO ratio ranging from 2.15 to 2.20 [9]. Their melts are considered to be crystallization resistant in a continuous commercial furnace. Specifically, the lowest log3 forming temperature that has a delta of 66°C is 1232°C (Table III), or 26 to 103°C lower than that of first-generation boron- and fluorine-free E-glass (Table II). This composition has a SiO<sub>2</sub>/RO ratio of 2.15.

### THIRD-GENERATION ENVIRONMENTALLY FRIENDLY E-GLASS

#### Background

The first boron- and fluorine-free E-glass compositions, which had forming temperatures below 1260°C, were made between 1985 and 1996. In relation to these first boron- and fluorine-free E-glass compositions (Table II, Examples 4 and 5) the optimum second-generation boron- and fluorine-free E-glass composition (Table III) was found to have a 26°C lower forming temperature, a slightly lower delta temperature that offers adequate crystallization resistance.

Addition of  $\leq 1.0\%$   $\text{Li}_2\text{O}$  and/or  $\leq 2\%$   $\text{B}_2\text{O}_3$  (Table IV) was expected to afford third-generation environmentally friendly E-glass with even lower log3 forming temperatures, while retaining, if properly designed [5], the required delta of 55–65°C temperature.

Table IV. Trend Line Design of New Third-Generation Fluorine-Free E-Glass Compositions

| Approach               | Addition of $\text{Li}_2\text{O}$ and/or $\text{B}_2\text{O}_3$ to Second-Generation E-Glass |     |     |
|------------------------|----------------------------------------------------------------------------------------------|-----|-----|
| Variant                | 1                                                                                            | 2   | 3   |
| $\text{Li}_2\text{O}$  | <1%                                                                                          | -   | <1% |
| $\text{B}_2\text{O}_3$ | -                                                                                            | <2% | <2% |

Environmental control systems being used for commercial fiberglass, may remove boron emissions resulting from E-glass compositions with up to 2%  $\text{B}_2\text{O}_3$ . One compositional variant is fluorine- and boron-free (Variant 1 in Table IV), the others are fluorine-free and contain <2%  $\text{B}_2\text{O}_3$  and either <1%  $\text{Na}_2\text{O}$  (Variant 2) or <1%  $\text{Li}_2\text{O}$  (Variant 3) as the key alkali oxide.

#### Addition of <1% $\text{Li}_2\text{O}$

Before initiating trend line design experiments it was necessary to determine whether third-generation environmentally friendly E-glass variants would, like the second-generation variants, have the lowest liquidus temperature at ~2.5%  $\text{MgO}$ . As a result, the lowest liquidus temperatures for potential third-generation environmentally friendly E-glass was again found to be near 2.5%  $\text{MgO}$  [7], a value that was accepted for the trend line design experiments.

The new  $\text{Li}_2\text{O}$  containing, boron- and fluorine-free E-glass compositions were again designed by the trend line design of experiments [5]. A  $\text{Li}_2\text{O}$ -containing composition with a relatively high  $\text{SiO}_2$  and a relatively low  $\text{CaO}$  (or  $\text{RO}$ ) level was selected as the starting point for the ensuing trend line analysis.

In consecutive experiments, the  $\text{SiO}_2$  level was stepwise reduced, the  $\text{CaO}$  level was stepwise increased at a constant level of  $\text{MgO}$  (~2.5%), and the  $\text{Al}_2\text{O}_3$  level was adjusted as needed. The resultant trend lines, relating percent  $\text{SiO}_2$ , percent  $\text{RO}$  and the  $\text{SiO}_2/\text{RO}$  ratio to forming, liquidus and delta temperature were obtained, but are not shown.

The results are summarized in Table V. At a high  $\text{SiO}_2/\text{RO}$  ratio (2.44), the log3 forming temperature of the starting composition (Example 104) was unnecessarily high. At a low ratio (1.16) the delta temperature of the final composition (Example 130) was only 42°C and no longer meets the minimum requirements of a continuous commercial fiberglass process.

The lowest log3 forming temperature (Example 86) among the new third-generation boron- and fluorine-free E-glass compositions having 0.9% Li<sub>2</sub>O and a delta temperature of 65°C is therefore 1211°C, or 47 to 124°C lower than that of the first-generation boron- and fluorine-free E-glass. It has a SiO<sub>2</sub>/RO ratio of 2.23.

Table V. New Third-Generation Boron- and Fluorine-Free E-Glass Containing <1% Li<sub>2</sub>O

| Examples [8]                         | <i>Controls</i> |       | 87    | 86    | 130   |
|--------------------------------------|-----------------|-------|-------|-------|-------|
| SiO <sub>2</sub> , wt%               | 59.30           | 60.09 | 58.25 | 58.35 | 57.85 |
| Al <sub>2</sub> O <sub>3</sub> , wt% | 12.10           | 13.00 | 13.40 | 13.40 | 13.40 |
| CaO, wt%                             | 22.60           | 22.13 | 23.65 | 23.55 | 23.95 |
| MgO, wt%                             | 3.40            | 2.50  | 2.55  | 2.55  | 2.55  |
| TiO <sub>2</sub> , wt%               | 1.50            | 1.10  | 1.10  | 1.10  | 1.10  |
| Fe <sub>2</sub> O <sub>3</sub> , wt% | 0.20            | 0.25  | 0.25  | 0.25  | 0.25  |
| Na <sub>2</sub> O, wt%               | 0.90            | -     | -     | -     | -     |
| Li <sub>2</sub> O, wt%               | -               | 0.90  | 0.90  | 0.90  | 0.90  |
| B <sub>2</sub> O <sub>3</sub> , wt%  | -               | -     | -     | -     | -     |
| F, wt%                               | -               | -     | -     | -     | -     |
| SiO <sub>2</sub> /RO                 | 2.28            | 2.44  | 2.23  | 2.23  | 2.18  |
| Log3 FT, °C                          | 1258            | 1223  | 1215  | 1211  | 1199  |
| LT, °C                               | 1185            | 1155  | 1153  | 1146  | 1157  |
| ΔT, °C                               | 73              | 68    | 62    | 65    | 42    |

The effect of Li<sub>2</sub>O was predictable but the specific composition and SiO<sub>2</sub>/RO ratio that yields the lowest forming temperature with a delta of 55-65°C was not obvious. In addition, the liquidus temperature should have increased with the major (1.75%) increase in RO from 24.63% (Example 104) to 26.20% (Example 87). Instead, the liquidus remained constant, suggesting the presence of Li<sub>2</sub>O inhibited the formation of crystal species that would otherwise have formed.

#### Addition of <2% B<sub>2</sub>O<sub>3</sub>

The design of third-generation low-boron E-glass compositions started with a composition that contained 1.8% B<sub>2</sub>O<sub>3</sub> and had been reported in 1999 [10] with a forming temperature of 1300°C. It had 60% SiO<sub>2</sub>, and a SiO<sub>2</sub>/RO ratio of 2.40.

Figure 5 shows the trends of forming and liquidus temperature that result from the stepwise reduction of SiO<sub>2</sub> until a composition is reached with a delta of 40°C. A delta of 55-65°C between its forming and liquidus temperature is required for the SiO<sub>2</sub> level and forming temperature of a crystallization resistant third-generation low-boron E-glass.

Figure 6 shows the concurrent trends of log3 forming and liquidus temperatures resulting from the stepwise increase in RO levels starting with the RO level that had been reported for the literature composition. Percent Al<sub>2</sub>O<sub>3</sub> was usually maintained in a range of 12.0-14.0%.

Figure 7 shows the trends of the forming and liquidus temperatures resulting from the stepwise decrease in the SiO<sub>2</sub>/RO ratios. This ratio relates to the delta between log3 forming temperature and liquidus temperature. A specific SiO<sub>2</sub>/RO ratio is required to achieve a goal

delta temperature of 55-65°C for any given compositional variant under investigation, and therefore a goal level of crystallization resistance in a continuous commercial furnace.

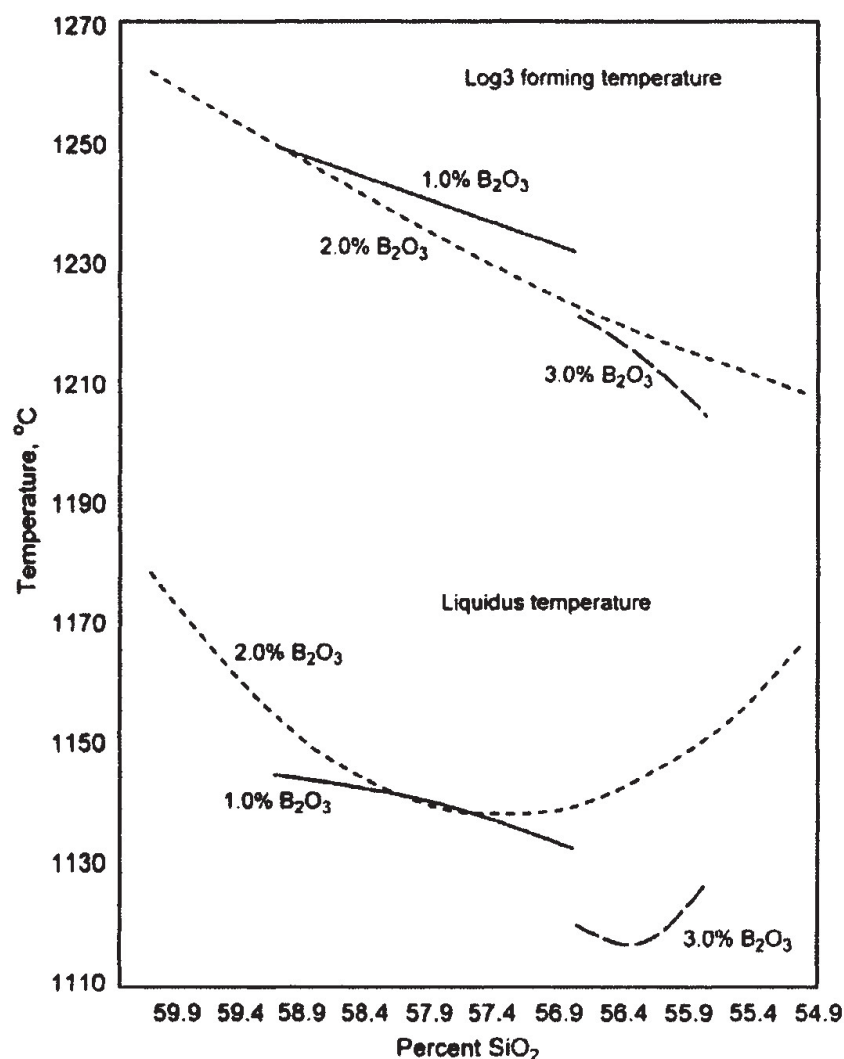


Figure 5. Trend Lines (SiO<sub>2</sub>) versus Melt Properties for Third Generation Fluorine-Free E-Glass Compositions Containing 1-3% B<sub>2</sub>O<sub>3</sub>

Table VI shows that the lowest log<sub>3</sub> forming temperature of new third-generation fluorine-free, low-boron E-glass with a delta temperature of 61°C is also 1211°C, or 47 to 124°C lower than that of the first-generation boron- and fluorine-free E-glass. It has a delta between forming and liquidus temperature of 58°C and a SiO<sub>2</sub>/RO ratio of 2.08.

In general, Table VI confirms that the lowest log<sub>3</sub> forming temperature of second-generation fluorine-free E-glass compositions containing <2% B<sub>2</sub>O<sub>3</sub> and having a delta temperature of 54-

61°C range from 1211 to 1220°C. These compositions have a  $\text{SiO}_2/\text{RO}$  ratio ranging from 2.08 to 2.09 [9]. Their melts are crystallization resistant in a continuous commercial furnace.

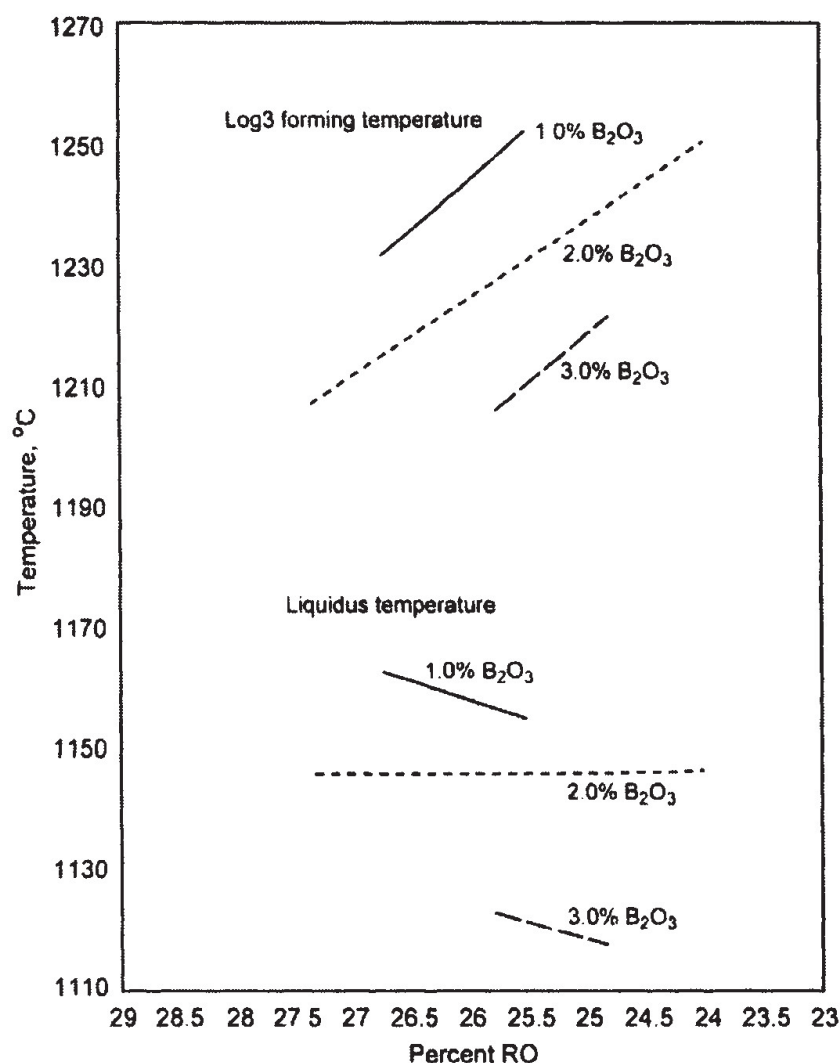


Figure 6. Trend Lines (%RO versus Melt Properties) for Third Generation Fluorine-Free E-Glass Compositions Containing 1-3%  $\text{B}_2\text{O}_3$

Specifically, the lowest log3 forming temperature of a new second-generation fluorine-free E-glass composition containing 1.3%  $\text{B}_2\text{O}_3$  and having a delta of 58°C is 1211°C, or 51°C lower than that of the control shown in Table VI, i.e., a literature composition [10] that served as the starting point of the trend line design for this compositional variant, or 47 to 124°C lower than that of first-generation boron- and fluorine-free E-glass shown in Table II. This composition has a  $\text{SiO}_2/\text{RO}$  ratio of 2.08.

The lowest log3 forming temperature, which was achieved by trend line design of experiments with a third generation environmentally friendly E-glass containing either containing 0.9%  $\text{Li}_2\text{O}$  or 1.3%  $\text{B}_2\text{O}_3$  was the same ( $1211^\circ\text{C}$ ).

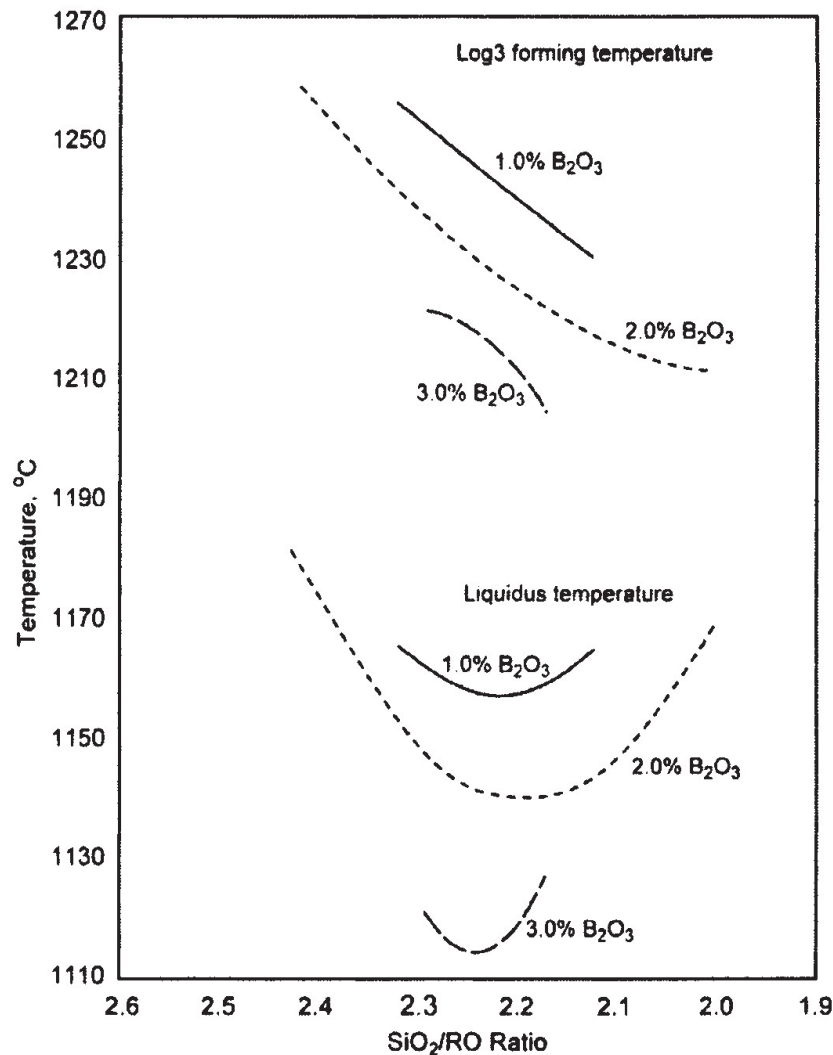


Figure 7. Trend Lines ( $\text{SiO}_2/\text{RO}$  Ratio versus Melt Properties) for Third Generation Fluorine-Free E-Glass Compositions Containing 1-3%  $\text{B}_2\text{O}_3$

Addition of <2%  $\text{B}_2\text{O}_3$  and <1%  $\text{Li}_2\text{O}$  [6]

Second-generation fluorine- and boron-free E-glass compositions [7] were found to have their lowest liquidus temperature at ~2.5%  $\text{MgO}$ . To establish this optimum  $\text{MgO}$  level for third generation fluorine-free E-glass compositions containing <2%  $\text{B}_2\text{O}_3$  and <1%  $\text{Li}_2\text{O}$ , the  $\text{MgO}$  level of a typical composition was varied from 3.4% to 1.5% [8]. The results show that the lowest liquidus temperature was again obtained near 2.5%  $\text{MgO}$  [8].

As shown in Table VII, the trend line design of third-generation fluorine-free E-glass compositions containing both 0.9%  $\text{Li}_2\text{O}$  and 1%  $\text{B}_2\text{O}_3$  started again with a specific composition, the control, that came as close as possible to the eutectic, i.e., had the lowest possible liquidus temperature within the given compositional variant.

Table VI. New Third-Generation Fluorine-Free E-Glass Compositions Containing <2%  $\text{B}_2\text{O}_3$

| Examples                      | Control | 41    | 40    | 39    | 38    | 35    | 34    | 33    |
|-------------------------------|---------|-------|-------|-------|-------|-------|-------|-------|
| $\text{SiO}_2$ , wt%          | 60.82   | 56.55 | 56.50 | 56.45 | 56.50 | 56.50 | 56.60 | 56.60 |
| $\text{Al}_2\text{O}_3$ , wt% | 11.70   | 13.35 | 13.45 | 13.48 | 13.49 | 13.45 | 13.45 | 13.25 |
| $\text{CaO}$ , wt%            | 21.20   | 24.55 | 24.50 | 24.52 | 24.46 | 24.50 | 24.50 | 24.60 |
| $\text{MgO}$ , wt%            | 2.80    | 2.55  | 2.55  | 2.55  | 2.55  | 2.55  | 2.55  | 2.55  |
| $\text{TiO}_2$ , wt%          | 0.10    | 0.55  | 0.55  | 0.55  | 0.55  | 0.55  | 0.55  | 0.55  |
| $\text{Fe}_2\text{O}_3$ , wt% | 0.16    | 0.25  | 0.25  | 0.25  | 0.25  | 0.25  | 0.25  | 0.25  |
| $\text{K}_2\text{O}$ , wt%    | 0.30    | -     | -     | -     | -     | -     | -     | -     |
| $\text{Na}_2\text{O}$ , wt%   | 1.10    | 0.90  | 0.90  | 0.90  | 0.90  | 0.90  | 0.90  | 0.90  |
| $\text{Li}_2\text{O}$ , wt%   | -       | -     | -     | -     | -     | -     | -     | -     |
| $\text{B}_2\text{O}_3$ , wt%  | 1.80    | 1.30  | 1.30  | 1.30  | 1.30  | 1.30  | 1.30  | 1.30  |
| F, wt%                        | -       | -     | -     | -     | -     | -     | -     | -     |
| $\text{SiO}_2/\text{RO}$      | 2.50    | 2.09  | 2.09  | 2.09  | 2.09  | 2.09  | 2.09  | 2.08  |
| Log3 FT, °C                   | 1262    | 1220  | 1220  | 1219  | 1218  | 1215  | 1212  | 1211  |
| LT, °C                        | 1180    | 1155  | 1160  | 1158  | 1161  | 1157  | 1158  | 1153  |
| $\Delta T$ , °C               | 82      | 65    | 60    | 61    | 57    | 58    | 54    | 58    |
| References                    | [10]    | [9]   | [9]   | [9]   | [9]   | [9]   | [9]   | [9]   |

This composition, which serves as the control (Example 297), had a very high  $\text{SiO}_2$  level (60.12%), a very low  $\text{CaO}$  level (21.13%), a very low RO level (23.63%) and a very high  $\text{SiO}_2/\text{RO}$  ratio (2.54). As a result, it had a very high forming temperature (1285°C) and a very high delta temperature (96°C).

To arrive at the final set of compositions (Table VII) according to the trend line design protocol, percent  $\text{SiO}_2$  was reduced stepwise downward from the starting composition, percent  $\text{CaO}$  was increased stepwise, percent  $\text{Al}_2\text{O}_3$  was kept in a narrow range of 12.0-13.5%, and percent  $\text{MgO}$  was kept constant at ~2.5, until the lowest log3 forming temperature emerged that has a delta temperature of 50°C, and therefore no longer et the design requirements.

Table VII summarizes the third set of third-generation fluorine-free E-glass compositions, which was ultimately obtained by the design study. All compositions contain 1.3%  $\text{B}_2\text{O}_3$  and 9%  $\text{Li}_2\text{O}$ . The specific trend lines relating percent  $\text{SiO}_2$ , percent RO and the  $\text{SiO}_2/\text{RO}$  ratio to forming, liquidus and delta temperature can be found elsewhere [6].

A delta temperature of 55-65°C is required. It identifies the  $\text{SiO}_2$  level, RO level and the  $\text{SiO}_2/\text{RO}$  ratio at the lowest log3 forming temperature and provides a suitably crystallization resistant third generation E-glass containing <2%  $\text{B}_2\text{O}_3$  and <1%  $\text{Li}_2\text{O}$ . As a result, the lowest possible log3 forming temperature for this compositional variant is 1192°C. It is has a goal delta between log3 forming and liquidus temperature of 55-65°C. It has a  $\text{SiO}_2/\text{RO}$  ratio of ~2.20.

Table VII. New Third-Generation Fluorine-Free E-Glass Containing <2% B<sub>2</sub>O<sub>3</sub> & <1% Li<sub>2</sub>O [6]

| Examples [9]                         | Control | 185   | 184   | 180   | 181   | 179   | 182   | 178   |
|--------------------------------------|---------|-------|-------|-------|-------|-------|-------|-------|
| SiO <sub>2</sub> , wt%               | 60.12   | 57.80 | 58.50 | 58.30 | 57.90 | 58.10 | 58.22 | 58.00 |
| Al <sub>2</sub> O <sub>3</sub> , wt% | 13.00   | 13.43 | 12.76 | 13.03 | 13.23 | 13.03 | 13.36 | 13.03 |
| CaO, wt%                             | 21.13   | 23.64 | 23.61 | 23.54 | 23.74 | 23.74 | 23.40 | 23.84 |
| MgO, wt%                             | 2.50    | 2.50  | 2.50  | 2.50  | 2.50  | 2.50  | 2.50  | 2.50  |
| TiO <sub>2</sub> , wt%               | 1.10    | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  |
| Fe <sub>2</sub> O <sub>3</sub> , wt% | 0.25    | 0.23  | 0.23  | 0.23  | 0.23  | 0.23  | 0.23  | 0.23  |
| Na <sub>2</sub> O, wt%               | -       | -     | -     | -     | -     | -     | -     | -     |
| Li <sub>2</sub> O, wt%               | 0.90    | 0.90  | 0.90  | 0.90  | 0.90  | 0.90  | 0.90  | 0.90  |
| B <sub>2</sub> O <sub>3</sub> , wt%  | 1.00    | 1.00  | 1.00  | 1.00  | 1.00  | 1.00  | 1.00  | 1.00  |
| F, wt%                               |         |       |       |       |       |       |       |       |
| SiO <sub>2</sub> /RO                 | 2.54    | 2.21  | 2.24  | 2.24  | 2.21  | 2.21  | 2.24  | 2.20  |
| Log <sub>3</sub> FT, °C              | 1285    | 1197  | 1196  | 1195  | 1195  | 1194  | 1192  | 1192  |
| LT, °C                               | 1189    | 1139  | 1139  | 1140  | 1137  | 1135  | 1133  | 1137  |
| ΔT, °C                               | 96      | 58    | 58    | 55    | 58    | 59    | 63    | 55    |

## CRYSTALLIZATION POTENTIAL

### Continuous Process

The trend line design of compositional variants described in this paper (Figures 2-7) was pursued for each variant until the delta temperature dropped to about +15°C, while that described in the immediately preceding paper [5] was pursued in some cases until the delta temperature dropped to about -150°C.

Figure 8 shows the change of the forming and liquidus temperature for the SiO<sub>2</sub>/RO ratio of a ternary eutectic SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO composition [5] that results when the SiO<sub>2</sub> level is stepwise reduced and the RO level is stepwise increased, and both well beyond the level where the forming and liquidus temperature are the same and the delta temperature is 0°C.

In a continuous process, the commercial batch ingredients are continuously added to the melt on one end of the glass furnace and glass fibers are continuously withdrawn from multiple-tip bushings on the other end. A delta temperature of 55-65°C is required as a safety zone between log<sub>3</sub> forming and liquidus temperature (or ΔT).

A glass composition that has a lower delta temperature does not provide an adequate safety zone, and crystallization may occur in a slow moving, or near stationary, section of the melt, e.g., in a corner of the furnace, in an individual tip of a commercial bushing, or in the glass melt above the bushing. A higher delta temperature (e.g., 75-100°C) might be more desirable for a continuous process, but it would raise the forming temperature that must be kept at a minimum.

### Stationary Process

In a stationary laboratory process only a small glass sample (~50 grams) is melted in a small platinum crucible and extruded in a very short time (<½ hour) through a single tip (orifice) bushing to form a single continuous pristine glass fiber. In such a process [4], almost any melt, except one that instantly crystallizes on cooling, can be down-drawn at a lower delta temperature

than 55-65°C because crystallization will not occur in such a short time. Glass melts having a higher liquidus than log<sub>3</sub> forming temperature are known as “fragile” melts [1] [5].

As a matter of fact, pristine glass fibers can be formed in a single tip bushing process from glass melts not only having a much higher forming temperature than liquidus temperature, thus having a highly positive delta temperature (e.g.,  $\Delta T = +150^\circ\text{C}$ ) but also from glass melts having a much higher liquidus temperature than forming temperature, thus having a highly negative delta temperature (e.g.,  $\Delta T = -150^\circ\text{C}$ ).

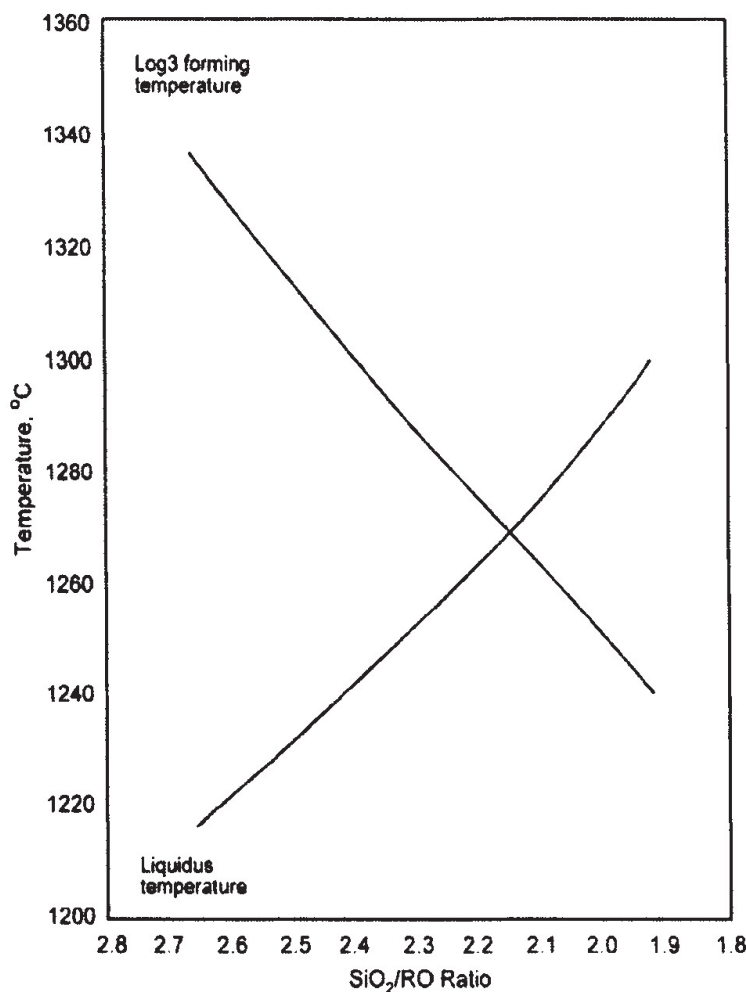


Figure 8. Typical Relationship between Log<sub>3</sub> Forming, Liquidus and Delta Temperature [5]

In both cases, the melt is extruded long before crystals can form at the liquidus temperature. One exceptional literature composition has been reported [12]. It has the highest negative delta temperature (-159°C) on record and reportedly crystallized while it was extruded through a single tip bushing.

## SUMMARY AND CONCLUSIONS

### Trend Line Design

Optimum second and third-generation environmentally friendly E-glass compositions were developed by the trend line design of experiments, an exploratory method aimed at discovering the path, with a limited number of trend-setting compositions, from a known composition with known properties to a goal composition with design-required properties. Compositional inputs (such as individual oxide levels) and melt property outputs (such as individual log3 forming temperatures, individual liquidus temperatures and individual delta temperatures) are codependent variables. Statistical tools, which treat compositional inputs and/or melt property outputs as independent variables, are not suitable for designing new glass compositions.

### Environmentally Friendly E-glass

The lowest log3 forming temperature has been achieved with a goal delta temperature for each compositional variant (Table VIII).

**Table VIII. Three Generations of Fluorine-Free Environmentally Friendly E-glass Compositions**

| Compositions                         | 621   | Control | First Generation E-Glass |       |       | Second | Third Generation |        |        |
|--------------------------------------|-------|---------|--------------------------|-------|-------|--------|------------------|--------|--------|
| SiO <sub>2</sub> , wt%               | 53.27 | 62.10   | 60.00                    | 60.00 | 60.10 | 57.75  | 58.35            | 56.60  | 58.00  |
| Al <sub>2</sub> O <sub>3</sub> , wt% | 13.98 | 14.60   | 15.00                    | 15.00 | 12.99 | 13.20  | 13.40            | 13.25  | 13.03  |
| CaO, wt%                             | 23.53 | 23.30   | 25.00                    | 20.00 | 22.13 | 24.25  | 23.55            | 24.60  | 23.84  |
| MgO, wt%                             | 0.61  | -       | -                        | 5.00  | 3.11  | 2.55   | 2.55             | 2.55   | 2.50   |
| TiO <sub>2</sub> , wt%               | 0.51  | -       | -                        | -     | 0.55  | 1.10   | 1.10             | 0.55   | 0.50   |
| Fe <sub>2</sub> O <sub>3</sub> , wt% | 0.36  | -       | -                        | -     | 0.25  | 0.25   | 0.25             | 0.25   | 0.23   |
| K <sub>2</sub> O, wt. %              | 0.10  | -       | -                        | -     | 0.14  | -      | -                | -      | -      |
| Na <sub>2</sub> O, wt%               | 0.93  | -       | -                        | -     | 0.63  | 0.90   | -                | 0.90   | -      |
| Li <sub>2</sub> O, wt. %             | -     | -       | -                        | -     | -     | -      | 0.90             | -      | 0.90   |
| B <sub>2</sub> O <sub>3</sub> , wt%  | 6.00  | -       | -                        | -     | -     | -      | -                | 1.30   | 1.00   |
| F, wt%                               | 0.48  | -       | -                        | -     | 0.04  | -      | -                | -      | -      |
| SiO <sub>2</sub> /RO                 | 2.21  | 2.67    | 2.40                     | 2.40  | 2.37  | 2.15   | 2.23             | 2.08   | 2.20   |
| Log3 FT, °C                          | 1174  | 1335    | 1294                     | 1299  | 1259  | 1232   | 1211             | 1211   | 1192   |
| LT, °C                               | 1068  | 1217    | 1235                     | 1225  | 1174  | 1166   | 1146             | 1153   | 1137   |
| ΔT, °C                               | 106   | 118     | 59                       | 74    | 85    | 66     | 65               | 61     | 55     |
| E-glass                              | +     | -       | +                        | +     | +     | +      | +                | +      | +      |
| References                           | [1]   | [5]     | [5]                      | [11]  | [4]   | [8]    | [6, 8]           | [6, 9] | [6, 9] |

The lowest log3 forming temperature of second-generation, environmentally friendly, boron- and fluorine-free E-glass is 26 to 103°C lower than that of the original first generation boron- and fluorine-free fiberglass compositions, and it has goal delta temperature of 55-65°C.

The lowest log3 forming temperature of fluorine-free third-generation E-glass containing either <2.0% B<sub>2</sub>O<sub>3</sub> or <1% Li<sub>2</sub>O is 47 to 124°C lower than that of the original first generation boron- and fluorine-free E-glass compositions. Both have a goal delta temperature of 55-65°C.

The lowest log3 forming temperature of fluorine-free third-generation E-glass containing both <2.0% B<sub>2</sub>O<sub>3</sub> and <1% Li<sub>2</sub>O is 65 to 143°C lower than that of the original first generation boron- and fluorine-free E-glass compositions, and it has goal delta temperature of 55-65°C.

The compositions, which have the lowest possible forming temperatures within each group along with a delta temperature of 55–65°C, have a specific SiO<sub>2</sub>/RO ratio that is characteristic of a melt that is crystallization resistant in a continuous commercial fiberglass furnace.

The log<sub>3</sub> forming temperatures for an incumbent E-glass composition that contains 6% B<sub>2</sub>O<sub>3</sub> and ~0.5% fluorine (621), for the ternary SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO eutectic control that is boron- and fluorine-free and for three successive environmentally friendly E-glass generations (I, II and III) are schematically represented in Figure 9. Third-generation E-glass compositions contain <1% Li<sub>2</sub>O (III-1), <2% B<sub>2</sub>O<sub>3</sub> (III-2) as well as <1% Li<sub>2</sub>O and <2% B<sub>2</sub>O<sub>3</sub> (III-3) respectively.

In summary, the new environmentally friendly E-glass compositions avoid emissions of particulates (boron) and hazardous vapors (fluorine) from fiberglass production furnaces with current environmental control systems.

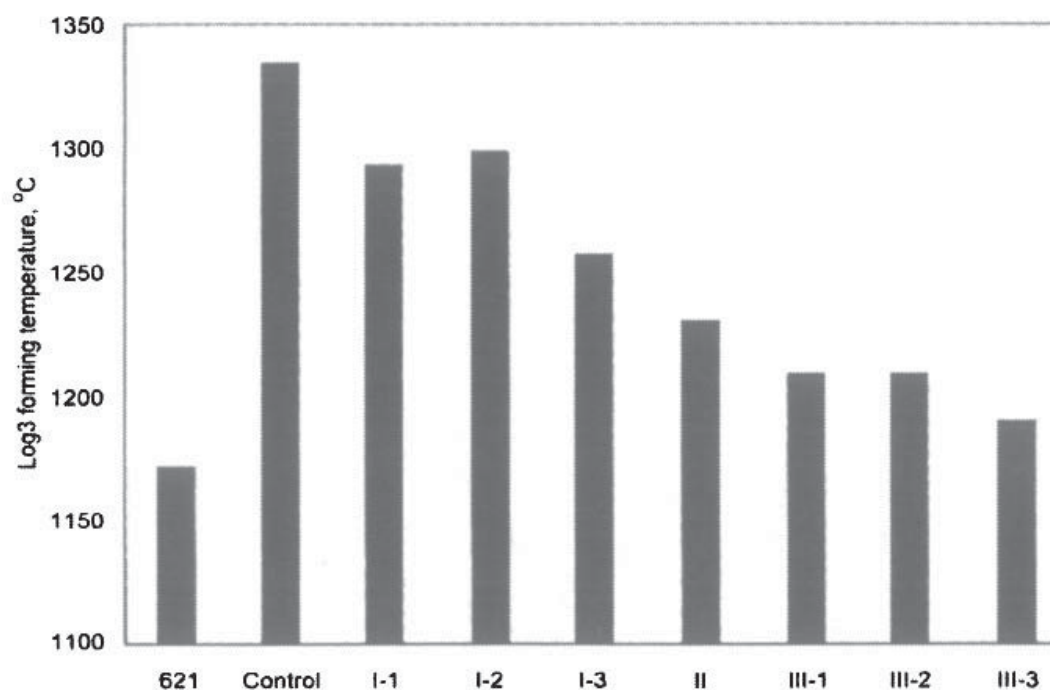


Figure 9. Log<sub>3</sub> Forming Temperatures of Environmentally Friendly E-Glass Compositions

In going from first- to second- and third-generation environmentally friendly E-glass compositions, the log<sub>3</sub> forming temperature decreases dramatically (Table VIII and Figure 9). The decrease suggests that increasing energy savings are possible. Consequently, the third-generation fluorine-free E-glass composition that contains 1% B<sub>2</sub>O<sub>3</sub> and 0.9% Li<sub>2</sub>O has a log<sub>3</sub> forming temperature that is only 18°C higher than that of the original incumbent E-glass composition that contains 6% B<sub>2</sub>O<sub>3</sub> and 0.5% fluorine.

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