

## **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 II: Fluorine-Free E-Glass Compositions Containing Low Levels of $\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O}$**

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### **Abstract**

Incumbent E-Glass compositions contain 6-8%  $\text{B}_2\text{O}_3$  and 0.1-1.0% fluorine. Partial emissions of these ingredients from commercial melt furnaces were recently identified as environmental hazards. Removal of all fluorine and of essentially all boron was required. But the resulting boron- and fluorine-free E-glass compositions posed another environmental concern. They had higher melt viscosities and fiber forming temperatures, and needed much more process energy. Second and third-generation fluorine-free E-glass compositions were therefore developed, which contained low levels of either  $\text{B}_2\text{O}_3$  or  $\text{Li}_2\text{O}$  and had a 26°C to 47°C lower forming temperature than optimum first generation compositions. This paper provides a detailed description of third-generation fluorine-free E-glass compositions, which contain low levels of both  $\text{B}_2\text{O}_3$  and  $\text{Li}_2\text{O}$ , have a 65°C lower forming temperature than optimum first generation boron and fluorine-free E-glass, and promise to offer major process energy savings.

### **Introduction**

Using a commercial glass furnace with a current environmental emission control system, incumbent high-boron and high-fluorine E-glass compositions (Table 1) emit boron and fluorine into the environment. First generation boron- and fluorine-free E-glass melts do not emit boron or fluorine from a fiberglass furnace into the environment, but they create another environmental concern. Removal of boron and fluorine increases the melt viscosity and the higher fiber forming temperatures. Due to the higher operating temperatures, the energy demand would increase and the lifetime of both the furnace linings and platinum bushings would decrease.

Several boron- and fluorine-free E-glass compositions are known [1] [2] [3] [4]. Two have been optimized, by earlier compositional design methods [3] [4] and one is shown in Table 1. All are environmentally friendly and those, which have been optimized [3] [4], also meet the ASTM specifications required for an E-glass.

Table 1. Incumbent E-glass Compositions and ASTM Specification

Incumbent E-Glass Compositions Meeting the ASTM Specifications	High Boron and High Fluorine 621	Boron- and Fluorine-Free 1 <sup>st</sup> Generation	Compositional Limits Required By ASTM
SiO <sub>2</sub> , weight %	53.27	59.30	52 to 62
Al <sub>2</sub> O <sub>3</sub> , weight %	13.98	12.10	12 to 16
CaO, weight %	23.53	22.60	16 to 25
MgO, weight %	0.61	3.40	0 to 5
TiO <sub>2</sub> , weight %	0.51	1.50	0 to 1.5
K <sub>2</sub> O, weight %	0.10	-	Alkali
Na <sub>2</sub> O, weight %	0.93	0.90	Oxides:
Li <sub>2</sub> O, weight %	-	-	0 to 2
Fe <sub>2</sub> O <sub>3</sub> , weight %	0.36	0.20	0.05 to 0.8
B <sub>2</sub> O <sub>3</sub> , weight %	6.00	-	0 to 10
F <sub>2</sub> , weight %	0.48	-	0 to 1.0
Forming T (log3 poise), °C	1174	1258	-
Liquidus T, °C	1068	1185	-
Delta (Δ) T, °C	106	73	-
SiO <sub>2</sub> /RO ratio	2.20	2.28	-
References	[1] [4] [5]	[1] [4] [5]	[1] [4] [5] [10]

To further reduce melt viscosity, forming temperature and energy demand, boron- and fluorine-free second-generation E-glass compositions were designed by trend line design of experiments [4], and were found to have a 26°C lower fiber forming temperature, shown in Table 1, than optimum first-generation boron- and fluorine-free E-glass composition [5].

Current environmental, or emission, control systems may not be able to remove fluorine at any level, but they may be able to remove boron emissions from melts containing <2% boron. However, a costly additional emission control system may be required for the commercial production of compositions containing >2% boron and/or more than barely minimal traces of fluorine.

As a result, fluorine-free third-generation E-glass compositions were designed by the trend line design of experiments [5] having either <2% B<sub>2</sub>O<sub>3</sub> or <1% Li<sub>2</sub>O (Table 2). Either compositional variant (Table 2, Examples 1 and 2) was found to offer a 47°C lower fiber forming temperature [5] than optimum first-generation boron- and fluorine-free E-glass versions [2] [3] shown in Table 1.

Table 2. Third-Generation Environmentally Friendly E-glass Types

Examples	1	2	3
Na <sub>2</sub> O	-	<1%	-
Li <sub>2</sub> O	<1%	-	<1%
B <sub>2</sub> O <sub>3</sub>	-	<2%	<2%
Reference	[5]	[5]	[5] [14]

The compositional design method has previously been discussed in detail [4] and the results of the final fluorine-free third generation E-glass composition (Table 2, Example 3) was included for comparison [5]. This paper analyzes in detail the specific trend lines that yielded optimum fluorine-free environmentally friendly E-glass compositions containing both <1% Li<sub>2</sub>O and <2% B<sub>2</sub>O<sub>3</sub> (Table 2, Example 3).

### Melt Properties

The standard for comparing the melt properties of fiberglass compositions is the temperature of a melt with a viscosity of 1000 (log3) poise. This temperature is also known as log3 fiber forming temperature. The viscosities were determined with a viscometer using ASTM method C965-81 [6]. The standard for determining, and inferring the crystallization potential of fiberglass melts is the liquidus temperature. It was determined in a gradient temperature furnace by ASTM method C829-81 [7]. At this temperature and below, crystals (solid) and melt (liquid) can form an equilibrium state.

The reference material for the viscosity of boron-free fiberglass compositions is the NIST Standard Reference Material (SRM) 710a [8], a soda lime silica glass. The reference material for the viscosity of fiberglass compositions containing 6-8% B<sub>2</sub>O<sub>3</sub> is the NIST Standard Reference Material (SRM) 717a, a borosilicate glass [9].

A useful parameter for comparing the crystallization potential of fiberglass melts is the delta temperature (ΔT) or the difference between the log3 forming temperature and the liquidus temperature since a continuous fiber forming process must be operated well above the liquidus temperature of the melt. In a commercial melt

furnace, the delta temperature must be 55-65°C. The ASTM Standard D 5290-81 (re-approved in 2000) states the composition limits for E-glass fiber strands [10].

### **Design Requirements**

Design of new glass compositions requires the discovery of new structure-property relationships to meet these demanding requirements: (1) The goal composition must have the lowest temperature at a melt viscosity of 1000 poise, or log3 fiber forming temperature, in a given compositional system to minimize the energy use. (2) It must have a delta between the log3 fiber forming and liquidus temperature of 55-65°C to avoid crystallization that might otherwise occur in a continuous melt furnace, and (3) it must meet the E-glass requirements as specified by ASTM.

### **Design Considerations**

A pure SiO<sub>2</sub> melt has a very high melt viscosity and a very low crystallization potential. A pure Al<sub>2</sub>O<sub>3</sub>, MgO or CaO melt has a very low melt viscosity, a high and sharp melting point and a very high crystallization potential. By combining SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and MgO (plus the other oxides) at a given weight ratio, each oxide makes its unique contribution to the resulting combination of melt viscosity (fiber forming temperature) and liquidus temperature (crystallization potential).

In a boron-free or low-boron E-glass composition, the melt viscosity that depends on the SiO<sub>2</sub> content, is much lower than that of pure SiO<sub>2</sub>, but it is much higher than that of pure CaO, MgO, Al<sub>2</sub>O<sub>3</sub> or the other oxides. And the crystallization potential that depends on the level of CaO, MgO, Al<sub>2</sub>O<sub>3</sub> and other oxides, is much lower than that of these ingredients in their pure state.

The contribution of Al<sub>2</sub>O<sub>3</sub> to both viscosity (fiber forming temperature) and liquidus temperature (crystallization potential) is predictable (Figure 1). The elastic modulus and, implicitly therefore, the forming temperature of oxide fibers containing both SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> [13], increases with increasing Al<sub>2</sub>O<sub>3</sub> content from borosilicate E-glass (14% Al<sub>2</sub>O<sub>3</sub>, 79 GPa, 1174°C) to sapphire fibers (100% Al<sub>2</sub>O<sub>3</sub>, 410 GPa, 2000°C). The resulting melt viscosity gradually drops and eventually results in a sharp melting point. And the resulting fiber morphology changes from amorphous (Quartzel, E-glass, S-glass, Sialon-1), to nanocrystalline (Sialon-2, Nextel, Altex), polycrystalline (Safimax, Almax, Fiber FP), and single crystal (Saphicon).

Moderately low levels of Al<sub>2</sub>O<sub>3</sub> (12-16%), which incidentally are required for a glass fiber to qualify as an E-glass, support the formation of crystallization resistant glass

fibers. This range of  $Al_2O_3$  is a key requirement but, per se, an insufficient condition to design new environmentally friendly E-glass composition having both an optimally low forming temperature and offering a crystallization resistant melt.

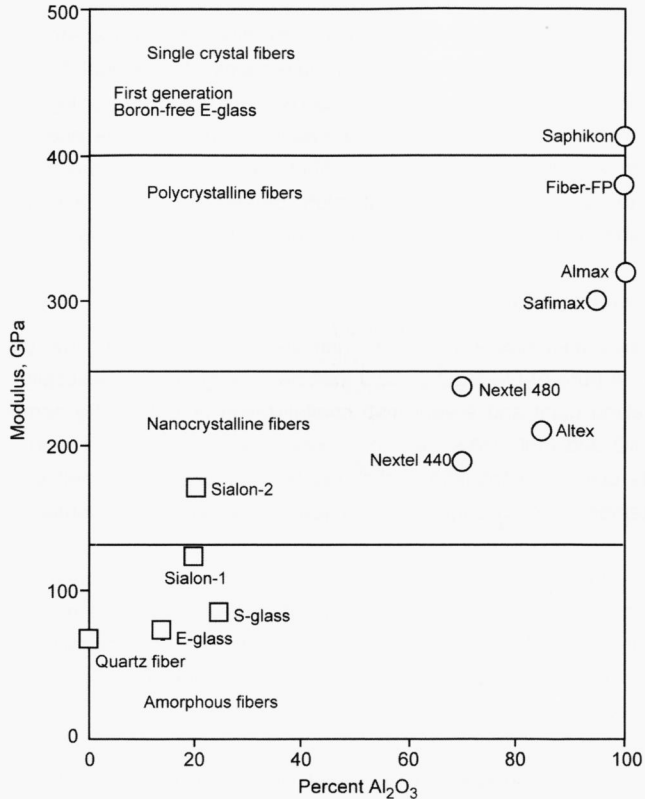


Figure 1. Elastic Modulus and Crystallization Potential of  $Al_2O_3$  Containing Fibers

Any further increase above 16%  $Al_2O_3$  will increase the crystallization potential of the resulting fiber, and it will eventually lead to a 100% single crystal  $Al_2O_3$  fiber (Saphikon). Any further decrease below 12%  $Al_2O_3$  will increase the melt viscosity and therefore the log3 fiber forming temperature. And it will eventually produce an amorphous 100%  $SiO_2$  fiber (Quartzel).

### Trend Line Design

Murach, Makat and Brückner [11] used a compositional design method that relies on a generic understanding of the contribution of each oxide. Aubourg and Wolf [12] additionally used "linear and complex regressions" in the design of experiments.

Trend line design takes these methodologies another step forward [4] [5] by quantifying the conceptual understanding of the contribution of each oxide in a given composition. 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 is not a statistical method, but it can and should be supplemented at each step in the design process, preferably near and around the goal composition, with statistical tools.

Trend line design is best started with a composition that comes as close as possible to the eutectic, i.e., having the lowest possible liquidus temperature. The eutectic of fluorine-free E-glass melts containing 1% B<sub>2</sub>O<sub>3</sub> and 0.9% Li<sub>2</sub>O [5] [15] was found at ~2.5% MgO (Figure 2). This starting composition (Figures 3 to 5) is accompanied by a very high forming temperature and therefore affords a high delta temperature.

Specifically, the design of third-generation environmentally friendly E-glass compositions containing 0.9% Li<sub>2</sub>O and 1% B<sub>2</sub>O<sub>3</sub> started with a composition that had a high SiO<sub>2</sub> level (60.12%), a low CaO level (21.13%), a low MgO level (2.50%), a low RO, or CaO plus MgO, level (25.5%) and a high SiO<sub>2</sub>/RO ratio (2.54). This composition had a very high log<sub>3</sub> forming temperature (1285°C), a very low liquidus temperature (1189°C), and a very high delta temperature (96°C).

Following the trend line design protocol, percent SiO<sub>2</sub> was reduced stepwise from that composition, percent CaO was increased stepwise, percent Al<sub>2</sub>O<sub>3</sub> was kept in a narrow range of 12.0-13.5%, and percent MgO was kept constant at ~2.5, until the lowest log<sub>3</sub> forming temperature emerged that has a delta temperature of 55-65°C.

Figure 3 shows the trends of the log<sub>3</sub> forming temperature (i.e., melt viscosity at 1000 poise) and liquidus temperature resulting from the stepwise reduction of SiO<sub>2</sub> until a composition had been reached with a delta of 50°C between its log<sub>3</sub> forming and liquidus temperatures. A delta temperature of 55-65°C identifies the SiO<sub>2</sub> level and log<sub>3</sub> forming temperature of a suitably crystallization resistant third generation, lithium-containing low-boron E-glass composition.

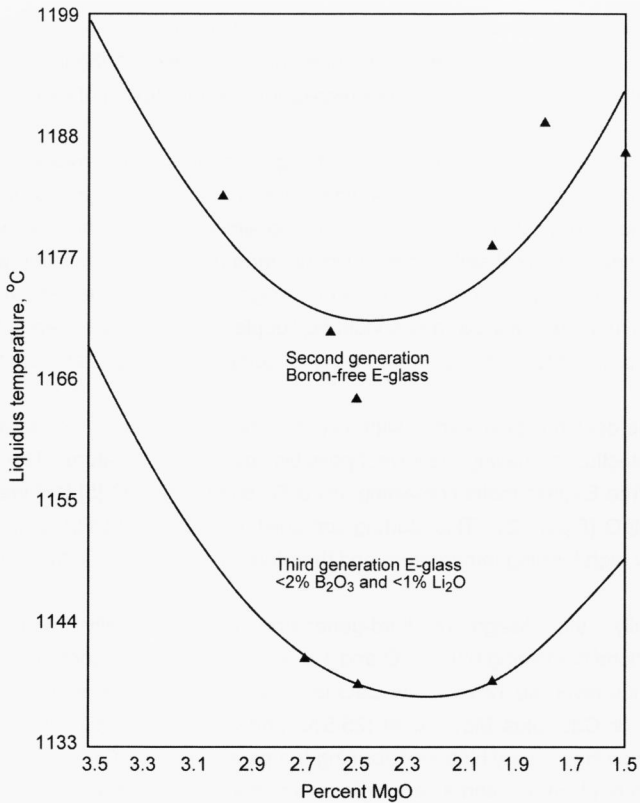


Figure 2. Eutectic with Regard to MgO for Fluorine-Free Third Generation E-Glass Compositions Containing <2% B<sub>2</sub>O<sub>3</sub> and <1% Li<sub>2</sub>O

Figure 4 shows the trends of log<sub>3</sub> forming and liquidus temperatures as the result of the stepwise increase of RO levels. Figure 5 shows the trends of the forming and liquidus temperatures as the result of the stepwise decrease of the SiO<sub>2</sub>/RO ratios [15]. A delta temperature of 55-65°C identifies the SiO<sub>2</sub>/RO ratio of a third-generation, lithium-containing low-boron E-glass composition that has the required crystallization resistance when used in a continuous commercial furnace.

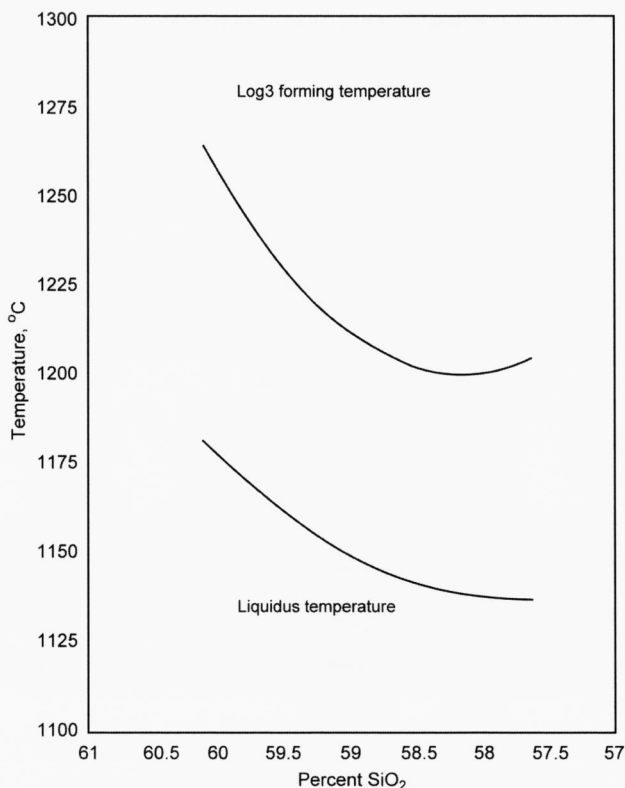


Figure 3. Trend Lines (%SiO<sub>2</sub> versus Melt Properties) for Third Generation Fluorine-Free E-Glass Compositions Containing 1% B<sub>2</sub>O<sub>3</sub> and 0.9% Li<sub>2</sub>O

In summary, the trend line design relies on a carefully planned sequence of individual compositions, each having a given percent SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO content. Although MgO is being kept constant, each composition has its own SiO<sub>2</sub>/RO ratio (RO=CaO+MgO). Each composition has a different combination of oxides. Compositional inputs (individual oxide levels) are co-dependent variables. Each composition has a different combination of forming, liquidus and delta temperature. These property outputs are also codependent. Trend line design of experiments can be further augmented with proper additional tools of regression analysis, statistical analysis and/or sigma logic. Statistical tools however, which treat



compositional inputs and melt property outputs as independent variables are not suitable for assisting in the design of new glass compositions.

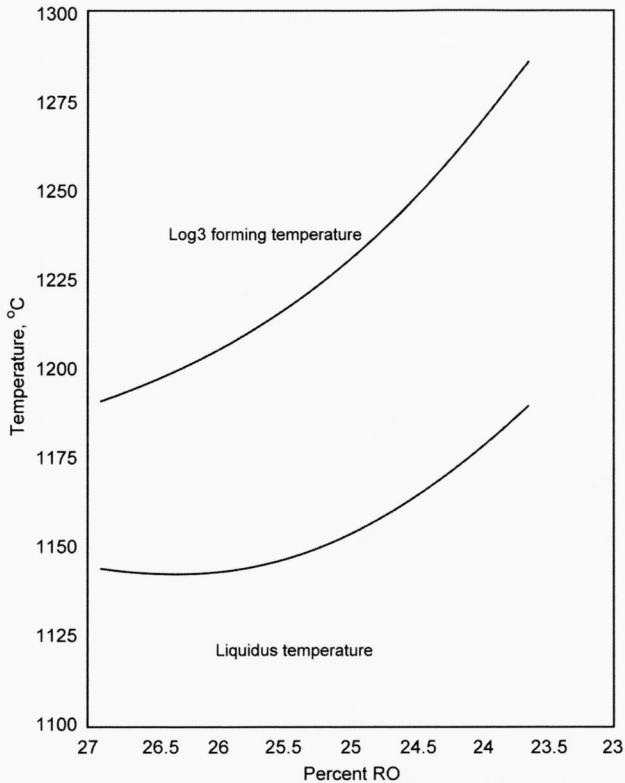


Figure 4. Trend Lines (%RO versus Melt Properties) for Third Generation Fluorine- Free E-Glass Compositions Containing 1%  $B_2O_3$  and 0.9%  $Li_2O$

Table 3 summarizes the final third-generation lithium-containing low-boron E-glass compositions, which were obtained by the design study. Thus, the lowest possible forming temperature for this compositional variant is  $\sim 1192^\circ C$ .

The specific composition that has the lowest forming temperature among fluorine-free E-glass compositions containing 1%  $B_2O_3$  and 0.9%  $Li_2O$  is accompanied by a

goal delta between forming and liquidus temperature of 55-65°C. This composition has a SiO<sub>2</sub>/RO ratio of ~2.20

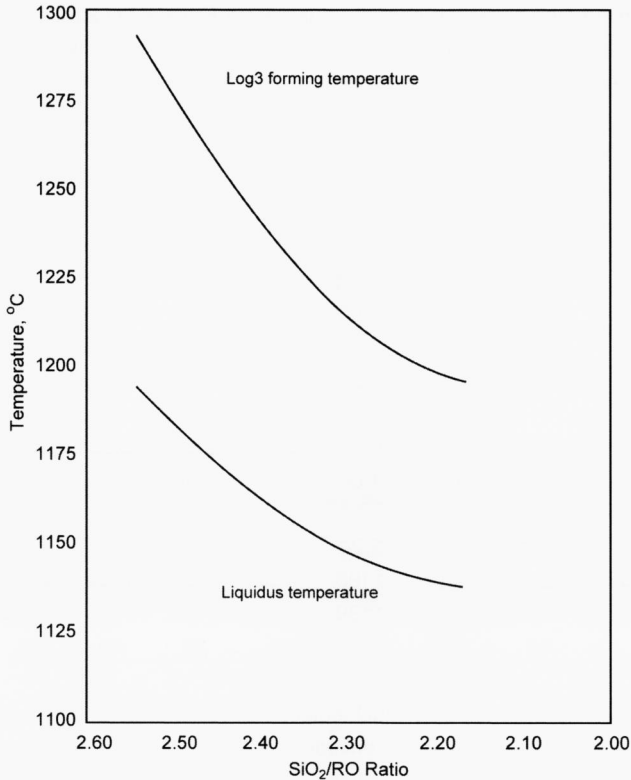


Figure 5. Trend Lines (SiO<sub>2</sub>/RO Ratio versus Melt Properties) for Third Generation Fluorine-Free E-Glass Compositions Containing 1% B<sub>2</sub>O<sub>3</sub> and 0.9% Li<sub>2</sub>O

### Summary and Conclusions

The lowest log3 forming temperature, as shown in Table 3, of the third-generation fluorine-free E-glass variant that contains <2.0% B<sub>2</sub>O<sub>3</sub> and <1% Li<sub>2</sub>O is 1192°C. It has a liquidus temperature of 1133-1137°C, a goal delta temperature of 55-62°C and a SiO<sub>2</sub>/RO ratio of 2.20-2.24. This composition is expected to be crystallization resistant in a continuous commercial fiberglass furnace.

Table 4 places the results in the perspective all E-glass compositions, which have so far been reported [1] [2] [3] [4] [5]. The ternary eutectic  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  composition from which the incumbent high-boron, high fluorine composition 621 E-glass is derived, serves as the control. It is not an E-glass because its  $\text{SiO}_2$  level exceeds 60%. The 621 composition is considered to be a derivative of the ternary eutectic since  $\text{MgO}$  is imported as tramp (impurity) from commercial ingredients.

Table 3. New Third-Generation Fluorine-Free E-Glass (<2%  $\text{B}_2\text{O}_3$  and <1%  $\text{Li}_2\text{O}$ )

Examples [9]	Control	185	184	180	181	179	182	178
$\text{SiO}_2$ , wt%	60.12	57.80	58.50	58.30	57.90	58.10	58.22	58.00
$\text{Al}_2\text{O}_3$ , wt%	13.00	13.43	12.76	13.03	13.23	13.03	13.36	13.03
$\text{CaO}$ , wt%	21.13	23.64	23.61	23.54	23.74	23.74	23.40	23.84
$\text{MgO}$ , wt%	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
$\text{TiO}_2$ , wt%	1.10	0.50	0.50	0.50	0.50	0.50	0.50	0.50
$\text{Fe}_2\text{O}_3$ , wt%	0.25	0.23	0.23	0.23	0.23	0.23	0.23	0.23
$\text{Na}_2\text{O}$ , wt%	-	-	-	-	-	-	-	-
$\text{Li}_2\text{O}$ , wt%	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
$\text{B}_2\text{O}_3$ , wt%	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
F, wt%								
$\text{SiO}_2/\text{RO}$	2.54	2.21	2.24	2.24	2.21	2.21	2.24	2.20
Log3 FT, °C	1285	1197	1196	1195	1195	1194	1192	1192
LT, °C	1189	1139	1139	1140	1137	1135	1133	1137
$\Delta\text{T}$ , °C	96	58	58	55	58	59	63	55

The quaternary  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$  eutectic shown in Table 4 serves as the control for successive fluorine-free environmentally friendly E-glass compositions and variants. All quaternary compositions shown in Table 4 are contain  $\text{MgO}$  that would have to be deliberately added from dolomite to a commercial composition.

Overall, the lowest log3 forming temperature of the optimum second-generation boron- and fluorine-free E-glass composition, as shown in Table 4, is 26 to 103°C lower than that of the original boron- and fluorine-free fiberglass compositions, but 85°C higher than that of the incumbent high-boron and high fluorine 621 E-glass.

The lowest log3 forming temperature of the third-generation fluorine-free E-glass variant containing either <2.0%  $\text{B}_2\text{O}_3$  or <1%  $\text{Li}_2\text{O}$  (Table 4) is 47 to 124°C lower than that of the original boron-free E-glass composition [1] [5], but still 58°C higher than that of the incumbent high-boron and high fluorine 621 E-glass composition.

Table 4. Three Generations of Environmentally Friendly E-glass Compositions [5]

Compositions	Ternary		Quaternary SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -CaO-MgO System**					
	<i>Eutectic</i>	621*	Eutectic	I	II	III-1	III-2	III-3
SiO <sub>2</sub> , wt%	62.10	53.27	60.00	60.10	57.75	58.35	56.60	58.00
Al <sub>2</sub> O <sub>3</sub> , wt%	14.60	13.98	15.00	12.99	13.20	13.40	13.25	13.03
CaO, wt%	23.30	23.53	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	2.67	2.21	2.40	2.37	2.15	2.23	2.08	2.20
Log3 FT, °C	1335	1174	1299	1259	1232	1211	1211	1192
LT, °C	1217	1068	1225	1174	1166	1146	1153	1137
ΔT, °C	118	106	74	85	66	65	61	55
E-glass	-	+	+	+	+	+	+	+
References	[5]	[1]	[11]	[4]	[8]	[6, 8]	[6, 9]	[6, 9]

\* MgO is imported as tramp (impurity) from commercial ingredients; \*\* MgO is deliberately added

The lowest log3 forming temperature of the third-generation fluorine-free E-glass variant containing both <2.0% B<sub>2</sub>O<sub>3</sub> and <1% Li<sub>2</sub>O (Table 4) is 65 to 143°C lower than that of the original boron-free E-glass composition [1] [5] [14] [16] but only 18°C higher than that of the incumbent high-boron and fluorine 621 E-glass composition.

The dramatic decrease in log3 forming temperatures shown in Table 4 suggests that increasing energy reductions have been achieved starting with the original ternary eutectic and by going from optimum first to optimum second and optimum third generation environmentally friendly E-glass compositions.

In summary, the effect of 1% B<sub>2</sub>O<sub>3</sub> and 0.9% Li<sub>2</sub>O on log3 forming temperature (and/or energy demand) in a properly designed third generation fluorine-free E-glass composition nearly equals that of 6% B<sub>2</sub>O<sub>3</sub> and 0.5% fluorine in the incumbent commercial E-glass, independent of which other specific composition in Table 4 one might selected as an additional control.

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