Glasses within the ternary system Li2O–B2O3–SiO2 containing less than 25.6% Li2O can be broadly classified into three groups according to their behavior during cooling or heating. One group, containing either more than 18% Li2O or less than 20% SiO2 yields clear glasses during slow or rapid cooling. The second group, containing approximately 5 to 15% Li2O and 26 to 90% SiO2 yields dense white opal glass during slow or rapid cooling. The third group, located at the outer edge of the second group, cools to room temperature as clear glasses but develops opacity when reheated to temperatures between 550° and 880°C. It has been shown by electron microscopy that the opacity is due to liquid immiscibility, the matrix glass containing well-formed phases of the dispersed phase. Some of the clear glasses of both groups have been shown to consist of two immiscible phases. The size of the dispersed units in the spontaneous opal glasses and also the reheat opal glasses can be controlled by the variation of the reheat treatments. The phase separation reported here is beyond the resolution of the petrographic microscope and can be detected only with the high resolution of the electron microscope. Accessory evidence is given to show that the phases are non-crystalline.

I. Introduction and Literature Survey

The existence of liquid immiscibility in three systems of the RO–B2O3–SiO2 type has been observed with the help of the petrographic microscope by several investigators. Among systems of the type R2O–B2O3–SiO2, a patent has been issued on a process for making high-silica glasses (Vycor brand) based on claims and descriptions of liquid immiscibility in the three systems forming Li2O, Na2O, and K2O. In the recent work of Morey on the system Na2O–B2O3–SiO2, flat liquidus curves were obtained on certain joins such as Na2O–4B2O3–SiO2 suggesting the possibility of immiscible liquids, but no claims were made for their existence, using the petrographic microscope as the method of phase identification.

Several other workers have concentrated on the system Na2O–B2O3–SiO2 with the electron microscope, low-angle X-
ray scattering, and light-scattering techniques and have claimed microheterogeneity or immiscibility effects.

Handwerk and McVay\(^4\) in reporting on the thermal expansion of some glasses in the system Li\(_2\)O-B\(_2\)O\(_3\)-SiO\(_2\) noted that glasses containing less than 20\% Li\(_2\)O by weight were not transparent.

Levin and Block\(^5\) recently have proposed structural models for the interpretation of liquid immiscibility in oxide systems, and much of the literature was reviewed during the course of this work.

The nature of the two-liquid separation in the system Li\(_2\)O-B\(_2\)O\(_3\)-SiO\(_2\) was presented in a brief summary of recent experimental work in the general field of liquid immiscibility.\(^7\) The purpose of this paper is to present a complete description of the nature and extent of two-liquid separation in the system Li\(_2\)O-B\(_2\)O\(_3\)-SiO\(_2\).

### II. Experimental Procedure

1. **Raw Materials and Preparation of Glasses**

C.p.-grade lithium carbonate\(^*\) and luminescent-grade boric acid and silicic acid were used. Mixing the batches in acetone or alcohol caused a slight discoloration of the mixture during the early stages of sintering and melting, probably owing to incomplete evaporation and subsequent decomposition of the mixing medium. Hence the batches were mixed dry, sintered on a low Bunsen flame, ground, screened, and finally melted to a glass in platinum in a Globar furnace. The quenched melt was repeatedly ground and melted (two or three times) until the glass looked homogeneous under the petrographic microscope.

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\(^*\) Supplied by the Lithium Corporation of America, Minneapolis, Minn.
(2) Methods

The glasses were examined in five different ways: (1) visual inspection of color and translucency, (2) petrographic examination of color, homogeneity, and appearance using transmitted light, (3) X-ray diffraction, (4) electron diffraction, and (5) electron microscopy.

For visual inspection, a 5- to 10-gm. melt of the glass was poured on a platinum sheet in the form of beads weighing about 1 gm. each. The beads cooled to room temperature in a few seconds. The visual appearance of rapidly chilled glass obtained by quenching the outside of the crucible in water also was studied.

For optical and X-ray study, glass prepared as described above was powdered and used. A Norelco wide-angle Geiger counter diffractometer was used for X-ray diffraction study. Relatively flat fractured surfaces of the glass were used for electron diffraction study by reflection using an RCA model EMU-2 electron diffraction unit. A conducting layer of platinum was evaporated on the underside of the glass sample to prevent accumulation of charge in the sample.

An RCA model EMU-2D unit was used for electron microscopy. The preparation of the sample is briefly described as follows: The glass obtained by quenching the melt in water or by cooling in air was fractured. Four to six representative pieces of glass with a relatively flat and smooth surface were evacuated. Platinum was evaporated at approximately 20° incidence followed by evaporation of carbon at normal incidence. The replica was floated either in distilled water or in hydrofluoric acid, mounted on 200-mesh electrolytically etched copper-grid screens in a diameter. In general, four to six screens for each composition of glass were examined.

III. Results and Discussion

(1) General

The compositions studied are listed in Table I and are indicated in Fig. 1. They comprise the major portion of the glassforming region in the system Li2O–B2O3–SiO2 and range in composition from 1 to 25.6 weight % Li2O, 2 to 80 weight % B2O3, and 15 to 90 weight % SiO2.

(2) Visual Characteristics

The glasses can be classified into three groups based on their visual appearance.

The first group of glasses contain either 18 weight % or more of Li2O or 20 weight % or less SiO2. The melts are fairly fluid and cool to clear glasses even during cooling in air from the temperatures mentioned in Table I. Such compositions are denoted by open circles in Fig. 1.

The second group of glasses contain 5 to 15 weight % Li2O and 26 to 90 weight % SiO2. The melts are clear and more viscous than those of the first group, and opacity develops very readily during cooling, whether slow or rapid. For instance, when the crucible containing the melt is cooled in air, intense white opacity develops first around the periphery of the melt and spreads into the bulk of the glass, resulting in a dense uniform opacity. When the outside of the crucible containing the melt is quenched in water, a thin layer of glass immediately adjacent to the walls of the crucible remains relatively clear while the bulk of the glass becomes opal. The appearance varies from light bluish white to dense white, depending on the composition, the temperature from which the melt is quenched, and the rapidity of quenching. All such light bluish-white opal glasses can be made dense white opal during subsequent reheating at a lower temperature. Glasses belonging to the second group are denoted by solid circles in Fig. 1.

The third group of glasses is located at the outer edge of the opal glass region mentioned above. The melts form clear glasses even during slow cooling in air. They develop opacity, however, during subsequent reheating at a temperature considerably below that at which they were initially melted. The intensity of opacity depends on the composition and on the temperature and duration of reheating. Such compositions are indicated by half-filled circles in Fig. 1. The boundary of the region wherein opal glasses can be obtained either spontaneously or during reheating is outlined in Fig. 1.

(3) Petrographic Study

The three types of glasses described above were examined under the petrographic microscope. No unusual appearance was present in the clear glasses. The opal glasses were a uniform light brown under transmitted light and a pale white under crossed Nicol, owing to scattered light. No evidence of crystallinity or inhomogeneity was present.

(4) X-Ray and Electron Diffraction

X-ray diffraction patterns of several powdered clear and opal glasses as well as a reflection electron diffraction pattern of opal glass No. 27 prepared by cooling the melt in air from 1075°C showed no evidence of crystallinity.

(5) Electron Microscopy

(A) General: In the absence of any evidence of crystallinity by optical, X-ray, and electron diffraction methods, the cause of the scattering of light was to be sought in the existence of two glassy phases, constituting liquid immiscibility. The necessary evidence was obtained by a detailed electron microscopic examination of glasses representing the three types described in section (1). The compositions, visual appearance, heat-treatment, an index to the electron micrographs, and the approximate size of the dispersed units are given in Table II.

The replica method used for the study of fractured surfaces already has been described. The nature of the immiscibility revealed by the electron microscope was generally uniform in several replicas prepared from a glass of the same composition. It is characterized by the presence of two phases, one of which is uniformly dispersed in the shape of more or less spherical particles in a matrix glass. The shape, size, and the density of distribution of the dispersed phase depend on the composition and the heat-treatment of the glass.

The positive prints of the electron micrographs are reproduced in this paper.
Table II. Electron Microscope Data on Li$_2$O-B$_2$O$_3$-SiO$_2$ Glasses

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Composition (wt. %)</th>
<th>Melting temp. and heat-treatment</th>
<th>Visual appearance</th>
<th>Approx. diameter of dispersed phase (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li$_2$O</td>
<td>BeO</td>
<td>SiO$_2$</td>
<td>1150°C, quenched</td>
</tr>
<tr>
<td>42</td>
<td>20.0</td>
<td>10.0</td>
<td>70.0</td>
<td>1000°C, quenched</td>
</tr>
<tr>
<td>43</td>
<td>20.0</td>
<td>15.0</td>
<td>65.0</td>
<td>1450°C, quenched</td>
</tr>
<tr>
<td>17</td>
<td>8.8</td>
<td>20.5</td>
<td>70.7</td>
<td>1205°C, quenched</td>
</tr>
<tr>
<td>18</td>
<td>9.0</td>
<td>65.0</td>
<td>26.0</td>
<td>1075°C, quenched</td>
</tr>
<tr>
<td>21</td>
<td>10.0</td>
<td>15.0</td>
<td>75.0</td>
<td>Melted in air from 1100°C.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1300°C, quenched</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Melted from 1300°C to 1200°C, held for 1 hour and quenched</td>
</tr>
<tr>
<td>27</td>
<td>10.3</td>
<td>48.1</td>
<td>41.6</td>
<td>1075°C, cooled in air</td>
</tr>
<tr>
<td>29</td>
<td>15.0</td>
<td>5.0</td>
<td>80.0</td>
<td>1300°C, quenched</td>
</tr>
<tr>
<td>27</td>
<td>10.3</td>
<td>48.1</td>
<td>41.6</td>
<td>Melted at 1500°C, for 1 hour, cooled to 1000°C, and held for 4 hr., quenched</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Above glass cooled to 600°-670°C, held for 4 days, quenched</td>
</tr>
<tr>
<td>27</td>
<td>10.3</td>
<td>48.1</td>
<td>41.6</td>
<td>1500°C, quenched</td>
</tr>
<tr>
<td>27</td>
<td>10.3</td>
<td>48.1</td>
<td>41.6</td>
<td>1400°C, quenched, reheated at 800°C for 2 hr.</td>
</tr>
<tr>
<td>27</td>
<td>10.3</td>
<td>48.1</td>
<td>41.6</td>
<td>1500°C, quenched, reheated at 800°C for 24 hr.</td>
</tr>
</tbody>
</table>

* Relatively clear portion of the glass from the periphery of the quenched melt was used.
† The top surface of the quenched melt, not a fractured surface, was used.

The results of electron microscopy of glasses representing the three types shown in Fig. 1 are discussed below. Freshly fractured surfaces of the glasses were used for electron microscopy unless otherwise stated.

(B) Clear Glasses: Compositions Nos. 42 and 43 (Table II) form clear glasses which are homogeneous under the petrographic microscope. The corresponding electron micrographs are shown in Figs. 2 and 3. Some variation in the appearance of the replicas made from glass No. 42 was present as shown in Fig. 2 (A) and (B). It nevertheless is apparent that no pronounced structure interpretable in terms of liquid immiscibility is noticeable in this case. The appearance of glass No. 43 after quenching from 1000°C is shown in Fig. 3. The presence of two phases, one of which exists as somewhat elongated channels dispersed in the matrix glass, is apparent.

It is significant, however, that this glass is completely homogeneous under the petrographic microscope.

(C) Glasses Which Develop Opacity Readily: Evidence of liquid immiscibility was more strikingly visible in the glasses which developed opacity spontaneously when the melt was cooled in air or quenched in water. In the latter case, the layer of glass immediately adjacent to the walls of the crucible remains relatively clear while the bulk of the glass develops a bluish to dense white opacity, depending on the composition of the glass and the temperature of quenching.

Figure 4 shows the variation in the appearance of immiscibility with temperature in glass No. 17. The melt was quenched from 1450°C, and the relatively clear pieces of glass near the periphery of the melt were examined. The structure (Fig. 4 (A)) shows a considerable degree of immiscibility,

![Fig. 2. Glass No. 42 (20% Li$_2$O, 10% BeO, 70% SiO$_2$) quenched from 1150°C. (A) and (B) show some variation in appearance of surface. (×27,000.)](image)

![Fig. 3. Glass No. 43 (20% Li$_2$O, 15% BeO, 65% SiO$_2$) quenched from 1000°C. (×15,000.)](image)
the dispersed phase being present in the form of very fine spherical to irregularly shaped particles.

A dense opal glass is obtained by quenching the melt from 1250°C. The relatively more pronounced nature of immiscibility is clearly visible from Fig. 4 (B). The dispersed phase consists of more or less spherical particles of nearly uniform size distributed in the matrix glass.

Figure 5 shows the appearance of immiscibility in opal glass No. 18. Melts rapidly quenched in water from 1075°C and cooled more slowly in air from 1100°C possessed the structure seen in Fig. 5 (A) and Fig. 5 (B) respectively. In both cases, the glass became opaque, more intensely in the latter. Although immiscibility exists in both cases, the relatively large size of the dispersed particles may be noted.

Figures 6 (A) and (B) show the effect of the variation of temperature on the nature of immiscibility in glass No. 21. On quenching the melt from 1300°C. (Fig. 6 (A)) the shape of the particles of the dispersed phase as well as their distribution indicates a certain amount of flow or spreading in the
matrix glass. Figure 6 (B) shows the appearance of the opal glass which was melted at 1300°C, cooled to 1200°C, held for 1 hour, and quenched. The appearance of immiscibility is more pronounced. The dispersed phase is more spherical in character and the spheres are larger in size. The amount of the dispersed phase also appears to have increased as compared with that in Fig. 6 (A).

To study the appearance of immiscibility at the surface of an opal glass as compared with that within the bulk, a replica was made from the top surface of a melt (not a fractured surface) quenched from 1300°C. Figure 6 (C) shows that the two phases do exist at the surface of the glass as well as in the interior mass (cf. Fig. 6 (A)). The appearance of immiscibility at the surface, however, is not brought out clearly in the electron micrograph owing to the smoother character of the surface.

The appearance of glass No. 27, which developed a dense opacity during cooling from 1075°C, is shown in Fig. 7. The nature of immiscibility present is again typical of that indicated by other dense opal glasses described above. It may be noted that the dispersed phase consists of nearly perfect spheres.

Figure 8 shows the immiscibility present in a light bluish opal glass prepared by quenching a melt of composition No. 29, near the lithium disilicate composition, from 1300°C. (X15,000.)

The change in the appearance of immiscibility produced by reheating a glass of composition No. 1 at a constant temperature for different periods of time is illustrated in Fig. 10. The appearance of a clear glass prepared by quenching a melt from 1500°C is shown in Fig. 10 (A). The presence of small spherical particles dispersed in the matrix glass is evident.

A clear glass prepared by quenching a melt from 1400°C became opal on reheating at 800°C for 2 hours. The distinct development of immiscibility consequent to this heat-treatment may be seen in Fig. 10 (B). In particular, an almost perfect sphericity of the particles, a relatively large size of the spheres (0.18 to 0.37 μ in diameter), and a difference in the microstructure within the spheres and that of the matrix glass may be noted. The glass quenched from 1500°C was reheated at 800°C for 24 hours. Corresponding to the increase in the duration of reheating, the size of the dispersed spheres increased further to a strikingly large diameter of about 0.44 to 0.67 μ as seen from Fig. 10 (C).

Effect of Replacing Na₂O by Li₂O: The effect of the successive replacement of Na₂O by Li₂O in a glass of composition Na₂O·B₂O₃·4SiO₂ was studied. The compositions,
Fig. 10. Glass No. 2 (2 % Li₂O, 33 % B₂O₃, 65 % SiO₂). (A) Quenched from 1300°C, (B) reheated at 800°C. for 2 hours, and (C) reheated at 800°C. for 24 hours. (×15,000)

Table III. Electron Microscope Data on Li₂O-Na₂O-B₂O₃-SiO₂ Glasses

<table>
<thead>
<tr>
<th>Mode ratio</th>
<th>Weight %</th>
<th>Heat-treatment</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O- B₂O₃·4SiO₂</td>
<td>Li₂O</td>
<td>Na₂O</td>
<td>B₂O₃</td>
</tr>
<tr>
<td>0.5 Li₂O</td>
<td>4.2</td>
<td>8.7</td>
<td>19.6</td>
</tr>
<tr>
<td>0.5 Na₂O</td>
<td>0.5 Li₂O</td>
<td>B₂O₃·4SiO₂</td>
<td></td>
</tr>
<tr>
<td>0.8 Li₂O</td>
<td>6.9</td>
<td>3.6</td>
<td>20.1</td>
</tr>
<tr>
<td>0.2 Na₂O</td>
<td>0.8 Li₂O</td>
<td>B₂O₃·4SiO₂</td>
<td></td>
</tr>
<tr>
<td>0.1 Na₂O</td>
<td>0.9 Li₂O</td>
<td>B₂O₃·4SiO₂</td>
<td></td>
</tr>
<tr>
<td>Li₂O· B₂O₃·4SiO₂</td>
<td>Li₂O</td>
<td>8.8</td>
<td>20.5</td>
</tr>
</tbody>
</table>
Fig. 1. Glasses in the system Li$_2$O–Na$_2$O–B$_2$O$_3$–SiO$_2$. (A) 16.7% Na$_2$O, 18.7% B$_2$O$_3$, 64.6% SiO$_2$ melted at 1250°C and reheated at 700°C for 2 days (X27,600). (B) 4.2% Li$_2$O, 8.7% Na$_2$O, 19.6% B$_2$O$_3$, 67.5% SiO$_2$ with same heat-treatment as (A) (X15,000). (C) 4.9% Li$_2$O, 3.6% Na$_2$O, 20.1% B$_2$O$_3$, 69.4% SiO$_2$ quenched from 1200°C (X15,000); (D) 7.8% Li$_2$O, 1.8% Na$_2$O, 20.3% B$_2$O$_3$, 70.1% SiO$_2$ with same heat-treatment as (C) (X15,000).

heat-treatment, and the index to the related electron micrographs are presented in Table III.

A gradual change in the appearance of the structure with increasing substitution of Li$_2$O is evident from Figs. 11 (A) through (D) and 4 (B). A corresponding increase in the degree of opacity was also observed.

IV. Conclusions

(1) Phase separations detectable by the electron microscope are easily achieved in quenched, slowly cooled, or reheated lithium borosilicate melts.

(2) In many cases, the phase separation takes the form of nearly perfect spheres, droplets, or lenses immersed in a matrix which might serve as an ideal medium for light-scattering studies or as a base for a fundamental approach to the effect of submicron particle size on light diffusion.

(3) In view of the lack of interconnecting channels or capillaries in these structures, it would appear that leaching with chemical reagents would be relatively ineffective in producing high-silica skeletons which could be subsequently reheated and reconstituted to clear glasses.

(4) The system can be considered as an intermediate link between the petrographically easily observable immiscibility in the alkaline-earth borosilicate systems and the difficultly interpretable heterogeneity of the soda and potash borosilicate systems.

Acknowledgment

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