Physico-Chemical Properties of
Tl₂O-B₂O₃-SiO₂ Glasses and Their Phase Separations

by

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Tl₂O—B₂O₃—SiO₂ 유리의 物理化學의 性質 및 그의 分相

金 基 成

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要 約

9 편의 選ば된 탈리움 네트리유리와 21 호의 鉄酸塩 유리에 對하여 物理化學的 性質을 評

定하였다. 이들 鋼성에 依한 性質의 變化曲線은 여러 點에서 異化 Slovakia, 소리 및 塩化塩などを 包容하는

다른 組成曲線에 順였았다. 탈리움 鉄酸塩 유리의 組成에 関한 性質의 變化曲線에 極少點이

나타났는데, 이는 Na₂O—B₂O₃—SiO₂ 유리에서 觀察된 마찬가지, 硅酸塩 유리의 變化에 基因하는 것 같다.

탈리움 이온이 鉄酸塩 유리에 미치는 主 影響은 綜合에 보면 明確하다. 1) 탈리움 이온을 添加함으로써 密度, 截折率, 頭에 對한 溶解度, 熱線膨脹係數, 溶電係數 등이 增加

되었었다.

2) 탈리움 溶解度 增加함으로써 유리의 軟化點이 降下되었고, 紫外線 散射에 順하여 結晶이 생겼으

며, 赤外線 15μ부근의 吸收帯이 不明確해 졌다.

Tl₂O—B₂O₃—SiO₂ 系에서 高纯度 無雜質不混合金이 電子顯微鏡에 依하여 影響이 민감하다. 不混合金은 B₂O₃—SiO₂

二成分系에 對하여 토 Tl₂O 55 wt. %의 組成範圍내에서 나타났다. 不混合金유리는 多 角錐과 多 四面角으

로 된 銀密이 있음을, 溶解度에 對하여, 影響이다.

ABSTRACT

The physico-chemical properties of nine selected thallium borosilicate glasses and other 21 supplementary compositions were investigated. Their composition-property curves are found to be in many respects analogous to those of other borosilicate glasses containing lithium, soda, and lead oxide. It is indicated that certain minima found in the composition-property curves of thallium borosilicate glasses might be caused by a change in boron coordination as has been observed to occur in the Na₂O-B₂O₃-SiO₂ glasses. Typical effects of thallium ions on the borosilicate glass are summarized as follows:

1) Addition of thallium ions increased density, refractive index, water solubility, linear coefficient of thermal expansion, and dielectric constant.

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2) Increased concentration of thallium decreased the softening point of the glasses, caused fluorescence under ultraviolet radiation and smeared out the absorption edges up to 15 μ in the infrared region.

An extensive liquid immiscibility was found by replication electron microscope technique in the Tl₂O—B₂O₃—SiO₂ system. The immiscibility covers a composition range roughly from 55 wt. % Tl₂O to the binary system B₂O₃—SiO₂. By acid treatment, it was found that the immiscible glass consists of separate silica-rich and boron-rich phases.

Introduction

The chemical properties of thallium compounds are quite interesting. In some respects they are similar to those of the alkali metals, and in other respects, they are similar to those of the heavy metals: lead, silver, and gold. The reason for this may be that the cations of thallium(1), the alkali metals, silver, and gold have the same valency and possess similar ionic radii. In the thallium and lead ions, Sidgwick's "inert pair" could play an important role in explaining their chemical stability.

In oxide glasses containing thallium and lead ions, the easy deformability of the ions having outer shells of (18 + 2) electrons leads to the unusually high optical refractivity and extensive solubility of the oxide glasses. Nevertheless, scant literature data for the system Tl₂O—B₂O₃—SiO₂ glasses are available in contrast to the abundant data available for the systems Li₂O—B₂O₃—SiO₂, Na₂O—B₂O₃—SiO₂ and PbO—B₂O₃—SiO₂. Because of the chemical similarities of the ions of lithium, sodium, lead and thallium, a liquid immiscibility may be postulated in the Tl₂O—B₂O₃—SiO₂ glasses analogous to those in the Li₂O—B₂O₃—SiO₂, Na₂O—B₂O₃—SiO₂ and PbO—B₂O₃—SiO₂ systems.

The main purpose of the present investigation is to explore physico-chemical properties of Tl₂O—B₂O₃—SiO₂ glasses and to determine the liquidus relationships, especially, the phase separation in the glassy state.

Experimental Procedure

Reagents and Preparation of Specimens

Chemically pure thallium oxide powder, fused boric acid and silicic acid, all supplied by Fisher Scientific Company, were used. The spectrochemical analysis of the thallium oxide is given in Appendix I.

The reagents were weighed using their correction factors, mixed in alcohol, dried, and then melted to a glass at temperature between 800°C and 1500°C for 1/2 to 6 hours in platinum ware using a Glober furnace. The quenched glasses were ground to —200 mesh, and then remelted in order to insure the uniformity of the melts. After this the melts were quenched over cold water in order to crack the glasses into a few large chunks.

A part of the melt was also poured directly into a graphite die in order to form a glass cylinder 0.64 cm (D) × 5.1 cm (L).

Methods of Analysis

Observations

The glasses were observed in various ways: 1) by visual examination of transparency, opacity, and color, 2) by petrographic microscope observation of the homogeneity and crystalline phases, 3) by X-ray diffraction, and 4) by electron microscope examination. In the X-ray diffraction study, a General Electric XRD-5 diffractometer unit was used employing CuKα radiation. The electron micrographs were obtained by using a Japan Electron-Optic Company GAS unit. For this purpose, the two step carbon replica technique was applied on the freshly fractured glass surface by using chrome as a shadowing material at approximately 30° incidence.

Measurements

1) The pycnometer density was measured at room temperature using —200 mesh (Taylor system) glass powder in a kerosene media.

2) The refractive index of the glasses was measured by the Becke line technique which used a petrographic microscope and a white light. Its precision was not more than ±0.003.

3) The water solubility was taken by measuring
the weight percent of the soluble portion after filtering
out the undissolved portion, over the initial weight.
Before filtering, the solution of —200 mesh glass
powder was held in boiling water for one hour.

4) The *coefficient of linear thermal expansion* (C.
T. E.) was measured at a range from room temperature
to 250°C by the dilatometer technique. The experimen-
tal details are described in ASTM-E-228-63T.

5) The *softening temperatures* were estimated by the
inflection point of D.T.A. curves by using —200 mesh
glass powders and calcined alumina as a reference
material. A du Pont 900 Differential Thermal Analyzer
was employed whose selected heating rate was set at
50°C per minute.

6) The *infrared absorption* was measured using a
Beckman IR 4 spectrophotometer with a sodium chloride
pallet, and the KBr pallet technique, unless otherwise
stated.

7) The *fluorescence* was qualitatively determined in
a dark room under filtered ultraviolet radiation. A Black
Raymaster made by Geo. W. Gates and Company
was used.

8) A *dielectric constant* measurement was made with
a flat piece of the glass at room temperature using a
frequency of one kilocycle per second; a 1615A cap-
acitance bridge unit, coupled with Type 1311-A audio
oscillator manufactured by General Radio Company
was used.

Results and Discussion

General

The physico-chemical properties of the nine glasses
compositions in the section of the phase diagram located
between Tl₂O apex and the 20 B₂O₃—50 SiO₂ (wt. %)
as shown in Figure 1 were extensively studied. The
other 21 compositions identified in Figure 1 were chosen
to determine the glass formation region and the liquid
immiscibility zone.

The melts containing 90 wt. % Tl₂O rapidly recrys-
tallized during the quenching process when 25 to 30 gram
batches were used. Since the batch containing 80 wt. %
Tl₂O and other compositions formed a glass easily,
the limit of glass formation in the system Tl₂O—B₂O₃
—SiO₂ lies approximately at a composition between
80 and 90 wt. % Tl₂O as shown in Figure 1.

A chemical analysis of three out of the nine glasses
showed approximately one wt. % loss of thallium oxide
during the glass preparation process.

In the following, Part I will be a discussion of the
physico-chemical properties of the nine glasses and in
Part II, the liquid immiscibility (phase separations) of
the ternary glasses will be presented.

Part I

Physico-Chemical Properties of Thallium
Borosilicate Glasses

The physico-chemical properties of the nine glasses
are summarized in Table 1:

1) The pycnometer density increased as a function
of increased Tl₂O concentration from 2.142 gm/cc to
5.906 gm/cc (at 80 wt. % Tl₂O). As shown in Figure 1
the 10, 20, 30, 40 and 50 wt. % glass compositions
showed an unusually high density deviating from the
linear density relationship.

![Figure 1. The compositions studied and the glass formation and liquid immiscibility regions.](image)

2) The refractive index showed an apparent disen-
tinuity near 7 mol % Tl₂O as shown in Figure 2,
and then increased as the concentration of Tl₂O
increased. The refractive index is similar to those of
the corresponding glasses in the PbO—SiO₂—SiO₂
system. ²

3) The water solubility curve inflected sharply near
the 7 mol % Tl₂O as presented in Figure 2. The water
solubility was in the range of 54 to 68 wt. %.

4) The C.T.E. curve did not show any significant inflection point at 7 mol % Tl₂O concentration, but did at 3 mol % Tl₂O concentration. According to Cousen and Turner(18), 50B₂O₃-50SiO₂ (wt. %) glass has a C.T.E. of \(5.0 \times 10^{-6}\) per °C. This would represent a minimum in this variation of C.T.E., if their data are directly comparable with ours.

5) The softening points of the glasses determined by D.T.A. presented a flat plateau as shown in Figure 8. The plateau area corresponds to the liquid separation region which will be discussed in Part II. It is interesting to note that the softening curve determined by the D.T.A. technique showed a flat plateau between the composition 10 and 50 wt. % Tl₂O. The significance of this will be discussed below in connection with the liquid immiscibility problem.

6) Fluorescence phenomena were observed among the compositions of 30 to 70 wt. % Tl₂O presenting weak yellowish to pinkish colors, as previously described by Weyl.(24)

7) The 80Tl₂O- 10B₂O₃-10SiO₂ glass had a dielectric constant, \(K\), of 24.4 and a dissipation factor of 0.036. Since borosilicate glasses have a dielectric constant of approximately 4, and lead glass about 7-8(19), the present glass possesses a significantly high dielectric constant, equivalent to that of tellurite glass reported by Stanworth(19), and Ulrich(20).

8) In the infrared absorption runs, the absorption peaks of approximately 6.9 μ (B-OH) and approximately 7.5 μ (Si-O) disappeared at near the 30Tl₂O concentration. At further increased Tl₂O concentration, no absorption peaks were distinguishable. The small fluctuations near 3 μ and 5-7.5 μ in the absorption, as shown in Figure 3, were due to the KBr pellets. Incidentally, thallium oxide presintered at 700°C for 3 hours did not show any absorption peaks up to 15μ and transmitted over 80 % of the infrared beam. The non-sintered thallium oxide had a lower transmission rate particularly below 10 μ range than the sintered thallium oxide.

The absence of infrared absorption peaks in the silicate glass below 15 μ wavelength range is an unusual phenomenon in silicate glasses, and perhaps attributable to the unusually large field strength of thallium ions.(21)

Furthermore, the disappearance of Si-O absorption at 7.5 μ and B-OH absorption at 6.9 μ suggests that thallium ions may perhaps directly replace or interact with the glass former position in the glass structure, suppressing the absorption peaks and forming a larger than 15 μ wavelength range absorption.

A plausible explanation for the pronounced minima in the property-composition curves of the densities, the refractive indices, and the linear thermal expansions is the “boron oxide anomaly” in which the coordination number of boron changes from 3 to 4 as well known in the alkali borate glass systems. (22) It appears to be plausible that the Tl₂O-B₂O₃ glasses may possess the “boron oxide anomaly” at approximately 3 to 7 mol % of thallium oxide causing in the minima of thermal expansion in the Tl₂O-B₂O₃-SiO₂ glass. Rietling(22) indicated the boron coordination change in sodium borosilicate glasses in correlation with the Na₂O-B₂O₃ system.

The high water solubility of the Tl₂O-B₂O₃-SiO₂ glasses was found to originate in the binary B₂O₃-SiO₂ system. The water solubility of the 50B₂O₃-50 SiO₂ glass powder was 45 wt. %. It is interesting to note that the Tl₂O-B₂O₃-SiO₂ glasses are more resistant to acid rather than water. For example, the solu-

![Figure 2. Refractive index, C.T.E., density, and water solubility in the selected Tl₂O-B₂O₃-SiO₂ glasses](image-url)
bility of the 40TiO\textsubscript{2}–30BO\textsubscript{2}–30SiO\textsubscript{2} glass showed 56 wt.% in water, and 31 % in 2N HCl solution after sitting for 5 days. The portion leached by acid presented higher silica and thallium concentration than the initial glass samples, as shown in Appendix II.

The D.T.A. curves of Ti\textsubscript{2}O–BO\textsubscript{2}–SiO\textsubscript{2} glasses listed in Table 1 are shown in Figure 4 as a function of Ti\textsubscript{2}O concentration. As the concentration of Ti\textsubscript{2}O was higher, the inflection points were sharper. The lower temperature inflection was tentatively identified as a second order transition\(^{(27)}\) and the higher inflection points are taken as softening points.

It should be borne in mind that the estimated softening points have a correlation with the softening points based on the viscosity measurements as described in A.S.T.M. C393–54T. In order to correlate the viscosity data with the thermal effect of glass, the NBS standard glass #711 containing 5.62 K\textsubscript{2}O–45.32 PbO–45.00 SiO\textsubscript{2} (wt.%) was examined by the D.T.A. method, and in the D.T.A. curve, the viscosity data given by the NBS was compared as shown in Figure 5.

The viscosity near the glass transformation temperature, \(T_d\), is always of the order 10\(^{13}\) poises.\(^{(27)}\) Therefore, it is reasonable to interpret the minima at approximately 460°C in Figure 5 as the glass transformation temperature.

The sharp endothermic inflection at approximately 270°C occurs where the viscosity of the glass exceeds 10\(^{14.6}\) poise. In such a high viscosity state, diffusion and rearrangement of the atomic structure of glass appears extremely sluggish and the endothermic inflection at 270°C may be attributed to a second order transition, perhaps, caused by an internal rotational contribution or to a relaxation effect of the modifier ions. Yamamoto\(^{(27)}\) attempted to correlate characteristic points in the D.T.A. curves to the viscosity data of
Table 1. Summary of physico-chemical data of the ThO₂-B₂O₃-SiO₂ glasses

<table>
<thead>
<tr>
<th>Weight Compositions (wt. %)</th>
<th>Prepared Temp.</th>
<th>Pycnometer Density (gms/c.c.)</th>
<th>Refractive Index</th>
<th>Water Solubility (wt. %)</th>
<th>C.T.E. * Softening Points**</th>
<th>Fluorescence</th>
<th>Infrared Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>ThO₂ B₂O₃ SiO₂ (°C/min)</td>
<td>(rpm. temp.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 45 45 1400</td>
<td>2.142</td>
<td>1.405</td>
<td>54.1</td>
<td>4.6</td>
<td>0.8</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>(1.4) (45.8) (52.8)</td>
<td>2.358</td>
<td>1.49—1.50</td>
<td>55.1</td>
<td>5.4</td>
<td>600</td>
<td>observed</td>
<td></td>
</tr>
<tr>
<td>20 40 40 1400</td>
<td>2.702</td>
<td>1.54—1.55</td>
<td>57.7</td>
<td>5.8</td>
<td>580</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3.9) (44.2) (51.9)</td>
<td>3.763</td>
<td>1.62</td>
<td>54.4</td>
<td>7.2</td>
<td>570</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 30 30 1200</td>
<td>3.168</td>
<td>1.50</td>
<td>56.0</td>
<td>6.2</td>
<td>550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5.8) (45.2) (48.1)</td>
<td>3.753</td>
<td>1.62</td>
<td>54.4</td>
<td>7.2</td>
<td>570</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 50 50 1200</td>
<td>4.097</td>
<td>1.66—1.67</td>
<td>58.4</td>
<td>7.8</td>
<td>560</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(12.8) (58.2) (38.4)</td>
<td>4.835</td>
<td>1.75</td>
<td>63.5</td>
<td>9.6</td>
<td>470</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 15 15 1200</td>
<td>4.136</td>
<td>1.75</td>
<td>63.5</td>
<td>9.5</td>
<td>470</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(25.0) (38.0) (38.0)</td>
<td>5.906</td>
<td>1.90—1.95</td>
<td>68.3</td>
<td>12.2</td>
<td>357</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 10 10 800</td>
<td>6.025</td>
<td>&gt;2.11</td>
<td>85.8</td>
<td>–</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(50.0) (45.0) (5.0)</td>
<td>7.845</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* From room temperature to 250°C.
** By the D.T.A. method.

Figure 4. D.T.A. curves of ThO₂—B₂O₃—SiO₂ glasses as a function of ThO₂ concentration

commercial glasses. However, he did not detect the sharp endothermic inflection points at temperatures lower than the strain point, perhaps, due to the lower sensitivity of his D.T.A. instrument.

It is clear that the NBS viscosity data have some correlation with the D.T.A. characteristic points in the glass. It may imply that in order to estimate with

Figure 5. D.T.A. curves of the N.B.S. 5711 standard glass 5.62 ThO₂—65.32 PbO—29.06 SiO₂ (wt. %)
little effort the viscosity of the glasses as defining the annealing point, strain point, softening point, etc., the characteristic points of glasses run by the D.T.A. technique are very useful, as pointed out by Yamamoto. (24)

The two minima (inflection points) in a soda-borosilicate glass (Figure 6) have been attributed to the boundaries of the phase separation according to Volb. (29) Pure fused silica, fused B₂O₃, 80SiO₂—20B₂O₃ and other commercial glasses, were also tested in the D.T.A. Instrument and were found to possess two minimum inflection points as shown in Figure 6 depending upon the glass compositions. The two minima were clearly seen in the thallium borosilicate system only when substantial amounts of ThO₂ were added to the B₂O₃—
SiO₂ system, as shown in Figure 4. That two such minima existed beyond the two-liquid separation as established by the electron micrograph investigations will be discussed in Part II. In the NBS K₂O—P₂O₅—SiO₂ glass, which does not contain phase separation phenomena, there were three distinctive inflection points. Therefore, it may be said that the inflection points in the D.T.A. are not dependent upon the phase separation of the glasses, but, in general, relate to the internal structural change as a function of thermal treatment, and particularly as a function of the amount of modifier cations such as Ti⁺⁺, alkali ions or lead ions.

The 40TlO—30B₂O₃—30SiO₂ (wt. %) glass was reheated at temperatures between 200°C and 600°C for 16 hours. Variation of the water solubility and the pycnometer density as a function of the temperature is illustrated in Figure 7. The original density obtained from the glass quenched from 1200°C was 2.168 where as that of the reheated glasses was approximately 2.00 g/cm³, indicating a considerable volume of expansion having taken place during thermal annealing, in agreement with the results of the soda borosilicate glass system. (26)

The original water solubility obtained from the quenched glass was 56 wt. % while that of the reheated glass showed a remarkable variation in solubility. At reheating temperatures between 300°C and 550°C, the water solubility was low and almost constant at 58 wt. %. A sharp increase of the solubility was observed at the 200°C and 600°C heat treatments. As shown in the following section, opal liquid separation developed below 575°C appears to decrease the water solubility.

Part II

Phase Separations in the Tl₂O—B₂O₃—SiO₂ Glasses

General

The positive prints of the electron micrographs which present evidence of phase separation within the glasses are listed in Table 2. The eight glasses were extensively studied as a function of heat treatment. Approximately liquid immiscibility regions in the Tl₂O—B₂O₃—SiO₂ system are shown in Figure 11. The liquid immiscibility as a function of temperature of heat treatment is shown in Figure 8, presenting the section "Tl₂O apex to 50 B₂O₃—50SiO₂ glass" in the Tl₂O—B₂O₃—SiO₂ system.

The significant electron micrographs are discussed below.

Electron Micrographs

Figure 9.
Composition 20Tl₂O—40B₂O₃—40SiO₂ (wt. %)

When the glass was melted at 1400°C for one hour, and quenched over cold water, it was clear and electron micrographs showed no evidence of liquid immiscibility. After the quenched glass was reheated at 500°C for 64 hours, it became slightly opaque. The electron micrographs of the reheated glass are given in Figure 9.

Figure 6. D.T.A. curves of fused quartz, 80SiO₂—20B₂O₃ (wt. %), Corning 7270, Harshaw Q—12 grade (lead borosilicate), B₂O₃ & 80 B₂O₃—10 Ti₂O (wt. %) glasses
Table 2. Electron micrograph data on TiO$_2$-B$_2$O$_3$-SiO$_2$ glasses

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>TiO$_2$ (wt. %)</th>
<th>B$_2$O$_3$ (wt. %)</th>
<th>SiO$_2$ (wt. %)</th>
<th>Heat Treatment</th>
<th>Description</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>40</td>
<td>1400°C/1hr.</td>
<td>No liquid separation. No liquid immiscibility.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1400°C/1hr.</td>
<td></td>
<td></td>
<td>+500°C/6hrs.</td>
<td>Anhedral microheterogeneities imbedded in the matrix glass.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200°C/1hr.</td>
<td></td>
<td></td>
<td>+500°C/6hrs.</td>
<td>No liquid separation. A dendrite growth in the matrix glass.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200°C/1hr.</td>
<td></td>
<td></td>
<td>+500°C/6hrs.</td>
<td>Immiscible liquids exist.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200°C/1hr.</td>
<td></td>
<td></td>
<td>+700°C/6hrs.</td>
<td>Round inclusions.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>35</td>
<td>35</td>
<td>1200°C/1hr.</td>
<td>No liquid separation. No liquid immiscibility.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200°C/1hr.</td>
<td></td>
<td></td>
<td>+500°C/6hrs.</td>
<td>Worm-like structure. Worm-like structure.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200°C/1hr.</td>
<td></td>
<td></td>
<td>+500°C/6hrs.</td>
<td>No liquid immiscibility.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>1200°C/1hr.</td>
<td>No liquid immiscibility. No liquid immiscibility.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200°C/1hr.</td>
<td></td>
<td></td>
<td>+500°C/6hrs.</td>
<td>Worm-like structures imbedded in the matrix glass.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200°C/1hr.</td>
<td></td>
<td></td>
<td>+500°C/6hrs.</td>
<td>Three kinds of liquid coexist.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200°C/1hr.</td>
<td></td>
<td></td>
<td>+500°C/6hrs.</td>
<td>Fine, roughly 500Å wide channels are imbedded in the matrix glass.</td>
<td></td>
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<tr>
<td>4</td>
<td>5</td>
<td>20</td>
<td>75</td>
<td>1500°C/6hrs.</td>
<td>Fine, dotty microstructures are imbedded in the matrix glass.</td>
<td></td>
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<tr>
<td></td>
<td>1500°C/6hrs.</td>
<td></td>
<td></td>
<td>+500°C/6hrs.</td>
<td>Round microstructures are imbedded in the matrix glass.</td>
<td></td>
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<tr>
<td></td>
<td>1500°C/6hrs.</td>
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<td></td>
<td>+500°C/6hrs.</td>
<td>Fine microheterogeneities are imbedded in the matrix glass.</td>
<td></td>
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<tr>
<td>5</td>
<td>10</td>
<td>70</td>
<td>20</td>
<td>1400°C/1hr.</td>
<td>Fine microheterogeneities are imbedded in the matrix glass.</td>
<td></td>
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<tr>
<td></td>
<td>1400°C/1hr.</td>
<td></td>
<td></td>
<td>+450°C/6hrs.</td>
<td>Round microstructures are imbedded in the matrix glass.</td>
<td></td>
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<tr>
<td>6</td>
<td>20</td>
<td>90</td>
<td>0</td>
<td>1200°C/6hrs.</td>
<td>Fine microheterogeneities are imbedded in the matrix glass.</td>
<td></td>
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Figure 7. Variation of density and water solubility of 40TiO$_2$-30B$_2$O$_3$-30SiO$_2$ glasses as a function of reheating

Figure 8. Section TiO$_2$-50B$_2$O$_3$-30SiO$_2$ in the TiO$_2$-B$_2$O$_3$-SiO$_2$ system
Figure 9: Electron micrograph of a fractured surface of 20Tl2O—40B2O3—40SiO2 glass. Melted at 1400 °C for one hour and reheated at 500°C for 64 hours. (×15,000)

Figure 10(a): Electron micrograph of a fractured surface of 30Tl2O—35B2O3—35SiO2 glass. Reheated at 500°C for 64 hours. (×15,000)

Figure 10(b): Replica electron micrograph of fractured glass 20Tl2O—35B2O3—35SiO2 (wt. %). Melted at 1200°C 1/2 hour and reheated at 700°C 16 hours (×50,000)
Figure 10(c). Replica electron micrograph of fractured glass 30TiO—35B₂O₃—35SiO₂ (wt. %).
Melted at 1200°C/1.5 hour + 700°C/16 hours, and quenched. (×50,000)

Figure 10(d). Replica electron micrograph of 30TiO—35B₂O₃—35SiO₂ (wt. %) glass. Melted at 1000°C/16 hours and quenched. (×10,000)

Figure 11(a). Electron micrograph of a fractured surface of 40TiO—30B₂O₃—30SiO₂ glass. Re-heated at 500°C for 64 hours. (×15,600)
Figure 11(b). Electron micrograph of a fractured surface of 40Tl₂O--20B₂O₃--30SiO₂ (wt. %) glass. Melted at 1200°C/1 hour and reheated at 500°C for 16 hours. (×10,000)

Figure 11(c). Electron micrograph of a fractured surface of 40Tl₂O--30B₂O₃--30SiO₂ glass. Reheated at 550°C for 16 hours. (×10,000)

Figure 12(a). Electron micrograph of a fractured surface of a quenched 3Tl₂O--20B₂O₃--75SiO₂ (wt. %) glass. Melting at 1500°C for 6 hours and quenched over water. (×15,000.)
Figure 12(b). Replica electron micrograph of fractured 5TiO₂—20B₂O₃—75SiO₂ (wt. %) glass. Melted at 1500°C for 6 hours, quenched to room temperature, and then reheated at 600°C for 16 hours. (×10,000)

Figure 13. Replica electron micrograph of 10TiO₂—70B₂O₃—20SiO₂ (wt. %) glass. Melted at 1400°C for one hour, quenched, and then reheated at 450°C for 64 hours and quenched. (×60,000)

Figure 14. Replica electron micrograph of 10TiO₂—90B₂O₃ (wt. %) glass. Melted at 1200°C for 6 hours and quenched. (×10,000)
The phases having various sizes and irregular shapes are dispersed in a continuous matrix. The length of the large inclusion ranges from 1/10 to 1 μ. X-ray analysis was unable to detect any crystalline phase.

The slightly opal glass lost opacity when it was heated at 600°C for two hours, but the opacity was regained after the glass was heated at 500°C for six hours, indicating the opacity phenomenon is reversible.

**Figure 10(a-d).**

**Composition 3TiO·3B2O3·3SiO2 (wt. %)**

The glass melted at 1200°C for one hour and quenched over cold water did not show evidence of the liquid immiscibility in the electron micrographs. When the quenched glass was reheated at 500°C for 64 hours, it became slightly opalescent. The electron micrograph of the opal glass is shown in Figure 10(a). Round and sinuous structures whose width is roughly 1/5 to 1/4 μ are imbedded in matrix glass. It is worth mentioning that the phase separation exists even above the temperatures where the opacity completely disappeared and the glass is freely flowing. The nature of the phase separation, however, is no longer the completely separated channel structure, but rather discontinuous dots as shown in Figure 10(b).

In Figure 10(c) which was obtained from a different replica under the same conditions (500°C/64 hrs. reheating treatment), a euhedral nuclei growth is visible. Plate-like rectangular crystals are imbedded in and growing from the matrix area. Since the glass remains in the liquid immiscibility region, the phase separation could be a prerequisite for crystallization as discussed by Filipovich, Cahn and Charles.

At 1000°C, 450°C above the opacity disappearing temperature, the glass remained fluid and transparent. However, the glass after quenching still showed a finely oriented structure as shown in Figure 10(d).

**Figure 11(a).**

**Composition 40TiO·20B2O3·30SiO2 (wt. %)**

The glass 40TiO·20B2O3·30SiO2 melted at 1200°C for 1 hour and quenched was clear, and no evidence of immiscible liquid was found. After reheating at 500°C for 64 hours and quenching, the glass was densely opaque, and the replica electron micrograph (Figure 11(a)) shows long worm-like phases dispersed with a matrix glass. After reheating the quenched glass for 16 hours at 500°C, it showed a dendrite growth (Figure 11(b)) which is explained in terms of spinel decomposition.

When the originally clear glass was reheated at 500°C for 16 hours, three liquid phase separations were observed (Figure 11(c)). Since there is evidence of phase separation in the TiO·B2O3 glass, it is possible that the portion separated from the matrix glass could be further separated into both thallium-rich borate glass and thallium-poor borate glass.

It is interesting to note that in the metastable liquid immiscibility the dendrite form proceeds at lower temperature prior to the spherical or channel type liquid separation perhaps due to the mechanical strain within the quenched glasses.

**Figure 12(a-b).**

**Composition 5TiO·20B2O3·75SiO2 (wt. %)**

(0.8TiO·18.7B2O3·80.5SiO2 mol %)

In order to determine the presence of liquid immiscibility near the binary system B2O3–SiO2, 5TiO·20B2O3·75SiO2 (wt. %) glass was melted at 1200°C for 6 hours and quenched over water. Figure 12(a) shows a characteristic channel structure imbedded in a matrix glass. The width of the channels are roughly 500 Å.

The originally quenched glass was reheated at 600°C for 16 hours. Figure 12(b) shows the metastable liquid immiscibility characteristics below the liquidus. All the glasses before and after the heat treatment remained clear.

These configurations in combination with the immiscibility data on the B2O3–SiO2 glass mentioned elsewhere indicate that the equilibrium and metastable liquid immiscibility may extend to the B2O3–SiO2 system.

**Figure 13.**

**Composition 10TiO·70B2O3·20SiO2 (wt. %)**

The 10TiO·70B2O3·20SiO2 (wt. %) glass was melted at 1400°C for one hour, quenched to room temperature, and reheated at 450°C for 64 hours. The glass was clear before and after the reheat treatment. Figure 13 was obtained from the reheated glass, and shows a typical microheterogeneity presumably at below
the liquidus temperature.

Figure 14.

Composition 10Tl₂O—90B₂O₃ (wt.%)

There is evidence that the binary system Tl₂O—B₂O₃ contains the microheterogeneity analogous to those which were recently reported in the alkali—B₂O₃ systems. Figure 14 was obtained from the 10Tl₂O—90B₂O₃ glass which was melted at 1200°C for 6 hours and then quenched over cold water.

Summary

Since “Pyrex” glass, borosilicate glasses containing soda and alumina as modifiers, was developed by Sullivan and Taylor, Corning Works, in 1915, the development of modern technical glasses has rapidly advanced. Two outstanding qualities of Pyrex glass are primarily the extraordinary thermal shock resistance due to the small linear coefficient of thermal expansion (3.2×10⁻⁵°C⁻¹), the high thermal conductivity (0.028 in C.G.S. unit), and the chemical durability. In 1938, Hood and Nordberg developed the Vycor glass process utilizing two immiscible liquid phases in alkali (Li, Na and K) containing borosilicate glasses. Nevertheless, no systematic investigation has been reported on borosilicate glass containing thallium whose chemical properties in many respects analogous to the alkalies.

In the present investigation, an exploratory investigation of the Tl₂O—B₂O₃—SiO₂ glass system has been made paying particular attention to a comparison with the alkali containing borosilicate glasses.

From the glass formation region and the softening curve, it is clear that thallium ions act as a strong fluxing agent, lowering the softening temperature of the glasses rapidly in similar manner to alkalis and lead ions. The system Tl₂O—B₂O₃—SiO₂ offers a glass formation which is large relative to that of the PbO—B₂O₃—SiO₂ system. ⁹⁻¹³

The refractive index, and the C.T.E. as a function of Tl₂O concentration may be explained in terms of the addition of the highly polarizable Tl⁺⁺ within the glass matrix. The refractive index is approximately similar to those of the system PbO—B₂O₃—SiO₂. The slight dip of the C.T.E. at near 10 wt.% Tl₂O concentration, if explored further, might be interesting because addition of less than 10 wt.% Tl₂O might produce a low expansion glass which is similar to the “Pyrex” glasses.

The variation of the glass density as a function of heating time is in agreement with those of Na₂O—B₂O₃—SiO₂ glasses. ⁹⁻¹⁴

A probable reason that the thallium borosilicate glass displays a higher dielectric constant ³⁺ in contrast to the Na₂O—B₂O₃—SiO₂ is the presence of the highly polarizable Tl⁺ ion.

Finally, the presence of a large liquid immiscibility region whose magnitude is equivalent to that in the PbO—B₂O₃—SiO₂ system ⁹⁻¹⁵, and apparently larger than that of Li₂O—B₂O₃—SiO₂ must be considered. It is interesting to note that the opacification due to the liquid immiscibility in the Tl₂O—B₂O₃—SiO₂ system is reversible by temperature cycling and that the liquid immiscibility persists at higher temperatures than does the opacification. It is also worth mentioning that liquid immiscibility is believed to exist in the binary systems B₂O₃—SiO₂ ⁹⁻¹⁰ and Tl₂O—B₂O₃ ⁹⁻¹¹. It is even predictable that in the Tl₂O—SiO₂ system, a liquid immiscibility might exist analogous to those of the Na₂O—SiO₂ and the Li₂O—SiO₂ systems. ⁹⁻¹⁰ The separated phases are also found to be leachable by acid or water similar to “Vycor.”

Conclusions

The following conclusions may be drawn from the Tl₂O—B₂O₃—SiO₂ glasses investigated:

1. The physico-chemical properties of thallium borosilicate glasses are in many respects analogous to those of glasses in the Li₂O—B₂O₃—SiO₂, Na₂O—B₂O₃—SiO₂, and PbO—B₂O₃—SiO₂ systems, especially in their composition-property curves.

2. An extensive liquid immiscibility was found by the electron microscope in the Tl₂O—B₂O₃—SiO₂ system below and above the liquidus temperature comparable to that of the PbO—B₂O₃—SiO₂ system. The thallium containing immiscible glass contains a silica-rich and boron deficient portion which can be leached from the original glass by acid treatment.

3. In the metastable liquid state the precipitation into dendrite forms takes place before the sphere and channel-like separation occurs.

4. Thallium borosilicate glasses possess a large dielectric constant comparable to those of tellurite glasses,
and a high infrared transmission tendency.

Acknowledgements

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Special gratitude is due to Dr. W. E. Parker, who has kindly permitted the publication of the present research work.

Appendix I

Spectrochemical Analysis of Thallium Oxide Tl₂O₃

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<th>Concentration (ppm)</th>
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<td>Tl</td>
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</tr>
<tr>
<td>Ba</td>
<td>600</td>
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<td>Fe</td>
<td>80</td>
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<tr>
<td>Si</td>
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<td>Na</td>
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<tr>
<td>Pb</td>
<td>300</td>
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<tr>
<td>In</td>
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</tr>
<tr>
<td>Cu</td>
<td>300</td>
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</table>

Appendix II

Chemical Analysis of the Leaching Test

Original glass composition: 40Tl₂O-30B₂O₃-30SiO₂ (wt. %). The glass was left in 2N HCl aq. solution for 5 days in ambient atmosphere.

<table>
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<th></th>
<th>Dissolved Portion (Chemical Analysis)</th>
<th>Undissolved Portion (Calculated)</th>
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<tr>
<td>20 Mesh Glass</td>
<td>Powder Glass</td>
<td>200 Mesh Glass</td>
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<tr>
<td></td>
<td>(wt. %)</td>
<td>Glass</td>
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<tr>
<td></td>
<td></td>
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<tr>
<td>Tl₂O</td>
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<td>B₂O₃</td>
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<td>SiO₂</td>
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</table>

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