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

by

KEE HYONG KIM*

Airco Speer Research

a Division of Air Reduction Company, Inc.

Niagara Falls, New York, U.S.A.

(Received June 13, 1968)

Tl₂O—B₂O₃—SiO₂系 유리의 物理化學的 性質 및 그의 分相

에어코 스피어 硏究所

金 基 衡

(1968. 6. 13. 受理)

要 約

9種의 選擇된 탈리움硼硅酸유리와 21種의 同類組成을 變化시킨 유리에 對하여 物理化學的 性質을 檢討하였다. 이들 組成에 依한 性質의 變化曲線은 여러 點에서 酸化리티움, 소다 및 酸化鉛들을 包含하는 다른 硼硅酸유리와 類似하였다. 탈리움 硼硅酸유리의 組成에 따른 性質의 變化曲線에 極少點이 나타났는데, 이는 Na₂O—B₂O₃—SiO₂ 유리에서 觀察된 바와 같이 硼素結合의 變化에 基因되는 것 같다.

탈리움 이온이 硼硅酸유리에 미치는 主 影響을 綜合해 보면 다음과 같다.

1) 탈리움 이온을 添加함으로써 密度, 屈折率, 물에 對한 溶解度, 熱線膨脹係數, 誘電恒數 等이 增加되었다.

2) 탈리움 濃度를 增加시킴으로써 유리의 軟化點이 降下되었고, 紫外線 照射에 依하여 螢光이 생겼으며, 赤外線 15μ 까지의 吸收端이 不明確해 졌다.

Tl₂O—B₂O₃—SiO₂ 系에서 廣範한 液體不混合性이 電子顯微鏡에 依해 밝혀졌다. 不混合性은 B₂O₃—SiO₂ 二成分系에 對하여 約 Tl₂O 55 wt.%의 組成範圍內에서 나타났다. 不混合性유리는 多硅酸과 多硼素相으로 分離 構成되어 있음이, 酸處理에 依하여, 밝혀졌다.

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 lithia, 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.

* The Present Address: Office of Minister, Ministry
of Science and Technology, Seoul

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 15μ in the infrared region.

An extensive liquid immiscibility was found by replication electron microscope technique in the Tl_2O-B_2O_3-SiO_2 system. The immiscibility covers a composition range roughly from 55 wt. % Tl_2O to the binary system B_2O_3-SiO_2. 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. [1] 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(I), the alkali metals, silver, and gold have the same valency and possess similar ionic radii. [1-2] In the thallium and lead ions, Sidgwick's "inert pair" could play an important role in explaining their chemical stability. [3-4]

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. [5] Nevertheless, scant literature data for the system Tl_2O-B_2O_3-SiO_2 glass are available in contrast to the abundant data available for the systems Li_2O—B_2O_3—SiO_2, Na_2O—B_2O_3—SiO_2 and PbO—B_2O_3—SiO_2. [6-13] Because of the chemical similarities of the ions of lithium, sodium, lead and thallium, a liquid immiscibility may be postulated in the Tl_2O—B_2O_3—SiO_2 glasses analogous to those in the Li_2O—B_2O_3—SiO_2, Na_2O—B_2O_3—SiO_2 and PbO—B_2O_3—SiO_2 systms.

The main purpose of the present investigation is to explore physico-chemical properties of Tl_2O—B_2O_3—SiO_2 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 Globar furnace. The quenched glasses were ground to —200 mesh, and then remelted in order to insure the uniformity of the melts. Afer 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 0.64cm (D) × 5.1cm (L).

Methods of Analyses

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 [14] 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 experimental 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 prism, and the KBr pellet 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 capacitance 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 50 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 recrystallized during the quenching process when 25 to 50 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
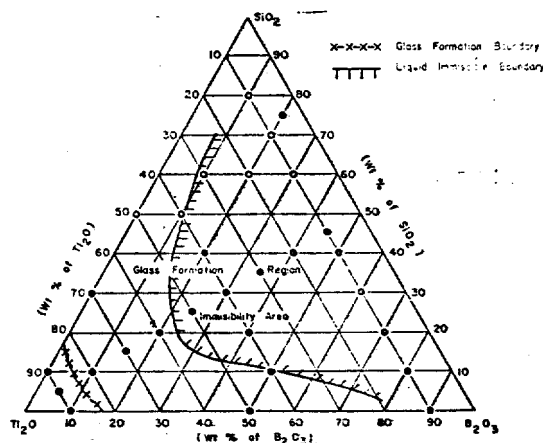

Figure 1. The compositions studied and the glass formation and liquid immiscibility regions. (wt. %)

2) The refractive index showed an apparent discontinuity 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—B₂O₃—SiO₂ system. [15]

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 88 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[15], 50B₂O₃—50SiO₂(wt. %) glass has a C. T. E. of 5.0× 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) Flourescence phenomena were observed among the compositions of 30 to 70 wt. % Tl₂O presenting weak yellowish to pinkish colors, as previously described by Weyl. [16]

7) The 80Tl₂O· 10B₂O₃·10SiO₂ glass had a dielectric constant, K, of 24.4 and a dissipation factor of 0.036. Since borosilicate glass has a dielectric consant of

approximately 4, and lead glass about 7—8[17], the present glass possesses a significantly high dielectric constant, equivalent to that of tellurite glass reported by Stanworth[18], and Ulrich. [19]

8) In the infrared absorption runs, the absorption peaks of approximately 6.9μ (B-OH) and approximately 7.5μ (Si-O) disappeared at near the 30Tl₂O concentration. At further increased Tl₂O concentration, no absorption peaks were distinguishable. The small fluctuations near 3μ and 5—7.5μ 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 nonsintered thallium oxide had a lower transmission rate particularly below 10μ range than the sintered thallium oxide.

The absense of infrared absorption peaks in the silicate glass below 15μ wavelength range is an unusual phenomenon in silicate glasses, and perhaps attributable to the unusually large field strength of thallium ions. [5]

Furthermore, the disappearance of SiO₄ absorption at 7.5μ and B—OH absorption at 6.9μ 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 15μ wevelength 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. [20] 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. Riebling[21] 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-
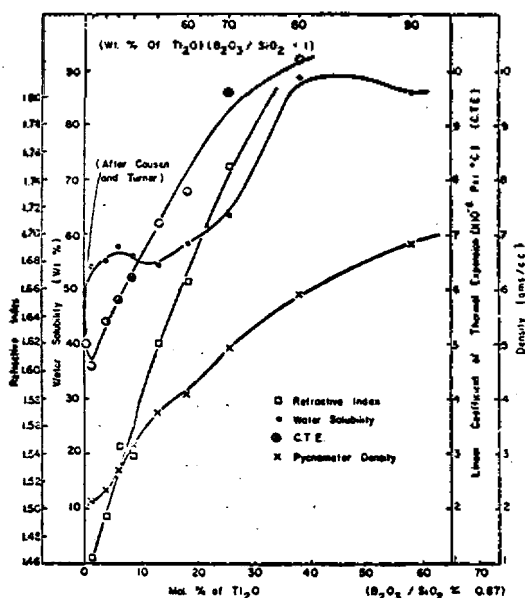

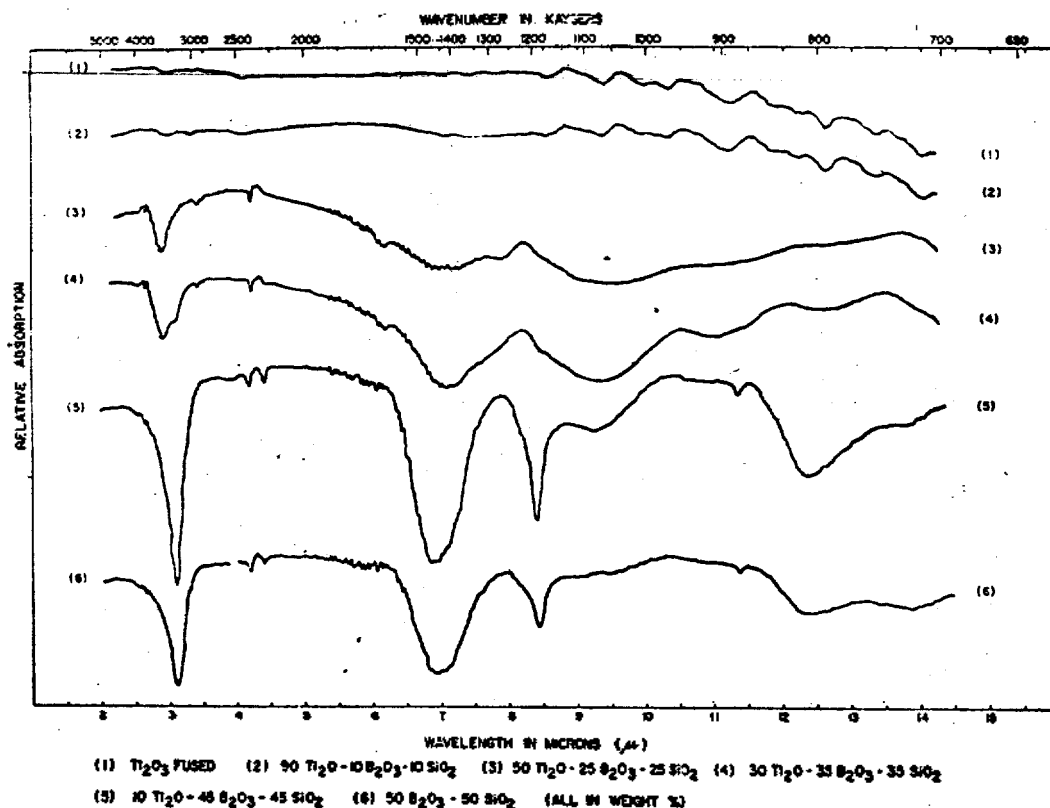Figure 2. Refractive index, C.T.E., density, and water solubility in the selected Tl₂O-B₂O₃-SiO₂ glasses

Figure 3.   Infrared absorption in the $Tl_2O-B_2O_3-SiO_2$ glasses along the section $Tl_2O-50B_2O_3-50SiO_2$

bility of the $40Tl_2O_3-30B_2O_3-30SiO_2$ 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 $Tl_2O-B_2O_3-SiO_2$ glasses listed in Table 1 are shown in Figure 4 as a function of Tl_2O concentration. As the concentration of Tl_2O was higher, the inflection points were sharper. The lower temperature inflection was tentatively identified as a second order transition[22] 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. C336—54T. In order to correlate the viscosity data with the thermal effect of glass, the NBS standard glass #711 containing 5. 62 $K_2O-45. 32$ PbO

—46. 00 SiO_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_g, is always of the order 10^{13} poises. [23] Therefore, it is reasonable to interpret the minima at approximately 460°C in Figure 5 as the glass transformation temperature.
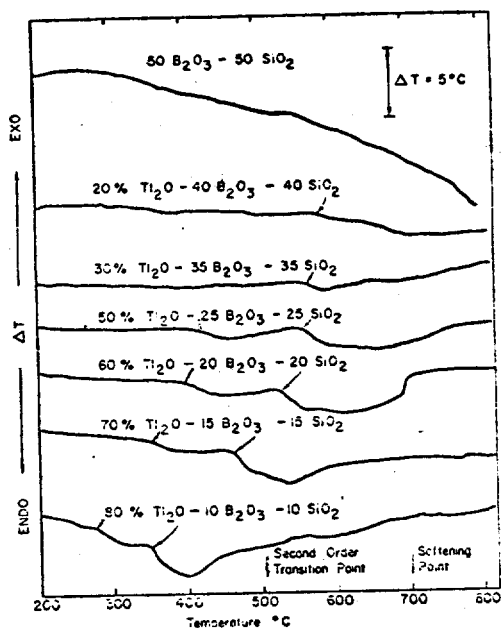
The sharp endothermic inflection at approximately 270°C occurs where the viscosity of the glass exceeds $10^{14.5}$ poise. In such a high viscosity state, diffusion and rearrangement of the atomic structure of glass appears extremely sluggish and the endothermic inflection at 270°C may be attributed to a second order transition, perhaps, caused by an internal rotational contribution or to a relaxation effect of the modifier ions. Yamamoto[24] 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 Tl₂O—B₂O₃—SiO₂ glasses

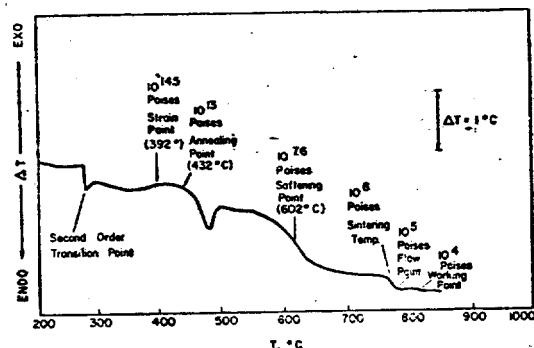| Weight % Compositions (mol. %)			Prepared Temp.	Pycnometer Density	Refractive Powder Index	Water Solubility	C.T.E.* (×10⁻⁶)	Softening Point**	Floures-cence	Infrared Absorption
Tl₂O	B₂O₃	SiO₂	(°C/30min)	(gms/c.c.)	(rm. temp.)	(wt. %)	(°C⁻¹)	(°C)	(ultraviolet)	(to 15μ range)
10 (1.4)	45 (45.8)	45 (52.8)	1400	2.142	1.465	54.1	4.6	—		B—OH (6.9μ) and Si—O(7.6μ) absorpsion edges exist.
20 (3.9)	40 (44.2)	40 (51.9)	1400	2.358	1.49—1.50	55.1	5.4	600	observed	
30 (6.1)	35 (43.5)	35 (50.4)	1400	2.702	1.54—1.55	57.7	5.8	580	"	
40 (8.8)	30 (42.2)	30 (49.0)	1200	3.168	1.539	56.0	6.2	550	"	No absorption edges were observed.
50 (13.3)	25 (40.0)	25 (46.7)	1200	3.578	1.62	54.4	7.2	570	"	
60 (18.4)	20 (38.2)	20 (43.4)	1200	4.097	1.66—1.67	58.4	7.8	540	"	
70 (25.8)	15 (33.9)	15 (40.3)	1200	4.816	1.75	63.5	9.6	470	"	
80 (38.0)	10 (28.0)	10 (34.0)	800	5.906	1.90—1.95	88.1	12.2	357		
90 (58.3)	5 (19.5)	5 (22.2)	800	6.825	>2.11	85.8	—	—		

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

Figure 4. D.T.A. curves of Tl₂O—B₂O₃—SiO₂ glasses as a function of Tl₂O concentration

Figure 5. D.T.A. curves of the N.B.S. #711 standard glass 5.62 K₂O—45.32 PbO—46.00 SiO₂ (wt. %)

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

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 Volf. [25] 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 Tl₂O 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—PbO—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 Tl⁺, alkali ions or lead ions.

The 40Tl₂O—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 3.168 whereas that of the reheated glasses was approximately 3.00 or less, indicating a considerable volume of expansion having taken place during thermal annealing, in agreement with the results of the soda borosilicate glass system. [28]

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. Approximate liquid immiscibility regions in the Tl₂O—B₂O₃—SiO₂ system are shown in Figure 1. 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.
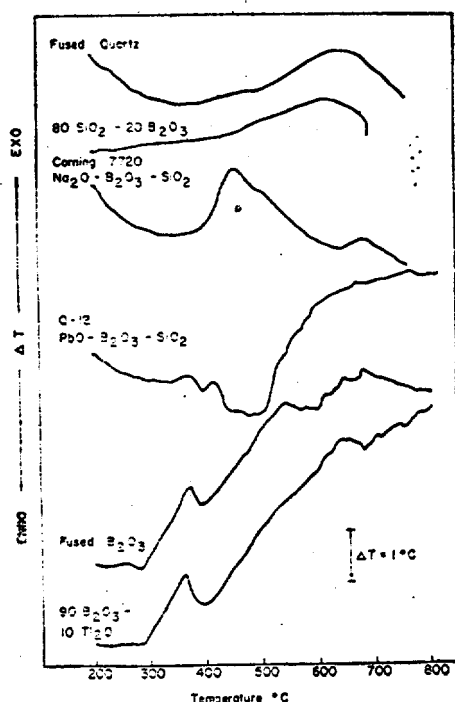

Figure 6. D.T.A. curves of fused quartz, 80SiO₂—20B₂O₃ (wt. %), Corning 7720, Harshaw Q—12 grade (lead boro silicate), B₂O₃ & 90 B₂O₃—10 Tl₂O (wt. %) glasses

Table 2. Electron micrograph data on Tl₂O—B₂O₃—SiO₂ glasses

Glass No.	Glass Composition(wt. %)			Heat Treatment	Description	Figure
	Tl₂O	B₂O₃	SiO₂			
1	20	40	40	1400°C/1hr.	No liquid separation.	—
				1400°C/1hr.	Anhedral microheterogeneities are imbedded in the matrix	9
				+500°C/64hs.	glass. The width of the microheterogeneity is 100Å to 1µ range.	—
2	30	35	35	1200°C/1hr.	No liquid separation.	
				1200°C/1hr.	Immiscible liquids exist.	10(a)
				+500°C/64hrs.	Worm-like structure.	
				1200°C/1hr.	Worm-like structure.	10(b)
				+700°C/16hrs.	Round inclusions.	
				1200°C/1hr.	Nucleation is observed from the immiscible matrix glass.	
				+700°C/16hrs.		10(c)
				1200°C/1hr.	Oriented microheterogeneities exist.	10(d)
				+1000°C/16hrs.		
3	40	30	30	1200°C/1hr.	No liquid immiscibilty.	—
				1200°C/1hr.	Worm-like structures are imbedded in the matrix glass.	
				+500°C/64hrs.		11(a)
				1200°C/1hr.	A dendrite growth in the matrix glass.	11(b)
				+500°C/16hrs.		
				1200°C/1hr.	Three kinds of liquid coexist.	11(c)
				+550°C/16hrs.		
4	5	20	75	1500°C/6hrs.	Fine, roughly 500Å wide channels are imbedded in the matrix glass.	12(a)
				1500°C/16hrs.		
				+600°C/16hrs.	Fine, dotty microstructures are imbedded in the matrix glass.	12(b)
5	10	70	20	1400°C/1hr.	Round microstructures are imbedded in the matrix glass.	
				+450°C/64hrs.		13.
6	10	90	0	1200°C/6hrs.	Fine microheterogeneities are imbedded in the matrix glass.	14
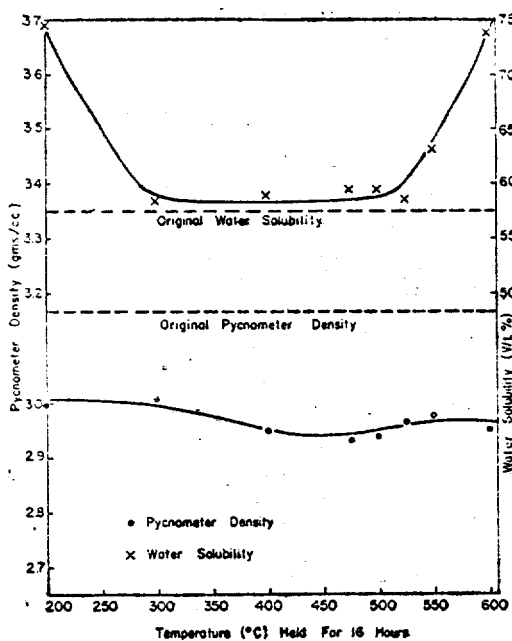
Figure 7. Variation of density and water solubility of 40Tl₂O—30B₂O₃—30SiO₂ glass as a function of reheating
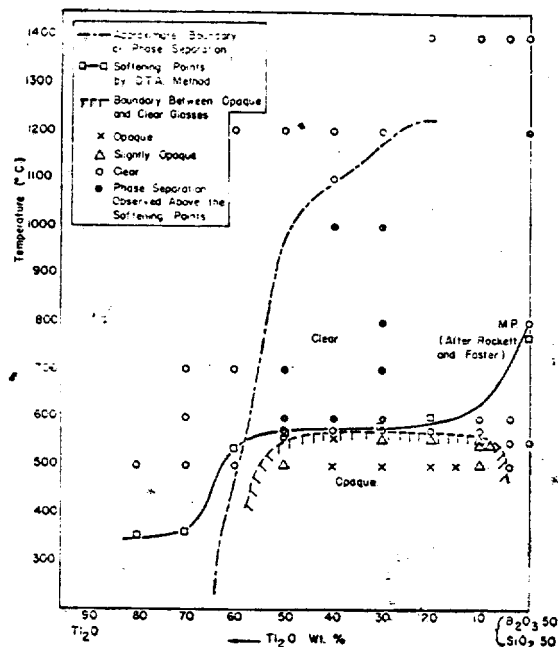
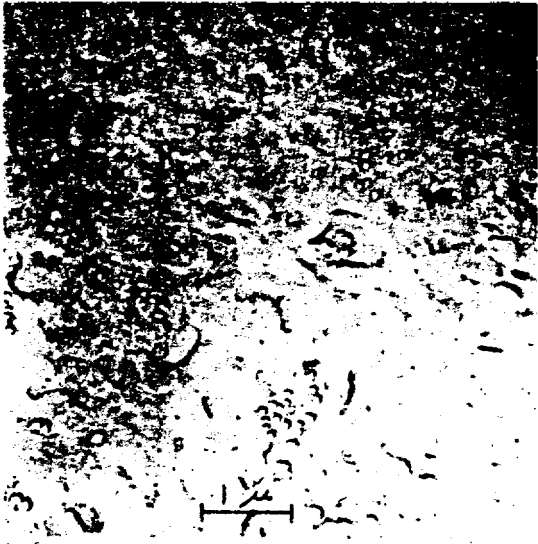Figure 8. Section Tl₂O—50B₂O₃·50SiO₂ in the Tl₂O—B₂O₃—SiO₂ system

Figure 9. Electron micrograph of a fractured surface of $20Tl_2O$—$40B_2O_3$—$40SiO_2$ glass. Melted at 1400 °C for one hour and reheated at 500°C for 64 hours. ($\times$15,000)

Figure 10(a). Electron micrograph of a fractured surface of $30Tl_2O$—$35B_2O_3$—$35SiO_2$ glass. Reheated at 500°C for 64 hours. ($\times$ 15,000)

Figure 10(b). Replica electron micrograph of fractured glass $30Tl_2O_3$—$35B_2O_3$—$35SiO_2$(wt. %). Melted at 1200° $\frac{1}{2}$ hour and reheated at 700°C 16 hours($\times$ 50,000)
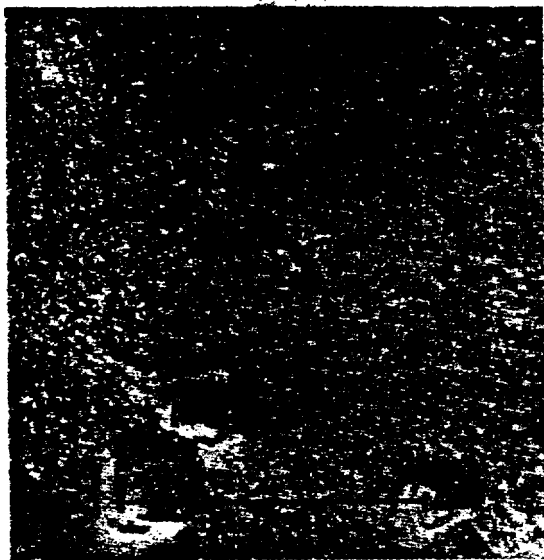
Figure 10(e). Replica electron micrograph of fractured
glass 30Tl₂O—35B₂O₃—35SiO₂ (wt. %).
Melted at 1200°C/½ hour+700°C/16 hours,
and quenched. (×50,000)

Figure 10(d). Replica electron micrograph of 30Tl₂O—
35B₂O₃—35SiO₂(wt. %) glass. Melted at
1000°C/16 hours and quenched. (×10,000)
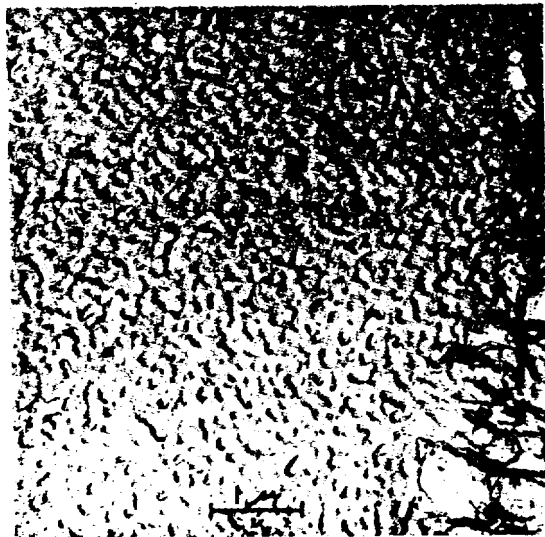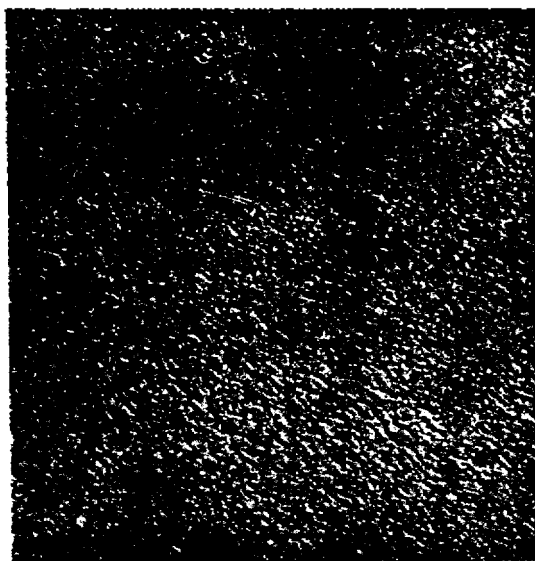
Figure 11(a). Electron micrograph of a fractured sur-
face of 40Tl₂O—30B₂O₃—30SiO₂ glass. Re-
heated at 500°C for 64 hours. (×15,000)
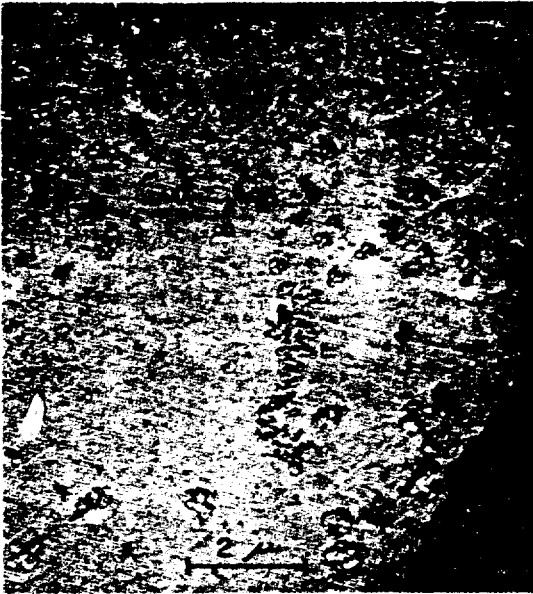
Figure 11(b). Electron micrograph of a fractured surface of 40Tl₂O—30B₂O₃—30SiO₂ (wt. %) glass. Melted at 1200°C/1 hour and reheated at 500°C for 16 hours. (×10,000)

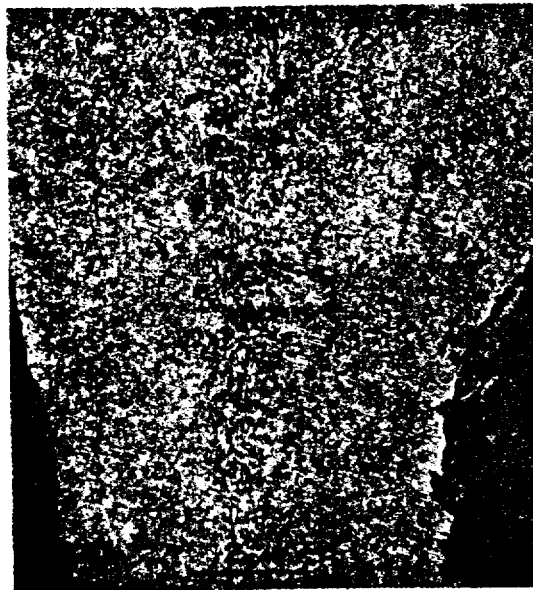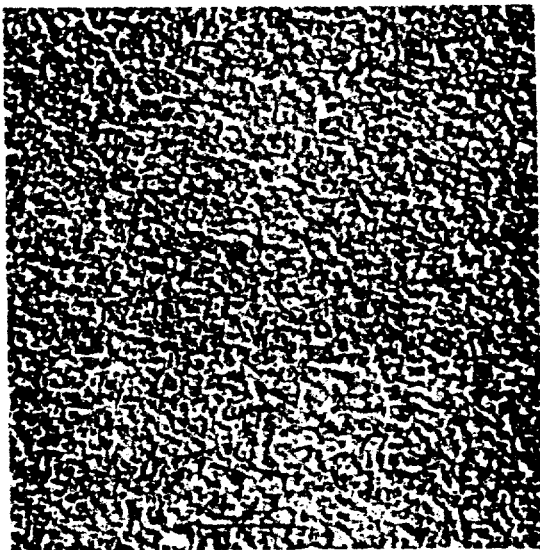Figure 11(c). Electron micrograph of a fractured surface of 40Tl₂O—30B₂O₃—30SiO₂ glass. Reheated at 550°C for 16 hours. (×10,000)

Figure 12(a). Electron micrograph of a fractured surface of a quenched 5Tl₂O—20B₂O₃—75SiO₂ (wt. %) glass. Melted at 1500°C for 6 hours and quenched over water. (×15,000.)
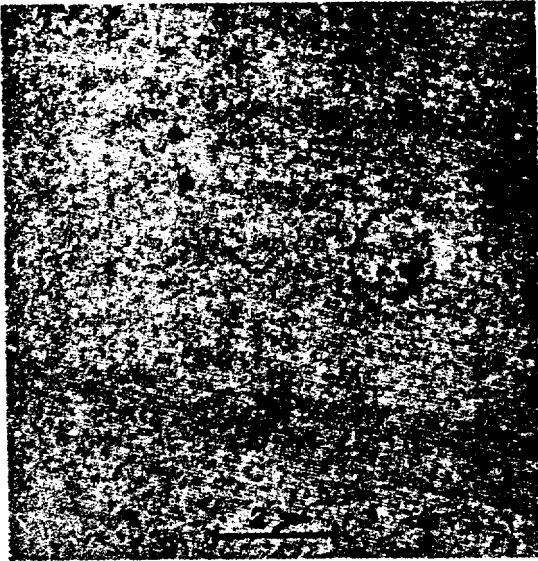
Figure 12(b). Replica electron micrograph of fractured 5Tl$_2$O—20B$_2$O$_3$—75SiO$_2$(wt. %) glass. Melted at 1500°C for 6 hours, quenched to room temperature, and then reheated at 600°C for 16 hours. (×10,000)

Figure 13. Replica electron micrograph of 10Tl$_2$O—70 B$_2$O$_3$—20SiO$_2$ (wt. %) glass. Melted at 1400°C for one hour, quenched, and then reheated at 450°C for 64 hours and quenched. (×60,000)
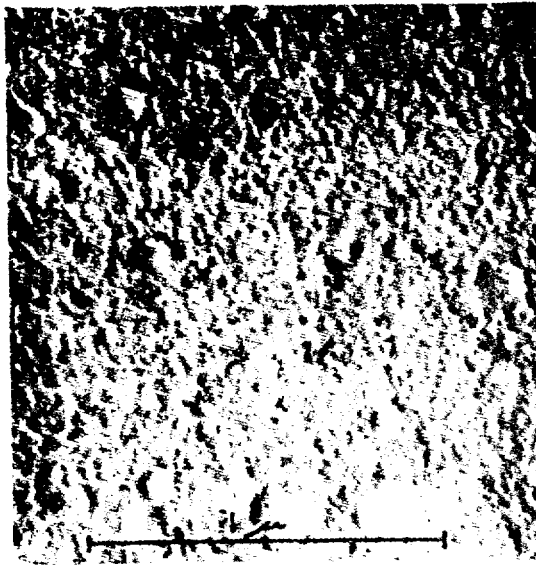
Figure 14. Replica electro micrograph of 10Tl$_2$O—90 B$_2$O$_3$(wt. %) glass. Melted at 1200°C for 6 hours and quenched. (×10,000)
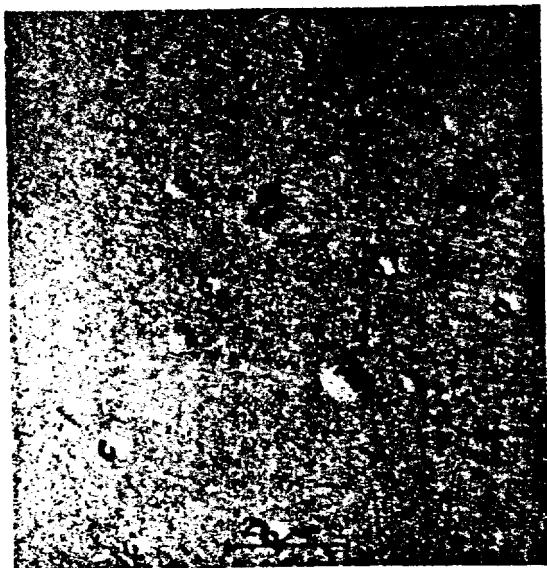
The phases having various sizes and irregular shapes are dispersed in a continuous matrix. The length of the large inclusion ranges from 1/10 to 1μ. X-ray analysis was unable to detect any crystalline phase.

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 30Tl₂O—35B₂O₃—35SiO₂(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 1/4μ 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. Platelike 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,[27] Cahn and Charles.[28]

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 40Tl₂O—30B₂O₃—30SiO₂(wt. %)

The glass 40Tl₂O—30B₂O₃—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 "spinodel decomposition."[26]

When the originally clear glass was reheated at 550°C for 16 hours, three liquid phase separations were observed (Figure 11(c)). Since there is evidence of phase separation in the Tl₂O—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.[27]

Figure 12(a—b).

Composition 5Tl₂O—20B₂O₃—75SiO₂(wt. %)

(0.8Tl₂O—18.7B₂O₃—80.5SiO₂, mol %)

In order to determine the presence of liquid immiscibility near the binary system B₂O₃—SiO₂, 5Tl₂O—20B₂O₃—75SiO₂(wt. %) glass was melted at 1500°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 500Å.

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[29] indicate that the equilibrium and metastable liquid immiscibility may extend to the B₂O₃—SiO₂ system.

Figure 13.

Composition 10Tl₂O—70B₂O₃—20SiO₂(wt. %)

The 10Tl₂O—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 $10Tl_2O-90B_2O_3$(wt. %)

There is evidence that the binary systm $Tl_2O-B_2O_3$ contains the microheterogeneity analogous to those which were recently reported in the alkali—B_2O_3 systems. [30-31] Figure 14 was obtained from the $10Tl_2O-90B_2O_3$ glass which was melted at 1200°C for 6 hours and then quenched over cold water.

Summary

Since "Pyrex" glass, borosilicate glass 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^{-6}/°C) the high thermal conductivity(0. 0028 in C. G. S. unit), and the chemical durability. In 1938, Hood and Nordbergs 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 is in many respects analogous to the alkalies.

In the present investigation, an exploratory investigation of the $Tl_2O-B_2O_3-SiO_2$ 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 alkalies and lead ions. The system $Tl_2O-B_2O_3-SiO_3$ offers a glass formation which is large relative to that of the PbO—$B_2O_3-SiO_2$ system. [13]

The refractive index, and the C. T. E. as a function of Tl_2O concentration may be explained in terms of the addition of the highly polarizable Tl^{1+} within the glass matrix. The refractive index is approximately similar to those of the system PbO—$B_2O_3-SiO_2$. The slight dip of C. T. E. at near 10 wt. % Tl_2O concentration, if explored further, might be interesting because addition of less than 10 wt. % Tl_2O 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 $Na_2O-B_2O_3-SiO_2$ glasses. [28]

A probable reason that the thallium borosilicate glass displays a higher dielectric constant[24] in contrast to the $Na_2O-B_2O_3-SiO_2$ 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—$B_2O_3-SiO_2$ system[13], and apparently larger than that of $Li_2O-B_2O_3-SiO_2$, must be considered. It is interesting to note that the opacification due to the liquid immiscibility in the $Tl_2O-B_2O_3-SiO_2$ 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 $B_2O_3-SiO_2$[29] and $Tl_2O-B_2O_3$. It is even predictable that in the Tl_2O-SiO_2 system, a liquid immiscibility might exist analogous to those of the Na_2O-SiO_2 and the Li_2O-SiO_2 systems. [32-33] 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 $Tl_2O-B_2O_3-SiO_2$ glasses investigated:

1. The physico-chemical properties of thallium borosilicate glasses are in many respects analogous to those of glasses in the $Li_2O-B_2O_3-SiO_2$, $Na_2O-B_2O_3-SiO_2$ and PbO—$B_2O_3-SiO_2$ systems, especially in their composition-property curves.

2. An extensive liquid immiscibility was found by the electron microscope in the $Tl_2O-B_2O_3-SiO_2$ system below and above the liquidus temperature comparable to that of the PbO—$B_2O_3-SiO_2$ 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

Appendix I

Spectrochemical Analysis of Thallium Oxide Tl₂O₃

	Concentration (ppm)
Tl	major
Ba	600
Fe	80
Si	200
Mg	10
Ca	400
Sn	300
Pb	300
In	300
Cu	300

Appendix II

Chemical Analysis of the Leaching Test

Original glass composition: $40Tl_2O-30B_2O_3-30SiO_2$ (wt. %). The glass was left in 2N HCl aq. solution for 5 days in ambient atmosphere.

Chemical Composition	Dissolved Portion (Chemical Analysis)		Undissolved Portion (Calculated)	
	−200 Mesh Glass Powder (wt. %)	Glass Chunk (wt. %)	−200 Mesh Glass Powder (wt. %)	Glass Chunk (wt. %)
	41.4	30.9	58.6	69.1
Tl₂O	44.0	46.9	37.2	36.9
B₂O₃	12.6	6.0	42.3	40.8
SiO₂	43.2	47.1	20.5	22.3

References

1) Korenman, L. M., Analytical Chemistry of Thallium, Academy of Sciences of the U. S. S. R.,

Vernadskii Institute of Geochemistry and Analytical Chemistry, Moskva, p. 408 (1960). (English Translation-Daniel Davey & Co., Inc., New York)

2) Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. V, p. 419-425 (1956), Longmans, Green and Co., New York.

3) Sidgwick, N. V., The Electronic Theory of Valency, p. 179, Clarendon Press, Oxford (1927).

4) Wells, A. F., Structural Inorganic Chemistry (3rd Edition). p. 887-890, Clarendon Press, Oxford (1962).

5) Stanworth, J. E., Physical Properties of Glass, p. 64, Clarendon Press, Oxford (1953).

6) Sastry, B. S. R., and Hummel, F. A., J. Am. Ceram. Soc., 42 (2) 81-88 (1959).

7) Sastry, B. S. R., and Hunmel, F. A., J. Am. Ceram. Soc., 43 (1) 23-33 (1960).

8) Morey, G. W., J. Soc. Glass Technol., 35 (167) 270-83 (1951).

9) Rockett, T. J., Foster, W. R., and Ferguson, R. G., Jr., J. Am. Ceram. Soc., 48 (6) 329-331 (1965).

10) Hood, H. P. and Nordberg, M. E., U. S. Pat. 2,106,744 (Feb. 1938).

11) Volf, M. B., Technical Glasses, p. 129-209, Sir Isaac Pitman and Sons, Ltd., London (1961).

12) Lebedev, A. A., Toropov, N. A., Barzakovskii, V. P. and Appen, A. A. (editors), Structure of Glass—Report of Symposium on the Structure of Glass, Leningrad, (Nov. 23-27, 1953), Akademiya Nauk S. S. S. R. Leningrad and Moscow (1955). (English translation—Consultants Bureau, Inc., New York)

13) Geller, R. F. and Bunting, E. N., J. Res. Natl. Bur. Std., 23 (2) 275-83 (1939) RP 1231.

14. Bradley, D. E., Replica and Shadowing Techniques, Techniques for Electron Microscopy, 2nd Edition (Editor Kay, D. E.), Chapter 5, p. 119-121, F. A. Davis Company, Philadelphia, Pa.

15) Cousen, A. and Turner, W. E. S., J. Soc. Glass Technol., 12 (47) 169-90 (1928).

16) Weyl, W. A., Colored Glasse   p. 485-487, Dowson's of Pall Mall, London (1959).

17) Volf, M. B., Technical Glasses, p. 69, Sir Isaac Pitman and Sons. Ltd., London (1961)

18) Stanworth, J. E., *J. Soc. Glass Technol.*, **36** 217-41 (1952).

19) Ulrich, D. R., *J. Am. Ceram. Soc.*, **47** (11) 595-6 (1964).

20) Warren, B. E., *J. Appl. Phys.*, **15** 602(1942). cf. Stanworth, J. E., *Physical Properties of Glass*, p. 22-29, Clarendon Press, Oxford (1950); Warren, B. E., *J. Am. Ceram. Soc.* **24** 256(1941).

21) Riebling, E. F., Structure of Sodium Silicoborate Melts at 1300°C, presented at the Annual Meeting of American Ceramic Society; *Ceram. Bull.* **45** (4) 420 (1966).

22) Gibbs, J. H., *Nature of the Glass Transition and the Vitreous States*, p. 152-187, *Modern Aspects of the Vitreous State*, Vol. I (Editor MacKenzie, J. D.), Butterworths, Washington, D. C. (1960).

23) Jones, G. O., *Glass*, p. 64, John Wiley & Sons, Inc., New York (1956).

24) Yamamoto, A., *Bunseki Kagaku* **14**(8) 692-6 (1965).

25) Volf, M. B., *Technical Glasses* p. 129-209 Sir Isaac Pitman and Sons, Ltd., London (1961).

26) Tool, A. Q. and Hill, E. E., *J. Soc. Glass Technol., Trans.* **9** 185 (1925); cf. Reference 5, p. 169-174.

27) Filipovich, V. N., Initial Stages in the Crystallization of Glasses and Formation of Glass Ceramics, p. 9-20, *The Structure of Glass*, Vol. 3, Catalyzed Crystallization of Glass (Editor-in-Chief Porai-Koshita, E. A.), Consultants Bureau, New York (1964).

28) Cahn, J. W. and Charles, R. J., *Phys. Chem. Glasses*, **6** (5) 181-91 (1965).

29) Charles, R. J. and Wagslatt, F. E., *J. Am. Ceram. Soc.*, **51**(1) 16-20 (1968).

30) Krogh-Moe, J. *Ark. Kemi* **14** 1 (1959). cf. Reference 21.

31) Wagstaff, F. E. and Charles, R. J., Metastable Liquid Immiscibility in the $Na_2O-B_2O_3$ System, presented at the Annual Meeting of American Ceramic Society, May 1966; *Ceram. Bull.*, **45** (4) 420 (1966).

32) Tran, T. L., *Glass Technol.*, **6**(5) 161-65(1967)

33. Charles, R. J., *J. Am. Ceram. Soc.*, **49**(2) 55-62 (1966).