Variation of the gel region with heat-treatment in the B_2O_3–Na_2O–TiO_2 system compared with the melt-quenched glass region

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Variation of the gel region with heat-treatment and variation of the melt-quenched glass region with cooling rates were compared for the B_2O_3–Na_2O–TiO_2 system. Gels were prepared by the sol–gel method without catalyst using boron tributoxide ($B(OBu)_3$) sodium methoxide ($NaOCH_3$) and titanium tetraisopropoxide ($Ti(OPr)_4$). The gel region was in the composition range B_2O_3 = 0 to 90, Na_2O = 0 to 60, and TiO_2 = 0 to 100 mol% at 50°C. The crystalline phases precipitated were boric acid (H_3BO_3), sodium metaborate hydrate ($NaBO_2 2H_2O$), and sodium hydroxide ($NaOH$), or sodium carbonate (Na_2CO_3). A 500°C, heat treatment for 2 h reduced the gel regions to a composition range of B_2O_3 = 50 to 90, Na_2O = 10 to 30 and TiO_2 = 0 to 20 mol%, but treatment at 800°C produced melts which became glassy upon cooling. On the other hand, a twin-roller method produced a wide range of glass region which includes a high concentration of TiO_2 up to 70 mol%. The as-prepared gel region was found to correspond fairly well to the twin-roller glass region and the thermally most stable gel region was close to the air-quenched glass region. It was speculated that the B_2O_3- or Na_2O-rich composition had not gelled because of the high water solubility of these gels.

1. Introduction

Gel to glass evolution is usually accomplished through a drying and sintering process under an appropriate heat treatment. The probability of crystallization of a gel during a heat-treatment depends on both the duration and temperature of heating. At present, however, it is not possible to predict the gel region of a system or the variation of a gel region with heat treatment.

However, evidence has proved that gel-derived glass resembles melt-quenched glass in structure as well as in physico-chemical properties. For example, the measurements of X-ray diffraction, Raman spectra [1] and infrared spectra [1] have indicated a structural resemblance between gel-derived and melt-quenched silica glass. At the same time, a strong similarity has been indicated between the gel-derived and melt-quenched glasses in properties [2–5] such as density, refractive index, Vicker's hardness, coefficient of thermal expansion, glass transition temperature and elastic modulus. Therefore, a strong resemblance can be anticipated in the thermal stability between the gel-derived and melt-quenched glasses.

Generally, the gel region depends on the preparation conditions (water content, pH, solvent concentration, etc.). For example, too much or too little water will produce no gel. In this respect, the gel region at a given temperature should be defined as a maximum gel region prepared under optimum conditions. Similarly, the melt-quenched glass region depends on quenching rate. Very slow quenching of the melt will induce entire crystallization of the system because the

glassy state is only metastable compared with the stable crystalline state. Contrary to this, theoretically speaking, a sufficiently high quenching rate would quench any liquid into a glass.

Kinetic evaluation of the melt-quenched glass region and its cooling rate dependence has been made in the alkali borate binary systems in terms of thermokinetic parameters, such as viscosity, fusion entropy, etc. [6–11]. However, it seems that comparatively few studies have been made on the thermal evolution of the gel region, despite a large number of works done on the synthesis and characterization of gels and gel-derived glasses.

The SiO_2–Na_2O system seems to be the only example [12] whose gel region can be compared with its melt-quenched glass region. The gel region under conditions of a water/TEOS ratio = 1/4 with no catalyst was SiO_2 = 50 to 100 mol% [12]. The glass region by water quenching was SiO_2 = 52 to 100 mol% [6]. Phalippou *et al.* [13] examined the crystallization tendency of various gels including $0.4Na_2O$–$99.6SiO_2$, $10Na_2O$–$90SiO_2$, $1Na_2O$–$11B_2O_3$–$88SiO_2$, $2.8Na_2O$–$10.8B_2O_3$–$86.4SiO_2$ and $27Li_2O$–$3Al_2O_3$–$70SiO_2$ compositions. It was noted that Na_2O enhances the crystallization tendency of a gel upon heating. Other gels included are of the binary borosilicate system of 5, 10, 15, $20B_2O_3$–95, 90, 85, $80SiO_2$ compositions. It has been mentioned that B_2O_3 addition reduces the crystallization tendency of an SiO_2 gel. However, Na_2O-rich sodium silicate gels of more than 40 mol% Na_2O have not been reported [13]. On the other hand,

Jabra et al. [14] prepared SiO_2-TiO_2, $SiO_2-P_2O_5$ and $SiO_2-B_2O_3$ gels. The contents of the minor components of the gels were 5, 10, 15 mol % TiO_2, 5, 10, 15 mol % P_2O_5, and 5 to 30 mol % B_2O_3. Tohge et al. [15] prepared $20Na_2O-80B_2O_3$ glass by the sol–gel method. However, neither P_2O_5 gel nor B_2O_3 gel have been prepared. The reason for this is not known.

Mackenzie [16] classified gel-derived amorphous solids into two categories, i.e. vitrification oxides and easily crystallizable amorphous solids. The former oxides include SiO_2 [17], $20B_2O_3-80SiO_2$ [13], $15P_2O_5-85SiO_2$ [14], $20Na_2O-80SiO_2$ [18], $34Li_2O-66B_2O_3$ [19], GeO_2 [16], $10PbO-90GeO_2$ [20] and $25CaO-25Al_2O_3-50SiO_2$ [21]; all are composed of glass formers SiO_2, B_2O_3, GeO_2 and P_2O_5 in a similar sense as used for melt-quenching glass formation. The crystallization temperatures, T_c, determined from the DTA curve for these glasses were found to be higher than their glass transition temperatures. The latter oxides include oxides such as Al_2O_3 [16], $4Y_2O_3-6Al_2O_3$ [22], TiO_2 [16], $BaTiO_3$ [23], $SrTiO_3$ [16], $PbTiO_3$ [16], $PbZr_{0.5}O_3$ [16], ZrO_2 [24], ZrO_2-2SiO_2 [25], $CoFeO_3$ [16], $Li_2O-Fe_2O_3$ [26], $KTa_{0.6}Nb_{0.4}O_3$ [16], V_2O_5 [16], Ta_2O_5 [16] and $2TiO_2-5Nb_2O_5$ [27]. The crystallization temperatures, T_c, of these amorphous solids were found to be lower than even half the liquidus temperature, $T_L/2$. The major components of these oxides are non-glass formers or modifiers in a conventional way as used for melt-quenching glass formation.

If a direct relationship is established between the gel region and the melt-quenched glass region or their thermal stability, the melt-quenched glass region might be predicted from the gel region, and vice versa. Conveniently, we could denote this relationship as a "correspondence principle". As is well known, amorphous substances can be prepared through a number of different techniques, in addition to sol–gel and melt-quenching methods, such as (a) evaporation, (b) sputtering, (c) chemical vapour deposition, (d) shock wave [28], (e) particle bombardment [28] or gamma-ray irradiation [28], (f) vapour oxidation (SiO_2), and (g) anodic oxidation (Ta_2O_5) [28]. Work in the future will no doubt investigate the validity of applying the "correspondent principle" to those methods.

2. Objective

The objective of the present study was to compare the gel region and its thermal stability in the binary systems $B_2O_3-Na_2O$, TiO_2-Na_2O and $TiO_2-B_2O_3$ and the ternary system $B_2O_3-Na_2O-TiO_2$ with the melt-quenched glass region determined at various cooling rates. We are curious to know why B_2O_3 would not gel while its melt would vitrify very easily upon cooling. It has been known that $B_2O_3-Na_2O$ melt produces one glass region (on air quenching) or two glass regions (on water quenching or twin-roller quenching) [7–9] and that TiO_2 addition enlarges the glass region in the $B_2O_3-Na_2O-TiO_2$ system [6] even though TiO_2 itself does not vitrify under normal quenching techniques. We wished to see if two gel regions might appear in the $B_2O_3-Na_2O$ system corresponding to the

melt-quenching glass region. It seems that no gel region or its thermal stability have been reported for the $B_2O_3-Na_2O-TiO_2$ system.

3. Experimental procedure

Variation of the gel region under various heat treatments was examined and compared with the glass region determined at various cooling rates.

3.1. Gel region in the $B_2O_3-Na_2O-TiO_2$ system

The procedure for gel preparation in the $B_2O_3-Na_2O-TiO_2$ system is shown in Fig. 1. A butanol solution of boron tributoxide, $B(OBu)_3$, and titanium tetraisopropoxide, $Ti(OPr)_4$, were mixed in a 200 cm³ glass beaker and stirred thoroughly for 5 min. Then a butanol solution of sodium methoxide was added dropwise to the $B(OBu)_3-Ti(OPr)_4$ mixture. The solution in the beaker was covered with pinholed plastic film and was kept at ambient temperature in air for gelation to occur. Gels were formed within 5 to 10 d.

3.2. Heat treatment of the gel

Wet gel was dried in an air bath at 50° C for 3 d, and the dried gel was heated in air to 200, 400, 500 and 800° C at a heating rate of 1° C min^{-1} and was held there for 2 h. X-ray diffraction was used to determine the gel region and to identify the precipitated crystals.

3.3. Melt-quenched glass regions in the $B_2O_3-Na_2O-TiO_2$ system

A mixture of reagent grade boric acid, H_3BO_3, sodium carbonate, Na_2CO_3, and titania, TiO_2, was melted in a PtRh crucible at a temperature of 1100 to 1550° C in an electric furnace. The melts were then quenched by twin-roller quenching, water-quenching or air-quenching methods. The glass region was determined by visual observation.

4. Results

4.1. The gel region in the $B_2O_3-Na_2O-TiO_2$ system

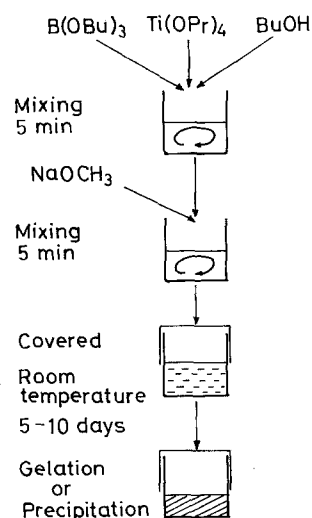The gel region after a 50° C, 3 d drying in the $B_2O_3-Na_2O-TiO_2$ system is illustrated in Fig. 2. The region

Figure 1 The sol-gel process in the $B_2O_3-Na_2O-TiO_2$ system.

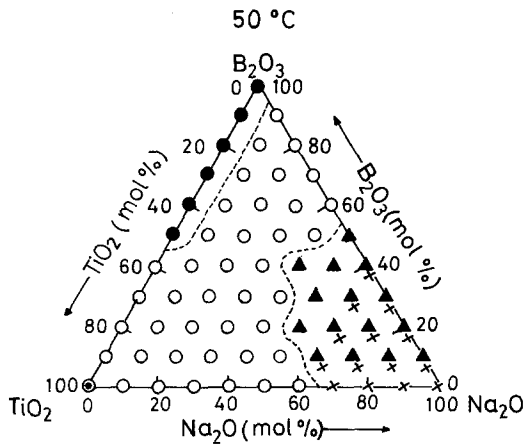Figure 2 The gel region obtained by a 50°C, 3 d drying in the B₂O₃–Na₂O–TiO₂ system. (O) Gel, (●) H₃BO₃, (⊙) amorphous TiO₂, (▲) NaBO₂ · 2H₂O, (x) Na₂CO₃ + NaOH.

Figure 4 The gel region after a 500°C, 2 h heat treatment in the B₂O₃–Na₂O–TiO₂ system. (O) Gel, (●) H₃BO₃, (◑) B₂O₃, (■) TiO₂ (anatase), (△) NaBO₂, (▲) NaBO₂ · 2H₂O.

covers a wide range of composition of B₂O₃ = 0 to 90, Na₂O = 0 to 60 and TiO₂ = 0 to 100 mol %. It should be pointed out here that B₂O₃ has not gelled, and TiO₂ has precipitated as an amorphous phase according to X-ray diffraction analysis. Crystalline precipitates consisted of partially dehydrated boric acid, H₃BO₃, sodium metaborate hydroxide, NaBO₂2H₂O, and sodium carbonate, Na₂CO₃, or sodium hydroxide, NaOH.

4.2. Variation of the gel region with heat treatment in the ternary system

Wet gel was heat treated at various temperatures from 200 to 800°C for 2 h. The gel region after a 400°C, 2 h treatment is illustrated in Fig. 3 together with pre-cipitated crystals. The region was reduced drastically by heat treatment from the original region (Fig. 2). Amorphous TiO₂ was transformed into anatase TiO₂ by heat treatment. Crystalline sodium metaborate, NaBO₂, has precipitated.

Fig. 4 illustrates the gel region after a 500°C, 2 h treatment together with precipitated crystals. The 500°C, 2 h treatment reduced the gel region further. Newly precipitated crystalline phases are boric oxide, B₂O₃, anatase, TiO₂, sodium titanate, 4Na₂O5TiO₂, and sodium metaborate (hydrate).
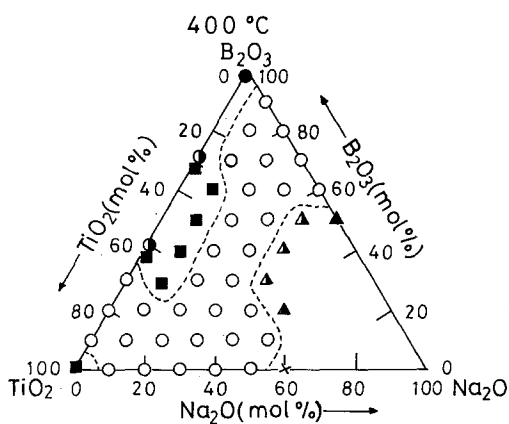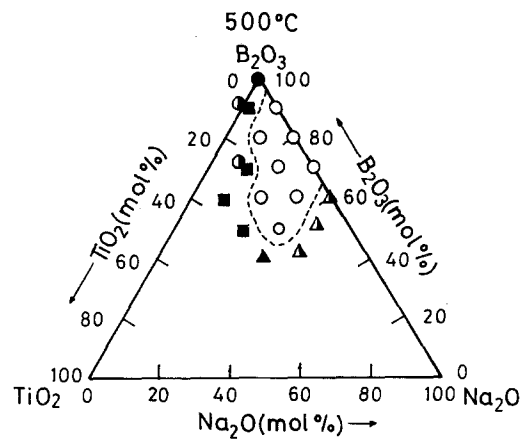
Fig. 5 shows the glass regions after a 800°C, 2 h heat treatment. The original gel region (Fig. 2) has totally vanished and amorphous regions have emerged in the B₂O₃-rich or Na₂O-rich composition.

4.3. Variation of gel region in the B₂O₃–Na₂O system with heat treatment

Figs 6 to 8 show details of the variation of the gel region with heating temperature (50 to 800°C, 2 h) for the B₂O₃–Na₂O, TiO₂–B₂O₃, and TiO₂–Na₂O systems, respectively. It follows from Fig. 6 that B₂O₃–Na₂O gel (B₂O₃ = 10 to 40 mol %) is thermally stable up to 500°C. Above 600°C, however, a B₂O₃-rich amorphous region emerged and above 800°C another amorphous region was seen, all above the liquidus temperature. Fig. 7 indicates that TiO₂–B₂O₃ gel (TiO₂ = 60 to 100 mol %) is thermally stable up to 400°C as also is TiO₂–Na₂O gel (TiO₂ = 40 to 100 mol %) (Fig. 8).

By analogy with Mackenzie's classification of the thermal stability of gels [16] the crystallization tem-peratures, T_c, at which gels crystallize are compared with the liquidus temperatures, T_L, of corresponding compositions [9, 28, 29] in Table I. It can be seen that gels in the B₂O₃–Na₂O system (T_c/T_L = 0.7 to 0.9) are relatively stable compared with those in the TiO₂–

Figure 3 The gel region after a 400°C, 2 h heat treatment in the B₂O₃–Na₂O–TiO₂ system. (O) Gel, (●) partially dehydrated H₃BO₃, (◑) B₂O₃, (■) TiO₂ (anatase), (△) NaBO₂, (▲) NaBO₂ · 2H₂O, (x) Na₂CO₃ + NaOH.
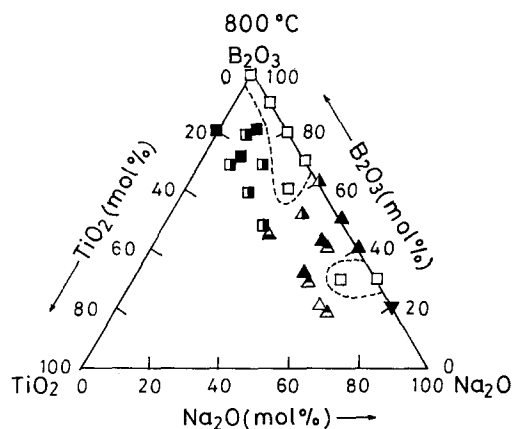

Figure 5 The gel region after a 500°C, 2 h heat treatment in the B₂O₃–Na₂O–TiO₂ system. (□) Glass, (■) TiO₂ (anatase), (▣) TiO₂ (rutile), (△) NaBO₂, (▲) NaBO₂ · 2H₂O, (▲) Na₂O · TiO₂, (▲) Na₂O · TiO₂, (▼) unknown.
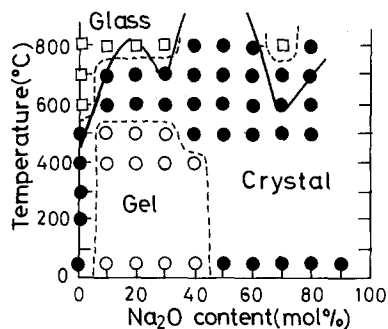
Figure 6 Variation of the gel region with heating temperature (2 h) in the B_2O_3-Na_2O system. (- - -) Gel and amorphous regions. (——) Liquidus temperature [8].

B_2O_3 system (T_c/T_L = 0.2 to 0.4) or in the TiO_2-Na_2O system (T_c/T_L = 0.2 to 0.6).

4.4. Melt-quenched glass region

Fig. 9 illustrates the glass region in the B_2O_3-Na_2O-TiO_2 system determined by twin-roller quenching (quenching rate $10^5\,^\circ C\,sec^{-1}$). The glass region covers a wide range of composition (B_2O_3 = 0 to 100, Na_2O = 0 to 60 and TiO_2 = 0 to 70 mol). A phase-separated glass region was obtained in the B_2O_3-rich composition. TiO_2-rich and Na_2O-rich compositions have also crystallized.

Fig. 10 illustrates the glass regions determined by water quenching (quenching rate $10^\circ C\,sec^{-1}$). The glass region was reduced drastically with the appearance of large crystalline regions extending to the TiO_2-rich compositions.

Fig. 11 shows the glass regions determined by air quenching (quenching rate $2^\circ C\,sec^{-1}$). The glass region was reduced to two separate composition ranges,

TABLE I Variation of crystallization temperature, T_c, of heat-treated gels and their relative temperature, T_c/T_L with the corresponding liquidus temperature, T_L. The higher the value of T_c/T_L, the higher is the thermal stability of the gel, while a lower value gives poor thermal stability

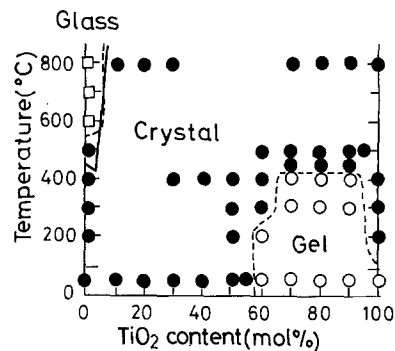| System (mol %)		T_c (K)	T_L (K)	T_c/T_L
B_2O_3-Na_2O				
100	0	—		
90	10	873	995	0.88
80	20	873	1092	0.80
70	30	873	1006	0.87
60	40	773	1166	0.66
50	50	—		
TiO_2-B_2O_3				
100	0	473	2083	0.23
90	10	723	2041	0.35
80	20	723	1989	0.36
70	30	723	1884	0.38
60	40	573	1778	0.32
50	50	—		
TiO_2-Na_2O				
100	0	473	2083	0.23
90	10	723	1919	0.38
80	20	723	1550	0.47
70	30	723	1381	0.52
60	40	723	1304	0.55
50	50	723	1290	0.56
40	60	673	1135	0.59
30	70	—		

Figure 7 Variation of the gel region with heating temperature (2 h) in the TiO_2-B_2O_3 system. (- - -) Gel region. (——) Liquidus temperature [29].

one in a B_2O_3-rich, and another in a Na_2O-rich composition.

5. Discussion

Comparison of the gel regions (Figs 2 to 8) and the melt-quenched glass regions (Figs 9 to 11) has disclosed some similarities as well as dissimilarities, as summarized below.

5.1. Similarities between the gel and the melt glass regions

1. Significant similarities can be observed between the $50^\circ C$ gel region (Fig. 2) and the twin-roller glass region (Fig. 9), extending to a composition of high concentration of B_2O_3 and TiO_2. The twin-roller glass region in the TiO_2-Na_2O system agrees fairly well with the splat-quenched glass region observed by Yoshimaru *et al.* [31] in the range TiO_2 = 55 to 80 mol %. However, $NaOCH_3$-rich sol did not gel and Na_2O-rich melt was not vitrified.

2. A strong similarity was noticed between the $500^\circ C$ gel region (Fig. 4) and the water-quenched (Fig. 10) or the air-quenched glass regions (Fig. 11) which covers the B_2O_3-rich compositions.

3. An amorphous region resulting from the $800^\circ C$ heat treatment (Fig. 8) almost coincides with the air-quenched glass region (Fig. 11). As Fig. 6 indicates, amorphous regions emerged only at the compositions whose liquidus temperatures lay below $800^\circ C$. Thus it seems certain that gels were melted at $800^\circ C$ and the melts were quenched into glasses after heat treatment.
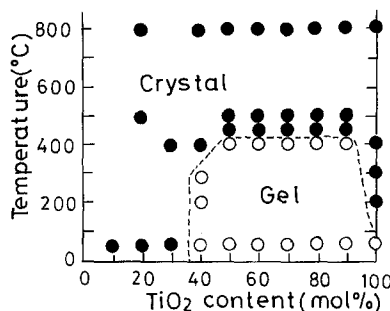

Figure 8 Variation of the gel region with heating temperature (2 h) in the TiO_2-Na_2O system. (- - -) Gel region. The liquidus temperature is over $800^\circ C$ [30].
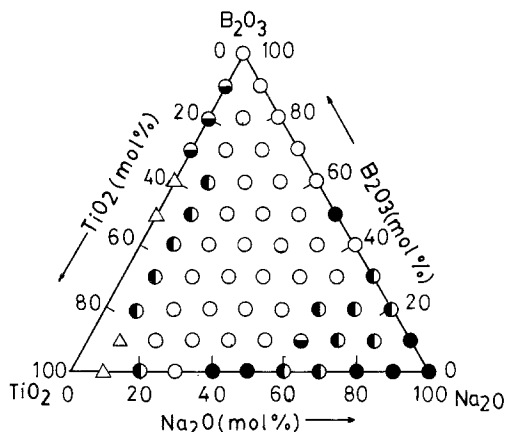
Figure 9 Variation of the glass-forming region in the B_2O_3-Na_2O-TiO_2 system determined by the twin-roller quenching method. (○) Glass, (◑) phase-separated glass, (◐) glass+crystal, (●) crystal, (△) not melted.

5.2. Dissimilarities between the gel and the melt glass regions

1. $B(OBu)_3$ sol does not gel but is precipitated as crystalline boric acid, H_3BO_3 (Fig. 2), while B_2O_3 melt is vitrified on quenching.

2. $NaOCH_3$-rich sol near the B_2O_3-Na_2O system ($Na_2O = 50$ to 70 mol %) is precipitated as a crystalline solid, but the Na_2O-rich melt ($Na_2O = 30$ mol %) produces a second glass region on quenching (Figs 9 to 11).

3. $B(OBu)_3$-rich sol in the TiO_2-B_2O_3 system ($B_2O_3 = 50$ to 100 mol %, Fig. 2) is precipitated as a crystalline solid, but the B_2O_3-rich melt ($B_2O_3 = 70$ to 90 mol %) produces a phase-separated glass region (Fig. 9).

4. $Ti(OPr)_4$ sol precipitates as amorphous TiO_2, but TiO_2 was not melted in the present study due to its high melting temperature ($1800°$ C). Direct comparison of gel regions with glass regions could not therefore be made for TiO_2-rich compositions.

5.3. Relation between the thermal stability of gels and glasses

1. The similarity between the gel and the melt glass regions in the B_2O_3-Na_2O-TiO_2 system, and that observed between the thermal stability of gel and the melt glass, indicate a strong structural resemblance of
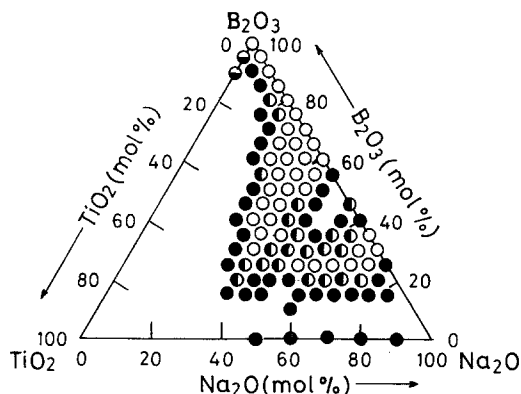

Figure 10 Glass-forming regions in the B_2O_3-Na_2O-TiO_2 system determined by the water quenching method. (○) Glass, (◑) phase-separated glass, (◐) glass+crystal, (●) crystal.
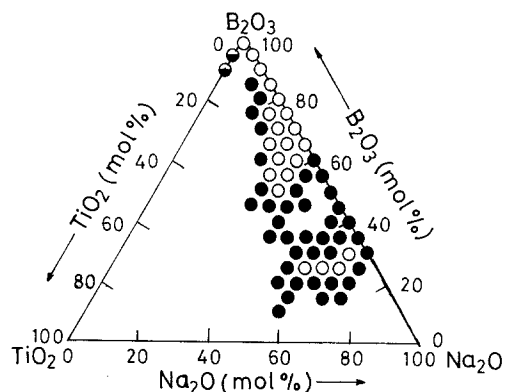

Figure 11 Glass-forming region in the B_2O_3-Na_2O-TiO_2 system determined by the air-quenching method. (○) Glass, (◑) phase-separated glass, (●) crystal.

the gels and glasses in accordance with the suggestions made by Mackenzie [16].

2. B_2O_3 is a well-known glass former, even stronger than SiO_2, because the critical cooling rate for glass formation estimated for B_2O_3 ($Q^* = 10^{-14}°C\,sec^{-1}$) [38] appears to be much smaller than that of SiO_2 [32]. It can be suggested, therefore, that the B_2O_3 system, as well as the SiO_2 system, has a strong polymerizing tendency which gives rise to a highly viscous liquid. Moreover, the thermal stability of B_2O_3 glass is amazingly high. It has been reported that B_2O_3 bulk glass could not be crystallized by any prolonged heat treatment [33, 34] if in a dried atmosphere, but in the presence of water and under shear stress, pulverized B_2O_3 glass would crystallize on heat treatment [33, 34]. Obviously hydration of B_2O_3 glass must trigger the nucleation and enhance crystal growth. From the superior polymerization tendency of the BO_3 unit, together with the high thermal stability of the B_2O_3 glass, we can expect $B(OBu)_3$ sol to gel under certain dry conditions.

3. As Na_2O glass has never been prepared from its melt by any high-quenching technique, Na_2O may well be said to be a typical glass modifier. The high fluidity of a Na_2O-rich melt (although 100% $NaOCH_3$
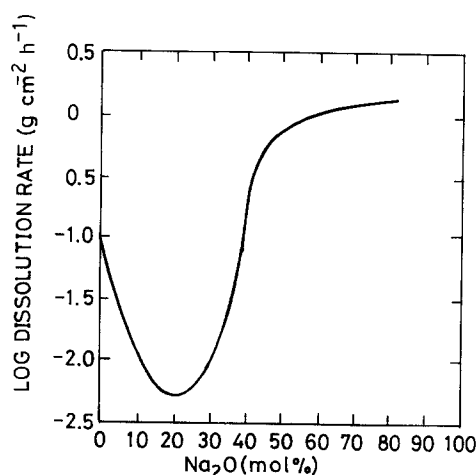

Figure 12 Dissolution rate of the B_2O_3-Na_2O system [35]. Glass or crystallized solid samples in cubic form or flakes were immersed in circulating water at $20°$ C, and the weight loss caused by dissolution was measured as a function of time. The dissolution rate was calculated from the weight loss, time, surface area, volume and density of the sample. The hydration tendency can be regarded to be closely related to the dissolution rate.

sol melt cannot be obtained) suggests a poor polymerizing tendency of the Na_2O component. Therefore, we cannot expect $NaOCH_3$ sol to gel under dry conditions.

5.4. Speculative mechanism of crystallization of gels in the B_2O_3-rich or Na_2O-rich composition

1. Secrist and Mackenzie [28] have shown that the synthesis of amorphous B_2O_3 is possible from $B(OC_2H_5)_3$ by a thermally activated CVD method in a vacuum environment. In view of this fact, together with the expectation mentioned in Section 5.3 (2), we can suppose *a priori* a gellation capability of $B(OBu)_3$ sol by Reaction 1. Yet, because $B(OBu)_3$ sol has not condensed as a gel or amorphous solids in the present study, we must consider a situation that might occur when B_2O_3 gel is coexistent with water. It is certain that B_2O_3 gel will be dissolved in an aqueous solution by Reaction 2, as implied from the high water solubility of B_2O_3 glass [35] (Fig. 12). As a result, crystalline boric acid, H_3BO_3, will be precipitated from the solution according to Reaction 3.

$$2B(OBu)_3 + 3H_2O \rightarrow B_2O_3 \text{ (gel)} + 6BuOH \quad (1)$$

$$B_2O_3 \text{ (gel)} + 3H_2O \rightarrow 2H_3BO_3 \text{ (aq)} \quad (2)$$

$$2H_3BO_3 \text{ (aq)} \rightarrow 2H_3BO_3 \text{ (c)} \quad (3)$$
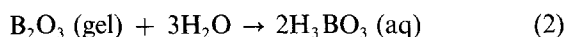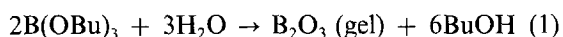
The same hydration reaction may be possible for the gel of a high concentration of $B(OBu)_3$ in the TiO_2-B_2O_3 system. In this case, however, phase segregation seems necessary for prompt precipitation of crystalline H_3BO_3, because TiO_2, which is water resistant, will hinder the hydration of B_2O_3 gel if B_2O_3 is interconnected with the TiO_2 network in the B_2O_3-TiO_2 gel.

2. For Na_2O-rich compositions a similar mechanism for gellation and hydration might be possible. We can postulate a gellation capability for $NaOCH_3$-rich sol covering the $NaBO_2$ composition. However, Na_2O gellation is doubtful, from the reason mentioned in Section 5.3 (3). The high water solubility of Na_2O-rich alkali borate glass (Na_2O = 40 to 100 mol %) can be shown in Fig. 12 [35]. Hydration of $NaBO_2$ gel, for example, would then result in a hydrated $NaBO_2 \cdot 2H_2O$ crystal by Reaction 4

$$NaBO_2 \text{ (gel)} + 2H_2O \rightarrow NaBO_2 \cdot 2H_2O \text{ (aq)} \quad (4)$$
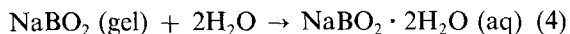
3. A wide range of composition, including TiO_2, has gelled. Hydration of TiO_2 gel seems unlikely due to its low water solubility. TiO_2 is an intermediate oxide which does not form glass by the usual quenching rate, but enhances the glass-forming tendency of a non-glass forming system, as is shown in Fig. 9.

6. Conclusions

1. The variation of the gel region with heat treatment has shown that the thermal stability of a gel in the B_2O_3-Na_2O-TiO_2 system is dependent on composition, as is the thermal stability of a melt-quenched glass of the same system. Generally, the gel region at 50° C agrees well with the melt glass region obtained

by the twin-roller method, and thermally the most stable gel region dried at 500° C for 3 d lies very close to the melt-quenched glass region obtained by the water- or air-quenching method, which suggests a correspondence between a gellation tendency and a glass-forming tendency.

2. However, a close comparison of the gel and melt-quenched glass regions has shown some disagreements between them: neither 100% B_2O_3 nor Na_2O-rich composition (Na_2O = 30 mol %) has gelled, but both of them were vitrified on melt-quenching.

3. The reason for conclusion 2 has been argued based on a hydration hypothesis, according to which B_2O_3 gel and Na_2O-rich gel are unstable in water, and the hydration of these gels will give crystalline precipitates. This hypothesis seems to be supported by a high dissolution rate observed for B_2O_3-rich and Na_2O-rich compositions in the B_2O_3-Na_2O-TiO_2 system.

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