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Phase equilibria in the system $ZnO–B_2O_3–SiO_2$ at 950° C

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Phase equilibria in the system $ZnO–B_2O_3–SiO_2$ were investigated at 950° C using quenching and X-ray powder diffraction techniques. The binary phases reported previously were confirmed but no ternary phases were found. Solid-solution effects were investigated for the primary and binary phases by comparison of patterns; no solid solutions were detected. There is a large liquid area in the high-B_2O_3 corner of the phase diagram. It is found that zinc orthosilicate, α-$2ZnO \cdot SiO_2$, dissolves in this to form a zinc-oxide-rich borosilicate liquid but $4ZnO \cdot 3B_2O_3$ does not. There is also a liquid eutectic at approximate composition $65ZnO–25B_2O_3–10SiO_2$ (wt%). The rate of volatilization and loss of B_2O_3 was also investigated for $4ZnO \cdot 3B_2O_3$ and it was concluded that although volatilization occurs, the loss was insufficient at the firing times and temperature used to invalidate the major features of the diagram.

1. Introduction

Compounds within both the $ZnO–SiO_2$ and $ZnO–B_2O_3$ binary systems are known to exhibit fluorescent properties. In the $ZnO–SiO_2$ system, the mineral, willemite (zinc orthosilicate, $2ZnO \cdot SiO_2$), gives a green fluorescence under ultraviolet radiation [1]. In addition, zinc orthosilicate may be activated by manganese to give a red-fluorescing form (γ-$2ZnO \cdot SiO_2$), a yellow-fluorescing form (β-$2ZnO \cdot SiO_2$) and a green-fluorescing form (α-$2ZnO \cdot SiO_2$, willemite) [1]; although it appears that both the γ and β forms may be changed to the α form, there is no record of the α form changing to either of the others [1].

During their study of the $ZnO–B_2O_3$ system, Harrison and Hummel [2] discovered that both the binary intermediates they found will fluoresce if activated with suitable amounts of manganese.

In spite of interest due to this fluorescence in both the binary systems there has been no attempt to determine the subsolidus phase equilibria of the ternary system, although some work has been reported on the $ZnO_2–B_2O_3–SiO_2$ glasses [1, 3].

1.1. Previous work

As already mentioned, the ternary system has not been investigated in the subsolidus region but some work has been reported on $ZnO–B_2O_3–SiO_2$ glasses [1, 3]. In one case [1] the liquidus phases are given and this shows that this phase diagram is dominated (about two-thirds of the diagram) by a field of two immiscible liquids. In the second case the paper is really concerned with nuclear radioactive waste disposal using $Na_2O–ZnO–B_2O_3–SiO_2$ glasses and the actual information on $ZnO_2–B_2O_3–SiO_2$ glasses is rather sparse. However, data exist for all three binary systems.

A considerable amount of work has been completed on the $ZnO_2–B_2O_3$ phase diagram [1, 2, 4–14], much of it confusing and contradictory. This was summarized [15] in an article in which further results were reported. This report concluded that in the range 640 to 900° C, three zinc borates may be found; α-$3ZnO \cdot B_2O_3$, $4ZnO \cdot 3B_2O_3$ and $ZnO \cdot 2B_2O_3$. Up to 700° C only α-$3ZnO \cdot B_2O_3$ and $ZnO \cdot 2B_2O_3$ are detected, while at 710° C $4ZnO \cdot 3B_2O_3$ is obtained accompanied by the decomposition of $ZnO \cdot 2B_2O_3$. However, the decomposition is very sluggish and all three compounds may coexist up to 900° C. According to one reference [2], $3ZnO_2 \cdot B_2O_3$ is dimorphic with a transition temperature of 964° C, the high-temperature form being called β (this reference actually places this phase at a composition of $5ZnO \cdot 2B_2O_3$, as does some of the others). Since the summarizing article [15], the crystal structure of $ZnO \cdot 2B_2O_3$ has been determined [16]; those of $3ZnO \cdot B_2O_3$ [14] and $4ZnO \cdot 3B_2O_3$ [8–10] had already been reported and so the doubts on the compositions of the phases must be considered settled.

The $ZnO–SiO_2$ phase system at temperatures above 1300° C was originally studied by Bunting [17] who concluded that the only stable binary phase was zinc orthosilicate ($2ZnO \cdot SiO_2$). However, Schleede and Gruhl [18] examined melts of manganese-activated zinc orthosilicate and found that, depending upon the rate of cooling, one could obtain either green fluorescence (slow cooling), a yellow-fluorescent form (faster cooling) or a red-fluorescent form (chilled). These forms were subsequently named α, β and γ forms respectively [19]; the α form corresponds to the mineral willemite. Ingerson, *et al.* [1] grew needle crystals of the β and γ forms and were able to determine the optical properties. In addition, they studied the

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thermal transitions and concluded that at temperatures in excess of 900° C, the γ form changes to the β form and then to the α form. Williamson and Glasser [20] redetermined the phase diagram at temperatures above 1300° C; essentially their work confirms that of Bunting [17], but they also showed that β and γ forms could be obtained without the addition of manganese, but only from divitrified glasses; they could not be prepared from crystalline starting materials heated at subsolidus temperatures. They also showed that α-zinc orthosilicate was the only stable binary compound at temperatures between 800° C and the liquidus.

Although other zinc orthosilicate polymorphs have been found at high pressures [21, 22] as well as one of zinc metasilicate, $ZnO \cdot SiO_2$ [22], none of these have been found at atmospheric pressure.

The phase diagram for B_2O_3–SiO_2 has been studied many times, often with confusing and conflicting results. The most thorough work [23] (which also reviews the earlier results) concludes that there is no binary phase in this system under equilibrium conditions. This has been confirmed [24, 25].

2. Experimental procedure

2.1. Choice of firing temperature

The choice of the subsolidus firing temperature was governed by several conflicting factors:

(i) The necessity of ensuring complete solid-state reaction in the ZnO–SiO_2 system. The lowest solidus temperature in the phase diagram is 1432° C [17] or 1421° C [20], while the melting point of willemite is variously given as 1512° C [1, 17] or 1498° C [20].

(ii) The melting points of the various zinc borates. These have been determined by Harrison and Hummel [2] but attributed to slightly incorrect compositions. According to them, $ZnO \cdot B_2O_3$ (really $4ZnO \cdot 3B_2O_3$) melts at 982 $\pm$ 2° C while α-$5ZnO \cdot 2B_2O_3$ (really α-$3ZnO \cdot B_2O_3$) transforms to β-$5ZnO \cdot 2B_2O_3$ at 964 $\pm$ 4° C and melts at 1045° C.

(iii) The volatilization of B_2O_3. The melting point is given as 450° C [25] or in the range 455 to 475° C [26]. Studies of B_2O_3 volatilization at 730° C have been carried out [23] and indicate that the weight loss of a pure B_2O_3 sample is 7% after 1000 h. The rate of weight loss would appear to be linear. The first factor would ideally suggest a temperature of 1400° C or so, the second about 950° C and the third even lower.

As a result, compacts were made in the manner given below (Section 2.2). These corresponded to a composition of $2ZnO \cdot SiO_2$ to which 3 wt % LiF was added as a mineralizer. Attempts were made to make α-$2ZnO \cdot SiO_2$ at 900° C; examination of X-ray patterns from compacts fired at times ranging from 21.0 to 100.0 h indicated that in all cases the major phase was ZnO, while α-$2ZnO \cdot SiO_2$ was a minor phase. What is more, the proportion of these phases (assessed from relative diffraction line strengths) was the same. In these circumstances it would appear that 900° C is too low for producing α-$2ZnO \cdot SiO_2$ under equilibrium conditions.

At 950° C, α-$2ZnO \cdot SiO_2$ could be made after firing for 89.3 h without need of a mineralizer, and so 950° C was chosen as the firing temperature and no mineralizer was used in later work.

2.2. Thermal equilibrium diagram

The investigation commenced with examination of the starting materials and by preparing the binary compounds.

The starting materials were Analar zinc oxide (not less than 99.7% pure), Analar boric acid (not less than 99.5% pure) and silica (BDH (Pool, UK), precipitated approximately 98% pure, the remainder being mainly loss at 1000° C). For those few compacts where a mineralizer was added (see Section 2.1) Analar lithium fluoride (not less than 98% pure) was added. Quantities of zinc oxide, silica and lithium fluoride were stored inside the furnace at the firing temperature, until required for compact preparation.

For compact preparation, the appropriate quantities were mixed, ground to a fine powder under acetone, and pressed for 5 min in a 0.5 in. (13 mm) diameter steel die at 6000 lb in^{-2} (41 MPa). No binder was used. All compacts were prefired at 400° C, removed, reground and repressed for the final firing.

Both prefiring and firing were carried out in air with the compacts in open platinum boats. The temperature of firing was controlled at 950° C and the specimens air-quenched. Various firing times were used and these are mentioned in Table I.

After firing, a little of the compact was ground and used as an X-ray powder specimen which was examined in an 11.46 cm diameter Debye–Scherrer camera using filtered copper radiation.

3. Results

3.1. Zinc oxide–boric oxide binary system

Only two zinc borates were found in the system: $4ZnO \cdot 3B_2O_3$ and α-$3ZnO \cdot B_2O_3$. The patterns agree with those reported previously [11, 13]. $ZnO \cdot 2B_2O_3$, which had been found to coexist with $4ZnO \cdot 3B_2O_3$ at temperatures up to 900° C [15], was not found at 950° C. It has already been mentioned that this zinc borate starts to decompose at a temperature of 710° C, but the decomposition was sluggish [15] and hence it could still be present at 900° C.

3.2. Zinc oxide–silicon dioxide binary system

It was confirmed that the only phase found in this system was α-$2ZnO \cdot SiO_2$, the mineral willemite.

3.3. Boric oxide–silicon dioxide binary system

It was confirmed that no binary was found in this system.

3.4. Thermal equilibrium diagram

During the course of the investigation into the thermal equilibrium diagram six binary and twenty-six ternary compacts were made and analysed. Table I lists these compacts, composition firing times, the interpretation of the X-ray diffraction patterns and the result of a visual inspection of the fired compacts. In some cases the presence of amorphous material was detected by X-rays, either by the lack of any crystalline phase or

TABLE I Specimens prepared, chemical analysis, firing times and X-ray analysis

Compound or specimen No.	Chemical composition (wt %)			Firing time (h)	Phase analysis			Visual inspection
					Major	Minor	Trace	
	ZnO	B_2O_3	SiO_2					
ZnO	100			24.0	ZnO			
SiO_2			100	24.0	α-cristobalite	Tridymite		
$3ZnO \cdot B_2O_3$	77.8	22.2		16.5	α-$3ZnO \cdot B_2O_3$			
$4ZnO \cdot 3B_2O_3$	60.9	39.1		5.9	$4ZnO \cdot 3B_2O_3$	α-$3ZnO \cdot B_2O_3$		
$ZnO \cdot 2B_2O_3$	36.9	63.1		89.7	$4ZnO \cdot 3B_2O_3$			
$2ZnO \cdot SiO_2$	73.0		27.0	89.2	α-$2ZnO \cdot SiO_2$		ZnO	
1		63.5	36.5	45.2	Amorphous			Glassy
2		10.0	90.0	45.7	Amorphous		Tridymite	Glazed
3	10.0	20.0	70.0	41.5	Amorphous	α-$2ZnO \cdot SiO_2$		Glassy
4	15.0	10.0	75.0	41.9	Tridymite α-$2ZnO \cdot SiO_2$			Glazed
5	15.0	70.0	15.0	21.5	Amorphous			Glassy
6	20.0	35.0	45.0	22.5	Amorphous	α-$2ZnO \cdot SiO_2$		Glassy
7	35.0	22.0	43.0	22.5	α-$2ZnO \cdot SiO_2$			Glassy
8	40.0	11.0	49.0	30.7	α-$2ZnO \cdot SiO_2$			Glazed
9	45.0	5.0	50.0	41.8	α-$2ZnO \cdot SiO_2$	Tridymite		Neither
10	45.0	20.0	35.0	22.5	α-$2ZnO \cdot SiO_2$			Glazed
11	60.0	7.0	33.0	41.8	α-$2ZnO \cdot SiO_2$			Neither
12	30.0	59.0	11.0	21.6	Amorphous		$4ZnO \cdot 3B_2O_3$	Glassy
13	49.6	31.9	18.5	41.5	α-$2ZnO \cdot SiO_2$			Glassy
14	60.7	17.0	22.3	41.5	α-$2ZnO \cdot SiO_2$			Glazed
15	25.0	70.0	5.0	20.4	$4ZnO \cdot 3B_2O_3$			Neither
16	45.0	45.0	10.0	21.5	Amorphous		$4ZnO \cdot 3B_2O_3$	Glassy
17	55.0	40.0	5.0	24.4	$4ZnO \cdot 3B_2O_3$	α-$2ZnO \cdot SiO_2$		Neither
18	58.0	30.0	12.0	20.5	$4ZnO \cdot 3B_2O_3$	α-$2ZnO \cdot SiO_2$		Glassy
19	65.0	15.0	20.0	24.4	α-$2ZnO \cdot SiO_2$	$4ZnO \cdot 3B_2O_3$		Neither
20	63.0	32.0	5.0	1.5	Amorphous			Glassy
21	67.0	19.0	14.0	41.5	α-$2ZnO \cdot SiO_2$			Glazed
22	70.0	10.0	20.0	45.7	α-$2ZnO \cdot SiO_2$		α-$3ZnO \cdot B_2O_3$	
23	76.0	15.0	9.0	92.0	α-$3ZnO \cdot B_2O_3$ α-$2ZnO \cdot B_2O_3$			
24	80.0	5.0	15.0	49.9	α-$2ZnO \cdot SiO_2$ ZnO		α-$3ZnO \cdot B_2O_3$	
25	82.0	13.0	5.0	28.0	ZnO	α-$3ZnO \cdot B_2O_3$ α-$2ZnO \cdot SiO_2$		
26	90.0	5.0	5.0	30.7	ZnO		α-$2ZnO \cdot SiO_2$ α-$3ZnO \cdot B_2O_3$	

by the high background recorded on the film; in others there was no evidence of this nature and the presence of amorphous material (glass) was obtained from a visual inspection alone. The compatibility triangles consistent with these results are given in Fig. 1.

X-ray patterns containing binary phases were compared. From this comparison there appeared to be no evidence of solid-solution effects in the binary phases; however, many patterns lacked sharp lines in the back-reflection region and because of this the existence of some solubility cannot be discounted.

4. Discussion

The lack of solid solution, mentioned in the previous section, is not unexpected. The published binary phase diagrams of zinc oxide–boric oxide [2], zinc oxide–silicon dioxide [17, 20] and boric oxide–silicon dioxide [23] suggest that there are no solid solutions in any of them. Van Vlack [26] points out that in close-packed crystal structures there can be extensive solid solution if the size of the host and substitutional ions do not differ by more than 15%, but that this limitation may be relaxed if the structures are not close-packed. In addition, solid solution is limited if the host and substitution atoms have different valency, or for compounds having different structures.

Based on the ionic radius of O^{2-} as 0.140 nm for sixfold coordination, Shannon and Prewitt [27] give the ionic radii for sixfold coordination as Zn^{2+} 0.075 nm, Si^{4+} 0.040 nm and B^{3+} 0.023 nm. In their oxides, zinc and silicon have fourfold coordination and boron threefold. The ionic radii corresponding to these coordination numbers are 0.060, 0.026 and 0.002 nm, respectively. Whichever figures are used, in either case the three ions have widely different radii. In addition, the three ions have different valencies. Thus it can be seen that the conditions are not favourable for the formation of solid solutions.

A major concern with firing at such a high temperature as 950° C was the inevitable loss of B_2O_3 due to volatilization. It has already been shown that the weight loss of a pure B_2O_3 sample is 7% after 1000 h at 730° C [23]. Thus the volatilization was studied at 950° C. Rather than use a pure B_2O_3 sample (which is rather artificial in view of the compositions studied), the binary $4ZnO \cdot 3B_2O_3$ was studied. This was chosen because of its relatively high B_2O_3 content (39.1 wt %); there were only six compacts richer in B_2O_3 that were

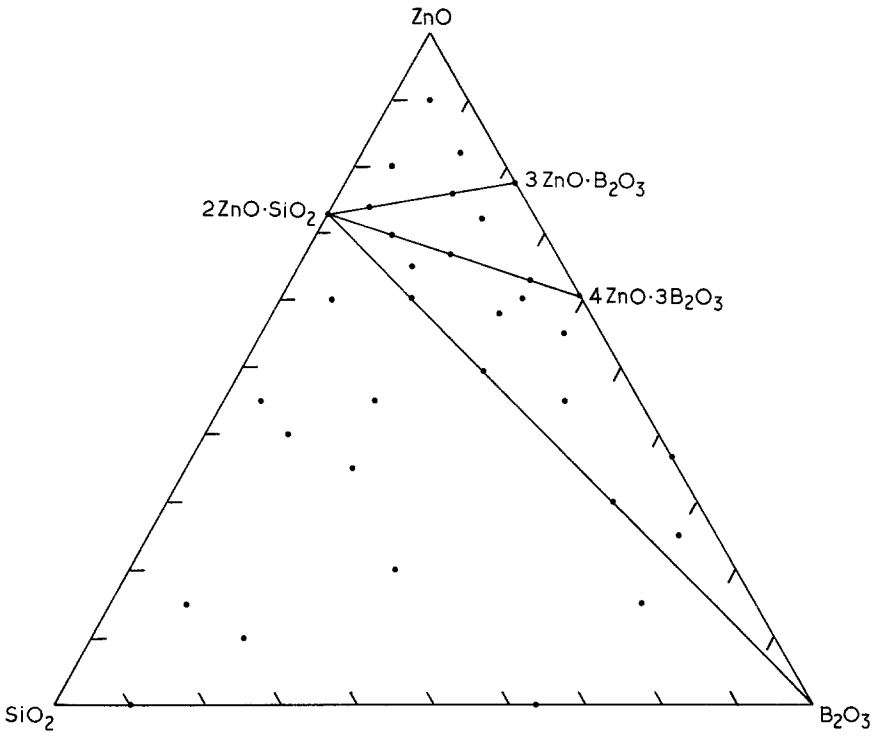

Figure 1 Phase equilibrium in the system $ZnO-B_2O_3-SiO_2$ at 950° C.

studied. Also this compound produces a very distinctive X-ray pattern which would allow for easier X-ray interpretation if required. The results given in Fig. 2 show that there is an initial higher B_2O_3 loss before the loss rate becomes linear and significantly smaller. This initial loss is no doubt due to volatilization from the surface. Even including this initial surface loss, the total loss corresponded to approximately 2% after 20 h and some 3.5% after 40 h. Thus, although the actual compositions must be somewhat different to the nominal values in Table I and Fig. 1, the difference is insufficient to invalidate the proposed phase diagram.

The proposed phase diagram suggests that silica exists in a considerable area of the sub-solidus phase diagram, yet tridymite was only detected in three specimens (Nos 2, 4 and 9). Of course this is because of the low melting point of B_2O_3, 450° C [28] or 455 to 475° C [29]; this means that the diagram determined is not subsolidus over a considerable area. In fact, according to the data on the $B_2O_3-SiO_2$ binary diagram [23], this system is liquid at 950° C from B_2O_3 to a composition of approximately $33B_2O_3-67SiO_2$ (wt %). Assuming that this boundary is not affected by the presence of $2ZnO \cdot SiO_2$, this means that tridymite would only be present in five specimens (Nos 2, 3, 4, 8 and 9) and in two of these (Nos 3 and 8) the amount would be less than 13%.

It has already been reported [1], that at the liquidus most of the phase diagram is dominated by two immiscible liquids, one of which is almost pure

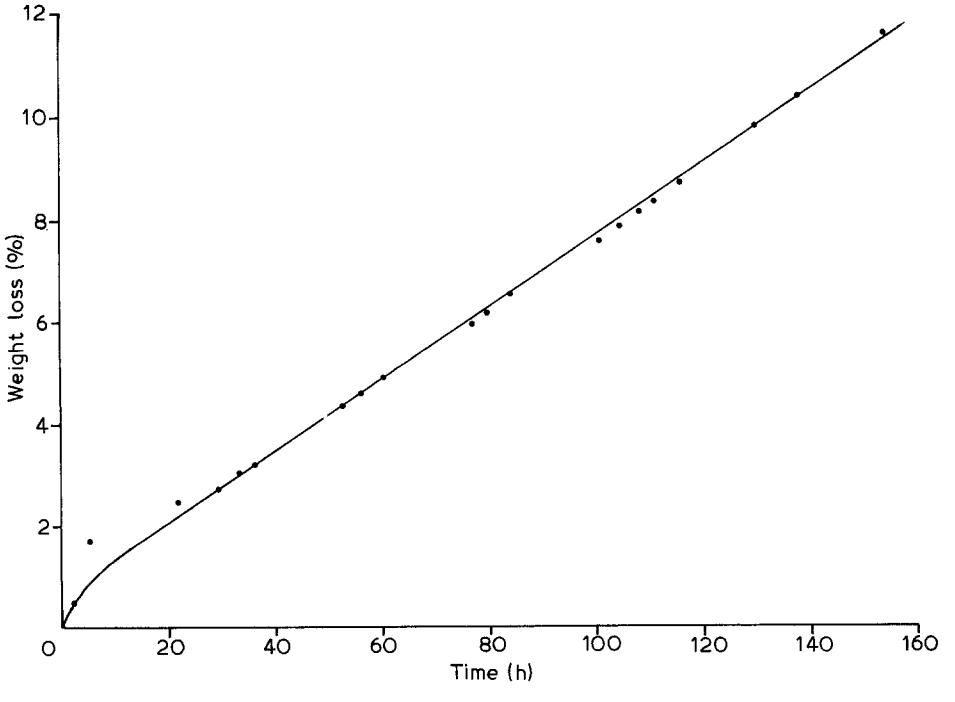

Figure 2 Volatilization of boric oxide from $4ZnO \cdot 3B_2O_3$ at 950° C.

TABLE II Specimens of $63.0ZnO-32B_2O_3-5SiO_2$ (wt %) fired at various temperatures

Temperature (° C)	Firing time (h)	Phase analysis		
		Major	Minor	Trace
800	24.5	$4ZnO \cdot 3B_2O_3$	$2ZnO \cdot SiO_2$	$3ZnO \cdot B_2O_3$
850	22.5	$4ZnO \cdot 3B_2O_3$	$2ZnO \cdot SiO_2$	$3ZnO \cdot B_2O_3$
900	21.0	$4ZnO \cdot 3B_2O_3$	$2ZnO \cdot SiO_2$	$3ZnO \cdot B_2O_3$
910	73.0	$4ZnO \cdot 3B_2O_3$	$2ZnO \cdot SiO_2$	$3ZnO \cdot B_2O_3$
930	24.0	$4ZnO \cdot 3B_2O_3$		$2ZnO \cdot SiO_2$
940	24.0	Sample melted		

$B_2O_3-SiO_2$ (probably containing less than 1% ZnO) and a zinc-oxide-rich borosilicate liquid, whose composition is believed to be near $60.7ZnO-19.1B_2O_3-20SiO_2$ [1] (i.e. near Specimen No. 14). The presence of this two-liquid region has been subsequently confirmed [3]. In addition, it is pointed out by Taylor and Owen [3] that there is secondary segregation of SiO_2-rich particles within the zinc-rich phase, but they only mention detailed work on one sodium-free composition ($18ZnO-18B_2O_3-64SiO_2$) at 1300° C, and so it is not known how extensively this secondary segregation occurs, particularly as the only composition reported contains such a large proportion of SiO_2.

This zinc-oxide-rich borosilicate liquid exists at 950° C but not with the same composition [1] as at the liquidus. Assuming the nominal compositions in Table I, a mineralogical analysis (i.e. a percentage phase analysis) suggests that Specimens 12 and 16 contain 40.7 and 37.0 wt % $2ZnO \cdot SiO_2$, respectively, but in neither case is $2ZnO \cdot SiO_2$ detected, while it is detected in Specimens 3 and 4 in which the amounts of $2ZnO \cdot SiO_2$ are 14.7 and 20.5 wt %, respectively. This is no doubt due to the $2ZnO \cdot SiO_2$ dissolving in the excess B_2O_3; excess B_2O_3 being defined as that remaining after allowing for the pure saturated borosilicate liquid mentioned earlier [1, 3], of approximate composition $33B_2O_3-67SiO_2$ [23] at 950° C. The amounts of excess B_2O_3 are 58.8 and 33.4 wt % in specimens 12 and 16, respectively, but zero in Specimens 3 and 4.In fact in the four specimens where $2ZnO \cdot SiO_2$ would be expected but not found (Nos. 5, 12, 15 and 16) there is a minimum of 33.4 wt % excess B_2O_3. However, with one exception, $4ZnO \cdot 3B_2O_3$ was detected in all specimens where it would be expected. As the exception, Specimen 14 contained only 0.7 wt % $4ZnO \cdot 3B_2O_3$; this would be too small to detect using X-ray powder techniques, and so it appears that $2ZnO \cdot SiO_2$ will dissolve in free liquid B_2O_3 while $4ZnO \cdot 3B_2O_3$ will not.

This analysis is not meant to imply that a pure borosilicate glass of the saturated composition exists over all the B_2O_3-rich part of the diagram, but simply that the solution of $2ZnO \cdot SiO_2$ to form a zinc-oxide-rich borosilicate glass appears to depend upon the amount of excess B_2O_3.

In addition to the large liquid (glassy) area in the high-B_2O_3 corner of the diagram, there is a small one in a region of Specimen 20 on the $2ZnO \cdot SiO_2-4ZnO \cdot 3B_2O_3$ tie-line. This suggests a eutectic along this tie-line, but to test that there was no intermediate ternary compound, a series of specimens all with the composition of Specimen 20 ($63.0ZnO-32.0B_2O_3-5.0SiO_2$) were made, fired at temperatures between 800 and 940° C and X-ray analysed (Table II). This indicates that there is no ternary phase along this tie-line and there there is a eutectic between Specimens 20 and 21 ($67ZnO-19B_2O_3-14SiO_2$).

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