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RESEARCH ON PHASE EQUILIBRIA BETWEEN BORON OXIDES AND REFRACTORY OXIDES, INCLUDING SILICON AND ALUMINUM OXIDES

W.C. Beard, W.C. Butterman, D.E. Koopman
H. E. Wenden, and W.R. Foster

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On: RESEARCH ON PHASE EQUILIBRIA BETWEEN BORON OXIDES AND REFRACTORY OXIDES, INCLUDING SILICON AND ALUMINUM OXIDES

For the period: 1 October 1961 - 31 December 1961

Submitted by: W. C. Beard, W. C. Butterman, D. E. Koopman,
H. E. Wenden, and W. R. Foster
Department of Mineralogy

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I. INTRODUCTION

This report summarizes the work done during the tenth quarterly report period, 1 October 1961 to 31 December 1961. During this period attention was directed to the systems TiO_2-B_2O_3, ZrO_2-B_2O_3, HfO_2-B_2O_3, and ThO_2-B_2O_3-Na_2O.

A literature survey was made for each of these systems. Preliminary experiments of a reconnaissance nature were also carried out. It is proposed to extend these studies so as to secure a phase diagram for each of the systems. Additional information is expected on the polymorphic relations of the refactory oxides TiO_2, ZrO_2 and HfO_2, and on the conditions for successful growth of single crystals.

II. THE SYSTEM TiO_2-B_2O_3

No study designed specifically to establish phase relations in the system TiO_2-B_2O_3 has yet been made. Ebelman[1] failed to obtain compound formation by prolonged heating of titanic oxide with boric acid. Guertler[2] reported that TiO_2 is dissolved in molten boric acid anhydride and yields an emulsion on cooling. Mixtures from pure B_2O_3 to the mol ratio 1 : 1 form homogeneous melts at high temperature, but on cooling, melts within a certain composition range becomes turbid and segregate immediately into two liquid phases. A two-liquid area is thus to be expected in the TiO_2-B_2O_3 phase diagram, but whether it affects the liquidus, or occurs metastably below the liquidus curve, is not known. Foex[3] established the solubility of TiO_2 in B_2O_3 at 1200° C as 4.4 mols in 100 mols of B_2O_3, or 4.8 weight percent. This observation strongly suggests either that the liqudus curve for TiO_2 rises sharply (almost vertically) from the melting point of B_2O_3 in a monotectic relation, or that an even more nearly vertical liquidus rises from a eutectic located very close to the B_2O_3 end-member. Dietzel and Tober[4] were unable to decide whether compound formation is to be expected in the system,

although the difference in field strengths of TiO_2 (1.25) and B_2O_3 (1.45) would appear to fall below the 0.30 limit believed necessary for compound formation. Imaska[5] has investigated the range of glass formation of B_2O_3 with numerous other oxides, including TiO_2. Considerations developed by Glasser, Warshaw and Roy[6] for prediction of the possibility of liquid immiscibility in silicate systems indicate that immiscibility in the TiO_2-B_2O_3 system is likewise probable, and consistent with the early suggestion of Guertler[2].

There is wide divergence of opinion as to the true relations between the three polymorphs of TiO_2, rutile, anatase and brookite. Most investigators, like Osborn[7], regard rutile as the form stable at all temperatures, with anatase and brookite as metastable forms which change monotropically to rutile. The anatase to rutile transition has been located as low as 100° C[8] and as high as 1200° C[9]. The synthesis of brookite has been claimed as low as 300° C[10] and as high as 1300° C[11], with one author assigning a 800°-1040° range[12]. Three separate forms of anatase and of rutile has been reported[13]. Obviously, additional study is called for in order to obtain clarification of these confused and conflicting relationships.

Failure to convert rutile directly to anatase under any laboratory conditions largely accounts for belief in the monotropic nature of the anatase-to-rutile inversion. A preliminary attempt has been made to effect the rutile-to-anatase transition with the aid of a low-melting flux. Rutile in a large excess of lithuim nitrate was heated slightly above the $LiNO_3$ melting point (268° C). On the assumption that anatase rather than rutile is the phase stable at low temperatures, it was hoped that the more soluble (because less stable) rutile would dissolve in the $LiNO_3$ and that the less soluble (because more stable) anatase would precipitate. No evidence of anatase was observed after 3 days, nor was there any evidence of recrystallization or grain growth of the original rutile. It is not even certain

that rutile dissolved in the flux. The results are therefore considered inconclusive, and further runs are scheduled at 300°, 400°, 500°, 600°, etc. in hope that more elevated temperatures will cause substantial solution of rutile, and that reprecipitation of either rutile or anatase will take place on cooling. Other low-melting fluxes may possess greater solvating ability, and will also be tried.

Another approach to the problem of the anatase - rutile relations was the following. Fine-grained rutile obtained by heat treatment of J. T. Baker C. P. anatase was ground in a mechanical mortar under liquid nitrogen for five minutes. Similar treatment has been found by Bredig to change calcite to aragonite. Previously, aragonite had widely been regarded as having a monotropic relation towards calcite, similar to the relation generally believed to exist between anatase and rutile. Thus far, however, no conversion of rutile to anatase has been effected. It is still hoped that more prolonged grinding in liquid nitrogen may produce the rutile-to-anatase transition, even although the density relations of anatase (3.84) and rutile (4.26) would appear unfavorable. In the course of these tests, some data on the sluggishness of the anatase-to-rutile transition at moderate temperatures were obtained. After 41 hours at 640° C, anatase showed no recognizable alteration. An additional 26½ hours at 700° C likewise failed to produce rutile. After further treatment at 950° C for 116 hours, it was found that all of the anatase had been converted to rutile. Earlier preliminary tests by one of the present authors (HEW) indicated the feasibility of synthesizing brookite hydrothermally at low temperatures, by heating saturated solutions of soluble titanium salts and hydrogen peroxide in a steel bomb. A series of experiments is now in progress, in an endeavor to establish brookite - anatase relations in the TiO_2-H_2O system, comparable to those reported by Osborn[7] for the anatase-rutile relations. The results of these and other preliminary experiments outlined above are presented in Table 1.

TABLE 1

EXPERIMENTS ON THE POLYMORPHIC INVERSION OF TiO_2

Starting Material	Temp. (° C)	Time	Products
Rutile in $LiNO_3$	270°	3 dys.	Rutile
Rutile	Liquid N_2	5 min.	Rutile
Anatase	640°	41 hrs.	Anatase
Anatase (preceding run)	700°	26½ hrs.	Anatase
Anatase (preceding run)	950°	116 hrs.	Rutile
Potassium Titanium Oxalate and Hydrogen Peroxide	275 ± 25	3 dys.	Brookite and Anatase
Titanium Sulfate and Hydrogen Peroxide	284°	5 dys.	Anatase and Rutile
Titanium Sulfate and Hydrogen Peroxide	200°	3 dys.	Anatase and Rutile
Potassium Titanium Oxalate and Hydrogen Peroxide	274°	3 dys.	Rutile and K-Titanite (?)

Some preliminary studies have been carried out in the system TiO_2 - B_2O_3. These had a fourfold purpose; to discover whether any intermediate compound is formed, a question left open by Dietzel and Tober; to check the possible existence of a two-liquid area, a feature suggested by the "emulsion" noted by Guertler; to ascertain whether the TiO_2-liquidus is close to B_2O_3 composition-vertical, as suggested by the solubility data of Foex; and to locate approximately the anatase - rutile transition temperature in the presence of B_2O_3.

Seven mixtures were prepared (Table 2) using Baker's C. P. anatase and Fisher's A-76 fused purified boric acid. Disks 1 inch in diameter and 1/16 inch thick were pressed with the aid of paraffin-carbon tetrachloride binder. For each mixture two disks, one on top of the other, were placed on coarse zirconia sand sprinkled on a slab of silica brick. Firing was for 24 or 71 hours at 800° or 900° C, respectively. It was hoped that the bottom disk would act as a buffer for the upper test disk. In the specimens containing over 60% B_2O_3, however, the entire disk-pair flowed into and penetrated the zirconia placing sand, and rendered the specimens useless. There was also evidence of considerable loss of B_2O_3 from volatilization.

The results of these experiments are presented in Table 2. No evidence for any intermediate compound was obtained. The firing temperatures of 800° and 900° C were apparently too low to reveal liquid immiscibility, if such does indeed exist. No reliable information on the location of the liquidus curve was obtained, because of the uselessness of the B_2O_3 - rich specimens for this purpose. Anatase was converted to rutile at both 800° and 900° C.

Tentatively, it appears that the anatase - rutile transition lies below 800° C. Whether or not B_2O_3 enters into the rutile thus formed is open to question. If it does, it would lower the transition temperature characteristic of pure TiO_2.

Samples containing 80, 85, 90, and 95% B_2O_3 were next fired for 1 hour in a platinum crucible, a container having been found necessary in the preliminary runs.

TABLE 2

PRELIMINARY FIRINGS IN THE SYSTEM TiO_2-B_2O_3

Composition (wt %) TiO_2	B_2O_3	Time (hrs)	Temp. (° C)	Phases Present
80	20	65½	900	Rutile + Glass
80	20	24	800	Rutile + Glass
60	40	65½	900	Rutile + Glass
60	40	24	800	Rutile + Glass
40	60	21½	900	Rutile + Glass
40	60	24	800	Rutile + Glass
20	80	1	1400	Rutile + 2 Glasses (?)
20	80	71	900	Rutile + Glass
20	80	24	800	Rutile + Glass
15	85	1	1400	Rutile + 2 Glasses (?)
15	85	71	900	Rutile + Glass
15	85	24	800	Rutile + Glass
10	90	1	1400	Rutile + 2 Glasses (?)
10	90	71	900	Rutile + Glass
10	90	24	800	Rutile + Glass
5	95	1	1400	Rutile + 2 Glasses (?)
5	95	71	900	Rutile + Glass
5	95	24	800	Rutile + Glass

All four samples showed crystals and glass, suggesting that the liquidus curve crosses the 1400° C isotherm between 95% and 100% B_2O_3. This tentative conclusion is in need of further confirmation because 1 hour runs, although minimizing B_2O_3 - volatilization, may not be sufficient to establish maximum solubility. There was some suggestion of liquid immiscibility in the 1400° runs. The glasses from these runs were brown in color and presented a finely-speckled appearance suggesting blebs of different refractive index than the matrix. In contrast, the glasses from the 900° and 800° runs were clear and colorless.

III. THE SYSTEM ZrO_2-B_2O_3

No full-scale investigation of the system zirconia-boric oxide appears ever to have been carried out. Venable and Clarke[14] stated that zirconia is not attacked by molten boric oxide. Guertler[2] reported that ZrO_2 is not dissolved by B_2O_3. However, Foex[3] established the solubility of ZrO_2 at 1200° C as 0.90 moles in 100 moles of B_2O_3, equivalent to a weight percent solubility of 1.57. The liquidus curve in the ZrO_2-B_2O_3 system must therefore descend almost parallel to the B_2O_3 composition vertical. Dietzel and Tober[4] left open the question of compound formation in the system, although the difference in field strength of B_2O_3 (1.45) and ZrO_2 (0.78) lies well beyond the 0.30 limit regarded as the minimum required for compound formation. Baskin, Harada and Handwerk[15] encountered no new phase when several ZrO_2 : B_2O_3 compositions were fired in air at 1200° C for 1 hour. The marked difference in ionic radius and in coordination number between zirconium and boron ions would suggest that molten mixtures of the two oxides might separate into two immiscible liquids[6].

There is no unanimous agreement as to the polymorphic relations of zirconium dioxide. A useful review has recently been presented by Weber and Schwartz[16]. Most workers agree on the existence of at least two polymorphs, a low temperature

monoclinic form corresponding to the mineral baddeleyite, and a higher temperature higher density tetragonal form. Considerable variation exists in the temperatures assigned by different authors to this transition, although most values lie between 950 and 1250° C, the observed differences are apparently due to differences in technique employed to locate the transition, with a lesser effect produced by impurities (notably hafnia) in the ZrO_2. Recent work by Mumpton and Roy[17] on especially pure zirconia places the inversion at 1170° C. Lynch, Vahldiek and Robinson[18], also working with pure ZrO_2, place it between 1182° and 1193° C, in essential agreement with Mumpton and Roy. Although a few workers[19] have maintained that tetragonal zirconia can be quenched through the inversion temperature to room temperature, most investigators agree that the inversion to the monoclinic form proceeds spontaneously, on cooling, causing cracking and destruction of the test specimen. There can be little doubt that tetragonal zirconia has been observed at low temperatures, as noted by Clark and Reynolds[20] and by Weber and Schwartz[16]. But in such instances it has formed metastably at low temperatures by thermal dissociation of zirconium salts, and changes monotropically to the stable monoclinic form upon heating to 500° or 600° C.

Several other forms of zirconia have also been reported. There is wide belief, although little or no direct evidence for it, that tetragonal zirconia inverts at 1700° to 1900° C to a cubic form, stable to the melting point of 2680° C. Cubic solid solutions of zirconia with MgO, CaO_3 etc., are known, and these are believed to represent the stabilized cubic form. Wittels and Sherrill[21] have recently reported conversion of monoclinic ZrO_2 into a cubic form at low temperatures by fast neutron bombardment. This they regard as equivalent to the alleged high temperature cubic form, and as existing metastably at low temperatures, changing to monoclinic zirconia when annealed at 800° C. Cohn[22] early suggested a hexagonal (trigonal) form produced by prolonged heating above 1900° C, which inverted to a pseudohexagonal

orthorhombic form at 625° C. This view has enjoyed little support, but recent work by Evans and Wildsmith[23] has revived the belief in a possible hexagonal form. Sense[24] has suggested the possibility that monoclinic zirconia reappears as a high-temperature phase above 2250° C. Much of the uncertainty existing in binary phase diagrams involving ZrO_2 as one of the components can be traced to the uncertainties still remaining in the polymorphic relations of zirconia.

Some preliminary studies have been made in the system ZrO_2-B_2O_3. These had the same fourfold purpose as similar studies in the TiO_2-B_2O_3 system, reported earlier. The experimental approach, too, was similar. Fine-grained ZrO_2 was obtained by thermal decomposition of zirconium adipate at 300° to 400° C, followed by ignition over a blast-burner to burn off carbonaceous material. X-ray diffraction revealed the product to consist of a mixture of monoclinic and tetragonal (presumably metastable) zirconia. The compositions investigated, and the results obtained, are given in Table 3. Compositions high in B_2O_3 were found to flow readily, and to run off the setting disks (three parts ZrO_2 and 1 part kaolin). This was attributed to the partial hydration of the fused B_2O_3 raw material on standing, to H_3BO_3, with resulting fluidity on firing. This behaviour led to the substitution of H_3BO_3 for the partially hydrated B_2O_3, and to the use of a platinum crucible as container.

X-ray patterns of all test specimens revealed monoclinic ZrO_2 as the only identifiable crystalline phase. No evidence for compound formation was obtained. No all-glass products were obtained, suggesting that the zirconia liquidus lies on the B_2O_3 - rich side of the 5 zirconia: 95 boric oxide composition. Optical examination of the glass phase (marked with an asterisk in Table 3) of some of the runs suggested a two-liquid condition.

In a further attempt to test the possible existence of an intermediate compound, zirconyl nitrate was heated in a large excess (20:1) of H_3BO_3 in a platinum crucible

TABLE 3

PRELIMINARY FIRINGS IN THE SYSTEM ZrO_2-B_2O_3

Composition (wt %) ZrO_2	B_2O_3	Time (hrs)	Temp. (° C)	Phases Present
80	20	16½	900	Glass, ZrO_2 (Mono)
60	40	16½	900	Glass, ZrO_2 (Mono)
40	60	16½	900	(Sample Contaminated)
20	80	16½	900	(Sample Contaminated)
20	80	1¼	1020	Glass,* ZrO_2 (Mono)
20	80	1	1183	Glass,* ZrO_2 (Mono)
20	80	1	1291	Glass,* ZrO_2 (Mono)
15	85	16½	900	(Sample Contaminated)
15	85	2	1010	Glass,* ZrO_2 (Mono)
15	85	1	1181	Glass,* ZrO_2 (Mono)
15	85	1	1291	Glass,* ZrO_2 (Mono)
10	90	16½	900	(Sample Contaminated)
10	90	1	1020	Glass,* ZrO_2 (Mono)
10	90	1	1175	Glass,* ZrO_2 (Mono)
5	95	16½	900	(Sample Contaminated)
5	95	1	1015	Glass,* ZrO_2 (Mono)
5	95	1	1175	Glass,* ZrO_2 (Mono)
5	95	1	1385	Glass,* ZrO_2 (Mono)

at 800° - 900° C for two weeks. Fused B_2O_3 was added during the test to insure a large excess. During cooling of the crucible on removal from the furnace, crystals could be observed to develop. This observation suggests the necessity for quenching samples used to delineate the liquidus curve. The sample was leached with boiling water, and left a residue of monoclinic zirconia crystals 1 to 3 millimeters long.

IV. THE SYSTEM HfO_2 - B_2O_3

Very little phase equilibrium work has been published for systems in which HfO_2 is one of the components. In general, hafnia shows close similarity to zirconia in physical and chemical properties. Like zirconia, it exhibits two polymorphic forms, a low temperature monoclinic form and a high temperature tetragonal form. According to Curtis, Doney and Johnson[25] the transition temperature is about 1700° C and involves a 3.4% density increase. This compares with a transition temperature of about 1180° C and a 7.5% density increase, for the corresponding zirconia inversion. These authors give 2900° ± 25° C as the melting point of HfO_2. A cubic form has also been reported[26]. Richardson, Scott and Shea[27] have synthesized $HfSiO_4$, isostructural with zircon ($ZrSiO_4$). Indeed, natural zircon always contains some $HfSiO_4$ in solid solution, amounting to about 2 percent (calculated as HfO_2 in the ZrO_2 extracted from the zircon). Durif[28] reports that both hafnia and zirconia form 1 : 1 compounds with GeO_2, and both $HfGeO_4$ and $ZrGeO_4$ possess the scheelite structure. As far as is known, no previous work has been reported on the HfO_2-B_2O_3 system. In view of such similarities in behavior between HfO_2 and ZrO_2 as noted above, the HfO_2-B_2O_3 might be expected to show great similarity to the system ZrO_2-B_2O_3. Thus, the discussion of the possibility of compound formation and liquid immiscibility in the system ZrO_2-B_2O_3 applies equally well to the system HfO_2-B_2O_3.

A preliminary study of relations in the HfO_2-B_2O_3 system has been undertaken. As in the TiO_2-B_2O_3 and ZrO_2-B_2O_3 studies, samples were fired in a platinum crucible

TABLE 4

PRELIMINARY FIRINGS IN THE SYSTEM HfO_2-B_2O_3

Composition (wt. %) HfO_2	B_2O_3	Time (hrs)	Temp. (° C)	Phases Present
75	25	2	1400	Glass, HfO_2 (Mono)
20	80	2	1400	2 Glasses (?), HfO_2 (Mono)
15	85	2	1400	2 Glasses (?), HfO_2 (Mono)
15	85	2	1400	2 Glasses (?), HfO_2 (Mono)
10	90	2	1400	2 Glasses (?), HfO_2 (Mono)
5	95	2	1400	2 Glasses (?), HfO_2 (Mono)

because of the fluidity of the B_2O_3 - rich compositions. The results of the few reconnaissance runs are given in Table 4. The only crystalline phase encountered was the monoclinic polymorph of hafnia. No evidence for an intermediate compound was found. The data from these 1400° runs suggests a liquidus curve close to the B_2O_3 end of the system. There is strong evidence for liquid immiscibility in the system. The 2 hour run on the 15 HfO_2 : 85 B_2O_3 sample was particularly revealing in this connection. Small spherical pellets of high refractive index, and approximating 2 microns in size, were clearly visible in a low-index glassy matrix. These pellets were slightly anisotropic, showing a "uniaxial cross" effect characteristic of strained isotropic material. An acetic acid solution completely leached the low index matrix and freed the pellets. It was tentatively concluded from their shape and optical characteristics that these pellets represent a hafnia-rich glass. Other runs showed similar pellets, although these were so much smaller in size that they could not be clearly resolved under the microscope. A distinctly "dingy" appearance characteristic of micro-heterogeneous materials was shown in these runs. Results to date suggest that the syntectic horizontal (the lower limit of the two liquid area) must lie below 1400° C, and that the two liquid area extends from less than 5 percent hafnia to at least 20 percent hafnia.

V. THE SYSTEM ThO_2-B_2O_3-Na_2O

Our interest in this system arises from the possibility that B_2O_3 or the various sodium borates might constitute practical fluxes for recrystallization of ThO_2. Two of the three limiting binary diagrams have been studied and phase diagrams have been published. Cole and Taylor[29] studied the Na_2O-B_2O_3 system in the temperature range 1150° - 1400° C. Morey and Merwin[30] published a phase diagram for the B_2O_3 - rich portion of the system, and Morey[31] later presented a complete diagram. The system ThO_2-B_2O_3 has been the subject of several recent investigations. Rase[32]

recently published a tentative phase diagram, and Baskin, Harada and Handwerk[33] reported additional information on the compound ThB_2O_5. No diagram has been presented for the system Na_2O-ThO_2.

Because of the intermediate compound ThB_2O_5, boric oxide is not a practical solvent or flux for the low temperature growth of thoria crystals. It was decided to investigate the possibility of borax ($Na_2B_4O_7 \cdot 10H_2O$) as a low temperature flux for thoria. Accordingly, some preliminary runs were made in the ThO_2-B_2O_3-Na_2O system to determine if the compatibility triangle configuration is favorable. The samples studied, and the results obtained, are presented in Table 5.

Samples 2 and 3 were prepared from pure ThO_2 and reagent grade sodium carbonate monohydrate; samples 1 and 4 from thoria and borax; samples 5, 6 and 8 from thoria, borax and boric oxide; samples 7 from thoria and sodium sulfate; and sample 9 from thoria and boric oxide.

It was first necessary to find out whether compounds exist along the Na_2O-ThO_2 binary system, as this would affect the Alkemade line arrangement within the ternary diagram. The purpose of samples 2, 3, and 7 was to find out whether such a compound or compounds could be synthesized. Sampes 2 and 3 gave no evidence of a compound. The X-ray pattern of sample 7 shows several small peaks which could not be matched with any compound listed in the A. S. T. M. card file. Optical examination of the same sample failed to disclose anything other than thoria and glass. Further attempts will be made to synthesize a compound in this binary system, but, except for the anomalous X-ray pattern of sample 7, the evidence thus far is against the existence of a compound.

Assuming there is no compound along the Na_2O-ThO_2 side of the diagram, all the possible joins within the ThO_2-B_2O_3-Na_2O ternary diagram have been added to the sketch (Fig. 1).

TABLE 5

PRELIMINARY FIRINGS IN THE SYSTEM ThO_2-B_2O_3-Na_2O

Sample No	Composition (wt. %) Na_2O	ThO_2	B_2O_3	Time (hrs)	Temp. (° C)	Phases Present
1.	9.0	70.0	21.0	½	900	ThO_2, Glass
2.	21.0	79.0	----	½	900	ThO_2, Na_2CO_3
3.	(ThO_2 in excess Na_2CO_3)			2½	1000-1100	ThO_2, Na_2CO_3
4.	28.5	7.0	64.5	5	750-800	ThO_2, Glass, $Na_2B_4O_7$
5.	11.5	48.5	40.0	5	750-800	ThO_2, Glass, $Na_2B_6O_{10}$ (?)
6.	11.5	37.0	51.5	5	750-800	ThO_2, Glass, $Na_2B_8O_{13}$ (?)
7.	21.0	79.0	----	2	1400	ThO_2, Glass, Unident. Phase
8.	15.0	13.0	72.0	2	1400	ThB_2O_5, ThO_2, Two Glasses (?)
9.	(ThO_2 in excess B_2O_3)			5	1400	ThB_2O_5, Two Glasses (?)

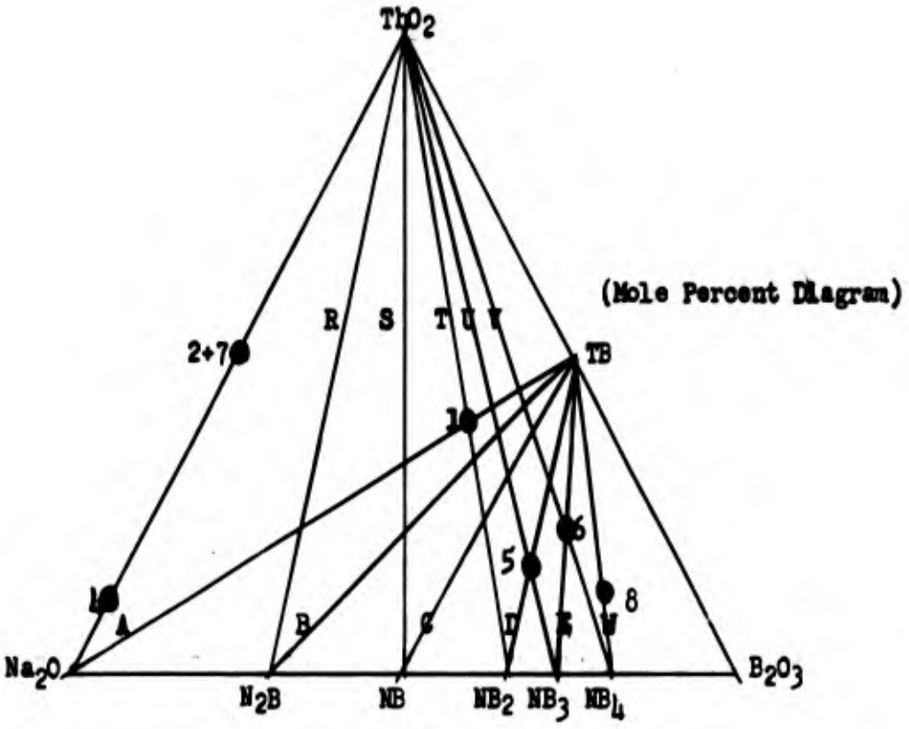

FIGURE 1

Diagram Showing all of the Theoretically Possible Compatibility Joins in the System ThO_2-B_2O_3-Na_2O.

Tentatively, the results tabulated in Table 5 may be interpreted thus: Sample 1 eliminates joins A, B, and C; sample 5 eliminates join D; sample 6 eliminates join E; sample 8 confirms join W.

It is not certain that samples 5 and 6 were fired long enough for ThB_2O_5 to form from the particular compositions used; however, Rase's success in synthesizing ThB_2O_5 at 325° C in two hours is reassuring. Thus, it appears that the actual arrangement of joins within the ThO_2-B_2O_3-Na_2O system is as shown below in Figure 2.

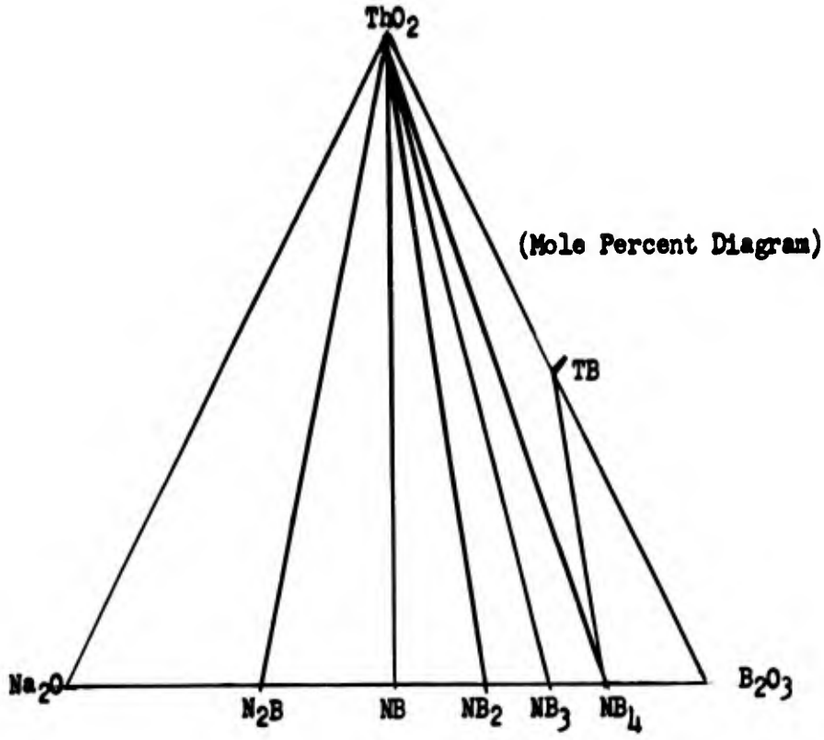

FIGURE 2

Tentative Compatibily Joins in the System ThO_2-B_2O_3-Na_2O.

Since the N_2B to ThO_2 join is valid, any compound, which, in the future, may be found in the Na_2O-ThO_2 binary system can be joined only with N_2B.

The liquid immiscibility evident in sample 8 will bear further investigation. If the ThB_2O_5 crystals represent quench growth, then the eutectic between NB_4 (m.p. 816° C) and TB (m.p. 1483° C) lies, in the ternary diagram, between sample 8 and NB_4, and sample 8 lies in a two-liquid area. Liquid immiscibility was also observed in sample 9.

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Investigator William C. Beard Date 5 Feb. 62

William C. Butterman Date 5 Feb. 62

Donald E. Kaufman Date 5 Feb. 62

Henry E. Wenden Date 5 Feb 62

Supervisor Wilfred R. Foster Date 2/5/62

For The Ohio State University Research Foundation

Executive Director Oran C. Worlpert Date 2/6/62

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