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THE SYSTEM $PbO-B_2O_3-SiO_2$

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ABSTRACT

The system was investigated by well-known methods of quenching and petrographic examination. One ternary compound, $5PbO.B_2O_3.SiO_2$, was established. Over 90 percent of the system is occupied by the fields of $PbO.2B_2O_3$ and of SiO_2 and these fields lie predominantly under a two-liquid area. That portion of the system containing less than 60 percent of PbO is incomplete.

CONTENTS

I. INTRODUCTION

This report covers the results of studies on the system $PbO-B_2O_3-SiO_2$, a combination of oxides of interest primarily to manufacturers of glazed semiporcelain ware and of colors used for decorating ceramic whiteware and glass. These oxides are used also in the production of some glasses and vitreous enamels. The study is a part of the general investigation on systems containing PbO.[1]

The study of phase equilibria was limited, with the exception of a few melts, to mixtures containing more than 50 percent by weight of PbO because melts containing lower percentages are of very high viscosity. This property, in conjunction with the continued volatilization of B_2O_3 and of PbO at crystallizing temperatures, makes the attaining of even partial equilibrium in these viscous mixtures extremely difficult and time-consuming. Furthermore, it is believed evident that the ternary compound established by this study is the only one to form in the system.

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[1] R. F. Geller, A. S. Creamer, and E. N. Bunting, J. Research NBS **13**, 237 (1934) RP705. R. F. Geller and E. N. Bunting, J. Research NBS **17**, 277 (1936) RP911; and **18**, 585 (1937) RP995.

II. EXPERIMENTAL PROCEDURE

1. PREPARATORY WORK

"End members" were sublimed litharge (PbO) containing 0.02 percent of total detected impurities, boric acid of reagent quality containing less than 0.01 percent of total detected impurities, and quartz crystal (SiO_2) containing 0.02 percent of nonvolatile residue on evaporation with HF and H_2SO_4.

All fusions were made in platinum, using electrically heated furnaces. One hundred and five melts were analyzed chemically and portions of these used in various combinations to obtain additional preparations. When preparing the melts, it was necessary to allow for volatilization of PbO and of B_2O_3 in order to approximate the desired composition.

The melts became increasingly unstable in air as the percentage of B_2O_3 exceeded about 30 and, for convenience, all preparations of melts and of crystallized samples were stored over P_2O_5.

To determine SiO_2, 0.5-g samples were fused with Na_2CO_3, dissolved in hot dilute HCl, evaporated almost to dryness, and the moist residue evaporated three times with 10 ml of CH_3OH saturated with HCl. This removed the B_2O_3. Silica was then determined in the usual way.

The PbO was determined as sulfate by double or, when necessary to obtain constant values, by triple evaporation with HF and H_2SO_4.

B_2O_3 was determined by difference.

All chemical analyses were made by A. S. Creamer.

2. TEST METHODS

Thermal studies were made by the quenching method.[2] The samples for quenching were held in capsules of platinum foil. Pt to Pt–Rh thermocouples were used for temperature measurements and were calibrated by observing the melting temperature of KCl (770.3° C). Usually air quenching was sufficient; otherwise the samples were dropped into CCl_4.

When working with compositions which crystallize readily, it is customary to quench from progressively lower temperatures and to note the temperature intervals within which crystals first appear. When, however, the melts are very viscous and the rates of crystallization extremely low, it is more feasible to obtain at least partial equilibrium at some temperature below the solidus and then quench from progressively higher temperatures. By this method, the investigator notes the temperature intervals within which the various crystal phases disappear.

The time required to crystallize the melts varied over a wide range. Compositions in which PbO exceeded 90 percent could be crystallized overnight, whereas many of those containing less than 80 percent were only partially crystallized after holding them several months at temperatures below the estimated solidus. In several instances, as illustrated in table 1 (for example, melts 110, 140, and 160), melts held at temperatures below the liquidus in the two-liquid area still contained two liquids. The time that melts could be held to attain equilibrium was limited in some cases by volatilization from the sample or by attack on the platinum capsules. For example, in the preliminary work some melts were held unnecessarily long and the index of refrac-

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[2] F. C. Kracek, N. L. Bowen, and G. W. Morey, J. Phys. Chem. **33**. 1857 (1929).

tion of the glass, after remelting, or even the primary phase if the melt was near a boundary, would be different from that found for the same melt held for a shorter time. It was assumed that the composition had been changed by volatilization.

With the exception of a few of the compositions highest in PbO, samples of the previously crystallized melts were held at least overnight before each quench. Frequently it was necessary to compromise between the time required to reach complete equilibrium and attack on the capsule. Such attack resulted in the capsules becoming black and brittle; and frequently the melts contained a scattering of small, prismatic crystals which probably were composed in part of platinum.

Table 1.—*Some compositions at approximately 10-percent intervals in the silica and lead diborate fields*

Melt number	Composition			Held to crystallize		Treatment before quenching		Phases present
	PbO	B_2O_3	SiO_2	Time	Temperature	Time held	Temperature	
	Percent	*Percent*	*Percent*	*Days*	*°C*	*hr*	*°C*	
110	10.1	48.9	41.0	260	650			Two glasses, lower index<(1.47
120	20.0	39.7	40.3	90	800			Two glasses, lower index 1.47.
120						23	845	Two glasses.
120						46	850	Glass index 1.505.
130	30.2	29.3	40.5	90	800			Two glasses.
130						24	865	Do.
130						23	875	Glass, index 1.54.
140	40.4	19.7	39.9	106	600			Quartz and two glasses.
140						6	960	Tridymite and two glasses.
140						18	975	Glass, opalescent.
150	50.2	10.2	39.6	106	600			Quartz and glass.
150						18	1070	Tridymite and glass.
150						5	1080	Glass, index 1.63.
160	10.2	59.5	30.3	260	650			$PbO.2B_2O_3$ and two glasses.
160						72	740	Do.
160						48	750	Two glasses, lower index<1.47.
160						48	760	Glass index, 1.485.
170	20.6	49.0	30.4	260	650			Minute crystals and two glasses.
170						48	750	$PbO.2B_2O_3$ and two glasses.
170						20	760	Two glasses.
170						48	800	Do.
170						48	820	Glass, index 1.505.
180	30.4	39.0	30.6	260	650			$PbO.2B_2O_3$ and two glasses.
180						72	750	Do.
180						72	770	Two glasses.
180						23	850	Do.
180						22	870	Glass, index 1.54.
200	50.2	19.9	29.9	91	800			Quartz and two glasses.
200						24	900	Tridymite and two glasses.
200						24	910	Two glasses, higher index 1.65.
210	60.1	10.3	29.6	107	600			Quartz and glass.
210						24	1025	Tridymite and glass.
210						47	1035	Glass, index 1.72.
250	40.2	39.6	20.2	30	600			Two glasses.
260	50.5	29.2	20.3	12	695			Two glasses, index—*a*, 1.75; *b*, 1.47.
270	60.4	19.4	20.2	122	490			Quartz and glass.
270						18	815	Do.
270						2	825	Glass, index 1.72.
280	69.9	10.2	19.9	122	490			Quartz, $PbO.SiO_2$ and glass.
280						1	625	Do.
280						1	630	Quartz and glass.
280						1	775	Do.
280						18	790	Glass, index 1.79.
330	50.2	39.8	10.0	13	650			Two glasses, upper index 1.76.
340	60.1	29.9	10.0	13	650			$PbO.2B_2O_3$ and two glasses.
340						23	735	$PbO.2B_2O_3$ and glass.
340						24	740	Glass, 1.72.
350	70.1	19.9	10.0	30	600			$PbO.2B_2O_3$ and glass.
350						18	680	Do.
350						18	685	Glass index, 1.80.

The petrographic microscope was used to determine the phases in quenched samples. Identification of the crystalline phases was limited practically to the establishment of optical character and indices of refraction. Samples in solid media (ranging in index of refraction from 1.74 to 2.58) were examined by means of white light passed through a No. 25 Wratten filter, which type of illumination had been used in determining the indices of the media.[3]

X-ray diffraction patterns were made and interpreted by H. F. McMurdie. Samples were pulverized and mounted with collodion on glass rods 0.1 to 0.2 mm in diameter. The sample, placed at the center of a cylindrical camera with a radius of 5.70 cm, was rotated constantly during 17 hours' exposure. Radiation was produced by a gas-type tube with copper target, the tube being operated at approximately 40 kv and 4 to 5 ma. The Kβ-radiation was removed by a nickel filter at the entrance to the camera.

III. BINARY SYSTEMS OF COMPONENTS

The systems PbO-SiO_2 and PbO-B_2O_3 have been described by the authors.[4]

The system B_2O_3-SiO_2 has been investigated by Greig [5] and by Cousen and Turner,[6] who believe these oxides as glasses to be completely miscible in all proportions.

Since the report by the authors on the system PbO-B_2O_3, the crystallization of B_2O_3 has been accomplished [7] and its properties reported.[8]

IV. TERNARY COMPOSITIONS AS GLASSES

The thermal expansion, softening temperature by interferometer method, and relative solubility of compositions at 10-percent intervals have been reported.[9] Index of refraction values of the same melts, and additional ones in the high PbO region, are shown in figure 1. In the majority of cases the melts were either too viscous to permit "fining" to clear, uniform glasses, or they were opalescent because of separation into two liquids. Consequently, the values given in the figure represent the average indices.

The value for B_2O_3 glass is taken from the work of Morey and Merwin [10] and the value for SiO_2 glass from Tilton and Tool.[11]

V. THE TWO-LIQUID AREA

At least 90 percent of the system is occupied by the fields of SiO_2 and of $PbO.2B_2O_3$, and the greater portion of both these fields lies under a region of liquid immiscibility (fig. 2). Very little is known about the two-liquid area. Its boundaries, as indicated in figure 2, were estimated largely by whether or not the melts developed opaqueness without the development of crystals discernible either micro-

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[3] These media had been prepared, during another investigation, by L. T. Brownmiller, using piperine and iodides, and sulfur and selenium mixtures, as recommended by Esper S. Larsen and Harry Berman in United States Geological Survey Bulletin 848 (1934).

[4] See footnote 1.

[5] J. W. Greig, Am. J. Sci. [5] **13**, 133 (1927).

[6] A. Cousen and W. E. S. Turner, J. Soc. Glass Tech. **12**, 169 (1928).

[7] L. McCulloch, J. Am. Chem. Soc. **59**, 2650 (1937).

[8] F. C. Kracek, G. W. Morey, and H. E. Merwin, Am. J. Sci. [5] **35A**, 143 (1938).

[9] R. F. Geller, E. N. Bunting, and A. S. Creamer, J. Research NBS **20**, 57 (1938) RP 1064.

[10] G. W. Morey and H. E. Merwin, J. Am. Chem. Soc. **58**, 2248 (1936).

[11] L. W. Tilton and A. Q. Tool, BS J. Research **3**, 619 (1929) RP112.

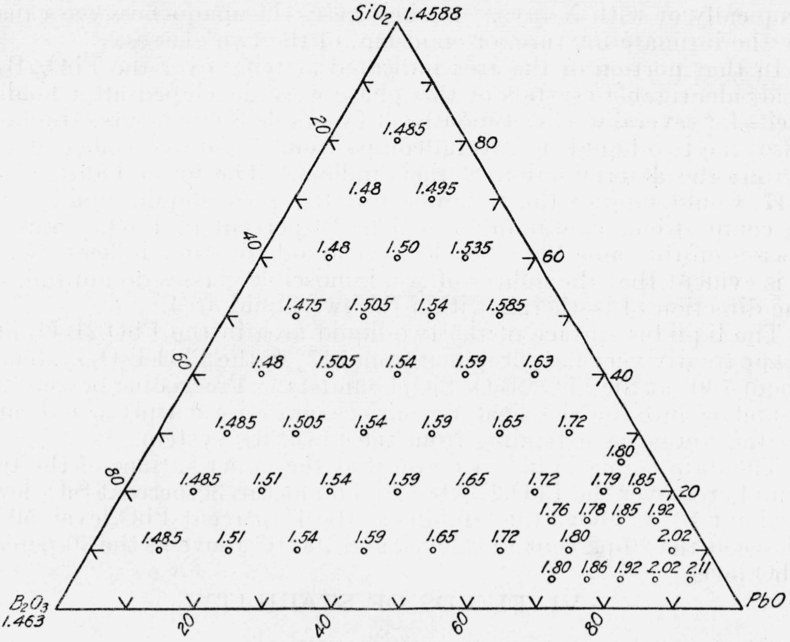

FIGURE 1.—*Average indices of refraction of compositions as glasses.*

Values below 1.72 are believed accurate within ±0.005, and higher values within ±0.01.

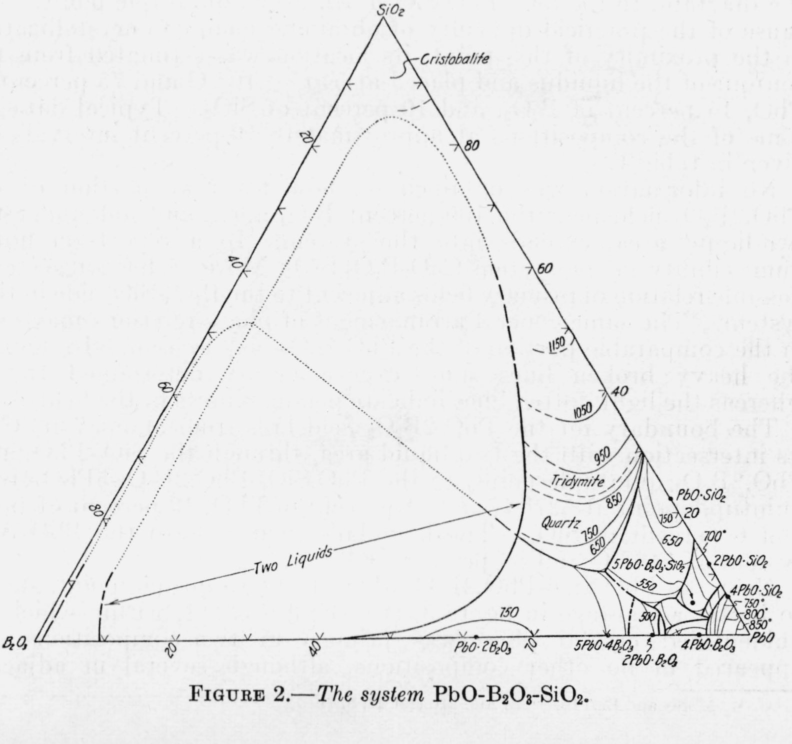

FIGURE 2.—*The system* $PbO-B_2O_3-SiO_2$.

scopically or with X-rays. In these cases the opaqueness was caused by the intimate mixture, or emulsion, of the two glasses.

In that portion of the area indicated as lying over the $PbO.2B_2O_3$ field, identifiable crystals of this phase were developed after holding melts for several weeks or months at favorable temperatures (table 1). Also, the two liquids in several compositions separated sufficiently to permit the determination of their indices. The lower index, about 1.47, would support the assumption that the two-liquid area extends to compositions containing less than 10 percent of PbO. Since all glasses on the same PbO "level" have about the same indices (fig. 1), it is evident that the indices of two immiscible glasses do not indicate the direction of isotherms within the two-liquid area.

The liquidus surface of the two-liquid area in the $PbO.2B_2O_3$ field is apparently very flat, dropping from 742° in the PbO-B_2O_3 system to about 730° at the $PbO.2B_2O_3$-SiO_2 boundary. Proceeding beyond this boundary into the SiO_2 field, the surface must rise sharply as indicated by the isotherms extending from the PbO-SiO_2 system.

The data (table 1) indicate also that the upper surface of the two-liquid area over the $PbO.2B_2O_3$ field, and at the 30-percent SiO_2 level, is about 10° C above the liquidus at the 10-percent PbO level, 50° C above at the 20-percent PbO level, and 100° C above at the 30-percent PbO level.

VI. FIELDS OF STABILITY

1. SiO_2 AND $PbO.2B_2O_3$

That portion of the SiO_2 field which is known not to be under the two-liquid area extends as a narrow belt, along the PbO-SiO_2 side of the diagram, to the SiO_2-$PbO.SiO_2$-$PbO.2B_2O_3$ quintuple point. Because of the practical difficulty of obtaining complete crystallization in the proximity of this point, its location was estimated from the contour of the liquidus and placed at 540° ±10° C and 75 percent of PbO, 15 percent of B_2O_3, and 10 percent of SiO_2. Typical data for some of the compositions at approximately 10-percent intervals are given in table 1.

No information was obtained on how far that portion of the $PbO.2B_2O_3$ field near the 100-percent B_2O_3 apex, and not under the two-liquid area, extends into the system. In a report on liquid immiscibility in the system CaO-B_2O_3-SiO_2, Morey [12] has suggested a possible relation of primary fields adjacent to the B_2O_3-SiO_2 side in that system. The same general arrangement of phase relations may exist in the comparable portion of the PbO-B_2O_3-SiO_2 system. In figure 2 the heavy broken lines show experimentally determined trends, whereas the light dotted lines indicate possible limits of the fields.

The boundary for the $PbO.2B_2O_3$ field falls from about 730° C at its intersection with the two-liquid area, through the SiO_2-$PbO.SiO_2$-$PbO.2B_2O_3$ quintuple point, to the $PbO.SiO_2$-$PbO.2B_2O_3$-$5PbO.4B_2O_3$ quintuple point at 527° C and 81 percent of PbO, 13 percent of B_2O_3, and 6 percent of SiO_2. The boundary then rises to the PbO-B_2O_3 system at 548° C and 83 percent of PbO.

Near the $PbO.SiO_2$-$PbO.2B_2O_3$-$5PbO.4B_2O_3$ quintuple point, shown to better advantage in figure 3, is a small area, *A*, within which an unidentified crystal phase was primary in two compositions. It appeared in no other compositions, although several in adjacent

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[12] G. W. Morey and Earl Ingerson, Am. Mineral. **22**, 37 (1937).

portions of this system begin to crystallize within the temperature range in which phase *A* was found in the binary system (530° to 580° C).[13] It is believed to be a metastable form either of $PbO.2B_2O_3$ or of $5PbO.4B_2O_3$. Adjacent boundaries are shown in broken lines to indicate that the field of phase *A* may or may not be completey enclosed by the field of $PbO.2B_2O_3$. It should be noted that the secondary phase in melt 445 (fig. 3), which phase appears on cooling at the intersection of the dotted line (crystallization curve) with the $PbO.SiO_2$ boundary, is $PbO.2B_2O_3$, and therefore field *A* does not extend to the quintuple point at 527° C.

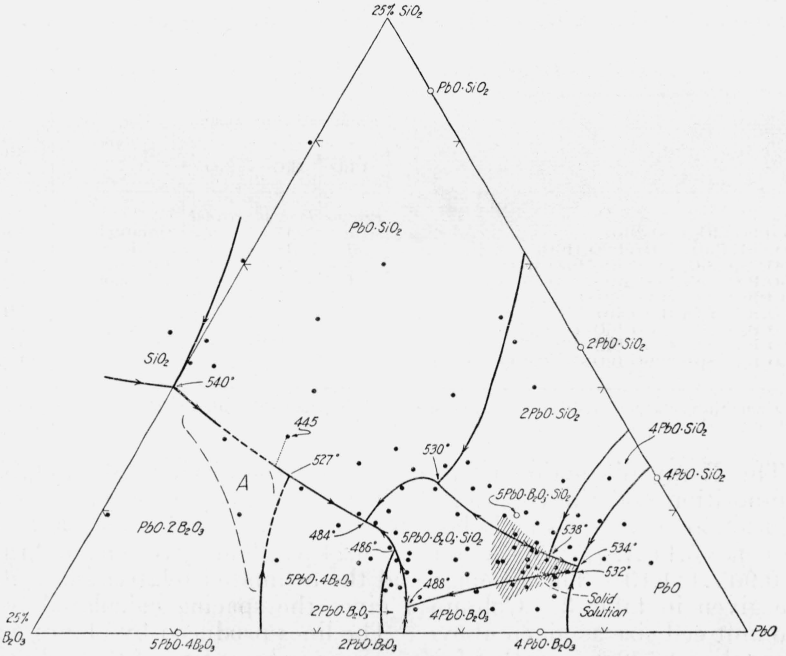

FIGURE 3.—*That portion of the system* PbO-B_2O_3-SiO_2 *containing over 75 percent (by weight) of* PbO.

2. $5PbO.B_2O_3.SiO_2$

Pentalead borosilicate (89.58 percent of PbO, 5.59 percent of B_2O_3, and 4.83 percent of SiO_2) is the only ternary compound found in this system. It melts incongruently at 551° C to form $2PbO.SiO_2$ and liquid.[14] Its field, although small (fig. 3), is bounded by the fields of seven other compounds, and its boundary includes the three eutectic points and all of the quintuple points, except the two already discussed, which are found in this system (table 2).

Optically the prismatic crystals of $5PbO.B_2O_3.SiO_2$ are nearly, or quite, uniaxial; character is negative; and the indices of refraction are ϵ (or α) 2.04 ± 0.005, and ω (or β and γ) 2.085 ± 0.005. At tempera-

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[13] This is the same phase which appeared in the PbO-B_2O_3 system. R. F. Geller and E. N. Bunting, J. Research NBS **18**, 585 (1937) RP995.

[14] It is interesting that the only ternary compound found at the liquidus in the system lime-boric oxide-silica has the same molecular ratio (see E. P. Flint and Lansing S. Wells, J. Research NBS **17**, 727 (1936) RP941).

tures above approximately 535° C, and in compositions occupying the central and "high-lead" portions of the shaded area (fig. 3), these crystals have indices of refraction equal to 2.09 (min) and 2.12 (max). In compositions at the "low-lead" fringe of the area, and at temperatures between about 535° and 545° C, the indices were found to be about 2.08 (min) and 2.10 (max). The interference figure appeared the same for all of these crystals. That the changes in indices result from solid solution and do not evidence polymorphism in the ternary compound is shown by the results of McMurdie's examinations:

TABLE 2.—*Invariant points in the system lead borosilicate*

	Composition by weight			Type	Temperature
	PbO	B_2O_3	SiO_2		
	Percent	*Percent*	*Percent*		*°C*
SiO_2-$PbO.SiO_2$-$PbO.2B_2O_3$	75	15	10	Quintuple	540±10
$PbO.SiO_2$-$PbO.2B_2O_3$-$5PbO.4B_2O_3$	81	13	6	do	527±5
$5PbO.B_2O_3.SiO_2$-$PbO.SiO_2$-$5PbO.4B_2O_3$	84.5	11.0	4.5	Eutectic	[a] 484±2
$5PbO.B_2O_3.SiO_2$-$PbO.SiO_2$-$2PbO.SiO_2$	86.3	7.6	6.1	Quintuple	530±3
$5PbO.B_2O_3.SiO_2$-$2PbO.SiO_2$-$4PbO.SiO_2$	91.5	5.3	3.2	do	538±2
$5PbO.B_2O_3.SiO_2$-$4PbO.SiO_2$-PbO	92.7	4.5	2.8	do	[a] 534±2
$5PbO.B_2O_3.SiO_2$-$4PbO.B_2O_3$-PbO	92.7	4.8	2.5	Eutectic	[a] 532±2
$5PbO.B_2O_3.SiO_2$-$4PbO.B_2O_3$-$2PbO.B_2O_3$	87.5	11.4	1.1	do	[a] 488±2
$5PbO.B_2O_3.SiO_2$-$2PbO.B_2O_3$-$5PbO.4B_2O_3$	86.0	10.6	3.4	Quintuple	[a] 486±2

[a] Under the particular conditions of test used in this investigation, this value is believed to be reproducible within ±1° C.

The X-ray diffraction pattern of the crystallized $5PbO.B_2O_3.SiO_2$ composition and the composition in the central portion of the solid solution area (crystals and glass) indicated an orthorhombic structure with $a_0=5.14$ A, $b_0=5.68$ A, and $c_0=6.24$ A. This gives an axial ratio of 0.905:1:1.10. The spacings and the estimated relative intensities are given in table 3. Column 4 gives the spacing calculated from the unit cell size as given above. The lines produced by planes with d less than 1.552 were rather faint owing to absorption of the radiation by the Pb.

TABLE 3.—*Interplanar spacings of* $5PbO.B_2O_3.SiO_2$

d_{hkl} observed	Relative intensity [a]	Miller indices	d_{hkl} calculated	d_{hkl} observed	Relatve intensity [a]	Miller indices	d_{hkl} calculated
A			*A*	*A*			*A*
4.19	*S*	011	4.19	2.07	*W*	003	2.08
3.96	*S*	101	3.97	1.98	*M*	202	1.98
3.25	*S*	111	3.25	1.928	*M*	103	1.932
3.12	*S*	002	3.12	1.867	*M*	212	1.868
2.84	*SS*	020	2.84	1.832	*S*	113	1.831
2.75	*M*	012	2.73	1.782	*SS*	130	1.777
2.30	*WW*	121	2.29	1.650	*WW*	301	1.650
2.19	*WW*	211	2.19	1.631	*WW*	222	1.631
2.11	*W*	022	2.10	1.552	*M*	132	1.550

[a] S, strong; SS, very strong; M, medium; W, weak; WW, very weak.

3. $PbO.SiO_2$, $2PbO.SiO_2$, $4PbO.SiO_2$, PbO, $4PbO.B_2O_3$, $2PbO.B_2O_3$ AND $5PbO.4B_2O_3$

There are no unusual features about the fields for these compounds. The boundary curves, and the important temperatures and invariant points, may be obtained from figures 2 and 3, and table 2.

VII. SUMMARY

The compositions studied have some potential value to those interested in stable, low-melting glasses of high refractive index. Their value as ceramic glazes is limited and has been discussed in a previous publication (see footnote 9).

Phase relations within the system resemble those for the system $CaO-B_2O_3-SiO_2$ in two particulars; the two-liquid area covers a large portion of the diagram; and the one ternary compound possessing a field in each system has the same molecular ratio (5:1:1).

The new compound, $5PbO.B_2O_3.SiO_2$, melts incongruently at 551° C to form $2PbO.SiO_2$ and liquid. It is negative in character and the X-ray pattern shows orthorhombic, and therefore biaxial, structure. Interference figures indicated the crystals to be nearly, or quite, uniaxial. The indices of refraction are ϵ (or α) 2.04 ± 0.005 and ω (or β and γ) 2.085 ± 0.005. Throughout a small area it forms solid solutions as a result of which the indices are raised to 2.10 (min) and 2.12 (max), but an X-ray pattern of solid solution crystals having these indices did not show a measurable shift as compared with the pattern for the compound composition.

The liquidus of the lowest-melting eutectic is at 484° C and 84.5 percent of PbO, 11.0 percent of B_2O_3, and 4.5 percent of SiO_2.

WASHINGTON, April 28, 1939.