THE SYSTEM PbO–B₂O₃

By R. F. Geller and E. N. Bunting

ABSTRACT

The system PbO-B₂O₃, of interest to investigators and manufacturers of ceramic glazes and glasses, was studied by well-known methods involving quenching and petrographic examination. In addition, limits of liquid immiscibility were obtained by direct observation. Seven crystalline forms of binary compounds were found and the chemical compositions of six of these established. A number of compositions were studied also as glasses to obtain data on thermal expansion, softening behavior, and relative solubility.

CONTENTS

I. INTRODUCTION

The study of this system is part of a general investigation of phase relations involving PbO with other oxide constituents of ceramic glazes and glasses. The first study [1] covered the system PbO-SiO₂ and the second [2] covered the system K₂O-PbO-SiO₂.

Although there are other oxides of lead, only the monoxide is stable above approximately 450° C.[3]

For mixtures containing over 30 percent of B₂O₃ the present study was limited to data at the liquidus only, partly because of their very high viscosity at temperatures below the liquidus and partly because of the hygroscopic nature of melts containing over approximately 40 percent of B₂O₃. The melting point of PbO is taken from the study referred to in footnote 1, and the melting point of B₂O₃ (294±1° C) is taken from a report by Cole and Taylor.[4] This value has been questioned by Morey and Merwin.[5]

[1] R. F. Geller, A. S. Creamer, and E. N. Bunting, J. Research NBS 13, 237 (1934) RP705.
[2] R. F. Geller and E. N. Bunting, J. Research NBS 17, 277 (1936) RP911.
[3] J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, 7, 672. (Longmans, Green and Co., New York, N. Y.)
[4] S. S. Cole and N. W. Taylor, J. Am. Ceram. Soc. 18, 55 (1935).
[5] G. W. Morey and H. E. Merwin, J. Am. Chem. Soc. 58, 2248 (1936).

II. PREPARATORY WORK

1. PREPARATION OF MIXTURES

"End members" were sublimed litharge (PbO) containing 0.02 percent of total detected impurities, and boric acid of reagent quality containing less than 0.01 percent of total detected impurities.

All fusions were made in platinum, using electrically heated furnaces. The well mixed ingredients were allowed to react overnight at about 800° C and were then taken to 1,000° C to drive off all water from the boric acid. As shown by the values in table 1, losses by volatilization during preparation of the melts were in direct relation to the percentage of each oxide in the batch mixture. Thirty melts were analyzed chemically and portions used in various combinations to obtain additional preparations.

Although melts containing less than 40 percent of B_2O_3 appeared stable in air many of higher B_2O_3 content were very hygroscopic and therefore, for convenience, all preparations were stored over P_2O_5. The variation in time required for crystal growth to attain equilibrium was also extreme. Because of quench growths clear glass could not be obtained with those melts in which the content of PbO was higher than 94 percent, while melts containing over 28 percent of B_2O_3 did not attain equlibrium when held as long as 1 month at temperatures below the solidus.

TABLE 1.—*Relative volatilization of PbO and of B_2O_3 from lead-borate melts*

PbO put in batch [a]	PbO found in melt	PbO put in batch [a]	PbO found in melt	PbO put in batch [a]	PbO found in melt
%	%	%	%	%	%
96.9	96.6	82.1	82.5	56.8	58.5
94.6	94.2	80.8	81.3	50.6	52.0
93.5	93.7	79.8	80.4	46.8	48.6
92.6	92.7	79.0	79.5	43.4	44.9
92.3	92.2	77.7	78.5	35.2	36.7
91.2	91.2	76.5	77.1	29.0	30.1
90.2	90.1	75.5	76.0	25.2	25.9
87.8	88.0	71.6	72.5	14.0	14.1
86.1	86.4	67.2	68.3	4.9	5.1
86.0	86.2	60.6	61.8	1.9	2.1

[a] Calculated on the anhydrous basis, the difference between the PbO content given and 100 percent being B_2O_3.

A higher "found" value for PbO shows that B_2O_3 volatilized more rapidly than did PbO. Equal values for "batch" and "found" content show that the PbO and B_2O_3 volatilized in equal proportionate amounts.

2. CHEMICAL ANALYSES

The PbO content was determined as sulfate by double or, when necessary to obtain constant values, by triple evaporation with HF and H_2SO_4. The B_2O_3 was determined by difference. All analyses were made by A. S. Creamer.

III. EXPERIMENTAL PROCEDURE

Thermal studies were made by the quenching, and by the differential thermocouple, method. The latter method was not productive of significant results. Both methods are well established.[6] Pt to Pt-Rh thermocouples were used for temperature measurements and were cal-

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

ibrated by observing the melting temperature of KCl (770.3° C). When air quenching did not suffice, the samples were dropped into CCl_4.

The petrographic microscope was used to determine the phases present 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.

Maximum temperatures in the area of liquid immiscibility were determined by direct observation of melts heated and cooled slowly through the critical range. Change from clear to opaque glass (or vice versa) usually occurred in a range of 4° C or less. The sample (approximately 1 g in a 25-ml crucible) was observed through fused-quartz windows. A spotlight was directed on the melt when the furnace was too cool to provide sufficient illumination. Accuracy of the method was determined by observing the melting and freezing of KCl.

Determinations of linear thermal expansion and observations of the temperature of initial softening (T_s values) of compositions as glasses were made by the interferometer method, using electrically heated furnaces, a temperature rise of from 2.0 to 2.5° C per minute, and chromel-alumel thermocouples for temperature measurements.

Values for relative solubility were obtained on approximately 0.5-g samples which passed a no. 200, and were retained on a no. 325, U. S. Standard sieve. Each sample was boiled for ½ hour, under reflux, in 100 ml of 4-percent acetic acid and the PbO dissolved was estimated by titration with ammonium molybdate solution, using tannic acid solution as the external indicator.

IV. RESULTS

1. PHASE RELATIONS

Results of the quenching tests are summarized in table 2, and the phase relations indicated by them are shown in figures 1 and 2.

PbO melts at $886 \pm 2°$ C and is the primary phase in melts containing from 93.7 to 100 percent of PbO.

$4PbO.B_2O_3$ is the primary phase, in the β form, from 88 percent to 91.7 percent of PbO and, in the α form, from 91.7 percent to 93.7 percent of PbO.

$\alpha 4PbO.B_2O_3$ melts congruently at 565° C[7] and reverts to the β form either very sluggishly or not at all. The eutectic composition between α4:1 and PbO melts at 560° C. Optical properties of the α form are: indices of refraction, maximum, 2.15, minimum, 2.20;[8] character was not established.

$\beta 4PbO.B_2O_3$ apparently melts congruently at about 555° C, and the eutectic temperature between the β form and PbO is about 549° C. Determination of the melting temperature is not shown clearly by the quenched samples because of the simultaneous process of transformation of the β to the α form, which transformation under equilibrium conditions is estimated to proceed at a maximum rate at about 552° C. Optical properties of the β form are: indices of refraction $\alpha 2.15$, $\beta 2.20$, $\gamma 2.24$; character biaxial negative; optic axial angle $(2V)$ about 80°.

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[7] For accuracy of temperatures given in the text see footnote (a) to table 2.
[8] All index of refraction values are accurate within ±0.01.

TABLE 2.—*Data from quenching and petrographic examination*

PbO	B₂O₃	t[a]	Primary phase	Reaction
%	%	°C		
96. 6	3. 4	[b]	PbO	
94. 5	5. 5	655 ±5	PbO	Liquidus.
93. 7	6. 3	560	PbO and α4:1	Eutectic.
93. 7	6. 3	549	PbO and β4:1	Do.
93. 7	6. 3	553	----------------	β4:1→α4:1 transformation.
93. 2	6. 8	564	α4:1	Liquidus.
92. 7	7. 3	565	α4:1	Melting of compound.
92. 7	7. 3	552	----------------	β4:1→α4:1 transformation.
92. 2	7. 8	561	α4:1	Liquidus.
92. 2	7. 8	554	----------------	β4:1→α4:1 transformation.
91. 2	8. 8	548	β4:1	Liquidus.
90. 1	9. 9	537	β4:1	Do.
88. 0	12. 0	493	α2:1 and β4:1	Eutectic.
88. 0	12. 0	473	----------------	β2:1→α2:1 transformation.
87. 3	12. 7	497	α2:1	Liquidus.
87. 3	12. 7	475	----------------	β2:1→α2:1 transformation.
86. 6	13. 4	517	5:4	Liquidus.
86. 6	13. 4	496	----------------	α2:1 melts incongruently.
86. 4	13. 6	517	5:4	Liquidus.
86. 4	13. 6	498	----------------	α2:1 melts incongruently.
86. 4	13. 6	472	----------------	β2:1→α2:1 transformation.
86. 2	13. 8	518	5:4	Liquidus.
86. 0	14. 0	525	5:4	Do.
84. 9	15. 1	535	5:4	Do.
83. 7	16. 3	542	5:4	Do.
82. 5	17. 5	583	1:2	Do.
82. 5	17. 5	545 ±5	----------------	5:4+liquid⇌1:2+liquid.
81. 3	18. 7	623	1:2	Liquidus.
81. 3	18. 7	545 to 580		(c)
80. 3	19. 7	642	1:2	Liquidus.
80. 3	19. 7	550 to 560	----------------	(c)
79. 5	20. 5	669	1:2	Liquidus.
79. 5	20. 5	545 to 580	----------------	(c)
78. 5	21. 5	675	1:2	Liquidus.
78. 5	21. 5	530 to 590	----------------	(d)
77. 1	22. 9	698	1:2	Liquidus.
77. 1	22. 9	530 to 595	----------------	(d)
76. 1	23. 9	705	1:2	Liquidus.
76. 1	23. 9	548	----------------	5:4+1:2⇌1:2+liquid.
72. 5	27. 5	738	1:2	Liquidus.
68. 3	31. 7	757	1:2	Do.
61. 8	38. 2	767	1:2	Do.
61. 4	38. 6	(e)	1:2	Melting of compound.
58. 5	41. 5	763	1:2	Liquidus.[f]
52. 0	48. 0	758	1:2	Do.
48. 6	51. 4	754	1:2	Do.
44. 9	55. 1	746	1:2	Do.
42. 8	57. 2	750 ±5	----------------	1 liquid⇌2 liquids.
36. 7	63. 3	744	1:2	Liquidus.[f]
36. 7	63. 3	777 ±5	----------------	1 liquid⇌2 liquids.
30. 1	69. 9	785 ±5	----------------	1 liquid⇌2 liquids.
25. 9	74. 1	742	1:2	1:2+liquid⇌2 liquids.[f]
25. 9	74. 1	780 ±5	----------------	1 liquid⇌2 liquids.
14. 1	85. 9	742	1:2	Liquidus.[f]
14. 1	85. 9	777 ±5	----------------	1 liquid⇌2 liquids.
5. 1	94. 9	700 ±5	----------------	1 liquid⇌2 liquids.
2. 1	97. 9	610 ±5	----------------	1 liquid⇌2 liquids.

[a] Accurate within ±3° C, unless otherwise stated.

[b] Quench growths only from temperatures above 830° C.

[c] Crystals of index of refraction 1.89 and 1.91 and glass. Above the temperature range indicated these crystals were replaced by PbO.2B₂O₃. (See A, fig. 2.)

[d] Between 530 and 545 to 550° C quenched samples contained the crystals of index 1.89 and 1.91 and 5PbO.4B₂O₃. Above 550° C, and below the maximum temperature indicated, the samples contained the crystals of index 1.89 and 1.91 and glass, while at higher temperatures they contained PbO.2B₂O₃ and glass. This change to the 1:2 compound and glass is apparently not reversible.

[e] This mixture was not prepared. The melting point is estimated to be 768±3° C.

[f] After holding from 4 to 6 weeks at crystallizing temperatures this composition contained PbO.2B₂O₃, clear glass, and an emulsion-like isotropic phase resembling the 2-liquid specimens of melts higher in B₂O₃ content.

2PbO.B₂O₃ exists in two allotropic forms, the α form being the primary phase in compositions containing from 87.3 to 88.0 percent of PbO, while the β form does not appear at the liquidus.

α2PbO.B₂O₃ melts incongruently at 497° C to form 5PbO.4B₂O₃ and liquid. The eutectic composition between α2:1 and β4:1 melts
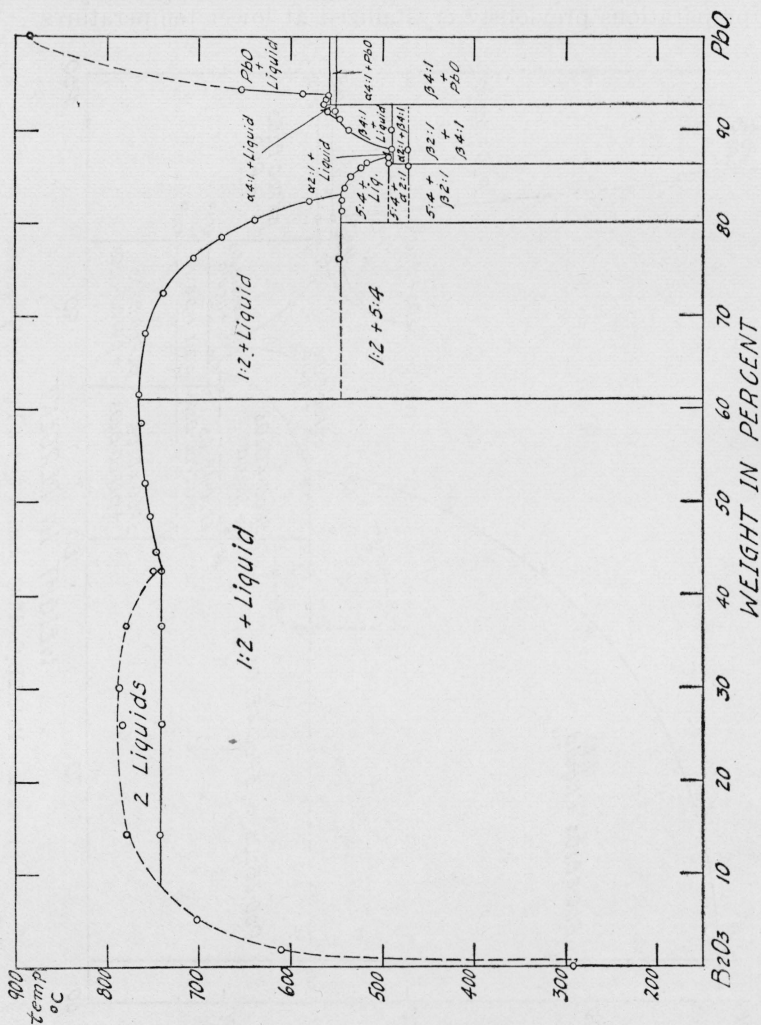
FIGURE 1.—The system PbO-B₂O₃.

at 493° C. Optical properties of the α form are: indices of refraction α1.965, γ2.025; biaxial negative character, $2V$ about 60°.

β2PbO.B₂O₃ inverts to the α form at about 473° C, and the reaction is apparently irreversible. The inversion is too rapid to permit determination of either the melting point of the compound or the temperature of melting of the β2:1-β4:1 eutectic composition, although the latter is indicated to be between 470 and 475° C. Indices of refraction are: α2.08, β2.10, γ2.11. The optic axial angle is very large and positive character is indicated.

$5PbO.4B_2O_3$ melts incongruently at 548° C to form liquid and crystals. The chemical composition of the crystals resulting from this decomposition has not been established. The crystals are doubly refracting, with a minimum index of 1.89 and a maximum of 1.91. They were found only in the area A (fig. 2) and apparently formed from preparations previously crystallized at lower temperatures. At
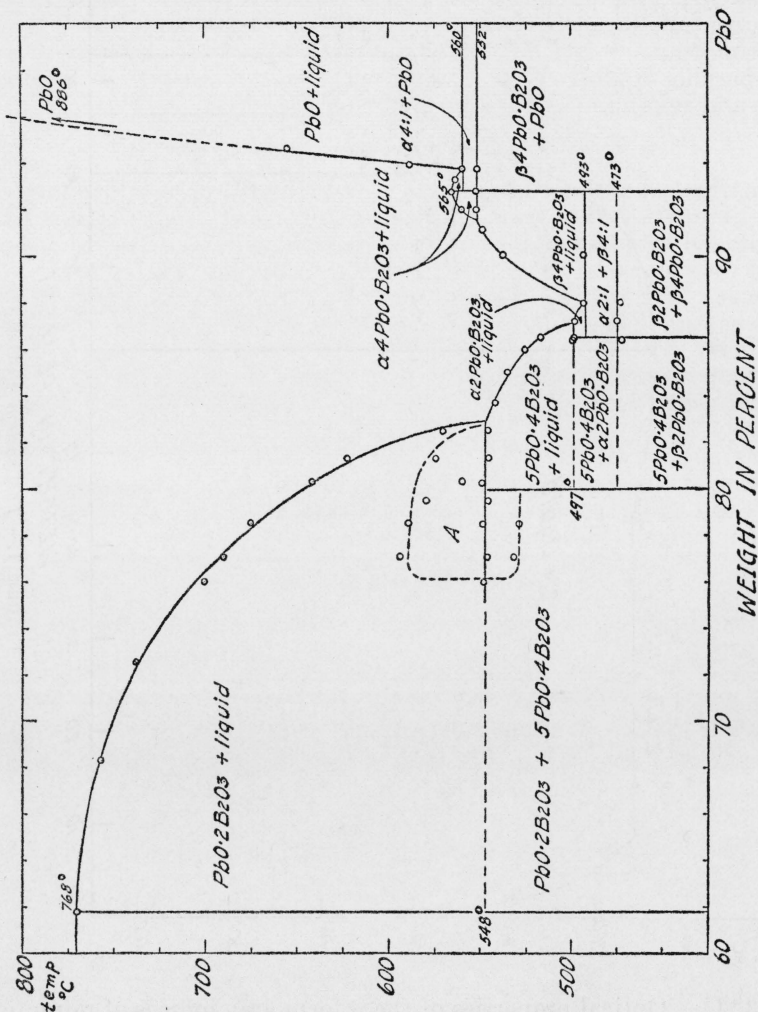
FIGURE 2.—$PbO.2B_2O_3$-PbO *portion of the* PbO-B_2O_3 *system.*

higher temperatures they were replaced by crystals of the 1:2 compound, but there was no consistent relation between composition and the temperature at which the unidentified phase disappeared. Their indices were constant over the composition range in which they formed, indicating that they are not the result of solid solution. The possibility that they might be the metaborate, or a polymorphic form of the diborate, was investigated by holding melts of these compositions for periods of 1 day to 3 weeks at temperatures in the range 500° C to 560° C. The results were negative.

5PbO.4B$_2$O$_3$ is the primary phase in compositions containing from 83 to 87.3 percent of PbO. The particles frequently were polysynthetically twinned. Character is biaxial negative; $2V$ about 65°; and the indices of refraction α1.91, β1.93, γ1.96.

PbO.2B$_2$O$_2$ predominates in the system, being the primary phase from the hypothetical PbO.2B$_2$O$_3$–B$_2$O$_3$ eutectic composition (containing less than 2 percent of PbO) to the composition containing 83 percent of PbO. It melts congruently at 768° C and, under favorable conditions, forms large, well defined laths with pointed ends and with parallel extinction. Character was not established but the maximum and minimum indices of refraction are 1.935 and 1.915.

2. TWO-LIQUID AREA

A narrow two-liquid area (fig. 1), extending from approximately 9 to 43 percent of PbO, was indicated. The upper limit of this area is determined by the temperatures at which change from clear to opaque liquid (or vice versa) could be observed, the crest being at 785° C for the melt containing 30.1 percent of PbO. The lower limit is at 742° C and was established by the disappearance of PbO.2B$_2$O$_3$ crystals from previously crystallized melts.

Actually, some immiscibility was observed in nearly all of the various partially crystallized specimens containing B$_2$O$_3$ in excess of the PbO–2B$_2$O$_3$ ratio. Even after holding for several weeks below the liquidus it was obvious that equilibrium had not been reached— evidence of the high viscosity of these melts. That a two-liquid area may exist under nonequilibrium conditions over this high B$_2$O$_3$ composition range is shown also by Guertler.[9]

3. COMPOSITIONS AS GLASSES

Index-of-refraction and thermal-expansion values, and the temperature of initial softening are given in table 3 for five glasses. Expressed in approximate mole ratios, these glasses represent compositions from 1PbO and 15B$_2$O$_3$ to 3PbO and 1B$_2$O$_3$. The test for relative solubility extracted 100 percent of the lead from each glass.

TABLE 3.—*Some properties of lead borate glasses*

PbO (by weight)	Index of refraction	Coefficient of linear thermal expansion from room temperature to 250° C	Beginning of softening, T_s
%			°C
36. 8[a]	{ 1. 46 { 1. 60	} 10. 3×10⁻⁶	476
52. 0	1. 66	6. 8	487
61. 8	1. 75	6. 9	491
79. 5	1. 92	9. 8	394
90. 1	2. 11	13. 2	286

[a] 2 immiscible glasses.

Glasses containing B$_2$O$_3$ in less than the 1:2 ratio (approximately 38 percent) appear stable in air. Those containing B$_2$O$_3$ in excess of this ratio are increasingly unstable as the content of B$_2$O$_3$ increases. 2 g

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[9] W. Guertler, Z. anorg. Chem. **40**, 225 (1904). The region of immiscibility, as reported by Guertler, extends from 41 percent to practically zero percent of PbO, and the maximum temperature is approximately 625° C.

each of glasses containing 38.2, 41.5, 55.1, 74.1, and 85.5 percent of B_2O_3 were digested in 100 ml of warm water, which treatment dissolved 4.5, 6.5, 13.0, 47.0, and 67.0 percent, respectively. When the composition containing 74.1 percent of B_2O_3 was exposed to room atmosphere for 30 minutes, crystals had developed sufficiently in the glass of lower index (1.46) to be identified as boric acid.

An extensive investigation of lead borate glasses has been reported by Drs. Klemm and Berger [10] who studied, in particular, the thermal expansion as influenced by previous thermal history, by load, and by heating rate. Their values for initial softening (T_s), when using a load of 60 g/cm^2, show a maximum variation of only 15° C from the values given in table 3. With a load of 15 g/cm^2 the maximum variation was 45° C, their values being invariably higher. They give also a curve for specific gravity versus composition of lead borate glasses, which curve may be expressed by the equation:

$$S=\frac{(PbO)^2}{1600}+2$$

where
S = true specific gravity.
PbO = weight percentage of PbO in the glass.

V. DISCUSSION

Determination of phase equilibria in the lead borate system had been attempted previously by Mazzetti and De Carli [11], whose data were obtained from heating curves and microscopic examination without, apparently, holding compositions at crystallizing temperatures for prolonged periods of time. Their results were interpreted as indicating compounds of PbO and B_2O_3 in the molecular ratios of 1:1, 1:2, 2:5, and 1:3 having melting points of 500°, 570°, 520°, and 560° C, respectively. They state that the smallness of the crystals in the devitrified glass prevented identification.

In the present investigation the following results were accepted as proof that the crystals of index 1.91 and 1.96 were the compound 5:4 rather than the metaborate: (a) melts approximating this composition, when held several weeks at $500 \pm 10°$ C, apparently crystallized to one phase; (b) previously crystallized mixtures containing slightly less than 80 percent of PbO (composition of $5PbO.4B_2O_3$ is 80.02% of PbO; 19.98% of B_2O_3) when held at temperatures between 500° and 540° C for 16 to 18 hours gave practically no liquid; (c) previously crystallized mixtures containing slightly more than 80 percent of PbO heated to the same temperatures gave liquid and the crystals designated as $5PbO.4B_2O_3$. However, certain heat treatments were productive of results which at first threw doubt on the conclusion that the crystals in question were the 5:4 compound. For example, compositions containing from 78 to 80 percent of PbO would contain crystals of PbO. $2B_2O_3$ and of $2PbO.B_2O_3$ if they were first held for several weeks at 600° to 650° C and then held at about 400° C. Evidently the melt was too viscous at the lower temperature to permit resorption of the 1:2 compound, thereby forcing crystallization of the 2:1 compound. The formation of the unidentified phase in area A (fig. 2) also might be

[10] A. Klemm and E. Berger, Glastech. Ber. 5, 405 (1927–28).
[11] C. Mazzetti and F. De Carli, Gazz. chim. ital. 40, 19 (1926).

misleading, but it is believed to be a metastable phase. $PbO.2B_2O_3$ and glass can be obtained by holding either glass or previously crystallized samples at temperatures between area A and the liquidus, while the unidentified phase was obtained only from melts previously crystallized at lower temperatures.

The melting temperature for $PbO.2B_2O_3$ given by Mazzetti and De Carli (570° C) is between the T_s value given in this report for the glass of similar composition (491° C) and the melting temperature given for the compound (768° C). It is probable that all of their determinations of liquidus temperatures were influenced by lack of complete crystallization. The high viscosity of this composition as a liquid, and the consequent slow growth of crystals, may be illustrated by the following data: the sample held 15 days at 475° C remained all liquid; the sample held 13 days at 650° C was partly crystallized, but the crystals were very small; the sample held 25 days at 560° C and then 25 days at 740° C was completely crystallized.

No evidence was obtained in this study of compounds higher in B_2O_3 than the lead diborate.

TABLE 4.—*Some optical properties of lead borate compounds*

Compound	Indices of refraction (values to ±0.01)			Optical character
	α	β	γ	
$\alpha 4PbO.B_2O_3$	(min 2.15; max 2.20)			Not established.
$\beta 4PbO.B_2O_3$	2.15	2.20	2.24	Biaxial negative; 2V 80°.
$\alpha 2PbO.B_2O_3$	1.965	--------	2.025	Biaxial negative; 2V 60°.
$\beta 2PbO.B_2O_3$	2.08	2.10	2.11	Biaxial positive; 2V 90°.
$5PbO.4B_2O_3$	1.91	1.93	1.96	Biaxial negative; 2V 65°.
$PbO.2B_2O_3$	(min 1.915; max 1.935)			Not established.

VI. SUMMARY

The system $PbO-B_2O_3$ was found to contain four compounds, the optical properties of which are summarized in table 4: $4PbO.B_2O_3$ occurring in two forms and melting congruently at 565° C; $2PbO.B_2O_3$ occurring in two forms and melting incongruently at 497° C; $5PbO.4B_2O_3$ melting incongruently at 548° C; and $PbO.2B_2O_3$ melting congruently at 768° C. The identity of an additional crystal phase was not established. The lowest melting eutectic has the composition 88 percent of PbO and 12 percent of B_2O_3, by weight, and melts at 493° C. Some properties of several of the compositions as glasses are given also.

WASHINGTON, March 13, 1937.