U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP911

Part of Journal of Research of the National Bureau of Standards, Volume 17, August 1936

THE SYSTEM K_2O-PbO-SiO_2

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ABSTRACT

The system was investigated by means of well known methods involving quenching, petrographic examination, and heating curves. Five ternary compounds were identified by optical properties and the chemical composition of four of these established. A number of melts were studied also as glasses to obtain data of interest to manufacturers of glasses, glazes, and enamels.

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I. INTRODUCTION

The simple oxides involved in this system are constituents of many ceramic glazes, glasses, and enamels. Consequently, the study of the glass and crystalline phases is an essential step in obtaining information upon which to base studies of the more complex systems encountered in ceramic practice. There remains the possibility, also, that ceramic products of both higher quality and of relatively simple composition may result from a thorough investigation of the basic ternary systems. Of these basic systems, the ones involving PbO as one component offer a virgin field for study. This report, the first on phase equilibria of the oxides K_2O, PbO, and SiO_2, is also, so far as the authors are aware, the first on any ternary system in which PbO is a component. However, some work has been done on glasses composed primarily of potassium oxide, lead oxide, and silica. A recent article [1] offers some new data of limited significance

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[1] R. Rieke and H. Mields. Ber. deut. keram. Ges. 16, 331 (1935).

(because of impurities in the melts) and contains references to earlier pertinent reports.

Although there are other oxides of lead, only the monoxide is stable above approximately 450° C.[2]

Phase equilibria have been established for the systems $K_2O.SiO_2$–SiO_2[3] and PbO–SiO_2.[4]

The present investigation was limited to studies of compositions in which the molecular ratio of K_2O to SiO_2 is unity, or less than unity, partly because of the extremely unstable nature of melts of higher $K_2O:SiO_2$ ratio, partly because of the physical impossibility (with available equipment) of obtaining or maintaining these melts free of CO_2 present as K_2CO_3, and partly because of excessive attack on the platinum crucibles and thermocouples. These facts were ascertained by preliminary tests, as was also the fact that K_2CO_3 and PbO were mutually insoluble in the solid and liquid states at atmospheric pressure, and that no binary compounds of K_2O and PbO were formed.

II. PREPARATORY WORK

1. PREPARATION AND PRESERVATION OF MIXTURES

The "end members" were sublimed litharge (PbO) containing 0.02 percent of total detected impurities; quartz crystal (SiO_2), which contained 0.02 percent of nonvolatile residue on evaporation with hydrofluoric and sulphuric acids; and potassium carbonate (K_2CO_3 as the source of K_2O) of which two 1-kg batches were used. The first batch, obtained in 1932, contained less than 0.037 percent of impurities and the second, obtained in 1935, contained less than 0.045 percent of impurities.[5]

All fusions were made in platinum, using electrically heated furnaces. The well mixed ingredients were allowed to react overnight at 700 to 800° C in order to drive off most of the CO_2 and were then taken to the minimum temperature required for fusion. By repeated grinding and remelting, instead of prolonged heating, the volatilized K_2O did not exceed 1 percent and was usually within 0.2 percent. No difficulty was experienced in obtaining melts within 0.2 percent of the desired PbO content, except with those melts approaching the potassium metasilicate in composition from which as much as 1 to 2 percent might be volatilized.

Seventy-four melts were analyzed chemically and portions used in various combinations to obtain additional preparations. A total of 165 melts was prepared (fig. 1).

Many compositions were so hygroscopic that they absorbed moisture except when kept over P_2O_5. Consequently, for convenience, all mixtures both as glass and in the crystallized form were kept over this material.

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[2] J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry (Longmans, Green & Co., New York, N. Y.) vol. 7, p. 672. Mellor states that PbO apparently goes to Pb_3O_4 when heated which, on higher heating, again goes to PbO, the temperature range of maximum Pb_3O_4 being about 425 to 450° C.

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

[4] R. F. Geller, A. S. Creamer, and E. N. Bunting, J. Research NBS. **13**, 237 (1934) RP705.

[5] Analyses were made by the Chemistry Division of the National Bureau of Standards. The litharge was analyzed for Cu (0.002%), Bi (0.018%), Fe (less than 0.001%), and for Zn, Ni, and Mn which were not detected. The potassium carbonate was analyzed for insoluble matter, silica and ammonium hydroxide precipitate, Ca and Mg, sulphates and chlorates, N, As, Fe, H_2S metals, phosphate, and Na. The principal impurity (loss on ignition not being considered as such) was Na, which was reported as "<0.02 percent" in each batch. In the first batch other impurities were present in quantities of 0.003 percent or less; the second contained "<0.02 percent of insoluble matter, <0.015 percent of Ca and Mg, and <0.005 percent of phosphate."

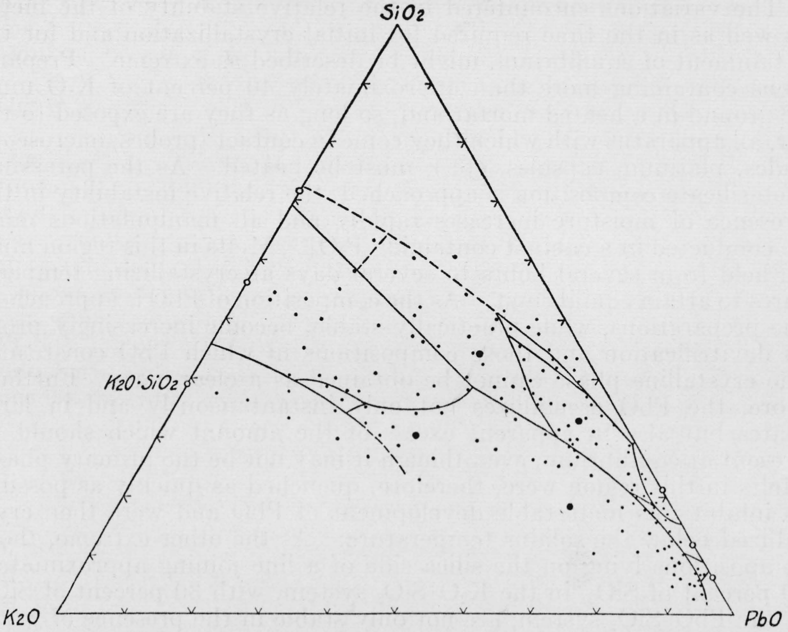

FIGURE 1.—*Points plotted in this figure show the compositions of the melts investigated.*

2. CHEMICAL ANALYSES

The PbO content was determined electrolytically and also as sulphate. The sample was treated with dilute nitric and hydrofluoric acids, dissolved in dilute nitric acid, the lead deposited on platinum gauze as PbO_2, dried at 110° C, and (by using the determined factor of 0.931) calculated to PbO. This deposit, after having been dissolved in dilute nitric acid and alcohol added to the solution, was converted with sulphuric acid to $PbSO_4$ and weighed as such. With few exceptions results by these two methods agreed within 0.1 percent. The electrolyte was evaporated to dryness, treated with hydrochloric acid, the KCl transferred to a small platinum dish and weighed. It was established by analysis that the SiO_2 content could be determined satisfactorily by difference.

All the chemical analyses of melts were made by A. S. Creamer. This involved modification of test methods as well as routine determinations.

III. EXPERIMENTAL PROCEDURE

1. THERMAL STUDIES

Thermal studies were made by the quenching method supplemented, in the case of a relatively small number of compositions, with heating curves obtained by the differential thermocouple method. Both of these methods are well established [6] and need no further description. Pt to Pt–Rh thermocouples were used for all temperature measurements and were calibrated by observing the inversion temperature of K_2SO_4 (583 ± 1° C), or the temperature of melting of K_2SO_4 (1069.1° C), or of KCl (770.3° C).

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

The variations encountered in the relative stability of the melts, as well as in the time required for initial crystallization and for the attainment of equilibrium, might be described as extreme. Preparations containing more than approximately 40 percent of K_2O must be ground in a heated mortar and, so long as they are exposed to the air, all apparatus with which they come in contact (probes, microscope slides, platinum capsules, etc.), must be heated. As the potassium metasilicate composition is approached, the relative instability in the presence of moisture increases rapidly and all manipulations must be conducted in a cabinet containing P_2O_5. Melts in this region must be held from several hours to several days at crystallizing temperatures to attain equilibrium. As the composition of PbO is approached, the preparations, while practically stable, become increasingly prone to devitrification and those compositions in which PbO constitutes one crystalline phase cannot be obtained as a clear glass. Furthermore, the PbO crystallizes not only instantaneously and in large plates but also in apparent excess of the amount which should be present at equilibrium, even though it may not be the primary phase. Melts in this region were, therefore, quenched as quickly as possible to inhibit this metastable development of PbO and were then crystallized below the solidus temperature. As the other extreme, those compositions lying on the silica side of a line joining approximately 70 percent of SiO_2, in the K_2O–SiO_2 system, with 30 percent of SiO_2, in the PbO–SiO_2 system, are not only stable in the presence of water vapor but require months to crystallize. One, held 6 months near the solidus temperature, had not crystallized sufficiently to establish the primary phase. Consequently the details of procedure were modified as the peculiarities of the preparations demanded.

2. MICROSCOPIC EXAMINATIONS

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. Solid media, ranging in index of refraction from 1.74 to 2.58, were available from a previous investigation.[7] Samples in solid media 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. LINEAR THERMAL-EXPANSION DETERMINATIONS

Determinations of linear thermal expansion 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.

IV. RESULTS

The results of the equilibrium studies are summarized in table 1 and plotted in figures 2, 3, and 4.

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[7] R. F. Geller, A. S. Creamer, and E. N. Bunting, J. Research NBS 13, 237 (1934) RP705.

TABLE 1.—*Invariant points*

[Compositions and melting temperatures]

Compounds	Composition, by weight						Temperature [a]
	$K_2O.SiO_2$	PbO	SiO_2	K_2O	PbO	SiO_2	
	%	%	%	%	%	%	°C
BINARY COMPOUNDS [b]							
$K_2O.SiO_2$	100.0	--------	--------	61.1	--------	38.9	976
$K_2O.2SiO_2$	72.0	--------	28.0	44.0	--------	56.0	1,036
$K_2O.4SiO_2$	46.2	--------	53.8	28.2	--------	71.8	765
$PbO.SiO_2$	--------	78.8	21.2	--------	78.8	21.2	764
$2PbO.SiO_2$	--------	88.1	11.9	--------	88.1	11.9	743
$4PbO.SiO_2$ [c]	--------	93.7	6.3	--------	93.7	6.3	725
TERNARY COMPOUNDS							
$K_2O.2PbO.2SiO_2$	23.4	67.5	9.1	14.3	67.5	18.2	918
$K_2O.4PbO.8SiO_2$	10.5	60.8	28.7	6.4	60.8	32.8	779
$K_2O.PbO.4SiO_2$	27.7	40.0	32.3	16.9	40.0	43.1	757
$2K_2O.PbO.3SiO_2$ [c]	52.1	37.7	10.2	31.8	37.7	30.5	735 ± 5
BINARY EUTECTICS [b]							
$K_2O.SiO_2$–$K_2O.2SiO_2$	89.2	--------	10.8	54.5	--------	45.5	775
$K_2O.2SiO_2$–$K_2O.4SiO_2$	50.7	--------	49.3	31.0	--------	69.0	752
$K_2O.4SiO_2$–SiO_2	45.8	--------	54.2	28.0	--------	72.0	764
SiO_2–$PbO.SiO_2$	--------	70.4	29.6	--------	70.4	29.6	732
$PbO.SiO_2$–$2PbO.SiO_2$	--------	84.6	15.4	--------	84.6	15.4	716
$2PbO.SiO_2$–$4PbO.SiO_2$	--------	91.8	8.2	--------	91.8	8.2	714
PbO–$4PbO.SiO_2$ [c]	--------	93.3	6.7	--------	93.3	6.7	725
BINARY EUTECTICS WITHIN THE TERNARY SYSTEM							
$K_2O.2SiO_2$–$K_2O.2PbO.2SiO_2$	44.5	38.0	17.5	27.2	38.0	34.8	806
$K_2O.2SiO_2$–$K_2O.PbO.4SiO_2$	37.0	31.8	31.2	22.6	31.8	45.6	740
$K_2O.4SiO_2$–$K_2O.PbO.4SiO_2$	38.5	16.5	45.0	23.5	16.5	60.0	715 ± 5
SiO_2–$K_2O.PbO.4SiO_2$	20.6	30.4	49.0	12.6	30.4	57.0	718
$K_2O.4PbO.8SiO_2$–$K_2O.PbO\ 4SiO_2$	18.8	50.7	30.5	11.5	50.7	37.8	719
$K_2O.2PbO.2SiO_2$–$K_2O.PbO.4SiO_2$	26.2	49.3	24.5	16.0	49.3	34.7	716
$K_2O.2PbO.2SiO_2$–$K_2O.4PbO.8SiO_2$	15.1	63.2	21.7	9.2	63.2	27.6	683
$PbO.SiO_2$–$K_2O.4PbO.8SiO_2$	2.9	73.7	24.4	1.8	73.7	24.5	737
$2PbO.SiO_2$–$K_2O.2PbO.2SiO_2$	3.3	85.2	11.5	2.0	85.2	12.8	704
PbO–$K_2O.2PbO.2SiO_2$	3.3	95.5	1.2	2.0	95.5	2.5	840
QUINTUPLE POINTS							
Points in figure 3:							
1 [d]	75	15	10	46	15	39	--------
2	65	26	9	40	26	34	--------
3	61	27	12	37	27	36	725 (?)
4 [d]	43	16	41	26	16	58	705 ± 10
5	29	19	52	18	19	63	--------
6 [d] [e]	16	39	45	10	39	51	--------
7 [e]	16	43	41	10	43	47	700 ± 5
8 [e]	5.2	60.0	34.8	3.2	60.0	36.8	742
9 [d]	.8	71.0	28.2	.5	71.0	28.5	730
10	4.9	78.0	17.1	3.0	78.0	19.0	676
11 [d]	2.5	91.7	5.8	1.5	91.7	6.8	705
12 [d]	2.9	88.0	9.1	1.8	88.0	10.2	693
13 [d]	8.2	74.5	17.3	5.0	74.5	20.5	637
14 [d]	18.0	59.5	22.5	11.0	59.5	29.5	682
15 [d]	32.7	41.7	25.6	20.0	41.7	38.3	708

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[a] Accurate within ± 3° C, unless otherwise stated. This does not apply to values taken from reports cited in footnote [b].

[b] Data for the system K_2O–SiO_2 are taken from F. C. Kracek, N. L. Bowen, and G. W. Morey, J. Phys. Chem. **33**, 1857 (1929). Data for the system PbO–SiO_2 are taken from R. F. Geller, A. S. Creamer, and E. N. Bunting, J. Research NBS **13**, 237 (1934) RP705.

[c] Melts incongruently.

[d] Eutectic.

[e] The composition of the primary phase within the area of which these points form the apices has not been established.

The extremely unstable nature of compositions along the join PbO–$K_2O.SiO_2$, and the rapidity with which they attack thermocouples and platinum containers, make the values obtained of little significance. Heating curves for 4 compositions, varying in PbO from 74 to 92 percent, show a break between 740 and 750° C and also at about 800° C. The ternary compound $K_2O.2PbO.2SiO_2$ is the primary phase in the composition containing 59 percent of PbO, which shows that the system is not binary, and the liquidus (by the quench method) is approximately 860° C. In the composition containing 42 percent of PbO the same ternary compound is the primary phase, the liquidus (by the quench method) is about 835° C, and heating curves have a well defined break at 780° C (which may be the melting temperature at the intersection with the $K_2O.SiO_2$–$K_2O.2PbO.2SiO_2$ boundary curve.) When the composition containing 42 percent of PbO is completely crystallized, or when held for a short time (30 min) at 810° C, the crystalline phase resembling the 1:2:2 compound in optical character, cleavage, and general appearance, has indices of refraction of ϵ 1.62, ω 1.72. However, when held for 48 hr at 810° C this crystalline phase, the only one present in addition to glass and constituting 5 to 10 percent of the total, has the correct indices of refraction for $K_2O.2PbO.2SiO_2$. The change in indices indicates solid solution, possibly with $K_2O.SiO_2$.

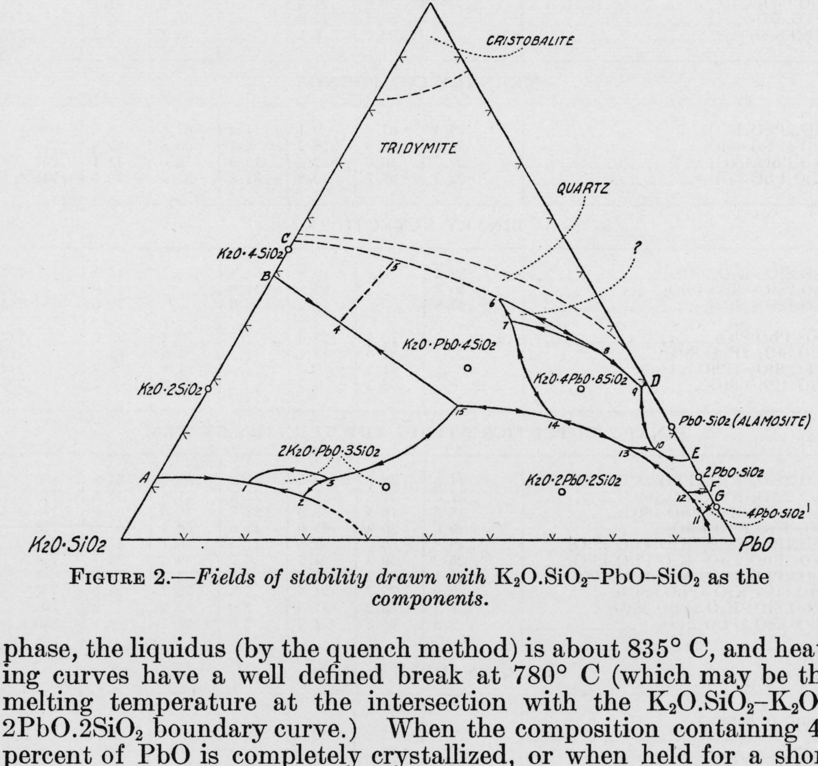

FIGURE 2.—*Fields of stability drawn with* $K_2O.SiO_2$–PbO–SiO_2 *as the components.*

1. TERNARY COMPOUNDS

The chemical composition, melting temperature, and optical properties of four ternary compounds were established, and the existence of a fifth is indicated by optical properties.

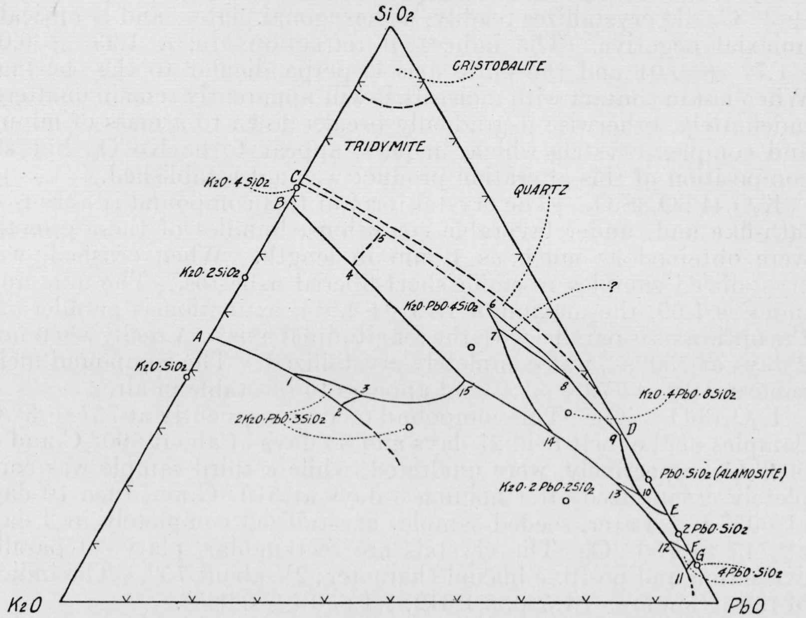

FIGURE 3.—*Fields of stability for the system* K_2O–PbO–SiO_2.

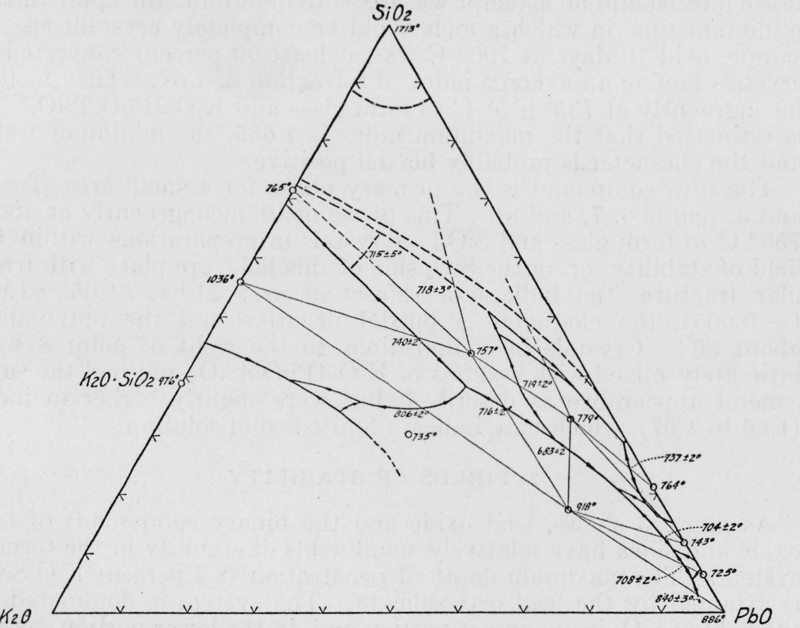

FIGURE 4.—*Tie-lines within the ternary system along which phase equilibria were investigated.*

$K_2O.2PbO.2SiO_2$.—This compound melts congruently at 918 ± 3° C. It crystallizes readily, as hexagonal plates, and is optically uniaxial negative. The indices of refraction are: ω 1.93 ± 0.01, ϵ 1.72 ± 0.01 and the optic axis is perpendicular to the cleavage. When not in contact with moisture it will apparently remain unaltered indefinitely, otherwise it gradually breaks down to a mass of minute and complex crystals which, in part, appear to be K_2CO_3, but the composition of this alteration product was not established.

$K_2O.4PbO.8SiO_2$.—The crystal form of this compound is fibrous or lath-like and, under favorable conditions, bundles of these growths were obtained as much as 1 mm in length. When crushed, well crystallized samples resemble short-fibered asbestos. The minimum index is 1.69, the maximum 1.79 (±0.01), extinction is parallel and the optic axis is parallel with the longitudinal axis. A melt, when held 2 days at 750° C, was completely crystallized. The compound melts congruently at 779 ± 3° C and appears to be stable in air.

$K_2O.PbO.4SiO_2$.—This compound melts congruently at 757 ± 3° C. Samples of the melt held 27 days and 33 days at about 690° C and at 600° C, respectively, were unaltered, while a third sample was completely crystallized after holding 8 days at 510° C and then 10 days at 605° C. Later, seeded samples crystallized completely in 3 days at 745 to 750° C. The crystals are rectangular, platy, of parallel extinction and positive biaxial character; 2V about 75°. The indices of refraction are: α 1.590, β 1.612, γ 1.650 (± 0.005).

$2K_2O.PbO.3SiO_2$.—This composition is so unstable that more than momentary exposure to ordinary air, except in heated containers, will destroy it for purposes of optical examination. Data concerning it are limited and no attempt was made to determine the approximate minimum time in which a melt could be completely crystallized. A sample held 10 days at 700° C was at least 90 percent converted to crystals having an average index of refraction of 1.67. They melted incongruently at 735 ± 5° C to form glass and $K_2O.2PbO.2SiO_2$. It is estimated that the maximum index is 1.685, the minimum 1.665, and the character is probably biaxial positive.

The fifth compound is the primary phase for a small area (figs. 2 and 3, points 6, 7, and 8). This phase melts incongruently at about 750° C to form glass and SiO_2. Crystals in preparations within the field of stability, or on the SiO_2 side of this field, are platy with irregular fracture, the indices of refraction are: α1.64, β1.65, γ1.655 (± 0.005), the character is biaxial negative and the optic angle about 80°. Crystals in compositions to the right of point 8 were intimately mixed with crystals of $K_2O.4PbO.8SiO_2$ and had the same general appearance as described, but were slightly higher in index (1.66 to 1.67), which may indicate limited solid solution.

2. FIELDS OF STABILITY

As figure 3 shows, lead oxide and the binary compounds of lead oxide and silica have relatively small fields of stability in the ternary system. The maximum depth of penetration (8.2 percent $K_2O.SiO_2$) is attained by the lead orthosilicate. The system is dominated by the field of SiO_2 in the upper portion and, in the lower portion, by the fields of $K_2O.2SiO_2$ and $K_2O.2PbO.2SiO_2$. In the former field it is possible that an area adjoining the composition of the potassium disilicate should be assigned to the "$K_2O.2SiO_2$ mix crystals" noted by Kracek, Bowen, and Morey.[8] A thorough investigation of this possibility was not made, but compositions on the tie-lines joining the disilicate with $K_2O.PbO.4SiO_2$ and with $K_2O.2PbO.2SiO_2$, and containing as little as 5 percent of PbO, apparently contained only crystals of $K_2O.2SiO_2$ and glass when held at temperatures which were expected to develop the mixed crystals.

(a) QUINTUPLE POINTS

Fourteen quintuple invariant points were located and another is indicated (point 5, figs. 2 and 3); of these, nine are ternary eutectics (table 1 and fig. 2). It is interesting to note the small range of temperatures covered by the melting points, from 637° C for point 13 to 742° C for point 8.

Point 1, ternary eutectic for the potassium metasilicate and disilicate and $2K_2O.PbO.3SiO_2$, and points 2 and 3 form the apices of the area in which the 2:1:3 compound is the primary phase. The compositions of these points, as given in table 1, are believed to be correct within ±1 percent, but the melting-temperature data were unsatisfactory because of the presence of K_2CO_3. The values indicate that the composition at point 1 melts above 700° C, and that at point 3 melts below 735° C.

Point 4, ternary eutectic for $K_2O.2SiO_2$, $K_2O.4SiO_2$, and $K_2O.PbO.4SiO_2$, is not definitely located because of insufficient data to locate either point 5 or the connecting boundary. In fact, no crystallization of $K_2O.4SiO_2$ as the primary phase was obtained in any composition. Kracek, Bowen, and Morey obtained this compound by hydrothermal crystallization.[9]

Points 6 and 7, although in an area of compositions which crystallize very slowly and usually incompletely even after months of treatment, are believed to be located within 0.5 percent of their true positions. Data for point 8, which composition melts at 742° C, are of satisfactory precision, practically complete crystallization of neighboring melts being obtainable in about 3 months. A melting temperature for point 6 is not given in table 1 but, from the contour of the liquidus surface in this region, is estimated to be about 690° C.

As table 1 shows, the melting temperatures of all of the other points are within 3° C of the correct values, the compositions are correct to ±0.1 percent and, with the exception of point 10, all are ternary eutectics. No. 10, the invariant point for $K_2O.4PbO.8SiO_2$, $PbO.SiO_2$, and $2PbO.SiO_2$, lies just outside the ternary system of these three compositions.

(b) BOUNDARY CURVES

The entire range of temperatures along the boundary curves is only about 200° (840° C maximum, 637° C minimum; table 1). The locations of the curves drawn as continuous lines in figures 1 to 4, inclusive, are believed to be sufficiently well established by determinations of primary phases. However, the isotherms (liquidus temperatures) were not always established, for reasons already elaborated upon, but may be deduced approximately from the general trends of the adjoining liquidus surfaces and by means of van Alkemade's theorem.[10]

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[8] F. C. Kracek, N. L. Bowen, and G. W. Morey. J. Phys. Chem. 33, 1857 (1929).
[9] See footnote 8.
[10] Bancroft, The Phase Rule, p. 149. Published by J. Phys. Chem. (1897).

For example, the data indicate that the melting temperature at point 1 is above 700° C, and it must also be below 735° C. The melting temperature at point 2 must be above that of point 1, may be above or below that of point 3, but probably does not differ much from the latter, and the very limited data obtainable indicate 720° C as the melting temperature. The curves from point 3 to point 1, and from point 2 to point 1, slope downward; but between points 2 and 3 there must be a maximum at the intersection of the curve with the tie-line, extended, from $K_2O.2PbO.2SiO_2$ to $2K_2O.PbO.3SiO_2$.

The curves from points 6 to 7 to 8, on the other hand, exemplify how their determined slopes may assist in establishing the identity of the phase which is primary within the area they circumscribe. In this case there is a maximum (750° C) along curve 6–8, and a maximum (743° C) along curve 7–8; both maxima are on or very near the intersection of these curves with the tie-line from the 1:4:8 compound to SiO_2. The composition 5 percent of K_2O, 47.3 percent of PbO, and 47.7 percent of SiO_2 (molecular ratio 1:4:15 or a base-acid ratio of 1:3) lies on this tie-line, slightly above the 6–8 curve. The suggestion is offered that this is the ternary compound described in section IV–2. A melt of this composition, held 2½ months at 700° C, was one-third crystals having the properties of the suggested 1:4:15 compound and the balance was glass. A specimen then held at 740° C for 4 hours was unchanged, but when held at 750° C for 4½ hours, contained less than 1 percent of these crystals in glass. A specimen held at 760° C for 2 hours before quenching contained only glass. Tridymite was identified in specimens held overnight above 940° C and below the liquidus (1,025 ± 10° C).

3. BINARY SYSTEMS WITHIN THE DIAGRAM

Phase relations in eight binary systems within the ternary system were established (fig. 4). Five of the eight involve $K_2O.2PbO.2SiO_2$ as one component, the other three connect the compounds $K_2O.2SiO_2$ with $K_2O.PbO.4SiO_2$; $K_2O.PbO.4SiO_2$ with $K_2O.4PbO.8SiO_2$; and $K_2O.4PbO.8SiO_2$ with $PbO.SiO_2$. They are all simple systems.

No compositions on the $K_2O.4SiO_2$ side of the $K_2O.4SiO_2$–$K_2O.PbO.4SiO_2$ eutectic were even partially crystallized after holding 3 months at 650 to 680° C. Location of a eutectic was approximated by extrapolation of the $K_2O.PbO.4SiO_2$ liquidus. The same method was used in approximating the composition of a SiO_2–$K_2O.PbO.4SiO_2$ eutectic. A composition on the SiO_2 side of the estimated eutectic showed no crystallization after holding 6 months at 700° C, while a composition on the other side was almost completely crystallized after 2 months at 600° C. It follows, therefore, that the existence of true binary systems between these compounds, although probable, was not established.

Binary systems do not exist between $K_2O.4PbO.8SiO_2$ and either SiO_2 or $2PbO.SiO_2$, or between $4PbO.SiO_2$ and $K_2O.2PbO.2SiO_2$. As figure 4 shows, each tie-line crosses a field in which a third compound is the primary phase. The break in the $4PbO.SiO_2$ liquidus, at the intersection of the PbO–$4PbO.SiO_2$ boundary curve with the $4PbO.SiO_2$–$K_2O.2PbO.2SiO_2$ tie line, occurs at a temperature of about 721° C and the composition must be very close to 0.5 percent of K_2O; 92.8 percent of PbO; and 6.7 percent of SiO_2.

4. COMPOSITIONS AS GLASSES

The values for index of refraction and also, in nine cases, for the linear thermal expansion and for the softening temperature (by the interferometer method) are summarized in figure 5. It is evident that a relatively small portion of the compositions produce glasses resistant to weathering. Although immiscibility is indicated in the lower portion of the diagram, the immiscibility is probably due wholly or in part to the presence of K_2CO_3. The limiting compositions were not determined, but it is known that the area does not cross the PbO–$K_2O.SiO_2$ tie-line. The liquids separate into two sharply defined layers which crystallize very rapidly upon solidification. Each layer of two melts was examined petrographically and also analyzed chemically. It was evident that the top layer in each case was composed primarily of K_2CO_3, the bottom layer primarily of PbO.

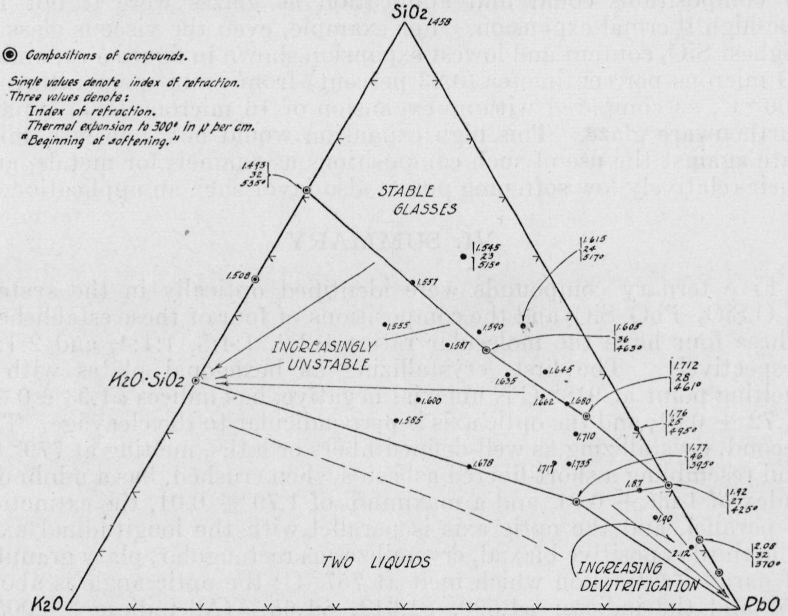

FIGURE 5.—*Summary of data obtained on melts as glasses.*

V. DISCUSSION

Since this report is the first dealing with a ternary system involving lead oxide, no comparisons can be made with systems of silica, lead oxide, and oxides of other elements, such as sodium and lithium, which systems might show trends similar to the one investigated.[11]

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[11] The following tests were made to obtain an indication of the probable behavior of a similar system substituting Na_2O for K_2O:

A melt of molecular composition $Na_2O.PbO.4SiO_2$ held at 500° C for 6 days contained about 10 percent of crystals in a glass of index of refraction 1.65. The crystals appeared as prisms radiating from a common center, or as rectangular plates, and of very low birefringence and average index 1.50.

A melt of molecular composition $Na_2O.4PbO.8SiO_2$ held at 500° C for 8 days contained less than 2 percent of glass (index 1.69) and two crystalline phases in about equal amounts. Phase A was prismatic, almost fibrous, with parallel extinction, very low birefringence, and average index 1.71. Phase B was platy and the indices of refraction ranged from 1.72 to 1.75.

A melt of molecular composition $Na_2O.2PbO.2SiO_2$ held at 500° C for 8 days had attacked the platinum capsule and was dark brown in color. Minute crystals of irregular fracture and indices ranging from 1.79 to 1.92 were identified.

The stable compounds crystallize from glasses which are so viscous, and crystal growth is relatively so slow, that their development as "stones" in glass under manufacturing conditions is very unlikely. The system itself will be important to those investigators studying similar, as well as more complex, systems encountered in glaze and glass technology. The difficulties to be encountered, should the need for completion of the present system arise, are indicated, and it is probable that similar difficulties would confront the student of, for example, the system Na_2O–PbO–SiO_2.

A narrow band of compositions along the silica side of the boundary separating the fields of stable and unstable glasses (fig. 5) have potential value as glasses. Those higher in SiO_2 would be so viscous that fusing them to a homogeneous glass, without excessive loss of K_2O and PbO by volatilization, would be impracticable; or, if this were accomplished, they would still be unworkable. The same band of compositions could find application as glazes were it not for the high thermal expansion. For example, even the viscous glass of highest SiO_2 content and lowest expansion shown in figure 5 expanded 23 microns per centimeter (0.23 percent) from room temperature to 300° C, as compared with an expansion of 16 microns for a typical earthenware glaze. This high expansion would not, however, militate against the use of such compositions as enamels for metals, and their relatively low softening points also favor such an application.

VI. SUMMARY

Five ternary compounds were identified optically in the system $K_2O.SiO_2$–PbO–SiO_2 and the compositions of four of these established. These four have the molecular ratios 1:2:2, 1:4:8, 1:1:4, and 2:1:3, respectively. The first, crystallizing as hexagonal plates with a melting point at 918° C is uniaxial negative, has indices $\omega 1.93 \pm 0.01$, $\epsilon 1.72 \pm 0.01$, and the optic axis is perpendicular to the cleavage. The second, crystallizing as well-defined fibers or laths, melting at 779° C, and resembling a short-fibered asbestos when crushed, has a minimum index of 1.69 ± 0.01, and a maximum of 1.79 ± 0.01, the extinction is parallel, and the optic axis is parallel with the longitudinal axis. The third is positive biaxial, crystallizes as rectangular, platy granules of parallel extinction which melt at 757° C; the optic angle is about 75° and the indices: $\alpha 1.590$, $\beta 1.612$, $\gamma 1.65$. (All indices ± 0.005.) The fourth is platy with an average index of approximately 1.67, melts incongruently at 735° C, and is very unstable. The crystalline phase of undetermined composition apparently melts incongruently at about 750° C to form glass and SiO_2. The crystals are platy, the indices $\alpha 1.64$, $\beta 1.65$, $\gamma 1.655$ ($\pm$ 0.005), 2V about 80°, character biaxial negative.

Glasses in that portion of the ternary diagram lying on the silica side of the tie-lines connecting the compound compositions $K_2O.4SiO_2$, $K_2O.PbO.4SiO_2$, $K_2O.4PbO.8SiO_2$, and $PbO.SiO_2$ are stable in air. Compositions in this area and near these tie-lines fuse to a homogeneous glass with sufficient ease to be of possible commercial application. However, the temperatures required to produce a glass, and the viscosity of the product, rise very rapidly with increase in silica. It is believed that the band or area of commercially usable compositions would be narrow. Compositions on the K_2O side of the tie-lines mentioned are either unstable in air or, in that area bounded by the tie-lines from $PbO.SiO_2$ and from PbO to $K_2O.2PbO.2SiO_2$, prone to devitrification. Also, many compositions below a line connecting PbO with the $K_2O.SiO_2$ composition separate into two immiscible liquids.

The usefulness or lack of usefulness of a composition as a glass will generally determine also its potential value as a glaze for porcelain or earthenware. In addition, a glaze must have the proper thermal dilatation to "fit" the ware upon which it forms a coating. Unfortunately, all the glasses examined, and which otherwise held promise of usefulness as glazes, on heating or cooling undergo volume changes so great as to preclude their use on clay ware as now manufactured, with the exception of certain "high silica" and "high talc" wall tile.

WASHINGTON, JUNE 3, 1936.