RESEARCH PAPER RP705

Part of *Journal of Research of the National Bureau of Standards*, volume 13
August 1934

THE SYSTEM: PbO-SiO_2

By R. F. Geller, A. S. Creamer, and E. N. Bunting

ABSTRACT

The system PbO-SiO_2 , of interest to investigators and manufacturers of ceramic glazes and glasses, was investigated. The following compounds were identified and their optical properties, linear thermal expansion, and melting temperatures determined: $4\text{PbO} \cdot \text{SiO}_2$, $2\text{PbO} \cdot \text{SiO}_2$, and $\text{PbO} \cdot \text{SiO}_2$. The compositions and melting points of three eutectics were determined also.

CONTENTS

	Page
I. Introduction.....	237
II. Preparatory work.....	238
1. Preparation of mixtures.....	238
2. Chemical analyses.....	238
3. Immersion media.....	238
III. Experimental procedure.....	238
1. Heating curves and quenches.....	238
2. Linear thermal expansion.....	239
3. Microscopic examinations.....	239
IV. Results.....	239
1. Compounds.....	239
2. Linear thermal expansion.....	240
3. The phase-equilibrium diagram.....	241
V. Discussion.....	242
VI. Summary.....	244

I. INTRODUCTION

The study of this system was preliminary to a study of the system $\text{K}_2\text{O-PbO-SiO}_2$, the purpose being to provide information of fundamental nature to manufacturers and investigators of ceramic glazes and glasses.

Much of the earlier data for the PbO-SiO_2 system is incomplete and often conflicting.¹ The most comprehensive report is that by Krakau and Vachrameev, who found maxima at 744 C and 765 C, corresponding to the compounds $2\text{PbO} \cdot \text{SiO}_2$ and $\text{PbO} \cdot \text{SiO}_2$, and who give detailed results of exhaustive petrographic studies. They suggest, but failed to identify, the compounds $3\text{PbO} \cdot \text{SiO}_2$ and $3\text{PbO} \cdot 2\text{Si}_2\text{O}_2$. The latter would correspond to the mineral barysilite.

¹ H. C. Cooper, L. I. Shaw, and N. E. Loomis; *Am. Chem. J.* 42, 461 (1909); S. Hilpert and P. Weiler, *B. d. Deut. Ker. Gesell.* 42 [III], 2969 (1909); S. Hilpert and R. Nacken, *B. d. Deut. Ker. Gesell.* 43 [II], 2565 (1910); H. C. Cooper, E. H. Krause and A. A. Klein, *Am. Chem. J.*, 47, 273 (1912); K. A. Krakau and N. A. Vachrameev, *Keram i Steklo*, 8, [1], 42 (1932).

II. PREPARATORY WORK

1. PREPARATION OF MIXTURES

The "end members" used in preparing the various mixtures were PbO (sublimed litharge) containing 0.02 percent total detected impurities,² and SiO₂ (quartz crystal) crushed to pass a no. 100 sieve and purified. It contained 0.02 percent nonvolatile residue on evaporation with HF and H₂SO₄.

All fusions were made in platinum, using electrically heated furnaces. For each "key" mixture the proper proportions of PbO and SiO₂ were mixed intimately and fused. By using temperatures only slightly higher than required for complete melting, and by repeated grinding and remelting instead of prolonged heating, it was possible to prepare microscopically homogeneous melts without detectable volatilization of PbO.³ These key mixtures were analyzed chemically and were used in various combinations to produce mixtures of intermediate composition.

2. CHEMICAL ANALYSES

The PbO content was determined as sulfate by double evaporation with HF and H₂SO₄, and also electrolytically by dissolving the sample in diluted HNO₃, depositing on platinum gauze, drying at 110 C, and using the previously determined factor of 0.931 to calculate the equivalent PbO. With few exceptions, results by these two methods agreed within 0.1 percent. It was established by test that the SiO₂ content could be determined satisfactorily by difference.

3. IMMERSION MEDIA

All of the compounds in this system, and also the PbO, have indices of refraction above the highest attainable with liquid immersion media. Solid media, ranging in index of refraction from 1.74 to 2.58 were available from a previous investigation.⁴ However, their indices were redetermined by means of a reflecting goniometer. White light passed through a no. 25 Wratten filter provided the illumination for the calibration of the immersion media.

III. EXPERIMENTAL PROCEDURE

1. HEATING CURVES AND QUENCHES

The thermal studies were made by the well established quenching method⁵ supplemented, in most cases, with heating curves by the differential thermocouple method.

All compositions in which PbO is the primary phase were prepared for thermal study by fusing portions of previously prepared mixtures, quenching in water, and then crystallizing slightly below the solidus temperature. This procedure was necessary because equilibrium was

² Furnished by the Eagle-Picher Lead Co., and analyzed by the chemistry division of the National Bureau of Standards for Cu (0.002 percent), Bi (0.018 percent), Fe (less than 0.001 percent), and for Zn, Ni, and Mn which were not detected.

³ Olaf Andersen, *J. Amer. Cer. Soc.* 2 [10], 784 (1919).

⁴ L. T. Brownmiller, *The Amer. Mineralogist* 12, 43 (1927).

⁵ E. S. Shepherd and G. A. Rankin; *Am. J. Sci.* 28,293(1909). F. C. Kracek, N. L. Bowen and G. W. Morey; *J. Phys. Chem.* 33,1857(1929).

not attained in these mixtures, when cooled slowly from the liquid state, due to the PbO crystallizing in large plates characteristic of this oxide. For this reason, and also because mixtures containing more than 8 to 10 percent SiO_2 by weight crystallize very slowly, it was found advisable to study all compositions by determining heating (rather than cooling) curves, and by using for quenching tests specimens of material which had first been completely crystallized and then held at the desired temperature for 15 min or more prior to quenching. The time required to complete crystallization varied from a few minutes to several days, increasing rapidly as the ratio of SiO_2 to PbO increased. PbO , for example, crystallized so rapidly that it could not be obtained as a glass while the crystallization of the $PbO.SiO_2$ composition required 2 days or more, depending on the crystallizing temperature.⁶

For the differential thermocouple method two average heating rates were used, $0.9^\circ C$ and $1.8^\circ C$ per min. Holding at constant temperatures ($\pm 0.5^\circ C$), or changing temperatures at a predetermined rate, was accomplished with automatically controlled furnaces. The type of control used is described in principle by Adams.⁷ Pt to Pt-Rh thermocouples were used for all temperature measurements and were calibrated periodically by using the inversion temperature of K_2SO_4 ($583 \pm 1^\circ C$), or the temperature of melting of either K_2SO_4 ($1069.1^\circ C$) or KCl ($770.3^\circ C$),⁸ as reference points.

2. LINEAR THERMAL EXPANSION

Determinations of linear thermal expansion were made by the interferometer method⁹ using an average heating rate of from 2.0° to $2.5^\circ C$ per min, and chromel-alumel thermocouples for measurements of temperature.

3. MICROSCOPIC EXAMINATIONS

The petrographic microscope was used to determine the phases present in the quenched samples.¹⁰ Identification of crystal phases was limited practically to the establishment of their optical character and also their indices of refraction which are believed to be accurate to ± 0.01 . White light passed through a no. 25 Wratten filter provided the illumination for observation of the quenched samples.

IV. RESULTS

1. COMPOUNDS

Three compounds were found in the system: $4PbO.SiO_2$, $2PbO.-SiO_2$, and $PbO.SiO_2$.

$4PbO.SiO_2$, *tetralead silicate*.—This compound melts incongruently to form PbO and liquid at $725 \pm 1^\circ C$ and is a final product of crys-

⁶ S. Hilpert and R. Nacken, see footnote 1 on p. 237.

⁷ J. Opt. Soc. Am. 9, 599 (1924).

⁸ H. S. Roberts, Some New Standard Melting Points at High Temperatures; Phys. Rev. 2, [23] 386 (1924).

⁹ G. E. Merritt, BS J. Research 10, 59 (1933); RP515.

¹⁰ E. S. Larsen and H. Berman, U.S. Geol. Sur. Bull. 848 (1934).

tallization in all mixtures containing up to 33.33 mol percent (11.85 wt percent) SiO_2 . It crystallizes readily and apparently occurs in 3 forms. The α form, stable above $720 \pm 1^\circ \text{C}$, crystallizes as irregular plates of high birefringence and is characterized by the clear blue to violet color, under crossed nicols, when the plates lie normal to the axis of the microscope. It is biaxial positive with an optic angle about 40° . The approximate indices of refraction are $\alpha = 2.31$, $\beta = 2.34$, $\gamma = 2.38$. The β form, stable between about 155 and 720°C , was not distinguished optically from the γ form, stable below about 120°C , except by relative birefringence. Specimens crystallized at or below 720°C appear as minute, probably prismatic, grains of

FIGURE 1.—The linear thermal expansion of $4\text{PbO} \cdot \text{SiO}_2$ showing reversal caused by crystal transformation.

medium birefringence and average index of refraction approximating 2.34.

$2\text{PbO} \cdot \text{SiO}_2$, *lead orthosilicate*.—This compound melts congruently at $743 \pm 3^\circ \text{C}$. It is the primary phase in mixtures containing approximately 25 to 40.5 mol percent (8.22 to 15.4 wt percent) SiO_2 and crystallizes in well-defined prismatic form with a characteristic cleavage normal to the prismatic axis. The extinction is parallel, the character biaxial negative, and the optic angle about 80° . Approximate indices of refraction are: $\alpha = 2.13$, $\beta = 2.15$, $\gamma = 2.18$.

$\text{PbO} \cdot \text{SiO}_2$, *lead metasilicate*.—This compound melts congruently at $764 \pm 3^\circ \text{C}$. It is the primary phase in mixtures containing approximately 40.5 to 61.0 mol percent (15.4 to 29.6 wt percent) SiO_2 . Crystals appear prismatic when formed in glass containing an excess of SiO_2 , but otherwise are of indefinite form. They are biaxial negative, optic angle about 60° , birefringence medium, and average index of refraction about 1.95.

2. LINEAR THERMAL EXPANSION

With the exception shown in figure 1, all of the expansion-temperature relations appear as smooth curves and the values are given as average coefficients in table 1. Tests made on the α form of the tetralead silicate were unsatisfactory because of the extreme friability of the specimens.

TABLE 1.—Average coefficients of linear thermal expansion for PbO, the compounds in the PbO-SiO₂ system, and two other mixtures

Mol ratio PbO:SiO ₂	Test number	Coefficients ^a			
		Room temperature to 200 C	200 to 300 C	300 to 400 C	400 to 500 C
37:63 Glass.....	2	8.5	7.9	8.1	^b (495)
1:1 (Glass.....	2	9.2	10.4	9.3	^b (425)
1:1 (Crystal.....	2	7.2	8.8	9.3	9.1
2:1 (Glass.....	2	10.5	13.1	^b (370)	-----
2:1 (Crystal.....	2	12.0	13.4	15.2	15.4
3:1 Crystals.....	2	^c 10.0	-----	-----	-----
4:1 Crystal.....	3	(^d)	15.5	13.8	12.5
PbO Crystal.....	2	25	30	30	28

^a Coefficients to be multiplied by 10⁻⁶.
^b Beginning of softening, degrees C.
^c Expansion retarded between 100 and 150 C due to presence of 4PbO.SiO₂.
^d Contracts between 137 and 153 C.

3. THE PHASE EQUILIBRIUM DIAGRAM

The phase equilibrium diagram is shown in figure 2.

From the melting point of PbO (886±2° C) the liquidus drops sharply to approximately 725 C at about 21 mol percent (6.7 wt percent) SiO₂, in which region PbO is the primary phase. At about 725 C the 4PbO.SiO₂ compound begins to separate out as large crystals of high double refraction (α form). However, when the fused sample is quenched and then held at or below 720 C, a form (designated β) develops which, in turn, undergoes a reversible inversion in the temperature range 120 to 155 C (fig. 1).¹¹ The results of heating curves, as well as of the quenching tests, are not entirely satisfactory as regards the establishment of the α⇌β inversion, but are believed to indicate that the tetralead silicate, on heating, undergoes an inversion at 720±2° C. The liquidus of 20 mol percent silica, which is the composition of the compound 4PbO.SiO₂, is about 735 C.

From the composition marking the limit of the region in which PbO is the primary phase, to the composition of the 4PbO.SiO₂-2PbO.SiO₂ eutectic at 25 mol percent (8.22 wt percent) SiO₂, the tetralead silicate is the primary phase and the liquidus drops gradually from 725±2° C to 714±3° C, the tetralead silicate-orthosilicate eutectic temperature.

The liquidus then rises to 743±3° C, the melting point of the orthosilicate, and as the content of SiO₂ is increased it drops gradually to 716±3° C at about 40.5 mol percent (15.4 wt percent) SiO₂, which values are the melting point and composition respectively of the orthosilicate-metasilicate eutectic. In this region the orthosilicate is the primary phase.

From the 2PbO.SiO₂-PbO.SiO₂ eutectic the liquidus rises, steeply at first, to 764±3° C, the melting point of the metasilicate. The liquidus then drops, gradually at first, to the metasilicate-silica eutectic temperature (732±2° C) at approximately 61 mol percent (29.6 wt percent) SiO₂. The metasilicate constitutes the primary phase in this region.

Increasing the silica over the composition of the metasilicate-silica eutectic causes the liquidus to rise very steeply from 732±3° C

¹¹ Heating curves showed a maximum differential temperature at 138 C while microscopic observations on a heated stage (made by C. P. Saylor of the chemistry division of the National Bureau of Standards) showed crystal movements, caused by volume changes, and increased birefringence beginning at temperatures as low as 100 C and continuing to temperatures as high as 170 C. On cooling, the evidence of a transformation was observable but less clearly defined by either method.

for 61 mol percent SiO_2 to $880 \pm 5^\circ \text{C}$ for 62.5 mol percent and approximately 930°C for 66 mol percent SiO_2 . Compositions higher in SiO_2 were not investigated, it being considered sufficient to have established that SiO_2 becomes the primary phase for compositions containing more than 61 mol percent SiO_2 and that the liquidus must therefore rise from the eutectic temperature at that composition to the melting point of SiO_2 at 1713°C .¹²

V. DISCUSSION

Values for critical temperatures determined from heating curves obtained by the differential thermocouple method were consistently higher than values obtained by the method of quenching. This variation ranged from a maximum of 8°C for the melting point of PbO to a minimum of 4°C for the melting point of the tetrasilicate-orthosilicate eutectic composition. The indicated values (fig. 2) for the melting temperatures of compounds and eutectics include the values obtained by each method but, in drawing the diagram, preference was given the values obtained by the quenching method with the exception of values for the liquidus temperatures of compositions in which PbO is the primary phase.

The establishment of the melting point of PbO by examination of quenched samples was difficult because of practically instantaneous crystallization; specimens of litharge heated to 875°C and quenched appeared unaffected, while those heated to 880°C and quenched had crystallized as large plates. The results of the differential thermocouple method indicated 886°C as the melting point, which value is in agreement with the value reported by V. A. Kroll¹³ and by Krakau and Vachrameev.¹⁴ Many other values have been reported from time to time ranging from 830 to 906°C .¹⁵ Neither the linear thermal expansion curve from room temperature to 500°C nor the heating curve above 500°C indicated a temperature for the massicot-litharge inversion.

The formation of the compound $4\text{PbO} \cdot \text{SiO}_2$ has not heretofore been mentioned in the literature; several investigators, however, attempted to identify the compound $3\text{PbO} \cdot \text{SiO}_2$ which would differ from the former, in composition, by only 1.92 wt percent SiO_2 . Krakau and Vachrameev¹⁶ describe crystals which they conclude to be $3\text{PbO} \cdot \text{SiO}_2$, but offer no direct supporting data. Their description of these crystals coincides with the description, given in this paper, of the compound $4\text{PbO} \cdot \text{SiO}_2$. Cooper Kraus and Klein¹⁷ and Hilpert and Nacken¹⁸ also were unable to prove the formation of trilead silicate. In this investigation mixtures containing 20 mol percent SiO_2 were found to crystallize as a single phase which, on heating to temperatures between approximately 725 and 735°C , formed PbO and glass.

Krakau and Vachrameev¹⁹ describe two biaxial crystal forms of the composition $2\text{PbO} \cdot \text{SiO}_2$, namely, prismatic and platy, the former having positive elongation and a small optic axial angle and the latter characterized by relatively low interference colors, irregular fracture,

¹² J. W. Greig, *Amer. J. Sci.* [5] 13, 1 (1927).

¹³ *Ztschr. Anorg. Chem.* 78, 95 (1912).

¹⁴ See footnote 1, p. 237.

¹⁵ J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*; Longmans, Green & Co., New York, N.Y.

¹⁶ See footnote 1, p. 237.

¹⁷, ¹⁸ See footnote 1, p. 237.

¹⁹ See footnote 1, p. 237.

and an optic axial angle of 50° . They obtained, also, by heating curves, indications of a transformation at 620°C . In this investigation no evidence of a polymorphic change at 620°C was obtained by

FIGURE 2.—Phase equilibrium diagram for the system PbO-SiO_2 .

means of heating curves, by linear thermal expansion determinations, or by quenching.

Heating curves of mixtures containing from 35 to 40 mol percent SiO_2 , which had been permitted to crystallize for 3 days or more at temperatures favoring crystal growth, showed two breaks correspond-

ing to the melting temperature of the eutectic mixture and to the liquidus. Conflicting results, such as the three breaks reported by Cooper Kraus and Klein,²⁰ were obtained when crystallization was not permitted to proceed to equilibrium.

The crystalline compound $3\text{PbO} \cdot 2\text{SiO}_2$ occurs in nature as the mineral barysilite. Specimens from Langban, Sweden²¹ were clear, transparent plates, uniaxial negative, of extremely low double refraction and having an estimated average index of refraction of 2.04.²² Attempts to produce this compound artificially proved unsuccessful. Specimens quenched after having been held at 705 C for 20 hours were completely crystallized to ortho- and meta-silicate. Specimens quenched after holding 3 hours or less at the same temperature consisted almost wholly of a phase resembling barysilite in color and index of refraction, but which was either all glass or glass containing extremely minute crystals.

The difficulties encountered in crystallizing and obtaining significant heating curves for mixtures containing more than 40 mol percent SiO_2 made it impracticable to use this method for mixtures higher in SiO_2 than the metasilicate ratio. The metasilicate occurs in nature as the mineral alamosite. Specimens from Alamos, Sonora, Mexico,²³ are yellow, of no well defined cleavage, biaxial negative, and have a very large optic axial angle and average index of refraction of approximately 1.96.²⁴

The optical properties reported for the three compounds of the system investigated are in substantial agreement with those reported by Krakau and Vachrameev with the exception of the refractive indices of the ortho and tetralead silicates. The discrepancy is apparently due to the fact that these investigators did not determine the actual indices of refraction of the sulfur-selenium immersion media used by them but used, instead, the calculated values as given by Larsen.²⁵

VI. SUMMARY

The system $\text{PbO}-\text{SiO}_2$ was found to contain three compounds: $4\text{PbO} \cdot \text{SiO}_2$, occurring in three forms and melting incongruently at $725 \pm 1^\circ \text{C}$; $2\text{PbO} \cdot \text{SiO}_2$, melting congruently at $743 \pm 3^\circ \text{C}$; and $\text{PbO} \cdot \text{SiO}_2$, melting congruently at $764 \pm 3^\circ \text{C}$. The PbO , melting at $886 \pm 2^\circ \text{C}$, is the primary phase for all mixtures containing less than approximately 21 mol percent (6.7 wt percent) SiO_2 ; the tetralead silicate-orthosilicate eutectic was found at 25 mol percent (8.22 wt percent) SiO_2 , having a melting point of $714 \pm 3^\circ \text{C}$; the orthosilicate-metasilicate eutectic melts at $716 \pm 3^\circ \text{C}$ and contains approximately 40.5 mol percent (15.4 wt percent) SiO_2 ; the metasilicate-silica eutectic, having a silica content of about 61 mol percent (29.6 wt percent), melts at $732 \pm 3^\circ \text{C}$.

WASHINGTON, June 11, 1934.

²⁰ See footnote 1, p. 237.

²¹ U.S. National Museum no. 95103.

²² Larsen (see footnote 10, p. 239) gives, for the indices of refraction: $\epsilon = 2.05$; $\omega = 2.07$.

²³ U.S. National Museum no. 92950.

²⁴ Larsen (see footnote 10, p. 239) gives, for the indices of refraction: $\alpha = 1.947$; $\beta = 1.961$; $\gamma = 1.968$.

²⁵ See footnote 10, p. 239.