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Phase Relations in the System PbO-$PbSiO_3$

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Phase relations in the system PbO–$PbSiO_3$ were determined at temperatures above 650 °C. Two new lead silicate phases, Pb_5SiO_7 and $Pb_{11}Si_3O_{17}$ were found to be stable. The former melts incongruently at 733±1 °C to solid PbO plus liquid, and decomposes below 702±1 °C. The latter melts congruently at 728±1 °C. The compound Pb_4SiO_6, which has been accepted as stable, could not be confirmed.

Considerable work has been done by various investigators[1–11] on the system PbO–SiO_2. These workers agree about the temperature region of liquidus and solidus lines of the PbO–SiO_2 system, and the phase diagram given by Geller *et al.*[6] has long been accepted as definitive by many investigators.[7–11] Beyond this, however, there is little agreement. Compounds with the PbO:SiO_2 molar ratios of 4:1, 3:1, 2:1, 3:2, 1:1, 5:8, and 1:2 have been reported. Billhardt,[7] Ott and McLaren,[8] and Smart and Glasser[9] have studied subsolidus reactions and compound formation in this system, with the result that there are 3 quite different sets of conclusions regarding the identity, polymorphism, and thermodynamic stability of the lead silicates.

In the present study, we re-examined the phase equilibrium relations of the system PbO–$PbSiO_3$ in the region above 650 °C, of which the phase diagram has been given by Geller *et al.*[6] Two new lead silicate phases, 5:1 and 11:3, were found to be stable.

Experimental

The reaction products quenched in the equilibration runs were examined by X-ray diffraction of powdered specimens, by electron probe microanalysis, and by microscopy. The approach to equilibrium was studied as a function of run durations. Starting from a mixture of PbO and SiO_2, a complex mixture of more than three phases was obtained when the run duration was too short to attain an equilibrium state. A quenched specimen was judged to be at equilibrium when two phases or a single phase only was found. The starting mixtures were enclosed by welding them in platinum capsules 6 mm in diameter and 35 mm long. Otherwise, sublimation of components during the run durations was not negligible.

A fine powder of SiO_2 used as the starting material was prepared from a commercial $SiCl_4$ (Shin-Etsu Chemical Co. Ltd.) prepared for semiconductor use. The $SiCl_4$ was added to water in a platinum dish. The product was dried on a sand bath. Then the product silica was crushed into a powder and heated at 1300 °C to eliminate the volatile impurities. The PbO used as starting material was prepared from a commercial basic lead carbonate (Nakarai Chemicals, Ltd., CP grade). About 10 ppm of Al and Ni were detected in the PbO by means of spectroscopic analysis. Further details of the experimental procedures are the same as those given in our previous report on the PbO–$PbGeO_3$ system.[12]

Results

Observed equilibrium phase relations are summarized in Fig. 1. In the PbO–$PbSiO_3$ system, three intermediate compounds, Pb_5SiO_7, $Pb_{11}Si_3O_{17}$, and Pb_2SiO_4, appear above 650 °C. The last one, Pb_2SiO_4 has been already reported by Krakau *et al.*,[5] but the former two phases have not yet been reported.

In the present investigation, electron probe microanalysis was used successfully for identification of phases in quenched samples. Results of analysis for equilibration runs are shown in Table 1. Each starting mixture was sealed by welding it inside a plutinum

TABLE 1. ANALYTICAL RESULTS OF THE PRODUCTS KEPT AT 718 °C FOR 820 h[a]

Starting materials Composition		Products							
		Phase 1		Phase 2		Phase 3		Phase 4	
SiO_2/wt%	PbO/wt%	SiO_2/wt%	PbO/wt%	SiO_2/wt%	PbO/wt%	SiO_2/wt%	PbO/wt%	SiO_2/wt%	PbO/wt%
3.0	97.0	0.0_5	$100._1$	5.1_2	$94._2$				
		0.0_2	$100._2$	5.3_2	$94._2$				
		0.0_0	$99._8$	5.2_4	$94._5$				
6.0	94.0			5.1_0	$94._9$	6.8_2	$92._9$		
				5.1_9	$94._5$	6.8_3	$93._7$		
				5.2_0	$94._5$	6.9_5	$93._9$		
9.0	91.0					6.7_4	$94._0$	11.6_9	$88._7$
						6.7_6	$92._7$	11.7_5	$88._7$
						6.9_4	$94._4$	11.9_4	$88._6$
Average		0.0_2	$100._0$	5.2_0	$94._5$	6.8_7	$93._3$	11.7_9	$88._7$
Formula		PbO		Pb_5SiO_7		$Pb_{11}Si_2O_{17}$		Pb_2SiO_4	
Calculated		0.00	100.0	5.10	94.90	6.83	93.17	11.85	88.15

[a] Computational method was taken from Bence and Albee.[13] Under experimental conditions of 20 kV accelerating potential and 40° take-off angle, the correction factors α were: $\alpha^{Pb}_{SiO_2}=1.60$ and $\alpha^{Si}_{PbO}=1.04$.

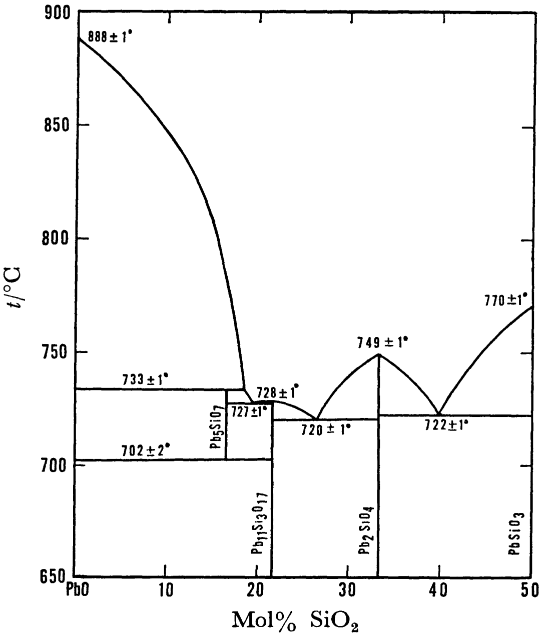

Fig. 1. Phase relations in the system $PbO-PbSiO_3$.

capsule. This was kept at 718 °C for 820 h and then quenched to room temperature. Only two phases were found in each capsule. Crystals in the quenched samples thus obtained were several tens of microns or more in size, and were large enough to allow the analysis. The standard deviation σ for SiO_2 concentration in the $Pb_{11}Si_3O_{17}$ phase was determined to be 0.08 wt% SiO_2; this was sufficient to determine the chemical composition of this phase.

Pb_5SiO_7. The Pb_5SiO_7 phase was determined to be stable only between 733 ± 1 °C and 702 ± 2 °C. By spontaneous crystallization of a melt of composition $5PbO\cdot SiO_2$, brown plates of Pb_5SiO_7, together with PbO and fine crystals of $Pb_{11}Si_3O_{17}$, were obtained. Well developed crystals of Pb_5SiO_7 were obtained by keeping a mixture of PbO and $Pb_{11}Si_3O_{17}$ for a week at 725 °C. The Pb_5SiO_7 decomposes slowly into PbO and $Pb_{11}Si_3O_{17}$ at temperatures below 702 °C. Runs of several weeks duration were necessary to attain an equilibrium state.

$Pb_{11}Si_3O_{17}$. The phase $Pb_{11}Si_3O_{17}$ melts congruently at 728 ± 1 °C. The composition of this phase was determined, at the first stage of investigation, by means of electron probe microanalysis. The results of this analysis were scattered in a range from 78.4_3 to 78.9_6 mol% PbO. The average value was 78.6_5 mol% PbO. The atomic ratio $Pb/Si=11/3$ (78.57 mol% PbO) is the simplest integral ratio for these analytical results. To confirm this conclusion, a mixture of the composition $11PbO\cdot 3SiO_3$ was enclosed in a platinum capsule by welding. Keeping the mixture at a temperature only slightly lower than that required for melting, and grinding repeatedly, it was possible to prepare a microscopically single-phase product of $Pb_{11}Si_3O_{17}$. A rapid and reversible structural inversion at 145 ± 5 °C was detected by X-ray powder diffraction measurement of this phase.

Discussion

In the early investigations,[1-5] the workers agree on the existence of the compounds Pb_2SiO_4 and $PbSiO_3$. The phase "Pb_4SiO_6" has been reported by Geller *et al.*[6] In their investigations, they came to the conclusion that "Pb_4SiO_6" has three crystal modifications: alpha form stable above 720 °C and melting incongruently at 725 °C to PbO and liquid, beta form stable between 720° and about 140 °C, and gamma form stable below 140 °C. The phase "Pb_4SiO_6" has been accepted by Billhaldt,[7] by Ott and McLaren[8] and by Smart and Glasser,[9] who studied subsolidus phase equilibria in the system $PbO-SiO_2$. In their investigations, a single phase "Pb_4SiO_6" was obtained both when the constituent oxides were sintered and when the glass was devitrified. X-Ray powder data for the alpha form and the gamma form were given by McMurdie and Bunting,[10] by Billhardt,[7] and by Argyle and Hummel.[11] Their data coincide with each other satisfactorily within their experimental errors.

But, as regards the alpha-beta inversion of "Pb_4SiO_6," some ambiguities have been pointed out. Geller *et al.*[6] reported that the results of heating curves obtained by a DTA method, as well as of the quenching tests, were not entirely satisfactory as regards the establishment of the alpha-beta inversion, but these results were believed to indicate that the tetralead silicate, on heating, undergoes an inversion at 720 ± 2 °C. Billhaldt[7] has reported that the questions whether the chemical formula given for the phase α-Pb_4SiO_6 is the right one and wherther the composition of this phase is Pb_3SiO_5 could not be solved. He also reported that a crystallized single phase sample is necessary to determine the chemical composition of this phase.

The synthesis of "α-Pb_4SiO_6" was readily repeated by Smart and Glasser.[9] But they reported that the available data are insufficient to prove that the composition ratio of this phase is 4:1. Irrespective of the bulk composition of the mixture or the time and temperature used in the experiment, a single-phase product was never obtained in either isothermal or dynamic runs. They also reported that the α-phase was sometimes obtained free of other crystalline phases, but these preparations always contained glass, and, more often, the α-phase occurred with β-Pb_4SiO_6, PbO, or both. They added that the narrow range of temperatures essential to formation of this phase makes more detailed investigation difficult.

It is possible to suspect that the "α-Pb_4SiO_6" is the Pb_5SiO_7 obtained in the present investigation. Certainly, X-ray powder data for this phase given by McMurdie and Bunting,[10] and Billhaldt[7] coincide with that for the Pb_5SiO_7 phase found in the present investigation. Practically all reflections in their X-ray powder data of "α-Pb_4SiO_6" are found also in that of Pb_5SiO_7 phase; these are shown in Table 2.

Similarly, the phases "β-Pb_4SiO_6" and "γ-Pb_4SiO_6" correspond with the compound $Pb_{11}Si_3O_{17}$ in the present investigation. X-Ray powder data for "γ-

TABLE 2. X-RAY DIFFRACTION DATA OF POWDERED SAMPLES

Spacing d/Å	Relative intensity	Spacing d/Å	Relative intensity	Spacing d/Å	Relative intensity
Pb_5SiO_7					
6.63	3	3.241	9	2.511	2
5.90	4	3.127	6	2.370	4
5.68	6	3.110	15	2.318	9
5.50	4	3.087	13	2.248	4
4.289	2	3.038	100	2.225	3
4.210	2	2.944	29	2.181	6
4.024	5	2.855	28	2.124	2
3.679	13	2.833	40	2.009	8
3.489	3	2.794	21	1.890	13
3.431	2	2.751	12	1.851	4
3.362	4	2.710	12	1.838	4
3.312	12	2.682	4	1.817	9
$Pb_{11}Si_3O_{17}$					
7.249	12	3.006	37	2.316	16
5.441	7	2.974	5	2.181	5
4.608	3	2.939	8	2.101	5
3.663	4	2.914	30	2.032	4
3.636	5	2.853	8	2.025	5
3.494	5	2.823	8	2.009	11
3.460	7	2.792	20	1.959	6
3.236	13	2.738	15	1.897	24
3.203	4	2.717	26	1.859	14
3.147	13	2.656	11	1.848	9
3.115	100	2.543	9	1.826	24
3.034	43	2.486	12		

Pb_4SiO_6" given by McMurdie and Bunting,[10] and X-ray powder data for "T-Pb_4SiO_6" given by Billhaldt[7] coincide with that of $Pb_{11}Si_3O_{17}$ at room temperature in the present investigation. The difference in composition between "Pb_4SiO_6" and $Pb_{11}Si_3O_{17}$ is only 0.534 wt% SiO_2. The experimental techniques used in the previous investigations may not have been sufficient to distinguish such a small difference in chemical compositions.

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