Experimental Study of Phase Equilibria in the System PbO-ZnO-SiO_2

EVGUENI JAK, BAOJUN ZHAO, NAIGANG LIU, and PETER C. HAYES

An experimental study on the ternary system PbO-ZnO-SiO_2 in air by high-temperature equilibration and quenching techniques followed by electron probe X-ray microanalysis was carried out as part of the wider research program on the six-component system PbO-ZnO-SiO_2-CaO-FeO-Fe_2O_3, which combines experimental and thermodynamic computer modeling techniques to characterize zinc and lead industrial slags. Liquidus and solidus data were reported for all primary phase fields in the system PbO-ZnO-SiO_2 in the temperature range 640 °C to 1400 °C (913 to 1673 K).

I. INTRODUCTION

THE overall research program combines experimental investigations with computer-aided thermodynamic modeling to develop a self-consistent thermodynamic database for the six-component system PbO-ZnO-SiO_2-CaO-FeO-Fe_2O_3 with the computer package FACT.[1] The research methodology and some results of this overall research program have already been described by the present authors in previous publications,[2–11] including work on the systems PbO-CaO-SiO_2,[2,3,4] PbO-ZnO-SiO_2,[5,6] Ca-O-Pb,[2,4] PbO-SiO_2,[6,7] Fe-O-Zn,[7] and six-component slag system PbO-ZnO-SiO_2-CaO-FeO-Fe_2O_3.[7–11]

In the present study, critical evaluations of all phase diagrams and thermodynamic data for the PbO-SiO_2, ZnO-SiO_2, and PbO-ZnO binary systems have been initially conducted. During that initial thermodynamic optimization of the PbO-ZnO-SiO_2 ternary system using the computer package FACT, it was found that there were significant inconsistencies between the data previously reported on binary subsystems and this ternary system.[12,13] The liquidus temperature data reported by Umetsu *et al.*[12] and lead oxide activity measurements by Toivonen and Taskinen[13] could not be reproduced simultaneously with one set of thermodynamic parameters with the FACT package. This indicated that either liquidus data[12] or lead oxide activity data[13] were not accurate. To resolve these discrepancies, this present new experimental investigation was initiated.

II. EXPERIMENTAL PROCEDURE

The experimental procedure in general is similar to that described in detail previously.[2,3,5,7,8,10,11] In brief, binary glassy lead and zinc silicate master slags were prepared from pure oxide powders, then mixed in the desired proportions with the addition of pure ZnO, SiO_2, and PbO powders where required, pelletized, and equilibrated in air in shallow-bottomed platinum crucibles first at higher temperature to homogenize the melt, and then at the final experimental temperature. The total equilibration time varied from a few hours to a few days. The temperature accuracy was estimated to be within ±5 K. After equilibration, the samples were quenched in air or in water, mounted, and analyzed using optical and scanning electron microscopy. The compositions of liquid and solid phases were measured with electron probe X-ray microanalysis (EPMA) using a JEOL* 8800L electron probe microanalyzer with wavelength dispersive detectors. Lead-silicate glass standard** (Pb = 65.67 ± 0.26, Si = 13.37 ± 0.24, and O = 20.35 wt pct) was used for the lead, willemite (Zn_2SiO_4) standard† was used for zinc, and wollastonite ($CaSiO_3$) standard‡ was used for silicon. The Duncumb–Philibert ZAF correction procedure supplied with a JEOL 8800L was applied. The average accuracy of the EPMA measurements was estimated to be within 1 wt pct.

*JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

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III. RESULTS ON THE TERNARY SYSTEM PbO-ZnO-SiO_2 AND BINARY SUBSYSTEMS

A. *Binary System PbO-SiO_2*

Results of experiments carried out in the high-silica region of the binary system PbO-SiO_2 are given in Table I. The diagram has been reported in a previous publication of the present authors (Reference 6, Figure 1). Liquidus data obtained from the present study are in good agreement with the experimental results of previous researchers[13–17] in the temperature range from 800 °C (1073 K) to 1100 °C (1373 K). The SiO_2 liquidus temperatures at high SiO_2 contents appear about 25 °C lower than those reported by Calvert and Shaw.[17] The results reported by Kuxman and Fischer[18] are significantly different from the results of the present study and the results of all other workers.

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A number of researchers[15,17–20] agree within experimental error about the liquidus of this binary in the composition range 0 to 60 mol pct SiO_2. However, there is disagreement regarding the stability of different lead silicate compounds. In the present study, only Pb_4SiO_6, Pb_2SiO_4, and $PbSiO_3$ primary phase fields were observed in the ternary system, and liquidus temperatures in the ternary region close to the binary PbO-SiO_2 are in general agreement with previous data.

B. *Binary System ZnO-PbO*

Equilibration and quenching experiments were conducted in the binary system PbO-ZnO. However, in contrast to silica-containing systems, it was not possible to retain the liquid phase present at temperature as a glass in the quenched samples. The liquidus in this system therefore could not be accurately characterized using EPMA. However, it was found that both hyper- and hypoeutectic samples equilibrated at 870 °C (1143 K) were molten. The samples held at 850 °C (1123 K) did not form a liquid phase. These results are consistent with the eutectic temperature of 861 °C (1134 K) reported by Bauleke and McDowell.[21] A new phase diagram has been reported in a previous publication of the present authors (Reference 6, Figure 5).

C. *Ternary System PbO-ZnO-SiO_2*

Initial bulk mixture compositions used in the present study and results of the experiments are reported in Table II. Solid solubilities in the crystalline compounds are given in Table III. These new experimental data have been used by the present authors to optimize this ternary system using the computer system FACT.[5,6] The liquidus surface for the ternary system PbO-ZnO-SiO_2 in air calculated using the new FACT model has been reported in a previous publication of the present authors (Reference 6, Figure 6).

The system has ten primary fields including three of mono-oxides (PbO, ZnO, and SiO_2); four of binary oxides (Zn_2SiO_4, $PbSiO_3$, Pb_2SiO_4, and Pb_4SiO_6); and three of incongruently melting ternary compounds (larsenite-Pb-$ZnSiO_4$, lead zinc melilite-$Pb_2ZnSi_2O_7$, and barysilite-$Pb_8ZnSi_6O_{21}$). Experiments have been carried out in all of these primary fields at temperatures from 640 °C (913 K) up to 1400 °C (1673 K).

Data on the binary subsystem ZnO-SiO_2 were taken from Bunting.[22] The system has one congruently melting binary compound Zn_2SiO_4, which forms binary eutectics with both zinc oxide and silica. These phase relations extend into the ternary region and form primary fields of ZnO, Zn_2SiO_4, and SiO_2, which dominate in this ternary diagram.

Figures 1 through 4 present some typical microstructures observed in the quenched samples with univariant equilibria between the phases (liquid + ZnO + willemite, Zn_2SiO_4), (liquid + tridymite, SiO_2 + willemite, Zn_2SiO_4), (liquid + ZnO + larsenite, $PbZnSiO_4$), and (liquid + larsenite, $PbZnSiO_4$ + lead-zinc melilite, $Pb_2ZnSi_2O_7$), respectively.

No data have been previously reported on the liquidus in the primary field of ZnO in the ternary system. The present experiments indicate that the ZnO primary field has univariant boundaries with PbO, $PbZnSiO_4$, and Zn_2SiO_4.

Table I. Results of Experiments on Silica Liquidus in the Binary System PbO-SiO_2 in Air

Temperature	Phases in Equilibrium	Composition of Liquid Phase			
		PbO	SiO_2	PbO	SiO_2
[°C]		(Mol Pct)		(Wt Pct)	
800	liquid+quartz	38.9	61.1	70.3	29.7
1000	liquid+tridymite	37.1	62.9	68.7	31.3
1100	liquid+tridymite	34.0	66.0	65.7	34.3
1200	liquid+tridymite	31.9	68.1	63.5	36.5
1300	liquid+tridymite	28.1	71.9	59.3	40.8
1200	liquid+tridymite	31.7	68.3	63.3	36.7
1100	liquid+tridymite	33.8	66.2	65.5	34.5
1000	liquid+tridymite	36.1	63.9	67.7	32.3

The ZnO liquidus surface determined in the ternary region is not consistent with the liquidus temperatures in the binary system ZnO-PbO suggested by Bauleke and McDowell.[21] Using a ''cooling curve technique,'' these authors[21] reported that the eutectic between ZnO and PbO was at 861 °C (1134 K) and 4.3 wt pct ZnO. Information obtained in the present investigation confirms the eutectic temperature, but a eutectic composition of 1.6 wt pct ZnO is predicted by extrapolation of results obtained in the ternary region in the present study. This latter value of the eutectic composition is in good agreement with the PbO liquidus of the PbO-ZnO system reported by Fisher.[23]

The primary field of the incongruently melting compound $PbZnSiO_4$, which corresponds to the naturally occurring mineral larsenite, is the third phase, in addition to ZnO and SiO_2, which limits the Zn_2SiO_4 liquidus surface and forms a univariant boundary line with it.

The three ternary incongruently melting compounds (larsenite-$PbZnSiO_4$, lead zinc melilite-$Pb_2ZnSi_2O_7$, and barysilite-$Pb_8ZnSi_6O_{21}$) and three binary compounds (Pb_4SiO_6, Pb_2SiO_4, and $PbSiO_3$) are involved in phase relations at liquidus temperatures in the low zinc region of the diagram.

Umetsu *et al.*[12] reported data on the ternary liquidus phase relations, which were obtained by the quenching technique followed by X-ray diffraction for phase identification. Although the work of Umetsu *et al.* and the present study are in agreement with respect to the temperature of the peritectic reaction $PbZnSiO_4 \rightarrow Zn_2SiO_4$ + liquid, there are significant differences in the liquidus surface and univariant lines.

In the low ZnO region of the system, Umetsu *et al.*[12] observed the ternary compound barysilite as a primary phase. However, the phase relations concerned with the barysilite were not explained by Umetsu *et al.* Umetsu *et al.* reported the formula $Zn_{0.5}Pb_{2.5}Si_2O_7$ for the barysilite. The EPMA measurements in the present study indicate that the stoichiometry of this compound is described by the formula $Pb_8ZnSi_6O_{21}$. This formula is consistent with that found by other researchers.[24,25,26] The primary field of the barysilite ($Pb_8ZnSi_6O_{21}$) has been constructed in the present study. It was found that the primary field of $Pb_8ZnSi_6O_{21}$ closely approaches the binary join PbO-SiO_2.

The primary fields of two other ternary incongruently melting compounds $PbZnSiO_4$ (larsenite) and $Pb_2ZnSi_2O_7$ (lead-zinc melilite) were also investigated.

Table II. Results of Experiments on the System PbO-ZnO-SiO_2 in Air

Starting Mixture Composition			Temperature	Phases in	Composition of Liquid Phase (Wt Pct)		
PbO	ZnO	SiO_2	(°C)	Equilibrium	PbO	ZnO	SiO_2
			Equilibria Involving One Condensed Phase				
78.2	2.8	19.0	750	L only	78.4	2.4	19.2
78.2	2.8	19.0	750	L only	77.3	2.5	20.2
77.6	1.5	20.9	760	L only	76.5	1.6	21.8
			Bivariant Equilibria				
Zincite primary field							
80.0	14.6	5.4	800	L + Z	90.3	3.5	6.1
93.0	5.0	2.0	900	L + Z	94.8	3.0	2.1
90.0	6.0	4.0	900	L + Z	92.1	3.8	4.2
80.0	14.6	5.4	900	L + Z	89.2	4.8	6.0
93.0	5.0	2.0	1000	L + Z	93.9	4.1	2.0
89.0	8.0	3.0	1000	L + Z	92.5	4.5	3.0
89.0	8.0	3.0	1000	L + Z	92.2	4.7	3.2
90.0	6.0	4.0	1000	L + Z	90.6	5.2	4.3
80.0	14.6	5.4	1000	L + Z	87.8	6.3	5.9
80.0	11.0	9.0	1000	L + Z	81.3	9.3	9.4
72.0	17.0	11.0	1000	L + Z	75.3	12.4	12.3
89.0	8.0	3.0	1100	L + Z	89.8	6.7	3.5
89.0	8.0	3.0	1100	L + Z	88.3	7.2	4.5
80.0	14.6	5.4	1100	L + Z	85.8	8.3	5.9
80.0	11.0	9.0	1100	L + Z	79.2	11.3	9.5
72.0	17.0	11.0	1100	L + Z	72.8	15.0	12.3
68.5	18.0	13.5	1100	L + Z	69.4	17.2	13.4
89.0	8.0	3.0	1200	L + Z	88.5	8.4	3.1
89.0	8.0	3.0	1200	L + Z	88.3	8.5	3.2
80.0	14.6	5.4	1200	L + Z	83.0	10.8	6.2
72.0	17.0	11.0	1200	L + Z	70.0	18.1	11.9
72.0	17.0	11.0	1200	L + Z	69.8	18.1	12.1
63.5	22.5	14.0	1200	L + Z	63.1	22.4	14.5
63.5	22.5	14.0	1200	L + Z	62.3	22.7	15.0
63.5	22.5	14.0	1200	L + Z	60.7	23.8	15.5
Willemite primary field							
62.0	10.0	28.0	850	L + Z2S	65.1	7.7	27.2
66.0	11.0	23.0	900	L + Z2S	67.9	8.5	23.6
62.0	10.0	28.0	900	L + Z2S	64.1	8.6	27.3
59.5	25.0	15.5	1000	L + Z2S	73.3	13.3	13.4
55.5	25.0	19.6	1000	L + Z2S	70.2	11.8	18.0
68.3	13.5	18.2	1000	L + Z2S	69.6	11.7	18.7
66.0	11.0	23.0	1000	L + Z2S	62.5	11.6	25.9
50.0	21.0	29.0	1000	L + Z2S	57.5	11.3	31.2
57.3	25.5	17.2	1020	L + Z2S	71.8	13.3	14.8
57.3	25.5	17.2	1100	L + Z2S	67.3	17.3	15.4
55.5	25.0	19.6	1100	L + Z2S	66.1	16.0	17.9
50.0	21.0	29.0	1100	L + Z2S	54.8	15.1	30.0
50.0	21.0	29.0	1100	L + Z2S	53.9	15.7	30.3
43.0	25.0	32.0	1100	L + Z2S	51.1	15.1	33.8
43.0	25.0	32.0	1100	L + Z2S	50.5	15.4	34.1
50.0	16.0	34.0	1100	L + Z2S	50.7	14.8	34.5
59.5	25.0	15.5	1200	L + Z2S	59.3	24.7	16.0
59.5	25.0	15.5	1200	L + Z2S	59.4	24.4	16.2
62.0	2.0	36.0	1200	L + Z2S	59.3	23.8	16.9
55.5	25.0	19.6	1200	L + Z2S	58.7	22.1	19.2
55.5	25.0	19.6	1200	L + Z2S	58.7	21.9	19.4
55.5	25.0	19.6	1200	L + Z2S	58.3	21.6	20.1
50.0	21.0	29.0	1200	L + Z2S	49.3	20.6	30.0
50.0	21.0	29.0	1200	L + Z2S	49.2	20.6	30.1
50.0	21.0	29.0	1200	L + Z2S	48.6	20.7	30.7
43.0	25.0	32.0	1200	L + Z2S	46.2	20.5	33.3
43.0	25.0	32.0	1200	L + Z2S	46.0	20.4	33.5
31.9	46.6	21.5	1300	L + Z2S	50.7	30.9	18.4
31.9	46.6	21.5	1400	L + Z2S	33.9	44.9	21.2

Table II. Continued Results of Experiments on the System PbO-ZnO-SiO_2 in Air

Starting Mixture Composition			Temperature	Phases in	Composition of Liquid Phase (Wt Pct)		
PbO	ZnO	SiO_2	(°C)	Equilibrium	PbO	ZnO	SiO_2
Quartz primary field							
65.7	2.2	32.1	800	L + S	68.6	1.9	29.6
61.9	5.1	33.0	800	L + S	64.4	6.0	29.6
65.7	2.2	32.1	800	L + S	67.5	2.9	29.6
Tridymite primary field							
61.9	5.1	33.0	900	L + S	65.2	4.6	30.1
62.0	2.0	36.0	900	L + S	68.0	1.7	30.3
59.0	5.0	36.0	900	L + S	64.3	5.4	30.3
65.7	2.2	32.1	900	L + S	67.7	2.0	30.4
62.0	2.0	36.0	1000	L + S	66.0	2.3	31.7
62.0	2.0	36.0	1000	L + S	65.7	2.6	31.7
59.0	5.0	36.0	1000	L + S	62.0	6.1	31.8
59.0	5.0	36.0	1000	L + S	61.8	6.4	31.8
62.0	2.0	36.0	1100	L + S	63.7	2.4	34.0
59.0	5.0	36.0	1200	L + S	59.2	5.3	35.5
59.0	5.0	36.0	1200	L + S	59.3	5.1	35.6
62.0	2.0	36.0	1200	L + S	61.7	2.7	35.6
62.0	2.0	36.0	1200	L + S	62.2	2.1	35.7
62.0	2.0	36.0	1200	L + S	61.6	2.7	35.8
37.0	22.0	41.0	1300	L + S	37.6	23.0	39.4
Larsenite primary field							
83.0	7.0	10.0	800	L + PZS	89.4	3.5	7.0
82.8	3.4	13.8	800	L + PZS	83.2	2.8	13.9
77.0	6.5	16.5	800	L + PZS	80.1	2.9	17.0
77.0	6.5	16.5	800	L + PZS	79.1	3.0	17.9
72.8	5.0	22.2	800	L + PZS	72.9	4.2	22.8
72.8	5.0	22.2	800	L + PZS	72.5	4.3	23.2
70.0	5.3	24.7	800	L + PZS	70.0	5.0	25.0
73.3	7.0	19.7	810	L + PZS	73.7	4.2	22.0
73.3	7.0	19.7	830	L + PZS	73.5	4.5	21.9
83.0	7.0	10.0	850	L + PZS	87.2	4.8	8.0
77.0	6.5	16.5	850	L + PZS	78.4	3.9	17.7
68.3	13.5	18.2	850	L + PZS	73.6	5.1	21.3
66.0	11.0	23.0	850	L + PZS	68.4	6.4	25.2
83.0	7.0	10.0	900	L + PZS	84.3	6.6	9.1
64.8	19.3	15.9	900	L + PZS	81.6	5.2	13.1
77.0	6.5	16.5	900	L + PZS	77.4	5.5	17.1
68.3	13.5	18.2	900	L + PZS	72.6	6.6	20.8
64.8	19.3	15.9	1000	L + PZS	73.3	12.1	14.6
Lead/zinc melilite primary field							
70.0	5.3	24.7	700	L + P2ZS2	70.8	1.9	27.3
73.3	7.0	19.7	740	L + P2ZS2	75.2	2.1	22.6
Lead/zinc barysilite primary field							
75.7	1.5	22.8	655	L + P8ZS6	71.6	0.9	27.5
77.6	1.5	20.9	675	L + P8ZS6	75.2	0.6	24.2
75.7	1.5	22.8	700	L + P8ZS6	74.5	1.1	24.4
78.2	2.8	19.0	700	L + P8ZS6	72.7	1.5	25.9
82.0	1.5	16.5	730	L + P8ZS6	82.8	0.3	16.9
82.0	1.5	16.5	730	L + P8ZS6	80.7	0.2	19.1
78.2	2.8	19.0	730	L + P8ZS6	75.5	1.5	23.0
78.2	2.8	19.0	730	L + P8ZS6	74.0	2.0	24.1
85.0	1.5	13.5	740	L + P8ZS6	86.2	1.1	12.7

Table II. Continued Results of Experiments on the System PbO-ZnO-SiO_2 in Air

Starting Mixture Composition			Temperature	Phases in	Composition of Liquid Phase (Wt Pct)		
PbO	ZnO	SiO_2	(°C)	Equilibrium	PbO	ZnO	SiO_2
				Univariant Equilibria			
93.0	5.0	2.0	800	L + Z + P	94.2	2.6	3.2
90.0	6.0	4.0	780	L + Z + P	92.5	2.9	4.6
93.0	5.0	2.0	780	L + Z + P	92.5	2.8	4.7
80.0	11.0	9.0	800	L + Z + PZS	89.6	3.7	6.7
80.0	11.0	9.0	900	L + Z + PZS	84.5	6.7	8.9
72.0	17.0	11.0	1000	L + Z + PZS	75.4	12.0	12.6
63.5	22.5	14.0	1100	L + Z + Z2S	67.4	18.3	14.3
50.0	16.0	34.0	850	L + Z2S + S	61.9	7.7	30.4
37.0	22.0	41.0	1100	L + Z2S + S	49.5	15.1	35.4
37.0	22.0	41.0	1200	L + Z2S + S	42.8	20.3	36.8
50.0	16.0	34.0	900	L + Z2S + S	60.2	8.7	31.1
43.0	25.0	32.0	1000	L + Z2S + S	54.5	11.9	33.6
50.0	16.0	34.0	1000	L + Z2S + S	54.5	11.7	33.8
37.0	22.0	41.0	1000	L + Z2S + S	54.1	11.8	34.1
37.0	22.0	41.0	1200	L + Z2S + S	42.8	20.2	37.0
37.0	22.0	41.0	1200	L + Z2S + S	42.6	20.2	37.1
80.0	14.6	5.4	750	L + PZS + P	90.6	2.5	6.8
83.0	7.0	10.0	740	L + PZS + P	91.0	2.1	6.8
88.0	4.0	8.0	740	L + PZS + P	91.1	1.9	6.9
88.0	4.0	8.0	710	L + PZS + P4S	90.6	1.7	7.6
86.0	3.5	10.5	710	L + PZS + P2S	89.3	1.6	9.1
70.0	5.3	24.7	740	L + PZS + P2ZS2	70.4	2.4	27.2
77.3	4.3	18.4	800	L + PZS + P2ZS2	78.3	3.0	18.7
82.8	3.4	13.8	740	L + PZS + P8ZS6	86.6	1.8	11.6
61.0	7.0	32.0	700	L + PZS + S	68.2	2.8	29.0
61.0	7.0	32.0	730	L + PZS + S	66.9	3.9	29.2
62.0	10.0	28.0	800	L + PZS + S	63.7	6.8	29.5
77.3	4.3	18.4	740	L + P8ZS6 + P2ZS2	75.4	2.1	22.5
78.2	2.8	19.0	740	L + P8ZS6 + P2ZS2	75.2	2.1	22.7
85.0	1.5	13.5	730	L + P8ZS6 + P2S	86.7	1.5	11.8
85.0	1.5	13.5	730	L + P8ZS6 + P2S	84.3	0.4	15.3
77.6	1.5	20.9	655	L + P8ZS6 + PS	72.7	0.6	26.7
72.8	5.0	22.2	645	S + P8ZS6 + PZS	—	—	—

L = liquid; P = PbO; Z = ZnO; S = silica; Z2S = willemite Zn_2SiO_4; P2S = Pb_2SiO_4; PS = alamosite $PbSiO_3$; PZS = larsenite $PbZnSiO_4$; P8ZS6 = Zn-Pb barysilite $Pb_8ZnSi_6O_{21}$; P2ZS2 = lead melilite $Pb_2ZnSi_2O_7$; and P4S = Pb_4SiO_6.

IV. CONCLUSIONS

An initial evaluation of the thermodynamic data and phase diagrams currently available on the PbO-ZnO-SiO_2 system was conducted using the computer system FACT. It was found that the experimental information previously available was not thermodynamically consistent. To resolve these discrepancies, new experimental work has been carried out providing extensive sets of liquidus and solidus data.

Using the new experimental data, obtained for a wide range of compositions, the liquidus surface of the ternary system PbO-ZnO-SiO_2 has been completely reconstructed. All ten primary phase fields were characterized in this investigation, including the primary fields of ZnO and $Pb_8ZnSi_6O_{21}$, where data were not previously available. The existence of the ternary compound $Pb_8ZnSi_6O_{21}$ has been confirmed from EPMA measurements.

These results have been used to develop a self-consistent database within the FACT package and can be used to predict the phase relations and thermodynamic properties of the multicomponent system PbO-ZnO-SiO_2-CaO-FeO-Fe_2O_3.

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Table III. Compositions of Solid Phases Measured by Electron Probe

Phase Name	Ideal Formula	Temperature (°C)	Composition in Mol Pct		
			PbO	ZnO	SiO_2
Tridymite	SiO_2		0.6 ± 0.5	0.1 ± 0.1	99.3
Zincite	ZnO		0.3 ± 0.4	99.7 ± 0.4	0.0
Willemite	Zn_2SiO_4		0.1 ± 0.1	66.6 ± 0.1	33.3
Larsenite	$PbZnSiO_4$		33.0 ± 0.5	33.7 ± 0.5	33.3
Zn/Pb barysilite	$Pb_8ZnSi_6O_{21}$		53.7 ± 0.5	6.3 ± 0.5	40.0
Zn/Pb melilite	$Pb_2ZnSi_2O_7$		39.6 ± 0.3	20.4 ± 0.3	40.0
Four lead silicate	Pb_4SiO_6		79.4 ± 0.1	0.6 ± 0.1	20.0
Lead oxide	PbO	710 °C	99.2	0.8	0.0
		730 °C	99.7	0.3	0.0
		730 °C	99.5	0.5	0.0
		750 °C	98.9	1.1	0.0
		800 °C	98.9	1.1	0.0
		800 °C	98.6	1.4	0.0
		850 °C	97.8	2.2	0.0

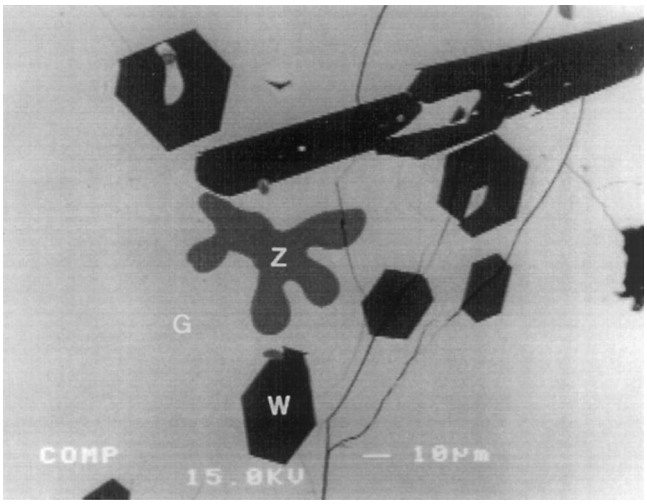

Fig. 1—Backscattered electron image of sample with univariant equilibrium (liquid + Zn_2SiO_4 + ZnO) in the system PbO-ZnO-SiO_2: G = glass (liquid), Z = zincite ZnO, and W = willemite Zn_2SiO_4.

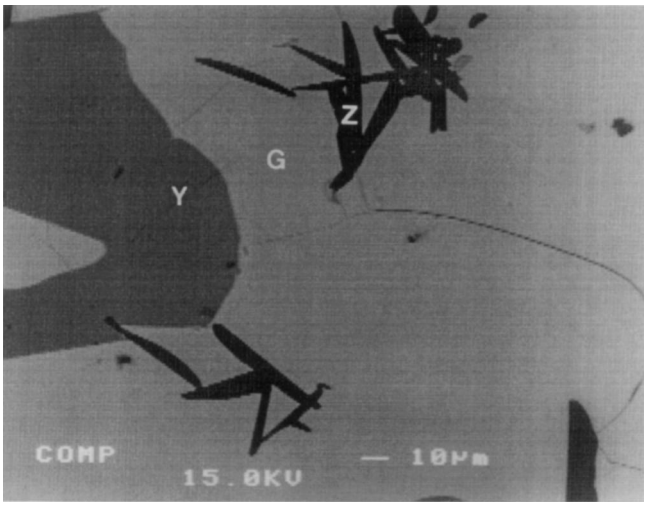

Fig. 3—Backscattered electron image of sample with univariant equilibrium (liquid + $PbZnSiO_4$ + ZnO) in the system PbO-ZnO-SiO_2: G = glass (liquid), Z = zincite ZnO, and Y = larsenite $PbZnSiO_4$.

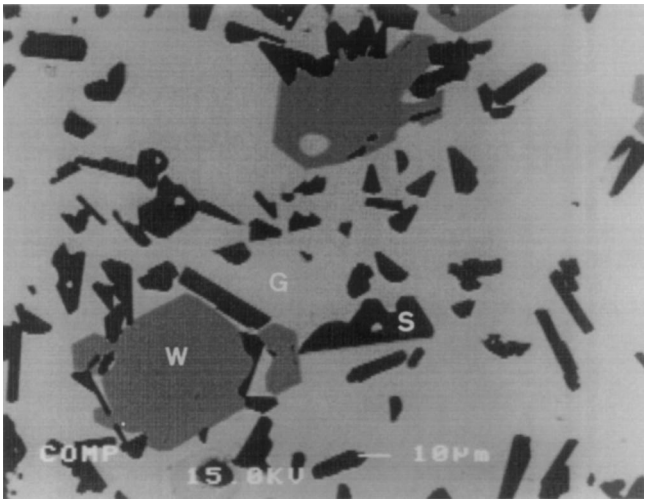

Fig. 2—Backscattered electron image of sample with univariant equilibrium (liquid + Zn_2SiO_4 + SiO_2) in the system PbO-ZnO-SiO_2: G = glass (liquid), S = tridymite SiO_2, and W = willemite Zn_2SiO_4.

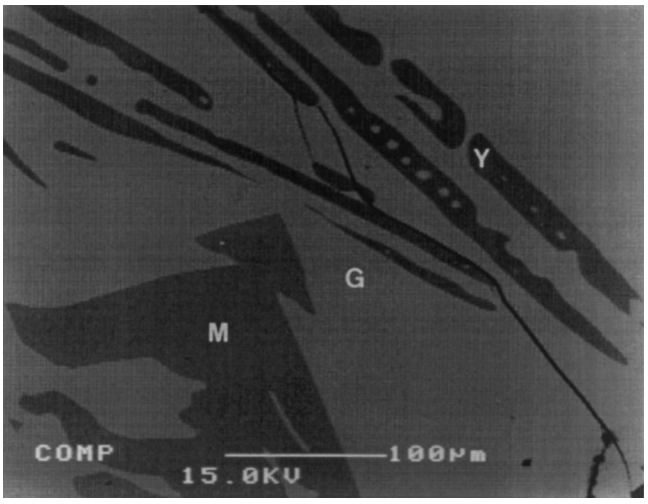

Fig. 4—Backscattered electron image of sample with univariant equilibrium (liquid + $PbZnSiO_4$ + $Pb_2ZnSi_2O_7$) in the system PbO-ZnO-SiO_2: G = glass (liquid), Y = larsenite $PbZnSiO_4$, and M = Zn-Pb melilite $Pb_2ZnSi_2O_7$.

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