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X-RAY STUDIES OF COMPOUNDS IN THE SYSTEM $PbO-SiO_2$

By Howard F. McMurdie and Elmer N. Bunting

ABSTRACT

X-ray diffraction powder patterns were made on various compositions in the system $PbO-SiO_2$ in order to check the presence of certain reported compounds. It was found that three binary compounds exist: $PbO.SiO_2$ (same as the mineral alamosite), $2PbO.SiO_2$, and $4PbO.SiO_2$. The latter occurs in at least two polymorphic forms. The powder patterns of the alpha and beta forms of PbO are also given.

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I. INTRODUCTION

Considerable work has been done by various investigators on the system $PbO-SiO_2$ [1, 2, 3, 4, 5, 6].[1] These workers agree on the existence of the compounds $2PbO.SiO_2$ and $PbO.SiO_2$. Beyond this there is little agreement. One worker [6] finds the compound $PbO.2SiO_2$. Another [5] suggests the existence of the compounds $3PbO.SiO_2$ and $3PbO.2SiO_2$. The last compound would correspond to the natural mineral barysilite.

Valenkov and Poray-Koshitz [8] studied the system with the X-ray, making powder diffraction patterns of various compositions. They concluded that 3:2, 4:1, and 3:1 compounds did not exist. Mixtures at the 4:1 composition gave, according to them, a pattern of a mixture of βPbO and $2PbO.SiO_2$.

Geller, Creamer, and Bunting [7] investigated the system by thermal studies, optical investigation, and thermal expansion tests, and came to the conclusion that three binary compounds existed: $PbO.SiO_2$ (corresponding to the natural mineral alamosite), $2PbO.SiO_2$, and $4PbO.SiO_2$. The last compound was thought to have three crystal modifications: an alpha form stable above 720° C and melting incongruently at 725° C to PbO and liquid, a beta form stable between 720 and about 140° C, and a gamma form stable below 140° C. The beta to gamma inversion was found to be so rapid that all samples of the beta form which were prepared changed quickly to gamma at room temperature. Heating curves and thermal-expansion measurements indicated the occurrence of the change at 140° C. It was found that the samples of $\alpha 4PbO.SiO_2$ crystallized between 720° and

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[1] Figures in brackets indicate the literature references at the end of this paper.

725° C could be quenched successfully to produce the alpha form at room temperature.

The present study was made as a supplement to the work of Geller, Creamer, and Bunting to check by X-ray patterns the compounds found by them.

II. MATERIALS AND METHODS

The samples of the binary compounds were made, using the methods employed in the previous work. The sample of $\alpha 4PbO.SiO_2$ was prepared at 723° C and quenched after holding for 18 hours. The $\gamma 4PbO.SiO_2$ was prepared by first crystallizing the compound for 18 hours at 710° C in the β form and then cooling below 140° C to obtain the γ form. A sample of the natural mineral alamosite was obtained from the United States National Museum, Washington, D. C.

The αPbO (massicotite) was a sample of sublimed "litharge." The βPbO (lithargite)[2] was prepared by precipitation from a hot solution of 15 *N* KOH [9].

The X-ray patterns were made in circular cameras with a radius of approximately 5.70 cm. The samples were mounted on fine glass rods with vaseline and rotated during the exposure period of about 17½ hours. The radiation used was from a gas type copper anticathode X-ray tube, operating at about 45 kv and 4 ma. The β radiation was filtered out with a thin sheet of nickel foil placed over the entrance to the camera slit.

III. RESULTS AND DISCUSSION

The diffraction data obtained on the two forms of PbO, on two forms of $4PbO.SiO_2$, and on $2PbO.SiO_2$ and $PbO.SiO_2$ are given in tables 1 to 6.

TABLE 1.—*Powder diffraction pattern of* α PbO

[*ww*=very weak; *w*=weak; *m*=medium; *s*=strong; *ss*=very strong]

Line	Intensity	d	Line	Intensity	d
		A			*A*
1	*ww*	5.89	17	*s*	1.463
2	*ss*	3.01	18	*w*	1.397
3	*m*	2.93	19	*m*	1.366
4	*s*	2.72	20	*m*	1.352
5	*s*	2.35	21	*w*	1.319
6	*ww*	2.26	22	*m*	1.289
7	*ww*	2.19	23	*m*	1.281
8	*s*	1.98	24	*m*	1.241
9	*w*	1.950	25	*m*	1.235
10	*s*	1.830	26	*m*	1.196
11	*s*	1.775	27	*m*	1.181
12	*s*	1.707	28	*m*	1.165
13	*s*	1.595	29	*m*	1.132
14	*w*	1.575	30	*m*	1.113
15	*s*	1.518	31	*s*	1.094
16	*w*	1.508	32	*m*	1.085

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[2] E. S. Larsen [14] showed the identity of the two natural minerals of PbO with the two artificial forms. In that article he proposed that "massicot" be used for the tetragonal (β) form and "litharge" for the orthorhombic (α) form. In a later paper [11] he proposed interchanging the names, which conforms to current practice.

TABLE 2.—*Powder diffraction pattern of* β PbO

[*ww*=very weak; *w*=weak; *m*=medium; *s*=strong; *ss*=very strong]

Line	Intensity	d	Line	Intensity	d
		A			*A*
1	*ww*	5.07	15	*w*	1.248
2	*ss*	3.10	16	*s*	1.218
3	*m*	2.79	17	*w*	1.193
4	*m*	2.49	18	*m*	1.146
5	*ww*	2.11			
			19	*w*	1.123
6	*ww*	2.06	20	*w*	1.075
7	*m*	1.97	21	*w*	1.060
8	*s*	1.862	22	*ww*	1.038
9	*s*	1.667	23	*ww*	1.020
10	*s*	1.530			
			24	*m*	.970
11	*ww*	1.432	25	*w*	.946
12	*w*	1.396	26	*m*	.935
13	*ww*	1.341			
14	*ww*	1.278			

TABLE 3.—*Powder diffraction pattern of* α $4PbO.SiO_2$

[*w*=weak; *m*=medium; *s*=strong; *ss*=very strong]

Line	Intensity	d	Line	Intensity	d
		A			*A*
1	*w*	3.64	13	*m*	2.010
2	*w*	3.36	14	*w*	1.958
3	*ss*	3.10	15	*w*	1.924
4	*s*	3.03	16	*m*	1.891
5	*w*	2.91	17	*w*	1.854
6	*m*	2.83	18	*m*	1.800
7	*m*	2.70	19	*m*	1.790
8	*w*	2.49	20	*m*	1.708
9	*w*	2.31	21	*s*	1.676
10	*w*	2.245	22	*w*	1.635
11	*w*	2.170	23	*w*	1.610
12	*w*	2.120	24	*m*	1.552

TABLE 4.—*Powder diffraction pattern of* γ $4PbO.SiO_2$

[*ww*=very weak; *s*=strong; *ss*=very strong; *w*=weak; *m*=medium]

Line	Intensity	d	Line	Intensity	d
		A			*A*
1	*ww*	3.69	12	*w*	2.02
2	*ww*	3.48	13	*w*	1.958
3	*s*	3.13	14	*m*	1.897
4	*ss*	3.02	15	*m*	1.853
5	*w*	2.93	16	*s*	1.819
6	*w*	2.83	17	*w*	1.730
7	*m*	2.72	18	*w*	1.676
8	*w*	2.65	19	*m*	1.610
9	*w*	2.55	20	*m*	1.563
10	*w*	2.47	21	*m*	1.539
11	*w*	2.31	22	*w*	1.486

TABLE 5.—*Powder diffraction pattern of* $2PbO.SiO_2$

[*m*=medium; *w*=weak; *ss*=very strong; *s*=strong; *ww*=very weak]

Line	Intensity	d	Line	Intensity	d
		A			*A*
1	*m*	9.80	13	*ww*	2.14
2	*m*	5.97	14	*ww*	2.10
3	*w*	3.71	15	*m*	1.99
4	*w*	3.55			
5	*ss*	3.21	16	*w*	1.93
			17	*m*	1.891
6	*ss*	3.11	18	*m*	1.855
7	*s*	2.98	19	*w*	1.790
8	*s*	2.78	20	*w*	1.750
9	*s*	2.56			
10	*w*	2.44	21	*w*	1.706
			22	*m*	1.635
11	*w*	2.36	23	*s*	1.597
12	*w*	2.22			

TABLE 6.—*Powder diffraction pattern of* $PbO\text{-}SiO_2$ (Alamosite)

[*ww*=very weak; *w*=weak; *m*=medium; *s*=strong]

Line	Intensity	d	Line	Intensity	d
		A			*A*
1	*m*	5.82	11	*w*	2.52
2	*s*	3.58	12	*w*	2.47
3	*s*	3.36	13	*w*	2.34
4	*m*	3.24	14	*m*	2.285
5	*m*	3.02	15	*w*	2.205
6	*w*	2.89	16	*w*	2.135
7	*m*	2.78	17	*ww*	2.080
8	*w*	2.73	18	*ww*	2.050
9	*w*	2.66	19	*w*	2.025
10	*w*	2.59	20	*m*	1.928

The diffraction patterns of the α and β $4PbO.SiO_2$ are similar, but show significant differences. It can be seen that neither of these patterns could be the result of a mixture of β PbO and $2PbO.SiO_2$, as suggested by Valenkov and Poray-Koshitz. Geller and Bunting [16] noted that in mixtures of similar composition, at temperatures considerably below the liquidus, PbO would sometimes crystallize out even though it was not the primary phase. To crystallize $4PbO.SiO_2$ in either form required that the composition be held at temperatures near the top of their stability ranges at least overnight.[3]

Thus, if a melted mixture were cooled before the 4:1 compound formed, PbO and $2PbO.SiO_2$ might result. The modification which was formed would presumably depend on the temperature at which the PbO first crystallized. Therefore, rapid cooling might reduce the temperature of the liquid below that of the α to β PbO inversion before crystallization could take place.

The α to β PbO inversion temperature is not agreed on by investigators. Cohen and Addink [12] report the temperature as 488.5° C. Other values reported are 530° C [13] and 587° C [15].

The entire liquidus curve of this system for compositions in which PbO is the primary phase lies above 725° C. An X-ray pattern of a

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[3] After completing this study, we note that Ernst Kordes [17] confirms the existence of $4PbO.SiO_2$. He also prepared $3PbO.2SiO_2$ crystals, but we have done no additional work to obtain it.

mixture of 97.5 percent of PbO and 2.5 percent of SiO_2 held at, and then quenched from, 740° C indicated that α PbO was present.

The inversion from α to β PbO would appear to be very sluggish. Geller, Creamer, and Bunting [7] obtained no breaks in cooling curves made with α PbO. However, the inversion from β to α PbO proceeds rapidly [15].

The α and β PbO patterns check within experimental error the results of the work of Darbyshire [10]. He stated that αPbO (yellow, massicotite) was orthorhombic with $a=5.46$ A, $b=4.72$ A, and $c=3.86$ A. β PbO (red, lithargite) was tetragonal with $a=3.97$ A and $c=5.01$ A.

A diffraction pattern of natural alamosite was also made. While Geller and his coworkers had found the optical properties of prepared $PbO.SiO_2$ very similar to alamosite, the X-ray patterns show conclusively their identity.

IV. SUMMARY

The X-ray examination of compounds in the system $PbO-SiO_2$ indicates the existence of $PbO.SiO_2$, $2PbO.SiO_2$, and $4PbO.SiO_2$, the last in at least two crystal modifications. The natural mineral alamosite was found to be identical with $PbO.SiO_2$.

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