Phase Equilibrium Relations in the Binary System Lead Oxide-Niobium Pentoxide

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The phase equilibrium diagram for the binary system lead oxide-niobium pentoxide has been constructed from observations of fusion characteristics and X-ray diffraction data. The system contains six binary compounds with $PbO:Nb_2O_5$ ratios of 3:1, 5:2, 2:1, 3:2, 1:1, and 1:2. The compound $PbO\cdot Nb_2O_5$ was found to melt congruently at 1,343° C and have a stable, reversible phase transformation temperature from the low-temperature rhombohedral form to the high-temperature tetragonal form at 1,150° C. The 5:2, 2:1, and 1:2 compounds melt congruently at 1,220°, 1,233°, and 1,337° C, respectively; the 3:1 and 3:2 compounds melt incongruently at 985° and 1,233° C, respectively.

1. Introduction

A study of phase relationships in the binary system $PbO-Nb_2O_5$ has been conducted as part of a program of fundamental phase equilibria studies of ceramic materials. The compounds $PbO\cdot Nb_2O_5$ and $2PbO\cdot Nb_2O_5$ have been previously reported by Goodman [1],[1] and a phase transformation in the $PbO\cdot Nb_2O_5$ compound has been reported by Francombe [2]. Cook and Jaffe [3, 4] have studied $2PbO\cdot Nb_2O_5$ and compositions deficient in PbO and report a cubic phase to occur at a composition of $3PbO\cdot2Nb_2O_5$. However, no systematic attempt has been made to study the phase-equilibrium relations in the entire binary system.

X-ray diffraction data, together with the determination of the melting points of the compounds and of the solidus and liquidus temperatures at various compositions across the system, have supplied data from which an equilibrium diagram has been constructed.

Because of the volatility of PbO, many of the experiments were conducted in sealed Pt tubes. As PbO tends to vaporize markedly at the temperature studied, all the data may not be exactly equivalent to the true values at atmospheric pressure. However, as these experiments could not be conducted in air and the pressure inside the tube was relatively small, it is felt that the data show the best available approach to the equilibrium conditions prevailing under atmospheric pressure.

2. Sample Preparation and Test Methods

The following starting materials were used in the preparation of samples:

PbO—Reagent grade yellow lead oxide. This material was found by X-rays to contain only the high-temperature modification of PbO, massicotite, and none of the tetragonal red lead oxide, lithargite. Spectroscopic analyses showed 0.01 to 0.1 percent Co, 0.001 to 0.01 percent Bi and Tl, 0.0001 to 0.001 percent Ag, Al, Ca, Cu, and Si and less than 0.0001 percent Mg.

Nb_2O_5—High-purity grade niobium pentoxide, over 99.7 percent. Spectroscopic analyses showed 0.01 to 0.1 percent Zr, 0.001 to 0.01 percent Fe and Si, and 0.0001 to 0.001 percent Ca and Mg.

Calculations of weight composition were made to ±0.01 percent, no correction being made for the percentage purity of the raw materials, except for a factor due to weight lost on ignition. The starting materials, in sufficient quantities to give a 5.0-g sample, were weighed to the nearest 0.1 mg. They were then mixed by hand, tumbled for 1 hr, ground for 1 hr in an agate mortar, and formed into 5/8-in.-diam disks at a pressure of 10,000 lb/in.². The pressed disks were fired for 1 hr at 750° C on platinum foil in an air atmosphere, using an electrically-heated furnace wound with 80 percent Pt–20 percent Rh wire.

Following the preliminary heat treatment, the disks were ground, and for those specimens selected for the X-ray study new disks about ¼ in. high were formed at 15,000 lb/in.² in a ½-in.-diam mold and refired for ½ to 1 hr at various appropriate temperatures between 800° C and 1,400° C. In order to reduce PbO loss, a system of inverted Pt crucibles similar to that reported by Jaffe, Roth, and Marzullo [5] was utilized. For those specimens which still indicated appreciable weight loss, a sealed Pt tube, containing a small amount of the ground, calcined mixture, was quenched from the appropriate temperature. Equilibrium conditions, except in the immediate vicinity of a phase transformation, could usually be obtained in the sealed tube in 10 to 15 min. X-ray diffraction powder patterns were made, using a high-angle recording Geiger-counter Spectrometer and Ni filtered Cu radiation, with the Geiger counter traversing the specimen at ¼°/min and the radiation being recorded on the chart at 1° 2θ/in.

Specimens for solidus and liquidus determinations were mixed with a few drops of a 20-percent solution of polyethylene glycol in water, pressed into disks in the same manner as for the X-ray specimens, and ground in the form of small four-sided pyramids grooved on each side as described by Geller et al. [6]. Solidus and liquidus determinations were made in

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

the electrically heated furnace using a Pt versus 90 Pt–10 Rh thermocouple and an indicating potentiometer for temperature measurements. The specimens were placed on a Pt disk which was on a support of mullite. An oxidizing atmosphere existed in the furnace at all times. The specimens were placed around the circumference of a circle, 1 in. away from the thermocouple, maintained at temperature for $\frac{1}{2}$ hr, and allowed to cool by shutting off the furnace. The solidus and liquidus temperatures were arrived at by visual inspection of the cooled specimen. The solidus temperature was recorded as the first sign of liquid formation, as indicated by rounding of the corners of the test pyramid. The temperature of complete melting, as indicated by the formation of a flat button, was recorded as the liquidus temperature. In all cases many tests had to be made to determine these two values.

In general, this pyramid method was only usable for those specimens containing less than 50 percent of PbO. Specimens containing more than 50 percent of PbO tended to change composition rapidly when heated in air and it was necessary to seal these compositions in small Pt tubes. For specimens which had been heated in the sealed tubes, visual observation of partial melting of the quenched specimens could usually locate the solidus temperature. In some cases, the appearance of a new phase in the X-ray pattern with different heat treatments was the best means of locating the solidus. The liquidus temperatures could probably be found only by detailed optical microscope examination. No attempt has been made to locate accurately the liquidus temperatures in that portion of the system containing greater than 50 percent of PbO.

The methods of determination of temperature limits of a particular phase are subject to a number of sources of error. Among these are the possible introduction of impurities into the specimens in the forming and grinding operations, the possibility of reduction of Nb_2O_5, oxidation and/or differential loss of PbO, difference of temperature between one or more specimens and the thermocouple, and the inherent difficulty in the visual determination of the solidus and liquidus temperatures. It is believed that the temperatures as recorded are accurate to $\pm 5°$ C.

3. Compounds Involved in the PbO–Nb₂O₅ System

3.1. Nb₂O₅

Brauer [7] has found Nb_2O_5 to occur in three polymorphic forms. The H-form or high-temperature form was reported as stable at temperatures above 1,200° to 1,250° C. In this study wherever free Nb_2O_5 was found, the high-temperature form was the one observed in all heated specimens, although the low-temperature form was used as the starting material. Holzberg, Reisman, Berry, and Berkenblit [8] concluded that Nb_2O_5 has only two crystalline polymorphs, the high- and the low-temperature

forms, with an irreversible phase transformation, γ to α (low to high) at 830° C. They gave the parameters of the high-temperature form as, monoclinic, $a=21.34$ A, $b=3.816$ A, $c=19.47$ A, and $\beta=120° 20'$. Magneli and Lagergren [9] have used the parameters $a=21.50$ A, $b=3.825$ A, $c=20.60$ A and $\beta=121° 45'$. Holzberg et al. have indexed the diffraction peak at 1.915 A as (712). The index of this peak should probably be (020). Holzberg [10] has agreed that the b value of 3.825 A is probably more correct. Table 1 shows the indexed X-ray pattern of high-temperature Nb_2O_5, as found in the present study, compared with the indexed values shown by Holzberg et al. [8] and Magneli and Lagergren [9]. The parameters found for the material used in the present study are $a=21.08$ A, $b=3.823$ A, $c=19.33$ A, and $\beta=119° 48'$.

3.2. PbO

PbO occurs in two polymorphic forms. The low-temperature form, stable at room temperature, is lithargite, red PbO, tetragonal with $a=3.976$ A, $c=5.023$ A [11]. It transforms to massicotite, yellow lead oxide, at 489° C [12]. Yellow PbO is orthorhombic, and the material used for the present study has the parameters $a=5.48$ A, $b=5.88$ A, $c=4.75$ A. The high-temperature polymorph is found to exist, metastably, at room temperature when quenched from any temperature in the sealed Pt tube. Even 65 hr at 470° C, just below the transformation temperature, showed no sign of red PbO. Petersen [12] has shown that it takes two to three weeks at 420° to 430° C to convert the yellow lead oxide into the red form.

3.3. Compound PbO·Nb₂O₅

The compound $PbO \cdot Nb_2O_5$ has been reported to occur in four different symmetry modifications.[2] The compound was first described by G. Goodman [1] as ferroelectric, orthorhombic. Francombe [2] first reported a low-temperature rhombohedral phase, and Roth [14] showed that a tetragonal modification probably also existed. Cook [15] has indicated that a pyrochlore-type phase is present if the material is not heated above 700° C.

a. Low-Temperature Rhombohedral Modification

Francombe [2] reported that the compound $PbO \cdot Nb_2O_5$ was polymorphic, having a phase transformation at about 1,200° to 1,250° C. The low temperature form is not ferroelectric and was reported to be rhombohedral with the "simplest-structure-cell" possessing the dimensions $a_R=6.206$ A and $\alpha_R=58° 18'$. However, the X-ray powder pattern given by Francombe [2] was indexed on a larger "pseudo-cubic-cell" with dimension $a'_R=8.664$ A and $\alpha'_R=88° 30'$.

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[2] A paper in Russian by Efimov et al. [13] discusses the reactions involved in producing $PbO \cdot Nb_2O_5$ and reports a face centered cubic lattice of 5.277 A for this compound. As only an abstract of this paper was available in English, this result cannot be critically analyzed. However, it seems likely that the X-ray pattern giving rise to this data was of the pyrochlore-type structure occurring at a ratio of 3PbO to 2Nb₂O₅, which has a parameter of approximately twice that given in the Russian work.

TABLE 1. *X-ray powder diffraction data for high temperature* Nb_2O_5

Magneli and Lagergren [9]			Holzberg et al. [8]			Present work $CuK\alpha_1$ radiation				
d_{obs}	I/I_o	hkl[a]	d_{obs}	I/I_o	hkl[b]	d	I/I_o	$1/d^2_{obs}$	$1/d^2_{calc}$ [c]	hkl[d]
17.0	30	10$\bar1$/001	16.9	10	001	16.66	6	0.0036	0.0036	001
10.6	40	20$\bar1$	10.6	20	20$\bar1$	10.517	5	.0090	.0090	20$\bar1$
						10.063	2	.0099	.0099	101
9.7	10	10$\bar2$	9.7	10	10$\bar2$	9.615	2	.0108	.0107	10$\bar2$
9.2	20	200	9.2	<10	200	9.148	5	.0120	.0120	200
8.5	20	002	8.4	<10	002	8.354	4	.0143	.0142	002
						6.942	2	.0208	.0207	30$\bar1$
						6.486	3	.0238	.0237	1$\bar0$2
6.35	30	10$\bar3$	6.32	10	10$\bar3$	6.285	11	.0253	.0253	10$\bar3$
5.60	10	003	5.60	<10	003	5.590	4	.0320	.0320	003
5.30	10	40$\bar2$	5.29	<10	40$\bar2$	5.273	6	.0360	.0361	40$\bar2$
5.15	60	40$\bar1$	5.13	20	40$\bar1$	5.116	48	.0382	.0384	40$\bar1$
			4.74	<10	103	4.734	4	.0446	.0447	103
4.63	50	10$\bar4$	4.63	20	10$\bar4$	4.616	36	.0469	.0469	10$\bar4$
						3.852	6	.0674	.0672	30$\bar5$
3.83	20	{ 20$\bar5$ / 010 }	3.83	<10	010	3.821	6	.0685	{ .0684 / .0684 }	010 / 20$\bar5$
3.75	100	110	{ 3.75 / 3.74 }	{ 70 / 50 }	{ 40$\bar5$ / 110 }	} 3.737	100	.0716	{ .0714 / .0717 / .0719 }	110 / 11$\bar1$ / 40$\bar5$
3.65	100	10$\bar5$	3.65	100	10$\bar5$	3.636	100	.0756	.0757	10$\bar5$
3.59	10	111	3.56	<10	111	3.577	4	.0782	.0782	111
3.56	20	11$\bar2$		0	11$\bar2$	3.553	4	.0792	.0791	11$\bar2$
						3.515	4	.0809	.0804	210
									.0812	60$\bar3$
									.0816	21$\bar2$
3.49	100	{ 60$\bar3$ / 60$\bar2$ / 012 }	} 3.49	50	21$\bar2$	3.483	100	.0824	{ .0826 / .0826 }	50$\bar5$ / 012
									.0829	60$\bar2$
3.41	10	60$\bar4$	3.41	<10	60$\bar4$	3.406	4	.0862	.0867	60$\bar4$
				0	402	3.383	4	.0874	.0879	402
3.36	60	005/31$\bar1$	3.36	10	005	3.351	28	.0891	{ .0889 / .0891 }	005 / 31$\bar1$
3.32	20	60$\bar1$	3.32	<10	211	3.316	5	.0909	{ .0904 / .0917 }	211 / 60$\bar1$
			3.28	<10	21$\bar3$				.0929	21$\bar3$
3.27	20	11$\bar3$		0	11$\bar3$	3.264	4	.0939	.0937	11$\bar3$
						3.247	4	.0949	.0948	204
3.17	40	013	3.17	<10	20$\bar6$	3.153	11	.1006	.1004	013
									.1045	41$\bar2$
3.09	20	50$\bar6$	3.09	<10	41$\bar2$	3.078	6	.1055	.1055	50$\bar6$
3.00	30	{ 10$\bar6$ / 214 }	} 3.01	<10	10$\bar6$	2.994	7	.1116	{ .1113 / .1116 }	21$\bar4$ / 10$\bar6$
2.95	10	114							.1153	114
2.84	90	{ 51$\bar2$ / 014 }	} 2.84	10	51$\bar2$	2.832	36	.1247	.1249	51$\bar2$
2.82	10	51$\bar3$	2.83	10	70$\bar1$	2.826	38	.1252	.1253	014
									.1265	51$\bar3$
									.1273	70$\bar1$
2.77	80	51$\bar1$	2.78	20	51$\bar1$	2.771	31	.1303	{ .1305 / .1306 }	51$\bar1$ / 601
2.73	10	51$\bar4$							.1352	51$\bar4$
2.70	80	21$\bar5$	2.71	20	21$\bar5$	2.701	34	.1371	.1369	21$\bar5$
2.70	10	70$\bar6$							.1383	70$\bar6$
2.67	10	41$\bar5$	2.677	{ <10 / 0 }	{ 41$\bar5$ / 20$\bar7$ }	} 2.668	3	.1405	{ .1403 / .1408 }	41$\bar5$ / 20$\bar7$
2.65	20	510				2.644	4	.1431	.1431	510
2.63	20	80$\bar3$	2.635	<10	11$\bar5$	2.628	5	.1448	{ .1441 / .1444 / .1454 }	11$\bar5$ / 804 / 80$\bar3$
2.58	10	{ 51$\bar5$ / 61$\bar2$ }	}						{ .1510 / .1513 }	51$\bar5$ / 61$\bar2$
2.54	70	{ 80$\bar2$ / 61$\bar4$ / 503 }	} 2.549	10	10$\bar7$	2.543	36	.1546	{ .1536 / .1545 / .1551 }	80$\bar2$ / 10$\bar7$ / 61$\bar4$
2.53	10	412	2.537	<10	503				.1553	503
				0	404				.1564	412
				0	412				.1565	313
									.1565	404
2.53	30	015	2.529	<10	31$\bar3$	2.523	5	.1571	.1573	015
2.49	50	70$\bar7$	2.496	10	80$\bar6$	2.491	26	.1612	.1619	70$\bar7$
2.48	30	214	2.483	<10	511	2.478	8	.1629	{ .1629 / .1632 }	511 / 214
									.1637	80$\bar6$
2.45	20	41$\bar6$	2.457	<10	61$\bar5$	2.452	5	.1664	.1665	41$\bar6$
									.1688	80$\bar1$

See footnotes at end of table.

TABLE 1. *X-ray powder diffraction data for high temperature* Nb_2O_5—Continued

Magneli and Lagergren [9]			Holzberg et al. [8]			Present work CuK$_{\alpha_1}$ radiation				
d_{obs}	I/I_o	hkl^a	d_{obs}	I/I_o	hkl^b	d	I/I_o	$1/d^2_{obs}$	$1/d^2_{calc}$ [c]	hkl^d
									0.1837	$71\bar{2}$
2.339	20	$71\bar{2}$	2.340	<10	$90\bar{3}$				.1840	$80\bar{7}$
									.1851	$90\bar{5}$
		$61\bar{6}$							.1865	$90\bar{3}$
2.315	80	413	2.319	10	$20\bar{8}$	2.314	29	0.1868	.1871	413
		$20\bar{8}$							.1873	$61\bar{6}$
									.1877	$20\bar{8}$
2.282	10	$70\bar{8}$							.1925	$70\bar{8}$
2.210	20	702							.2060	702
2.175	10	907	2.181	<10	$81\bar{4}$				.2121	$90\bar{7}$
									.2128	$81\bar{4}$
2.162	20	617		0	$81\bar{3}$				.2139	$81\bar{3}$
									.2141	617
2.111	20	414	2.112	<10	513	2.111	4	0.2244	.2237	513
				0	414				.2249	414
									.2316	207
2.075	80	$10,0,\bar{3}$	2.079	10	207	2.076	38	.2321	.2321	$81\bar{6}$
									.2324	$10,0,\bar{6}$
									.2328	315
									.2336	$10,0,\bar{3}$
			2.041	20	$10,0,\bar{7}$					
				0	809					
2.036	80	$20\bar{9}$	2.037	10	604	2.037	34	.2411	.2410	$71\bar{1}$
									.2411	$51\bar{8}$
									.2416	$20\bar{9}$
									.2422	604
									.2459	$80\bar{9}$
									.2462	$10,0,\bar{7}$
1.985	10	817							.2524	$81\bar{7}$
1.931	10	$6,0,\bar{10}$	1.934	<10	117				.2683	117
									.2687	$6,0,\bar{10}$
		$11\bar{8}$							.2730	$11\bar{8}$
		020							.2736	020
1.912	100	901	1.915	20	712	1.912	29	.2736	.2738	712
		$11,0,\bar{6}$							.2744	901
									.2747	$11,0,\bar{6}$
									.2827	$22\bar{1}$
		$11,0,\bar{7}$							.2853	$3,0,\bar{10}$
1.872	30	220	1.876	<10	$22\bar{1}$	1.873	5	.2852	.2856	220
									.2862	$11,0,\bar{7}$
		022							.2879	022
1.865	10	009							.2880	009
									.2890	$61\bar{9}$
1.855	20	208	1.857	<10	$10,1,\bar{4}$	1.856	3	.2903	.2891	811
				0	208				.2914	$20\bar{8}$
									.2945	$10,1,\bar{4}$
1.840	10	$31\bar{9}$							.2958	$31\bar{9}$
		$22\bar{3}$							.2981	$22\bar{3}$
1.830	10	$12\bar{3}$							.2989	$12\bar{3}$
									.3005	320
		$2,0,\bar{10}$							.3020	$10,1,\bar{3}$
1.820	60	$11,0,\bar{8}$	1.822	10	320	1.819	20	.3020	.3027	$2,0,\bar{10}$
									.3039	$11,0,\bar{8}$
									.3120	$42\bar{1}$
			1.793	10	902	1.789	16	.3124	.3127	407
									.3128	222
									.3145	902
			1.762	<10	$10,0,\bar{10}$	1.765	5	.3211	.3214	420
			1.744	10	$11\bar{9}$	1.742	23	.3295	.3294	$11,0,\bar{1}$
									.3302	$11\bar{9}$
									.3303	$10,0,\bar{10}$
									.3355	$4,0,\bar{11}$
						1.727	25	.3353	.3355	$10,1,\bar{8}$
									.3357	$52\bar{1}$
									.3421	$22\bar{5}$
						1.709	10	.3424	.3422	$4,1,\bar{10}$
									.3483	520
			1.694	10	$52\bar{0}$	1.692	20	.3493	.3493	$12\bar{5}$
			1.685	10	$3,1,\bar{10}$	1.683	51	.3529	.3522	606
									.3537	$3,1,\bar{10}$
						1.627	8	.3776	.3778	$10,0,\bar{2}$
			1.590	<10	522	1.592	27	.3945	.3946	$1,1,\bar{10}$
									.3949	522
			1.584	10	$10,1,\bar{1}$	1.582	20	.3994	.3997	$11,0.\bar{11}$
						1.579	18	.4012	.4009	$72\bar{1}$
									.4016	026
									.4031	10,1,1
			1.557	10	904	1.556	22	.4130	.4138	$13,0,\bar{9}$
									.4140	$12,1,\bar{3}$
									.4155	904

[a] The parameters upon which these *hkl* values are based are a=21.50 A, b=3.825 A, c=20.60A, β=121° 45'.
[b] The parameters upon which these *hkl* values are based are a=21.34 A, b=3.816 A, c=19.47 A, β=120° 20'.
[c] Only those values are listed which were either found as peaks in the present study or reported as peaks by previous workers.
[d] The parameters upon which these *hkl* values are based are a=21.08 A, b=3.823 A, c=19.33 A, β=119° 48'.

It can easily be seen that the larger "pseudo-cell" is related to the smaller "simplest-cell" by a doubling of the hexagonal a axis. For the "simplest-cell" $a_H = 6.04$ A, $c_H = 15.394$ A and for the "pseudo-cell" $a_H = 12.093$ A, $c_H = 15.394$ A. The pattern was indexed by Francombe using hexagonal hkl values for the larger cell. However, a simple examination of this indexing reveals that many of the hkl values used are not allowed by a rhombohedral cell, where $h - k + l = 3n$. Furthermore, the observed versus calculated d spacings do not fit for many of the lines. The same observations are true for the "simplest-cell."

Cook [15] has given the rhombohedral unit cell of the low-temperature form of $PbO \cdot Nb_2O_5$ as $a_R = 7.168$ A and $\alpha_R = 93° 52'$. These parameters correspond to a hexagonal unit cell of $a = 10.473$ A and $c = 11.549$ A. This cell is related to Francombe's "simplest-cell" by a multiplication and rotation of the unit-cell parameters of the hexagonal cell:

$$a_H \text{ (Cook)} = \sqrt{3}\, a_H \text{ (Francombe)},$$
$$c_H \text{ (Cook)} = 3/4\, c_H \text{ (Francombe)}.$$

An X-ray powder pattern of the rhombohedral form of $PbO \cdot Nb_2O_5$, indexed on the basis of the cell suggested by Cook, is shown in table 2. The unit-cell parameters of this material are found to be $a_R = 7.184$ A, $\alpha_R = 93° 55'$; $a_H = 10.510$ A, $c_H = 11.562$ A.

b. Metastable Orthorhombic Ferroelectric Modification

The orthorhombic modification was the first form of $PbO \cdot Nb_2O_5$ to be reported. It was discovered to be ferroelectric by G. Goodman [1] who reported an orthorhombic unit cell having the approximate dimensions $a = 25$ A, $b = 25$ A, $c = 7.0$ A. Francombe [2] found that the ferroelectric form only occurred when the specimen had been heated above the phase transformation temperature of 1,200° to 1,250° C. He reported this form to be orthorhombic with $a = 17.51$ A, $b = 17.81$ A, $c = 7.73$ A. In a previous publication arising from the present work [14] the X-ray powder diffraction pattern of the ferroelectric modification of $PbO \cdot Nb_2O_5$ was indexed on the basis of an orthorhombic unit cell with $a = 17.63$ A, $b = 17.93$ A, $c = 3.868$ A. Long film exposures using single-crystal techniques have shown that the true unit cell actually has a c axis value of twice that given [15]. This larger value does not show up in a Geiger counter tracing of the powder diffraction pattern. It has been shown [14] that the ferroelectric modification is only metastable, reverting to the rhombohedral form if heated several times from room temperature to 700° C. It, therefore, has no field of stability in the binary system $PbO - Nb_2O_5$.

c. High-Temperature Tetragonal Modification

Goodman [1] added small amounts of ZrO_2 and/or TiO_2 to his materials in order to obtain dense ceramics. Roth [14] has shown that the addition of such impurities has the effect of producing the

TABLE 2. *X-ray diffraction powder data for low temperature, rhombohedral* $PbNb_2O_6$ *(CuK$_{\alpha_1}$ Radiation)*

d	I/I_0	$1/d^2_{obs}$	$1/d^2_{calc}$ [a]	Rhombohedral hkl	Hexagonal hkl
7.184	5	0.0194	0.0196	010	011
5.270	13	.0360	.0363	01$\bar{1}$	110
4.889	3	.0418	.0420	110	102
4.231	7	.0559	.0558	11$\bar{1}$	201
3.109	100	.1035	.1036	120	113
3.034	100	.1086	.1088	11$\bar{2}$/$\bar{1}$2$\bar{1}$	300
2.957	10	.1144	.1146	12$\bar{1}$	212
2.626	11	.1450	.1451	02$\bar{2}$	220
2.383	7	.1760	.1761	030/22$\bar{1}$	033
2.170	69	.2123	.2124	13$\bar{1}$	223
2.116	6	.2233	.2234	22$\bar{2}$	402
2.061	5	.2353	.2354	131	025
2.054	10	.2371	.2372	03$\bar{2}$	231
1.9840	48	.2541	.2539	12$\bar{3}$/13$\bar{2}$	410
1.9270	9	.2693	.2693	222	006
1.9012	5	.2767	.2769	23$\bar{1}$	314
1.8093	10	.3055	.3056	231	116
1.7964	8	.3099	.3097	22$\bar{3}$	501
1.7640	100	.3214	.3212	04$\bar{1}$/23$\bar{2}$	143
1.7502	58	.3265	.3264	033	330
1.6477	4	.3683	.3685	04$\bar{2}$	242
1.6263	40	.3781	.3781	141/330	036
1.5530	7	.4146	{ .4144 / .4149 }	240 / 331	226 / 207
1.5156	22	.4353	.4353	22$\bar{4}$/24$\bar{2}$	600
1.3826	10	.5231	.5232	150/34$\bar{1}$	146
1.3620	18	.5391	.5389	05$\bar{2}$/24$\bar{3}$	253
1.3483	20	.5501	.5498	$\bar{1}$52	162
1.3360	5	.5603	.5600	151	047
1.3336	5	.5623	.5618	34$\bar{2}$	515
1.3126	13	.5804	.5803	044	440
1.2955	22	.5958	.5957	25$\bar{1}$	336
1.2542	6	.6357	.6359	251	138
1.2481	5	.6420	.6422	342	119
1.2425	4	.6478	.6477	15$\bar{3}$	443
1.1912	11	.7047	.7046	060/44$\bar{2}$	066
1.1613	7	.7415	.7414	160	157
1.1536	6	.7514	.7510	351	229
1.1493	100	.7571	.7565	34$\bar{4}$/$\bar{1}$62	713
1.1421	8	.7666	.7674	154	542
1.1314	4	.7812	{ .7810 / .7813 }	161 / 33$\bar{5}$	058 / 801
1.1067	6	.8165	.8157	35$\bar{3}$	625
1.0958	5	.8328	.8327	352	1, 2, 10
1.0846	12	.8501	.8496	26$\bar{2}$	446
1.0782	28	.8602	.8598	261/450	149

[a] These values are based on the unit-cell parameters $a_H = 10.501$ A, $c_H = 11.562$ A, $a_R = 7.184$ A, $\alpha_R = 93° 55'$.

orthorhombic structure in a form apparently stable at room temperature regardless of further heat treatments in laboratory time. A solid solution, of $PbO \cdot Nb_2O_5$ plus 2 weight percent of $ZrO_2 \cdot TiO_2$, was examined by high-temperature X-rays at 600° C, above the ferroelectric Curie point. The resulting pattern could be indexed on the basis of a tetragonal unit cell with $a = 12.56$ A and $c = 3.925$ A [14]. It is still not known whether the c axis should be doubled for the true tetragonal cell.

High-temperature X-ray patterns made in this laboratory, indicate that pure $PbO \cdot Nb_2O_5$ has tetragonal symmetry, as a stable modification, from the temperature of the high-low phase transformation to the melting point. If the high-temperature modification is cooled quickly below the transformation point, it will maintain the tetragonal structure in a metastable condition. When it reaches the Curie point, reported as 590° C by Goodman [1], it transforms metastably and reversibly to the orthorhombic ferroelectric modification.

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d. Pyrochlore-Type Modification

Cook [15] has claimed that another low-temperature form of $PbO \cdot Nb_2O_5$ exists below 700° C and that it "appears to be a pyrochlore structure previously unreported for lead niobate of this formula." Examination of the X-ray pattern of $PbO \cdot Nb_2O_5$ heated at 550° C for 16 hr as well as that of a specimen supplied by Cook, showed that the pyrochlore-type phase reported actually was $3PbO \cdot 2Nb_2O_5$, and that rhombohedral $PbO \cdot Nb_2O_5$ and free Nb_2O_5 also were present. It can therefore be concluded that $PbO \cdot Nb_2O_5$ does not form a pyrochlore-type structure under any conditions.

3.4. Compound $2PbO \cdot Nb_2O_5$

The compound $2PbO \cdot Nb_2O_5$ has been studied by Cook and Jaffe [3,4], Shirane and Pepinsky [17], Hulm [18], and Jona, Shirane, and Pepinsky [19]. Cook and Jaffe [3] list the compound $2PbO \cdot Nb_2O_5$ as rhombohedral with $a=5.285$ A and $\alpha=89°$ 15'. They later [4] imply that the a axis should be doubled, thus suggesting a rhombohedral distortion of the pyrochlore-type structure. Jona, Shirane, and Pepinsky [19] give values of $a=10.674$ A, $\alpha=88°$ 50'. The values obtained in the present study are $a=10.676$ A, $\alpha=88°$ 44', and the indexed X-ray diffraction pattern is given in table 3. Shirane and Pepinsky [17] and Hulm [18] have shown a dielectric anomaly in $2PbO \cdot Nb_2O_5$ at about 14° K, indicating a phase transformation, but nothing is known of the structure of this phase.

3.5. Compound $3PbO \cdot 2Nb_2O_5$

Cook and Jaffe [4] reported the observation of a cubic pyrochlore-type phase at approximately "the composition $Pb_{1.5}Nb_2O_{6.5}$" but did not definitely call it a compound. They observed a unit-cell parameter for this composition of 10.561 A. In the present study this phase has been identified as a compound with little or no solid solution, of the composition $3PbO \cdot 2Nb_2O_5$. It has been found to melt incongruently at 1,233° C to liquid plus $PbO \cdot Nb_2O_5$.

3.6. Compound $5PbO \cdot 2Nb_2O_5$

This compound has not been previously reported. It was discovered in the present work by observing that compositions in the area containing a single-phase rhombohedral pyrochlore-type structure did not begin melting at temperatures to be expected from a simple solid-solution region. It was obvious that a new compound of approximately the ratio 5:2 had to be introduced in order to explain the melting-point data. This composition containing 71.43 mole percent of PbO is the high PbO end member of this solid-solution series. The composition containing 72 mole percent of PbO shows some of the compound $3PbO \cdot Nb_2O_5$. The compound $5PbO \cdot 2Nb_2O_5$ apparently has the same symmetry as the 2:1 compound, probably rhombohedral. The 5:2 compound shows a larger distortion from the ideal cubic pyrochlore-type structure than does the compound

d	I/I_0	I/I^2_{obs}	$1/d^2_{calc}$ [a]	Rhombohedral hkl	Hexagonal hkl [b]
7.10	3	0.0199	--------	--------	(b)
6.29	7	.0253	0.0252	111	003
3.543	4	.0796	.0791	030/22$\bar{1}$	303
3.393	3	.0869	.0867	130	124
3.142	65	.1013	.1009	222	006
3.056	100	.1071	.1069	22$\bar{2}$	402
2.667	100	.1406	.1405	040	044
2.438	3	.1683	{ .1657 / .1703	33$\bar{1}$ / 13$\bar{3}$	405 / 421
2.410	7	.1722	.1726	240	226
2.390	5	.1751	.1787	04$\bar{2}$	242
2.015	8	.2464	.2449	342	119
1.9064	39	.2751	.2750	440	408
1.8664	45	.2871	.2871	04$\bar{4}$	440
1.6305	27	.3762	.3759	262	0, 4, 10
1.6053	33	.3881	.3879	26$\bar{2}$	446
1.5935	18	.3938	.3940	$\bar{2}6\bar{2}$	082
1.5744	7	.4034	.4034	444	0, 0, 12
1.5297	19	.4274	.4276	44$\bar{4}$	804
1.3333	9	.5625	.5621	080	088
1.2450	4	.6452	.6448	662	4, 0, 14
1.2282	7	.6629	.6629	66$\bar{2}$	8, 0, 10
1.2122	14	.6805	.6810	266	842
1.2028	9	.6912	.6905	480	4, 4, 12
1.1832	11	.7143	.7147	08$\bar{4}$	484
1.1092	3	.8128	.8129	484	0, 4, 16
1.0857	6	.8484	.8491	48$\bar{4}$	848
1.0781	4	.8604	.8612	448/48$\bar{4}$	12, 0, 0

$2PbO \cdot Nb_2O_5$. The parameters observed for the 5:2 compound are $a_R=10.709$ A; $\alpha_R=88°$ 14'.

The composition of the 5:2 compound can be arrived at by analogy to the pyrochlore-type structure. The theoretical cubic pyrochlore-type structure contains 16 A ions, 16 B ions, and 56 negative ions. Of the negative ions, 48 occupy one set of equivalent positions and 8 ions occupy another. In the $PbO \cdot Nb_2O_5$ system a unique compound is formed at a ratio of 1½ Pb^{+2} ions to $2Nb^{+5}$ ions or $Pb_{1.5}Nb_2O_{6.5}$ ($Pb_{12}Nb_{16}O_{48}O_4$). On the high-PbO side of the pyrochlore-type formula a likely compound is one in which 8 oxygen ions are missing, those belonging to the 8-fold equivalent position. This type of compound would be $Pb_2Nb_{1.6}O_6$ ($Pb_{16}Nb_{12.8}O_{48}$) which has a $PbO:Nb_2O_5$ ratio of 5:2. This composition is observed to be the high-PbO end of the solid solution series.

3.7. Compound $3PbO \cdot Nb_2O_5$

The compound $3PbO \cdot Nb_2O_5$ has also not been previously reported. It has a distorted pyrochlore-type structure which resembles $2PbO \cdot Nb_2O_5$, except that the distortion is of a pseudo-tetragonal rather than a rhombohedral type. The face-centered tetragonal parameters for this phase are $a=10.658$ A, $c=10.824$ A. As can be seen in the X-ray pattern of table 4, there are some diffraction peaks which cannot be indexed on the basis of this face-centered cell, but do fit a primitive cell of the same dimen-

TABLE 4. *X-ray diffraction powder data for the compound* $3PbO \cdot Nb_2O_5$ *(CuK$_{\alpha_1}$ radiation)*

d	I/I_0	$1/d^2_{obs}$	$1/d^2_{calc}$ a	hkl
6.78	7	0.0217	--------	--------
6.18	16	.0262	0.0262	111
5.886	3	.0289	--------	--------
5.611	5	.0318	--------	--------
3.419	7	.0856	.0856	b 103
3.218	12	.0966	.0966	311
3.093	100	.1045	.1046	222
2.943	14	.1154	.1144	b 320
2.706	69	.1366	.1366	004
2.662	100	.1411	.1408	400
2.461	13	.1651	.1649	313
2.444	8	.1674	.1670	331
2.404	4	.1731	--------	--------
2.354	5	.1805	.1806	b 214
2.077	4	.2319	.2310	115
2.051	8	.2378	.2374	511
1.8989	100	.2773	.2774	404
1.8834	54	.2819	.2817	440
1.6268	58	.3779	.3777	226
1.6091	100	.3862	.3863	622
1.5461	41	.4183	.4183	444
1.3530	8	.5463	.5463	008
1.3323	15	.5634	.5634	800
1.2317	37	.6592	.6594	626
1.2247	13	.6667	.6679	662
1.2224	13	.6692		
1.2066	17	.6869	.6871	408
1.1953	17	.6999	.6999	804
1.1923	18	.7034	.7042	840
1.0991	11	.8278	.8280	448
1.0912	16	.8398	.8408	844
1.0406	7	.9235	.9240	2, 2, 10
1.0313	7	.9402	.9411	666
1.0262	16	.9496	.9496	10, 2, 2

a These values are based on a tetragonal unit cell with $a = 10.658$ A, $c = 10.824$ A.
b These peaks are not allowed by a face-centered cell.

TABLE 5. *X-ray diffraction powder data for the compound* $PbO \cdot 2Nb_2O_5$ *(CuK$_{\alpha_1}$ radiation)*

d	I/I_0	hkl a	d	I/I_0	hkl a
8.84	7	110	2.441	9	041
6.24	15	020	2.313	4	250
5.576	15	120	2.139	7	-------
3.948	32	001	2.126	9	350
3.857	6	-------	2.073	6	060
3.601	5	-------	1.996	5	260
3.528	8	-------	1.972	35	002
3.455	14	230	1.858	7	-------
3.333	16	021	1.850	5	-------
3.218	55	121	1.757	4	451
3.109	5	040	1.739	4	-------
3.067	8	-------	1.711	4	-------
3.020	100	140	1.681	8	-------
2.942	32	330/221	1.649	16	142
2.861	5	-------	1.637	6	-------
2.786	60	240/131	1.604	15	242
2.627	4	-------	1.508	4	-------
2.596	23	231	1.450	5	-------
2.520	4	-------	1.312	7	-------

a The *hkl* values are given by analogy to the tetragonal structure of high temperature $PbO \cdot Nb_2O_5$. This is only a pseudo-cell, as there are many peaks which cannot be indexed on this basis. The pseudo-tetragonal cell has unit-cell parameters of $a = 12.44$ A, $c = 3.94$ A.

sions. However, there are still other d-spacings which cannot be indexed at all on this tetragonal cell. Although the pattern is very strongly pseudo-tetragonal, it must be concluded that the true symmetry is still unknown.

3.8. Compound $PbO \cdot 2Nb_2O_5$

The compound $PbO \cdot 2Nb_2O_5$ has not been previously reported. This new compound can easily be observed by X-ray diffraction studies of specimens of the 1:2 composition, or of compositions between 1:1 and 1:2, heated in the range in which the rhombohedral form of $PbO \cdot Nb_2O_5$ would be expected. It was found in the present study to have an X-ray pattern very similar to the orthorhombic and tetragonal forms of $PbO \cdot Nb_2O_5$. However, there are some lines in the pattern that cannot be indexed on either basis, as shown in table 5. This compound is isostructural with $BaO \cdot 2Nb_2O_5$ which also has these extra lines. It must be concluded that the true symmetry of $PbO \cdot 2Nb_2O_5$ is, as yet, unknown.

4. Discussion of Phase Equilibria

The phase-equilibrium diagram of the binary system $PbO-Nb_2O_5$ is shown in figure 1. The data from which this diagram has been constructed are given in table 6. The system contains four

congruently melting compounds $5PbO \cdot 2Nb_2O_5$, $2PbO \cdot Nb_2O_5$, $PbO \cdot Nb_2O_5$, and $PbO \cdot 2Nb_2O_5$; and two incongruently melting compounds $3PbO \cdot Nb_2O_5$ and $3PbO \cdot 2Nb_2O_5$.

PbO has been accepted as melting at $883 \pm 5°$ C [20]. There is an eutectic between PbO and $3PbO \cdot Nb_2O_5$ at approximately 94 mole percent of PbO and $835°$ C. The eutectic temperature was located by X-ray diffraction analyses of quenched specimens from sealed Pt tubes (see section 5). When a specimen in the two-phase region was quenched from below the solidus, yellow PbO and $3PbO \cdot Nb_2O_5$ were found to coexist. Changes in d-spacings of the X-ray patterns indicate that a small amount of solid solution, less than 2 mole percent, probably exists in the yellow PbO phase.

The compound $3PbO \cdot Nb_2O_5$ was found to melt incongruently to $5PbO \cdot 2Nb_2O_5$ plus liquid at $985°$ C. Specimens containing 75 mole percent of PbO, in a sealed Pt tube, quenched from below this temperature showed only the compound $3PbO \cdot Nb_2O_5$. Specimens of the same composition quenched from just above this temperature showed some of the compound $5PbO \cdot 2Nb_2O_5$. The compound $5PbO \cdot 2Nb_2O_5$ is essentially isostructural with $2PbO \cdot Nb_2O_5$, and there is apparently complete solid solution between the two. The compound $5PbO \cdot 2Nb_2O_5$ appears to melt congruently at approximately 1,220° C. There may be a very small eutectic or minimum in the solid-solution area close to the 5-2 compound or this compound might actually melt incongruently; however, any such discrepancies from the situation shown in figure 1 are so small as to be undetectable with the present experimental equipment.

The compound $2PbO \cdot Nb_2O_5$ was observed to melt congruently at about 1,233° C. Specimens sealed in a Pt tube and quenched from below this temperature showed no sign of melting. Above this temperature, the specimen appeared to be completely melted.
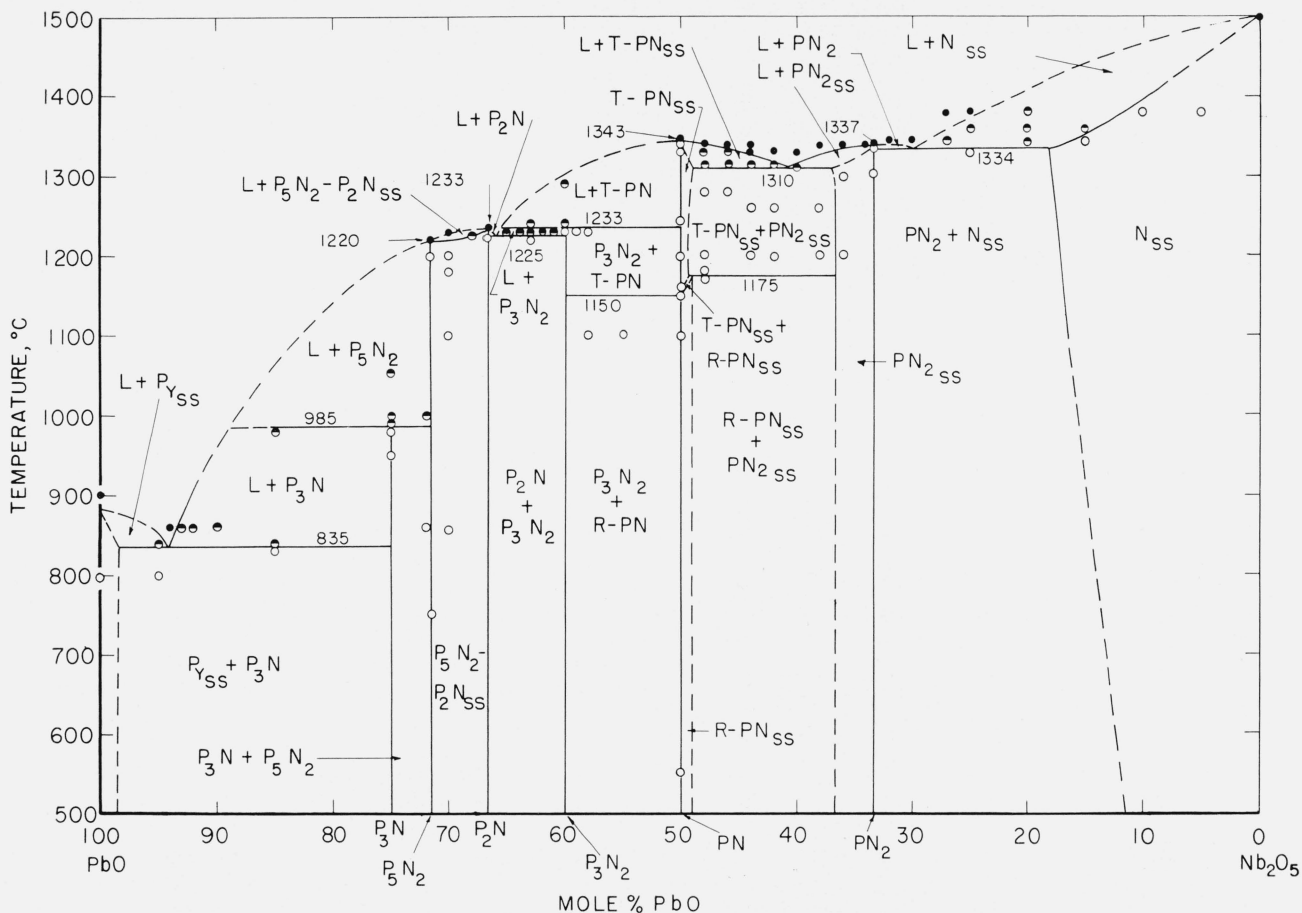
FIGURE 1. *Phase equilibrium diagram for the system* $PbO—Nb_2O_5$.

P_y—yellow PbO, orthorhombic; P_3N—$3PbO \cdot Nb_2O_5$; P_5N_2—$5PbO \cdot 2Nb_2O_5$; P_2N—$2PbO \cdot Nb_2O_5$; P_3N_2—$3PbO \cdot 2Nb_2O_5$; T-PN—tetragonal $PbO \cdot Nb_2O_5$; R-PN—rhombohedral $PbO \cdot Nb_2O_5$; PN_2—$PbO \cdot 2Nb_2O_5$; N—Nb_2O_5; SS—solid solution; ◯—no melting; ◗—partial melting; ●—completely melted.

No phase other than that of $2PbO \cdot Nb_2O_5$ was observed in the X-ray pattern of a quenched specimen of the melted material, thus strongly indicating congruent melting.

Compositions between $2PbO \cdot Nb_2O_5$ and $PbO \cdot Nb_2O_5$ give conflicting data when examined as quenched specimens from sealed tubes and as ceramic pellets heated in air. Cook and Jaffe [4] observed a single-phase cubic pyrochlore-type structure at a composition corresponding to "$Pb_{1.5}Nb_2O_{6.5}$" or 60 mole percent of PbO. This observation was confirmed in the present study for both air and sealed-tube techniques. However, Cook [21] has stated that in "a closely spaced series of compositions between Pb_2-Nb_2O_7 and $Pb_{1.5}Nb_2O_{6.5}$ . . . extra lines of the rhombohedral splitting do not draw closer to the main lines of the pattern, as you would expect. They just fade out." A similar phenomena was observed in the present study for specimens prepared at 1-mole-percent intervals between 65 and 60 mole percent of PbO, when heated in covered Pt crucibles.

When these specimens were quenched in sealed Pt tubes a clear picture of a two-phase region with little or no solid solution was observed for temperatures of 1,220° C or below. At 1,230° C the cubic $3PbO \cdot 2Nb_2O_5$ phase greatly predominated throughout all the specimens from 65 to 61 mole percent of PbO. The rhombohedral $2PbO \cdot Nb_2O_5$ phase was found to coat the walls of the Pt tube and was difficult to recover, thus indicating that this phase had been in the vapor state and that these specimens had been above the eutectic temperature. The eutectic composition could not be located exactly but is probably close to 66 percent of PbO. The eutectic temperature was thus located at 1,225 ±5° C. In the sealed tube, the composition containing 60 mole percent of PbO was found to melt incongruently at 1,233° C, forming some $PbO \cdot Nb_2O_5$. Compositions of 59 and 58 mole percent of PbO contained both cubic $3PbO \cdot 2Nb_2O_5$ and $PbO \cdot Nb_2O_5$ when quenched in the sealed tube from below the solidus. Therefore, a compound of the ratio $3PbO \cdot 2Nb_2O_5$ has been fully established.

TABLE 6. *Experimental data for compositions in the binary system PbO–Nb_2O_5*

PbO	Nb_2O_5	Air	Sealed Pt tube, quenched	Temperature	Time	Physical observation	X-Ray diffraction analyses [d]
mol %	mol %			°C	hr		
		X	-----	470	30	Bright red	Pb_3O_4.
100	0	-----	X	471	65	Yellow	Orth.–PbO.
		-----	X	487	16	Yellow	Do.
		-----	X	798	1.5	Yellow	Do.
		-----	X	900	0.16	Yellow, melted	Do.
95	5	X	-----	786	1		Orth·PbO+$3PbO \cdot Nb_2O_5$.
		-----	X	471	65	Orange-yellow	Do.
		-----	X	487	16	Orange-yellow	Do.
		-----	X	798	1.5	Yellow with red spots, partially melted	Orth·PbO+tet·PbO_{ss}.
94	6	-----	X	832	0.11	Dark reddish brown, melted	Tet·PbO_{ss}+trace of $3PbO \cdot Nb_2O_5$ and orth·PbO.
		-----	e X	824	16.00	Black-metallic luster, grinds to yellowish brown	Orth·PbO+$3PbO \cdot Nb_2O_5$ (no tet·PbO_{ss}).
93	7	-----	X	860	0.03	Reddish brown, melted	Tet·PbO_{ss}+$3PbO \cdot Nb_2O_5$.
92	8	-----	X	860	.03	Reddish brown, melted	Do.
90	10	X	-----	750	1		Orth. PbO+$3PbO \cdot Nb_2O_5$.
		-----	X	860	.05	Mostly melted, vesicular	Tet. PbO_{ss}+$3PbO \cdot Nb_2O_5$.
85	15	X	-----	786	1		$3PbO \cdot Nb_2O_5$+orth.PbO.
		-----	X	830	.08	Not melted	Do.
		-----	X	840	.08	Some melting	Tet·PbO_{ss}+$3PbO \cdot Nb_2O_5$.
		-----	X	978	.08	Mostly melted, vesicular	Do.
80	20	X	-----	786	1		$3PbO \cdot Nb_2O_5$+orth. PbO.
75	25	X	-----	753	1		$3PbO \cdot Nb_2O_5$.
		X	-----	870	1		Do.
		X	-----	900	1		Do.
		X	-----	920	1	Lost weight	$3PbO \cdot Nb_2O_5$+$5PbO \cdot 2Nb_2O_5$.
		X	-----	950	1	Lost weight	Do.
		X	-----	1,008	1	Lost weight	$5PbO \cdot 2Nb_2O_5$.
		-----	X	951	0.25	No melting	$3PbO \cdot Nb_2O_5$.
		-----	X	980	.16	No melting	Do.
		-----	X	990	.16	Melting (?)	$3PbO \cdot Nb_2O_5$+$5PbO \cdot 2Nb_2O_5$+tet. PbO_{ss}.
		-----	X	1,000	.16	Some melting	$5PbO \cdot 2Nb_2O_5$+tet. PbO_{ss}.
		-----	X	1,053	.16	Some melting	Do.
72	28	-----	X	860	1.5		$5PbO \cdot 2Nb_2O_5$+$3PbO \cdot Nb_2O_5$.
		-----	X	1,000	0.33	Some melting (?)	$5PbO \cdot 2Nb_2O_5$+tet. PbO_{ss}.
		-----	X	1,225	.08	Some melting (?)	
71.4285 (5:2)	28.5715	-----	X	1,200	.08	No melting	$5PbO \cdot 2Nb_2O_5$.
		-----	X	1,220	.08	Melted	$5PbO \cdot 2Nb_2O_5$+$2PbO \cdot Nb_2O_{5ss}$+tet. PbO_{ss}.
		-----	X	1,230	.02	Completely melted	
70	30	X	-----	753	1		$3PbO \cdot Nb_2O_5$+$5PbO \cdot 2Nb_2O_5$−$2PbO \cdot Nb_2O_{5ss}$.
		X	-----	1,100	1	Lost weight	$5PbO \cdot 2Nb_2O_5$−$2PbO \cdot Nb_2O_{5ss}$.
		-----	X	747	64		Do.
		-----	X	856	0.5		Do.
		-----	X	1,100	.08	No melting	Do.
		-----	X	1,180	.16	No melting	Do.
		-----	X	1,230	.08	No melting	Do.
		-----	X	1,250	.08	Melted	$5PbO \cdot 2Nb_2O_5$−$2PbO \cdot Nb_2O_{5ss}$+tet. PbO_{ss}.
68	32	-----	X	860	1.5		$5PbO \cdot 2Nb_2O_5$−$2PbO \cdot Nb_2O_{5ss}$.
		-----	X	1,225	0.02	Considerable melting	$5PbO \cdot 2Nb_2O_5$−$2PbO \cdot Nb_2O_{5ss}$+tet. PbO_{ss}.
66.67	33.33	X	-----	1,075	1		$2PbO \cdot Nb_2O_5$.
		-----	X	1,225	0.25	Not melted	Do.
		-----	X	1,230	.16	----do	Do.
		-----	X	1,235	.25	Melted	Do.
		-----	X	1,247	.16	----do	Do.
		-----	X	1,260	.16	----do	Do.
65	35	X	-----	1,100	1		$3PbO \cdot 2Nb_2O_5$+$2PbO \cdot Nb_2O_5$.
		X	-----	1,100	1		e $2PbO \cdot Nb_2O_5$+$3PbO \cdot 2Nb_2O_5$.
		-----	X	1,230	0.5	Some melting	$2PbO \cdot Nb_2O_5$+$3PbO \cdot 2Nb_2O_5$.
64	36	X	-----	1,100	1		$3PbO \cdot 2Nb_2O_5$+$2PbO \cdot Nb_2O_5$.
		-----	X	1,230	0.25	Some melting	Do.
63	37	X	-----	1,100	1		Do.
		-----	X	1,220	1.5	No melting	$2PbO \cdot Nb_2O_5$+$3PbO \cdot 2Nb_2O_5$.
		-----	X	1,230	0.16	Melting (?)	$3PbO \cdot 2Nb_2O_5$+$2PbO \cdot Nb_2O_5$.
		-----	X	1,240	.08	Some melting	
62	38	X	-----	1,100	1		$3PbO \cdot 2Nb_2O_5$+$2PbO \cdot Nb_2O_5$.
		-----	X	1,230	0.5	Some melting	Do.
61	39	X	-----	1,100	1		Do.
		-----	X	1,230	0.16	Some melting (?)	Do.
60	40	X	-----	1,100	1		$3PbO \cdot 2Nb_2O_5$.
		-----	X	1,225	0.25	No melting	Do.
		-----	X	1,235	.25	Some melting	$3PbO \cdot 2Nb_2O_5$+orth. $PbO \cdot Nb_2O_5$.
		-----	X	1,285	0.08	Mostly melted	Do.
59	41	X	-----	1,100	1		$3PbO \cdot 2Nb_2O_5$.
		-----	X	1,230	0.11	No melting	$3PbO \cdot 2Nb_2O_5$+$PbO \cdot Nb_2O_5$.
58	42	X	-----	1,100	1		$3PbO \cdot 2Nb_2O_5$.
		-----	X	1,230	0.11	No melting	$3PbO \cdot 2Nb_2O_5$+orth. $PbO \cdot Nb_2O_5$.
56.5	43.5	X	-----	1,259	1		$3PbO \cdot 2Nb_2O_5$− rhom·$PbO \cdot Nb_2O_5$.
55	45	X	-----	1,100	1		Do.
53.5	46.5	X	-----	1,259	1		Rhom· $PbO \cdot Nb_2O_5$+$3PbO \cdot 2Nb_2O_5$.
52	48	X	-----	1,299	1		Orth. $PbO \cdot Nb_2O_5$+$3PbO \cdot 2Nb_2O_5$.

Composition		Experimental procedure		Heat treatment		Results	
PbO	Nb₂O₅	Air	Sealed Pt tube, quenched	Temperature	Time	Physical observation	X-Ray diffraction analyses [d]
mol %	*mol %*			*° C*	*hr*		
		X	------	550	16	Not completely reacted_____	$3PbO \cdot 2Nb_2O_5 + $ rhom. $PbO \cdot Nb_2O_6 + $ mon. Nb_2O_5
		X	------	800	0.5	Completely reacted_____	Rhom. $PbO \cdot Nb_2O_5$.
		X	------	1,200	.5		Do.
		X	------	1,300	.5		Rhom. $PbO \cdot Nb_2O_5 + $ orth. $PbO \cdot Nb_2O_5$.
		X	------	1,350	.5	Melted	Orth. $PbO \cdot Nb_2O_5$.
		------	X	1,150	2		Rhom. $PbO \cdot Nb_2O_5$.
		------	X	1,150	24		Rhom. $PbO \cdot Nb_2O_5 + $ orth. $PbO \cdot Nb_2O_5$.
		------	X	1,160	2		Do.
50	50	------	X	1,200	0.5		Do.
		------	X	1,243	.25		Orth. $PbO \cdot Nb_2O_5 + $ rhom. $PbO \cdot Nb_2O_5$.
		------	X	1,329	.5	No melting	Orth. $PbO \cdot Nb_2O_5$.
		------	X	1,340	.25	No melting	Do.
		------	X	1,345	0	Melted	Do.
		[a] X	------	1,000	0		Rhom. $PbO \cdot Nb_2O_5$.
		[a] X	------	1,236	0		Rhom. $PbO \cdot Nb_2O_5 + $ tet. $PbO \cdot Nb_2O_5$.
		[a] X	------	1,287	0		Tet. $PbO \cdot Nb_2O_5 + $ rhom. $PbO \cdot Nb_2O_5$.
		[a] X	------	1,287	2		Tet. $PbO \cdot Nb_2O_5$.
		X	------	1,280	1		Orth. $PbO \cdot Nb_2O_{5ss} + PbO \cdot 2Nb_2O_{5ss}$.
		[b] X	------	1,296	0.5	No melting	
		[b] X	------	1,314	.5	Some melting	
		[b] X	------	1,330	.5	Considerable melting	
48	52	[b] X	------	1,338	.5	Completely melted	
		------	X	1,170	.25		Rhom. $PbO \cdot Nb_2O_{5ss} + PbO \cdot 2Nb_2O_{5ss}$.
		------	X	1,180	1		Rhom. $PbO \cdot Nb_2O_{5ss} + $ orth. $PbO \cdot Nb_2O_{5ss} + PbO \cdot 2Nb_2O_{5ss}$.
		------	X	1,200	0.25		Orth. $PbO \cdot Nb_2O_{5ss} + PbO \cdot 2Nb_2O_{5ss}$.
		X	------	1,280	1		Do.
		[b] X	------	1,296	0.5	No melting	
46	54	[b] X	------	1,314	.5	Some melting	
		[b] X	------	1,330	.5	Almost completely melted	
		[b] X	------	1,338	.5	Completely melted	
		X	------	1,200	.16		Rhom. $PbO \cdot Nb_2O_{5ss} + PbO \cdot 2Nb_2O_{5ss}$.
		X	------	1,265	0		Orth. $PbO \cdot Nb_2O_{5ss} + PbO \cdot 2Nb_2O_{5ss}$.
44	56	[b] X	------	1,296	0.5	No melting	
		[b] X	------	1,314	.5	Considerable melting	
		[b] X	------	1,330	.5	Completely melted	
		X	------	1,200	1		Rhom $PbO \cdot Nb_2O_{5ss} + PbO \cdot 2Nb_2O_{5ss}$.
		X	------	1,265	0		Orth. $PbO \cdot Nb_2O_{5ss} + PbO \cdot 2Nb_2O_{5ss}$.
42	58	[b] X	------	1,296	0.5	No melting	
		[b] X	------	1,314	.5	Almost completely melted	
		[b] X	------	1,330	.5	Completely melted	
		X	------	1,265	0		$PbO \cdot 2Nb_2O_{5ss} + $ orth. $PbO \cdot Nb_2O_{5ss}$.
		[b] X	------	1,296	0.5	No melting	
40	60	[b] X	------	1,314	.5	Almost completely melted	
		[b] X	------	1,330	.5	Completely melted	
		------	X	1,310	.25	Partly melted	
		------	X	1,330	.25	Completely melted	
38	62	X	------	1,200	1		$PbO \cdot 2Nb_2O_{5ss} + $ rhom. $PbO \cdot Nb_2O_{5ss}$.
36	64	X	------	1,200	1		$PbO \cdot 2Nb_2O_{5ss}$.
		X	------	1,299	1		Do.
34	66	X	------	1,304	1		Do.
		X	------	1,257	0		$PbO \cdot 2Nb_2O_5$.
		X	------	1,301	48		Do.
		X	------	1,350	0.5	Melted	Do.
33.33	66.67	[b] X	------	1,296	.5	No melting	
		[b] X	------	1,314	.5	No melting	
		[b] X	------	1,330	.5	No melting	
		[b] X	------	1,338	.5	Completely melted	
		------	X	1,336	.25	No melting	$PbO \cdot 2Nb_2O_5$.
		------	X	1,338	.16	Completely melted	Do.
32	68	X	------	1,304	1		$PbO \cdot 2Nb_2O_5 + $ mon. Nb_2O_{5ss}.
30	70	X	------	1,304	1		Do.
		[b] X	------	1,340	0.5	Completely melted	
		------	X	1,338	.16	Completely melted	
27	73	[b] X	------	1,340	.5	Almost completely melted	
		[b] X	------	1,360	.5	Completely melted	
		X	------	1,265	0		$PbO \cdot 2Nb_2O_5 + $ mon. Nb_2O_{5ss}.
		[b] X	------	1,296	0.5	No melting	
25	75	[b] X	------	1,314	.5	No melting	
		[b] X	------	1,330	.5	No melting	
		[b] X	------	1,338	.5	Considerable melting	
		[b] X	------	1,340	.5	Considerable melting	
		[b] X	------	1,360	.5	Almost completely melted	
		[b] X	------	1,380	.5	Completely melted	
		X	------	1,300	65		Mon. $Nb_2O_{5ss} + PbO \cdot 2Nb_2O_5$.
20	80	[b] X	------	1,340	0.5	Some melting	
		[b] X	------	1,360	.5	Moderate melting	
		[b] X	------	1,380	.5	Considerable melting	
		X	------	1,300	65		Mon. $Nb_2O_{5ss} + PbO \cdot 2Nb_2O_5$.
15	85	[b] X	------	1,340	0.5	No melting	
		[b] X	------	1,360	.5	Some melting	
		[b] X	------	1,380	.5	Moderate melting	
		X	------	1,257	0		Mon. $Nb_2O_{5ss} + PbO \cdot 2Nb_2O_5$.
10	90	[b] X	------	1,340	0.5	No melting	
		[b] X	------	1,360	.5	No melting	
		[b] X	------	1,380	.5	No melting	
		X	------	770	1.0		Mon. Nb_2O_{5ss}.
		X	------	1,300	65		Do.
5	95	[b] X	------	1,340	0.5	No melting	
		[b] X	------	1,360	.5	No melting	
		[b] X	------	1,380	.5	No melting	

[a] This experiment was conducted in a high-temperature X-ray furnace.

[b] The specimens had been ground into the shape of four-sided-grooved pyramids.

[c] The melted specimen was sealed in another Pt tube and reheated to determine if equilibrium could be obtained from the nonequilibrium tetragonal PbO solid solution.

[d] The phases identified are given in the order of the amount present at room temperature. The phases are not necessarily those present at the temperature to which the specimen was heated: Mon.—monoclinic; orth.—orthorhombic; tet.—tetragonal; rhom.—rhombohedral; ss—solid solution.

[e] This X-ray pattern was made on the same specimen as preceding after grinding the surface of the specimen.

The compound $PbO \cdot Nb_2O_5$ was found to melt congruently at 1,343 ±2° C by both the sealed-Pt-tube method and the grooved-pyramid method. However, the temperature of the rhombohedral-tetragonal phase transformation could not be arrived at by heating in air. It appears that this phase transformation is quite sluggish. High-temperature X-ray patterns in air show that several hours at 1,287° C are required to convert all of the low-temperature rhombohedral form to the high-temperature tetragonal form. A specimen heated at 1,200° C for 1 hr in air and examined at room temperature showed only the low-temperature form. However, the same material heated in a sealed Pt tube for 30 min at 1,200° C was converted in part to the high-temperature form. A 2-hr heat treatment as low as 1,160° C gave some of the high-temperature form while the same time at 1,150° C gave only low-temperature $PbO \cdot Nb_2O_5$. However, holding the 1:1 composition at 1,150° C for 24 hr did convert a small amount of the material to the high-temperature form. It seems that a maximum temperature of 1,150° C is as close to the transformation temperature as can be obtained in reasonable laboratory time.

$PbO \cdot Nb_2O_5$ will accept a small amount of Nb_2O_5 into solid solution as shown by significant changes in d-spacings of the X-ray patterns. However, the composition containing 48 mole percent of PbO has two phases, indicating that solid solution is less than 2 mole percent. This small amount of solid solution is enough to raise the temperature of the phase transformation from the rhombohedral to the tetragonal form by about 25° C, as shown by quenching experiments in sealed Pt tubes.

A eutectic exists between $PbO \cdot Nb_2O_5$ and $PbO \cdot 2Nb_2O_5$ at about 41 mole percent of PbO and 1,310° C. This eutectic was found by the grooved-pyramid technique and checked with experiments using sealed Pt tubes. The compound $PbO \cdot 2Nb_2O_5$ was found to melt, probably congruently, at 1,337° ±2° C. $PbO \cdot 2Nb_2O_5$ takes more than 2 but less than 4 mole percent of PbO into solid solution at the solidus temperature. This solid solution is retained on relatively slow cooling, as shown by X-ray patterns of specimens containing 36 and 38 mole percent of PbO.

Although $PbO \cdot 2Nb_2O_5$ appears to melt sharply, no eutectic has been definitely located on the high Nb_2O_5 side. However, some melting-point data of the compositions containing 32 and 30 mole percent of PbO indicate a eutectic in this region. Both of these compositions appear completely melted, by the pyramid method, at 1,344° C. If the 1:2 compound melted incongruently, these specimens would be only partially melted at 1,344° C. A eutectic can, therefore, be placed at about 30 mole percent of PbO and 1,334 ±4° C.

Nb_2O_5 is found to accept a little over 15 mole percent of PbO into solid solution at the eutectic temperature. As shown by X-ray diffraction this amount decreases to a little less than 10 mole percent at room temperature. The addition of PbO to Nb_2O_5 seems to lower the temperature of the phase transformation from the low to the high form of Nb_2O_5. The specimen containing 5 mole percent of PbO heated to 770° C for 1 hr contained only the high-temperature form of Nb_2O_5. This form was also found in the nonequilibrium assemblage of the 50:50 specimen at 550° C for 16 hr. No attempt has been made to locate accurately the temperature of this phase transformation in the presence of PbO. The low temperature form of Nb_2O_5 has not been indicated on the phase diagram of figure 1 as it seems likely that this polymorph is only metastable and has no true equilibrium position in the binary system. The melting point of Nb_2O_5 was accepted as 1,500 ±10° C as found by Roth and Coughanour [22].

5. Occurrence of a Nonequilibrium Red PbO Solid Solution

When specimens of composition between pure PbO and the 2:1 compound are quenched from above the solidus, a phase similar to the tetragonal red PbO is observed in the X-ray patterns. This phase has an a parameter about the same as pure tetragonal PbO but a c parameter which is much larger. This c parameter is always approximately the same, regardless of the temperature or composition of the quenched specimen. It has a value of about 5.08 A as compared to the value of 5.023 A for pure PbO. Specimens containing 95 percent of PbO consisted only of yellow PbO and this red PbO solid solution, when quenched from above the solidus. When the composition is on the high-Nb_2O_5 side of the eutectic, the tetragonal solid solution occurs with the compound $3PbO \cdot Nb_2O_5$. When specimens of $3PbO \cdot Nb_2O_5$ are heated above the incongruent melting point, about 985° C, this tetragonal phase is observed to occur with the $5PbO \cdot 2Nb_2O_5$ compound. Specimens of the 5:2 compound and compositions between 5:2 and 2:1 contain, upon quenching from above the solidus, red PbO solid solution plus a rhombohedral pyrochlore-type solid solution.

A specimen of the eutectic composition, 94 mole percent of PbO, showed almost entirely the red PbO solid solution when quenched from above the melting point. This specimen was put back in a sealed Pt tube and held overnight just below the melting point. The resulting product was an equilibrium mixture of yellow PbO and the compound $3PbO \cdot Nb_2O_5$. Thus the red PbO solid solution has been proven to be metastable.

There are several possible explanations of this nonequilibrium phenomenon. The most obvious conclusion would be that oxidation of PbO and reduction of Nb_2O_5 occur when they are heated together in a closed tube. However, this oxygen solid solution would then have parameters depending upon the amount of Nb_2O_5 present, which is not observed to be the case. Another possibility is that the tetragonal PbO solid solution represents the composition of the liquid in equilibrium at the temperature from which the material was quenched.

That is, the liquid when quenched devitrifies into a single-phase crystalline solid of the same composition. However, this explanation also would require different parameters of the solid solution for different temperatures and compositions. An alternative hypothesis is that the phase does not represent the equilibrium liquid but that the liquid follows its regular course of crystallization until it reaches the eutectic composition. This composition then crystallizes out as a single-phase nonequilibrium solid solution, having a structure similar to the low-temperature form of PbO.

It does not seem likely that this solid solution is of the substitutional type. The radius of Pb^{+2} is 1.20 A and that of Nb^{+5} is 0.69 A [23]. The ratio between the two is well beyond the limit at which even partial substitution might be expected. Therefore, it must be concluded that this nonequilibrium solid solution is of an interstitial type.

There is also the possibility that this apparent red PbO solid solution is a true compound in the system, having a minimum thermal stability at the temperature indicated here for the eutectic temperature, 835° C, and a composition equal to the hypothesized eutectic composition. That such a compound should have the same structure as red PbO seems highly unlikely and is not considered to be the true explanation of the observed phenomena.

6. Summary

The system PbO-Nb₂O₅ was studied by means of solid-state reactions, fusion characteristics, and X-ray diffraction data. The existence of six compounds in this system was shown. They are $3PbO \cdot Nb_2O_5$ which melts incongruently at about 985° C, $5PbO \cdot 2Nb_2O_5$ which melts congruently at 1,220° C, $2PbO \cdot Nb_2O_5$ which melts congruently at about 1,233° C, $3PbO \cdot 2Nb_2O_5$ which melts incongruently at about 1,233° C, $PbO \cdot Nb_2O_5$ which melts congruently at about 1,343° C, and $PbO \cdot 2Nb_2O_5$ which melts congruently at about 1,337° C. The four eutectic points are located as follows: about 94 mole percent of PbO and 835° C, about 66 mole percent of PbO and 1,225° C, 41 mole percent of PbO and 1,310° C, and about 30 mole percent of PbO and 1,334° C.

Complete solid solution was noted between $2PbO \cdot Nb_2O_5$ and $5PbO \cdot 2Nb_2O_5$. Partial solid solution occurred between the two compounds $PbO \cdot Nb_2O_5$ and $PbO \cdot 2Nb_2O_5$. Nb₂O₅ accepts about 15 mole percent PbO in solid solution at the eutectic temperature. No solid solution occurs on either side of the compound $3PbO \cdot 2Nb_2O_5$.

The rhombohedral-tetragonal inversion of $PbO \cdot Nb_2O_5$ was found to take place very sluggishly at approximately 1,150° C in a sealed Pt tube. The temperature of this phase transition is raised by the Nb₂O₅ solid solution to about 1,175° C.

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A recent paper by M. H. Francombe and B. Lewis [24] suggests a solid-solution region from $PbO:1.5Nb_2O_5$ to $PbO:3Nb_2O_5$. This covers a range in which two phases have been found, for the most part, in the present work. No explanation can be found for the observation of such a large amount of solid solution in the PbO-Nb₂O₅ system.

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