

Crystal Growth and X-Ray Data of the Lead Phosphates $Pb_4P_2O_9$ and $Pb_8P_2O_{13}$

L. H. BRIXNER AND C. M. FORIS

Central Research Department,* E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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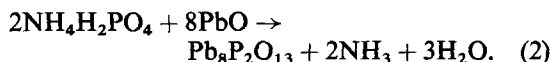
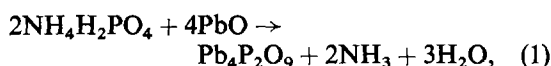
Single crystals of the title compounds have been grown by the Czochralski technique. $Pb_4P_2O_9$ crystallizes in the space group $P2_1/c$ with the parameters $a = 9.4812 \text{ \AA}$, $b = 7.1303 \text{ \AA}$, $c = 14.390 \text{ \AA}$, $\beta = 104.51^\circ$ and $Pb_8P_2O_{13}$ in $C2/m$ with $a = 10.641 \text{ \AA}$, $b = 10.206 \text{ \AA}$, $c = 14.342 \text{ \AA}$, $\beta = 98.34^\circ$.

Introduction

In two previous publications (1, 2) we have indicated that of the seven different lead phosphates described by Argyle and Hummel (3), only one, namely $Pb_3(PO_4)_2$, had been structurally characterized by Keppler (4). The present paper is an extension of our previous work aimed at a more detailed characterization of the remaining two lead phosphates, $Pb_4P_2O_9$ and $Pb_8P_2O_{13}$.

Experimental Methods

Both lead phosphates were prepared from high purity $(NH_4)H_2PO_4$ (BDH Chemicals, Ltd., England, Analytical grade) and PbO (5-9s Spex Industries Inc., No. 1233) according to



Both compounds were first pre-fired at $300^\circ C$ for 10-14 hr to drive off all water and ammonia and obtain partial reaction. After homogenization of this reaction product heating at a rate of $100^\circ C/hr$ was continued until a clear melt was obtained in a platinum dish. The material was then transferred into a pure platinum crucible and remelted by means of RF heating using an Ecco 20 KVA generator. Since in neither case

seeds were available, growth was initiated on a platinum wire at pulling speeds of 0.5-1 cm/hr and rotation of the wire at 40 rpm. The grown crystals were analyzed by wet chemical methods for Pb only. $Pb_4P_2O_9$ gave 79.8% Pb and $Pb_8P_2O_{13}$, 85.5%, in good agreement with the calculated amounts of 80.09 and 85.99%, respectively.

X-Ray

Single crystal photographs were taken with a precession camera and Mo radiation. X-ray powder patterns were obtained with a Guinier-Hägg camera at $25^\circ C$ with $CuK\alpha_1$ radiation and an internal standard of KCl ($a = 6.2931 \text{ \AA}$). Refined cell dimensions were obtained by a least-squares treatment of the Guinier data. In the case of $Pb_4P_2O_9$, the refinement is based on 145 observations. 144 of these have been accounted for and only one extremely weak line at $d = 3.6299 \text{ \AA}$ was not used. The refinement was terminated after 7 least-squares cycles. The errors at that stage are reported in Table I. For the $Pb_8P_2O_{13}$ refinement 65 reflections were used and all lines were accounted for. The errors after 8 cycles are also reported in Table I.

Results and Discussion

In his work on thermal expansion, Argyle and Hummel (3) observed that $Pb_4P_2O_9$ undergoes a destructive "inversion" at $256^\circ C$ which

* Contribution No. 1959.

TABLE I
CELL DIMENSIONS AND SPACE GROUPS FOR THE LEAD PHOSPHATES

Compound	a (Å)	b (Å)	c (Å)	β (°)	ρ , pycnom. (g ml ⁻¹)	ρ X-ray (g ml ⁻¹)	Z	Space group
Pb ₄ P ₂ O ₉	9.4812 ± 6	7.1304 ± 4	14.390 ± 1	104.51 ± 1	7.31	7.294	4	$P2_1/c$
Pb ₈ P ₂ O ₁₃	10.641 ± 1	10.206 ± 1	14.342 ± 3	98.34 ± 1	8.29	8.306	4	$C2/m$

did not permit measurements on this compound. During crystal growth of Pb₄P₂O₉, which melts congruently without detectable vapor pressure at 949°C, we observed the same phenomenon. A clear boule would totally disintegrate when taken through this transition. The small crystalline fractions were nevertheless large enough for single crystal X-ray work. The exact temperature for this transition was established by differential scanning calorimetry (DSC) as 294°C. No such transition was noticed for Pb₈P₂O₁₃, which melts congruently at 820°C. Similarly to Pb₂P₂O₇ and Pb₃(PO₄)₂, this compound also has a strong tendency to cleave into thin sheets. While Pb₈P₂O₁₃ does not exhibit any temperature-dependent polymorphism, we have to assume that Pb₄P₂O₉ does undergo a structural transformation at 294°C. The high-temperature structure is not known at this point. Although no structural transformation was indicated by DTA for Pb₈P₂O₁₃, a prominent subcell could

be seen on the single crystal photograph with face-centered monoclinic symmetry and the parameters $a = 5.685 \pm 1$ Å, $b = 5.107 \pm 1$ Å, $c = 5.318 \pm 1$ Å, $\beta = 92.36 \pm 1^\circ$.¹ Space group and lattice parameters for the two compositions are summarized in Table I. Tables II and III compare the observed and measured d -spacings. We also compare these data with those of Argyle and Hummel (3) and find that the agreement is generally good although he missed many of the weaker reflections. In order to obtain d -values for the weaker lines, the Guinier pattern was overexposed. Relative intensities were then determined by comparison with a pattern that was not overexposed.

Since the space group determination for Pb₈P₂O₁₃ was not unequivocal, with $C2$, Cm , and $C2/m$ all being possible, a second harmonic generation test was run in equipment similar to that described by Perry and Kurtz (5). As this test was negative, centric $2/m$ is strongly indicated as the correct point group. The refractive index of Pb₈P₂O₁₃ was found to be 2.35. With Pb₈P₂O₁₃ being the compound richest in lead in the PbO/P₂O₅ phase diagram, it appears worthwhile to comment once more on the large number of well-defined stoichiometric compounds in this simple binary system. What is even more amazing is the fact that five of the seven compounds melt congruently and permit the growth of single crystals by the Czochralski technique. The first two lead phosphates, Pb(PO₃)₂ and Pb₃P₄O₁₃, form glasses and cannot be pulled in the crystalline state from the melt. Table IV gives a summary of the structural information known to date on the different lead phosphates. It appears from the habit of some of the crystals as well as the pronounced cleavage characteristics that layer-type structures are preferred in these systems and it would be an intriguing challenge to crystallo-

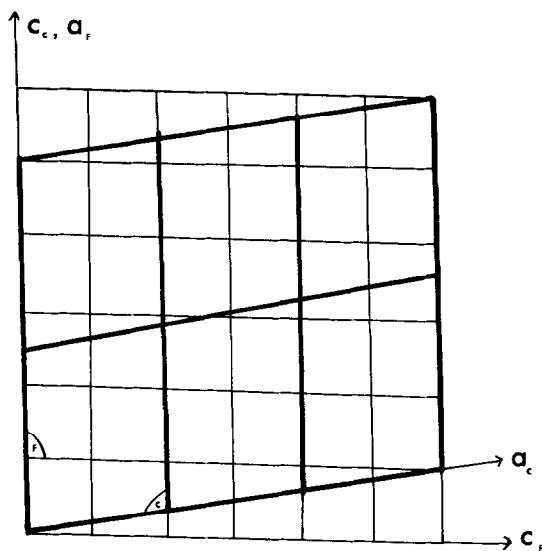


FIG. 1. Relationship between C -centered monoclinic and face-centered monoclinic subcell of Pb₈P₂O₁₃.

¹ The relationship between the two cells is shown in Fig. 1.

TABLE II
OBSERVED AND CALCULATED D-VALUES FOR $\text{Pb}_4\text{P}_2\text{O}_9$

<i>I</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i>		Ref. (3)
				Obsd	Calcd	
15	0	0	2	6.9658	6.9658	
30	-1	0	2	6.3660	6.3704	6.37
50	1	1	0	5.6290	5.6310	5.64
25	1	0	2	4.9791	4.9804	5.01
65	-1	1	2	4.7488	4.7506	4.77
50	2	0	0	4.5870	4.5894	4.60
30	-2	0	2	4.3676	4.3679	4.33
25	1	1	2	4.0818	4.0830	4.13
15	-1	1	3	3.8862	3.8880	3.87
50	2	1	0	3.8584	3.8591	
25	-2	1	2	3.7241	3.7246	3.72
50	-1	0	4	3.5657	3.5661	3.56
25	2	1	1	3.5311	3.5325	
85	0	0	4	3.4837	3.4829	3.48
10	0	2	1	3.4530	3.4539	
50	-2	1	3	3.3325	3.3332	3.39
30	1	2	0	3.3243	3.3233	3.34
25	-1	2	1	3.3002	3.3009	3.27
35	-2	0	4	3.1855	3.1852	3.19
50	0	2	2	3.1729	3.1736	
100	2	1	2	3.1097	3.1094	3.12
85	-3	0	2	3.1040	3.1020	
100	3	0	0	3.0603	3.0596	3.06
60	1	0	4	3.0154	3.0154	2.99
75	-2	1	4	2.9063	2.9082	2.96
95	1	2	2	2.8988	2.8990	2.88
15	-3	1	2	2.8451	2.8445	
75	2	2	0	2.8146	2.8155	2.82
35	1	1	4	2.7765	2.7773	2.77
60	-2	2	2	2.7617	2.7619	
5	-3	1	3	2.6975	2.6958	
15	-1	1	5	2.6640	2.6654	
60	-3	0	4	2.6520	2.6514	
5	-2	2	3	2.5906	2.5905	
20	3	0	2	2.5735	2.5739	
20	-1	2	4	2.5212	2.5213	2.53
30	2	0	4	2.4901	2.4902	2.49
15	2	2	2	2.4814	2.4812	
30	-2	2	4	2.3751	2.3753	
15	-3	2	1	2.3640	2.3643	
30	-3	2	2	2.3400	2.3402	
15	-2	0	6	2.3192	2.3190	
15	1	3	0	2.2991	2.3009	
35	-1	3	1	2.2937	2.2934	2.29
25	-1	1	6	2.2728	2.2732	2.28
5	-3	1	5	2.2563	2.2557	
40	-4	1	2	2.2423	2.2425	
5	0	1	6	2.2072	2.2078	2.20
10	0	2	5	2.1951	2.1954	
15	-4	1	3	2.1870	2.1877	

TABLE III
OBSERVED AND CALCULATED D-VALUES FOR $\text{Pb}_8\text{P}_2\text{O}_{13}$

<i>I</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i>		Ref. (3)
				Obsd	Calcd	
7	0	0	1	14.1753	14.1893	
12	1	1	0	7.3111	7.3264	
23	0	0	2	7.0847	7.0946	7.14
27	-1	1	1	6.7824	6.7967	6.81
12	1	1	1	6.2511	6.2566	
7	2	0	0	5.2538	5.2611	
5	-2	0	1	5.1800	5.1850	
20	0	2	1	4.7978	4.8024	4.82
18	2	0	1	4.7141	4.7144	4.72
7	-2	0	2	4.5528	4.5549	
4	-1	1	3	4.1714	4.1709	4.37
11	1	1	3	3.8025	3.8020	
25	-2	2	1	3.6340	3.6372	3.63
4	2	2	1	3.4655	3.4630	3.48
4	3	1	0	3.3165	3.3170	
7	2	0	3	3.2883	3.2875	
85	3	1	1	3.1321	3.1357	3.13
100	-2	2	3	3.0524	3.0496	3.05
5	0	2	4	2.9121	2.9128	2.95
55	0	0	5	2.8386	2.8378	2.84
4	2	2	3	2.7635	2.7637	
50	-4	0	1	2.6565	2.6567	2.66
5	1	3	3	2.6181	2.6174	
45	0	4	0	2.5513	2.5518	2.56
11	4	0	1	2.5253	2.5215	
5	3	3	0	2.4416	2.4421	
11	2	2	4	2.4287	2.4283	
4	0	4	2	2.4008	2.4012	
4	-2	2	5	2.3610	2.3623	
5	4	2	0	2.3385	2.3382	
7	-3	1	5	2.3177	2.3198	
11	-4	2	2	2.3114	2.3114	
5	-4	0	4	2.2782	2.2774	
11	2	4	1	2.2441	2.2441	
9	0	2	6	2.1464	2.1457	2.15
4	-3	3	4	2.1133	2.1140	
11	3	3	3	2.0859	2.0855	
4	-5	1	2	2.0598	2.0594	
4	0	0	7	2.0274	2.0270	2.03
4	2	4	3	2.0158	2.0158	
18	4	0	4	1.9820	1.9796	1.985
25	0	4	5	1.8990	1.8975	1.899
45	-4	4	1	1.8407	1.8403	1.841
7	-5	1	5	1.7944	1.7936	
4	-1	5	4	1.7662	1.7659	
21	-2	4	6	1.7031	1.7022	1.704
4	0	6	1	1.6885	1.6891	
4	-6	2	1	1.6745	6.6741	
23	-2	2	8	1.6649	1.6639	1.667
4	-4	2	7	1.63991	1.6402	

TABLE IV
SUMMARY OF STRUCTURAL INFORMATION ON VARIOUS LEAD PHOSPHATES

Composition	ΔPbO^a	Lattice parameters (Å)			α (°)	β (°)	γ (°)	Space group	Transition mp temp (°C)	Ref.
		a	b	c						
PbP_2O_6	0.5	—	—	—	—	—	—	—	Forms glass (3)	(3)
$\text{Pb}_{1.5}\text{P}_2\text{O}_{6.5}$	0.5	6.923	6.975	12.764	96.8	91.1	89.7	$P\bar{1}$	831	(3, 1)
$\text{Pb}_2\text{P}_2\text{O}_7$	0.5	12.399	18.453	24.756	—	92.3	—	$P2_1/c$	251	(3, 2)
$\text{Pb}_{2.5}\text{P}_2\text{O}_{7.5}$	0.5	13.816	5.692	9.429	—	102.4	—	$C2/c$	171	(3 and 4)
$\text{Pb}_3\text{P}_2\text{O}_8$	1.0	9.481	7.130	14.390	—	104.5	—	$P2_1/c$	294	(3) and present paper
$\text{Pb}_4\text{P}_2\text{O}_9$	4.0	10.641	10.206	14.342	—	98.3	—	$C2/m$	—	(3) and present paper

^a This column indicates the amount of PbO on a comparative molar basis which separates this compound from the previous one.

graphers to determine all these structures in detail and establish their respective relationships. It is interesting to note that with the exception of $\text{Pb}_2\text{P}_2\text{O}_7$, apparently all lead phosphates crystallize in a monoclinic structure.

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