

THE CRYSTAL STRUCTURES OF  $\text{PbO.PbXO}_4$  ( $X = \text{S, Cr, Mo}$ )  
AT 5K BY NEUTRON POWDER PROFILE REFINEMENT.

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ABSTRACT

The structures of  $\text{PbO.PbXO}_4$  monobasic lead oxide- lead sulphate, chromate and molybdate have been determined at 5K by neutron powder profile refinement. They are all isostructural with Lanarkite (the sulphate), being based on the red  $\text{PbO}$  structure with  $\text{PbO}_2^{2-}$  and its lone pair electrons replaced by  $\text{XO}_4^{2-}$ . A similar mechanism apparently produces the di-basic and tetra-basic oxides  $n\text{PbO.PbXO}_4$ . These materials are of relevance to solid state reactions in lead - acid battery electrodes.

Introduction

The solid solutions  $\text{PbO-PbSO}_4$  are of interest in the study of reactions at lead - acid battery electrodes; we are examining the structures of these materials in an attempt to understand the mechanism of the incorporation of sulphate in lead monoxide.

Until now only the structures of Lanarkite  $\text{PbO.PbSO}_4$  (1) and  $\alpha\text{-2PbO.PbSO}_4$  (2) have been solved, the most recent attempt at  $4\text{PbO.PbSO}_4$  being only partially successful (3). There are two difficulties in applying conventional crystallographic methods to these materials: the heavy atoms, forming a distorted metallic lead lattice, obscure the details of the oxygen, and the materials themselves are usually twinned or otherwise disordered.

Both of these problems might be solved by using neutron powder profile refinement (4,5), which is equally successful with heavy atom structures (6). We have even had success with X-ray powder diffraction techniques for materials such as  $\text{PbO.PbSO}_4$  (7). As a first step in this program, we have refined the structure of  $\text{PbO.PbSO}_4$  at 5K from neutron powder data to check that there is no phase transition at low temperature, and shown that  $\text{PbO.PbCrO}_4$  and  $\text{PbO.PbMoO}_4$  are isomorphous, as assumed in (8) and (9). The present results give more precise heavy metal - oxygen bond lengths, and permit calculations of the effective cation valence charges according to the ideas of Brown, Shannon and Wu (10,11).

#### Experimental

Synthetic samples of the three materials were ground to fine powders and held at 5K for the 20 hours needed to collect each neutron powder diffraction pattern on the high resolution diffractometer D1A at the ILL Grenoble (12). Vanadium sample containers, fine collimators, and appropriate diffraction geometry ensured perfectly clean, sharp patterns with no trace of any other phase, wavelength contamination or other extraneous lines. Data was collected to scattering angles of  $158^\circ$ , except for the molybdate, where an electronic fault stopped the experiment at  $107^\circ$ ; the standard deviations for this refinement are then a little larger.

The profile refinement was performed with the Rietveld program (5,6) after calibrating and averaging the ten separate counters to produce a single average profile, and subtraction of the measured background (fig. 1). The crosses represent the measured points, and the solid line the calculated profile: also shown is the difference between these two (upper solid line) and the positions and intensities of the contributing reflexions (vertical bars).

Table 1 shows the refined lattice constants, with standard deviations not including the possible error in the neutron wavelength ( $1.909 \pm 0.001 \text{ \AA}$ ).  $R_p$  is the refined profile R-factor, and  $R_I$  the R-factor for integrated intensities, about twice the usual crystallographic R-factor (5). Table 2 shows the atomic co-ordinates. For lead they are obtained equally well with neutrons or X-rays, but the positions of all the other atoms are obtained much more precisely with neutrons, especially at low temperature.

TABLE 1. Lattice dimensions  $a$ ,  $b$ ,  $c$  ( $\text{\AA}$ ), and R-factors.

	Sahl (1970)	$\text{PbO.PbSO}_4$	$\text{PbO.PbCrO}_4$	$\text{PbO.PbMoO}_4$
$a$	13.7690(50)	13.7576(1)	14.0076(2)	14.2058(3)
$b$	5.6980(30)	5.6578(1)	5.6445(1)	5.7592(1)
$c$	7.0790(20)	7.0322(1)	7.1028(1)	7.2844(1)
$V$	115.933 (17)	115.885 (1)	115.330 (1)	114.286 (1)
$R_p$	499.46 (15)	492.46 (1)	507.60 (2)	543.23 (2)
$R_I$		5.2	8.4	4.7
		2.3	6.2	2.6

All numbers in parentheses here and elsewhere are standard deviations in the last digits quoted for the preceding value.

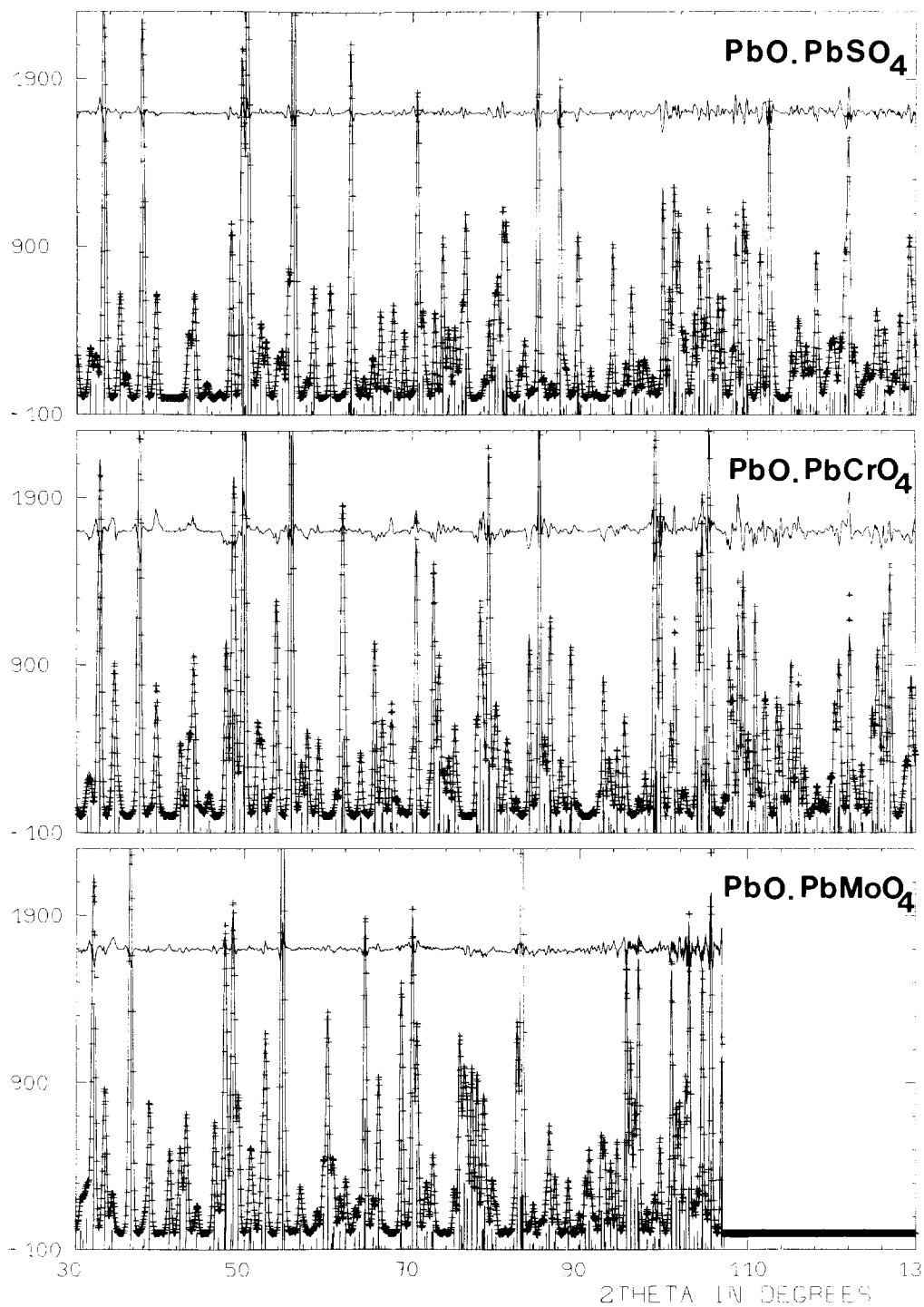


FIG. 1

TABLE 2. Atomic co-ordinates for the various compounds x10000.  
Order: Sahl(1970), PbO.PbSO<sub>4</sub>, PbO.PbCrO<sub>4</sub>, PbO.PbMoO<sub>4</sub>.

Atoms	x	y	z	Bav	n
PB1	1466( 1)	0	1050( 2)	1.30	4.0
	1473( 1)	0	1087( 2)	0.20	4.0
	1438( 1)	0	1146( 2)	0.21	4.0
	1374( 1)	0	1166( 2)	0.07	4.0
PB2	258( 1)	5000	2715( 2)	1.22	4.0
	255( 1)	5000	2731( 2)	0.24	4.0
	203( 1)	5000	2692( 2)	0.19	4.0
	132( 1)	5000	2580( 2)	0.18	4.0
X	3290(10)	5000	3440(20)	1.20	4.0
	3317( 3)	5000	3414( 5)	0.16	4.0
	3298( 3)	5000	3385( 6)	0.26	4.0
	3324( 1)	5000	3390( 3)	0.77	4.0
O1	1110(30)	0	4290(60)	2.10	4.0
	1024( 1)	0	4264( 3)	0.54	4.0
	911( 2)	0	4066( 4)	0.50	4.0
	848( 2)	0	3985( 3)	0.51	4.0
O2	3550(20)	7110(50)	2510(40)	2.00	8.0
	3560( 1)	7133( 2)	2474( 2)	0.45	8.0
	3523( 1)	7371( 3)	2243( 3)	0.49	8.0
	3529( 1)	7453( 3)	2142( 2)	0.51	8.0
O3	2130(30)	5000	2840(60)	2.00	4.0
	2150( 1)	5000	2915( 3)	0.64	4.0
	2039( 2)	5000	2987( 4)	0.42	4.0
	2007( 2)	5000	3075( 3)	0.48	4.0
O4	0	2460(60)	0	1.70	4.0
	0	2535( 3)	0	0.30	4.0
	0	2540( 4)	0	0.30	4.0
	0	2541( 4)	0	0.45	4.0

Note our low Bav factors at 5K compared with Sahl's at 300K.

### Discussion

Table 3 shows the calculated bond lengths and angles, together with the effective valence charge  $S$  for the metal ions. The standard deviations for Sahl's data are slightly different from those quoted in the original paper (1) having been recalculated from his quoted co-ordinate and lattice constant deviations. The standard deviations obtained from the Rietveld refinement do not include the absolute error in the wavelength, and appear to be a little lower than expected. However, the internal agreement between the different experiments is very good: the lead environment hardly changes with substitution of the different cations ( $X = S, Cr, Mo$ ), while the X-oxygen distances expand to accommodate the larger cations. The valence charge on both lead sites remains  $2+$ , and that on the X-site  $6+$ . The calculated standard deviations on these charges do not include possible errors in the Brown-Shannon-Wu parameters, which are less precisely known for  $Cr^{6+}$  and  $Mo^{6+}$ .

TABLE 3. Bond lengths and angles for Lanarkite at 300K (Sahl) with our neutron powder diffraction results at 5K.

			Sahl (1970)	PbO.PbSO <sub>4</sub>	PbO.PbCrO <sub>4</sub>	PbO.PbMoO <sub>4</sub>
Pb1	-O4	2x	2.298(23)	2.323( 1)	2.318( 2)	2.304( 2)
	-O1		2.546(49)	2.565( 2)	2.481( 4)	2.456( 3)
	-O2	2x	3.069(30)	3.063( 2)	3.065( 2)	3.200( 2)
	-O2	2x	2.784(30)	2.762( 2)	2.775( 3)	2.845( 2)
	-O3	2x	3.090(14)	3.079( 1)	3.073( 1)	3.163( 1)
	-MEAN		2.781(**)	2.780(**)	2.771(**)	2.831(**)
	-S		2.135(**)	2.085( 6)	2.147(11)	2.075( 9)
O1	-O4	2x	3.076(43)	3.057( 2)	2.979( 3)	3.024( 2)
O4	-O4		2.803(48)	2.869( 2)	2.867( 4)	2.927( 3)
O1	-Pb1	-O4	2x 78.7 ( 6)	77.2 ( 0)	76.7 ( 1)	78.8 ( 1)
O4	-	-O4	75.2 (10)	76.3 ( 1)	76.4 ( 1)	78.9 ( 1)
Pb2	-O4	2x	2.306(22)	2.273( 1)	2.280( 2)	2.299( 2)
	-O3		2.540(45)	2.554( 2)	2.488( 3)	2.537( 3)
	-O2	2x	2.822(29)	2.780( 2)	2.683( 2)	2.615( 2)
	-O2	2x	3.461(35)	3.444( 2)	3.583( 2)	3.813( 2)
	-O1	2x	3.097(14)	3.048( 1)	3.012( 1)	3.085( 1)
	-MEAN		2.879(**)	2.849(**)	2.845(**)	2.907(**)
	-S		1.986(**)	2.113( 6)	2.211(10)	2.142( 9)
O3	-O4	2x	3.095(44)	3.099( 2)	3.066( 3)	3.146( 3)
O4	-O4		2.895(48)	2.789( 2)	2.778( 4)	2.833( 3)
O4	-O4		2.803(48)	2.869( 2)	2.867( 4)	2.927( 3)
O3	-Pb2	-O4	79.2 ( 7)	79.6 ( 0)	79.9 ( 1)	81.0 ( 3)
O4	-	-O4	77.8 ( 9)	75.7 ( 1)	75.0 ( 1)	76.1 ( 1)
X	-O1		1.450(41)	1.482( 3)	1.670( 4)	1.786( 3)
	-O2	2x	1.488(32)	1.483( 3)	1.664( 4)	1.768( 2)
	-O3		1.462(43)	1.486( 4)	1.662( 5)	1.789( 3)
	-MEAN		1.472(16)	1.483( 1)	1.665( 2)	1.778(10)
	-S		6.074(**)	5.868(55)	5.698(72)	5.635(47)
	-O2	2x	2.423(47)	2.429( 2)	2.741( 3)	2.947( 3)
	-O3		2.386(55)	2.428( 2)	2.736( 3)	2.916( 3)
O2	-O3	2x	2.392(51)	2.417( 2)	2.708( 3)	2.888( 3)
	-O2		2.405(40)	2.414( 1)	2.676( 3)	2.826( 2)
O1	-X	-O2	2x111.1 (14)	110.0 ( 1)	110.6 ( 2)	112.0 ( 1)
O1	-	-O3	110.0 (27)	109.8 ( 3)	110.4 ( 3)	109.3 ( 2)
O2	-	-O3	2x108.4 (14)	109.0 ( 1)	109.0 ( 2)	108.6 ( 1)
O2	-	-O2	107.8 (20)	108.9 ( 3)	107.1 ( 3)	106.1 ( 1)
O4	-O4		2.895(48)	2.789( 2)	2.778( 4)	2.833( 3)
	-O4		2.803(48)	2.869( 2)	2.867( 4)	2.927( 3)
	-Pb1	2x	2.298(23)	2.323( 1)	2.318( 2)	2.304( 2)
	-Pb2	2x	2.306(22)	2.273( 1)	2.280( 2)	2.299( 2)
Pb1	-Pb1		3.641(25)	3.654( 2)	3.642( 2)	3.559( 2)
	-Pb2		3.740( 8)	3.720( 1)	3.713( 2)	3.737( 2)
Pb2	-Pb2		3.603(10)	3.554( 2)	3.560( 3)	3.695( 2)
Pb1	-O4	-Pb1	104.8 (14)	103.7 ( 1)	103.6 ( 1)	101.1 ( 1)
Pb2	-	-Pb2	102.3 (13)	104.3 ( 1)	105.0 ( 1)	103.9 ( 1)
Pb1	-	-Pb2	2x108.7 ( 0)	108.1 ( 0)	107.7 ( 0)	108.6 ( 0)
Pb1	-	-Pb2	2x116.5 ( 1)	116.6 ( 0)	116.7 ( 1)	117.7 ( 1)

The valence charges S are according to Brown &amp; Wu (1976).

References

1. K. Sahl: Z. Kristallogr., 132, 99 (1970).
2. K. Sahl: Z. Kristallogr., 156, 209 (1981).
3. B. F. Mentzen, J. C. Viala, A. Sartre and J. Bouix: C. R. Acad. Sc.,  
293, 1053 (1981).
4. H. M. Rietveld: J. Appl. Cryst. 2, 65 (1969).
5. A. W. Hewat: J. Phys. C 6, 2559 (1973).
6. A. Bogacz, J. Bros, M. Gaune-Escard, A. W. Hewat and J. C. Taylor:  
J. Phys. C 13, 5273 (1980).
7. B. F. Mentzen and A. Latrach: J. Appl. Cryst. 16, 430 (1983).
8. J. C. Ruckman, R. T. W. Morrison and R. H. Buck: J. C. S. Dalton Trans.  
426 (1972).
9. Sh. Miyazawa and H. Iwasaki: J. Cryst. Growth, 8, 359 (1971).
10. I. D. Brown and R. D. Shannon: Acta Cryst. A29, 266 (1973).
11. I. D. Brown and K. K. Wu: Acta Cryst. B32, 1957 (1976).
12. A. W. Hewat and I. Bailey: Nucl. Inst. Methods 137, 463 (1976).