Structure and Lattice Parameters of Dilead(II) Pentaoxochromate(VI)

By **J. C. Ruckman,* R. T. W. Morrison,** and **R. H. Buck,** Atomic Weapons Research Establishment, Aldermaston, Berkshire

Samples of dilead(II) pentaoxochromate(VI) Pb_2CrO_5, have been synthesised by direct fusion of PbO and $PbCrO_4$, and the composition characterised by gravimetric and neutron activation analysis. *X*-Ray powder diffraction measurements of *d*-spacings and line intensities revealed that the structure is monoclinic and isomorphous with lead pentaoxo-sulphate and -selenate. A computer method was employed to aid in fixing the position of the lead and chromium atoms in the unit cell and indexing the high angle Bragg reflections. The lattice parameters were found to be $a = 14{\cdot}01$, $b = 5{\cdot}68$, $c = 7{\cdot}15$ Å, $\beta = 115{\cdot}1°$.

IN the course of an investigation into the glazing of vacuum-evaporated duplex gold–chromium films with a lead-containing glass it became necessary to identify a red deposit at the site of a glazing defect in order to find the reasons for the occurrence of the defect.[1] Electron-probe microanalysis suggested that the deposit was Pb_2CrO_5. In order to confirm this by electron diffraction it was necessary first to establish the *X*-ray diffraction parameters using bulk samples since this data was not available.

Samples were synthesised by direct fusion at 1000 °C using calculated quantities of PbO and $PbCrO_4$. Gravimetric analysis for chromium and lead gave results within 0·5 wt. % of the calculated values for Pb_2CrO_5. The oxygen figure, determined by neutron activation analysis, was within 1 wt. % of the theoretical figure.

Metallographic examination of a thin section of the compound showed it to be a single phase. The melting point, determined by simple cooling curves and visual observation was found to be 920 °C.

X-Ray diffraction, using a Philips diffractometer gave patterns with similar '*d*-spacings' and intensities to Pb_2SO_5 and Pb_2SeO_5;[2-4] and to a compound stated to be Pb_2CrO_5 by Negas,[5] suggesting isomorphism of Pb_2CrO_5 with these two compounds.

Assuming a monoclinic unit cell and values of lattice parameters determined from low-angle lines an iterative computer programme, based on least-squares analysis, was used to give refined values of the lattice parameters until all the lines up to a Bragg angle of 30° had been indexed.

The results of this analysis, shown in Table 1, fit a

TABLE 1

'*d*-Spacings' and intensities of *X*-ray reflections from dilead(II) pentaoxochromate(VI)

hkl	d_o	d_c	I_o	I_c
001	6·5	6·471	14	18
200	6·4	6·339	14	15
$20\bar{1}$	6·0	5·972	14	16
110	5·2	5·186	2	5
$11\bar{1}$	4·4	4·441	14	18
201	3·79	3·793	9	12
111	3·74	3·742	3	3
$20\bar{2}$	3·54	3·559	8	12
$31\bar{1}$		3·541		
310	3·39	3·391	100	100
002	3·24	3·236	10	6
$11\bar{2}$	2·988	2·988	130	106
$40\bar{2}$		2·986		
$31\bar{2}$	2·884	2·884	25	16
020	2·841	2·842	42	38
311	2·648	2·654	5	2
021	2·591	2·602	3	7
220		2·593		
$22\bar{1}$	2·566	2·566	7	4
112		2·553		
$51\bar{1}$	2·512	2·511	20	21
202	2·480	2·486	22	23
401	2·460	2·463	10	7
$20\bar{3}$	2·369	2·373	5	3
$51\bar{2}$		2·368		
$60\bar{1}$	2·317	2·321	8	6
510		2·316		
221	2·267	2·274	20	11
$60\bar{2}$		2·264		

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[1] R. H. Buck, G. D. Lawrence, and J. C. Ruckman, *Corrosion Sci.*, 1971, **11**, 81.

[2] W. P. Binnie, *Acta Cryst.*, 1951, **4**, 471.

[3] J. J. Lander, *J. Electrochem. Soc.*, 1949, **95**, 174.

[4] R. O. Jones and S. Rothschild, *J. Electrochem. Soc.*, 1959, **105**, 206.

[5] T. Negas, *J. Amer. Ceram. Soc.*, 1969, **51**, 716.

Table 1 (*Continued*)

hkl	d_o	d_c	I_o	I_c
$31\bar{3}$	2·188	2·189	6	5
022	2·131	2·135	8	5
$11\bar{3}$		2·127		
420	2·114	2·116	8	8
600		2·113		
$42\bar{2}$	2·061	2·058	22	21
312	2·020	2·022	3	1
$51\bar{3}$		2·016		
$60\bar{3}$	1·992	1·991	12	6
511	1·951	1·953	5	5
113	1·865	1·879	39	38
130		1·874		
222		1·871		
$71\bar{2}$		1·869		
$71\bar{1}$		1·866		
421		1·861		
$13\bar{1}$	1·830	1·831	3	2
$22\bar{3}$	1·820	1·821	1	2
203		1·820		
423	1·779	1·785	15	5
404		1·779		
622		1·771		
131		1·770		
$20\bar{4}$	1·756	1·757	6	8
$33\bar{1}$		1·748		
$71\bar{3}$	1·728	1·733	17	16
330		1·729		
710		1·726		
023	1·718	1·718	9	7
$80\bar{1}$		1·717		
$31\bar{4}$	1·695	1·703	8	8
620		1·696		
$13\bar{2}$	1·663	1·667	14	15
514		1·664		
$33\bar{2}$	1·650	1·649	4	3
$62\bar{3}$	1·625	1·630	18	12
$11\bar{4}$		1·627		
512	1·607	1·610	14	9
$53\bar{1}$	1·576	1·569	5	5
223	1·530	1·532	10	6
$71\bar{4}$		1·529		
711	1·520	1·521	15	9
530		1·518		
403	1·508	1·510	10	7
$42\bar{4}$		1·508		
$91\bar{2}$	1·502	1·501	8	2
$22\bar{4}$		1·494		

Table 2

Comparison of the lattice parameters of lead pentaoxo-chromate, -sulphate and -selenate

Compound	a/Å	b/Å	c/Å	°	Reference
Pb_2CrO_5	14·01	5·68	7·15	115·1	This work
Pb_2SO_5	13·75	5·68	7·05	116·2	Ref. 2
Pb_2SeO_5	13·94	5·78	7·25	115·9	Ref. 4

monoclinic unit cell with the lattice parameters shown in Table 2 where they are compared with the lattice parameters for Pb_2SO_5 and Pb_2SeO_5.

The '*d*-spacings' calculated from these parameters (d_c); listed in Table 1 have a standard deviation of 12×10^{-5} compared with the observed '*d*-values', over the range $d = 6{\cdot}4$—$1{\cdot}5$ Å.

The theoretical density calculated from the above unit cell parameters and assuming 4 molecules of Pb_2CrO_5 per unit cell is 7·044 g ml^{-1} which agrees very well with the pyknometric density, determined as 7·033 g ml^{-1}.

The calculated intensities (I_c) in Table 1 were obtained by assuming the *c*2/*m* space group found for Pb_2SO_5 [2] and using a second computer programme (developed by Powell [6]), in which the positions of the lead, chromium, and oxygen atoms were varied until the best match was obtained between the observed and calculated intensities. The atomic scattering factors for Pb^{2+}, O^{2-}, and Cr^{6+} were used in this calculation. The positions of the lead and chromium atoms resulting from this analysis are given in Table 3.

Table 3

Positions of lead and chromium atoms in the Pb_2CrO_5 unit cell (fractional co-ordinates)

	x	*y*	*z*
Pb_1	0·445	0	0·105
Pb_2	0·024	0·5	0·257
Cr_1	0·318	0·5	0·369

Since the positions of the oxygen atoms could not be determined with any degree of accuracy using this method they are not included in Table 3. It seems likely that they occupy the positions described by Binnie [2] for the Pb_2SO_5 structure.

The results of the structure factor analysis and the good agreement between measured and calculated intensities reinforce the validity of the assumed isomorphism of Pb_2CrO_5 with Pb_2SO_5 and Pb_2SeO_5 and provide a firmer basis for indexing the high angle reflections.

The results of this study were usefully employed in an electron diffraction study to characterise thin red needles of a corrision product as single crystals of lead pentaoxochromate and to determine the direction of growth as the (020) direction.

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[6] M. J. D. Powell, *Computer J.*, 1964, **6**, 155.