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Powder Neutron Diffraction Study of Chemically Prepared β-Lead Dioxide

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Abstract. β-PbO_2, tetragonal, $P4_2/mnm$, $a = 4{\cdot}9578\ (2)$, $c = 3{\cdot}3878\ (2)$ Å, $Z = 2$, with the Pb atoms located in positions 2(*a*) and the O atoms in positions 4(*f*). The structure was refined with the Rietveld method utilizing powder neutron diffraction data collected with a multiple-channel detector up to $\sin\theta/\lambda = 0{\cdot}6$ Å^{-1}. Anisotropic thermal parameters were included in the refinement. The O positional parameter was found to be $x = 0{\cdot}3067\ (2)$. The Pb atoms are coordinated by six O atoms, forming an irregular octahedron in which the four equatorial Pb—O distances are 2·1689 (7) Å and the two axial distances 2·150 (1) Å.

Introduction. β-PbO_2 is the major constituent of the lead-acid battery. A detailed knowledge of its structure is essential in correlating electrochemical activity with the atomic arrangement of the electrode constituents of the battery. Such knowledge is also important in understanding the nature of the chemical bonds in compounds with rutile-type structures (Baur, 1956, 1958, 1961; Baur & Khan, 1971). Structural studies of β-PbO_2 have been carried out by X-ray (Tolkacev, 1958) and neutron powder diffraction techniques (Leiciejewicz & Padlo, 1962; indicated LP hereafter). The O positions in the structure could not be determined with any precision in the X-ray work. On the other hand, in the neutron diffraction experiment only data up to $\sin\theta/\lambda = 0{\cdot}3$ Å^{-1} were used, and the structure was only partially refined because no temperature factors were introduced in the calculations. More importantly, in this study the value of the positional parameter of the O atoms was obtained with such a large standard deviation that it is impossible to establish if the PbO_6 octahedra are compressed or elongated along their axial direction (Baur & Kahn, 1971). As the distortions of octahedra in rutile-type AB_2 oxides are of theoretical interest, we thought it worthwhile to refine the structure of β-PbO_2 with the Rietveld (1969) method.

The sample used to collect the neutron diffraction data was chemically prepared (Baker reagent grade, β-PbO_2, lot No. 4604). The measurements were made at room temperature with a five-detector diffractometer at the National Bureau of Standards reactor (Prince & Santoro, 1980), using the experimental conditions summarized in Table 1.

The powder pattern of β-PbO_2 consists of isolated peaks as well as resolved and unresolved clusters. The distribution of the reflections is such that the angular interval scanned by each detector contains a sufficient number of points free from diffraction lines to permit a reliable evaluation of the background contribution to the observed intensities at all the 2θ diffraction angles. Some of the diffracted lines were slightly asymmetric near the Gaussian tails. This may be caused by impurities in the sample or by crystallite-size effects. In any event, the regions affected were excluded from all subsequent calculations.

The structure was refined with the Rietveld (1969) method modified to process simultaneously the data from the five channels of the multiple-detector diffractometer. The neutron scattering amplitudes were $b(\mathrm{Pb}) = 9{\cdot}4$ and $b(\mathrm{O}) = 5{\cdot}8$ fm. The initial values of the lattice parameters and of the positional parameter x of the O atoms were those obtained by LP and the initial profile parameters U, V, and W were calculated theoretically (Caglioti, Paoletti & Ricci, 1958). The anisotropic temperature factors of the Pb and O atoms were refined together with the other parameters. Their introduction in the calculations is justified because the data were measured to a sufficiently high $\sin\theta/\lambda$ and

Table 1. *Experimental conditions used to measure the powder pattern of* β-PbO_2

Monochromatic beam: reflection 220 of a Cu monochromator
Wavelength: 1·5416 (3) Å
Horizontal divergences: (*a*) in pile collimator: 10′ arc; (*b*) monochromatic beam collimator: 20′ arc; (*c*) diffracted beam collimator: 10′ arc
Monochromator mosaic spread: ~15′ arc
Sample container: vanadium can ~10 mm in diameter
Angular ranges scanned by each detector: 15–40, 35–60, 55–80, 75–100, 95–120°; step: 0·05°
Number of independent Bragg reflections: 44

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Table 2. *Results of the refinement of the structure of* β-PbO_2

	a (Å)	c (Å)	c/a	x	x_m‡
This work*	4·9578 (2)	3·3878 (2)	0·68333 (5)	0·3067 (2)	0·30835
Naidu†	4·9568 (5)	3·3866 (2)	0·68322 (8)		
LP	4·955 (3)	3·383 (2)	0·6827 (7)	0·309 (4)	0·3083
Tolkacev (1958)	4·946	3·379	0·6832	0·308	0·3083

	Position	$\beta_{11} = \beta_{22}$	β_{33}	β_{12}	$\beta_{13} = \beta_{23} \times 10^4$§
Pb	2(*a*)	55 (4)	50 (1)	3 (6)	0
O	4(*f*)	97 (5)	80 (2)	−50 (7)	0

Profile parameters: $U = 0{\cdot}50\ (2)$, $V = -0{\cdot}36\ (3)$, $W = 0{\cdot}210\ (8)$ (deg^2)
$R = 4{\cdot}71\%$, $R_p = 12{\cdot}28\%$, $R_w = 14{\cdot}44\%$, $R_{\text{expected}} = 6{\cdot}05\%$, $\chi = 2{\cdot}4$¶

* The cell-dimension errors obtained in the neutron refinement do not include the error in the neutron wavelength.

† As quoted by Baur & Khan (1971).

‡ $x_m = \frac{c^2}{8a^2} + \frac{1}{4}$, with c and a measured by Naidu.

§ The thermal parameters are of the form
$\exp|-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})|$.

¶ The R factors are defined in several publications (*e.g.*, Rietveld, 1969).

because the background intensity was reliably determined. The initial values of these parameters were set equal to those of comparable oxides (for example, Baur & Khan, 1971). All parameters were allowed to vary simultaneously until the shifts were less than 0·3 times the standard deviation. The results of the refinement are given in Table 2 and the observed and calculated profiles are shown in Fig. 1.*

Discussion. The lattice parameters obtained in the refinement agree closely with those measured by LP with a back-reflection camera and with those determined by Naidu (as quoted by Baur & Khan, 1971). The small systematic deviations are probably due to the uncertainty with which the neutron wavelength is known (Table 2) and therefore Naidu's parameters are used in all subsequent calculations. The values of the profile parameters U, V, and W are in agreement with those observed for other compounds analyzed with the same experimental conditions (for example, Santoro, Roth & Minor, 1979). The anisotropic thermal factors are of the same order as those reported for similar compounds (Baur & Khan, 1971). From Fig. 2 it can be seen that the major vibrational motion of the O atoms is perpendicular to the planes {110}, in agreement with the results of Baur & Khan (1971) for rutile-type SiO_2 and for GeO_2.

The structure of β-PbO_2 is shown in Fig. 2 with the atoms represented by their thermal ellipsoids. The six O atoms surrounding the Pb atoms form slightly distorted octahedra. In Fig. 3 the O atoms are connected to show

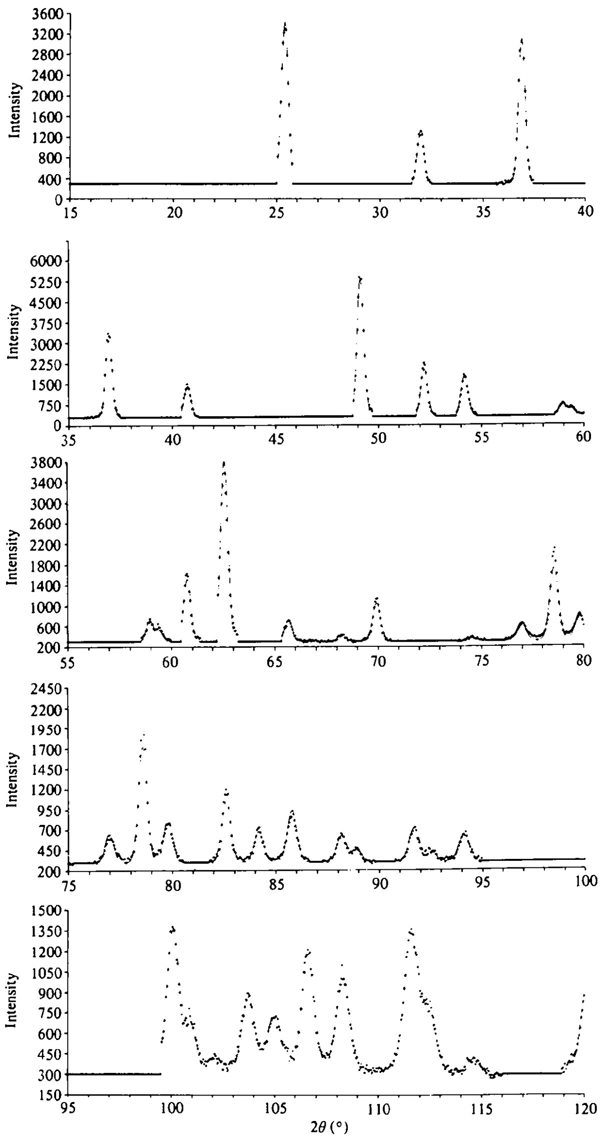

Fig. 1. Observed (dots) and calculated (continuous line) profiles for β-PbO_2. Each section is recorded with a different detector of the five-detector diffractometer with an overlapping of the patterns of 5° in 2θ.

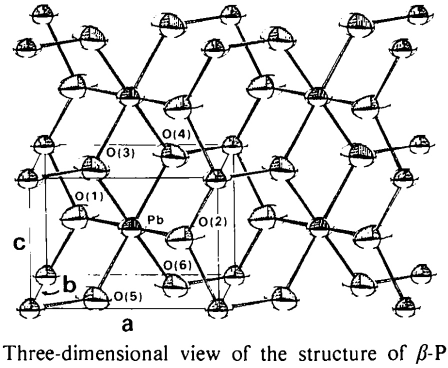

Fig. 2. Three-dimensional view of the structure of β-PbO_2. The atoms are represented by their thermal ellipsoids. The labeling of the atoms is the same as that used in Table 3.

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* A table of observed and calculated profile intensities has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35354 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the packing sequence of the octahedra. The structure consists of vertical columns of edge-sharing PbO_6 octahedra. These columns are oriented along the [001] direction and form sequences of corner-sharing octahedra along the ⟨110⟩ directions, with the octahedra alternately rotated by 90° about [001].

The principal interatomic distances and angles in the PbO_6 octahedron are compared with the results of LP in Table 3 (the values reported in column 3 have been recalculated to facilitate comparison and to correct some errors in the results of LP). The four equatorial bonds $(Pb—O)_1$ lie in the planes {110} and the two axial bonds $(Pb—O)_2$ are normal to these planes.

According to our results, and contrary to those of LP, $(Pb—O)_1 > (Pb—O)_2$, *i.e.* the octahedron of the O atoms surrounding the Pb atom is slightly compressed along the axial direction. This result, however, is significant only if the value of the standard deviation σ_x associated with the positional parameter x can be considered reliable. In a recent analysis of the profile-fitting procedure, Sakata & Cooper (1978) have concluded that the Rietveld method weights the observations incorrectly and that the estimated standard deviations are smaller by a factor of at least 2 than those given by a refinement based on integrated intensities. On the other hand, Prince (1980) has pointed out that the high precision of the Rietveld method is a consequence of the fact that each peak is assumed to be Gaussian, so that each data point within the peak becomes an independent measurement of the intensity. This results in a more precise estimate of the diffracted intensity. In agreement with Prince's conclusions, it has been shown in a number of cases (for example, Andresen, Hewat & Sabine, 1978; Cheetham & Taylor, 1977) that the Rietveld method gives quite realistic standard deviations associated with the atomic coordinates. The high precision of the Rietveld method translates into high accuracy only if the model is adequate, *i.e.* free of hidden factors such as unrecognized structural distortions, non-Gaussian peak shape, *etc.* No problems of this kind are apparent in our experiment. All the parameters calculated in the refinement are quite reasonable, including the thermal and profile parameters which are very sensitive to errors in the adopted structural model and to the physical conditions of the sample used to collect the data. Finally, the correlation coefficients involving x and the other refined quantities are low, the largest being only 10%.

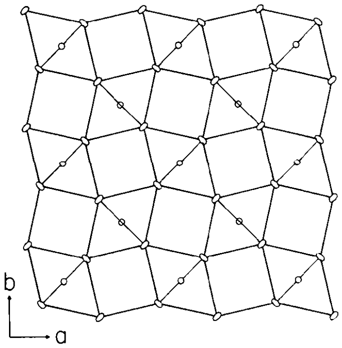

Fig. 3. Projection of the structure of β-PbO_2 on the plane (001). Atoms are joined to show the packing of the PbO_6 octahedra.

Table 3. *Principal distances* (Å) *and angles* (°) *in the octahedral coordination sphere of* β-PbO_2

	This work	LP
Pb—O(3,4,5,6)* ≡ $(Pb—O)_1$	2·1689 (7)†	2·157 (12)
Pb—O(1,2) ≡ $(Pb—O)_2$	2·1500 (11)	2·165 (20)
O(3)—O(4) O(5)—O(6)	2·7107 (22)	2·677 (40)
O(1)—O(3,4,5,6) O(2)—O(3,4,5,6)	3·0542 (5)	3·056 (8)
O(3)—O(6) O(4)—O(5)	3·38668 (2)	3·383 (2)
O(3)—Pb—O(4) O(5)—Pb—O(6)	77·35 (5)	76·7 (8)

* The labeling of the atoms is given in Fig. 2.

† These distances were calculated by using $x = 0{\cdot}3067\ (2)$ and the lattice parameters measured by Naidu (Baur & Khan, 1971). The distance $(Pb—O)_m$ corresponding to x_m of Table 2 is 2·1615 Å.

To remove any doubts, a second evaluation of the positional parameter was obtained by carrying out a refinement based on integrated intensities. These were obtained by fitting least-squares Gaussian peaks to 27 single or separable reflections. This refinement gave $x = 0{\cdot}3066\ (6)$ with an R factor, based on structure factors, of 2·0%[*] (the R factor based on F^2 was 3·6%). As expected, the standard deviation σ_x is larger than that obtained with the Rietveld method (the same is true for the standard deviations associated with the thermal parameters). Even in this case, however, the difference between the value of x obtained in the refinement and that reported by LP can be considered significant. Thus, the point representing β-PbO_2 in the plot of x *versus* c/a shown in Fig. 2 of Baur & Khan (1971) is located below the line corresponding to the conditions for undistorted octahedra in the structure. It follows that β-PbO_2 is in the same category with the fluorides of Mg, Mn, Fe, Co, and Zn[†] and the oxides of Cr, Ru, and Os. A conclusion of this study is that β-PbO_2 is closer to the Born model, and its bonding has more ionic character, than previous structural investigations implied.

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[*] The calculations were made with the program *ORFLS* of Busing, Martin & Levy (1962).

[†] Neutron-diffraction analysis (Taylor & Wilson, 1974) has shown that in NiF_2 the F atoms form an undistorted octahedron.

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$Sc_5T_4Si_{10}$ (T = Co, Rh, Ir) and $Y_5T_4Ge_{10}$ (T = Os, Ir) with a New Tetragonal Structure Type

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Abstract. $Sc_5Co_4Si_{10}$, $P4/mbm$, $Z = 2$, $a = 12{\cdot}01$ (1), $c = 3{\cdot}936$ (5) Å, $D_c = 4{\cdot}34$ (1), $D_o = 4{\cdot}33$ (1) Mg m^{-3}, μ(Mo $K\alpha$) = 9·7 mm^{-1}. Final $R = 0{\cdot}04$ for 419 reflections. Isostructural compounds are $Sc_5Rh_4Si_{10}$ [$a = 12{\cdot}325$ (6), $c = 4{\cdot}032$ (3) Å], $Sc_5Ir_4Si_{10}$ [$a = 12{\cdot}316$ (5), $c = 4{\cdot}076$ (3) Å], $Y_5Os_4Ge_{10}$ [$a = 13{\cdot}006$ (8), $c = 4{\cdot}297$ (5) Å] and $Y_5Ir_4Ge_{10}$ [$a = 12{\cdot}927$ (5), $c = 4{\cdot}308$ (5) Å].

Introduction. During a seach for superconductivity in rare-earth–transition-metal silicides, a series of tetragonal compounds of formula $R_5T_4X_{10}$ (R = Sc, Y, T = Co, Rh, Ir, Os, X = Si, Ge) was found (Braun, 1979). Most of them are good superconductors with critical temperatures up to 8·6 K (Braun & Segre, 1980). Their composition was determined by microprobe analysis of a sample belonging to the Sc–Rh–Si system (Braun, Burri & Rinderer, 1979). In the analogous Co system, Kotur, Bodak & Gladyshevskii (1977) reported a tetragonal phase of approximate composition $Sc_3Co_2Si_5$. To our knowledge, the structure has not been determined. In view of the space group indicated ($P4/mbm$) and the similarity of the lattice parameters ($a = 11{\cdot}99$, $c = 3{\cdot}96$ Å) their $Sc_3Co_2Si_5$ and our $Sc_5Co_4Si_{10}$ are likely to be identical.

Prior to the present study, single crystals of $Sc_5Ir_4Si_{10}$ were examined by Weissenberg and precession photographs. The Laue class $4/mmm$ and the systematic absences ($0kl$: $k = 2n + 1$) led to the possible space groups $P4bm$, $P\bar{4}b2$ or $P4/mbm$. A model was obtained by direct methods, but despite corrections for isotropic absorption and extinction, anisotropic refinement in non-centrosymmetric $P4bm$ yielded only an unsatisfactory $R = 0{\cdot}18$. Thus, it became desirable to collect a new set of data, preferably for a compound in which Ir was replaced by a lighter transition metal. A sample of $Sc_5Co_4Si_{10}$ was prepared by arc-melting and subsequently cooled slowly (6 K h^{-1}) from 1700 to 1100 K. A single crystal, isolated from the crushed sample, was mounted on a four-circle diffractometer (Philips PW 1100, Mo $K\alpha$, graphite monochromator). Integrated intensities were collected

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