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Pb_2PtO_4, A New Platinum–Lead Oxide with Edge-Shared PtO_6 Octahedral Chains

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Pb_2PtO_4 was prepared by the solid state reaction between lead monoxide and platinum metal in the appropriate ratio at 690–720°C. It decomposed to PbO and Pt at 735°C. The symmetry is orthorhombic: $a = 9.115(4)$, $b = 7.941(4)$, $c = 6.306(4)$ Å, $Z = 2$, space group *Pbam*. The crystal structure was solved by conventional methods to $R = 0.049$ using 851 independent reflections. The structure consists of chains of edge-shared PtO_6 octahedra extending along the *c*-axis direction. Lead atoms are stacked in rows in the channels between the chains. The conductivity of Pb_2PtO_4 is low ($\sigma(300\text{ K}) \simeq 10^{-5}\ (\Omega \cdot \text{cm})^{-1}$), in agreement with the presence of fully oxidized tetravalent platinum. © 1987 Academic Press, Inc.

Introduction

As pointed out in an exhaustive recent review on binary and ternary platinum oxides (*1*), some were accidentally discovered as the result of chemical attack on platinum containers. This was the case for the tetragonal $Bi_{2-x}Pb_xPtO_4$ ($0.33 \le x \le 0.52$) which contains columnar stacks of PtO_4 groups extending along the *c*-axis direction (*2, 3*).

Attempts were made to prepare the family end members Bi_2PtO_4 ($x = 0$) and Pb_2PtO_4 ($x = 2$) which would contain only divalent and tetravalent platinum, respectively. While there was no evidence of formation of the former (*3*), a high-temperature X-ray powder investigation carried out on a mixture of divalent orthorhombic lead oxide and platinum metal in a molar ratio of 2 : 1 disclosed the formation of a new phase in the vicinity of 700°C. The present paper deals with the characterization and structure of this phase, which proved to be a new mixed platinum–lead oxide.

Experimental

Polycrystalline Pb_2PtO_4 was prepared by solid state reaction of appropriate amounts of yellow lead monoxide (Johnson Matthey) and platinum powder (Heraeus, 99.9%). The mixture (0.5 to 1 g) was heated in air between 690 and 720°C for several days, with frequent regrindings. The resulting dark brown powder was examined by X-ray diffraction using a Guinier-De Wolff focusing camera (Cu*Kα* radiation). Least-squares refinement of unit-cell dimensions was carried out on a powder diffraction pattern standardized against KCl. A Guinier-

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TABLE I

POWDER DIAGRAM OF Pb_2PtO_4

$h\,k\,l$	d_{obs} (Å)	d_{calc} (Å)	$h\,k\,l$	d_{obs} (Å)	d_{calc} (Å)
1 1 0	5.9713	5.9875	3 2 0	2.4110	2.4129
0 2 0	3.9636	3.9705	2 2 2	2.1723	2.1710
2 1 0		3.9528	2 3 1	2.1533	2.1516
2 1 1	3.3442	3.3492	4 1 1	2.0692	2.0691
0 0 2	3.1507	3.1530	1 3 2	1.9774	1.9789
1 2 1		3.1526	4 2 0		1.9764
2 2 0	2.9931	2.9937	2 1 3	1.8550	1.8559
3 1 0	2.8352	2.8377	4 0 2	1.8469	1.8469
1 1 2	2.7857	2.7898	2 4 0	1.8185	1.8201
3 1 1	2.5886	2.5879	3 3 2	1.6873	1.6864
1 3 0	2.5435	2.5420	4 3 1	1.6665	1.6656
2 1 2	2.4681	2.4649	5 2 1	1.6025	1.6023

Lenne camera was used for high-temperature X-ray investigations (HTXR).

Single crystals were prepared by a flux method. A small amount (0.05 g) of platinum powder was added to 2.5 g of a mixture of lead oxide and lead fluoride in the molar ratio (14 : 9). The material was held for 1 hr at 690°C in a platinum crucible and then slowly cooled ($3°C \cdot hr^{-1}$) to room temperature. Blackening of the crucible indicated that it took part in the formation of the phase. The resulting solid was then roughly crushed and treated with a 2 *M* acetic acid solution at room temperature. Needle-shaped crystals could then be removed. Increasing the platinum powder to flux weights ratio resulted in crystals of poorer quality. Thermogravimetric (TG), differential thermal (DT) and differential scanning calorimetric (DSC) measurements were carried out using a Dupont 1090 thermoanalyzer. Density determination was made using the method described by Barker (*4*).

Conductivity measurements were carried out by a two probe dc method on cold-pressed pellets (5 mm diameter, 2.7 mm thick) which were sintered at 700°C for 3 days. Flat faces were provided with vacuum-deposited gold electrodes.

Results

Thermal Stability and Formula Determination

From examination of a HTXR photograph carried out in air on an unreacted sample of nominal composition 2 PbO: 1 Pt, it appeared that lead monoxide began to react with platinum at about 650°C. Although the heating rate of the experiment was rather low ($12°C \cdot hr^{-1}$), the reaction did not go to completion and decomposition occured at about 750°C, resulting in a mixture of orthorhombic lead monoxide, platinum metal and a phase which was identified, from its X-ray pattern, as the pyrochlore $Pb_2Pt_2O_{7-y}$ (*5*). DT and TG analyses were carried out in air on Pb_2PtO_4 samples which were prepared as described in the experimental section. They confirm that decomposition of the phase occurred at 735 ± 5°C. However, only lead monoxide and platinum metal could be identified as decomposition products, according to the stoichiometry $Pb_2PtO_4 \rightarrow 2PbO + Pt + O_2$. The weight loss measured between 730 and 770°C (4.65%) was in agreement with the loss of two oxygen atoms per formula (4.75%). At higher temperatures, a continuous weight change was observed which was attributed to lead monoxide volatilization.

As described in the next section, the unit cell is orthorhombic. Table I gives the X-ray powder pattern which was indexed using the parameters reported on Table II. Increasing the temperature resulted in a decrease of a and an increase of b, so that the following parameters were measured at 720°C, just before decomposition (using Pt reflexions as standard): $a = 8.927(4)$, $b = 8.275(6)$, $c = 6.302(5)$ Å. The symmetry would perhaps become tetragonal (like Pb_3O_4) if decomposition did not occur.

TABLE II

UNIT CELL PARAMETERS

Crystal symmetry	Orthorhombic
a(Å)	9.115(4)
b(Å)	7.941(4)
c(Å)	6.306(4)
d_{calc}(g · cm^{-3})	9.79
Z	4
Space group	*Pbam*
μ(cm^{-1}) (for $K\alpha$ = 0.7107 Å)	1039

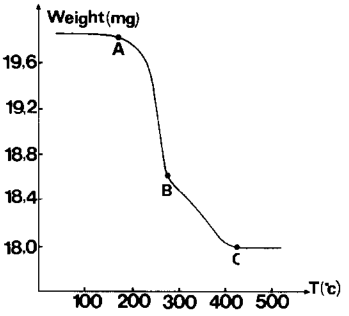

FIG. 1. Thermogravimetric analysis of Pb_2PtO_4 under a hydrogen stream.

Several samples which appeared cristallographically pure from X-ray powder diagrams were analyzed to determine the oxygen content of the phase. TG analyses were carried out under a hydrogen stream. Figure 1 shows a typical curve: reduction occurred between 175°C (point *A*) and 425°C (point *C*). The total weight loss (9.4%) is in good agreement with the postulated formula (9.5%). An X-ray powder diagram indicated that the reduced sample was a mixture of two lead–platinum alloys, hexagonal PbPt and tetragonal Pb_4Pt, together with a small amount of metallic lead. A TG experiment was stopped at 275°C (point *B*): an X-ray analysis showed the presence of hexagonal PbPt and tetragonal lead monoxide PbO. It seems that the reduction proceeds in two steps:

$$Pb_2PtO_4 + 3\ H_2 \rightarrow PbO + PbPt + 3\ H_2O$$

$$PbO + PbPt + H_2 \rightarrow \tfrac{2}{3}PbPt + \tfrac{1}{3}Pb_4Pt + H_2O$$

Attempts were made to determine lead and platinum contents by wet chemical analyses: they failed because the phase could not be dissolved, even in aqua regia, but in these conditions a new phase appeared which is presently under investigation. As a consequence, the lead to platinum ratio could only be estimated by X-ray analysis: it was believed that a possible formula for the phase was Pb_2PtO_4. This was later confirmed by the results of the crystal structure determination.

Crystal Structure Determination

The selected crystal was a needle with the following dimensions: 0.034, 0.018, and 0.0053 cm. Intensity data were collected by means of the automated Philips PW 1100 diffractometer of the "Centre Commun de Mesures de l'Université des Sciences et Techniques de Lille" using the conditions for data collection given in Table III. Ab-

TABLE III

DATA COLLECTION AND REFINEMENT CONDITIONS

Data collection	Pb_2PtO_4
Equipment	Philips PW 1100 diffractometer
Radiation (Å)	Mo$K\alpha$, graphite monochromator, λ = 0.7107
Scan mode	$\omega - 2\theta$
Scan angle(°)	ω = 1.4
Recording angular range (θ°)	2 – 35
Recording reciprocal space	$-14 \leq h \leq 14, 0 \leq k \leq 10, 0 \leq l \leq 11$
Number of measured reflections	2229
Number of reflections $I > 3\sigma(I)$	1582
Number of independent reflections (used in refinement)	851
Refinement	
Number of variables	29
$R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$	0.049
$R_w = [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma F_o^2]^{1/2}$ with $w = 1$	0.059

TABLE IV

ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS

Atom	Site	x	y	z	B or B_{eq} (Å^2)[a]
Pb(1)	$4g$	0.3273(1)	0.1093(1)	0	0.85
Pb(2)	$4h$	0.8435(1)	0.6399(1)	0.5	0.83
Pt	$4e$	0	0	0.2510(2)	0.49
O(1)	$8i$	0.169(2)	0.168(2)	0.247(3)	1.5(3)
O(2)	$4h$	−0.092(2)	0.129(3)	0.5	1.0(3)
O(3)	$4g$	−0.110(3)	0.110(3)	0	1.3(4)

[a] Equivalent isotropic temperature factors are computed according to the relation $B_{eq} = \frac{4}{3}\Sigma_{ij}\beta_{ij}a_i a_j$.

TABLE V

ANISOTROPIC THERMAL PARAMETERS (×10^5) FOR Pb AND Pt ATOMS[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pb(1)	135(9)	295(15)	846(28)	36(8)	0	0
Pb(2)	165(9)	284(4)	774(27)	28(8)	0	0
Pt	92(8)	225(12)	373(19)	−17(7)	0	0

[a] The anisotropic temperature factor is defined by $e^{(-\Sigma_{ij}\beta_{ij}h_i h_j)}$.

sorption corrections were applied to 1582 reflections with $I > 3\sigma(I)$, assuming that Pb_2PtO_4 was the correct formula (μ = 1039 cm^{-1}) using the method of De Meulenaer and Tompa (*6*): transmission coefficients ranging from 0.13 to 0.42 were obtained. Averaging of the equivalent reflections led to 851 independent data which were used in the structure determination. Scattering factors for cations were taken from (*7*) and corrected for anomalous dispersion effects (*7*). Oxygen scattering factors were taken from Tokonami (*8*).

Diffractometer data were in agreement with Weissenberg photographs which displayed orthorhombic symmetry. Extinction conditions indicated that the space group was *Pba*2 or *Pbam*. The structure was successfully solved in the latter space group. Cell parameters were used to compute a theoretical density of 9.79 g · cm^{-3}, which was in fair agreement with the measured density (9.6(3)g · cm^{-3}) assuming four formula in the unit cell.

The three-dimensional Patterson synthesis was interpreted by locating heavy atoms in 4(e) ($z \simeq 0.25$), 4(g) ($x \simeq 0.33$, $y \simeq 0.11$), and 4(h) ($x \simeq 0.84$, $y \simeq 0.64$) positions of space group *Pbam*. Assuming that the former was occupied by platinum atoms and the others by lead atoms, the calculations led to an R index of 0.09. Oxygen atoms were then located from a Fourier difference map in 4(g), 4(h), and 8(i) positions. Anisotropic thermal vibrations were assigned to Pb and Pt atoms whereas isotropic vibrations were assigned to other atoms. A secondary extinction correction was introduced in the form $F^2_{\text{corr}} = F^2_{\text{calc}}(1 + SF^2_{\text{obs}})$, the final value of S being 0.7(1) × 10^{-7}. Refined atomic and thermal parameters are listed in Tables IV and V.* Table VI gives the most significant distances and angles.

Description of the Structure

A projection along the c-axis direction of the structure is shown in Fig. 2. It consists of isolated chains of edge-shared PtO_6 octahedra extending along [0 0 1]. The chains are connected by means of Pb(1) and Pb(2) atoms. Pt–O distances within an octahedron (Table VI) are in agreement with the sum of ionic radii of tetravalent platinum and oxygen (*9*). These values rule out the presence of a significant amount of tetravalent lead in place of platinum, since this would result in longer distances (*10*). The octahedra common edges O(2)–O(2) and O(3)–O(3) are nearly equal and much shorter than other edges O(1)–O(2), O(1)–O(3), and O(2)–O(3). The latter is far greater than twice the ionic radius of oxygen, so that octahedra are elongated in the

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[1] Lists of observed and calculated structure factors are available on request to the authors.

TABLE VI

MAJOR DISTANCES (Å) AND ANGLES (°) IN Pb_2PtO_4

Pb(1) environment		Pb(2) environment	
$Pb(1)-O(1)^{i}$	2.17(2)	$Pb(2)-O(1)^{ii}_{111}$	2.21(2)
$Pb(1)-O(1)^{iv}$		$Pb(2)-O(1)^{iii}_{110}$	
$Pb(1)-O(3)^{ii}$	2.64(3)	$Pb(2)-O(2)^{ii}_{111}$	2.92(2)
$Pb(1)-O(3)^{v}$	2.30(2)	$Pb(2)-O(2)^{vi}$	2.29(2)
PtO_6 octahedron			
Pt–O(1)	2.04(2)	$O(1)-O(2)^{iii}$	2.93(3)
$Pt-O(1)^{iii}$		O(1)–O(3)	3.02(3)
Pt–O(2)	2.05(1)	$O(1)-O(3)^{iii}$	2.75(3)
$Pt-O(2)^{iii}$			
Pt–O(3)	2.07(2)	O(1)–Pt–O(2)	89.5(11)
$Pt-O(3)^{iii}$		O(1)–Pt–O(3)	94.6(14)
$O(2)-O(2)^{iii}$	2.65(4)	O(2)–Pt–O(3)	100.2(7)
$O(3)-O(3)^{iii}$	2.66(5)		
O(2)–O(3)	3.16(1)		
O(1)–O(2)	2.88(2)		

Note. The notation $O(n)^{x}_{pqr}$ represents atom O(*n*) to which the symmetry *x* has been applied, followed by a translation of **pa** + **qb** + **rc**. Symmetry code: (i) x, y, z; (ii) $\bar{x}, \bar{y}, \bar{z}$; (iii) $\bar{x}, \bar{y}, z$; (iv) $x, y, \bar{z}$; (v) $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y; z$.

direction of the chain. This elongation is comparable to that of PtO_6 octahedra in β-PtO_2 which has a distorted rutile structure formed by chains of edge-shared PtO_6 octahedra sharing corners with adjacent chains to form a three-dimensional framework (*10*); the Pt–Pt distance along the chain is 3.14 Å.

Lead atoms Pb(1) and Pb(2) have very similar oxygen coordination, with three nearest neighbors at distances ranging from 2.17 to 2.30 Å, the next nearest oxygen atom being located at 2.64 (Pb(1)) or 2.92 Å (Pb(2)).

Discussion

The structure of Pb_2PtO_4 is very similar to those of Pb_3O_4 (*11*), on the one hand, and Sr_2PbO_4 (*12*), (Cd_2PtO_4 (*13*), and Sr_2PtO_4 (*14*) have probably the same structure), on the other. All are characterized by one-dimensional linkage of edge-shared $M^{4+}O_6$ octahedra. The chains are held together by divalent cations. The main differences are observed in the coordination of the latter and, from this point of view, Pb_2PtO_4 is very similar to Pb_3O_4: the highly dissymmetric coordination of divalent lead atoms (three nearest-neighbor oxygen atoms instead of seven in Sr_2PbO_4 and isostructural A_2MO_4 compounds) results in doubling of the *c* parameter. It may be that the origin of the phenomena is to be found in the stereoactivity of the $6s^2$ lone pairs of divalent Pb atoms. From simple spatial considerations, it can be inferred that lone pairs of Pb(1) and Pb(2) atoms are located in the channels between MO_6 octahedra chains. Such a situation had already been observed in $(Bi,Pb)_2PtO_4$(2).

The lower symmetry of Pb_2PtO_4 (orthorhombic *Pbam*) compared to Pb_3O_4 (tetragonal *P4₂/mbc*) results in slight distortions of PtO_6 octahedra which are no longer perfectly stacked along the *c*-axis direction.

Conductivity values of 10^{-5}–10^{-6} $(\Omega \cdot cm)^{-1}$ were observed at 300 K. These values must be considered as lower limits since they were obtained on samples of high porosity (35%). Nevertheless, Pb_2PtO_4 is obviously a rather poor conductor:

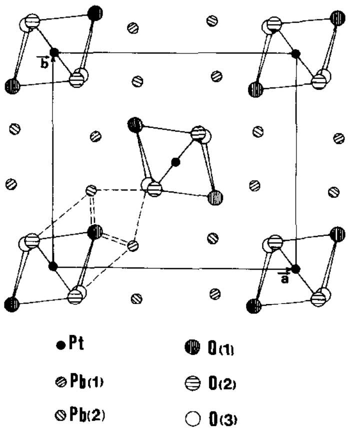

FIG. 2. A projection of the structure of Pb_2PtO_4 along the **c** axis.

metal–metal interactions across the octahedra common edges are therefore weak, in agreement with the shortening of the latter and with Schwartz and Prewitt's observation (*1*) that valence state (here fully oxidized tetravalent state) is a much more reliable indicator of possible electronic interactions than metal–metal distances.

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