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Tetravalent lead in nature – plattnerite crystals from Mine du Pradet (France) and Mount Trevasco (Italy)

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Abstract: Natural lead dioxide samples (β modification) from Cap Garonne, Mine du Pradet, France and Mount Trevasco, Italy were studied by single crystal X-ray and electron diffraction, clearly manifesting the rutile-type structure. A needle from the Mount Trevasco sample was investigated on a single crystal diffractometer: $P4_2/mnm$, $a = 495.81(10)$, $c = 338.66(7)$ pm, $wR = 0.0513$, 117 $F^2$ values (all data) and nine variables (293 K data). An additional data set at $T = 90$ K gave no hint for structural distortions.

Keywords: crystal structure; lead dioxide; Mine du Pradet; Trevasco Mount.

1 Introduction

Lead forms three technologically important oxides: divalent PbO, mixed-valent Pb$_2$PbIVO$_4$ and tetravalent PbIVO$_2$ [1–4] which are well-known for the following applications. PbO is an important precursor for glass varieties with high refractive index [3, 4] or for transparent conducting films [5]. Pb$_3$O$_4$ has long-time been used as long-lasting anti-corrosive paint (as suspension in linseed or turpentine oil), and PbO$_2$ is the outstanding cathode material of the lead-acid battery. However, since the implementation of the RoHS (Restriction of Hazardous Substances) directive by the European Union in 2002, the use of lead compounds is strongly diminishing. The lead-acid battery is the only lead-based product used on a large scale and with an almost complete recycling rate.

The two modifications of PbO and also Pb$_3$O$_4$ are synthetically accessible under ambient pressure conditions, while the synthesis of the two modifications of PbO$_2$ requires high oxygen pressures, an electrochemical synthesis route or strongly oxidizing agents [6–8]. Studies of the thermal decomposition reactions of lead dioxide led to the discovery of the mixed-valent phases Pb$_2$O$_3$ and Pb$_{12}$O$_{19}$.

Several inorganic chemistry textbooks [9, 10] state, that naturally occurring lead compounds are all divalent. However, meanwhile it is known that besides the divalent minerals litharge ($\alpha$-PbO) and massicot ($\beta$-PbO), also minium ($\alpha$-Pb$_3$O$_4$), scrutinyite ($\alpha$-PbO$_2$) and plattnerite ($\beta$-PbO$_2$) with tetravalent lead have been found as minerals [11–13]. Lead dioxide is formed as an oxidation product during hydrothermal mineralization [12]. Plattnerite crystals can also be generated from Cu-Fe-Pb oxysulfide precursors under suitable Eh-pH conditions [14]. In this context it is interesting to note that plattnerite ($\beta$-PbO$_2$) has also been observed as product of the “black darkening” process (not to be confused with “brown darkening” of paints due to PbS formation with atmospheric hydrogen sulfide) of red lead pigments in artworks [15–17]. Humidity and hydrogen peroxide resulting from bacteria metabolism are discussed as parameters for the oxidation process.

The present contribution focuses on the structural characterization of natural plattnerite ($\beta$-PbO$_2$). So far, only X-ray and neutron powder diffraction data were reported, mostly for synthetic material [18–21] and for lead dioxide of charged electrodes of lead-acid batteries [22]. Plattnerite is a rare mineral. The historical background and details for the different deposits were summarized by White Jr. [23]. Several specimens are documented in diverse internet data bases, e.g. www.mineralienatlas.de, www.johnbetts-fineminerals.com or www.webmineral.com. Further mineral localities can be found

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through a simple internet search for the mineral name. Although most of these samples show well-shaped single crystals, to the best of our knowledge, no single crystal diffraction data of plattnerite have been published. Herein we report on single crystal X-ray and electron diffraction studies of plattnerite crystals from two different deposits.

2 Experimental

2.1 Sample selection

The first sample originated from Cap Garonne (Département du Var, région Provence-Alpes-Côte d’Azur), Mine du Pradet [24], one of the mineralogically most important places in France. Plattnerite crystallized in a small fissure on a quartz matrix. The neighboring phases were mimetite (Pb₅(AsO₄)₃Cl), cerusite (PbCO₃) and duftite (PbCu(AsO₄)OH). The plattnerite specimen was localized in the north mine (mine Nord) on pillar no. 20. A piece of this plattnerite specimen is shown in Fig. 1. The sample consists of thin intergrown platelets and the surface shows a blue black luster. The sample color and habit is similar to the plattnerite from Ojuela mine, Mapimí, Durango, Mexico (RRUFF data base entry R070605) [25].

The second sample is plattnerite AN12 from Mount Trevasco, Parre, Seriana Valley, Bergamo, Italy, (U07). The thin needles (Fig. 2) grew on a smithsonite (ZnCO₃) matrix. They have a slightly reddish luster. This is similar to plattnerite from Snake Pit, lower Mex-Tex mine, Hansonburg District, Socorro County, New Mexico, USA (RRUFF data base entry 080019) [25].

2.2 X-ray diffraction

The Cap Garonne sample was studied first. Plattnerite pieces were mechanically broken from the quartz matrix. A light-microscopic study of these pieces showed the strong crystal intergrowth and a slate-like structure. Several pieces were fixed on glass fibers using varnish and their quality was checked using a Buerger precession camera with white Mo radiation and an image plate technique. The Laue photographs showed split and elongated reflections, already pointing to multi-domain crystals. Intensity data of one of these pieces was subsequently collected at room temperature by using a STOE IPDS-II image plate system (graphite-monochromatized Mo radiation; \( \lambda = 71.073 \text{ pm} \)) in oscillation mode. The image plate data confirmed the multi-domain character. A reasonable integration of the data was not possible. Nevertheless, the refined lattice parameters of the domains of \( a = 494.7 \text{ pm} \) and \( c = 339.3 \text{ pm} \) confirmed the rutile type unit cell and were in good agreement with all previous literature data [18–22]. These multi-domain pieces were also used for an electron-microscopic study (vide infra).

Subsequently thin needles of the Mount Trevasco sample were broken from the zinc carbonate matrix, mounted to glass fibers and tested by Laue photographs. These needles (Fig. 3) were of good quality and showed sharp reflections in the Laue photographs. A first data set was collected at room temperature on the same STOE IPDS-II image plate diffractometer. A numerical absorption correction was applied to the data set.

Since the oxygen atoms showed a slight anisotropy at room temperature, we also collected data of the same crystal at \( T = 90 \text{ K} \) using a STOE StadiVari diffractometer (Mo microfocus source; Pilatus detection system). Due to a Gaussian-shaped profile of the StadiVari X-ray source
scaling was applied along with the numerical absorption correction. Details of both collections and the crystallographic parameters are listed in Table 1.

### 2.3 Structure refinements

The room temperature and 90 K data sets showed primitive tetragonal lattices and the systematic extinctions were in agreement with space group $P4_2/mnm$. The atomic parameters of the neutron powder diffraction study [19] were taken as starting values and both data sets were refined on $F^2$ values with the JANA2006 software package [26] with anisotropic atomic displacement parameters for all atoms. Separate refinements of the oxygen occupancy parameter revealed full occupancy within two standard deviations. The final difference Fourier syntheses revealed no significant residual electron density. The refined atomic positions and displacement parameters are given in Table 2.

CCDC 1900207 and 1900297 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

### 2.4 EDX data

Several mechanically broken fragments of the Cap Garonne sample and carefully selected needles of the Mount Trevasco sample were mounted on glass fibers with beeswax and studied by energy dispersive analyses of X-rays (EDX) using a Zeiss EVO® MA10 scanning electron microscope in variable pressure mode (60 Pa). The EDX analyses were conducted especially with respect to metal

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**Table 1:** Crystal data and structure refinement parameters for PbO$_2$ (Mount Trevasco specimen), space group $P4_2/mnm$, $Z=2$ and 239.2 g mol$^{-1}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature, K</th>
<th>293(1)</th>
<th>90(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters (single crystal data)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$, pm</td>
<td></td>
<td>495.81(10)</td>
<td>495.33(5)</td>
</tr>
<tr>
<td>$c$, pm</td>
<td></td>
<td>338.66(7)</td>
<td>338.67(4)</td>
</tr>
<tr>
<td>Unit cell volume $V$, nm$^3$</td>
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<td>0.0833</td>
<td>0.0831</td>
</tr>
<tr>
<td>Calculated density, g cm$^{-3}$</td>
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<td>9.54</td>
<td>9.56</td>
</tr>
<tr>
<td>Crystal size, $\mu$m$^3$</td>
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<td>$10 \times 10 \times 190$</td>
<td>$10 \times 10 \times 190$</td>
</tr>
<tr>
<td>Diffractometer type</td>
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<td>StadiVari (STOE)</td>
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<tr>
<td>Transmission (min/max)</td>
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</tr>
<tr>
<td>Detector distance, mm</td>
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<td>60</td>
<td>40</td>
</tr>
<tr>
<td>Exposure time, min</td>
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<td>7</td>
<td>53</td>
</tr>
<tr>
<td>$\omega$ range/increment, deg.</td>
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<td>0–180/1.0</td>
<td>0–180/0.3</td>
</tr>
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<td>Integr. Param. (A/B/EMS)</td>
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<td>14.0/-1.0/0.030</td>
<td>5.0/-2.0/0.030</td>
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<tr>
<td>Absorption coefficient, mm$^{-1}$</td>
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<tr>
<td>$F(000), e$</td>
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<td>196</td>
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<td>5.8–32.2</td>
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<td>$\pm 7, \pm 7, \pm 4$</td>
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<td>Total no. reflections</td>
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<td>Independent reflections/$R_{int}$</td>
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<td>117/0.0245</td>
<td>96/0.0208</td>
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<td>Reflections with $I &gt; 3 \sigma(I)$/$R_s$</td>
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<td>69/0.0031</td>
</tr>
<tr>
<td>Data/rel. parameters</td>
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<td>96/9</td>
</tr>
<tr>
<td>$R/WR$ for $I &gt; 3 \sigma(I)$</td>
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<td>0.0149/0.0503</td>
<td>0.0136/0.0491</td>
</tr>
<tr>
<td>$R/WR$ for all data</td>
<td></td>
<td>0.0303/0.0513</td>
<td>0.0181/0.0499</td>
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<tr>
<td>Extinction coefficient</td>
<td></td>
<td>52(11)</td>
<td>17(9)</td>
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<tr>
<td>Goodness-of-fit on $F^2$</td>
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<td>2.01</td>
</tr>
<tr>
<td>Largest diff. peak/hole, $e$ Å$^{-3}$</td>
<td></td>
<td>1.42/–1.43</td>
<td>1.00/–0.73</td>
</tr>
</tbody>
</table>
impurities. Some of the Cap Garonne fragments showed only lead as metal basis while few of them revealed up to 0.4 at% iron content. The needles of the Mount Trevasco sample showed similar behavior. Besides pure ones we observed iron and zinc contaminations in the same quantity as for the Cap Garonne sample. These are most likely surface contaminations.

### 2.5 Transmission electron microscopy (TEM)

Selected-area electron diffraction (SEAD) patterns and EDX analysis data of a small plattnerite single crystal (Cap Garonne sample; see Fig. 4) were recorded using a Philips CM-200 STEM transmission electron microscope (super twin objective lens, point resolution 0.23 nm, \(U_0 = 200\) kV) combined with a double-tilt low-background sample holder (Gatan) and an EDAX system. To obtain electron transparent particles a polycrystalline piece of plattnerite (approx. 50×50×20 \(\mu m^3\)) was crushed on a microscope slide under one drop of ethanol. The obtained crystal fragments were transferred as a suspension on a copper grid coated with holey carbon film (Plano GmbH, 200 mesh). Simulations of the experimental SAED patterns were done (kinematical intensities) using the JEMS software [27, 28]. TEM-EDX investigations confirmed the presence of Pb and O and small amounts of Fe up to 0.9 at% in accordance with previous SEM-EDX measurements (vide supra).

### 3 Crystal chemistry

The single crystal and electron diffraction data (see Figs. 5 and 6) confirm the rutile type structure for the naturally grown plattnerite crystals from Cap Garonne and Mount Trevasco. SAED patterns of the Cap Garonne sample showed no additional reflections hence excluding superstructure formation. This clearly manifests that contrary to some textbook opinions [9, 10] tetravalent lead minerals occur in nature, although rarely. Our lattice and positional parameters agree well with all previous work on synthetic lead dioxide [18–22]. The 293 and 90 K data sets gave no hints for additional reflections or structural distortions. This is in agreement with synthetic PbO\(_2\) which shows only pressure-induced phase transitions [29, 30]. The slight anisotropy of the oxygen displacement parameters at 293 K vanishes for the 90 K data and this is in line with the general observations for rutile-type oxides [31].

The plattnerite unit cell is presented in Fig. 7. Each lead cation has distorted octahedral oxygen coordination with 2×215.8 and 4×216.5 pm Pb–O. The compression of the octahedra in the unit cell \(c\) direction leads to \(O–Pb–O\) angles of 77.1 and 102.9°. As is well-known for this basic structure type, the PbO\(_6\) octahedra show a trans-edge condensation along the \(c\) axis to form rows which are condensed with neighboring rows (which are shifted by half the translation period \(c\)) through common corners. This leads to a slightly distorted trigonal planar lead coordination for the oxygen atoms (1×102.9 and 2×128.5° Pb–O–Pb). The plattnerite structure nicely fits into the rutile family of AB\(_2\) oxides [32, 33].

In the Experimental Section we mentioned the blue black, respectively slightly reddish luster of the dark samples. Crushed pieces of the minerals are similar to the dark brown-black synthetic PbO\(_2\) powders; however, the color cannot be described with the valence precise formulation Pb\(^{4+}\)2O\(^{2-}\). Recent high resolution valence band X-ray photoelectron and electron energy loss spectra showed that the metallic state (and thus the dark color)
of $\beta$-PbO$_2$ result from partial occupation of a conduction band that corresponds to strongly hybridized Pb6s-O2p states [34].

Finally we comment on minerals with tetravalent lead. Besides plattnerite ($\beta$-PbO$_2$) reported herein, and scrutinyite ($\alpha$-PbO$_2$) the mineral murdochite also contains tetravalent lead. Murdochite is a secondary mineral that formed in oxidized zones of lead-copper deposits. Originally, murdochite was reported with the composition Cu$_6$PbO$_8$ [35, 36]. This would result in an electron-precise formula 6Cu$^{2+}$Pb$^{4+}$8O$^{2-}$. Subsequently presented analytical data revealed that natural murdochite contains small amounts of chlorine and bromine, and the composition is in fact Cu$_x$PbO$_{8-x}$ (Cl, Br)$_{2x}$ ($x \leq 0.5$) [37–39]. With the highest halide ($X^-$) content the formula is 12Cu$^{2+}$2Pb$^{4+}$15O$^{2-}$2$X^-$. 

Fig. 5: Experimental and calculated SAED patterns of plattnerite (Cap Garonne sample) recorded along different zone axes. The calculation (kinematical intensities) was carried out by using crystal structure data from ref. [22].

Fig. 6: Goniometer positions and comparison of experimental (black font) and calculated (red font) tilt angles between the zone axes obtained by the recorded SAED series of the investigated plattnerite crystal (Cap Garonne sample).
Fig. 7: The crystal structure of PbO₂ (room temperature data). Lead and oxygen atoms are drawn as blue and magenta ellipsoids (90% probability level). The network of edge- and corner-sharing PbO₆ octahedra is emphasized.

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References