# PbWO₄-III (A High-Pressure Form)

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**Abstract.** PbWO₄-III, monoclinic, $P2_1/n$, $a = 12 \cdot 709$ (5), $b = 7 \cdot 048$ (3), $c = 7 \cdot 348$ (3) Å, $\beta = 90 \cdot 57$ (4)°, $Z = 8$, $D_c = 9 \cdot 19$ g cm⁻³. Crystals were prepared under high pressure at high temperature in the presence of water. PbWO₄-III is formally isomorphous with BaWO₄-II, but the coordination number of both sets of Pb atoms is eight.

**Introduction.** PbWO₄ occurs in nature as tetragonal stolzite (PbWO₄-I, scheelite-type) and monoclinic raspite (PbWO₄-II, unique structure, not wolframite-type). PbWO₄-II is 1·3% less dense than PbWO₄-I (Shaw & Claringbull, 1955), and has not yet been prepared synthetically. PbWO₄-III exists above the pressure $P$(kbar) $= 0 \cdot 7 + 0 \cdot 039\,T$(°C) ($T = 350$–$650$°C), and is quenchable to normal pressure (Chang, 1971).

Single crystals of PbWO₄-III were prepared by sealing precipitated PbWO₄-I with a small amount of distilled water in a thin-walled Pt capsule, treating this for 4h in a piston-cylinder device (Kennedy & LaMori, 1961) at 500°C, 32 kbar, and cooling slowly before release of pressure.

Intensities were collected on a Philips PW1100 four-circle diffractometer in the $\omega$–$2\theta$ mode with graphite-monochromated Mo $K\alpha$ radiation. A roughly spherical crystal with radius 0·1 mm was used. Data were collected to the limit of the Cu sphere ($\theta = 3 - 27 \cdot 4°$) at a scan rate of $0 \cdot 04°$ s⁻¹ and a constant scan width of 1·4°. The background was counted for half the total scanning time on each side of the reflexion. Of the 1501 independent reflexions measured, 399 were considered unobserved with $I < 2\sigma(I)$. The systematic absences were $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, indicating the space group $P2_1/n$. The large $\mu R$ of 8·73 necessitated absorption corrections, and corrections for a spherical crystal were applied.

Since the cell dimensions and space group indicated that PbWO₄-III is probably isomorphous with the high-pressure phase BaWO₄-II (Kawada, Kato & Fujita, 1974), the fractional coordinates found there were used as the starting point for full-matrix least-squares refinement. The temperature factors of the O atoms were refined isotropically. The function minimized was $\sum\omega(\Delta F)^2$ with $1/\sigma_F^2$ weights. $R = \sum\Delta F/\sum F_o$ and $R_w = [\sum\omega(\Delta F)^2/\sum\omega F]^{1/2}$ converged to final values of 0·056 and 0·066, respectively. The atomic parameters are listed in Table 1.*
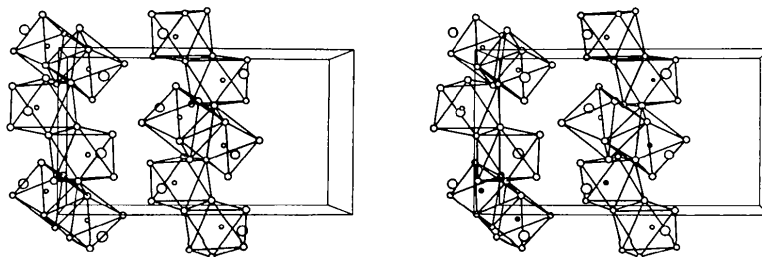
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Fig. 1. A stereo view (Johnson, 1971) of PbWO₄-III down $b$. $a$ is horizontal and $c$ vertical, down. Pb and W atoms are represented by the largest and smallest circles, respectively.

Table 1. *Fractional coordinates* ($\times 10^4$) *and thermal parameters* (Å² $\times 10^4$) *with e.s.d.'s*

Anisotropic thermal parameters are of the form $T = \exp[-2\pi^2(a^{*2}h^2 U_{11} + \ldots 2b^*c^*kl U_{23})]$.

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Pb(1) | 1486 (1) | 6887 (2) | 1568 (2) | 146 (7) | 152 (8) | 195 (7) | 14 (6) | 30 (5) | 21 (6) |
| Pb(2) | 1445 (1) | 9410 (2) | 6316 (2) | 165 (7) | 191 (8) | 148 (6) | −23 (6) | 41 (5) | 5 (6) |
| W(1) | 840 (1) | 1642 (2) | 876 (2) | 77 (7) | 67 (7) | 53 (6) | −4 (5) | 28 (4) | −4 (5) |
| W(2) | 894 (1) | 4520 (2) | 6499 (2) | 64 (6) | 70 (7) | 59 (6) | 2 (5) | 29 (4) | 11 (5) |

## Table 1 (cont.)

|  | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| O(1) | 958 (22) | 175 (43) | 2849 (37) | 157 (56) |
| O(2) | 1837 (20) | 5856 (40) | 7837 (34) | 116 (51) |
| O(3) | 559 (19) | 6450 (37) | 4755 (31) | 63 (46) |
| O(4) | 2159 (21) | 2556 (42) | 554 (38) | 155 (56) |
| O(5) | 522 (21) | 2726 (42) | 8267 (37) | 145 (53) |
| O(6) | 1754 (20) | 3099 (40) | 5238 (34) | 116 (51) |
| O(7) | 261 (20) | 3779 (40) | 1862 (35) | 121 (52) |
| O(8) | 789 (19) | 9198 (40) | 9416 (34) | 111 (50) |

All calculations were done with the X-RAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The scattering factors were taken from Cromer & Mann (1968). Cell dimensions were obtained from a least-squares fit of high-angle peaks in the powder pattern.

**Discussion.** PbWO₄-III is isomorphous with BaWO₄-II. The structure contains densely packed two-dimensional networks of slightly distorted WO₆ octahedra linked by Pb atoms. Fig. 1 illustrates two of these layers and their positions relative to the unit cell.

The bond lengths and angles are listed in Tables 2 and 4. The only significant differences between the structures of BaWO₄-II and PbWO₄-III are in the coordination around the Pb atoms. The average Pb–O distance is 2·67 Å for both sets of Pb atoms, while the average Ba–O distances are 2·83 and 2·76 Å for Ba(1) and Ba(2), respectively. Pb(1) is surrounded by eight O atoms between 2·43 and 2·88 Å with the next nearest, O(4), at 3·28 Å, whereas Ba(1) has nine O atoms, including O(4), surrounding it at distances between 2·72 and 3·05 Å with the next nearest at 3·20 Å. The comparison in Table 4 between the bond lengths in BaWO₄-II and PbWO₄-III clearly shows that the environments of the Ba and Pb atoms differ significantly. The lower effective coordination about Pb(1) compared to Ba(1) is reflected in the density. BaWO₄-II is 12·7% denser than scheelite-type BaWO₄-I, whereas PbWO₄-III is only 8·7% denser than scheelite-type PbWO₄-I.

## Table 2. Interatomic distances (Å) around W atoms

W–O

|  | W(1) |  | W(2) |
|---|---|---|---|
| O(1) | 1·79 (3) | O(2) | 1·81 (3) |
| O(4) | 1·81 (3) | O(3) | 1·91 (3) |
| O(7) | 1·83 (3) | O(5) | 1·88 (3) |
| O(5ⁱ) | 2·10 (3) | O(6) | 1·76 (3) |
| O(8ⁱⁱ) | 2·03 (3) | O(3ⁱⁱⁱ) | 2·17 (3) |
| O(8ⁱⁱⁱ) | 2·16 (3) | O(7ⁱⁱⁱ) | 2·26 (3) |
| Average | 1·95 | Average | 1·97 |

O–O

|  |  |  |  |
|---|---|---|---|
| Min. | 2·47 (3) | Min. | 2·51 |
| Max. | 3·06 | Max. | 2·96 |
| Average | 2·75 | Average | 2·75 |

Symmetry code: i $x,y,-1+z$; ii $x,-1+y,-1+z$; iii $-x,1-y,1-z$.

## Table 3. Bond angles (°) around W atoms (all angles have an e.s.d. of ±1°)

Around W(1) atom

|  | O(4) | O(7) | O(5ⁱ) | O(8ⁱⁱ) | O(8ⁱⁱⁱ) |
|---|---|---|---|---|---|
| O(1) | 104 | 101 | 165 | 87 | 90 |
| O(4) |  | 98 | 85 | 105 | 166 |
| O(7) |  |  | 89 | 154 | 83 |
| O(5ⁱ) |  |  |  | 80 | 80 |
| O(8ⁱⁱ) |  |  |  |  | 72 |

Around W(2) atom

|  | O(3) | O(5) | O(6) | O(3ⁱⁱⁱ) | O(7ⁱⁱⁱ) |
|---|---|---|---|---|---|
| O(2) | 98 | 98 | 100 | 162 | 82 |
| O(3) |  | 152 | 101 | 76 | 81 |
| O(5) |  |  | 98 | 82 | 80 |
| O(6) |  |  |  | 97 | 177 |
| O(3ⁱⁱⁱ) |  |  |  |  | 81 |

## Table 4. Interatomic distances (Å) between Pb and O atoms in PbWO₄-III, compared to the corresponding Ba–O distances in BaWO₄-II

Pb–O and Ba–O

|  | Pb(1) | Ba(1) |  | Pb(2) | Ba(2) |
|---|---|---|---|---|---|
| O(1ⁱ) | 2·59 (3) | 2·95 | O(1ⁱ) | 2·67 (3) | 2·67 |
| O(2ⁱⁱ) | 2·88 (3) | 2·76 | O(2) | 2·79 (3) | 2·79 |
| O(3) | 2·65 (3) | 2·81 | O(2ᵛ) | 2·49 (3) | 2·64 |
| O(4) | [3·28 (3)]* | 3·05 | O(3) | 2·63 (3) | 2·74 |
| O(4ⁱⁱⁱ) | 2·76 (3) | 2·76 | O(4ⁱⁱⁱ) | 2·61 (3) | 2·83 |
| O(5ⁱᵛ) | 2·57 (3) | 2·80 | O(5ⁱ) | 2·99 (3) | 3·05 |
| O(6ⁱⁱⁱ) | 2·75 (3) | 2·91 | O(6ⁱ) | 2·75 (3) | 2·85 |
| O(7) | 2·70 (3) | 2·75 | O(8) | 2·44 (3) | 2·52 |
| O(8ⁱⁱ) | 2·43 (3) | 2·72 | Average | 2·67 | 2·76 |
| Average | 2·67 | 2·83 |  |  |  |

Symmetry code: i $x,1+y,z$; ii $x,y,-1+z$; iii $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; iv $-x,1-y,1-z$; v $\frac{1}{2}-x,\frac{1}{2}+y,\frac{3}{2}-z$.

\* Not included in average value.

Phases similar to BaWO₄-II and PbWO₄-III may possibly occur at high pressures also in the corresponding molybdates. No ABO₄-type phases are known as yet that are more densely packed than BaWO₄-II.

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