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BaWO₄-II (A High-Pressure Form)

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Abstract. Monoclinic, $P2_1/n$, $a=13.159(12)$, $b=7.161(3)$, $c=7.499(6)$ Å, $\beta=93.76(5)^\circ$. $Z=8$. $D_m=7.17$, $D_x=7.26$ g cm⁻³. Crystals were synthesized under high pressure at high temperature. The structure has no direct resemblance either to the scheelite- or to the wolframite-type. It consists of densely packed layers of WO₆ octahedra, which are connected by edge- and corner-sharing; barium atoms are located between them. The coordination number of the barium atoms has increased in comparison with the structure under ordinary conditions.

Introduction. This phase exists above the pressure $P(\text{kbar})=26.7+0.0265 T(^\circ\text{C})$, ($T=600\text{--}1000^\circ\text{C}$), and is quenchable to normal pressure (Fujita, Yamaoka & Fukunaga, 1974).

The intensity data were collected on a Rigaku four-circle diffractometer with Mo $K\alpha_1$ ($\lambda=0.70926$ Å) radiation monochromatized by graphite. In the range $2\theta \leq 90^\circ$, 6099 independent reflexions were measured, of which 3791 were considered not observed. The systematic absences were $h0l$, $h+l=2n+1$, and $0k0$, $k=2n+1$, giving the space group $P2_1/n$ (No.14).

The positions of the barium and tungsten atoms were obtained by the Patterson superposition method. A difference Fourier synthesis revealed the positions of the oxygen atoms. In the subsequent full-matrix least-squares refinement using the program *ORFLS* (Busing, Martin & Levy, 1962), the temperature factors of the barium and tungsten atoms were assumed to be anisotropic. A uniform isotropic thermal parameter $B=0.0993$ was assigned to the oxygen atoms. This value corresponds to the mean of their B values at the refinement stage when $R=0.08$; individual B values vary from $-0.06(13)$ to $0.43(13)$. The final R value was 0.077 and the weighted R 0.096 for 2308 observed reflexions.*

The atomic scattering-factors for Ba and W were taken from *International Tables for X-ray Crystallography* (1962). That for O was taken from Hanson, Herman, Lea & Skillman (1964). The absorption correction was not applied ($\mu R=1.15$).

Discussion. Except for a few examples the ABO₄-type molybdates and tungstates generally crystallize either in the scheelite-type or in the wolframite-type structure (Sleight, 1972). The normal-pressure phase of BaWO₄ has the scheelite-type structure, whereas the high-pressure phase, has a new type of structure, containing densely packed two-dimensional networks of WO₆ octahedra. The increase in density of about 12.7% reflects this.

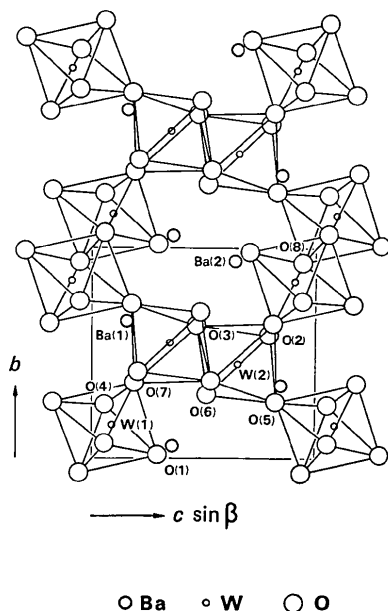


Fig. 1. Projection of the structure along the a axis. Atoms between $-\frac{1}{4} < x < \frac{1}{4}$ are depicted.

Table 1. Atomic coordinates

	x	y	z
Ba(1)	0.15779 (14)	0.65295 (34)	0.15643 (27)
Ba(2)	0.14304 (15)	0.93648 (33)	0.64178 (27)
W(1)	0.08053 (10)	0.15756 (20)	0.09206 (17)
W(2)	0.08515 (9)	0.44516 (20)	0.65503 (17)
O(1)	0.1091 (16)	0.0245 (32)	0.2972 (29)
O(2)	0.1745 (16)	0.5851 (32)	0.7973 (29)
O(3)	0.0524 (16)	0.6357 (33)	0.4705 (28)
O(4)	0.2110 (16)	0.2530 (32)	0.0571 (29)
O(5)	0.0499 (16)	0.2709 (32)	0.8235 (29)
O(6)	0.1716 (16)	0.3095 (32)	0.5222 (29)
O(7)	0.0219 (16)	0.3651 (33)	0.1887 (29)
O(8)	0.0740 (16)	0.9304 (33)	0.9467 (29)

* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30442 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Thermal parameters expressed as $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ Values are $\times 10^5$. The isotropic thermal parameter of the oxygen atoms was fixed at $B=0.0993$ (see text).

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba(1)	90 (8)	386 (32)	305 (25)	-11 (15)	6 (12)	-1 (29)
Ba(2)	123 (9)	397 (34)	258 (24)	-45 (15)	47 (12)	-10 (28)
W(1)	52 (5)	170 (18)	84 (14)	-3 (9)	-14 (7)	-16 (17)
W(2)	38 (5)	172 (19)	87 (14)	-2 (9)	-20 (7)	47 (17)

Tables 1 and 2 list the positional and thermal parameters. Projections of the structure along the a and b axes are shown in Figs. 1 and 2. For simplicity, only the atoms between $-\frac{1}{4} < x < \frac{1}{4}$ are shown in Fig. 1. As can be observed in these projections, the structure of this high-pressure phase is built up of zigzag layers of WO_6 octahedra parallel to (100); these zigzag layers are linked by barium atoms.

Each layer consists of eight- and four-membered rings of WO_6 octahedra; in the former type of ring each pair of edge-shared octahedra is linked with another by corner-sharing, while in the latter all octahedra are linked by corner-sharing.

The WO_6 octahedra are slightly distorted and the tungsten atoms are slightly shifted from their centres. W(1) has four near oxygen atoms at distances from 1.83 to 1.96 Å, and two oxygen atoms at greater

distances of 2.13 and 2.18 Å. Likewise W(2) also has four near oxygen atoms at distances from 1.83 to 1.97 Å, and two oxygens at greater distances of 2.07 and 2.33 Å. It is to be noted that these distances and bond angles (Tables 3 and 4) around the tungsten atoms are not significantly different from those of WO_6 octahedra at normal pressure (Gebert & Kihlborg, 1969; Kihlborg & Gebert, 1970).

In comparison with the structure at normal pressure, however, the barium atoms have essentially higher coordination numbers. Ba(1) is surrounded by nine oxygen atoms at distances from 2.72 to 3.05 Å, and Ba(2) by eight oxygen atoms at distances from 2.52 to 3.05 Å (Fig. 3, Table 5). They have next nearest oxygen atoms at 3.20 and 3.37 Å respectively.

Table 3. Interatomic distances (Å) around W atoms

	W(1)		W(2)
W-O			
O(1)	1.83 (2)	O(2)	1.83 (2)
O(4)	1.88 (2)	O(3)	1.97 (2)
O(7)	1.84 (2)	O(5)	1.86 (2)
O(5 ⁱ)	2.18 (2)	O(6)	1.84 (2)
O(8 ⁱⁱ)	1.96 (2)	O(3 ⁱⁱⁱ)	2.07 (2)
O(8 ⁱⁱⁱ)	2.13 (2)	O(7 ⁱⁱⁱ)	2.33 (2)
Average	1.97	Average	1.98
O-O			
Min.	2.37 (4)	Min.	2.44 (5)
Max.	3.01 (3)	Max.	2.98 (3)
Average	2.76	Average	2.77

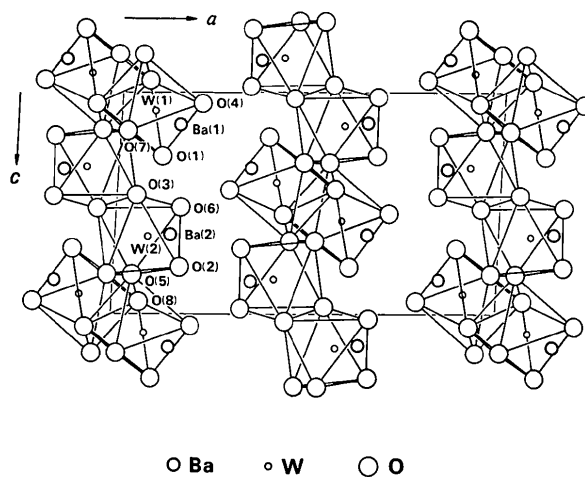
Symmetry code

i	$x,$	$y,$	$-1+z$
ii	$x,$	$-1+y,$	$-1+z$
iii	$-x,$	$1-y,$	$1-z$

Table 4. Bond angles around W atoms ($\angle \text{O-W-O}$)

For symmetry code see Table 3.

Around W(1) atom					
	O(4)	O(7)	O(5 ⁱ)	O(8 ⁱⁱ)	O(8 ⁱⁱⁱ)
O(1)	99.6 (0.9)	99.1 (1.0)	170.2 (0.9)	92.0 (1.0)	95.9 (0.9)
O(4)		99.8 (1.0)	81.5 (0.9)	103.4 (0.9)	163.7 (0.9)
O(7)			90.4 (0.9)	152.2 (0.9)	82.6 (0.9)
O(5 ⁱ)				78.3 (0.9)	82.4 (0.8)
O(8 ⁱⁱ)					70.9 (1.0)
Around W(2) atom					
	O(3)	O(5)	O(6)	O(3 ⁱⁱⁱ)	O(7 ⁱⁱⁱ)
O(2)	97.6 (0.9)	98.7 (1.0)	102.0 (1.0)	158.0 (0.9)	77.0 (0.9)
O(3)		152.9 (0.9)	95.8 (0.9)	74.3 (1.0)	80.7 (0.8)
O(5)			101.8 (1.0)	82.6 (0.9)	82.1 (0.9)
O(6)				99.2 (0.9)	176.0 (0.9)
O(3 ⁱⁱⁱ)					81.5 (0.8)

Fig. 2. Projection along the b axis.

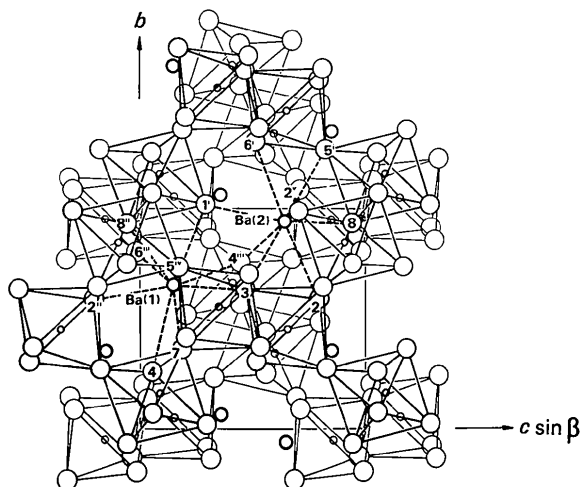


Fig. 3. Coordination of barium atoms (broken lines). Oxygen atoms are identified only by numbers. For the symmetry-operation superscripts see Table 5.

The calculations were carried out on the FACOM 270-20 of the National Institute for Researches in Inorganic Materials. Bond lengths and angles were calculated using the program *ORFFE* (Busing, Martin & Levy, 1964).

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Table 5. *Interatomic distances (Å) between Ba and O atoms and between metal atoms*

Ba-O	Ba(1)	Ba(2)
O(1 ⁱ)	2.95 (2)	O(1 ⁱ) 2.67 (2)
O(2 ⁱⁱ)	2.76 (2)	O(2) 2.79 (2)
O(3)	2.81 (2)	O(2 ^v) 2.64 (2)
O(4)	3.05 (2)	O(3) 2.74 (2)
O(4 ⁱⁱⁱ)	2.76 (2)	O(4 ⁱⁱⁱ) 2.83 (2)
O(5 ^{iv})	2.80 (2)	O(5 ⁱ) 3.05 (2)
O(6 ⁱⁱⁱ)	2.91 (2)	O(6 ⁱ) 2.85 (2)
O(7)	2.75 (2)	O(8) 2.52 (2)
O(8 ⁱⁱ)	2.72 (2)	
Average	2.83	Average 2.76
Next nearest neighbour		Next nearest neighbour
O(1 ⁱⁱⁱ)	3.20 (2)	O(7 ^{iv}) 3.37 (2)
Ba—Ba	Min.	3.878 (4)
W—W	Min.	3.219 (3)
Ba(1)—W(1)		3.713 (3)
Ba(2)—W(2)		3.603 (3)

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	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$

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3,5-Dinitropyridine

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Abstract. 3,5-Dinitropyridine, $C_5H_3N_3O_4$, is orthorhombic, space group $P2_12_12_1$; $a=19.918(3)$, $b=6.465(1)$, $c=5.272(1)$ Å, $Z=4$, $D_m=1.65$, $D_c=1.654$ g cm⁻³. One of the two nitro groups is approximately coplanar with the ring system; the other is rotated by 7°. This small but significant rotation is very likely due to packing interactions.

Introduction. Crystals of 3,5-dinitropyridine are pale yellow prisms elongated along the chosen crystallo-

graphic b axis. The cell dimensions were obtained by a least-squares fit to the $\sin^2\theta$ values of 48 hkl reflexions measured on a diffractometer. The density was measured by flotation in dilute Thoulet (K_2HgI_4) solution. Crystal data are given in Table 1. For the data collection, a crystal with approximate dimensions $0.40 \times 0.20 \times 0.15$ mm was sealed in a Lindemann-glass capillary. Intensities were collected on a Syntex automated diffractometer with Mo $K\alpha$ radiation [λ (Mo $K\alpha$) = 0.7107 Å; graphite monochromator] and a variable