THE CRYSTAL STRUCTURE OF $PbWO_4$

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Translated from Kristallografiya, Vol. 15, No. 5,
pp. 1067-1068, September-October, 1970
Original article submitted April 14, 1970

$PbWO_4$ is historically the first member of the morphotropic [1] series of tungstates and molybdates of divalent cations (Ca, Sr, Cd, Ba, Pb) with the general formula ABX_4 and with a scheelite structure.

Single crystals of Pb tungstates were synthesized by I. S. Potkin in the Institute for the Synthesis of Mineral Raw Materials. The experimental data for the structural determination was provided by layer lines ($h0l - h3l$) with 90 independent and nonzero reflections (Weissenberg r meter, Mo radiation). The intensity of the reflections was estimated by the normal $2^{1/4}$ scale of blackening. The symmetry of the x-ray photographs and the regular extinctions indicated the tetragonal space group $C_{4h}^6 = I4_1/a$. The unit cell parameters (a = 5.50 ± 0.01 Å and c = 12.12 ± 0.02 Å) were determined from x-ray rotation photographs using further reflections.

The structure was interpreted from the lateral xz projection. With fixed positions of the heavy atoms of Pb and W the coordinates of the two quasi-independent O atoms were found. These were confirmed by normal and differential Fourier syntheses. The coordinates of the basic oxygen were refined, by the use of the least-squares method based on a three-dimensional program using the intensities from $h0l$-$h3l$ scans, with an M-20 computer at the Moscow University Computer Center. The final dispersion factor for the $PbWO_4$ structure was $R_{hkl} = 5\%$ (B = 0.1 Å^2). The coordinates of the basis atoms are given in Table 1. The interatomic distances in the W tetrahedron calculated from these coordinates are found to be: W–O = 1.804; O_1–O_3 = 2.948, O_1–O_4 = 2.943 Å. These values correspond to those normally found in a Pb polyhedron (Table 2).

TABLE 1. Coordinates of the Basis Atoms in $PbWO_4$ (origin at one of the centers of inversion*)

Atom	x/a	y/b	z/c
Pb	0.500	0.750	0.125
W	0.000	0.250	0.125
O	0.221	0.401	0.389

*At the common edge of two Pb polyhedra (see Fig. 1).

A comparison of the interatomic distances in Ca, Ba, Sr, Cd and Pb polyhedra (Table 2) indicates that the distance in the Pb tungstate polyhedron is

TABLE 2. Interatomic Distances (Å) in Ca, Ba, Sr, Cd, and Pb Polyhedra

Distance	$CaWO_4$	$SrWO_4$	$SrMoO_4$	$CdMoO_4$	$BaWO_4$	$BaMoO_4$	$PbWO_4$
$Me - O_1$ (4)	2.438	2.49	2.46	2.28	2.68	2.615	2.645
$Me - O_6$ (4)	2.479	2.59	2.50	2.51	2.688	2.761	2.670
$O_5 - O_6$ (4)	2.767	3.09	2.90	2.92	2.994	2.901	2.907
$O_1 - O_7$ (4)	2.870	3.14	2.91	2.96	3.286	2.979	3.135
$O_1 - O_6$ (4)	2.93	2.84	3.01	2.99	3.292	3.060	3.393
$O_1 - O_5$ (2)	3.03	3.07	3.13	2.94	3.328	3.239	3.494
$O_7 - O_6$ (4)	3.14	3.84	3.84	3.84	4.081	3.964	4.055

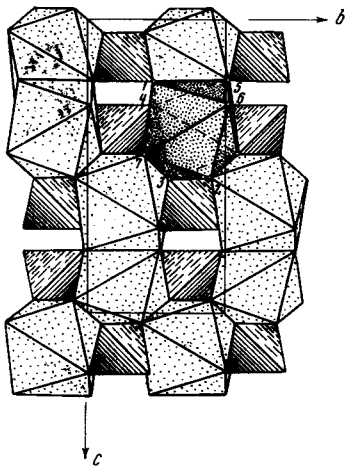

Fig. 1. The structure of $PbWO_4$ in terms of polyhedra: xz projection; designated O atoms at one of the four sets of eight apices around the Pb in the cell.

closest to the analogous distance in $BaWO_4$ with respect to the closeness of the ionic radii Ba^{2+} (r = 1.42 Å) and Pb^{2+} (r = 1.29 Å). In the $PbWO_4$ structure (Fig. 1) the $CaWO_4$ scheelite motif is qualitatively repeated.

LITERATURE CITED

1. A. V. Chichagov, L. N. Dem'yanets, V. V. Ilyukhin, and N. V. Belov, Kristallografiya, 11, 4, 686 (1966) [Sov. Phys. – Crystallogr., 11, 588 (1967)].