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A neutron crystallographic investigation of lead molybdenum oxide, $PbMoO_4$

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With 1 figure

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Auszug

Die Sauerstoffparameter der Struktur eines Vertreters des Scheelit-Typs des Bleimolybdänoxyds oder Wulfenits, wurden mittels Neutronenbeugung an einem Kristall bestimmt. Die Koordinaten des Sauerstoffs ergaben sich nach der Verfeinerung mit der Methode der kleinsten Quadrate zu $x_0 = 0{,}2352$, $y_0 = 0{,}1134$, $z_0 = 0{,}0439$. Die Struktur besteht aus MoO_4-Tetraedern mit dem Mo—O-Abstand von 1,772 Å, was auf kovalente Bindung weist. Jedes Bleiatom ist von 8 Sauerstoffatomen umgeben, die zu 8 verschiedenen MoO_4-Tetraedern gehören. Die Pb—O-Abstände betragen 2,610 Å und 2,630 Å, je viermal.

Abstract

The oxygen parameters in one representative of the scheelite-type structure: lead molybdenum oxide, wulfenite, were determined by neutron diffraction using a single crystal. The following coordinates of the oxygen atom were found:

$$x_0 = 0.2352, \quad y_0 = 0.1134, \quad z_0 = 0.0439.$$

The refinement was carried out by a least-squares procedure on an electronic computer. The structure consists of MoO_4 tetrahedra. The Mo—O distance within this tetrahedron is 1.772 Å indicating a covalent link. Each lead atom is surrounded by 8 oxygen atoms belonging to 8 different MoO_4 units. The Pb—O distances are: 2.610 Å, four times, and 2.630 Å, four times.

1. Introduction

The problem of the oxygen parameters in the scheelite-type structure has been a point of interest in crystal chemistry for a long time. Since Vegard[1] published the determination of the crystal structure

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[1] L. Vegard, Results of crystal analysis, space lattices and atomic dimensions. Skr. Norske Vid. Akad. Oslo (1925) No. 11.

of $CaWO_4$ it has been firmly established that the space group of scheelite is $I4_1/a$; calcium atoms occupying the $4b$ sites and tungsten atoms the $4a$ sites respectively, forming two interpenetrating diamond-like arrangements. Consequently the oxygen atoms were placed at $16f$ sites. The crystallographic data are summarized in Table 1.

Table 1. *Crystallographic data on the scheelite-type structure*[2]

Space group: C_{4h}^{6}—$I4_1/a$				
4 X atoms (X = Ca,Pb) at $4b$	$0\,\frac{1}{4}\,\frac{5}{8}$,	$0\,\frac{3}{4}\,\frac{3}{8}$,	$\frac{1}{2}\,\frac{3}{4}\,\frac{1}{8}$,	$\frac{1}{2}\,\frac{1}{4}\,\frac{7}{8}$
$4A$ atoms (A = W,Mo) at $4a$	$0\,\frac{1}{4}\,\frac{1}{8}$,	$0\,\frac{3}{4}\,\frac{7}{8}$,	$\frac{1}{2}\,\frac{3}{4}\,\frac{5}{8}$,	$\frac{1}{2}\,\frac{1}{4}\,\frac{3}{8}$
16 oxygen atoms at $16f$				

$$(0\,0\,0,\ \tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}) \pm (x\,y\,z,\ \ \bar{x}\ \ \tfrac{1}{2}-y\ \ z,\ \ \tfrac{3}{4}-y\ \ \tfrac{1}{4}+x\ \ \tfrac{1}{4}+z,\ \ \tfrac{1}{4}+y\ \ \tfrac{1}{4}-x\ \ \tfrac{1}{4}+z)$$

The cell dimensions of all crystals belonging to this type of structure differ very little. On the other hand, very different parameters have been assigned to the oxygen atoms suggesting considerable differences in the shapes and orientations of XO_4 tetrahedra. The oxygen coordinates in a number of molybdates and wolframates were critically revised by SILLÉN and NYLANDER[3] by the use of stereochemical considerations supported by powder and single-crystal x-ray data. However, it should be noted, that the majority of AXO_4 compounds with the scheelite structure contain atoms with high atomic numbers. These are dominating in the scattering of x-rays causing considerable inaccuracy in the determination of the coordinates of the oxygen atoms. The neutron-diffraction method is here of advantage, since the coherent scattering amplitudes for thermal neutrons are of the same order of magnitude. For example, in the case of $PbMoO_4$ they are[4]:

$$b_{Pb} = 0.960 \pm 0.005 \times 10^{-12}\,\mathrm{cm}$$

$$b_{O} = 0.58 \pm 0.02 \times 10^{-12}\,\mathrm{cm}$$

$$b_{Mo} = 0.661 \pm 0.005 \times 10^{-12}\,\mathrm{cm}.$$

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[2] International tables for x-ray crystallography, Vol. 1. Kynoch Press, Birmingham (1952) p. 178.

[3] L. G. SILLÉN and A. NYLANDER, On the oxygen positions in tungstates and molybdates with the scheelite structure. Ark. Kemi, Min. Geol. **17** A (1943) No. 4.

The lead molybdenum oxide has been chosen for investigation because of the author's interest in the crystal chemistry of divalent lead-oxygen compounds. Besides, sufficiently large single crystals of wulfenite suitable for a single-crystal neutron-diffraction study were available.

2. Experiment

A single crystal of wulfenite from Los Lamentos, Mexico, $2 \times 2 \times 4$ mm in dimension was examined under a polarizing microscope, cut to an approximately spherical shape with a diameter of about 2 mm and mounted on a goniometer head. The crystal was subsequently oriented by x-rays and neutrons making the [001] axis vertical. The tetragonal symmetry was confirmed in preliminary measurements by checking the equality of the intensity of equivalent reflections of $hk0$ type. The space-group absences of $I4_1/a$ were found to be absences for neutron diffraction also. The reflections of the $h0l$ and $hk0$ zones were collected on a spectrometer placed at the reactor JEEP I operating at a power of 550 kW. The wavelength used was 1.05 Å. Only reflections up to $2\theta = 115°$ were measured due to the geometrical limitations of the spectrometer. All the reflections in the $h0l$ zone within the limits mentioned were recorded, as the structure factors $F(h0l)$, $F(\bar{h}0l)$, $F(h0\bar{l})$, $F(\bar{h}0\bar{l})$ are equal owing to symmetry, an average of these was used. In the $hk0$ zone there are two groups of reflections:

1. $h + k = 4n + 2$. In this case $F(hk0) \neq F(h\bar{k}0)$. However, the structure factors $F(hk0)$ and $F(h\bar{k}0)$ are of the same absolute value but differ in sign.
2. $h + k = 4n$. Here, $F(hk0) = F(k\bar{h}0) \neq F(h\bar{k}0)$.

All reflections occurring in this zone were measured within the limits mentioned. The intensities of equivalent reflections were averaged.

The integrated intensities were derived by measuring the areas under the diffraction peaks. From these the experimental structure factors were obtained in the usual way. The lattice constants were determined by x-rays using a standard 114 mm diameter camera with Straumanis film mounting. They were refined on a Ferranti Mercury computer using a least-squares programme written by E. WAIT[5].

$$a = 5.4312 \pm 0.0016 \text{ Å}, \qquad c = 12.1065 \pm 0.0039 \text{ Å}.$$

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[4] D. I. HUGHES and R. B. SCHWARTZ (1958), Neutron cross sections, 2nd. Ed., Upton, New York, Brookhaven National Laboratory.

[5] E. WAIT, A Mercury computer programme for the analytical refinement of crystal unit cell parameters by the method of least squares. A.E.R.E.-R 3598 (1961).

3. The refinement procedure

The approximate parameters of the oxygen atoms were found by Fourier projections of the "nuclear" density on the (001) and (010) planes respectively. Only higher-than-average structure factors were used for preparing both projections. The assignment of the signs to the experimental structure factors was made on the basis of lead and molybdenum atomic coordinates. In this way the following trial parameters for oxygen were found:

$$x_O = 0.26, \qquad y_O = 0.12, \qquad z_O = 0.04.$$

For comparison SILLÉN and NYLANDER[3] reported:

$$x_O = 0.25 \qquad y_O = 0.13 \qquad z_O = 0.075$$

The oxygen parameters derived from the Fourier projections were refined further by a three-dimensional treatment using only observable reflections and varying the above parameters, the scaling factor and the isotropic temperature factor for all atoms. A least-squares programme for the Ferranti Mercury computer prepared by H. KEILHAU and H. M. SEIP[6] was adopted. No correction for extinction has been introduced. However the reflections which could possibly be affected were left out in the two initial cycles. The weights were taken equal to $(A+F_o+cF_o^2)^{-1}$ where: $A = 2F_{\min}$, $c = 0.01$. Temperature factors with $B = 1.2$ Å^2 for oxygen and $B = 0.8$ Å^2 for the metal atoms were adopted at the initial stage of the refinement. After four cycles the following data were obtained, the discrepancy factor being $6.03\,{}^0/_0$:

$$\begin{aligned} x_O &= 0.2352 & \sigma(x) &= 0.00068 \\ y_O &= 0.1134 & \sigma(y) &= 0.00073 \\ z_O &= 0.0439 & \sigma(z) &= 0.00024. \end{aligned}$$

The isotropic temperature factors:

$$\begin{aligned} B_O &= 1.317 \text{ Å}^2 & \sigma(B_O) &= 0.0507 \\ B_{Pb} &= 1.079 \text{ Å}^2 & \sigma(B_{Pb}) &= 0.0502 \\ B_{Mo} &= 0.678 \text{ Å}^2 & \sigma(B_{Mo}) &= 0.0641. \end{aligned}$$

A list of observed and calculated structure factors for all independent reflections is presented in Table 2.

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[6] H. KEILHAU and H. M. SEIP (1962), unpublished.

Table 2. *Observed and calculated structure factors*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	4	117.82	-110.86	2	0	4	392.73	-411.49	3	0	11	89.59	83.25	5	0	9	105.55	-109.10
0	0	8	52.77	53.17	2	0	8	397.64	409.47	3	0	13	126.41	107.61	6	0	0	180.41	178.96
0	0	12	511.78	-583.91	2	0	10	149.73	136.17	3	0	15	85.91	- 86.41	6	0	2	159.55	-164.11
0	0	16	142.57	142.22	2	0	12	73.64	- 73.79	4	0	0	273.69	278.75	6	0	4	257.73	-260.64
0	2	0	68.73	- 60.62	2	0	14	83.46	88.21	4	0	2	293.32	307.26	6	0	8	273.69	235.10
0	4	0	273.69	278.75	2	0	16	245.46	251.57	4	0	4	279.82	-278.97	6	0	10	148.50	142.75
0	6	0	180.41	-178.98	2	2	0	331.37	-361.61	4	0	8	262.64	259.98	6	0	12	144.82	-150.92
0	8	0	432.01	371.87	2	4	0	445.51	479.51	4	0	10	268.78	-267.28	6	6	0	102.97	-114.50
1	0	1	27.00	16.61	2	6	0	97.69	- 94.07	4	0	12	196.37	-224.86	7	0	1	57.68	- 60.98
1	0	3	54.00	- 50.70	2	-6	0	283.87	-294.50	4	0	14	169.37	-173.14	7	0	3	142.37	-124.83
1	0	5	186.55	183.85	3	0	1	141.14	-142.04	4	0	16	200.05	193.91	7	0	5	116.59	120.29
1	0	7	166.91	-169.97	3	0	3	126.41	127.42	4	2	0	335.42	-367.45	7	0	7	109.23	- 96.39
1	0	9	46.64	27.72	3	0	5	152.18	-137.20	4	6	0	425.26	-430.75	8	0	0	432.01	371.87
2	0	0	68.73	60.62	3	0	7	131.32	131.55	4	-6	0	278.84	-309.35	8	0	4	125.18	-118.22
2	0	2	163.23	-156.64	3	0	9	90.82	- 82.04	5	0	3	141.14	131.72	8	-2	0	200.05	-175.62

4. Discussion

The main feature of the structure is the existence of four short Mo—O bonds of 1.772 Å each, directed towards the corners of a slightly compressed regular tertahedron. The interatomic distances with their standard deviations and the bond angles within this tetrahedron are shown below (for numbering of atoms, see Fig. 1):

$$\left.\begin{array}{l} \mathrm{Mo_I{-}O_I} \\ \mathrm{Mo_I{-}O_{III'}} \\ \mathrm{Mo_I{-}O_V} \\ \mathrm{Mo_I{-}O_{VII'}} \end{array}\right\} \quad 1.772\ \text{Å} \qquad \sigma(d) = 0.006\ \text{Å}$$

$$\begin{array}{ll} \mathrm{O_I{-}Mo_I{-}O_{III'}} & 112^\circ 50' \\ \mathrm{O_I{-}Mo_I{-}O_V} & 107^\circ 40' \end{array}$$

The standard deviations for both angles are approximately 1 °.

The edges of the coordination tetrahedron are:

$$\left.\begin{array}{l} \mathrm{O_I{-}O_V} \\ \mathrm{O_V{-}O_{III'}} \\ \mathrm{O_{III'}{-}O_{VII'}} \\ \mathrm{O_{VII'}{-}O_I} \end{array}\right\} \quad 2.865\ \text{Å}$$

$$\left.\begin{array}{l} \mathrm{O_I{-}O_{III'}} \\ \mathrm{O_V{-}O_{VII'}} \end{array}\right\} \quad 2.955\ \text{Å}$$

The observed Mo—O bonds are shorter than the sum of Pauling ionic radii which is 1.92 Å after coorrection for a tetrahedral coordination, indicating a contribution of covalent bonding. The Mo—O distance of 1.77 Å was also found[3] in $SrMoO_4$. The next four oxygen atoms are at the much larger distance of 3.150 Å. The MoO_4 tetrahedra do not share common oxygen atoms but are linked through Pb—O bonds rather than by O—O interactions. The latter distances are greater than the sum of van-der-Waals radii for oxygen.

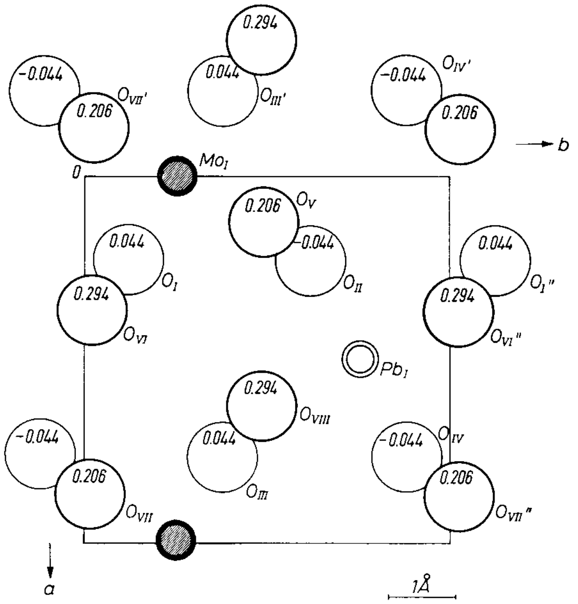

Fig. 1. A projection along the c axis of a section of the $PbMoO_4$ structure. Only atoms occurring between $z/c = -0.05$ and $z/c = +0.30$ are shown

Each lead atom is surrounded by 8 oxygens belonging to 8 different MoO_4 units. Four of them are at a distance of 2.610 Å and four others at the slightly larger distance of 2.630 Å. The next nearest oxygens are: two at 3.872 Å and two at 4.547 Å. The sum of the Pauling ionic radii for lead and oxygen corrected for the coordination number 8 is 2.70 Å. These eight oxygen atoms are at the corners of two interpenetrating tetrahedra forming an eightfold coordination group around each Pb atom.

Each Pb atom is surrounded by 8 molybdenum atoms: four at the corners of a square with $d_{\text{Pb-Mo}} = 3.840$ Å and further four at the corners of a tetrahedron with $d_{\text{Pb-Mo}} = 4.064$ Å. Similarly, each Mo atom is in turn surrounded by 8 lead atoms with the same coordination.

5. Acknowledgements

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