A neutron crystallographic investigation of lead molybdenum oxide, PbMoO$_4$

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With 1 figure (Received March 3, 1963)

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 CaWO₄, it has been firmly established that the space group of scheelite is I₄₁/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

<table>
<thead>
<tr>
<th>Space group: C₁₅₁₄₁/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>4X atoms (X = Ca, Pb) at 4b</td>
</tr>
<tr>
<td>4A atoms (A = W, Mo) at 4a</td>
</tr>
<tr>
<td>16 oxygen atoms at 16f</td>
</tr>
</tbody>
</table>

\[ \{0 0 0, \frac{1}{2} \frac{1}{2} \} \pm \{x y z, \frac{2}{3} - y z, \frac{1}{3} - y + x \frac{1}{2} + z, \frac{1}{2} + y \frac{1}{2} - x \frac{1}{2} + z\} \]

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 XO₄ tetrahedra. The oxygen coordinates in a number of molybdates and wolframates were critically revised by Sillén and Nylander by the use of stereochemical considerations supported by powder and single-crystal x-ray data. However, it should be noted, that the majority of AXO₄ 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 PbMoO₄ they are:

\[ b_{\text{Mo}} = 0.960 \pm 0.005 \times 10^{-12} \text{ cm} \]
\[ b_{\text{O}} = 0.58 \pm 0.02 \times 10^{-12} \text{ cm} \]
\[ b_{\text{Mo}} = 0.661 \pm 0.005 \times 10^{-12} \text{ cm} \]


\(^3\) 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, $2 \times 2 \times 4 \text{ mm}$ 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 $h0l\theta$ type. The space-group absences of $I4_1/a$ were found to be absences for neutron diffraction also. The reflections of the $h0l$ and $hk0\theta$ 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 $\theta = 115^\circ$ 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 $F(h0l)$, $F(h0l)$, $F(h0l)$, $F(h0l)$ are equal owing to symmetry, an average of these was used. In the $hk0\theta$ zone there are two groups of reflections:

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

2. $h + k = 4n$. Here, $F(hk0\theta) = F(kh0\theta) \neq F(hk0\theta)$. 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 Straumann's film mounting. They were refined on a Ferranti Mercury computer using a least-squares programme written by E. Wait.

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

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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:

\[ x_o = 0.26, \quad y_o = 0.12, \quad z_o = 0.04. \]

For comparison SILLÉN and NYLANDER\(^3\) reported:

\[ x_o = 0.25, \quad y_o = 0.13, \quad z_o = 0.075. \]

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: \(A = 2F_{\text{min}}, c = 0.01\). Temperature factors with \(B = 1.2 \, \text{Å}^2\) for oxygen and \(B = 0.8 \, \text{Å}^2\) 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\(^9\)%:

\[ x_o = 0.2352 \quad \sigma(x) = 0.00068 \]
\[ y_o = 0.1134 \quad \sigma(y) = 0.00073 \]
\[ z_o = 0.0439 \quad \sigma(z) = 0.00024. \]

The isotropic temperature factors:

\[ B_O = 1.317 \, \text{Å}^2 \quad \sigma(B_O) = 0.0507 \]
\[ B_{\text{Pb}} = 1.079 \, \text{Å}^2 \quad \sigma(B_{\text{Pb}}) = 0.0502 \]
\[ B_{\text{Mo}} = 0.678 \, \text{Å}^2 \quad \sigma(B_{\text{Mo}}) = 0.0641. \]

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.
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 tetrahedron. The interatomic distances with their standard deviations and the bond angles within this tetrahedron are shown below (for numbering of atoms, see Fig. 1):

\[
\begin{align*}
\text{Mo}_1-\text{O}_1 & \quad 1.772 \ \text{Å} & \quad \sigma(d) = 0.006 \ \text{Å} \\
\text{Mo}_1-\text{O}_{11'} & \\
\text{Mo}_1-\text{O}_v & \\
\text{Mo}_1-\text{O}_{v11'} & \\
\text{O}_1-\text{Mo}_1-\text{O}_{11'} & \quad 112°50' \\
\text{O}_1-\text{Mo}_1-\text{O}_v & \quad 107°40' \\
\end{align*}
\]

The standard deviations for both angles are approximately 1°.

The edges of the coordination tetrahedron are:

\[
\begin{align*}
\text{O}_1-\text{O}_v & \quad 2.865 \ \text{Å} \\
\text{O}_v-\text{O}_{11'} & \\
\text{O}_{11'}-\text{O}_{v11'} & \\
\text{O}_{v11'}-\text{O}_1 & \\
\end{align*}
\]

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 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.

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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