MEMOIRS OF THE COLLEGE OF SCIFNCE, UNIVERSITY OF KYOTO, SERIES B,
Vol. XXIV, No. 2 Geology and Mineralogy, Article 3, 1957

The Crystal Structure of Wulfenite, $PbMoO_4$

By

Takaharu ARAKI

Geological and Mineralogical Institute, University of Kyoto

(Received July 25, 1957)

Abstract

The crystal structure of wulfenite, $PbMoO_4$ was determined by means of X-ray oscillation photographing. The unit cell has the dimensions of a=5.47Å, c=12.18Å and the space group is $C_{4h}^6-I4_1/a$. There are four chemical units of $PbMoO_4$ in the unit cell. The coordinates of atoms were found by two dimensional Fourier synthesis and those of oxygen atoms were further refined by the difference synthesis.

Introduction

Hitherto several authors have determined lattice constants, numbers of chemical unit, space groups and atomic coordinates of the minerals of scheelite type structure. But, only a few results of X-ray studies on wulfenite have so far been reported. DICKINSON (1920) was the first to examine the structure of wulfenite and soon after VEGARD and REFSUM (1927). The atomic coordinates of oxygen atoms in the structure were, however, not fully determined. On the other hand, SILLÉN and NYLANDER (1943) found coordinates of oxygen atoms of this mineral, applying the rigid sphere method which based on certain assumption. It is desirable, however, that these coordinates are checked X-ray crystallographically.

Experimental

Specimens found in Bolivia, South America, were submitted to the present study. X-ray photographings were carried out using unfiltered Cu-K radiations throughout.

The lattice constants were determined by the a- and c-axis rotation photographings. The lattice constants thus obtained are as follows:

$$a = 5.47 \pm 0.01 \text{ Å} \quad c = 12.18 \pm 0.02 \text{ Å}$$

the annexed errors being the probable errors. The result is in good agreement with that reported by previous authors. The ratio, a : c = 1 : 2.226 is also in good agreement with axial ratio given in the Dana's System of Mineralogy. The number

of chemical unit of $PbMoO_4$ in the unit cell is 4. The space group is $C_{4h}^6-I4_1/a$, hkl reflexions being present only when $h+k+l=2n$, $hk0$ reflexions only when $h=2n$, $k=2n$ and $00l$ reflexions only when $l=4n$. The results are also in good agreement with those reported by the previous authors.

Structure analysis

Intensities of the reflexions on the oscillation photographs were estimated

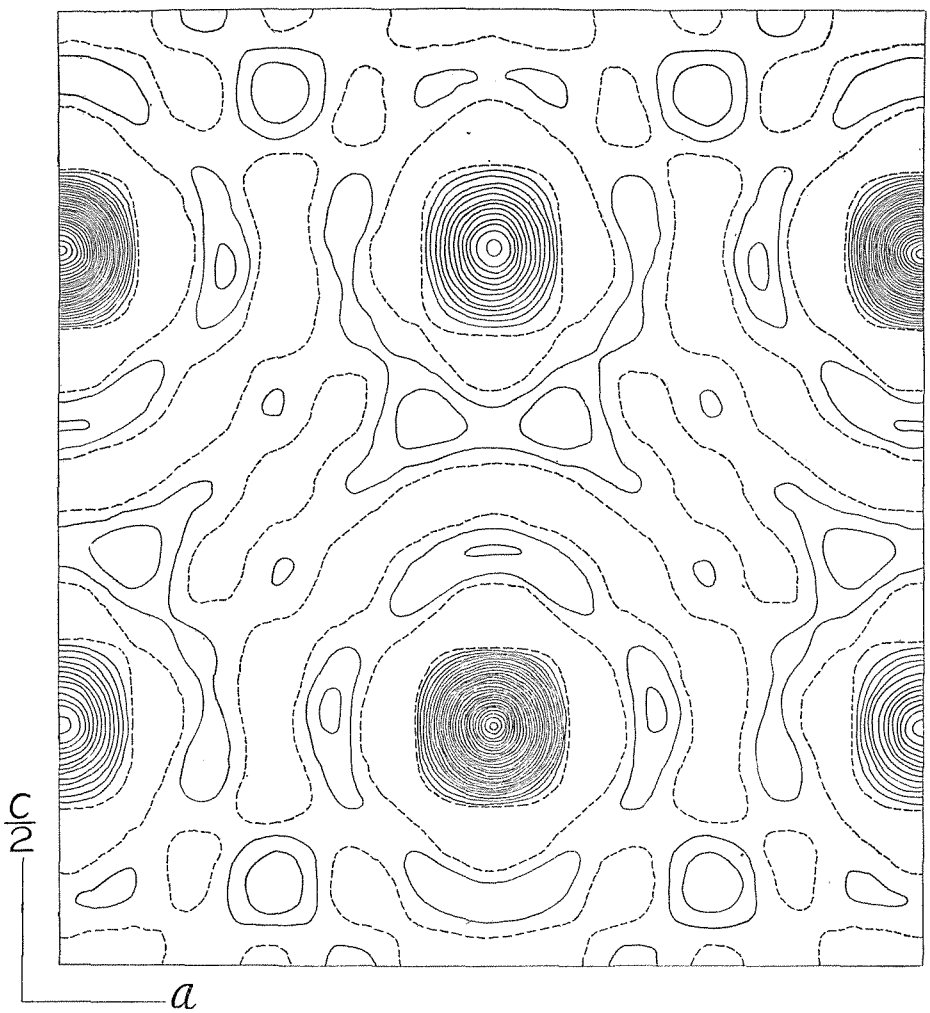

Fig. 1. Electron density in the [010] projection, obtained in the final summation. Contours at intervals of 10 e. $Å^{-2}$. Zero contours are broken.

visually with the aid of intensity edge and corrected for the Lorentz and polarization factors, but not for absorption nor temperature factors. The corrected intensities, which approximately proportional to the structure factors were then converted to a set of numbers.

It was proposed by the previous authors that metal atoms of some compounds of scheelite type structure were located on the special positions and in the present case it was confirmed that heavy atoms were located on that positions from the observation of strong reflexions. Therefore, the signs of F_0's whose values were relatively large could be easily found. At the outset, the electron densities in the [010] and the [001] projections were evaluated by means of two dimensional Fourier synthesis using F_0's whose signs could be determined, and the maxima in the electron density maps, which represent the positions of heavy atoms, were found to coincide exactly with the special positions. Subsequently, the coordinates of oxygen atoms were searched for by the method of trial and error using the intensities of reflexions, to which heavy atoms do not contribute. Then, the approximate structure of wulfenite could be found.

For the refinement of the coordinates of atoms, two dimensional Fourier summations were carried out using F_0's at first, whose signs were settled from the approximately determined structure, at intervals of 1/60 of the cell edges with the aid of Beevers and Lipson strips. But, final summation were at intervals of 1/60 and 1/120 of a- and c-cell edge respectively. For scattering factors Thomas-Fermi's values for heavy atoms and Viervoll and Ögrim's values for oxygen atoms were used. After repeating the summation several times, giving necessary corrections for the coordinates of oxygen atoms, the maxima in the electron density map, which represent the positions of oxygen atoms, almost coincided with coordinates of the atoms. In Fig. 1 are shown the electron density in the [010] projection, obtained in the final summation.

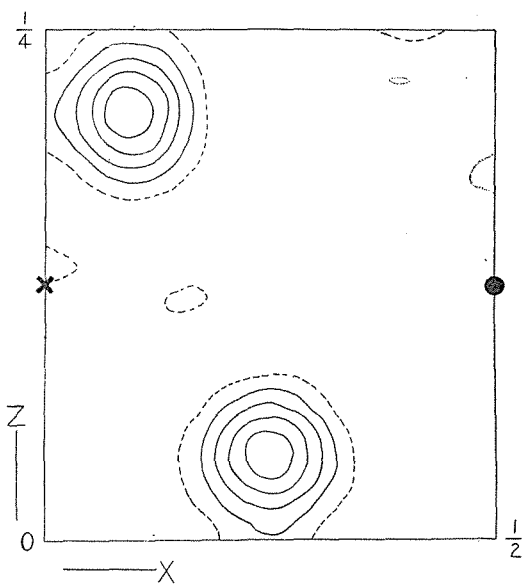

Fig. 2. Electron density in the [010] projection, obtained in the final difference synthesis. Contours at intervals of 4 e.Å^{-2}. Zero contours are broken, negative contours dotted. Positions of *Pb* and *Mo* atoms are marked by solid circle and cross respectively.

For further refinement of the coordinates of oxygen atoms, difference synthesis was then carried out, using the differences between F_0's and $F(Pb, Mo)$'s. Where, $F(Pb, Mo)$'s are the calculated structure factors

to which only *Pb* and *Mo* atoms contribute. After repeating this synthesis several times, giving necessary corrections, the maxima in the electron density map satisfactorily coincided with the coordinates of oxygen atoms chosen. In Fig. 2 are shown the electron density in the [010] projection, obtained in the final difference synthesis.

The coordinates of atoms found in the final structure are given in Table 1. The termination errors of the atomic coordinates in the [010] projection are given in Table 2.

Table 1. Coordinates of atoms in the structure of wulfenite.

Atom	Number of atoms in the unit cell	x/a	y/b	z/c
Pb	4	0.000	0.250	0.625
Mo	4	0.000	0.250	0.125
O	16	0.247	0.342	0.040

Table 2. Termination errors.

Atom	x (Å)	y (Å)	z (Å)
Pb	0.000		0.000
Mo	0.000		0.000
O	0.003	0.005	0.020

In Table 3 are summarized F_0's and F_c's. F_c's are calculated with atomic coordinates finally obtained and F_0's are rendered, at the final stage of the analysis, comparable on an approximately absolute scale by multiplying a factor which minimumizes the sum of differences between corresponding F_0 and F_c.

Table 3. Observed and calculated structure factors for *hk*0 and *h*0*l* reflexions.

hkl	F_0	F_c	*hkl*	F_0	F_c	*hkl*	F_0	F_c	*hkl*	F_0	F_c
020	246	−376	$4\bar{6}0$	202	−221	10.13	55	66	30.13	72	66
040	287	326	600	265	213	10.15	48	−56	402	57	45
060	299	−213	620	235	−254	202	21	−61	404	264	−297
200	245	376	$6\bar{2}0$	271	−259	204	188	−388	406	—	3
220	224	−335	640	235	221	206	—	−3	408	191	266
$2\bar{2}0$	273	−335	$6\bar{4}0$	202	223	208	232	319	40.10	22	−28
240	231	326	004	273	−362	20.10	38	29	40.12	191	−242
$2\bar{4}0$	310	331	008	307	304	20.12	207	−246	501	87	−78
260	315	−259	0012	328	−316	20.14	23	24	503	86	90
$2\bar{6}0$	271	−254	101	25	−95	301	102	−96	505	84	50
400	279	326	103	32	73	303	84	93	507	55	−49
420	266	−331	105	69	133	305	31	79	509	64	−81
$4\bar{2}0$	310	−326	107	97	−122	307	34	−75	602	—	−1
440	252	232	109	81	−63	309	61	−77	604	264	−266
$4\bar{4}0$	252	232	10.11	87	66	30.11	80	71	606	—	0
460	235	−223									

The reliability numbers, $R=\frac{\sum||F_o|-|F_c||}{\sum|F_o|}$, are 0.20 for $hk0$ and 0.29 for $h0l$ reflexions.

Description of the structure

The structure of wulfenite is illustrated in Fig. 3. It is essentially of the scheelite type structure reported by the previous authors. However, comparing the coordinates of oxygen atoms with those obtained by the rigid sphere method, there

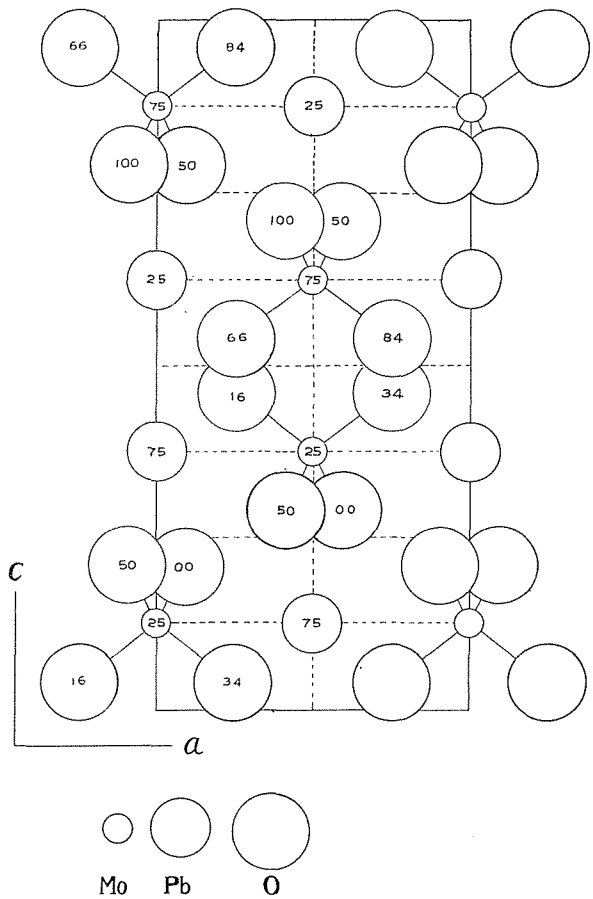

Fig. 3. The crystal structure of wulfenite, projected on (010) plane. Numbers denote the heights of atoms expressed by the percentage of b-translation.

are appreciable differences especially in y-coordinate and with those of scheelite and $BaWO_4$, there are also considerable differences in coordinates.

Mo atom is situated at the center of tetrahedron of four oxygen atoms, whereas *Pb* atom is surrounded by eight oxygen atoms which form somewhat irregular polyhedron. Each *O* atom is shared by one *Mo* and two *Pb* atoms. Interatomic distances are given in Table 4.

Table 4. Interatomic distances.

Atom Atom	Distance (Å)	Atom Atom	Distance (Å)
Mo——O	1.77	O_1——O_2'	2.94
Pb_1——O	2.49	O_1——O_6	3.28
Pb_2——O	2.82	O_1——O_7	3.34
O_1——O_2	2.88	O_1——O_7'	3.40
O_1——O_3	2.90	O_1——O_8	4.02
O_1——O_4	2.90	O_1——O_9'	4.03
O_2——O_3	2.90	O_1——O_{10}'	4.25
O_2——O_4	2.90	O_1——O_3'	4.32
O_3——O_4	2.88	O_1——O_{11}'	4.53
O_1——O_5'	2.90		

Acknowledgment

The writer wishes to express his sincere thanks to Prof. Dr. T. ITO and Mr. T. UEDA who kindly gave him advice in this work. He is also indebted to Dr. K. SAKURAI who sent him precious specimens used in the present experiment. He is also grateful to Dr. K. TANAKA, and to Messrs. Y. FUJIWARA, T. SETO who afforded facilities in taking X-ray photographs.

References

DICKINSON, R. G. (1920): J. Am. Chem. Soc., **42**, 85.
SILLÉN, L. G. and NYLANDER, A. (1943): Arkiv. Kem. Min. Geol., **17 A**, No. 4, 1.
VEGARD, L. and REFSUM, A. (1927): Norsk. Geol. Tidsskr., **9**, 24.