

The Crystal Structure of $\text{Li}_2\text{WO}_4(\text{IV})$ and Its Relation to the Wolframite-Type Structure

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$\text{Li}_2\text{WO}_4(\text{IV})$, the densest phase among four polymorphs, crystallizes with monoclinic symmetry, $C2/c$, $a = 9.753(1) \text{ \AA}$, $b = 5.954(1) \text{ \AA}$, $c = 4.994(1) \text{ \AA}$, $\beta = 90.58(2)^\circ$, $Z = 4$, $D_{\text{calc}} = 6.00 \text{ g cm}^{-3}$. The structure was determined by 1765 counter-measured independent reflections with a single crystal synthesized at 40 kbar and 850°C , and refined to $R = 0.067$ by the full-matrix least-squares method. It is based on a hexagonal closest arrangement of oxygen atoms and is structurally closely related to the wolframite-type structure. Both the tungsten and the lithium atoms are in octahedral sites. The structure consists of four octahedral layers parallel to (100). The first and the third layers are filled by lithium atoms, resulting in LiO_6 octahedral sheets, while the second and the fourth contain zigzag chains of WO_6 octahedra observed in the wolframite structure.

Introduction

Four polymorphic phases of Li_2WO_4 were studied by Yamaoka *et al.* (1) and by Pistorius (2) under high pressures and high temperatures. $\text{Li}_2\text{WO}_4(\text{I})$ has a structure similar to that of phenakite, Be_2SiO_4 (3), i.e., both the tungsten and the lithium atoms are tetrahedrally coordinated by oxygen atoms in the structure. $\text{Li}_2\text{WO}_4(\text{II})$ has a structure based on the cubic closest packing of oxygen atoms and is closely related to the β -phase of Mg_2SiO_4 (4-6). $\text{Li}_2\text{WO}_4(\text{III})$ has a structure with orthorhombic symmetry based on the hexagonal closest packing of oxygen atoms (7) but no detailed structure data have been

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reported. $\text{Li}_2\text{WO}_4(\text{IV})$ has a structure with monoclinic symmetry based on the hexagonal closest packing of oxygen atoms in which both the tungsten and the lithium atoms are in octahedral sites (4, 8). The detail of the structure analyzed with a single crystal, however, has not been reported.

In this paper, the structure of $\text{Li}_2\text{WO}_4(\text{IV})$ and its relationship to the wolframite-type structure are discussed.

Experimental

The specimen of $\text{Li}_2\text{WO}_4(\text{IV})$ used in this work was synthesized at 40 kbar and 850°C by means of an uniaxial piston-cylinder press. A fragment of single crystal with an approximate size of $0.130 \times 0.100 \times 0.115 \text{ mm}^3$ was used to determine the space

group and lattice constants, and to collect intensity data. The monoclinic symmetry and systematic absences of reflections with l odd for $h0l$ observed in precession photographs establish the space group $C2/c$. Cell dimensions were precisely determined by the least-squares method using 53 high-angle reflections ($27 K\alpha_1$ and $26 K\alpha_2$ reflections) which were measured on a four-circle diffractometer. The crystal data are summarized in Table I. The intensities of 1765 independent reflections within the range $0^\circ < 2\theta \leq 107^\circ$ were obtained using a four-circle diffractometer employing the 2θ - ω scan technique. $MoK\alpha$ radiation monochromatized by pyrolytic graphite was used. Conventional polarization and Lorentz corrections were carried out in the process of data collection. Of all reflections measured, 52 had zero intensity and 111 had high standard deviations ($F_0 < 3\sigma_{hkl}$).

Structure Analysis and Refinement

The positions of tungsten and oxygen atoms were found from the diagrams of the Patterson syntheses. After a few cycles of least-squares refinements of positions, lithium atoms were found by the $F_o - F'_c$ syntheses in which the F'_c 's were calculated with tungsten and oxygen atoms. Further refinements of positional and thermal parameters with isotropic temperature factors gave an R factor of 0.081 for all reflections. Anisotropic temperature factors for all atoms, and the parameter C for the secondary extinction effect (ρ), were introduced in the final stage of refinement. The value of C is 3.5×10^{-6} . Unit weight was used for all reflections. The final R value is 0.067 for refinement with all reflections. The R values for 1713 reflections omitting undetectable intensities and for 1602 reflections with lower standard deviations

TABLE I
CRYSTALLOGRAPHIC DATA AND REFINED POSITIONAL AND THERMAL PARAMETERS OF
 $Li_2WO_4(IV)^a$

Crystallographic data							
Synthesized at 40 kbar and 850°C, monoclinic, space group $C2/c$ (No. 15), $a = 9.753(1) \text{ \AA}$, $b = 5.954(1) \text{ \AA}$, $c = 4.994(1) \text{ \AA}$, $\beta = 90.58^\circ$, $V = 290.00 \text{ \AA}^3$, $Z = 4$. $D_{\text{calc}} = 6.00 \text{ g cm}^{-3}$, molecular weight = 261.73, $\mu(MoK\alpha) = 405.4 \text{ cm}^{-1}$.							
Positional parameters							
Atom	Position	Mult.	x	y	z		
W	$4e$	$\frac{1}{2}$	0	0.32837(6)	$\frac{1}{4}$		
O(1)	$8f$	1	0.3927(6)	0.1002(10)	0.4415(11)		
O(2)	$8f$	1	0.1263(6)	0.1420(10)	0.1221(13)		
Li	$8f$	1	0.299(3)	0.353(5)	0.246(5)		
Thermal parameters							
Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{eq}/A^2
W	0.00113(2)	0.00198(5)	0.00180(11)	0	-0.00010(3)	0	0.30
O(1)	0.0013(3)	0.0037(9)	0.0034(11)	-0.0008(4)	-0.0010(5)	0.0004(8)	0.42
O(2)	0.0013(3)	0.0028(9)	0.0090(15)	-0.0013(4)	0.0008(6)	0.0001(9)	0.54
Li	0.006(3)	0.012(6)	0.007(6)	-0.002(3)	0.002(3)	-0.005(5)	1.51

^a Anisotropic temperature factors in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. B_{eq} : Equivalent isotropic temperature factors computed according to the relation $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij}(a_i \cdot a_j)$. Estimated standard deviations are given in parentheses.

($F_0 \geq 3\sigma_{hkl}$) are 0.063 and 0.045, respectively. Fully ionized scattering factors were taken from the International Tables for X-ray Crystallography, Vol. IV (10), for W^{6+} and Li^+ , and from Tokonami (11) for O^{2-} ions. All computations of the Patterson and Fourier syntheses, least-squares refinements of the structure, and interatomic distances were carried out using the programs 3DFR (Iitaka, private communication), RSFLS (12), and BADTEA (13) at the Computation Center of Osaka University. The F_0 and F_c table has been deposited¹. The final atomic parameters are given in Table I. Interatomic distances and angles are listed in Table II.

Discussion of the Structure

The structure of Li_2WO_4 (IV) is based on a distorted hexagonal closest arrangement of oxygen atoms parallel to (100) like a wolframite-type structure. The crystal structure of Li_2WO_4 (IV) with the a -axis twice that of wolframite, $(\text{Mn, Fe})\text{WO}_4$, is shown in Fig. 1. The tungsten and the lithium atoms occupy one-half and all of the octahedral holes of the oxygen octahedral layers, respectively, which are alternated along the a -axis. Li_2WO_4 (I) (3) crystallizes with phenakite structure, i.e., both the tungsten and the lithium atoms are in tetrahedral sites. In the structure of Li_2WO_4 (II) (4-6), the tungsten and one-half of the lithium atoms occupy one-half of the octahedral sites while the other half of the lithium atoms occupy

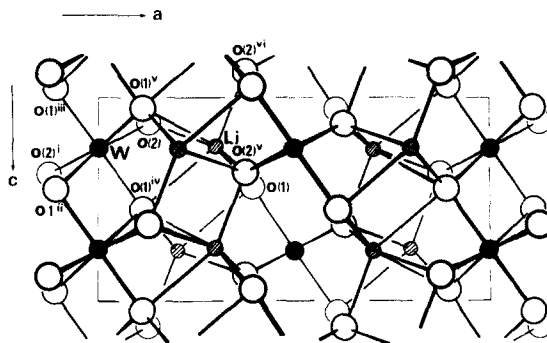


FIG. 1. Crystal structure of Li_2WO_4 (IV) projected along the b -axis.

one-eighth of the tetrahedral sites. Thus the number of co-ordinated oxygen atoms around the cations increases from the lower to the higher pressure phases: $\text{Li}_2^{\text{IV}}\text{W}^{\text{IV}}\text{O}_4$ (I) \rightarrow $\text{Li}^{\text{IV}}\text{Li}^{\text{VI}}\text{W}^{\text{VI}}\text{O}_4$ (II) \rightarrow $\text{Li}_2^{\text{VI}}\text{W}^{\text{VI}}\text{O}_4$ (IV). Although the details of the structure of Li_2WO_4 (III) is still unknown, the fundamental framework of the structure was reported by Wilhelmi *et al.* (7).

The LiO_6 octahedra in the structure of Li_2WO_4 (IV) build sheets parallel to (100), sharing their octahedral edges. The WO_6 octahedra construct zigzag chains running along the c -axis, sharing their octahedral edges, which are commonly observed in the wolframite-type structures. The LiO_6 octahedral sheets and octahedral layers including the WO_6 zigzag chains alternate along the a -axis. There are four oxygen octahedral layers in the unit translation along the a -periodicity of Li_2WO_4 (IV).

The schematic representation of the cation distribution is given in Fig. 2, in which ferberite, FeWO_4 , one of the typical tungstates with the wolframite-type structures (14), and one of the double tungstates closely related to the wolframite-type structures, $\text{LiYb}(\text{WO}_4)_2$ (15), are also shown. In the structure of ferberite, layers I and III, and II and IV, are equivalent by the lattice translation, respectively. In the structure of Li_2WO_4 (IV), the second and the fourth layers contain the WO_6 zigzag chains. These

¹ To obtain F_0 and F_c tables, see NAPS document No. 03554 for 12 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering, however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are \$5.00. Microfiche are \$3.00. Outside the U.S. and Canada add postage of \$3.00 for photocopy and \$1.00 for microfiche.

TABLE II
 INTERATOMIC DISTANCES (Å) AND ANGLES (DEGREES) OF $\text{Li}_2\text{WO}_4(\text{IV})^a$

WO_6 octahedron				LiO_5 octahedron			
W-O(1) ⁱⁱ	2.155(6)	[2]		Li-O(1) ^{iv}	2.47(3)		
-O(1) ⁱⁱⁱ	1.903(6)	[2]		-O(1) ^v	2.56(3)		
-O(2)	1.781(6)	[2]		-O(2)	2.18(3)		
Mean	1.946			-O(1)	1.99(3)		
	Angle	Distance		-O(2) ^{vi}	1.98(3)		
	O-W-O	O-O		-O(2) ^v	1.99(3)		
				Mean	2.20		
				Angle	Distance		
	O-Li-O	O-O					
O(1) ⁱⁱ -O(1) ⁱⁱⁱ	85.8(2)	2.769(5)	[2] _{f_{WL}}	O(1) ^{iv} -O(1) ^v	66.9(8)	2.769(5)	<i>f_{WL}</i>
-O(1) ^{iv}	74.9(3)	2.476(12)	[2] _{e_{WW}}	-O(2)	69.9(9)	2.674(9)	<i>f_{WL}</i>
-O(1) ^v	82.6(3)	2.845(12)		-O(1)	97.1(10)	3.360(12)	<i>e_{LL}</i>
-O(2) ⁱ	88.1(3)	2.750(8)	[2] _{f_{WL}}	-O(2) ^v	88.0(10)	3.114(9)	<i>e_{LL}</i>
O(1) ⁱⁱⁱ -O(2)	102.9(3)	2.881(8)	[2]	O(1) ^v -O(2)	70.5(9)	2.750(8)	<i>f_{WL}</i>
-O(2) ⁱ	93.0(3)	2.674(9)	[2] _{f_{WL}}	-O(2) ^{vi}	85.6(10)	3.114(9)	<i>e_{LL}</i>
O(2)-O(2) ⁱ	103.1(4)	2.789(13)		-O(2) ^v	83.1(10)	3.045(9)	<i>e_{LL}</i>
Mean		2.728		O(2)-O(1)	93.6(12)	3.045(9)	<i>e_{LL}</i>
				-O(2) ^{vi}	92.1(11)	2.999(12)	<i>e_{LL}</i>
				O(1)-O(2) ^{vi}	107.3(14)	3.203(9)	
				-O(2) ^v	108.9(13)	3.240(8)	
				O(2) ^{vi} -O(2) ^v	98.9(13)	3.015(6)	
				Mean		3.027	

Symmetry operations				
None	<i>x</i>	<i>y</i>	<i>z</i>	
i	- <i>x</i>	<i>y</i>	$\frac{1}{2}-z$	
ii	$-\frac{1}{2}+x$	$\frac{1}{2}+y$	<i>z</i>	
iii	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$	
iv	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$1-z$	
v	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	
vi	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$-z$	

^a *f_{WL}*, face shared between WO_6 and LiO_6 octahedra; *e_{WW}*, edge shared between two WO_6 octahedra; *e_{LL}*, edge shared between two LiO_6 octahedra. Numbers in brackets are multiplicity factors.

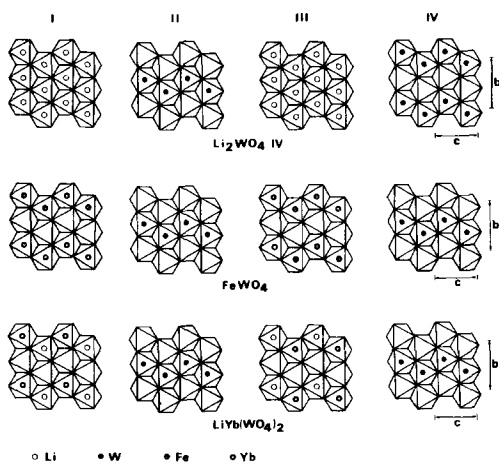


FIG. 2. Cation arrangement in oxygen octahedra of $\text{Li}_2\text{WO}_4(\text{IV})$ and its comparison with other tungstates. The structures of FeWO_4 and $\text{LiYb}(\text{WO}_4)_2$ were obtained from the results of Ülkü (14) and Klevtsova and Belov (15), respectively.

zigzag chains can also be found in FeWO_6 and $\text{LiYb}(\text{WO}_4)_2$. The only difference in the octahedral layers including the WO_6 zigzag chains between $\text{Li}_2\text{WO}_4(\text{IV})$ and the other tungstates is the relative arrangement of layers II and IV. There is no shift in FeWO_4 and $\text{LiYb}(\text{WO}_4)_2$; however, layers II and IV in $\text{Li}_2\text{WO}_4(\text{IV})$ are mutually displaced by $b/2$. In the structure of $\text{Li}_2\text{WO}_4(\text{IV})$, all the oxygen octahedra of layers I and III are filled by lithium atoms, resulting in LiO_6 octahedral sheets. On the other hand, only one-half of the oxygen octahedra are filled by such cations as Fe, Li, and Yb in layers I and III of FeWO_4 and $\text{LiYb}(\text{WO}_4)_2$, resulting in octahedral zigzag chains of the same type as the WO_6 zigzag chains. Thus, the distribution of the cations in layers I and III differs markedly between $\text{Li}_2\text{WO}_4(\text{IV})$ and the

other tungstates in Fig. 2. The same structural relationship as discussed above can also be observed between $\text{Li}_2\text{WO}_4(\text{IV})$ and other tungstates related to the wolframite-type structure such as $\text{LiR}(\text{WO}_4)_2$, where R is Ga, Fe, and so on (15, 16).

The mean distances between cations and oxygen atoms are 1.946 and 2.20 Å for WO_6 and LiO_6 , respectively. The difference is almost attributed to the ionic radii of Li^+ , 0.78 Å, and W^{6+} , 0.65 Å. The mean distances of $\text{W}-\text{O}$ and $\text{Li}-\text{O}$ are almost comparable with those of other tungstates such as $\text{Li}_2\text{WO}_4(\text{II})$, 1.951 and 2.14 Å (5), $\text{LiGa}(\text{WO}_4)_2$, 1.95 and 2.14 Å (16), and $\text{LiYb}(\text{WO}_4)_2$, 1.97 and 2.21 Å (15). The $\text{O}-\text{O}$ distances surrounding tungsten atoms are in the range of 2.476 to 2.881 Å, while those of LiO_6 vary from 2.674 to 3.360 Å, resulting in mean distances of 2.728 and 3.027 Å, respectively.

The $\text{O}(1)^{\text{ii}}-\text{O}(1)^{\text{iv}}$ bond, which is a shared edge in the WO_6 zigzag chain, is the shortest, 2.476 Å, and the $\text{O}-\text{O}$ bonds which form the shared faces between WO_6 and LiO_6 octahedra are smaller than the others. The shortening of distances between oxygens involved in edge and face sharing are due to the results of strong $\text{W}^{6+}-\text{W}^{6+}$ and $\text{W}^{6+}-\text{Li}^+$ repulsion. This phenomenon was discussed for olivine and spinel by Kamb (17). The repulsion between W^{6+} and Li^+ causes the lithium atom to shift markedly its position from the center of the octahedron. This results in a considerable deviation from 90° of the $\text{O}-\text{Li}-\text{O}$ angles and a wide range of the $\text{Li}-\text{O}$ distances in the LiO_6 octahedron.

References

1. S. YAMAOKA, O. FUKUNAGA, T. ONO, E. IZUKA, AND S. ASAMI, *J. Solid State Chem.* **6**, 280 (1973).
2. C. W. F. T. PISTORIUS, *J. Solid State Chem.* **13**, 325 (1975).
3. W. H. ZACHARIASEN AND H. A. PLETINGER, *Acta Crystallogr.* **14**, 229 (1961).
4. H. HORIUCHI, N. MORIMOTO, AND S. YAMAOKA, "1975 Annual Meeting Abstracts", p.44, Mineralogical Society of Japan (in Japanese) (1975).
5. H. HORIUCHI, N. MORIMOTO, AND S. YAMAOKA, *J. Solid State Chem.* **30**, 129 (1979).
6. K. WALTERSSON, P.-E. WERNER, AND K.-A. WILHELM, *Cryst. Struct. Commun.* **6**, 231 (1977).
7. K.-A. WILHEMI, K. WALTERSSON, AND P. LÖFGREN, *Cryst. Struct. Commun.* **6**, 219 (1977).
8. K. WALTERSSON, P.-E. WERNER, AND K.-A. WILHELM, *Cryst. Struct. Commun.* **6**, 225 (1977).
9. W. H. ZACHARIASEN, *Acta Crystallogr.* **16**, 1139 (1963).
10. "International Tables for X-Ray Crystallography," Vol. IV, pp. 71-98, Kynoch Press, Birmingham (1974).
11. M. TOKONAMI, *Acta Crystallogr.* **19**, 486 (1965).
12. T. SAKURAI, "Universal Crystallographic Computation Program System (I) (UNICS)", pp. 61-65, Crystallographic Society of Japan (1967).
13. L. W. FINGER, "University of Minnesota program for computing Bond Angles and Distances, and Thermal Ellipsoids with error Analysis" (1968).
14. D. ÜLKÜ, *Z. Kristallogr.* **124**, 192 (1967).
15. R. F. KLEVTSOVA AND M. V. BELOV, *Sov. Phys. Crystallogr.*, **15**, 32 (1970).
16. P. V. KLEVTSOVA, A. V. DEMENEV, AND R. F. KLEVTSOVA, *Sov. Phys. Crystallogr.* **16**, 440 (1971).
17. B. KAMB, *Amer. Mineral.* **53**, 1439 (1968).