The Crystal Structure of Li₂WO₄II: A Structure Related to Spinel

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Li₂WO₄II, synthesized at 3 kbar and 630°C, has tetragonal symmetry, $I4_1/amd$, $a = 11.954(2)$ and $c = 8.410(1)$Å, $Z = 16$, $D_{calc} = 5.78$ g cm^{-3}. The structure was determined by countermeasuring 469 independent reflections from a single crystal and was refined up to $R = 0.032$ by the full-matrix least-squares method. It is based on cubic closest packing of oxygen atoms and is closely related to the β-phase structure of Mg₂SiO₄. W and Li(2) are in octahedral sites and Li(1), in tetrahedral sites. Four Li(1)O₄ tetrahedra form a Li₄O₁₂ group, WO₆ and Li(2)O₆ construct a octahedral double chain along the a axis, and four WO₆ octahedra build a W₄O₁₆ group by sharing their octahedral edges.

Introduction

The crystal structures and phase relations of M_2XO_4 compounds have been extensively investigated because of the interests not only in crystal chemistry but also in earth science. Li₂WO₄ is one of the typical compounds with the phenacite (Be₂SiO₄)-type structure under atmospheric pressure. Goldschmidt (1) suggested that the higher pressure form of Li₂WO₄ would be spinel-type structure. Since then, the higher pressure form of Li₂WO₄ had been presumed to take spinel-type structure. In fact, in the case of Li₂MoO₄ in which Mo⁶⁺ has almost the same ionic radius as W⁶⁺, the phenacite-type structure transforms to a spinel-type structure at pressures above 5 kbar and at a temperature of 400°C (2).

Phase relations of Li₂WO₄ were studied in detail up to 160 kbar and 800°C by Yamaoka *et al.* (*3*). They found that the phase behavior of Li₂WO₄ is completely different from that of Li₂MoO₄ at high pressures and temperatures and reported the following four polymorphs: Li₂WO₄I, phenacite-type structure which is stable at atmospheric pressure; Li₂WO₄II, the phase obtained at about 3 kbar, a measurable limit of the lowest pressure with the piston–cylinder apparatus; Li₂WO₄III, an orthorhombic phase obtained above 3 kbar and at higher temperature than that at which Li₂WO₄II was obtained; Li₂WO₄IV, monoclinic phase[1] which is stable at pressures higher than those for Li₂WO₄II and Li₂WO₄III. Pistorius (4) reported that Li₂WO₄II is stable at

[1] The crystallographic data previously reported by Yamaoka *et al.* (1973) are incorrect. Li₂WO₄IV takes monoclinic $C2/c$, $a = 9.753(1)$, $b = 5.954(1)$, $c = 4.994(1)$ Å, and $\beta = 90.58(2)$°. The structure will be published very soon.

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atmospheric pressure and temperature below $\sim310°C$ and yields phase transformation to Li_2WO_4I around this temperature. He determined the space group and the lattice constants of Li_2WO_4II by the X-ray powder method: tetragonal $I4_1/amd$, $a = 11.941$, $c = 8.409$ Å, and $Z = 16$.

The present study has been carried out to determine the structure of Li_2WO_4II and to examine the structural relationship among Li_2WO_4II, β-phase [described for higher pressure form of $(Mg, Fe)_2SiO_4$ and Co_2SiO_4 by Ringwood and Major (5)], and spinel.

Experimental

Crystals of Li_2WO_4II were synthesized at 3 kbar and 630°C by means of a uni-axial piston–cylinder press. The systematic absences of reflections and tetragonal symmetry observed in precession photographs establish the space group $I4_1/amd$. The cell dimensions were determined from high Bragg-angle reflections collected by diffractometer. The results are in good

agreement with those reported by Pistorius (4). Diffraction intensities were measured with a four-circle automatic diffractometer (RGAKU AFC-3) using a single-crystal specimen of size of $0.06 \times 0.04 \times 0.04$ mm^3. Zr-Filtered $MoK\alpha$ radiation was used. A total of 471 independent reflections were collected in the range $0 < 2\theta \leqslant 60°$ by the $\omega/2\theta$ scan technique with scan rate 2°/min. The intensities were corrected for Lp effects in the process of data collection. No absorption correction was applied.

Structure Solution and Refinement

A three-dimensional Patterson synthesis clearly showed peaks due to vectors between symmetrically related tungsten atoms and those between tungsten and oxygen atoms. A few possible models of crystal structures with tungsten and oxygen atoms were built up from the Patterson synthesis diagram. The correct structure was finally determined by comparison between observed and calculated structure factors and by Fourier and

TABLE I

REFINED POSITIONAL AND THERMAL PARAMETERS IN $Li_2WO_4II^a$

Atom	Position	x	y	z	β_{11}	β_{22}
W	$16h$	$0.36394(4)^c$	$\frac{1}{4}$	$-0.02805(6)$	$0.00063(3)$	$0.0008(6)$
O(1)	$16h$	0	$0.1273(9)$	$0.0175(12)$	$0.0031(7)$	$0.0015(7)$
O(2)	$16h$	0	$0.1449(8)$	$0.4852(12)$	$0.0004(5)$	$0.0006(6)$
O(3)	$32i$	$0.1150(6)$	$0.0223(5)$	$0.2542(10)$	$0.0013(4)$	$0.0003(4)$
Li(1)	$16g$	$0.1300(18)$	$0.8800(18)$	$\frac{1}{8}$	$0.0025(11)$	0.0025
Li(2)	$16f$	$0.374(6)$	0	0	$0.013(5)$	$0.0009(17)$

β_{33}	β_{12}	β_{13}	β_{23}	$B_{eq}/Å^{2b}$
$0.00175(6)$	0	$-0.00016(3)$	0	0.40
$0.0018(13)$	0	0	$0.0002(7)$	1.10
$0.0030(12)$	0	0	$-0.0009(7)$	0.24
$0.0052(9)$	$0.0002(3)$	$-0.0006(6)$	$-0.0003(5)$	0.63
$0.005(3)$	$0.0010(14)$	$-0.0004(10)$	0.0004	1.81
$0.012(6)$	0	0	$-0.0030(25)$	3.02

^{a} Origin at center $(2/m)$.
^{b} B_{eq}: Equivalent isotropic temperature factors computed according to the relation, $B_{eq} = (\frac{4}{3}) \sum_{ij} \beta_{ij}(a_i \cdot a_j)$.
^{c} Estimated standard deviations are given in parentheses.

difference-Fourier syntheses. Lithium atoms were found by difference-Fourier synthesis in which the structure factors were calculated without lithium atoms.

The positional parameters for all atoms and an isotropic temperature factor for tungsten atom were refined first using the full-matrix least-squares method. The isotropic temperature factors for other atoms were fixed to 0.6 Å^2. The reflections with the

FIG. 1. Sections of the difference electron density in Li$_2$WO$_4$II synthesized using $F_{obs} - F'_{calc}$ as coefficients, where F'_{calc} are structure factors computed without Li atoms. Contours begin at $1e/Å^3$; intervals of $1e/Å^3$; negative contours are shown as broken lines; zero contours are omitted.

two strongest intensities, 440 and 004, were omitted at this stage because of the effect due to secondary extinction. Further refinement of positional and thermal parameters with anisotropic temperature factors for all atoms gave an R factor of 0.032. The R factor including 440 and 004 (471 reflections) is 0.035. Unit weight was applied in the procedure of refinement.

Atomic coordinates and anisotropic temperature factors are shown in Table I. Fo and Fc values are listed in Table II.[2] The electron density distribution from lithium atoms is shown in Fig. 1. Roothaan–Hartree–Fock and modified Dirac–Slater scattering factors for Li$^+$ and W^{6+} were taken, respectively, from the International Tables for X-ray Crystallography, Vol. 4 (5). The scattering factors O^{2-} were used from the results by Tokonami (7). The computer programs used in this analysis are ORFLS (8) for least-squares refinement of the structure, 3DFR (9) for Fourier and difference-Fourier syntheses, and RSDA-4 (10) for interatomic distances and angle calculations. The computations were carried out at the Computation Center, Osaka University.
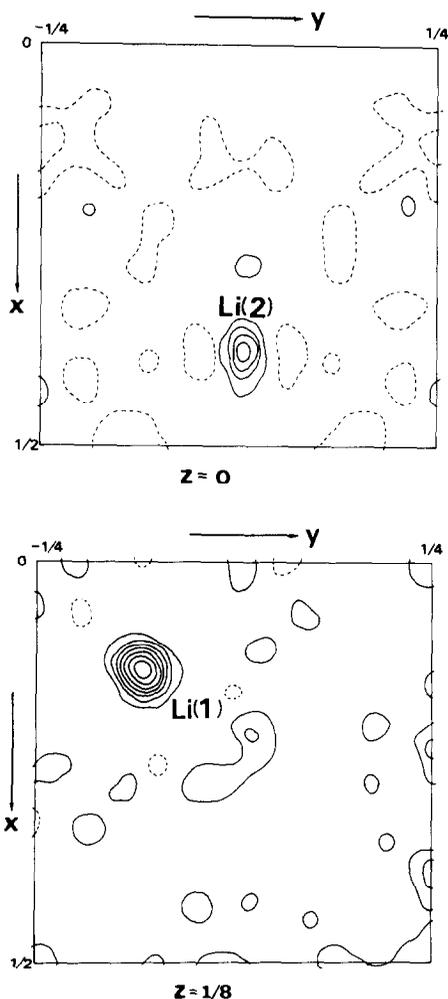
Discussion of the Structure

The structure of Li$_2$WO$_4$II is based on a distorted cubic closest packing arrangement of oxygen atoms as in spinel and β-phase. The relationship between their lattices is shown in Fig. 2. The a_1 and a_2 axes of Li$_2$WO$_4$II are in common with the diagonal of the a_1 and a_2 of spinel and with the b axis
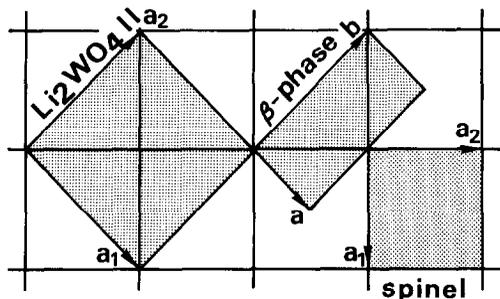
FIG. 2. Relationship of lattices among Li_2WO_4II, β-phase, and spinel.

of the β-phase. The c axis is in common with the a_3 axis of spinel and the c axis of β-phase. Compared with the spinel structure, there are twice as many numbers of tetrahedral and octahedral holes surrounded by oxygen atoms in the unit cell of Li_2WO_4II, which are 128 and 64, respectively. One-eighth of the tetrahedral holes and one-half of the octahedral holes are occupied by cations in the Li_2WO_4II as well as in the spinel and β-phase structures. The crystal structure of Li_2WO_4II is shown in Figs. 3a and b.

Cations are completely ordered. There are two types of Li atoms in the structure. Li(1) occupies a tetrahedral site and forms a Li_4O_{12} group by sharing tetrahedral corners with each other. The M_4O_{12} group, where M represents Li atoms in Li_2WO_4II, corresponds to a coupling of the M_2O_7 group in β-phase structures (11, 12). On the other hand, $Li(2)O_6$ and WO_6 octahedra alternate by sharing edges and construct an octahedral chain. This chain shares edges with another chain related by a mirror plane, resulting in an octahedral double chain running along a_1 and a_2 at different heights. An edge-shared octahedral group, W_2O_{10}, shares edges with another W_2O_{10} of octahedral chain at different height and forms W_4O_{16} group.

The configurations of tetrahedral and octahedral groups in spinel, β-phase, and Li_2WO_4II are schematically compared in Fig. 4. Spinel has octahedral single chains and isolated tetrahedra; β-phase, octahedral single and double chains and a T_2O_7 group, where T represents a tetrahedral cation;
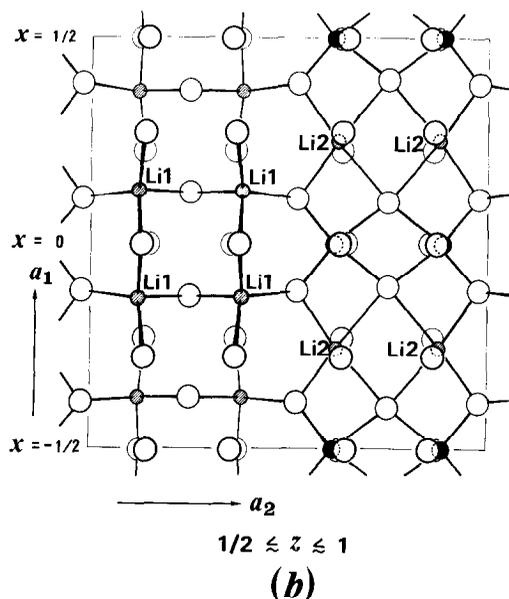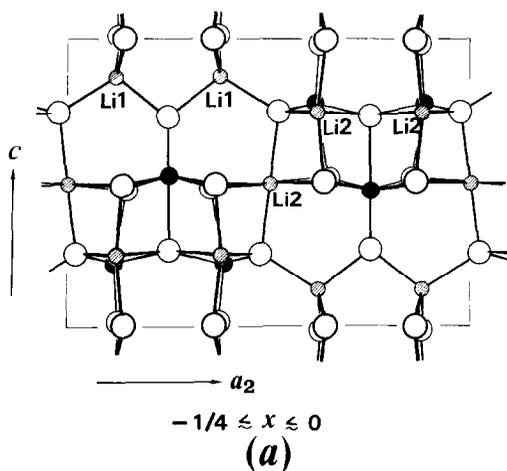

FIG. 3. The crystal structure of Li_2WO_4II: (a) projected along a axis in the range $-\frac{1}{4} \le x \le 0$, (b) projected along c axis in the range $-\frac{1}{2} \le z \le 0$. Open, shaded, and solid circles represent oxygen, lithium, and tungsten atoms, respectively. Li1 and Li2 are lithium atoms symmetrically related to Li(1) and Li(2), respectively.
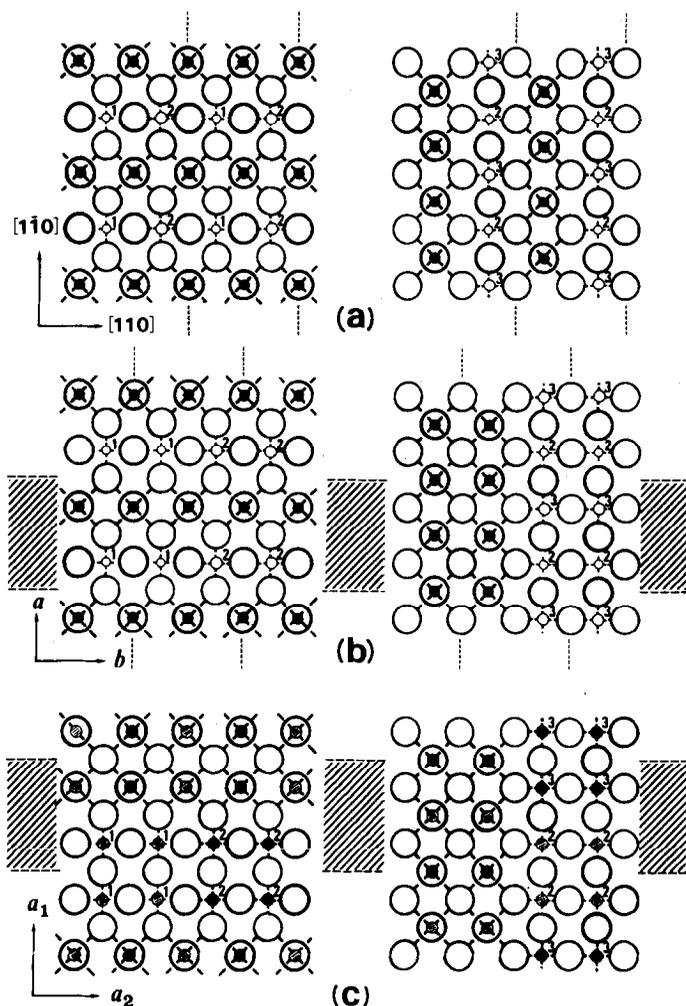
FIG. 4. Comparison of the arrangement of octahedra and tetrahedra in (a) spinel, (b) β-phase, and (c) Li$_2$WO$_4$II: (left) projection of the range $-1/8 \leq z \leq 1/4$, (right) projection of the range $1/8 \leq z \leq 1/2$. The open and shaded circles with numbers of 1, 2, and 3 represent tetrahedral cations at heights of $-\frac{1}{8}, \frac{1}{8}$, and $\frac{3}{8}$, respectively. Large open circles show anions, and solid or shaded circles (without numbers) represent octahedral cations. Shaded circles of (c) are lithium atoms.

Li$_2$WO$_4$II, octahedral double chains and a T_4O_{12} group. The same slabs can be observed both in spinel and in β-phase (lightly shaded area in Figs. 4a and b). In spinel, the slabs are translationally arranged along [110]. On the other hand, β-phase is constructed by an alternation of slabs along [010] which are mutually related by a mirror plane. A similar relationship can be found between β-phase and Li$_2$WO$_4$II. The same

type of slabs, which are formed by an octahedral chain and 1-1-2-2 arrangement of tetrahedra, can be observed in β-phase and Li$_2$WO$_4$II (heavily shaded area in Figs. 4b and c). The slabs in β-phase alternate translationally along [100]; on the other hand, those in Li$_2$WO$_4$II are related by a mirror plane perpendicular to (100). Thus, the structure of Li$_2$WO$_4$II is considered to be a derivative of spinel and β-phase structures.

Interatomic distances and angles are shown in Fig. 5. The W–O distances vary from 1.727 to 2.245, and the average is 1.951 Å. The average O–O distance of WO_6 octahedron is 2.741 Å. The Li–O distances of LiO_6 octahedra are in the range from 2.02 to 2.30 Å, and the average is 2.14 Å. The O–O distances of LiO_6 octahedra vary from 2.726 to 3.472 Å, and the average is 3.009 Å. The shared edges between WO_6 octahedra give the shortest O–O distances, 2.513 and 2.568 Å, and those between WO_6 and LiO_6 are 2.726 and 2.795 Å, while the shared edges between LiO_6 octahedra are 2.79 and 3.47 Å. The Li–O distances of LiO_4 tetrahedra are 1.96 and 2.03 Å, and the average is 2.00 Å. The O–O distances of LiO_4 tetrahedra vary from 3.17 to 3.43 Å and the average is 3.26 Å. This value is fairly large as compared to O–O distances of LiO_6 and WO_6. The distances from cations to oxygen atoms of the WO_6 octahedron and the LiO_4 tetrahedron are comparable with those of WO_6 and LiO_4 of other wolframates such as $Li_2W_2O_7$ (13).

The electron density of Li(1) is relatively higher than that of Li(2) (Fig. 1). This result can be explained by the following reasons: (1) substitution of Li by W of the type $(Li_{1-x}W_{x/6}{}^{IV}Li^{VI}W^{VI}O_4$. The crystal is colorless. Therefore, there will be no possibility of the type $Li_{2-x}WO_4$. If nonstoichiometry of the type $Li_{2-x}WO_4$ were true, the crystal would have a color due to the reduced tungsten ion from W^{6+}; (2) spreading of electron density of Li(2) due to strong thermal motion or due to stretching of potential energy minima. Further experi-

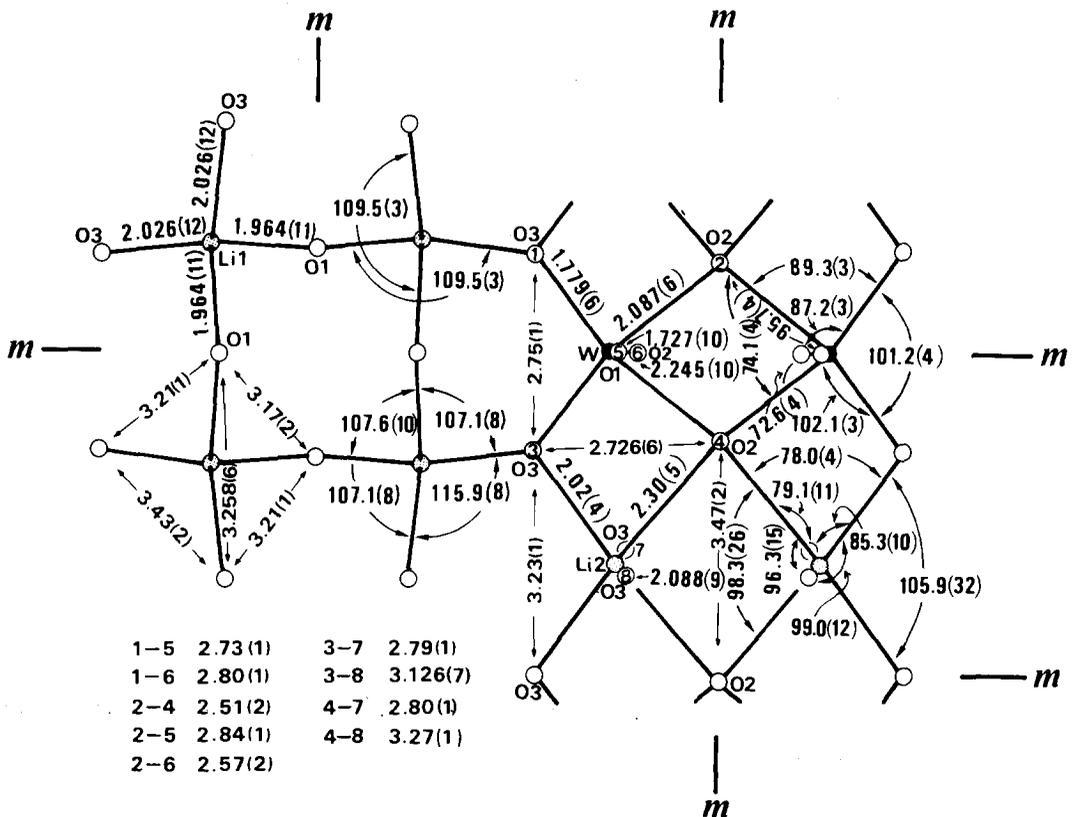| 1–5 | 2.73(1) | 3–7 | 2.79(1) |
1–6	2.80(1)	3–8	3.126(7)
2–4	2.51(2)	4–7	2.80(1)
2–5	2.84(1)	4–8	3.27(1)
2–6	2.57(2)		

FIG. 5. Interatomic distances (Å) and angles (degrees) with estimated standard deviations in parentheses.

ments would be needed to decide whether (1) or (2), or a combination of the two, is correct.

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