JOURNAL OF SOLID STATE CHEMISTRY 6, 280–285 (1973)

Phase Transformations in Li_2WO_4 at High Pressure

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Received May 9, 1972

The phase diagram of Li_2WO_4 has been determined at high pressure up to 160 kbars and a temperature of 800°C. Three new high-pressure phases have been found in the present study. Crystallographic data are given for Li_2WO_4 III and Li_2WO_4 IV by means of single crystal and powder X-ray analyses. Li_2WO_4 III is orthorhombic with the large unit cell containing 16 molecules and having the edges: $a_0 = 10.12(4)$ Å, $b_0 = 10.07(1)$ Å, $c_0 = 11.68(6)$ Å. Li_2WO_4 IV has an orthorhombic unit cell with the parameters: $a_0 = 4.96(7)$ Å, $b_0 = 9.72(8)$ Å, $c_0 = 5.93(8)$ Å and $Z = 4$. The total volume decrease is estimated to be 24.8% through the high pressure transformations in Li_2WO_4. No spinel-like structure could be found in the present study.

Introduction

Pressure-induced phase transformations in complex oxides have been studied extensively for the past 10 yr in the field of crystal chemistry as well as of earth science. Various types of transformations have been reported so far. One of the typical transformations among them is that of phenacite-spinel. Be_2SiO_4, Be_2GeO_4, Zn_2SiO_4, Zn_2GeO_4, Li_2MoO_4, Li_2WO_4, $LiAlGeO_4$, $LiGaGeO_4$ and $LiZnVO_4$ crystallize in the phenacite structure at atmospheric pressure (*1*), in which three cations are all in the tetrahedral coordination. All the compounds except Be_2SiO_4, Be_2GeO_4 and Li_2WO_4 transform to the more closely packed spinel (*2–6*) or modified spinel (*7*) structure under pressure; the change of two thirds of the cations from four- to sixfold coordination results in a decrease in volume of about 20 to 23%. Because the ionic radius of Be^{2+} is far smaller than that of the other cations, in Be_2SiO_4 and Be_2GeO_4 it cannot occupy the octahedrally coordinated sites in the spinel structure even under very high pressure.

Under these circumstances, Li_2WO_4 is expected to transform to spinel, because it is quite similar to Li_2MoO_4 in the crystal chemical properties at atmospheric pressure. According to the preliminary experiment by Liebertz and Rooymans (*6*), three modifications probably exist in Li_2WO_4, none of them having a spinel structure. No further information has been given so far.

It is the object of the present study to throw light upon the high pressure phase transformations in Li_2WO_4 up to 160 kbars and 800°C. For comparison with that of Li_2MoO_4, which transforms to spinel under relatively low pressure (*6*), phase behavior of the binary system Li_2WO_4–Li_2MoO_4 was also examined at high pressure in some detail.

Experimental Procedures

The atmospheric pressure phase of Li_2WO_4 was prepared by mixing intimately Li_2CO_3 and WO_3 of guaranteed quality obtained from Kanto Chemical Co., Tokyo, loading into a platinum crucible, firing at 450–500°C for 3 days, and crushing and grinding. The product was refined at this temperature for 3 days and crushed again. This procedure was repeated more than 10 times. The specimen so prepared was found to be single phase by X-ray diffraction and by microscopic examination in immersion liquids, having unit cell dimensions of the hexagonal lattice, $a_0 = 14.363$ Å, $c_0 = 9.606$ Å, which are in good agreement with the value previously reported (ASTM card No. 12-760).

Starting materials of the binary system Li_2WO_4–Li_2MoO_4 were prepared by mixing intimately in the required proportions Li_2WO_4 and Li_2MoO_4, prepared as mentioned above, loading into a gold capsule, putting into a test-tube type microbomb under oxygen pressures of about 100 atm, in order to prevent the reduction and vaporization of the constituent oxides, and then heating at 600°C for 2 hr, at 750°C for 20 min and at 600°C for 1 hr. The specimen thus obtained was found to be homogeneous single phase with phenacite structure by X-ray and microscopic examinations. Linear relations between the lattice parameters and the composition in the $Li_2W_{1-x}Mo_xO_4$ system are shown in Fig. 1, indicating that a complete solid solution is formed in this system.

A piston-cylinder type of high pressure apparatus was used with the furnace assembly in the pressure cell as previously described (*8*). Samples were sealed by dc carbon arc welding in a gold capsule 10 mm long and 3 mm in diameter. The temperature was measured with chromel–alumel thermocouples without any corrections for the pressure effect on the emf. Friction loss in the solid pressure media of pyrophyllite and talc was also ignored by adopting the so called "piston-out" procedure suggested by Boyd et al. (*9*). Temperature and pressure are considered to be accurate within ±10°C and ±5%, respectively.

In the runs for pressures of 40 to 60 kbars, a belt type high pressure apparatus (*10*) was used and for ultrahigh pressures up to 160 kbars, a Bridgman anvil type high pressure apparatus with internal heating system (*11*) was used. In these cases, the pressure was calibrated at room temperature based on the NBS pressure scale (*12*) (Bi I–II, 26 kbars; Ba I–II, 55 kbars; Bi III–V, 77 kbars) and the new Drickamer's scale (*13*) (Ba II–III, 120 kbars).

The experimental method used in the phase equilibrium study was a conventional quenching method. The atmospheric pressure phase of Li_2WO_4 was held at a certain temperature–pressure condition for a time interval sufficient for a reaction (for example, 0.5 hr at 700°C and 6 hr at 420°C were needed) and then quenched to room temperature by turning off the heating power. The pressure was then released slowly. To confirm the reversibility of the reactions, the high pressure phases thus obtained by quenching were also used as the starting materials.

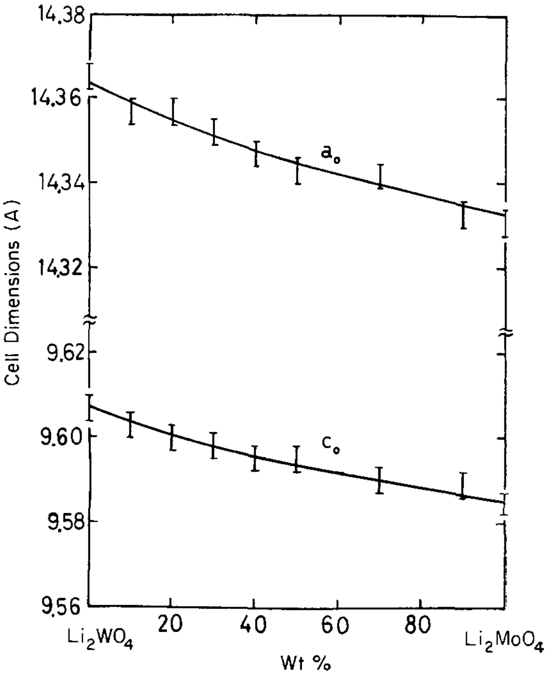

FIG. 1. Composition dependence of the unit cell parameters for Li_2WO_4–Li_2MoO_4 system with the hexagonal lattice of the phenacite structure.

Identification of the phases present in the recovered specimen was made by X-ray powder analysis and by microscopic observation. The crystal symmetry of the polymorphs of Li_2WO_4, newly found in the course of the study, were determined on a single crystal using a Weissenberg camera with Ni filtered Cu$K\alpha_1$ radiation. An accurate determination of the unit cell parameters was made by a least-squares refinement of the powder data which were collected with an X-ray diffractometer with scanning speed of 1/4° (2θ) per min. Diffraction angles were calibrated with pure silicon standard. Cu$K\alpha_1$ radiation was used throughout.

Single crystals of Li_2WO_4 III and Li_2WO_4 IV (which are designated below) were obtained by heating for 3 hr at temperature about 50°C above the melting point and then cooling slowly to about 550°C at a programmed rate of 0.5°C/min with a PID temperature controller, while pressure was kept constant at a designed value.

Experimental Result

a. Li_2WO_4

Experimental results on the phase equilibrium study for Li_2WO_4 up to 30 kbars are summarized in Fig. 2. In the figure, the ratio of the phases present in the run products, which was roughly estimated from X-ray powder data, is shown in proportion to the area in the circles. Reverse reactions are also indicated by the rectangular symbols with arrows showing the directions of reactions. The broken line is the melting curve of Li_2WO_4, which was roughly determined by DTA method similar to that reported by Jayaraman, Klement and Kennedy (*14*). High pressure runs were carried out up to 160 kbars and 800°C and four polymorphs of Li_2WO_4 were found in the present study. Each phase is hereafter designated as Li_2WO_4 I–IV, in the order of phases with increasing pressure and temperature as shown in Fig. 2.

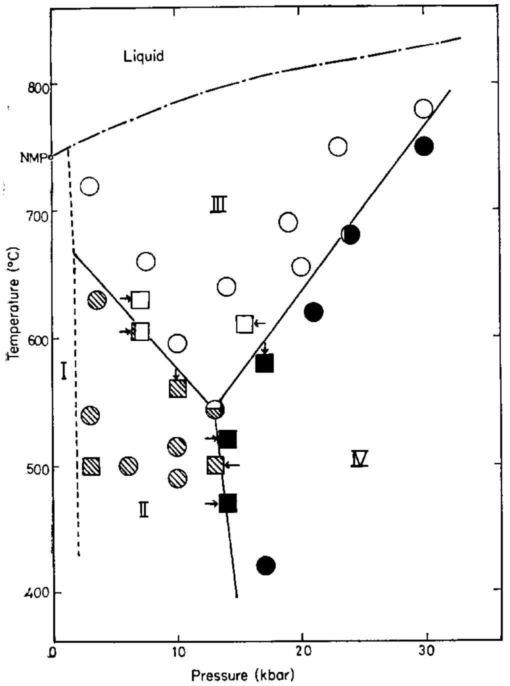

FIG. 2. Phase diagram for Li_2WO_4. Symbols are: I = Li_2WO_4 I; II = Li_2WO_4 II; III = Li_2WO_4 III; IV = Li_2WO_4 IV; (◍) I → II; (○) I → III; (●) I → IV; (▨) II → II; ($\overset{\downarrow}{▨}$) III → II; (▨←) IV → II; (→□) II → III; (□←) IV → III; (→■) II → IV; ($\overset{\downarrow}{■}$) III → IV; (broken line) the melting curve determined by DTA.

The atmospheric pressure phase of Li_2WO_4 I with the phenacite structure was found to transform to two other phases, Li_2WO_4 II and Li_2WO_4 III, at pressures at least above 3 kbars, the lower pressure limit available in the piston-cylinder apparatus. Li_2WO_4 III was a high temperature–high pressure phase compared to Li_2WO_4 II. That is, at 3 kbars and at temperatures higher than 665°C Li_2WO_4 II was found to transform to Li_2WO_4 III, and at temperatures of 665 to 545°C, the former transformed to the latter with increasing pressure. The equilibrium phase boundary curve between Li_2WO_4 II and Li_2WO_4 III has a negative slope and can be expressed by $P(\text{kbar}) = 64 - 0.093\ T\ (°\text{C})$.

At temperatures higher than 545°C, Li_2WO_4 III was found to transform to Li_2WO_4 IV with increasing pressure. The equilibrium phase boundary between Li_2WO_4 III and Li_2WO_4 IV was determined and can be expressed by the equation, $P(\text{kbar}) = -29 + 0.077\ T(°\text{C})$. At temperatures lower than 545°C, Li_2WO_4 II also transformed to Li_2WO_4 IV with increasing pressure. The equilibrium phase boundary curve was almost independent of temperature and can be expressed by $P(\text{kbar}) = 19 - 0.012\ T(°\text{C})$. The triplet point Li_2WO_4 II–Li_2WO_4 III–Li_2WO_4 IV was located at 545°C, 13 kbars. Li_2WO_4 IV, the densest form among all the polymorphs of Li_2WO_4, was found to be stable up to 160 kbars and 800°C. No spinel phase was observed in the present P–T regions. All the high pressure phases of Li_2WO_4 II, III and IV completely transformed to the atmospheric pressure phase of Li_2WO_4 I when they were heated at both temperatures of 600 and 700°C in air.

The crystal symmetry of Li_2WO_4 II could not be determined lacking single crystals for the Weissenberg camera. The observed *d*-values of the X-ray powder analysis are tabulated in Table I.

Li_2WO_4 III was found to have orthorhombic symmetry by Weissenberg photographs taken for a single crystal of 100 μm size. Powder X-ray diffraction lines were completely indexed using the single crystal data. No extra peaks could be found. Unit cell dimensions determined by the least-squares method are summarized in Table II, together with the observed and calculated *d*-values. The unit cell of Li_2WO_4 III contains 16 molecular units, which was determined by a pycnometrical density measurement (the

TABLE I

POWDER DIFFRACTION DATA FOR Li_2WO_4 II

d_{obs}	I_{obs}	d_{obs}	I_{obs}
6.89	40	2.141	25
5.975	60	2.112	90
4.514	100	1.991	20
3.770	10	1.910	10
3.601	90	1.838	20
3.440	70	1.819	30
3.082	65	1.743	15
2.736	85	1.654	10
2.671	35	1.610	25
2.484	10	1.566	10
2.435	30	1.550	20
2.340	10	1.542	20
2.298	25	1.491	40
2.255	20	1.457	45

measured density $d = 5.8 \pm 0.3$ g ml^{-1}. This gives a volume decrease of 21.9% for the Li_2WO_4 I to Li_2WO_4 III transformation.

The crystal symmetry of Li_2WO_4 IV was found to be orthorhombic very close to hexagonal, from the single crystal data. Powder diffraction lines were well indexed on the basis of the orthorhombic lattice. Cell dimensions together with both the observed and calculated d-values are tabulated in Table III. The pycnometrically measured density was $d = 6.2 \pm 0.3$ g ml^{-1}, which indicated a cell containing four formula units. The volume decrease during the transformation is estimated to be 2.9% from Li_2WO_4 III to Li_2WO_4 IV and 24.8% from Li_2WO_4 I to Li_2WO_4 IV.

Detailed crystal structure analyses of Li_2WO_4 III and IV, now being carried out by Morimoto and his colleagues at Osaka University, will be reported elsewhere.

b. Li_2WO_4–Li_2MoO_4 System

Among the four polymorphs of Li_2WO_4, no spinel-like structure could be found. In order to make the situation clear, the binary system of Li_2WO_4–Li_2MoO_4 was investigated at high pressure up to 60 kbars at constant temperature of 750°C. The starting material was the solid solution of $Li_2W_{1-x}Mo_xO_4$ with the phenacite structure. The experimental results are summarized in Fig. 3. The figure shows that this system is substantially a pseudobinary one in this experimental range. It is confirmed, however, that at

TABLE II

POWDER DIFFRACTION DATA FOR Li_2WO_4 III

Orthorhombic
$a_0 = 10.12(4)$ Å, $b_0 = 10.07(1)$ Å, $c_0 = 11.68(6)$ Å, $V_0 = 1191$ Å^3, $Z = 16$

$h\,k\,l$	d_{calc}	d_{obs}	I	$h\,k\,l$	d_{calc}	d_{obs}	I
1 0 1	7.652	7.65	10	1 4 2	2.254	2.259	10
0 0 2	5.843	5.86	10	2 4 0	2.354		
2 0 1	4.645	4.652	70	4 2 0	2.261		
2 1 0	4.523	4.526	20	2 2 4	2.261		
2 0 2	3.826	3.822	60	4 1 2	2.263		
0 1 3	3.633	3.640	30	2 4 1	2.213	2.215	30
1 0 3	3.635			4 2 1	2.220		
2 1 2	3.576	3.582	10	2 0 5	2.122	2.124	5
2 2 1	3.414	3.414	5	4 0 3			
0 3 1	3.226	3.229	20	4 2 2	2.109	2.110	15
2 3 0	2.798	2.799	25	2 1 5	2.076	2.078	10
2 2 3	2.632	2.635	100	4 1 3	2.077		
0 2 4	2.527	2.530	55	4 3 1	1.991	1.992	5
2 0 4	2.530			2 4 3	1.951	1.953	15
4 0 0	2.531			2 2 5	1.955		
2 1 4	2.454	2.457	20	4 2 3	1.956		
4 1 0	2.455			4 4 0	1.785	1.789	60
4 1 1	2.402	2.401	5	4 2 4	1.788		
				2 1 6	1.789		

TABLE III

POWDER DIFFRACTION DATA FOR Li_2WO_4 IV

Orthorhombic

$a_0 = 4.96(7)$ Å, $b_0 = 9.72(8)$ Å, $c_0 = 5.93(8)$ Å, $V_0 = 287$ Å^3, $Z = 4$

hkl	d_{calc}	d_{obs}	*I*	*hkl*	d_{calc}	d_{obs}	*I*
0 1 1	5.07	5.05	30	0 5 1	1.849	1.850	1
0 2 0	4.86	4.85	100	2 2 2	1.772	1.766	10
1 1 1	3.547	3.548	40	1 4 2	1.759	1.757	5
0 0 2	2.969	2.963	5	2 4 0	1.738	1.740	5
0 3 1	2.846	2.844	10	1 5 1	1.733	1.729	5
1 0 2	2.548	2.547	5	0 3 3	1.689	1.690	10
0 2 2	2.534	2.531	5	0 6 0	1.621	1.623	15
2 0 0	2.483	2.479	15	3 1 1	1.574	1.577	2
1 1 2	2.465	2.462	10	2 5 0	1.531	1.531	5
0 4 0	2.432	2.431	20	3 0 2	1.446	1.450	1
1 2 2	2.257	2.262	10	0 6 2	1.423	1.423	2
2 2 0	2.212	2.209	5	2 3 3	1.397	1.402	1
0 1 3	1.940	1.938	5	1 1 4	1.407		
2 0 2	1.905	1.908	1	0 5 3	1.387	1.388	5
0 4 2	1.881	1.882	5	3 4 0	1.369	1.367	10
2 1 2	1.869	1.867	1	0 7 1	1.353	1.355	1

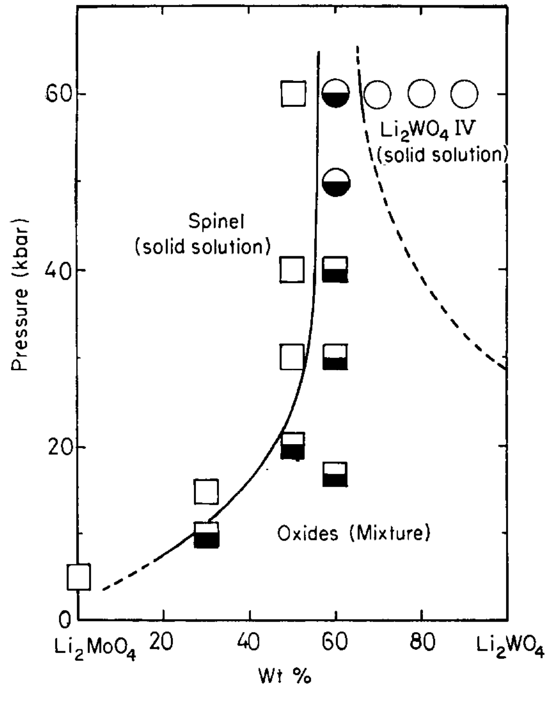

FIG. 3. Phase diagram for Li_2WO_4–Li_2MoO_4 system at 750°C. (□) Spinel solid solution; (⬓) mixture of spinel solid solution and unknown phases; (○) Li_2WO_4 IV solid solution; (◒) mixture of Li_2WO_4 IV solid solution and unknown phases.

higher the pressure, two other solid solutions of Li_2WO_4 IV and spinel phase became more stable in the two separate regions of Li_2WO_4– and Li_2MoO_4-rich compositions, respectively. A phase gap was observed at around the composition of 60 wt% Li_2WO_4.

Conclusion and Discussion

In the present work it was found that Li_2WO_4 I finally transforms to the orthorhombic Li_2WO_4 IV with a total volume decrease of 24.8%, passing through two intermediate phases. On the other hand, Li_2MoO_4 directly transforms to the spinel structure with a volume decrease of 21%, although both compounds crystallize in the phenacite structure having nearly identical unit cell parameters at atmospheric pressure. This experimental fact shows that Li_2WO_4 IV has a rather denser structure than the "virtual" spinel Li_2WO_4. Therefore it may be concluded that Li_2WO_4 would not transform to the spinel structure even under ultrahigh pressure. This presumption is also supported by the phase behavior in the pseudobinary system Li_2WO_4–Li_2MoO_4 at high pressure.

The difference between the phase behaviors of the two compounds at high pressure suggests that the analogy in crystal chemical properties such as ionic radius and electronegativity between W^{6+} and Mo^{6+} at atmospheric pressure breaks down at high pressure. More detailed discussions can be done when the structure analyses of the new high pressure polymorphs are completed.

However, the opposite case has been known in the compounds containing Mo and W. The WO_3 structure consists of the BO_3 array of the perovskite structure having the general composition ABO_3, where A is a larger cation and B is a smaller cation able to accept octahedral coordination. Because the A-cation interstices are vacant, A cations are inserted into these interstices to form the so-called A_xWO_3 bronzes. MoO_3 has a more complex layer structure and no A_xMoO_3 perovskite bronze has been prepared at atmospheric pressure. However, Bither, Gillson and Young (*15*) found that the cubic perovskite system Na_xMoO_3 and K_xMoO_3 are present at 65 kbars. These two different results will present an interesting problem in the field of high-pressure crystal chemistry.

Acknowledgment

We are very grateful to Professor N. Morimoto and Dr. H. Horiuchi of the Institute for Industrial Science, Osaka University, for X-ray analyses and useful suggestions. We are also indebted to Professor S. Akimoto of University of Tokyo, and Dr. M. Nakahira and Mr. H. Ohashi of the National Institute for Researches in Inorganic Materials, for their stimulating discussions and helpful comments on the manuscript. Ultrahigh pressure experiments using a Bridgman anvil type apparatus were carried out with the aid of Dr. B. Okai and Mr. Yoshimoto of this Institute.

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