

Synthesis and Crystal Structure of a New Layered Phosphate, Li_2VPO_6

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The compound Li_2VPO_6 was separated from a solidified melt in the Li/V/P/O system, and the structure was solved from single crystal X-ray diffraction data. The crystal class is orthorhombic with a space group of $Pna2_1$, $a = 10.3219(3)$ Å, $b = 4.6355(1)$ Å, $c = 8.5620(4)$ Å, and $Z = 4$. In Li_2VPO_6 , phosphate tetrahedra and vanadate octahedra link to form layers perpendicular to the a -axis. Two different types of lithium cations are found between the sheets. An unusual feature of the structure is edge sharing between the phosphate tetrahedra and the vanadate octahedra, leading to a strained four-membered ring. Measurements of ionic conductivity were made over the temperature range 337 to 458°C. Incongruent melting of Li_2VPO_6 occurs at about 545°C. © 1993 Academic Press, Inc.

Introduction

Phase diagram studies have not been reported for the Li/V/P/O system, and apparently no compounds are known which contain these four elements. We have been investigating the Li/V/P/O system under conditions where one would expect vanadium and phosphorous to be fully oxidized. Thus, we may consider this to be the three component system $\text{Li}_2\text{O}/\text{P}_2\text{O}_5/\text{V}_2\text{O}_5$. The only compound which we have found that contains substantial quantities of the three components is Li_2VPO_6 . We have also discovered (1) new compounds of analogous stoichiometry in the $\text{Na}_2\text{O}/\text{P}_2\text{O}_5/\text{V}_2\text{O}_5$ and $\text{K}_2\text{O}/\text{P}_2\text{O}_5/\text{V}_2\text{O}_5$ systems. However, isostructural Na_2VPO_6 and K_2VPO_6 have a distinctly different structure from that which we report here for Li_2VPO_6 .

Experimental

Reactants used were LiNO_3 (Mallinckrodt, reagent), NH_4VO_3 (Matthey Electron-

ics, 99%), and $(\text{NH}_4)_2\text{HPO}_4$ (EM Science, reagent). Various mixtures were ground together and heated in air using platinum crucibles. The synthesis temperature ranged from 500 to 650°C; some melting normally occurred at the higher temperature. Light yellow crystals of Li_2VPO_6 were found in samples where melting had occurred. X-ray powder diffraction always showed some LiV_3O_8 and Li_3PO_4 in such products, even for the 2Li:1V:1P stoichiometry. However, LiV_3O_8 could be removed by dissolving in 30% H_2O_2 , and Li_3PO_4 was a fine powder which could be separated from the Li_2VPO_6 crystals using sieves.

A crystal of dimensions $0.063 \times 0.188 \times 0.313$ mm was mounted on a glass fiber for collection of single crystal X-ray diffraction data. Details of the data collection, reduction, and refinement are summarized in Table I. The cell dimensions were refined by least squares refinement of 25 reflections in the range 28° to $30^\circ 2\theta$ that had been centered on a Rigaku AFC6R diffractometer. A total of 1090 reflections were collected using the

ω - 2θ scan technique at a scan width of $(1.63 + 0.3 \tan \theta)^\circ$. The intensities of three standard reflections measured every 300 reflections throughout the data collection exhibited no significant excursions. An empirical absorption correction was made using psi scan data which resulted in transmission factors ranging from 0.65 to 1.0 with an average of 0.91. The structure was solved and refined with programs from the TEXSAN crystallographic software package (2). The vanadium atoms were located by direct methods using SHELXS (3). The phosphorous, oxygen, and lithium atoms were found in subsequent analysis of difference electron density maps. The structure was refined by full matrix least-squares cycles. Atomic scattering factors (4) were corrected for anomalous dispersion (5). The weighting scheme was based on the counting statistics, and a factor accounting for secondary extinction was refined and applied to the calculated structure factors. A final residual of $R = 0.041$ was obtained using anisotropic thermal parameters for 763 structure factors and 91 variables. Refinement in the enantiomorph setting resulted in an R -value slightly higher ($R = 0.042$). The acentric space group was confirmed by showing second harmonic generation when using a YAG: Nd laser.

X-ray diffraction powder patterns were obtained on a Siemens D5000 diffractometer using $\text{CuK}\alpha$ radiation and a Si ($a = 5.43094 \text{ \AA}$) internal standard. The cell dimensions were refined by least squares, and they are in good agreement with those obtained from the four circle diffractometer (Table I). An indexed powder X-ray diffraction pattern for Li_2VPO_6 is listed in Table II. Intensity calculations (6) based on the positional parameters of the refined structure facilitated the identification of diffraction lines.

The final atomic position and isotropic thermal parameters are given in Table III. Anisotropic thermal parameters are given in

TABLE I
CRYSTAL DATA AND INTENSITY COLLECTION
FOR Li_2VPO_6

Empirical formula	Li_2VPO_6
Formula weight (g/mol)	191.79
Crystal system	Orthorhombic
Space group	$Pna2_1$ (no. 33)
Lattice parameters from single crystal	
a (Å)	10.314(2)
b (Å)	4.6328(6)
c (Å)	8.562(1)
V (Å ³)	409.1(1)
Lattice parameters from powder diffractometer	
a (Å)	10.3219(3)
b (Å)	4.6355(1)
c (Å)	8.5620(4)
V (Å ³)	409.69(2)
Z	4
Diffractometer	Rigaku AFC6R
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71069 \text{ \AA}$) Graphite-monochromated
Temperature	23°C
Maximum 2θ (°)	70
Data collected	$0 < h < 14, 0 < k < 17, 0 < l < 7$
Scan speed (°/min)	16.0 in ω and 32.0 in 2θ
No. unique data with $F_o^2 > 3\sigma(F_o^2)$	763
Data/parameter ratio	8.38
Extinction parameter	1.858×10^{-5}
R	0.041
R_w	0.046

Table IV, and selected interatomic distances and angles are given in Table V.

Differential thermal analysis was carried out using a Netzsch STA 409 system. Incongruent melting of Li_2VPO_6 commenced at about 545°C. Polycrystalline Li_2VPO_6 may be prepared single phase by carrying out the synthesis below 545°C.

Conductivity measurements were made on a Solartron 1260 impedance analyser over the frequency range of 15 MHz to 1 mHz using platinum blocking electrodes. To ensure that the conductivity measured was bulk conductivity, two pellets of area 1.267 cm² but with lengths 0.132 cm and 0.288 cm were used. The data were fitted to the relationship $\sigma = \sigma_0 e^{-(E/RT)}$ from 337 to 458°C which gave a σ_0 value of 85 ohm⁻¹·cm⁻¹ and an activation energy (E) of about 28.7 kcal/mol. The apparent Li^+ conductivity at 450°C is 1.7×10^{-7} ohm⁻¹·cm⁻¹.

TABLE II
OBSERVED AND CALCULATED VALUES FOR d -SPACING AND INTENSITY FROM
POWDER X-RAY DIFFRACTION DATA

d_{calc}	d_{obs}	I_{calc}	I_{obs}	hkl	d_{calc}	d_{obs}	I_{calc}	I_{obs}	hkl
5.1611	5.1630	14	28	200	1.6921	—	1	—	314
4.4202	4.4193	100	100	201	1.6904	—	1	—	421
4.2811	4.2820	15	9	002	1.6867	1.6865	1	1	601
4.2287	4.2284	35	36	110	1.6475	1.6477	2	1	404
4.0764	4.0744	11	10	011	1.6253	1.6253	8	4	205
3.7915	3.7882	49	51	111	1.6129	—	<1	—	610
3.4487	3.4461	4	4	210	1.6063	—	<1	—	015
3.2950	3.2935	34	25	202	1.5995	1.5999	11	8	422
3.1989	3.1979	13	14	211	1.5963	—	1	—	602
3.0085	3.0086	56	42	112	1.5944	1.5948	3	3	323
2.7628	2.7618	1	2	310	1.5872	—	<1	—	115
2.6857	2.6836	1	1	212	1.5850	1.5849	2	2	611
2.6293	2.6288	45	48	311	1.5734	—	<1	—	513
2.5805	2.5799	1	2	400	1.5725	1.5725	5	4	024
2.4976	2.4979	5	5	203	1.5545	1.5546	1	1	124
2.4708	2.4713	6	6	401	1.5524	1.5528	1	1	414
2.4303	—	1	—	013	1.5416	1.5414	1	2	520
2.3656	2.3653	26	18	113	1.5338	—	<1	—	215
2.3214	2.3204	13	9	312	1.5281	—	1	—	130
2.3178	—	1	—	020	1.5206	1.5207	1	1	031
2.2614	2.2610	5	4	120	1.5172	1.5169	2	2	521
2.2547	2.2552	16	17	410	1.5093	—	<1	—	612
2.2100	2.2094	9	7	402	1.5044	—	1	—	131
2.1987	2.1987	30	25	213	1.5042	1.5040	3	2	224
2.1865	—	1	—	121	1.4803	—	<1	—	230
2.1804	2.1810	2	2	411	1.4759	—	2	—	423
2.1405	2.1399	4	2	004	1.4734	1.4733	16	8	603
2.1143	—	<1	—	220	1.4586	1.4586	2	1	231
2.0527	2.0524	9	7	221	1.4555	1.4555	10	4	315
2.0382	2.0384	4	3	022	1.4504	—	<1	—	522
1.9996	2.0000	6	4	122	1.4392	1.4391	1	1	132
1.9949	—	<1	—	412	1.4302	—	<1	—	324
1.9851	1.9845	5	3	313	1.4270	1.4271	9	3	006
1.9772	1.9761	2	1	204	1.4268	—	1	—	405
1.9223	1.9223	4	3	320	1.4150	1.4152	5	3	514
1.9141	1.9137	5	4	403	1.4096	1.4097	1	1	330
1.9098	1.9100	8	4	114	1.4052	1.4051	1	1	400
1.8957	1.8952	1	1	222	1.4042	—	<1	—	613
1.8859	1.8862	8	8	510	1.3990	1.3987	1	1	232
1.8756	—	1	—	321	1.3908	1.3907	4	2	331
1.8417	1.8417	3	2	511	1.3867	1.3867	4	2	711
1.8187	1.8189	2	1	214	1.3814	—	<1	—	620
1.7725	1.7721	<1	1	123	1.3754	—	1	—	206
1.7692	—	<1	—	413	1.3652	—	<1	—	125
1.7536	—	<1	—	322	1.3637	1.3636	3	2	621
1.7258	—	4	—	512	1.3588	—	1	—	415
1.7243	1.7246	11	6	420	1.3564	—	<1	—	033
1.7204	1.7205	3	4	600	1.3521	—	<1	—	523
1.6989	1.6990	24	18	223	1.3472	1.3472	2	1	116

TABLE III
ATOMIC AND ISOTROPIC THERMAL PARAMETERS
FOR Li_2VPO_6

Atom	x	y	z	$B_{\text{eq}}(\text{\AA}^2)^a$
V	0.60978(8)	0.0169(2)	0	0.57(3)
P	0.2181(1)	0.0854(3)	0.8041(2)	0.55(4)
Li1	0.411(1)	0.519(2)	0.821(1)	1.2(4)
Li2	0.363(1)	0.035(3)	0.122(1)	1.8(5)
O1	0.2803(5)	0.193(1)	0.6506(5)	0.6(1)
O2	0.0818(4)	0.2316(8)	0.8114(6)	0.7(1)
O3	0.7160(4)	0.7409(8)	0.8139(6)	0.8(1)
O4	0.2857(4)	0.237(1)	0.9419(5)	0.7(1)
O5	0.4888(4)	0.7963(9)	0.9732(5)	0.7(1)
O6	0.5478(5)	0.241(1)	0.1272(5)	0.9(2)

$$^a B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j a_i$$

Discussion

The structure of Li_2VPO_6 may be considered as phosphate tetrahedra and vanadate octahedra linked to form a covalently bonded layer (Fig. 1) with an overall negative charge which is balanced by lithium cations between the layers. The lithium coordination is irregular (Fig. 2), as might be expected in such a situation, but both lithium cations can be viewed as six-coordinated to oxygen (Table V). In this description, most of the oxygen atoms have a coordination number of four, but O5 and O6 have a coordination number of only three. The average Li-O distance for Li2 is 2.12

TABLE IV
ANISOTROPIC THERMAL PARAMETERS ($\times 10^{-4}$ \AA)
FOR Li_2VPO_6

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	59(3)	91(4)	65(3)	-8(4)	3(4)	11(4)
P	75(5)	63(6)	72(5)	-1(5)	8(6)	-4(6)
Li(1)	140(10)	130(10)	190(10)	-5(4)	1(4)	2(5)
Li(2)	280(10)	300(10)	8(5)	2(6)	1(5)	3(5)
O(1)	110(10)	5(2)	8(2)	-1(2)	1(2)	-1(1)
O(2)	8(2)	5(2)	140(10)	1(1)	-1(2)	-2(2)
O(3)	140(10)	4(2)	110(10)	1(2)	-3(2)	-3(2)
O(4)	110(10)	6(2)	9(2)	-1(2)	-1(1)	-1(1)
O(5)	6(2)	8(2)	140(10)	-2(1)	-2(1)	-1(1)
O(6)	140(10)	110(10)	9(2)	1(2)	-1(2)	-3(2)

TABLE V
BOND DISTANCES (\AA) AND ANGLES ($^\circ$) FOR Li_2VPO_6

V	O5	1.629(4)	P	O3	1.514(4)
	O6	1.633(5)		O4	1.539(5)
	O1	1.973(4)		O1	1.545(5)
	O2	2.012(5)		O2	1.563(4)
	O4	2.202(5)			
	O3	2.318(5)			
Li1	O5	2.00(1)	Li2	O4	1.97(1)
	O6	2.04(1)		O3	2.11(1)
	O4	2.11(1)		O5	2.13(1)
	O2	2.11(1)		O6	2.13(1)
	O3	2.30(1)		O1	2.18(1)
	O1	2.50(1)		O2	2.22(1)
O3-V-O6	173.2(2)	O1-V-O6	95.9(2)		
O4-V-O5	157.7(2)	O1-V-O4	85.9(2)		
O1-V-O2	153.2(2)	O3-V-O5	85.4(2)		
O1-V-O5	102.9(2)	O1-V-O3	84.6(2)		
O5-V-O6	101.1(2)	O2-V-O3	80.6(2)		
O4-V-O6	98.3(2)	O3-V-O4	75.0(2)		
O2-V-O5	98.1(2)	O2-V-O4	68.7(2)		
O2-V-O6	96.4(2)				
O3-P-O4	114.8(3)	O1-P-O4	108.5(2)		
O2-P-O3	114.7(2)	O1-P-O2	105.6(3)		
O1-P-O3	112.0(3)	O2-P-O4	100.4(2)		
O2-Li1-O3	174.1(6)	O3-Li1-O5	93.3(5)		
O1-Li1-O5	170.9(6)	O2-Li1-O5	92.5(5)		
O4-Li1-O6	149.7(6)	O1-Li1-O6	88.1(5)		
O4-Li1-O5	109.1(6)	O3-Li1-O6	84.0(4)		
O2-Li1-O4	101.0(5)	O1-Li1-O3	78.7(4)		
O1-Li1-O2	95.5(4)	O3-Li1-O4	77.1(4)		
O5-Li1-O6	95.4(5)	O1-Li1-O4	65.2(3)		
O2-Li1-O6	95.4(5)				
O2-Li2-O4	167.0(7)	O2-Li2-O6	92.2(5)		
O3-Li2-O5	163.4(7)	O4-Li2-O5	91.5(5)		
O1-Li2-O6	158.2(7)	O1-Li2-O3	90.3(5)		
O3-Li2-O4	102.7(6)	O2-Li2-O5	87.2(5)		
O4-Li2-O6	99.7(6)	O2-Li2-O3	80.8(4)		
O1-Li2-O4	99.0(6)	O5-Li2-O6	72.6(5)		
O3-Li2-O6	96.3(6)	O1-Li2-O2	68.3(4)		
O1-Li2-O5	95.9(6)				

\AA whereas the average Li-O distance for Li1 is 2.18 \AA. The significantly longer average distance for Li1 is consistent with the greater distortion of the Li1 octahedron. In fact, if the two long Li1-O bonds are eliminated, we may describe Li1 as in distorted tetrahedral coordination with an average Li-O distance of 2.06 \AA. If this view is

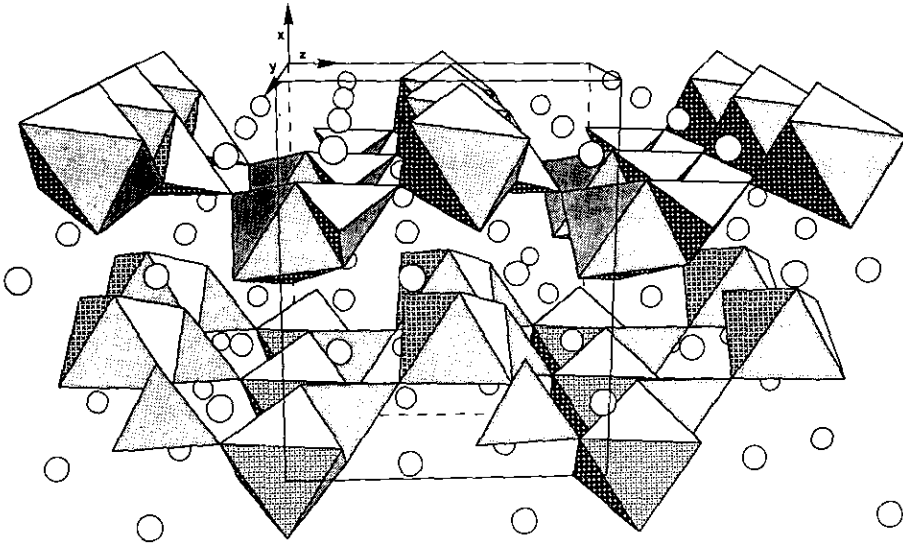


FIG. 1. The structure of Li_2VPO_6 as vanadate octahedra and phosphate tetrahedra connected to form layers within lithium cations (open circles) between the layers.

adopted, the coordination numbers for O1 and O3 also drop to three.

The coordination of vanadium to oxygen is distorted octahedral (Fig. 3), typical of

pentavalent vanadium. However, the sharing of this octahedron with an edge of the phosphate tetrahedron leads to an additional distortion caused by the repulsion between

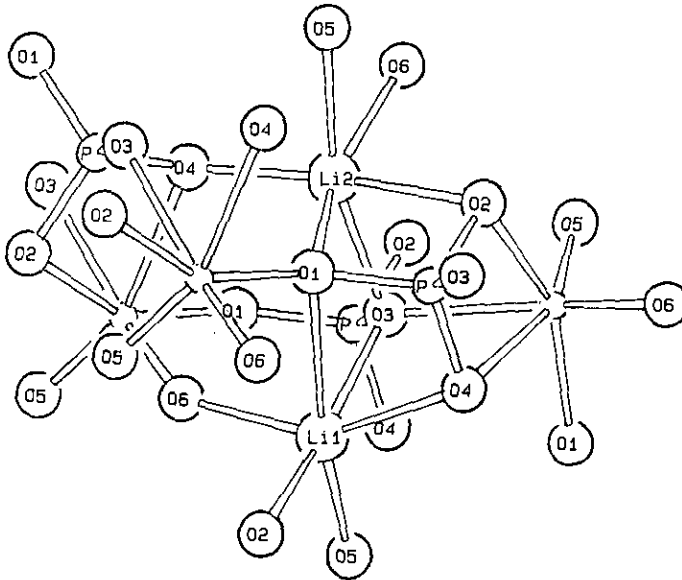


FIG. 2. Vanadium-oxygen-phosphorous ring, showing the lithium coordination.

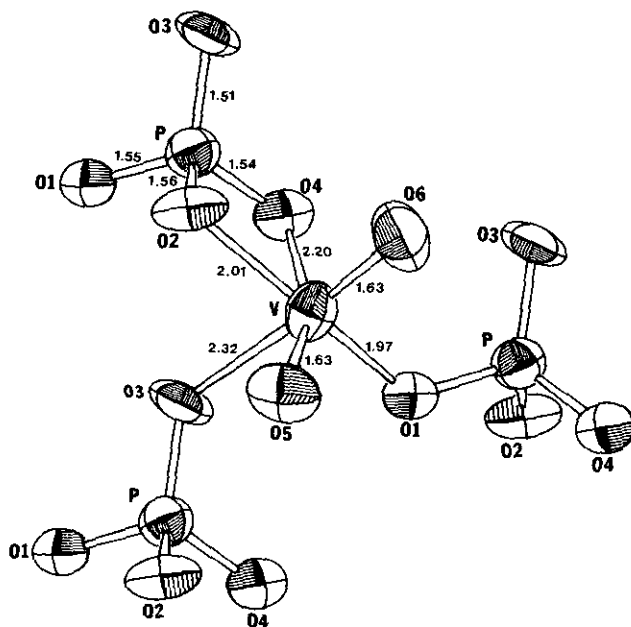


Fig. 3. The environment of vanadium and phosphorous in Li_2VPO_6 .

vanadium and phosphorus across this edge. The O2–V–O4 angle of this edge is only 68.7° , considerably smaller than the ideal octahedral value. Likewise, the O2–P–O4 for this edge is only 100.4° , much smaller than the ideal tetrahedral value.

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