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Crystal structure of a new vanadium(IV) diphosphate: VP_2O_7 , prepared by lithium extraction from LiVP_2O_7

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Abstract

A new vanadium(IV) diphosphate, VP_2O_7 , was obtained by lithium extraction from LiVP_2O_7 . The parent compound, LiVP_2O_7 , is built on $[\text{P}_2\text{O}_7]$ groups and $[\text{VO}_6]$ octahedra and its structure has been confirmed by Synchrotron X-ray powder diffraction. The extraction of one lithium, both electrochemically or chemically, leads to VP_2O_7 which presents a totally different diffraction pattern diagram. The crystal structure of this new compound was determined from Synchrotron X-ray powder diffraction on the chemically prepared sample. The framework of LiVP_2O_7 is maintained upon lithium extraction, and VP_2O_7 crystallizes in space group $P2_1$. Compared to LiVP_2O_7 , there is a very large cell distortion due to a modification of the shape of the tunnels that contained lithium ions along with an oxidation of the vanadium V^{III} to V^{IV} that induces shorter V–O bond lengths. The phase transformation from LiVP_2O_7 to VP_2O_7 is found to be displacive and not reconstructive. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There is a large number of crystalline materials containing pyrophosphate $[\text{P}_2\text{O}_7]$ groups in the literature, with general formula AMP_2O_7 (A=monovalent cation, M=transition metal) [1]. Due to their open 3D structure, they can accommodate a large number of different alkaline ions. Most of them are isostructural, with space group $P2_1/c$, as for example NaVP_2O_7 [2], KVP_2O_7 [3], RbVP_2O_7 [4] and CsVP_2O_7 [5]. When the alkaline ion is lithium, the compounds present a different structure with loss of the inversion center. LiVP_2O_7 [6], LiFeP_2O_7 [7], LiMoP_2O_7 [8,9] and LiInP_2O_7 [10] crystallize indeed in the space group $P2_1$. High ionic conductivity and presence of transition metal oxide make these compounds interesting as alternative positive electrodes for lithium batteries [11]. We

recently undertook a general study on the electrochemical properties of LiMX_2O_7 (M=Fe, V; X=P, As) [12].

Lithium may be inserted into LiFeX_2O_7 (reduction Fe^{3+} to Fe^{2+}) at potentials of 2.95 and 2.50 V versus Li^+/Li for X=P and As, respectively, or into LiVP_2O_7 (reduction of V^{3+} to V^{2+}) at 2 V. On the other hand, lithium can also be extracted from LiVP_2O_7 (oxidation V^{3+} to V^{4+}) at a higher potential of 4.2 V versus Li^+/Li , making this compound attractive for lithium battery applications.

This paper deals with the determination and analysis of the crystal structure of VP_2O_7 obtained by electrochemical or chemical extraction from LiVP_2O_7 and is part of our general study searching for new cathode materials for lithium batteries. It was indeed quite interesting to know whether this new compound would be isostructural to the Li-parent compound (space group $P2_1$) or the result of a reconstructive transformation during lithium extraction. Reconstructive transformations are known to occur through the additional plateau at 3.3 V in LiMn_2O_4 (spinel to double-hexagonal transformation [13]) or at high values of x in $\text{Li}_{1-x}\text{CoO}_2$ at which oxygen stacking goes from ABCABC to ABAB [14]. Reconstructive transformations

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lead to either poor reversible cyclability (LiCoO_2) or high polarization in the charge–discharge curve (LiMn_2O_4) partly due to the displacement energy.

2. Experimental

2.1. Sample preparation

LiVP_2O_7 was prepared as a pure green polycrystalline single phase using a general chemical route that we recently developed [12]. VP_2O_7 was obtained by both chemical and electrochemical extractions of lithium from LiVP_2O_7 . Chemical extraction was carried out in an argon-filled glove box by mixing LiVP_2O_7 with NO_2BF_4 (3-fold excess) dissolved in acetonitrile for 2 weeks. The obtained product was washed several times with acetonitrile and dried. Chemical analysis revealed that the lithium content was smaller than 300 ppm. The electrochemical extraction of one lithium was undertaken in a standard swagelok cell configuration with metallic lithium as the negative and reference electrodes, using LiPF_6 (1M) EC:DMC 1:1 under slow potentiodynamic mode up to 4.5 V versus Li^+/Li . The active oxidized material was then removed from the cell in the glove box, washed three times with DMC. Both chemically and electrochemically made VP_2O_7 were placed in a sealed-capillary for Synchrotron X-ray diffraction at LURE (Orsay, France).

2.2. Synchrotron X-ray diffraction

High-resolution Synchrotron X-ray diffraction patterns were recorded on the WD4C wiggler beamline of the DCI ring of LURE. A Si(111) monochromator was used to provide a wavelength of 1.0705 Å. The program FullProf [15] was used for crystal structure refinements using the Rietveld method [16], and the anomalous dispersion

Table 2

Structural parameters of LiVP_2O_7 determined from Synchrotron X-ray diffraction at 290 K (space group $P2_1$)

LiVP_2O_7	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso} (Å ²)
V(1)	0.2163(4)	0.5	0.7285(3)	1.29(4)
P(1)	0.2115(7)	0.7846(4)	0.0850(5)	1.09(6)
P(2)	0.3996(5)	0.1812(5)	0.5220(4)	1.23(6)
O(1)	−0.184(1)	0.5345(9)	0.5190(9)	0.87(5) ^a
O(2)	0.398(1)	0.678(1)	0.6076(8)	0.87(5) ^a
O(3)	0.056(1)	0.3219(8)	0.8546(9)	0.87(5) ^a
O(4)	0.246(1)	0.3467(8)	0.5050(8)	0.87(5) ^a
O(5)	0.125(1)	0.6944(9)	0.8871(9)	0.87(5) ^a
O(6)	0.599(1)	0.4350(8)	0.9191(9)	0.87(5) ^a
O(7)	0.407(1)	0.6506(8)	0.2443(8)	0.87(5) ^a
Li	0.172(5)	0.865(2)	0.680(3)	1.64(45)

^a Constrained to the same value.

correction for 1.0705 Å was taken into account for the refinement.

3. Results and discussion

3.1. Crystal structure of LiVP_2O_7 from powder diffraction

The quality and purity of the parent compound, LiVP_2O_7 , was first carefully checked by Synchrotron X-ray diffraction. It is the first time, to our knowledge, that this compound is prepared pure as a polycrystalline powder. This compound was discovered and studied 10 years ago by Lii et al. [6] from single-crystal X-ray diffraction. They determined its crystal structure and realized that the space group $P2_1/c$, common to all the vanadium analogs, did not match. LiVP_2O_7 was found to be isostructural with the iron analog LiFeP_2O_7 [7] with space group $P2_1$. We refined the crystal structure of LiVP_2O_7 from our powder X-ray diffraction data at room temperature, starting from the atomic positions of Lii et al. [6]. There are 11 independent atomic positions in the cell,

Table 1

Unit cell parameters of LiVP_2O_7 and VP_2O_7 determined from Synchrotron X-ray diffraction at 290 K, compared with the values for LiVP_2O_7 obtained by Lii et al. [6] from single-crystal X-ray diffraction

	LiVP_2O_7 our data synchrotron X-ray powder diffraction ^a	LiVP_2O_7 from Lii et al. [6] single-crystal X-ray diffraction	VP_2O_7 synchrotron X-ray powder diffraction ^b
Temperature	$T=290$ K	$T=290$ K	$T=290$ K
Wavelength	$\lambda=1.0705$ Å	$\lambda=0.7093$ Å	$\lambda=1.0705$ Å
Space group	$P2_1$	$P2_1$	$P2_1$
<i>a</i>	4.8085(1) Å	4.8048(6) Å	4.7725(1) Å
<i>b</i>	8.1151(1) Å	8.113(1) Å	7.8710(2) Å
<i>c</i>	6.9379(1) Å	6.9393(9) Å	6.8618(2) Å
β	108.9705(9) °	109.01(1) °	106.1417(10) °
Volume	256.02(1) Å ³	255.75(7) Å ³	247.59(1) Å ³

^a R_p , 12.6; R_{wp} , 13.3; R_{exp} , 6.30; χ^2 , 4.48; Bragg *R*-factor, 4.06; $N - P + C$, 6904; total number of ‘independent’ reflections, 502.

^b R_p , 12.8; R_{wp} , 14.2; R_{exp} , 7.13; χ^2 , 3.99; Bragg *R*-factor, 3.50; $N - P + C$, 6815; total number of ‘independent’ reflections, 484.

all in general position $2a$ ($x, y, z; -x, y+1/2, -z$). The vanadium coordinate along $[010]$ was set to $1/2$ to fix the floating origin along the b axis. The thermal parameters were refined and constrained to be equal for the seven oxygen atoms of the asymmetric unit cell. The lattice parameters and reliability factors are reported in Table 1 together with the structural parameters obtained by Lii et al., on single crystal. The atomic positions are listed in Table 2 and are in perfect agreement with the single-crystal study. Selected interatomic distances and angles are given in Table 3. The average M–O distances (M=V, P, Li) are also reported, as well as the bond valence sum (BVS) calculated using the Zachariasen formula: $V_i = \sum_j s_{ij} = \sum_j \exp\{(d_0 - d_{ij})/0.37\}$ using the parameters d_0 , characterizing a cation–anion pair, from Ref. [17]. In Table 3 we have also calculated the distortion parameter Δ of each coordination polyhedron BO_N , defined as: $\Delta = (1/N) \sum_{n=1,N} \{(d_n - \langle d \rangle) / \langle d \rangle\}^2$ with an average B–O distance $\langle d \rangle$. The BVS confirms the expected valence of each cation, i.e., V(+III), P(+V) and Li(+I). The average V–O bond length is of 2.002 Å, characteristic of vanadium in the oxidation state +3 in octahedral environment. Note also that the longest P–O bond lengths (1.618 Å) involves the ‘bridging’ oxygen O(7) common to both P(1)O₄ and P(2)O₄ tetrahedra. Fig. 1 shows a view of the structure of LiVP₂O₇ that presents cavities into which the lithium ions are located. This structure differs from that of NaVP₂O₇ and CsVP₂O₇ by the shape of these cavities. This has been

explained in detail by Lii et al. [6]. The cavities are interconnected through tunnels running along $[100]$ and we found that lithium ions could be extracted reversibly from the structure.

3.2. Crystal structure of VP₂O₇

The electrochemical extraction of one electron from LiVP₂O₇ occurs as a two phases process from a pretty high equilibrium potential of 4.26 V versus Li⁺/Li, as shown in Fig. 2. The compound obtained at the end of the oxidation (either electrochemically or chemically) is totally exempt of lithium and its diffraction pattern differs significantly from that of the starting LiVP₂O₇ (Fig. 3). A close look at the electrochemical data of Fig. 2, that shows a small hysteresis between the oxidation and reduction processes, suggested that the transformation between LiVP₂O₇ and VP₂O₇ is displacive, i.e., without breaking of V–O and P–O bonds. This process, followed by in situ X-ray diffraction, will be discussed in much more detail in a forthcoming paper [12].

Both electrochemically and chemically made VP₂O₇ present very similar patterns (Fig. 3), indicating that Li was indeed removed from the structure during the charge of the battery. The number of electrons involved in the electrochemical process does not result from an oxidation of the electrolyte or some other parasitic process. The only difference between the two samples is the shape of the

Table 3
M–O distances (Å, diagonal) and O–M–O angles (°) in VO₆/PO₄/LiO₄ polyhedra (M=V, P, Li) for LiVP₂O₇

V(1)	O(1)i	O(2)i	O(3)i	O(4)i	O(5)i	O(6)i	
O(1)i	2.016(7)						Average distance: 2.003(3)
O(2)i	92.3 (4)	2.014(7)					Distortion: 2.8×E-04
O(3)i	90.2 (4)	177.5 (6)	1.969(7)				B.V. Sum: 2.98(2)
O(4)i	79.8 (4)	88.5 (5)	91.6 (4)	2.020(6)			
O(5)i	87.5 (4)	82.2 (4)	98.2 (5)	164.0 (5)	2.050(7)		
O(6)i	172.2 (5)	92.2 (5)	85.3 (4)	94.0 (4)	99.3 (4)	1.951(4)	
P(1)	O(3)ii		O(5)i		O(6)ii	O(7)i	
O(3)ii	1.510(8)						Average distance: 1.538(4)
O(5)i	110.2 (6)		1.492(7)				Distortion: 9.8×E-04
O(6)ii	114.6 (7)		111.5 (6)		1.534(7)		B.V. Sum: 4.99(5)
O(7)i	107.6 (6)		102.7 (5)		109.5 (6)	1.618(7)	
P(2)	O(1)ii		O(2)ii		O(4)i	O(7)ii	
O(1)ii	1.545(8)						Average distance: 1.552(4)
O(2)ii	113.6 (7)		1.526(6)				Distortion: 4.7×E-04
O(4)i	112.9 (7)		110.7 (6)		1.527(8)		B.V. Sum: 4.80(5)
O(7)ii	101.7 (6)		108.5 (5)		108.8 (6)	1.609(6)	
Li	O(1)ii		O(2)i		O(4)ii	O(5)i	
O(1)ii	1.96(2)						Average distance: 2.01(1)
O(2)i	101.9(8)		2.01(2)				Distortion: 3.1×E-04
O(4)ii	81.5(8)		107.2 (8)		2.00(2)		B.V. Sum: 0.92(2)
O(5)i	175.5		81.9(7)		95.0(8)	2.06(2)	

The average distance in each polyhedron, the distortion Δ of the polyhedron and a bond strength analysis for each cation are also indicated (see text) (i, x, y, z ; ii, $-x, y+1/2, -z$).

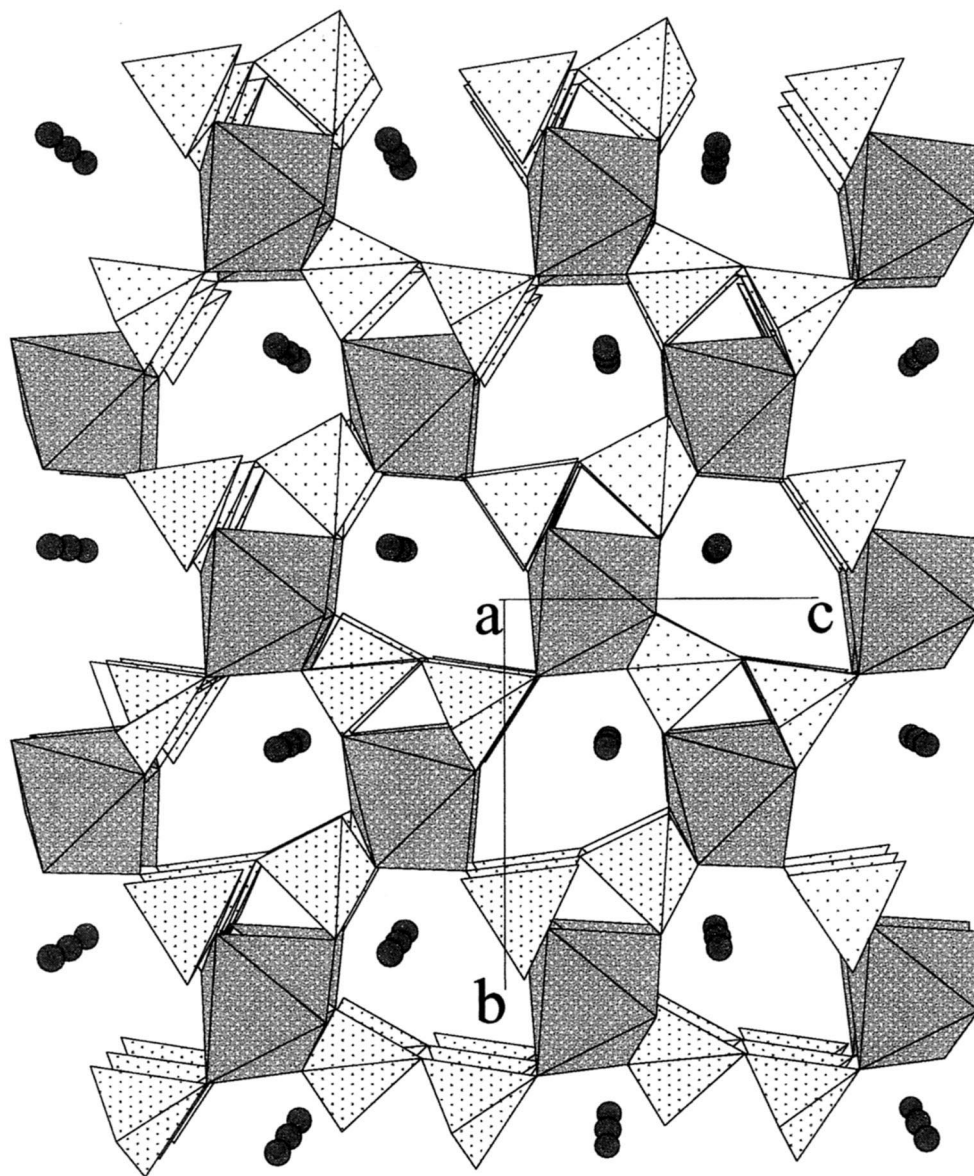


Fig. 1. Structure of LiVP_2O_7 . The $[\text{P}_2\text{O}_7]$ diphosphate groups and VO_6 octahedra delimit tunnels from/into which lithium can be extracted/reinserted.

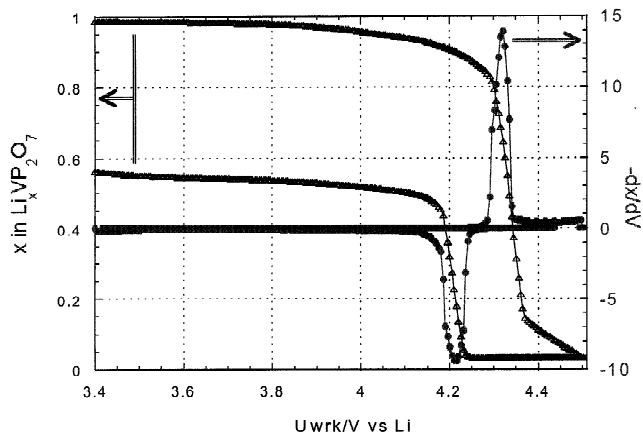


Fig. 2. Electrochemical extraction of lithium in a $\text{LiVP}_2\text{O}_7/\text{Li}$ cell between 3.4 and 4.5 V in a potentiodynamic cycling with galvanostatic acceleration mode (PCGA) at an equivalent rate of C/SO.

background, that is much higher for the electrochemically made sample, due to the presence of amorphous carbon that was used to ensure electronic conduction from the current collector to the active material. For that reason, Rietveld refinements were performed on the chemically made sample, and the structural model obtained was subsequently compared to that of the electrochemically made sample.

The determination of the structure of VP_2O_7 was performed from a multi-steps procedure: we first tried to determine the cell parameters starting from LiVP_2O_7 , but unsuccessfully. The program Dicvol 91 [18,19] was then used to determine the unit cell parameters that could index the diffraction pattern of VP_2O_7 . Two possible unit cells were found, both in the space group $P2_1$, that indexed perfectly the diffraction pattern. At this stage, the two possible sets of lattice parameters were: $a=4.77 \text{ \AA}$, $b=$

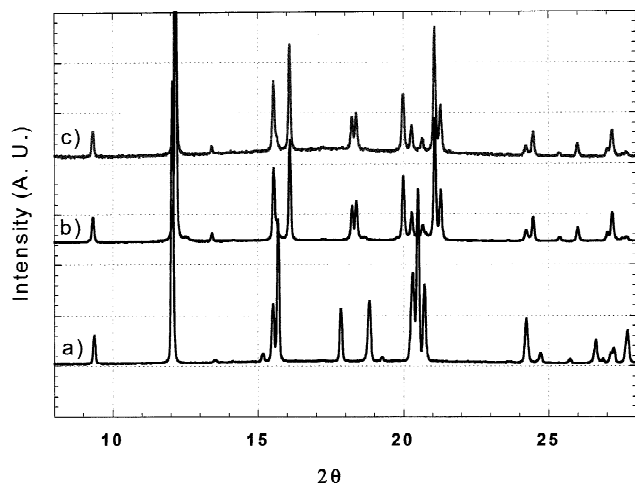


Fig. 3. Comparison between LiVP_2O_7 (a) and VP_2O_7 (b) obtained by chemical extraction, (c) obtained by electrochemical extraction diffraction patterns ($\lambda=1.0705 \text{ \AA}$).

7.87 \AA , $c=7.19 \text{ \AA}$, $\beta=113.49^\circ$ and $a=4.77 \text{ \AA}$, $b=7.87 \text{ \AA}$, $c=6.86 \text{ \AA}$, $\beta=106.14^\circ$. Both cells present the same values for a and b , but significantly different ones for c and β . Note that these two cells are both strongly distorted when compared to that of LiVP_2O_7 . In a second stage, the atomic positions of V, P and O of LiVP_2O_7 were used for Rietveld refinements in each of the two cells determined

Table 4

Structural parameters of VP_2O_7 determined from Synchrotron X-ray diffraction at 290 K (space group $P2_1$)

VP_2O_7	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$
V(1)	0.2158(5)	0.5	0.7270(3)	1.26(4)
P(1)	0.2309(7)	0.7685(5)	0.1007(6)	1.29(8)
P(2)	0.3965(7)	0.1828(5)	0.5069(5)	1.69(8)
O(1)	-0.156(1)	0.546(1)	0.537(1)	0.81(6)
O(2)	0.412(1)	0.673(1)	0.6284(9)	0.81(6) ^a
O(3)	0.042(2)	0.3229(9)	0.8321(9)	0.81(6) ^a
O(4)	0.262(1)	0.3593(9)	0.5111(9)	0.81(6) ^a
O(5)	0.144(1)	0.664(1)	0.915(1)	0.81(6) ^a
O(6)	0.578(1)	0.411(1)	0.910(1)	0.81(6) ^a
O(7)	0.412(1)	0.6412(9)	0.2695(9)	0.81(6) ^a

^a Constrained to the same value.

previously. It turned out that only the second solution gave satisfactory results and that the parent framework is maintained (but distorted) upon extraction of Li from LiVP_2O_7 . Rietveld refinements were processed for the atomic positions of the seven oxygen, two phosphorus and one vanadium atoms, with thermal parameters constrained to be equal for the oxygen atoms. This resulted in a very satisfactory refinement (Fig. 4), with final structural parameters and atomic positions listed in Tables 1 and 4, respectively. The cell volume decreases by 3.3% upon lithium extraction, mostly due to a strong contraction along

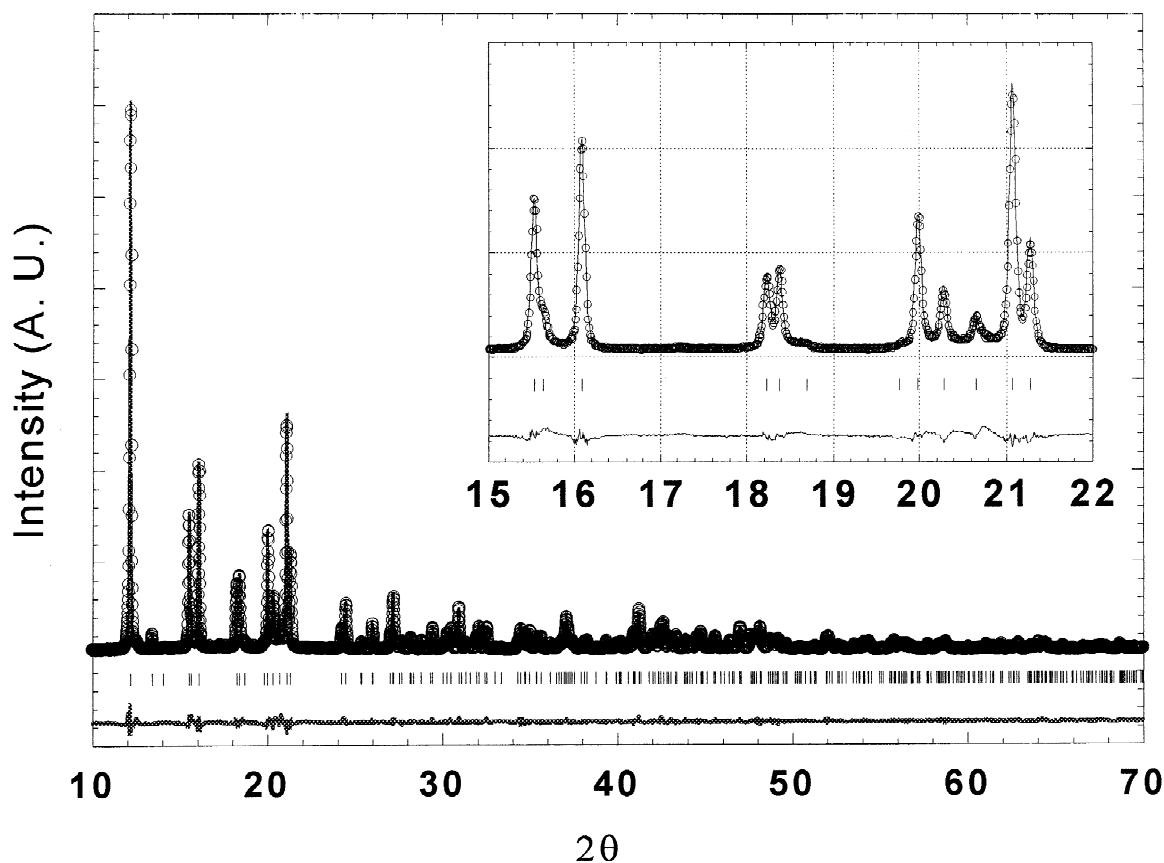


Fig. 4. Observed (circles) versus calculated (continuous line) Synchrotron X-ray powder diffraction patterns of the chemically prepared VP_2O_7 compound ($\lambda=1.0705 \text{ \AA}$). Position of the Bragg reflections are represented by vertical bars (space group $P2_1$). The insert is a zoom on the low-angles region.

Table 5

M–O distances (Å, diagonal) and O–M–O angles (°) in VO₆/PO₄ polyhedra (M=V, P) for VP₂O₇

V(1)	O(1)i	O(2)i	O(3)i	O(4)i	O(5)i	O(6)i
O(1)i	1.924(7)					Average distance: 1.910(3)
O(2)i	94.4 (6)	1.882(8)				Distortion: 2.7×E-04
O(3)i	88.7 (5)	176.7 (8)	1.862(8)			B.V. Sum: 4.28(4)
O(4)i	82.2 (5)	87.9 (6)	91.5 (6)	1.908(7)		
O(5)i	91.4 (6)	87.5 (5)	93.4 (6)	171.0 (7)	1.922(8)	
O(6)i	169.9 (7)	92.9 (6)	83.9 (6)	91.2 (5)	95.8 (6)	1.960(7)
P(1)	O(3)ii	O(7)i	O(6)ii	O(7)i		
O(3)ii	1.56(1)				Average distance: 1.524(4)	
O(5)i	110.4 (8)	1.477(9)			Distortion: 12.9×E-04	
O(6)ii	112.8 (9)	114.7 (9)	1.463(9)		B.V. Sum: 5.20(6)	
O(7)i	106.5 (8)	103.9 (7)	107.5 (8)	1.592(8)		
P(2)	O(1)ii	O(2)ii	O(4)i	O(7)ii		
O(1)ii	1.544(9)				Average distance: 1.536(4)	
O(2)ii	113.5 (8)	1.474(8)			Distortion: 7.1×E-04	
O(4)i	110.0 (8)	113.4 (8)	1.537(9)		B.V. Sum: 5.00(1)	
O(7)ii	104.0 (7)	107.7 (7)	107.6 (7)	1.589(7)		

The average distance in each polyhedron, the distortion Δ of the polyhedron and a bond strength analysis for each cation are also indicated (see text) (i, x, y, z; ii, -x, y+1/2, -z).

[010]. The list of interatomic distances and bond angles is reported in Table 5. Note that the electrochemically made VP₂O₇ presents exactly the same structural parameters.

The crystal structure of VP₂O₇ is somewhat similar to that of LiVP₂O₇ but some interesting subtle differences arise from (i) the oxidation of vanadium and (ii) the absence of lithium. The vanadium atom is octahedrally coordinated by oxygen atoms and, not surprisingly, the average V–O distance is decreased from 2.00 to 1.91 Å upon oxidation of V³⁺ to V⁴⁺ which is supported by the values found from the bond-valence analysis (Tables 3 and 5) and is in agreement with the forecasted oxidation of the compound upon the extraction of one lithium ion.

VO₆ octahedra are not directly connected to each other through common oxygen atoms, but through phosphate groups each VO₆ octahedron is linked to five P₂O₇, one of them acting as a ‘chelating’ group through the oxygen atoms O(6) and O(4), as observed in many diphosphates of transition metal elements [1] (Fig. 5). Fig. 5 shows clearly also the peculiar role of O(7) which acts as the bridging atom common to two PO₄ tetrahedra consequently, the value of the P–O(7) bond length is somewhat larger than that of the other PO bonds. The reduction in size of the VO₆ octahedron may induce some sort of stress within the ‘chelating’ P₂O₇ group as this would logically lead to a decrease of the P(2)–O(7)–P(1) angle. On going from LiVP₂O₇ to VP₂O₇ we surprisingly observed that this angle (roughly 127.5°) does not significantly change. In fact, we observe an anisotropic reduction in size of the VO₆ octahedron, as the V–O(6) bond length basically does not change.

One peculiar feature of the structure of LiVP₂O₇ is the existence of large cavities running as tunnels along [100]

where lithium ions are located, shown in Fig. 1. Due to their small size, lithium ions are located at the periphery of the tunnels, with, as explained by Lii et al. [6], an irregular coordination of six oxygen atoms. Four oxygen neighbours (O(1), O(2), O(4) and O(5)) are located at an average distance of 2.01 Å (Table 3). O(6) and O(7) lie at distances of 2.7 and 3.0 Å, respectively (Fig. 6). The bond valence sum considering the first four Li–O bonds is 0.92(2), very close to the expected value. The four oxygen neighbours do not define a tetrahedron around lithium but rather a geometry similar to that found in the molecule

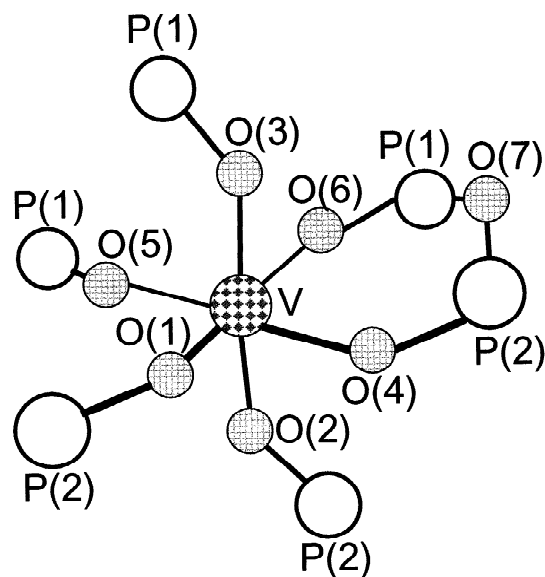


Fig. 5. Local environment of the vanadium ion in VP₂O₇. O(7) is linking the two [PO₄] tetrahedra to form the bidentate pyrophosphate group [P₂O₇].

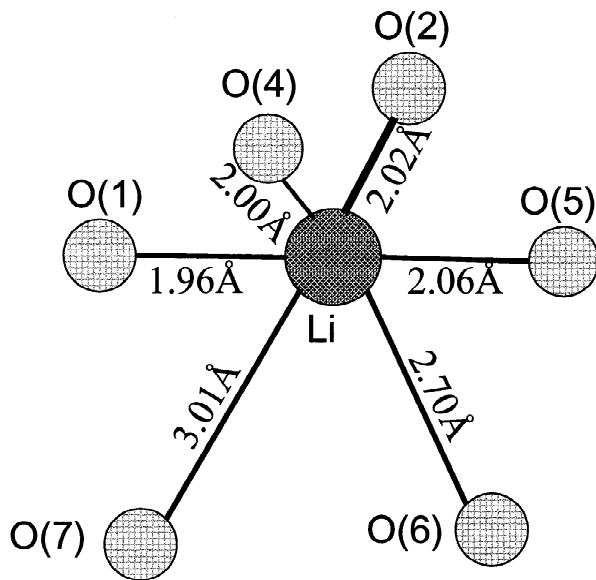


Fig. 6. Local environment of the lithium ion in LiVP_2O_7 . Li is surrounded by four first oxygen neighbours in a SF_4 geometry.

SF_4 . When lithium is removed from the structure, this cage is largely modified. Distances between the four closest neighbours increase strongly (for instance, the distance between O(4) and O(5) increases from 2.99 to 3.39 Å, the distance between O(1) and O(2) increases from 3.09 to 3.27 Å. When lithium is removed, the ‘cage’ relaxes as a result of electrostatic repulsions between neighbouring oxygen atoms. This is illustrated in Fig. 7 where the ‘tunnels’ are represented for both compounds. The dashed line on each figure corresponds to the tunnel shape in the other compound.

The distortion induced by the extraction of lithium, along with the oxidation of the vanadium that requires

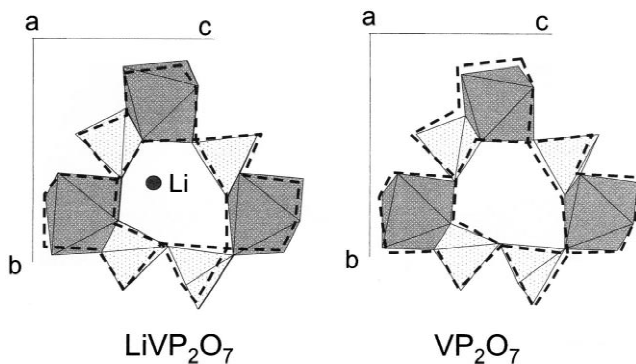


Fig. 7. Tunnels for lithium ions in LiVP_2O_7 (left) and VP_2O_7 (right). The shape of the tunnel of the other structure is represented by dashed lines to facilitate the observation of the distortion.

shorter V–O distances, is at the origin of the distortion of the cell that modifies drastically the diffraction pattern. Note that the bond sequences in the framework itself are not modified, in agreement with the electrochemical data. This distortion is reversible, as the diffraction pattern of LiVP_2O_7 is restored from electrochemical insertion of lithium into VP_2O_7 (reduction of V^{4+} to V^{3+}). However, an apparent irreversibility of 0.4 Li was observed at the first cycle. Figuring out the reason for such an important irreversibility that does not result from a reconstructive phase transformation (as for the 3.3 V plateau of LiMn_2O_4 or for high potential phases Li_xCoO_2) is the purpose of a future work.

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