

$wR(F^2) = 0,068$
 $S = 1,133$
 1512 réflexions
 141 paramètres
 $w = 1/[\sigma^2(F_o^2) + (0,0233P)^2]$
 où $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0,004$

Correction d'extinction:
 SHELXL93 (Sheldrick,
 1993)
 Coefficient d'extinction:
 0,00035 (7)
 Facteurs de diffusion des
 International Tables for
 Crystallography (Tome C)

Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: DU1175). Les processus d'accès à ces archives sont donnés au dos de la couverture.

Tableau 1. Paramètres géométriques (Å, °)

Cs1—O3	3,062 (5)	(As,V)1—O5	1,630 (5)
Cs1—O3 ⁱ	3,062 (5)	(As,V)1—O8	1,635 (4)
Cs1—O9 ⁱⁱ	3,275 (7)	(As,V)1—O4	1,719 (3)
Cs1—O1 ⁱⁱⁱ	3,318 (5)	(As,V)2—O3	1,613 (5)
Cs1—O1 ^{iv}	3,318 (5)	(As,V)2—O7	1,627 (5)
Cs1—O8 ⁱⁱⁱ	3,386 (5)	(As,V)2—O6	1,644 (5)
Cs1—O8 ^v	3,386 (5)	(As,V)2—O2	1,716 (3)
Cs1—O7 ⁱ	3,425 (5)	V1—O11 ^s	1,583 (8)
Cs1—O7	3,425 (5)	V1—O7 ^{xi}	1,983 (5)
Cs1—O6 ^v	3,551 (5)	V1—O7 ^{xii}	1,983 (5)
Cs1—O6 ⁱⁱ	3,551 (5)	V1—O8	1,989 (5)
Cs2—O4 ^{vi}	3,201 (7)	V1—O8 ⁱ	1,989 (5)
Cs2—O11	3,250 (7)	V2—O9	1,593 (7)
Cs2—O2 ^{vii}	3,293 (7)	V2—O5	1,967 (5)
Cs2—O8 ^v	3,344 (5)	V2—O5 ^{xiii}	1,967 (5)
Cs2—O8 ⁱⁱ	3,344 (5)	V2—O6 ^{xiii}	1,972 (5)
Cs2—O5 ^{viii}	3,431 (5)	V2—O6	1,972 (5)
Cs2—O5 ^{vi}	3,431 (5)	V3—O10 ⁱⁱⁱ	1,636 (3)
Cs2—O7 ^{ix}	3,486 (5)	V3—O1 ^{iv}	1,979 (9)
Cs2—O7 ^{vii}	3,486 (5)	V3—O3 ⁱ	1,985 (9)
Cs2—O6 ^{viii}	3,522 (5)	V3—O3 ^{iv}	1,992 (8)
Cs2—O6 ^{vi}	3,522 (5)	V3—O1 ⁱ	1,993 (9)
Cs2—O5 ^v	3,561 (5)	V3—O10 ^{xiv}	2,190 (3)
(As,V)1—O1	1,619 (5)		
O1—(As,V)1—O5	111,2 (3)	O5—V2—O5 ^{xiii}	85,2 (3)
O1—(As,V)1—O8	111,2 (2)	O9—V2—O6 ^{xiii}	103,1 (2)
O5—(As,V)1—O8	109,4 (2)	O5—V2—O6 ^{xiii}	153,0 (2)
O1—(As,V)1—O4	109,8 (3)	O5 ^{xiii} —V2—O6 ^{xiii}	86,4 (2)
O5—(As,V)1—O4	105,7 (3)	O9—V2—O6	103,1 (2)
O8—(As,V)1—O4	109,4 (3)	O5—V2—O6	86,4 (2)
O3—(As,V)2—O7	109,6 (3)	O5 ^{xiii} —V2—O6	153,0 (2)
O3—(As,V)2—O6	115,9 (3)	O6 ^{xiii} —V2—O6	89,5 (3)
O7—(As,V)2—O6	114,5 (2)	O10 ⁱⁱⁱ —V3—O1 ^{iv}	96,3 (4)
O3—(As,V)2—O2	107,3 (3)	O10 ⁱⁱⁱ —V3—O3 ⁱ	97,4 (4)
O7—(As,V)2—O2	100,9 (3)	O1 ^{iv} —V3—O3 ⁱ	87,1 (4)
O6—(As,V)2—O2	107,2 (3)	O10 ⁱⁱⁱ —V3—O3 ^{iv}	98,6 (4)
O11 ^s —V1—O7 ^{xii}	103,0 (2)	O1 ^{iv} —V3—O3 ^{iv}	91,1 (4)
O11 ^s —V1—O7 ^{xii}	103,0 (2)	O3 ⁱ —V3—O3 ^{iv}	164,0 (2)
O7 ^{xii} —V1—O7 ^{xii}	89,8 (3)	O10 ⁱⁱⁱ —V3—O1 ⁱ	99,8 (4)
O11 ^s —V1—O8	103,5 (2)	O1 ^{iv} —V3—O1 ⁱ	164,0 (2)
O7 ^{xii} —V1—O8	153,5 (2)	O3 ⁱ —V3—O1 ⁱ	90,9 (4)
O7 ^{xii} —V1—O8	83,5 (2)	O3 ^{iv} —V3—O1 ⁱ	86,5 (4)
O11 ^s —V1—O8 ⁱ	103,5 (2)	O10 ⁱⁱⁱ —V3—O10 ^{xiv}	179,9 (4)
O7 ^{xii} —V1—O8 ⁱ	83,5 (2)	O1 ^{iv} —V3—O10 ^{xiv}	83,7 (3)
O7 ^{xii} —V1—O8 ⁱ	153,5 (2)	O3 ⁱ —V3—O10 ^{xiv}	82,6 (3)
O8—V1—O8 ⁱ	91,1 (3)	O3 ^{iv} —V3—O10 ^{xiv}	81,3 (3)
O9—V2—O5	103,8 (2)	O1 ⁱ —V3—O10 ^{xiv}	80,3 (3)
O9—V2—O5 ^{xiii}	103,9 (2)		

Codes de symétrie: (i) $x, \frac{1}{2} - y, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$; (iii) $-x, 1 - y, -z$; (iv) $-x, y - \frac{1}{2}, -z$; (v) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} - z$; (vii) $1 - x, 1 - y, -z$; (viii) $\frac{1}{2} + x, y, -\frac{1}{2} - z$; (ix) $1 - x, y - \frac{1}{2}, -z$; (x) $x - 1, y, z$; (xi) $x - \frac{1}{2}, \frac{1}{2} - y, -\frac{1}{2} - z$; (xii) $x - \frac{1}{2}, y, -\frac{1}{2} - z$; (xiii) $x, \frac{3}{2} - y, z$; (xiv) $x, y - 1, z$.

Collection des données: CAD-4 EXPRESS (Duisenberg, 1992; Macíček & Yordanov, 1992). Affinement des paramètres de la maille: CAD-4 EXPRESS. Réduction des données: MolEN (Fair, 1990). Programme(s) pour la solution de la structure: SHELXS86 (Sheldrick, 1990). Programme(s) pour l'affinement de la structure: SHELXL93 (Sheldrick, 1993). Logiciel utilisé pour préparer le matériel pour publication: SHELXL93.

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Acta Cryst. (1998). **C54**, 1204–1206

Electrochemically Lithiated Vanadium Oxide, Li₃V₆O₁₃

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(Received 20 October 1997; accepted 18 March 1998)

Abstract

Single crystals of V₆O₁₃ were grown by chemical vapour transport (CVT) and subsequently electrochemically lithiated. The title compound, trilithium hexavanadium tridecaoxide, was the phase formed during electrochemical lithiation at 2.45 V versus Li/Li⁺. The Li₃V₆O₁₃ structure comprises single and double layers of VO₆ octahedra stacked in the *c* direction. Lithiation results in a 6.5% expansion along the *b* axis with respect to V₆O₁₃. Li atoms are located in two types of crystallographically independent sites: (i) a fully occupied 4i site with fivefold square-pyramidal O-atom coordination [Li—O distances in the range 1.960(1)–2.031(5) Å]; (ii) one 50% occupied 4i site with planar quadratic O-atom coordination [Li—O distances in the range 1.99(1)–2.08(5) Å].

Comment

Precise knowledge of the crystal structures of successive phases formed during lithium insertion/extraction is crucial to an understanding of cycling behaviour in electrochemical materials relevant to lithium-ion batteries. Earlier work (Berg *et al.*, 1997) has indicated the need for single-crystal data to reveal the subtleties of lithium intercalation processes in transition metal oxides. In the single-crystal study of an electrochemically lithiated sample presented here, we were able to determine the lithiated structure of V_6O_{13} at 2.45 V versus Li/Li^+ .

The V_6O_{13} structure can be described in terms of layers of VO_6 octahedra parallel to the ab plane. Two types of layer occur in the structure: a single layer at $z = 0$ containing V1, and a double layer at $z = 0.5$ containing V2 and V3. The two layers are connected via corner sharing of O5 and O6 atoms (Wilhelmi *et al.*, 1971). After the insertion of lithium into V_6O_{13} to form $Li_2V_6O_{13}$, each Li atom is located in a fully occupied $4i$ site with fivefold O-atom coordination in a tetragonal pyramid between the vanadium–oxygen layers (Bergström *et al.*, 1997). This lithiation process coincides with a 7.6% c -axis expansion with respect to V_6O_{13} . The $Li_3V_6O_{13}$ phase (see Fig. 1) is reached on further lithium insertion with a c -axis contraction almost back to that of pure V_6O_{13} , and a 5.6% b -axis expansion compared with V_6O_{13} . In $Li_3V_6O_{13}$, Li atoms occupy two crystallographically independent sites. One type of Li-atom site is a fully occupied $4i$ site with fivefold O-atom coordination in a pyramidal arrangement in the double layer, with Li–O distances in the range 1.960(1)–2.031(5) Å; this site has coordination similar to that found in $Li_2V_6O_{13}$. The second Li-atom site is also of the $4i$ type, with distorted planar quadratic

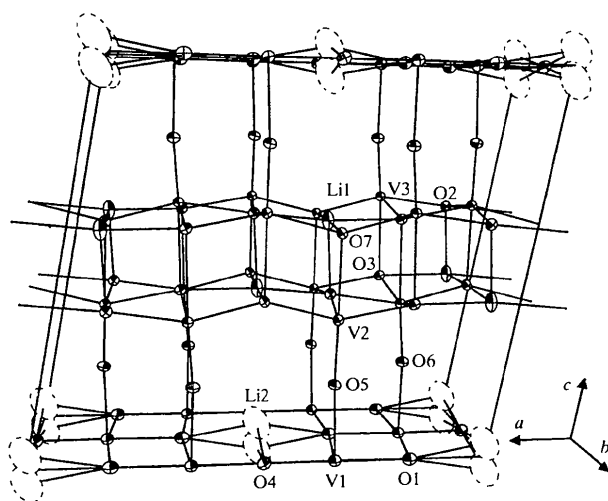


Fig. 1. The structure of $Li_3V_6O_{13}$. The possible positions of the disordered Li2 atom are indicated schematically by dashed ellipsoids. Displacement ellipsoids are drawn at a 50% level of probability.

coordination within the single layer and Li–O distances in the range 1.99(1)–2.08(5) Å; this site has a 50% Li occupation.

The Li^+ ion can diffuse along channels perpendicular to the b axis (Murphy *et al.*, 1979). The relatively large equivalent isotropic displacement parameter for Li2 [$B = 5(2) \text{ \AA}^2$] suggests ion mobility, and that this ion can find a diffusion path between adjacent channels. Although it is clear that the data here are of quite poor quality (as indicated by the high R values), single-crystal data are indeed rare in such situations, and the structural information derived will prove crucial to the ultimate understanding of lithiation mechanisms in this material.

Experimental

Single crystals of V_6O_{13} were grown by a CVT process (Saeki *et al.*, 1973); the starting material was a mixture of crystallographically phase-pure V_6O_{13} [synthesis described by Lampe-Önnerud & Thomas (1995)] and $TeCl_4$ (Merck, used as received) in the mass ratio 20:1. Electrochemical lithiation was performed by incorporating suitably sized single crystals into the composite cathode of an (Li|polymer electrolyte| V_6O_{13}) battery. The battery was maintained at a slightly elevated temperature (323 K) in a sand bath to enhance reaction kinetics and Li-ion diffusion rate. As described previously, *in-situ* XRD studies (Gustafsson *et al.*, 1992) confirm that V_6O_{13} passes through stepwise lithium insertion involving a sequence of lithiated phases. The battery was slowly discharged from an initial 3.0 V down to 2.45 V versus Li/Li^+ over a period of eight weeks and held at this potential for several months. The single crystals were then recovered from the cathode (in a glove box under argon) and mounted on a goniometer.

Crystal data

$Li_3V_6O_{13}$
 $M_r = 534.46$
 Monoclinic
 $C2/m$
 $a = 11.776(6) \text{ \AA}$
 $b = 3.918(2) \text{ \AA}$
 $c = 10.189(7) \text{ \AA}$
 $\beta = 100.59(4)^\circ$
 $V = 462.1(4) \text{ \AA}^3$
 $Z = 2$
 $D_x = 3.841 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 14 reflections
 $\theta = 5.49\text{--}12.61^\circ$
 $\mu = 5.67 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Plate
 $0.07 \times 0.06 \times 0.05 \text{ mm}$
 Black

Data collection

Stoe four-circle diffractometer
 ω scan
 Absorption correction: integration (ABSSTOE; Lundgren, 1983)
 $T_{\min} = 0.712$, $T_{\max} = 0.807$
 5232 measured reflections
 2225 independent reflections

$R_{\text{int}} = 0.060$
 $\theta_{\text{max}} = 48^\circ$
 $h = -14 \rightarrow 24$
 $k = -8 \rightarrow 8$
 $l = -21 \rightarrow 17$
 4 standard reflections
 frequency: 240 min
 intensity decay: 6.5%

Refinement

Refinement on F^2 $R(F) = 0.095$ $wR(F^2) = 0.082$ $S = 1.69$

5232 reflections

72 parameters

 $w = 1/\sigma^2(F^2)$ $(\Delta/\sigma)_{\max} = 0.10$ $\Delta\rho_{\max} = 2.2 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -2.3 \text{ e } \text{\AA}^{-3}$

Extinction correction: Becker & Coppens (1974), isotropic (type 1)

Extinction coefficient: $3.2(5) \times 10^2$ Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)Table 1. Selected bond lengths (\AA)

V1—O1	1.998 (3)	V3—O3 ⁱⁱⁱ	2.005 (1)
V1—O1 ⁱ	1.968 (1)	V3—O3 ^{viii}	2.005 (1)
V1—O1 ⁱⁱ	1.968 (1)	V3—O6	1.643 (3)
V1—O4	1.854 (1)	V3—O7	1.954 (3)
V1—O5	1.990 (3)	Li1—O2 ^{ix}	2.032 (5)
V1—O6 ⁱⁱⁱ	2.022 (3)	Li1—O2 ^{vi}	2.009 (7)
V2—O2 ^{iv}	1.979 (1)	Li1—O3	2.031 (5)
V2—O2 ^v	1.979 (1)	Li1—O7 ^{iv}	1.960 (1)
V2—O3	2.007 (3)	Li1—O7 ^v	1.960 (1)
V2—O5	1.664 (3)	Li2—O1	2.06 (5)
V2—O7	1.956 (3)	Li2—O1 ^x	2.08 (5)
V2—O7 ^{vi}	2.201 (3)	Li2—O4 ^{iv}	1.99 (1)
V3—O2	1.985 (3)	Li2—O4 ^v	1.99 (1)
V3—O3 ^{vi}	2.321 (3)		

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, -z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, -z$; (iii) $1-x, y, -z$; (iv) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (v) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (vi) $1-x, y, 1-z$; (vii) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (viii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (ix) $x-1, y, z$; (x) $-x, y, -z$.

The large cell-parameter changes (described above) which occur during the lithiation process introduce severe stress and cracks in the crystal, resulting in poor crystal quality and weak broad peaks. The reflections were thus measured with a large-interval ω -step scan (70 steps of 0.05°). The net intensities obtained have large standard deviations due to the smeared-out character of the reflections. The structure was solved from a sequence of difference Fourier syntheses in space group $C2/m$, based on the atomic coordinates of V₆O₁₃ (Wilhelmi *et al.*, 1971). Some features of the refined model indicate that the structure should be described with lower symmetry. The disordered positions of Li2 close to a centre of symmetry show that, at least locally, the structure is non-centrosymmetric. Peaks in the range $0.8\text{--}2.2 \text{ e } \text{\AA}^{-3}$ close to the V-atom positions in the $\Delta\rho$ maps also indicate deficiencies in the model. Systematic refinements in the non-centrosymmetric space groups Cm and $C2$ did not improve the model significantly; moreover, displacement parameters for atoms breaking the $2/m$ symmetry acquired physically unreasonable large values. It is possible, nevertheless, that the structure does not have the space group $C2/m$; the present data cannot resolve this, however. A refinement of the final model based on averaged data but with a lower cut-off at $2\sigma(F^2)$ gave a weighted $wR(F^2)$ value of 0.0696.

Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: *STOEDATRED*, *LSQLIN* and *ABS-STOE* (Lundgren, 1983). Program(s) used to solve structure: *FORDUP* (Lundgren, 1983). Program(s) used to refine structure: *DUPALS* (Lundgren, 1983). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *DISTAN* (Lundgren, 1983).

This work is currently supported by The Swedish Natural Science Research Council (NFR) and The

Swedish Board for Technical Development (NUTEK). The authors also wish to thank Mr Hilding Karlsson for his skilled technical assistance throughout this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1007). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 1206–1209

Rubidium Antimony(V) Titanium Oxide, Rb₅Sb₇TiO₂₂

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(Received 22 August 1997; accepted 6 March 1998)

Abstract

In the title compound, three Sb atoms have octahedral coordination and there is a 50/50 disorder of Sb and Ti at a site with trigonal-bipyramidal coordination. These polyhedra form an open network with the Rb⁺ ions in two types of channels, both types running in perpendicular directions, along [110] and [1 $\bar{1}$ 0]. The structure is pseudo-tetragonal and similar to the cubic pyrochlore structure.