LiMnVO$_4$

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Key indicators

Single-crystal X-ray study
$T = 297$ K
Mean σ(V–O) = 0.001 Å
R factor = 0.022
wR factor = 0.033
Data-to-parameter ratio = 64.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of lithium manganese vanadate, LiMnVO$_4$, is characterized by chains of edge-sharing MnO$_6$ octahedra, bridged by pairs of edge-sharing LiO$_4$ and VO$_4$ tetrahedra. Cation–cation repulsions displace the V and Li ions from the tetrahedral centres and deform the tetrahedra further by shortening the mutually shared O—O edges. The smallest r.m.s. atomic displacements in thermal motion for Li and V are parallel to the shortest Li$\cdots$V vector with maximum vibrational motion normal to that direction. Cation–cation interactions between the Li and V tetrahedral sites play an important role.

Comment

Li$_x$Mn$_2$O$_4$ ($0 < x < 2$) and vanadium oxides such as V$_2$O$_5$ and LiV$_3$O$_8$ have been widely investigated as candidates for cathode materials in lithium batteries. The LiMnVO$_4$ phase has been found in the pseudo-binary system of LiMn$_2$O$_4$–LiV$_2$O$_4$. The structure of the phase was proposed by Rietveld analysis (Sato & Kano, 1994), and consists of an arrangement of edge-sharing MnO$_6$ octahedral chains, linked by VO$_4$ and LiO$_4$ tetrahedra sharing a common edge.

The lithium ion, which has a low mass and is monovalent, usually exhibits a large anisotropic thermal motion in ionic conductors. However, although the displacement modes contain much information about possible lithium migration
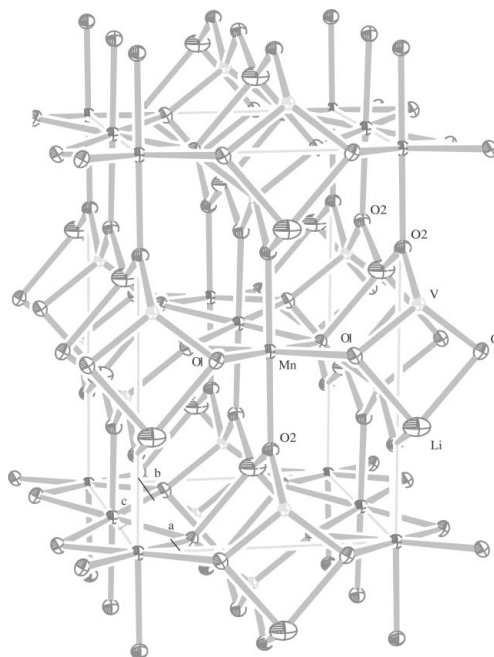

Figure 1
Perspective view of the LiMnVO$_4$ structure. Displacement ellipsoids are drawn at the 50% probability level.

paths, no detailed single-crystal structure analysis of LiMnVO₄ has been published. In this study, we have succeeded in synthesizing a large single crystal of $LiMnVO_4$ and the structure refinement with full anisotropic displacement parameters is reported. The large anisotropic thermal motion of Li in the edge-sharing LiO_4 tetrahedral site is discussed.

Sato & Kano (1994), Sato *et al.* (1996), and Padhi *et al.* (1997) have investigated the crystal structure of $LiMnVO_4$ *via* the Rietveld method, with an isotropic displacement model for all atoms. We find good agreement between the atomic coordinates of their powder determination and those of our single-crystal study.

The crystal structure of $LiMnVO_4$ (Fig. 1) is characterized by chains of edge-sharing MnO_6 octahedra, running parallel to the *c* axis. These chains are bridged by pairs of LiO_4 and VO_4 tetrahedra. Both tetrahedral sites are linked to each other by sharing an edge. Both the $Mn \cdots Mn$ [3.1815 (2) Å] and $V \cdots Li$ [2.684 (6) Å] distances parallel to the *c* and *b* axes, respectively, are relatively short, resulting in a strong repulsion between cations.

Interatomic distances for the MnO_6, VO_4 and LiO_4 polyhedra are listed in Table 1. The distances of $O1 \cdots O1^{iv}$ between MnO_6 octahedra themselves and $O1 \cdots O1^{iii}$ shared-edges between VO_4 and LiO_4 tetrahedra are 2.992 (1) and 2.772 (1) Å, respectively (symmetry codes as in Table 1). The $O1 \cdots O1^{iii}$ edges are shortened, due to cation–cation repulsion, which accompanies the significant off-centering of V and Li in each tetrahedral site.

An additional measure of the distortion of the VO_4 and LiO_4 tetrahedra is given by the deviation of the bond angles from the ideal 109.48°.

Fig. 1 shows the r.m.s. displacements of Mn, V, Li and O atoms rendered as ellipsoids. The smallest Li atom mean atomic displacements are oriented along the $Li \cdots V$ vectors and the maximal displacement vector is normal to this direction. The cation–cation interaction between the Li and V tetrahedral sites play an important role.

Many Li cathode materials, such as the spinel-type structure and layer structure (Sato & Kano, 1994), have an Li-ion conduction path in the structure. On the other hand, the Li sites in this $LiMnVO_4$ structure are widely separated from each other and no vacant site which the Li ion could occupy is located near the Li site, though the amplitude and anisotropy of thermal vibration for Li is large enough. It is, therefore, inferred that this phase does not suit a cathode material. This phase transforms to a spinel-type phase (Padhi *et al.*, 1997) under high pressure and temperature. The spinel-type phase should be appropriate for a cathode material. It is emphasized that the largest amplitude of the Li ion in this phase corresponds to the direction of displacement in the transition from this phase to the spinel-type phase, and the transition is achieved only by the displacement of Li ions.

Experimental

A single crystal of $LiMnVO_4$ was grown using an $LiVO_3$ flux. A mixture of Li_2CO_3 (0.1 mol), V_2O_5 (0.1 mol) and $MnCO_3$ (0.05 mol)

was heated at 1570 K for 24 h under atmospheric conditions. After slow cooling to 1070 K at a rate of 1 K h^{-1}, the product was quenched. A flat $LiMnVO_4$ single crystal of $10 \times 10 \times 1$ mm was ground into a sphere. The stoichiometric composition was confirmed by an ICP emission spectrochemical analysis.

Table 1
Selected geometric parameters (Å, °).

Li—O1	2.123 (4)	Mn—O2	2.1602 (10)
Li—O2^i	1.962 (2)	V—O1	1.7544 (9)
Mn—O1^{ii}	2.1909 (6)	V—O2	1.6896 (10)
O1—Li—O1^{iii}	81.5 (2)	O1^v—Mn—O2	90.65 (6)
O1—Li—O2^{iv}	107.7 (2)	O1—V—O1^{iii}	104.35 (10)
O2^i—Li—O2^{iv}	132.5 (3)	O1—V—O2	110.55 (2)
O1^v—Mn—O1^{vi}	86.12 (6)	O2—V—O2^{vii}	110.2 (1)

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

Precession photographs showed an orthorhombic unit cell with systematic absences of hkl; $h + k = 2n + 1$ and $h0l$; h and $l = 2n + 1$. The possible space groups were therefore $Cmcm$, $Cmc2_1$ and $C2cm$. The space group was initially assumed to be $Cmcm$ before the remaining two space groups were tested. Calculations gave the reliability factor $R = 0.0217$ for $Cmcm$, $R = 0.0217$ for $Cmc2_1$ and $R = 0.0223$ for $C2cm$, all with anisotropic displacement parameters. Since all structure models converged to the $Cmcm$ model and were essentially identical, within errors, the space group $Cmcm$ was adopted. The minimum electron-density peak was located near the position (0, 0.08, 0). All atoms are located on special positions. Crystallographically equivalent reflections were averaged.

Data collection: *MSC Software* (Rigaku, 1996); cell refinement: *MSC Software*; data reduction: *MSC Software*; program(s) used to solve structure: *RADY*89 (Sasaki, 1989); program(s) used to refine structure: *RADY*89; molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997).

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