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Li_2VOSiO_4: a Natisite-Type Structure

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Abstract

The structure of dilithium vanadyl silicate was determined from single-crystal data. It is isotypic with $Li_2TiOSiO_4$ and is therefore a new natisite-type structure.

Comment

The title compound is isostructural with $Li_2TiOSiO_4$ (Ziadi *et al.*, 1994), $Na_2TiOSiO_4$ (Nyman *et al.*, 1978) and $Na_2TiOGeO_4$ (Verkhovskii *et al.*, 1970).

The double-bond character of the vanadyl bond in Li_2VOSiO_4 is more pronounced (1.54 v.u.) than that of the titanyl bond (1.37 v.u.) in $Li_2TiOSiO_4$. [Bond-valence calculations were carried out using parameters given by Brese & O'Keeffe (1991) according to the Brown & Altermatt (1985) method.] Accordingly, the opposite O atom in the distorted $M^{IV}O_6$ octahedron is even less tightly bonded [V—O2 2.826 (6) Å] in the vanadium compound than in $Li_2TiOSiO_4$ [Ti—O2 2.701 (3) Å].

Within the $[VOSiO_4]^{2-}$ framework, the *M*—O bonds are rather strongly covalent and, accordingly, the Li—O bonds are mainly ionic. As has been observed in other such cases, the atomic displacement parameter for Li is rather large.

Experimental

Single crystals of the title compound were prepared in a platinum crucible by heating, under nitrogen, a mixture of Li_2CO_3, VO_2 and SiO_2 in a 1:1:1 ratio at 1073 K for one day.

Crystal data

Li_2VOSiO_4
M_r = 172.91
Tetragonal
*P*4/*nmm*
a = 6.3550 (9) Å
c = 4.4490 (9) Å
V = 179.68 (5) Å^3
Z = 2
D_x = 3.196 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 4.57–13.72°
μ = 2.980 mm^{-1}
T = 293 (2) K
Parallelepiped
0.05 × 0.05 × 0.03 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: by integration (*SHELXTL*; Sheldrick, 1994)
T_{min} = 0.865, T_{max} = 0.903
701 measured reflections
252 independent reflections
165 reflections with $I > 2\sigma(I)$
R_{int} = 0.111
θ_{max} = 34.96°
h = −1 → 10
k = −1 → 10
l = −1 → 7
3 standard reflections
frequency: 60 min
intensity decay: 0.0017%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.088
S = 1.016
252 reflections
16 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0095P)^2 + 0.6350P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.925 e Å^{-3}
$\Delta\rho_{min}$ = −0.917 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\sum_i\sum_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
Li	1/2	0	1/2	0.022 (3)
V	1/4	1/4	0.0857 (4)	0.0037 (3)
Si	3/4	1/4	0	0.0027 (5)
O1	0.5433 (4)	1/4	0.2180 (7)	0.0057 (6)
O2	1/4	1/4	−0.2791 (14)	0.0117 (14)

Table 2. *Selected geometric parameters (Å, °)*

Li—O1^{i} × 4	2.043 (2)	V—O1^{iii} × 4	1.955 (3)
Li—O2^{ii} × 2	2.452 (2)	Si—O1 × 4	1.633 (3)
V—O2	1.623 (6)		
O1^{i}—Li—O1^{iv}	80.3 (2)	O1^{iii}—V—O1^{vi}	84.80 (6)
O1^{i}—Li—O2^{ii}	80.2 (1)	O1—Si—O1^{vii}	110.6 (1)
O2—V—O1^{iii}	107.5 (1)	O1—Si—O1^{viii}	107.1 (2)
O1^{iii}—V—O1^{v}	145.0 (2)		

Symmetry codes: (i) $1-y, x-\frac{1}{2}, 1-z$; (ii) $1-x, -y, -z$; (iii) $\frac{1}{2}-y, x, z$; (iv) $1-x, -y, 1-z$; (v) $y, \frac{1}{2}-x, z$; (vi) $\frac{1}{2}-x, \frac{1}{2}-y, z$; (vii) $1-y, x-\frac{1}{2}, -z$; (viii) $\frac{3}{2}-x, \frac{1}{2}-y, z$.

Data collection: CAD-4 software (Enraf–Nonius, 1988). Cell refinement: CAD-4 software. Data reduction: *XPREP* in *SHELXTL* (Sheldrick, 1994). Program(s) used to solve structure: *XS* in *SHELXTL*. Program(s) used to refine structure: *XL* in *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1196). Services for accessing these data are described at the back of the journal.

References

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.

Enraf–Nonius (1988). *CAD-4 Manual.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Nyman, H., O'Keeffe, M. & Bovin, J.-O. (1978). *Acta Cryst.* **B34**, 905–906.

Sheldrick, G. M. (1994). *SHELXTL. Structure Determination Programs.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Verkhovskii, V. Ya., Kuz'min, E. A., Ilyukhin, V. V. & Belov, N. V. (1970). *Sov. Phys. Dokl.* **15**, 7–8.

Ziadi, A., Thiele, G. & Elouadi, B. (1994). *J. Solid State Chem.* **109**, 112–115.