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Lithium Vanadium Metasilicate, $LiVSi_2O_6$

CHRISTINE SATTO, PATRICE MILLET AND JEAN GALY

Centre d'Elaboration de Matériaux et d'Etudes Structurales, CNRS, 29 rue Jeanne Marvig, BP 4347, 31055 Toulouse CEDEX, France. E-mail: millet@cemes.fr

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Abstract

The title compound has been synthesized by solid-state reaction. Its structure is isomorphous with those of other lithium pyroxenes and is composed of infinite isolated chains of edge-sharing VO_6 octahedra linked together by corner-sharing SiO_4 tetrahedra. These form a three-dimensional framework within which each Li^+ ion occupies a highly distorted octahedron.

Comment

The alkali metal pyroxenes denoted $AM^{3+}Si_2O_6$ (A = alkali metal) have been studied for a long time since many of them are naturally occurring minerals (Cameron, Sueno, Prewitt & Papike, 1973). The structures of these compounds are very versatile and can accommodate a wide variety of cations at the M site. Interestingly, the sodium pyroxene family is much larger than the corresponding lithium family; nine sodium compounds have been discovered to date with M = Al^{3+}, Fe^{3+}, Cr^{3+}, Ga^{3+}, V^{3+}, Mn^{3+}, Ti^{3+}, Sc^{3+} or In^{3+} (Ohashi, Osawa & Tsukimura, 1987). For the lithium family, the following compounds have been isolated: $LiAlSi_2O_6$ and $LiFeSi_2O_6$ (Clark, Appleman & Papike, 1969), $LiScSi_2O_6$ (Hawthorne & Grundy, 1977), $LiInSi_2O_6$ (Grotepass, Behruzi & Hahn, 1983) and $LiGaSi_2O_6$ (Sato, Osawa & Ohashi, 1994). We were thus interested in synthesizing further lithium equivalents of the sodium family. We report here the crystal structure of a new lithium pyroxene, $LiVSi_2O_6$, synthesized in our laboratory.

This new lithium vanadium(III) metasilicate exhibits the $LiAlSi_2O_6$ structure. Its framework is composed of infinite isolated chains of edge-sharing VO_6 octahedra linked together by corner-sharing SiO_4 tetrahedra. A polyhedral representation of the structure showing the isolated chains running along the [001] direction is presented in Fig. 1. An *ORTEP*II (Johnson, 1976) view of the unit cell, slightly tilted for clarity, is given in Fig. 2 and shows the atom labelling. Both Li and V occupy the special position 4(e) (0, y, 1/4). The main difference between the structures of the lithium and sodium pyroxenes is related to the alkali metal radius. In lithium compounds, the small Li atom is sixfold coordinated and occupies a highly distorted octahedron (Fig. 3) with two short Li—O bonds of 2.065 (4) Å and two longer ones of 2.444 (4) Å, while for sodium compounds, the Na atom is eightfold coordinated in a very distorted cubic antiprism. The Si atom is located in a slightly distorted tetrahedron (mean Si—O = 1.621 Å), while V^{III} has octahedral coordination with V—O distances in the range 1.920–2.072 Å.

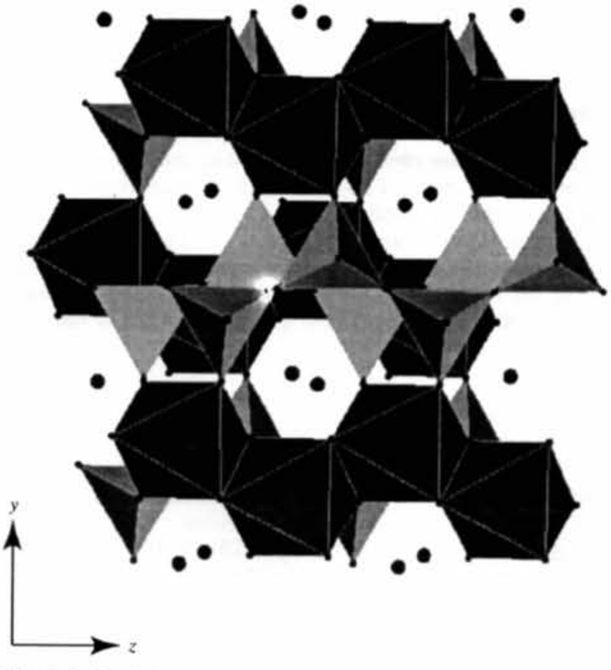

Fig. 1. Polyhedral representation of the $LiVSi_2O_6$ structure down the a^* axis showing the infinite chains of VO_6 octahedra.

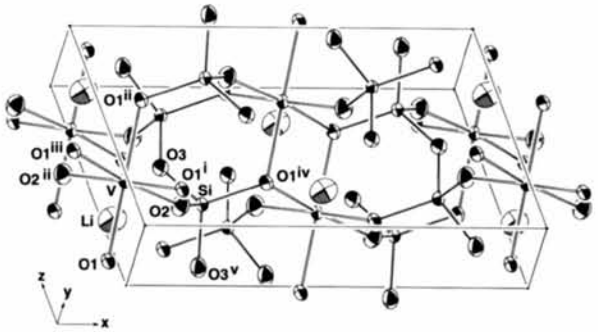

Fig. 2. *ORTEP*II (Johnson, 1976) representation of the structure of $LiVSi_2O_6$ showing the atom labels. Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, y, \frac{1}{2} - z$; (iii) $x, -y, \frac{1}{2} - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $x, 1 - y, z - \frac{1}{2}$. Displacement ellipsoids are plotted at the 90% probability level.

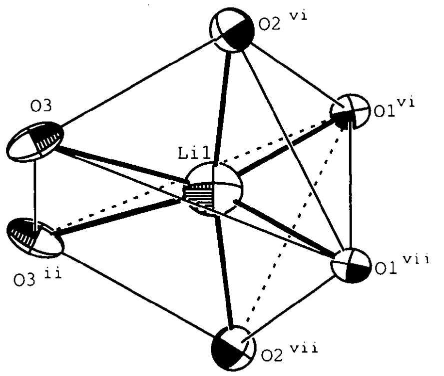

Fig. 3. The lithium coordination polyhedron. Symmetry codes: (ii) $-x, y, \frac{1}{2}-z$; (vi) $x, 1-y, \frac{1}{2}+z$; (vii) $-x, 1-y, -z$. Displacement ellipsoids are plotted at the 90% probability level.

Experimental

Single crystals were obtained by solid-state reaction of a mixture of Li_2SiO_3, SiO_2, V_2O_5 and V_2O_3 in proportions corresponding to the chemical formula $Li_{1.6}SiVO_5$. The mixture, ground in an agate mortar, was placed in a platinum crucible and heated at 1373 K for 96 h under a primary vacuum. Slow cooling led to the formation of small green crystals. Energy dispersive X-ray analysis (EDX) gave an Si/V molar ratio of 2.

Crystal data

$LiVSi_2O_6$
$M_r = 210.04$
Monoclinic
$C2/c$
$a = 9.634\,(4)$ Å
$b = 8.586\,(2)$ Å
$c = 5.304\,(2)$ Å
$\beta = 109.69\,(3)°$
$V = 413.1\,(2)$ Å^3
$Z = 4$
$D_x = 3.38$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 3.25$–$19.30°$
$\mu = 2.84$ mm^{-1}
$T = 293\,(2)$ K
Parallelepiped
$0.12 \times 0.06 \times 0.04$ mm
Translucent pale green

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.786$, $T_{max} = 0.893$
1190 measured reflections
481 independent reflections

427 reflections with $I > 3\sigma(I)$
$R_{int} = 0.01$
$\theta_{max} = 28°$
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 6$
6 standard reflections frequency: 3 every 60 min intensity decay: 0.4%

Refinement

Refinement on F
$R = 0.019$
$wR = 0.016$
$S = 1.078$
427 reflections
48 parameters
Weights: Chebychev polynomial (Carruthers & Watkin, 1979)
$(\Delta/\sigma)_{max} = 0.0005$

$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 4.7 (8)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å)*

V1—O1	2.067 (1)	Si1—O3^{iii}	1.631 (1)
V1—O1^{i}	2.072 (1)	Li1—O1^{iv}	2.065 (4)
V1—O2	1.920 (1)	Li1—O2^{iv}	2.184 (1)
Si1—O1^{ii}	1.634 (1)	Li1—O3	2.444 (4)
Si1—O2	1.593 (1)	V1···V1^{i}	3.105 (1)
Si1—O3	1.625 (1)	Si1···Si1^{iv}	3.075 (1)

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

The V1, Si1 and O1 atoms were localized by the Patterson technique and the other atoms were localized from a series of difference Fourier maps and refinements (Watkin, Carruthers & Betteridge, 1985).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1217). Services for accessing these data are described at the back of the journal.

References

Cameron, M., Sueno, S., Prewitt, C. T. & Papike, J. J. (1973). *Am. Mineral.* **58**, 594–618.
Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* A**35**, 698–699.
Clark, J. R., Appleman, D. E. & Papike, J. J. (1969). *Mineral. Soc. Am. Spec. Pap.* **2**, 31–50.
Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Grotepass, M., Behruzi, M. & Hahn, T. (1983). *Z. Kristallogr.* **162**, 90–91.
Hawthorne, F. C. & Grundy, H. D. (1977). *Can. Mineral.* **15**, 50–58.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Ohashi, H., Osawa, T. & Tsukimura, K. (1987). *Acta Cryst.* C**43**, 605–607.
Sato, A., Osawa, T. & Ohashi, H. (1994). *Acta Cryst.* C**50**, 487–488.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, University of Oxford, England.