

## LiInSiO<sub>4</sub>: a new monovalent–trivalent olivine

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The structure of the olivine LiInSiO<sub>4</sub> (lithium indium silicate) is isotypic with LiScSiO<sub>4</sub> and MgMgSiO<sub>4</sub> (forsterite). The main differences between the title compound and the divalent–divalent olivines are found for the bond lengths and angles opposite common edges between the tetrahedron and the Li<sup>+</sup> and In<sup>3+</sup> ion sites. The tetrahedron shares one common edge with the Li<sup>+</sup> site and two common edges with the In<sup>3+</sup> site. The tetrahedron is distinctly distorted, as are the Li<sup>+</sup> and In<sup>3+</sup> sites.

### Comment

The structure of LiInSiO<sub>4</sub> (I), is isotypic with that of LiScSiO<sub>4</sub> (Streele *et al.*, 1978; Hazen *et al.*, 1996), which is the only monovalent–trivalent (1:3) olivine for which the crystal structure has been determined. The ionic radii (Shannon & Prewitt, 1969) of the <sup>VI</sup>Li<sup>+</sup> and <sup>VI</sup>In<sup>3+</sup> (the first superscripts refer to the coordination numbers of the specific cations) ions are 0.75 and 0.79 Å, respectively, and thus are close to the

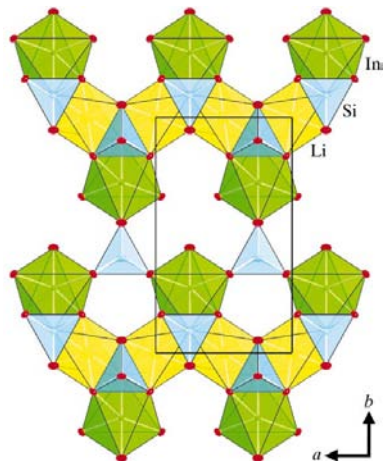


Figure 1

Part of the crystal structure of (I), showing the atomic labelling. Displacement ellipsoids have been plotted at the 95% probability level.

values for <sup>VI</sup>Mg<sup>2+</sup> (0.72 Å) and <sup>VI</sup>Fe<sup>2+</sup> (0.78 Å). Structural differences between forsterite, MgMgSiO<sub>4</sub>, and fayalite, FeFeSiO<sub>4</sub> (a divalent–divalent or 2:2 olivine), and (I) are mainly due to charge differences. In the following, the structure of (I) is compared with that of LiScSiO<sub>4</sub> (Streele *et al.*, 1978) and MgMgSiO<sub>4</sub> (Fujino *et al.*, 1981). Part of the structure of (I) is shown in Figs. 1 and 2.

The M1–O (Li–O; Table 1) bond lengths in (I) are on average 3.9% longer than those in MgMgSiO<sub>4</sub> and 0.4% shorter than those in LiScSiO<sub>4</sub>. The M1–O3 bond lengths show the largest (4.8%) and the M1–O1 bond lengths the smallest (2.7%) difference between the Mg<sup>2+</sup> and the In<sup>3+</sup> compounds. The longer M1–O bond lengths in forsterite can be explained by the fact that the Li<sup>+</sup> cation is larger than Mg<sup>2+</sup>. However, it is interesting to note that the mean Li–O bond length in LiScSiO<sub>4</sub> (2.186 Å) is larger than that in (I) (2.177 Å), although the Sc<sup>3+</sup> ion on the edge-sharing neighbouring M2 octahedron has a smaller radius than the In<sup>3+</sup> ion (<sup>VI</sup>Sc<sup>3+</sup> = 0.745 Å). The individual Li–O2 bond lengths are similar in both Li olivines; the Li–O3 bond lengths are shorter by 2.3% in (I), whereas the Li–O1 bond lengths are longer by only 1.3%. The O1–M1–O3 angle is therefore 0.6% smaller. These alterations are mainly due to the increase in size of the InO<sub>6</sub> octahedron (M2 site) that shares the O1–O3 edge with the neighbouring M1 sites. The above facts indicate that the M2 site is more dominant than the M1 site. The deviation of individual bond lengths from their mean value (bond-length distortion, BLD; Renner & Lehmann, 1986)

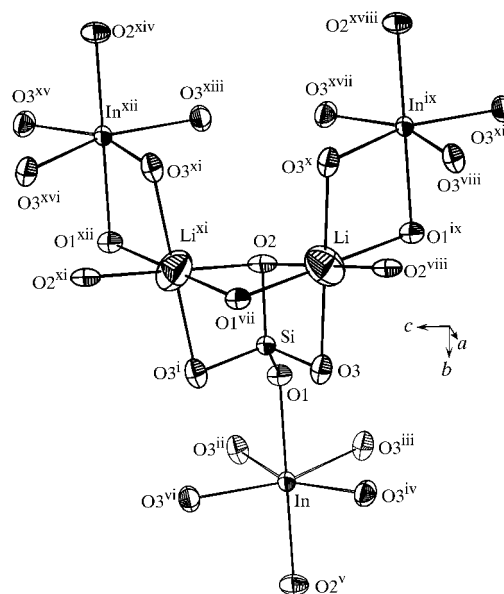


Figure 2

Polyhedral representation of part of the structure of (I), viewed along the *a* axis, showing the connection of individual tetrahedral and octahedral M1 and M2 sites. [Symmetry codes: (i)  $x, y, \frac{1}{2} - z$ ; (ii)  $1 + x, y, \frac{1}{2} - z$ ; (iii)  $1 + x, y, z$ ; (iv)  $\frac{1}{2} + x, \frac{1}{2} - y, -z$ ; (v)  $\frac{3}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$ ; (vi)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (vii)  $x - 1, y, z$ ; (viii)  $-x, -y, -\frac{1}{2} + z$ ; (ix)  $1 - x, -y, -\frac{1}{2} + z$ ; (x)  $-x, -y, -z$ ; (xi)  $-x, -y, \frac{1}{2} + z$ ; (xii)  $1 - x, -y, \frac{1}{2} + z$ ; (xiii)  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (xiv)  $-\frac{1}{2} + x, -\frac{1}{2} - y, 1 - z$ ; (xv)  $\frac{1}{2} - x, -\frac{1}{2} + y, 1 + z$ ; (xvi)  $-x, -y, 1 - z$ ; (xvii)  $\frac{1}{2} - x, -\frac{1}{2} + y, z$ ; (xviii)  $-\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$ ; (xix)  $\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$ .]

decreases from MgMgSiO<sub>4</sub> (BLD = 1.59%), via LiScSiO<sub>4</sub> (BLD = 1.19%), to (I) (BLD = 0.86%).

The largest angular change within the *M1* site is observed for the O1–*M1*–O2 angle, which is opposite the common edge between neighbouring *M1* sites and which increases from 86.5 (1)° in MgMgSiO<sub>4</sub> to 89.9 (1)° in (I). This increase indicates a decrease of repulsion forces across the shared edge between the two neighbouring *M1* octahedra. The octahedral angle variance (OAV; Robinson *et al.*, 1971) in (I) [OAV = 111.6 (2)°] is larger than that in MgMgSiO<sub>4</sub> [OAV = 95.1 (2)°] but smaller than that in LiScSiO<sub>4</sub> [OAV = 123.6 (2)°]. Although distinctly distorted, the *M1*O<sub>6</sub> octahedron in (I) appears to be more regular than that in both LiScSiO<sub>4</sub> and MgMgSiO<sub>4</sub>.

The mean *M2*–O bond lengths reflect the substitution of In<sup>3+</sup> ions. The mean *M2*–O distance in (I) is 2.1% larger than that in LiScSiO<sub>4</sub>, and individual In<sup>3+</sup>–O distances are 1.8–2.4% longer than the corresponding Sc<sup>3+</sup>–O bond lengths. The mean Mg–O bond length in MgMgSiO<sub>4</sub> is 1.7% below the mean In–O bond length. The BLD of the *M2* site in (I) (BLD = 3.05%) is intermediate between that in LiScSiO<sub>4</sub> (BLD = 2.82%) and MgMgSiO<sub>4</sub> (BLD = 4.6%). With respect to the BLD and the OAV, the *M2* site appears to be more distorted than the *M1* site. The *M2* OAV is 106.1 (2)° for (I), which is larger than the values for LiScSiO<sub>4</sub> and MgMgSiO<sub>4</sub> [96.3 (2) and 89.5 (2)°, respectively].

The O3–Si–O3 tetrahedral angle, which is opposite the common edge between the tetrahedron and the *M2* (In<sup>3+</sup>) site, decreases from 104.8 (1)° in forsterite to 98.9 (1)° in (I) (–5.7%). The O3–Si–O3 angle is close to the value found in LiScSiO<sub>4</sub> [98.6 (1)°], these O3–Si–O3 angles being among the smallest values found for condensed silicates. The decrease in the O3–Si–O3 angle is accompanied by an increase of 1.3% in the Si–O3 bond length, from 1.635 (2) Å in forsterite to 1.658 (2) Å in (I). These two effects result from the increased charge (In<sup>3+</sup> versus Mg<sup>2+</sup>) at the *M2* site. Conversely, the O2–Si–O3 angle, opposite a common edge between the tetrahedral and the *M1* (Li<sup>+</sup>) site, increases from 101.9 (1)° in MgMgSiO<sub>4</sub> to 105.4 (1)° in (I) (+3.5%), and the Si–O2 bond length decreases by 1.8%, from 1.655 (2) to 1.626 (3) Å. The lower charge (Li<sup>+</sup> versus Mg<sup>2+</sup>) at the *M1* site can be seen as the driving force for the observed alterations. The mean Si–O bond length in (I) is 1.635 Å and thus is close to the values found in LiScSiO<sub>4</sub> (1.633 Å) and MgMgSiO<sub>4</sub> (1.636 Å). Except for the Si–O2 bond lengths [1.626 (3) and 1.616 (2) Å in (I) and LiScSiO<sub>4</sub>, respectively], the Si–O bond lengths are identical within 1 s.u. in the Li olivines. The BLD increases from the Mg<sup>2+</sup> (0.66%) to the In<sup>3+</sup> (1.39%) and the Sc<sup>2+</sup> (1.52%) compound. The mean O–Si–O angle is 109.1° in all three compounds, and although the O3–Si–O3 angle is very small and the O–Si–O angles differ distinctly between MgMgSiO<sub>4</sub> and the Li olivines, the tetrahedral angle variance (TAV; Robinson *et al.*, 1971) is similar in (I) and MgMgSiO<sub>4</sub> [48.2 (2) and 49.5 (2)°, respectively], thus indicating similar tetrahedral distortions in both compounds. LiScSiO<sub>4</sub> exhibits a lower overall tetrahedral distortion (TAV = 42.4°), which again indicates small O3–Si–O3 angles.

## Experimental

Single crystals were obtained as a by-product during high-temperature solution growth of the clinopyroxene compound LiInSi<sub>2</sub>O<sub>6</sub> (Redhammer & Roth, 2003). Li<sub>2</sub>CO<sub>3</sub>, In<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> were mixed in proportions corresponding to the chemical formula LiInSi<sub>2</sub>O<sub>6</sub>. This mixture and Li<sub>2</sub>MoO<sub>4</sub> (1:10), serving as the high-temperature solution, were placed in a covered platinum crucible, heated to 1473 K, maintained at this temperature for 24 h and then cooled slowly (5 K h<sup>–1</sup>) to 873 K. Besides the transparent prismatic crystals of the clinopyroxene sample, a small number of cuboid transparent crystals of (I), of up to 0.5 mm in size, were found in the synthesized material.

### Crystal data

LiInSiO <sub>4</sub>	Mo K $\alpha$ radiation
<i>M<sub>r</sub></i> = 213.85	Cell parameters from 2311 reflections
Orthorhombic, <i>Pb</i> <i>nm</i>	$\theta$ = 3.4–32.0°
<i>a</i> = 4.8448 (9) Å	$\mu$ = 7.87 mm <sup>–1</sup>
<i>b</i> = 10.5043 (19) Å	<i>T</i> = 293 (2) K
<i>c</i> = 6.0634 (13) Å	Cuboid, colourless
<i>V</i> = 308.57 (10) Å <sup>3</sup>	0.25 × 0.17 × 0.16 mm
<i>Z</i> = 4	
<i>D<sub>x</sub></i> = 4.603 Mg m <sup>–3</sup>	

### Data collection

Stoe IPDS-I diffractometer	553 independent reflections
$\omega$ scans	552 reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )
Absorption correction: numerical ( <i>X-SHAPE</i> and <i>X-RED</i> ; Stoe & Cie, 1996)	<i>R</i> <sub>int</sub> = 0.060
<i>T</i> <sub>min</sub> = 0.23, <i>T</i> <sub>max</sub> = 0.34	$\theta$ <sub>max</sub> = 32.0°
2460 measured reflections	<i>h</i> = –7 → 7
	<i>k</i> = –15 → 13
	<i>l</i> = –8 → 8

### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 0.431P]$
<i>R</i> ( <i>F</i> ) = 0.025	where $P = (F_o^2 + 2F_c^2)/3$
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.061	( $\Delta/\sigma$ ) <sub>max</sub> = 0.001
<i>S</i> = 1.39	$\Delta\rho$ <sub>max</sub> = 1.38 e Å <sup>–3</sup>
553 reflections	$\Delta\rho$ <sub>min</sub> = –2.63 e Å <sup>–3</sup>
41 parameters	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.324 (9)

**Table 1**

Selected geometric parameters (Å, °).

Li–O1 <sup>i</sup>	2.1888 (18)	In–O3 <sup>iv</sup>	2.2331 (18)
Li–O2	2.1578 (18)	Si–O1	1.599 (3)
Li–O3	2.1829 (18)	Si–O2	1.626 (3)
In–O1	2.158 (2)	Si–O3	1.6581 (19)
In–O2 <sup>ii</sup>	2.103 (3)	Si–O3 <sup>v</sup>	1.6581 (19)
In–O3 <sup>iii</sup>	2.1312 (18)		
O2–Li–O3	74.00 (8)	O3 <sup>vi</sup> –In–O3 <sup>iv</sup>	89.21 (4)
O2–Li–O1 <sup>i</sup>	89.88 (7)	O1–In–O3 <sup>iv</sup>	82.39 (7)
O3–Li–O1 <sup>i</sup>	82.86 (8)	O3 <sup>iv</sup> –In–O3 <sup>vii</sup>	68.69 (9)
O2 <sup>ii</sup> –In–O3 <sup>iii</sup>	89.54 (6)	O1–Si–O2	116.10 (14)
O3 <sup>iii</sup> –In–O3 <sup>vi</sup>	112.48 (10)	O1–Si–O3 <sup>v</sup>	114.58 (9)
O3 <sup>iii</sup> –In–O1	91.14 (6)	O2–Si–O3 <sup>v</sup>	105.41 (10)
O2 <sup>ii</sup> –In–O3 <sup>iv</sup>	96.62 (7)	O3–Si–O3 <sup>v</sup>	98.90 (13)

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

A data set collected previously on the same crystal, up to  $\theta = 28.1^\circ$  on a Stoe IPDS-I system [399 unique reflections, 41 parameters, *R*(*F*) = 0.020 and *wR*(*F*<sup>2</sup>) = 0.049], yielded identical structural parameters within 1 s.u. but lower electron-density residuals ( $\Delta\rho$ <sub>max</sub> = 0.81 and  $\Delta\rho$ <sub>min</sub> = –1.06 e Å<sup>–3</sup>).

Data collection: *EXPOSE* (Stoe & Cie, 1997); cell refinement: *CELL* (Stoe and Cie, 1997); data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999) and *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1621). Services for accessing these data are described at the back of the journal.

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