

## Crystal synthesis of a new olivine, $\text{LiScSiO}_4$

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### Abstract

$\text{LiScSiO}_4$ , a new silicate olivine, orthorhombic,  $Pbnm$   $a = 4.8200(4)$   $b = 10.4392(8)$   $c = 5.9720(4)$  Å, and the binary solid solution series extending to  $\text{Mg}_2\text{SiO}_4$  have been synthesized both from oxide mixes in air and by high-temperature solvent growth using lithium molybdo-vanadate as a solvent. Substitution of 2  $\text{Mg}^{2+}$  for  $\text{Li}^{1+} + \text{Sc}^{3+}$  confirmed Goldschmidt's proposed  $\text{Sc}^{3+}$ - $\text{Mg}^{2+}$  diadochy in ferromagnesian silicates.

### Introduction

The early investigations of Eberhard (1908), Goldschmidt and Peters (1931), and Oftedal (1943) showed that scandium is almost always present in ferromagnesian silicates (pyroxene, amphibole, olivine, and biotite) of igneous rocks. Goldschmidt's dominant theme of diadochy of  $\text{Sc}^{3+}$  with  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$ , based on the similarity of ionic radii (Goldschmidt, 1927), has been well supported by a vast number of modern trace analyses of rocks and minerals.

Owing to the lack of direct experimental evidence of  $\text{Mg}^{2+} \rightleftharpoons \text{Sc}^{3+}$  substitution and the significant difference of ionic radii values between  $\text{Sc}^{3+}$  (0.81 Å) and  $\text{Mg}^{2+}$  (0.66 Å) later given by Ahrens (1952), arguments have been made against  $\text{Sc}^{3+} \rightleftharpoons \text{Mg}^{2+}$  heterovalency substitution. However, the effective ionic radii were recently revised by Shannon and Prewitt (1969) and Whittaker and Muntus (1970). This reestablished the close similarity of ionic radii of  $\text{Mg}^{2+}$  and  $\text{Sc}^{3+}$  in 6-fold condition as follows:

$$\begin{aligned} \text{Mg}^{2+} 0.725 < \text{Si}^{3+} 0.745 < \text{Fe}^{2+} 0.780 \\ & \text{(Shannon and Prewitt, 1969)} \\ \text{Mg}^{2+} 0.80 < \text{Sc}^{3+} 0.83 < \text{Fe}^{2+} 0.87 \\ & \text{(Whittaker et al., 1970)}^1 \end{aligned}$$

Crystal synthesis of Sc-aegirine,  $\text{NaScSi}_2\text{O}_6$ , and Sc-spodumene,  $\text{LiScSi}_2\text{O}_6$ , using high-temperature solvents (Ito and Frondel, 1968) and subsequent crystal-structure refinement by Hawthorne and Grundy

(1972) demonstrated that the metal sites in the pyroxene structure readily accommodate  $\text{Sc}^{3+}$  if valency is compensated by alkalis.

Experimental studies of  $(\text{Sc}^{3+} + \text{Li}^+) \rightleftharpoons \text{Mg}^{2+}$  coupled substitution in the silicates now includes synthesis of a new olivine,  $\text{LiScSiO}_4$ , and its binary solid-solution series extending to  $\text{Mg}_2\text{SiO}_4$ , forsterite.

### Experimental

#### Method of Synthesis 1

Fine-grain crystalline olivines of the solid-solution series  $\text{LiScSiO}_4$ - $\text{Mg}_2\text{SiO}_4$  were synthesized at subsolidus temperatures by the solid-state reaction of a mixture of reagent grade (99.9%) lithium carbonate, scandium oxide, magnesium oxide, and silicic acid. The thoroughly-mixed charge was placed in a covered platinum crucible, sintered at 650°C for one hour, and then ground in an agate mortar. The temperature was then raised to 1050°C and maintained for 24 hours. After further grinding, the temperature was raised to a final firing temperature (1100-1250°C, 48 hours, see Table 2), depending on the solidus temperature of the composition. Repeated grinding of the sample was made at 50°C intervals. A single-phase crystalline olivine was thus obtained; no peaks belonging to the extraneous phases were observed among X-ray powder diffraction data. A sudden surge of temperature or over-heating of the charge caused a loss of  $\text{Li}_2\text{O}$ , resulting in the appearance of second phases, notably  $\text{Sc}_2\text{Si}_2\text{O}_7$  ( $d = 3.13, 3.11, \text{ and } 2.93$  Å), and a shift of unit-cell dimensions of the olivine solid-solution toward those of  $\text{Mg}_2\text{SiO}_4$ .

<sup>1</sup> Relative differences between the two sets of ionic radii are due to the different oxygen bond length used.

These results of the direct synthesis experiment without flux suggest a complete and stable solid solution series between Mg<sub>2</sub>SiO<sub>4</sub> and LiScSiO<sub>4</sub> at subsolidus temperatures.

### Method of Synthesis 2

High-temperature solvent synthesis of single-phase euhedral crystals up to 2 × 1 × 1 mm in size was effected, using a lithium vanadomolybdate solvent (Grandin de L'Épervier, 1972; Ito, 1975). The charges (Table 1) were placed in a platinum crucible of 30 ml capacity, heated slowly to a maximum of 1250°C in air, and held for 4 days to ensure complete dissolution. The melt was then cooled at 4°C per hour to 650°C, then cooled more rapidly. The excess solvent was dissolved in hot water, and some remaining insoluble matter was rinsed out by hot dilute HCl. Typical experimental data are given in Table 1. The crystals are colorless, transparent, somewhat elongated along the *c* direction (up to 2 mm in length), with well-developed {110} {120} prisms, {021} {101} domes, and {010} {001} pinacoids.

### Chemical analysis

Bulk chemical analysis and emission spectrographic analysis of the olivine were performed to determine the average composition and purity of the crystals. Electron-probe analyses by I. M. Steele were made, using an energy dispersive detector and data reduction procedure described by Reed and Ware (1973).

Emission spectrographic analysis showed, in addition to the major components (Li, Sc, Mg, Si), solvent components (Mo, V), and a small amount of Fe; impurities possibly derived from reagents and furnace walls (Al, Ca, Na, Ag, Mn, Pb, Ni, Cr, Cu, Ag) were detected at the 0.00x or less level. Using atomic absorption spectrometry, Li, Mg, Fe, Mo, and V were determined, and SiO<sub>2</sub> was determined by gravimetric analysis. After removal of SiO<sub>2</sub>, Sc<sub>2</sub>O<sub>3</sub> was determined by EDTA titration. The results are summarized in Table 2.

Probe analysis indicates that the major portion of MoO<sub>3</sub> found in the bulk analyses is flux inclusion, but V<sub>2</sub>O<sub>5</sub> concentration could be as much as 0.1–0.2 weight percent. Dr. Ian M. Steele noted that V<sub>2</sub>O<sub>5</sub> was found often in the core rather than rim, and some clean areas contained less than 0.05 weight percent.

### X-ray studies

Single-crystal X-ray precession photographs of LiScSiO<sub>4</sub> and Li<sub>0.587</sub>Sc<sub>0.587</sub>Mg<sub>0.826</sub>SiO<sub>4</sub> showed no de-

Table 1. Synthesis data for the Li-Sc-Mg silicate olivines

Run No.	1	2
Li <sub>2</sub> CO <sub>3</sub>	0.350 g	0.200 g
Li <sub>2</sub> MoO <sub>4</sub>	14.15 g	14.15 g
V <sub>2</sub> O <sub>5</sub>	2.08 g	2.08 g
Li <sub>2</sub> SiO <sub>3</sub>	1.43 g	1.25 g
Sc <sub>2</sub> O <sub>3</sub>	1.41 g	0.775 g
MgO	----	0.454 g
Soaking temperature	1250°C	1250°C
Soaking time	4 days	4 days
Cooling rate	4°C/h	4°C/h
Cutoff temperature	680°C	580°C
Crucible size	15 ml	30 ml
Yield	1.3 g	1.7 g
Crystal size	max. 2 mm	1 mm
Products	olivine	olivine
Bulk compositions	LiScSiO <sub>4</sub>	Li <sub>0.75</sub> Sc <sub>0.75</sub> Mg <sub>0.50</sub> SiO <sub>4</sub>

parture from the established olivine space group of *Pbnm*. Observed extinction rules were *0kl k = 2n* and *h0l h + l = 2n* only.

Crystal-structure refinement of the LiScSiO<sub>4</sub> established that Li and Sc are almost perfectly ordered in *M*(1) and *M*(2) sites respectively (Steele, Pluth and Ito, in preparation), analogous to the ordered olivine structure of triphylite, LiFePO<sub>4</sub> (Finger and Rapp, 1970).

Unit-cell dimensions of both end members and intermediate compositions of the solid-solution series were refined, using the X-ray powder diffraction method with CuKα<sub>1</sub> radiation with Si standard (*a* = 5.43062 Å) using the program of Appleman and Evans (1973) (Table 3). Unit-cell volumes and *a* and *b* of the series increased linearly with the corresponding amounts of Li and Sc, but *c* showed slight minima near the middle of the binary solid solution. Slightly larger cell dimensions for the flux-grown LiScSiO<sub>4</sub> compared to those of directly synthesized LiScSiO<sub>4</sub> are probably due to the entrance of the minor elements, mainly V<sub>2</sub>O<sub>5</sub>.

Indexed *d*-spacing data for LiScSiO<sub>4</sub> are given in Table 4. The observed intensities are consistent with those obtained from the single crystal.

Specific gravity of the two analyzed crystals were determined by floating several crystals in Clerici solution at room temperature, and simultaneously measuring the specific gravity of the liquid. Measured data agree well with the calculated values given in Table 2.

Table 2. Chemical analysis of the flux grown Li-Sc olivine crystals

Run No.	1		2	3		
	Bulk*	Grains**	Bulk*	Bulk*	Rim**	Core**
$\text{Li}_2\text{O}$	10.23	N. D.	7.9	6.2	N. D.	N. D.
$\text{Sc}_2\text{O}_3$	47.10	46.48	36.2	28.4	27.06	29.06
$\text{MgO}$	0.09	0.0	14.0	23.4	24.68	21.18
$\text{SiO}_2$	41.9	41.54	41.9	41.9	42.64	41.19
Total	99.32	88.02	100.0	99.9	94.38	91.43
$\text{Fe}_2\text{O}_3$	0.06	0.0	0.06	0.06	0.0	0.0
$\text{V}_2\text{O}_5$	0.28	N. A.	0.10	0.20	Nil	0.1 - 0.05
$\text{MnO}_3$	0.08	Nil	0.18	0.06	Nil	Nil
Specific gravity	3.19 (measured)		N. D.	3.21 (measured)		
	3.18 (calculated)		N. D.	3.20 (calculated)		

N. D. - Not determined; Nil = Not observed (Detection limit 0.05 wt%); N. A. = Not available  
 \*Bulk chemical analysis by J. Ito.  
 \*\*Electron probe analysis; analyzed by I. M. Steele; mean value from the analysis of representative points.

#### Melting relations on the join $\text{Mg}_2\text{SiO}_4$ - $\text{LiScSiO}_4$

A complete equilibrium study of this series is beyond the scope of this note, partly because a large portion of the liquidus lies above the present temperature limit of this laboratory. Observations made during the synthesis experiments indicate, however, that  $\text{LiScSiO}_4$  decomposes to liquid + olivine +  $\text{Sc}_2\text{Si}_2\text{O}_7$  on prolonged heating in platinum above  $1150^\circ\text{C}$  in air, but melts incongruently to liquid +  $\text{Sc}_2\text{Si}_2\text{O}_7$  +  $\text{Sc}_2\text{O}_3$  by rapid heating to temperatures above  $1450^\circ\text{C}$ . This melting trend extends from  $\text{LiScSiO}_4$  toward the composition containing approximately 25 mole percent  $\text{Mg}_2\text{SiO}_4$ , but with increasing thermal stability with higher  $\text{Mg}_2\text{SiO}_4$  component. Rapid melting and cooling of this olivine series using an induction furnace suggests that a primary liquidus field probably extends from  $\text{Mg}_2\text{SiO}_4$  to at least (Li,Sc)  $\text{MgSiO}_4$ .

#### On scandium in natural olivine

The scandium concentration in olivines from ultramafic and mafic rocks in general is much lower than that in pyroxenes and amphiboles (e.g. Borisenko, 1963). An exceptionally high concentration of

$\text{Sc}^{3+}$  (50 ppm and 39 ppm) was found in two hortonolite-dunites by Liebenberg (1960). Frykland and Fleischer (1963) concluded that the lower concentration of  $\text{Sc}^{3+}$  in olivines relative to that in pyroxenes and amphiboles is due to a greater ease in charge compensation in the latter two minerals, both of which readily accommodate heterovalency substitutions, rather than to structural incompatibility of  $\text{Sc}^{3+}$  in olivine. This study confirms Frykland and Fleischer's argument that if an appropriate valency compensation is made,  $\text{Sc}^{3+}$  can readily enter the olivine structure.

Other trivalent elements, such as  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$ , have also been incorporated in the synthetic forsterite using the same technique. Trivalent oxide contents in individually doped synthetic forsterites were determined by the electron microprobe analysis by I. M. Steele as follows: Cr-doped forsterite (green)  $\text{Cr}_2\text{O}_3 = 1.25$  weight percent, Fe-doped forsterite (yellowish brown)  $\text{Fe}_2\text{O}_3 = 0.39$  weight percent (total iron), and Al-doped forsterite  $\text{Al}_2\text{O}_3 = 0.32$  weight percent. The maximum limit of this type of substitution is not known; in each case, an equimolar amount of Li was detected in the bulk analysis by atomic absorption spectrometry.

Table 3. Unit-cell dimensions of the synthetic olivines in the binary  $\text{LiScSiO}_4$ - $\text{Mg}_2\text{SiO}_4$  system

Formula	a	b	c	Synthesis Conditions
<b>Flux Grown</b>				
$\text{LiScSiO}_4^*$	4.8214 (7)	10.444 (1)	5.9729 (9)	300.76 (6) 1250–600°C
$\text{LiScSiO}_4^{**}$	4.8200 (4)	10.439 (1)	5.9720 (5)	300.49 (3) 1250–600°C
$\text{Li}_{.75}\text{Sc}_{.75}\text{Mg}_{.50}\text{SiO}_4^{***}$	4.8002 (10)	10.404 (2)	5.9650 (13)	297.91 (7) 1250°C–580°C
$\text{Li}_{.59}\text{Sc}_{.59}\text{Mg}_{.82}\text{SiO}_4^{****}$	4.7867 (8)	10.367 (1)	5.9592 (8)	295.71 (6) 1000°C–500°C
$\text{Mg}_2\text{SiO}_4$	4.7544 (7)	10.201 (1)	5.9839 (9)	290.23 (6) 1400°C–1000°C
<b>Direct Synthesis</b>				
$\text{LiScSiO}_4$	4.8168 (6)	10.436 (1)	5.9686 (8)	300.04 (4) 1100°C, 48h
$\text{Li}_{.80}\text{Sc}_{.80}\text{Mg}_{.40}\text{SiO}_4$	4.8040 (8)	10.405 (2)	5.9632 (11)	298.08 (7) 1150°C, 48h
$\text{Li}_{.60}\text{Sc}_{.60}\text{Mg}_{.80}\text{SiO}_4$	4.7886 (6)	10.366 (2)	5.9612 (9)	295.91 (5) 1150°C, 48h
$\text{Li}_{.40}\text{Sc}_{.40}\text{Mg}_{1.20}\text{SiO}_4$	4.7794 (4)	10.325 (1)	5.919 (6)	294.21 (4) 1250°C, 48h
$\text{Li}_{.20}\text{Sc}_{.20}\text{Mg}_{1.60}\text{SiO}_4$	4.7676 (4)	10.265 (1)	5.9696 (4)	292.15 (3) 1250°C, 48h
*	4 circle diffractometer data (Steele, Pluth and Ito, in preparation)			
**	Analysis from Run No. 1 in Table 2, flux grown.			
***	Analysis from Run No. 2 in Table 2, flux grown.			
****	Analysis from Run No. 3 in Table 2, flux grown.			

In spite of the above results, noticeable concentration of  $\text{Sc}^{3+}$  in natural olivines has not been reported except in Liebenberg's (1960) dunites. The overall low concentration of  $\text{Sc}^{3+}$  in natural olivines might be due in part to their high crystallization temperature, where volatile elements, such as Li, would not enter concomitantly with  $\text{Sc}^{3+}$  into the olivine structure. This suggestion is supported by the low concentration of Li in mafic silicates crystallized in an early state of magmatic differentiation (Nockolds and Allen, 1956; Beus, 1964).

More careful analysis of the dunite described by Liebenberg (1960), especially that of separate grains of olivine, using ion probe microanalysis, might reveal more clues to an understanding of Sc geochemistry, and perhaps effects of Li. An example of Sc–Li, replacing Mg– $\text{Fe}^{2+}$ , is shown in the chemical analysis reported by Kukharenko and Kler (1962) of pyroxenes from the alkali gabbro from the Kola Peninsula.

Also, a quantitative analysis of Sc in the Li-bearing silicates from various localities may be a worthwhile geochemical study.

### Conclusion

Synthesis of a new olivine,  $\text{LiScSiO}_4$ , and the presence of a solid-solution series between  $\text{Mg}_2\text{SiO}_4$  and  $\text{LiScSiO}_4$  provides conclusive evidence of the direct  $\text{Sc}^{3+}$  substitution for  $\text{Mg}^{2+}$  in silicates. Charge balance is maintained by the simultaneous entry of  $\text{Li}^+$  into  $\text{Mg}^{2+}$  octahedra. Goldschmidt and Peters's observation (1931) of  $\text{Sc}^{3+} \rightleftharpoons \text{Mg}^{2+}$  diadochy in ferromagnesian silicates (Whittaker and Muntus, 1970) is thus confirmed experimentally, although a large number of trace analyses of  $\text{Sc}^{3+}$  in basic rocks have indicated this result. Any arguments made, based on improbability of the  $\text{Mg}^{2+} \rightleftharpoons \text{Sc}^{3+}$  isomorphous substitution in inorganic systems should, therefore, be refuted.

Table 4. X-ray powder diffraction for synthetic lithium scandium olivine,  $\text{LiScSiO}_4$  ( $\text{CuK}\alpha_1$  radiation, Si standard)

h	k	l	$V/I_0$	d obs	d calc	h	k	l	$V/I_0$	d obs	d calc
0	2	0	20	5.23	5.22	1	2	3	8	1.735	1.735
1	1	0	70	4.377	4.366	2	4	1	20	1.697	1.697
0	2	1	40	3.931	3.930	0	6	1	10	1.670	1.670
1	0	1	10	3.751	3.751	1	3	3	20	1.627	1.627
1	2	0	10	3.541	3.539	0	4	3	10	1.583	1.583
1	1	1	50	3.526	3.530	3	0	1	5	1.551	1.551
1	2	1	5	3.045	3.046	3	1	1	5	1.535	1.535
0	0	2	60	2.984	2.986	2	5	1	5	1.525	1.525
1	3	0	20	2.822	2.821	2	4	2	3	1.523	1.523
1	3	1	100	2.551	2.551	2	1	3	5	1.519	1.519
1	1	2	35	2.468	2.467	0	6	2	40	1.504	1.504
0	4	1	7	2.391	2.391	0	0	4	40	1.493	1.493
2	1	0	5	2.347	2.348	1	7	0	8	1.424	1.425
1	4	0	25	2.296	2.295	3	3	1	20	1.417	1.417
1	2	2	35	2.282	2.283	1	1	4	15	1.413	1.413
2	1	1	40	2.186	2.185	2	6	0	8	1.411	1.411
2	2	1	3	2.053	2.054	3	2	2	20	1.366	1.366
0	4	2	2	1.965	1.965	3	4	1	5	1.334	1.334
2	0	2	10	1.875	1.875	2	4	3	3	1.323	1.323
1	5	1	5	1.825	1.824	1	3	4	5	1.320	1.320
1	1	3	10	1.812	1.812	3	3	2	8	1.311	1.311
2	4	0	20	1.770	1.770	0	6	3	5	1.310	1.310
2	2	2	5	1.765	1.765	1	7	2	10	1.286	1.286
0	6	0	5	1.740	1.740						

$\text{LiScSiO}_4$ , Orthorhombic  $\text{Pbnm}$ ,  $a=4.8200$  (4),  $b=10.4392$  (8),  $c=5.9720$  (4)  
 $V=300.49$  (3), synthesized at temperature between 1250 and 600°C using solvent

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