the lattice parameters a and c, but also of c/a. In hypothetical $LaV(CN)_6.5H_2O$ the hole between the $[FeC_6]$ octahedra and the $[LaN_6O_3]$ polyhedra might even be too large for the two non-bonded H_2O molecules.

We are highly indebted to Dr Volker Gramlich and Professor Walter Petter of the Crystallography Institute, ETH, for their facilities, advice and active help. Moreover, we thank Professor Hans-Christoph Siegmann as well as the Swiss National Science Foundation for generous support.

References

BAILEY, W. E., WILLIAMS, R. J. & MILLIGAN, W. O. (1973). Acta Cryst. B29, 1365–1368.

BRAUER, G. (1981). Handbuch der Präparativen Anorganischen Chemie, Vol. 3, p. 1514. Stuttgart: Ferdinand Enke Verlag.

FIGGIS, B. N., KUCHARSKI, E. S., REYNOLDS, P. A. & WHITE, A. H. (1983). Acta Cryst. C39, 1587–1588.

FIGGIS, B. N., REYNOLDS, P. A. & WILLIAMS, G. A. (1981). Acta Cryst. B37, 504–508.

HULLIGER, F., LANDOLT, M. & VETSCH, H. (1976). J. Solid State Chem. 18, 283–291.

MULLICA, D. F., MILLIGAN, W. O., BEALL, G. W. & REEVES, W. L. (1978). Acta Cryst. B34, 3558–3561.

MULLICA, D. F., MILLIGAN, W. O. & KOUBA, W. T. (1979). J. Inorg. Nucl. Chem. 41, 967–973.

MULLICA, D. F. & SAPPENFIELD, E. L. (1989). J. Solid State Chem. 82, 168–171.

Nicolet Instrument Corporation (1988). XLS Structure Refinement Package. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

PETTER, W., GRAMLICH, V. & HULLIGER, F. (1989). J. Solid State Chem. 82, 161–167.

RYAN, R. R. & SWANSON, B. I. (1974). Inorg. Chem. 13, 1681–1684.

Synthesis and Structure of Magnesium Iron Thiosilicates (Mg₁₋ₓFeₓ)₂SiS₄

BY J. FUHRMANN AND J. PICKARDT*

Institut für Anorganische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12, Federal Republic of Germany

Abstract. $Mg_{1.4}Fe_{0.6}SiS_4$, $M_r = 223.88$, orthorhombic, $Pnma$, $a = 12.633$ (5), $b = 7.348$ (3), $c = 5.901$ (2) Å, $V = 547.7$ (4) Å³, $Z = 4$, $D_x = 2.715$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 32.9$ cm⁻¹, $F(000) = 442$, $T = 298$ K, $R = 0.025$, $wR = 0.022$ for 690 unique reflections, $F_o > 4\sigma(F_o)$. $Mg_{1.86}Fe_{0.14}SiS_4$, $M_r = 209.37$, orthorhombic, $Pnma$, $a = 12.677$ (4), $b = 7.405$ (2), $c = 5.913$ (2) Å, $V = 555.1$ (3) Å³, $Z = 4$, $D_x = 2.505$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 21.68$ cm⁻¹, $F(000) = 416$, $T = 298$ K, $R = 0.029$, $wR = 0.025$ for 1873 unique reflections, $F_o > 4\sigma(F_o)$. The two metal cations are not evenly distributed between the $M(1)$ and $M(2)$ positions of the olivine structure. The type of order [enrichment of Fe in the $M(1)$ position] is the same in both compounds. The degree of order is greater than in olivines of the forsterite–fayalite series.

Introduction. In the course of our studies of thiosilicates which crystallize in the olivine structure type we have carried out X-ray structure analyses of

Mn_2SiS_4 (Fuhrmann & Pickardt, 1989a), $(Mn,Mg)_2$-SiS_4, $(Mn,Fe)_2SiS_4$ and $(Mg,Fe)_2SiS_4$ (Fuhrmann & Pickardt, 1989b). The structure determination of the magnesium iron thiosilicate, combined with an electron microprobe analysis, yielded ordering effects of the metal cations in the two different positions of the olivine structure: the $M(1)$ position is enriched in Fe relative to $M(2)$. In order to verify these remarkable results [based on the cation size, Fe^{2+} should prefer the larger $M(2)$ octahedral site], we prepared single crystals of the solid-solution series Mg_2SiS_4–Fe_2SiS_4 and determined the crystal structures of $Mg_{1.4}$-$Fe_{0.6}SiS_4$ and $Mg_{1.86}Fe_{0.14}SiS_4$. The formulae assigned to these compounds are based on the refined occupancies of the metal sites.

Experimental. Single crystals of the title compounds were obtained by chemical transport reactions carried out in sealed quartz ampoules at 1173/1073 K for two weeks using Mg_2Si, Fe, Si and S_8 as starting materials. A red, transparent $Mg_{1.4}Fe_{0.6}SiS_4$ crystal (0.22 × 0.18 × 0.2 mm) and a yellow transparent $Mg_{1.86}Fe_{0.14}SiS_4$ crystal (0.26 × 0.14 × 0.18 mm) were

---

chosen for data collection on a Syntex $P2_1$ diffractometer operated in ω-scan mode (Mo $K\alpha$ radiation, graphite monochromator).

In the following, experimental details for $Mg_{1\cdot4}Fe_{0\cdot6}SiS_4$ are given before those for $Mg_{1\cdot86}Fe_{0\cdot14}SiS_4$. Cell parameters were obtained from a least-squares refinement of 15 reflections in the range $8 \le 2\theta \le 25°$, $6 \le 2\theta \le 25°$. Two standard reflections, measured periodically every 50 reflections, showed no significant change during data collection. 1017, 2796 reflections in the range $2 < 2\theta < 60°$. $0 \le h \le 17$, $0 \le k \le 10$, $0 \le l \le 8$, $2 < 2\theta < 90°$, $0 \le h \le 25$, $0 \le k \le 14$, $0 \le l \le 11$, were measured and yielded 856, 2407 unique reflections ($R_{int} = 0\cdot089$, $0\cdot09$), of which 690, 1873 were considered as observed ($F_o > 4\sigma F_o$). The data were corrected for Lorentz polarization effects and for absorption (numerical integration), range of transmission factors $0\cdot688$–$0\cdot778$, $0\cdot719$–$0\cdot831$; secondary-extinction effects on $Mg_{1\cdot86}Fe_{0\cdot14}SiS_4$ were corrected by refinement of an empirical extinction coefficient $X = 3\cdot6$ (2) $\times 10^{-7}$, $F_o = F_o(1 - XF_o^2/\sin\theta)$. Based on the coordinates of earlier structure determinations of M_2SiS_4 compounds (Vincent, Bertaut, Baur & Shannon, 1976; Fuhrmann & Pickardt, 1989a) the full-matrix least-squares refinements (43, 44 parameters) on F yielded the final R values $R = 0\cdot025$, $wR = 0\cdot022$, $w = 0\cdot58/\sigma^2(F_o)$, $R = 0\cdot029$, $wR = 0\cdot025$, $w = 1\cdot77/\sigma^2(F_o)$. The cation distributions in the equipoints $4(a)$ [$M(1)$ position] and $4(c)$ [$M(2)$ position] were also refined, using common anisotropic thermal parameters for Mg and Fe on the same position. Residual electron densities in the final difference syntheses were $0\cdot62$, $-0\cdot75$ e Å^{-3}, $0\cdot67$, $-0\cdot75$ e Å^{-3} near the Si atom, $(\Delta/\sigma)_{max}$ $0\cdot002$, $0\cdot002$. Atomic scattering factors for neutral Si and S atoms were taken from *SHELX*76 (Sheldrick, 1976), for Mg^{2+} and Fe^{2+} from Cromer & Mann (1968), anomalous-dispersion coefficients for all atoms from Cromer & Liberman (1970). Programs used were *SHELX*76 (Sheldrick, 1976) for structure calculations and *PLATON* (Spek, 1982) for geometric calculations.

Discussion. The stoichiometry and homogeneity of the crystals were proved by X-ray microanalysis using a scanning electron microscope. The results of these analyses (see Table 1*) agree well with the cation distributions calculated from the crystal structure refinements. Table 2 lists the atomic parameters, equivalent isotropic thermal parameters and the

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53067 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Chemical analyses (scanning electron microscope)*

$Mg_{1\cdot4}Fe_{0\cdot6}SiS_4$	Mg	Fe	Si	S
Measured (weight %)	13·50	17·11	12·68	56·15
Measured (atom %)	18·12	10·00	14·73	57·15
Calculated (atom %)*	20·00	8·57	14·29	57·14
$Mg_{1\cdot86}Fe_{0\cdot14}SiS_4$	Mg	Fe	Si	S
Measured (weight %)	22·73	2·21	14·10	61·61
Measured (atom %)	27·51	1·17	14·77	56·54
Calculated (atom %)*	26·57	2·00	14·29	57·14

* From the refined occupancies in Table 2.

metal cation occupancies; bond distances and angles are given in Table 3. Compared with Mg_2SiS_4 (Vincent, 1975) and Fe_2SiS_4 (Vincent, Bertaut, Baur & Shannon, 1976), no significant change of the mean $M(1)$—S and $M(2)$—S bond distances or distortion of the octahedra could be observed. The mean $M(1)$—S and $M(2)$—S bond distances increase with the Fe/(Fe + Mg) ratio.

The cation-ordering effects of the compounds $(Mg,Fe)_2SiS_4$, synthesized for the first time by us, agree well with the results of crystal structure refinements of lunaric and terrestic $(Mg,Fe)_2SiO_4$ olivines reported by Finger (1970) and Wenk & Raymond (1973), who also observed an enrichment of Fe in the $M(1)$ position. This type of Mg/Fe order in olivines was also proven with Mössbauer spectroscopy (Bush, Hafner & Virgo, 1970). The degree of order in the $(Mg,Fe)_2SiO_4$ olivines is much lower than in our samples, since the distribution coefficients, K_D, for the exchange reaction $Fe_{M(2)} + Mg_{M(1)} \rightleftharpoons Fe_{M(1)} + Mg_{M(2)}$ are 3·69 and 4·26 for our thiosilicates, much greater than the values calculated for the $(Mg,Fe)_2SiO_4$ olivines (0·97–1·39). (Here K_D is defined as $X[Mg_{M(2)}]X[Fe_{M(1)}]/X[Mg_{M(1)}]X[Fe_{M(2)}]$, where X is the cation-site occupancy.)

The detected enrichment of Fe in the $M(1)$ position conflicts with the cation size (Shannon & Prewitt, 1969, 1970), since Fe^{2+} (high spin: $r = 0\cdot78$ Å) is larger than Mg^{2+} ($r = 0\cdot72$ Å) and should prefer the larger $M(2)$ octahedron. The sense of ordering in our compounds also disagrees with results of Burns (1969), who investigated several $(Mg,Fe)_2SiO_4$ olivines by measurements of polarized absorption spectra and found an enrichment of Fe in the $M(2)$ position.

This study suggests that there may be cation-ordering effects in $(Mg,Fe)_2SiS_4$ comparable to olivines of the forsterite–fayalite series and detectable by X-ray methods. It will be necessary to carry out further investigations on thiosilicates of the olivine structure type to find out whether the ordering effects can also be detected by other analytical methods (*e.g.* Mössbauer and IR spectroscopy), especially since the crystal structure refinement

Table 2. *Fractional atomic coordinates, occupancies and equivalent isotropic thermal parameters* $(Å^2)$

$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	Equipoint	x	y	z	Occupancy	B_{eq}
$Mg_{1.4}Fe_{0.6}SiS_4$						
$M(1)$	$4(a)$	0	0	0	0.283 (2) Mg / 0.217 (2) Fe	0.90
$M(2)$	$4(c)$	0.23039 (7)	¼	0.50848 (18)	0.414 (2) Mg / 0.086 (2) Fe	0.82
Si	$4(c)$	0.41096 (8)	¼	0.09344 (16)	0.5	0.60
S(1)	$4(c)$	0.40830 (6)	¼	0.73625 (14)	0.5	0.70
S(2)	$4(c)$	0.56613 (6)	¼	0.24055 (15)	0.5	0.71
S(3)	$8(d)$	0.33430 (4)	0.02186 (7)	0.24750 (10)	1.0	0.73
$Mg_{1.86}Fe_{0.14}SiS_4$						
$M(1)$	$4(a)$	0	0	0	0.444 (1) Mg / 0.056 (1) Fe	0.98
$M(2)$	$4(c)$	0.23044 (4)	¼	0.50820 (9)	0.487 (1) Mg / 0.013 (1) Fe	0.93
Si	$4(c)$	0.41038 (3)	¼	0.09352 (7)	0.5	0.63
S(1)	$4(c)$	0.40767 (3)	¼	0.73832 (6)	0.5	0.74
S(2)	$4(c)$	0.56518 (3)	¼	0.23935 (6)	0.5	0.74
S(3)	$8(d)$	0.33372 (2)	0.02360 (3)	0.24687 (4)	1.0	0.76

Table 3. *Bond distances* (Å) *and angles* (°)

	$Mg_{1.4}Fe_{0.6}SiS_4$	$Mg_{1.86}Fe_{0.14}SiS_4$
Si tetrahedra		
Si—S(1^{vi})	2.108 (1)	2.101 (1)
Si—S(2)	2.144 (1)	2.143 (1)
Si—S(3),S(3^{ii})	2.139 (1)	2.139 (1)
S(1^{vi})—Si—S(3),S(3^{ii})*	114.7 (1)	114.6 (1)
S(1^{vi})—Si—S(2)	114.8 (1)	114.7 (1)
S(3)—Si—S(3^{ii})	103.2 (1)	103.2 (1)
S(2)—Si—S(3),S(3^{ii})*	104.0 (1)	104.2 (1)
$M(1)$ octahedra		
$M(1^{iv})$—S(1),S(1^{v})*	2.581 (1)	2.604 (1)
$M(1^{iv})$—S(2),S(2^{v})*	2.533 (1)	2.547 (1)
$M(1^{iv})$—S(3^{ii}),S(3^{v})*	2.574 (1)	2.591 (1)
S(1),S(1^{v})—$M(1^{iv})$—S(2),S(2^{v})*	87.6 (1)	87.5 (1)
S(1),S(1^{v})—$M(1^{iv})$—S(2^{v}),S(2)*	92.4 (1)	92.5 (1)
S(1),S(1^{v})—$M(1^{iv})$—S(3^{ii}),S(3^{v})*	84.5 (1)	84.2 (1)
S(1),S(1^{v})—$M(1^{iv})$—S(3^{v}),S(3^{ii})*	95.6 (1)	95.8 (1)
S(2),S(2^{v})—$M(1^{iv})$—S(3^{ii}),S(3^{v})*	82.7 (1)	82.2 (1)
S(2),S(2^{v})—$M(1^{v})$—S(3^{v}),S(3^{i})*	97.3 (1)	97.8 (1)
$M(2)$ octahedra		
$M(2)$—S(2^{i})	2.543 (1)	2.555 (1)
$M(2)$—S(3^{iii}),S(3^{iv})*	2.578 (1)	2.600 (1)
$M(2)$—S(1)	2.619 (1)	2.627 (1)
$M(2)$—S(3),S(3^{ii})*	2.628 (1)	2.629 (1)
S(2^{i})—$M(2)$—S(3),S(3^{ii})*	94.0 (1)	94.1 (1)
S(2^{i})—$M(2)$—S(3^{iii}),S(3^{iv})*	93.3 (1)	93.1 (1)
S(3^{iii})—$M(2)$—S(3^{iv})	101.6 (1)	102.4 (1)
S(3^{iii}),S(3^{iv})—$M(2)$—S(1)*	89.5 (1)	89.2 (1)
S(3),S(3^{ii})—$M(2)$—S(3^{iii}),S(3^{iv})*	89.1 (1)	88.7 (1)
S(1)—$M(2)$—S(3),S(3^{ii})*	82.7 (1)	83.0 (1)
S(3)—$M(2)$—S(3^{ii})	79.3 (1)	79.2 (1)
S(2^{i})—$M(2)$—S(1)	175.6 (1)	176.2 (1)
S(3),S(3^{ii})—$M(2)$—S(3^{iv}),S(3^{iii})*	166.7 (1)	166.3 (1)

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

* Two equivalent distances or angles.

(Fuhrmann & Pickardt, 1989*b*) of $(Mg,Mn)_2SiS_4$ showed no evidence of a significant Mg/Mn order and in $(Mn,Fe)_2SiS_4$ a distinction between Mn and Fe by X-ray methods was not possible. The detected degree of Mg/Fe order in $(Mg,Fe)_2SiS_4$, which is much greater than in $(Mg,Fe)_2SiO_4$ olivines, should also cause thermochemical effects.

References

BURNS, R. G. (1969). *Am. Mineral.* **55**, 1608–1632.
BUSH, W. R., HAFNER, S. S. & VIRGO, D. (1970). *Nature (London)*, **227**, 1339–1341.
CROMER, D. T. & LIBERMAN, D. (1970), *J. Chem. Phys.* **53**, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
FINGER, L. W. (1970). *Carnegie Inst. Washington Yearb.* **69**, 302–305.
FUHRMANN, J. & PICKARDT, J. (1989*a*). *Acta Cryst.* **C45**, 1808–1809.
FUHRMANN, J. & PICKARDT, J. (1989*b*). *Z. Anorg. Allg. Chem.* In the press.
SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 926–946.
SHANNON, R. D. & PREWITT, C. T. (1970). *Acta Cryst.* **B26**, 1046–1048.
SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.
SPEK, A. L. (1982). *The EUCLID Package.* In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.
VINCENT, H. (1975). *Thèse d'Etat*, Univ. Grenoble, France.
VINCENT, H., BERTAUT, E. F., BAUR, W. H. & SHANNON, R. D. (1976). *Acta Cryst.* **B32**, 1749–1755.
WENK, H.-R. & RAYMOND, K. N. (1973). *Z. Kristallogr.* **137**, 86–105.