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Ferrosilite III, the High-Temperature Polymorph of $FeSiO_3$

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Abstract. $M_r = 2374{\cdot}74$, triclinic, $P\bar{1}$, $a = 6{\cdot}628$ (1), $b = 7{\cdot}467$ (1), $c = 22{\cdot}607$ (3) Å, $\alpha = 115{\cdot}32$ (1), $\beta = 80{\cdot}56$ (1), $\gamma = 95{\cdot}49$ (2)°, $V = 997{\cdot}2$ (3) Å^3, D_m (flotation) $= 3{\cdot}89$ (5), $D_x = 3{\cdot}95$ Mg m^{-3} for $Z = 18$, $\mu(\text{Mo } K) = 7{\cdot}025$ mm^{-1}, $\lambda = 0{\cdot}7107$ Å. The title compound was synthesized at 2 GPa and 1523 K and then quenched. Its structure was solved by direct methods and the refinement by full-matrix least squares converged to $R_w = 0{\cdot}06$ for 11 233 reflections with $F_o > 3\sigma$. $FeSiO_3$ is made up structurally of bands of Fe—O octahedra which are linked together by SiO_4 tetrahedra. The latter form chains of their own which run parallel to the bands. Along the chain the tetrahedra exhibit a uniform increase in the extent of their distortion. The ellipsoid of thermal motion of Fe at the $M(22)$ site is strikingly anisotropic and its largest axis points to the center of the octahedral face towards which the atom is shifted.

Introduction. Pyroxenoid minerals are silicates in which bands of close-packed O^{2-} anions are joined by Si^{4+} cations. The SiO_4 tetrahedra themselves are further corner-linked to form linear chains. The length of the repeat unit within this chain and the distribution pattern of the metal cations within the oxygen bands mainly distinguish one pyroxenoid from another. Repeat units of three, five and seven SiO_4 tetrahedra occur in the minerals wollastonite, rhodonite and pyroxmangite, respectively (*e.g.* Liebau, 1980). A longer repeat unit has so far only been observed in a compound synthesized in the laboratory: ferrosilite III. This phase was first encountered (Lindsley, Davis, MacGregor, 1964) during the mapping of the subsolidus relations of ferrosilite, the Fe analog of enstatite ($MgSiO_3$). The monoclinic and orthorhombic $FeSiO_3$ polymorphs which occur at lower temperatures were demonstrated to be isostructural with clino- and orthoenstatite, respectively (Burnham, 1965). For the high-temperature, triclinic form a pyroxenoid-type structure with a repeat length of nine SiO_4 tetrahedra in the chain was proposed, mainly on the basis of the close relationship of its triclinic cell with the unit cells of other pyroxenoids (Burnham, 1966). Lately, the existence of the nine-unit repeat within ferrosilite III has been confirmed by electron microscopy (Czank & Simons, 1981). This paper presents the three-dimensional crystal structure of ferrosilite III.

Experimental. Grayish-green crystals synthesized in a solid-media piston-and-cylinder press at 2 GPa and 1523 K for 20 h, starting mix of metallic Fe, Fe_2O_3, SiO_2 in stoichiometric proportions and a trace of water; long-exposure precession photographs of several crystals displayed the expected triclinic symmetry and no diffuse streaks between reflections along **c***; Philips PW 1100 automated four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, crystal $0{\cdot}15 \times 0{\cdot}20 \times 0{\cdot}40$ mm, longest dimension ($\sim c$ axis) at 15° to diffractometer φ axis; unit-cell parameters obtained from a least-squares fit of weighted $\sin^2\theta$ values for 45 reflections with $2{\cdot}0 < \theta < 37{\cdot}8°$, each reflection centered at $+\theta$ and $-\theta$; integrated intensities measured by $\omega/2\theta$ scans, scan width $\Delta(2\theta) = 3°$, ω scan rate 1·2° min^{-1}, background measured for 38 s at each end of a scan; 18 843 symmetry-unrelated reflections measured to $(\sin\theta/\lambda)_{\max} = 1{\cdot}1$ Å^{-1}, variance of an integrated reflection, $\sigma^2(I)$, obtained from counting statistics and augmented by $(0{\cdot}02I)^2$, all intensity data corrected for absorption, transmission factor ranged from 0·73 to 0·87; a statistical survey of all diffracted intensities yielded a distribution close to hypercentric (Lipson & Woolfson, 1952), space group $P\bar{1}$ subsequently assumed; direct methods (program *MULTAN*; Germain, Main & Woolfson, 1971), 280 $E_{\mathbf{h}}$'s greater than 1·2, 3849 $\sum_2$ relationships; of four different solutions proposed that with the second highest combined figure-of-merit (1·74) proved correct; E maps revealed seven Fe, five Si atoms and 13 O atoms, remaining 20 atoms obtained from computation of a series of electron density maps; these atom locations were then introduced as initial guesses in a full-matrix least-squares refinement (program *POP*; Craven & Weber, 1977) of positional parameters and isotropic temperature factors; atomic scattering factors and dispersion corrections taken from Cromer & Waber (1974); in final three cycles of refinement

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temperature factors were refined anisotropically, an isotropic extinction parameter was added, and only the 11 233 reflections with $F_o > 3\sigma$ were included; upon convergence $R(F) = 0{\cdot}071$, $R_w(F) = 0{\cdot}060$ and $\mathrm{QME} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO}-\mathrm{NV})]^{1/2} = 1{\cdot}294$; extinction was moderate, giving 1339 (124) rad^{-1}, $F(000) = 1152$.

Discussion. The atomic coordinates* of ferrosilite III are contained in Table 1 and its atomic arrangement is pictured in Fig. 1. The nomenclature follows that proposed recently for other pyroxenoids (Takéuchi, 1977). The structure is projected onto (110), the plane parallel to the close-packed O layer; this orientation most clearly displays the structural relationship with the other pyroxenoid minerals.

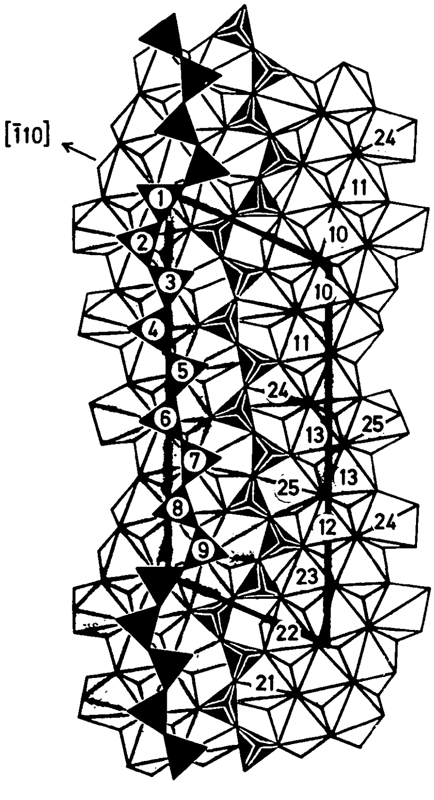

Fig. 1. The structure of ferrosilite III, as seen in a projection onto (110). The cell outlined is the C-centered one. SiO_4 tetrahedra and Fe—O polyhedra are labeled by single-digit and double-digit numbers, respectively.

Table 1. *Atomic parameters for ferrosilite* III

The positional parameters are $\times 10^5$; the equivalent isotropic thermal parameter $U_{\mathrm{eq}} = [\frac{1}{3}\sum\sum U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j]^{1/2}$ is $\times 10^4$. The e.s.d.'s given in parentheses refer to the least significant digit in the parameter value. M refers to Fe and the numbering follows the scheme proposed by Takéuchi (1977).

	x	y	z	U_{eq}(Å)
M(10)	5134 (8)	45492 (7)	41889 (2)	777 (6)
M(11)	19183 (8)	31543 (7)	25993 (2)	760 (6)
M(12)	2977 (7)	46190 (7)	80630 (2)	755 (6)
M(13)	11189 (7)	38982 (7)	3356 (2)	773 (6)
M(21)	38922 (8)	13267 (8)	34072 (3)	880 (7)
M(22)	19151 (11)	16975 (11)	48612 (3)	1481 (14)
M(23)	14528 (8)	32746 (7)	65097 (2)	794 (8)
M(24)	30572 (8)	19380 (8)	10798 (3)	889 (8)
M(25)	22018 (8)	27055 (8)	88125 (3)	860 (8)
Si(1)	23845 (15)	86110 (14)	55161 (5)	765 (11)
Si(2)	10381 (15)	97742 (14)	69403 (5)	693 (11)
Si(3)	29602 (14)	78413 (14)	76288 (5)	697 (11)
Si(4)	17754 (14)	90786 (14)	91198 (5)	701 (11)
Si(5)	37389 (14)	71303 (14)	98406 (5)	710 (11)
Si(6)	25880 (14)	83834 (13)	13461 (5)	689 (11)
Si(7)	45657 (14)	63640 (14)	20414 (5)	676 (11)
Si(8)	33723 (15)	75381 (14)	35205 (5)	725 (11)
Si(9)	51498 (15)	58620 (15)	43131 (5)	782 (11)
O(A1)	94446 (40)	30076 (37)	47750 (13)	949 (48)
O(A2)	8465 (38)	18252 (36)	32587 (12)	882 (45)
O(A3)	87004 (37)	39786 (34)	25959 (12)	873 (46)
O(A4)	986 (37)	25258 (36)	9949 (13)	919 (46)
O(A5)	79999 (38)	46107 (35)	2991 (13)	916 (45)
O(A6)	92235 (36)	32797 (34)	87490 (12)	846 (45)
O(A7)	72228 (38)	53275 (36)	80546 (12)	870 (45)
O(A8)	15208 (38)	59449 (36)	34803 (13)	887 (45)
O(A9)	64791 (40)	59199 (37)	57816 (13)	930 (48)
O(A10)	75615 (39)	55188 (39)	42593 (14)	1004 (48)
O(B1)	82961 (44)	93322 (40)	44377 (14)	1098 (50)
O(B2)	4924 (41)	20247 (35)	71484 (13)	973 (49)
O(B3)	47985 (37)	25909 (37)	27872 (12)	933 (45)
O(B4)	12298 (40)	13712 (35)	94131 (13)	973 (38)
O(B5)	60186 (37)	65214 (39)	94768 (13)	987 (47)
O(B6)	20211 (40)	6798 (36)	17184 (13)	944 (47)
O(B7)	31271 (38)	42892 (37)	82596 (13)	894 (47)
O(B8)	28470 (41)	98120 (37)	39679 (13)	956 (47)
O(C1)	27855 (39)	89803 (38)	62649 (13)	926 (47)
O(C2)	78920 (38)	3138 (36)	24698 (13)	896 (47)
O(C3)	68131 (40)	13666 (40)	15953 (13)	1028 (49)
O(C4)	32208 (41)	87839 (38)	95909 (13)	1080 (48)
O(C5)	37516 (41)	83064 (39)	6372 (12)	1040 (48)
O(C6)	57162 (39)	21431 (37)	83012 (13)	951 (47)
O(C7)	56301 (39)	22825 (38)	71604 (12)	943 (47)
O(C8)	52014 (38)	67906 (39)	37630 (13)	920 (47)
O(C9)	45147 (39)	77366 (37)	50325 (13)	979 (47)

In fact, the structure of pyroxmangite, for example, can easily be developed from the ferrosilite III structure by the removal of a pyroxene-type cluster (two octahedra and two tetrahedra). The similarity extends to the metrics of the polyhedra. The 'inner' FeO_6 octahedra, those embedded within the octahedral bands and labelled $M(1i)(i = 0$ to $3)$, are quite regular as evidenced by their bond-length variance $\{\langle \mathrm{Fe[VI]—O}\rangle = 2{\cdot}17\ (8), 2{\cdot}16\ (8), 2{\cdot}16\ (7), 2{\cdot}16\ (5)$ Å, respectively$\}$ while the 'outer' FeO_6 octahedra, labelled $M(2i)(i = 1$ to $5)$, are distorted and all contain five- or seven-coordinated Fe $\{\langle \mathrm{Fe[VII]—O}\rangle = 2{\cdot}3\ (4), 2{\cdot}3\ (4), 2{\cdot}3\ (4), 2{\cdot}4\ (4), 2{\cdot}4\ (4)$ Å$\}$. Thus the average Fe—O distances in ferrosilite III are longer than for the corresponding polyhedra in orthoferrosilite, which in turn are longer than in clinoferrosilite; this is a remnant

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* Lists of structure factors and anisotropic thermal parameters, and selected interatomic distances, angles and polyhedral distortions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38080 (130 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of its high-temperature origin. The shortest Fe—Fe interaction [3·1023 (8) Å] is found between $M(12)$ and $M(25)$; in orthoferrosilite it is only 2·9938 (7) Å (Seifert & Weber, 1982). The SiO_4 tetrahedra, which link the octahedral bands zipper-like, display an almost steady increase in the degree of their distortion as manifested in their bond-angle variance, from 19·6 deg^2 for Si(1) to 47·8 deg^2 for Si(9). This feature is found in all pyroxenoids and may be caused by an increasing out-of-registry of the octahedra from neighbouring bands which are linked by the Si atoms. As observed in all other pyroxenoids the cation at the $M(22)$ site is shifted far off-center and has an abnormally large amplitude of vibration. In the case of ferrosilite III, the only pyroxenoid where the temperature factors have been refined anisotropically, the ellipsoid of thermal motion is unusually anisotropic and the axis of its largest amplitude points to the center of the octahedral face towards which the atom has been displaced; this is roughly towards the more remote [2·879 (2) Å] of the two O(B1) oxygen atoms. Whether the potential at this site is of an anharmonic or a double-well nature will be discussed in a forthcoming publication, which will also deal with the electron distribution within the present compound.

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Structure of Basic Sodalite, $Na_8Al_6Si_6O_{24}(OH)_2.2H_2O$

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Abstract. $M_r = 968·34$, cubic, $P\bar{4}3n$, $a = 8·890$ (1) Å, $V = 702·6$ (1) Å^3, $Z = 1$, $D_x = 2·29$ Mg m^{-3}, $F(000) = 480$, graphite-monochromatized Mo $K\alpha$ radiation, $\lambda K\alpha_1 = 0·71069$ Å, $\mu = 0·775$ mm^{-1}. Final $R = 0·022$ for 152 observed reflexions. The 1:1 alumino-silicate framework is completely ordered whereas the O of the hydroxyl group and water molecule is disordered about the body diagonal of the cubic cell due to spatial requirements and the presence of hydrogen bonds; thus only four of the 24(i) cavity O positions can be occupied simultaneously and the chemical formula above is ideal.

Introduction. Basic sodalite is isotypic with sodalite $Na_8Al_6Si_6O_{24}Cl_2$ (Pauling, 1930) and polymorphic with basic cancrinite (Pahor, Calligaris, Nardin & Randaccio, 1982) the latter being the low-temperature polymorph (Anderson & Burley, 1982). Zeolites are distinguished on the basis of their structural type (Meier & Olsen, 1971) which is defined by the topology of their alumino-silicate frameworks. Accordingly, basic sodalite and basic cancrinite may be considered members of the zeolite family. As in the zeolites, these minerals contain interframework ions which can be replaced without disrupting the framework bonds. Basic sodalite is stable at higher temperatures than other zeolites and therefore offers a means of gas storage at these higher temperatures, with possible controlled release of the gas (Barrer & Vaughan, 1971).

Bukin & Makarov (1967) reported a single-crystal neutron diffraction structure of a synthetic basic sodalite $Na_{7·1}Al_6Si_{5·5}H_{0·5}Cl_{0·4}(OH)_{0·7}.0·7H_2O$, space group $P\bar{4}3n$ and $a = 8·887$ Å. They found that $\frac{1}{12}$ of the Si atoms were replaced by four H atoms arranged in tetrahedral fashion on the midway point of the O—O edges of the original SiO_4 tetrahedron, giving an H_4O_4

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