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# Samarium Pyrosilicate Sulfide, Sm4S3Si2O7

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**Abstract.** $Sm_4S_3Si_2O_7$, space group $I4_1/amd$, $a = 11\cdot839$ (5), $c = 13\cdot928$ (5) Å, $Z = 8$, $D_x = 5\cdot89$ g cm$^{-3}$. The final $R$ value was $0\cdot054$ for 937 observed reflections. $Sm_4S_3Si_2O_7$ has been found to crystallize in a new tetragonal structure type. The structure contains two kinds of Sm atoms. Sm(1) is coordinated to three O and three S atoms and Sm(2) to six O and three S atoms. The $[Si_2O_7]$ double tetrahedra are in the eclipsed configuration.

**Introduction.** In an attempt to grow $SmS_2$ single crystals by an iodine-transport reaction in a closed silica tube at 1073 to 1173 K we obtained transparent crystals the largest of which had dimensions of about $1 \times 1 \times 0\cdot5$ mm. Thin plates have a yellowish color whereas bulky crystals look greenish. The crystals are stable in air. An electron-beam microprobe analysis yielded within the experimental accuracy the composition $Sm_4S_3Si_2O_7$. Obviously this silicate sulfide decomposes peritectically since all attempts to reproduce this phase, as well as other rare-earth analogs, by melting or sintering failed.

The shape of the single crystal was approximated by 11 faces, dimensions about $0\cdot4 \times 0\cdot3 \times 0\cdot2$ mm. Precession patterns revealed tetragonal symmetry with the unambiguous systematic extinctions of space group $I4_1/amd$ (No. 141). For the structure determination we used a Syntex $P2_1$ four-circle diffractometer, mono-chromatized Mo $K\alpha$ radiation, $2\theta-\theta$ scan to $\sin \theta/\lambda = 0\cdot76$ Å$^{-1}$ ($2\theta_{max} = 65°$), Lehmann–Larsen algorithm (Blessing, Coppens & Becker, 1972), absorption correction by *ORABS* program of the XRAY system 72 (1972) ($\mu_{MoK\alpha} = 250$ cm$^{-1}$), 2405 reflections, 1053 unique reflections, 1017 observed $I > 3\sigma(I)$, Patterson and Fourier methods, and the XRAY system 72 (1972). The Patterson map was analyzed with a program written by Walpen (Walpen & Niggli, 1979). Scattering factors were taken from Cromer & Mann (1968) and the anomalous-dispersion factors for Sm from *International Tables for X-ray Crystallography* (1974). The structure was refined by the full-matrix least-squares method. An isotropic refinement with an extinction correction applied led to an $R$ value of $0\cdot064$, all reflections included. An anisotropic refinement with 937 reflections in the range of $\sin \theta/\lambda$ from $0\cdot3$ to $0\cdot8$ Å$^{-1}$ lowered the $R$ value to $0\cdot054$. A difference Fourier map showed only weak peaks in the vicinity of the Sm atoms. The final positional and thermal parameters are listed in Table 1.* Interatomic distances up to $3\cdot3$ Å are given in Table 2.

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters for* Sm₄S₃Si₂O₇, *origin at center* (2/m)

$$B_{eq} = \tfrac{4}{3}\, \text{trace } B_{ij}$$

| Position | | x | y | z | $B_{eq}$ (Å²) |
|---|---|---|---|---|---|
| Sm(1) | 16(h) | 0 | 0·0137 (1) | 0·3422 (1) | 0·52 (4) |
| Sm(2) | 16(g) | 0·1714 (1) | $x + \tfrac{1}{4}$ | $\tfrac{7}{8}$ | 0·36 (3) |
| Si | 16(h) | 0 | 0·3740 (4) | 0·0971 (3) | 0·3 (2) |
| S(1) | 16(f) | 0·3523 (3) | 0 | 0 | 0·8 (2) |
| S(2) | 4(b) | 0 | $\tfrac{1}{4}$ | $\tfrac{3}{8}$ | 0·7 (2) |
| S(3) | 4(a) | 0 | $\tfrac{3}{4}$ | $\tfrac{1}{8}$ | 0·7 (2) |
| O(1) | 32(i) | 0·1200 (7) | 0·1103 (8) | 0·0433 (6) | 0·6 (3) |
| O(2) | 16(h) | 0 | 0·0207 (9) | 0·1746 (8) | 0·6 (3) |
| O(3) | 8(e) | 0 | $\tfrac{1}{4}$ | 0·603 (1) | 1·2 (6) |

Table 2. *Coordination and interatomic distances, including non-bonding distances up to* 3·3 Å

For Sm(1) and Sm(2) see Figs. 2 and 3.

S(1)—4 Sm at 2·813 (3) (2×) and 2·912 (5) Å (2×)
  6 O at 3·10 (1) (2×), 3·27 (1) (2×) and 3·29 (1) Å (2×)
S(2)—4 Sm at 2·834 (1) Å
  2 O at 3·18 (2) Å
S(3)—4 Sm at 2·870 (1) Å
  12 O at 3·20 (1) (8×) and 3·28 (1) Å (4×)
Si—4 O at 1·617 (9) (2×), 1·623 (9) (bridging O) and 1·65 (1) Å
  1 Si at 2·936 (7) Å
O(1)—3 Sm at 2·451 (9), 2·469 (9) and 2·582 (9) Å
  1 Si at 1·617 (9) Å
  5 O at 2·54 (1), 2·61 (1) Å, 2·84 (1), 2·88 (1) and 2·94 (1) Å
O(2)—3 Sm at 2·34 (1) and 2·445 (6) Å (2×)
  1 Si at 1·65 (1) Å
  5 O at 2·54 (1) (2×), 2·74 (1) and 2·94 (1) Å (2×)
O(3)—2 Si at 1·623 (9) Å
  6 O at 2·61 (1) (4×) and 2·74 (1) Å (2×)

**Discussion.** The crystal structure contains two kinds of Sm atoms and S and O atoms both in three different symmetry positions (Figs. 1–3, Table 1). One of the O atoms is located distinctly closer to the central Sm atom than the other two. Similar short distances, however, are also met in Sm₂Si₂O₇, where Sm(1)—O = 2·345–2·663 (13) Å, Sm(2)—O = 2·333–2·954 (13) Å, Sm(3)—O = 2·271–2·662 (13) Å, and Sm(4)—O = 2·377–2·853 (13) Å (Smolin, Shepelev & Butikova, 1970). The top and bottom planes of the trigonal-prismatic coordination polyhedron around Sm(1) are tilted against each other by an angle of 12·2 (2)°, the symmetry of the prism being m. The three S atoms lie at almost equal distances which are about 16% larger than those of the O atoms. At considerably larger distances three additional atoms [two S at 3·21 (1) Å and one O at 3·39 (1) Å] are located outside the trigonal prism nearly perpendicular to the centers of its lateral faces. The Sm(2) atom is more regularly coordinated by nine atoms, three S and six O (Fig. 3), the mean oxygen distance being 2·49 (1) Å and the mean sulfur distance 2·90 (1) Å. These distances are

about 3% larger than those of Sm(1). Taking the site parameters of Dy₂O₂S (Abbas, Rossat-Mignod, Quezel & Vettier, 1974), we calculated the following distances for Sm₂O₂S (Eick, 1958): Sm—O = 2·32 (1), 2·47 (1) Å, Sm—S = 2·90 (1) Å, which agree well with our data for Sm₄S₃Si₂O₇.

The [Si₂O₇] double tetrahedra have the symmetry mm. The Si—O distances cover the range 1·62–1·65 (1) Å and the O—Si—O angles are 102·5, 107·5, 113·9 and 122·9 (5)°. The non-bonding Si—Si distance of 2·936 (7) Å is fairly short compared with the average in silicates of 3·06 Å (O'Keeffe & Hyde,
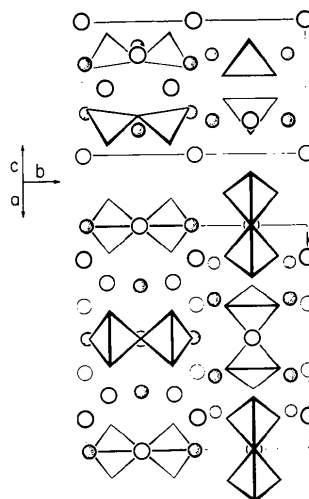


Fig. 1. Half the cell of Sm₄S₃Si₂O₇ projected along |00$\bar{1}$| and |$\bar{1}$00|. The Si₂O₇ anions are represented by double tetrahedra. Large spheres: S atoms; small stippled spheres: Sm atoms.
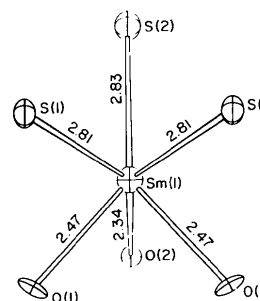


Fig. 2. Coordination of the Sm(1) atoms. Thermal ellipsoids of 75% probability are used for all the atoms. Distances in Å (errors 0·01 Å; exact values in Table 2).
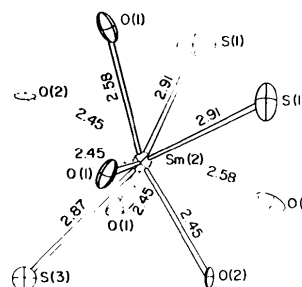


Fig. 3. Coordination of the Sm(2) atoms, analogous to Fig. 2.

1978). As a consequence, the bridging Si—O—Si angle of 129 (1)° is rather small.

For comparison we may note that in the various rare-earth pyrosilicate modifications the [$Si_2O_7$] groups occur mainly in two configurations (Felsche, 1973): (1) A centrosymmetric staggered configuration is met in the thortveitite-type silicates (type $C'$), such as $Yb_2Si_2O_7$, and in type $D$, as realized in $Er_2Si_2O_7$. In this configuration the Si—O—Si angle is 180°. (2) A non-centrosymmetric eclipsed configuration, similar to the one in $Sm_4S_3Si_2O_7$, is also found in type $A$ [$Sm_2Si_2O_7$: Si—O—Si = 129·7 (10) and 136 (1)°; Si—Si = 2·99 (2) and 3·05 (2) Å] (Smolin et al., 1970), type $E$ [$Eu_2Si_2O_7$: Si—O—Si = 158·3 (4)°; Si—Si = 3·28 (1) Å] and type $G$ pyrosilicates [$Pr_2Si_2O_7$: Si—O—Si = 131·7 (4)°; Si—Si = 2·96 (1) Å] as well as in $Na_3ScSi_2O_7$ [Si—O—Si = 136·0 (4)°; Si—Si = 3·12 (1) Å] (Felsche, 1973).

Structures containing a mixture of sulfide and silicate ions appear to be rather seldom. We are aware only of three examples, namely helvite $Mn_4(BeSiO_4)_3S$ (Holloway, Giordano & Peacor, 1972), $Ag_8S_2SiO_4$ (Schultze-Rhonhof, 1974) and $Ca_{22}(SiO_4)_8O_4S_2$ (Dent Glasser & Lee, 1981). Geometrically, the $Sm_4S_3Si_2O_7$ structure would also be appropriate for such exotic compounds as $Ca_2Ln_2^{3+}(P_2O_7)S_3$ or $Ln_2^{3+}Zr_2(Al_2O_7)S_3$.

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# Neutron Diffraction Study of Sodium Sesquicarbonate Dihydrate

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**Abstract.** $Na_2CO_3.NaHCO_3.2H_2O$, $M_r = 220·0$, monoclinic, $C2/c$, $a = 20·36$ (2), $b = 3·48$ (1), $c = 10·29$ (1) Å, $\beta = 106·48$ (1)°, $Z = 4$, $D_x = 2·147$ Mg m$^{-3}$. The final $R$ value after full-matrix least-squares refinement was 0·040 for 754 observed reflections. In this structure, water molecules and $(CO_3.H.CO_3)^{3-}$ anions form a two-dimensional hydrogen-bonded network. The $(HC_2O_6)^{3-}$ anion is almost planar and consists of two $CO_3^{2-}$ anions linked by an H atom with an O$\cdots$H$\cdots$O distance of 2·46 Å. Least-squares refinements revealed that this H atom is dynamically disordered between two equivalent sites separated by 0·211 (9) Å.

**Introduction.** The crystal structure of sodium sesquicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$, was first determined by Brown, Peiser & Turner-Jones (1949) with single-crystal X-ray diffraction data. It was refined