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$NaY_3S_3[SiS_4]$: a sodium-containing yttrium sulfide thiosilicate with channel structure

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Abstract

The reaction of sodium bromide (NaBr), yttrium (Y), sulfur (S) and silicon disulfide (SiS_2) in the molar ratio 1:4:6:2 with an excess of NaBr as flux in evacuated silica ampoules at 850°C for 7 days leads to the formation of deep red, hexagonal pillar-shaped single crystals of the title compound. $NaY_3S_3[SiS_4]$ crystallizes hexagonally in the space group $P6_3$ ($a = 976.57(7)$, $c = 570.61(5)$ pm; $Z = 2$). The sodium cations are situated in the trigonal antiprismatic holes (CN = 6) of a channel along [001] that is built by *non*-silicon bonded sulfide anions, which on their part are surrounded by four Y^{3+} and two Na^+ cations. The yttrium cations are surrounded by eight sulfur atoms in the shape of a square antiprism divided into four silicon- and four non-silicon-bonded sulfide anions. Finally, all discrete $[SiS_4]^{4-}$ tetrahedra point in the same direction along the polar *c*-axis. Therefore, the whole structure of $NaY_3S_3[SiS_4]$ remains non-centrosymmetric.

Keywords: Yttrium; Thiosilicates; Channel structures

1. Introduction

Thiosilicate derivatives of the trivalent rare-earth elements are already known with large halide anions such as Cl^-, Br^- and I^- [1–3] according to $M_3X[SiS_4]_2$ (M = rare-earth metal, X = halogene) and also with the heavy alkali metal cations ($A^+ = K^+$ [4–7] Rb^+ and Cs^+ [7, 8]) in compounds with the formula $AM[SiS_4]$ (A = alkali metal) which largely crystallize isotypical to the analogous thiogermanates (e.g., $KLa[GeS_4]$ [9]). All these compounds contain isolated $[SiS_4]^{4-}$ tetrahedra in their crystal structures and the derivatizing ion plays a structure dominating role, as it is forming layers either alone (in $AM[SiS_4]$) or together with rare-earth trications (in $M_3X[SiS_4]_2$). This is no longer possible on transition to the smaller Na^+ cation [10], so an alternative structure requiring a different composition ($NaM_3S_3[SiS_4]$) is built, in which the alkali cation does not have a coordination sphere of eight [4–7] like the potassium or nine (*plus two*) like the rubidium and caesium cations in the $AM[SiS_4]$-type compounds [7,8], but a coordination number of only six, situated in a channel of a hexagonal crystal structure which is naturally very open for cationic exchange. This structure type of rare-earth thiosilicates exists also with a total substitution of Na^+ (in $NaLa_3S_3[SiS_4]$ [10]) by Cu^+ cations to form $CuLa_3S_3[SiS_4]$ [11] as well as the case in which two sodium cations are replaced by one small divalent cation (e.g., M' = Mg [12], Mn [13], Co, Ni [14]) in $M'La_6S_6[SiS_4]_2$ that occupies only half of the former Na^+ position. There is a tolerance even in consideration of the exchange of sulfur by selenium which is realized in $AgLa_3Se_3[SiSe_4]$ [15]. Since all these compounds exist exclusively with lanthanum, it was obvious to carry out attempts with smaller rare-earth representatives to reach the existence range limits of this structure type.

2. Experimental

While attempting to react beryllium (ChemPur, 99.9%), yttrium (ChemPur, 99.9%) and sulfur (ChemPur, 99.999%) in an excess of sodium bromide (ChemPur, 99.9%) as flux to obtain a ternary sulfide of the formula BeY_2S_4 in evacuated silica ampoules for 5 days at 950°C, the beryllium accidentally reacted with

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the ampoule and according to

$$2\mathrm{NaBr} + 6\mathrm{Y} + 14\mathrm{S} + 5\mathrm{Be} + 4\mathrm{SiO_2} \rightarrow 2\mathrm{NaY_3S_3[SiS_4]} + 2\mathrm{Be_2[SiO_4]} + \mathrm{BeBr_2},$$

the title compound was obtained. The experiment to reach this sodium yttrium sulfide thiosilicate on purpose using yttrium (ChemPur, 99.9%), sulfur (ChemPur, 99.999%), silicon disulfide (ChemPur, 95%) and again an excess of sodium bromide (ChemPur, 99.9%) both as educt (sodium source) and as flux according to

$$\mathrm{NaBr} + 4\mathrm{Y} + 6\mathrm{S} + 2\mathrm{SiS_2} \rightarrow \mathrm{NaY_3S_3[SiS_4]} + \mathrm{YSBr}$$

for 7 days at 850°C in evacuated silica ampoules was successful as well. Whether the first or the second reaction path was used the main product consists of air- and water-resistant single crystals in the shape of thick hexagonal pillars (Fig. 1) with dark red, in larger thickness almost black colour and with a yield of about 80%. The crystals were examined by single crystal X-ray diffraction on an κ-CCD diffractometer (Nonius, Delft/NL) and by electron beam X-ray microanalysis on a SX100 electron probe microanalyzer (Cameca, Paris/F) to verify that the crystals really contain sodium but neither beryllium nor bromine. The results of the structure determination as well as important internuclear distances can be taken from Tables 1–3 [16–18].

3. Structure description and discussion

$\mathrm{NaY_3S_3[SiS_4]}$ crystallizes hexagonally with space group $P6_3$ ($Z = 2$) and the lattice constants $a = 976.57(7)$, $c = 570.61(5)$ pm (Table 1). The $\mathrm{Na^+}$ cations at the Wyckoff position $2a$ (Table 2) are located in the trigonal antiprismatic holes (CN = 6, Fig. 2, top) of a channel along [001] built by the *non*-silicon bonded $(\mathrm{S3})^{2-}$ anions with distances, $d(\mathrm{Na^+{-}S^{2-}})$, of 253 and 262 pm (Table 3) which are shorter than common ionic sodium–sulfur distances (e.g., $\mathrm{Na_2S}$: $d(\mathrm{Na^+}$–

Table 1
Crystallographic data and their determination for $\mathrm{NaY_3S_3[SiS_4]}$

Formula	$\mathrm{NaY_3S_3[SiS_4]}$
Crystal system	Hexagonal
Space group	$P6_3$ (No. 173), $Z=2$
Lattice constants	$a = 976.57(7)$ pm $c = 570.61(5)$ pm
c/a ratio	0.584
Calculated density ($D_x/\mathrm{g\,cm^{-3}}$)	3.821
Molar volume ($V_m/\mathrm{cm^3\,mol^{-1}}$)	141.903
Diffractometer	κ-CCD (Nonius)
Wavelength	Mo$K\alpha$: $\lambda = 71.07$ pm
Index range	$\pm h = \pm k = 12$, $\pm l = 7$
2θ range	$2° \leqslant 2\theta \leqslant 55°$
Absorption coefficient ($\mu/\mathrm{mm^{-1}}$)	19.97
Data corrections	Numerical absorption correction by the program X-SHAPE [16]
Collected reflections (unique)	9634 (709)
$R_{\mathrm{int}}/R_\sigma$	0.069/0.026
Flack-x parameter	–0.01(1)
Structure solution and refinement	Program-package SHELX-97 [17]
Scattering factors	International Tables, Vol. C [18]
R_1/R_1 with $\lvert F_o\rvert \geqslant 4\sigma(F_o)$	0.035/0.033
wR_2/goodness of fit (GooF)	0.074/1.067
Extinction (g)	0.003(2)
Residual electron density ($\rho/e^- \times 10^{-6}\,\mathrm{pm^{-3}}$)	max.: 2.57, min.: –0.58

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-412445.

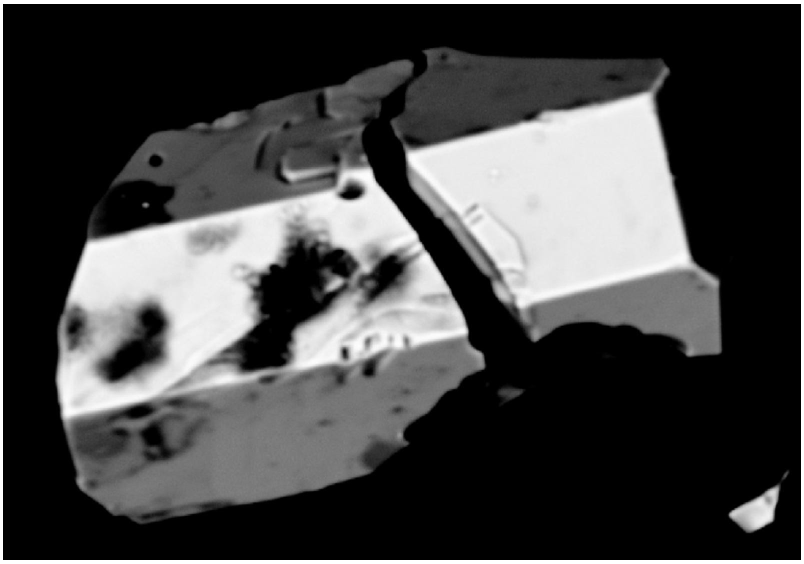

Fig. 1. Electron microscopic picture of a (broken) $\mathrm{NaY_3S_3[SiS_4]}$ single crystal emphasizing its hexagonal pillar shape.

Table 2
Atomic coordinates and anisotropic displacement parameters (U_{ij}/pm^2) for $NaY_3S_3[SiS_4]$

Atom	Wyckoff position	x/a	y/b	z/c
Na	2*a*	0	0	0.0510(7)
Y	6*c*	0.35846(7)	0.13271(7)	1/4[a]
Si	2*b*	1/3	2/3	0.1656(6)
S1	2*b*	1/3	2/3	0.5346(6)
S2	6*c*	0.5230(2)	0.4187(2)	0.5184(4)
S3	6*c*	0.2502(2)	0.0939(2)	0.7870(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	156(17)	$=U_{11}$	167(24)	0	0	$=1/2U_{11}$
Y	191(3)	163(3)	323(4)	–24(3)	–20(3)	96(2)
Si	149(9)	$=U_{11}$	167(14)	0	0	$=1/2U_{11}$
S1	183(9)	$=U_{11}$	136(13)	0	0	$=1/2U_{11}$
S2	141(7)	196(8)	183(7)	–4(7)	0(6)	102(6)
S3	217(7)	144(7)	278(9)	–1(6)	–70(7)	92(6)

[a] Arbitrarily fixed to define the origin.

Table 3
Motifs of mutual adjunction, selected interatomic distances (d/pm) and bond angles ($\sphericalangle$/deg) for $NaY_3S_3[SiS_4]$

	S1	S2	S3	CN
Na	0/0	0/0	6/2 252.7, 261.5	6
Y	1/3 291.7	3/3 278.6, 287.1, 296.8	4/4 271.9, 274.3, 280.0, 320.2	8
Si	1/1 210.6 –S2: 113.2	3/1 213.0 –S2: 105.5	0/0	4
CN	4	4	6	

S^{2-}) = 283 pm [19]). However, this bond length is not unusually small, as seen in ternary compounds like $NaFeS_2$ ($d(Na^+–S^{2-})$ = 257–258 pm [20]). These channel building $(S3)^{2-}$ anions also exhibit a coordination number of six, consisting of two sodium and four yttrium cations in the shape of a strongly distorted octahedron (Fig. 2, mid). The Y^{3+} cation has a slightly distorted square-antiprismatic environment of four silicon bonded S^{2-} anions and four "free" ones of the position S3. Two of the four silicon bonded sulfur atoms (S2 and S2′) work as part of the thiosilicate unit as edge-spanning ligands (Fig. 2, bottom). The internuclear distances between Y^{3+} and S^{2-} show values, $d(Y^{3+}–S^{2-})$, of 272–320 pm (Table 3) which compare very well with other compounds containing yttrium and sulfur (e.g., *D*-type Y_2S_3: $d(Y^{3+}–S^{2-})$ = 263–299 pm [21]). The isolated thiosilicate units $[SiS_4]^{4-}$ have exclusive contact

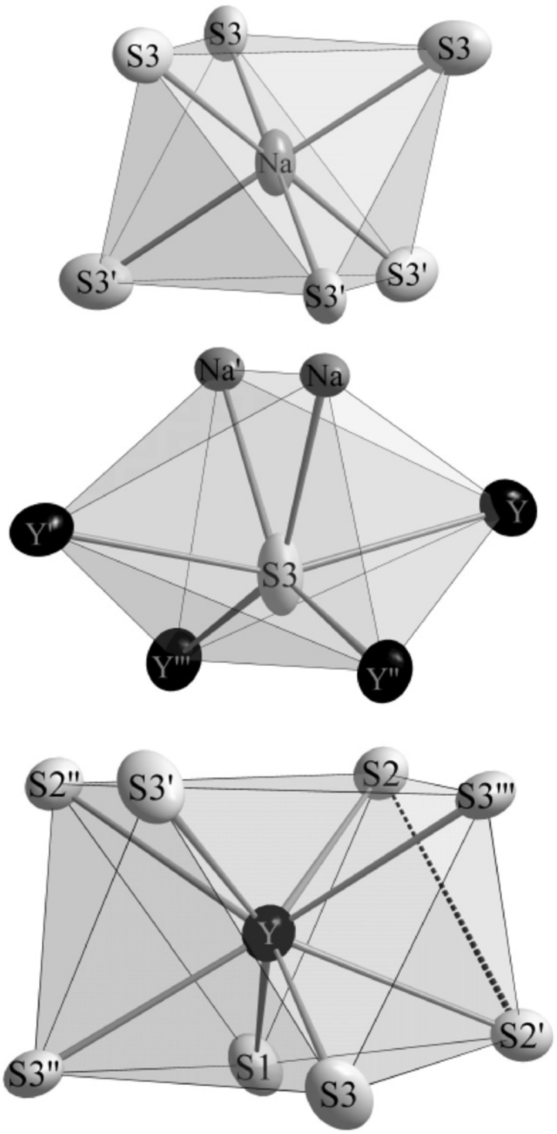

Fig. 2. Coordination environment about the Na^+ cations (top), the *non*-silicon bonded $(S3)^{2-}$ anions (mid) and the Y^{3+} cations (bottom) in $NaY_3S_3[SiS_4]$ (thermal ellipsoid representation with a probability factor of 95%).

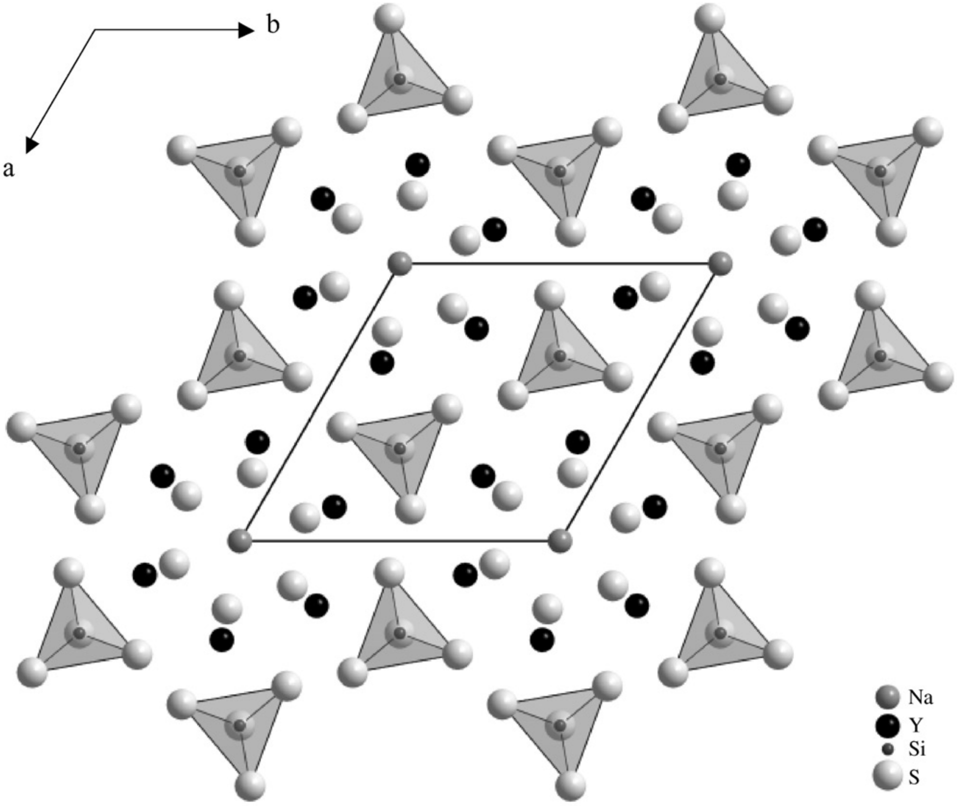

Fig. 3. View at the crystal structure of $NaY_3S_3[SiS_4]$ along the polar *c*-axis.

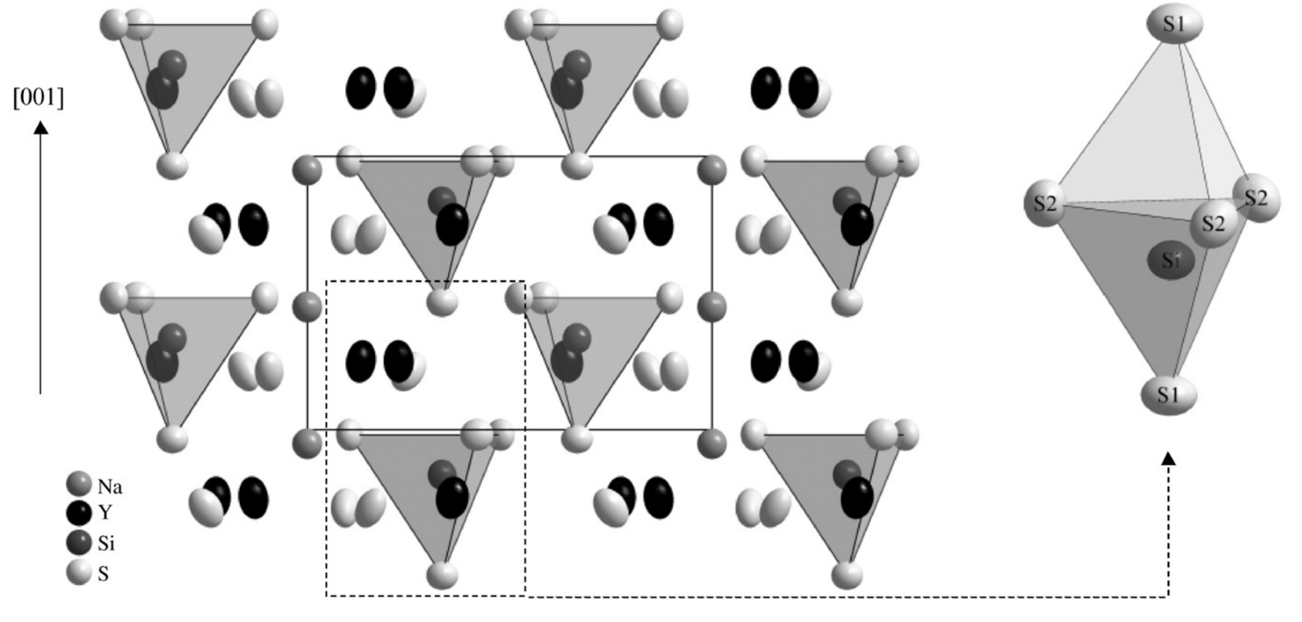

Fig. 4. View at the unit cell of $NaY_3S_3[SiS_4]$ perpendicular to [001] with special emphasis on the "trigonal bipyramidal" thiosilicate unit, in which only the lower partial tetrahedron is occupied with a Si^{4+} cation to form the discrete $[SiS_4]^{4-}$ anion.

to Y^{3+} cations as every S^{2-} interacts with three yttrium and one silicon but no sodium atom. These tetrahedral units are better considered as a trigonal pyramid with three sulfur atoms of the position S2 forming the base and one $(S1)^{2-}$ anion building the top. The basal sulfide anions are surrounded once terminal and twice edge-spanning by yttrium whereas the one at the top has contact to three terminal Y^{3+} ligands. The Si–S bond lengths in $NaY_3S_3[SiS_4]$ show values, $d(Si^{4+}–S^{2-})$, of 211 and 213 pm (Table 3) which are similar either to other thiosilicate compounds (e.g., $Ba_2[SiS_4]$: $d(Si^{4+}–S^{2-}) = 210$ and 213 pm [22]) or to SiS_2 itself ($d(Si^{4+}–S^{2-}) = 213$ pm [23]). The bond angles of the isolated $[SiS_4]^{4-}$ units ($\sphericalangle(S–Si–S) = 106°$ and 113°) are comparable to other thiosilicates as well (e.g., $Ba_2[SiS_4]$: $\sphericalangle(S–Si–S) = 105–116°$ [22]) or even SiS_2 ($\sphericalangle(S–Si–S) = 99–116°$ [23]) again.

A view on the crystal structure along the polar *c*-axis (Fig. 3) emphasizes the sodium cations situated in the channel at [001] built by the *non*-silicon bonded sulfide anions $(S3)^{2-}$ which are for their part surrounded by the Y^{3+} cations. This structural arrangement now leaves two other channels at the positions $[\frac{1}{3}, \frac{2}{3}, z]$ and $[\frac{2}{3}, \frac{1}{3}, z]$ which are occupied by the thiosilicate units such that all of these trigonal pyramids point in the same direction along [001]. The structure therefore proves to be non-centrosymmetric (space group $P6_3$) with a Flack-x parameter of –0.01(1) and no tendency of inversion twinning. Considering (pseudo-) hexagonally crystallizing oxosilicate derivatives of the rare-earth elements like $M_3Cl_5[SiO_4]$ [7,24] predominantly a centrosymmetric structure is found although the situation of the oxosilicate units is almost the same. It is possible to describe the "silicate situation" of the title compound as chains of apically vertex-shared trigonal bipyramids along [001] in which the Si^{4+} central cation always occupies strictly the same partial tetrahedron of the bipyramid (≡ face-shared bitetrahedron), enabling the structure to remain non-centrosymmetric. Whereas oxosilicates very often show statistically mixed occupation of the upper and the lower partial tetrahedron so the structure can be solved properly as centrosymmetric by X-ray diffraction ($\lambda \approx 70$ pm). In the case of $NaY_3S_3[SiS_4]$ the silicon atom occupies exclusively the lower part of the "trigonal bipyramid" with no tendency to switch between the two possible central positions of the tetrahedra seen by looking at the well-balanced thermal ellipsoids for silicon (Fig. 4 and Table 2). It is obviously impossible for the Si^{4+} central cation to switch between the centers of the two partial thiosilicate tetrahedra because here it has to travel almost the triple way compared to the oxosilicates ($NaY_3S_3[SiS_4]$ $d(Si–Si') = 153$ pm vs $Pr_3Cl_5[SiO_4]$ $d(Si–Si') = 58$ pm [7]). This is supposed to be such a strong restraint that it might not be possible to transform the structure $NaY_3S_3[SiS_4]$ into a centrosymmetric form by a thermal-induced phase transition by so-called "rattling".

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