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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{S}-\text{Si}) = 0.001\text{ \AA}$
 R factor = 0.019
 wR factor = 0.040
Data-to-parameter ratio = 25.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Lanthanum iodide thiosilicate, $\text{La}_3\text{I}[\text{SiS}_4]_2$

The title compound displays isolated $[\text{SiS}_4]^{4-}$ tetrahedra and a chain of I atoms along $[001]$. Iodine, which lies on a twofold axis, is coordinated by three lanthanum cations, one of which lies on the same twofold axis, forming an isosceles triangle. The compound is isotypic with $\text{Ce}_3\text{I}[\text{SiS}_4]_2$ [Gauthier *et al.* (1998). *J. Alloys Compd.*, **275–277**, 46–49].

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Comment

The cerium iodide thiosilicate $\text{Ce}_3\text{I}[\text{SiS}_4]_2$ (Gauthier *et al.*, 1998) was the first compound in a large series of thio-analogs of the *A*-type lanthanide chloride oxosilicates $\text{Ln}_3\text{Cl}[\text{SiO}_4]_2$, first discovered by Gravereau *et al.* (1988).

In the case of the lanthanide halide thiosilicates, up to now the stability of this structure type has been verified for the iodides from cerium to terbium (exceptions being Pm, Eu and Gd), for the bromides from lanthanum to europium (exception Pm), and for the chlorides from lanthanum to praseodymium (Hatscher & Urland, 2001, 2002*a,b*). Riccardi *et al.* (1999) succeeded in synthesizing powder samples of the compound $\text{La}_3\text{I}[\text{SiS}_4]_2$; we present here its first single-crystal structure determination.

Lanthanum iodide thiosilicate crystallizes in the monoclinic space group $C2/c$. A view of the structure is given in Fig. 1. A main feature is the tunnel along c , in which a chain of iodide ions can be found. The surrounding network is composed of lanthanum, silicon and sulfur.

Two crystallographically different La atoms are found in the compound. Both are coordinated by eight sulfide ions and one iodide ion, forming a strongly distorted tricapped trigonal prism. The La–S distances lie between 2.9328 (10) and 3.2988 (11) Å. Although this range is rather large, the mean value of about 3.08 Å is close to that reported for ortho-

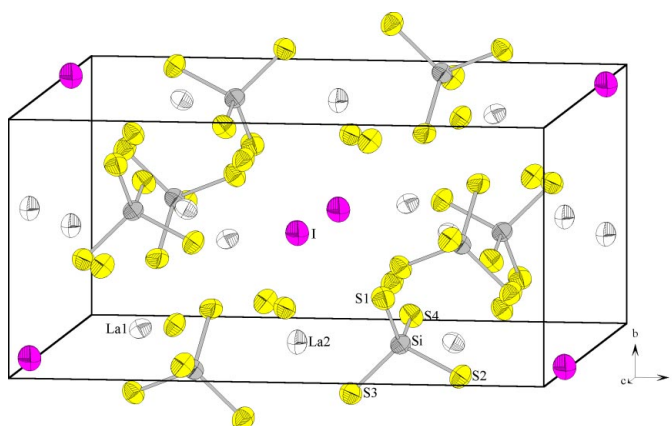


Figure 1
View of the crystal structure of $\text{La}_3\text{I}[\text{SiS}_4]_2$, approximately along the c axis. Displacement ellipsoids are shown at the 99% probability level.

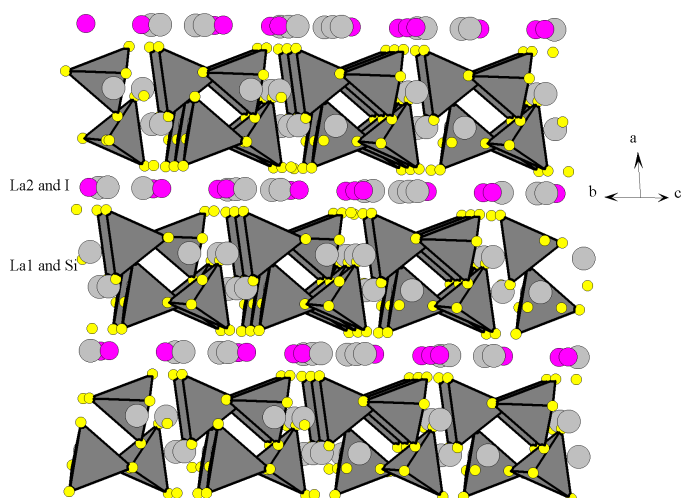


Figure 2
View of the crystal structure of $\text{La}_3\text{I}[\text{SiS}_4]_2$ from a direction in the bc plane. The $[\text{SiS}_4]^{4-}$ tetrahedra are colored grey.

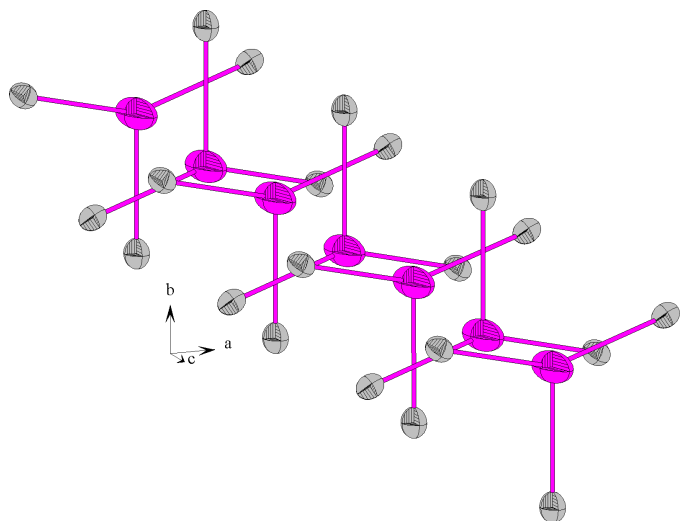


Figure 3
The chain of iodide ions with surrounding lanthanum ions. Displacement ellipsoids are shown at the 99% probability level.

rhombic La_2S_3 (Basacon *et al.*, 1969), of about 3.01 Å. The La—I distances are 3.3335 (7) and 3.4571 (7) Å (two instances). In $\text{La}_2\text{I}_2[\text{SiO}_4]$ (Beck *et al.*, 1993), the La—I distances range from 3.288 to 3.470 Å.

The Si atom is connected to four sulfide ions, resulting in a nearly perfect tetrahedron. The Si—S distances range from 2.1048 (14) to 2.1322 (13) Å. Similar distances in SiS_4 building blocks can be found in other lanthanide thiosilicates, *e.g.* $\text{Tb}_4[\text{SiS}_4]_3$ (Hatscher & Urland, 2002c) and $\text{Dy}_4[\text{SiS}_4]_3$ (Hatscher & Urland, 2002d). A typical feature also observed in these compounds is the isolated SiS_4 building block in the structure. As can be seen in Fig. 2, the $[\text{SiS}_4]^{4-}$ tetrahedra form, together with the LaS_8 polyhedra for La1, a layered structure in the bc plane. The spaces between the layers are filled with La2 and iodide ions.

The iodide ion is coordinated by two La1 and one La2 ion, forming an isosceles triangle. As the bonding of the halide ions

is rather weak in the [001] direction, an increased displacement parameter, U^{33} , results, as shown in Fig. 3. Two successive iodide ions are separated by 5.471 (1) Å.

A more detailed description of the structure type is given in the literature (Hatscher & Urland, 2002b).

Experimental

Single crystals of the title compound were prepared from the elements. Lanthanum metal chips (Heraeus, 99.9%), sulfur powder (Aldrich, 99.98%), silicon powder (Merck, >99%), and iodine (Heraeus, >99.999%) were loaded into a quartz glass tube in a ratio of 1:3.3:1.03:0.4. The ampoule was evacuated, sealed, and heated for 10 d in a temperature gradient of 1273 to 1073 K. After cooling, the molten reaction mixture was finely ground, and once more sealed in an evacuated quartz glass tube with some iodine (molar ratio about 0.15). The ampoule was placed in a furnace following the temperature program described above. This procedure had to be repeated a second time to obtain air-stable white crystals of $\text{La}_3[\text{SiS}_4]_2$ of high quality.

Crystal data

$\text{La}_3\text{I}(\text{SiS}_4)_2$
 $M_r = 856.29$
Monoclinic, $C2/c$
 $a = 16.110$ (3) Å
 $b = 7.9175$ (12) Å
 $c = 10.931$ (2) Å
 $\beta = 97.94$ (2)°
 $V = 1380.9$ (4) Å³
 $Z = 4$

$D_x = 4.119$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 11586 reflections

$\theta = 2.6$ – 28.1°

$\mu = 12.69$ mm⁻¹

$T = 293$ (2) K

Tablet, white

$0.20 \times 0.13 \times 0.09$ mm

Data collection

Stoe IPDS diffractometer

φ scans

Absorption correction: Gaussian

(*X-RED*; Stoe & Cie, 1998)

$T_{\min} = 0.120$, $T_{\max} = 0.256$

11586 measured reflections

1671 independent reflections

1467 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 28.1^\circ$

$h = -21 \rightarrow 21$

$k = -10 \rightarrow 10$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.040$

$S = 0.95$

1671 reflections

66 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.89$ e Å⁻³

$\Delta\rho_{\min} = -1.22$ e Å⁻³

Extinction correction: *SHELXL97*

Extinction coefficient: 0.00359 (8)

Table 1

Selected geometric parameters (Å).

La1—S2 ⁱ	2.9467 (10)	La2—S4 ^{iv}	2.9328 (10)
La1—S4 ⁱⁱⁱ	2.9828 (10)	La2—S1 ⁱ	2.9747 (10)
La1—S3 ⁱⁱⁱ	2.9885 (11)	La2—S3 ^{viii}	3.2640 (12)
La1—S2 ^{iv}	3.0006 (11)	La2—S3 ^{viii}	3.2988 (11)
La1—S4 ^{iv}	3.0580 (10)	La2—I ^{ix}	3.3335 (7)
La1—S2 ⁱⁱⁱ	3.0614 (10)	Si—S1	2.1048 (14)
La1—S1 ^v	3.1009 (10)	Si—S4	2.1070 (14)
La1—S1 ⁱ	3.1213 (12)	Si—S3	2.1189 (14)
La1—I ^{vi}	3.4571 (7)	Si—S2	2.1322 (13)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $x, y, 1 + z$; (iii) $x, 1 - y, \frac{1}{2} + z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (v) $x, -y, \frac{1}{2} + z$; (vi) $-x, 1 - y, 1 - z$; (vii) $\frac{1}{2} + x, y - \frac{1}{2}, 1 + z$; (viii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ix) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$.

Data collection: *IPDS Software* (Stoe & Cie, 1998); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s)

used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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