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La_2SiS_5

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Key indicators: single-crystal X-ray study; T = 293 K; mean σ(S–Si) = 0.002 Å; R factor = 0.023; wR factor = 0.040; data-to-parameter ratio = 24.9.

The lattice parameters and space group for dicerium pentathiosilicate, La_2SiS_5, have been reported previously [Michelet, Perez, Etienne & Darriet-Duale (1970.) *C. R. Seances Acad. Sci. Ser. C* **271**, 513–515]. Moreover, isotypism with the La_2GeS_5 structure (space group $P2_1/c$) has been assigned, but a structure refinement was not performed. The present single-crystal study reveals that the two independent La atoms are surrounded by 8 and 9 S atoms, forming bi- and tricapped trigonal prisms, respectively, whereas the Si atom has a slightly distorted tetrahedral coordination. The capped trigonal prisms are linked to tetrahedra *via* corners and edges; they are also connected to each other by sharing faces.

Related literature

For a previous study of the title compound, see: Michelet *et al.* (1970).

Experimental

Crystal data

La_2SiS_5
M_r = 466.21
Monoclinic, $P2_1/c$
a = 7.6208 (12) Å
b = 12.6407 (15) Å
c = 7.8998 (12) Å
β = 101.559 (13)°
V = 745.57 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 12.75 mm^{-1}
T = 293 (2) K
0.13 × 0.09 × 0.06 mm

Data collection

Kuma KM-4 diffractometer with CCD area-detector
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.208, T_{max} = 0.567
9434 measured reflections
1818 independent reflections
1465 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.040
S = 0.97
1818 reflections
73 parameters
$\Delta\rho_{max}$ = 0.97 e Å^{-3}
$\Delta\rho_{min}$ = −1.22 e Å^{-3}

Table 1
Selected bond lengths (Å).

La1—S1	3.1154 (13)	La2—S3^{vii}	2.9767 (13)
La1—S2^{i}	2.9213 (13)	La2—S4^{vi}	3.0850 (13)
La1—S2^{ii}	2.9767 (13)	La2—S4	3.1453 (12)
La1—S3^{iii}	2.8456 (12)	La2—S5^{vi}	3.1040 (13)
La1—S3	2.8635 (13)	La2—S5^{vii}	3.2936 (13)
La1—S4^{iv}	2.9670 (13)	La2—S1^{viii}	3.3745 (13)
La1—S5	3.0184 (13)	Si—S1	2.1015 (18)
La1—S5^{ii}	3.0420 (13)	Si—S2	2.0980 (17)
La2—S1^{v}	3.1226 (14)	Si—S4	2.1249 (18)
La2—S2	2.9350 (13)	Si—S5	2.1522 (19)
La2—S3^{vi}	2.8991 (12)		

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *publCIF* (Westrip, 2007).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2163).

References

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supplementary materials

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La_2SiS_5

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Comment

The formation of the ternary compound La_2SiS_5 has been reported previously (Michelet *et al.*, 1970), but only lattice parameters were determined and isotypism with the La_2GeS_5 structure was established during the original study. The crystal structure of La_2SiS_5 has now been investigated by means of single-crystal X-ray diffraction data and is presented in this communication.

The unit cell and coordination polyhedra of the La and Si atoms are shown in Fig. 1. Six S atoms surround both independent La atoms leading to a distorted trigonal-prismatic arrangement. For La1, two additional S atoms and for La2 three additional S augment these basic polyhedra to bi- and tri-capped trigonal prisms, respectively. The Si atom has a slightly distorted tetrahedral environment of S atoms. The capped trigonal prisms are linked to the [SiS_4] tetrahedra by corners and edges, whereas the capped trigonal prisms are connected to each other also by sharing faces.

Experimental

Single crystals of the title compound were grown by fusion of the elemental constituents (Alfa Aesar; purity > 99.9%$_{wt}$) in the stoichiometric ratio of La:Si:*S* = 2:1:5 in an evacuated silica ampoule. The ampoule was heated in a tube furnace with a heating rate of 30 K/h to 1420 K and was kept at this temperature for 4 h. It was then cooled down slowly (10 K/h) to 770 K and annealed at this temperature for further 240 h and finally quenched in cold water. The obtained yellow crystals were selected from the brown-coloured compact product. The crystals had a prismatic habit and maximal lengths of 0.2 mm.

Refinement

The highest peak is located 2.19 Å away from Si and the deepest hole 0.02 Å away from La2.

Figures

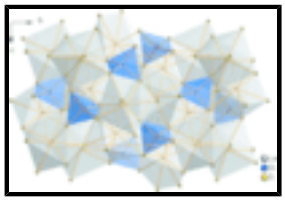

Fig. 1. The structure of La_2SiS_5 viewed along the *a* axis. Displacement ellipsoids are shown at the 50% probability level.

dicerium pentathiosilicate

Crystal data

La_2SiS_5 $F_{000} = 832$

M_r = 466.21	D_x = 4.153 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 1465 reflections
a = 7.6208 (12) Å	θ = 3.1–28.3°
b = 12.6407 (15) Å	μ = 12.75 mm^{-1}
c = 7.8998 (12) Å	T = 293 (2) K
β = 101.559 (13)°	Prism, yellow
V = 745.57 (19) Å^3	0.13 × 0.09 × 0.06 mm
Z = 4	

Data collection

KUMA KM-4 with CCD area-detector diffractometer	1818 independent reflections
Radiation source: fine-focus sealed tube	1465 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.052
Detector resolution: 1024x1024 with blocks 2x2, 33.133pixel/mm pixels mm^{-1}	θ_{max} = 28.3°
T = 293(2) K	θ_{min} = 3.1°
ω–scan	h = −10→9
Absorption correction: numerical (CrysAlis-RED; Oxford Diffraction, 2006)	k = −15→16
T_{min} = 0.208, T_{max} = 0.567	l = −9→10
9434 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.023	$w = 1/[\sigma^2(F_o^2) + (0.0134P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.040	$(\Delta/\sigma)_{max}$ = 0.001
S = 0.97	$\Delta\rho_{max}$ = 0.97 e Å^{-3}
1818 reflections	$\Delta\rho_{min}$ = −1.22 e Å^{-3}
73 parameters	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculat-

ing *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
La1	0.74054 (4)	0.09529 (2)	0.04559 (3)	0.00735 (8)
La2	0.66488 (4)	0.66522 (2)	0.13363 (4)	0.00926 (8)
Si	0.83032 (18)	0.38347 (10)	0.09619 (16)	0.0080 (3)
S1	1.02312 (17)	0.27396 (9)	0.05064 (15)	0.0111 (3)
S2	0.92134 (17)	0.50034 (9)	0.28160 (15)	0.0092 (3)
S3	0.36080 (16)	0.12101 (9)	0.00203 (15)	0.0085 (3)
S4	0.67558 (17)	0.47033 (9)	−0.11162 (15)	0.0103 (3)
S5	0.62829 (17)	0.29811 (9)	0.19537 (15)	0.0100 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.00743 (15)	0.00657 (14)	0.00813 (14)	0.00046 (11)	0.00170 (11)	0.00066 (11)
La2	0.00955 (16)	0.00836 (15)	0.00978 (14)	0.00071 (12)	0.00175 (12)	0.00164 (11)
Si	0.0087 (7)	0.0075 (7)	0.0078 (6)	−0.0011 (5)	0.0019 (5)	−0.0009 (5)
S1	0.0101 (7)	0.0090 (6)	0.0154 (6)	−0.0001 (5)	0.0056 (5)	−0.0010 (5)
S2	0.0098 (7)	0.0081 (6)	0.0094 (6)	−0.0015 (5)	0.0011 (5)	−0.0023 (5)
S3	0.0071 (6)	0.0074 (6)	0.0110 (6)	0.0005 (5)	0.0021 (5)	−0.0007 (5)
S4	0.0119 (7)	0.0107 (6)	0.0078 (6)	0.0013 (5)	0.0012 (5)	−0.0003 (5)
S5	0.0111 (7)	0.0084 (6)	0.0109 (6)	−0.0025 (5)	0.0029 (5)	−0.0009 (5)

Geometric parameters (Å, °)

La1—S1	3.1154 (13)	Si—S1	2.1015 (18)
La1—S2^{i}	2.9213 (13)	Si—S2	2.0980 (17)
La1—S2^{ii}	2.9767 (13)	Si—S4	2.1249 (18)
La1—S3^{iii}	2.8456 (12)	Si—S5	2.1522 (19)
La1—S3	2.8635 (13)	S1—La2^{v}	3.1226 (13)
La1—S4^{iv}	2.9670 (13)	S1—La2^{i}	3.3745 (13)
La1—S5	3.0184 (13)	S2—La1^{viii}	2.9213 (13)
La1—S5^{ii}	3.0420 (13)	S2—La1^{iv}	2.9767 (13)
La2—S1^{v}	3.1226 (14)	S3—La1^{iii}	2.8456 (12)
La2—S2	2.9350 (13)	S3—La2^{vi}	2.8991 (12)
La2—S3^{vi}	2.8991 (12)	S3—La2^{ix}	2.9767 (13)
La2—S3^{vii}	2.9767 (13)	S4—La1^{ii}	2.9670 (13)
La2—S4^{vi}	3.0850 (13)	S4—La2^{vi}	3.0850 (13)
La2—S4	3.1453 (12)	S5—La1^{iv}	3.0420 (13)
La2—S5^{vi}	3.1040 (13)	S5—La2^{vi}	3.1040 (13)
La2—S5^{vii}	3.2936 (13)	S5—La2^{ix}	3.2936 (13)

La2—S1^{viii}	3.3745 (13)		
S3^{iii}—La1—S3	81.50 (4)	S4^{vi}—La2—S5^{vii}	71.00 (3)
S3^{iii}—La1—S2^{i}	81.81 (3)	S5^{vi}—La2—S5^{vii}	80.42 (3)
S3—La1—S2^{i}	151.44 (4)	S1^{v}—La2—S5^{vii}	135.08 (3)
S3^{iii}—La1—S4^{iv}	76.21 (3)	S4—La2—S5^{vii}	139.07 (3)
S3—La1—S4^{iv}	77.99 (4)	S3^{vi}—La2—S1^{viii}	83.05 (3)
S2^{i}—La1—S4^{iv}	75.61 (4)	S2—La2—S1^{viii}	71.37 (3)
S3^{iii}—La1—S2^{ii}	70.65 (3)	S3^{vii}—La2—S1^{viii}	62.28 (3)
S3—La1—S2^{ii}	124.09 (4)	S4^{vi}—La2—S1^{viii}	136.72 (3)
S2^{i}—La1—S2^{ii}	70.84 (4)	S5^{vi}—La2—S1^{viii}	147.19 (3)
S4^{iv}—La1—S2^{ii}	135.33 (3)	S1^{v}—La2—S1^{viii}	75.80 (3)
S3^{iii}—La1—S5	141.01 (4)	S4—La2—S1^{viii}	132.30 (3)
S3—La1—S5	65.90 (3)	S5^{vii}—La2—S1^{viii}	85.67 (3)
S2^{i}—La1—S5	117.29 (3)	S2—Si—S1	116.02 (8)
S4^{iv}—La1—S5	76.55 (3)	S2—Si—S4	103.31 (7)
S2^{ii}—La1—S5	145.78 (3)	S1—Si—S4	120.45 (8)
S3^{iii}—La1—S5^{ii}	106.62 (3)	S2—Si—S5	105.04 (7)
S3—La1—S5^{ii}	75.35 (4)	S1—Si—S5	107.93 (7)
S2^{i}—La1—S5^{ii}	131.91 (4)	S4—Si—S5	102.33 (8)
S4^{iv}—La1—S5^{ii}	152.37 (4)	Si—S1—La1	88.54 (6)
S2^{ii}—La1—S5^{ii}	68.16 (3)	Si—S1—La2^{v}	122.78 (6)
S5—La1—S5^{ii}	85.99 (2)	La1—S1—La2^{v}	139.60 (4)
S3^{iii}—La1—S1	150.10 (3)	Si—S1—La2^{i}	123.71 (6)
S3—La1—S1	126.77 (3)	La1—S1—La2^{i}	95.57 (3)
S2^{i}—La1—S1	75.47 (3)	La2^{v}—S1—La2^{i}	87.44 (3)
S4^{iv}—La1—S1	115.61 (3)	Si—S2—La1^{viii}	138.84 (7)
S2^{ii}—La1—S1	83.54 (3)	Si—S2—La2	96.97 (6)
S5—La1—S1	68.20 (3)	La1^{viii}—S2—La2	110.42 (4)
S5^{ii}—La1—S1	76.01 (3)	Si—S2—La1^{iv}	93.92 (6)
S3^{vi}—La2—S2	143.07 (4)	La1^{viii}—S2—La1^{iv}	109.16 (4)
S3^{vi}—La2—S3^{vii}	121.32 (3)	La2—S2—La1^{iv}	101.69 (4)
S2—La2—S3^{vii}	69.46 (3)	La1^{iii}—S3—La1	98.50 (4)
S3^{vi}—La2—S4^{vi}	120.21 (3)	La1^{iii}—S3—La2^{vi}	148.24 (5)
S2—La2—S4^{vi}	96.52 (3)	La1—S3—La2^{vi}	98.16 (4)
S3^{vii}—La2—S4^{vi}	74.50 (3)	La1^{iii}—S3—La2^{ix}	103.86 (4)
S3^{vi}—La2—S5^{vi}	64.36 (3)	La1—S3—La2^{ix}	99.54 (4)
S2—La2—S5^{vi}	138.56 (3)	La2^{vi}—S3—La2^{ix}	99.78 (3)
S3^{vii}—La2—S5^{vi}	131.45 (4)	Si—S4—La1^{ii}	113.10 (6)
S4^{vi}—La2—S5^{vi}	65.14 (3)	Si—S4—La2^{vi}	94.98 (6)
S3^{vi}—La2—S1^{v}	66.39 (3)	La1^{ii}—S4—La2^{vi}	94.91 (3)

S2—La2—S1^{v}	81.49 (3)	Si—S4—La2	90.44 (5)
S3^{vii}—La2—S1^{v}	134.48 (3)	La1^{ii}—S4—La2	144.17 (4)
S4^{vi}—La2—S1^{v}	145.17 (3)	La2^{vi}—S4—La2	110.15 (4)
S5^{vi}—La2—S1^{v}	93.47 (4)	Si—S5—La1	90.20 (6)
S3^{vi}—La2—S4	120.70 (3)	Si—S5—La1^{iv}	91.02 (5)
S2—La2—S4	65.91 (3)	La1—S5—La1^{iv}	133.05 (4)
S3^{vii}—La2—S4	117.61 (3)	Si—S5—La2^{vi}	93.88 (5)
S4^{vi}—La2—S4	69.85 (4)	La1—S5—La2^{vi}	90.66 (3)
S5^{vi}—La2—S4	72.80 (3)	La1^{iv}—S5—La2^{vi}	136.01 (4)
S1^{v}—La2—S4	77.85 (3)	Si—S5—La2^{ix}	176.92 (6)
S3^{vi}—La2—S5^{vii}	71.04 (3)	La1—S5—La2^{ix}	89.79 (3)
S2—La2—S5^{vii}	130.63 (3)	La1^{iv}—S5—La2^{ix}	86.74 (3)
S3^{vii}—La2—S5^{vii}	61.17 (3)	La2^{vi}—S5—La2^{ix}	89.20 (3)

Symmetry codes: (i) −*x*+2, *y*−1/2, −*z*+1/2; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) −*x*+1, −*y*, −*z*; (iv) *x*, −*y*+1/2, *z*+1/2; (v) −*x*+2, −*y*+1, −*z*; (vi) −*x*+1, −*y*+1, −*z*; (vii) −*x*+1, *y*+1/2, −*z*+1/2; (viii) −*x*+2, *y*+1/2, −*z*+1/2; (ix) −*x*+1, *y*−1/2, −*z*+1/2.

Fig. 1