

A new lanthanum titanium oxysulfide, $\text{La}_{16}\text{Ti}_5\text{S}_{17+x}\text{O}_{17}$, with $x = 0.75$ (9)

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The title compound, hexadecalanthanum pentatitanium heptadecasulfide heptadeca-oxide, $\text{La}_{16}\text{Ti}_5\text{S}_{17+x}\text{O}_{17}$ [$x = 0.75$ (9)], has been obtained as a by-product in the preparation of new oxychalcogenide compounds in the La/Ti/Ag/S/O system. $\text{La}_{16}\text{Ti}_5\text{S}_{17+x}\text{O}_{17}$ crystallizes in the tetragonal system (space group $I4/m$) and is isostructural with $\text{Nd}_{16}\text{Ti}_5\text{S}_{17}\text{O}_{17}$. The structure of the title compound consists of an $[\text{La}_2\text{S}_2]$ rock-salt-type framework, which delimits $[001]$ square channels containing two types of chains of corner-sharing $\text{Ti}(\text{O,S})_6$ octahedra. These chains are connected through $\text{La}(\text{O,S})_n$ polyhedra.

Comment

Recent investigations into the chemistry of oxychalcogenides, and particularly quaternary systems of the type $M/T/X/O$ (M is a rare earth metal, T is a transition metal, and $X = \text{S}$ and Se), show that M and T atoms always bond preferentially to a particular anion (O or X), thus leading to segregated oxide or chalcogenide building blocks in the structure. For instance, such a segregation occurs in the structures of the $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ compounds ($\text{Ln} = \text{Pr}–\text{Er}$; Boyer *et al.*, 1999; Goga *et al.*, 1999). In these compounds, a sulfide slab of composition $[\text{Ln}_2\text{S}_2]$ is separated by an oxide slab built from the corner-sharing O atoms of two adjacent layers of Ti octahedra.

The present structural study of $\text{La}_{16}\text{Ti}_5\text{S}_{17+x}\text{O}_{17}$ shows that the structure can be described on the basis of an $[\text{La}_2\text{S}_2]$ framework that delimits channels of squared sections. These channels contain chains of corner-sharing $\text{Ti}(\text{O,S})_6$ octahedra (four Ti1 chains for one Ti2 chain) parallel to the c direction, which are connected by La4 polyhedra (Fig. 1). Note that a similar $[\text{La}_2\text{S}_2]$ framework (with a rock-salt-type structure) was encountered in the two-dimensional misfit layered chalcogenides (Wiegiers & Meerschaut, 1992), as well as in oxychalcogenides (Gardberg & Ibers, 2001; Meignen *et al.*, 2001).

The title compound is isostructural with $\text{Nd}_{16}\text{Ti}_5\text{S}_{17}\text{O}_{17}$ (Boyer-Candalen *et al.*, 2000). The $[\text{La}_2\text{S}_2]$ framework consists of two-atom-thick layers with La atoms (La1 , La2 and La3)

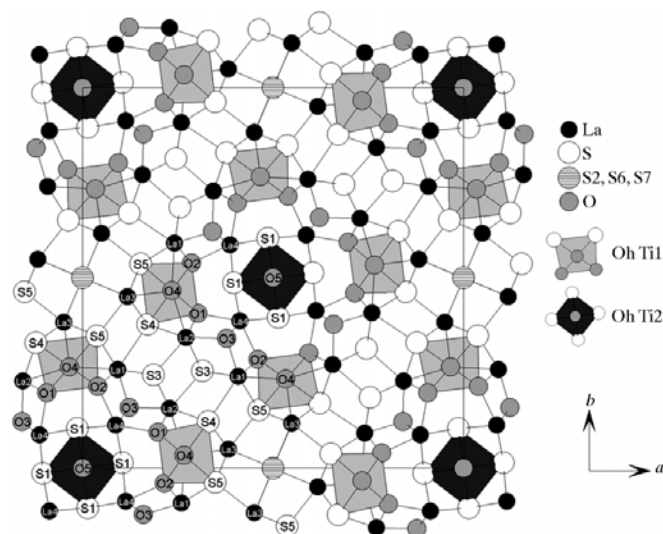


Figure 1

The structure of $\text{La}_{16}\text{Ti}_5\text{S}_{17+x}\text{O}_{17}$, projected on to the ab plane.

protruding from the plane of S atoms. This structure arises because these La atoms are also bonded to O atoms belonging to the Ti octahedra. A complex atomic arrangement is observed at the intersection of two adjacent $[\text{La}_2\text{S}_2]$ building blocks. This atomic junction involves La3 polyhedra that are connected by S5 atoms, and this 'knot' of four La3 polyhedra encloses a channel filled with S atoms. The La derivative differs from the Nd homologue in that, in the former, a third S -atom site (S7) is found in this channel. The higher S -atom content in the channel results in a slightly modified chemical composition, *viz.* $\text{La}_{16}\text{Ti}_5\text{S}_{17+x}\text{O}_{17}$ [$x = 0.75$ (9)]. This difference led us to consider the existence of an $(\text{S}_2)^{2-}$ pairing, which would be required for charge balance. Not all combinations of atoms S2 , S6 and S7 give a pair with a reasonable $\text{S}–\text{S}$ bond distance, and the most probable pairing is between two S2 atoms (~ 2.10 Å). Similar $(\text{S}_2)^{2-}$ dianions were also encountered in $\text{Sr}_6\text{V}_9\text{S}_{22}\text{O}_2$ (Litteer *et al.*, 2000). Another difference between the Nd and La analogues concerns the splitting of the Ti2 -atom position. A high U_{eq} value for atom Ti2 was also obtained in the case of the Nd compound (although not as high as that for the present La compound), but the splitting of this position was not considered for the Nd compound. Finally, note that the high U_{eq} value for atom O5 could also be related to the splitting of the Ti2 -atom site. The resulting $\text{Ti2}–\text{O5}$ distances range from 1.769 (3) to 2.256 (3) Å (Table 1). A comparable short $\text{Ti}–\text{O}$ distance of 1.768 Å was encountered in $\text{La}_2\text{Ti}_2\text{O}_7$ (Gasparin, 1975).

Experimental

The title compound was obtained as a small number of needle-shaped translucent orange single crystals, as a by-product of a solid-state reaction of a mixture of La_2O_3 , La_2S_3 , TiO_2 and Ag_2O in the molar ratio 1:1.5:2:0.5. The reaction was carried out at 1273 K for 160 h in a quartz ampoule sealed *in vacuo*. After initial heating, the product of the reaction was reground and a small amount of iodine was added to favor crystallization during a second heating.

Crystal data

La₁₆Ti₅S_{17.75}O₁₇
M_r = 3303.0
 Tetragonal, *I4/m*
a = 22.633 (3) Å
c = 4.0252 (8) Å
V = 2061.9 (6) Å³
Z = 2
D_x = 5.28 Mg m⁻³
 Mo *K*α radiation

Cell parameters from 21 662 reflections
 $\theta = 3.6\text{--}34.9^\circ$
 $\mu = 17.97\text{ mm}^{-1}$
T = 293 K
 Needle, orange
 0.12 × 0.02 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: Gaussian
 (Petricek & Dusek, 2000)
T_{min} = 0.332, *T_{max}* = 0.727
 4503 measured reflections
 2028 independent reflections

1799 reflections with *I* > 2σ(*I*)
R_{int} = 0.027
 $\theta_{\text{max}} = 32.2^\circ$
h = −33 → 33
k = −24 → 25
l = −6 → 6

Refinement

Refinement on *F*
R = 0.023
wR = 0.1032
S = 1.11
 2028 reflections
 95 parameters
w = 1/(σ²*F* + 0.0004*F*²)

(Δ/σ)_{max} = 0.004
 Δρ_{max} = 1.64 e Å⁻³
 Δρ_{min} = −1.55 e Å⁻³
 Extinction correction: B–C type 1
 Gaussian isotropic (Becker & Coppens, 1974)
 Extinction coefficient: 0.017 (4)

During the refinement, the last positions to be found were those of atoms S2, S6 and S7. The largest residual peak in the difference Fourier map at (0, $\frac{1}{2}$, $\frac{1}{4}$) (4*d* site) was introduced and refined (S2-atom position). Because the resulting displacement parameter of atom S2 was large and the contact between equivalent S2-atom positions (*c*/2 = 2.013 Å) was shorter than the minimum distance for an (S₂)²⁻ pairing (>2.05 Å), the site-occupancy factor for atom S2 was halved. Later, the adoption of a more general position for atom S2 [8*g* site at (0, $\frac{1}{2}$, *z*), with *z* ≈ 0.20] very slightly improved the refinement. A subsequent Fourier difference calculation revealed two further residual peaks at (0, $\frac{1}{2}$, 0) and (0.461, 0.043, 0), which were introduced as atoms S6 and S7, respectively. A constraint was initially imposed on the sum of the occupancy factors (S2 + S6 + S7 = half the occupancy of the 4*d* site) for a total of two S atoms without formation of an (S₂)²⁻ pairing. In addition, the displacement parameters for atoms S2, S6 and S7 were constrained to be identical. However, the refinement at this stage led to a negative *U_{iso}* value for these sites (−0.006 Å²). When the constraint on the occupancies was removed, the refinement was improved and yielded a positive *U_{iso}* value [0.027 (3) Å²]. Initially, atom Ti2 in the 2*b* site, at ($\frac{1}{2}$, $\frac{1}{2}$, 0), showed a large value of the *U₃₃* component, which led us to adopt a more general 4*e* site [($\frac{1}{2}$, $\frac{1}{2}$, *z*), with *z* ≈ 0], with a statistical occupancy of 50%. Under these conditions, the final refinement converged to an *R* value of 0.023 and yielded a featureless Fourier difference map [1.64 e Å⁻³ at (0.405, 0.241, 0.245) and −1.55 e Å⁻³ at ($\frac{1}{2}$, $\frac{1}{2}$, 0.377)].

Table 1

Selected bond lengths (Å).

La1—S3 ⁱ	2.9495 (9)	La3—O4	2.656 (4)
La1—S4 ⁱⁱ	3.2170 (14)	La3—S7 ^{ix}	2.695 (7)
La1—S5 ⁱⁱⁱ	3.0971 (10)	La3—S7 ^x	2.567 (10)
La1—O2	2.554 (2)	La4—S1	3.0455 (9)
La1—O3	2.366 (4)	La4—S1 ^x	3.0480 (9)
La1—O4	2.849 (4)	La4—O1 ^v	2.541 (4)
La2—S3	2.9444 (13)	La4—O2	2.527 (4)
La2—S3 ⁱ	2.9907 (10)	La4—O3	2.401 (2)
La2—S4 ^{iv}	3.1420 (11)	La4—O5	3.2318 (7)
La2—O1 ^{iv}	2.562 (2)	Ti1—S4	2.7122 (16)
La2—O3	2.407 (4)	Ti1—S5	2.7406 (16)
La2—O4 ^v	2.915 (4)	Ti1—O1	1.805 (4)
La3—S2 ^{vi}	3.07 (3)	Ti1—O2	1.824 (4)
La3—S2 ^{vii}	3.04 (3)	Ti1—O4	2.0489 (8)
La3—S4	2.8711 (10)	Ti2—S1	2.3977 (14)
La3—S5	2.9190 (10)	Ti2—S1 ^v	2.3977 (14)
La3—S5 ^{viii}	2.9498 (14)	Ti2—O5 ⁱⁱⁱ	2.256 (3)
La3—S6 ^{ix}	3.5150 (3)	Ti2—O5	1.769 (3)
La3—S6 ^{vii}	2.8817 (3)		

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

Data collection: *COLLECT* (Nonius, 1997–2001); cell refinement: *COLLECT*; data reduction: *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *JANA2000* (Petricek & Dusek, 2000); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *JANA2000*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1010). Services for accessing these data are described at the back of the journal.

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