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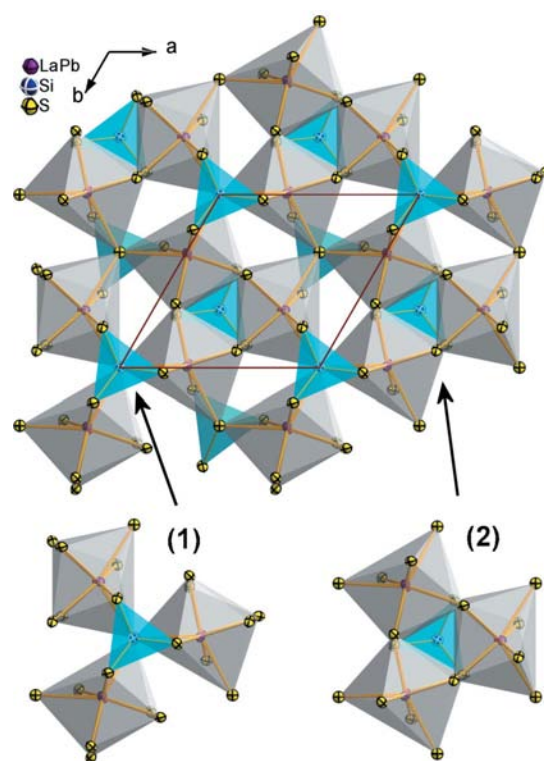
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Crystals of La₂Pb(SiS₄)₂, dilanthanum(III) lead(II) bis[tetra-sulfidosilicate(IV)], were obtained from the La–Pb–Si–S system and structurally characterized using X-ray single-crystal diffraction. The La and Pb atoms are coordinated in bicapped trigonal prisms of S atoms, with the Si atoms in tetrahedra. An occupational disorder of the La and Pb centres was refined for one position in the structure. The bicapped trigonal prisms and tetrahedra share edges. A gap located 2.629 (1) Å from the sulfide anions was found around the coordination polyhedra, which makes La₂Pb(SiS₄)₂ a prospective material in crystal engineering. The Si and one S atom lie on a threefold axis.

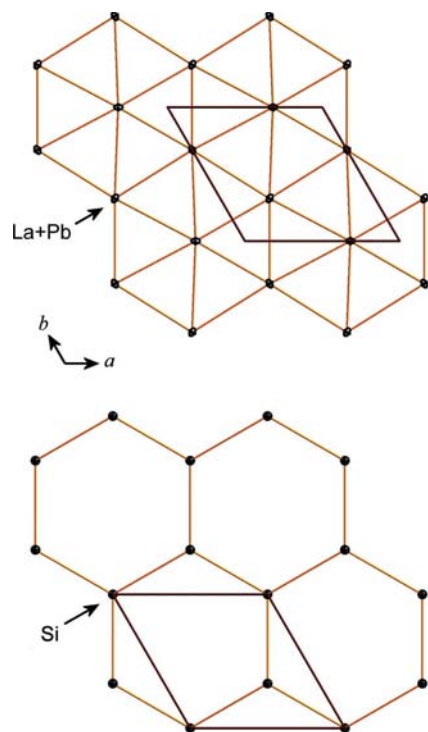
Comment

The synthesis of compounds with increasingly complex compositions, such as ternary, quaternary, *etc.*, has become a principal direction in modern materials science (Eliseev & Kuzmichyeva, 1990; Mitchell & Ibers, 2002). Among multi-component systems, an important place belongs to the complex rare-earth chalcogenides. They have been intensively studied over recent years owing to their specific thermal, electrical and optical properties, which make them prospective materials in the field of IR and nonlinear optics. Therefore, the synthesis and investigation of the crystal structures of complex chalcogenides are important in the search for new materials. So far, a series of quaternary rare-earth chalcogenides with Pb have been obtained from the R₂S₃–PbS–SnS₂ system (Marchuk *et al.*, 2007; Gulay *et al.*, 2008). These R₂Pb₃Sn₃S₁₂ (R = La–Nd, Sm, Gd–Tm) compounds crystallize in the non-centrosymmetric space group *Pmc*2₁ (Y₂Pb₃Sn₃S₁₂ structure type). However, a thorough investigation of the similar La₂S₃–PbS–SiS₂ system shows that a different quaternary compound of formula La₂Pb(SiS₄)₂ can be obtained. The crystal structure of this new chalcogenide is presented here.

Relevant interatomic distances and coordination numbers of the La, Pb and Si atoms in the structure of La₂Pb(SiS₄)₂ are listed in Table 1. Overall, the distances are close to the sums of the respective ionic radii (Wiberg, 1995). The Si atom lies on a threefold rotation axis and is surrounded by one S1 and three S2 atoms, resulting in a slightly elongated [SiS₁S₂₃] tetrahedron of C_{3v} point-group symmetry. A similar, but compressed, environment for an Si atom was found in the recently published hexagonal compound La₃Ag_{0.90}SiS₇ (Daszkiewicz *et al.*, 2008). In the title compound, the La and Pb atoms occupy the same site, with occupancy factors of 0.696 (9) and 0.304 (9), respectively. Therefore, these atoms have the same coordination environment of eight S atoms, creating an [(La1/Pb1)S₁S₂S₆] bicapped trigonal prism (Fig. 1). Similar values for La–S and Pb–S distances have also been observed in the previously reported lanthanum and lead sulfides. For example, the shortest La–S distance in La₂S₃ (Basañcon *et al.*, 1969) is 2.91 (1) Å and the shortest Pb–S distance in Ho₅Cu_{1+x}Pb_{3–x/2}S₁₁ (x = 1/4) is 2.822 (8) Å (Gulay *et al.*, 2007). In the title compound, the two longest (La/Pb)–S distances of 3.2784 (10) Å contribute 0.178 of a valence unit (Brown, 1996). However, the bond-valence sums of the La³⁺, Pb²⁺ and Si⁴⁺ ions are 2.722, 2.040 and 4.077, respectively. These values suggest that the La³⁺ ion is underbonded in its eight-coordinate site. On the other hand, the bond-valence sums for both symmetry-independent S atoms are 1.901 for S1 and 2.087 for S2. Thus, atom S1 is underbonded and S2 is

**Figure 1**

The unit cell and the coordination polyhedra of the La, Pb and Si atoms in the structure of La₂Pb(SiS₄)₂, viewed down the *c* axis. Displacement ellipsoids are shown at the 50% probability level. See *Comment* for descriptions of (1) and (2).


Figure 2

The 3^6 net of the (La+Pb) atoms (top) and the honeycomb-like 6^3 net of the Si atoms (bottom), both viewed down the c axis.

overbonded, despite both anions having similar pyramidal trigonal surroundings, *viz.* [(La1/Pb1) $_3$ Si1].

The [(La1/Pb1)S $_1$ S $_2$ S $_6$] bicapped trigonal prisms and [Si1S1S $_2$ S $_3$] tetrahedra are connected to each other in two ways. Firstly, three prisms connect the tetrahedra by the edges and the prisms are connected to each other only by one corner [denoted (1) in Fig. 1], and secondly three prisms are connected by edges around the threefold axis and an empty trigonal prism exists inside this block [denoted (2) in Fig. 1]. In addition, two [Si1S1S $_2$ S $_3$] tetrahedra share edges, resulting in a closed empty trigonal prism in the structure. The centre of gravity of this gap is located 2.629 (1) Å from the S atoms, which makes La $_2$ Pb(SiS $_4$) $_2$ a prospective material in crystal engineering.

Overall, the (La+Pb) and Si atoms in the structure of La $_2$ Pb(SiS $_4$) $_2$ form separated two-dimensional nets which are parallel to the ab plane (Fig. 2). A 3^6 net is created by the (La+Pb) atoms, whereas the Si atoms form a honeycomb-like 6^3 net. However, the S atoms do not create a layer. Thus, the cationic (La $^{3+}$ +Pb $^{2+}$) and Si $^{4+}$ layers are arranged in an alternating manner and they are immersed in the anionic sublattice.

Experimental

The sample was prepared by sintering the elemental constituents (La:Pb:Si:S atomic ratio = 2:1:2:8), of purity better than 99.9 wt%, in an evacuated quartz ampoule in a tube furnace. The ampoule was heated at a rate of 30 K h $^{-1}$ to a maximum temperature of 1370 K and kept at this temperature for 4 h. It was then cooled slowly

(10 K h $^{-1}$) to 770 K and annealed at this temperature for 500 h. After annealing the ampoule, the sample was quenched in cold water. A diffraction-quality single crystal of the title compound was selected from the sample.

Crystal data

La $_2$ Pb(SiS $_4$) $_2$	$Z = 6$
$M_r = 797.67$	Mo $K\alpha$ radiation
Trigonal, $R\bar{3}c$	$\mu = 21.19 \text{ mm}^{-1}$
$a = 9.0522 (13) \text{ \AA}$	$T = 295 \text{ K}$
$c = 26.964 (5) \text{ \AA}$	$0.25 \times 0.15 \times 0.08 \text{ mm}$
$V = 1913.5 (5) \text{ \AA}^3$	

Data collection

Kuma KM-4 diffractometer with a CCD area detector	6359 measured reflections
Absorption correction: numerical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007)	487 independent reflections
$T_{\min} = 0.059$, $T_{\max} = 0.414$	475 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.015$	23 parameters
$wR(F^2) = 0.043$	$\Delta\rho_{\max} = 0.53 \text{ e \AA}^{-3}$
$S = 1.22$	$\Delta\rho_{\min} = -0.67 \text{ e \AA}^{-3}$
487 reflections	

Table 1

Selected bond lengths (Å).

La1—S1	3.0868 (5)	La1—S2 $^{\text{iv}}$	3.2784 (10)
La1—S1 $^{\text{i}}$	3.0867 (5)	La1—S2 $^{\text{v}}$	3.2784 (10)
La1—S2	2.8801 (8)	Si1—S1 $^{\text{vi}}$	2.1277 (17)
La1—S2 $^{\text{i}}$	2.8800 (8)	Si1—S2	2.1203 (9)
La1—S2 $^{\text{ii}}$	3.0143 (9)	Si1—S2 $^{\text{vii}}$	2.1203 (9)
La1—S2 $^{\text{iii}}$	3.0144 (9)		

Symmetry codes: (i) $y + \frac{1}{3}, x - \frac{1}{3}, -z + \frac{1}{6}$; (ii) $-x + y + \frac{1}{3}, y - \frac{1}{3}, z + \frac{1}{6}$; (iii) $y, -x + y, -z$; (iv) $x - y + \frac{1}{3}, -y + \frac{2}{3}, -z + \frac{1}{6}$; (v) $-y + 1, x - y, z$; (vi) $-x + 1, -y, -z$; (vii) $-x + y + 1, -x + 1, z$.

The formation of La $_2$ Pb(SiS $_4$) $_2$ was established during the investigation of the phase relations in the respective La $_2$ S $_3$ –PbS–SiS $_2$ system. The systematic absences were found to be consistent with the space group $R\bar{3}c$, which was applied for the crystal structure determination. One position for La and Pb, one position for Si and two positions for S were determined at the first stage of refinement. However, a statistical mixture of La and Pb was assumed in the refinement, with the same anisotropic displacement parameters for the La and Pb atoms. The site-occupancy factors for the positions of the La and Pb atoms refined to 0.696 (9) and 0.304 (9), respectively. These values are in good agreement with the requirements of charge balance. The positions of the other atoms are fully occupied.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3045). Services for accessing these data are described at the back of the journal.

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