Crystal structure of trilanthanum monosilver monosilicon heptasulfide, La_3AgSiS_7

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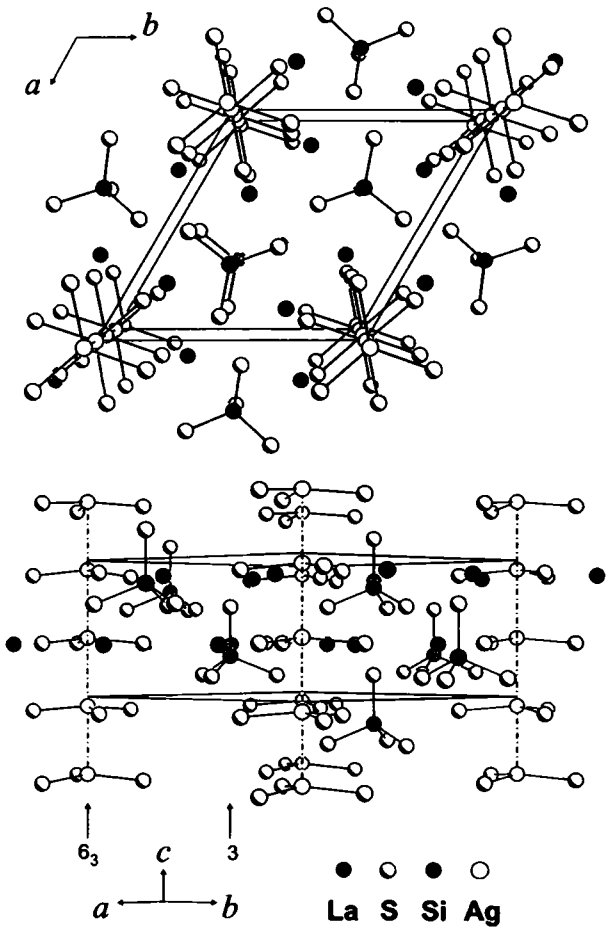

Abstract

$AgLa_3S_7Si$, hexagonal, $P6_3$ (no. 173), $a = 10.421(2)$ Å, $c = 5.785(3)$ Å, $V = 544.1$ Å^3, $Z = 2$, $R_{gt}(F) = 0.042$, $wR_{ref}(F^2) = 0.099$, $T = 293$ K.

Source of material

The title compound was obtained by the reaction of stoichiometric amount of elemental commercial products (La 99.9 %, Ag 99.5 %, Si 99.99 %, and S 99.95%) in a KBr flux. The mixture was loaded under argon, sealed under a 10^{-2} Pa vacuum in a silica tube. The tube was placed and heated in a computer-controlled furnace to 1173 K, kept at 1123 K for 72 h, cooled at a rate of 0.05 K/min to 723 K, and finally cooled to room temperature. The reaction mixture was washed with distilled water and dried with acetone. The reaction products comprised hexagonal pale greenish-yellow needles, which were modestly stable in air.

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Discussion

Although La_3AgSiS_7 crystallizes in the hexagonal system and also belongs to the extensively studied compound family of $Ln_3MM'Q_7$, where M is main-group metal or first-row transition-metal and M' is tetrahedrally coordinated main-group metal, some difference arises owing to coordination number of silver atom in 2*a* site which decreases compared with usual octahedrally coordinated main-group metals (figure, top). For instance, Ni or Mg (Co/Mg/Mn or Fe etc.) in the corresponding compounds ($La_6MSi_2S_{14}$, M = Ni, Co [1]; $La_6MgM'_2S_{14}$, M' = Ge, Si [2]; La_3MAlS_7 and La_3MFeS_7, M = Mg, Mn, Fe, Co, Ni, or Zn [3]) are coordinated with six sulfur atoms and form one-dimensional chains of face-sharing MS_6 octahedra along *c* axis.

In the crystal structure of La_3AgSiS_7, the silver atom is only bonded to three S1 atoms with Ag—S distances of 2.441(3) Å. The Ag atoms are strongly anisotropic, the value of U_{33} is much larger than that of U_{11} and U_{22}. This might be explained by the coordination of the atoms. Each Ag in 2*a* site is three-coordinated and located in the center of the triangular sulfur plane, so stood unconstrained perpendicular to the plane. The silicon atom forms a slightly distorted tetrahedron with three S2 parallel to the *a,b* plane and one S3 on the *c* axis, leaving one shorter Si—S3 bond of 2.086(9) Å and other three Si—S2 bonds of 2.138(5) Å (figure, bottom). The lanthanum atom is eight-coordinated to four S1 atoms, three S2 and one S3 atoms, which strongly resembles its analogues like La_3AgGeS_7 [4], $La_3AgSiSe_7$ [5], La_3CuGeS_7, $La_3CuGeSe_7$ [6] and other lanthanide chalcogenide compounds ($Dy_3CuGeSe_7$ [7], Y_3NaSiS_7 [8]). The La—S distances of the bicapped trigonal prism LaS_8 polyhedron range from 2.905(4) Å to 3.120(3) Å, well comparable to 2.910 Å to 3.121 Å (no errors cited) in La_3AgGeS_7 [4]. In brief, three structural motifs make up of the title compound, i.e. LaS_8 bicapped trigonal prisms, planar AgS_3 triangles, and SiS_4 tetrahedra. The LaS_8 prisms form corner-sharing chains along *c* axis, whereas the isolated AgS_3 triangles are staggered on 6_3 axis with a distance of 2.892(4) Å, and distorted AgS_4 tetrahedra packed along the threefold axis (figure, bottom).

Table 1. Data collection and handling.

Crystal:	pale greenish-yellow needle, size 0.20 × 0.22 × 0.68 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	147.02 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω/φ
$2\theta_{max}$:	49.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3867, 648
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 642
$N(param)_{refined}$:	39
Program:	SHELXTL [9]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La(1)	6c	0.12133(7)	0.35947(7)	0.1175(2)	0.0128(4)	0.0118(4)	0.0166(5)	0.0062(3)	0.0007(4)	0.0006(4)
Ag	2a	0	0	0.0682(5)	0.0171(6)	U_{11}	0.066(2)	$½U_{11}$	0	0
S(1)	6c	0.2644(3)	0.1764(3)	0.1083(8)	0.018(2)	0.014(2)	0.020(2)	0.009(1)	0.002(2)	0.002(2)
S(2)	6c	0.5262(4)	0.1181(4)	0.3447(7)	0.017(2)	0.012(2)	0.022(2)	0.006(2)	−0.001(2)	0.000(1)
S(3)	2b	⅓	⅔	0.341(1)	0.020(2)	U_{11}	0.018(4)	$½U_{11}$	0	0
Si	2b	⅓	⅔	0.702(1)	0.021(2)	U_{11}	0.014(4)	$½U_{11}$	0	0

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