

Crystal structure of $Y_{1.5}La_{1.5}Si_{1.75}Se_7$

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The existence of the new quaternary compound $Y_{1.5}La_{1.5}Si_{1.75}Se_7$ was established, and its crystal structure was studied by X-ray powder diffraction: space group $P6_3$, Pearson code $hP23.5$, $a = 10.5968(2)$ Å, $c = 5.9995(2)$ Å, $R_I = 0.0414$. The coordination polyhedra of the rare-earth atoms ($R = Y_{0.5}La_{0.5}$) are trigonal prisms with two additional atoms, those of the Si atoms are octahedra and tetrahedra.

Rare-earth metals / Crystal structure / X-ray powder diffraction

Introduction

The development of new functional materials is one of the areas of modern science and semiconductor technology. Among the most extensively studied multicomponent systems, an important place is occupied by systems that include chalcogenides of rare-earth metals (R) [1,2]. The study of the nature of the interaction of the components in complex R -containing chalcogenide systems, and the investigation of the crystal structures of the compounds that exist in these systems, form the basis for the creation of new materials with new physicochemical characteristics [3].

Experimental

The samples for the study were prepared from components of semiconductor purity. The synthesis of the alloys was performed in evacuated quartz containers in an MP-30 programmable electric muffle furnace according to the following regime: heating to 1150°C at a rate of 12°C/h; 4-h exposure at this temperature; cooling to 500°C at a rate of 12°C/h; homogenizing annealing for 240 h; quenching into cold water.

The powder X-ray diffraction pattern used to determine the crystal structure of the quaternary compound was recorded on a DRON 4-13 diffractometer (Cu $K\alpha$ radiation, $10^\circ \leq 2\theta \leq 100^\circ$, step scan mode with a step size of 0.05° and a counting

time of 20 s per data point). The refinement of the structure was performed using the WinCSD software package [4].

Results and discussion

The X-ray diffraction pattern of $Y_{1.5}La_{1.5}Si_{1.75}Se_7$ was indexed in hexagonal symmetry (space group $P6_3$). The conditions of the X-ray experiment and crystallographic parameters of the quaternary compound are listed in Table 1.

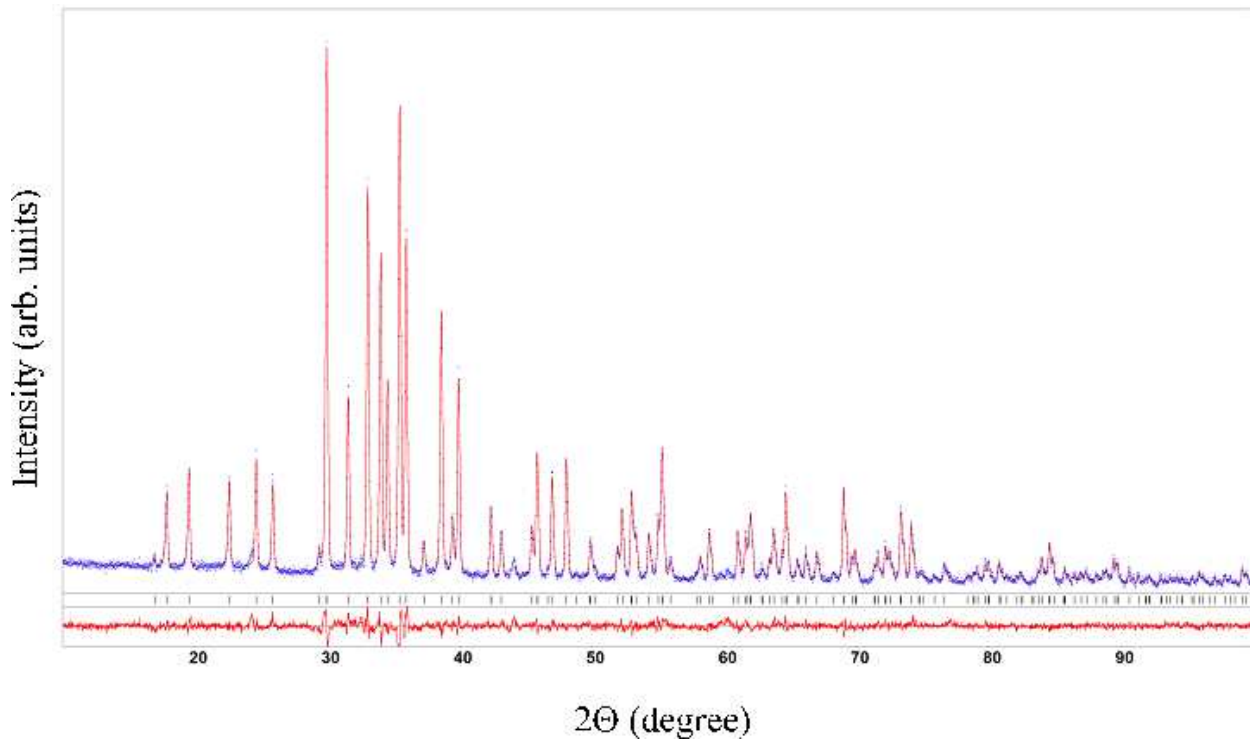
The experimental and theoretical powder patterns of $Y_{1.5}La_{1.5}Si_{1.75}Se_7$ and their difference are shown in Fig. 1. Satisfactory reliability factors were obtained. The refined atomic coordinates and displacement parameters are shown in Tables 2 and 3, interatomic distances and coordination numbers are listed in Table 4.

The occupation factor of the site R in the structure was fixed, assuming that La and Y atoms fill this site by 50% each. Based on the chemical formula, the occupation of site Si1 in Wyckoff position 2b was fixed to 0.75. With these constraints, the computation produced satisfactory values of the thermal and geometric parameters.

The structure of the compound $Y_{1.5}La_{1.5}Si_{1.75}Se_7$ is similar to the isopointal structure of the compound $Pr_3Si_{1.25}Se_7$. In this structure the position of the Pr atoms have prismatic environment with additional atoms [5]. This is also the case in $Y_{1.5}La_{1.5}Si_{1.75}Se_7$, where the rare-earth atoms are located in

Table 1 Crystallographic data and X-ray experiment details.

Compound	$Y_{1.5}La_{1.5}Si_{1.75}Se_7$
Space group	$P6_3$ (No. 173)
a (Å)	10.5968(2)
c (Å)	5.9995(2)
V (Å ³)	583.44(4)
$F(000)$ (electrons)	813.0
Number of atoms per cell	23.5
Calculated density (g/cm ³)	5.3707(4)
Absorption coefficient (cm ⁻¹)	810.62
Radiation, wavelength (Å)	Cu $K\alpha$, 1.54185
Diffractometer	DRON 4-13
Mode of refinement	Full profile
Number of atom sites	6
Max 2θ (°) and $\sin\theta/\lambda$ (1/Å)	100.02 0.497
R_I	0.0414
R_p	0.1126
Scale factor	0.30328(1)
Texture axis and parameter	[3 2 0] 0.49(1)

**Fig. 1** Experimental and calculated powder diffraction patterns of $Y_{1.5}La_{1.5}Si_{1.75}Se_7$ and their difference.**Table 2** Atomic coordinates and equivalent displacement parameters (Å²) of the atoms in the structure of $Y_{1.5}La_{1.5}Si_{1.75}Se_7$.

Atoms	x/a	y/b	z/c	B_{eq}^a	Wyckoff	Occupation
R	0.1296(1)	0.3591(1)	0.0357(4)	1.47(5)	6c	0.5Y + 0.5La
Se1	0.2573(2)	0.1645(2)	0.0193(5)	2.01(8)	6c	1.0
Se2	0.5215(2)	0.1080(2)	0.2714(4)	1.40(7)	6c	1.0
Se3	$\frac{1}{3}$	$\frac{2}{3}$	0.2525(6)	1.19(8)	2b	1.0
Si1	$\frac{1}{3}$	$\frac{2}{3}$	0.6182(15)	1.8(3)	2b	0.75
Si2	0	0	-0.204(3)	0.5(2)	2a	1.0

$$^a B_{eq} = 4/3[B_{11} a^{*2} a^2 + \dots + 2B_{23} b^* c^* b c \cos(\alpha)]$$

Table 3 Anisotropic displacement parameters (\AA^2) of the atoms in the structure of $Y_{1.5}La_{1.5}Si_{1.75}Se_7$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
R^a	1.53(5)	1.39(6)	1.61(5)	0.81(5)	0.10(9)	0.64(9)
Se1	1.59(8)	2.59(10)	1.97(11)	1.14(8)	0.09(15)	0.29(14)
Se2	1.45(9)	1.56(8)	1.23(8)	0.79(8)	0.44(10)	-0.21(7)
Se3	0.55(9)	B_{11}	2.1(2)	$\frac{1}{2}B_{11}$	0	0
Si1	2.2(4)	B_{11}	0.4(7)	$\frac{1}{2}B_{11}$	0	0
Si2	0.4(2)	B_{11}	0.4(6)	$\frac{1}{2}B_{11}$	0	0

$$^a R = 0.5Y + 0.5La$$

Table 4 Interatomic distances (δ) and coordination numbers (C.N.) in the structure of $Y_{1.5}La_{1.5}Si_{1.75}Se_7$.

Atoms		δ (\AA)	C.N.
R	1Se1	2.981(2)	8
	1Se1	2.982(2)	
	1Se2	2.988(2)	
	1Se1	3.052(4)	
	1Se2	3.057(2)	
	1Se3	3.153(2)	
	1Se2	3.181(2)	
	1Se1	3.240(4)	
Se1	2R1	2.981(2)	6
	1R1	3.052(4)	
	1R1	3.240(4)	
	1Si1	2.740(9)	
	1Si2	2.911(11)	
Se2	1R1	2.988(4)	4
	1R1	3.057(2)	
	1R1	3.181(2)	
	1Si1	2.290(4)	
Se3	3R1	3.153(2)	4
	1Si1	2.194(10)	
Si1	1Se3	2.193(10)	4
	3Se2	2.290(4)	
Si2	3Se1	2.740(9)	6
	3Se1	2.911(11)	

trigonal prisms with two additional atoms. The Si1 atoms center tetrahedra, and the Si2 atoms center octahedra, as shown in Fig. 2.

An analysis of the composition of the synthesized compound indicated an excess of cations. This can mean either a lower oxidation state of the cations, or the existence of pairs of cations. Silicon is more electronegative than the rare-earth elements, and only Si could form pairs of atoms, the existence of which could explain the chemical composition of the compound. The analysis of previously studied compounds confirms that this is a possible option. The $Na_4PbSi_2Se_6$ compound ($C2/m$, No. 12, $a = 7.070 \text{ \AA}$, $b = 12.214 \text{ \AA}$, $c = 7.969 \text{ \AA}$, $\beta = 107.29^\circ$) [6] appears to have an excess of cations, but in this case Si–Si pairs show an interatomic distance of 2.344 \AA . The arrangement of the polyhedra of selenium atoms around the silicon atoms in $Na_4PbSi_2Se_6$ is shown in

Fig. 3, where the interatomic distances within one $Se_3Si-SiSe_3$ unit are also indicated. Such an atom arrangement can explain the charge balance and oxidation states in the compound. The $CoSi_2Se_4$ compound ($C2/m$, No. 12, $a = 12.4313 \text{ \AA}$, $b = 3.5860 \text{ \AA}$, $c = 5.9450 \text{ \AA}$, $\beta = 116.73^\circ$) [7] also has a “strange” formula with apparently too many cations, if the oxidation state of silicon is considered to be +4. The unit cell is similar to that of the Cr_3S_4 type, where the S atoms form a hexagonally close-packed arrangement, in which the cations occupy $\frac{3}{4}$ of the available octahedral voids. However, also $CoSi_2Se_4$, for which no complete structure refinement was carried out, is likely to contain Si–Si dumbbells. The authors state that Co atoms and Si–Si dumbbells occupy the octahedral voids in every second interlayer, as in the parent structure type CdI_2 .

A crystal-chemical analysis of compounds containing selenium and silicon showed that the distance of a Si–Si pair is shorter than the shortest distance Si2–Si2 = 3.00 Å in the $Y_{1.5}La_{1.5}Si_{1.75}Se_7$

compound. Therefore this option must be excluded in our case. A lower oxidation state of the cations remains to be considered, and part of the Si atoms may have the formal oxidation state Si^{II}.

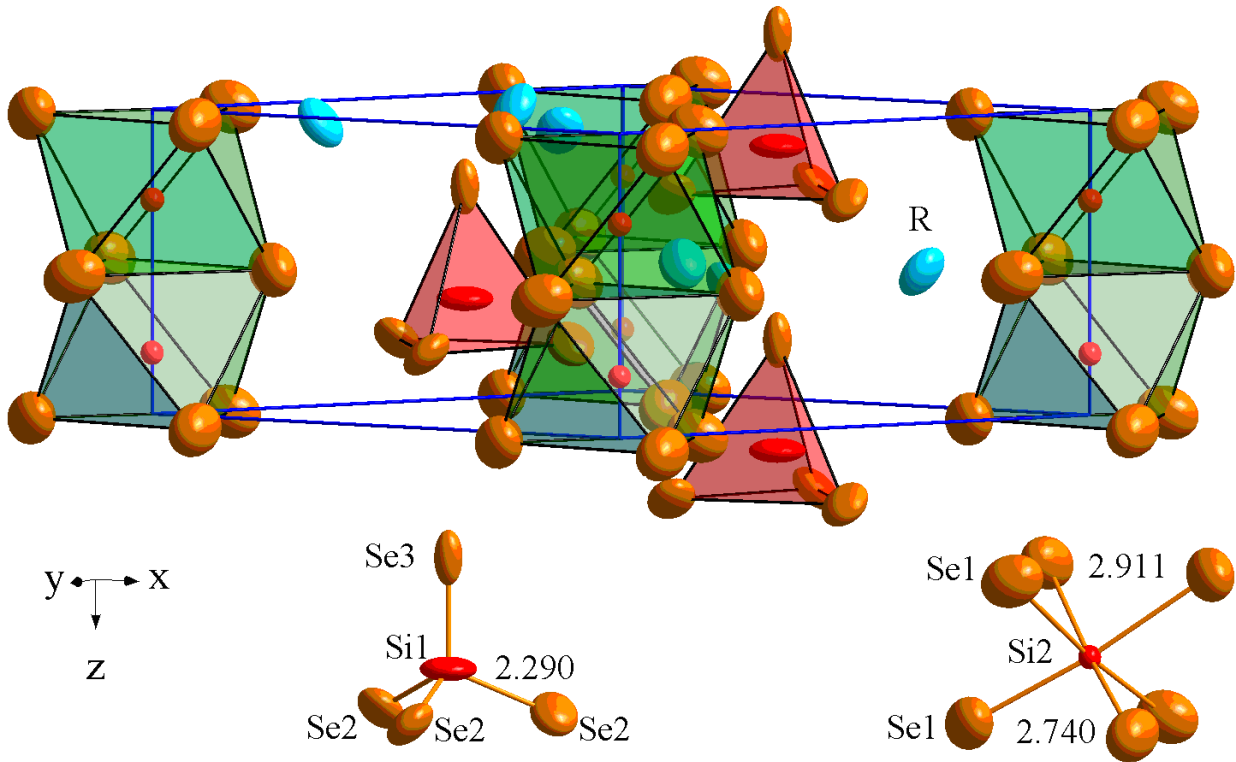


Fig. 2 Stacking of polyhedra of selenium atoms around the silicon atoms in the structure of $Y_{1.5}La_{1.5}Si_{1.75}Se_7$.

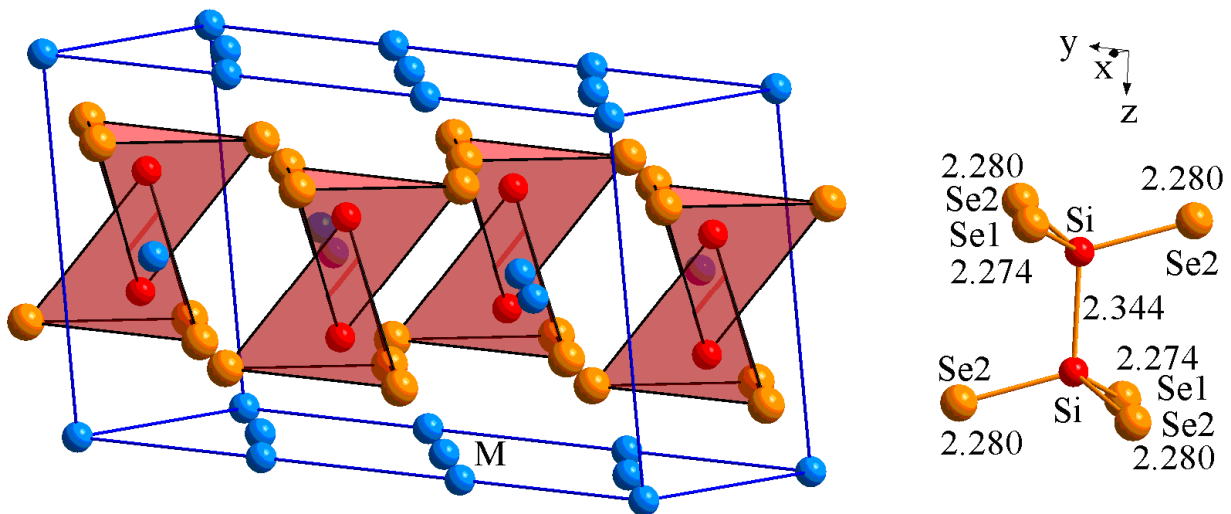


Fig. 3 Stacking of polyhedra of selenium atoms around the silicon atoms in the structure of $Na_4PbSi_2Se_6$.

Conclusions

The study of the structural parameters of the $Y_{1.5}La_{1.5}Si_{1.75}Se_7$ compound and the analysis of the interatomic distances and immediate coordination environment of the atoms in the structure indicate that, in our opinion, the silicon atoms exists in two oxidation states, +2 and +4. It would be interesting to find and investigate the structure of similar chalcogenides in related systems.

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