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Crystal structures of the $Ln_{4-x}In_{5-y}S_{13}$ (Ln = La, Ce, Pr and Nd; $x = 0.08$–0.12, $y = 0.21$–0.24), $La_3In_{1.67}S_7$, Gd_3InS_6 and $La_4Ag_2In_4S_{13}$ compounds

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ABSTRACT

The orthorhombic crystal structures of the series of $Ln_{4-x}In_{5-y}S_{13}$ (Ln = La, Ce, Pr and Nd; $x = 0.08$–0.12, $y = 0.21$–0.24) compounds were investigated by means of X-ray crystal diffraction. The crystals of $La_3In_{1.67}S_7$ and Gd_3InS_6 were also obtained unexpectedly from the La–In–S and Gd–In–S systems and no respective $Gd_{4-x}In_{5-y}S_{13}$ was obtained. In the structures of the orthorhombic $Ln_{4-x}In_{5-y}S_{13}$ series and hexagonal $La_3In_{1.67}S_7$ indium atoms occupy disordered positions in the octahedral and trigonal antiprismatic arrangement of the sulphur atoms. The crystal structure of the $La_4Ag_2In_4S_{13}$ is also given and discussed as an example of quaternary sulphide related to a ternary La–In sulphide.

1. Introduction

Syntheses of the compounds with increasingly complex compositions, such as ternary, quaternary, etc. became a principle direction in a modern material science [1,2]. Among the multi-component systems, an important place belongs to the complex rare-earth chalcogenides, which have been intensively studied during the last years due to their specific thermal, electrical and optical properties [2,3].

The Ln–In–S system has been intensively studied and so far, the crystal structures of several indium chalcogenides have been established: La_3InS_6—space group $P2_12_12$ [4], Sm_3InS_6–$Pnnm$ [5], $Ln_4In_5S_{13}$ (Ln = La and Nd)—$Pbam$ [6,7], $Tb_3In_5S_{12}$–$P2_1/m$ [8], $YbIn_2S_4$–$P3$ [9], $Yb_{18}In_{7.33}S_{36}$–$P6_3/m$ [10] and $Yb_{4/3}In_{4/3}S_4$–$Fd\bar{3}m$ [11]. Later on, investigations on the series of ternary chalcogenides provided structural information on the Ln_3InS_6–$P2_12_12$ [12], $LnIn_3S_6$–$Pbam$ [13], $Ln_3In_5S_{12}$–$P2_1/m$ (Ln = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) [14], $LnInS_3$ (Ln = Y, La, Ce, Pr, Nd, Sm and Gd)—$Pbam$ [1] and $EuIn_2S_4$—$Cccm$ [15].

The present paper describes the crystal structure of the series of lanthanide indium sulphides with general formula $Ln_{4-x}In_{5-y}S_{13}$, Ln = La, Ce, Pr and Nd, $x = 0.08$–0.12, $y = 0.21$–0.24, isolated from the Ln–In–S system (Table 1). The La–In–S system appears to be more complex as the hexagonal crystals of $La_3In_{1.67}S_7$ were also found (Table 2). Besides, the crystals of Gd_3InS_6 were obtained although an attempt to obtain a respective $Gd_{4-x}In_{5-y}S_{13}$ compound was made. The crystal structure of the $La_4Ag_2In_4S_{13}$ is also given and discussed as an example of quaternary sulphide related to a ternary La–In sulphide.

2. Experimental details

The samples with the compositions $LnInS_3$ (Ln = La, Ce, Pr, Nd and Gd) and La_2AgInS_5 were prepared by sintering the elemental constituents with purity better than 99.9 wt% in evacuated quartz ampoules. The syntheses were carried out in a tube furnace. The ampules were heated at a rate of 30 K/h to a maximum temperature of 1420 K and kept at this temperature for 3 h. Afterwards, they were cooled slowly (10 K/h) to 870 K and annealed at this temperature for 240 h. After annealing the ampules, they were quenched in cold water.

Diffraction-quality single crystals for the crystal structure determination were selected from the reaction products. X-ray diffraction data were obtained on a KUMA Diffraction KM-4 four-circle single-crystal diffractometer equipped with CCD detector using graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.071073$ nm). The raw data were treated with the CrysAlis Data Reduction

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Table 1
Crystal data and structure refinement details of the $Ln_{4-x}In_{5-y}S_{13}$ (Ln = La, Ce, Pr and Nd; $x = 0.08$–0.12, $y = 0.21$–0.24) compounds

Empirical formula	$La_{3.92}In_{4.76}S_{13}$	$Ce_{3.88}In_{4.79}S_{13}$	$Pr_{3.92}In_{4.76}S_{13}$	$Nd_{3.90}In_{4.76}S_{13}$
Formula weight	1506.00	1509.74	1513.84	1526.58
Space group	*Pbam* (no. 55)	*Pbam* (no. 55)	*Pbam* (no. 55)	*Pbam* (no. 55)
Unit cell dimensions	$a = 1.1814(1)$ nm $b = 2.1280(2)$ nm $c = 0.40384(4)$ nm	$a = 1.1794(2)$ nm $b = 2.1247(4)$ nm $c = 0.39933(8)$ nm	$a = 1.1758(1)$ nm $b = 2.1197(3)$ nm $c = 0.39695(5)$ nm	$a = 1.1754(2)$ nm $b = 2.1211(4)$ nm $c = 0.39514(8)$ nm
Volume (nm^3)	1.0152(1)	1.0007(3)	0.9893(2)	0.9852(3)
Number of formula units per unit cell	2	2	2	2
Calculated density (g/cm^3)	4.926	5.010	5.082	5.146
Absorption coefficient (mm^{-1})	14.651	15.369	16.222	16.912
$F(000)$	1328	1335	1343	1351
Crystal size (mm)	0.28 × 0.14 × 0.06	0.07 × 0.06 × 0.04	0.11 × 0.06 × 0.05	0.14 × 0.05 × 0.04
Θ Range for data collection	4.20–29.57	3.36–29.57	3.96–29.55	3.36–28.06
Index ranges	$-16 \leqslant h \leqslant 15$ $-28 \leqslant k \leqslant 27$ $-4 \leqslant l \leqslant 5$	$-15 \leqslant h \leqslant 16$ $-28 \leqslant k \leqslant 28$ $-3 \leqslant l \leqslant 5$	$-15 \leqslant h \leqslant 16$ $-25 \leqslant k \leqslant 29$ $-5 \leqslant l \leqslant 5$	$-14 \leqslant h \leqslant 16$ $-27 \leqslant k \leqslant 27$ $-4 \leqslant l \leqslant 5$
Reflections collected	12155	13105	12306	10608
Independent reflections	1586 [R(int.) = 0.0392]	1510 [R(int.) = 0.0412]	1533 [R(int.) = 0.0472]	1313 [R(int.) = 0.0395]
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Data/restraints/parameters	1586/0/85	1510/0/85	1533/0/85	1313/0/85
Goodness-of-fit on F^2	1.169	1.083	1.040	1.121
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0236$, $wR2 = 0.0537$	$R1 = 0.0254$, $wR2 = 0.0417$	$R1 = 0.0253$, $wR2 = 0.0370$	$R1 = 0.0256$, $wR2 = 0.0452$
R indices (all data)	$R1 = 0.0247$, $wR2 = 0.0542$	$R1 = 0.0431$, $wR2 = 0.0451$	$R1 = 0.0371$, $wR2 = 0.0397$	$R1 = 0.0336$, $wR2 = 0.0473$
Extinction coefficient	0.00162(9)	0.00118(5)	0.00027(4)	0.00044(5)
Largest diff. peak and hole $\times 10^{-3}$	1.893 and −0.925 e/nm^3	1.565 and −1.048 e/nm^3	1.484 and −1.513 e/nm^3	1.517 and −1.034 e/nm^3

Table 2
Crystal data and structure refinement details of the $La_3In_{1.67}S_7$, Gd_3InS_6 and $La_4Ag_2In_4S_{13}$ compounds

Empirical formula	$La_3In_{1.67}S_7$	Gd_3InS_6	$La_4Ag_2In_4S_{13}$
Formula weight	832.90	778.93	1647.44
Space group	$P6_3$ (no. 173)	*Pnnm* (no. 58)	*Pbam* (no. 55)
Unit cell dimensions	$a = 1.0196(1)$ nm $c = 0.62792(7)$ nm	$a = 1.3544(1)$ nm b = 1.6502(1) nm c = 0.38686(4) nm	$a = 2.0523(1)$ nm b = 2.5118(1) nm c = 0.40241(1) nm
Volume (nm^3)	0.5653(1)	0.8646(1)	1.0744(1)
Number of formula units per unit cell	2	4	4
Calculated density (g/cm^3)	4.893	5.983	5.275
Absorption coefficient (mm^{-1})	15.681	26.702	15.533
$F(000)$	730	1348	2904
Crystal size (mm)	0.15 × 0.09 × 0.06	0.15 × 0.05 × 0.02	0.21 × 0.03 × 0.03
Θ range for data collection	3.98–30.49	2.89–26.72	2.56–30.02
Index ranges	$-10 \leqslant h \leqslant 14$ $-13 \leqslant k \leqslant 13$ $-8 \leqslant l \leqslant 8$	$-17 \leqslant h \leqslant 17$ $-20 \leqslant k \leqslant 20$ $-4 \leqslant l \leqslant 4$	$-28 \leqslant h \leqslant 26$ $-32 \leqslant k \leqslant 35$ $-3 \leqslant l \leqslant 5$
Reflections collected	7839	10083	24366
Independent reflections	1132 [R(int.) = 0.0364]	1051 [R(int.) = 0.0607]	3161 [R(int.) = 0.0444]
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Data/restraints/parameters	1132/1/38	1051/0/63	3161/0/152
Goodness-of-fit on F^2	1.028	0.994	1.088
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0166$, $wR2 = 0.0274$	$R1 = 0.0264$, $wR2 = 0.0384$	$R1 = 0.0294$, $wR2 = 0.0462$
R indices (all data)	$R1 = 0.0195$, $wR2 = 0.0279$	$R1 = 0.0407$, $wR2 = 0.0414$	$R1 = 0.0418$, $wR2 = 0.0488$
Extinction coefficient	0.0042(1)	0.00010(5)	0.00003(1)
Largest diff. peak and hole $\times 10^{-3}$	1.083 and −1.340 e/nm^3	1.708 and −1.632 e/nm^3	1.186 and −1.107 e/nm^3

programme [16] taking into account an absorption correction. The intensities of the reflections were corrected for Lorentz and polarization effects. The crystal structures were solved by Patterson methods [17] and refined by full-matrix least-squares method using SHELXL-97 programme [17].

3. Results and discussion

3.1. Crystal structure of the $Ln_{4-x}In_{5-y}S_{13}$ (Ln = La, Ce, Pr and Nd; $x = 0.08$–0.12, $y = 0.21$–0.24) compounds

Needle-like single crystals were observed in the course of visual assessment of the $LaInS_3$ sample. Additionally, ellipsoid crystals were found for the $LaInS_3$ sample and the crystal structure is described in the next section. Orthorhombic unit cell was determined for the needle-like crystals and *Pbam* space group was applied for the crystal structure solution and refinement (Table 1). The dependence of the lattice parameters (a, b and c) and unit cell volume (V) of the $Ln_{4-x}In_{5-y}S_{13}$ series on the ionic radius of the rare-earth elements [18] (Fig. 1) reflects the well-known lanthanide contraction. The increase of the unit cell volume agrees well with the increase of the ionic radius of rare-earth element and the general growing tendency of the lattice parameters is observed.

Initially, the positions for all the atoms were determined in the structure solution and refinement. However, high values of anisotropic displacement parameters for two In atoms (In2 and In4) and residual electron densities near these atoms were observed. $R1$ factor was ~0.05 and 70 parameters were refined.

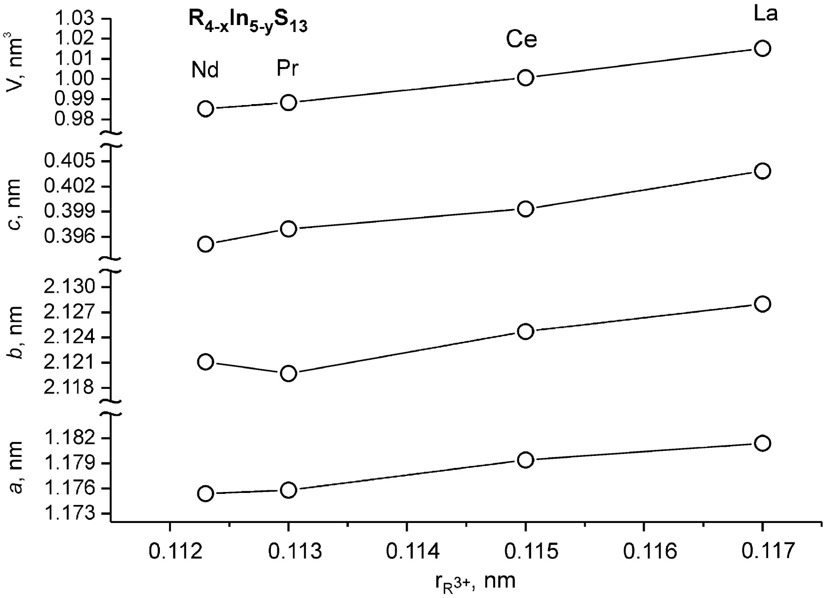

Fig. 1. The dependence of the lattice parameters (*a*, *b* and *c*) and unit cell volume (*V*) of the $Ln_{4-x}In_{5-y}S_{13}$ (*Ln* = La, Ce, Pr and Nd; $x = 0.08–0.12$, $y = 0.21–0.24$) compounds on the ionic radii of the rare-earth elements.

Therefore, two additional In atoms (In3 and In5) were located at extra positions. At this stage, the anisotropic parameters for the In atoms were significantly reduced and the final value of *R*1 factor was also improved. The site occupancy factors for the deficient sites of the lanthanum and indium atoms were free to refine. They were fixed when maximum shift/standard uncertainty of the parameter became smaller than 0.002. Finally, 85 parameters were refined. Among all the five positions of the indium atoms determined for all the $Ln_{4-x}In_{5-y}S_{13}$ compounds only the one position is fully occupied, In1. The site occupancy factors for the In2–In5 atoms were fixed at the values close to the calculated ones in order to satisfy charge balance requirement. Final calculated compositions of $La_{3.92}In_{4.76}S_{13}$, $Ce_{3.88}In_{4.79}S_{13}$, $Pr_{3.92}In_{4.76}S_{13}$ and $Nd_{3.90}In_{4.76}S_{13}$ were determined. A noteworthy fact is that the previous model of the crystal structures for two $Ln_4In_5S_{13}$ (*Ln* = La and Nd) compounds contained ordered positions of all the indium atoms despite that large displacement parameter for one of the In atoms was observed [6,7].

Generally, the crystal structures of the $Ln_{4-x}In_{5-y}S_{13}$ (*Ln* = La, Ce, Pr and Nd; $x = 0.08–0.12$, $y = 0.21–0.24$) compounds are essentially isostructural to the structures of $Ln_4In_5S_{13}$ (*Ln* = La and Nd) [6,7] and non-stoichiometric $Ln_4In_{4.72}Se_{13}$ (*Ln* = La and Ce) [19]. In both series of compounds sulphur atoms surround each of the Ln and In atoms. Tetrahedral and octahedral arrangements can be distinguished for the In atoms (Fig. 2), where the tetrahedral In1 position is similar to the respective In3 in $Ln_4In_5S_{13}$ compounds (Fig. 2b). The octahedral In2 and In4 positions in the structure of the title $Ln_{4-x}In_{5-y}S_{13}$ compounds relate to the In2 and In1 positions in the $Ln_4In_5S_{13}$. Overall, the interatomic distances agree well with the sum of the respective ionic radii [18]. However, such close contact between the In2 and In3 (In4 and In5) atoms do not really exist, because the In2 and In3 (In4 and In5) occupy the same octahedral arrangement of the sulphur atoms and indicate a disorder of the indium atoms. The octahedrons are shortened along the opposite corners. Especially, large axial distortion for the In4 octahedron occurs, as the ~0.4 Å difference of the In4–S interatomic distances is observed. Such deformation can be a reason that the In3 and In5 extra positions were found in the horizontal plane of the respective octahedrons. Besides, five and four coordination spheres can be reasonably considered for the In3 and In5 atoms, because some of the In3–S and In5–S distances are too long to consider them as a noteworthy interatomic (bonding) interaction (Table 3). A bond valence sum

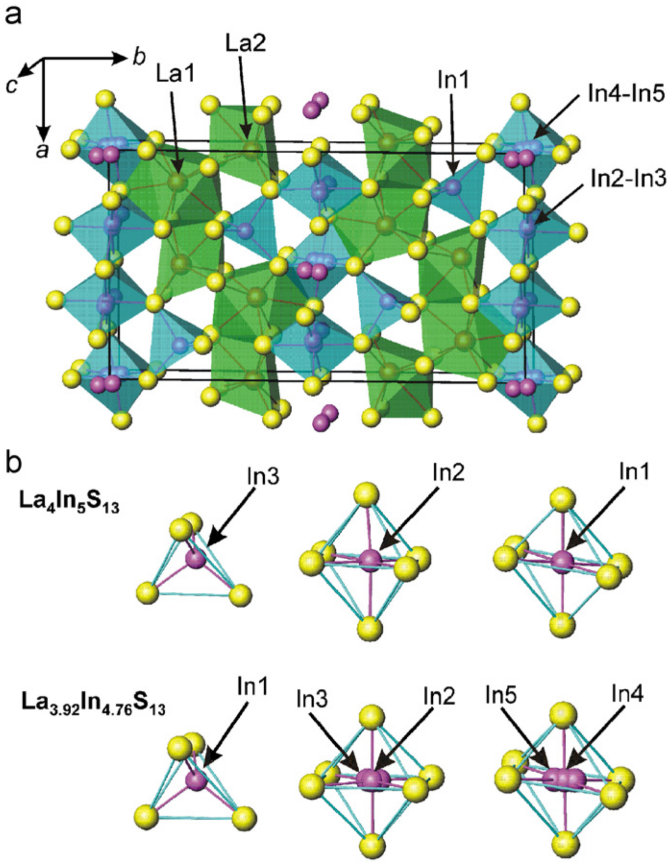

Fig. 2. (a) The packing of the unit cell in the crystal structure of the $La_{3.92}In_{4.76}S_{13}$ compound and (b) coordination spheres of the indium atoms in the structures of the $Ln_4In_5S_{13}$ (*Ln* = La and Nd) and $Ln_{4-x}In_{5-y}S_{13}$ (*Ln* = La, Ce, Pr and Nd; $x = 0.08–0.12$, $y = 0.21–0.24$) compounds.

Table 3
Relevant interatomic distances (δ, nm) and coordination numbers (c.n.) of the Ln and In atoms in the structure of the $Ln_{4-x}In_{5-y}S_{13}$ (Ln = La, Ce, Pr and Nd; x = 0.08–0.12, y = 0.21–0.24) compounds

Atoms	δ (nm)				c.n.
	Ln = La	*Ln* = Ce	*Ln* = Pr	*Ln* = Nd	
Ln1					
2S2	0.29186(9)	0.2891(1)	0.2873(1)	0.2862(1)	8
1S7	0.2976(1)	0.2964(1)	0.2938(1)	0.2934(1)	
1S4	0.3029(1)	0.2993(1)	0.2981(1)	0.2971(1)	
2S1	0.30361(9)	0.3012(1)	0.2993(1)	0.2984(1)	
2S5	0.3060(1)	0.3047(1)	0.3023(1)	0.3014(1)	
Ln2					
2S3	0.29071(9)	0.2888(1)	0.2874(1)	0.2867(1)	7
2S2	0.29197(9)	0.2891(1)	0.2875(1)	0.2864(1)	
2S1	0.29821(9)	0.2951(1)	0.2936(1)	0.2925(1)	
1S4	0.3171(1)	0.3114(1)	0.3063(1)	0.3031(1)	
In1					
2S4	0.24603(8)	0.2452(1)	0.24537(8)	0.2453(1)	4
1S5	0.2460(1)	0.2462(1)	0.2453(1)	0.2455(1)	
1S3	0.2532(1)	0.2529(1)	0.2518(1)	0.2516(1)	
In2					
1S3	0.2476(5)	0.246(1)	0.2441(8)	0.243(1)	6
1S1	0.2580(5)	0.260(1)	0.2638(8)	0.265(1)	
2S7	0.2640(3)	0.2636(6)	0.2630(5)	0.2627(7)	
2S6	0.2765(3)	0.2733(7)	0.2717(5)	0.2710(7)	
In3					
1S7	0.2294(4)	0.234(1)	0.2340(7)	0.235(1)	5
1S3	0.2528(5)	0.255(1)	0.2577(8)	0.259(1)	
1S1	0.2570(5)	0.255(1)	0.2531(9)	0.252(1)	
1S7	0.2676(8)	0.262(1)	0.261(1)	0.261(1)	
1S6	0.2792(8)	0.278(1)	0.2770(9)	0.276(1)	
In4					
2S7	0.2367(1)	0.2364(1)	0.2358(1)	0.2357(2)	6
4S5	0.2807(1)	0.2799(1)	0.2799(1)	0.2804(1)	
In5					
1S7	0.237(1)	0.237(5)	0.237(9)	0.233(4)	4
1S7	0.241(1)	0.239(5)	0.23(1)	0.244(4)	
2S5	0.2571(9)	0.263(3)	0.265(5)	0.255(1)	

for the five and four coordinate indium is 3.22 (In3) and 3.04 (In5) [20].

Sulphur atoms also surround the La1 and La2 atoms and the coordination spheres can be described as bi- and mono-capped trigonal prismatic, respectively (Fig. 2). The trigonal prisms are connected to each other and form zigzag chains along the *a*-axis. The zigzags are connected to the straight chains built by the octahedral indium atoms. However, from the theoretic point of view, a close-packed arrangement cannot simply be formed by the connection of the zigzag and straight chains as the interstitial voids occur. In the crystal structure of $Ln_{4-x}In_{5-y}S_{13}$ compounds, these voids are filled by the tetrahedrally coordinated indium atoms. Thus, the In1 atoms play a meaningful role in the crystal structure arrangement when it is treated as a linker of two chains (Fig. 2).

It is worth noticing that the crystal structure of the $Ln_{4-x}In_{5-y}S_{13}$ compounds cannot be created by the tri-valent lanthanide and indium and bi-valent sulphur atoms giving merely a $Ln_4In_5S_{13}$ compound. The structure must contain a deficiency of the cations by the reason of charge balance requirement. However, the ordered crystal structure can be formed when indium is replaced by the cations with larger ionic radius e.g. zinc, calcium and/or bismuth. This substitution give a new crystal structure of $Ln_4Tv_4BvS_{13}$ (Tv = tri-valent element, Bv = bi-valent element) e.g. $La_4Bi_4ZnS_{13}$, where a position of the bi-valent element relates to the In4 position in the crystal structure of $Ln_{4-x}In_{5-y}S_{13}$. Moreover, bi-valent element can substitute one of the In1 and In2 sites or both. However, in the former case, there must be a tetra-valent (Tev) element occupying the In4 position in the related $Ln_{4-x}In_{5-y}S_{13}$ compound to balance one negative charge. Then, a $Ln_4Dv_2Tv_2TevS_{13}$ can be formed. In the latter case, a hexavalent element (Hv) should substitute In4 position and a $Ln_4Dv_4HvS_{13}$ can be formed. All these cases provide new crystal structures and maintain the same set of the symmetry elements of the *Pbam* space group.

3.2. Crystal structure of the $La_3In_{1.67}S_7$ compound

A hexagonal unit cell for the ellipsoid-like single crystals was established and the space group $P6_3$ was applied for the crystal structure solution and refinement. The $La_3In_{1.67}S_7$ is isostructural with $La_3In_{1.67}Se_7$ ($Ce_3Al_{1.67}S_7$ type of structure, space group $P6_3$) reported in Ref. [21]. Crystal structure of the $La_3In_{1.67}Se_7$ is very similar to the previously reported $Ln_3Ag_{1-d}TX_7$ (Ln = La–Nd, Sm, Gd–Dy; T = Si, Ge, Sn; X = S, Se; d = 0–0.30) [22–24] (Fig. 3). However, the main difference concerns two positions occupied by the silver atoms in the $Ln_3Ag_{1-d}TX_7$ series. These positions are located in the centre and near the one face of trigonal antiprism created by the six sulphur atoms. Silver atoms occupy two positions with different site occupancy factors and the former is less occupied than the latter one. However, the In1 atom occupies the central position in the $La_3In_{1.67}Se_7$ compound and its position is disordered as $U_{33} \gg U_{11}$. On the other hand, the second indium atom, In2, is situated in a well-established position of tetrahedral surroundings of the sulphur atoms. This tetrahedron is trigonally compressed along the 3 axis and relates to the arrangement of the T atom in the $Ln_3Ag_{1-d}TX_7$ compounds (Table 4).

3.3. Crystal structure of the Gd_3InS_6 compound

In order to synthesize respective gadolinium compound with general formula $Gd_{4-x}In_{5-y}S_{13}$, the Gd–In–S system was investigated, but the needle-like crystals of the Gd_3InS_6 were obtained. A material of composition Gd_3InS_6 has been reported previously [25], however $P2_12_12$ space group was determined by means of powder diffraction. The Gd_3InS_6 crystallize in space group *Pnnm* adopting the U_3ScS_6 structure type and it is isostructural to several compounds including Sm_3InS_6 [5], Ln_3TSe_6 (Ln = Sm, Gd; T = In, Cr) and Tb_3CrSe_6 [26].

Sulphur atoms surround each of the Gd and In atoms (Fig. 4). The coordination sphere for the Gd1 and Gd3 atoms can be decribed as bi-capped trigonal prismatic, whereas Gd2 atom is

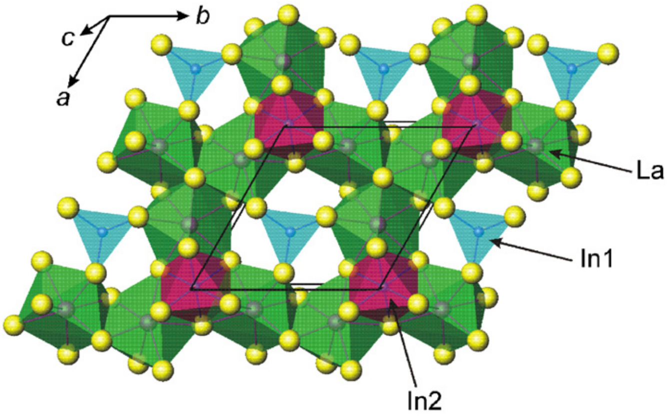

Fig. 3. The packing of the unit cell in the structure of the $La_3In_{1.67}S_7$.

situated in the mono-capped trigonal prism. Six sulphur atoms surround each of the two symmetry independent indium atoms, In1 and In2 (Table 5). The trigonal prismatic and octahedral coordination spheres of each gadolinium and In1 atoms relate to the lanthanum and In1 atoms in the La_3InS_6 (La_3InS_6 structure type, space group $P2_12_12$), respectively [4] (Fig. 4). However, the coordination sphere of the In2 atom in the La_3InS_6 is tetrahedral and the tetrahedrons are not connected to each other. On the other hand, in the Gd_3InS_6 the adjacent $[In2S1_2S2_4]$ octahedrons are connected to each other by edges and they form a chain along the *c*-axis (Fig. 4). Thus, the main difference in the crystal structure of the Gd_3InS_6, Sm_3InS_6 [5], Ln_3TSe_6 (Ln = Sm, Gd; T = In, Cr), Tb_3CrSe_6 [26] (space group *Pnnm*) and La_3InS_6 (space group $P2_12_12$) concerns a different position of the In2 atom. Relevant interatomic distances and the coordination numbers of the atoms are listed in Table 5. All the interatomic distances agree well with the sum of the respective ionic radii [18].

Table 4
Interatomic distances (δ, nm) and coordination numbers (c.n.) of the La and In atoms in the structure of the $La_3In_{1.67}S_7$ compound

Atoms	δ (nm)	c.n.
La		
1S1	0.28747(7)	7
1S3	0.2878(1)	
1S2	0.29193(9)	
2S3	0.2980(1)	
1S2	0.3054(1)	
1S3	0.3078(1)	
In1		
1S1	0.2392(1)	4
3S3	0.2451(1)	
In2		
3S2	0.2658(1)	6
3S2	0.2722(1)	

3.4. *Crystal structure of the $La_4Ag_2In_4S_{13}$ compound*

The ternary La–In–S system was expanded to the respective quaternary one and $La_4Ag_2In_4S_{13}$ was obtained. The lanthanum system was chosen as the formation of the La_2CuInS_5 compound

Table 5
Interatomic distances δ (nm) and coordination numbers (c.n.) of the Gd and In atoms in the Gd_3InS_6 compound

Atoms	δ (nm)	c.n.
Gd1		
2S1	0.2809(2)	8
2S6	0.2865(2)	
1S5	0.2866(3)	
2S3	0.2918(1)	
1S2	0.2924(3)	
Gd2		
1S1	0.2737(3)	7
2S6	0.2760(2)	
2S4	0.2839(1)	
1S3	0.2910(3)	
1S5	0.2924(3)	
Gd3		
2S3	0.2785(1)	8
2S2	0.2856(2)	
2S4	0.2961(2)	
1S6	0.3044(3)	
1S5	0.3118(3)	
In1		
4S5	0.2603(1)	6
2S4	0.2606(3)	
In2		
2S1	0.2438(3)	6
4S2	0.2718(1)	

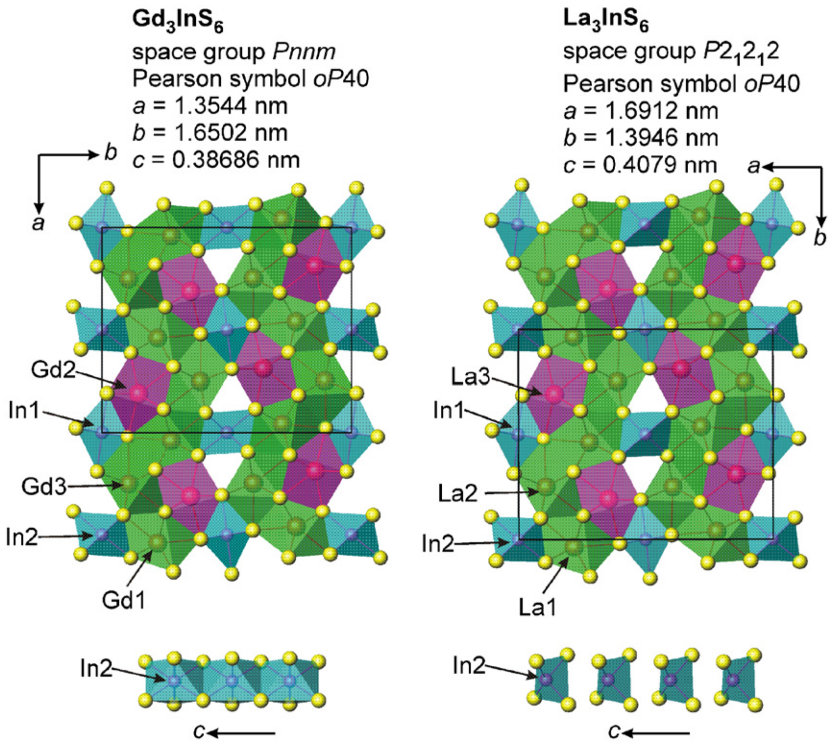

Fig. 4. The packing of the unit cell in the structures of the Gd_3InS_6 and La_3InS_6 compounds.

(space group *Pnma*) has been determined recently in Ref. [27] and in order to check the possibility of the formation of isostructural La_2AgInS_5 compound the sample of the respective composition was prepared. However, lattice parameters significantly differ from those of La_2CuInS_5 and the space group *Pbam* was determined. The positions of all the atoms were determined at the first stage of the refinement, similarly to the crystal structure determination of the $Ln_{4-x}In_{5-y}S_{13}$ compounds. However, unreal values of anisotropic parameters for two In atoms, In4 and In6, and residual electron densities of about 23 and 21 $e/10^{-3}\,nm^3$ at the distances 0.037 and 0.049 nm from these atoms were observed. Therefore, two additional indium atoms (In5 and In7) were located at the extra positions. Refining the site occupancy factors for In4–In7 atoms as a free parameter, the numerical values close to 0.40, 0.30 for In4, In5 and 0.56, 0.22 for In6, In7 were determined, respectively. These values relate to the charge balance requirements and by this reason they were fixed. At this stage, reasonable values of the anisotropic parameters were obtained. The final value of *R*1 factor (~0.03) was also improved significantly from ~0.08 (142 parameters refined). Since atomic scattering factors of the Ag (47) and In (49) atoms differ slightly the analysis of the Ag–S and In–S distances was additional proof of the selection of the Ag and In positions during the crystal structure determination of $La_4Ag_2In_4S_{13}$. Since the ionic radii of Ag^+ are larger than ionic radii of In^{3+} the Ag–S distances are longer than In-S distances (see Table 6).

Table 6
Interatomic distances δ (nm) and coordination numbers (c.n.) of the La, Ag and In atoms in the $La_4Ag_2In_4S_{13}$ compound

Atoms	δ (nm)	c.n.
La1		
2S1	0.2937(1)	8
2S2	0.2962(1)	
2S5	0.2972(1)	
1S6	0.3087(1)	
1S12	0.3186(1)	
La2		
2S3	0.2949(1)	8
2S2	0.2969(1)	
2S7	0.2995(1)	
1S12	0.3001(1)	
1S6	0.3030(1)	
La3		
2S4	0.2933(1)	8
2S9	0.2952(1)	
2S3	0.3009(1)	
1S11	0.3180(1)	
1S12	0.3331(1)	
La4		
2S10	0.2955(1)	8
2S5	0.2962(1)	
2S7	0.2962(1)	
1S13	0.3078(1)	
1S6	0.3197(1)	
Ag1		
1S8	0.2659(1)	6
2S1	0.2747(1)	
2S9	0.2755(1)	
1S11	0.2933(1)	
Ag2		
1S8	0.2647(2)	6
1S13	0.2760(1)	
2S4	0.2785(1)	
2S10	0.2830(1)	
In1		
1S1	0.2490(1)	6
1S3	0.2559(1)	
2S6	0.2634(1)	
2S11	0.2824(1)	
In2		
2S8	0.2436(1)	4
1S2	0.2537(1)	
1S7	0.2538(1)	
In3		
1S4	0.2511(1)	6
2S12	0.2588(1)	
1S5	0.2598(1)	
2S13	0.2837(1)	
In4		
2S9	0.2430(1)	6
4S11	0.2848(1)	
In5		
2S9	0.2459(3)	4
2S11	0.260(1)	
In6		
2S10	0.2401(1)	6
4S13	0.2932(1)	
In7		
2S10	0.2452(3)	4
2S13	0.2618(6)	

In the crystal structure of the $La_4Ag_2In_4S_{13}$ compound one indium atom, In2, is placed in a tetrahedral surroundings and four other are located in octahedral positions (Table 6). However, a displacive disorder for two octahedral positions is observed, $[In4/5S11_4S9_2]$ and $[In6/7S13_4S10_2]$ (Fig. 5). The central position of these two octahedrons is occupied by In4 and In6 atoms with 0.40 and 0.56 site occupancy factors, respectively. The In5 and In7 atoms occupy extra sites which are displaced from the central position of octahedron in the direction of one octahedron's edge. So, there are three positions of the indium atom in one octahedron i.e. one central and two symmetrically dependent displaced positions. Although each of the In4 and In5 positions have fractional value of the site occupancy factor, the sum of the factors of the In4 and two symmetrically dependent In5 positions indicates that this octahedron is fully occupied by the indium atom. The $[In6/7S13_4S10_2]$ octahedron is also fully occupied, since the respective sum related to the In6 and In7 atoms is equal to 1. Overall, the interatomic distances agree well with the sum of the respective ionic radii [18]. However, such close contacts between the In4 and In5 (0.037 nm) and In6–In7 (0.049 nm) atoms do not really exist. Since the In4–S9 and In6–S10 bonds are shorter than the four In4–S11 and In6–S13 distances in the $[In4/5S11_4S9_2]$ and $[In6/7S13_4S10_2]$ octahedrons, these polyhedrons appear to be axially compressed. However, in a more precise description the octahedrons should be considered as horizontally elongated polyhedrons, because the In4–S11 and In9–S13 are greater than the sum of the respective ionic radii. In the elongated octahedrons, the central and the displaced positions of the indium atoms lie in the horizontal plane. Thus, a relatively rigid arrangement of the sulphur atoms make the opportunity to occupy displaced In5

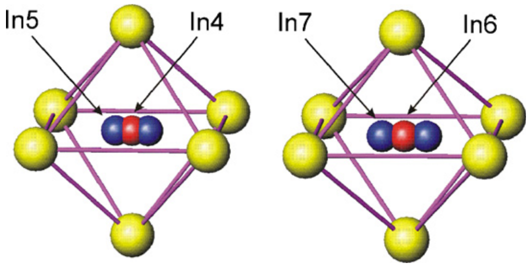

Fig. 5. The octahedral arrangement of the sulphur atoms around the indium atoms in the structure of the $La_4Ag_2In_4S_{13}$.

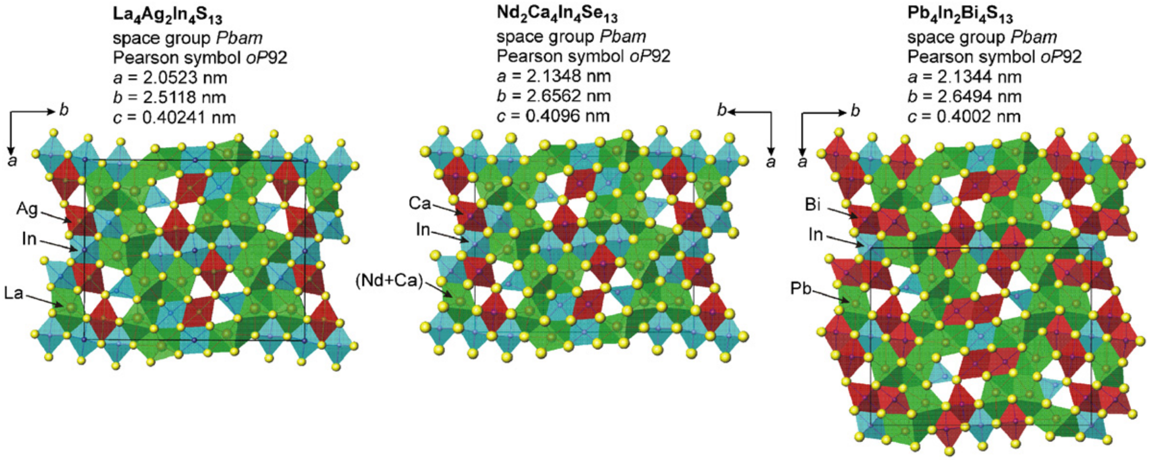

Fig. 6. The structures of the $La_4Ag_2In_4S_{13}$, $Nd_2Ca_4In_4Se_{13}$ and $Pb_4In_2Bi_4S_{13}$ compounds viewed down the *c*-axis.

and In7 sites by the indium atoms and therefore the four coordination sphere can be reasonably considered for these atoms.

The crystal structure of the $La_4Ag_2In_4S_{13}$ compound is similar to the structures of $Nd_2Ca_4In_4Se_{13}$ (space group *Pbam*) [28] and $Pb_4In_2Bi_4S_{13}$ (space group *Pbam*) [29] (Fig. 6). The positions of the S or Se atoms in these structures are similar. The positions of La in $La_4Ag_2In_4S_{13}$ correspond to the positions of the 0.5Nd+0.5Ca statistical mixture in $Nd_2Ca_4In_4Se_{13}$ and the positions of Pb in $Pb_4In_2Bi_4S_{13}$. All these atoms are located in the face-shared bi-capped trigonal prisms (green colour) stacked along the *c*-axis. Silver atoms occupy octahedral sites in $La_4Ag_2In_4S_{13}$ and correspond to the remaining positions of Ca in $Nd_2Ca_4In_4Se_{13}$ and half-occupied positions of Bi in $Pb_4In_2Bi_4S_{13}$. These octahedra are linked into edge-shared chain along the *c*-axis. The indium atoms occupy octahedral and tetrahedral sites in $La_4Ag_2In_4S_{13}$ and $Nd_2Ca_4In_4Se_{13}$. However, indium atoms show disordered position in two octahedrons in the former structure. On the other hand, a half of all the octahedral positions of the bismuth atoms in $Pb_4In_2Bi_4S_{13}$ correspond to the ordered octahedral positions in $La_4Ag_2In_4S_{13}$. So, each site can be occupied by different atoms and also with different site occupancy factors, but overall the pattern created by trigonal prisms, octahedrons and tetrahedrons remain unchanged.

The size of cation [18] seems to play a meaning role on the type of coordination polyhedron in the structures of investigated ternary and quaternary compounds. The largest lanthanide cations are located in mono- or bi-capped trigonal prisms. The medium-sized silver cations adopt octahedral geometry. The smallest indium cations are located in the octahedral or tetrahedral cavities. However, the tetrahedral arrangement of the sulphur atoms appears to be more privileged for the indium, since the larger octahedral cavities can involve a disordered position of the indium atom and the four coordination sphere is reasonably considered for the extra positions.

4. Supplementary material

Further details of the crystal structure investigation(s) can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number: $La_{3.92}In_{4.76}S_{13}$—419,274, $Ce_{3.88}In_{4.79}S_{13}$—419,273, $Pr_{3.92}In_{4.76}S_{13}$—410,272, $Nd_{3.90}In_{4.76}S_{13}$—419,271, $La_3In_{1.67}S_7$—419,270, Gd_3InS_6—419,269, $La_4Ag_2In_4S_{13}$—419,268.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.06.037

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