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Crystal structures of the compounds $YCuS_2$, Y_3CuSnS_7 and $YCuPbS_3$

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Abstract

The crystal structure of the $YCuS_2$ compound was investigated using X-ray powder diffraction (space group $P2_12_12_1$, $a = 0.62756(2)$ nm, $b = 1.33863(4)$ nm, $c = 0.39704(1)$ nm, Pearson symbol *oP*16, $R_I = 0.0628$). The S atoms are stacked in a close-packed arrangement with layers in the sequence AB. The Y atoms occupy half of the octahedral interstices, the Cu atoms occupy quarter of the tetrahedral interstices. Using X-ray powder diffraction, the crystal structures of the compounds Y_3CuSnS_7 (La_3CuSiS_7 structure type, space group $P6_3$, $a = 0.96766(1)$ nm, $c = 0.61717(1)$ nm, Pearson symbol *hP*24, $R_I = 0.0694$) and $YCuPbS_3$ (β-$BaLaCuSe_3$ structure type, space group *Pnma*, $a = 1.01957(7)$ nm, $b = 0.39370(2)$ nm, $c = 1.29625(6)$ nm, Pearson symbol *oP*24, $R_I = 0.0765$) were determined.

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Keywords: Chalcogenides; Y compounds; Cu compounds; Sn compounds; Pb compounds; S compounds; Crystal structure; X-ray powder diffraction

1. Introduction

The crystal structure of the $YCuS_2$ compound has been described as $ErAgSe_2$ structure type (space group $P2_12_12_1$) in [1] and $YCuS_2$ structure type (space group *Pnma*) in [2]. The existence of the YCu_3S_3 compound with $ErCu_3S_3$ structure type (space group $P\bar{3}$) has been determined in [3]. One quaternary Y_3CuSnS_7 compound ($Ce_6Al_{10/3}S_{14}$ structure type, space group $P6_3$) [4] has been found in the Y_2S_3–Cu_2S–SnS_2 system. The lattice parameters have been refined. No quaternary compounds of the Y_2S_3–Cu_2S–PbS system have been reported yet in literature.

The crystal structures of the compounds $YCuS_2$, Y_3CuSnS_7 and $YCuPbS_3$ are given in the present paper.

2. Experimental details

The alloys were prepared by fusion of the high purity elements (the purity of the ingredients was better than 99.9 wt.%) in evacuated quartz ampoules. The synthesis was realized in a shaft furnace with a heating rate of 20 K/h. The ampoules with the samples were heated to a maximal temperature of 1420 K. The samples were kept at the maximal temperature during 4 h. After that they were cooled slowly to 870 K with a rate of 10 K/h and annealed at respective temperature during 240 h. After annealing the ampoules with the samples were quenched in cold water.

X-ray powder diffraction patterns of the samples for the crystal structure determination were recorded using a DRON-4–13 powder diffractometer (CuKα radiation, $10^\circ \le 2\Theta \le 100^\circ$, step scan mode with a step size of 0.05° and counting time of 20 s per data point).The crystal structure determination was performed using the CSD [5] and DBWS-9411 [6] programs.

3. Results and discussion

3.1. Crystal structure of the $YCuS_2$ compound

The formation of the ternary $YCuS_2$ compound was conformed during an investigation of the phase relations

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Table 1
Results of the crystal structure determination of the $YCuS_2$, Y_3CuSnS_7 and $YCuPbS_3$ compounds

Compound	$YCuS_2$	Y_3CuSnS_7	$YCuPbS_3$
Structure type	$YCuS_2$	La_3CuSiS_7	β-$BaLaCuSe_3$
Number of formula units per unit cell	4	2	4
Space group	$P2_12_12_1$	$P6_3$	*Pnma*
a (nm)	0.62756(2)	0.96766(1)	1.01957(7)
b (nm)	1.33863(4)	0.96766(1)	0.39370(2)
c (nm)	0.39704(1)	0.61717(1)	1.29625(6)
Cell volume (nm^3)	0.33354(3)	0.50048(2)	0.52032(9)
Number of atoms in cell	16.00	24.00	24.00
Calculated density (g/cm^3)	4.3125	4.4680	5.818
Radiation and wavelength (nm)	Cu 0.154178	Cu 0.154178	Cu 0.154178
Diffractometer	Powder DRON-4–13	Powder DRON-4–13	Powder DRON-4–13
Mode of refinement	Full profile	Full profile	Full profile
Number of atom sites	4	6	6
Structure solution and refinement	CSD	CSD	DBWS-9411
R_I	0.0628	0.0694	0.0765
R_P	0.0981	0.0969	0.0377[a]
Texture axis and parameter	[1 0 0] 1.15(2)	[1 1 0] 0.99(3)	[0 0 1] 0.910(5)

[a] Presence of the phases $YCuS_2$ and PbS was taken into account during the refinement procedure (see Fig. 7).

Table 2
Atomic coordinates and isotropic temperature factors for the $YCuS_2$ compound

Atom	Position	*x/a*	*y/b*	*z/c*	$B_{iso} \times 10^2$ (nm^2)
Y	4(a)	0.2420(2)	0.13515(7)	0.249(1)	0.55(2)
Cu	4(a)	0.6431(3)	0.0550(1)	0.779(1)	2.19(5)
S1	4(a)	0.0129(4)	0.0386(2)	0.765(3)	0.30(8)
S2	4(a)	0.4806(4)	0.2093(2)	0.730(3)	0.12(9)

in the Y_2S_3–Cu_2S system. The peaks of the X-ray powder diffraction pattern of the sample $YCuS_2$ were indexed conclusively on the basis of a primitive orthorhombic lattice with $a = 0.62756(2)$ nm, $b = 1.33863(4)$ nm and $c = 0.39704(1)$ nm. The obtained lattice parameters are close to those reported for $YCuS_2$ in [1]. According to [1] the $ErAgSe_2$ structure type (space group $P2_12_12_1$) [7] as a starting model was use by us for the crystal structure investigation of the $YCuS_2$ compound. Our attempts to determine the positional parameters in the model of $ErAgSe_2$ were not successful. No reasonable results were obtained. Finally, the crystal structure of the $YCuS_2$ compound was determined in an independent way. By assuming space group symmetry $P2_12_12_1$ we were able to extract a plausible structural model from the powder X-ray intensities by means of direct methods and difference Fourier syntheses. Table 1 contains the essential technical and crystallographic data of the structure refinements. The atomic coordinates and isotropic temperature factors are listed in Table 2. All crystallographic positions are fully occupied. The experimental and calculated diffractograms and the corresponding difference diagram for $YCuS_2$ are shown in Fig. 1. Relevant interatomic distances and coordination numbers of the atoms are listed in Table 3. The

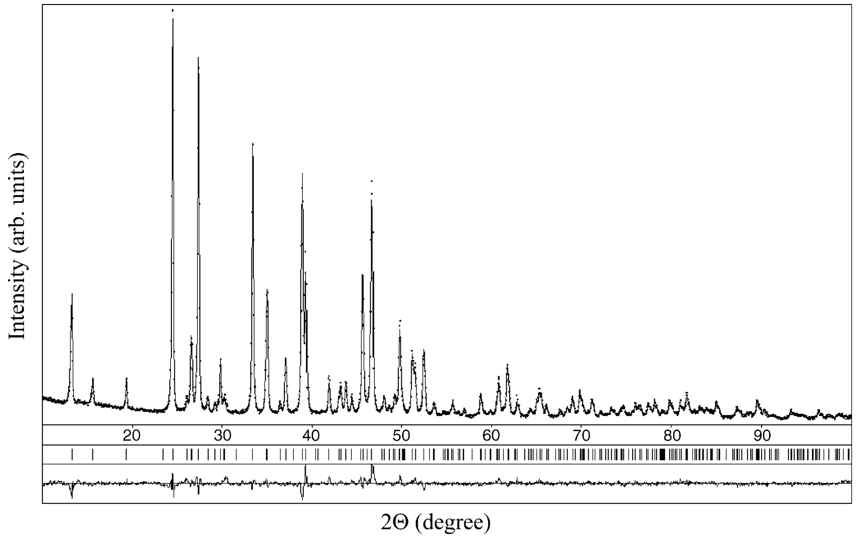

Fig. 1. The experimental and calculated diffractograms and the corresponding difference diagram for $YCuS_2$.

Table 3
Interatomic distances δ (nm) and coordination numbers (C.N.) of the atoms in the $YCuS_2$ structure

Atoms		δ (nm)	C.N.
Y	–1S2	0.2619(9)	6
	–1S2	0.2652(3)	
	–1S1	0.2728(9)	
	–1S2	0.2736(9)	
	–1S1	0.2789(3)	
	–1S1	0.281(1)	
Cu	–1S2	0.2312(4)	4
	–1S1	0.2332(3)	
	–1S1	0.250(1)	
	–1S1	0.258(1)	
S1	–1Cu	0.2332(3)	6
	–1Cu	0.250(1)	
	–1Cu	0.258(1)	
	–1Y	0.2728(9)	
	–1Y	0.2789(3)	
	–1Y	0.281(1)	
S2	–1Cu	0.2312(4)	4
	–1Y	0.2619(9)	
	–1Y	0.2652(3)	
	–1Y	0.2736(9)	

interatomic distances agree well with the sum of the respective ionic radii [8].

A crystal structure refinement of the $YCuS_2$ compound in the model of space group *Pnma* [2] was also performed. Better agreements between observed and calculated intensities were observed for space group $P2_12_12_1$ ($R_I = 0.0628$) compared with space group *Pnma* ($R_I = 0.0699$).

The unit cell, coordination polyhedra of the Y (a), Cu (b), S1 (c) and S2 (d) atoms and the layers of S atoms of hexagonal topology in the structure of the $YCuS_2$ compound are shown in Fig. 2. The Y and S1 atoms are surrounded by octahedra, the Cu and S2 atoms by tetrahedra. The atoms of S in the structure of the $YCuS_2$ compound are stacked in a close-packed arrangement with layers in the sequence AB. The Y atoms occupy half of the octahedral interstices, the Cu atoms occupy quarter of the tetrahedral interstices (see Fig. 3). The Se atoms in the structure of the $ErAgSe_2$ compound are stacked also in a close-packed arrangement with layers in the sequence AB, but these layers are significantly distorted compared with the respective layers of the $YCuS_2$ compound. Half of the octahedral interstices are occupied by Er atoms. The remaining octahedral interstices are occupied by Ag atoms (Fig. 3). The Er atoms are located in the centres of the octahedra. The Ag atoms are shifted from the centres of the respective octahedra in a way as shown in Fig. 4. Two of the Se atoms in the Ag-centered octahedra are located at the longer distances from Ag compared with the remaining four Se atoms. Accordingly, a tetrahedral surrounding exists for the Ag atoms. The surroundings of the S atoms in the structure of the $YCuS_2$ compound and the Se atoms in the structure of the $ErAgSe_2$ compound are different. The atoms of S1(S2) have octahedral (tetrahedral) surrounding in $YCuS_2$. Five neighbours exist for Se1(Se2) atoms in $ErAgSe_2$.

The projections of the unit cells of the compounds $YCuS_2$ and $ErAgSe_2$ on the XY plane are shown in Fig. 5. The locations of the Y(Er) and S(Se) atoms in both structures are similar. Significant differences exist in the locations of the Cu and Ag atoms.

3.2. *Crystal structure of the Y_3CuSnS_7 compound*

The formation of quaternary compound with composition Y_3CuSnS_7 was confirmed during the investigation of the phase relations in the Y_2S_3–Cu_2S–SnS_2 system. The peaks of the X-ray powder diffraction pattern were indexed on the basis of a hexagonal unit cell with the lattice parameters a = 0.96766(1) nm and c = 0.61717(1) nm. The obtained lattice parameters are close to those reported for Y_3CuSnS_7 in [4]. The $Ce_6Al_{10/3}S_{14}$ structure type (space group $P6_3$) [9], as proposed in [4], was used as a starting model for the crystal structure determination. Results of the crystal structure

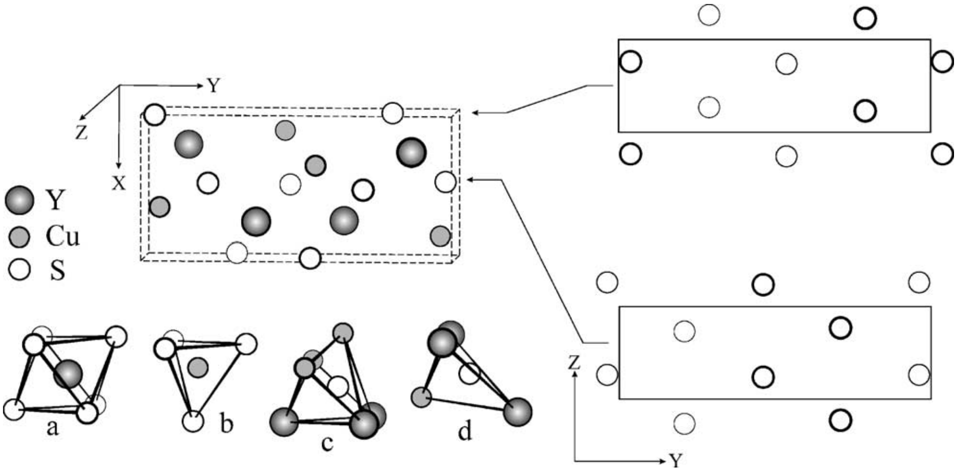

Fig. 2. The unit cell, coordination polyhedra of the Y (a), Cu (b), S1 (c) and S2 (d) atoms and the layers of S atoms of hexagonal topology in the structure of the $YCuS_2$ compound.

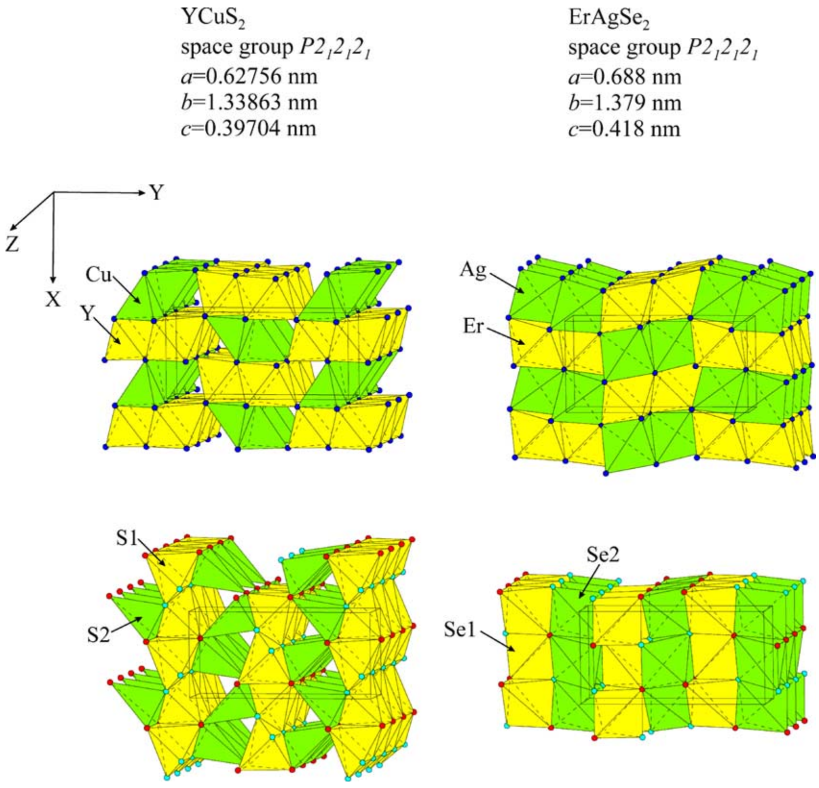

Fig. 3. The packing of cation- and anion-centered polyhedra in the structures of the $YCuS_2$ and $ErAgSe_2$ compounds.

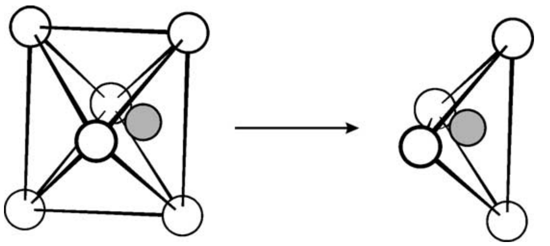

Fig. 4. Transformation from octahedron to tetrahedron for Ag-centered polyhedron in the structure of the $ErAgSe_2$ compound.

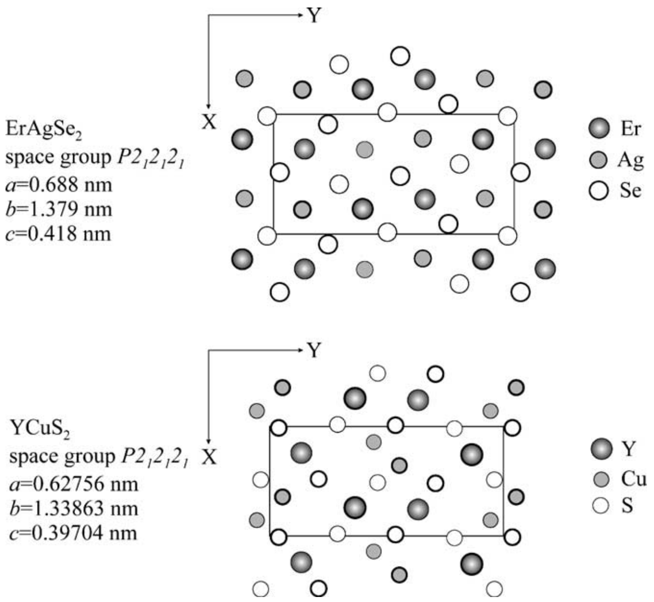

Fig. 5. The projections of the unit cells of the compounds $YCuS_2$ and $ErAgSe_2$ on XY plane.

determination are given in Table 1, whereas, atomic coordinates and isotropic temperature factors are listed in Table 4. Since the Cu and Sn atoms occupy independent crystallographic positions, the La_3CuSiS_7 structure type (space group $P6_3$) [10] is used for the description of the crystal structure of the Y_3CuSnS_7 compound. The experimental and calculated diffractograms and the corresponding difference diagram for Y_3CuSnS_7 are shown in Fig. 6. The interatomic distances (Table 5) agree well with the sum of the ionic radii [8]. The coordination surroundings of the respective atoms in

Table 4
Atomic coordinates and isotropic temperature factors for the Y_3CuSnS_7 compound

Atom	Position	*x/a*	*y/b*	*z/c*	$B_{iso} \times 10^2$ (nm^2)
Y	6(c)	0.3623(2)	0.1552(2)	0.3737(8)	0.63(3)
Cu	2(a)	0	0	0.0000[a]	0.83(8)
Sn	2(b)	1/3	2/3	0.3095(8)	0.20(5)
S1	6(c)	0.2617(4)	0.1135(5)	0.9485(9)	0.3(1)
S2	6(c)	0.5200(6)	0.4351(6)	0.6307(9)	0.5(1)
S3	2(b)	1/3	2/3	0.692(1)	0.6(2)

[a] Fixed.

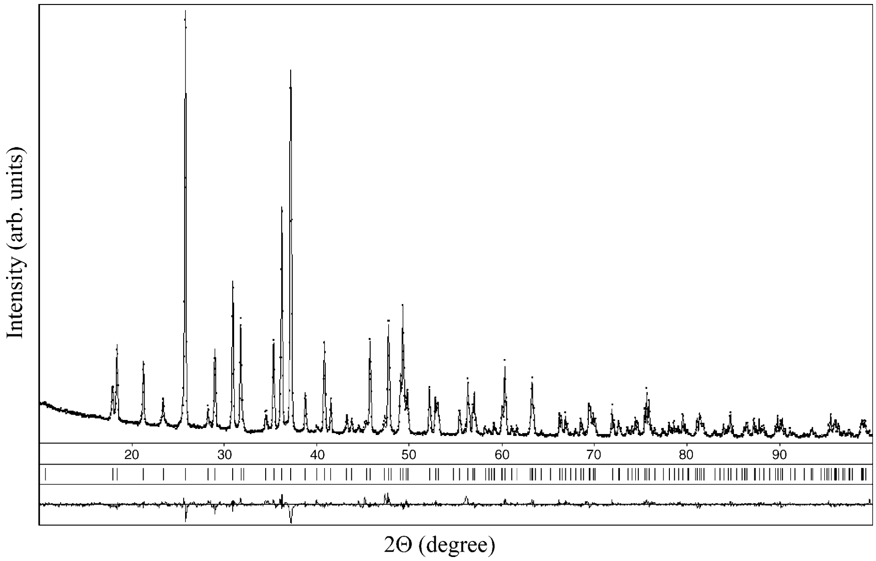

Fig. 6. The experimental and calculated diffractograms and the corresponding difference diagram for Y_3CuSnS_7.

Table 5
Interatomic distances δ (nm) and coordination numbers (C.N.) of the atoms in the Y_3CuSnS_7 structure

Atoms		δ (nm)	C.N.
Y	–1S1	0.2750(5)	7
	–1S1	0.2757(7)	
	–1S1	0.2775(5)	
	–1S3	0.2797(4)	
	–1S2	0.2837(6)	
	–1S2	0.2856(7)	
	–1S2	0.3127(6)	
Cu	–3S1	0.2223	3
Sn	–1S3	0.236(1)	4
	–3S2	0.2366(7)	
S1	–1Cu	0.2223	4
	–1Y	0.2750(5)	
	–1Y	0.2757(7)	
	–1Y	0.2775(5)	
S2	–1Sn	0.2366(7)	4
	–1Y	0.2837(6)	
	–1Y	0.2856(6)	
	–1Y	0.3127(7)	
S3	–1Sn	0.236(1)	4
	–3Y	0.2797(4)	

the structures of the compounds Y_3CuSnS_7 and $Y_3CuSnSe_7$ [11] are similar.

3.3. *Crystal structure of the $YCuPbS_3$ compound*

The formation of a new quaternary $YCuPbS_3$ compound was observed during an investigation of the phase relations in the Y_2S_3–Cu_2S–PbS system. The sample with composition $YCuPbS_3$ was used for the crystal structure determination of this compound. The presence of peaks of the $YCuS_2$ and PbS phases was observed in the X-ray powder diffraction pattern of the sample. The remaining peaks were indexed on the basis of a primitive orthorhombic lattice with a = 1.01957(7) nm, b = 0.39370(2) nm, c = 1.29625(6) nm. The similarity of the X-ray powder diffraction patterns of the $YCuPbS_3$ and $YCuPbSe_3$ [11] compounds allows us to conclude that these compounds are isostructural. Accordingly, the crystal structure of the β-$BaLaCuSe_3$ (space group *Pnma*) compound [12] was used as a starting model for the crystal structure determination of the $YCuPbS_3$ compound. Table 1 contains the essential technical and crystallographic data of the structure determination. The atomic coordinates and isotropic temperature factors are listed in Table 6. The Y, Pb and S atoms in $YCuPbS_3$ occupy the positions of the La, Ba and Se atoms, respectively, in β-$BaLaCuSe_3$. The positions of the Cu atoms in both compounds are identical. All crystallographic positions are fully occupied. The presence of the phases $YCuS_2$ and PbS was taking into account during the refinement procedure. The experimental and calculated diffractograms and the corresponding difference diagram for $YCuPbS_3$ (1: $YCuPbS_3$, 2: $YCuS_2$ and 3: PbS) are shown in Fig. 7. Relevant interatomic distances and coordination numbers of the atoms are listed in Table 7. The interatomic distances are close to the sum of the respective ionic radii [8]. The coordination polyhedra of the respective atoms in the structures of the compounds $YCuPbS_3$ and $YCuPbSe_3$ [11] are similar except S2(Se2)

Table 6
Atomic coordinates and isotropic temperature factors for the $YCuPbS_3$ compound

Atom	Position	*x/a*	*y/b*	*z/c*	$B_{iso} \times 10^2$ (nm^2)
Y	4(c)	0.499(2)	1/4	0.248(2)	0.5
Cu	4(c)	0.766(2)	1/4	0.7836(5)	0.5
Pb	4(c)	0.749(1)	1/4	0.5043(3)	0.5
S1	4(c)	0.258(5)	1/4	0.3278(8)	0.5
S2	4(c)	0.455(3)	1/4	0.600(2)	0.5
S3	4(c)	0.073(2)	1/4	0.619(2)	0.5

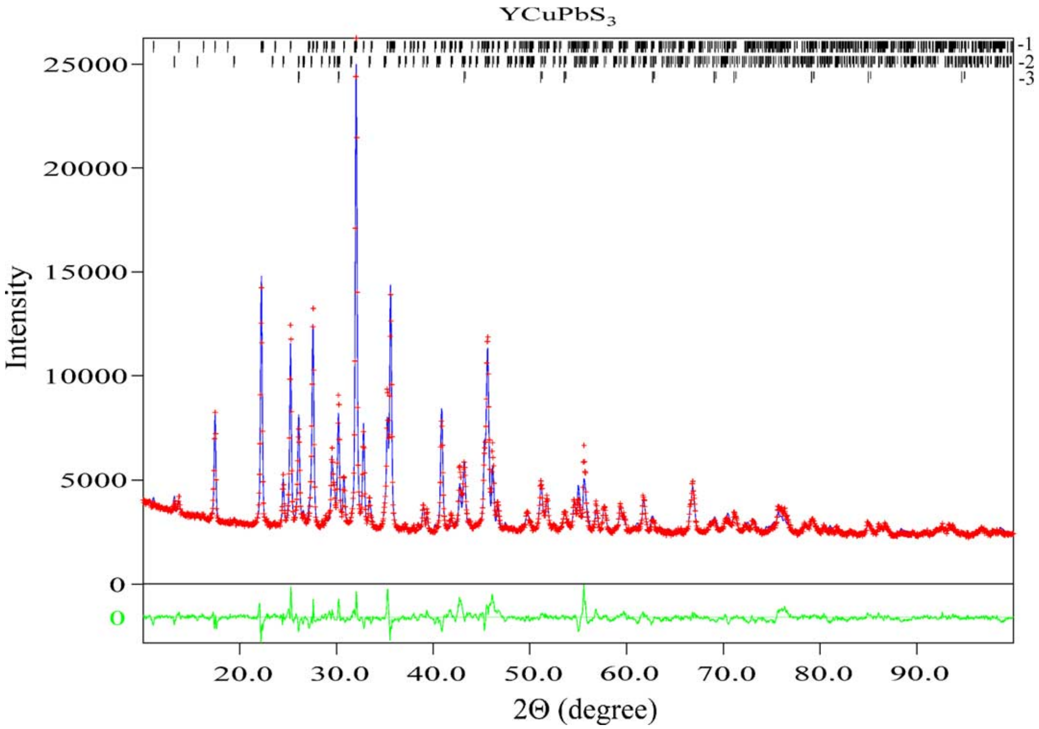

Fig. 7. The experimental and calculated diffractograms and the corresponding difference diagram for YCuPbS$_3$ (1: YCuPbS$_3$, 2: YCuS$_2$ and 3: PbS).

Table 7
Interatomic distances δ (nm) and coordination numbers (C.N.) of the atoms in the YCuPbS$_3$ structure

Atoms		δ (nm)	C.N.
Y	–1S1	0.267(5)	6
	–2S3	0.269(2)	
	–1S1	0.282(5)	
	–2S2	0.282(3)	
Cu	–1S3	0.234(3)	4
	–1S2	0.245(3)	
	–2S1	0.2454(9)	
Pb	–2S1	0.2935(8)	7
	–2S3	0.312(2)	
	–2S2	0.317(2)	
	–1S2	0.324(3)	
S1	–2Cu	0.2454(9)	6
	–1Y	0.267(5)	
	–1Y	0.282(5)	
	–2Pb	0.2935(8)	
S2	–1Cu	0.245(3)	6
	–2Y	0.282(3)	
	–2Pb	0.317(2)	
	–1Pb	0.324(3)	
S3	–1Cu	0.234(3)	5
	–2Y	0.269(2)	
	–2Pb	0.312(2)	

and S3(Se3). In the case of the YCuPbSe$_3$ structure the Se2 and Se3 atoms have five and six neighbors, respectively. The S2 and S3 atoms are surrounded by six and five cations in the structure of the YCuPbS$_3$ compound. This fact can be explained by slight shifting of the atoms in the case of YCuPbS$_3$ compared with YCuPbSe$_3$.

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