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Crystal structures of the $R_3CuSnSe_7$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) compounds

L.D. Gulay*, I.D. Olekseyuk

Department of General and Inorganic Chemistry, Volyn State University, Voli Ave 13, 43009 Lutsk, Ukraine

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Abstract

The crystal structures of the $R_3CuSnSe_7$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) compounds (La_3CuSiS_7 structure type, space group $P6_3$, Pearson symbol hP24) were determined by means of X-ray powder diffraction: a = 1.07211(1) nm, c = 0.62770(1) nm, R_I = 0.0613 ($La_3CuSnSe_7$); a = 1.06310(2) nm, c = 0.62562(1) nm, R_I = 0.0737 ($Ce_3CuSnSe_7$); a = 1.05613(4) nm, c = 0.62532(3) nm, R_I = 0.0964 ($Pr_3CuSnSe_7$); a = 1.05002(4) nm, c = 0.62523(2) nm, R_I = 0.0808 ($Nd_3CuSnSe_7$); a = 1.03809(2) nm, c = 0.62848(2) nm, R_I = 0.0745 ($Sm_3CuSnSe_7$); a = 1.02435(2) nm, c = 0.63409(2) nm, R_I = 0.0834 ($Gd_3CuSnSe_7$); a = 1.01894(2) nm, c = 0.63642(2) nm, R_I = 0.0881 ($Tb_3CuSnSe_7$); a = 1.01359(3) nm, c = 0.63809(3) nm, R_I = 0.0916 ($Dy_3CuSnSe_7$).
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Keywords: Chalcogenides; Rare earth compounds; Cu compounds; Sn compounds; Se compounds; Crystal structure; X-ray powder diffraction

1. Introduction

The $RCuSe_2$ (R = La, Ce, Pr, Nd, Sm and Gd) compounds ($LaCuS_2$ structure type, space group $P2_1/c$) have been investigated in [1]. The compounds with the compositions $RCuSe_2$–$R_{2/3}Cu_2Se_2$ (R = Y, Tb, Dy, Ho, Er, Tm, Yb and Lu) and $GdCu_3Se_3$ ($ErCu_3S_3$ structure type, space group $P\bar{3}$) have been reported in [2]. The existence of the R_5CuSe_8 (R = La, Ce, Pr, Nd, Sm and Gd) compounds (Th_3P_4 structure type, space group $I\bar{4}3d$) has been reported in [3]. Recently, the existence of the Sm_3CuSe_6 compound (Sm_3CuSe_6 structure type, space group $Pbcm$) has been established in [4]. The crystal structures of the compounds $Y_3Cu_{0.685}Se_6$ (Sm_3CuSe_6 structure type, space group $Pbcm$) and $Y_3CuSnSe_7$ (La_3CuSiS_7 structure type, space group $P6_3$) have been reported in [5].

The crystal structures of new quaternary $R_3CuSnSe_7$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) compounds are given in the present paper.

* Corresponding author.
E-mail address: gulay@lab.univer.lutsk.ua (L.D. Gulay).

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2. Experimental details

The samples were prepared by melting high purity elements (the purity of the ingredients was better than 99.9 wt.%). Calculated amounts of the components were sealed in evacuated quartz ampoules. The synthesis was realized in a shaft furnace. The ampoules with the components were heated with a heating rate of 30 K/h to the maximal temperature, 1420 K. They were kept at the maximal temperature during 4 h. After that the furnace with the samples was cooled slowly (10 K/h) to 870 K. Homogeneous annealing was applied at this 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 (Cu Kα radiation, $10^\circ \leq 2\Theta \leq 100^\circ$, 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 [6] and DBWS-9411 [7] programs.

Table 1
Results of the crystal structure determination of the $R_3CuSnSe_7$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) compounds

Compound	a (nm)	c (nm)	c/a	V (nm^3)	Calculated density (g/cm^3)	R_I	R_P
$La_3CuSnSe_7$	1.07211(1)	0.62770(1)	0.585	0.62483(2)	6.1208	0.0613	0.1008
$Ce_3CuSnSe_7$	1.06310(2)	0.62562(1)	0.588	0.61234(3)	6.2654	0.0737	0.0997
$Pr_3CuSnSe_7$	1.05613(4)	0.62532(3)	0.592	0.60404(7)	6.3645	0.0964	0.0426
$Nd_3CuSnSe_7$	1.05002(4)	0.62523(2)	0.595	0.59699(6)	6.4953	0.0808	0.0297
$Sm_3CuSnSe_7$	1.03809(2)	0.62848(2)	0.605	0.58654(4)	6.7148	0.0745	0.1469
$Gd_3CuSnSe_7$	1.02435(2)	0.63409(2)	0.619	0.57620(4)	6.9545	0.0834	0.1446
$Tb_3CuSnSe_7$	1.01894(2)	0.63642(2)	0.625	0.57223(2)	7.0319	0.0881	0.1418
$Dy_3CuSnSe_7$	1.01359(3)	0.63809(3)	0.630	0.56773(6)	7.1505	0.0916	0.1633

3. Results and discussion

New quaternary $R_3CuSnSe_7$ compounds were observed during the investigation of the phase relations in the R_2Se_3-Cu_2Se-$SnSe_2$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) systems. The similarity of the X-ray powder diffraction patterns of these compounds and that of $Y_3CuSnSe_7$ (La_3CuSiS_7 structure type, space group $P6_3$) investigated in [5] allows us to conclude that the $R_3CuSnSe_7$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) compounds are isostructural with La_3CuSiS_7 [8].

The samples of the $R_3CuSnSe_7$ (R = La, Ce, Sm, Gd, Tb and Dy) compounds seem to be single-phase. The X-ray powder diffraction pattern of the sample with Pr contains peaks of the main phase $Pr_3CuSnSe_7$ and weak additional peaks of $PrCuSe_2$ and Cu_2SnSe_3. The presence of weak additional peaks of the phases $NdSe_{1.9}$ and Cu_2SnSe_3 was observed in the X-ray powder diffraction pattern of the $Nd_3CuSnSe_7$ sample. The peaks of the X-ray powder diffraction patterns of these samples were indexed on the basis of hexagonal unit cells with the lattice parameters listed in

Table 2
Atomic coordinates and isotropic temperature factors for the $R_3CuSnSe_7$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) compounds

Compound	R 6(*c*) *x y z* $B_{iso} \times 10^2$ (nm^2)	Cu 2(*a*) 0 0 *z* (*z* = 0.0000*) $B_{iso} \times 10^2$ (nm^2)	Sn 2(*b*) 1/3 2/3 *z* $B_{iso} \times 10^2$ (nm^2)	Se1 6(c) *x y z* $B_{iso} \times 10^2$ (nm^2)	Se2 6(*c*) *x y z* $B_{iso} \times 10^2$ (nm^2)	Se3 2(*b*) 1/3 2/3 *z* $B_{iso} \times 10^2$ (nm^2)
$La_3CuSnSe_7$	*x* = 0.3568(1) *y* = 0.1357(2) *z* = 0.4633(4) *B* = 0.82(3)	*B* = 1.6(2)	*z* = 0.3845(4) *B* = 0.74(9)	*x* = 0.2561(1) *y* = 0.0980(2) *z* = 0.9856(5) *B* = 0.81(7)	*x* = 0.5158(3) *y* = 0.4272(3) *z* = 0.7183(5) *B* = 1.11(8)	*z* = 0.7760(7) *B* = 0.7(2)
$Ce_3CuSnSe_7$	*x* = 0.3564(1) *y* = 0.1354(2) *z* = 0.4546(4) *B* = 0.59(4)	*B* = 1.3(2)	*z* = 0.3764(5) *B* = 0.8(1)	*x* = 0.2577(2) *y* = 0.1002(3) *z* = 0.9786(5) *B* = 0.73(8)	*x* = 0.5146(4) *y* = 0.4289(3) *z* = 0.7033(5) *B* = 0.86(9)	*z* = 0.7691(7) *B* = 0.4(2)
$Pr_3CuSnSe_7$	*x* = 0.3546(5) *y* = 0.1350(5) *z* = 0.466(7) *B* = 0.5	*B* = 0.5	*z* = 0.381(7) *B* = 0.5	*x* = 0.2522(9) *y* = 0.097(1) *z* = 0.992(7) *B* = 0.5	*x* = 0.511(1) *y* = 0.430(1) *z* = 0.719(7) *B* = 0.5	*z* = 0.785(7) *B* = 0.5
$Nd_3CuSnSe_7$	*x* = 0.3576(4) *y* = 0.1396(4) *z* = 0.458(5) *B* = 0.7(1)	*B* = 1.4(5)	*z* = 0.382(5) *B* = 1.0(3)	*x* = 0.2603(7) *y* = 0.1015(8) *z* = 0.995(5) *B* = 0.6(1)	*x* = 0.514(1) *y* = 0.4346(8) *z* = 0.714(5) *B* = 0.3(2)	*z* = 0.774(6) *B* = 0.8(5)
$Sm_3CuSnSe_7$	*x* = 0.3582(2) *y* = 0.1424(2) *z* = 0.4414(5) *B* = 0.44(5)	*B* = 1.4(3)	*z* = 0.3679(6) *B* = 0.3(1)	*x* = 0.2598(4) *y* = 0.1055(4) *z* = 0.9844(7) *B* = 0.3(1)	*x* = 0.5172(5) *y* = 0.4353(4) *z* = 0.6930(7) *B* = 0.4(1)	*z* = 0.763(1) *B* = 0.4(2)
$Gd_3CuSnSe_7$	*x* = 0.3581(2) *y* = 0.1490(2) *z* = 0.4154(5) *B* = 0.65(7)	*B* = 1.1(3)	*z* = 0.3401(6) *B* = 0.8(2)	*x* = 0.2623(3) *y* = 0.1138(4) *z* = 0.9743(6) *B* = 0.3(1)	*x* = 0.5181(5) *y* = 0.4377(4) *z* = 0.6657(7) *B* = 0.4(2)	*z* = 0.735(1) *B* = 0.4(3)
$Tb_3CuSnSe_7$	*x* = 0.3597(2) *y* = 0.1535(2) *z* = 0.4027(5) *B* = 0.69(5)	*B* = 1.9(3)	*z* = 0.3298(5) *B* = 0.8(1)	*x* = 0.2617(3) *y* = 0.1135(4) *z* = 0.9676(6) *B* = 0.38(9)	*x* = 0.5181(5) *y* = 0.4390(4) *z* = 0.6537(6) *B* = 0.5(1)	*z* = 0.7186(9) *B* = 0.3(2)
$Dy_3CuSnSe_7$	*x* = 0.3588(3) *y* = 0.1557(3) *z* = 0.3958(7) *B* = 0.5(1)	*B* = 1.1(1)	*z* = 0.3229(8) *B* = 0.6(3)	*x* = 0.2632(5) *y* = 0.1240(8) *z* = 0.9657(9) *B* = 0.6(2)	*x* = 0.5165(9) *y* = 0.4381(7) *z* = 0.638(1) *B* = 1.2(2)	*z* = 0.715(1) *B* = 0.6(3)

* Fixed.

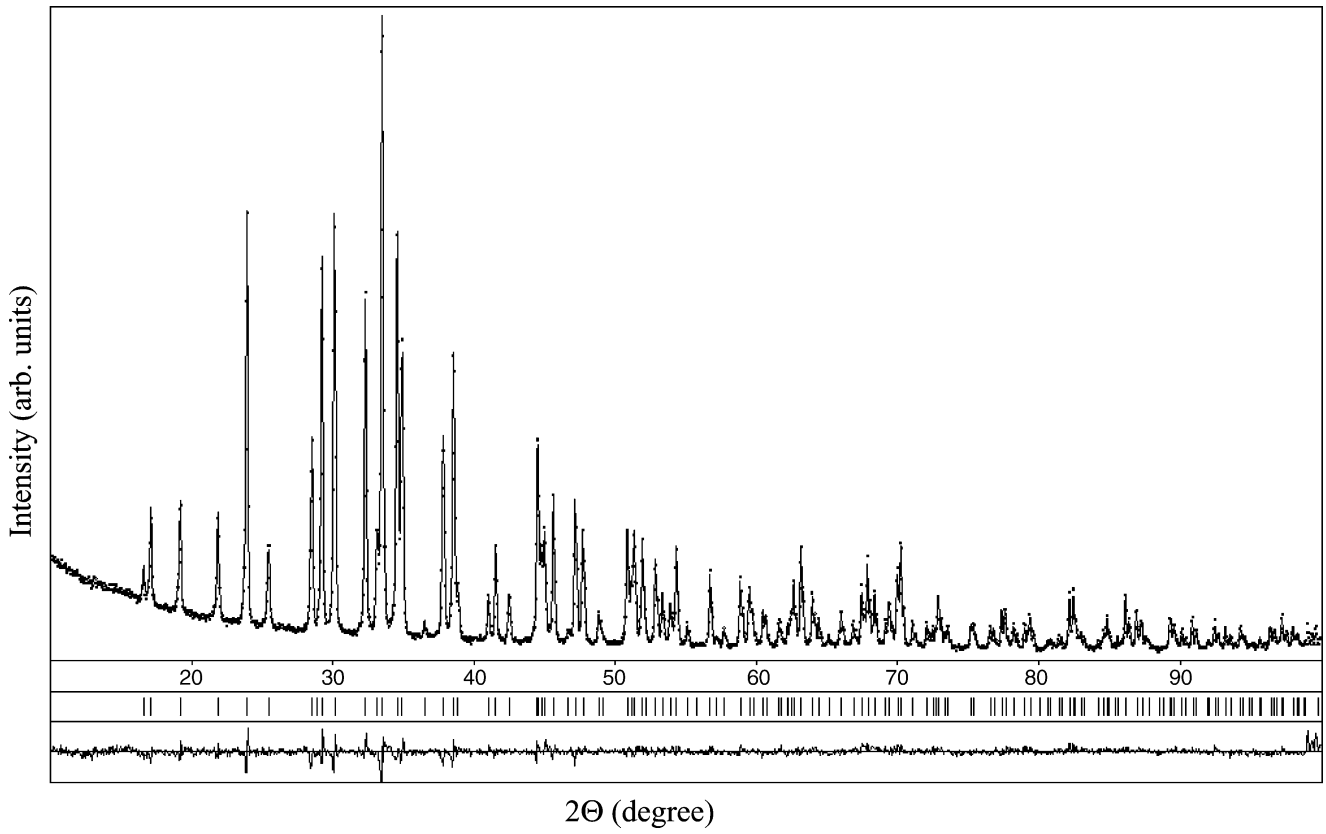

Fig. 1. The experimental and calculated diffractograms and the corresponding difference diagram for $La_3CuSnSe_7$.

Table 1. Results of the crystal structure determination of the $R_3CuSnSe_7$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) compounds (La_3CuSiS_7 structure type, space group $P6_3$) are given in Table 1. Atomic coordinates and isotropic temperature factors are listed in Table 2. The CSD software package was used in the refinement procedure of the $R_3CuSnSe_7$ (R = La, Ce, Sm, Gd, Tb and Dy) compounds for which single-phase samples were obtained. The DBWS-9411 program was used for the crystal structure determination of the $R_3CuSnSe_7$ (R = Pr and Nd) compounds. The presence of the phases $PrCuSe_2$ [1,9], Cu_2SnSe_3 [10] and $NdSe_{1.9}$ [11], Cu_2SnSe_3 [10] was taken into account during the refinement procedure of the samples $Pr_3CuSnSe_7$ and $Nd_3CuSnSe_7$, respectively. All crystallographic positions are fully occupied. The experimental and calculated diffractograms and the corresponding difference diagram for $La_3CuSnSe_7$ are shown in Fig. 1.

The dependence of the lattice constants (a, c) and unit cell volumes (V) of the $R_3CuSnSe_7$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) and $Y_3CuSnSe_7$ [5] compounds on the ionic radii of the rare earth elements [12] are shown in Fig. 2. The unit cell volumes agree well with the ionic radii of the rare earth elements. The lattice constants a correlate well with the sizes of the rare earth ions. The differences between the c parameters of the $R_3CuSnSe_7$ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) compounds are not significant compared with the differences between the a parameters. The dependence of the lattice parameter c from the sizes of the rare earth ions is not regular.

Relevant interatomic distances and coordination numbers of the atoms in the structure of the $La_3CuSnSe_7$ compound are listed in Table 3. The interatomic distances agree well with

Table 3
Interatomic distances δ (nm) and coordination numbers (C.N.) of the atoms in the $La_3CuSnSe_7$ structure

Atoms		δ (nm)	C.N.
La	–1Se1	0.2983(3)	7
	–1Se1	0.2996(3)	
	–1Se2	0.3057(4)	
	–1Se3	0.3141(2)	
	–1Se1	0.3144(4)	
	–1Se2	0.3147(3)	
	–1Se2	0.3246(4)	
Cu	–3Se1	0.2401	3
Sn	–1Se3	0.2458(5)	4
	–3Se2	0.2518(4)	
Se1	–1Cu	0.2401	4
	–1La	0.2983(3)	
	–1La	0.2996(3)	
	–1La	0.3144(4)	
Se2	–1Sn	0.2518(4)	4
	–1La	0.3057(4)	
	–1La	0.3147(3)	
	–1La	0.3246(4)	
Se3	–1Sn	0.2458(5)	4
	–3La	0.3141(2)	

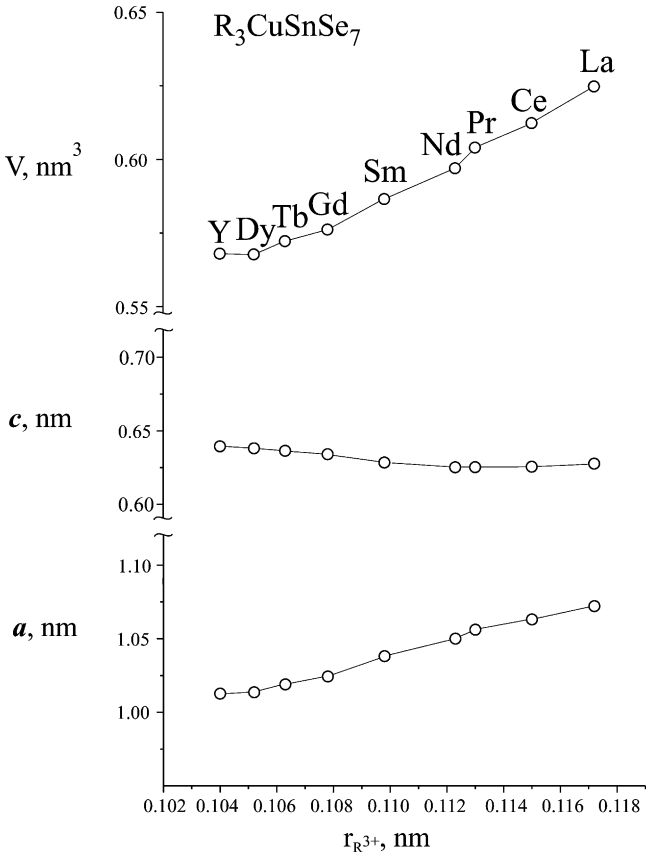

Fig. 2. The dependence of the lattice constants (*a*, *c*) and unit cell volumes (*V*) of the $R_3CuSnSe_7$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) and $Y_3CuSnSe_7$ [5] compounds from the ionic radii of the rare earth elements.

the sum of the respective ionic radii. Taking into account C.N. = 7 for the R atoms, C.N. = 3 for the Cu atoms and C.N. = 4 for the Sn atoms the average interatomic distances $\bar{d}_{R–Se}$, $\bar{d}_{Cu–Se}$ and $\bar{d}_{Sn–Se}$ were calculated (Table 4). The dependence of the average interatomic distances $\bar{d}_{R–Se}$, $\bar{d}_{Cu–Se}$ and $\bar{d}_{Sn–Se}$ on the ionic radii of the rare earth elements are shown in Fig. 3. The values of the average R–Se distances are in good accordance with the sizes of the rare earth ions.

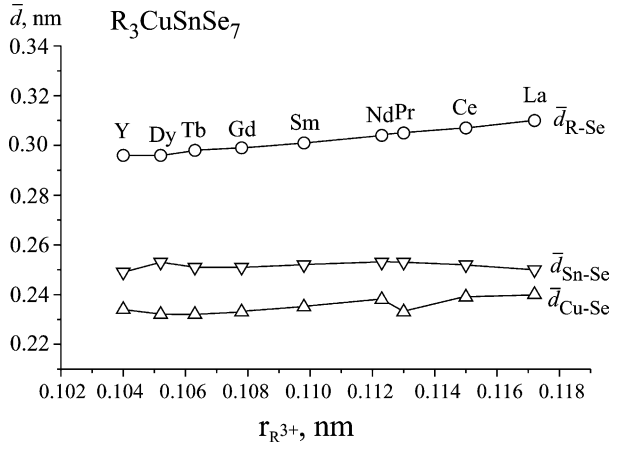

Fig. 3. The dependence of the average interatomic distances $\bar{d}_{R–Se}$, $\bar{d}_{Cu–Se}$ and $\bar{d}_{Sn–Se}$ from the ionic radii of the rare earth elements.

Table 4
Average interatomic distances $\bar{d}_{R–Se}$, $\bar{d}_{Cu–Se}$ and $\bar{d}_{Sn–Se}$ in the structures of the $R_3CuSnSe_7$ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) compounds

Compound	$\bar{d}_{R–Se}$ (nm)	$\bar{d}_{Cu–Se}$ (nm)	$\bar{d}_{Sn–Se}$ (nm)
$Y_3CuSnSe_7$	0.297	0.234	0.249
$La_3CuSnSe_7$	0.310	0.240	0.250
$Ce_3CuSnSe_7$	0.307	0.239	0.252
$Pr_3CuSnSe_7$	0.305	0.233	0.253
$Nd_3CuSnSe_7$	0.304	0.238	0.253
$Sm_3CuSnSe_7$	0.301	0.235	0.252
$Gd_3CuSnSe_7$	0.299	0.233	0.251
$Tb_3CuSnSe_7$	0.298	0.232	0.251
$Dy_3CuSnSe_7$	0.296	0.232	0.253

The packing of La-centered distorted trigonal prisms, Cu-centered octahedra and Sn-centered tetrahedra in the structure of the $La_3CuSnSe_7$ compound is shown in Fig. 4. Three

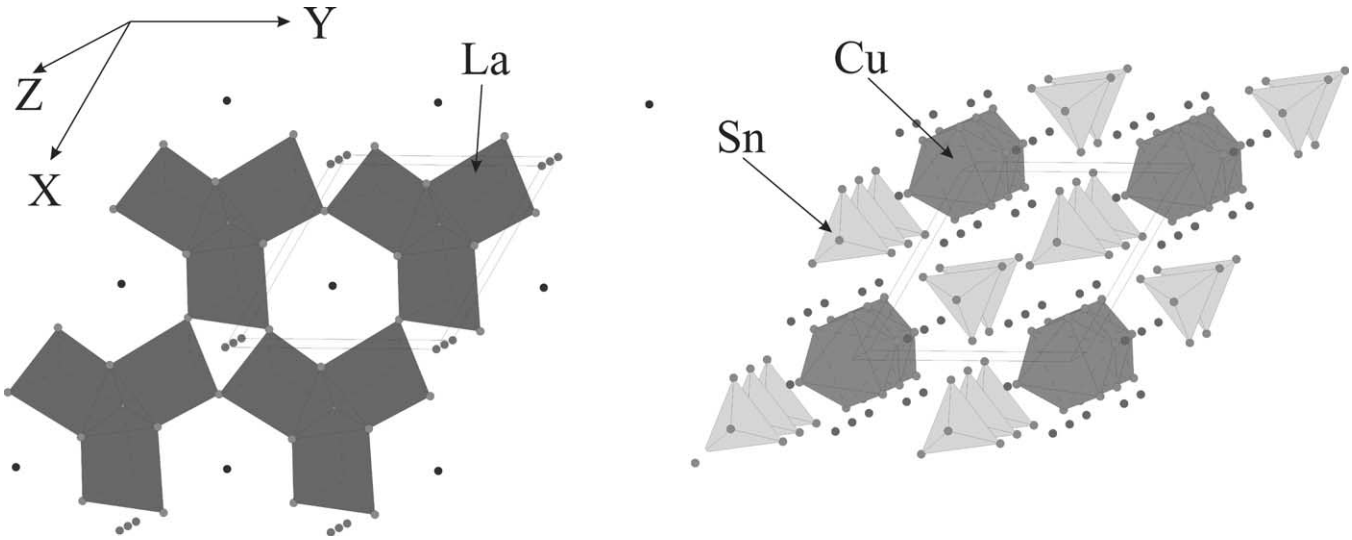

Fig. 4. The packing of La-centered distorted trigonal prisms, Cu-centered octahedra and Sn-centered tetrahedra in the structure of the $La_3CuSnSe_7$ compound.

La-centered prisms form the block. The prisms inside the block are connected to each other by edges. These blocks form the layers perpendicular to the *Z* axis. Three blocks connected by corners form the circles inside the layer. The prisms of the neighboring layers are connected by corners also. The Cu atoms are located in the octahedra. Since, the Cu atom is shifted from the center of the respective octahedron to an octahedron face and since three Se atoms are located at significantly larger distances from Cu compared with remaining three Se atoms, the real coordination surrounding of the Cu atom is triangular. Columns of Cu-centered octahedra connected by faces and isolated Sn-centered tetrahedra along the *Z* axis can be discerned in the structure of the $La_3CuSnSe_7$ compound.

References

[1] M. Julien-Pouzol, M. Guittard, Ann. Chim. Paris 7 (1972) 253.
[2] M. Julien-Pouzol, M. Guittard, J. Flahaut, Bull. Soc. Chim. Fr. (1968) 533.
[3] M. Julien-Pouzol, M. Guittard, Bull. Soc. Chim. Fr. (1968) 2293.
[4] S. Strobel, Th. Schleid, J. Solid State Chem. 171 (2003) 424.
[5] L.D. Gulay, V.Ya. Shemet, I.D. Olekseyuk, J. Alloys Compd. (2004) in press, doi:10.1016/j.jallcom.2004.04.123.
[6] L.G. Aksel'rud, Yu.N. Grin', P.Yu. Zavalij, V.K. Pecharsky, V.S. Fundamensky, Collected Abstract 12th European Crystallographic Meet, Moscow, August 1989. vol. 3, Izv. Acad. Nauk SSSR, Moscow, 1989, p. 155.
[7] R.A. Young, A. Sakthivel, T.S. Moss, C.O. Paria-Santos, in: Program DBWS-9411 for Rietveld Analysis of X-ray and Neutron Powder Diffraction Patterns, Georgia Institute of Technology, Atlanta GA (1995).
[8] G. Collin, P. Laruelle, Bull. Soc. Fr. Miner. Cristallogr. 94 (1971) 175.
[9] I. Ijjaali, K. Mitchell, J.A. Ibers, J. Solid State Chem. 177 (2004) 760.
[10] G. Marcano, L.M. de Chalbaud, C. Rincón, G. Sánchez Pérez, Mater. Lett. 53 (2002) 151.
[11] W. Urland, P. Plambeck-Fischer, M. Grupe, Z. Naturforschung B 44 (1989) 261.
[12] N. Wiberg, Lehrbuch der Anorganischen Chemie, Walter de Gruyter, Berlin, 1995.