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Synthesis and crysal structure of selenides $R_3Ag_{4k}Ge_{1.25-k}Se_7$ (R – La, Ce; k = 0.05; 0.10; 0.15)

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The paper presents the results of the study of the crystal structure of six selenides of the composition $R_3Ag_{4k}Ge_{1.25-k}Se_7$ (R – La, Ce; k = 0.05; 0.10; 0.15) as promising materials for use in various semiconductor technologies. Due to their potentially interesting nonlinear optical, magnetic and electrical properties, as well as other unique characteristics, these selenides can find application in scientific research and engineering developments, which opens up opportunities for the creation of modern materials with new functional properties.

The crystal structure of the selenides $La_3Ag_{0.20}Ge_{1.20}Se_7$ (A) [a = 10.779(1) Å, c = 6.0876(8) Å, R_I = 0.0982, R_P = 0.2544], $La_3Ag_{0.40}Ge_{1.15}Se_7$ (B) [a = 10.7821(9) Å, c = 6.0927(7) Å, R_I = 0.0950, R_P = 0.2377], $La_3Ag_{0.60}Ge_{1.10}Se_7$ (C) [a = 10.7977(5) Å, c = 6.0997(5) Å, R_I = 0.0920, R_P = 0.2156], $Ce_3Ag_{0.20}Ge_{1.20}Se_7$ (D) [a = 10.6948(5) Å, c = 6.0635(6) Å, R_I = 0.1130, R_P = 0.2649], $Ce_3Ag_{0.40}Ge_{1.15}Se_7$ (E) [a = 10.7074(6) Å, c = 6.0697(7) Å, R_I = 0.0977, R_P = 0.2529] and $Ce_3Ag_{0.60}Ge_{1.10}Se_7$ (F) [a = 10.7147(4) Å, c = 6.0729(4) Å, R_I = 0.0985, R_P = 0.2100] was studied by powder X-ray diffraction. The structure is represented by various geometric units, trigonal prisms with two additional atoms [R 8Se], tetrahedra [Ge 4Se], and monohedra [M 3Se]. These structural elements indicate a complex structure of selenides, which includes various types of chemical bonds and interactions between atoms in the crystal lattice.

The synthesized selenides crystallize in the hexagonal symmetry (La_3CuSiS_7 structure type; space group $P6_3$; Pearson symbol $hP24,173$). La or Ce atoms are localized in the 6c site (x y z), atoms of the statistical mixtures M(Ag + Ge) in the 2a site (0 0 z), and Ge atoms are in the 2b site (1/3 2/3 z). Selenium in the crystal lattice has three atomic sites, Se1 (2b site), Se2 and Se3 (6c site). The primitive hexagonal unit cell contains two $La(Ce)_3Ag_{4k}Ge_{1.25-k}Se_7$ formula units. The trigonal prisms [R 8Se] are connected by edges and form “blocks” of three prisms in each. The [R(Ag + Ge) 6Se] octahedra have common faces and form “columns” in the direction of the main axis. Trigonal prisms and octahedra form common faces. The [Ge 4Se] tetrahedra are isolated from each other.

Keywords: crystal structure, rare earth elements, quaternary non-centrosymmetric selenides, X-ray powder method.

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Introduction

One of the key areas of modern materials science is the search and development of multifunctional materials that do not contain toxic elements and are ecologically safe for humans and the environment [1-3]. Given the relevance of this problem, significant attention in research in the field of modern semiconductor materials science is focused on complex chalcogenides, in particular those whose structure is formed on the basis of rare earth (RE) metals [4-6]. Such materials have special physico-chemical properties due to the large coordination number of RE atoms which form coordination complexes or coordination units. Such polyhedral structures occupy most of the space of the unit cell [7-12], which contributes to the structural and thermodynamic stability of the substance. The study of such materials opens new prospects for the development of highly efficient, safe and

environmentally friendly clean technologies that significantly improve productivity and reduce environmental impact. These innovative materials can be implemented in various industries, starting from energy where they contribute to the creation of more sustainable and effective energy sources, to electronics where they will help develop devices with improved characteristics and reduced use of toxic materials. In addition, such technology can find applications in biomedicine, environmental monitoring and even in the production of new materials for renewable energy.

Here, we present results of a detailed study of the crystal structure of the $La(Ce)_3Ge_{1.25}Se_7 : Ag^+$ phases, doped with monovalent silver. The structure studies show that such materials can exhibit unique optical properties that have considerable potential for application in various fields, in particular in optoelectronics and laser technologies. Silver doping affects the structural and physical characteristics of materials, which allows to predict their ability to effectively interact with light, making these phases promising for further research of new functional materials with improved optical properties.

I. Experimental

Six samples of the stoichiometric compositions $R_3Ag_{4k}Ge_{1.25-k}Se_7$ (R – La, Ce; k = 0.05; 0.10; 0.15) were synthesized from high purity lanthanum, cerium, silver, germanium and selenium in quartz ampoules evacuated to the residual pressure of 10^{-2} Pa. The total batch mass of each sample was 1.0 g. The synthesis was held in an MP-30 electric muffle furnace by heating to 1150 °C at a rate of 12 °C/h; exposure to 1150 °C for four hours; cooling to 500 °C at a rate of 12 °C/h; homogenizing annealing at 500 °C for two months; quenching in room temperature water. The crystal structure of the synthesized selenides was studied by the X-ray powder method. Experimental diffraction patterns of the synthesized samples were obtained at a DRON 4-13 X-ray diffractometer (CuK_α radiation, $\lambda = 1.54185$ Å, $10° \le 2\Theta \le 100°$ range, scan step 0.05°, 10 s exposure at each point). The crystal structures were computed by the Rietveld method, which allows get accurate parameters structures through analysis diffraction data. For this used realized in WinCSD software package [13] which provides automated processing and interpretation X - ray results diffraction. The VESTA software was used for visualization and detailed analysis of the structure [14].

II. Results and discussion

The selenides of the composition $R_3Ag_{4k}Ge_{1.25-k}Se_7$ (R – La, Ce; k = 0.05; 0.10; 0.15) are based on the ternary compounds $R_3Ge_{1.25}Se_7$ [15, 16] by partial substitution of germanium atoms in the 2a site with monovalent silver atoms.

Crystal structure of selenides was studied by powder diffraction. Analysis of Miller indices hkl and intensities of the diffraction pattern reflections indicate that the structures of the synthesized selenides belong to the La_3CuSiS_7 structure type [17]. The experiment conditions and the crystallographic characteristics of the synthesized selenides are listed in Tables 1 and 2. Experimental and theoretically calculated diffraction patterns and their difference are plotted in Figure 1.

Table 1.

Shooting conditions and results of refinement of the crystal structure of (ПГ $P6_3$ (№ 173)) $La_3Ag_{4k}Ge_{1.25-k}Se_7$ (k = 0.05; 0.10; 0.15) selenides.

Parameters	$La_3Ag_{0.20}Ge_{1.20}Se_7$	$La_3Ag_{0.40}Ge_{1.15}Se_7$	$La_3Ag_{0.60}Ge_{1.10}Se_7$
Pearson's Symbol	*hP*22.8	*hP*23.1	*hP*23.4
a, (Å)	10.779(1)	10.7821(9)	10.7977(5)
c, (Å)	6.0867(8)	6.0927(7)	6.0997(5)
Cell volume (Å^3)	612.5(2)	613.4(2)	615.89(10)
Calculated Density (g/cm^3)	5.845(2)	5.934(2)	6.0068(9)
Absorption coefficient (1/cm)	1105.56	1127.91	1147.23
Number of atom sites	6	6	6
2Θ and sinΘ/λ (max.)	100.00; 0.497	100.00; 0.497	100.00; 0.497
R_I / R_P	0.0982 / 0.2544	0.0950 / 0.2377	0.0920 / 0.2156
Scale factor	0.4553(4)	0.481(1)	0.5095(5)

Table 2.

Shooting conditions and results of refinement of the crystal structure of (ПГ $P6_3$ (№ 173)) $Ce_3Ag_{4k}Ge_{1.25-k}Se_7$ (k = 0.05; 0.10; 0.15) selenides.

Parameters	$Ce_3Ag_{0.20}Ge_{1.20}Se_7$	$Ce_3Ag_{0.40}Ge_{1.15}Se_7$	$Ce_3Ag_{0.60}Ge_{1.10}Se_7$
Pearson's Symbol	*hP*22.8	*hP*23.1	*hP*23.4
a, (Å)	10.6926(9)	10.7074(6)	10.7147(4)
c, (Å)	6.0622(7)	6.0697(5)	6.0729(4)
Cell volume (Å^3)	600.2(2)	602.6(1)	603.80(9)
Calculated Density (g/cm^3)	5.985(2)	6.060(1)	6.1470(9)
Absorption coefficient (1/cm)	1160.57	1180.34	1202.45
Number of atom sites	6	6	6
2Θ and sinΘ/λ (max.)	100.00; 0.497	100.00; 0.497	100.00; 0.497
R_I / R_P	0.0911 / 0.2422	0.0977 / 0.2529	0.0985 / 0.2100
Scale factor	0.3735(2)	0.3045(2)	0.4257(1)

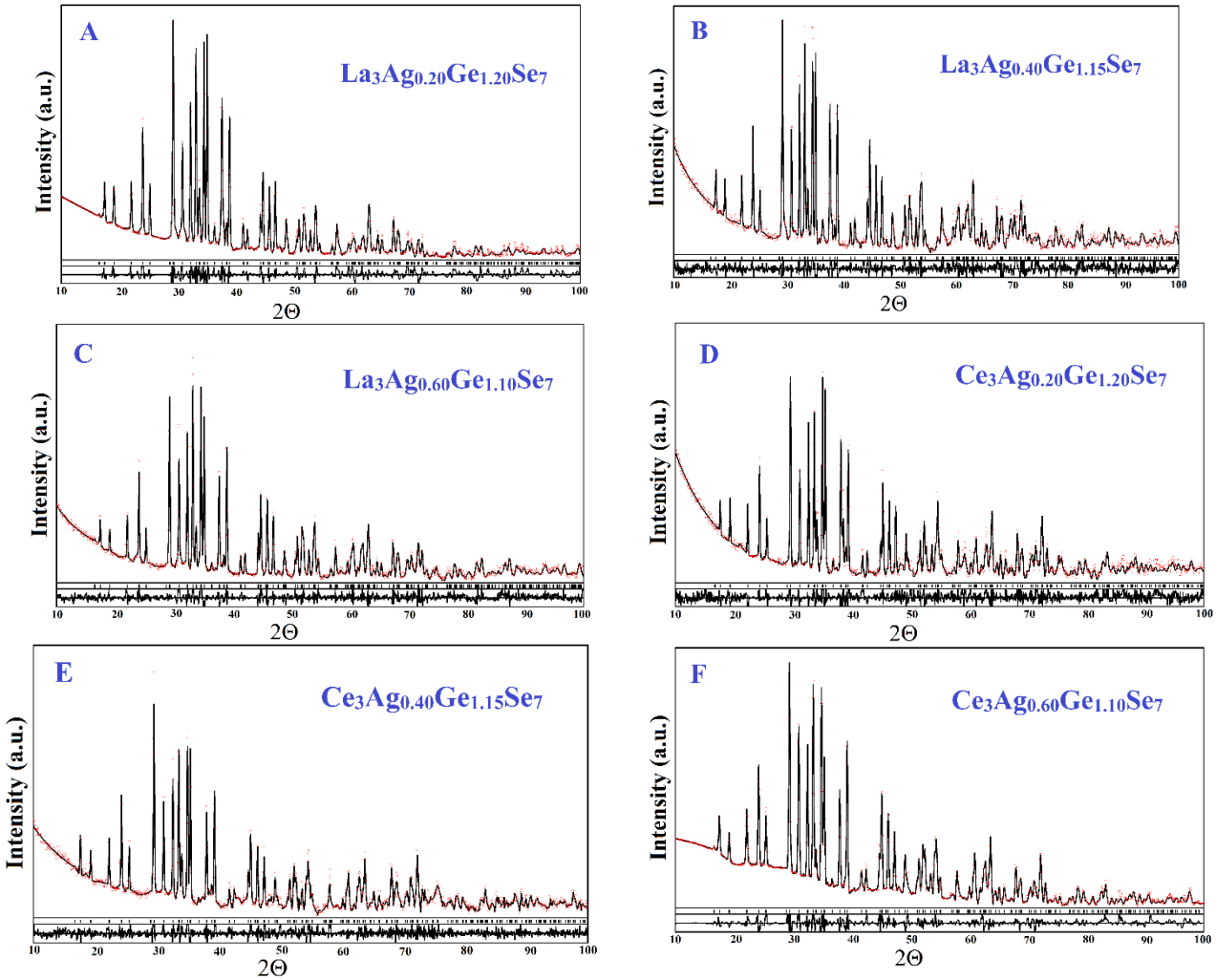

Fig. 1. Theoretical (−), experimental (°°°) and difference diffraction patterns between them for $La_3Ag_{0.20}Ge_{1.20}Se_7$ (A), $La_3Ag_{0.40}Ge_{1.15}Se_7$ (B), $La_3Ag_{0.60}Ge_{1.10}Se_7$ (C), $Ce_3Ag_{0.20}Ge_{1.20}Se_7$ (D), $Ce_3Ag_{0.40}Ge_{1.15}Se_7$ (E) and $Ce_3Ag_{0.60}Ge_{1.10}Se_7$ (F). [CuK$_\alpha$-radiation (λ = 1.54185 Å)].

Refinement of the standardized atomic coordinates and the isotropic thermal displacement parameters of atoms (B_{iso}) in the structures of synthesized selenides (Table 3, Table 4) led to relatively satisfactory values of fit factors.

The unit cell and the stacking of [La(Ce) 8Se], [Ge 4Se] and [M 3Se] polyhedra in the structure of the studies selenides are shown in Figure 2.

La(Ce) atoms in the structures of these phases occupy one 6c site (x y z) and coordinate eight Se atoms, forming trigonal prisms with two additional atoms [R 8Se]. These prisms have common corners and edges.

Ge atoms fully occupy the 2b site (1/3 2/3 z) and coordinate four Se atoms, forming highly symmetrical tetrahedra [Ge 4Se], that are isolated from each other and occupy the voids between the blocks of trigonal prisms as shown in Fig. 3.

The statistical mixture of M (Ag + Ge) atoms is localized in the 2a site (0 0 z). The composition of these mixtures is 50% Ag and 50% Ge (for $La(Ce)_3Ag_{0.20}Ge_{1.20}Se_7$), 73 % Ag and 27 % Ge (for $La(Ce)_3Ag_{0.40}Ge_{1.15}Se_7$), and 86 % Ag and 14 % Ge (for $La(Ce)_3Ag_{0.60}Ge_{1.10}Se_7$). The M (Ag + Ge) atoms are located quite close to one of the faces of the [M (Ag + Ge) 6Se] octahedra, and thus may be viewed as planar triangles [M 3Se].

The unit cell parameters predictably increase with the silver content. Parameter a increases from 10.779(1) to 10.7977(5) Å, parameter c from 6.0867(8) to 6.0997(5) Å, cell volume V from 612.5(2) to 615.89(10) Å^3 for lanthanum-containing selenides; and a from 10.6926(9) to 10.7147(4) Å, c from 6.0622(7) to 6.0729(4) Å, V from 600.2(2) to 603.80 (9) Å^3 for cerium-containing compositions, respectively. The parameters a, c and V monotonously decrease in the La → Ce transition due to the size decrease of $r(La^{3+})$ = 1.300 Å and $r(Ce^{3+})$ = 1.283 Å (for C.N. = 8). Trigonal prisms become more symmetrical ($C.N._{eff.}$ = 7.66 – 7.78; χ = 0.02587 – 0.02011 (for La-containing selenides) and $C.N._{eff}$ = 7.70 – 7.81; χ = 0.02230 – 0.01930 (for Ce-containing selenides)).

Average bond lengths δ(R – Se), δ(Ge – Se) and δ(M – Se) vary non-monotonously. The shortest and longest values are $\delta(R - Se_2)_{min}$ = 2.957(12) Å (for $Ce_3Ag_{0.20}Ge_{1.20}Se_7$) and $\delta(R - Se_2)_{max}$ = 3.34(4) Å (for $La_3Ag_{0.20}Ge_{1.20}Se_7$); $\delta(Ge - Se_1)_{min}$ = 2.354(18) Å (for $La_3Ag_{0.60}Ge_{1.10}Se_7$) and $\delta(Ge - Se_3)_{max}$ = 2.53(3) Å (for $La_3Ag_{0.20}Ge_{1.20}Se_7$); $\delta(M - Se_2)_{min}$ = 2.4932 Å (for $Ce_3Ag_{0.20}Ge_{1.20}Se_7$) and $\delta(M - Se_2)_{max}$ = 2.5286 Å (for

Table 3.

Coordinates and isotropic thermal parameters of atoms in the structure $La_3Ag_{4k}Ge_{1.25-k}Se_7$ (k = 0.05; 0.10; 0.15) selenides.

$La_3Ag_{0.20}Ge_{1.20}Se_7$					
Atom	Wyck	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
La	6*c*	0.1258(5)	0.3596(5)	0.134(4)	1.10(10)
M1	2*a*	0	0	0.00000*	1.0(5)
Ge	2*b*	1/3	2/3	0.692(6)	1.1(5)
Se1	2*b*	1/3	2/3	0.288(5)	0.8(3)
Se2	6*c*	0.2532(8)	0.1683(9)	0.111(4)	1.2(5)
Se3	6*c*	0.5148(9)	0.0959(9)	0.384(4)	1.0(2)
M1 – 0.20 Ag + 0.20 Ge					
$La_3Ag_{0.40}Ge_{1.15}Se_7$					
Atom	Wyck	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
La	6*c*	0.1258(4)	0.3594(4)	0.1321(12)	0.62(4)
M2	2*a*	0	0	0.00000*	1.7(4)
Ge	2*b*	1/3	2/3	0.696(2)	1.3(3)
Se1	2*b*	1/3	2/3	0.291(2)	1.0(3)
Se2	6*c*	0.2540(6)	0.1676(7)	0.113(2)	0.85(12)
Se3	6*c*	0.5145(7)	0.0968(7)	0.3835(14)	0.41(12)
M2 – 0.40 Ag + 0.15 Ge					
$La_3Ag_{0.60}Ge_{1.10}Se_7$					
Atom	Wyck	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
La	6*c*	0.1267(4)	0.3583(3)	0.1319(12)	0.93(5)
M3	2*a*	0	0	0.00000*	1.2(3)
Ge	2*b*	1/3	2/3	0.698(2)	1.0(3)
Se1	2*b*	1/3	2/3	0.311(2)	1.2(3)
Se2	6*c*	0.2559(6)	0.1687(6)	0.113(2)	0.97(11)
Se3	6*c*	0.5151(7)	0.0999(7)	0.3635(12)	1.04(11)
M3 – 0.60 Ag + 0.10 Ge; * – fixed					

Table 4.

Coordinates and isotropic thermal parameters of atoms in the structure $Ce_3Ag_{4k}Ge_{1.25-k}Se_7$ (k = 0.05; 0.10; 0.15) selenides.

$Ce_3Ag_{0.20}Ge_{1.20}Se_7$					
Atom	Wyck	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
Ce	6*c*	0.1272(4)	0.3584(4)	0.1334(13)	0.98(6)
M4	2*a*	0	0	0.00000*	1.4(8)
Ge	2*b*	1/3	2/3	0.697(3)	1.2(4)
Se1	2*b*	1/3	2/3	0.291(3)	1.1(4)
Se2	6*c*	0.2547(7)	0.1689(8)	0.113(2)	0.84(14)
Se3	6*c*	0.5142(8)	0.0989(8)	0.353(2)	1.0(2)
M4 – 0.20 Ag + 0.20 Ge					
$Ce_3Ag_{0.40}Ge_{1.15}Se_7$					
Atom	Wyck	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
Ce	6*c*	0.1258(4)	0.3593(4)	0.130(2)	0.45(8)
M5	2*a*	0	0	0.00000*	0.8(7)
Ge	2*b*	1/3	2/3	0.692(3)	0.5(5)
Se1	2*b*	1/3	2/3	0.285(3)	0.9(5)
Se2	6*c*	0.2551(7)	0.1671(8)	0.116(2)	0.8(2)
Se3	6*c*	0.5159(9)	0.1009(8)	0.363(2)	0.6(2)
M5 – 0.40 Ag + 0.15 Ge					
$Ce_3Ag_{0.60}Ge_{1.10}Se_7$					
Atom	Wyck	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
Ce	6*c*	0.1261(3)	0.3595(3)	0.1287(8)	1.31(9)
M6	2*a*	0	0	0.00000*	1.0(2)
Ge	2*b*	1/3	2/3	0.693(2)	1.8(2)
Se1	2*b*	1/3	2/3	0.301(2)	1.2(2)
Se2	6*c*	0.2575(4)	0.1680(5)	0.1139(12)	1.08(8)
Se3	6*c*	0.5165(5)	0.1014(5)	0.3637(9)	0.91(8)
M6 – 0.60 Ag + 0.10 Ge; * – fixed					

$La_3Ag_{0.60}Ge_{1.10}Se_7$). Calculated values of the average bond lengths agree well with the sum of the corresponding ionic radii [18].

Geometric parameters of polyhedra in the structures of synthesized selenides are given in Table 5 and 6.

A comparison with the crystal structure and properties of isostructural materials $R_3Ag_{1-\delta}Si(Sn)S_7$ ($\delta = 0.10 – 0.23$) [7, 8] is of interest. Silver atoms occupy two separate sites Ag1 and Ag2 in the crystal lattice of these compounds. The Ag1 site is located quite close to the plane of the monohedron, and Ag2 is located almost in the center of the octahedron. Such compounds are characterized by higher Ag concentration and significantly lower Ge content compared to Ag^+-doped phases presented in this work. Due to the atomic content of Ag and Ge, the size factor of the elements of Group IV-A and differing structure types of compounds, as well as their defects in our work, the above atoms are statistically

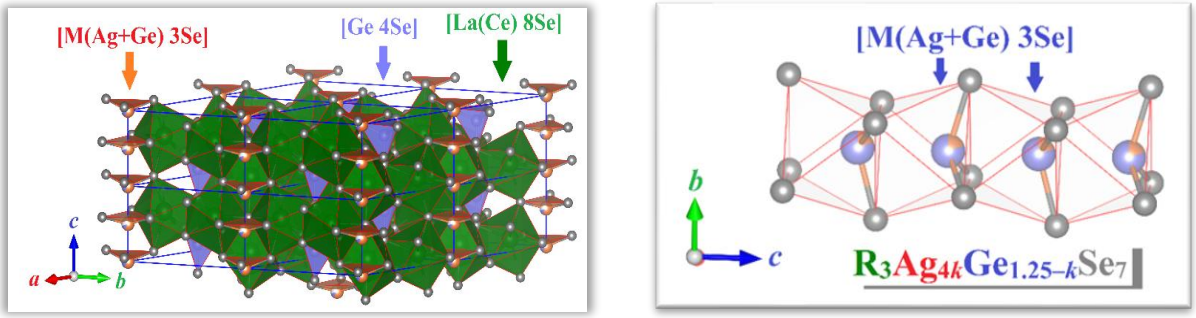

Fig. 2. Packing of polyhedra in the crystal structure of selenides $R_3Ag_{4k}Ge_{1.25-k}Se_7$ (R– La(Ce); $k = 0.05$; 0.10; 0.15).

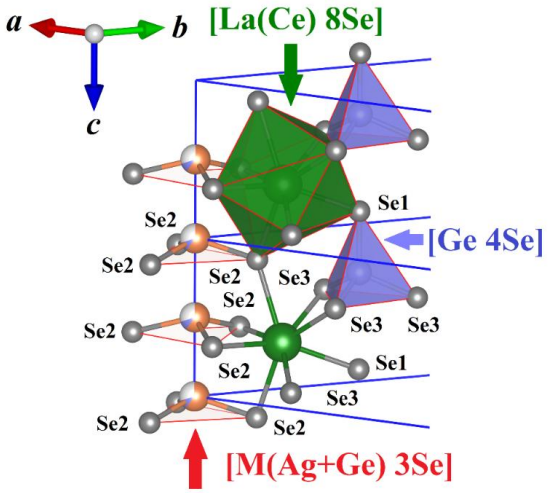

Fig. 3. Coordination polyhedra [La(Ce) 8Se], [Ge 4Se] and [M(Ag + Ge) 3Se] in the structure of selenides $La(Ce)_3Ag_{4k}Ge_{1.25-k}Se_7$ ($k = 0.05$; 0.10; 0.15).

Table 5.

Parameters of polyhedra [La 8Se], [Ge 4Se] and [M 3Se] in the structure selenides $La_3Ag_{4k}Ge_{1.25-k}Se_7$ ($k = 0.05$; 0.10; 0.15)

Parameters	$La_3Ag_{0.20}Ge_{1.20}Se_7$	$La_3Ag_{0.40}Ge_{1.15}Se_7$	$La_3Ag_{0.60}Ge_{1.10}Se_7$
[La 8Se]			
δ(La – Se), Å	2.98(3) – 3.34(4)	2.988(11) –3.315(14)	3.002(10) –3.304(14)
$\delta(La – Se)_{mean}$, Å	3.1026	3.1044	3.1222
Distortion index (χ)	0.02587	0.02290	0.02011
V, Å ^{3}	51.2819	51.4617	52.6899
C.N. / $C.N._{eff.}$	8 / 7.66	8 / 7.72	8 / 7.78
[Ge 4Se]			
δ(Ge – Se), Å	2.45(5) – 2.53(3)	2.461(18) –2.516(10)	2.354(18) –2.436(8)
$\delta(Ge – Se)_{mean}$, Å	2.5117	2.5020	2.4154
∠ Se1 – Ge – Se3, (°)	117.5(9)	117.1(4)	114.6(3)
∠ Se3 – Ge – Se3, (°)	100.4(12)	100.9(5)	103.9(4)
Distortion index (χ)	0.01179	0.00812	0.01261
V, Å ^{3}	7.9066	7.8344	7.1546
C.N. / $C.N._{eff.}$	4 / 3.97	4 / 3.99	4 / 3.97
[M(Ag+Ge) 3Se]			
δ(M – Se), Å	2.4961	2.5072	2.5286
$C.N._{eff.}$	3	3	3

Table 6.

Parameters of polyhedra [Ce 8Se], [Ge 4Se] and [M 3Se] in the structure selenides $Ce_3Ag_{4k}Ge_{1.25-k}Se_7$ (k = 0.05; 0.10; 0.15).

Parameters	$Ce_3Ag_{0.20}Ge_{1.20}Se_7$	$Ce_3Ag_{0.40}Ge_{1.15}Se_7$	$Ce_3Ag_{0.60}Ge_{1.10}Se_7$
[Ce 8Se]			
δ(Ce – Se), Å	2.957(12) – 3.303(17)	3.002(10) –3.2729(16)	3.016(8) – 3.275(8)
$\delta(Ce – Se)_{mean}$, Å	3.0957	3.0925	3.0980
Distortion index (χ)	0.02230	0.02048	0.01930
V, Å ^{3}	51.1194	50.9094	51.3945
C.N. / $C.N._{eff.}$	8 / 7.70	8 / 7.80	8 / 7.81
[Ge 4Se]			
δ(Ge – Se), Å	2.398(11) – 2.46(3)	2.422(6) –2.467(19)	2.387(18) –2.471(7)
$\delta(Ge – Se)_{mean}$, Å	2.4136	2.4332	2.4097
∠ Se1 – Ge – Se3, (°)	113.2(5)	115.45(6)	115.4(3)
∠ Se3 – Ge – Se3, (°)	105.5(6)	102.89(8)	103.0(4)
Distortion index (χ)	0.00984	0.00697	0.00479
V, Å ^{3}	7.1629	7.2646	7.0701
C.N. / $C.N._{eff.}$	4 / 3.98	4 / 3.99	4 / 3.99
[M(Ag+Ge) 3Se]			
δ(M – Se), Å	2.4932	2.5032	2.5211
$C.N._{eff.}$	3	3	3

$\delta(R – Se)_{mean} = 0{,}125*\sum\delta(R – Se)$;
$\delta(Ge – Se)_{mean} = 0{,}25*[3*\ \delta(Ge–Se3) + \delta(Ge–Se1)]$;

distributed in monohedra.

Analysis of the symmetry elements of polyhedra in the structure of synthesized selenides indicates that the introduction of atoms of chemical elements of different nature into the structure of chalcogenides enables a purposeful change in their geometric parameters. This is due to the influence of the chemical nature and electronic configuration of admixture atoms on the symmetry and spatial organization of the crystal lattice. By changing the composition of the compounds, it is possible to tune the interatomic distances, bond angles, and the overall symmetry of the crystal. This opens up opportunities for the creation of materials with predictable crystal structure and physico-chemical properties, which is promising for applications in optoelectronics, spintronics, thermoelectrics, and other semiconductor technologies.

Conclusions

New tetrahedral selenides of the composition $La(Ce)_3Ag_{4k}Ge_{1.25-k}Se_7$ (k = 0.05; 0.10; 0.15) were synthesized for the first time, and their crystal structure was studied by X-ray powder diffraction.

Based on the analysis of experimentally obtained results, it was established that these selenides crystallize in the hexagonal symmetry (La_3CuSiS_7 structure type, S.G. $P6_3$) with the unit cell parameters: a = 10.779(1) Å, c = 6.0867(8) Å and V = 612.5(2) Å^3, R_I = 0.0982, R_p = 0.2544 (for $La_3Ag_{0.20}Ge_{1.20}Se_7$); a = 10.7821(9) Å, c = 6.0927(7) Å and V = 613.4(2) Å^3, R_I = 0.0950, R_p = 0.2377 (for $La_3Ag_{0.40}Ge_{1.15}Se_7$); a = 10.7977(5) Å, c = 6.0997(5) Å and V = 615.98(10) Å^3, R_I = 0.0920, R_p = 0.2156 (for $La_3Ag_{0.60}Ge_{1.10}Se_7$); a = 10.6926(9) Å, c = 6.0622(7) Å and V = 600.2(2) Å^3, R_I = 0.0911, R_p = 0.2422 (for $Ce_3Ag_{0.20}Ge_{1.20}Se_7$); a = 10.7074(6) Å, c = 6.0697(5) Å and V = 602.6(1) Å^3, R_I = 0.0977, R_p = 0.2529 (for $Ce_3Ag_{0.40}Ge_{1.15}Se_7$) and a = 10.7147(4) Å, c = 6.0729(4) Å and V = 603.80(9) Å^3, R_I = 0.0985, R_p = 0.2100 (for $Ce_3Ag_{0.60}Ge_{1.10}Se_7$).

Since the synthesized selenides have non-centrosymmetric structure, this opens up possibilities for their use in the field of nonlinear optics. Such a structure is an important condition for effective interaction with intense light fields, which allows selenide-based materials to exhibit effects such as harmonic generation, coherent emission, and self-focusing of light. Due to unique optical properties, these materials can find applications in lasers, optical converters and others devices that work on the principles of nonlinear optics.

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Синтез та кристалічна структура селенідів $R_3Ag_{4k}Ge_{1.25-k}Se_7$ (R – La, Ce; k = 0.05; 0.10; 0.15)

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У роботі представлено результати дослідження кристалічної структури шести селенідів складу $R_3Ag_{4k}Ge_{1.25-k}Se_7$ (R – La, Ce; k = 0.05; 0.10; 0.15) як перспективних матеріалів для використання у різних напівпровідникових технологіях. Завдяки своїм потенційно цікавим нелінійно-оптичним, магнітним та електричним властивостям, а також іншим унікальним характеристикам, ці селеніди можуть знайти застосування в наукових та інженерних розробках, що відкриває можливості для створення сучасних матеріалів з новими функціональними властивостями.

Кристалічна структура селенідів $La_3Ag_{0.20}Ge_{1.20}Se_7$ (A) [a = 10.779(1) Å, c = 6.0876(8) Å, R_I = 0.0982, R_P = 0.2544], $La_3Ag_{0.40}Ge_{1.15}Se_7$ (Б) [a = 10.7821(9) Å, c = 6.0927(7) Å, R_I = 0.0950, R_P = 0.2377], $La_3Ag_{0.60}Ge_{1.10}Se_7$ (B) [a = 10.7977(5) Å, c = 6.0997(5) Å, R_I = 0.0920, R_P = 0.2156], $Ce_3Ag_{0.20}Ge_{1.20}Se_7$ (Г) [a = 10.6948(5) Å, c = 6.0635(6) Å, R_I = 0.1130, R_P = 0.2649], $Ce_3Ag_{0.40}Ge_{1.15}Se_7$ (Д) [a = 10.7074(6) Å, c = 6.0697(7) Å, R_I = 0.0977, R_P = 0.2529] та $Ce_3Ag_{0.60}Ge_{1.10}Se_7$ (E) [a = 10.7147(4) Å, c = 6.0729(4) Å, R_I = 0.0985, R_P = 0.2100] вивчена методом порошкової дифрактометрії. Структура представлена різноманітними геометричними одиницями: тригональними призмами з двома додатковими атомами [R 8Se], тетраедрами [Ge 4Se] та моноедрами [M 3Se]. Ці елементи структури вказують на складну будову селенідів, що включає різні види хімічних зв'язків та взаємодій між атомами в кристалічній решітці.

Синтезовані селеніди кристалізуються в гексагональній сингонії (СТ La_3CuSiS_7; ПГ $P6_3$; СП hP24,173). Атоми La або Ce локалізовані в правильній системі точок (ПСТ) 6*c* (*x y z*), атоми статистичних сумішей M(Ag + Ge) в ПСТ 2*a* (0 0 *z*), а атоми Ge в ПСТ 2*b* (1/3 2/3 *z*). Селен в кристалічній ґратці має три атомні позиції: Se1(ПСТ 2*b*), Se2 та Se3 (ПСТ 6*c*). На примітивну гексагональну елементарну комірку припадає дві формульні одиниці $La(Ce)_3Ag_{4k}Ge_{1.25-k}Se_7$. Тригональні призми [R 8Se] з'єднанні між собою ребрами і формують "блоки" (по три призми в кожному). Октаедри [R(Ag + Ge) 6Se] мають спільні грані і утворюють "колони" в напрямку головної осі. Тригональні призми з октаедрами утворюють спільні грані. Тетраедри [Ge 4Se] є ізольовані один від одного.

Ключові слова: кристалічна структура, рідкісноземельні елементи, тетрарні нецентросиметричні селеніди, метод порошкової дифрактометрії.