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Synthesis and crystal structure of the $R_3Fe_{0.1}Ga_{1.6}Se_7$ selenides (R – La, Ce, Pr, Nd)

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Samples of the stoichiometric composition $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce, Pr, Nd) were synthesized from high purity elements in evacuated quartz containers at a maximum synthesis temperature of 1100°C. Obtained alloys were homogenized by annealing at 500°C for a month. The crystal structure of the selenides that was investigated by X-ray powder method found that they belong to the structural type La_3CuSiS_7 (S.G. $P6_3$, Pearson symbol *h*P24). The lattice parameters are: a = 10.5358(8) Å, c = 6.3796(6) Å, V = 613.2(2) Å^3, R_I = 0.0846, R_p = 0.1575 (sample A, $La_3Fe_{0.1}Ga_{1.6}Se_7$); a = 10.4379(5) Å, c = 6.3550(5) Å, V = 599.6(1) Å^3, R_I = 0.0878, R_p = 0.2137 (sample B, $Ce_3Fe_{0.1}Ga_{1.6}Se_7$); a = 10.3431(4) Å, c = 6.3735(8) Å, V = 590.49(8) Å^3, R_I = 0.0846, R_p = 0.1575 (sample C, $Pr_3Fe_{0.1}Ga_{1.6}Se_7$); a = 10.2817(4) Å, c = 6.3819(4) Å, V = 548.26(8) Å^3, R_I = 0.0939, R_p = 0.2409 (sample D, $Nd_3Fe_{0.1}Ga_{1.6}Se_7$). Obtained chalcogenides are derived from the $R_3Ga_{1.67}Se_7$ selenides (R – La, Ce, Pr, Nd) by partial substitution of Ga atoms in the 2*a* site (0 0 *z*) with divalent Fe atoms. Rare-earth atoms in the studied structures occupy the 6*c* site (*x y z*) and, together with Se atoms, form trigonal prisms with one additional atom [R 7Se]. Trigonal prisms share edges to form 3 [R 7Se] blocks. Fe and Ga atoms are statistically distributed in the 2*a* site (0 0 *z*) and have an octahedral environment. Octahedra [M (2*a* site) 6Se] share faces to form spatial columns $[M(Fe + Ga)Se_6]_n$ along the *c axis*, which are connected to the trigonal prisms by common edges. Part of Ga atoms is located in the center of the [Ga 4Se] tetrahedra in the 2*b* site (1/3 2/3 z).

Keywords: rare earth elements, selenides, crystal structure, X-ray powder method, energy-dispersive X-ray spectroscopy.

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Introduction

One of the principal tasks of modern semiconductor materials science is oriented development of functional materials with predetermined physical properties [1-3]. A special place among such materials belongs to chalcogenide compounds doped with *d*-elements, particularly lanthanide-based, which are promising research objects due to the combination of structural order and multifunctionality.

Quaternary chalcogenides of the compositions $R_3A^I_{4x}Ga_{1.67-x}X_7$ [4] and $R_3B^{II}_{2x}Ga_{1.65-x}X_7$ [5], [6] (R – lanthanide; A^I, B^{II} – monovalent and divalent *d*-elements, respectively; X = S or Se – chalcogen atoms) deserve special attention. The presence of *d*-element atoms in the cell creates the corresponding crysta-ochemical ordering in which lanthanides occupy internalvolume sites [7], [8]. Due to the non-centrosymmetric hexagonal structure (Pearson symbol *hP*24, S.G. $P6_3$) and the presence of anisotropy in the structure, such materials can exhibit a wide range of nonlinear optical effects, such as second and third harmonic generation, optical decantation, piezo- and magneto-optical effects [9-12]. This makes them extremely promising for use in laser technologies, optoelectronics and photonics. Additional properties can be generated by varying the Ga composition and doping with other metals.

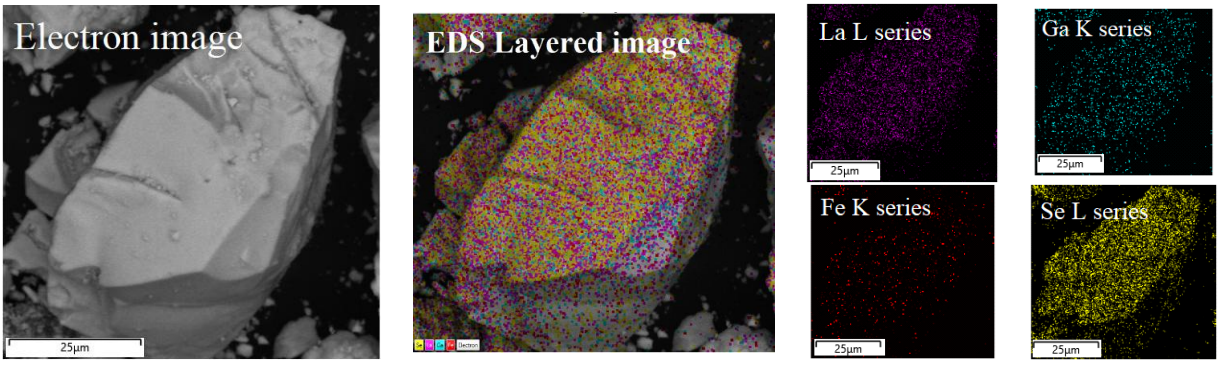
Here, we present for the first time the results of an experimental study of the crystal structure of selenides that crystallize in the La_3CuSiS_7 structural type (S.G. $P6_3$, Pearson symbol *h*P24). The presence of heavy metal

atoms in the crystal lattice of such phases can improve their thermoelectric properties. Synthesized selenides demonstrate stability at high temperatures and the ability to form homogeneous crystalline phases. Thus, we consider them as promising materials for modern materials science, particularly in the field of creation new thermoelectric transducers, sensors or optoelectronic elements. Obtained results create foundation for further research in the direction of optimization of the composition of multicomponent selenides and their implementation into functional devices of new generation.

I. Experimental

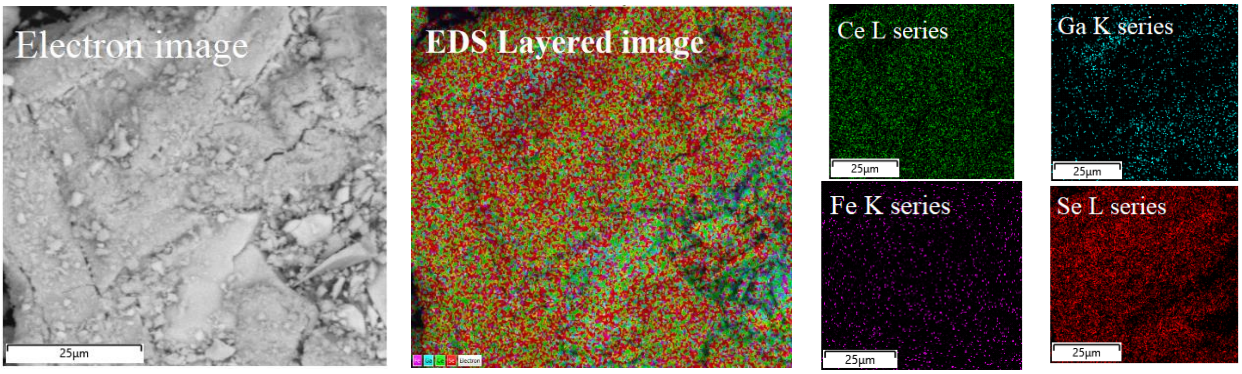
The alloys for studying the crystal structure of the $R_3Fe_{0.1}Ga_{1.6}Se_7$ selenides (R – La, Ce, Pr, Nd) of total weight 1 g each were synthesized from high-purity elements (at least 99.99 mass % of the principal) in an MP-30 electric muffle furnace. The synthesis in evacuated to 10^{-2} Pa quartz containers followed the route of heating to 700°C at the rate of 36°C/h; 10-h exposure to 700°C; heating to 1100°C at the rate of 12°C/h; 2-h exposure to 1100°C; cooling to 500°C at the rate of 6°C/h; homogenizing annealing at 500°C for over 700 h; quenching into room-temperature water without depressurization of the containers with the synthesized material.

Elemental composition of the synthesized selenides was confirmed using energy-dispersive X-ray (EDX) spectroscopy (Tescan Vega 3 LMU scanning electron microscope with an Oxford Instruments energy-dispersive X-ray analyzer). SEM images and element distribution are shown in Figures 1-4.



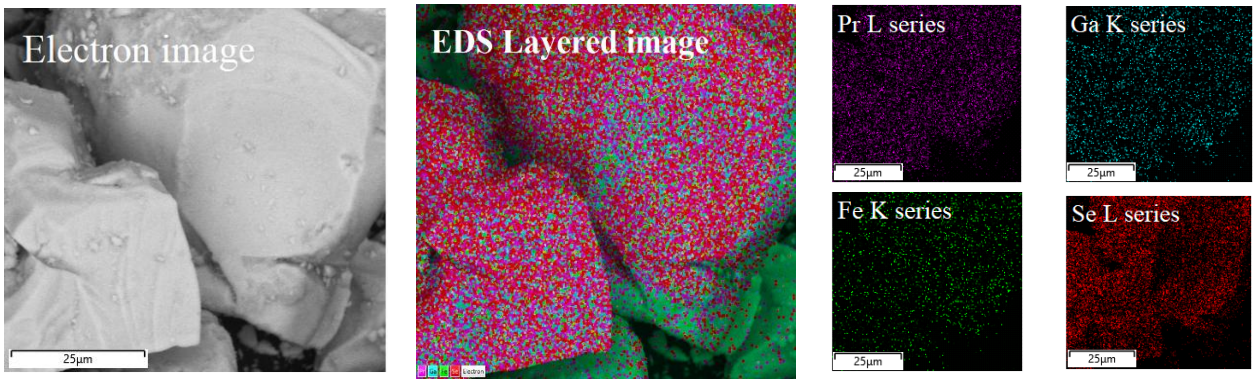
a) b)

Fig. 1. SEM image (*a*) and element distribution over the surface (*b*) of the $La_3Fe_{0.1}Ga_{1.6}Se_7$ alloy.



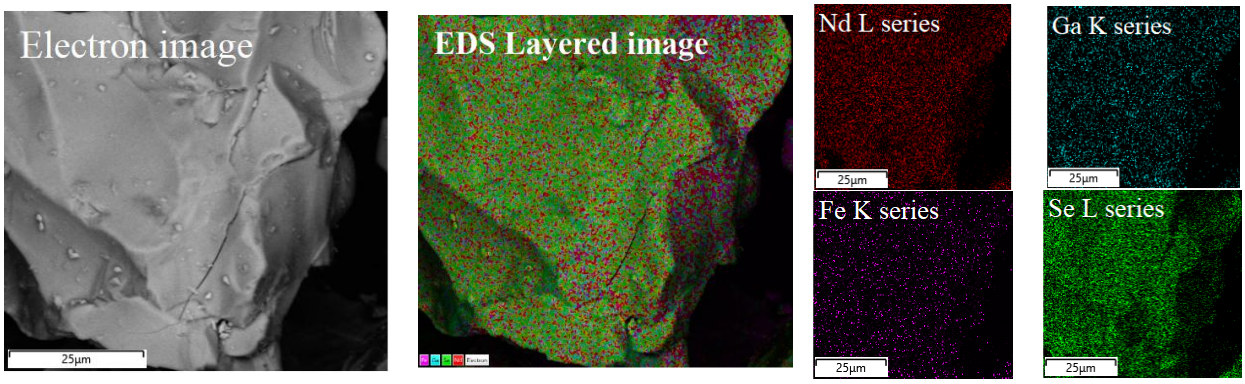
a) b)

Fig. 2. SEM image (a) and element distribution over the surface (b) of the $Ce_3Fe_{0.1}Ga_{1.6}Se_7$ alloy



a) b)

Fig. 3. SEM image (a) and element distribution over the surface (b) of the $Pr_3Fe_{0.1}Ga_{1.6}Se_7$ alloy.



a) b)

Fig. 4. SEM image (a) and element distribution over the surface (b) of the $Nd_3Fe_{0.1}Ga_{1.6}Se_7$ alloy.

For $La_3Fe_{0.1}Ga_{1.6}Se_7$ the calculated % La: 25.64, % Fe: 0.85, % Ga: 13.68, % Se: 59.83, and the found % La: 24.95, % Fe: 0.25, % Ga: 14.72, % Se: 60.07. For $Ce_3Fe_{0.1}Ga_{1.6}Se_7$ the calculated % Ce: 25.64, % Fe: 0.85, % Ga: 13.68, % Se: 59.83, and the found % Ce: 26.01, % Fe: 0.38, % Ga: 12.69, % Se: 60.92. For $Pr_3Fe_{0.1}Ga_{1.6}Se_7$ the calculated % Pr: 25.64, % Fe: 0.85, % Ga: 13.68, % Se: 59.83, and the found % Pr: 24.27, % Fe: 2.07, % Ga: 14.23, % Se: 59.43. For $Nd_3Fe_{0.1}Ga_{1.6}Se_7$ the calculated % Nd: 25.64, % Fe: 0.85, % Ga: 13.68, % Se: 59.83, and the found % Nd: 23.76, % Fe: 0.46, % Ga: 14.15, % Se: 61.63. The results of the element mapping demonstrate high levels of homogeneity and confirm the existence of the elements in the corresponding compounds.

The main structure parameters of the synthesized phases were calculated from the diffraction patterns obtained on the DRON 4-13 X-ray diffractometer (CuK_α radiation, 2Θ range 10–100°,: scan step 0.05°, 10 s exposure at each point. The crystal structure was calculated by the Rietveld method realized in WinCSD software package [13], and visualized using VESTA software [14].

II. Results and discussion

The selenides of the stoichiometric composition $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce, Pr, Nd) were obtained from the known ternary compounds $R_3Ga_{1.67}Se_7$ by isostructural modification of the crystal lattice. A targeted partial substitution of gallium atoms located in the 2*a* site with divalent iron atoms resulted in new chalcogenide phases. This approach preserved the general type of structure of the original compounds while providing the possibility of modifying their physico-chemical properties. The main crystal-chemical characteristics of the original ternary selenides are presented in Table 1.

The crystal structure of selenides was studied by X-ray powder method. Analysis of *hkl* indices and their intensities indicated that the structures of the synthesized chalcogenides belong to to structural type La_3CuSiS_7 [17]. The conditions of the X-ray experiment and crystallographic characteristics of the synthesized phases are shown in Tables 2 and 3.

Theoretical and experimental diffraction patterns and their difference for $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce, Pr, Nd) are presented in Figure 5. Refinement of the coordinates and isotropic thermal parameters of atoms in the structure of synthesized chalcogenides (Table 4) led to relatively satisfactory values of fit factors.

The crystal structure of synthesized selenides (Figures 6 and 7) belongs to the hexagonal symmetry and is formed by the trigonal prisms with one additional atom [R 7Se] (R – La, Ce, Pr, Nd). Rare earth atoms occupy the crystallographic site 6*c* and coordinate seven Se atoms. The trigonal prisms with one additional atom form blocks 3 [R 7Se] where they are connected by common edges which ensures the stability and integrity of the structural framework.

Introduction of divalent iron atoms to the structure of selenides $R_3Ga_{1.67}Se_7$ contributes to the fact that the trigonal prisms [R 7Se] become more symmetrical compared to those of the original compounds as evidenced by the values of the effective coordination number and the distortion index of the polyhedra. This indicates more regular geometry of the coordination environment of rare earth atoms in the doped structures.

In the structure $La_3Ga_{1.67}Se_7$ $CN_{eff}(\chi)$[La 7Se] = = 6.78(0.02325), in the structure $La_3Fe_{0.1}Ga_{1.6}Se_7$ $CN_{eff}(\chi)$[La 7Se] = 6.87(0.01784); in the structure $Ce_3Ga_{1.67}Se_7$ $CN_{eff}(\chi)$[Ce 7Se] = 6.79(0.02506), in the structure $Ce_3Fe_{0.1}Ga_{1.6}Se_7$ $CN_{eff}(\chi)$[Ce 7Se] = = 6.81(0.02029); in the structure $Pr_3Ga_{1.67}Se_7$ $CN_{eff}(\chi)$[Pr 7Se] = 6.77(0.02380), in the structure $Pr_3Fe_{0.1}Ga_{1.6}Se_7$ $CN_{eff}(\chi)$[Pr 7Se] = 6.91(0.00689); in the structure $Nd_3Ga_{1.67}Se_7$ $CN_{eff}(\chi)$[Nd 7Se] = 6.71(0.02723), in the structure $Nd_3Fe_{0.1}Ga_{1.6}Se_7$ $CN_{eff}(\chi)$[Nd 7Se] = = 6.88(0.01560).

Atoms of statistical mixtures M1–M4(Fe+Ga) occupy the 2*a* site and have octahedral coordination (C.N. = 6). The $Nd_3Fe_{0.1}Ga_{1.6}Se_7$ structure has the most symmetrical octahedra (χ=0.00418), the least symmetrical ones are in the $La_3Fe_{0.1}Ga_{1.6}Se$ structure (χ= 0.02690). The [M 6Se] octahedra have and form infinite columns by joint faces in the direction of the *c* axis.

Ga atoms occupy the 2*b* site and are characterized by the tetrahedral coordination (C.N. = 4). The most symmetrical [Ga 4Se] tetrahedra are in the $Pr_3Fe_{0.1}Ga_{1.6}Se_7$ structure (χ = 0.01214), the least symmetrical in the $La_3Fe_{0.1}Ga_{1.6}Se$ structure (χ = 0.02578).

Table 1.

Crystal-chemical characteristics of the selenides $R_3Ga_{1.67}Se_7$ (R – La, Ce, Pr, Nd)

Selenid	Space Group	Unit Cell, Å			Ref
		a	*b*	*c*	
$La_3Ga_{1.67}Se_7$	$P6_3$	10.44	–	6.20	[15]
$Ce_3Ga_{1.67}Se_7$	$P6_3$	10.41	–	6.18	
$Pr_3Ga_{1.67}Se_7$	$P6_3$	10.38	–	6.17	
$Nd_3Ga_{1.67}Se_7$	$P6_3$	10.30	–	6.25	[16]

Table 2.

Shooting conditions and results of refinement of the crystal structure of $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce)

Parameters	$La_3Fe_{0.1}Ga_{1.6}Se_7$	$Ce_3Fe_{0.1}Ga_{1.6}Se_7$
Space group and its number	$P6_3$ (173)	$P6_3$ (173)
a, (Å)	10.5358(8)	10.4379(5)
c, (Å)	6.3793(6)	6.3550(5)
Cell volume (Å^3)	613.2(2)	599.6(1)
Number of atom in cell	23.4	23.4
Calculated Density (g/cm^3)	5.884(2)	6.037(1)
Absorption coefficient (1/cm)	1093.41	1150.73
Number of atom sites	6	
2Θ та sinΘ/λ (max.)	100.00; 0.497	100.05; 0.497
R_I /R_P	0.0846/0.1575	0.0878/0.2137
Scale factor	0.25866(3)	0.5465(4)

Table 3.

Shooting conditions and results of refinement of the crystal structure of $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – Pr, Nd)

Параметри	$Pr_3Fe_{0.1}Ga_{1.6}Se_7$	$Nd_3Fe_{0.1}Ga_{1.6}Se_7$
Space group and its number	$P6_3$ (173)	$P6_3$ (173)
a, (Å)	10.3431(4)	10.2817(4)
c, (Å)	6.3735(4)	6.3819(4)
Cell volume (Å^3)	590.49(8)	584.26(8)
Number of atom in cell	23.4	23.4
Calculated Density (г/cm^3)	6.1455(9)	6.2668(9)
Absorption coefficient (1/cm)	1199.36	1259.80
Number of atom sites	6	
2Θ та sinΘ/λ (max.)	100.00; 0.497	100.00; 0.497
R_I / R_P	0.0739/0.1987	0.0939/0.2409
Scale factor	0.5156(3)	0.5401(4)

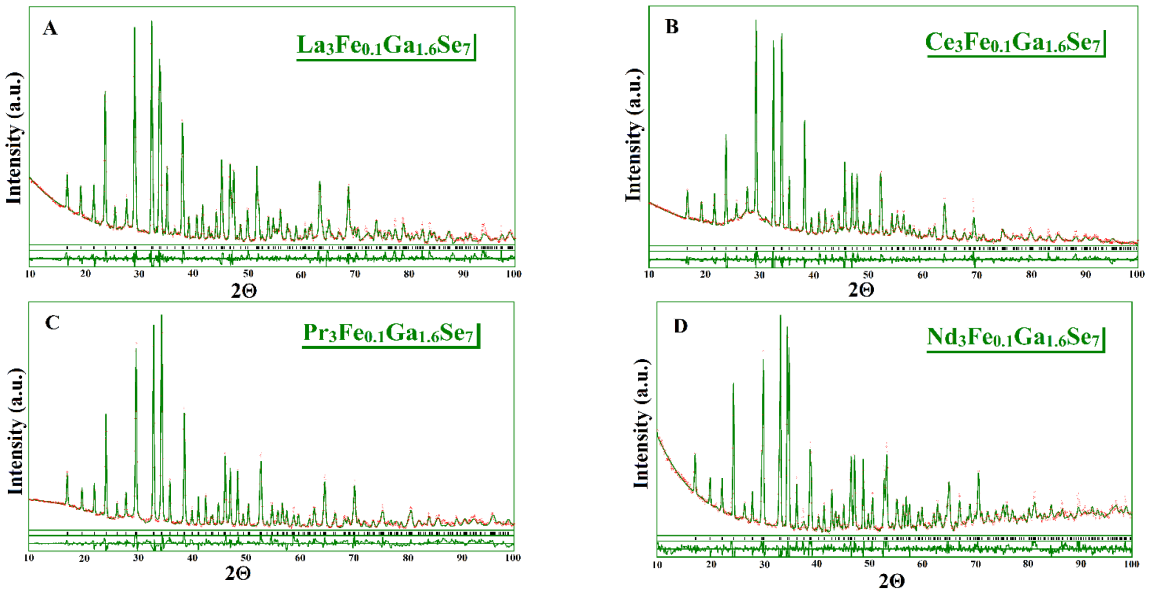


Fig. 5. Theoretical (−), experimental (°°°) and difference diffraction patterns between them for $La_3Fe_{0.1}Ga_{1.6}Se_7$ (sample A), $Ce_3Fe_{0.1}Ga_{1.6}Se_7$ (sample B), $Pr_3Fe_{0.1}Ga_{1.6}Se_7$ (sample C) and $Nd_3Fe_{0.1}Ga_{1.6}Se_7$ (sample D). [CuK_α-radiation (λ = 1.54185 Å)].

Table 4.

Coordinates and isotropic thermal parameters of atoms in the structure $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce, Pr та Nd)

$La_3Fe_{0.1}Ga_{1.6}Se_7$					
Atom	Site	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
La	6*c*	0.3755(3)	0.2252(3)	0.2081(8)	0.98(4)
Ga	2*b*	1/3	2/3	0.1495(14)	0.7(2)
M1	2*a*	0	0	0.000(3)	1.8(4)
Se1	2*b*	1/3	2/3	0.507(2)	1.3(2)
Se2	6*c*	0.1061(6)	0.2438(5)	0.2700(8)	1.16(10)
Se3	6*c*	0.5145(5)	0.0917(5)	0.4904(9)	1.02(10)
M1 – 0.1 Fe + 0.6 Ga					
$Ce_3Fe_{0.1}Ga_{1.6}Se_7$					
Atom	Site	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
Ce	6*c*	0.3752(5)	0.2252(4)	0.2089(13)	1.13(7)
Ga	2*b*	1/3	2/3	0.146(3)	1.2(4)
M2	2*a*	0	0	0.011(5)	1.1(6)
Se1	2*b*	1/3	2/3	0.508(3)	1.3(4)
Se2	6*c*	0.1082(10)	0.2426(8)	0.2714(13)	0.9(2)
Se3	6*c*	0.5125(9)	0.0931(8)	0.489(2)	1.0(2)
M2 – 0.1 Fe + 0.6 Ga					
$Pr_3Fe_{0.1}Ga_{1.6}Se_7$					
Atom	Site	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
Pr	6*c*	0.3771(3)	0.2226(2)	0.2093(7)	0.95(5)
Ga	2*b*	1/3	2/3	0.1355(13)	1.03(3)
M3	2*a*	0	0	0.028(3)	1.9(4)
Se1	2*b*	1/3	2/3	0.4996(14)	1.0(2)
Se2	6*c*	0.1034(6)	0.2443(5)	0.2720(7)	1.04(10)
Se3	6*c*	0.5151(5)	0.0891(5)	0.4890(8)	1.01(11)
M3 – 0.1 Fe + 0.6 Ga					
$Nd_3Fe_{0.1}Ga_{1.6}Se_7$					
Atom	Site	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
Nd	6*c*	0.3782(4)	0.2222(4)	0.2093(9)	0.48(8)
Ga	2*b*	1/3	2/3	0.136(2)	0.1(4)
M4	2*a*	0	0	0.025(4)	1.9(7)
Se1	2*b*	1/3	2/3	0.499(3)	0.1(3)
Se2	6*c*	0.1043(6)	0.2441(5)	0.2729(13)	0.3(2)
Se3	6*c*	0.5166(6)	0.0870(5)	0.4880(13)	0.2(2)
M4 – 0.1 Fe + 0.6 Ga					

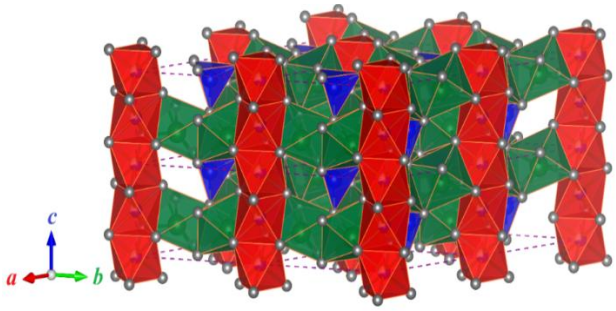


Fig. 6. Packing of polyhedra in the structure of selenides $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce, Pr, Nd).

The presence of divalent iron atoms in the structure of $R_3Ga_{1.67}Se_7$ selenides has virtually no effect on the symmetry of octahedra and tetrahedra, unlike the trigonal prisms.

The introduction of atoms of chemical elements of various nature (mainly divalent *d*-elements) into the structure of chalcogenides containing rare-earth metals opens up the possibility of targeted effect on the geometry of coordination polyhedra. Spatial organization of the crystal lattice can be modified in this approach, thus in turn creating materials with specified crystal structure parameters and controlled physical properties. Calculated parameters of polyhedra in chalcogenide structures $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce, Pr, Nd) are presented in Tables 5 and 6.

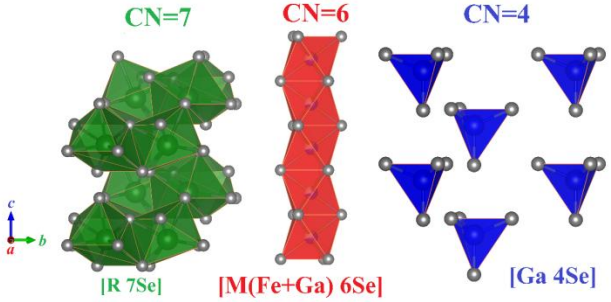


Fig. 7. Coordiation polyhedra [R 7Se], [M 6Se] and [Ga 4Se] in the structure of selenides $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce, Pr, Nd).

Table 5.

Parameters of polyhedra [La(Ce) 7Se], [M 6Se] and [Ga 4Se] in chalcogenide structures $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce)

Parameters	$La_3Fe_{0.1}Ga_{1.6}Se_7$	$Ce_3Fe_{0.1}Ga_{1.6}Se_7$
	[La 7Se]	[Ce 7Se]
δ(La(Ce) – Se), Å	2.967(8) – 3.154(6)	2.911(13) – 3.135(11)
$\delta(La(Ce) – Se)_{mean}$, Å	3.0618	3.0352
Distortion index (χ)	0.01784	0.02092
V, Å ^{3}	39.8324	38.8077
C.N. / $C.N._{eff.}$	7 / 6.87	7 / 6.81
	[M1 (Fe+Ga) 6Se]	[M2 (Fe+Ga) 6Se]
δ(M – Se), Å	2.669(12) – 2.817(13)	2.67(3) – 2.75(3)
$\delta(M – Se)_{mean}$, Å	2.7430	2.7114
Distortion index (χ)	0.02690	0.01373
V, Å ^{3}	27.4575	26.5547
C.N. / $C.N._{eff.}$	6 / 5.83	6 / 5.96
	[Ga 4Se]	
δ(Ga – Se1), Å	2.284(19)	2.30(3)
δ(Ga – Se3), Å	2.449(7)	2.417(12)
$\delta(Ga – Se)_{mean}$, Å	2.4076	2.3880
∠ Se1 – Ga – Se3, (°)	114.4(4)	114.4(5)
∠ Se3 – Ga – Se3, (°)	104.1(4)	104.1(6)
Distortion index (χ)	0.02578	0.01831
V, Å ^{3}	7.0971	6.9225
C.N. / $C.N._{eff.}$	4 / 3.82	4 / 3.92

Table 6.

Parameters of polyhedra [Pr(Nd) 7Se], [M 6Se] and [Ga 4Se] in chalcogenide structures $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – Pr, Nd)

Параметри	$Pr_3Fe_{0.1}Ga_{1.6}Se_7$	$Nd_3Fe_{0.1}Ga_{1.6}Se_7$
	[Pr 7Se]	[Nd 7Se]
δ(Pr(Nd) – Se), Å	2.941(7) – 3.138(5)	2.921(10) – 3.135(9)
$\delta(Pr(Nd) – Se)_{mean}$, Å	3.0250	3.0150
Distortion index (χ)	0.01337	0.01560
V, Å ^{3}	38.5372	38.1259
C.N. / $C.N._{eff.}$	7 / 6.91	7 / 6.88
	[M3 (Fe+Ga) 6Se]	[M4 (Fe+Ga) 6Se]
δ(M – Se), Å	2.695(13) – 2.733(13)	2.690(16) – 2.713(17)
$\delta(M – Se)_{mean}$, Å	2.7140	2.7018
Distortion index (χ)	0.00689	0.00418
V, Å ^{3}	26.6406	26.2732
C.N. / $C.N._{eff.}$	6 / 5.99	6 / 5.99
	[Ga 4Se]	
δ(Ga – Se1), Å	2.320(15)	2.31(6)
δ(Ga – Se3), Å	2.397(5)	2.404(9)
$\delta(Ga – Se)_{mean}$, Å	2.3777	2.3807
∠ Se1 – Ga – Se3, (°)	112.84(19)	113.1(4)
∠ Se3 – Ga – Se3, (°)	105.9(3)	105.6(5)
Distortion index (χ)	0.01214	0.01480
V, Å ^{3}	6.8676	6.8358
C.N. / $C.N._{eff.}$	4 / 3.97	4 / 3.95

Experimentally determined values of bond lengths $\delta(R\text{-}Se)_1$ and $\delta(R\text{-}Se)_2$ in the structure of the $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce, Pr, Nd) chalcogenides are in the range between the δ(R-Se) bond lengths calculated as the sum of covalent radii [18] and the sum of ionic radii [19] (Fig. 8).

The $\delta(R\text{-}Se)_3$, $\delta(R\text{-}Se)_4$ and $\delta(R\text{-}Se)_5$ values are close to the sum of the ionic radii. For $La_3Fe_{0.1}Ga_{1.6}Se_7$ and $Ce_3Fe_{0.1}Ga_{1.6}Se_7$ the values of $\delta(R\text{-}Se)_6$ and $\delta(R\text{-}Se)_7$ are larger than the bond length δ(R-Se) calculated as the sum of the ionic radii. For the selenides $Pr_3Fe_{0.1}Ga_{1.6}Se_7$ and $Nd_3Fe_{0.1}Ga_{1.6}Se_7$ only the $\delta(R\text{-}Se)_7$ values are larger than the sum of the ionic radii, whereas the bond lengths $\delta(R\text{-}Se)_6$ are close to the sum of the ionic radii.

Analysis of the bond lengths δ(R-Se) in the structures of the synthesized selenides demonstrates a gradual decrease in the distances in the La → Nd series due to the decreasing $r(R^{3+})$. This is consistent with the increase in

the symmetry of the coordination environment of R^{3+} as evidenced by the decreasing values of the distortion index (Tables 5 and 6). The non-uniform change in the value of individual bonds δ(R-Se) indicates local anisotropy of distortions within the coordination polyhedra.

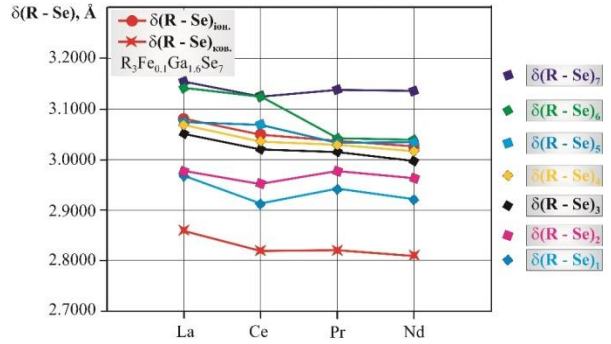


Fig. 8. Bond lengths δ(R - Se) in the structure of the $R_3Fe_{0.1}Ga_{1.6}Se_7$.

The changes in lattice parameters *a* and *c* (Å) and volume *V* (Å^3) for synthesized selenides depending on the nature of the rare earth element are plotted in Figure 9.

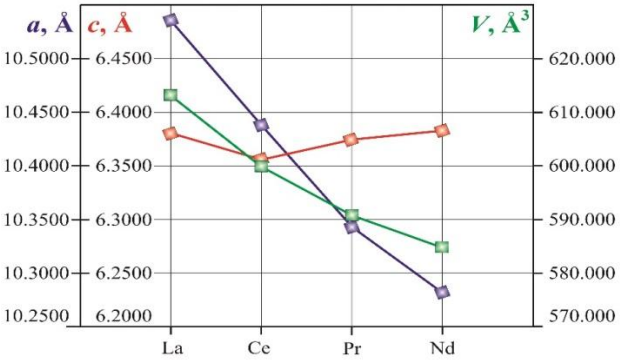


Fig. 9. Parameters of unit cell in the structure of the $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce, Pr, Nd).

A clear decrease is observed for the lattice parameter *a* (blue line), from La (10.5358(6) Å) to Nd (10.2817(4) Å). Observed pattern corresponds to the decrease in the ionic radius of the rare earth element. The unit cell volume *V* (green line) also gradually decreases from La (613.2(2) Å^3) to Nd (548.26(8) Å^3), which is consistent with the effect of lanthanide compression. The behavior of the parameter *c* (red line) is nontrivial: the initial decrease from La (6.3796(6) Å) to Ce (6.3550(5) Å) is followed by a slight increase (from Ce (6.3550(5) Å) to Nd (6.3819(4) Å)). Such a change may be associated with local distortion of the structure due to a change in the spatial orientation of the polyhedra.

Conclusions and prospects for further research.

New selenides $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce, Pr, Nd) were synthesized for the first time, and their crystal structure studied analyzed by X-ray powder method. Based on the analysis of experimentally obtained data sets, it was established that these chalcogenides crystallize in the hexagonal symmetry (La_3CuSiS_7 srtucture type, S.G. $P6_3$, Pearson symbol *hP*24) with unit cell parameters a = 10.5358(8) Å, c = 6.3796(6) Å, V=613.2(2) Å^3 ($La_3Fe_{0.1}Ga_{1.6}Se_7$); a = 10.4379(5) Å, c=6.3550(5) Å, V = 599.6(1) Å^3 ($Ce_3Fe_{0.1}Ga_{1.6}Se_7$); a=10.3431(4) Å, c = 6.3735(8) Å, V = 590.49(8) Å^3 ($Pr_3Fe_{0.1}Ga_{1.6}Se_7$); and a = 10.2817(4) Å, c= 6.3819(4) Å, V = 548.26(8) Å^3 ($Nd_3Fe_{0.1}Ga_{1.6}Se_7$). The inclusion of divalent iron atoms into the structure of the $R_3Ga_{1.67}Se_7$ selenides contributes not only to a variation in the elemental composition, but also significantly affects the geometry of coordination polyhedra. As a result of a decrease in the ionic radius of the rare earth elements (La → Nd), the structure adapts by reducing the bond lengths and volumes of polyhedra, which leads to a more compact packing of the crystal structure, more symmetrical polyhedral fragments, and optimization of the spatial interaction between structural blocks. These changes can significantly affect the physical properties of materials, such as electrical conductivity, magnetic characteristics or heat resistance, which makes such structure control a promising tool in materials science.

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Синтез та кристалічна структура селенідів $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce, Pr, Nd)

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Зразки стехіометричного складу $R_3Fe_{0.1}Ga_{1.6}Se_7$ (R – La, Ce, Pr, Nd) синтезовано з високочистих елементів у вакуумованих кварцових контейнерах при максимальній температурі синтезу 1100°C. Отримані сплави гомогенізували відпалом при 500°C протягом місяця. Кристалічна структура селенідів, досліджена методом рентгеноструктурного аналізу, показала, що вони належать до структурного типу La_3CuSiS_7 (S.G. P63, символ Пірсона hP24). Параметри кристалічної гратки: a = 10,5358(8) Å, c = 6,3796(6) Å, V = 613,2(2) Å3, RI = 0,0846, Rp = 0,1575 (зразок A, $La_3Fe_{0.1}Ga_{1.6}Se_7$); a = 10,4379(5) Å, c = 6,3550(5) Å, V = 599,6(1) Å3, RI = 0,0878, Rp = 0,2137 (зразок B, $Ce_3Fe_{0.1}Ga_{1.6}Se_7$); a = 10,3431(4) Å, c = 6,3735(8) Å, V = 590,49(8) Å3, RI = 0,0846, Rp = 0,1575 (зразок C, $Pr_3Fe_{0.1}Ga_{1.6}Se_7$); a = 10,2817(4) Å, c = 6,3819(4) Å, V = 548,26(8) Å3, RI = 0,0939, Rp = 0,2409 (зразок D, $Nd_3Fe_{0.1}Ga_{1.6}Se_7$). Отримані халькогеніди походять від селенідів $R_3Ga_{1,67}Se_7$ (R – La, Ce, Pr, Nd) шляхом часткового заміщення атомів Ga в позиції 2a (0 0 z) двовалентними атомами Fe. Атоми рідкісноземельних елементів у досліджуваних структурах займають позицію 6c (x y z) та разом з атомами Se утворюють тригональні призми з одним додатковим атомом [R 7Se]. Тригональні призми мають спільні ребра, утворюючи 3 блоки [R 7Se]. Атоми Fe та Ga статистично розподілені в позиції 2a (0 0 z) та мають октаедричне оточення. Октаедри [M (позиція 2a) 6Se] мають спільні грані, утворюючи просторові колони [M(Fe + Ga)Se_6]n вздовж осі c, які з'єднані з тригональними призмами спільними ребрами. Частина атомів Ga розташована в центрі тетраедрів [Ga 4Se] в позиції 2b (1/3 2/3 z).

Ключові слова: рідкісноземельні елементи, селеніди, кристалічна структура, рентгенівський порошковий метод, енергодисперсійна рентгенівська спектроскопія.