CRYSTAL STRUCTURE OF $R_3GaGe_{0.5}Se_7$ (R – Ce, Nd, Sm)

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Selenides of stoichiometric composition $R_3GaGe_{0.5}Se_7$ (R – Ce, Nd, Sm) are separate compositions of solid solutions formed in the $R_3Ga_{1.67}Se_7 – R_3Ge_{1.48}Se_7$ (R – Ce, Nd, Sm) systems.

The principal structure parameters of the synthesized selenides were calculated by the Rietveld method (WinCSD software package [1]) from the diffraction patterns (fig.1) recorded at a DRON 4-13 X-ray diffractometer in 2Θ range of 10 – 100°. Visualization of the crystal structure utilized the VESTA software [2].

The coordinates and thermal parameters of atoms for the synthesized selenides are presented in Table 1.

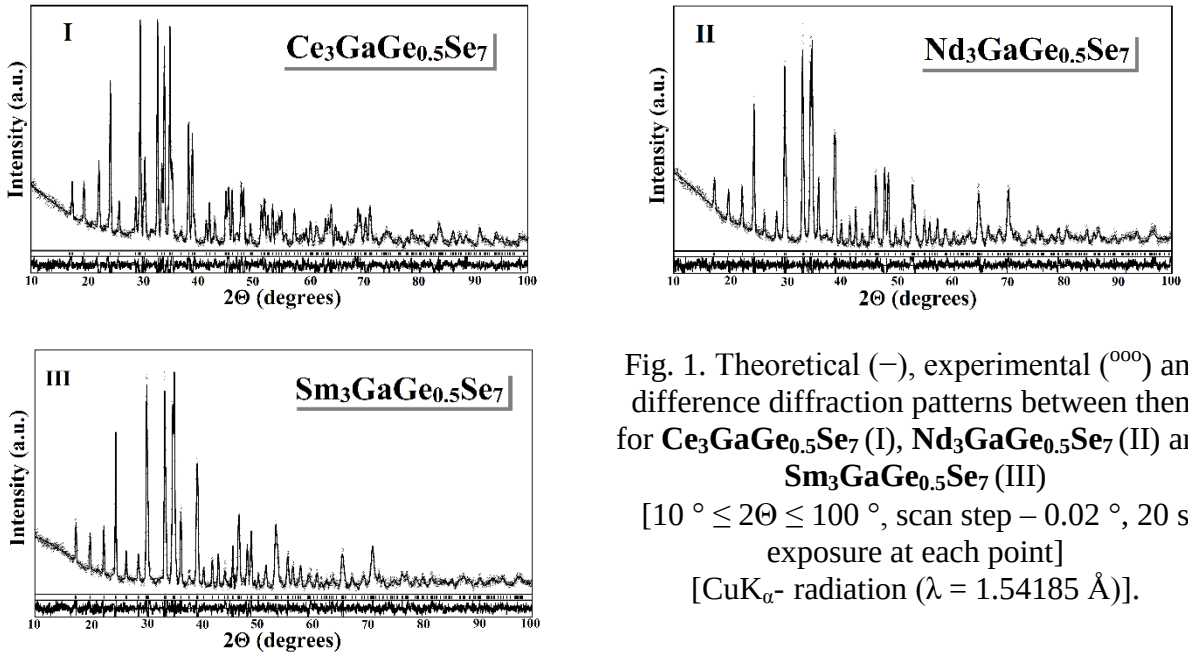

Fig. 1. Theoretical (−), experimental (ᵒᵒᵒ) and difference diffraction patterns between them for **$Ce_3GaGe_{0.5}Se_7$** (I), **$Nd_3GaGe_{0.5}Se_7$** (II) and **$Sm_3GaGe_{0.5}Se_7$** (III) [10 ° ≤ 2Θ ≤ 100 °, scan step – 0.02 °, 20 s exposure at each point] [CuK_α- radiation (λ = 1.54185 Å)].

The crystal structure of selenides **$Ce_3GaGe_{0.5}Se_7$** (I) {a = 10.5395(4) Å, c = 6.1900(3) Å, V=595.47(7) Å^3, R_I = 0.0743, R_P = 0.2100}, **$Nd_3GaGe_{0.5}Se_7$** (II) {a = 10.3643(7) Å, c = 6.2672(6) Å, V=583.0(1) Å^3, R_I = 0.0968, R_P = 0.2120} and **$Sm_3GaGe_{0.5}Se_7$** (III) {a = 10.2734(4) Å, c = 6.2185(4) Å, V=568.39(8) Å^3, R_I = 0.0937, R_P = 0.2176} was studied by X-ray powder diffraction. The structure of the synthesized phases belongs to the hexagonal symmetry (**La_3CuSiS_7** structure type; space group $P6_3$; symbol Pearson hP23, № 173).

The structures of synthesized selenides are characterized by the formation of trigonal prisms [R 7Se] with one additional atom, octahedra [M1 6Se], and tetrahedra [M2 4Se]. The packing of these polyhedra is presented in Fig. 2. Ce, Nd, and Sm atoms are localized in the 6c site and coordinate seven Se atoms each, forming trigonal prisms with one additional atom. These prisms are connected to each other by common edges and form "blocks" 3[R 7Se]. Ga and Ge atoms are statistically distributed in two sites, 2a (1/3Ga + 1/6Ge) and 2b (2/3Ga + 1/3Ge). Statistical mixtures M1-2 are characterized by a high Ga content and have the following composition: 66.7% Ga and 33.3% Ge in each of the two-fold sites. The M1 atoms center the octahedra, and the M2 atoms center the tetrahedra.

Table. 1. Coordinates and thermal parameters of atoms for **$R_3GaGe_{0.5}Se_7$ (R – Ce, Nd, Sm)**

	$Ce_3GaGe_{0.5}Se_7$	**$Nd_3GaGe_{0.5}Se_7$**	**$Sm_3GaGe_{0.5}Se_7$**
R 6*c* (x y z)			
x	0.1405(3)	0.1436(3)	0.1459(3)
y	0.3678(3)	0.3691(3)	0.3684(3)
z	0.2431(6)	0.2356(3)	0.2326(7)
$B_{iso}\times10^2$ (Å^2)	1.09(4)	0.13(4)	1.86(4)
M1 2*a* (0 0 0*)			
$B_{iso}\times10^2$ (Å^2)	1.3(4)	0.95(9)	1.03(8)
M2 2*b* (1/3 2/3 z)			
z	0.6719(11)	0.6744(11)	0.6680(11)
$B_{iso}\times10^2$ (Å^2)	0.7(2)	0.07(8)	2.02(8)
Se1 6*c* (x y z)			
x	0.0976(4)	0.0963(5)	0.0975()
y	0.2461(4)	0.2472(4)	0.2461(5)
z	0.7796(6)	0.7599(8)	0.7689(7)
$B_{iso}\times10^2$ (Å^2)	1.08(8)	0.36(7)	2.02(6)
Se2 6*c* (x y z)			
x	0.4221(5)	0.4310(5)	0.4298(5)
y	0.5178(5)	0.5187(7)	0.5231(6)
z	0.5371(7)	0.5149(8)	0.5068(8)
$B_{i3o}\times10^2$ (Å^2)	1.19(9)	0.77(7)	1.68(7)
Se3 2*b* (1/3 2/3 z)			
z	0.0445(11)	0.0516(13)	0.0439(12)
$B_{iso}\times10^2$ (Å^2)	0.14(13)	0.36(8)	0.08(7)
* - fixed; **M1** – 1/3Ga + 1/6Ge; **M2** – 2/3Ga + 1/3Ge			

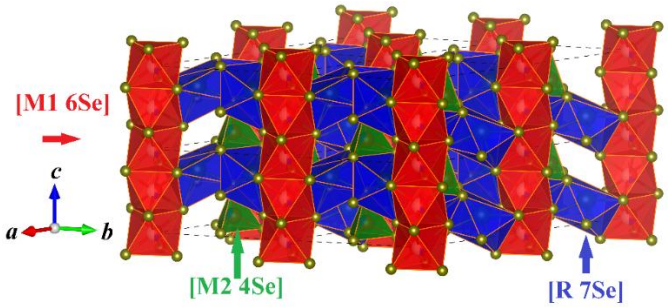

Fig. 2. Packing of polyhedra in the structure **$R_3GaGe_{0.5}Se_7$ (R – Ce, Nd, Sm)**

The [M1 6Se] octahedra in the c-axis direction form "columns" with common faces. The [M2 4Se] tetrahedra are located isolated from each other and are connected to the "blocks" of prisms by one vertex and three edges.

The unit cell parameter *a* decreases from 10.5395(4) Å (for **$Ce_3GaGe_{0.5}Se_7$**) to 10.2734(4) Å (for **$Sm_3GaGe_{0.5}Se_7$**) in the Ce → Nd → Sm series, *b* changes non-monotonously, and the volume *V* decreases from 595.47(7) Å (for **$Ce_3GaGe_{0.5}Se_7$**) to 584.26(2) Å^3 (for **$Sm_3GaGe_{0.5}Se_7$**) due to the decrease in the

$r_{R^{3+}}$ value: $r(Ce^{3+})$ = 1.210 Å, $r(Nd^{3+})$ = 1.186 Å, $r(Sm^{3+})$ = 1.160 Å (for C.N.=7). These values of the R^{3+} ionic radii also affect the bond lengths and geometric parameters of the polyhedra, namely, as $r_{R^{3+}}$ decreases, the average bond length δ(R – Se), δ(M1 – Se) and δ(M2 – Se) decreases monotonously in the Ce → Nd → Sm series; the volumes of trigonal prisms [R 7Se] decrease, while the values of the effective coordination numbers for R (6.75-6.78) indicate only a slight distortion of these polyhedra. A non-monotonous decrease of the above parameters is observed for the [M1 6Se] octahedra. The [M2 4Se] tetrahedra in the structure of these phases retain their symmetry ($C.N._{eff}$=3.99) and occupy voids formed by the trigonal prisms.

The parameters of the polyhedra are presented in Table 2. The calculated bond lengths (Table 3) are consistent with the sums of the corresponding ionic radii [3].

Table. 2. Parameters of polyhedra in structures
$Ce_3GaGe_{0.5}Se_7$ (I), **$Nd_3GaGe_{0.5}Se_7$** (II) та **$Sm_3GaGe_{0.5}Se_7$** (III)

Phase	Polyhedron	Average bond length , Å	Polyhedral volume, Å^3	Distortion index (bond length), χ	C.N. eff
I	[Ce 7Se]	3.0579	39.0817	0.02573	6.78
	[M1 6Se]	3.0775	37.7975	0.03000	5.79
	[M2 4Se]	2.3755	6.8273	0.00504	3.99
II	[Nd 7Se]	3.0311	38.0770	0.02875	6.75
	[M1 6Se]	2.7309	27.1401	0.01302	5.96
	[M2 4Se]	2.4199	7.2034	0.00897	3.98
III	[Sm 7Se]	3.0006	36.9960	0.02769	6.77
	[M1 6Se]	2.7002	26.1998	0.02516	5.86
	[M2 4Se]	2.3594	6.6573	0.00464	3.99

Table. 3. Bond lengths and coordination number in
$R_3GaGe_{0.5}Se_7$ (R – Ce, Nd, Sm) structures

Atoms		δ(R – Se), Å			C.N.
		$Ce_3GaGe_{0.5}Se_7$	$Nd_3GaGe_{0.5}Se_7$	$Sm_3GaGe_{0.5}Se_7$	
R	– Se1	2.96445(18)	2.93496(18)	9207(4)	7
	– Se1	2.97987(12)	2.9496(2)	2.9218(4)	
	– Se2	3.00330(10)	2.9534(2)	2.92797(11)	
	– Se3	3.00868(11)	2.98146(17)	2.94118(10)	
	– Se2	3.08223(11)	3.10044(18)	3.05645(11)	
	– Se2	3.15574(11)	3.11826(18)	3.085(5)	
	– Se1	3.21112(13)	3.1797(3)	3.15149(11)	
δ(M1 – Se), Å					
M1	– 3Se1	2.98513(10)	2.69536(15)	2.632(3)	6
	– 3Se1	3.16981(11)	2.76646(16)	2.768(3)	
δ(M2 – Se), Å					
M2	– Se3	2.35158(16)	2.3765(3)	2.338(7)	4
	– 3Se2	2.38351(8)	2.43441(15)	2.367(3)	

[1] L. Akselrud, Y. Grin, *WinCSD: Software package for crystallographic calculations (Version 4)*, J. Appl. Cryst., 47, 803 (2014); https://doi.org/10.1107/s1600576714001058
[2] K. Momma, F. Izumi, *VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data*, J. Appl. Cryst., 44, 1272 (2011); https://doi.org/10.1107/S002188981103897
[3] N. Wiberg, E. Wiberg, A. Holleman, *Lehrbuch der Anorganischen Chemie., Walter de Gruyter. 102. Auflage*, 2003 (2007).