PHYSICS AND CHEMISTRY
OF SOLID STATE
V. 25, No.4 (2024) pp. 677-683

Section: Chemistry

DOI: 10.15330/pcss.25.4.677-683

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 25, № 4 (2024) С. 677-683

Хімічні науки

UDC: 544.022.242

ISSN 1729-4428 (Print)
ISSN 2309-8589 (Online)

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The crystal structure of $R_3Fe_{0.1}Ga_{1.6}S_7$ chalcogenides (R – La, Ce, Pr and Tb)

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The paper reports the study of the crystal structure of chalcogenides of the composition $R_3Fe_{0.1}Ga_{1.6}S_7$ (R = La, Ce, Pr and Tb) as promising materials predicted to possess interesting nonlinear optical and electrical properties. The 1 g samples of stoichiometric composition were synthesized by co-melting the elements in quartz containers evacuated to a residual pressure of 10^{-2} Pa at the maximum synthesis temperature of 1100 °C. The crystal structure of the chalcogenides $La_3Fe_{0.1}Ga_{1.6}S_7$ (A) {a = 10.1884(6) Å, c = 6.0515(4) Å, R_I = 0.0940, R_P = 0.2503}, $Ce_3Fe_{0.1}Ga_{1.6}S_7$ (B) {a = 10.0864(4) Å, c = 6.0440(3) Å, R_I = 0.0695, R_P = 0.1935}, $Pr_3Fe_{0.1}Ga_{1.6}S_7$ (C) {a = 9.9853(3) Å, c = 6.0648(2) Å, R_I = 0.0730, R_P = 0.1777} and $Tb_3Fe_{0.1}Ga_{1.6}S_7$ (D) {a = 9.6692(7) Å, c = 6.0799(5) Å, R_I = 0.0909, R_P = 0.2742} was studied by X-ray powder method. It was determined that the structure of the synthesized phases belongs to the hexagonal symmetry (La_3CuSiS_7 structure type; space group $P6_3$ (No. 173); Pearson symbol *hP24*). The structure of the complex chalcogenides (A), (B), (C) and (D) is based on the $R_3Ga_{1.67}S_7$ sulfides (R = La, Ce, Pr, and Tb) by substituting gallium atoms in the 2a sites with atoms of statistical mixture M1{0.57(2) Ga + 0.10(2) Fe}, M2{0.56(1) Ga + 0.10(2) Fe}, M3 {0.61(8) Ga + 0.09(1) Fe} and M4 {0.57(2) Ga + 0.10(2) Fe}, respectively. Rare earth atoms are localized in the 6c sites and center sulfur atoms to form trigonal prisms with an additional atom [R $3S_13S_21S_3$]. The trigonal prisms form "blocks" 3[R 7S] where they share edges. Atoms of statistical mixtures M1, M2, M3, M4 are localized in the 2a sites forming [M $6S_2$] octahedra. These octahedra are face-sharing and form columns in the direction of the c axis. Ga atoms in the 2b sites are surrounded by four sulfur atoms [Ga $3S_11S_3$].

Key words: crystal structure, rare earth elements, chalcogenides, X-ray powder method, EDAX analysis.

Received 12 March 2024; Accepted 11 October 2024.

Introduction

A rather promising area of the development of modern chemical technology and crystal chemistry is the study of chalcogenides containing elements of the lanthanide family [1, 2]. Such compounds have interesting optical [3], magnetic [4], thermal [5], electrical [6, 7] and other properties. The presence of transition metal atoms in the cell creates a corresponding crystal-chemical order in which lanthanides occupy internal sites [8, 9]. Such chalcogenides crystallize in a non-centrosymmetric hexagonal space group $P6_3$ and can have nonlinear optical properties [10-14]. The paper presents the results of the study of the crystal structure of four chalcogenides $La_3Fe_{0.1}Ga_{1.6}S_7$, $Ce_3Fe_{0.1}Ga_{1.6}S_7$, $Pr_3Fe_{0.1}Ga_{1.6}S_7$ and $Tb_3Fe_{0.1}Ga_{1.6}S_7$ by the Rietveld method. One of the goals of the research is to obtain complex rare-earth-containing chalcogenides within the search for materials with predicted physical properties.

I. Experimental

Four 1 g alloys to study the crystal structure of the $R_3Fe_{0.1}Ga_{1.6}S_7$ chalcogenides (R = La, Ce, Pr, and Tb) were synthesized from high-purity elements (at least 99.99 mass %) in an MP-30 electric muffle furnace. The synthesis in evacuated to 10^{-2} Pa quartz containers was step-wise by heating to 700°C at the rate of 40°C/h; exposure for 10 h; heating to 1100°C at 12°C/h; exposure for 2 h; cooling to 500°C at 6°C/h; homogenizing annealing for 240 h; quenching into room-temperature water without unsealing the containers.

The principal structure parameters of the synthesized phases were calculated from the diffraction patterns recorded at a DRON 4-13 diffractometer (CuK$_\alpha$ radiation; 2Θ range = 10–100°; scan step 0.02°; 10 s exposure at each point). The crystal structure was calculated using the Rietveld method realized in WinCSD software package [15]. Visualization of the crystal structure utilized VESTA software [16].

II. Results and discussion

The structure of the sulfides of stoichiometric composition $R_3Fe_{0.1}Ga_{1.6}S_7$ (R = La, Ce, Pr and Tb) is obtained from the ternary compounds $R_3Ga_{1.67}S_7$ (R = La, Ce, Pr and Tb) by partial substitution of gallium atoms in the 2*a* sites with divalent ferrum. The crystallographic characteristics of the original chalcogenides are presented in Table 1.

Table 1.

Crystallographic characteristics of $R_3Ga_{1.67}S_7$ (R – La, Ce, Pr, Tb) compounds

Compound	*Space group*	Unit Cell, Å			Ref.
		a	***b***	***c***	
$La_3Ga_{1.67}S_7$	$P6_3$	10.15	–	6.08	[17, 18]
$La_3Ga_{1.67}S_7$	$P6_3$	10.17	–	6.082	[19]
$Ce_3Ga_{1.67}S_7$	$P6_3$	10.03	–	6.08	[17, 18]
$Pr_3Ga_{1.67}S_7$	$P6_3$	9.94	–	6.08	[18]
$Tb_3Ga_{1.67}S_7$	$P6_3$	9.67	–	6.08	[18, 20]

The crystal structure of sulfides was studied by X-ray powder method. Analysis of Miller indices *hkl* of the reflections and their intensities indicated that the structure of the synthesized chalcogenides belongs to the structural type La_3CuSiS_7 [21]. The conditions of the X-ray experiment and the crystallographic characteristics of the

Table 2.

Shooting conditions and results of refinement of the crystal structure of $R_3Fe_{0.1}Ga_{1.6}S_7$ chalcogenides (R – La, Ce)

Parameters	$La_3Fe_{0.1}Ga_{1.6}S_7$	$Ce_3Fe_{0.1}Ga_{1.6}S_7$
Space group	$P6_3$ (173)	$P6_3$ (173)
a, (Å)	10.1884(6)	10.0864(4)
c, (Å)	6.0515(4)	6.0440(3)
Cell volume (Å^3)	544.0(1)	532.51(6)
Number of atoms in cell	23.3	23.3
Calculated Density (g/cm^3)	4.6130(9)	4.7351(6)
Absorption coefficient (1/cm)	1044.88	1104.07
Radiation and wavelenght (Å)	Cu 1.54185	
Diffractometer	Dron 4-13	
Mode of refinement	Full Profile	
Program	WinCSD	
Number of atom sites	6	
Number of free parameters	19	
2Θ and sinΘ/λ (max.)	100.00; 0.496	100.05; 0.497
R_I	0.0940	0.0695
R_P	0.2503	0.1935
Scale factor	0.25030(5)	0.5262(3)

Table 3.

Shooting conditions and results of refinement of the crystal structure of $R_3Fe_{0.1}Ga_{1.6}S_7$ chalcogenides (R – Pr, Tb)

Parameters	$Pr_3Fe_{0.1}Ga_{1.6}S_7$	$Tb_3Fe_{0.1}Ga_{1.6}S_7$
Space group	$P6_3$ (173)	$P6_3$ (173)
a, (Å)	9.9853(3)	9.6692(7)
c, (Å)	6.0648(2)	6.0799(5)
Cell volume (Å^3)	523.68(4)	492.3(1)
Number of atoms in cell	23.3	23.3
Calculated Density (g/cm^3)	4.8462(4)	5.505(1)
Absorption coefficient (1/cm)	1158.18	1174.46
Radiation and wavelenght (Å)	Cu 1.54185	
Diffractometer	Dron 4-13	
Mode of refinement	Full Profile	
Program	WinCSD	
Number of atom sites	6	
Number of free parameters	19	
2Θ and sinΘ/λ (max.)	100.02; 0.497	100.00; 0.497
R_I	0.0730	0.0909
R_P	0.1777	0.2742
Scale factor	0.17824(0)	0.22804(2)

synthesized chalcogenides are shown in Tables 2 and 3.

The observed, calculated and difference diffraction patterns of $R_3Fe_{0.1}Ga_{1.6}S_7$ chalcogenides (R – La, Ce, Pr and Tb) are shown in Figure 1.

Refinement of coordinates and isotropic thermal displacement parameters of atoms (Table 4) resulted in relatively satisfactory values of fit factors.

Unit cell and coordination polyhedra [R 7S], [M 6S] and [Ga 4S] in the structure of synthesized sulfides are shown in Figure 2.

The crystal structure of the synthesized sulfides belongs to hexagonal symmetry and contains by the trigonal prisms [R $3S_1 3S_2 1S_3$] (R – La, Ce, Pr or Tb). Rare earth atoms occupy the 6*c* sites and coordinate seven sulfur atoms. The trigonal prisms with an additional atom form "blocks" 3[R 7S] where the prisms share edges.

Atoms of statistical mixtures M1–M4 occupying the 2*a* sites are characterized by the octahedral coordination (C.N. 6). The [M $6S_2$] octahedra have joint faces and form columns in the direction of the *c* axis.

The introduction of divalent metal atoms to the structure of the sulfides $La_3Ga_{1.67}S_7$ and $Ce_3Ga_{1.67}S_7$ results in more symmetrical octahedra [M $6S_2$] compared to [Ga $6S_2$]: χ([Ga $6S_2$]) = 0.03891 in the $La_3Ga_{1.67}S_7$ structure *vs* χ([M $6S_2$]) = 0.02398 in $La_3Fe_{0.1}Ga_{1.6}S_7$; χ([Ga $6S_2$]) = 0.03955 in $Ce_3Ga_{1.67}S_7$ *vs* χ([M $6S_2$]) = 0.02379 in the structure of $Ce_3Fe_{0.1}Ga_{1.6}S_7$

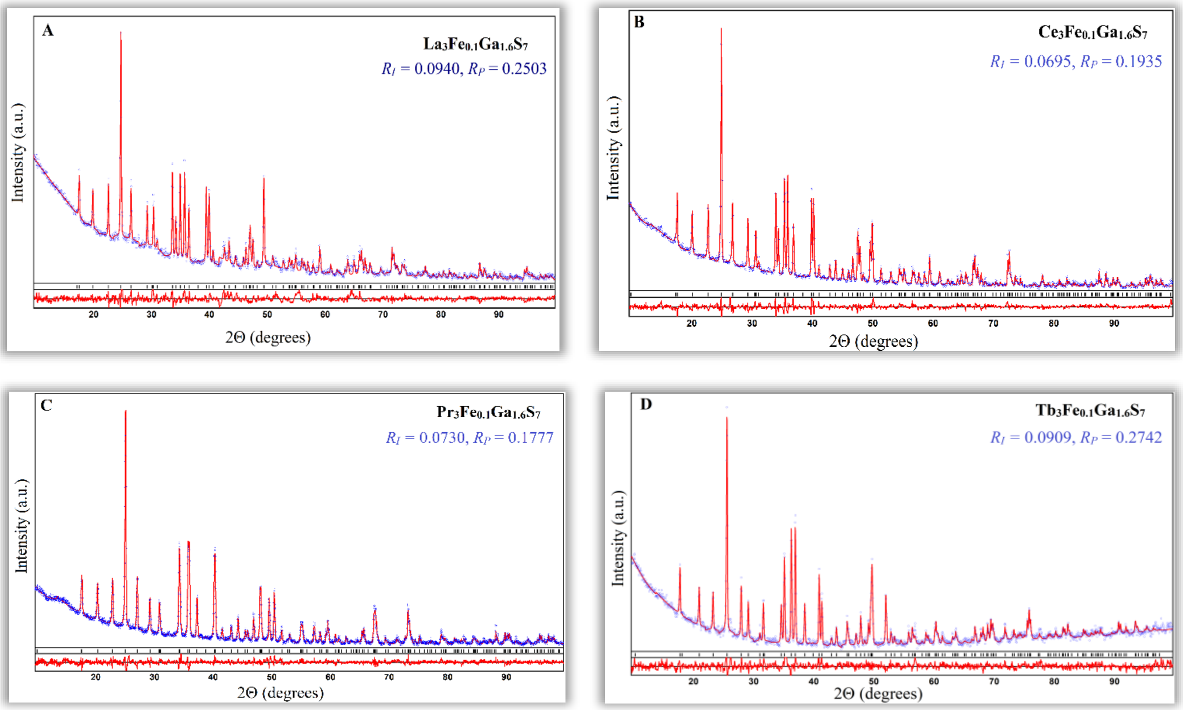

Fig. 1. Observed, calculated and difference diffraction patterns of chalcogenides: $La_3Fe_{0.1}Ga_{1.6}S_7$ (A), $Ce_3Fe_{0.1}Ga_{1.6}S_7$ (B), $Pr_3Fe_{0.1}Ga_{1.6}S_7$ (C) and $Tb_3Fe_{0.1}Ga_{1.6}S_7$ (D).

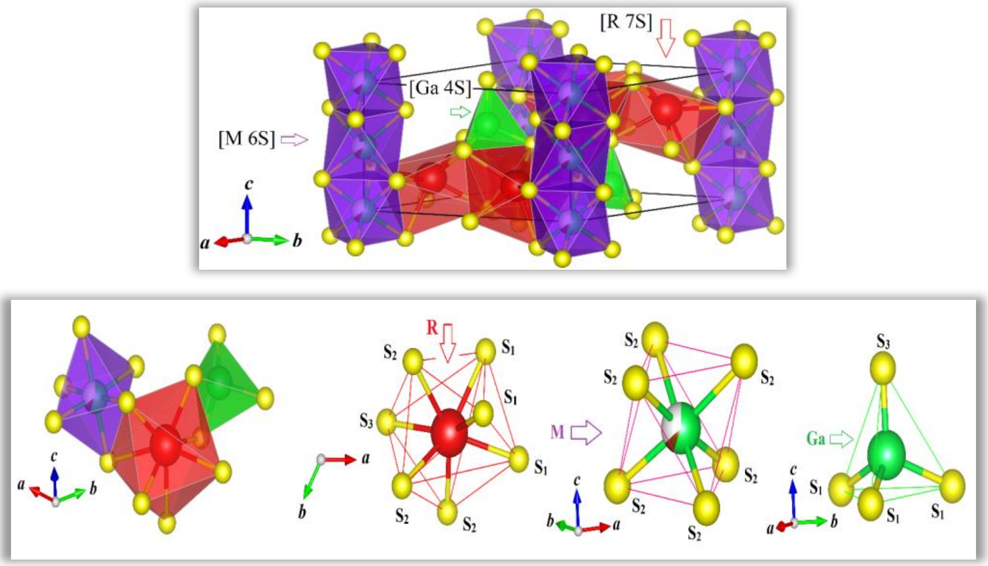

Fig. 2. Unit cell and coordination polyhedra [R 7S], [M 6S] and [Ga 4S] in the structure $R_3Fe_{0.1}Ga_{1.6}S_7$ (R – La, Ce, Pr and Tb).

Table 4.

Coordinates and isotropic thermal parameters of atoms in the structure $R_3Fe_{0.1}Ga_{1.6}S_7$ chalcogenides (R – La, Ce, Pr та Tb).

$La_3Fe_{0.1}Ga_{1.6}S_7$					
Atom	Wyck	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
La	6*c*	0.3746(3)	0.2324(3)	0.2224(11)	1.12(4)
Ga	2*b*	1/3	2/3	0.1399(15)	1.4(3)
M1	2*a*	0	0	0.00000	1.5(3)
S1	6*c*	0.507(2)	0.0985(12)	0.486(2)	0.9(3)
S2	6*c*	0.0888(11)	0.2303(11)	0.267(2)	0.7(3)
S3	2*b*	1/3	2/3	0.483(3)	1.1(5)
M1 – 0.57(2) Ga + 0.10(2) Fe					
$Ce_3Fe_{0.1}Ga_{1.6}S_7$					
Atom	Wyck	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
Ce	6*c*	0.3743(2)	0.2328(2)	0.2286(8)	0.62(4)
Ga	2*b*	1/3	2/3	0.1502(11)	0.3(2)
M2	2*a*	0	0	0.00000	0.9(3)
S1	6*c*	0.0912(9)	0.2435(9)	0.269(2)	0.3(2)
S2	6*c*	0.1519(13)	0.0925(11)	0.4982(15)	0.7(3)
S3	2*b*	1/3	2/3	0.518(3)	0.3(4)
M2 – 0.56(1) Ga + 0.10(2) Fe					
$Pr_3Fe_{0.1}Ga_{1.6}S_7$					
Atom	Wyck	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
Pr	6*c*	0.3742(2)	0.1453(2)	0.2345(5)	1.04(5)
Ga	2*b*	1/3	2/3	0.1568(6)	0.65(13)
M3	2*a*	0	0	0.018(2)	1.7(2)
S1	6*c*	0.1008(7)	0.5218(8)	0.0074(9)	0.9(3)
S2	6*c*	0.1470(7)	0.2394(6)	0.2969(9)	0.8(3)
S3	2*b*	1/3	2/3	0.5167(15)	0.6(3)
M3 – 0.61(8) Ga + 0.09(1) Fe					
$Tb_3Fe_{0.1}Ga_{1.6}S_7$					
Atom	Wyck	*x/a*	*y/b*	*z/c*	$B_{iso}\times10^2$ (Å^2)
Tb	6*c*	0.3779(3)	0.2244(11)	0.2142(11)	1.06(6)
Ga	2*b*	1/3	2/3	0.1475(15)	0.7(3)
M4	2*a*	0	0	0.001(3)	1.3(4)
S1	6*c*	0.491(2)	0.074(2)	0.488(2)	1.4(3)
S2	6*c*	0.0944(14)	0.2620(13)	0.292(2)	1.0(4)
S3	2*b*	1/3	2/3	0.513(4)	0.6(5)
M4 – 0.57(2) Ga + 0.10(2) Fe					

$Pr_3Ga_{1.67}S_7$ and $Tb_3Ga_{1.67}S_7$ exhibit the opposite behavior, with the [M $6S_2$] octahedra becoming less symmetrical than [Ga $6S_2$] ones: χ([Ga $6S_2$]) = 0.00845 in $Pr_3Ga_{1.67}S_7$ *vs* χ([M $6S_2$]) = 0.04118 in $Pr_3Fe_{0.1}Ga_{1.6}S_7$; and χ([Ga $6S_2$]) = 0.00876 in $Tb_3Ga_{1.67}S_7$ *vs* χ([M $6S_2$]) = 0.05194 in the $Tb_3Fe_{0.1}Ga_{1.6}S_7$ structure.

Gallium atoms occupying 2*b* sites are characterized by the tetrahedral coordination (C.N. 4). The [Ga 4S] tetrahedra are the most symmetrical in the $Pr_3Fe_{0.1}Ga_{1.6}S_7$ structure (χ = 0.00759), and the least symmetrical in $La_3Fe_{0.1}Ga_{1.6}S_7$ (χ= 0.03405).

The above-mentioned regularities in the symmetry of polyhedra allow us to state that the geometric parameters of polyhedra can be corrected by introducing atoms of chemical elements of different nature into the structure of rare-earth-containing chalcogenides. And therefore, to synthesize materials with predetermined crystal structure and physical properties.

Calculated parameters of polyhedra in the structures of $R_3Fe_{0.1}Ga_{1.6}S_7$ chalcogenides (R – La, Ce, Pr, Tb) are presented in Tables 5 and 6.

Interatomic distances in the structure of synthesized chalcogenides were calculated using WinCSD software [15].

Certain trends were discerned as the $r_{R^{3+}}$ value decreases.

The value of the interatomic distance δ(La–S1) in the $La_3Fe_{0.1}Ga_{1.6}S_7$ structure (Fig. 3) is the average between the sum of covalent radii $\delta(La–S)_{cov}$ and the sum of ionic radii $\delta(La–S)_{ion}$ [22].

Bond lengths δ(La–S2), δ(La–S3) and δ(La–S4) are commensurate with the sum of ionic radii $\delta(La–S)_{ion}$, and the values of δ(La–S5), δ(La–S6) and δ(La–S7) are larger than $\delta(La–S)_{ion}$. Bond lengths $\delta(Ce–S)_{1–5}$ in the $Ce_3Fe_{0.1}Ga_{1.6}S_7$ structure are commensurate with the the sum of ionic radii $\delta(Ce–S)_{ion}$, while the values of

Table 5.

Parameters of polyhedra [La(Ce) 7S], [M 6S] and [Ga 4S] in the structure $R_3Fe_{0.1}Ga_{1.6}S_7$ chalcogenides (R – La, Ce)

Parameters	**$La_3Fe_{0.1}Ga_{1.6}S_7$**	**$Ce_3Fe_{0.1}Ga_{1.6}S_7$**
	[La(Ce) $3S_13S_21S_3$]	
δ(La(Ce) – S), Å	2.834(19) – 3.040(13)	2.880(19) – 3.012(13)
δ(La(Ce) – S)$_{\text{mean}}$, Å	2.9491	2.9265
Distortion index (χ)	0.01628	0.01153
V, Å^3	35.5051	34.7442
CN / CN$_{\text{effective}}$	7 / 6.87	7 / 6.95
	[M $6S_2$]	
δ(M – S), Å	2.486(11) – 2.609(11)	2.566(10) – 2.691(10)
δ(M – S)$_{\text{mean}}$, Å	2.5475	2.6288
Distortion index (χ)	0.02398	0.02379
V, Å^3	21.9801	24.1801
CN / CN$_{\text{effective}}$	6 / 5.87	6 / 5.87
	[Ga $3S_11S_3$]	
δ(Ga – S1), Å	2.11(3)	2.22(2)
δ(Ga – S3), Å	2.318(11)	2.326(10)
δ(Ga – S)$_{\text{mean}}$, Å	2.2663	2.3009
∠ S1 – Ga – S3, (°)	113.7(4)	113.3(4)
∠ S1 – Ga – S1, (°)	104.9(5)	105.4(4)
Distortion index (χ)	0.03405	0.01668
V, Å^3	5.9359	6.2173
CN / CN$_{\text{effective}}$	4 / 3.66	4 / 3.94

Table 6.

Parameters of polyhedra [Pr(Tb) 7S], [M 6S] and [Ga 4S] in the structure $R_3Fe_{0.1}Ga_{1.6}S_7$ chalcogenides (R – Pr, Tb)

Parameters	**$Pr_3Fe_{0.1}Ga_{1.6}S_7$**	**$Tb_3Fe_{0.1}Ga_{1.6}S_7$**
	[Pr(Tb) $3S_13S_21S_3$]	
δ(Pr(Tb) – S), Å	2.829(8) – 3.046(6)	2.731(12) – 2.98(3)
δ(Pr(Tb) – S)$_{\text{mean}}$, Å	2.9068	2.8180
Distortion index (χ)	0.01369	0.03186
V, Å^3	34.2436	31.5331
CN / CN$_{\text{effective}}$	7 / 6.89	7 / 6.68
	[M $6S_2$]	
δ(M – S), Å	2.478(9) – 2.690(10)	2.56(2) – 2.84(2)
δ(M – S)$_{\text{mean}}$, Å	2.5840	2.7007
Distortion index (χ)	0.04118	0.05194
V, Å^3	22.8827	26.0173
CN / CN$_{\text{effective}}$	6 / 5.58	6 / 5.32
	[Ga $3S_11S_3$]	
δ(Ga – S1), Å	2.179(13)	2.23(3)
δ(Ga – S3), Å	2.224(7)	2.426(16)
δ(Ga – S)$_{\text{mean}}$, Å	2.2126	2.3750
∠ S1 – Ga – S3, (°)	114.03(17)	113.5(4)
∠ S1 – Ga – S1, (°)	104.6(2)	105.5(5)
Distortion index (χ)	0.00759	0.03154
V, Å^3	5.5103	6.8358
CN / CN$_{\text{effective}}$	4 / 3.99	4 / 3.72

δ(Ce–S6) and δ(Ce–S7) are larger than δ(Ce–S)$_{\text{ion}}$. Bond length δ(Pr–S7) in the $Pr_3Fe_{0.1}Ga_{1.6}S_7$ structure is significantly increased in comparison with δ(Pr–S)$_{\text{ion}}$. Experimentally determined values of bond lengths δ(Tb–S)$_{1–5}$ for $Tb_3Fe_{0.1}Ga_{1.6}S_7$ are in the range between the sum of covalent radii δ(Tb–S)$_{\text{cov}}$ and the sum of ionic radii δ(Tb–S)$_{\text{ion}}$. The values of δ(Tb–S6) and δ(Tb–S7) are greater than the bond length calculated as the sum of the ionic radii.

For the chalcogenide series $R_3Fe_{0.1}Ga_{1.6}S_7$, the unit cell parameter *a* decreases with the decrease of the radius of R^{3+} ion from 10.1884(6) Å for $La_3Fe_{0.1}Ga_{1.6}S_7$ to 9.6692(7) Å for $Tb_3Fe_{0.1}Ga_{1.6}S_7$; the unit cell volume decreases from 544.0(1) Å^3 for $La_3Fe_{0.1}Ga_{1.6}S_7$ to 492.3(1) Å^3 for $Tb_3Fe_{0.1}Ga_{1.6}S_7$. Such a change in the unit cell parameters correlates with a decrease in the volumes of trigonal prisms [R 7S] from 35.5051 Å^3 in the $La_3Fe_{0.1}Ga_{1.6}S_7$ structure to 31.5331 Å^3 in $Tb_3Fe_{0.1}Ga_{1.6}S_7$.

Elemental composition of the $Pr_3Fe_{0.1}Ga_{1.6}S_7$

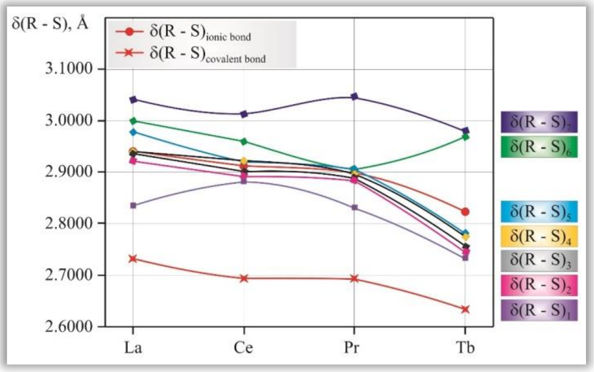

Fig. 3. Interatomic distances and R – S in structure $R_3Fe_{0.1}Ga_{1.6}S_7$ (R – La, Ce, Pr and Tb).

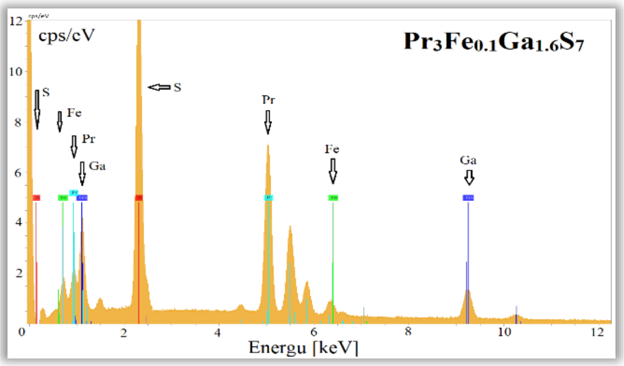

Fig. 4. EDAX spectrum $Pr_3Fe_{0.1}Ga_{1.6}S_7$ chalcogenide.

chalcogenide was further evaluated using EDAX analysis. Calculated atomic percentage of elements are Pr, 25.64%, Fe, 0.86%, Ga, 13.68%, S, 59.83%; found values are Pr, 26.74 ± 4.70%, Fe, 1.2 ± 0.17%, Ga, 14.12 ± 1.34%, S, 57.94 ± 3.12%. The results are presented in Figure 4 and show that structure calculation and elemental analysis are in good agreement.

Conclusions

Four quaternary chalcogenides $R_3Fe_{0.1}Ga_{1.6}S_7$ (R – La, Ce, Pr and Tb) were synthesized for the first time, and their crystal structure was analyzed by X-ray powder method. It was established from experimentally obtained data sets that these phases crystallize in hexagonal symmetry (La_3CuSiS_7 structure type; S.G. $P6_3$; Pearson symbol hP 24) with unit cell parameters $a = 10.1884(6)$ Å, $c = 6.0515(4)$ Å and $V = 544.0(1)$ Å^3 for $La_3Fe_{0.1}Ga_{1.6}S_7$; $a = 10.0864(4)$ Å, $c = 6.0440(3)$ Å and $V = 532.51$ (6) Å^3 for $Ce_3Fe_{0.1}Ga_{1.6}S_7$; $a = 9.9853(3)$ Å, $c = 6.0648(2)$ Å and $V = 523.68(4)$ Å^3 for $Pr_3Fe_{0.1}Ga_{1.6}S_7$; $a = 9.6692(7)$ Å, $c = 6.0799(5)$ Å and $V = 492.3(1)$ Å^3 for $Tb_3Fe_{0.1}Ga_{1.6}S_7$).

Given that the synthesized chalcogenides are characterized by a non-centrosymmetric structure, they can be used as materials for studying their nonlinear optical and other characteristics.

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Кристалічна структура халькогенідів $R_3Fe_{0.1}Ga_{1.6}S_7$ (R – La, Ce, Pr та Tb)

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У роботі представлено результати дослідження кристалічної структури халькогенідів складу $R_3Fe_{0.1}Ga_{1.6}S_7$ (R = La, Ce, Pr та Tb) як перспективних матеріалів, що прогнозовано володіють цікавими нелінійно-оптичними та електричними властивостями. Синтез зразків стехіометричного складу, загальною масою один грам кожен, отримано сплавлянням простих речовин у вакуумованих кварцевих контейнерах до залишкового тиску 10^{-2} Па за максимальної температури синтезу 1100 °C. Кристалічна структура халькогенідів $La_3Fe_{0.1}Ga_{1.6}S_7$ (A) {a = 10.1884(6) Å, c = 6.0515(4) Å, R_I = 0.0940, R_P = 0.2503}, $Ce_3Fe_{0.1}Ga_{1.6}S_7$ (B) {a = 10.0864(4) Å, c = 6.0440(3) Å, R_I = 0.0695, R_P = 0.1935}, $Pr_3Fe_{0.1}Ga_{1.6}S_7$ (C) {a = 9.9853(3) Å, c = 6.0648(2) Å, R_I = 0.0730, R_P = 0.1777} та $Tb_3Fe_{0.1}Ga_{1.6}S_7$ (D) {a = 9.6692(7) Å, c = 6.0799(5) Å, R_I = 0.0909, R_P = 0.2742} вивчена рентґенівським методом порошку. Встановлено приналежність структури синтезованих фаз до гексагональної сингонії (структурний тип La_3CuSiS_7; просторова група $P6_3$; символ Пірсона *hP24*,173). Складні халькогеніди (A), (B), (C) і (D) синтезовані на основі сульфідів $R_3Ga_{1.67}S_7$ (R = La, Ce, Pr та Tb) шляхом заміщення атомів галію в правильній системі точок (ПСТ) 2*a* атомами статистичних сумішей M1 {0.57(2) Ga + 0.10(2) Fe}, M2 {0.56(1) Ga + 0.10(2) Fe}, M3 {0.61(8) Ga + 0.09(1) Fe} і M4 {0.57(2) Ga + 0.10(2) Fe} відповідно. У структурі одержаних халькогенідів атоми рідкісноземельних елементів локалізовані в ПСТ 6*c* і разом з атомами сульфуру формують тригональні призми, що мають один додатковий атом [R $3S_13S_21S_3$]. Тригональні призми з одним додатковим атомом утворюють “блоки” 3[R 7S]. У цих “блоках” тригональні призми між собою з’єднані ребрами. Атоми статистичних сумішей M1, M2, M3 і M4, що локалізовані в ПСТ 2*a*, формують октаедри [M1 $6S_2$], [M2 $6S_2$], [M3 $6S_2$] і [M4 $6S_2$] відповідно. Ці октаедри між собою з’єднані гранями та в напрямку осі *c* утворюють колони. В ПСТ 2*b* атоми Ga оточені чотирма атомами сульфуру [Ga $3S_11S_3$].

Ключові слова: кристалічна структура, рідкісноземельні елементи, хальогеніди, рентґенівський метод порошку, EDAX аналіз.