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Crystal and band energy structure of $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$ sulfides

O.V. Marchuk[1]*, N.M. Blashko[1], M.Ya. Rudysh[2], O.A. Yakymchuk[3]

[1] Lesya Ukrainka Volyn National University, 13 Voli Ave., 43025 Lutsk, Ukraine
[2] Ivan Franko National University of Lviv, 8 Kyrylo and Mefodii Str., 79005 Lviv, Ukraine
[3] Frantsevych Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, 3 Omeliana Pritsaka Str., 03142 Kyiv, Ukraine
* Marchuk.Oleg@vnu.edu.ua

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Two sulfide phases of composition $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$ were obtained from high-purity simple substances in evacuated quartz ampoules at a maximum synthesis temperature of 1100 °C. The synthesized alloys were homogenized by annealing at a temperature of 500 °C for one month. The crystal structure of the sulfides $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ (a = 9.720(1) Å, c = 6.103(1) Å, R_I = 0.0804, R_p = 0.2806) and $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ (a = 9.8866(7) Å, c = 6.0877(6) Å, R_I = 0.0800, R_p = 0.2536) was studied by powder X-ray diffraction. Their structure belongs to the structural type La_3CuSiS_7 (space group $P6_3$; Pearson symbol $hP24$). In these structures, the rare-earth (R) atoms [Nd and Y(Tb)] are statistically distributed in the site 6c (x y z) and together with the S atoms form trigonal prisms with one additional atom [R S_{6+1}]. The Ga1 site 2a is defective with an atomic packing factor APF = 66.7 %, and Ga2 site 2b with full atomic occupancy. The Ga1 and Ga2 atoms have octahedral and tetrahedral environments, respectively. Sulfur in the crystal lattice has three atomic positions: S1, S2 (site 6c) and S3 (site 2b). The primitive hexagonal unit cell contains two formula units $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$. Trigonal prisms [R S_{6+1}] are connected by edges and form "blocks" (three prisms each). Octahedrons [Ga1 S_6] have common faces and form "columns" in the direction of the main axis. Trigonal prisms with octahedra form common faces. Tetrahedra [Ga2 S_4] are isolated from each other. Using density functional theory within the framework of the Kohn-Shem formalism, the band-energy structure of synthesized sulfides was studied.

Keywords: rare earth metals, sulfides, crystal structure, X-ray powder method, band-energy structure.

Кристалічна та зонно-енергетична структура сульфідів $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$. *О.В. Марчук, Н.М. Блашко, М.Я. Рудиш, О.А. Якимчук*

Дві сульфідні фази складу $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$ були отримані з високочистих простих речовин у вакуумованих кварцових ампулах за максимальної температура синтезу 1100 °C. Синтезовані сплави гомогенізували відпалом за температури 500 °C протягом одного місяця. Кристалічна структура сульфідів $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ (a = 9.720(1) Å, c = 6.103(1) Å, R_I = 0.0804, R_p = 0.2806) та $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ (a = 9.8866(7) Å, c = 6.0877(6) Å, R_I = 0.0800, R_p = 0.2536), вивчена методом рентґенівської дифракції порошку. Їх структура належить до структурного типу La_3CuSiS_7 (просторова група $P6_3$; символ Пірсона $hP24$). У цих структурах атоми рідкісноземельних елементів (R) [Nd та Y(Tb)] статистично розподілені в правильній системі точок 6c (x y z) і разом з атомами S формують тригональні призми з одним додатковим атомом [R S_{6+1}]. Позиція Ga1 (2a) дефектна із коефіцієнтом упаковки атомів 66,7 %, а Ga2 (ПСТ 2b) характеризується повною атомною зайнятістю. Атоми Ga1

та Ga2 мають окта- та тетраедричне оточення, відповідно. Сірка в кристалічній решітці має три атомні позиції: S1, S2 (6*c*) та S3 (2*b*). На примітивну гексагональну елементарну комірку припадає дві формульні одиниці $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$. Тригональні призми [R S_{6+1}] з'єднанні між собою ребрами і формують "блоки" (по три призми в кожному). Октаедри [Ga1 S_6] мають спільні грані і утворюють "колони" в напрямку головної осі. Тригональні призми з октаедрами утворюють спільні грані. Тетраедри [Ga2 S_4] є ізольовані один від одного. Використовуючи теорію функціоналу густини в рамках формалізму Кона-Шема досліджено зонно-енергетичну структуру синтезованих сульфідів.

1. Introduction

The past decade oversaw a noticeable increase in interest to multicomponent chalcogenides, particularly compounds containing rare earth elements in combination with *p*-elements [1-8], etc. This is explained by the variety of their crystallographic types, the diversity of electronic structures, as well as the clear prospect of applications in nonlinear optics, infrared photonics, and thermoelectric technology. Analysis of the results of modern research indicates that rare-earth-based chalcogenides are promising materials for both fundamental research and applied developments [9, 10].

The family of crystal structures of the La_3CuSiS_7 type (space group $P6_3$; Pearson symbol $hP24$) attract attention as a scaffold for implementation of complex coordination polyhedra (isolated tetrahedra and columnar stacking of octahedra), as well as for the introduction of statistical mixtures of cations. Such structural motifs create a much wider range of local symmetry in the crystal matrix of material significantly, which significantly increases the flexibility in tuning its physical properties. This, in turn, provides wide opportunities for precise control of electronic characteristics such as carrier mobility, as well as optical properties. This can be achieved by selective cation substitution that affects local electronic structure, and by defect engineering that controls defect concentration, creating optimal conditions for practical applications of multicomponent chalcogenides [11, 12].

The special crystal-chemical organization of the $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ and $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ sulfides, where the combination of 4*f*-elements with gallium and sulfur forms a complex multicomponent lattice with a characteristic distribution of cations, distinguishes these compounds by a unique combination of structural and electronic properties. This architecture causes high localization of *f*-electrons, low dispersion of electronic states, and the appearance of pronounced optical resonances in a wide spectral range, from visible to infrared. These characteristics open up possibilities for the application of synthesized sulfides in photonics, including infrared sensors, laser systems, and a new generation of optoelectronic devices. In addition, the combination of crystal chemical stability and functional flexibility makes these chalcogenides also promising for applications in modern energy technologies where precise tuning of electronic and optical properties is important.

2. Experimental

Two samples of stoichiometric compositions $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ and $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ were synthesized by co-melting high-purity elements neodymium Nd, yttrium Y, terbium Tb, gallium Ga and sulfur S in quartz ampoules evacuated to a residual pressure of 10^{-2} Pa (to minimize oxidation and loss of material during heating). The total mass of the initial batch for each sample was 1.0 g. The synthesis was carried out in an MP-30 electric muffle furnace by heating to 1100°C at a rate of 12 °C/h; then holding at this temperature for four hours; cooling to 500 °C at a rate of 12 °C/h; homogenizing annealing at 500 °C for one month; quenching into room temperature water without damaging the containers.

Experimental diffraction patterns were recorded on a DRON 4-13 diffractometer (Cu-*K*α radiation, λ = 1.54185 Å; in the scanning range of $10° \le 2\Theta \le 100°$; with a scanning step of 0.02 °; exposure time of 20 s at each point). Data processing and calculation of crystal structure parameters were performed by the Rietveld method using the WinCSD software package [13], which provides automated analysis of X-ray diffraction data. VESTA software was used for 3D visualization and detailed structural analysis [14].

The band-energy structure of $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ and $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ sulfides was studied using the density functional theory within the framework of the Kohn-Shem formalism [15] implemented in the CASTEP software [16, 17]. The initial parameters for calculations of the properties of materials were the crystallographic data for $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$

Table 1. Data collection conditions and Rietveld refinement results for the crystal structure of $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$

Parameters	$Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$	$Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$
Space group and its number	$P6_3$ (173)	$P6_3$ (173)
a, (Å)	9.720(1)	9.8866(7)
c, (Å)	6.103(1)	6.0877(6)
Cell volume (Å^3)	499.3(2)	515.3(1)
Number of atoms in cell	23.3	23.3
Calculated density (g/cm^3)	5.290(2)	4.449(1)
Absorption coefficient (1/cm)	1205.56	816.37
2Θ and sinΘ/λ (max)	100.00; 0.497	100.00; 0.497
R_I	0.0804	0.0800
R_P	0.2806	0.2536
Scale factor	0.26898(2)	0.21605(1)

Table 2. Coordinates and isotropic thermal parameters of atoms in the structure of $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ sulfide

Atoms	site	*x/a*	*y/b*	*z/c*	Atomic packing factor (APF)	$B_{iso}\times10^2$ (Å^2)
R2	6*c*	0.1515(2)	0.3785(2)	0.0460(8)	0.5Nd + 0.5Y	0.33(3)
Ga1	2*a*	0	0	0.236(3)	0.667	2.9(3)
Ga2	2*b*	1/3	2/3	0.6383(10)	1.0	0.1(4)
S1	6*c*	0.1028(9)	0.2461(9)	0.4825(13)	1.0	0.1(3)
S2	6*c*	0.4735(11)	0.9137(9)	0.771(2)	1.0	0.1(3)
S3	2*b*	1/3	2/3	0.276(3)	1.0	0.7(5)

Table 3. Coordinates and isotropic thermal parameters of atoms in the structure $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ sulfide

Atoms	site	*x/a*	*y/b*	*z/c*	Atomic packing factor (APF)	$B_{iso}\times10^2$ (Å^2)
R1	6*c*	0.1513(2)	0.3749(2)	0.0608(10)	0.5Nd + 0.5Tb	1.08(3)
Ga1	2*a*	0	0	0.249(2)	0.667	1.0(4)
Ga2	2*b*	1/3	2/3	0.6139(13)	1.0	1.0(3)
S1	6*c*	0.0894(9)	0.2240(8)	0.4875(12)	1.0	0.5(2)
S2	6*c*	0.4878(10)	0.9124(8)	0.7699(14)	1.0	2.1(3)
S3	2*b*	1/3	2/3	0.261(2)	1.0	1.5(4)

and $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ obtained in this work by the XRD method. The crystal structure with a statistical arrangement of atoms of certain chemical elements was simulated by the mixed-atom method in the virtual crystal approximation [18]. No geometric optimization was applied before calculations. The system energy was derived from a self-consistent solution of the Kohn-Shem equations. Wave functions of the valence electrons were described by Bloch type flat functions. The electronic configuration of the valence electrons was as follows: Nd – $4f^4$ $5s^2$ $5p^6$ $6s^2$; Y– $4d^1 5s^2$; Tb – $4f^9$ $5s^2$ $5p^6$ $6s^2$; Ga – $3d^{10}$ $4s^2$ $4p^1$; S – $3s^2 3p^4$. The plane wave cutoff energy was E_{cut} = 900 eV. The norm-conserving pseudopotential method was used to describe core electrons [19]. The exchange-correlation interaction was described by the generalized gradient approximation (GGA) with the Perdue-Burke-Ernzerhoff (PBE) parameterization [20, 21]. The integration was performed on a 4×4×6 *k*-grid which was selected by the Monkhorst-Pack method [22].

3. Crystal structure of sulfides

The crystal structure of the synthesized compounds was studied in detail by X-ray diffraction. Analysis of the composition of the samples, the intensities of diffraction reflections, and the calculated cell parameters showed that the sulfide phases $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$ crystallize in the La_3CuSiS_7 structural type [23]. Detailed

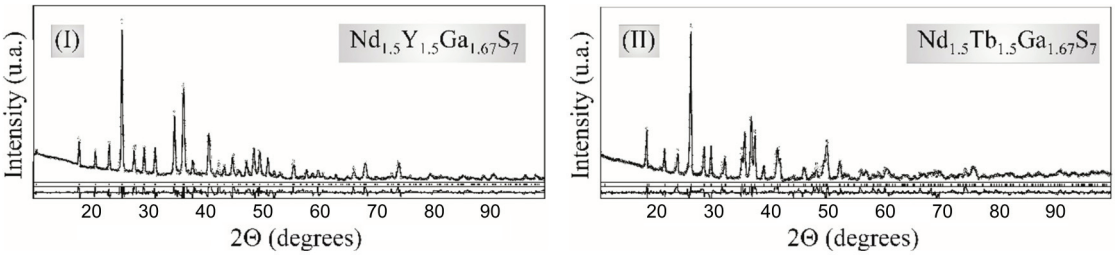

Fig. 1. Experimental and theoretical diffraction patterns of the sulfides $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ (I),

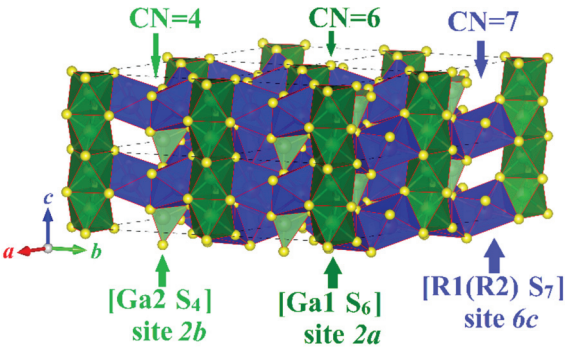

Fig. 2. Packing of polyhedra in the structure of $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$ sulfides.

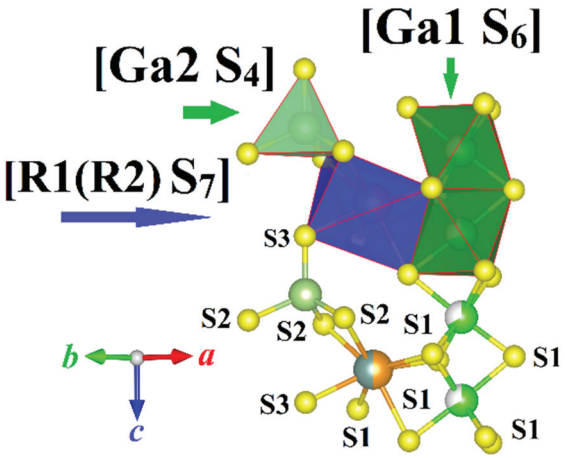

Fig. 3. The sequence of the connection of coordination polyhedra [R1(R2) S_{6+1}], [Ga1 S_6] and [Ga2 S_4] with each other in the structure of the $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$ sulfides.

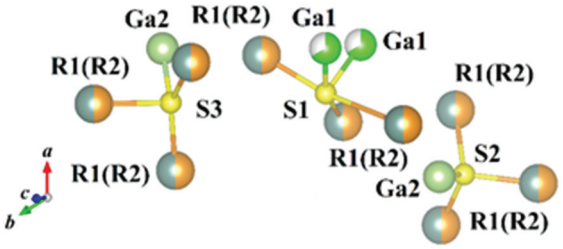

Fig. 4. Coordination environment of S1, S2 and S3 atoms in the structure of the $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$ sulfides.

conditions of the X-ray experiment and basic crystallographic characteristics of the synthesized compounds are given in Table 1 to evaluate accuracy and reproducibility of the results.

Refinement of atomic coordinates and isotropic thermal displacement parameters (B_{iso}) for atoms in the structure of the synthesized sulfides (Tables 2, 3) provided relatively satisfactory values of the fit factors R that indicates a high quality of experimental data. The structure was considered correctly defined when the value of $R_I < 0.1$, which confirms adequacy of the models and the accuracy of obtained cell parameters and location of atoms in the crystal lattice.

Experimental and theoretically calculated diffraction patterns of the sulfides and their difference are presented in Fig. 1. The unit cell and the stacking of polyhedra in the structure of the synthesized sulfides are shown in Fig. 2.

The structure of the sulfide phases $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$ includes atoms of the statistical mixture R1(R2) [Nd + Y(Tb)] in the 6*c* site centered trigonal prisms with one additional S atom. Trigonal prisms with one additional S atom form "blocks" 3 [R1(R2) S_{6+1}] where the trigonal prisms are connected by edges. To preserve the electric neutrality of the formulas, the compositions of the statistical mixture and of the defect position Ga1 were fixed and not refined.

Ga atoms occupy two atomic sites Ga1 and Ga2. Ga1 site (2*a*) is defective with 66.7 % occupancy, and Ga2 site (2*b*) has full occupancy. Ga1 and Ga2 atoms have octahedral and tetrahedral environment, respectively. The [Ga1 S_6] octahedra share faces and form infinite columns in the direction of the *c* axis. The [Ga2 S_4] tetrahedra are isolated and are located between the columns of the [Ga1 S_6] octahedra and between the voids formed by the [R1(R2) S_{6+1}] polyhedra. The sequence of the connection of coordination polyhedra in the structure of the sulfides is shown in Fig. 3.

Sulfur in the crystal lattice has three atomic positions, S1, S2 (both are the 6*c* sites) and S3 (the 2*b* site). The S2 and S3 atoms have tet-

Table 4. Parameters of polyhedra in the structures of $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ (I) and $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ (II)

Sulfides	Polyhedron	Average bond length, Å	Polyhedral volume, Å^3	Distortion index, χ	C.N.$_{eff}$
I	[R1 S_{6+1}]	2.8735	33.1695	0.02346	6.72
	[Ga1 S_6]	2.5794	22.8614	0.00420	5.99
	[Ga2 S_4]	2.2298	5.6823	0.00469	3.99
II	[R2 S_{6+1}]	2.8896	33.5032	0.01646	6.91
	[Ga1 S_6]	2.4592	19.6558	0.01762	5.93
	[Ga2 S_4]	2.2838	6.0660	0.02935	3.76

Table 5. Interatomic distances (δ, Å) and C.N. of atoms in the $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ and $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ structures

Bonds	$Nd_{1,5}Y_{1,5}Ga_{1,67}S_7$	$Nd_{1,5}Tb_{1,5}Ga_{1,67}S_7$	C.N.
	R – 0,5 Nd + 0,5 Y	R – 0,5 Nd + 0,5 Tb	
R – 1S1	2.804(11)	2.935(9)	7
R – 1S1	2.885(9)	2.937(13)	
R – 1S1	2.890(8)	2.948(12)	
R – 1S2	2.723(12)	2.840(11)	
R – 1S2	2.956(13)	2.860(12)	
R – 1S2	2.998(9)	2.904(13)	
R – 1S3	2.827(10)	2.802(9)	
Ga1 – 3S1	2.569(14)	2.416(18)	6
Ga1 – 3S1	2.590(14)	2.503(19)	
Ga2 – 3S2	2.21(2)	2.15(3)	4
Ga2 – 1S3	2.237(9)	2.329(10)	

rahedral environment. The S1 atoms are surrounded by five cations. The coordination environment of the S1, S2 and S3 atoms in the structure of the sulfides is shown in Fig. 4.

The unit cell parameter *a* increases from 9.720(1) Å for $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ to 9.8866(7) Å for $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$, while *b* decreases from 6.103(1) Å to 6.0877(6) Å , and the volume *V* increases from 499.3(2) Å^3 to 515.3(1) Å^3 due to the increase in the value of the ionic radii $r(Y^{3+})$ = 1.10 Å and $r(Tb^{3+})$ = 1.12 Å (for coordination number C.N. = 7), respectively. Trigonal prisms in the $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ structure are characterized by higher symmetry (C.N.$_{eff}$ = 6.91; distortion index χ = 0.01646) compared to $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ (C.N.$_{eff}$ = 6.72; χ = 0.02346), while octahedra and tetrahedra are the most symmetrical in yttrium-containing sulfide. The calculated parameters of polyhedra in the structures of $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$ sulfides are presented in Table 4.

Average bond length δ(R – S), δ(Ga1 – S) and δ(Ga2 – S) vary non-monotonously. Both the smallest value of

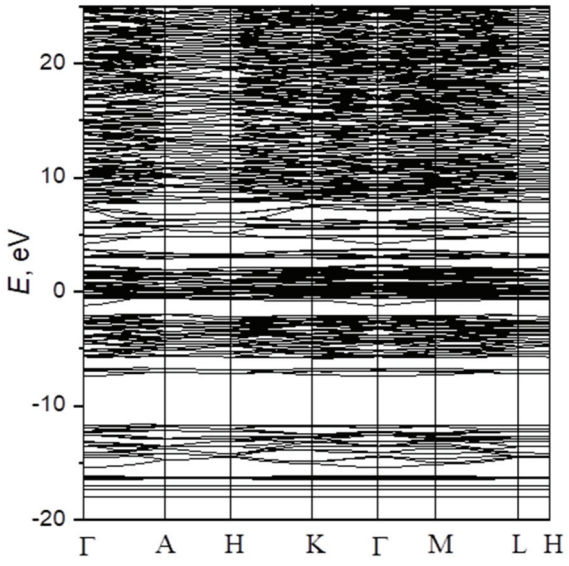

Fig. 5. Energy band structure of $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ sulfide.

$\delta(R-S_2)_{min}$ = 2.723(12) Å and the largest $\delta(R-S_2)_{max}$ = 2.998(9) Å are found in $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$. The smallest

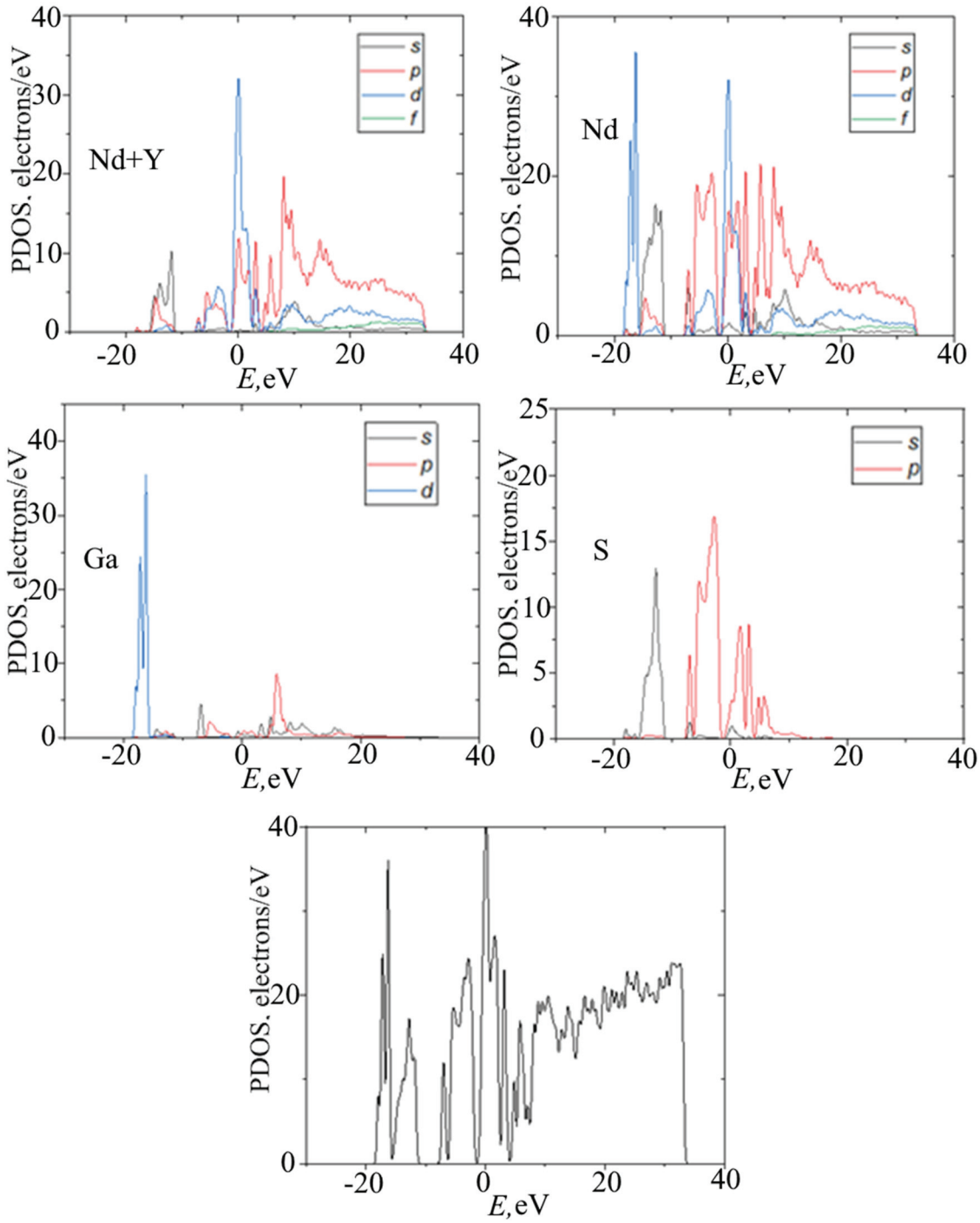

Fig. 6. Local partial and total densities of states (PDOS/DOS) of $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ calculated in the GGA-PBE approximation.

value of $\delta(Ga1 - S_1)_{min}$ = 2.416(18) Å (for $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$), and the largest is $\delta(Ga1 - S_1)_{max}$ = 2.590(14) Å (for $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$). The smallest value of $\delta(Ga2 - S_2)_{min}$ = 2.15(3) Å, and the largest is $\delta(Ga2 - S_3)_{max}$ = 2.329(10) Å (both $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$). The interatomic distances agree well with the sums of the radii of the corresponding ions [24]. The interatomic distances (δ, Å) and coordination numbers of atoms in the structure of the $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$ sulfides are presented in Table 5.

4. Energy band structure of sulfides

The calculated energy band structure of the $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ sulfide shown in Fig. 5 is constructed along the lines connecting the following points of the first Brillouin zone, Γ → A → H → K → Γ → M → L → H for the energy range from –20 to 25 eV. The zero mark corresponds to the top of the valence band of the material and coincides with the Fermi level. The band structure of the $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ crystal in the energy range from –7 to 25 eV is represented by a set of closely spaced bands corresponding to the levels of the constituent atoms. This part of the electronic spectrum is virtually continuous in the specified range. A somewhat separated set of electronic levels is observed near the energy 0 eV, which may correspond to localized electronic states. At lower energies, a set of narrow levels is observed corresponding to states tightly bound to nuclei.

The structure of electronic states of $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ can be analyzed in more detail using partial contributions to the total density of states (DOS). The total DOS and local partial densities of states (PDOS) of $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ calculated in the GGA-PBE approximation are plotted in Fig. 6. A narrow band of high intensity corresponding to the *f*-states of Nd atom lies near 0 eV. This band is formed by localized electrons with an energy corresponding to the boundary of the valence band and the conduction band. The band formed by a mixture of *d* -states of Nd+Y and *p*-states of S lies at higher energies near 3 eV. The higher levels of the conduction band of the material are formed by the overlap in the energies of the *s*, *p* and *d* states of the constituent atoms.

The valence band near the 0 eV mark is formed in the range from 0 to –12 eV and arises from the *d*-states of Ga2 atoms and the *p*-states of S atoms. The narrow band of *s*-states of sulfur atoms lies at an energy of –11 eV, and the band of *p*-states of Ga2 atoms lies at –18 eV. The *s*-states of Nd+Y atoms in the valence band are observed at energies of –15 eV, while the lowest levels are located at –6 eV and originate from *s*-electrons of Ga.

The band structure of the $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ crystal calculated by the GGA-PBE method is shown in Fig. 7. The band structure of the $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ crystal is clearly similar to that of $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$. A broad band is observed in the region from –5 to 0 eV forming the upper part of the valence band. The band is characterized by weak dispersion.

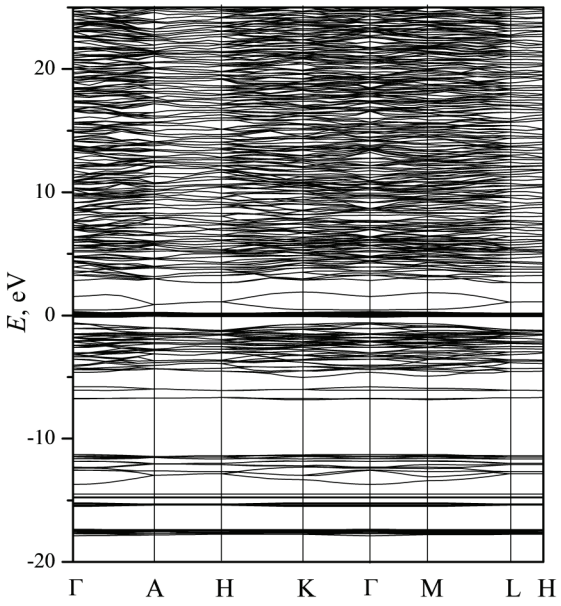

Fig. 7. Energy band structure of $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ sulfide.

Lower energy levels form a series of sets of electronic bands, in particular, near the energies of –6, –12, –15 and –17 eV. Compared to the $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ crystal, the deep levels of the valence band of $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ are characterized by a somewhat greater localization of levels. The conduction band is formed by narrow levels, probably localized *f*-states, and a broad band from 3 to 25 eV.

The calculated total and partial densities of states of $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ are shown in Fig. 8. The band formed by localized 4*f* states of Nd and Tb lies near the 0 eV mark which corresponds to the top of the valence band. Similar to the Y-containing sulfide, the slightly higher levels of the conduction band correspond to *p*-states of S atoms and a mixture of *p*/*d*-states of Nd+Tb. A wide conduction band at higher energies is formed by the overlap of *s*, *p* and *d* states of the constituent atoms of the $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ sulfide. The valence band of $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ in the range from 0 to –8 eV is formed by *p*-states of sulfur atoms with a minor contribution from *s*- and *p*-states of gallium. The main contribution of Ga atoms falls on the band near the energy of –15 eV and corresponds to *d*-states. Also, the intense peak of the sulfur states corresponds to the energy of –12 eV, which is slightly shifted towards lower energies compared to the Y-containing crystal. The *p*-states of the Nd+Tb mixture are represented by a narrow band located beyond –17 eV.

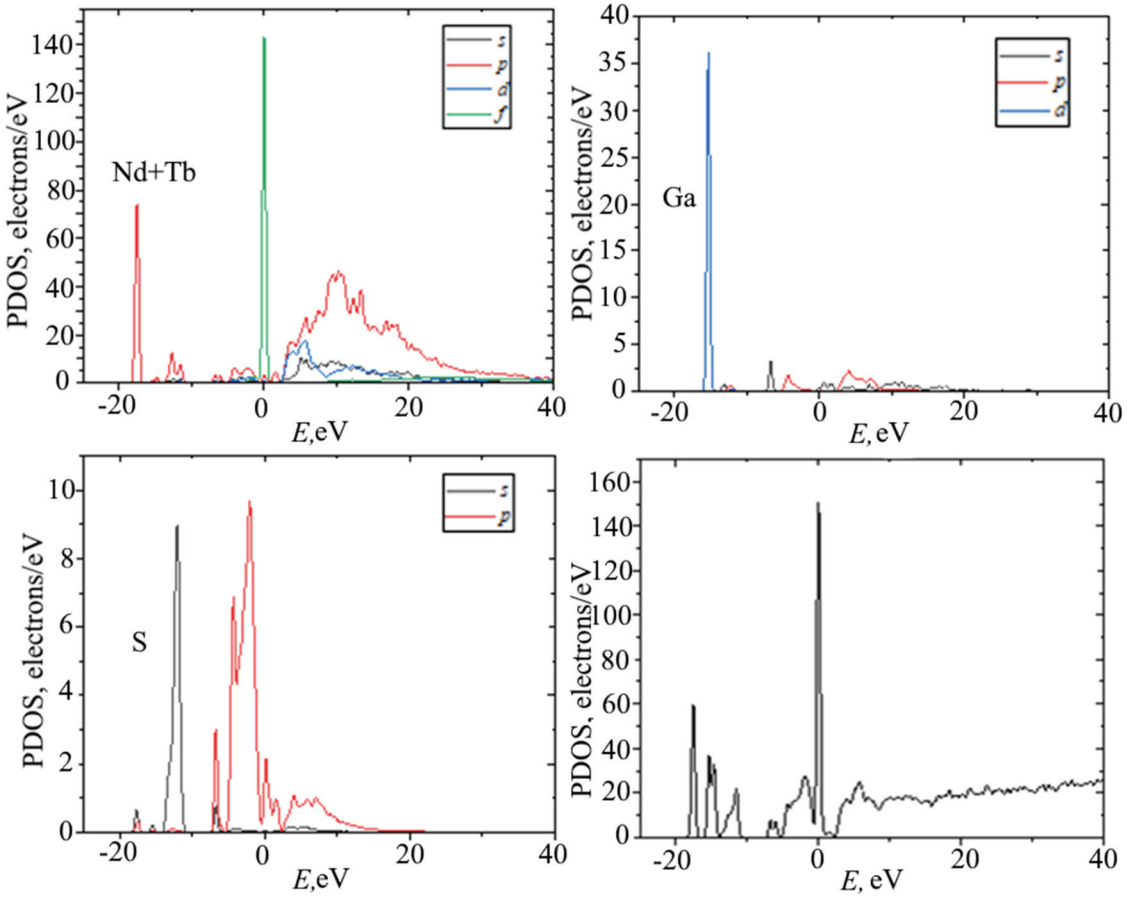

Fig. 8. Local partial and total densities of states (DOS/PDOS) for $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ calculated in the GGA-PBE approximation.

The studied materials are characterized by a relatively weak anisotropy of electronic states in *k*-space and low dispersion which is inversely proportional to the effective mass of charge carriers. Narrow localized levels of the valence band indicate their strong interaction with the nucleus. Of particular interest is the location of the *f*-levels of Nd+Y and Nd+Tb mixtures, as well as *d*-levels of sulfur, which form states near 0 eV. Taking into account the features and limitations of the DFT method in combination with the used GGA functional, it can be asserted that the studied material may belong to narrow-band materials or metals.

5. Conclusions

Two new sulfide phases of the composition $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$ and $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$ were synthesized for the first time, and their crystal structure was studied by X-ray powder diffraction and analyzed in detail. Summarizing the set of experimental data, it can be concluded that these sulfides crystallize in hexagonal symmetry (La_3CuSiS_7 structure type, S.G. $P6_3$, Pearson symbol $hP24$) with unit cell parameters a = 9.720(1) Å, c = 6.103(1) Å, R_I = 0.0804, R_p = 0.2806 (for $Nd_{1.5}Y_{1.5}Ga_{1.67}S_7$) and a = 9.8866(7) Å, c = 6.0877(6) Å, R_I = 0.0800, R_p = 0.2536 (for $Nd_{1.5}Tb_{1.5}Ga_{1.67}S_7$). A careful analysis of the obtained results shows that the simultaneous presence of atoms of different rare-earth elements in the structure of the studied sulfides leads to significant changes in the unit cell parameters and the degree of symmetry of the coordination polyhedra. This indicates the potential of using cation substitution as a tool for targeted modifications of structure characteristics.

The non-centrosymmetric nature of the crystal lattice makes the synthesized sulfides promising objects for nonlinear optics, in particular for the generation of second and third harmonics, creation of infrared sensors and for laser media. The discovered features of the electronic structure, in particular the localized 4*f* levels of Nd and Tb near the Fermi level, indicate the possibility of the appearance of pronounced optical resonances and luminescent

effects. This allows the use of the synthesized sulfides in photonics, infrared spectroscopy and optoelectronic devices.

Furthermore, the weak dispersion of electronic states and potentially large effective carrier mass make these sulfides interesting for further study with regard to thermoelectric properties. In this context, the research of the heat transfer coefficient, electrical conductivity and thermal conductivity, as well as the synthesis of multicomponent solid solutions based on $Nd_{1.5}Y(Tb)_{1.5}Ga_{1.67}S_7$ for increasing their thermoelectric efficiency are promising.

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