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New Quaternary Compounds $R_3Ni_{0.5}SiS_7$ ($R - Y, Sm, La$) with the $La_3Mn_{0.5}SiS_7$ Structure

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The new sulfides $Y_3Ni_{0.5}SiS_7$, $Sm_3Ni_{0.5}SiS_7$, and $La_3Ni_{0.5}SiS_7$ exist in the quasi-ternary systems $Y_2S_3 - NiS - SiS_2$, $Sm_2S_3 - NiS - SiS_2$, and $La_2S_3 - NiS - SiS_2$, respectively, for which the isothermal sections at 770 K were investigated. The crystal structure of the sulfides was determined by X-ray powder method. It belongs to the $La_3Mn_{0.5}SiS_7$ structure type (S.G. $P6_3$; Pearson symbol $hP23$), with the lattice parameters $a = 0.97643(4)$ nm; $c = 0.56377(4)$ nm ($Y_3Ni_{0.5}SiS_7$), $a = 0.99599(8)$ nm; $c = 0.56583(5)$ nm ($Sm_3Ni_{0.5}SiS_7$), and $a = 1.02830(6)$ nm; $c = 0.57412(4)$ nm ($La_3Ni_{0.5}SiS_7$). The structure of obtained sulfides is as follows: Y, Sm, and La atoms are located in the $6c$ site and center trigonal prisms with two additional S atoms. Ni atoms occupy the $2a$ site (0.5 occupancy) and have octahedral surrounding of S atoms. The coordination number of Si atoms (the $2b$ site) is 4. The Ni-centered octahedra form infinite chains $[Ni_6S]_n$.

Keywords: quaternary sulfides, rare-earth metal, crystal structure, X-ray powder method.

Received 14 July 2022; Accepted 10 October 2022.

Introduction

The search for multifunctional materials that do not contain toxic elements has a prominent place among the scientific areas of modern materials science [1, 2]. Many investigations are dedicated to determination of crystal structure and properties of quaternary chalcogenides $R_3B^{II}_{0.5}D^{IV}X_7$ ($R -$ rare-earth element, $B^{II} -$ Mn, Fe, Co, Ni, Zn, Cd; $D^{IV} -$ Si, Ge, Sn; $X -$ S, Se) [3–6] and others. The $R_3B^{II}_{0.5}D^{IV}X_7$ compounds crystallize in the hexagonal symmetry ($La_3Mn_{0.5}SiS_7$ structure type, (S.G.) $P6_3$, Pearson symbol $hP23$). Particular features of these structures are the large coordination number of R atoms whose polyhedra fill most of the space of the unit cell, octahedra of X atoms surrounding B^{II} atoms stretch along the c axis, and D^{IV} -centered tetrahedra fill the voids between the polyhedra of R atoms. The compounds exhibit non-linear optical properties due to non-centrosymmetric crystal structure. Functional materials based on this type of the compounds may be used as elements of modern devices [7]. Among the large family of chalcogenides, rare earth-containing ones have much

more complex electronic configuration compared to d - and p -electron-containing chalcogenides, which in turn improves their thermoelectric, magnetic and optical characteristics [8, 9].

In this work, we present the results of investigation of the crystal structure of three new rare earth-containing chalcogenides $Y_3Ni_{0.5}SiS_7$, $Sm_3Ni_{0.5}SiS_7$, and $La_3Ni_{0.5}SiS_7$ that contain d -blocks of Ni. The compounds were synthesized by solid state reactions. Their crystal structure was determined by X-ray powder method.

I. Experimental details

The samples of 0.8 g total mass for the investigation of the $Y_2S_3 - NiS - SiS_2$, $Sm_2S_3 - NiS - SiS_2$, and $La_2S_3 - NiS - SiS_2$ system were synthesized from elementary substances of at least 99.99 wt.% purity in quartz containers in an MP-30 programmable electric muffle furnace. The containers were evacuated to a residual pressure of 10^{-2} Pa and soldered in oxygen-gas burner flame. The alloys were synthesized step-wise as follows: heating the mixtures to 1320 K at the rate of 12 K/h;

exposure for 2 h; cooling to 770 K at the rate of 12 K/h; homogenizing annealing for 500 h at 770 K. After reaching the equilibrium state of the synthesized alloys, the ampoules were quenched into room-temperature water without breaking. The diffraction patterns for X-ray phase analysis were recorded at a DRON 4-13 diffractometer over 2θ range of $10\text{--}80^\circ$ ($CuK\alpha$ radiation, scan step 0.05° , 4 s exposure in each point). The diffraction patterns for X-ray structure analysis of $Y(Sm, La)_3Ni_{0.5}SiS_7$ sulfides (Figs. 1–3) were recorded at a DRON 4-13 diffractometer over 2θ range of $10\text{--}100^\circ$ ($CuK\alpha$ radiation, scan step 0.02° , 20 s exposure in each point).

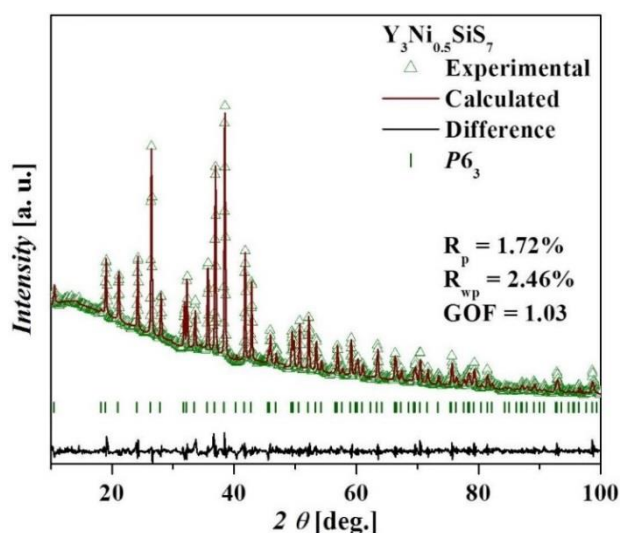


Fig. 1. Experimental and calculated diffraction patterns for $Y_3Ni_{0.5}SiS_7$ and their difference.

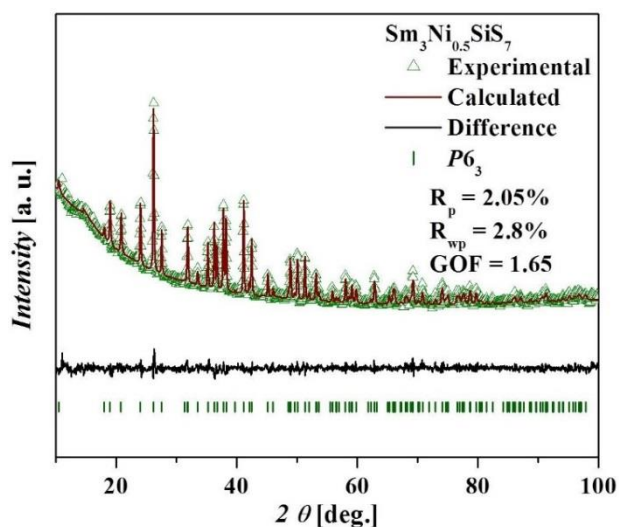


Fig. 2. Experimental and calculated diffraction patterns for $Sm_3Ni_{0.5}SiS_7$ and their difference.

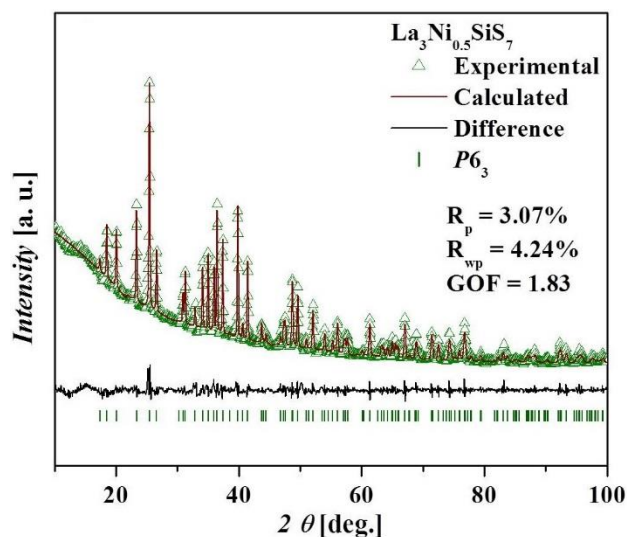


Fig. 3. Experimental and calculated diffraction patterns for $La_3Ni_{0.5}SiS_7$ and their difference.

II. Results and discussion

2.1. Isothermal sections of the $Y(Sm, La)_2S_3 - NiS - SiS_2$ systems at 770 K

The existence of four ternary compounds $Y_3Si_{1.25}S_7$ (S.G. $P6_3$, [12]), $Sm_4Si_3S_{12}$ (S.G. $R3c$, [13]), La_2SiS_5 (S.G. $P2_1/c$, [14, 15]), and La_4NiS_7 (S.G. $P6_3$, [16]) in the quasi-binary systems $Y_2S_3 - SiS_2$, $Sm_2S_3 - SiS_2$, $La_2S_3 - SiS_2$, and $La_2S_3 - NiS$ was confirmed. No compounds form in the $Y_2S_3 - NiS$, $Sm_2S_3 - NiS$, and $NiS - SiS_2$ systems. Under the conditions of the experiment, the existence of new quaternary chalcogenides $Y_3Ni_{0.5}SiS_7$, $Sm_3Ni_{0.5}SiS_7$, and $La_3Ni_{0.5}SiS_7$ was established in the studied systems (Table 1). Their crystal structure belongs to the $La_3Mn_{0.5}SiS_7$ structure type [17].

Isothermal sections of the quasi-ternary systems $Y_2S_3 - NiS - SiS_2$, $Sm_2S_3 - NiS - SiS_2$, and $La_2S_3 - NiS - SiS_2$ at 770 K were plotted from the results of the performed investigation.

Isothermal section of the $Y_2S_3 - NiS - SiS_2$ system (Fig. 4) consists of five single-phase points that correspond to the crystallization of binary Y_2S_3 , NiS , SiS_2 , ternary $Y_3Si_{1.25}S_7$, and quaternary $Y_3Ni_{0.5}SiS_7$ compounds, eight two-phase regions, and four three-phase regions. The $Y_3Ni_{0.5}SiS_7$ compound that is formed at the component ratio 3 : 1 : 2 has thermodynamic equilibria with Y_2S_3 , NiS , SiS_2 and $Y_3Si_{1.25}S_7$.

Isothermal section of the $Sm_2S_3 - NiS - SiS_2$ system (Fig. 5) differs from the former by the existence of the equilibrium between binary NiS and ternary $Sm_4Si_3S_{12}$ compounds. $Sm_3Ni_{0.5}SiS_7$ takes part in the formation of three two-phase equilibria $Sm_2S_3 + Sm_3Ni_{0.5}SiS_7$, $NiS + Sm_3Ni_{0.5}SiS_7$, and $Sm_4Si_3S_{12} + Sm_3Ni_{0.5}SiS_7$.

Isothermal section of the $La_2S_3 - NiS - SiS_2$ system (Fig. 6) is more complex due to two ternary compounds La_2SiS_5 and La_4NiS_7 that form in the quasi-binary systems $La_2S_3 - SiS_2$ and $La_2S_3 - NiS$, respectively. The quaternary compound $La_3Ni_{0.5}SiS_7$ takes part in four two-phase equilibria $La_2S_3 + La_3Ni_{0.5}SiS_7$, $La_4NiS_7 + La_3Ni_{0.5}SiS_7$, $NiS + La_3Ni_{0.5}SiS_7$, and $La_2SiS_5 + La_3Ni_{0.5}SiS_7$.

Table 1

Experimental details and crystallographic data for $Y_3Ni_{0.5}SiS_7$, $Sm_3Ni_{0.5}SiS_7$ and $La_3Ni_{0.5}SiS_7$.

Parameters	$Y_3Ni_{0.5}SiS_7$	$Sm_3Ni_{0.5}SiS_7$	$La_3Ni_{0.5}SiS_7$
S.G. / Pearson symbol	$P6_3 / hP23$		
a , (nm)	0.97643(4)	0.99599(8)	1.02830(6)
c , (nm)	0.56377(4)	0.56583(5)	0.57412(4)
Cell volume (nm ³)	0.46549(8)	0.4861(1)	0.5257(1)
Number of atoms in cell	23	23	23
Calculated density (g/cm ³)	3.9141(6)	5.008(1)	4.4130(9)
Absorption coefficient (1/cm)	419.38	1380.82	1043.17
Radiation and wavelength (nm)	CuK α , 0.154185		
Diffractometer	DRON 4-13		
Mode of refinement	Full Profile		
Program	WinCSD		
Number of atom sites	6	6	6
Number of free parameters	2	2	2
2 Θ ; sin Θ / λ (max.)	100.00; 0.497	100.00; 0.497	100.00; 0.497
R_I	0.0455	0.0668	0.0478
R_P	0.1460	0.2742	0.2152
Scale factor	0.01720(3)	0.23094(6)	0.21882(4)
Goodness of fit	1.025	2.690	2.830

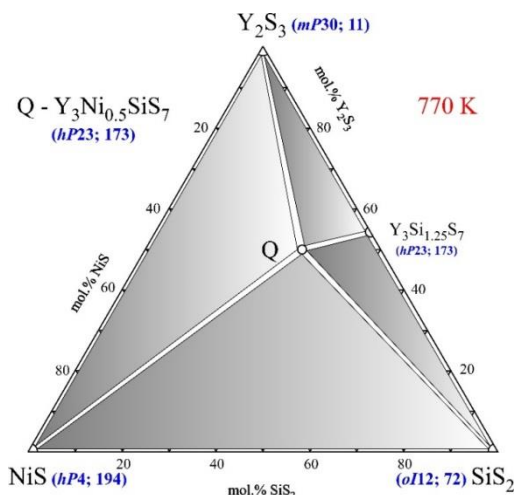


Fig. 4. Isothermal section of the quasi-ternary system $Y_2S_3 - NiS - SiS_2$.

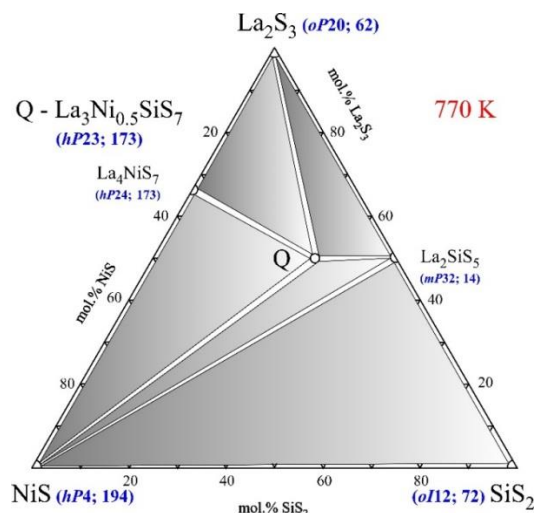


Fig. 6. Isothermal section of the quasi-ternary system $La_2S_3 - NiS - SiS_2$.

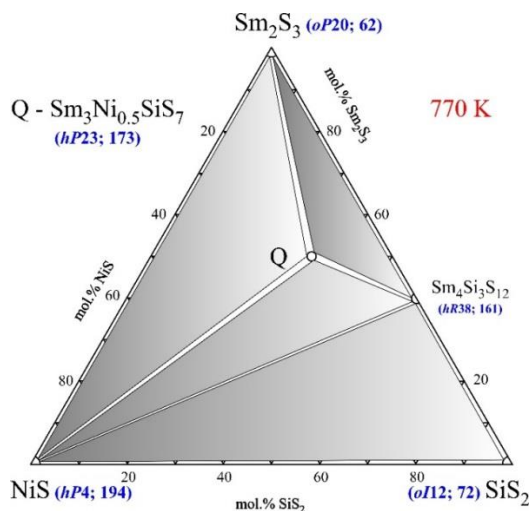


Fig. 5. Isothermal section of the quasi-ternary system $Sm_2S_3 - NiS - SiS_2$.

2.2. Crystal structure of the sulfides $Y(Sm, La)_3Ni_{0.5}SiS_7$

The calculated unit cell parameters are $a = 0.97643(4)$ nm, $c = 0.56377(4)$ nm for $Y_3Ni_{0.5}SiS_7$; $a = 0.99599(8)$ nm, $c = 0.56583(5)$ nm for $Sm_3Ni_{0.5}SiS_7$; $a = 1.02830(6)$ nm, $c = 0.57412(4)$ nm for $La_3Ni_{0.5}SiS_7$ (Fig. 7). The values are consistent with the unit cell parameters of the $R_3Ni_{0.5}SiS_7$ chalcogenides ($R - Ln$) [18–22].

Atomic coordinates and temperature displacement parameters in the investigated $R_3Ni_{0.5}SiS_7$ structures are given in Table 2. Polyhedral representation of the structures is depicted in Fig. 8. Interatomic distances are listed in Table 3 and shown in Fig. 9.

Rare-earth atoms occupy the $6c$ sites in the structure of the quaternary compounds and are surrounded by eight S atoms that form trigonal prisms with two additional atoms. Ni atoms are located in the $2a$ sites (occupancy 0.5) and coordinate six sulfur atoms forming octahedra. The

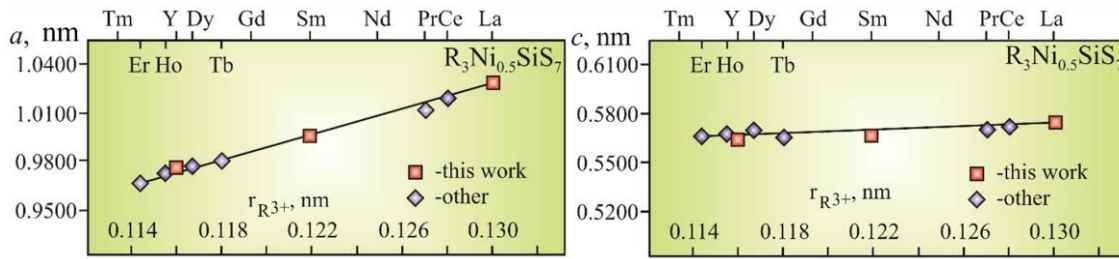


Fig. 7. Dependence of cell parameters (a and c) on ionic radii of rare earth elements for the $R_3Ni_{0.5}SiS_7$ compounds.

Table 2

Atomic coordinates and equivalent displacement parameters for $Y_3Ni_{0.5}SiS_7$, $Sm_3Ni_{0.5}SiS_7$ and $La_3Ni_{0.5}SiS_7$.

$Y_3Ni_{0.5}SiS_7$					
Atom	Wyck.	x/a	y/b	z/c	$B_{iso} \times 10^2$ (nm ²)
Y	6(c)	0.6439(2)	0.8701(2)	0.0141(10)	1.00(4)
Ni*	2(a)	0	0	0.2900**	1.2(4)
Si	2(b)	1/3	2/3	0.427(2)	0.9(3)
S1	6(c)	0.4775(9)	0.5792(7)	0.2773(13)	0.94(15)
S2	6(c)	0.9087(7)	0.1523(7)	0.0402(14)	1.04(13)
S3	2(b)	1/3	2/3	0.804(2)	1.1(3)
$Sm_3Ni_{0.5}SiS_7$					
Sm	6(c)	0.6433(3)	0.8716(3)	0.012(2)	0.91(5)
Ni*	2(a)	0	0	0.2900**	1.1(7)
Si	2(b)	1/3	2/3	0.435(4)	0.8(7)
S1	6(c)	0.478(2)	0.5856(14)	0.282(3)	0.8(3)
S2	6(c)	0.9149(13)	0.1553(12)	0.027(5)	0.8(3)
S3	2(b)	1/3	2/3	0.803(4)	1.3(6)
$La_3Ni_{0.5}SiS_7$					
La	6(c)	0.6435(2)	0.8754(2)	0.0162(15)	0.93(4)
Ni*	2(a)	0	0	0.2900**	0.8(5)
Si	2(b)	1/3	2/3	0.445(3)	1.1(5)
S1	6(c)	0.4141(12)	0.8849(10)	0.291(2)	1.1(3)
S2	6(c)	0.8444(9)	0.7595(9)	0.030(4)	1.0(2)
S3	2(b)	1/3	2/3	0.782(3)	0.9(4)

* occupation 0.5 Ni; ** - fixed value.

octahedra have shared faces and form “columns” in the direction of c axis. Si atoms occupy the $2b$ sites and are characterized by the tetrahedral surrounding. Analysis of the crystal structure of quaternary chalcogenides that exist in the quasi-ternary system should involve particularities of the crystal structure of initial binary and ternary compounds. The subjects of such analysis are the interatomic distances and the possibility of the formation of variously shaped polyhedra.

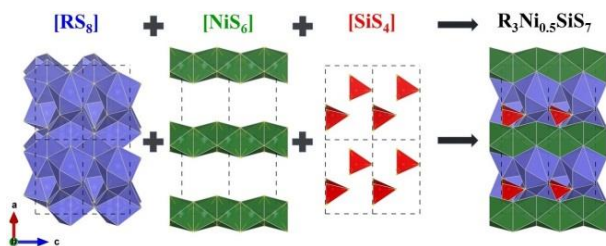


Fig. 8. Packing of polyhedra of cations in the structure of $Y(Sm, La)_3Ni_{0.5}SiS_7$ compounds.

The interatomic distance δ_{Si-S} nm in the $[SiS_4]$ tetrahedra in SiS_2 (S.G. *Ibam*; Pearson symbol *oI12*; [23]) is 0.2133. At the same time, Si atoms have varying

coordination surrounding in the ternary compounds in the $R_2S_3 - SiS_2$ systems. In the structure of $Y_3Si_{1.25}S_7$ (S.G. *P6₃*; Pearson symbol *hP23*; [12]), Si atoms that occupy the site $2a$ (occupancy 0.25) center tetrahedra of S atoms and the interatomic distances $\delta_{Si-S} = 0.2042$ nm. The interatomic distances (δ_{Si-S}) of Si atoms that occupy the $2b$ site and have octahedral surrounding of S atoms vary from 0.2429 до 0.2659 nm. Si atoms in the $Sm_4Si_3S_{12}$ structure (S.G. *R3c*; Pearson symbol *hR38*; [13]) are located in the $18b$ site and coordinate four S atoms (δ_{Si-S} vary from 0.2065 to 0.2109 nm). Si atoms in the $La_2Si_5S_5$ structure (S.G. *P2₁/c*; Pearson symbol *mP32*; [15]) are located in the $4e$ site and form $[SiS_4]$ tetrahedra where δ_{Si-S} ranges from 0.2098 до 0.2152 nm. The quaternary compounds $R_3Ni_{0.5}SiS_7$ ($R = Y, Sm, La$) crystallize in hexagonal symmetry (S.G. *P6₃*; Pearson symbol *hP23*). Si atoms occupy the $2b$ site (Table 3, Fig. 9) and coordinate four sulfur atoms

($\delta_{Si-S} = 0.2120 - 0.2151$ nm (for $Y_3Ni_{0.5}SiS_7$); $\delta_{Si-S} = 0.2080 - 0.2150$ nm (for $Sm_3Ni_{0.5}SiS_7$); $\delta_{Si-S} = 0.1957 - 0.2150$ nm (for $La_3Ni_{0.5}SiS_7$)). Ni atoms in the NiS structure (S.G. *P6₃/mmc*; Pearson symbol *hP4*; [24]) center octahedra $[NiS_6]$ of S atoms with

Table 3

Interatomic distances δ (nm) and coordination numbers (CN) of atoms in the structure of $Y_3Ni_{0.5}SiS_7$, $Sm_3Ni_{0.5}SiS_7$ and $La_3Ni_{0.5}SiS_7$ compounds.

Distances δ (nm)	$Y_3Ni_{0.5}SiS_7$	$Sm_3Ni_{0.5}SiS_7$	$La_3Ni_{0.5}SiS_7$	CN
$\delta(R-S)_{min}$	0.2679(7)	0.2742(13)	0.2839(9)	8
$\delta(R-S)_{max}$	0.3119(10)	0.3090(3)	0.3130(2)	
$\delta(Ni-S)_{min}$	0.2513(1)	0.2495(1)	0.2572(1)	6
$\delta(Ni-S)_{max}$	0.2514(1)	0.2575(1)	0.2637(1)	
$\delta(Si-S)_{min}$	0.2123(15)	0.208(3)	0.193(2)	4

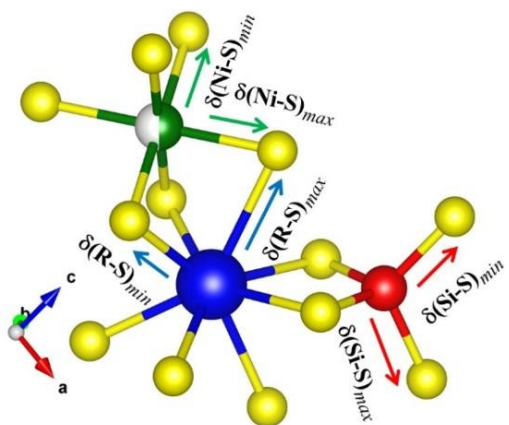


Fig. 9. The range of the interatomic distances of $R_3Ni_{0.5}SiS_7$ ($R = Y, Sm, La$) compounds.

$\delta_{Ni-S} = 0.2384$ nm. The interatomic distances of Ni atoms in the structure of the quaternary compounds $R_3Ni_{0.5}SiS_7$ ($R = Y, Sm, La$) are $\delta_{Ni-S} = 0.2514$ nm (for $Y_3Ni_{0.5}SiS_7$); $\delta_{Ni-S} = 0.2497 - 0.2580$ nm (for $Sm_3Ni_{0.5}SiS_7$); $\delta_{Ni-S} = 0.2599 - 0.2605$ nm (for $La_3Ni_{0.5}SiS_7$). As the atomic radii of the rare-earth atoms increase, we observe a decrease in the distortion of the nickel-centered octahedra. Interatomic distances δ_{R-S} in the binary compounds decrease somewhat with the decreasing atomic radii of a rare-earth element. At the same time, the crystal structure transforms from the monoclinic (for Y_2S_3) to orthorhombic (for Sm_2S_3 and La_2S_3) with the increasing atomic radii of R. Y atoms in the Y_2S_3 structure (S.G. $P2_1/m$; Pearson symbol $mP30$; [25]) occupy the $2e$ site and form two types of polyhedra of S atoms, trigonal prisms $[YS_6]$ (δ_{Y-S} from 0.2687 to 0.2831 nm) and trigonal prisms with one additional atom $[YS_7]$ (δ_{Y-S} from 0.2725 to 0.2919 nm). Sm and La atoms in the crystal structure of Sm_2S_3 [26] and La_2S_3 [27] (S.G. $Pnma$; Pearson symbol $oP20$) are coordinated in the $4c$ site and also form two types of polyhedra, trigonal prisms with one additional atom $[Sm(La)S_7]$ (δ_{Sm-S} from 0.2772 to 0.2945 nm; δ_{La-S} from 0.2915 to 0.3079 nm) and trigonal prisms with two additional atoms $[Sm(La)S_8]$ (δ_{Sm-S} – from 0.2777 to 0.3077 nm; δ_{La-S} from 0.2926 to 0.3207 nm). The hexagonal crystal structure of $Y_3Si_{1.25}S_7$ is characterized by Y atoms in the $6c$ sites centering trigonal prisms with two additional atoms $[YS_8]$ (δ_{Y-S} from 0.2690 to 0.3199 nm). Sm atoms in the $Sm_4Si_3S_{12}$ structure occupy the $6a$ sites (coordination number CN = 9) and the $18b$ sites (CN = 7). The interatomic distance δ_{Sm-S} ranges from 0.2834 to 0.3335 nm for the

former, and from 0.2801 to 0.3034 nm for the latter. La atoms in the La_2SiS_5 structure are located in the $4e$ sites (CN = 8; δ_{La-S} varies from 0.28456 to 0.32936 nm). Rare-earth atoms in the structure of the quaternary compounds form trigonal prisms with two additional atoms with sulfur atoms (CN = 8). The interatomic distances δ_{Ln-S} vary from 0.2679 to 0.3119 nm for $Y_3Ni_{0.5}SiS_7$, from 0.2742 to 0.3090 nm for $Sm_3Ni_{0.5}SiS_7$, and from 0.2839 to 0.3130 nm in $La_3Ni_{0.5}SiS_7$.

Conclusions

The thermodynamic conditions of the co-existence of binary, ternary, and quaternary compounds in the quaternary systems $Y_2S_3 - NiS - SiS_2$, $Sm_2S_3 - NiS - SiS_2$, and $La_2S_3 - NiS - SiS_2$ at 770 K were established using X-ray phase analysis methods. The crystal structure of the new quaternary sulfides $Y_3Ni_{0.5}SiS_7$ was determined by X-ray powder method. The quaternary chalcogenides belongs to the structure type of $La_3Mn_{0.5}SiS_7$ (Pearson symbol $hP23$, S.G. $P6_3$) and due to non-centrosymmetric structure are prospective objects for the investigation of their non-linear optical properties.

Ethics Declarations

Funding:

No funding was received to assist with the preparation of this manuscript.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Availability of data and material

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

The research did not involve human participants and/or animals.

Code availability

All data generated or analysed during this study are included in this published article.

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Нові четвертинні сполуки $R_3Ni_{0.5}SiS_7$ ($R - Y, Sm, La$) зі структурою $La_3Mn_{0.5}SiS_7$

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Сульфідні $Y_3Ni_{0.5}SiS_7$, $Sm_3Ni_{0.5}SiS_7$ і $La_3Ni_{0.5}SiS_7$ утворюються у системах $Y_2S_3 - NiS - SiS_2$, $Sm_2S_3 - NiS - SiS_2$ і $La_2S_3 - NiS - SiS_2$ відповідно, для яких за температури 770 К побудовано ізотермічні перерізи. Кристалічна структура сульфідів $Y_3Ni_{0.5}SiS_7$ ($a = 0.97643(4)$ нм; $c = 0.56377(4)$ нм), $Sm_3Ni_{0.5}SiS_7$ ($a = 0.99599(8)$ нм; $c = 0.56583(5)$ нм) і $La_3Ni_{0.5}SiS_7$ ($a = 1.02830(6)$ нм; $c = 0.57412(4)$ нм) вивчена рентгенівським методом порошку. Їх структура належить до структурного типу $La_3Mn_{0.5}SiS_7$ (space group $P6_3$; Pearson symbol $hP23$). У структурі вивчених сульфідів атоми Y, Sm і La розташовані в ПСТ 6c і разом з атомами сульфуру формують тригональні призми із двома додатковими атомами. Атоми Ni розташовані в ПСТ 2a (КЗП = 0.5) і для них характерним є октаедричне оточення з атомів сульфуру. Для атомів Si (ПСТ 2b) характерним є КЧ = 4. Центровані атомами Ni октаедри утворюють нескінченні ланцюжки $[Ni_6S]_n$.

Ключові слова: тетрарні сульфідні, РЗМ, кристалічна структура, рентгенівський метод порошку.