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$LaNi_9Si_4$: CRYSTAL STRUCTURE AND ELECTRICAL PROPERTIES

B. Belan[1], S. Pukas[1], M. Dzevenko[2*], M. Manyako[1], B. Kuzhel[1], R. Gladyshevskii[1]

[1]Department of Inorganic Chemistry, Ivan Franko National University of Lviv,
6 Kyryla i Mefodia Str., 79005 L'viv, Ukraine;
[2]Kruty Heroes Lviv Lyceum with intensive military and physical training,
68 Pasichna Str., 79038 L'viv, Ukraine
e-mail: m_dzevenko.teacher@lgk.ukr.education

The structure of $LaNi_9Si_4$ compound has been investigated by X-ray powder ans single crystal method. This silicide crystalize in $CeNi_{8.5}Si_4$ structure type: space group *I*4 *mcm*, Pearson symbol *tI*56, a = 7.86415(6), c = 11.5101(1) Å, R_B = 0.0653; a = 7.83933(17), c = 11.4472(5) Å, R = 0.0220, wR = 0.0734 for X-ray single crystal data. Unlike the prototype $CeNi_{8.5}Si_{4.5}$, where the Wyckoff position 4*d* is occupied by mixture of Ni and Si atoms, in the structure of the ternary silicide $LaNi_9Si_4$, the atoms are ordered in all Wyckoff positions. Additionally, the electrical properties for the compound were investigated. The temperature dependence of the electrical resistivity exhibits metal behaviour (ρ_0 = 121.60 μΩ·cm, θ_D = 191 K, $A = 2.2 \cdot 10^{-9}$ μΩ·m·K^{-3}).

Key words: lanthanum, nickel, silicon, crystal structure, electrical resistivity.

INTRODUCTION

The ternary systems *RE*-Ni-Si (*RE* = rare earth metals) have attracted interest of scientist due to complicated interaction of the components. A high number of compounds with various crystal structures and interesting physical properties exists in these systems [1–5]. Probably the La-Ni-Si system is the most interesting among them. The isothermal section of this system has been constructed in the whole concentration range at 400 °C [6] and twenty ternary compounds have been found, but full crystal structure determination has been performed not for all of them. Given this, we conducted research the part of the La-Ni-Si system, namely the section 7.14 at. % La. Previously we reported on the study of the compound $LaNi_{11.8\text{-}11.4}Si_{1.2\text{-}1.6}$, which adopts the cubic structure type $CaCu_{6.5}Al_{6.5}$ (space group *Fm*-3*c*, Pearson code *cF*112) [7]. Another phase exist on this section is $LaNi_9Si_4$ compound, which is isotypic to $CeNi_{8.5}Si_{4.5}$-type according to *Refs.* [8, 9]. Since we were lucky enough to synthesize a single-phase sample and obtain a single crystal, the detailed crystal structure determination of $LaNi_9Si_4$ and investigation of electrical resistivity was performed. Herein we present the results of these investigations.

EXPERIMENT AND DISCUSSION OF THE RESULTS.

X-ray powder investigations

12 ternary samples along the isoconcentrate 7.14 at.% La were melted under an argon atmosphere in an arc furnace, and annealed at 870 K under vacuum for 720 h.

In the beginning, the structure of the investigated phase was studied by X-ray powder diffraction of sample with composition $La_{7.14}Ni_{61.43}Si_{31.43}$. The powder intensity data was collected on automatic diffractometer STOE STADI P with linear PSD detector (transmission mode, $2\theta/\omega$-scan; Cu $K\alpha_1$ radiation, curved germanium [1 1 1] monochromator; 2θ-range $6.000 \leq 2\theta \leq 120.225°$ with step 0.015 °2θ; PSD step 0.480 °2θ, scan time 250 s/step). The value of linear absorption coefficient was estimated from the logarithmic ratio between the primary beam intensity and its intensity after passing through background and measured samples. A preliminary data processing, X-ray profile and phase analyses were performed using the STOE WinXPOW (version 2.21) program package [10]. The program DBWS [11] was used for the refinement of the crystal structure. The crystallographic data and the results of crystal structure refinements of the silicide are listed in the Table 1. Fig. 1 shows the X-ray diffraction patterns of $La_{7.14}Ni_{61.43}Si_{31.43}$ sample. The results of investigation confirmed that the investigated silicide is isotypical to the structure of $CeNi_{8.5}Si_{4.5}$ type. However, in the structure of our compound, all crystallographic positions are occupied by atoms in an orderly manner, and the composition of the compound is described by the formula $LaNi_9Si_4$, while in the prototype one of the positions occupied by mixture of Ni and Si atoms.

Table 1.

Crystal data and structure refinements for $LaNi_9Si_4$ compound.

Structure type	$CeNi_{8,5}Si_{4,5}$
Pearson symbol	*tI*56
Space group	*I*4/*mcm*
Unit cell dimensions, Å	a = 7.86415(6), b = 11.5101(1)
Volume, Å^3	711.84(1)
No. formula units per unit cell	4
Calculated density D_X, g/sm^3	7.285
Number of reflects	162
Zero value of 2θ, °	0.0109(6)
Profile parameters U; V; W	0.034(1); -0.012(2); 0.0116(4)
Reliability factors R_B; R_p; R_{wp}	0,0653; 0,0513; 0,0650
La 4*a* (0 0 1/4)	
B_{iso}, Å^2	0.59(2)
Ni1 16*l* (*x y z*)	x = 0,6294(1); y = 0,1294(1); z = 0,1824(1)

Structure type	$CeNi_{8,5}Si_{4,5}$
B_{iso}, Å^2	1,20(2)
Ni2 16*k* (*x y* 0)	x = 0,0692(2); y = 0,2047(2)
B_{iso}, Å^2	1,20(2)
Ni3 4*d* (0 ½ 0)	
B_{iso}, Å^2	1,20(2)
Si 16*l* (*x y z*)	x = 0,1715(2); y = 0,6715(2); z = 0,1176(2)
B_{iso}, Å^2	1,06(2)

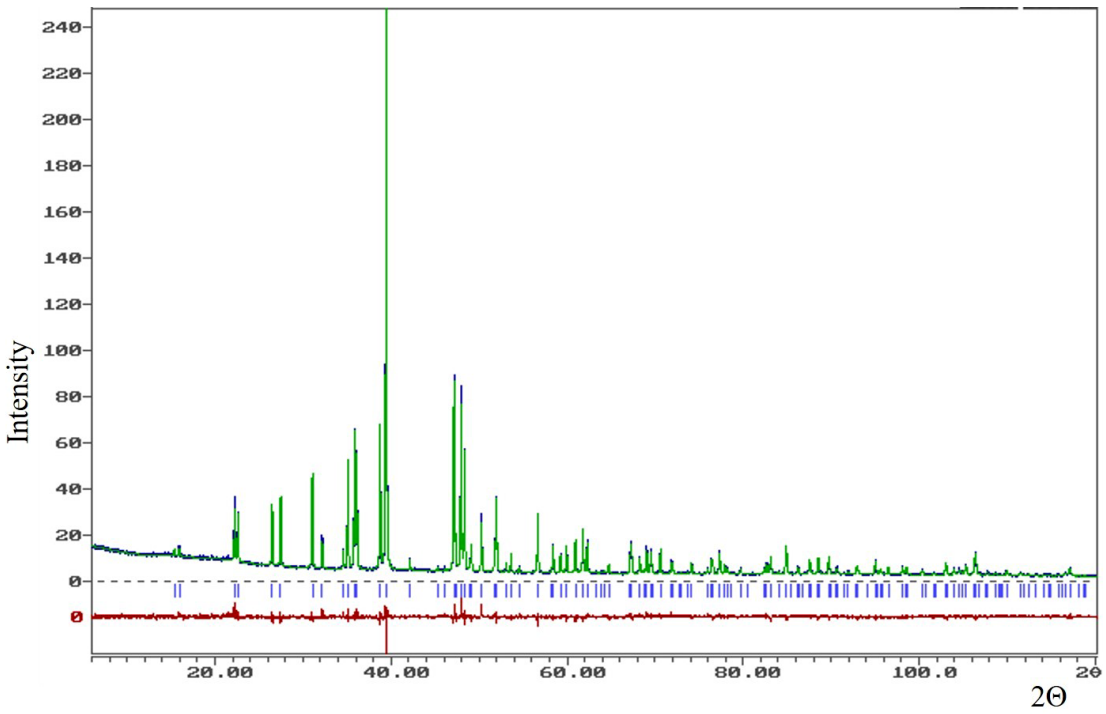

Fig. 1. Observed (•), calculated (-) and difference X-ray diffraction patterns of $LaNi_9Si_4$.

X-ray single crystal investigations

More detail crystal structure investigation was performed by X-ray single crystal method. Single crystals were selected from the sample by mechanical fragmentation from the sample with composition $La_{7.14}Ni_{67.86}Si_{25}$. They exhibit metallic lustre whereas the ground powders are dark grey. The reflections intensities were measured with graphite-monochromatized Mo *K*α radiation on an STOE IP diffractometer at

295(2) K. The structures were solved by direct methods and refined by the SHELX program package [12] with anisotropic atomic displacement parameters. After the data collection, the single crystal was analyzed by EDX spectroscopy with a Leica420i scanning electron microscope. The experimentally determined composition of the grain of is close to the composition calculated from the structure refinements.

The crystallographic data and details on the data collection for $LaNi_9Si_4$ are listed in Table 2. The structure was refined in space group *I*4/*mcm* with anisotropic atomic displacement parameters. A final electron-density difference map was flat and did not reveal any significant residual peaks. Concerning the occupations of crystallographic positions, the results of single crystal investigations correlate with the results of the X-ray powder study, namely, the fully and orderly occupations of all crystallographic positions. Final atomic positional and displacement parameters of $LaNi_9Si_4$ compound are presented in Table 3.

Table 2.

Crystal data and structure refinement details for $LaNi_9Si_4$.

Empirical formula	$LaNi_9Si_4$
Formula weight	779.66
T, K	295(2)
Structure type	$CeNi_{8.5}Si_{4.5}$
Space group	*I*4/*mcm*
Pearson code	*tI*56,140
Unit cell dimensions, Å	$a = 7.83933(17)$, $c = 11.4472(5)$
Volume, Å^3	703.49(4)
No. formula units per unit cell	4
Calculated density, g·cm^{-3}	7.361
Absorption coefficient, mm^{-1}	30.005
Crystal color	metallic
Index ranges	$-11 \le h \le 11$, $-9 \le k \le 10$, $-16 \le l \le 17$
Measured reflections	2177
Independent reflections / Reflections with $I > 2\,\sigma(I)$	352 / 343
Data / restraints / parameters	352 / 0 / 24
Goodness-of-fit on F^2	1.053
Final *R*1 / *wR*2 [$I > 2\,\sigma(I)$]	0,0220 / 0,0734
Largest diff. peak / hole, *e* Å^{-3}	2.525 / –1.408

Table 3.

Atomic coordinates and thermal displacement parameters for $LaNi_9Si_4$.

Atom	Wyckoff Site	G	x	y	z	U_{eq}, Å^2
La	4*a*	1	0	0	1/4	0.0039(2)
Ni1	16*l*	1	0.63048(7)	0.13048(7)	0.18442(6)	0.0070(2)
Ni2	16*k*	1	0.06884(10)	0.20317(9)	0	0.0065(2)
Ni3	4*d*	1	0	1/2	0	0.0061(3)
Si	16*l*	1	0.17072(14)	0.67072(14)	0.11833(14)	0.0066(3)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La	0.0028(2)	0.0028(2)	0.0062(3)	0	0	0
Ni1	0.0073(3)	0.0073(3)	0.0064(3)	–0.0004(2)	0.0007(2)	-0.0007(2)
Ni2	0.0051(3)	0.0058(3)	0.0085(4)	–0.0003(2)	0	0
Ni3	0.0047(4)	0.0047(4)	0.0089(6)	–0.0006(5)	0	0
Si	0.0062(4)	0.0062(4)	0.0074(7)	0.0016(5)	0.0001(3)	-0.0001(3)

The interatomic distances (δ), the values of interatomic distances reductions from the sum of atomic radii and coordination numbers of atoms for $LaNi_9Si_4$ listed in Table 4 (values of the atomic radii are taken from [13]: *r*(La) = 1.877 Å, *r*(Ni) = 1.240 Å, *r*(Si) = 1.320 Å). The majority of interatomic distances are in good agreement with the sum of atomic sizes. Some Ni-Si interatomic distances are rather short and a few Ni-Ni distances are rather long in comparison with the sum of the respective atomic radii.

Table 4.

Interatomic distances (δ), *Δ* values ($\Delta = 100(\delta - \Sigma r)/\Sigma r$, where Σr is the sum of the respective atomic radii) and coordination numbers (CN) of of $LaNi_9Si_4$ compound.

Atoms		δ, Å	*Δ*, %	CN	Atoms		δ, Å	*Δ*, %	CN
La	8 Ni1	3.1625(6)	1.5	24	Ni2	2 Ni2	2.3782(11)	–4.1	12
	8 Si	3.2751(12)	7.5			1 Ni3	2.3887(7)	–3.7	
	8 Ni2	3.3193(4)	6.5			2 Si	2.4633(14)	–3.8	
Ni1	1 Si	2.3016(17)	–10.1	13		2 Si	2.5177(14)	–1.7	
	1 Si	2.3302(13)	-9.0			1 Ni2	2.5276(11)	1.9	
	2 Si	2.4994(13)	–2.4			2 Ni1	2.5280(8)	1.9	
	2 Ni2	2.5280(8)	1.9			2 La1	3.3193(4)	6.5	
	2 Ni1	2.5376(9)	2.3		Ni3	4 Si	2.3275(13)	–9.1	12

Atoms		δ, Å	Δ, %	CN	Atoms		δ, Å	Δ, %	CN
	1 Ni3	2.5591(7)	3.2			4 Ni2	2.3887(8)	–3.4	
	1 Ni1	2.8931(8)	16.7			4 Ni1	2.5591(7)	3.2	
	1 Ni1	3.0459(8)	22.8		Si	1 Ni1	2.3016(17)	–10.1	12
	2 La	3.1625(6)	1.5			1 Ni3	2.3275(13)	–9.1	
						1 Ni1	2.3302(13)	–9.0	
						2 Ni2	2.4633(14)	–3.8	
						2 Ni1	2.4994(13)	–2.4	
						2 Ni2	2.5177(14)	–1.7	
						1 Si	2.7091(19)	2.6	
						2 La1	3.2751(12)	7.5	

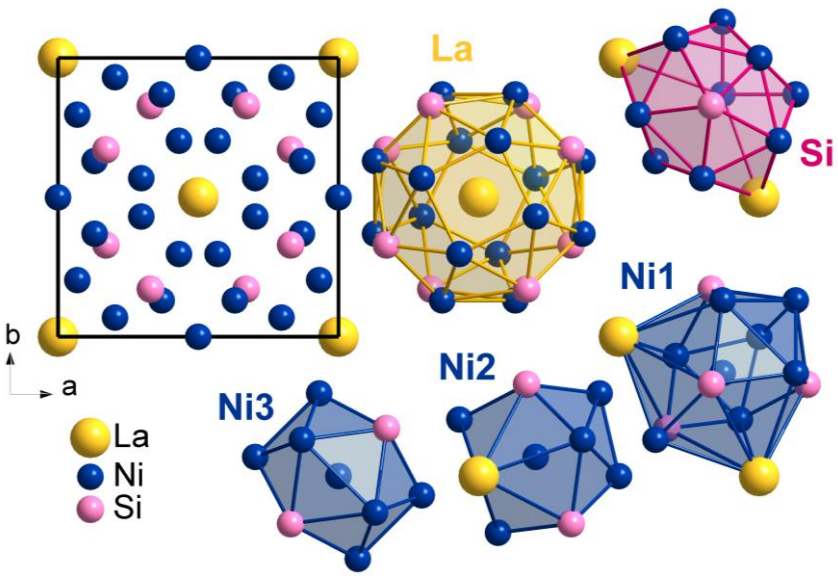

Fig. 2. A projection of the $LaNi_9Si_4$ unit cell on *ab* plane and a view of the coordination polyhedra of the atoms.

The projection of the crystal structure of $LaNi_9Si_4$ on the *ab* plane and the coordination polyhedral (CP) of the atoms are shown in Fig. 2. The $LaNi_9Si_4$ compounds belong to the family of transition-metal rich compounds, which have complex multilayer structures with high values for the coordination numbers of all atom types. The lanthanium atoms have the largest coordination number (CN = 24) and its pseudo Frank-Kasper polyhedron [$La(Ni_{16}Si_8)$] can be described as a combination of three antiprisms, two of which consists from eight

nickel atoms each, and the third of eight silicon atoms. A distorted icosahedron with one additional atom [Ni1($La_2Ni_7Si_4$)] is the CP of the Ni1 atoms (CN = 13). The similar types of polyhedra were observed for Ni2 and Ni3 atoms. The coordination polyhedrons of the these atoms (CN = 12 for both) can be described as distorted icosahedrons, [Ni2($La_2Ni_6Si_4$)] and [Ni3(Ni_8Si_4)], respectively. The first difference lies in the greater deformation of the Ni2 polyhedra. Furthemore, the environment of these atoms is also somewhat different. The atoms of all sorts form the CP of the Ni2 atoms and only nickel and silicon atoms surround the Ni3 atoms. The Si atoms have 12 neighbors and the polyhedron [Si1(La_2Ni_9Si1)] can be described as a strongly distorted icosahedron.

The structure of $LaNi_9Si_4$ compound can be considered as a packing of the tetragonal prism and antiprism, which are built from the eight silicon atoms each (Fig. 2). These prisms and antiprisms alternate along the *c* direction, forming endless columns that form a three-dimensional framework. The La atoms center the antiprism, and a square from the four Ni atoms situate in one prism. The columns from such clusters connect to each other by common edges and empty trigonal Si_6 prisms or Si_4 tetrahedra, which are formed in layers of tetragonal prisms or tetragonal antiprisms, respectively.

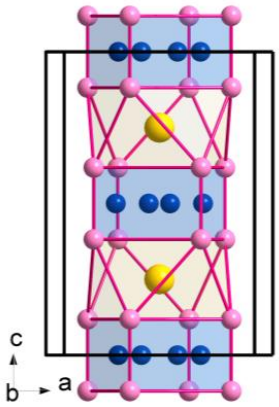

Fig. 3. The arrangement of the tetragonal prisms (blue) and antiprisms (yellow) in the $LaNi_9Si_4$ structure.

The alternative representation as packing of CP around lanthanium and nickel atoms shows even more compact filling (Fig. 3). The structure of $LaNi_9Si_4$ can be described as a 3D compact packing of two types of polyhedron: 24-vertex pseudo Frank – Kasper polyhedra around the La atoms in Wyckoff position 4*a* and icosahedra around the Ni atoms in Wyckoff position 4*d*. These both polydrons consists of nickel and silicon atonms and have the compositions [$Ni_{16}Si_8$] and [Ni_8Si_4], respectively.

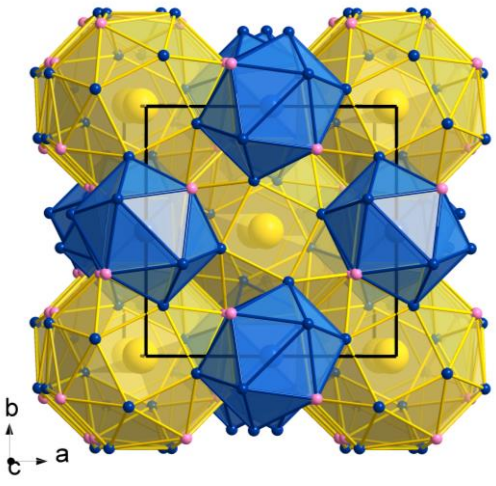

Fig. 4. Packing of [La($Ni_{16}Si_8$)] (yellow) and [Ni3(Ni_8Si_4)] (blue) slabs in the $LaNi_9Si_4$ structure.

Investigation of electrical properties

The specific electrical resistance of a polycrystalline $La_{7.14}Ni_{61.43}Si_{31.43}$ sample of regular geometric shape was measured in the temperature range of 11–290 K on a potentiometric setup by the standard two-probe method. The temperature dependence of electrical resistance, with slight nonlinearity, was approximated using the Bloch-Grüneisen-Mott formula [14].

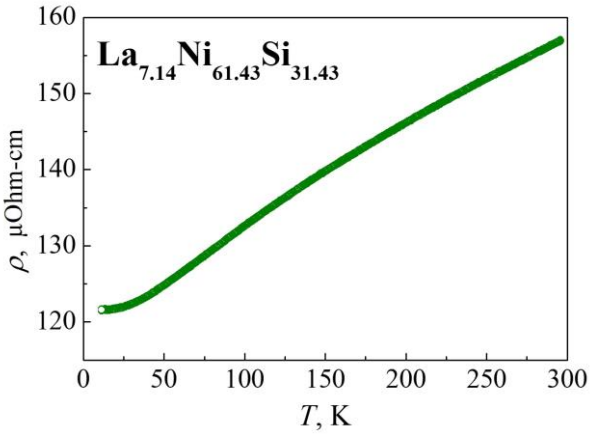

Fig. 5. Temperature dependence of specific electrical resistance for the $LaNi_9Si_4$ compound.

Fig. 5 shows the temperature dependence of the specific electrical resistance for the $LaNi_9Si_4$ compound. The temperature dependence of the specific electrical resistance indicates the metallic nature of the conductivity at relatively low absolute values of the specific electrical resistance of the investigated alloy ($\rho_{290\,K}$ / $\rho_{11\,K}$ = 156.26 μΩ•cm / 121.60 μΩ•cm). The slight nonlinearity of the temperature dependence of the resistivity at higher temperatures indicates that, in addition to scattering by lattice phonons, there is an additional mechanism, which can be explained by the process of scattering of *s-d* conduction electrons of a transition metal. Calculation of the obtained experimental results using the Bloch – Gruneisen – Mott formula gives the following parameters: ρ_0 = 121.60 μΩ•cm, θ_D = 191 K, A = $2.2•10^{-9}$ μΩ•m•K^{-3}.

CONCLUSIONS

The crystal structure of ternary compound $LaNi_9Si_4$ have been reinvestigated in detail using powder and single crystal X-ray data. This compound is isotypical to the structure of $CeNi_{8.5}Si_{4.5}$-type. Additionaly, the investigation of electrical resistivity was performed.

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$LaNi_9Si_4$: КРИСТАЛІЧНА СТРУКТУРА ТА ЕЛЕКТРИЧНІ ВЛАСТИВОСТІ

Б. Белан[1]*, С. Пукас[1], М. Дзевенко[2]*, М. Маняко[1], Б. Кужель[1], Р. Гладишевський[1]

[1] Львівський національний університет імені Івана Франка, вул. Кирила і Мефодія, 6, Львів 79005, Україна;
[2] Львівський ліцей з посиленою військово-фізичною підготовкою імені Героїв Крут, вулиця Пасічна, 68, Львів 79000, Україна
**e-mail: m_dzevenko.teacher@lgk.ukr.education*

Відомим є факт існування вздовж ізоконцентрати 7,14 ат.% La сполук складу $LaNi_{11,6-9,5}Si_{1,4-3,5}$, $LaNi_{8,8-8,4}Si_{4,2-4,6}$ і $LaNi_{7,8-4,5}Si_{5,2-8,5}$.

Під час детального вивчення системи La–Ni–Si за температури 600 °C підтверджено існування сполуки $LaNi_9Si_4$ та проведено комплексне дослідження її кристалічної структури методом порошку та монокристалу.

Уточнення кристалічної структури сполуки $LaNi_9Si_4$ спочатку здійснено методом порошку на основі масиву рентгенівських дифракційних даних від полікристалічного зразка складу $La_{7,14}Ni_{61,43}Si_{31,43}$ (дифрактометр STOE Stadi P, довжина хвилі λ = 1,5406 Å, діапазон кутів $6 \le 2\theta \le 120{,}225$ із кроком 0,015° і часом сканування 250 с): структурний тип $CeNi_{8,5}Si_{4,5}$, a = 7,86415(6), c = 11,5101(1) Å. Оскільки зі зразку складу $La_{7,14}Ni_{67,86}Si_{25}$ вдалося отримати монокристал, то подальше детальне дослідження проведено рентгеноструктурним методом монокристалу. Масив експериментальних інтенсивностей відбить отримано на автоматичному монокристальному дифрактометрі STOE IP (Mo K_α-випромінювання). Структуру визначено прямими методами за допомогою комплексу програм SHELX. Параметри теплового зміщення всіх атомів уточнено в анізотропному наближенні. Підтверджено приналежність структури досліджуваної сполуки до структурного типу $CeNi_{8,5}Si_{4,5}$ (СП *tI*56, ПГ *I*4/*mcm*): a = 7,86415(6), **c** = 11,5101(1) Å, R_B = 0,0653; a = 7,83933(17), **c** = 11,4472(5) Å, R = 0,0220, wR = 0,0734. Слід відмітити, що на відміну від прототипу $CeNi_{8,5}Si_{4,5}$, де положення 4*d*-просторової групи *I*4/*mcm* зайняте статистичною сумішшю атомів Ni та Si у співвідношенні 1:1, у структурі тернарного силіциду $LaNi_9Si_4$ атоми розміщені впорядковано в усіх правильних системах точок.

Окрім того, досліджено температурну залежність питомого електроопору для сполуки $LaNi_9Si_4$, що вказує на металічний характер провідності (ρ_0 = 121,60 мкОм·см, θ_D = 191 K, $A = 2{,}2\cdot10^{-9}$ мкОм·м·K^{-3}).

Ключові слова: лантан, нікель. силіцій, кристалічна структура, електричний опір.

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