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Crystal structure of the new silicide $LaNi_{11.8–11.4}Si_{1.2–1.6}$

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Abstract: The intermetallic compound $LaNi_{11.8–11.4}Si_{1.2–1.6}$ was synthesized by arc-melting and its crystal structure was determined using powder and single-crystal X-ray diffraction data. The compound adopts the cubic $CaCu_{6.5}Al_{6.5}$-type structure (space group $Fm\bar{3}c$, Pearson code *cF*112, Z = 8), which is a partially ordered ternary derivative of the $NaZn_{13}$ type: a = 11.256(4) Å, V = 1426.1(15) Å^3, R = 0.0133, wR = 0.0285 for 93 reflections with $I > 2\,\sigma(I)$ for $LaNi_{11.4}Si_{1.6}$; a = 11.25486(8) Å, V = 1425.68(2) Å^3, R_p = 4.17%, R_{wp} = 5.85%, R_B = 3.44% for $LaNi_{11.8}Si_{1.2}$. One of its crystallographic positions (96*i*) is occupied by a mixture of Ni and Si atoms. The structure of this new silicide can be represented as a packing of Ni-centered icosahedra and La-centered snub cubes, which are packed in a CsCl-related manner.

Keywords: crystal structure; intermetallic; rare earth silicide; X-ray diffraction.

1 Introduction

The most efficient method to discover new ternary materials with various characteristics is the investigation of the complicated interactions of the components and the construction of the isothermal sections. From this point of view, the *RE*–Ni–Si systems have attracted particular interest (*RE* is lanthanoid). These ternary systems are characterized by a variety of interactions of the components. A fairly high number of compounds with various crystal structures and interesting physical properties have been found in many of the *RE*–Ni–Si systems [1–4]. Twenty ternary compounds were found to exist in the La–Ni–Si system [5]. However, despite the fact that the isothermal section of this system has been constructed, the crystal structures of some compounds have not yet been determined. A good example is the series of ternary compounds with the approximate composition La(Ni, Si)$_{13}$, which exists within the section of 7.14 wt% La [6]. According to references [7, 8], $LaNi_9Si_4$ is isotypic to $CeNi_{8.5}Si_{4.5}$. The crystal structure of the other two compounds, namely $LaNi_{11.6–9.5}Si_{1.4–3.5}$ and $LaNi_{8.8–8.4}Si_{4.2–4.6}$, are known to be derived from the $NaZn_{13}$ type [6, 9], though only the cell parameters for these compounds have been determined. Therefore, we decided to investigate their crystal structures in more detail. The results of this investigation are reported herein.

2 Experimental details

Starting materials for the preparation of the samples were ingots of lanthanum, nickel, and silicon with nominal purities La ≥ 99.85 wt%, Ni ≥ 99.99 wt% and Si ≥ 99.999 wt%. The samples were synthesized by arc-melting under a purified argon atmosphere, using Ti as a getter and a tungsten electrode. To achieve complete reactions, the samples were melted twice. The ingots were annealed at 600 °C in evacuated quartz ampoules for 720 h and subsequently quenched in cold water. The weight loss during the preparations was less than 1% of the total mass, which was 2 g.

Initially, the samples were studied by X-ray powder diffraction (DRON-2.0 powder diffractometer) using Fe$K\alpha$ radiation. The indexing of the obtained diffraction data for the ternary samples was performed by comparison with calculated data using the program Powder Cell [10]. The compounds were further investigated using X-ray powder data: diffractometer STOE STADI P with a linear PSD detector (Cu$K\alpha_1$ radiation, curved germanium [1 1 1] monochromator; 2θ range 6.0 ≤ 2θ ≤ 111.060° with a step width of 0.015° in 2θ; PSD step 0.480° in 2θ, scan time 250 s per step). The crystal structure refinement was performed using the Dbws software [11].

Single crystals were selected by mechanical fragmentation from the sample with the composition

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$La_{7.1}Ni_{78.6}Si_{14.3}$. Laue and rotation diffraction patterns of selected single crystals showed cubic symmetry. Integrated intensities were measured at room temperature with graphite-monochromatized Mo$K\alpha$ radiation (λ = 0.71073 Å) on an Oxford Diffraction Xcalibur four-circle diffractometer equipped with an Atlas CCD camera. Data collection and reduction were carried out using the programs CrysAlis CCD and CrysAlis Red [12] taking into account a numerical absorption correction. The structure was solved by Direct Methods and refined using the Shelxl-2014 program package [13].

Further details on the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247 808-666; E-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-2062187.

Table 1: Results of structure refinements of the $LaNi_{11.8}Si_{1.2}$ phase (powder data).

Phase		$LaNi_{11.8}Si_{1.2}$[a]
Content, wt%		97(3)
Structure type		$CaCu_{6.5}Al_{6.5}$
Pearson code		*cF*112
Space group		$Fm\bar{3}c$ (No. 226)
Unit cell dimensions, Å		a = 11.25486(8)
Volume, Å^3		1425.68(2)
No. formula units per unit cell		8
Calculated density, g•cm^{-3}		8.06
R_p, %		4.17
R_{wp}, %		5.85
R_{Bragg}, %		3.44
B_{iso}, Å^2	La (8*a*) 1/4 1/4 1/4	0.56(3)
	Ni (8*b*) 0 0 0	0.83(6)
	Ni/Si (96*i*) 0 *y z*	0.88(3)
		y = 0.1178(1); z = 0.1798(1)
		G = 0.897(6)Ni/0.103(6)Si

[a]Additional phase: Ni (Cu type), space group $Fm\bar{3}m$, a = 3.51962(8) Å, V = 43.60(1) Å^3, R_B = 11.66%; 3(2) wt%.

3 Results and discussion

The powder X-ray diffraction patterns of $La_{7.1}Ni_{85.9}Si_{7.0}$, $La_{7.1}Ni_{82.9}Si_{10.0}$ and $La_{7.1}Ni_{78.6}Si_{14.3}$ showed reflections of a new compound with cubic structure and some additional phases: binary Ni_2Si (Co_2Si type), $LaNi_9Si_2$ ($CeNi_{8.6}Si_{2.4}$ type) and $LaNi_2Si_2$ ($CeAl_2Ga_2$ type) or pure Ni (Cu type) [14]. First we assumed that the compounds are isostructural to the $NaZn_{13}$ type. However, the analysis of the powder X-ray diffraction patterns of the $La_{7.1}Ni_{82.9}Si_{10.0}$ sample revealed that the structure of this compound is more complex and may be related to the $CaCu_{6.5}Al_{6.5}$ structure type (Pearson code *cF*112, space group $Fm\bar{3}c$, a = 11.935 Å [15, 16]), which is a distortion variant of $NaZn_{13}$ [17]. All further calculations have confirmed this supposition. Crystal data and details of structure refinement are listed in Table 1. Figure 1 illustrates the X-ray diffraction pattern of the respective sample.

Because a single crystal suitable for intensity data collection was available, the following part of the investigation was performed using single-crystal X-ray diffraction. The crystallographic data and details on the data collection for a single crystal obtained from the $La_{7.1}Ni_{78.6}Si_{14.3}$ sample are listed in Table 2. An analysis of systematic absences in the data set of the single crystal has pointed towards the possible space group $Fm\bar{3}c$ (no. 226), and the structure refinement confirmed that conclusion. The initial atomic parameters were deduced from an automatic interpretation of Direct Methods, and the structure was successfully refined with the $CaCu_{6.5}Al_{6.5}$ structure type with anisotropic atomic displacement parameters for all the atoms. The final electron density difference map was smooth and did not reveal any significant residual peaks. Therefore, from the reasonable values of the residual factors of the structure reliability, it may be concluded that the investigated compound adopts the $CaCu_{6.5}Al_{6.5}$ type. The final atomic positional and displacement parameters for the silicide are presented in Table 3. All the crystallographic positions are fully occupied, but the Wyckoff site (96*j*) is occupied by a mixture of nickel

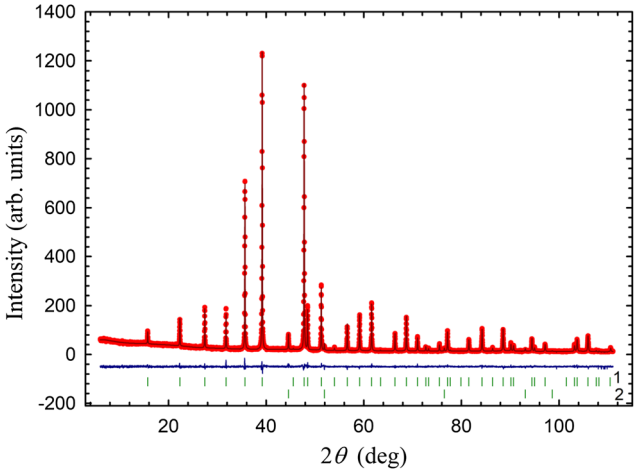

Figure 1: Observed (circles), calculated (solid line) and difference powder X-ray diffraction patterns of the sample $La_{7.1}Ni_{82.9}Si_{10.0}$ (1: $LaNi_{11.8}Si_{1.2}$; 2: Ni).

Table 2: Crystal data and data collection and structure refinement details for $LaNi_{11.4}Si_{1.6}$ (single-crystal data).

Empirical formula	$LaNi_{11.4}Si_{1.6}$
Formula weight	854
T, K	295(2)
Space group	$Fm\bar{3}c$ (No. 226)
Pearson code	*cF*112
Unit cell dimensions, Å	a = 11.256(4)
Volume, Å^3	1426.1(15)
No. formula units per unit cell	8
Calculated density, g•cm^{-3}	7.96
Absorption coefficient, mm^{-1}	35.41
F(000), e	3192
Crystal color	Metallic
Crystal size, mm^3	0.113 × 0.07 × 0.031
θ range for data collection, deg	3.597–28.412
Index ranges *hkl*	−14 → +15, ±15, ±15
Measured reflections	3132
Independent reflections/R_{int}	100/0.0275
Reflections with $I > 2\,\sigma(I)/R_\sigma$	93/0.0078
Data/restraints/parameters	100/0/10
Goodness-of-fit on F^2	1.247
Final $R1/wR2$ [$I > 2\,\sigma(I)$]	0.0133/0.0285
Final $R1/wR2$ (all data)	0.0155/0.0289
Largest diff. peak/hole, e Å^{-3}	0.84/−0.68

and silicon atoms. Based on this data, the refined composition $LaNi_{11.4}Si_{1.6}$ was deduced for the investigated crystal.

When the cell parameters of the refined phases together with the occupancy of the positions (a = 11.25486(8) Å and $G(96j)$ = 0.897Ni/0.103Si for $LaNi_{11.8}Si_{1.2}$; a = 11.256(4) Å and $G(96j)$ = 0.869Ni/0.131Si for $LaNi_{11.4}Si_{1.6}$) are compared with each other, the existence of a small homogeneity range with the composition $LaNi_{11.8-11.4}Si_{1.2-1.6}$ may be assumed. Herewith, the increase in the unit cell parameters is in good agreement with the increase in the silicon content of the compound (r(Ni) = 1.24 Å < r(Si) = 1.32 Å [18]). It should be noted, that the coordination of atoms in positions with mixed occupation is also slightly different for both phases (see Table 1 and 3).

The main interatomic distances and their reduced values from the sum of the atomic radii ($\Delta = 100(\delta - \sum r)/\sum r$, where $\sum r$ is the sum of the respective atomic radii), and the coordination numbers of the atoms for $LaNi_{11.4}Si_{1.6}$ are listed in Table 4 (values of the atomic radii are taken from [18]: r(La) = 1.87, r(Ni) = 1.24, r(Si) = 1.32, and calculated $r(M)$ = 1.25 Å). Deviations in the interatomic distances deduced from the sums of the relevant atomic radii are very small (no more than 6%). Some M–M and M–Ni interatomic distances are slightly shorter when compared with the sum of the respective atomic radii. Hence, the feature of our compound is that within its structure, the lanthanum atoms are not in contact with each other.

Projections of the unit cell and the coordination polyhedra of the atoms are shown in Figure 2. The lanthanum atoms are confined within 24-vertex snub cubes [La(M_{24})]. The nickel atoms are located inside the icosahedra [Ni(M_{12})] with coordination number 12. The environment of the Ni/Si atoms on sites with mixed occupancy consists of atoms of all three kinds with the coordination polyhedron [M($La_2Ni_1M_9$)], that has 12 vertices.

The $LaNi_{11.4}Si_{1.6}$ structure can be considered as a packing of different polyhedra (Figure 3). To the first type of the polyhedra one can attribute the Ni-centered icosahedra [Ni(M_{12})], which are isolated and mutually rotated by 90°. The other type of polyhedra includes the coordination polyhedra around the lanthanum atoms [La(M_{24})], which are connected with each other through common faces. These basic polyhedral building units almost completely fill the space in the structure of the compound. Moreover, the Ni-centered icosahedra and the La-centered snub cubes are packed in a CsCl manner (Figure 3).

According to previous reports [6, 9], the compound with the approximate composition $LaNi_{11.6-9.5}Si_{1.4-3.5}$ and an unknown crystal structure exists partly in the range of the

Table 3: Atomic coordinates and displacement parameters for $LaNi_{11.4}Si_{1.6}$.[a]

Atom	Wyck.	Occupation	x	y	z	U_{iso}
La	8a	1	1/4	1/4	1/4	0.0098(2)
Ni	8*b*	1	0	0	0	0.0114(4)
M	96*i*	0.869(6) Ni+0.131(6)Si	0	0.11765(5)	0.18020(5)	0.0116(2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
La	0.0098(2)	U_{11}	U_{11}	0	0	0
Ni	0.0114(4)	U_{11}	U_{11}	0	0	0
M	0.0104(3)	0.0152(3)	0.0092(3)	0.0033(2)	0	0

[a]U_{iso} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

Table 4: Interatomic distances (d, Å), Δ values ($\Delta = 100(d-\Sigma r)/\Sigma r$, where Σr is the sum of the respective atomic radii [16]) and atomic coordination numbers (C.N.) for $LaNi_{11.4}Si_{1.6}$.[a]

Atom		d (Å)	Δ (%)	C.N.
La	24 *M*	3.2795(9)	4.9	24
Ni	12 *M*	2.4224(9)	−3.0	12
M	2 *M*	2.3818(11)	−4.8	12
	1 Ni	2.4224(9)	−3.0	
	2 *M*	2.4447(8)	−2.2	
	4 *M*	2.5226(8)	0.9	
	1 *M*	2.6485(12)	5.9	
	2 La	3.2795(9)	4.9	

[a]*M* = 0.869(6)Ni + 0.131(6)Si.

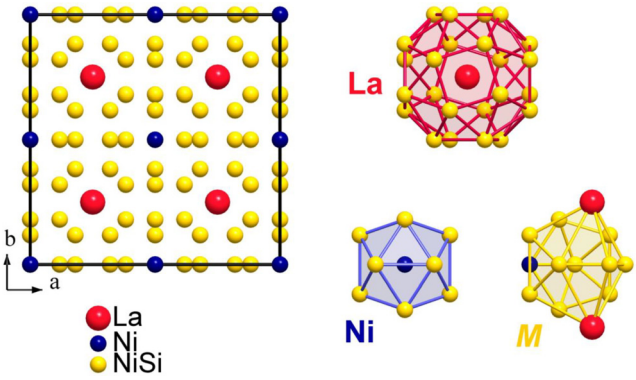

Figure 2: Projection of the unit cell of $LaNi_{11.4}Si_{1.6}$ onto the crystallographic *ab* plane and coordination polyhedra of the atoms.

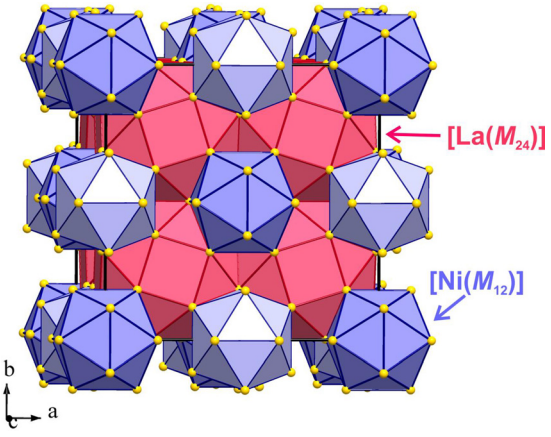

Figure 3: The packing of the icosahedra [Ni(M_{12})] and the snub cubes [La(M_{24})] in the crystal structure of $LaNi_{11.4}Si_{1.6}$.

compound $LaNi_{11.8-11.4}Si_{1.2-1.6}$. Taking into account that the area of existence of $LaNi_{11.6-9.5}Si_{1.4-3.5}$ has been determined approximately by using Debye-Scherrer techniques, it can be argued that the aforementioned silicide investigated by us is a completely new compound. In view of our results and the inaccuracy of literature data, new precise investigations of the existence region and the crystal structure of the ternary compound which can form across the section with 7.14 wt% La need to be performed in future work.

4 Conclusions

The crystal structure of $LaNi_{11.8-11.4}Si_{1.2-1.6}$ has been investigated using powder and single crystal X-ray diffraction data. The investigated silicide belongs to a larger class of compounds which derives from the $NaZn_{13}$ family. The $LaNi_{11.8-11.4}Si_{1.2-1.6}$ compound forms a cubic $CaCu_{6.5}Al_{6.5}$-type unit cell (space group $Fm\bar{3}c$, a = 11.25486(8)–11.256(4) Å). A mixture of Ni/Si atoms occupies one crystallographic position and the remaining two positions are occupied by La and Ni atoms.

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