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New ternary phases in the Lu–Ni–Si system

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The existence of three new ternary compounds, $LuNiSi_3$, LuNiSi, and $LuNi_{0.61}Si_{1.39}$, was established in the Lu–Ni–Si system, and their crystal structures were refined from X-ray powder diffraction data. The structure of the compound $LuNiSi_3$ belongs to the structure type $SmNiGe_3$, Pearson symbol *oS*20, space group *Cmmm*, $a = 3.88279(8)$, $b = 20.8179(4)$, $c = 3.89111(8)$ Å, that of LuNiSi to the structure type TiNiSi, *oP*12, *Pnma*, $a = 6.67857(10)$, $b = 4.09340(6)$, $c = 7.11618(10)$ Å, and that of $LuNi_{0.61(2)}Si_{1.39(2)}$ to the structure type AlB_2, *hP*3, *P*6/*mmm*, $a = 3.94594(10)$, $c = 3.87276(10)$ Å. The compound $LuNi_{0.61}Si_{1.39}$ has a homogeneity range of $LuNi_{0.27\text{-}0.67}Si_{1.73\text{-}1.33}$ at 600°C and is characterized by a statistical mixture of Ni and Si atoms. The other two compounds have point compositions and ordered distribution of the atoms.

Intermetallic compound / Lutetium / Nickel / Silicon / X-ray powder diffraction / Crystal structure

1. Introduction

The results presented in this paper are part of a systematic investigation of crystal structures of ternary compounds formed in *R*–*T*–Si systems (where *R* is a rare-earth element and *T* is a transition element), in this case in the system Lu–Ni–Si. This system has to our knowledge not been investigated in the whole concentration range; the literature contains information about six ternary compounds [1,2], for which crystallographic data are given in Table 1.

Three new phases, $LuNiSi_3$, LuNiSi, and $LuNi_{0.61}Si_{1.39}$, were found during our investigation of the phase equilibria in the system Lu–Ni–Si at 600°C. We present here results of the crystal structure determination of the three new silicides using X-ray powder diffraction. Preliminary results of the investigation were presented in [3].

2. Experimental

The samples were prepared from pure elements by arc melting under an argon atmosphere. The alloys were remelted to ensure homogeneity. The composition of the samples was controlled by comparing the mass of the obtained alloy with the mass of the initial load. The weight losses did not exceed 2% after melting. The samples were annealed at 600°C under vacuum in quartz ampoules for one month and subsequently quenched in cold water. The crystal structures of the compounds $LuNiSi_3$, LuNiSi, and $LuNi_{0.61}Si_{1.39}$ were determined from X-ray powder diffraction data collected at room temperature on a diffractometer Stoe Stadi P equipped with a linear position-sensitive detector and Cu $K\alpha_1$-radiation (range 6-110° 2θ, step size 0.015°) on alloys of nominal compositions $Lu_{20}Ni_{20}Si_{60}$, $Lu_{33.3}Ni_{33.3}Si_{33.3}$, and $Lu_{33.3}Ni_{21.3}Si_{45.3}$, respectively. Experimental details and parameters from the structure refinements by the Rietveld method using the program package FullProf Suite [10] are given in Table 2. Starting atom coordinates for the refinements were taken from the corresponding prototypes [1]. In the final cycles the following parameters were allowed to vary for each single-phase pattern: sample shift, scale factor, cell parameters, profile parameters (pseudo-Voigt profile function), atom positional and displacement parameters, site occupancy (in the case of $LuNi_{0.61}Si_{1.39}$), and preferred orientation parameter. For the refinement of the structure of $LuNiSi_3$, the isotropic displacement parameters of atoms of the same chemical element were constrained to be equal. The background was defined by linear interpolation between manually assigned points ($LuNiSi_3$), or by polynomial functions using a Fourier filtering technique (LuNiSi and $LuNi_{0.61}Si_{1.39}$). Fig. 1 shows the powder diffraction patterns of the alloys $Lu_{20}Ni_{20}Si_{60}$, $Lu_{33.3}Ni_{33.3}Si_{33.3}$, and $Lu_{33.3}Ni_{21.3}Si_{45.3}$. The cell parameters within the homogeneity range of the ternary AlB_2-type phase, $LuNi_{0.27\text{-}0.67}Si_{1.73\text{-}1.33}$, were refined using the program package FullProf Suite [10].

Table 1 Crystallographic data of the ternary compounds in the system Lu–Ni–Si.

Compound	Structure type	Pearson symbol	Space group	Cell parameters, Å			Literature
				a	*b*	*c*	
$LuNi_{10}Si_2$	$Nd(Mn_{0.5}Fe_{0.5})_4Fe_8$	*tI*26	*I*4/*mmm*	8.164	–	4.650	[4]
$LuNi_5Si_3$	YNi_5Si_3	*oP*36	*Pnma*	18.49	3.739	6.710	[5]
$LuNi_2Si_2$	$CeAl_2Ga_2$	*tI*10	*I*4/*mmm*	3.905	–	9.495	[6]
$LuNiSi_3$	$SmNiGe_3$	*oS*20	*Cmmm*	3.88279(8)	20.8179(4)	3.89111(8)	This work
$Lu_3Ni_6Si_2$	$Ce_3Ni_6Si_2$	*cI*44	*Im*-3*m*	8.659	–	–	[7]
$Lu_2Ni_3Si_5$	$Lu_2Co_3Si_5$	*mS*40	*C*2/*c*	11.032	11.942 β=120.18°	5.919	[8]
$LuNiSi_2$	$CeNiSi_2$	*oS*16	*Cmcm*	3.851	15.810	3.851	[9]
LuNiSi	TiNiSi	*oP*12	*Pnma*	6.67857(10)	4.09340(6)	7.11618(10)	This work
$LuNi_{0.61(2)}Si_{1.39(2)}$	AlB_2	*hP*3	*P*6/*mmm*	3.94594(10)	–	3.87276(10)	This work

Table 2 Experimental details and crystallographic data for the compounds $LuNiSi_3$, LuNiSi, and $LuNi_{0.61}Si_{1.39}$.

Compound		$LuNiSi_3$	LuNiSi	$LuNi_{0.61(2)}Si_{1.39(2)}$
Structure type		$SmNiGe_3$	TiNiSi	AlB_2
Pearson symbol		*oS*20	*oP*12	*hP*3
Space group		*Cmmm*	*Pnma*	*P*6/*mmm*
Cell parameters:	*a*, Å	3.88279(8)	6.67857(10)	3.94594(10)
	b, Å	20.8179(4)	4.09340(6)	–
	c, Å	3.89111(8)	7.11618(10)	3.87276(10)
Cell volume *V*, $Å^3$		314.525(11)	194.543(5)	52.222(2)
Number of formula units in the cell *Z*		4	4	1
Density D_X, g/cm^3		6.714	8.937	7.948
Preferred orientation: value / [direction]		0.935(3) / [101]	0.9158(13) / [010]	0.915(3) / [110]
Profile parameters:	*U*	0.054(2)	0.089(12)	0.023(2)
	V	-0.0232(16)	0.0070(14)	-0.001(2)
	W	0.0154(3)	0.0107(3)	0.0110(5)
Shape parameter		0.511(12)	0.214(3)	0.176(14)
Asymmetry parameters:	P_1	0.0806(14)	0.078(3)	0.091(5)
	P_2	0.0211(6)	0.0126(9)	0.0151(13)
Number of refined parameters		20	21	14
Reliability factors:	R_B	0.0658	0.0543	0.0758
	R_F	0.0535	0.0482	0.0543
	R_p	0.0714	0.0613	0.0883
	R_{wp}	0.102	0.0823	0.126
	χ^2	16.1	5.01	7.54

3. Results and discussion

The crystal structures of the compounds $LuNiSi_3$, LuNiSi, and $LuNi_{0.61}Si_{1.39}$ were refined in the space groups *Cmmm*, *Pnma*, and *P*6/*mmm*, as belonging to the structure types $SmNiGe_3$ [11], TiNiSi [12], and AlB_2 [13], respectively. Atom coordinates, isotropic displacement parameters, interatomic distances, and coordination numbers for the compounds $LuNiSi_3$, LuNiSi, and $LuNi_{0.61}Si_{1.39}$ are listed in Tables 3-8.

The structure of the compound $LuNiSi_3$ ($SmNiGe_3$ type) is an intergrowth of slabs sliced from the simple structure types $BaAl_4$ (or its ternary variant $CeAl_2Ga_2$), AlB_2, and α-Po [14]. The fragments have the following compositions: $Lu_{0.5}NiSi$ ($CeAl_2Ga_2$ type), $LuSi_2$ (AlB_2 type), and Si_2 (α-Po type). They are stacked along the crystallographic direction [010] *via* common atoms forming square meshes. The composition of the compound can be obtained from the stacking of eight slabs in the translation unit: $2(Lu_{0.5}NiSi + LuSi_2 + Lu_{0.5}NiSi + Si_2) \equiv 4LuNiSi_3$. It should be noted that the parent structure types $CeAl_2Ga_2$ and AlB_2 are represented in the system Lu–Ni–Si by the ternary compounds $LuNi_2Si_2$ and $LuNi_{0.61}Si_{1.39}$ (or binary $LuSi_{1.67}$ [15]), respectively.

The structure of the compound LuNiSi (TiNiSi type) is a deformation derivative of the structure type ZrBeSi, which is a ternary substitution variant of the structure type AlB_2 [14].

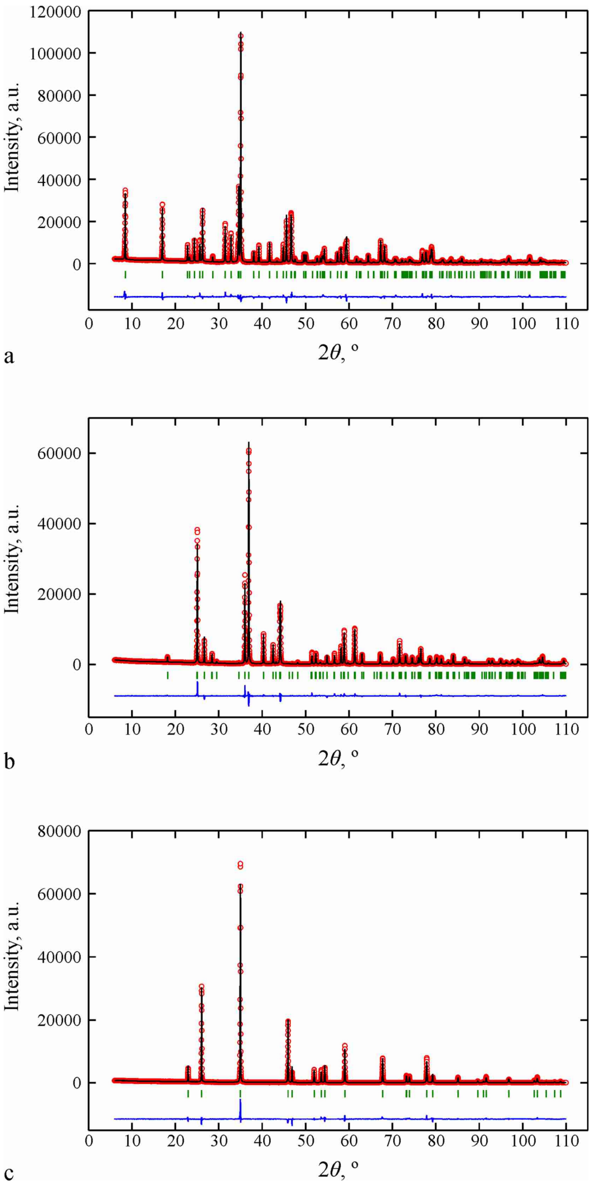

Fig. 1 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the samples $Lu_{20}Ni_{20}Si_{60}$ (a), $Lu_{33.3}Ni_{33.3}Si_{33.3}$ (b), and $Lu_{33.3}Ni_{21.3}Si_{45.3}$ (c) (Cu $K\alpha_1$-radiation). Vertical bars indicate the positions of reflections from the compounds $LuNiSi_3$ (a), LuNiSi (b), and $LuNi_{0.61}Si_{1.39}$ (c).

The phase $LuNi_{0.61}Si_{1.39}$, which has a statistical mixture of Ni and Si atoms (unlike the phases $LuNiSi_3$ and LuNiSi, which are ternary compounds with point compositions and ordered distribution of all the atoms in the crystal structure), could be part of the solid solution based on the binary silicide $LuSi_{1.67}$. However, our investigations show that at 600°C the composition $LuNi_{0.61}Si_{1.39}$ is inside the homogeneity range $LuNi_{0.27\text{-}0.67}Si_{1.73\text{-}1.33}$ of a ternary phase with hexagonal AlB_2-type structure. The cell parameters within the homogeneity range are shown in Fig. 2. With increasing Ni content (from 9 to 22.3 at.%) the *a*-parameter increases (3.88700(7)-3.94674(6) Å), whereas the *c*-parameter decreases (3.94298(10)-3.86807(7) Å), the *c*/*a*-ratio changing from 1.014 to 0.979. Consequently, the distances between the small atoms in the hexagonal nets increase from 2.244 to 2.279 Å. Considering the atomic and covalent radii of Si and Ni (r_{at} = 1.32 and r_{cov} = 1.11 Å for Si, r_{at} = 1.24 and r_{cov} = 1.15 Å for Ni), one can conclude that these atoms are connected *via* covalent bonding. The ratio c/a = 1 (which corresponds to an ideal trigonal prism Lu_6 around the small atoms) should be observed for 15.7 at.% Ni ($LuNi_{0.47}Si_{1.53}$). The binary compound $LuSi_{1.67}$ dissolves about 4 at.% Ni. The cell parameters within this solid solution change in the same way as for the isotypic ternary phase $LuNi_{0.27\text{-}0.67}Si_{1.73\text{-}1.33}$.

The structures of the three new compounds belong to class 10 of the systematic by P. Kripyakevich [16], which groups structure types with coordination number 6+*n* and coordination polyhedra having the form of a trigonal prism with 0-5 additional vertices for the small atoms. In the case of $LuNiSi_3$ (structure type $SmNiGe_3$), the trigonal prisms around the Si atoms have the composition Lu_6 or Lu_2Si_4 and their faces are capped by 1Ni + 2Si or 2Ni + 1Si atoms, respectively. In LuNiSi (TiNiSi) and $LuNi_{0.61}Si_{1.39}$ (AlB_2), the trigonal prisms around the Si are built up exclusively from Lu atoms and the additional atoms are four Ni (LuNiSi) or 3*M* ($LuNi_{0.61}Si_{1.39}$, *M* = 0.307Ni + 0.693Si). The coordination polyhedra of the Ni atoms are square antiprisms of composition Lu_4Si_4 with one additional Si atom ($LuNiSi_3$), or trigonal prisms of composition Lu_6 with four Si (LuNiSi) or three *M* additional atoms ($LuNi_{0.61}Si_{1.39}$). The closest atoms around the Lu atoms form 20- ($LuNiSi_3$ and $LuNi_{0.61}Si_{1.39}$) or 16- (LuNiSi) vertex polyhedra.

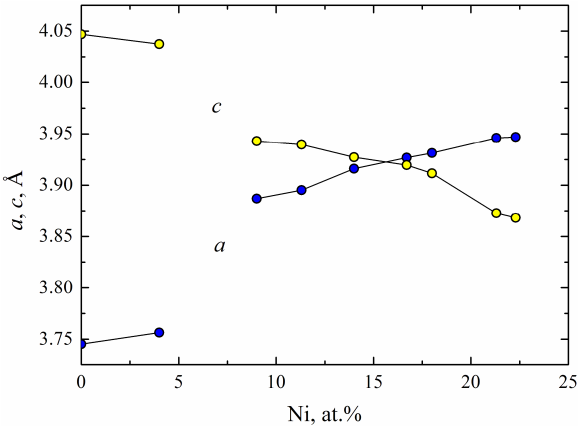

Fig. 2 Cell parameters *versus* Ni content within the homogeneity range of the ternary phase $LuNi_{0.27\text{-}0.67}Si_{1.73\text{-}1.33}$ with AlB_2-type structure.

Table 3 Atom coordinates and isotropic displacement parameters for the compound $LuNiSi_3$ (structure type $SmNiGe_3$, *oS*20, *Cmmm*).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Lu	4*j*	0	0.33119(3)	½	0.411(17)
Ni	4*i*	0	0.11183(9)	0	1.00(5)
Si1	4*j*	0	0.05683(18)	½	0.89(5)
Si2	4*i*	0	0.21541(18)	0	0.89(5)
Si3	4*i*	0	0.44459(18)	0	0.89(5)

Table 4 Interatomic distances and coordination numbers for the compound $LuNiSi_3$ (structure type $SmNiGe_3$, *oS*20, *Cmmm*).

Atom	*δ*, Å		CN
Lu	– 4 Si2	2.9147(13)	20
	– 4 Ni	2.9935(9)	
	– 2 Si1	3.034(3)	
	– 2 Si3	3.059(3)	
	– 2 Si2	3.098(3)	
	– 2 Lu	3.88279(8)	
	– 2 Lu	3.89111(8)	
	– 2 Lu	3.8982(8)	
Ni	– 1 Si2	2.156(4)	9
	– 2 Si1	2.257(2)	
	– 2 Si3	2.269(2)	
	– 4 Lu	2.9935(9)	

Atom	*δ*, Å		CN
Si1	– 2 Ni	2.257(2)	9
	– 1 Si1	2.366(5)	
	– 4 Si3	2.74865(7)	
	– 2 Lu	3.034(3)	
Si2	– 1 Ni	2.156(4)	9
	– 2 Si2	2.417(3)	
	– 4 Lu	2.9147(13)	
	– 2 Lu	3.098(3)	
Si3	– 2 Ni	2.269(2)	9
	– 1 Si3	2.307(6)	
	– 4 Si1	2.74865(7)	
	– 2 Lu	3.059(3)	

Table 5 Atom coordinates and isotropic displacement parameters for the compound LuNiSi (structure type TiNiSi, *oP*12, *Pnma*).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Lu	4*c*	-0.00555(16)	¼	0.70197(8)	0.390(13)
Ni	4*c*	0.1882(4)	¼	0.0777(5)	0.53(6)
Si	4*c*	0.3034(9)	¼	0.4090(9)	1.67(12)

Table 6 Interatomic distances and coordination numbers for the compound LuNiSi (structure type TiNiSi, *oP*12, *Pnma*).

Atom	*δ*, Å		CN
Lu	– 2 Ni	2.852(2)	16
	– 1 Ni	2.854(3)	
	– 2 Si	2.860(4)	
	– 1 Si	2.933(6)	
	– 2 Si	2.961(4)	
	– 1 Ni	2.970(3)	
	– 1 Si	3.048(6)	
	– 2 Ni	3.076(2)	
	– 2 Lu	3.4085(15)	
	– 2 Lu	3.5295(7)	

Atom	*δ*, Å		CN
Ni	– 2 Si	2.374(4)	10
	– 1 Si	2.480(7)	
	– 1 Si	2.572(7)	
	– 2 Lu	2.852(2)	
	– 1 Lu	2.854(3)	
	– 1 Lu	2.970(3)	
	– 2 Lu	3.076(2)	
Si	– 2 Ni	2.374(4)	10
	– 1 Ni	2.480(7)	
	– 1 Ni	2.572(7)	
	– 2 Lu	2.860(4)	
	– 1 Lu	2.933(6)	
	– 2 Lu	2.961(4)	
	– 1 Lu	3.048(6)	

Table 7 Atom coordinates and isotropic displacement parameters for the compound $LuNi_{0.61}Si_{1.39}$ (structure type AlB_2, *hP*3, *P*6/*mmm*).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Lu	1*a*	0	0	0	0.48(2)
M [a]	2*d*	⅓	⅔	½	1.36(7)

[a] *M* = 0.307(9)Ni + 0.693(9)Si.

Table 8 Interatomic distances and coordination numbers for the compound $LuNi_{0.61}Si_{1.39}$ (structure type AlB_2, *hP*3, *P*6/*mmm*).

Atom	*δ*, Å		CN
Lu	– 12 *M* [a]	2.98994(5)	20
	– 2 Lu	3.87276(10)	
	– 6 Lu	3.94594(10)	

Atom	*δ*, Å		CN
M	– 3 *M* [a]	2.27820(6)	9
	– 6 Lu	2.98994(5)	

[a] *M* = 0.307(9)Ni + 0.693(9)Si.

Conclusions

In addition to the previously known six ternary compounds in the system Lu–Ni–Si, three new silicides were found: $LuNiSi_3$, LuNiSi, and $LuNi_{0.61}Si_{1.39}$. The latter compound has a homogeneity range of $LuNi_{0.27-0.67}Si_{1.73-1.33}$ at 600°C and is characterized by a statistical mixture of Ni and Si atoms. The former two compounds have point compositions and ordered distribution of the atoms. In the structures of the three new compounds the Si atoms are coordinated by trigonal prisms with three or four additional atoms.

Acknowledgments

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References

[1] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds, Release 2013/14*, ASM International, Materials Park (OH), 2013.

[2] P. Villars, K. Cenzual, R. Gladyshevskii (Eds.), *Handbook of Inorganic Substances 2014*, De Gruyter, Berlin, 2014, 1717 p.

[3] B. Belan, Ya. Tokaychuk, M. Manyako, B. Kuzhel, R. Gladyshevskii, *Coll. Abstr. XII Int. Conf. Cryst. Chem. Intermet. Compd.*, Lviv, 2013, p. 57.

[4] V.I. Yarovets, *Coll. Abstr. III All-Union Conf. Cryst. Chem. Intermet. Compd.*, Lviv, 1978, p. 124 (in Russian).

[5] O.I. Bodak, Yu.K. Gorelenko, V.I. Yarovets, *Fiz. Khim. Tverd. Tila* 4 (2003) 141-145.

[6] O.I. Bodak, E.I. Gladyshevskii, P.I. Krypyakevych, *Inorg. Mater.* 2 (1966) 1861-1864.

[7] E.I. Gladyshevskii, P.I. Krypyakevych, O.I. Bodak, *Z. Anorg. Allg. Chem.* 344 (1966) 95-101.

[8] C. Mazumdar, K. Ghosh, S. Ramakrishnan, R. Nagarajan, L.C. Gupta, G. Chandra, B.D. Padalia, P.R. Vijayaraghavan, *Phys. Rev. B* 50 (1994) 13879-13882.

[9] O.I. Bodak, E.I. Gladyshevskii, *Sov. Phys. Crystallogr.* 14 (1970) 859-862.

[10] J. Rodriguez-Carvajal, *Commission on Powder Diffraction (IUCr), Newsletter* 26 (2001) 12-19.

[11] O.I. Bodak, V.K. Pecharskii, O.Ya. Mruz, V.E. Zavodnik, G.M. Vytvytska, P.S. Salamakha, *Dopov. Akad. Nauk Ukr. RSR, Ser. B* (2) (1985) 36-38.

[12] C. Brink-Shoemaker, D.P. Shoemaker, *Acta Crystallogr.* 18 (1965) 900-905.

[13] W. Hofmann, W. Jäniche, *Naturwissenschaften* 23 (1935) 851.

[14] E. Parthé, L. Gelato, B. Chabot, M. Penzo, K. Cenzual, R. Gladyshevskii, *TYPIX – Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types, Gmelin Handbook of Inorganic and Organometallic Chemistry*, Springer-Verlag, Berlin, 1993, Vols. 1-4, 1596 p.

[15] P. Villars, K. Cenzual, J.L.C. Daams, F. Hulliger, T.B. Massalski, H. Okamoto, K. Osaki, A. Prince (Eds.), *Pauling File Binaries Edition, Version 1.0, Release 2002/1*, ASM International, Materials Park (OH), 2002.

[16] P.I. Kripyakevich, *Structure Types of Intermetallic Compounds*, Nauka, Moscow, 1977, 288 p. (in Russian).