Chemistry of Metals and Alloys

Chem. Met. Alloys 4 (2011) 113-118
Ivan Franko National University of Lviv
www.chemetal-journal.org

Synthesis and crystal structure of $LaNi_5In$ and $Sm_2Ni_{2-x}In$ (x = 0.20)

Mykola PUSTOVOYCHENKO[1], Volodymyr PAVLYUK[1], Yaroslav KALYCHAK[1]*

[1] *Faculty of Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine*
* *Corresponding author. Tel.: +380-32 2600389; e-mail: Kalychak@franko.lviv.ua*

Received November 2, 2010; accepted May 18, 2011; available on-line November 8, 2011

$LaNi_5In$ and $Sm_2Ni_{2-x}In$ (x = 0.20) were obtained by arc-melting of compact metals under argon. Their crystal structures were refined from X-ray single crystal data: $LaNi_5In$ crystallizes in the $CeNi_5Sn$ structure type, space group $P6_3/mmc$, Z = 4, a = 4.9570(7), c = 19.969(4) Å; $Sm_2Ni_{2-x}In$ (x = 0.20) crystallizes in the Mo_2FeB_2 structure type, space group $P4/mbm$, Z = 2, a = 7.523(4), c = 3.790(6) Å. The structure of $LaNi_5In$ can be decomposed into slabs from $CaCu_5$ and two hypothetical compounds "$LaNi_2In$" and "Ni_3In" in the ratio 2:4:8. The compound $Sm_2Ni_{2-x}In$ is constructed from trigonal (AlB_2 type) and tetragonal (CsCl type) prisms in the ratio 2:2.

Intermetallic compound / Crystal structure / Lanthanum / Samarium / Nickel / Indium

Introduction

The ternary systems rare-earth metal (*RE*) – transition metal (*T*) – indium are a very rich source of intermetallic compounds with a large variety of compositions, crystal structures and physical properties [1]. This concerns especially the systems where the transition metal is nickel or cobalt. Preliminary data of investigations of the phase equlibria in *RE*–Ni–In systems show that more than ten compounds exist in each system [1].

The compounds $LaNi_5In$ [2], $Sm_2Ni_{2-x}In$ [3] and Sm_2Ni_2In [4] were reported some 20 years ago. The crystal structures of these compounds were found to belong to the structure types $CeNi_5Sn$ (space group $P6_3/mmc$) [5], Mo_2FeB_2 (space group $P4/mbm$) [6,7] and Mn_2AlB_2 (space group $Cmmm$) [8], respectively, but only the lattice parameters were determined from X-ray powder diffraction data. In this paper we present our results on the synthesis and crystal structure refinement of $LaNi_5In$ and $Sm_2Ni_{2-x}In$ from single crystal data.

Experimental section

Compact metals of the following purity: lanthanum 99.85 wt.%, samarium 99.85 wt.%, cobalt 99.92 wt.%, and indium 99.999 wt.%, were used as starting materials for the synthesis. Samples of nominal compositions $La_{14}Ni_{72}In_{14}$ and $Sm_{44.5}Ni_{33.3}In_{22.2}$ were prepared by arc-melting under argon at a pressure of 0.7-0.8 atm. The argon was purified by melting titanium sponge. To ensure the homogeneity of the samples, they were remelted twice. No weight loss occurred. The samples were wrapped in tantalum foil and sealed in evacuated silica tubes. The $La_{14}Ni_{72}In_{14}$ sample was annealed for 4 months at 870 K and quenched in cold water. The thermal treatment of the $Sm_{44.5}Ni_{33.3}In_{22.2}$ sample was performed as follows: the sample was quickly heated to 1170 K and after one hour the temperature was reduced to 870 K. Then the sample was annealed at 870 K for two months and finally quenched in cold water. After annealing no reaction with the tantalum foil was observed and irregularly-shaped single crystals had grown on the surface of the specimens. Single crystals were selected by mechanical fragmentation and investigated by Laue photographs and the rotation method (RKV-camera, Mo radiation) in order to check the crystal quality and symmetry, and determine the lattice parameters. Intensity data were collected at room temperature on an Xcalibur diffractometer with a CCD camera. Details of the data collection are listed in Table 1.

Results and discussion

The diffractometer data confirmed the hexagonal and tetragonal symmetry for $LaNi_5In$ and $Sm_2Ni_{2-x}In$, respectively, and also the values of the lattice parameters obtained by the photographic method. The starting atomic parameters were deduced from automatic interpretations of direct methods with SHELXS-97 [9], and the structures were refined using SHELXL-97 [10] with anisotropic atomic displacement parameters. The results of the crystal structure refinements are presented in Tables 2

Table 1 Crystal data and details of the structure refinements for $LaNi_5In$ and $Sm_2Ni_{1.8}In$.

	$LaNi_5In$	$Sm_2Ni_{1.80}In$
Molar mass	444.28	521.20
Crystal system	hexagonal	tetragonal
Space group	$P6_3/mmc$	$P4/mbm$
Pearson symbol	$hP28$	$tP9.60$
Unit cell dimension a (Å)	4.9570(7)	7.253(4)
Unit cell dimension c (Å)	19.969(4)	3.790(6)
Unit cell volume (Å^3)	424.94(12)	214.5(14)
Formula units per cell	4	2
Calculated density (g/cm^3)	7.56	8.07
Absorption coefficient (mm^{-1})	32.8	39.8
$F(000)$	878	447
θ range for data collection	2.04 – 27.47	3.83 – 26.31
Range in hkl	$-6 \le h \le 6$	$-9 \le h \le 7$
	$-6 \le k \le 6$	$-9 \le k \le 7$
	$-25 \le l \le 25$	$-3 \le l \le 4$
Total no. reflections	918	564
Independent reflections	231	141
Reflections with $I > 2\sigma(I)$	227	132
Data/parameters	227/21	132/14
Goodness-of-fit on F^2	1.272	1.118
R[$I > 2\sigma(I)$] (R1=)	0.0585	0.0759
R[$I > 2\sigma(I)$] (wR2=)	0.1888	0.1970
R [all] (R1=)	0.0586	0.0775
R [all] (wR2=)	0.1888	0.1991
Extinction coefficient	–	0.021(7)
Largest peak and hole	3.74 / -3.89	5.53 / -4.70

Table 2 Atomic coordinates, site occupations (G) and isotropic displacement parameters (Å^2) for $LaNi_5In$ and $Sm_2Ni_{1.80}In$.

Atom	Wyckoff position	x	y	z	G	U_{eq}
$LaNi_5In$						
La1	2c	⅓	⅔	¼	1	0.0162(8)
La2	2a	0	0	0	1	0.0195(9)
Ni1	12k	0.8292(4)	0.6584(9)	0.14333(19)	1	0.0419(11)
Ni2	4f	⅓	⅔	0.5361(4)	1	0.0411(17)
Ni3	2d	⅓	⅔	¾	1	0.039(2)
Ni4	2b	0	0	¼	1	0.037(2)
In	4f	⅓	⅔	0.08802(13)	1	0.0189(8)
$Sm_2Ni_{1.80}In$						
Sm	4h	0.1759(2)	0.6759(2)	½	1	0.0138(14)
Ni	4g	0.3789(6)	0.8789(6)	0	0.90(2)	0.015(2)
In	2a	0	0	0	1	0.0118(14)

and 3 and in Figs. 1 and 2. The refinement readily confirmed isotypism of $LaNi_5In$ with the $CeNi_5Sn$ structure type [2], and of $Sm_2Ni_{2-x}In$ with the Mo_2FeB_2 structure type [3].

In the case of the compound $LaNi_5In$ (Fig. 1), the cell parameters correlate well with the literature data (a = 4.957, c = 19.969 Å) [2] and all the atom positions are fully occupied. The coordination polyhedra of the lanthanum atoms are hexacapped hexagonal prisms with two capped bases for La1 (CN = 20) and polyhedra with 18 vertices for La2. The coordination polyhedra of the nickel atoms are icosahedra (CN = 12) for Ni1, polyhedra with 10 vertices (a combination of icosahedra and trigonal prisms) for Ni2, and 12-vertex polyhedra for Ni3 and Ni4. The indium atoms are situated at the center of polyhedra with 14 vertices. Compounds with the $CeNi_5Sn$ structure type are known only for light rare-earth metals when the transition metal is Ni (*RE* = La, Ce, Pr, Nd, Sm, Eu) [1,2]. It is known that the

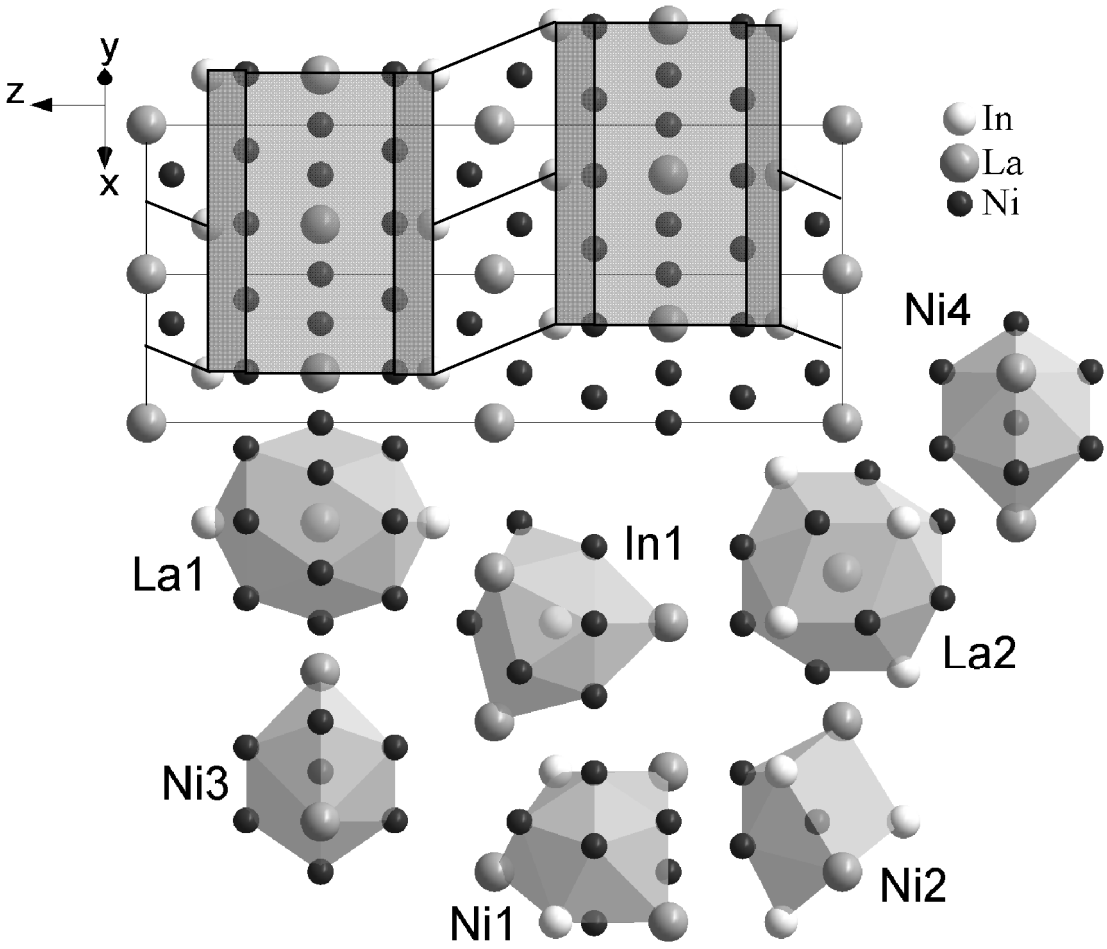

Fig. 1 Projection of the structure of $LaNi_5In$ onto the [110][001] plane and coordination polyhedra of the different atom sites; $LaNi_5$ ($CaCu_5$ structure type), "Ni_3In", and "$LaNi_2In$" slabs are light grey, dark grey, and colorless, respectively.

crystal structures of the transition metal-rich ternary indides consist of fragments of simple structures. The hexagonal $CeNi_5Sn$ type [5] and the related orthorhombic structure type $CeCu_{4.38}In_{1.62}$ [11] are among these. They have similar metric ratios (taking the orthorhombic setting for $CeNi_5Sn$) and both can be divided into identical fragments: $CaCu_5$ slabs and slabs of two hypothetical compounds "RNi_2In" and "Ni_3In" in the ratio 2:4:8. The difference between the two types is that the arrangement of the slabs is linear for $CeNi_5Sn$ but mosaic-like for $CeCu_{4.38}In_{1.62}$.

The refinement of the structure of $Sm_2Ni_{1.80}In$ (Fig. 2), which belongs to the Mo_2FeB_2 structure type, was satisfactory only when vacancies were considered on site 4*g*, which is occupied by nickel atoms (Table 2). This is in good agreement with [3], where $x \sim 0.2$ was estimated from the results of an X-ray phase analysis. A similar situation occurs for $Gd_2Ni_{1.78}In$ [3]. The value of the lattice parameters for the samarium compound, a = 7.448, c = 3.728 Å, calculated in [3] are slightly different from the values of the present investigation, a = 7.253, c = 3.790 Å. This is an evidence of the existence of a homogeneity range for this compound, just as for $Tb_{2+x}Pd_{1.80}In_{1-x}$ and $Ho_{2+x}Pd_{1.80}In_{1-x}$ [12], or the double-branched solid solutions $Ce_{1.95}Pd_{2+x}In_{1-x}$ and $Ce_{2+x}Pd_{1.85}In_{1-x}$ near the ideal stoichiometry 2:2:1 [13].

Ternary compounds of composition Mo_2FeB_2 exist in the systems *RE*–*T*–In for all the rare-earth metals, except for Eu (*T* = Ni, Cu, Rh, Pd, Pt, Au) [1]. In the systems *RE*–Ni–In, the compounds with Mo_2FeB_2 structure type are formed at the stoichiometric composition RE_2Ni_2In for the light rare-earth metals (La, Ce, Pr, Nd) at 670 K, but at the composition $RE_2Ni_{2-x}In$ ($x \sim 0.2$) for *RE* = Sm (at 670 K), Gd, Tb, Dy, Ho, Er, Tm, Lu, Y (all at 870 K). For Sm, Gd-Tm, Lu, and Y, compounds with Mn_2AlB_2 structure type exist at the stoichiometric composition. Both the Mo_2FeB_2 and the Mn_2AlB_2 structures contain trigonal [NiRE_6] (AlB_2 type) and tetragonal [InRE_8]

Table 3 Anisotropic displacement parameters (Å^2) for $LaNi_5In$ and $Sm_2Ni_{1.80}In$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$LaNi_5In$						
La1	0.0161(10)	U_{11}	0.0166(14)	0.0080(5)	0	0
La2	0.0193(11)	U_{11}	0.0197(14)	0.0097(5)	0	0
Ni1	0.0415(17)	0.042(2)	0.042(2)	0.0210(12)	0.0002(7)	0.0003(15)
Ni2	0.041(2)	U_{11}	0.041(3)	0.0205(12)	0	0
Ni3	0.040(3)	U_{11}	0.037(4)	0.0199(16)	0	0
Ni4	0.038(3)	U_{11}	0.037(4)	0.0188(15)	0	0
In	0.0189(10)	U_{11}	0.0188(13)	0.0095(5)	0	0
$Sm_2Ni_{1.80}In$						
Sm	0.0128(15)	U_{11}	0.0157(18)	-0.0005(7)	0	0
Ni	0.013(3)	U_{11}	0.018(3)	-0.002(3)	0	0
In	0.0087(17)	U_{11}	0.018(2)	0	0	0

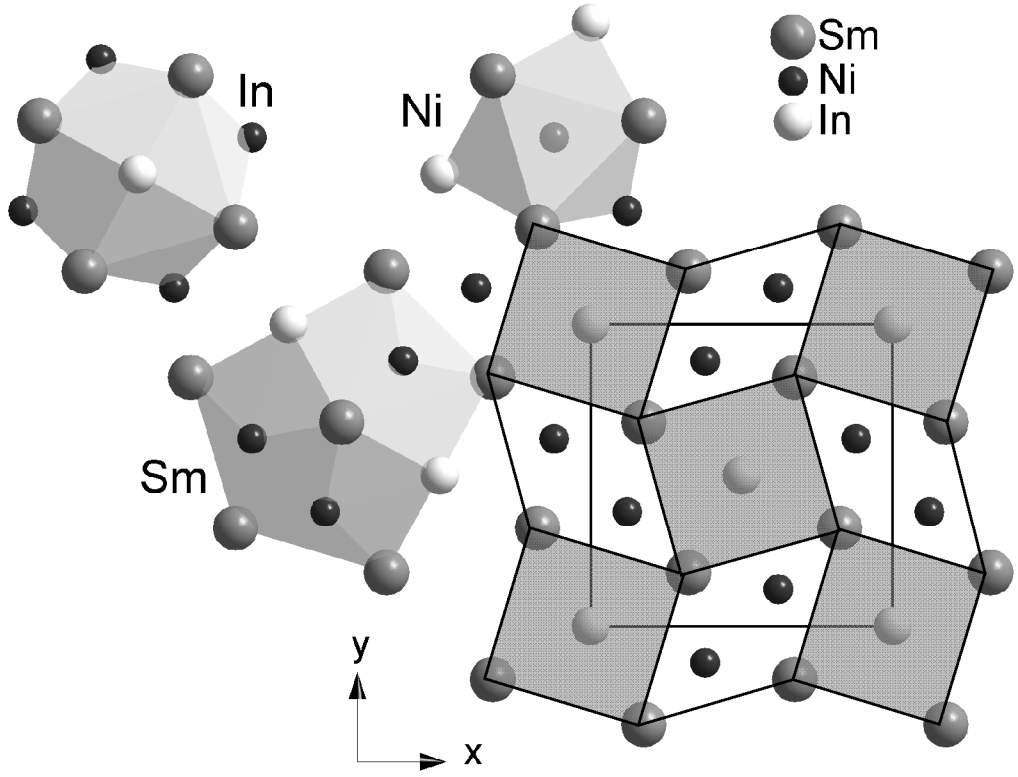

Fig. 2 Projection of the structure of $Sm_2Ni_{1.8}In$ onto the [100][010] plane and coordination polyhedra of the different atom sites. SmIn slabs (CsCl-structure type) are grey and $SmNi_2$ slabs (AlB_2-structure type) colorless.

(CsCl type) prisms in the ratio 2:2, but in the Mo_2FeB_2 type the arrangement of prisms is mosaic-like and in the Mn_2AlB_2 type linear. In $Sm_2Ni_{1.80}In$ the coordination polyhedra of the Sm atoms are pentacapped pentagonal prisms (CN = 17), and those of the Ni atoms trigonal prisms with three additional atoms (CN = 9). The indium atoms are situated at the center of tetrahexahedrons (CN = 14).

The interatomic distances (δ) and the values of Δ ($\Delta = 100(\delta-\Sigma r)/\Sigma r$, where Σr is the sum of the atomic radii [14]) are listed in Table 4. The strongest interactions were found for the following atom pairs in $LaNi_5In$: Ni2-In (Δ = -13.68 %), La1-Ni3 (Ni4) (Δ = -8.36 %), and La1-In (Δ = -7.65 %). In the other cases the interatomic distances correspond approximately to the sum of the atomic radii.

Table 4 Coordination numbers of the atoms (CN), interatomic distances (δ), and Δ ($\Delta = 100(\delta-\Sigma r)/\Sigma r$, where Σr is the sum of the atomic radii) for $LaNi_5In$ and $Sm_2Ni_{1.80}In$.

Atoms		δ (Å)	Δ (%)
$LaNi_5In$			
La1 (CN = 20)	3Ni3	2.8619(4)	-8.36
	3Ni4	2.8619(4)	-8.36
	2In	3.235(3)	-7.65
	12Ni1	3.268(3)	4.64
La2 (CN = 18)	6Ni2	2.9513(18)	-5.50
	6Ni1	3.216(4)	2.98
	6In	3.3586(14)	-4.12
Ni1 (CN = 12)	2Ni1	2.418(6)	-2.97
	2Ni1	2.539(6)	1.89
	Ni3	2.547(4)	2.21
	Ni2	2.556(7)	2.57
	Ni4	2.586(4)	3.77
	2In	2.714(2)	-5.50
	La2	3.216(4)	2.98
	2La1	3.268(2)	4.64
Ni2 (CN = 10)	In	2.479(8)	-13.68
	3Ni1	2.556(7)	2.57
	3La2	2.9513(18)	-5.50
	3In	3.044(3)	5.99
Ni3 (CN = 12)	6Ni1	2.547(4)	2.21
	3La1	2.8619(4)	-8.36
	3Ni4	2.8619(4)	14.84
Ni4 (CN = 12)	6Ni1	2.586(4)	3.77
	3La1	2.8619(4)	-8.36
	3Ni3	2.8619(4)	14.84
In (CN = 14)	Ni2	2.479(8)	-13.68
	6Ni1	2.714(2)	-5.50
	3Ni2	3.044(3)	5.99
	La1	3.235(3)	-7.65
	3La2	3.3586(14)	-4.12
$Sm_2Ni_{1.80}In$			
Sm (CN = 17)	2Ni	2.874(5)	-5.71
	4Ni	2.958(4)	-2.95
	4In	3.360(2)	-1.98
	Sm	3.742(5)	3.83
	2Sm	3.790(6)	5.16
	4Sm	3.923(6)	8.85
Ni (CN = 9)	Ni	2.576(12)	3.37
	2Sm	2.874(5)	-5.71
	4Sm	2.959(4)	-2.92
	2In	2.993(3)	4.21
In (CN = 14)	4Ni	2.993(3)	4.21
	8Sm	3.360(2)	-1.98
	2In	3.790(6)	16.54

References

[1] Ya.M. Kalychak, V.I. Zaremba, R. Pöttgen, M. Lukachuk, R.-D. Hoffmann, *Rare Earth–Transition Metal–Indides*, In: K.A. Gschneidner Jr., V.K. Pecharsky, J.-C. Bünzli (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 34, Elsevier, Amsterdam, 2005, pp. 1-133.

[2] V.M. Baranyak, Ya.M. Kalychak, L.V. Sysa, *Kristallografiya* 37 (1992) 1022.

[3] Ya.M. Kalychak, V. I. Zaremba, V.M. Baranyak, P.Yu. Zavalij, V.A. Bruskov, L.V. Sysa, O.V. Dmytrakh, *Neorg. Mater*. 26 (1990) 94.

[4] V.I. Zaremba, V.A. Bruskov, P.Yu. Zavalij, Ya.M. Kalychak, *Neorg. Mater.* 24 (1988) 409.

[5] R.V. Skolozdra, L.P. Komarovskaya, *Izv. Akad. Nauk SSSR, Met.* (2) (1988) 214.

[6] W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.* 95 (1964) 1417.
[7] E.I. Gladyshevsii, T.F. Fedorov, Yu.B. Kuz'ma, R.V. Skolozdra, *Poroshk. Metall.* (4) (1966) 55.
[8] H.J. Becher, R. Krogmann, E. Piesker, *Z. Anorg. Chem. B* 344 (1966) 140.
[9] G.M. Sheldrick, *SHELXS-97*, University of Göttingen, Germany, 1997.
[10] G.M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, 1997.
[11] Ya.M. Kalychak, V.M. Baranyak, V.K. Bel'skii, O.V. Dmytrakh, *Dopov. Akad. Nauk Ukr. RSR, Ser. B* (9) (1988) 39.
[12] M. Giovannini, A. Saccone, S. Delfino, P. Rogl, *Intermetallics* 11 (2003) 1237.
[13] M. Giovannini, A. Saccone, P. Rogl, R. Ferro, *Intermetallics* 11 (2003) 197.
[14] J. Emsley, *The Elements*, Clarendon Press, Oxford, 1991.