New Quaternary Indides $RE_7Ni_{5-x}Ge_{3+x}In_6$ (*RE* = La, Nd, Sm)

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The quaternary indides $RE_7Ni_{5-x}Ge_{3+x}In_6$ (*RE* = La, Nd, Sm) were synthesized from the elements by arc-melting. Single crystals were grown by slow cooling of the polycrystalline samples. The structures were characterized by powder and single-crystal X-ray diffraction: $Ce_7Ni_{4.73}Ge_{3.27}In_6$ type, $P6/m$, $Z = 1$, $a = 1147.05(9)$, $c = 426.82(4)$ pm, $wR2 = 0.0652$, 528 F^2 values for $La_7Ni_{4.46}Ge_{3.54}In_6$, $a = 1134.5(7)$, $c = 407.1(7)$ pm, $wR2 = 0.0419$, 441 F^2 values for $Nd_7Ni_{4.91}Ge_{3.09}In_6$, and $a = 1133.5(2)$, $c = 404.3(1)$ pm, $wR2 = 0.0619$, 498 F^2 values for $Sm_7Ni_{4.31}Ge_{3.69}In_6$, with 25 parameters per refinement. Characteristic features of the $RE_7Ni_{5-x}Ge_{3+x}In_6$ structures are hexagonal, AlB_2-related prisms around the *RE*1 atoms and a tricapped, trigonal-prismatic coordination of the nickel atoms.

Key words: Indide, Rare Earth Compounds, Crystal Structure

Introduction

Several structure types of binary intermetallic compounds RE_xM_y (*RE* = rare earth element; *M* = element of the 3rd, 4th, or 5th main group) have ternary and quaternary representatives formed by an ordered occupancy of the *RE* or *M* positions by two different elements. Typical examples are the series $RE_{11}Ge_4In_6$ with an ordered $Ho_{11}Ge_{10}$-type structure [1, 2], RE_3GeIn with an ordered Gd_3Ga_2-type [3, 4], RE_2Ge_2In with an ordered U_3Si_2-type [5 – 9], $RE_4Ni_2InGe_4$ with an ordered Mg_5Si_6-type [10], and $Yb_3AuGe_2In_3$ with an ordered ZrNiAl-type structure [11].

Besides these ordered versions of binaries, also some individual structure types of ternary and quaternary indium germanides exist. SrInGe and EuInGe [12] are ternary Zintl phases with an anionic network derived from the $ThSi_2$ type. $AE_2LiInGe_2$ (*AE* = Ca, Sr) [13] and $SrCa_2In_2Ge$ [14] contain chain-like polyanions which are separated and charge balanced by the alkali and alkaline earth metal cations. A more complex three-dimensional $[Co_4InGe_{12}]$ network with corner-sharing $CoGe_5$ square pyramids occurs for the series $RE_7Co_4InGe_{12}$ (*RE* = Dy, Ho, Yb) [15]. $Yb_7Co_4InGe_{12}$ exhibits mixed ytterbium valency.

Recently we reported on the quaternary compounds $Ce_7Ni_{5\pm x}Ge_{3\pm x}In_6$ and $Pr_7Ni_{5\pm x}Ge_{3\pm x}In_6$ [16]. The latter crystallize with a new structure type which derives from the AlB_2 type by substitution of the aluminum and boron sites by $RE(Ni/Ge)_{12}$ and $NiIn_6RE_3$ building groups. During our phase-analytical studies of quaternary *RE*–Ni–Ge–In systems we obtained the isotypic compounds $RE_7Ni_{5-x}Ge_{3+x}In_6$ (*RE* = La, Nd, Sm) which are reported herein.

Experimental Section

Synthesis

Starting materials for the synthesis of the $RE_7Ni_{5-x}Ge_{3+x}In_6$ samples were pieces of the rare earth elements (smart elements or Kelpin, > 99.9 %), nickel wire (Johnson Matthey, ∅ 1 mm), germanium lumps (Wacker), and indium tear drops (Chempur), all with stated purities better than 99.9 %. Pieces of the rare earth metals were first arc-melted [17] to small buttons under an argon pressure of *ca.* 700 mbar. The argon was purified with titanium sponge (900 K), silica gel, and molecular sieves. The four elements were then weighed in the ideal 7 : 5 : 3 : 6 ratio and arc-melted. To ensure homogeneity of the samples, the buttons were turned over and remelted twice. In all cases the total weight loss was smaller than 0.5 %. The $RE_7Ni_{5-x}Ge_{3+x}In_6$ samples were obtained as polycrystalline powders after this heat treatment. For crystal growth, parts of these samples were placed in tantalum crucibles which were sealed into evacuated silica ampoules. The samples were then heated to 1280 K within 5 h and kept at that temperature for another 5 h. The temperature was then decreased at a rate of 5 K h^{-1} to 1000 K, and to 700 K at a rate of 15 K h^{-1}. Finally the samples were cooled to r.t. by switching off the furnace. These heat treatments resulted in brittle, air-stable samples with small single crystals which exhibited metallic luster.

Table 1. Crystal data and structure refinement for $RE_7Ni_{5-x}Ge_{3+x}In_6$ (RE = La, Nd, Sm), space group $P6/m$, Z = 1.

Refined composition	$La_7Ni_{4.46}Ge_{3.54}In_6$	$Nd_7Ni_{4.91}Ge_{3.09}In_6$	$Sm_7Ni_{4.31}Ge_{3.69}In_6$
Formula weight, g mol^{-1}	2180.11	2211.17	2262.27
Unit cell dimensions (Guinier data)			
a, pm	1147.05(9)	1134.5(7)	1133.5(2)
c, pm	426.82(4)	407.1(7)	404.3(1)
Cell volume, nm^3	0.4863	0.4538	0.4499
Calculated density, g cm^{-3}	7.44	8.09	8.35
$F(000)$, e	931	950	967
Crystal size, μm^3	10 × 10 × 30	15 × 15 × 20	10 × 15 × 35
Transm. ratio (max / min)	0.645 / 0.263	0.287 / 0.233	0.341 / 0.206
Absorption coefficient, mm^{-1}	31.5	37.0	40.3
Detector distance, mm	80	–	–
Exposure time, min	3	–	–
ω range; increment, deg	0 – 180, 1.0	–	–
Integr. param. A, B, EMS	12.6, 1.8, 0.018	–	–
θ range for data collection, deg	2.0 – 30.0	2.0 – 28.5	2.0 – 30.0
Range in hkl	±16, ±16, ±6	±15, ±15, ±5	±15, ±15, ±5
Total no. reflections	4257	4444	5230
Independent reflections / R_{int}	528 / 0.0822	441 / 0.2062	498 / 0.1897
Reflections with $I \geq 2\sigma(I)$ / R_σ	380 / 0.0645	305 / 0.0683	345 / 0.0589
Data / ref. parameters	528 / 25	441 / 25	498 / 25
$R1$ / $wR2$ for $I \geq 2\sigma(I)$	0.0311 / 0.0624	0.0327 / 0.0667	0.0312 / 0.0680
$R1$ / $wR2$ for all data	0.0508 / 0.0562	0.0359 / 0.0419	0.0528 / 0.0619
Extinction coefficient	0.0058(3)	0.00111(6)	0.00025(7)
Goodness-of-fit on F^2	0.885	1.033	1.057
Largest diff. peak / hole, e Å^{-3}	2.03 / −2.16	3.81 / −2.77	2.50 / −2.54

EDX data

The three single crystals investigated on the diffractometers were studied by EDX using a Zeiss EVO MA10 scanning electron microscope with LaB_6, NdF_3, SmF_3, Ni, Ge, and InAs as standards for the semiquantitative measurements. The results of the analyses were in agreement with the compositions refined from the single crystal X-ray data. No impurity elements were observed.

X-Ray diffraction

The polycrystalline $RE_7Ni_{5-x}Ge_{3+x}In_6$ samples were studied through Guinier patterns (image plate system Fujifilm, BAS-1800) using Cu$K_{\alpha1}$ radiation and α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. The hexagonal lattice parameters were deduced from least-squares refinements. Correct indexing of the patterns was ensured by intensity calculations [18] using the positional parameters obtained from the structure refinements.

Irregularly shaped crystal fragments of $RE_7Ni_{5-x}Ge_{3+x}In_6$ were separated from the annealed samples by mechanical fragmentation. The crystals were glued to quartz fibers using beeswax and characterized by Laue photographs (Buerger camera, white molybdenum radiation, image plate technique, Fuji-film, BAS-1800) in order to check their suitability for intensity data collections. The data sets of $Nd_7Ni_{4.91}Ge_{3.09}In_6$ and $Sm_7Ni_{4.31}Ge_{3.69}In_6$ were collected at r. t. by use of a four-circle diffractometer (CAD4) with graphite-monochromatized MoK_α radiation and a scintillation counter with pulse height discrimination. Scans were taken in the $\omega/2\theta$ mode. Empirical absorption corrections were applied on the basis of Ψ-scan data, accompanied by spherical absorption corrections. The $La_7Ni_{4.46}Ge_{3.54}In_6$ crystal was measured at r.t. by use of an IPDS II diffractometer (graphite-monochromatized MoK_α radiation; oscillation mode). A numerical absorption correction was applied to the data set. All relevant crystallographic data and details of the data collections and evaluations are listed in Table 1.

Structure refinements

The isotypy of the $RE_7Ni_{5-x}Ge_{3+x}In_6$ indides with $Ce_7Ni_{4.73}Ge_{3.27}In_6$ [16] was evident from the Guinier patterns. The three data sets showed low hexagonal Laue symmetry and no further systematic extinctions, in agreement with space group $P6/m$. The atomic positions of $Ce_7Ni_{4.73}Ge_{3.27}In_6$ [16] were taken as starting values, and the structures were refined with anisotropic displacement parameters for all atoms with SHELXL-97 (full-matrix least-squares on $F_o{}^2$) [19]. Similar to the cerium and praseodymium compound [16], the 6k sites showed mixed Ni/Ge (M) occupancy. These occupancies were refined as least-squares variables, leading to the compositions listed in Table 1. The atomic parameters and interatomic distances are listed in Tables 2 and 3.

Further details of 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-

Table 2. Atomic coordinates and anisotropic displacement parameters (pm^2) for RE_7Ni$_{5-x}$Ge$_{3+x}$In$_6$ (RE = La, Nd, Sm). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)2U_{11} + ...+2hka^*b^*U_{12}]$. $U_{23} = U_{13}$ = 0.

Atom	Wyck. site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
$La_7Ni_{4.46}Ge_{3.54}In_6$									
La1	1*a*	0	0	0	79(5)	U_{11}	117(9)	40(3)	92(4)
La2	6*j*	0.30466(7)	0.38123(7)	0	103(4)	79(3)	103(3)	39(3)	98(2)
In	6*k*	0.16972(9)	0.51796(9)	1/2	101(5)	74(5)	131(4)	32(4)	107(2)
Ni2	2*c*	1/3	2/3	0	148(9)	U_{11}	107(14)	74(5)	135(6)
M^a	6*k*	0.2397(2)	0.1571(2)	1/2	142(10)	106(9)	143(9)	79(7)	123(7)
$Nd_7Ni_{4.91}Ge_{3.09}In_6$									
Nd1	1*a*	0	0	0	69(6)	U_{11}	73(9)	35(3)	70(4)
Nd2	6*j*	0.30003(8)	0.37968(8)	0	108(4)	75(4)	80(3)	40(3)	90(2)
In	6*k*	0.16350(11)	0.51651(11)	1/2	99(5)	89(5)	98(5)	38(5)	99(2)
Ni2	2*c*	1/3	2/3	0	145(10)	U_{11}	81(15)	73(5)	124(7)
M^b	6*k*	0.2392(2)	0.1599(2)	1/2	143(11)	84(11)	103(9)	69(8)	104(7)
$Sm_7Ni_{4.31}Ge_{3.69}In_6$									
Sm1	1*a*	0	0	0	82(5)	U_{11}	72(7)	41(3)	79(4)
Sm2	6*j*	0.29795(8)	0.37921(8)	0	116(4)	82(3)	54(3)	39(3)	89(2)
In	6*k*	0.16082(11)	0.51572(11)	1/2	112(5)	97(5)	89(4)	52(4)	99(2)
Ni2	2*c*	1/3	2/3	0	136(10)	U_{11}	76(13)	68(5)	116(6)
M^c	6*k*	0.2387(2)	0.1611(2)	1/2	166(11)	114(10)	97(9)	101(8)	112(7)

[a] M = 0.59(7) Ge + 0.41(7) Ni; [b] M = 0.51(7) Ge + 0.49(7) Ni; [c] M = 0.62(7) Ge + 0.38(7) Ni.

Table 3. Interatomic distances (pm) in $La_7Ni_{4.46}Ge_{3.54}In_6$. All distances within the first coordination spheres are listed.

La1:	12 *M*	322.6(1)	In:	2 Ni2	279.0(1)
	6 La2	400.7(1)		1 *M*	282.8(2)
La2:	2 *M*	308.9(1)		2 In	311.3(2)
	1 Ni2	312.3(1)		2 La2	340.7(1)
	2 *M*	313.1(1)		2 La2	344.1(1)
	2 In	340.7(1)		2 La2	346.6(1)
	2 In	344.1(1)		1 In	370.5(2)
	2 In	346.6(1)	Ni2:	6 In	279.0(1)
	1 La2	391.1(1)		3 La2	312.3(1)
	3 La2	400.7(1)	*M*:	2 *M*	241.9(1)
				1 In	282.8(2)
				2 La2	308.9(1)
				2 La2	313.1(1)
				2 La1	322.6(1)

informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-422612 ($La_7Ni_{4.46}Ge_{3.54}In_6$), CSD-422613 ($Nd_7Ni_{4.91}Ge_{3.09}In_6$), and CSD-422614 ($Sm_7Ni_{4.31}Ge_{3.69}In_6$).

Discussion

The intermetallic compounds $RE_7Ni_{5-x}Ge_{3+x}In_6$ (RE = La, Nd, Sm) are isotypic with the recently reported phases $Ce_7Ni_{5\pm x}Ge_{3\pm x}In_6$ and $Pr_7Ni_{5\pm x}Ge_{3\pm x}In_6$ [16]. All five compounds show small homogeneity ranges due to Ni/Ge mixing on the 6*k* site. No hints for Ni/Ge ordering were evident from the single-crystal X-ray data.

A projection of the $La_7Ni_{4.46}Ge_{3.54}In_6$ structure is exemplarily given in Fig. 1. The indium and germanium atoms build up layers at z = 1/2 which leave trigonal prismatic voids for the Ni2, distorted pentagonal prismatic voids for the La2, and hexagonal prismatic voids for the La1 atoms. These three types of prisms are capped by three, five, and six atoms on the rectangular faces, leading to coordination numbers 9, 15, and 18, respectively, as frequently observed for related intermetallic phases [20].

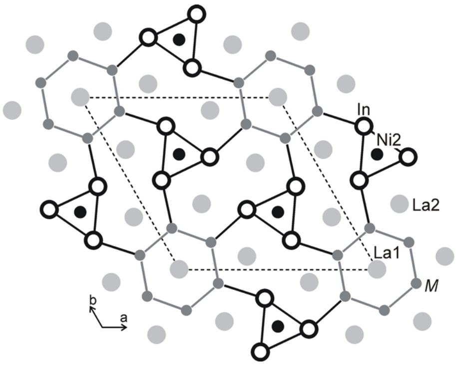

Fig. 1. Projection of the $La_7Ni_{4.46}Ge_{3.54}In_6$ structure onto the *xy* plane. Lanthanum, nickel, germanium, and indium atoms are drawn as light-grey, black filled, small medium-grey, and black open circles, respectively. All atoms lie on mirror planes at z = 0 (La1, La2, Ni2) and z = 1/2 (M, In). The hexagonal-prismatic and trigonal-prismatic coordinations of La1 and Ni2, respectively, are emphasized.

The M–M distances of 242 pm within the M_6 hexagons are slightly longer than the sum of the covalent radii of 237 pm (Ni + Ge) [21], but shorter than in *fcc* nickel (249 pm) and elemental germanium (245 pm) [22]. We can therefore assume substantial Ni–Ge bonding within the hexagons. The triangular edges of the $Ni2In_6$ prisms have In–In distances of 311 pm. These distances are even shorter than in elemental tetragonal body-centered indium. There, each indium atom has four nearest indium neighbors at 325 pm and eight further neighbors at 338 pm [22]. The planar M_6In_6 layers are condensed to a three-dimensional network *via* the Ni2 atoms within the trigonal prisms. The La1 and La2 atoms are connected to the network *via* weaker La1–*M* (323 pm) and La2–*M* (309 pm) bonds. These distances are longer than the sums of the covalent radii [21] of 284 pm (La + Ni) and 291 pm (La + Ge).

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