# Crystal structure of the Ca<sub>16</sub>Ni<sub>173.14</sub>In<sub>62.61</sub> compound

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The new ternary indide  $Ca_{16}Ni_{173.14}In_{62.61}$  was synthesized from the elements by arc-melting and its crystal structure was determined by means of X-ray single crystal diffraction. The compound crystallizes in its own structure type: space group  $P2_1/m$  (No. 11), Z = 1, mP254, a = 1.5374(3) nm, b = 1.6565(9) nm, c = 1.5911(2) nm,  $\beta = 115.434(7)^\circ$ , wR2 = 0.0715,  $6674 F^2$  values, 691 variable parameters. The compound  $Ca_{16}Ni_{173.14}In_{62.61}$  exists only in as-cast samples and decomposes during annealing at 1070 K with the formation of  $CaNi_{9.x}In_{2+x}$ . In the structure of  $Ca_{16}Ni_{173.14}In_{62.61}$  the nickel atoms build complex puckered two-dimensional Ni-slabs, which are interconnected along the [110] direction by indium atoms into a  $[Ni_{173.14}In_{62.61}]$  network, in the cavities of which the calcium atoms are situated.

Indide / Crystal structure / Single crystal

## Introduction

Ternary systems containing rare-earth metals (RE), transition *d*-metals and *p*-elements have attracted considerable interest among researchers, due to the interesting structural and physical properties of their compounds [1-4].

Ternary systems AE - d-metal – In (AE = alkaline earth metal) have not been studied systematically, and investigations have been carried out only for the synthesis of new ternary compounds of certain stoichiometric compositions. The only exceptions are the Ca–T–In (T = Cu, Ni) systems, for which the composition range 0-50 at.% Ca has been studied and the isothermal sections of the phase diagrams at 670 K constructed [5,6]. It should be highlighted that the existence of six ternary indides in each of the chemical systems shows the complex nature of the interaction of the components. In the *d*-metal rich region of the studied ternary systems, the  $CaT_{9-x}In_{2+x}$  (T = Cu, Ni) compounds that appear with YNi<sub>9</sub>In<sub>2</sub> structure type [7] exist in a small homogeneity region at 8.33 at.% Ca [8]. Further investigations of the Ni-rich region of the Ca-Ni-In system indicated the existence of a new ternary compound, with a yet unknown structure. Herein we report on the synthesis and crystal structure of the  $Ca_{16}Ni_{173.1}In_{62.6}$  compound. A brief account of this work has been presented at a conference [9].

#### Experimental

#### **Synthesis**

The starting materials for the synthesis of the alloy were: Ca ingots (>99.8 %), Ni electrolytic pieces (99.9 %) and In tear drops (>99.9 %). The sample was synthesized by arc melting of compact metals in the ratio 1:8:3 (Ca:Ni:In) in an atmosphere of purified argon (Ti sponge was used as an oxygen absorber). Considering the high volatility of calcium in comparison to nickel and indium, the starting amount contained an excess of 2 mass % calcium. The sample was arc-melted three times in order to achieve homogeneity. The weight loss after the arc-melting procedure was smaller than 1 mass %.

Rather small single crystals, in the form of thin plates, suitable for structural investigations, were isolated from the as-cast alloy. Further attempts to synthesize high-quality single crystals using a special heat treatment in an induction furnace (Hüttinger Elektronik, Freiburg, Typ TIG 2.5/300 equipped with a Sensor Therm Metis MS06 pyrometer for temperature monitoring) were made. Small pieces of the sample were heated in a welded Ta-ampoule to 1320 K and held at this temperature for 30 min. Then the temperature was slowly reduced to 1070 K, with further annealing at this temperature for 2 h. After that the sample was cooled to room temperature by switching off the oven. The sample easily separated from the crucible after the synthesis and no reaction with the Ta-ampoule could be detected. Single crystals were obtained, but in the form of deformed parallelepipeds. Further investigations showed that they crystallized in tetragonal symmetry and belong to the YNi<sub>9</sub>In<sub>2</sub> structure type [7]. A detailed description of these investigations will be the subject of a forthcoming publication.

## X-ray investigations

Phase analyses of the samples were carried out by powder X-ray diffraction (powder diffractometer Stoe Stadi P, Cu  $K\alpha$  radiation). Powder patterns were obtained for the as-cast sample and after annealing at 1070 K. For the annealed sample, the reflections of strong intensity correspond to the main tetragonal phase and were indexed in the YNi<sub>9</sub>In<sub>2</sub> structure type [7]. Some additional reflections of low intensity were assigned to the CaNiIn<sub>2</sub> (MgCuAl<sub>2</sub> structure type) and Ca<sub>2</sub>Ni<sub>8.5</sub>In<sub>8.5</sub> (Th<sub>2</sub>Zn<sub>17</sub> structure type ) impurity phases. The tetragonal lattice parameters (a = 0.8326(4) nm, c = 0.4997(3) nm) obtained from a least-squares refinement are in good agreement with earlier reported values [5]. The powder pattern of the as-cast sample is different and very complex.

Single crystals in the form of small thin plates were isolated by mechanical fragmentation from the as-cast sample after the arc-melting procedure. Intensity data for one of them were collected at room temperature using an Oxford Diffraction Xcalibur 3 diffractometer with graphite monochromatized Mo Ka  $(\lambda = 71.073 \text{ pm})$  radiation. The raw data were corrected for background, polarization and Lorenz factor. A numerical absorption correction was applied  $Ca_{16}Ni_{173,14}In_{62,61}$  [10,11]. data of to the Crystallographic data and relevant data for the data collection and structure determination are listed in Table 1

After the data collection the single crystal was investigated by energy-dispersive X-ray (EDX) analysis with a JEOL SEM 5900LV scanning electron microscope equipped with an Oxford Instruments INCA energy-dispersive X-ray microanalysis system. No impurity elements heavier than sodium were observed. The composition determined by EDX (7(1) at.% Ca : 70(2) at.% Ni : 23(2) at.% In) is in good agreement with the refined composition, *i.e.* 6.6 at.% Ca : 68.4 at.% Ni : 25.0 at.% In.

Table 1 Crystal data and details of the structure refinement for Ca<sub>16</sub>Ni<sub>173.14</sub>In<sub>62.6</sub>.

Chemical formula		$Ca_{16}Ni_{173.14(3)}In_{62.61(3)}$		
Molar mass		1799.52		
Space group, Z		$P2_1/m$ (No.11), 1		
Pearson symbol		mP254		
Cell parameters	<i>a</i> (nm)	1.5374(3)		
	<i>b</i> (nm)	1.6565(9)		
	<i>c</i> (nm)	1.5911(2)		
	β (°)	115.434(7)		
	$V(nm^3)$	3.659(9)		
$d_{\rm calc} ({\rm g/cm}^3)$		8.165		
Radiation, $\lambda$ (nm)		Μο Κα, 0.071073		
Absorption coefficient	(mm <sup>-1</sup> )	31.817		
F(000)		8236		
Index ranges		$-18 \le h \le 18$		
		$-19 \le k \le 19$		
		$-18 \le l \le 18$		
$\theta$ range for data collect	tion (°)	2.84-25.00		
Total no. reflections / Independent reflections		30096/6674		
Observed reflections [	<i>I</i> >2σ( <i>I</i> )]	2605		
Parameters / restraints		691/0		
Goodness of fit S		0.757		
R1/wR2 [ <i>I</i> >2σ( <i>I</i> )]		0.0497/0.0843		
R1/wR2 all data		0.1462/0.0715		
Largest diff. peak and	hole (e/Å <sup>3</sup> )	3.245 and -2.495		

## **Results and discussion**

#### Structure refinement

The diffractometer data showed a primitive monoclinic lattice, and the observed extinction conditions were in agreement with the space group  $P2_1/m$ . The starting atomic parameters were determined by an interpretation of direct methods with SHELXS-97 [12] and the structure was refined with anisotropic displacement parameters for all of the atoms with SHELXL-97 [13] (full-matrix least-squares on  $F_o^2$ ). As a check for the correct composition and site assignment, the occupancy parameters were refined in a separate series of least-squares cycles. Refinement of the occupancy parameters revealed mixed Ni/In (shown as M1...M7)

occupancy for three 4f and four 2e sites, as well as two defective sites: 4f Ni11 and 4f In11. These occupancy parameters were refined in the final cycles and are in good agreement with the EDX data. All the other sites were fully occupied within two standard uncertainties. The final difference Fourier synthesis revealed no significant residual peaks (Table 1). The refined atomic positions and equivalent isotropic displacement parameters are given in Table 2.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (e-mail: crysdata@fiz-karlsruhe.de; web: http://www.fiz-karlsruhe.de/request\_for\_deposited\_data.html) on quoting the depositing number CSD-426834.

**Table 2** Atomic coordinates, isotropic displacement parameters (×10<sup>4</sup>) and coordination numbers of the atoms in the structure of Ca<sub>16</sub>Ni<sub>173.14</sub>In<sub>62.61</sub>.  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

					2	
Atom	Wyckoff site	x	У	Z	$U_{\rm eq},{\rm nm}^2$	CN
Ni1	4f	0.0025(3)	0.1066(2)	0.8105(2)	2.17(1)	12
Ni2	4f	0.0289(3)	0.5062(2)	0.7205(2)	1.98(9)	12
Ni3	4f	0.0333(3)	0.0313(2)	0.1551(3)	2.02(9)	12
Ni4	4f	0.0409(3)	0.6240(2)	0.3614(3)	2.26(1)	12
Ni5	4f	0.0603(3)	0.1760(2)	0.1352(3)	2.16(9)	12
Ni6	4f	0.0974(3)	0.0085(2)	0.4336(2)	2.09(9)	12
Ni7	4f	0.1156(3)	0.6097(2)	0.5370(3)	2.89(1)	12
Ni8	4f	0.1330(3)	0.1191(2)	0.7509(3)	2.34(1)	12
Ni9	4f	0.1372(3)	0.5320(2)	0.3056(3)	2.13(9)	12
Ni10	4f	0.1500(3)	0.1766(2)	0.9074(3)	2.50(1)	12
Ni11 <sup>a</sup>	4f	0.1530(3)	0.6776(2)	0.3024(3)	1.76(2)	12
Ni12	4f	0.1791(3)	0.1309(2)	0.5024(3)	2.09(9)	12
Ni13	4f	0.2189(3)	0.6037(2)	0.4580(3)	2.33(1)	12
Ni14	4f	0.2303(3)	0.6791(2)	0.0842(2)	1.98(9)	12
Ni15	4f	0.2405(3)	0.5319(2)	0.0654(3)	2.00(9)	12
Ni16	4f	0.2443(3)	0.0045(2)	0.5796(2)	1.93(9)	12
Ni17	4f	0.2595(3)	0.0391(2)	0.4341(3)	1.97(9)	12
Ni18	4f	0.2669(3)	0.1067(2)	0.0374(3)	2.19(1)	12
Ni19	4f	0.2790(3)	0.1776(2)	0.4160(2)	2.19(1)	12
Ni20	4f	0.2910(3)	0.1175(2)	0.8811(3)	2.34(1)	12
Ni21	4f	0.3418(3)	0.6033(2)	0.2171(2)	1.93(9)	12
Ni22	4f	0.3837(3)	0.6229(2)	0.0865(2)	2.02(9)	12
Ni23	4f	0.3888(3)	0.1782(2)	0.1693(3)	2.20(9)	12
Ni24	4f	0.4280(3)	0.1174(2)	0.0377(2)	2.30(1)	12
Ni25	4f	0.4711(3)	0.5279(2)	0.3485(3)	2.00(9)	12
Ni26	4f	0.4932(3)	0.1185(2)	0.3240(3)	2.10(9)	12
Ni27	4f	0.5138(3)	0.6219(2)	0.2414(3)	2.18(1)	12
Ni28	4f	0.5432(3)	0.1757(2)	0.6445(2)	2.02(9)	12
Ni29	4f	0.5544(3)	0.1238(2)	0.2011(3)	232(1)	12
Ni30	4f	0.5981(3)	0.0014(2)	0.2942(3)	2.31(1)	12
Ni31	4f	0.6149(3)	0.0429(2)	0.4518(2)	1.99(9)	12
Ni32	$\dot{4f}$	0.6587(3)	0.0084(2)	0.0209(3)	2.24(1)	12
Ni33	4f	0.7707(3)	0.1266(2)	0.0618(2)	2.02(9)	12
Ni34	$\dot{4f}$	0.9125(3)	0.1025(2)	0.0248(2)	2.12(9)	12
Ni35	4f	0.9291(3)	0.1266(2)	0.1860(2)	2.20(1)	12

**Table 2** Atomic coordinates, isotropic displacement parameters (×10<sup>4</sup>) and coordination numbers of the atoms in the structure of Ca<sub>16</sub>Ni<sub>173.14</sub>In<sub>62.61</sub>.  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. (*continued*)

Atom	Wyckoff site	x	У	Z	$U_{\rm eq},{\rm nm}^2$	CN
Ni36	2 <i>e</i>	0.0133(4)	1/4	0.2455(4)	2.18(1)	12
Ni37	2 <i>e</i>	0.1326(4)	1⁄4	0.4042(3)	2.25(1)	12
Ni38	2 <i>e</i>	0.1846(4)	1⁄4	0.2684(3)	2.01(1)	12
Ni39	2 <i>e</i>	0.2220(4)	1⁄4	0.8009(4)	2.35(1)	12
Ni40	2 <i>e</i>	0.2729(4)	1⁄4	0.5572(3)	1.90(1)	12
Ni41	2 <i>e</i>	0.4183(4)	1⁄4	0.5203(3)	2.10(1)	12
Ni42	2 <i>e</i>	0.4236(4)	1⁄4	0.6829(4)	2.40(1)	12
Ni43	2 <i>e</i>	0.4968(4)	1⁄4	0.1109(4)	1.86(1)	12
Ni44	2 <i>e</i>	0.5346(4)	1⁄4	0.2812(4)	1.79(1)	12
Ni45	2 <i>e</i>	0.6636(4)	1⁄4	0.2291(4)	2.51(1)	12
Ni46	2 <i>e</i>	0.6841(4)	1⁄4	0.9920(3)	2.20(1)	12
Ni47	2 <i>e</i>	0.8364(4)	1⁄4	0.3705(4)	2.94(2)	12
In1	4f	0.0197(2)	0.6500(1)	0.6275(1)	2.57(6)	15
In2	4f	0.0768(2)	0.0488(1)	0.5835(1)	2.12(5)	15
In3	4f	0.0804(2)	0.0729(1)	0.0118(2)	2.67(6)	16
In4	4f	0.1489(2)	0.5865(1)	0.1582(1)	2.00(5)	14
In5	4f	0.2869(2)	0.1414(1)	0.7043(1)	2.31(5)	16
In6	4f	0.3235(2)	0.5837(1)	0.3701(1)	2.03(5)	14
In7	4f	0.4482(2)	0.0897(1)	0.4676(1)	2.32(5)	16
In8	4f	0.5497(2)	0.5391(1)	0.1071(2)	2.68(6)	16
In9	4f	0.6073(2)	0.1508(1)	0.0704(1)	2.08(5)	14
In10	4f	0.6898(2)	0.1488(1)	0.3687(1)	2.26(5)	14
In11 <sup>a</sup>	4f	0.3688(3)	0.1152(2)	0.5857(3)	2.41(2)	14
In12	2 <i>e</i>	0.0257(2)	1⁄4	0.7523(2)	2.24(8)	14
In13	2 <i>e</i>	0.2007(2)	1⁄4	0.0992(2)	2.61(8)	16
In14	2 <i>e</i>	0.3820(2)	1⁄4	0.3275(2)	2.18(7)	15
In15	2 <i>e</i>	0.8126(2)	1⁄4	0.1936(2)	2.54(8)	15
In16	2 <i>e</i>	0.8526(2)	1⁄4	0.5433(2)	2.25(7)	14
Ca1	4f	0.2618(5)	0.0829(3)	0.2395(4)	2.35(2)	20
Ca2	4f	0.7662(5)	0.0535(4)	0.2406(4)	2.85(2)	20
Ca3	2 <i>e</i>	0.0807(6)	1⁄4	0.5782(5)	2.00(2)	20
Ca4	2 <i>e</i>	0.4497(6)	1⁄4	0.8854(6)	2.50(2)	20
Ca5	2 <i>e</i>	0.6092(6)	1⁄4	0.5020(6)	2.50(2)	21
Ca6	2 <i>e</i>	0.9700(6)	1⁄4	0.9280(6)	2.40(2)	20
$M1^{\rm b}$	4f	0.1126(2)	0.1179(2)	0.3078(2)	2.63(2)	14
$M2^{\rm b}$	4f	0.1559(2)	0.0159(2)	0.8887(2)	2.41(1)	14
M3 <sup>b</sup>	4f	0.4123(2)	0.0224(1)	0.1714(2)	2.24(1)	14
<i>M</i> 4 <sup>b</sup>	2 <i>e</i>	0.8885(3)	1⁄4	0.0668(3)	1.43(2)	14
$M5^{\rm b}$	2 <i>e</i>	0.3195(2)	1⁄4	0.9896(2)	1.62(1)	14
$M6^{\rm b}_{\rm c}$	2 <i>e</i>	0.7244(2)	1⁄4	0.7443(2)	2.08(1)	14
$M7^{\mathrm{b}}$	2 <i>e</i>	0.5986(4)	1⁄4	0.8108(3)	3.50(2)	14

<sup>a</sup> Ni11 - s.o.f. = 0.85(14), In11 - s.o.f. = 0.587(8);

<sup>b</sup> M1 - Ni0.72(2)/In0.28(2), M2 - Ni0.42(2)/In0.58(2), M3 - Ni0.26(2)/In0.74(2), M4 - Ni0.81(3)/In0.19(3), M5 - Ni0.28(3)/In0.72(3), M6 - Ni0.27(3)/In0.73(3), M7 - Ni0.71(3)/In0.29(3).

## Crystal chemistry

The nickel-rich indide Ca<sub>16</sub>Ni<sub>173.14</sub>In<sub>62.61</sub> crystallizes with a new monoclinic structure type, space group  $P2_1/m$ , Pearson code mP254. The structure contains seventy six crystallographically independent sites with the Wyckoff sequence  $e^{25}f^{51}$ . A projection of the unit cell of Ca<sub>16</sub>Ni<sub>173.14</sub>Ni<sub>62.61</sub> onto the XZ plane and typical coordination polyhedra are presented in Fig. 1. For clarity only typical coordination polyhedra for the different kinds of atom are shown.

The coordination environment of the calcium atoms can be described by two types of polyhedron having 20 and 21 vertices. The first of them can be represented as a hybrid of two hexagonal antiprisms



**Fig. 1** Projection of the structure of  $Ca_{16}Ni_{173.14}In_{62.61}$  onto the *XZ* plane and typical coordination polyhedra. Calcium, nickel and indium atoms are drawn as medium grey, black filled, and open circles, respectively. The mixed-occupied sites are emphasized by segments. The site symmetries are indicated in parentheses.

with capped basal faces. These polyhedra are similar to the coordination polyhedra of the europium atoms in the EuAu<sub>4</sub>In<sub>8</sub> compound [14], but are significantly deformed, as a result of the lower symmetry of the reported structure. The polyhedra of the Ca5 atoms are very complex and possess 21 vertices; in a first approximation they can be described as strongly deformed heptagonal antiprisms with 3 and 4 additional atoms above opposite basal faces.

Typical coordination polyhedra of the nickel atoms are deformed (to different degrees) icosahedra (CN 12).

The coordination environment of the indium atoms can be described by three different types of polyhedron (14-, 15- and 16-vertex polyhedra), which can be interpreted as more or less deformed hexagonal antiprisms with 2, 3 and 4 additional atoms capping opposite bases.

The coordination polyhedra of the M sites with Ni/In statistical occupancy can be considered as deformed hexagonal Ni-antiprisms with their bases capped by In and Ca atoms (CN 14).

The analysis of the coordination environment of the atoms in the compound Ca<sub>16</sub>Ni<sub>173.14</sub>In<sub>62.61</sub>, as well as in other compounds of the Ca-Ni-In ternary system in the region with high nickel content (> 50 at.%), namely CaNi<sub>9-x</sub>In<sub>2+x</sub> [8] and Ca<sub>3</sub>Ni<sub>8</sub>In<sub>4</sub> [15], indicated certain regularities in the first coordination sphere. With increasing calcium content and decreasing nickel content, within the series of compounds  $Ca_{16}Ni_{173.14}In_{62.61} \ - \ CaNi_{9\text{-}x}In_{2\text{+}x} \ - \ Ca_3Ni_8In_4, \ a$ decrease of the coordination number (CN) of the large atoms (Ca, In, M) is observed, while the coordination environment of the smallest atoms (Ni) remains unchanged (deformed icosahedra). A similar situation has been observed for ternary indides in the 3d-metal rich region of rare-earth – 3d-metal – In ternary systems [1].

"building The main blocks" of the Ca<sub>16</sub>Ni<sub>173,14</sub>In<sub>62,61</sub> structure are two-dimensional puckered Ni-slabs (Fig. 2a,b), in which interconnected clusters, that are identical in shape and composition, can be identified (Fig. 2d). The coordination polyhedra of the calcium atoms share common edges or faces and form infinite two-dimensional slabs (Fig. 2c), which are sandwiched between the slabs of nickel clusters. From a geometrical point of view, the structure of the Ca<sub>16</sub>Ni<sub>173,14</sub>In<sub>62,61</sub> compound can be described as a stacking of slabs formed by calcium polyhedra and Ni-cluster slabs (Fig. 2e).

Table 3 shows the most characteristic values of the interatomic distances in the structure of the  $Ca_{16}Ni_{173.14}In_{62.61}$  compound. Analysis of the values of the interatomic distances indicates very strong interaction between the atoms in the structure. For almost all pairs of atoms, these distances are shorter than the sum of their atomic radii [16]. Significant bond length shortening is observed between the nickel atoms within the Ni-clusters (d(Ni-Ni) = 0.233-0.284 nm), as well as for the Ca-Ni, Ca-In and Ca-*M* distances. The values indicate that the stability of the whole structure mainly relies on these interactions.

The existence of *d*-metal clustering is a characteristic feature of the ternary indides that form in the ternary systems AE - 3d-metal – In in the transition metal rich region. Examples of such clustering, as it occurs in the compounds  $SrCu_7In_6$  [17],  $CaNi_{9.x}In_{2+x}$  [8],  $Ca_3Ni_8In_4$  [15] and  $Ca_{16}Ni_{173.14}In_{62.61}$ , are presented in Fig. 3.

Ni1 – Ni10 0.2421	Ni2 – Ni6 0.2386	Ni3 – Ni34 0.2415
– In4 0.2602	– M2 0.2574	– In4 0.2626
Ni10 – Ni18 0.2379	Ni12 – Ni40 0.2378	Ni17 – Ni19 0.2347
– In12 0.2678	– In2 0.2781	– In11 0.2598
Ni27 – Ni30 0.2371	Ni33 – Ni35 0.2388	Ni40 – Ni42 0.2321
– In11 0.2564	– In9 0.2604	– In11 0.2606
In1 – Ni7 0.2553	In6 – Ni13 0.2565	In15 – Ni45 0.2584
– M1 0.2696	– M6 0.3209	– M4 0.2730
Ca1 – M1 0.2988	Ca2 – M2 0.3017	Ca5 – Ni41 0.3071
– Ni23 0.3071	– Ni2 0.3041	– In6 0.3315

**Table 3** Selected interatomic distances (nm) in the structure of  $Ca_{16}Ni_{173.14}In_{62.61}$ . The standard deviations are equal or smaller than 0.0009 nm.



Fig. 2 Stacking of slabs formed by calcium polyhedra and nickel clusters, respectively, in the structure of  $Ca_{16}Ni_{173.14}In_{62.61}$ .



Fig. 3 Cutouts of the nickel (copper) cluster units from structures with high 3*d*-metal content in AE - 3d-metal – In systems.

Crystals of similar shape (thin plates) were also found in an as-cast SrNi<sub>9</sub>In<sub>2</sub> sample. EDX analysis indicated the following composition:  $Sr_{0.06(1)}Ni_{0.67(4)}In_{0.27(3)}$ . The poor quality of the crystals did not allow performing a full structural but the refined investigation, unit cell parameters, a = 1.5429(3) nm, b = 1.6599(3) nm, c = 1.5985(3) nm,  $\beta = 15.56(3)^{\circ}$  (Stoe IPDS 2T single crystal diffractometer, Mo Ka radiation), indicate possible isotypism of this compound with Ca<sub>16</sub>Ni<sub>173.14</sub>In<sub>62.61</sub>. No single crystals were found in the sample annealed at 670 K. The powder pattern of the as-cast sample (powder diffractometer Stoe Stadi P, Cu K $\alpha$  radiation) was similar to that of the calcium ascast sample and also very complex.

# References

 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. Bunzli (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier, Amsterdam, 2005, Vol. 34, pp. 1-133.

- [2] P.S. Salamakha, Crystal Structures and Crystal Chemistry of Ternary Rare-Earth Germanides, In: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Elsevier, Amsterdam, 1999, Vol. 27, pp. 225-338.
- R.V. Skolozdra, Stannides of Rare-Earth and Transition Metals, In: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Elsevier, Amsterdam, 1997, Vol. 24, pp. 399-517.
- [4] R. Pöttgen, U.Ch. Rodewald, Rare Earth Transition Metal Plumbides, In: K.A. Gschneidner Jr., V.K. Pecharsky, J.-C. Bunzli (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Elsevier, Amsterdam, 2008, Vol. 38, pp. 55-104.

- [5] I. Muts, L. Sysa, Ya. Galadzhun, V. Zaremba, Ya. Kalychak, Visn. Lviv. Univ., Ser. Khim. 52 (2011) 27-32.
- [6] L.V. Sysa, Ya.M. Kalychak, *Neorg. Mater.* 30(6) (1994) 779-782.
- [7] Ya.M. Kalychak, L.G. Akselrud, V.I. Zaremba, V.M. Baranyak, *Dopov. Akad. Nauk Ukr. RSR*, *Ser. B* (8) (1984) 35-37.
- [8] I.R. Muts, V.V. Baran, V. Hlukhyy, T.F. Fässler, R. Pöttgen, V.I. Zaremba, *Coll. Abstr. 17 Int. Conf. Solid Compd. Trans. Elements*, Annecy, France, 2010, p. 70.
- [9] A. Kharkhalis, V. Baran, I. Muts, V. Hlukhyy, T.F. Fässler, V. Zaremba, *Coll. Abstr. XII Int. Conf. Cryst. Chem. Intermet. Compd.*, Lviv, Ukraine, 2013, p. 129.
- [10] X-RED32, Data Reduction Program, Version 1.48 STOE & Cie GmbH, Darmstadt, Germany, 2008.
- [11] X-SHAPE, Crystal Optimization for Numerical Absorption Correction, Version 2.11 STOE & Cie GmbH, Darmstadt, Germany, 2008.

- [12] G.M. Sheldrick, SHELXS-97, SHELXL-97 Programs for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [13] G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112.
- [14] L.V. Sysa, Ya.M. Kalychak, I.M. Stets, Ya.V. Galadzhun, *Kristallografiya* 39(4) (1994) 821-824.
- [15] V.I. Zaremba, I.R. Muts, Ya.M. Kalychak, R.-D. Hoffmann, R. Pöttgen, J. Solid State Chem. 160 (2001) 415-420.
- [16] J. Emsley, *The Elements*, Oxford University Press, Oxford, U.K., 1999.
- [17] V.I. Zaremba, I.R. Muts, R.-D. Hoffmann, R. Pöttgen, Z. Anorg. Allg. Chem. 629(12-13) (2003) 2330-2336.