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Crystal structure of the new ternary thorium indide $\text{Th}_3\text{Ni}_4\text{In}_{13}$

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Abstract

The title compound was prepared by arc melting the elemental components and subsequent annealing at 870 K. The crystal structure of $\text{Th}_3\text{Ni}_4\text{In}_{13}$ was refined from single crystal X-ray data: $Pm\bar{3}n$, $a=9.574(1)$, $V=877.6 \text{ \AA}^3$, $Z=2$, $R=0.0258$ for 242 F^2 values and 13 parameters. It crystallizes with a $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ -type structure. The crystal chemistry and relationships of this phase are briefly discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Actinide compounds; Transition metal compounds; Crystal structure; X-ray diffraction

1. Introduction

No systematical investigations of the interaction between the components of the Th–3d-metal–In ternary systems have so far been carried out. Only the existence of the ThNiIn (structure type Fe_2P , space group $P\bar{6}2m$) [1] and ThCu_5In (structure type CeCu_5Au , space group $Pnma$) [2] ternary compounds has been known up to now. The present paper contains the results of the crystal structure investigation of a new ternary thorium indide, $\text{Th}_3\text{Ni}_4\text{In}_{13}$, of which the existence is here reported for the first time.

2. Experimental

The samples were first obtained by arc melting the components thorium (99.9 wt.%), nickel (99.9 wt.%, Johnson Matthey) and indium tear drops (99.9 wt.%, Johnson Matthey) in the corresponding mass ratios under a purified argon atmosphere (titanium sponge was used as a getter). All samples were remelted several times in order to obtain homogeneous alloys. The weight losses after the melting were less than 1% of the total mass. Then, the alloys were homogenized by annealing the samples at 870 K in evacuated quartz ampoules for 1 month. All samples were single phase and stable in air.

The analysis of the reflections of the X-ray diffraction pattern of the ThNiIn_4 alloy (STOE powder diffractometer, $\text{CuK}\alpha$ radiation) indicated that the structure of the unknown compound is of cubic symmetry. Besides the presence of reflections of the unknown compound, reflections belonging to the ThIn_3 (structure type AuCu_3) were also detected.

The subsequent investigation of the crystal structure of this compound was carried out with a single crystal method. After annealing we obtained no single crystals suitable for X-ray investigation. Therefore synthesis in a special temperature regime was required. An alloy with a composition of $\text{Th}_{0.17}\text{Ni}_{0.17}\text{In}_{0.66}$, weighing 2 g was placed into a tantalum container and then closed in an evacuated quartz ampoule. It was heated in a muffle oven up to 1170 K and kept at this temperature for 6 h. The temperature was controlled by a CrNi–Ni thermocouple with an Eurotherm 818 thermoregulator. After annealing, the ampoule with the alloy was cooled at a rate of 10 K per hour down to room temperature. As a result, we obtained single crystals that were stable in air, and were suitable for the X-ray investigation. They had metallic luster and had the shape of deformed cubes. Quantitative and qualitative EDAX analyses of the single crystals, were carried out by means of a Philips 515-PV9800 scanning electron microscope. These analyses gave the following results (in atomic percentage): Th — 13.7, Ni — 19.3, In — 67.0, which does not differ greatly from the initial composition of the mixture of the elemental components. No impurities have been found.

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Single crystals, selected from the $\text{Th}_{0.17}\text{Ni}_{0.17}\text{In}_{0.66}$ alloy, were then tested and one of them turned out to be suitable for X-ray investigation. It was examined with Laue and rotation methods (camera RKV-86, MoK radiation). The results have indicated cubic symmetry of the crystal (Laue class $m\bar{3}m$) and the lattice parameter of the alloy was determined. The subsequent investigation of this single crystal was made by means of a KUMA DIFFRACTION KM-4 four-circle automatic diffractometer equipped with a CCD camera using graphite — monochromatized MoK α radiation. The intensities of the reflections were corrected considering the Lorentz and polarization factors as well as the absorptions of the crystal.

3. Results and discussion

The crystal structure of $\text{Th}_3\text{Ni}_4\text{In}_{13}$ was solved by direct methods and refined by a full matrix squares method using the SHELXL-97 program [3].

The crystal data, data collection and refinement information are listed in Table 1. The final atomic positional parameters with thermal displacement coefficients and interatomic distances are given in Tables 2 and 3, respectively. Final differences in the Fourier syntheses have not revealed any significant residual peaks.

One can see from Table 2, that all the crystallographic positions in the structure are completely occupied by only a single type of atom. The composition of the compound can be described with the chemical formula of $\text{Th}_3\text{Ni}_4\text{In}_{13}$

Table 1
Crystal data and structure refinement for $\text{Th}_3\text{Ni}_4\text{In}_{13}$

Empirical formula	$\text{Th}_3\text{Ni}_4\text{In}_{13}$
Formula weight	2423.58
Temperature	293(2) K
Wavelength	MoK α , 0.71073 Å
Crystal system	Cubic
Space group	$Pm\bar{3}n$ (No. 223)
Unit cell dimensions	$a=9.574(1)$ Å
Volume	877.6 Å ³
Unit per cell	$Z=2$
Density (calculated)	9.172 g/cm ³
Absorption coefficient	46.14 mm ⁻¹
$F(000)$	2038.0
2θ range for data collection	$2-59^\circ$
Index range	$-11 \leq h \leq 12, -13 \leq k \leq 13, -12 \leq l \leq 13$
Reflections collected	8767
Independent reflections	242 ($R_{\text{int}}=0.0727$)
Reflections with $I > 2\sigma(I)$	238 ($R_{\text{sigma}}=0.0239$)
Data/restraints/parameters	242/0/13
Goodness-of-fit on F^2	1.294
Final R indices [$I > 2\sigma(I)$]	$R1=0.0258$
R indices (all data)	$R1=0.0262, \omega R2=0.0561$
Extinction coefficient	0.00314
Largest diff. peak and hole	1.62 and -3.17 e Å ⁻³

Table 2

Atomic coordinates and thermal displacement parameters (Å² × 10⁴) for $\text{Th}_3\text{Ni}_4\text{In}_{13}$

Atom	Wyckoff site	x/a	y/b	z/c	U_{eq}^a
Th	6c	1/4	0	1/2	119(3)
In ¹	2a	0	0	0	339(8)
In ²	24k	0	0.1554(1)	0.3030(1)	150(3)
Ni	8e	1/4	1/4	1/4	124(5)

^a U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

and there are 40 atoms per unit cell. These results correlate well with the results of the EDAX analysis.

The $\text{Th}_3\text{Ni}_4\text{In}_{13}$ compound is the first representative of the $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ structure type [4] among ternary indides. The projection of the unit cell on the XY plane and coordination polyhedra of the atoms are shown in Fig. 1.

The polyhedra for the atoms having the largest size (Th) can be considered as deformed cubooctahedra with four additional Ni atoms located on the opposite side faces (CN=16). For the Ni atoms, trigonal prisms with three additional atoms located on the opposite side faces (CN=9) are typical. The polyhedra for the indium atoms are icosahedra (CN=12 for In¹) and 14-vertices (CN=14 for In²). The same polyhedra are typical for the atoms in the structure of the $\text{Gd}_6\text{Co}_8\text{Sn}_{26}$ compound [5].

The analysis of the interatomic distances in the $\text{Th}_3\text{Ni}_4\text{In}_{13}$ structure indicates the absence of a significant reduction (δ) compared with the sum of the atomic radii of the elements. The most characteristic reductions $\delta=10.4\%$ and 10.0% were found for the atoms: In²–In² (2.975 Å) and In²–Ni (2.609 Å), respectively.

$\text{Th}_3\text{Ni}_4\text{In}_{13}$ is closely related to the rare earth indides RPTIn_3 (R=La, Ce, Pr, Nd, Sm) [6] previously investigated. They crystallize with the LaRuSn_3 type structure [7]. The difference between these two types of structures lies in different occupations of the $2a(000)$ site. In the $\text{Th}_3\text{Ni}_4\text{In}_{13}$ structure ($\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ -type), this site is occupied by the atoms of medium size (e.g. In), while in the LnPtIn_3 crystal structure (LaRuSn_3 -type) — by the atoms of the largest size (e.g. La) (see Table 4).

Table 3
Interatomic distances (Å) in the structure of $\text{Th}_3\text{Ni}_4\text{In}_{13}$

Th —	4 In ²	3.339	In ² —	2 Ni	2.609
(CN=16)	4 Ni	3.385	(CN=14)	1 In ²	2.975
	8 In ²	3.391		2 In ²	3.224
				1 In ¹	3.260
Ni —	6 In ²	2.609		1 Th	3.339
(CN=9)	3 Th	3.385		2 Th	3.391
				4 In ²	3.553
In ¹ —	12 In ²	3.260		1 In ²	3.771
(CN=12)					

Standard deviations are all equal or less than 0.002 Å.

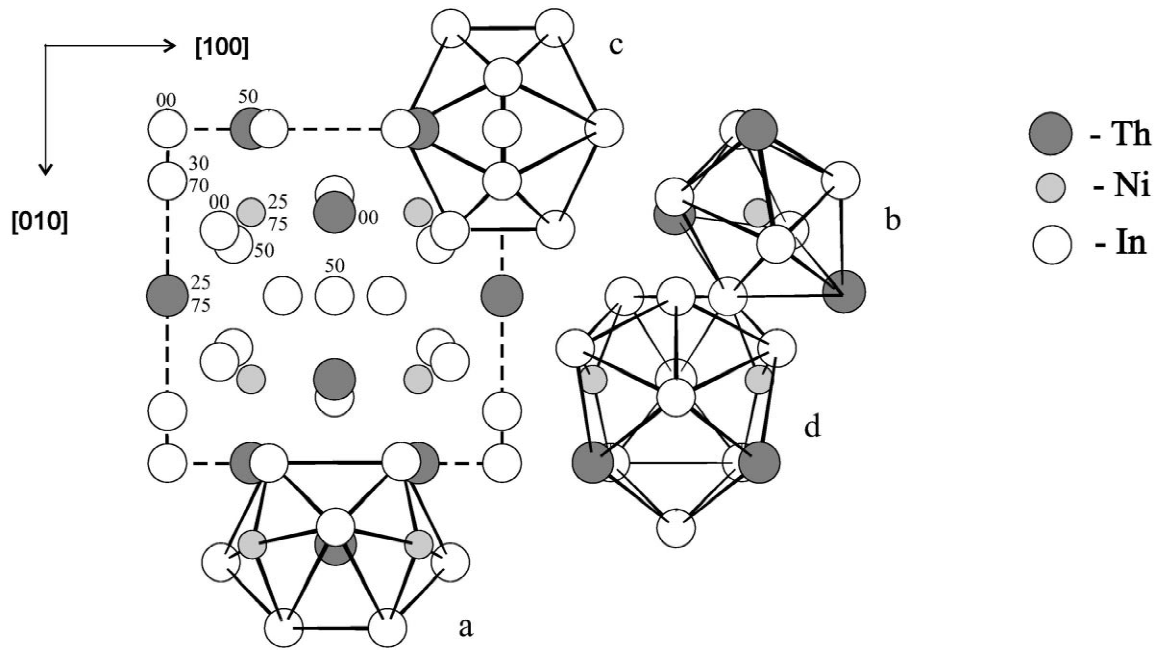


Fig. 1. The projection of the $\text{Th}_3\text{Ni}_4\text{In}_{13}$ ($Pm\bar{3}n$) structure and coordination polyhedra of the atoms (*a* — for Th atoms, *b* — for Ni atoms, *c* and *d* — for In atoms).

It appears that the structures of $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ and LaRuSn_3 types are representatives of the whole series of intermetallic compounds, which are formed in the R–M–Sn systems in the region with high content of tin and have been described in Refs. [5,8–17]. They are derived from the $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ structure type by means of the lattice deformation or multiple substitution of the atoms.

The $\text{Th}_3\text{Ni}_4\text{In}_{13}$ structure can be considered as close packing of polyhedra of different types, $[\text{ThNi}_4\text{In}_{12}^2]$ (deformed cubooctahedra with four additional Ni atoms) and icosahedra $[\text{In}^1\text{In}_{12}^2]$ with tetrahedral holes of two

types between them: $[\text{E In}_4^2]$ and $[\text{E In}_3^2\text{Ni}]$ (Fig. 2). Such a description of the structure of the $\text{Th}_3\text{Ni}_4\text{In}_{13}$ compound slightly differs from the description of the $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ structure, suggested in [4]. There, the authors present a close packing in the $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ structure of the three polyhedra $[\text{YbSn}_{12}]$ (deformed cubooctahedron), $[\text{SnSn}_{12}]$ (icosahedron) and $[\text{RhSn}_6]$ (trigonal prism), with tetrahedral holes $[\text{E Sn}_4]$ between them. It is impossible to apply this kind of stacking to the compound investigated by us, as far as the Ni atoms are enclosed into the coordination sphere of the Th atoms (CN=16). In our case the deformed cubooctahedron, which is typical for the Yb atoms in the $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ structure, transforms into 16 vertices $[\text{ThNi}_4\text{In}_{12}^2]$, while the trigonal prism $[\text{RhSn}_6]$ splits into two empty tetrahedra $[\text{E In}_3^2\text{Ni}]$ and three empty tetragonal pyramids with the Ni atoms in the vertices (Fig. 3).

The structure of the RPtIn_3 compounds (LaRuSn_3 -type) can be described by a similar close packing of the polyhedra, analogous to the description of the $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ structure.

Table 4
The relationship between the $\text{Th}_3\text{Ni}_4\text{In}_{13}$ ($\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ -type) and the RPtIn_3 (LaRuSn_3 -type) compounds

Wyckoff site	$\text{Th}_3\text{Ni}_4\text{In}_{13}$ ($\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ -type) $a=9.574(1)$ Å Space group $Pm\bar{3}n$ (No. 223)	RPtIn_3 (LaRuSn_3 -type) $a=9.804(2)$ Å (for LaPtIn_3)
6c	Th	La^1
1/4 0 1/2		
8e	Ni	Pt
1/4 1/4 1/4		
2a	In^1	La^2
0 0 0		
24k	In^2	In
0 y z	$y=0.1554(1)$ $z=0.3030(1)$	$y=0.1524(1)$ $z=0.3091(1)$

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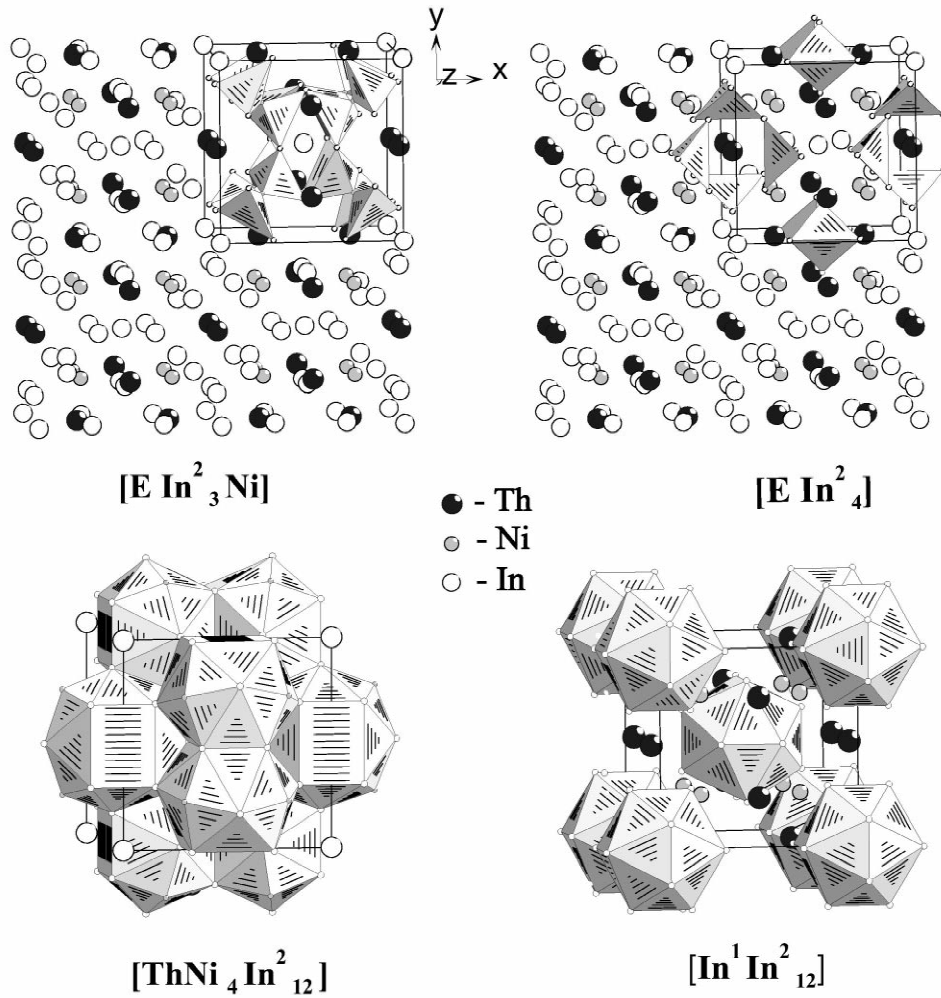


Fig. 2. The packing of the polyhedra and tetrahedral holes in the $Th_3Ni_4In_{13}$ structure.

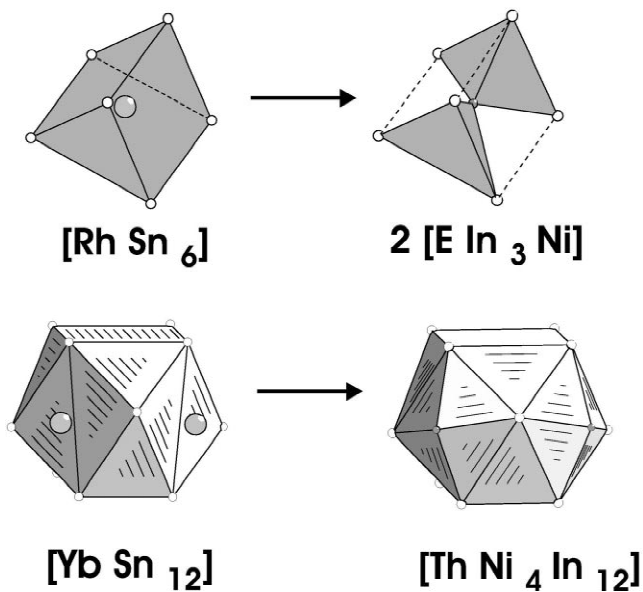


Fig. 3. Scheme of formation of tetrahedral holes and polyhedra of the Th atoms in the $Th_3Ni_4In_{13}$ structure.

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