

New Indium-rich Indides SrTIn_4 ($T = \text{Ni, Pd, Pt}$)

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The indium-rich indides SrTIn_4 ($T = \text{Ni, Pd, Pt}$) were synthesized from the elements by arc-melting and subsequent annealing at 670 K (SrNiIn_4) or by induction melting in sealed tantalum tubes. The three samples were investigated by powder and single crystal X-ray diffractometer data: YNiAl_4 -type, space group $Cmcm$, $a = 448.1(1)$, $b = 1707.3(3)$, $c = 732.6(1)$ pm, $wR2 = 0.067$, 717 F^2 values for SrNiIn_4 , $a = 454.7(2)$, $b = 1708.8(4)$, $c = 750.1(2)$ pm, $wR2 = 0.056$, 746 F^2 values for SrPdIn_4 , and $a = 455.6(2)$, $b = 1706.4(9)$, $c = 748.7(4)$ pm, $wR2 = 0.055$, 508 F^2 values for SrPtIn_4 with 24 variables per refinement. The transition metal and indium atoms build up complex three-dimensional $[\text{TIn}_4]$ polyanionic networks in which the strontium atoms fill distorted hexagonal channels. The indium atoms show distorted bcc indium cubes with short In–In distances as substructures within the $[\text{TIn}_4]$ networks. Each transition metal atom has seven nearest indium neighbors: 257–275 pm Ni–In in SrNiIn_4 and 267–281 pm Pd–In and Pt–In in SrPdIn_4 and SrPtIn_4 , respectively.

Key words: Intermetallics, Indium, Alkaline Earth Compounds

Introduction

Indium-rich intermetallic compounds $R_x\text{T}_y\text{In}_z$ (R = alkaline earth metal, Eu or Yb; T = late transition metal) show similar indium substructures. The indium atoms build up distorted bcc indium cubes within the two- or three-dimensional $[\text{T}_y\text{In}_z]$ networks. The different types of cubes have been summarized in [1] and [2]. The In–In distances are often smaller than in the tetragonal body-centered structure of elemental indium (4×325 and 8×338 pm) [3], indicating strong In–In bonding.

Among the indium-rich compounds, the indides with composition RTIn_4 crystallize with two different structure types. The indides CaTIn_4 ($T = \text{Ni, Pd}$) [1, 4], EuTIn_4 ($T = \text{Ni, Cu, Pd}$) [2, 4–7], and YbTIn_4 ($T = \text{Ni, Pd}$) [2, 6] adopt the orthorhombic YNiAl_4 -type [8], space group $Cmcm$, while CaTIn_4 ($T = \text{Rh, Ir}$) [1], SrIrIn_4 [9], and YbRhIn_4 [2] crystallize with the LaCoAl_4 -type [10], space group $Pmma$. Both structure types have similar structural fragments. The occurrence of a structure type depends on the valence electron concentration (VEC), with the LaCoAl_4 -type occurring for the lower VEC.

We have extended our studies of these indium-rich indides with respect to strontium as the divalent metal

cation. In these systems, so far, only the crystal structure of the LaCoAl_4 -type SrIrIn_4 [9] has been determined. Herein we report on the synthesis and the structures of the indides SrTIn_4 ($T = \text{Ni, Pd, Pt}$) with YNiAl_4 -type. A brief account on the SrNiIn_4 structure has been given in a university report [11].

Experimental Section

Synthesis

Starting materials for the synthesis of the SrTIn_4 ($T = \text{Ni, Pd, Pt}$) samples were a strontium rod (Johnson Matthey, > 99.8 %), nickel wire (Johnson Matthey, \varnothing 0.38 mm, > 99.9 %), palladium and platinum powder (Degussa-Hüls, 200 mesh, > 99.9 %), and indium tear drops (Merck, > 99.9 %). The strontium rods were mechanically cut into smaller pieces under paraffin oil and cleaned with n -hexane. Both the paraffin oil and n -hexane were dried over sodium wire. The strontium pieces were kept in Schlenk tubes under dried argon. The argon was purified over molecular sieves, silica gel, and titanium sponge (900 K).

SrNiIn_4 was prepared by arc-melting of the elements (1 : 1 : 4 atomic ratio) with a low current in order to minimize the evaporation of strontium. The button was remelted twice to ensure homogeneity. The total weight loss after the melting was smaller than one weight percent. The arc-melted button was put into a tantalum container, sealed in an evac-

Empirical formula	SrNiIn ₄	SrPdIn ₄	SrPtIn ₄
Molar mass	605.61	653.3	741.99
Crystal size, μm^3	$30 \times 30 \times 60$	$20 \times 40 \times 60$	$10 \times 30 \times 90$
<i>Unit cell dimensions (Guinier powder data):</i>			
<i>a</i> , pm	448.1(1)	454.7(2)	455.6(2)
<i>b</i> , pm	1707.3(3)	1708.8(4)	1706.4(9)
<i>c</i> , pm	732.6(1)	750.1(2)	748.7(4)
<i>V</i> , nm ³	0.5605(2)	0.5829(3)	0.5821(5)
Calculated density, g cm ⁻³	7.18	7.45	8.47
<i>F</i> (000), e	1048	1120	1248
Abs. coefficient, mm ⁻¹	28.8	27.5	48.5
θ range, deg	2–35	2–35	2–30
Range in <i>hkl</i>	$0 \leq h \leq 7, -27 \leq k \leq 27, -11 \leq l \leq 11$	$-7 \leq h \leq 7, -27 \leq k \leq 27, -12 \leq l \leq 10$	$-6 \leq h \leq 2, -23 \leq k \leq 23, -10 \leq l \leq 10$
Total no. reflections	2485	4373	2388
Indep. Reflections; <i>R</i> _{int}	717; 0.060	746; 0.055	508; 0.081
Refl. with $I \geq 2\sigma(I)$; <i>R</i> _{σ}	667; 0.041	618; 0.032	421; 0.052
Data/parameters	717/24	746/24	508/24
Goodness-of-fit on <i>F</i> ²	1.211	1.229	1.038
Final <i>R</i> 1; <i>wR</i> 2 [$I \geq 2\sigma(I)$]	0.030; 0.065	0.029; 0.053	0.029; 0.052
Final <i>R</i> 1; <i>wR</i> 2 (all data)	0.034; 0.067	0.042; 0.056	0.043; 0.055
Extinction coefficient	0.037(1)	0.0018(1)	0.0016(1)
$\Delta\rho_{\text{min}}$ (max/min), e Å ⁻³	2.05/–1.49	1.79/–2.27	1.75/–1.87

Table 1. Crystal data and structure refinements for SrTIn₄ (*T* = Ni, Pd, Pt), YNiAl₄-type, *Cmcm*, *Z* = 4, Pearson code oC24.

uated silica ampoule and annealed at 670 K for four weeks. After the annealing procedure the sample was stable in air and did not decompose over a long period of time.

Single crystals suitable for X-ray diffraction could not be extracted from the annealed button. In order to get single crystals the sample was exposed to a special heat treatment in a muffle oven. First it was heated up to 1123 K and kept at this temperature for 3 h. Subsequently the sample was cooled down to r. t. at a rate of 5 K per hour. The temperature was controlled using a Eurotherm 818 thermoregulator. This way single crystals with metallic lustre were obtained. They were stable in air and suitable for X-ray investigations.

The SrPdIn₄ and SrPtIn₄ samples were synthesized from the elements (1 : 1 : 4 atomic ratio) in sealed tantalum tubes under an argon pressure of *ca.* 600 mbar [12]. The latter were placed in a water-cooled sample chamber of a high-frequency furnace (Hüttinger Elektronik, Freiburg, and type TIG 1.5/300) under flowing argon [13] and were annealed at 1600 K for about one minute followed by slow cooling to 900 K. Finally the samples were annealed for four h at that temperature.

The temperature was controlled through a Sensor Therm Methis MS09 pyrometer with an accuracy of ± 30 K. The samples could easily be separated from the crucible material. No reaction with the container was observed. The SrTIn₄ samples are stable in air over months in powdered as well as in polycrystalline form. Single crystals exhibit metallic lustre while ground powders are grey.

EDX data

Quantitative and qualitative EDX analyses were carried out by use of a Philips EDX 515 scanning elec-

tron microscope (SEM) on the SrNiIn₄ single crystal used for the structure determination. Semi-quantitative analyses of this crystal gave the composition (in atomic percentage) Sr: Ni: In = 17 ± 1 : 15 ± 1 : 68 ± 1 , close to the ideal one (16.6 : 16.6 : 66.6). No impurity elements heavier than sodium were found. The SrPdIn₄ and SrPtIn₄ crystals were studied by energy dispersive analyses of X-rays (EDX) using a Leica 420i scanning electron microscope with SrF₂, palladium, platinum, and InAs as standards. The experimentally observed compositions (18 ± 3 at.-% Sr: 19 ± 3 at.-% Pd: 63 ± 3 at.-% In and 17 ± 3 at.-% Sr: 17 ± 3 at.-% Pt: 64 ± 3 at.-% In) were close to the ideal one. The standard uncertainties account for the measurements at different points on the irregularly shaped crystals.

X-Ray diffraction

The polycrystalline samples were studied through Guinier powder patterns (imaging plate technique, Fujifilm BAS-1800) using CuK α ₁ radiation and α -quartz (*a* = 491.30 and *c* = 540.46 pm) as an internal standard. The orthorhombic lattice parameters were obtained from least-squares fits of the powder data. The correct indexing of the patterns was ensured through intensity calculations [14] taking the atomic positions from the structure refinements. The powder lattice parameters compared well with the single crystal data.

Suitable single crystals of the three compounds were selected from the annealed samples and first investigated *via* Laue and rotation photographs (RKV-86 and Buerger cameras, Mo radiation) in order to check the quality for intensity data collection.

Single crystal intensity data of the SrNiIn₄ crystal were collected at r. t. by use of single crystal diffractometer KM-4

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) of SrTIn_4 ($T = \text{Ni, Pd, Pt}$). (U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor).

Atom	Wyckoff site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
SrNiIn₄					
Sr	4 <i>c</i>	0	0.12135(4)	1/4	85(2)
Ni	4 <i>c</i>	0	0.77383(6)	1/4	83(2)
In1	8 <i>f</i>	0	0.31058(2)	0.05073(6)	83(1)
In2	4 <i>c</i>	0	0.92412(3)	1/4	122(2)
In3	4 <i>b</i>	0	1/2	0	139(2)
SrPdIn₄					
Sr	4 <i>c</i>	0	0.12390(5)	1/4	132(2)
Pd	4 <i>c</i>	0	0.77416(4)	1/4	121(2)
In1	8 <i>f</i>	0	0.31516(3)	0.05160(6)	123(1)
In2	4 <i>c</i>	0	0.93010(4)	1/4	176(2)
In3	4 <i>b</i>	0	1/2	0	191(2)
SrPtIn₄					
Sr	4 <i>c</i>	0	0.12586(9)	1/4	117(4)
Pt	4 <i>c</i>	0	0.77526(4)	1/4	95(2)
In1	8 <i>f</i>	0	0.31521(5)	0.05000(11)	104(2)
In2	4 <i>c</i>	0	0.93182(7)	1/4	159(3)
In3	4 <i>b</i>	0	1/2	0	174(3)

(KUMA Diffraction, graphite-monochromatized $\text{MoK}\alpha$ radiation). An empirical absorption correction was applied on the basis of Ψ -scan data. The SrPdIn_4 and SrPtIn_4 crystals were measured at r.t. by use of a four-circle diffractometer (CAD4) with graphite monochromatized $\text{MoK}\alpha$ radiation and a scintillation counter with pulse height discrimination. The scans were taken in the $\omega/2\theta$ mode and empirical absorption corrections were applied on the basis of Ψ -scan data, accompanied by spherical absorption corrections. All relevant details concerning the data collections are listed in Table 1.

Structure refinements

The isotypy with the orthorhombic YNiAl_4 -type [8], space group $Cmcm$, was already evident from the powder pattern. The atomic parameters of CaPdIn_4 [1] were taken as starting values and the structures were refined using SHELXL-97 [15] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms. As a check for the correct composition, the occupancy parameters of all sites were refined in separate series of least-squares cycles. All sites were fully occupied within two standard deviations, and in the final cycles the ideal occupancy parameters were assumed again. The final difference Fourier syntheses were flat (Table 1). The positional parameters and interatomic distances of the refinements are listed in Tables 2 and 3.

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, [Table 3. Interatomic distances \(pm\) in the structures of \$\text{SrTIn}_4\$ \(\$T = \text{Ni, Pd, Pt}\$ \), calculated with the lattice parameters obtained from X-ray powder data. \(Standard deviations are all equal to or smaller than 0.2 pm. All distances within the first coordination spheres are listed\).](http://www.fiz-</p></div><div data-bbox=)

SrNiIn₄			SrPdIn₄			SrPtIn₄		
Sr:	4	In1 335.0	Sr:	1	In2 331.2	Sr:	1	In2 331.1
1	In2 336.7		4	In1 337.2		4	In1 335.3	
2	Ni 343.5		2	Pd 343.0		2	Pt 341.9	
2	In1 354.5		2	In1 359.1		2	In1 356.1	
4	In3 355.9		4	In3 362.9		4	In3 364.8	
2	In2 374.4		2	In2 386.2		2	In2 387.1	
Ni:	1	In2 256.6	Pd:	1	In2 266.5	Pt:	1	In2 267.2
2	In1 263.3		2	In1 272.9		2	In1 272.6	
4	In1 274.7		4	In1 280.6		4	In1 281.0	
2	Sr 343.5		2	Sr 343.0		2	Sr 341.9	
In1:	1	Ni 263.3	In1:	1	Pd 272.9	In1:	1	Pt 272.6
2	Ni 274.7		2	Pd 280.6		2	Pt 281.0	
1	In1 292.0		1	In1 297.6		1	In1 299.5	
2	In1 313.9		1	In3 318.2		1	In3 317.5	
1	In3 325.5		2	In1 327.5		2	In1 327.2	
2	In2 330.3		2	In2 335.3		2	Sr 335.3	
2	Sr 335.0		2	Sr 337.2		2	In2 337.5	
1	Sr 354.5		1	Sr 359.1		1	Sr 356.1	
In2:	1	Ni 256.6	In2:	1	Pd 266.5	In2:	1	Pt 267.2
4	In3 317.1		4	In3 318.0		4	In3 317.0	
4	In1 330.3		1	Sr 331.2		1	Sr 331.1	
1	Sr 336.7		4	In1 335.3		4	In1 337.5	
2	Sr 374.4		2	Sr 386.2		2	Sr 387.1	
In3:	4	In2 317.1	In3:	4	In2 318.0	In3:	4	In2 317.0
2	In1 325.5		2	In1 318.2		2	In1 317.5	
4	Sr 355.9		4	Sr 362.9		4	Sr 364.8	
2	In3 366.3		2	In3 375.1		2	In3 374.4	

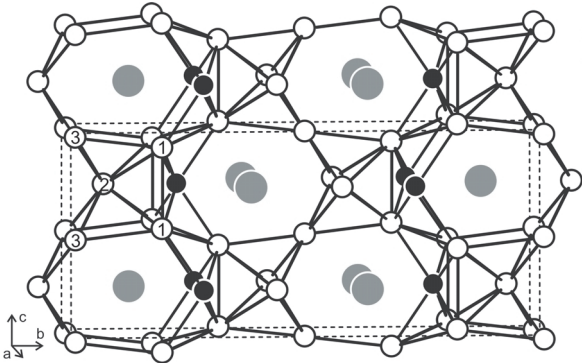


Fig. 1. The crystal structure of SrPdIn_4 (view approximately along the x axis). The strontium, palladium, indium atoms are drawn as medium grey, black, open circles, respectively. The three-dimensional $[\text{PdIn}_4]$ network and the three crystallographically independent indium sites within the indium-centered indium cubes are emphasized.

[fachinformationsdienste.de/en/DB/icsd/depot_anforderung.html](http://www.fachinformationsdienste.de/en/DB/icsd/depot_anforderung.html)) on quoting the deposition number CSD-418178 (SrNiIn_4), CSD-418179 (SrPdIn_4) and CSD-418180 (SrPtIn_4).

Discussion

The new indides SrTIn_4 ($T = \text{Ni, Pd, Pt}$) crystallize with the orthorhombic YNiAl_4 -type structure, similar to EuNiIn_4 [6, 7] and EuPdIn_4 [2]. In both cases, the cell volumes are slightly larger for the strontium compounds. A similar trend is observed for the pairs $\text{CaRhIn}_4 / \text{YbRhIn}_4$ and $\text{CaPdIn}_4 / \text{YbPdIn}_4$ [1, 2], where the calcium compounds have slightly larger cell volumes. As an example we present the SrPdIn_4 structure in Fig. 1. The structure is built up from a complex $[\text{PdIn}_4]$ polyanionic network in which the strontium atoms fill distorted hexagonal channels that extend in a direction.

Within the $[\text{PdIn}_4]$ network each palladium atom has seven nearest indium neighbors at Pd–In distances ranging from 267 to 281 pm, close to the sum of the covalent radii of 278 pm [16]. We can thus assume a significant degree of Pd–In bonding. Each of the three crystallographically independent indium atoms has between six and ten indium neighbors. The various In–In distances cover the broad range from 298 to 375 pm. Most of the In–In distances (Table 3) are even shorter than in the tetragonal body-centered structure of elemental indium (4×325 and 8×338 pm) [3], leading to strong In–In bonding. This pattern of chemical

bonding is similar to isotypic CaPdIn_4 [1], where the largest crystal orbital overlap populations have been calculated for the Pd–In and In–In interactions. A rigid band model can safely be applied to SrPdIn_4 reported herein.

A slightly different bonding pattern has been observed for the gallide YbNiGa_4 [17]. Calculation of the electron localization function revealed strong Ga–Ga bonds, but despite short Ni–Ga distances, no discrete attractors have been observed between the nickel and gallium atoms, suggesting that the ytterbium and nickel atoms serve as cations which transfer part of their valence electrons, leading to homoatomic Ga–Ga bonding. The difference in bonding with respect to SrPdIn_4 is certainly related to the higher electronegativity of palladium, where we observe filling of the d bands, leading to a negative net charge [1]. For further crystal chemical details we refer to the previous work [1, 2, 17].

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