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Quaternary indides $LaTIn_3Mg$ (T = Rh and Ir) and $CeIrIn_3Mg$ with $LaCoAl_4$ type structure

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Abstract The quaternary indides $LaTIn_3Mg$ (T = Rh and Ir) and $CeIrIn_3Mg$ were prepared from the elements in sealed tantalum ampoules in an induction furnace. The samples were characterized by X-ray powder and single crystal data: $LaCoAl_4$ type, *Pmma*, $Z = 2$, $a = 830.5(1)$, $b = 436.1(1)$, $c = 745.1(1)$ pm, $wR2 = 0.038$, 467 F^2 values for $LaRhIn_{3.075}Mg_{0.925}$, $a = 832.9(1)$, $b = 436.5(1)$, $c = 746.9(1)$ pm, $wR2 = 0.077$, 471 F^2 values for $LaIrIn_{3.091}Mg_{0.909}$, and $a = 832.2(1)$, $b = 434.1(1)$, $c = 743.9(1)$ pm, $wR2 = 0.066$, 465 F^2 values for $CeIrIn_{3.07}Mg_{0.93}$ with 25 variables for each refinement. The transition metal, indium, and magnesium atoms build up three-dimensional [TIn_3Mg] networks which leave pentagonal prismatic voids for the lanthanum and cerium atoms. The transition metal atoms have tricapped trigonal prismatic coordination and the magnesium atoms fill distorted square prisms. All three crystals revealed a small degree of Mg/In mixing on the latter site.

Keywords Rare earth compounds; Indides; Solid solution; Crystal chemistry.

Introduction

Depending on the electron count, the $AETIn_4$ and $RETIn_4$ indides (AE = alkaline earth element; RE = rare earth element; and T = late transition metal) crystallize with two different structure types. The indides $CaTIn_4$ (T = Ni, Cu, and Pd) [1, 2], $SrTIn_4$ (T = Ni, Pd, and Pt) [3], $EuTIn_4$ (T = Ni, Cu, and Pd) [5–7], and $YbTIn_4$ (T = Ni and Pd) [5, 6] adopt the orthorhombic $YNiAl_4$ type [8], space group *Cmcm*, while $CaTIn_4$ (T = Rh and Ir) [1], $SrIrIn_4$ [9], and $YbRhIn_4$ [5] crystallize with the $LaCoAl_4$ type [10], space group *Pmma*. Both structure types have similar structural fragments. The occurrence of the structure type depends on the valence electron concentration (VEC), where the $LaCoAl_4$ type occurs for the lower VEC.

Recently we synthesized the indides $CeRhIn_{4-x}Mg_x$ ($x = 0.79$ and 0.84), where the VEC was reduced by indium–magnesium substitution [11]. This way it was possible to stabilize this compound with a trivalent rare earth element in a $LaCoAl_4$ type structure. In continuation of these substitution studies we obtained $LaRhIn_{3.075}Mg_{0.925}$, $LaIrIn_{3.091}Mg_{0.909}$, and $CeIrIn_{3.07}Mg_{0.93}$ reported herein.

Discussion

Three new indides $LaRhIn_{3.075}Mg_{0.925}$, $LaIrIn_{3.091}Mg_{0.909}$, and $CeIrIn_{3.07}Mg_{0.93}$ with orthorhombic $LaCoAl_4$ type structure have been synthesized and structurally characterized. The lattice parameters of the cerium compounds (Table 1) are slightly smaller than those of the lanthanum compounds as expected from the lanthanoid contraction. As an example, a

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Table 1 X-Ray powder and single crystal (*) lattice parameters of the orthorhombic $LaCoAl_4$ type indides. For comparison, also the lattice parameters of $CeRhIn_{3.21}Mg_{0.79}$ and $CeRhIn_{3.16}Mg_{0.84}$ [11] are listed

Compound	a/pm	b/pm	c/pm	V/nm^3
$LaRhIn_3Mg$	832.0(2)	436.8(1)	746.3(2)	0.2712
$LaRhIn_{3.075}Mg_{0.925}$*	830.5(1)	436.1(1)	745.1(1)	0.2699
$CeRhIn_{3.21}Mg_{0.79}$	829.5(2)	433.56(9)	740.2(2)	0.2662
$CeRhIn_{3.16}Mg_{0.84}$	831.44(10)	433.49(10)	741.04(10)	0.2671
$LaIrIn_3Mg$	834.2(1)	436.8(1)	747.2(1)	0.2723
$LaIrIn_{3.091}Mg_{0.909}$*	832.9(1)	436.5(1)	746.9(1)	0.2716
$CeIrIn_3Mg$	830.7(7)	437.3(1)	740.7(2)	0.2691
$CeIrIn_{3.07}Mg_{0.93}$*	832.2(1)	434.1(1)	743.9(1)	0.2687

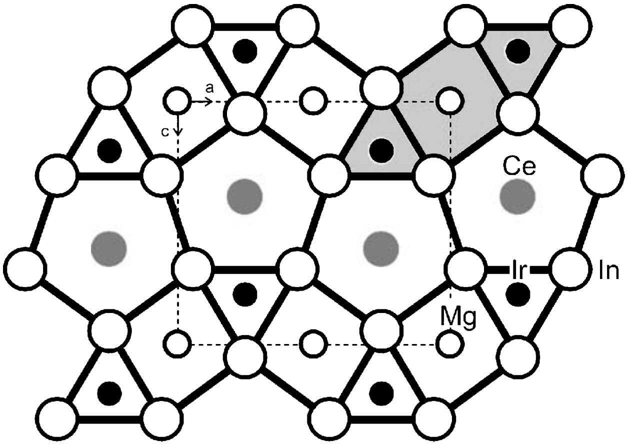

Fig. 1 Projection of the $CeIrIn_3Mg$ structure along the y axis. All atoms lie on mirror planes at $y = 0$ (thin lines) and $y = 1/2$ (thick lines). The different prismatic slabs are emphasized

projection of the $CeIrIn_{3.07}Mg_{0.93}$ structure onto the xz plane is presented in Fig. 1. The In2 and In3 atoms build up two-dimensional networks in the xz plane which leave trigonal prismatic voids for the iridium, square prismatic voids for the magnesium, and pentagonal prismatic voids for the cerium atoms. All these prisms are capped on the rectangular sites, leading to coordination numbers 9, 12, and 15. The size of the prisms scales with the size of the centering atoms.

The shortest interatomic distances in the $CeIrIn_{3.07}Mg_{0.93}$ structure occur between the iridium and magnesium atoms. The Ir–Mg distance of 259 pm is even slightly shorter than the sum of the covalent radii of 262 pm for Ir + Mg [15] and one can assume substantial Ir-Mg bonding. The cerium atoms bind to the three-dimensional $[IrIn_{3.07}Mg_{0.93}]$ network *via* one short Ce–Ir distance (298 pm), only slightly longer than the sum of the covalent radii of 291 pm [15]. Similar short Ce–Ir distances have been observed for CeIrGe (295–305 pm) [16] and CeIrSn (303–308 pm) [17], where the cerium atoms bind to the three-dimensional [IrGe] and [IrSn] networks.

Each magnesium atom has eight indium neighbors building the square prisms. The Mg–In distances range from 303 to 320 pm, somewhat longer than the Mg–In distances in SmMgIn (294–299 pm) [18] with an ordered three-dimensional [MgIn] polyanionic network. The various In–In distances within the two-dimensional indium networks range from 301 to 320 pm. They are all shorter than in tetragonal body-centered indium (8 × 325 and 4 × 338 pm) [19], indicating strong In–In bonding.

Although all samples had the ideal 1:1:3:1 starting compositions, the structure refinements of the crystals always revealed a small degree of Mg/In mixing on the 2a sites. Thus, for all compounds small homogeneity ranges $RETIn_{4-x}Mg_x$ exist and the $LaCoAl_4$ structure type has certain flexibility for the electron count. An exact rule for the borders of the homogeneity ranges like for the well known Hume-Rothery phases is not yet known. More detailed studies on chemical bonding in these structures are planned in order to get a better understanding of the structural behavior in terms of structure, bonding, stability and VEC.

Experimental

Synthesis

Starting materials for the preparation of the $RETIn_3Mg$ samples were ingots of lanthanum and cerium (*Johnson Matthey*), rhodium and iridium powder (*ca.* 200 mesh, Degussa-Hüls), indium tear drops (*Johnson Matthey*), and a magnesium rod (*Johnson Matthey*, Ø 16 mm). The surface of the magnesium rod was cut on a turning lathe in order to remove surface impurities. The lanthanum and cerium ingots were cut into smaller pieces and arc-melted [12] to small buttons (*ca.* 400 mg) under an argon atmosphere. The argon was purified with titanium sponge (900 K), silica gel, and molecular sieves.

The lanthanum (cerium) buttons were then mixed with rhodium (iridium) powder and pieces of the indium tear drops and the magnesium rod in the ideal 1:1:3:1 atomic ratio and sealed in small tantalum tubes under an argon pressure of ca. 800 mbar. The ampoules were then heated in a water-cooled sample chamber of an induction furnace with the same annealing sequence as for the CeRhIn$_{4\text{-}x}$Mg$_x$ samples [11]. The polycrystalline samples are brittle and stable in air over months. Finely ground powders are dark gray and single crystals exhibit metallic luster.

Scanning electron microscopy

The single crystals investigated on the diffractometers have been analyzed by EDX measurements using a LEICA 420 I scanning electron microscope with LaF$_3$, CeO$_2$, rhodium, iridium, MgO, and InAs standards. Since the crystals were mounted by beeswax on glass fibres, they were first coated with a thin carbon film. No impurity elements were detected. The semiquantitative analyses were in agreement with the compositions obtained from the structure refinements, *vide infra*.

X-Ray film data and structure refinements

The *RET*In$_3$Mg samples were characterized by Guinier powder patterns using Cu Kα_1 radiation and α-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The Guinier camera was equipped with an imaging plate system (Fujifilm BAS-1800). The orthorhombic lattice parameters (Table 1) were refined from the powder data by least-squares fits. To ensure proper indexing, the experimental patterns were compared to calculate ones [13], taking the atomic positions obtained from the structure refinements.

Small single crystals of LaRhIn$_{3.075}$Mg$_{0.925}$, CeIrIn$_{3.091}$-Mg$_{0.909}$ and CeIrIn$_{3.07}$Mg$_{0.93}$ were selected from the annealed samples and examined by Laue photographs on a Buerger precession camera (equipped with an imaging plate system Fujifilm BAS-1800) in order to establish suitability for intensity data collection. Intensity data were collected on a Nonius CAD4 four-circle diffractometer with graphite monochromatized Mo K$_\alpha$ radiation ($\lambda = 71.073$ pm) and a scintillation counter with pulse-height discrimination. Scans were taken in the $\omega/2\theta$ mode. Absorption corrections were applied on the basis of psi-scan data followed by spherical absorption corrections. All relevant crystallographic details for the data collections and evaluations are listed in Table 2.

The systematic extinctions of the three data sets were compatible with space group *Pmma*, in agreement with the earlier investigations on the CeRhIn$_{4\text{-}x}$Mg$_x$ indides [11]. The atomic parameters of CeRhIn$_{3.21}$Mg$_{0.79}$ [11] were used as starting values and the structures were refined using SHELXL-97 (full-matrix least-squares on ${F_0}^2$) [14] with anisotropic atomic displacement parameters for all sites. The 2*a* site was refined with mixed Mg/In occupancy for all crystals, similar to CeRhIn$_{3.21}$Mg$_{0.79}$ [11]. As a check for further In/Mg mixing, the occupancy parameters of the 2*f* and 4*j* indium sites were refined in separate series of least-squares cycles. These sites were fully occupied within three standard deviations and in the final cycles full indium occupancy was assumed again. Final difference Fourier syntheses revealed no significant residual peaks (Table 2). The largest peaks for LaIrIn$_{3.091}$Mg$_{0.909}$ and CeIrIn$_{3.075}$In$_{0.925}$ were close to the iridium sites as typically observed for such highly absorbing compounds. The positional parameters and inter-

Table 2 Crystal data and structure refinement for LaRhIn$_{3.075}$Mg$_{0.925}$, LaIrIn$_{3.091}$Mg$_{0.909}$, and CeIrIn$_{3.07}$Mg$_{0.93}$, LaCoAl$_4$ type, space group *Pmma*, Z = 2

Empirical formula	LaRhIn$_{3.075}$Mg$_{0.925}$	LaIrIn$_{3.091}$Mg$_{0.909}$	CeIrIn$_{3.07}$Mg$_{0.93}$
Molar mass	617.83 g/mol	708.03 g/mol	707.88 g/mol
Unit cell dimensions	Table 1	Table 1	Table 1
Calculated density	7.60 g/cm^3	8.66 g/cm^3	8.75 g/cm^3
Crystal size	$15 \times 40 \times 40\ \mu$m^3	$20 \times 30 \times 40\ \mu$m^3	$10 \times 20 \times 20\ \mu$m^3
Transm. ratio (max/min)	1.55	1.96	4.41
Absorption coefficient	23.6 mm^{-1}	45.0 mm^{-1}	45.9 mm^{-1}
F(000)	528	593	594
θ range	2° to 30°	2° to 30°	2° to 30°
Range in *hkl*	±11, ±6, ±10	±11, ±6, ±10	±11, ±6, ±10
Total no. reflections	2984	3034	2616
Independent reflections	467 ($R_{\text{int}} = 0.048$)	471 ($R_{\text{int}} = 0.055$)	465 ($R_{\text{int}} = 0.186$)
Reflections with $I > 2\sigma(I)$	444 ($R_\sigma = 0.021$)	458 ($R_\sigma = 0.024$)	356 ($R_\sigma = 0.087$)
Data/parameters	467/25	471/25	465/25
Goodness-of-fit on F^2	1.258	1.507	1.005
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.016$	$R1 = 0.031$	$R1 = 0.037$
	$wR2 = 0.038$	$wR2 = 0.076$	$wR2 = 0.060$
R indices (all data)	$R1 = 0.018$	$R1 = 0.032$	$R1 = 0.059$
	$wR2 = 0.038$	$wR2 = 0.077$	$wR2 = 0.066$
Extinction coefficient	0.0156(7)	0.0201(13)	0.0019(2)
Largest diff. peak and hole	0.91/−1.52 e/Å^3	3.86/−4.19 e/Å^3	2.97/−3.60 e/Å^3

Table 3 Atomic coordinates and isotropic displacement parameters (pm^2) for $LaRhIn_{3.075}Mg_{0.925}$, $LaIrIn_{3.091}Mg_{0.909}$ and $CeIrIn_{3.07}Mg_{0.93}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	Wyckoff site	Occupancy (%)	*x*	*y*	*z*	U_{eq}
$LaRhIn_{3.075}Mg_{0.925}$						
La	2*e*	100	1/4	0	0.39228(5)	90(1)
Rh	2*e*	100	1/4	0	0.79654(6)	80(1)
In1/Mg	2*a*	7.5(4)/92.5(4)	0	0	0	110(6)
In2	2*f*	100	1/4	1/2	0.05157(6)	100(1)
In3	4*j*	100	0.05927(4)	1/2	0.69367(4)	95(1)
$LaIrIn_{3.091}Mg_{0.909}$						
La	2*e*	100	1/4	0	0.39101(9)	103(2)
Ir	2*e*	100	1/4	0	0.79433(6)	85(2)
In1/Mg	2*a*	9.1(7)/90.9(7)	0	0	0	123(12)
In2	2*f*	100	1/4	1/2	0.04948(11)	111(3)
In3	4*j*	100	0.05964(8)	1/2	0.69228(8)	107(2)
$CeIrIn_{3.07}Mg_{0.93}$						
Ce	2*e*	100	1/4	0	0.39259(18)	112(3)
Ir	2*e*	100	1/4	0	0.79275(13)	87(2)
In1/Mg	2*a*	7(1)/93(1)	0	0	0	120(23)
In2	2*f*	100	1/4	1/2	0.05132(22)	110(4)
In3	4*j*	100	0.05865(14)	1/2	0.69136(16)	110(3)

Table 4 Interatomic distances (pm), calculated with the powder lattice parameters in $CeIrIn_{3.07}Mg_{0.93}$. Standard deviations are all equal or smaller than 0.2 pm. All distances within the first coordination spheres are listed. *M* denotes 7(1)% In 1/93(1)% Mg

Ce	1	Ir	297.7	In2	2	Ir	290.0
	2	In2	334.0		2	*M*	303.1
	4	In3	342.0		2	In3	311.6
	4	In3	349.1		2	In3	320.3
	2	*M*	358.6		1	Ce	334.0
	2	Ce	434.1	In3	1	Ir	279.6
Ir	2	*M*	258.9		1	In3	301.0
	4	In3	279.6		1	In2	311.6
	2	In2	290.0		1	In3	318.5
	1	Ce	297.7		1	*M*	319.7
M	2	Ir	258.9		2	In2	320.3
	4	In2	303.1		2	Ce	342.0
	4	In3	319.7		2	Ce	349.1
	2	Ce	358.6				

atomic distances (exemplarily for $CeIrIn_{3.075}Mg_{0.925}$) are listed in Tables 3 and 4. Further details on the structure refinements are available.*

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* Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD-418620 ($LaRhIn_{3.075}Mg_{0.925}$), CSD-418621 ($LaIrIn_{3.091}Mg_{0.909}$), and CSD-418622 ($CeIrIn_{3.07}Mg_{0.93}$).

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