Synthesis and Structure of $YbPdSn_2$

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New ternary stannide $YbPdSn_2$ was synthesized from the elements in a sealed tantalum tube in a high-frequency furnace. $YbPdSn_2$ was characterized through X-ray powder and single crystal data: *Cmcm*, a = 442.4(2), b = 1108.6(3), c = 738.4(2) pm, $wR2$ = 0.0450, 317 F^2 values, and 16 variable parameters. $YbPdSn_2$ crystallizes with the $MgCuAl_2$ type structure, a ternary ordered variant of the Re_3B type. The tin sublattice of $YbPdSn_2$ corresponds to a distorted lonsdaleite-like arrangement with Sn-Sn distances varying from 303 to 336 pm.

Introduction

The crystal chemistry and chemical bonding of the alkaline earth metal indides $CaTIn_2$ (T = Ni, Cu, Rh, Pd, Ir, Pt, Au) [1–4], $SrTIn_2$, and $BaTIn_2$ (T = Rh, Pd, Ir, Pt) [5, 6] has intensively been studied in recent years. These indides crystallize with the $MgCuAl_2$ structure [7], a ternary ordered version of Re_3B [8], however, this is only a geometrical picture. A description of the $AETIn_2$ (AE = Ca, Sr, Ba) compounds as transition metal filled variants of the Zintl phases $CaIn_2$, $SrIn_2$, and $BaIn_2$ [9–11] is more appropriate. The transition metals tend to fill their *d*-bands and hence they partially oxidize the indium networks to meet their electronic requirements. Although a binary stannide $CaSn_2$ is not known, and a Sn^- sublattice would adopt a structure similar to gray arsenic or antimony, we were recently sucessful in synthesizing the transition metal filled stannides $CaTSn_2$ (T = Rh, Pd, Ir) [12] and $EuIrSn_2$ [13]. Since ytterbium (r_{atomic} = 194 pm; r_{cov} = 170 pm) has an atomic and covalent radius similar to calcium (r_{atomic} = 197 pm; r_{cov} = 174 pm) [14], we extended our investigations with respect to ytterbium. The synthesis and structure refinement of $YbPdSn_2$ are reported herein.

Experimental

Synthesis

Starting materials for the preparation of $YbPdSn_2$ were ytterbium ingots (Johnson Matthey), palladium powder (Degussa, 200 mesh), and a tin bar (Heraeus), all with stated purities better than 99.9%. Small ytterbium and tin pieces were mixed with the palladium powder in the ideal 1:1:2 atomic ratio and sealed in a small tantalum tube (tube volume about 1 cm^3) under an argon atmosphere of about 800 mbar [15]. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves. The tantalum tube was placed in a water-cooled quartz glass sample chamber in a high-frequency furnace (KONTRON Roto-Melt, 1.2 kW) under flowing argon [16]. It was first heated for 1 min with the maximum power output (about 1500 K) and subsequently annealed at about 900 K for another 4 h. After the annealing procedure the sample could easily be separated from the tantalum tube. No reactions with the tube could be detected. Compact pieces are light gray with metallic luster. The sample is stable in moist air. No decomposition was observed after several months.

Table I. Crystal data and structure refinement for $YbPdSn_2$.

Empirical formula	$YbPdSn_2$
Molar mass [g/mol]	516.82
Unit cell dimensions [pm]	a = 442.4(2)
	b = 1108.6(3)
	c = 738.4(2)
Volumen [nm^3]	V = 0.3621
Space group	*Cmcm* (No. 63)
Calculated density [g cm^{-3}]	9.48
Crystal size [μm^3]	20 × 25 × 30
Transm. ratio (max/min)	2.46
Absorption coefficient [mm^{-1}]	43.8 mm
θ Range [°]	2 to 30
Range in *hkl*	±6, ±15, ±10
Total no. reflections	2062
Independent reflections	317 (R_{int} = 0.0571)
Reflections with $I>2\sigma(I)$	284 (R_{sigma} = 0.0262)
Data/parameters	317 / 16
Goodness-of-fit on F^2	1.210
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0186
	$wR2$ = 0.0420
R Indices (all data)	$R1$ = 0.0248
	$wR2$ = 0.0450
Extinction coefficient	0.0053(3)
Largest diff. peak and hole [e/Å^3]	2.39 and −1.90

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X-ray film data

$YbPdSn_2$ was characterized through its Guinier powder pattern using Cu–$K_{\alpha 1}$ radiation and α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. The lattice parameters (Table I) were obtained from least-squares fits of the X-ray powder data. The correct indexing of the pattern was ensured by an intensity calculation [17] taking the atomic positions from the structure refinement. The lattice parameters determined from the powder and the single crystal agreed well.

Irregularly shaped single crystals were isolated from the annealed sample by mechanical fragmentation. They were examined on a Buerger precession camera camera in order to establish both symmetry and suitability for intensity data collection. The extinction conditions for the reciprocal layers $0kl$ and $1kl$ were compatible with space group *Cmcm*, in agreement with previous results on the alkaline earth stannides [12].

Structure refinement

Single crystal intensity data were collected at room temperature by use of a four-circle diffractometer (CAD4) with graphite monochromatized Mo–K_α radiation (71.073 pm) and a scintillation counter with pulse height discrimination. The scans were performed in the $\omega/2\theta$ mode. An empirical absorption correction was applied on the basis of ψ-scan data. All relevant crystallographic data and experimental details for the data collection are listed in Table I.

The atomic positions of $CaPdSn_2$ [12] were taken as starting values and the structure was successfully refined using SHELXL-97 (full-matrix least-squares on F_o^2) [18] with anisotropic atomic displacement parameters for all sites. As a check for the correct composition, the occupancy parameters were refined in a separate series of least-squares cycles. All sites were fully occupied within two standard deviations. A final difference Fourier synthesis revealed no significant residual peaks (see Table I). The positional parameters and interatomic distances are listed in Tables II and III. Listings of the observed and calculated structure factors are available.*

Table III. Interatomic distances (pm), calculated with the lattice parameters taken from X-ray powder data of $YbPdSn_2$. All distances within the first coordination sphere are listed. Standard deviations are equal or less than 0.1 pm.

Yb: 1	Pd	303.0	Pd: 4	Sn	276.8	Sn: 2	Pd	276.8
4	Sn	319.7	2	Sn	279.1	1	Pd	279.1
2	Pd	334.8	1	Yb	303.0	1	Sn	303.0
2	Sn	354.2	2	Yb	334.8	1	Sn	317.9
4	Sn	356.0	2	Yb	396.9	2	Yb	319.7
2	Pd	396.9				2	Sn	335.5
2	Yb	401.4				1	Yb	354.2
2	Yb	442.4				2	Yb	356.0

Discussion

$YbPdSn_2$ is the fifth stannide with $MgCuAl_2$ type structure [7], besides $EuIrSn_2$ [13] and $CaTSn_2$ (T = Rh, Pd, Ir) [12]. A view of the $YbPdSn_2$ unit cell is presented in Fig. 1. The structure is best described as a palladium filled $YbSn_2$ host lattice. The ytterbium and tin atoms build a strongly distorted $CaIn_2$-like arrangement in which the palladium atoms are located in every other Yb_3 triangle within the *ab* plane.

The tin sublattice reminds of the lonsdaleite structure (hexagonal diamond) [19]. Each tin atom has a distorted tetrahedral tin environment with Sn-Sn distances ranging from 303 to 336 pm. The shorter ones compare well with the Sn-Sn bond lengths of 302 pm (4×) and 318 pm (2×) in the β-tin structure [19]. The shortest interatomic distances in $YbPdSn_2$, however, occur for the Pd-Sn contacts which range from 277 to 279 pm, somewhat larger than the sum of Pauling's single bond radii of 268 pm [20] for palladium and tin.

* Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD-411798.

Table II. Atomic coordinates and anisotropic displacement parameters (pm^2) for $YbPdSn_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. $U_{12} = U_{13} = 0$.

Atom	Wyckoff position	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{eq}
Yb	4*c*	0	0.42899(4)	1/4	101(3)	119(3)	91(3)	0	104(2)
Pd	4*c*	0	0.70228(7)	1/4	101(4)	138(4)	95(4)	0	111(2)
Sn	8*f*	0	0.14024(4)	0.04483(7)	97(3)	124(3)	55(3)	−6(2)	92(2)

The lattice parameters and consequently all interatomic distances in $YbPdSn_2$ are very close to the values derived recently for $CaPdSn_2$ [12]. We can therefore conclude that ytterbium is most likely divalent in $YbPdSn_2$. Since the crystal chemistry and chemical bonding have been described in detail for $CaTSn_2$ (T = Rh, Pd, Ir) [12], we refer to this work for further information.

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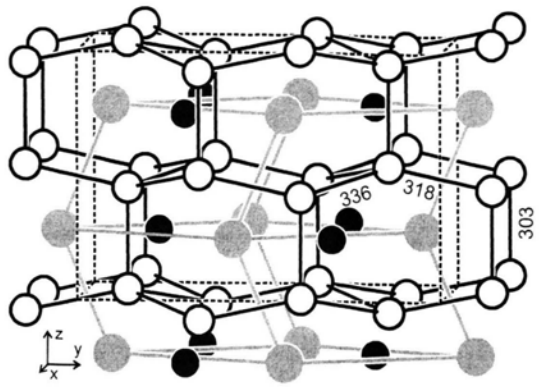

Fig. 1. Cutout of the $YbPdSn_2$ structure. Large gray, medium open, and black filled circles represent ytterbium, palladium, and tin, respectively. Selected bond lengths within the tin sublattice are given in pm.

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