

## Structure Refinements of $REAuSn$ ( $RE = Sm, Gd, Tm$ )

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Well-shaped single crystals of the stannides  $REAuSn$  ( $RE = Sm, Gd, Tm$ ) were obtained from arc-melted ingots. The samples were investigated on the basis of X-ray powder and single crystal data: NdPtSb type,  $P6_3mc$ ,  $Z = 2$ ,  $a = 467.3(1)$ ,  $c = 748.9(2)$  pm,  $wR2 = 0.0468$ ,  $BASF = 0.273(14)$ ,  $273 F^2$  values, 12 variables for  $SmAuSn$ ,  $a = 465.14(9)$ ,  $c = 742.4(1)$  pm,  $wR2 = 0.0686$ ,  $265 F^2$  values, 11 variables for  $GdAuSn$ , and  $MgAgAs$  type,  $F\bar{4}3m$ ,  $Z = 4$ ,  $a = 658.54(9)$  pm,  $wR2 = 0.0384$ ,  $120 F^2$  values, 5 variables for  $TmAuSn$ . The  $[AuSn]$  networks in  $SmAuSn$  and  $GdAuSn$  are two-dimensional with intralayer Au–Sn distances of 278 and 277 pm in the slightly puckered  $Au_3Sn_3$  hexagons, respectively. The interlayer Au–Sn distances of 308 and 302 pm are much longer.  $TmAuSn$  has a network of corner-sharing  $AuSn_{4/4}$  tetrahedra with Au–Sn distances of 285 pm. The thulium atoms fill octahedral sites formed by the tin atoms. The crystal chemistry of these  $REAuSn$  stannides is briefly discussed.

**Key words:** Rare Earth Compounds, Stannides,  
Crystal Chemistry

## Introduction

The series of equiatomic  $REAuSn$  ( $RE =$  rare earth metal) stannides has thoroughly been investigated in recent years in view of the fascinating magnetic and transport properties. The literature on these stannides has recently been summarized [1]. Despite the extensive spectroscopic and magnetic studies, so far, only the structures of  $ScAuSn$  [1],  $YAuSn$  [1],  $CeAuSn$  [2],  $EuAuSn$  [3],  $YbAuSn$  [4], and  $LuAuSn$  [1] have been refined on the basis of single crystal data. In the course of our systematic studies of structure-property relations of equiatomic  $RETX$  intermetallics we obtained well shaped crystals of  $SmAuSn$ ,  $GdAuSn$ , and

$TmAuSn$ . The structure refinements of these stannides are reported herein.

## Experimental Section

### Synthesis

Starting materials for the preparation of the  $REAuSn$  stannides were ingots of the rare earth metals (Johnson Matthey, Chempur or Kelpin), a gold bar (Heraeus, rolled to a foil), and tin granules (Merck), all with stated purities better than 99.9%. All samples were prepared directly from the elements *via* arc-melting [5] under an atmosphere of *ca.* 600 mbar argon. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves. The elements were weighed in the ideal 1 : 1 : 1 atomic ratios. After the first melting stage, all samples were turned over and remelted three times in the arc-melting crucible in order to achieve homogeneity. The weight losses were always smaller than 0.5 weight-%. The  $REAuSn$  stannides were obtained as silvery buttons with metallic luster that are stable in air for months.

### X-ray film data and structure refinements

The samples were investigated through Guinier powder diagrams using  $Cu-K\alpha_1$  radiation and  $\alpha$ -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). To facilitate correct indexing, the experimental patterns were compared to calculated ones [6] using the atomic positions obtained from the structure refinements. The lattice parameters (Table 1) are in good agreement with the Debye-Scherrer data originally published by Dwight [7].

Well-shaped single crystals of  $SmAuSn$ ,  $GdAuSn$ , and  $TmAuSn$  were isolated from the arc-melted samples by mechanical fragmentation 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 of  $SmAuSn$  and  $TmAuSn$  were collected at r.t. by use of a four-circle diffractometer (CAD4) with graphite monochromatized  $Mo-K\alpha$  (71.073 pm) 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 psi-scan data, followed by spherical absorption corrections. The  $GdAuSn$  data set was collected at room temperature by use of a Stoe IPDS-II diffractometer with graphite monochromatized  $Mo-K\alpha$  radiation. The absorption correction was numerical. All relevant crystallographic data for the data collections and evaluations are listed in Table 1.

Empirical Formula	SmAuSn	GdAuSn	TmAuSn
Molar mass [g/mol]	466.01	472.91	484.59
Unit cell dimensions [pm]	$a = 467.3(1)$	$a = 465.14(9)$	$a = 658.54(9)$
(Guinier powder data) [pm]	$c = 748.9(2)$	$c = 742.4(1)$	
$V$ [nm <sup>3</sup> ]	0.1416	0.1391	0.2856
$Z$	2	2	2
Space group	$P6_3mc$ (No. 186)	$P6_3mc$ (No. 186)	$F\bar{4}3m$ (No. 216)
Calculated density [g/cm <sup>3</sup> ]	10.93	11.29	11.27
Crystal size [ $\mu\text{m}^3$ ]	$45 \times 65 \times 65$	$45 \times 45 \times 90$	$20 \times 20 \times 45$
Transm. ratio (max/min)	2.55	2.88	3.63
Absorption coefficient [mm <sup>-1</sup> ]	80.5	84.7	90.4
$F(000)$	382	386	792
$\theta$ range [°]	5 to 35	5 to 35	5 to 40
Range in $hkl$	$\pm 7, \pm 7, \pm 12$	$\pm 7, -6/+7, \pm 11$	$\pm 11, \pm 11, -11/+10$
Total no. reflections	2310	1934	1586
Independent reflections	273	265	120
	( $R_{\text{int}} = 0.0965$ )	( $R_{\text{int}} = 0.0497$ )	( $R_{\text{int}} = 0.1181$ )
Reflections with $I > 2\sigma(I)$	239	235	113
	( $R_{\text{sigma}} = 0.0347$ )	( $R_{\text{sigma}} = 0.0236$ )	( $R_{\text{sigma}} = 0.0404$ )
Data/parameters	273 / 12	265 / 11	120 / 5
Goodness-of-fit on $F^2$	1.119	1.145	1.111
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0198$	$R1 = 0.0260$	$R1 = 0.0288$
	$wR2 = 0.0453$	$wR2 = 0.0644$	$wR2 = 0.0369$
$R$ Indices (all data)	$R1 = 0.0261$	$R1 = 0.0347$	$R1 = 0.0337$
	$wR2 = 0.0468$	$wR2 = 0.0686$	$wR2 = 0.0384$
Extinction coefficient	0.024(1)	0.027(3)	0.0018(2)
Flack parameter	—	0.01(2)	−0.04(8)
BASF	0.273(14)	—	—
Largest diff. peak and hole [e/Å <sup>3</sup> ]	2.10 and −1.68	3.27 and −3.53	1.85 and −1.96

Table 1. Crystal data and structure refinement for SmAuSn, GdAuSn, and TmAuSn.

Atom	Wyckoff position	$x$	$y$	$z$	$U_{11}$	$U_{33}$	$U_{12}$	$U_{eq}$
SmAuSn (space group $P6_3mc$ )								
Sm	2a	0	0	0.00859(13)	84(2)	35(3)	42(1)	68(2)
Au	2b	2/3	1/3	0.82033(6)	87(2)	124(3)	44(1)	99(2)
Sn	2b	2/3	1/3	0.23088(15)	72(4)	53(5)	36(2)	66(2)
GdAuSn (space group $P6_3mc$ )								
Gd	2a	0	0	0.00000(16)	62(3)	33(4)	31(1)	52(2)
Au	2b	2/3	1/3	0.18489(6)	52(3)	126(4)	26(1)	77(2)
Sn	2b	2/3	1/3	0.77829(18)	35(4)	57(6)	17(2)	42(3)
TmAuSn (space group $F\bar{4}3m$ )								
Tm	4b	1/2	1/2	1/2	42(5)	$U_{11}$	0	$U_{11}$
Au	4c	1/4	1/4	1/4	62(2)	$U_{11}$	0	$U_{11}$
Sn	4a	0	0	0	64(5)	$U_{11}$	0	$U_{11}$

Table 2. Atomic coordinates and anisotropic displacement parameters (pm<sup>2</sup>) for SmAuSn, GdAuSn and TmAuSn.  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.  $U_{11} = U_{22}$ ,  $U_{13} = U_{23} = 0$ .

In agreement with our previous investigations [1], the SmAuSn and GdAuSn data sets were compatible with space group  $P6_3mc$ , and the TmAuSn data set with  $F\bar{4}3m$ . The atomic parameters of YAuSn and LuAuSn [1] were taken as starting values and the structures were refined using SHELXL-97 (full-matrix least-squares on  $F_o^2$ ) [8] with anisotropic atomic displacement parameters for all sites. Refinement of the occupancy parameters in separate series of least-squares cycles revealed no deviations from the ideal compositions. For each data set the Flack parameter [9, 10] was carefully checked in order to refine the correct absolute structure. The data set of SmAuSn revealed twinning by inversion. Final difference Fourier synthesis revealed no sig-

nificant residual peaks (see Table 1). The refined positional parameters and interatomic distances are listed in Tables 2 and 3. Further details on the structure refinements are available.\*

#### EDX analyses

The bulk samples and the single crystals measured on the diffractometers were analyzed by EDX using a LEICA 420 I

\*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD-416420 (SmAuSn), CSD-416418 (GdAuSn), and CSD-416419 (TmAuSn).

Table 3. Interatomic distances (pm), calculated with the lattice parameters taken from X-ray powder data of SmAuSn, GdAuSn and TmAuSn. All distances within the first coordination spheres are listed. Standard deviations are equal or less than 0.1 pm.

Sm:	3	Au	304.4	Gd:	3	Au	301.6	Tm:	4	Au	285.2
	3	Sn	317.0		3	Sn	315.0		6	Sn	329.3
	3	Sn	340.7		3	Sn	338.8	Au:	4	Sn	285.2
	3	Au	356.8		3	Au	356.2		4	Tm	285.2
Au:	3	Sn	278.0	Au:	3	Sn	277.4	Sn:	4	Au	285.2
	3	Sm	304.4		3	Gd	301.6		6	Tm	329.3
	1	Sn	307.5		1	Sn	301.9				
	3	Sm	356.8		3	Gd	356.2				
Sn:	3	Au	278.0	Sn:	3	Au	277.4				
	1	Au	307.5		1	Au	301.9				
	3	Sm	317.0		3	Gd	315.0				
	3	Sm	340.7		3	Gd	338.8				

scanning electron microscope with SmF<sub>3</sub>, GdF<sub>3</sub>, TmF<sub>3</sub>, Au, and Sn as standards. The single crystals mounted on the quartz fibres were coated with a carbon film. Pieces of the bulk samples were polished with different silica and diamond pastes and left unetched for the analyses in the scanning electron microscope in backscattering mode. The EDX analyses revealed non impurity elements and were in agreement with the refined compositions.

## Discussion

### Crystal chemistry

The structure refinements clearly revealed the hexagonal NdPtSb type structure for SmAuSn and

GdAuSn, and the cubic MgAgAs type for TmAuSn. These results fully parallel our recent investigations on ScAuSn, YAuSn, and LuAuSn. For drawings of these simple structures and further crystal chemical details we refer to a published review [1]. Here we discuss only the relevant interatomic distances in SmAuSn, GdAuSn, and TmAuSn.

The intralayer Au–Sn distances in the slightly puckered Au<sub>3</sub>Sn<sub>3</sub> hexagons of SmAuSn (277 pm) as well as the Au–Sn distance within the three-dimensional network of corner-sharing AuSn<sub>4/4</sub> tetrahedra in TmAuSn (285 pm) are close to the sum of the covalent radii [11] of 274 pm. These contacts can be considered as strongly bonding. In contrast, the interlayer Au–Sn distances in SmAuSn (308 pm) and GdAuSn (302 pm) are significantly longer. These interlayer Au–Sn distances are a function of the size of the rare earth atom (lanthanoid contraction). With decreasing radius of the rare earth element, the puckering of the Au<sub>3</sub>Sn<sub>3</sub> hexagons becomes more pronounced, and the interlayer Au–Sn distances decrease, *i. e.* 323 pm in CeAuSn [2], 308 pm in SmAuSn, 302 pm in GdAuSn, and 297 pm in YAuSn [1].

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- [1] C. P. Sebastian, H. Eckert, S. Rayaprol, R.-D. Hoffmann, R. Pöttgen, *Solid State Sci.* **8**, 506 (2006).
- [2] D. Niepmann, R. Pöttgen, K. M. Poduska, F. J. Di-Salvo, H. Trill, B. D. Mosel, *Z. Naturforsch.* **56b**, 1 (2001).
- [3] R. Pöttgen, R.-D. Hoffmann, R. Müllmann, B. D. Mosel, G. Kotzyba, *Chem. Eur. J.* **3**, 1852 (1997).
- [4] R.-D. Hoffmann, R. Pöttgen, D. Kußmann, R. Müllmann, B. D. Mosel, *Chem. Mater.* **13**, 4019 (2001).
- [5] R. Pöttgen, Th. Gulden, A. Simon, *GIT Labor Fachzeitschrift* **43**, 133 (1999).
- [6] K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Crystallogr.* **10**, 73 (1977).
- [7] A. E. Dwight, *Proc. Rare Earth Res. Conf.*, 12<sup>th</sup>, Colorado **1**, 480 (1976).
- [8] G. M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, University of Göttingen, Germany (1997).
- [9] H. D. Flack, G. Bernardinelli, *Acta Crystallogr. A* **55**, 908 (1999).
- [10] H. D. Flack, G. Bernardinelli, *J. Appl. Crystallogr.* **33**, 1143 (2000).
- [11] J. Emsley, *The Elements*, Oxford University Press, Oxford (1999).