High-pressure High-temperature Synthesis, Magnetic Properties and X-ray Absorption Spectroscopy of Phases RE_3Sn_7 and $\text{hp-RESn}_3\text{-x}$ ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$)

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Katrin Meier, Leonid Vasylechko, Raul Cardoso-Gil, Ulrich Burkhardt, Walter Schnelle, et al.. High-pressure High-temperature Synthesis, Magnetic Properties and X-ray Absorption Spectroscopy of Phases RE_3Sn_7 and $\text{hp-RESn}_3\text{-x}$ ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$). *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2010, 636 (9-10), pp.1695. 10.1002/zaac.201000147 . hal-00552475

HAL Id: hal-00552475

<https://hal.science/hal-00552475>

Submitted on 6 Jan 2011

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Zeitschrift für Anorganische und
Allgemeine Chemie

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Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.201000147.R1
Wiley - Manuscript type:	Article
Date Submitted by the Author:	27-Apr-2010
Complete List of Authors:	Meier, Katrin; MPI CPfS, Chemical Metals Science Vasylechko, Leonid; Lviv PNU, Semiconductor Electronics Cardoso-Gil, Raul; MPI CPfS, Chemical Metals Science Burkhardt, Ulrich; MPI CPfS, Chemical Metals Science Schnelle, Walter; MPI CPfS, Chemical Metals Science Schmidt, Marcus; MPI CPfS, Chemical Metals Science Grin, Yuri; MPI CPfS, Chemical Metals Science Schwarz, Ulrich; MPI CPfS, Chemical Metals Science
Keywords:	high-pressure synthesis, tin, terbium, holmium, erbium

ARTICLE

DOI: 10.1002/zaac.200((will be filled in by the editorial staff))

High-pressure High-temperature Synthesis, Magnetic Properties and X-ray Absorption Spectroscopy of Phases RE_3Sn_7 and $hp-RESn_{3-x}$ ($RE = Tb, Ho, Er$)

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Dedicated to Prof. Dr. Bernd Harbrecht on the Occasion of his 60th Birthday

Keywords: terbium; holmium; erbium; tin; high-pressure synthesis

The high-temperature high-pressure syntheses of binary phases $hp-RESn_{3-x}$ ($RE = Tb, Ho, Er$) was reinvestigated showing good agreement with previously determined stability fields concerning pressure and temperature conditions. Phases $hp-RESn_{3-x}$ adopt a cubic Cu_3Au arrangement ($a = 466.52(6)$ pm for $hp-TbSn_{3-x}$; $a = 465.44(8)$ pm for $hp-HoSn_{3-x}$ and $a = 464.98(9)$ pm for $hp-ErSn_{3-x}$). Superstructure reflections observed in experiments with synchrotron radiation indicate an ordered arrangement for $HoSn_{3-x}$ prepared at 8.4(8) GPa and 1270 K (space group $Pm\bar{3}m$). $hp-HoSn_{3-x}$ transforms exothermally at 460 K and ambient pressure into the low-pressure modification $HoSn_{3-x}$ indicating that the ordered Cu_3Au -type arrangement is a metastable high-pressure phase.

A second set of phases are identified as compounds RE_3Sn_7 ($RE = Ho, Er$) being isotypic to the ambient pressure modifications Gd_3Sn_7 and Tb_3Sn_7 (space group $Cmmm$; lattice parameters $a = 434.95(7)$ pm, $b = 2615.6(6)$ pm, $c = 442.09(7)$ pm for Ho_3Sn_7

and $a = 434.29(5)$ pm, $b = 2607.2(4)$ pm, $c = 441.49(5)$ pm) for Er_3Sn_7). The crystal structure of compounds RE_3Sn_7 are interpreted as an intergrowth of AlB_2 -, CaF_2 - and $AuCu_3$ -like segments. Analysis of the chemical bonding in Er_3Sn_7 by means of the electron localizability approach reveals two-centre Sn-Sn bonding in the AlB_2 -like segment and multi-centre bonding in the $AuCu_3$ - and CaF_2 -like motifs.

The electrical resistivity of $\rho \approx 31 \mu\Omega \text{ cm}$ at 300 K reveals that $hp-HoSn_{3-x}$ is a metallic conductor. The phases $hp-RESn_{3-x}$ and RE_3Sn_7 ($RE = Ho, Er$) show paramagnetic Curie-Weiss behaviour of the rare earth metal ions Ho^{3+} and Er^{3+} , respectively. Ho_3Sn_7 and Er_3Sn_7 order antiferromagnetically at 10.0 K and 8.2 K, respectively. The high-pressure phases $RESn_{3-x}$ show no magnetic order above 2 K. XAS measurements on the compounds Tb_3Sn_7 and $hp-TbSn_{3-x}$ indicate a $4f^8$ configuration evidencing the oxidation state +3 for terbium.

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Introduction

In the context of recent high-pressure high-temperature syntheses of new binary silicon- and germanium-rich intermetallic compounds [1-11], the tin-rich parts of the phase diagrams $RE-Sn$ ($RE = Tb, Ho, Er$) were reinvestigated. An earlier study reports on the formation of cubic close packed Cu_3Au -type phases $RESn_3$ ($RE = Tb, Ho, Er$) at high-pressure high-temperature conditions [12]. Lowering of the synthesis pressure yielded hitherto unidentified products.

At ambient pressure the tin-richest compounds in the binary systems $RE-Sn$ ($RE = Tb, Ho, Er$) have the composition $RESn_{3-x}$. At slightly lower tin contents, phases with a composition RE_2Sn_5 have been described for $RE = Ho$ and Er while for $RE = Tb$ a Gd_3Sn_7 -like orthorhombic crystal structure [13] was observed. This atomic pattern comprises a manifold of different tin coordination

environments ranging from coordination number seven via nine to twelve [14].

Complete definitions of stability fields in high-pressure high-temperature synthesis have to address a three-dimensional parameter space with the consequence that even a course grid with respect to each variable would result in a large number of experiments. Thus, the present investigation focuses on the characterisation of the prepared phases RE_3Sn_7 and $hp-RESn_{3-x}$ with regards to crystal structure and composition as well as electrical conductivity and magnetic susceptibility. Additionally, thermal decomposition at ambient pressure will be discussed for $hp-HoSn_{3-x}$ in the context of *in-situ* X-ray diffraction experiments.

Results and Discussion

Compounds RE_3Sn_7 ($RE = Tb, Ho, Er$)

At ambient pressure, arc melting of samples with compositions $Ho : Sn$ between 1 : 2.2 and 1 : 3 results in mixtures of phases isotypic to $HoSn_2$ [15] and a tin-rich solid solution $Sn(Ho)$ with $\beta-Sn$ structure. Subsequent high-pressure high-temperature treatments basically confirm the earlier phase diagrams [12], e.g., the formation of an hitherto unidentified orthorhombic phase and a tin-rich solid solution $Sn(Ho)$ at 2 GPa and a temperature of 720 K for starting compositions $Ho : Sn$ between 1 : 2.2 and 1 : 2.85.

Determining the chemical composition of the product Ho_3Sn_7 (starting composition 1 : 2.33) by EDXS (Fig. 1 top) results in a Ho : Sn ratio of 1 : 2.31(5). The low-pressure phase in the system Tb–Sn is identified as Tb_3Sn_7 which can be synthesized already at ambient pressures [14]. Energy dispersive X-ray spectroscopy (EDXS) of a polished sample grown in a tin flux at 1370 K and ambient pressure (annealing time 96 h) indicates a composition Tb:Sn = 1 : 2.22(8) in satisfactory agreement with a ratio of 1 : 2.33 calculated for a composition 3 : 7 (Fig. 1 bottom). Conditions for the syntheses of compounds RE_3Sn_7 ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$) are summarized in Table 1.

Fig. 1. Electron back scattering images of compounds RE_3Sn_7 ($\text{RE} = \text{Ho}, \text{Tb}$). Top: Sample with a nominal composition Ho : Sn 3 : 7 showing the main phase Ho_3Sn_7 (grey), tin-rich solid solution (dark spots) and Ho : Sn 1 : 0.60(1) (bright spot on the left). Bottom: Tb_3Sn_7 grown in a tin flux. The main phase is light grey, dark spots represent tin-rich solid solution. On the left, residuals of the crucible are visible.

Table 1. Starting composition, P, T -reaction conditions, identified phases and composition of the reaction products as determined by EDXS for syntheses of compounds RE_3Sn_7 ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$).

Starting Composition	T / K P / GPa	Phases	Composition EDX
Tb : Sn 1 : 7	1370 0.0001	Tb_3Sn_7 Sn(Ho)	1 : 2.22(8)
Tb : Sn 1 : 3	920 1.0(1)	Tb_3Sn_7 Sn(Ho)	
Ho : Sn 1 : 2.2 – 2.85	720 2.0(2)	Ho_3Sn_7 Sn(Ho) $\text{Ho}_{1.6}\text{Sn}$	1 : 2.31(5) 1 : 0.60(1)
Er : Sn 1 : 2.33	1078 5.0(5)	Er_3Sn_7 Sn(Ho)	

After subtracting the contributions of the phase with β -Sn-type crystal structure from the mixtures, the remaining X-ray powder diffraction lines can be indexed on the basis of an orthorhombic lattice. A comparison of experimental and calculated intensities indicates crystal structures isotopic to the ambient pressure modification of Gd_3Sn_7 or Tb_3Sn_7 [13, 14]. Crystallographic data and refinement results for the synthesized phases RE_3Sn_7 ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$) are shown in Table 2 and Table 3.

Table 2. Crystallographic data and refinement parameters of compounds RE_3Sn_7 ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$) using the ordered model of Gd_3Sn_7 [13] (see Fig. 2) Refinement of a disordered Tb_3Sn_7 -type model [14] did not result in a significant improvement concerning residuals or displacement parameters.

Temperature, K	296(2)
Diffractometer type	Huber Image Plate Guinier Camera G670
Wavelength / Å	1.54056 (Cu $K\alpha_1$)
Crystal system	orthorhombic
Space group (No.); Z	$Cmmm$ (65); 2
Tb_3Sn_7 : unit cell parameters / pm; unit cell volume / 10^6 pm^3	$a = 436.6(1)$; $b = 2634.1(1)$ $c = 443.7(1)$; $V = 510.28$
Ho_3Sn_7 : unit cell parameters / pm; Unit cell volume / 10^6 pm^3	$a = 4.3495(7)$; $b = 26.156(6)$ $c = 4.4209(7)$; $V = 502.95$
Er_3Sn_7 : unit cell parameters / pm; Unit cell volume / 10^6 pm^3	$a = 4.3429(5)$; $b = 26.072(4)$ $c = 4.4149(5)$; $V = 499.89$
Measurement range / Degree	$15 < 2\theta < 85$
$N(\text{meas})$ ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$)	14984; 14184; 13984
Reflections ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$)	140, 141, 139
Refinement method	Full profile (Rietveld)
Refined structure parameters	14
R_{wp} ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$)	0.107, 0.101, 0.099
R_p ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$)	0.160, 0.123, 0.110
R_1 ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$)	0.083, 0.085, 0.086

Table 3. Atomic coordinates and isotropic displacement parameters of compounds RE_3Sn_7 ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$).

Atom	Wyckoff position	x	y	z	$U_{\text{iso}} / 10^4 \text{ pm}^2$
Tb1	2d	0	0	$\frac{1}{2}$	0.011(1)
Tb2	4i	0	0.3115(1)	0	0.014(1)
Sn1	2b	$\frac{1}{2}$	0	0	0.011(1)
Sn2	4j	0	0.4043(1)	$\frac{1}{2}$	0.009(1)
Sn3	4i	0	0.0955(1)	0	0.009(1)
Sn4	4j	0	0.2123(1)	$\frac{1}{2}$	0.008(1)
Ho1	2d	0	0	0	0.012(1)
Ho2	4i	0	0.3102(1)	0	0.008(1)
Sn1	2b	$\frac{1}{2}$	0	0	0.017(2)
Sn2	4j	0	0.4041(1)	$\frac{1}{2}$	0.012(1)
Sn3	4i	0	0.0948(1)	0	0.007(1)
Sn4	4j	0	0.2100(1)	$\frac{1}{2}$	0.014(1)
Er1	2d	0	0	$\frac{1}{2}$	0.003(1)
Er2	4i	0	0.3106(1)	0	0.007(1)
Sn1	2b	$\frac{1}{2}$	0	0	0.013(1)
Sn2	4j	0	0.4029(1)	$\frac{1}{2}$	0.008(1)
Sn3	4i	0	0.0957(1)	0	0.011(1)
Sn4	4j	0	0.2108(1)	$\frac{1}{2}$	0.011(1)

The crystal structure of the compounds RE_3Sn_7 may be interpreted as an intergrowth [17, 18] of 2D segments of the structural patterns of AlB_2 ($RESn_2$) and $AuCu_3$ ($RESn_3$) prototypes [19] in the ratio 1:1 (Fig. 2). They are separated by fragments adopting the CaF_2 motif ($RESn_2$). The total composition of the unit cell can thus be expressed as $[RESn_2]_4[RESn_3]_2 = RE_6Sn_{14}$. Within the AlB_2 segments, tin atoms are located in the centre of trigonal prisms formed by RE atoms and form zig-zag-like chains along the [100] direction. Characteristic features of the CaF_2 -, $AuCu_3$ - and $AuCu$ -like segments are rectangular networks formed either by Sn atoms alone or by a mixture of Sn and RE atoms in the ratio 1:1 (Fig. 2).

Fig. 2. Left: Gd_3Sn_7 -type crystal structure [13] of phases RE_3Sn_7 ($RE = Tb, Ho, Er$), viewed along [001]. Fragments of the atomic pattern adopting AlB_2 -, $AuCu_3$ - and CaF_2 -motifs [13] are indicated (left). Right: Parent structures of the AlB_2 -, $AuCu_3$ - and CaF_2 -motifs in corresponding orientations. Please notice that the unit cell of the $AuCu_3$ and the CaF_2 segments have been shifted with respect to the usual setting. The sequence CaF_2 - $AuCu_3$ - CaF_2 can be alternatively considered to correspond to the $TiAl_3$ sequence.

Phases $hp-RESn_{3-x}$

Pressure increase with respect to the stability fields of the 3 : 7 phases results for starting compositions $RE : Sn = 1 : 3$ in the formation of cubic phases and tin-rich solid solution $Sn(Ho)$ (Fig. 3). The presence of the β - Sn phase indicates that the composition of the nominal Cu_3Au -type phase is tin-deficient. Thus, samples with a slightly lower $Ho : Sn$ ratio of 1 : 2.85 were prepared. Determining the chemical composition of the product $hp-HoSn_{3-x}$ with EDXS by averaging the results of measurements at eight different spots of an ingot result in a $Ho : Sn$ ratio of 1 : 2.7(2)

Fig. 3. Electron backscattering image of $hp-HoSn_{3-x}$ (grey, main phase, $x = 0.3(2)$) containing traces of tin-rich solid solution $Sn(Ho)$ (black spotty area top left).

Table 4. Starting composition, P,T -reaction conditions, identified phases and composition of the reaction products as determined by EDXS for phases $hp-RESn_{3-x}$ ($RE = Tb, Ho, Er$).

Starting Comp.	P / GPa	T / K	Phases	Composition EDX
Tb : Sn	4.0(4)	– 920 –	$hp-TbSn_{3-x}$	1 : 2.7(2)
1 : 3	5.7(6)	1270	$Sn(Ho)$	
Ho : Sn	5.7(6)	– 870 –	$hp-HoSn_{3-x}$	
1 : 3	8.5(9)	1270	$Sn(Ho)$	
Ho : Sn	5.7(6)	– 870 –	$hp-HoSn_{3-x}$	1 : 2.7(2)
1 : 2.85	8.5(9)	1270	$Sn(Ho)$	
Er : Sn	11(1)	1173	$hp-ErSn_{3-x}$	
1 : 3			$Sn(Ho)$	

(Fig. 3). Reaction conditions for the preparation of high-pressure phases $hp-RESn_{3-x}$ ($RE = Tb, Ho, Er$) are summarized in Table 4.

With respect to the crystal structures of the phases $hp-RESn_{3-x}$ adopting a Cu_3Au -type atomic pattern, two idealized situations of these substitution varieties of an fcc arrangement can be distinguished: A randomly disordered face-centred cubic crystal structure (space group $Fm\bar{3}m$) and an –at least partially– site-ordered, primitive cubic arrangement (space group $Pm\bar{3}m$). A synchrotron powder X-ray diffraction measurement of a sample $hp-HoSn_{3-x}$ with a nominal composition 1 : 2.85 reveals broad reflection profiles which are attributed to sample inhomogeneities. However, the presence of weak reflections, e.g., slightly above 6 degrees and 8 degrees two theta (Fig. 4), indicate a primitive cubic lattice.

Using the same thermal displacement parameter for both atomic positions, the refinements indicate an occupation of Wyckoff position $3c$ ($\frac{1}{2}, \frac{1}{2}, 0$) mainly by tin with s.o.f. $Sn = 0.95(1)$ and s.o.f. $Ho = 0.05(1)$. For $1a$ ($0, 0, 0$), the results converge to s.o.f. $Ho = 0.90(1)$ and s.o.f. $Sn = 0.05(1)$ indicating approximately 5% defects on position $1a$. These refined occupancies result in a composition $HoSn_{2.76(15)}$ consistent with the EDX results. Thus, contrary to the findings of the earlier investigation [12], the synchrotron diffraction data evidence that the high-pressure phase $hp-HoSn_{3-x}$ adopts a partially ordered Cu_3Au -type arrangement [16].

Fig. 4. Powder X-ray diffraction pattern of hp-HoSn_{3-x}. The weak reflections (see inset) at above six and eight degrees, respectively, indicate a partially ordered arrangement of the holmium and tin atoms in a primitive cubic crystal structure. Stars indicate reflections of a tin-rich solid solution Sn(Ho) with β -Sn-like crystal structure.

In order to study the thermal stability of the cubic high-pressure phase hp-HoSn_{3-x}, differential scanning calorimetry measurements (Fig. 5) have been combined with temperature-dependent *in-situ* powder X-ray diffraction experiments (Fig. 6). The exothermic character of the first transition as revealed by DSC indicates a monotropic transformation. The diffraction data show that Cu₃Au-type hp-HoSn_{3-x} transforms into the low-pressure modification HoSn_{3-x} (GdSn_{3-x} type [13]) below 470 K (Fig. 7). The upper limit of the transition temperature of 450 K which is measured in the diffraction experiments is in good agreement with the onset temperature of 460 K as determined by DSC measurements. The remaining difference is assigned to the kinetic control of the transformation and the different heating rates. The effect at temperatures slightly above this transformation is attributed to the melting of tin-rich solid solution Sn(Ho). According to the phase diagram [14], lp-HoSn_{3-x} decomposes into Ho₂Sn₅ and a solid solution Sn(Ho) at 701 K.

Fig. 5. Differential scanning calorimetry measurement of hp-HoSn_{3-x} using a heating rate of 10 K min⁻¹. The exothermic effect at 460 K is attributed to the phase transition from hp-HoSn_{3-x} to the orthorhombic ambient pressure modification of HoSn_{3-x}. Black curve: increasing temperature; grey curve: decreasing T .

Fig. 6. Powder X-ray diffraction patterns of hp-HoSn_{3-x} and its transformation products at elevated temperatures. The transformation of hp-HoSn_{3-x} into HoSn_{3-x} is already visible at 448 K and completed at 473 K. In the pattern recorded in the transition range, squares indicate reflections of residual hp-HoSn_{3-x}.

Fig. 7. Crystal structures of phases RESn_{3-x} (left) isotypic to GdSn_{3-x} [13] and the constituting segments (right). The phases hp-RESn_{3-x} are isotypic to AuCu₃. (RE = Tb, Ho, Er).

Finally, at 800 K Ho₂Sn₅ decomposes into HoSn₂ and a solid solution Sn(Ho) with β -Sn arrangement. Upon cooling the effect at 704 K is attributed to the crystallisation of a mixture of tin-rich holmium phases and that around 500 K to the recrystallization of the solid solution Sn(Ho) adopting a β -Sn pattern. In accordance with these assignments, powder X-ray diffraction data of samples measured after the

heating cycle evidence the formation of a solid solution $\text{Sn}(\text{Ho})$ with $\beta\text{-Sn}$ crystal structure, the compound Ho_2Sn_5 and a third phase. After reaching the maximum temperature of the experiment (483 K), the formed modification HoSn_{3-x} remains stable upon cooling to ambient conditions indicating the metastable character of hp-HoSn_{3-x} .

Chemical bonding in Er_3Sn_7

The differentiation within the structure fragments in phases RE_3Sn_7 ($\text{RE} = \text{Tb}, \text{Ho}, \text{Er}$) facilitates different atomic interactions within the crystal structure. This indication was investigated by an analysis of the chemical bonding in direct space applying the electron localizability indicator technique.

In Er_3Sn_7 , a characteristic feature of ELI within the AlB_2 segment is the formation of maxima close to the Sn-Sn contacts (Fig. 8 bottom) indicating 2c (two-centre) Sn-Sn bonding. ELI attractors above and below each Sn atoms would reflect lone pairs if the zigzag chains were completely isolated. In the crystal structure of RE_3Sn_7 , they are attributed to multi-centre interactions. In all segments the bonds within mixed RE-Sn square nets have 3c character (Fig. 8 top), in the square Sn nets 2c Sn-Sn bonding is observed. The ELI attractors above and below the tin atoms indicate 5c Sn_5 or SnEr_4 interactions between adjacent nets.

The presence of multi-centre bonds suggests a rather metallic behaviour of the RE_3Sn_7 phases. This is confirmed by the calculated total electronic density of states (Fig. 9). Even assuming a strongly localized character of the Er 4f states, there is a significant density of states at the Fermi level originating from Sn 5p states.

Fig. 8. Chemical bonding in Er_3Sn_7 : Distribution of the electron localizability indicator (ELI) within the CaF_2 - and AuCu_3 -like segments (top) and the AlB_2 -like fragment (bottom) visualized by isosurfaces of $\gamma = 1.04$, $\gamma = 1.07$ and $\gamma = 1.11$, respectively. Atomic arrangement and distribution of ELI in the unit cell of Er_3Sn_7 (middle).

Fig. 9. Computed total electronic density of states (DOS) with partial atomic contributions for Er_3Sn_7 .

Physical properties of phases RE_3Sn_7 and hp-RESn_{3-x}

With respect to the electronic states of the terbium compounds, X-ray absorption spectra reveal that the white line (WL) of TbSn_{3-x} is located at the same position as the low-energy contribution of mixed-valent Tb_4O_7 ($[\text{Tb}^{3+}]_2[\text{Tb}^{4+}]_2\text{O}_7$) and coincides within the experimental resolution of 1 eV with the WL of $\text{Tb}^{3+}\text{PO}_4$ (Fig. 10). Consequently, terbium is assigned to the electronic state $4f^8$. In Tb_3Sn_7 , the WL is located at the same position as that of $\text{Tb}^{3+}\text{PO}_4$ also evidencing Tb^{3+} .

The magnetic susceptibilities $\chi(T) = M/H$ of hp-HoSn_{3-x} and Ho_3Sn_7 are well described by a Curie-Weiss law at high temperatures (Fig. 11 top). From fits to the data above 20 K the following effective moments and paramagnetic Weiss temperatures are obtained: $\text{HoSn}_{2.85}$, $\mu_{\text{eff}} = 10.46 \mu_B$, $\theta_P = -14.9 \text{ K}$; Ho_3Sn_7 , $\mu_{\text{eff}} = 10.54 \mu_B$, $\theta_P = -10.5 \text{ K}$. The observed behaviour confirms the presence of trivalent Ho ions with $4f^{10}$ configuration (5I_8 multiplet, $\mu_{\text{free}} = 10.61 \mu_B$).

Fig. 10. X-ray absorption spectra of hp-TbSn_{3-x} (top) and Tb_3Sn_7 (bottom) indicating a $4f^8$ configuration of terbium in both compounds consistent with the oxidation state Tb^{3+} .

Fig. 11. Inverse magnetic susceptibilities $1/\chi$ versus temperature T for polycrystalline samples of hp-HoSn_{3-x} and Ho_3Sn_7 (top) as well as hp-ErSn_{3-x} and Er_3Sn_7 (bottom) in a field $\mu_0 H = 1$ T. The insets show $\chi(T)$ for low temperatures and $\mu_0 H = 0.01$ T.

and suggests antiferromagnetic interactions. A broad cusp in $\chi(T)$ due to antiferromagnetic ordering of the Ho moments is observed (Fig. 11 top, inset) at $T_N = 13.6$ K for Ho_3Sn_7 . For hp-HoSn_{3-x} no sharp anomaly but only a very broad hump is visible at approximately 10 K.

In isothermal magnetization curves measured at $T = 1.8$ K on both holmium compounds $M(H)$ increases sub-linearly up to ~ 2 T and then becomes linear. Saturation is not reached for the maximum field (hp-HoSn_{3-x} : $M(7\text{ T}) \sim 5.1 \mu_B$; Ho_3Sn_7 : $M(7\text{ T}) \sim 4.3 \mu_B$). The presence of tin at the grain boundaries of both samples is concluded from a superconducting transition at 3.6 K in a field of 1 mT. As can be deduced from the field-cooling Meissner effect the volume of Sn metal is small (flux expulsion $< 1\%$), however the shielding (zero-field cooling) of the crystallites of the main phase by the surrounding superconducting tin is almost perfect. The electrical resistivity $\rho(T)$ of the hp-HoSn_{3-x} sample is typically metallic with a room temperature value $\rho(300\text{ K}) = 31 \mu\Omega\text{ cm}$ and a residual resistivity $\rho_0 = 2.1 \mu\Omega\text{ cm}$. In accordance with the susceptibility data, no sharp anomaly is visible in $\rho(T)$ (especially not around 10 K) which would indicate a magnetic ordering of the moments in residual elemental holmium. The Er compounds also show Curie-Weiss behaviour at elevated temperatures (Fig. 11 bottom). Fits above 50 K yield for ErSn_3 $\mu_{\text{eff}} = 10.00 \mu_B$ and $\theta_p = -12.4$ K and for Er_3Sn_7 $\mu_{\text{eff}} = 9.79 \mu_B$ and $\theta_p = -6.3$ K. Thus, the Er ions have the $4f^{11}$ configuration ($^4I_{5/2}$ ground state, $\mu_{\text{free}} = 9.58 \mu_B$, Er^{3+}) and interact predominantly antiferromagnetic. While for hp-ErSn_{3-x} again no signature of magnetic ordering is found, there is a clear but broad cusp

at 8.2(3) K suggesting an antiferromagnetic ordering in Er_3Sn_7 . The isothermal magnetization curve of hp-ErSn_{3-x} ($T = 1.8$ K) tends to saturate for $\mu_0 H = 7$ T at $\approx 6.6 \mu_B$ which is well below the theoretical value $gJ = 9 \mu_B$ for the multiplet. For Er_3Sn_7 a similar value of $M(7\text{ T})$ per Er atom is observed, however, there is a very broad metamagnetic transition between 0.8 T

and ≈ 4.0 T which has a field hysteresis. According to low-field data there is only little free tin in the samples of the Er compounds, but more homogeneous samples of all phases are required for further investigations of the magnetism.

Summary

Phases RE_3Sn_7 and hp-RESn_{3-x} ($\text{RE} = \text{Tb}, \text{Ho}$ and Er) adopting Gd_3Sn_7 -type and Cu_3Au -type crystal structures, respectively, were synthesized at high-pressure high-temperature conditions. For hp-HoSn_{3-x} , a partially ordered Cu_3Au -type with defects is verified. Measurements of the magnetic susceptibilities and X-ray absorption spectra evidence oxidation state +3 for the rare-earth metal atoms in all investigated compounds. A study of the chemical bonding in Er_3Sn_7 by the electron localizability approach reveals multi-centre tin-tin and tin-rare earth interactions. In zig-zag chains formed by tin, two-centre bonding is observed.

Experimental Section

Preparation of the precursors by arc melting and sample handling is performed in argon-filled glove boxes (MBraun , $\text{H}_2\text{O} < 0.1$ ppm; $\text{O}_2 < 0.1$ ppm). In order to avoid contamination with oxygen or moisture, the high-pressure assembly is transferred to the press directly before synthesis. After the experiment, the set-up is immediately removed from the Walker module and transported into a glove box where the sample is recovered from the crucible.

High-pressure and high-temperature preparation experiments are performed in an octahedral assembly. The redistribution of the uniaxial force of the hydraulic press is realized by a Walker module with inserted MgO octahedra of 14 mm edge length [20]. Elevated temperatures are realized by resistive heating in a graphite cylinder. Pressure and temperature calibration is performed prior to the experiments by *in-situ* monitoring of the resistance changes of bismuth [21] and by adjusting the heating power with a thermocouple, respectively. Typical annealing times amount to 2 h. As crucible material served hexagonal boron nitride. At the reaction conditions, the containers remain inert in contact to the samples as evidenced by X-ray powder diffraction data and energy dispersive X-ray analysis, respectively. For the high-pressure syntheses, typical annealing times amount to two hours. Quenching to ambient temperature is realized by disconnecting the heating current before decompression.

In order to investigate the phase distribution within the samples by light- and electron-optical microscopy on metallographic microstructures, the air and moisture sensitive samples are prepared in an inert gas atmosphere of a glove box using dried hexane as lubricant. The compositions of the phases are determined by energy dispersive x-ray spectrometry (Phoenix system, EDAX) on a scanning electron microscope (FEI XL30). The X-ray spectra have been collected with an acceleration voltage of 25 kV. The semi-quantitative analyses using X-ray intensities of the Ho L (6.72 keV) and the Sn L (3.44 keV) lines yield for, e.g., HoSn_{3-x} the following composition after matrix correction according to the ZAF model: Ho: 29.1(6) at.% and Sn: 70.9(6) at.%. The accuracy is estimated from the relative error of Ho L and Sn L intensities $dI/I = 1.6\%$ and 0.1% , respectively. The variation of the intensity of the Ho L line corresponds to 0.6 wt.% assuming a linear relation between X-ray

intensity and Ho content (in wt.%). Presence and composition of additional phases like β -Sn-type solid solutions is also verified by EDXS analysis.

X-ray powder diffraction data are collected in transmission alignment with a Huber Image Plate Guinier Camera G670 employing $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). In order to avoid oxidation during powder preparation, samples are ground in an inert atmosphere. After adding LaB_6 as an internal standard ($a = 4.1569 \text{ \AA}$) the mixture is fixed between two mylar foils. For lattice parameters refinements sets of about 5 (RESn_{3-x}) or 10 (RE_3Sn_7) reflections are used. WinXPOW was used for phase identification on the basis of X-ray powder diffraction data [22]. Profile fitting and lattice parameter calculations are performed with the program package WINCSD [23]. Structure visualisation is realized by means of the computer program DIAMOND [24].

The *in-situ* high-temperature diffraction experiments were performed at the Beamline B2 of HASYLAB at DESY in the temperature range from 298 K to 483 K with a powder diffractometer equipped with an on-site readable image plate detector OBI [25] and a STOE furnace. The wavelength ($\lambda = 0.49953 \text{ \AA}$) was calibrated using the reflection positions of a silicon reference material (NIST SRM 640b). The polycrystalline powdered sample was filled in a quartz glass capillary under inert gas atmosphere and closed with two-components adhesive.

Differential Scanning Calorimetry (DSC) measurements at ambient pressure are performed with a Netzsch STA 449 C equipment using Al_2O_3 crucibles at temperatures between 295 and 1473 K.

Electronic structure calculation and bonding analysis were carried out for Er_3Sn_7 using the TB-LMTO-ASA program package [26]. The ordered model was used for calculations with the position of Sn4 being completely occupied. The Barth-Hedin exchange potential [27] was employed for the LDA calculations. The radial scalar-relativistic Dirac equation was solved to get the partial waves. Because the calculation within the atomic sphere approximation (ASA) includes corrections for the neglect of interstitial regions and partial waves of higher order [28] an addition of empty spheres was not necessary. The following radii of the atomic spheres were applied for the calculations: $r(\text{Er1}) = 184.8 \text{ pm}$, $r(\text{Er2}) = 194.1 \text{ pm}$, $r(\text{Sn1}) = 180.2 \text{ pm}$, $r(\text{Sn2}) = 182.7 \text{ pm}$, $r(\text{Sn3}) = 182.7 \text{ pm}$, $r(\text{Sn4}) = 161.9 \text{ pm}$. A basis set containing $\text{Er}(6s, 5d, 4f)$ and $\text{Sn}(5s, 5p)$ orbitals was employed for a self-consistent calculation with $\text{Er}(6p)$, and $\text{Sn}(5d, 4f)$ functions being downfolded. The calculations were performed in a spin-polarized manner. The electron localizability indicator (ELI, γ) [29] was evaluated in the ELI-D representation according to Refs. [30, 31] with an ELI-D module within the TB-LMTO-ASA [26] program package.

The magnetization of polycrystalline samples was measured at external fields $\mu_0 H$ between 1 mT and 7 T (temperature range 1.8 K – 400 K) in a SQUID magnetometer (MPMS XL-7, Quantum Design). The electrical resistivity $\rho(T)$ of HoSn_3 was determined by a dc four-point method (4 K – 320 K). Due to the small size of the sample the inaccuracy of the absolute resistivity values is estimated to be $\pm 30 \%$.

The valence state of Tb was investigated by X-ray absorption spectroscopy at the Tb L_{III} edge. The spectra were recorded in transmission arrangement at the EXAFS Beamline E4 of the Hamburg synchrotron radiation laboratory (HASYLAB) at DESY. Wavelength selection was realized by means of a Si(111) double crystal monochromator which yields an experimental resolution of approximately 1.0 eV for the experimental setup at the Tb L_{III} edge threshold of 7514 eV. Polycrystalline sample were mixed under argon atmosphere with B_4C and filled in a stainless steel cell with beryllium windows. The Experimental data were measured using TbPO_4 or Tb_4O_7 as external references.

Acknowledgments

The authors thank Mrs. Susann Leipe for supporting high pressure synthesis, Dr. Stefan Hoffmann and Mrs. Susann Scharsach for the DSC measurements, and Dr. D. Trots for assistance in the powder X-ray synchrotron diffraction experiments at HASYLAB (project II-20060043). We thank Dr. Yurii Prots and Dr. Roman Gumeniuk for helpful discussions. U.S. gratefully acknowledges nocturnal conversations with Bernd, e.g., under a blue Caribbean sky.

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Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

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