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The stannides $RE_3Co_6Sn_5$ (RE = Y, Nd, Sm, Gd, Tb, Ho–Tm) with $Dy_3Co_6Sn_5$-type structure

Rainer Pöttgen

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

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Abstract

The title compounds were prepared from the elements by arc-melting and subsequent annealing at 1020 K. While most of the compounds were already present in the as cast samples, $Y_3Co_6Sn_5$ and $Tm_3Co_6Sn_5$ form only after the annealing process. All stannides have the $Dy_3Co_6Sn_5$-type structure, a ternary ordered version of the La_3Al_{11}-type. The structure of $Sm_3Co_6Sn_5$ was refined from single-crystal X-ray data: *Immm*, $a = 432.8(1)$ pm, $b = 1246.6(2)$ pm, $c = 978.5(1)$ pm, $V = 0.5279(2)$ nm^3, $Z = 2$, $R_1 = 0.0178$, 571 F^2 values and 28 variable parameters.

Keywords: Stannides; Arc melting; Annealing

1. Introduction

Numerous investigations in the ternary systems rare earth metal–cobalt–tin resulted in the syntheses of several isotopic series with different structure types, e.g. RECoSn [1–3] (TiNiSi-type), $RECo_6Sn_6$ [4] (YCo_6Ge_6-type) and $RE_7Co_6Sn_{23}$ [5,6] ($Ho_7Co_6Sn_{23}$-type). In the tin-rich corner of these phase diagrams, several compounds with compositions close to 3:4:13 (presumably $Pr_3Rh_4Sn_{13}$-type) have been discovered while searching for new superconducting materials [7–9]. For the lanthanum and scandium systems, the compounds $LaCo_{0.52}Sn_2$ [10] ($CeNiSi_2$-type), $La_3Co_2Sn_7$ [11] and $ScCo_2Sn$ [3,12] ($MnCu_2Al$-type) have also been communicated.

Recently, we reported on the crystal structure of $Dy_3Co_6Sn_5$ [13], a new ternary ordered version of the La_3Al_{11}-type [14]. We have now extended these investigations to several other rare earth metal–cobalt–tin systems and discovered new compounds that are isotypic with $Dy_3Co_6Sn_5$. The syntheses of these compounds and the structure refinement of $Sm_3Co_6Sn_5$ are reported in the present paper.

2. Sample preparation

Starting materials for the preparation of the ternary stannides were ingots of the rare earth metals (Johnson Matthey), cobalt powder (Ventron, 325 mesh) and tin granules (Merck), all with stated purities greater than 99.9%. The rare earth ingots were mechanically cut into small pieces, mixed with the cobalt powder in the ideal atomic ratio and cold-pressed to small pellets. These pellets were melted together with the tin granules in an arc-melting furnace under an argon atmosphere (about 600 mbar). The argon had been purified before by molecular sieves, titanium sponge at 900 K and an oxisorb catalyst [15]. All samples were turned over and remelted several times to ensure good homogeneity. After several meltings, the weight loss of the samples was always smaller than 1%. For the subsequent annealing process (two weeks at 1020 K), the samples were enclosed into evacuated silica tubes. While most of the samples were already present in the arc-melted samples, $Y_3Co_6Sn_5$ and $Tm_3Co_6Sn_5$ were formed during the annealing process.

All stannides are stable in air. No decomposition could be observed after several weeks. While powder samples are dark grey, single crystals exhibit a silvery, metallic lustre.

3. Lattice constants

Guinier powder diagrams of all samples were recorded with Cu $K\alpha_1$ radiation and silicon ($a = 543.07$ pm) as

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Table 1
Lattice constants of the orthorhombic stannides $RE_3Co_6Sn_5$ with ordered La_3Al_{11}-type structure (standard deviations in parentheses)

Compound	*a* (pm)	*b* (pm)	*c* (pm)	*V* (nm³)	Ref.
$Y_3Co_6Sn_5$	430.3(1)	1236.9(2)	970.1(1)	0.5163(2)	This work
$Nd_3Co_6Sn_5$	434.8(1)	1253.1(2)	984.9(1)	0.5366(2)	This work
$Sm_3Co_6Sn_5$	432.8(1)	1246.6(2)	978.5(1)	0.5279(2)	This work
$Gd_3Co_6Sn_5$	431.4(1)	1242.2(1)	974.2(1)	0.5221(2)	This work
$Tb_3Co_6Sn_5$	430.7(1)	1238.1(1)	970.4(1)	0.5175(2)	This work
$Dy_3Co_6Sn_5$	430.3(1)	1235.0(2)	967.6(3)	0.5142(2)	[13]
$Ho_3Co_6Sn_5$	429.8(1)	1231.6(2)	965.5(1)	0.5111(2)	This work
$Er_3Co_6Sn_5$	429.5(1)	1229.2(1)	962.6(1)	0.5082(2)	This work
$Tm_3Co_6Sn_5$	429.4(1)	1226.3(2)	960.0(2)	0.5055(2)	This work

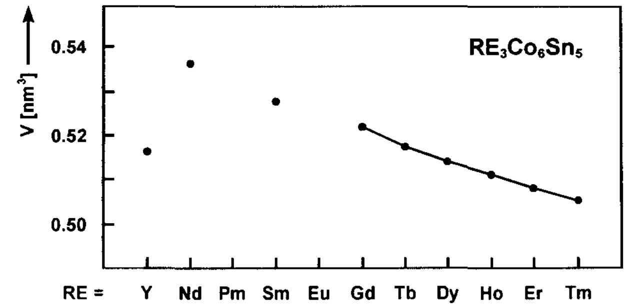

Fig. 1. Cell volumes of the stannides with $Dy_3Co_6Sn_5$-type structure. The size of the dots corresponds approximately to the standard deviation.

Table 2
Crystal data and structure refinement for $Sm_3Co_6Sn_5$

Empirical formula	$Sm_3Co_6Sn_5$
Formula weight	1398.08 g mol^{-1}
Temperature	293(2) K
Wavelength	56.087 pm
Crystal system	orthorhombic
Space group	Immm
Unit cell dimensions	see Table 1
Formula units per cell	$Z=2$
Calculated density	8.795 Mg m^{-3}
Crystal size	$20\times23\times53$ μm³
Absorption correction	from ψ-scan data
Transmission ratio (max:min)	1:0.969
Absorption coefficient	19.55 mm^{-1}
F (000)	1196
θ range for data collection	2.09–24.91°
Range in *hkl*	$0\leq h\leq6$, $-18\leq k\leq18$, $-14\leq l\leq14$
Scan mode	ω/θ
Total No. reflections	1940
Independent reflections	571 ($R_{int}=0.0256$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	571/0/28
Goodness-of-fit on F^2	1.024
Final *R* indices [$I>2\sigma(I)$]	$R_1=0.0178$, $wR_2=0.0253$
R indices (all data)	$R_1=0.0240$, $wR_2=0.0263$
Extinction coefficient	0.00117(5)
Largest diff. peak and hole	1365 and -1402 e nm^{-3}

an internal standard. Indices could be assigned on the basis of the orthorhombic unit cell found in the single crystal investigations. The identification of the diffraction lines was ensured by intensity calculations [16], taking the positional parameters of the refined structures of $Dy_3Co_6Sn_5$ and $Sm_3Co_6Sn_5$. The lattice constants (Table 1) were obtained by least-squares fits of the powder data. The cell parameters of the samarium compound determined on the four-circle diffractometer from 25 selected reflections in the range $43.0° < 2\theta < 46.9°$ [$a=432.44(2)$ pm, $b=1246.64(4)$ pm, $c=977.97(4)$ pm and $V=0.52723(3)$ nm³] are in excellent agreement with the powder data.

The plot of the cell volumes (Fig. 1) shows the expected lanthanoid contraction. The cell volume of the yttrium compound is between those of the terbium and dysprosium compounds. This was also noted for the phase series $RE_7Co_6Sn_{23}$ [5,6] and RECoSn [1–3]. In contrast, in the series $RECo_6Sn_6$ [4] the cell volume of the yttrium compound is comparable to the cell volume of the corresponding holmium compound.

4. Structure refinement of $Sm_3Co_6Sn_5$

Single crystals used for the structure refinement were isolated from a crushed ingot of the annealed sample. They were investigated by use of Buerger precession photographs to establish their suitability for intensity data collection. The precession photographs showed orthorhombic symmetry and only systematic extinctions of a body-centred lattice. This led to the space groups *Immm*, *Imm*2, $I2_12_12_1$ and *I*222, of which the centrosymmetric group *Immm* (No. 71) was found to be correct during structure refinement, in agreement with the earlier results for $Dy_3Co_6Sn_5$ [13].

Intensity data were collected with an automated four-circle diffractometer (CAD4) using graphite monochromatized Ag Kα radiation and a scintillation counter with pulse height discrimination. Experimental details are listed in Table 2.

Table 3
Atomic coordinates and anisotropic displacement parameters (pm^2) for $Sm_3Co_6Sn_5$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11}+\ldots+2hka^*b^*U_{12}]$

Atom	Immm	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	$U_{12}=U_{13}$
Sm1	2*a*	0	0	0	83(1)	97(2)	69(2)	82(2)	0	0
Sm2	4*g*	0	0.31512(3)	0	69(1)	65(2)	69(2)	73(2)	0	0
Co1	4*j*	0	1/2	0.19990(10)	86(2)	66(4)	64(4)	128(5)	0	0
Co2	8*l*	0	0.10777(5)	0.27435(7)	76(1)	62(3)	87(3)	77(3)	11(2)	0
Sn1	2*c*	0	0	1/2	75(1)	84(3)	67(3)	75(3)	0	0
Sn2	8*l*	0	0.32366(2)	0.34161(4)	70(1)	62(1)	80(1)	67(2)	14(1)	0

Table 4
Interatomic distances (pm) in the structure of $Sm_3Co_6Sn_5$. All distances shorter than 475 pm (Sm–Co, Sm–Sn), 430 pm (Sm–Sm, Co–Sn, Sn–Sn) and 390 pm (Co–Co) are listed. Standard deviations are all equal or less than 0.1 pm

Sm_1:	4	Co_2	300.2
	8	Sn_2	345.2
	4	Co_1	364.8
	2	Sm_2	392.8
Sm_2:	2	Co_1	302.3
	2	Sn_1	316.1
	4	Sn_2	317.5
	4	Co_2	323.8
	2	Sn_2	334.4
	2	Co_2	372.7
	1	Sm_1	392.8
Co_1:	4	Co_2	256.0
	2	Sn_2	259.9
	2	Sn_1	291.7
	2	Sm_2	302.3
	2	Sm_1	364.8
Co_2:	2	Co_1	256.0
	1	Sn_1	258.5
	2	Sn_2	258.9
	1	Co_2	268.7
	1	Sn_2	277.1
	1	Sm_1	300.2
	2	Sm_2	323.8
	1	Sm_2	372.7
Sn_1:	4	Co_2	258.5
	4	Co_1	291.7
	4	Sm_2	316.1
Sn_2:	2	Co_2	258.9
	1	Co_1	259.9
	1	Co_2	277.1
	1	Sn_2	310.0
	2	Sm_2	317.5
	1	Sm_2	334.4
	2	Sn_2	335.7
	2	Sm_1	345.2

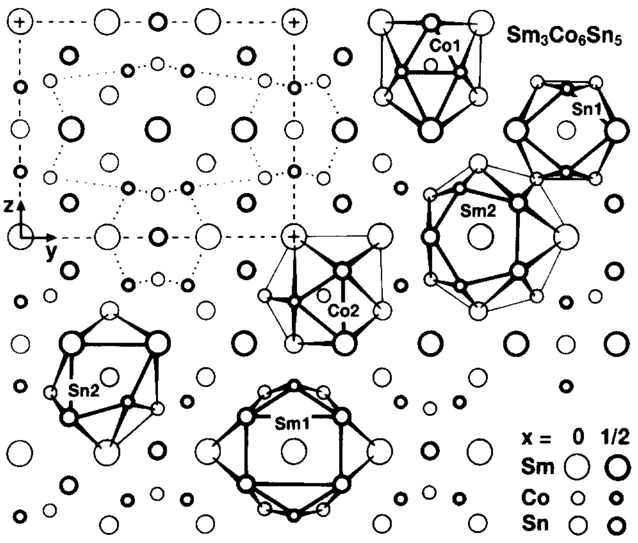

Fig. 2. Crystal structure and coordination polyhedra of $Sm_3Co_6Sn_5$ projected onto the *yz* plane. All atoms are situated on mirror planes at $x=0$ and $x=1/2$ indicated by thin and thick lines, respectively. The distorted $ThCr_2Si_2$- and Cu_3Au-like slabs are emphasized by dotted lines in the upper left-hand part.

The atomic parameters determined for $Dy_3Co_6Sn_5$ [13] were taken as starting values. The structure was then successfully refined using SHELXL-93 [17] with anisotropic displacement parameters for all atoms. A final difference Fourier synthesis revealed no significant residual peaks. The results of the refinement are listed in Table 2. Atomic coordinates and anisotropic displacement parameters are given in Table 3; interatomic distances are given in Table 4. Structure factor tables may be obtained from the author on request.

5. Discussion

Eight ternary stannides of composition $RE_3Co_6Sn_5$ (RE = Y, Nd, Sm, Gd, Tb, Ho–Tm) were reported for the first time. They crystallize in the orthorhombic $Dy_3Co_6Sn_5$-type structure [13], a ternary ordered variant of the La_3Al_{11}-type [14]. The present structure refinement of $Sm_3Co_6Sn_5$ fully confirms the structure determination for the prototype $Dy_3Co_6Sn_5$.

A projection of the crystal structure of $Sm_3Co_6Sn_5$ is shown in Fig. 2. It is built up from distorted $ThCr_2Si_2$- and Cu_3Au-like slabs of composition $SmCo_2Sn_2$ and $SmCo_2Sn$. The periodic intergrowth of these slabs may be rationalized by the formula $Sm_3Co_6Sn_5 \equiv 2SmCo_2Sn_2 + SmCo_2Sn$. The different slabs are outlined in the upper left-hand part of Fig. 2. A more detailed description of the crystal chemistry of this structural family is given in Ref. [13]. As already discussed for the dysprosium compound, the $SmCo_2Sn_2$ and $SmCo_2Sn$ slabs do not exist as ternary phases. The Cu_3Au structure is only known for $SmSn_3$ [18].

The cell volume of the samarium compound is about 3% larger than that of the dysprosium compound as expected from the lanthanoid contraction. This is also reflected by the interatomic distances which are slightly larger in $Sm_3Co_6Sn_5$, although, there are no significant differences in the coordination shells when compared to $Dy_3Co_6Sn_5$.

The structure determinations of $Dy_3Co_6Sn_5$ and $Sm_3Co_6Sn_5$ show two crystallographically different rare earth positions. These rare earth atoms form three orthorhombically distorted body-centred subcells like in the $ThCr_2Si_2$ and $CaBe_2Ge_2$ structures. Thus, one might expect interesting magnetic and electrical properties for this new family of ternary stannides.

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