



# Syntheses and crystal structures of $Y_7Co_6Sn_{23}$ and $RE_5Co_6Sn_{18}$ (RE = Sc, Ho)

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## ABSTRACT

Single crystals of  $Y_7Co_6Sn_{23}$  and  $RE_5Co_6Sn_{18}$  (RE = Sc, Ho) have been obtained by solid-state reactions of the corresponding pure elements in welded tantalum tubes at high temperature. Their crystal structures have been established by single-crystal X-ray diffraction studies.  $Y_7Co_6Sn_{23}$  belongs to the  $Ho_7Co_6Sn_{23}$  type and crystallizes in the trigonal space group  $P-3m1$  (No. 164) whereas  $RE_5Co_6Sn_{18}$  (RE = Sc, Ho) adopt the  $Tb_5Rh_6Sn_{18}$  type structure and crystallizes in the tetragonal space group  $I4_1/acd$  (No. 142). Their structures all feature a three-dimensional (3D) anionic framework based on  $[CoSn_6]$  trigonal prisms. The structure of  $Y_7Co_6Sn_{23}$  is made from the ordinal stacking one type of 2D slab composed of the same  $[CoSn_6]$  trigonal prisms via corner-sharing, forming two types of narrow tunnels along the  $c$ -axis, which are occupied by Y or residual Sn atoms. The 3D structure of  $RE_5Co_6Sn_{18}$  is built up from alternately stacking two types of 2D slabs, which are composed of different  $[CoSn_6]$  trigonal prisms via corner-sharing and Sn–Sn bonds, respectively. The RE and residual Sn atoms are located in the spacers of the 3D framework. Band structure calculations indicate that  $Y_7Co_6Sn_{23}$  and  $Sc_5Co_6Sn_{18}$  are metallic.

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## 1. Introduction

Ternary A–M–Sn systems (A represents alkali, alkaline earth or rare earth metal, M = transition metal) have been extensively investigated in recent years due to their richness in structural chemistry and tunable physical properties [1–8]. Such ternary compounds containing a late transition metal element (such as Ni, Cu, Zn) are now comparatively well-known, and most of compounds have been structurally determined by single-crystal X-ray diffraction studies [9–15]. Several examples include  $Ca_6Cu_2Sn_7$  with a novel structure type, whose structure features a 3D open-framework composed of  $[Cu_2Sn_3]$  layers interconnected by unusual  $[Sn_4]$  tetramers [9];  $Ce_3Ni_2Sn_7$  features a 3D network composed of 2D  $[Ni_2Sn_5]$  layers linked by 1D zigzag Sn chains [10];  $La_{4.87}Ni_{12}Sn_{24}$  features 3D network built from the condensation of  $[NiSn_6]$  trigonal prisms [11];  $SrNiSn_2$  with the  $CeNiSi_2$  structure type [12];  $RE_3Cu_3Sn_4$  (RE = La, Pr, Nd, Sm) with the  $Gd_3Cu_4Ge_4$  structure type [13], and  $Sm_2NiSn_4$  with the intermediate type structure between  $ZrSi_2$  and  $CeNiSi_2$ , and features 2D corrugated  $[NiSn_4]^{6-}$  layers in which the 1D Sn zigzag chains and the 2D Sn square sheets are bridged by Ni atoms [14].

As for the RE–Co–Sn (RE=rare earth metal) systems, a number of tin-rich phases have also been prepared and their structures elucidated [16–26]. For example, the ternary compounds RECoSn

(RE=Dy–Er) feature 3D framework built from the condensation of  $[CoSn_4]$  tetrahedrons [16]. With a higher tin content, stannides such as  $RECoSn_2$  (RE=Gd–Er),  $RE_4Co_2Sn_5$  (RE=La, Ce),  $Yb_3CoSn_6$ , and  $La_3Co_2Sn_7$  with various 3D framework based on Co-centered  $[CoSn_5]$  square pyramids have been reported [17–20]. The more tin-rich compounds including  $RE_3Co_4Sn_{13}$  (RE=La–Nd, Sm, Gd, Tb, Yb) [21–23],  $RE_5Co_6Sn_{18}$  (RE=Dy, Er, Tm) and  $RE_7Co_6Sn_{23}$  (RE=Dy, Ho) [24–26] have attracted considerable interest in recent years due to their outstanding physical properties. Their structures are all constructed by condensation of Co-centered  $[CoSn_6]$  trigonal prisms. We are especially interested in the effect of “lanthanide contraction” on the structures of phases formed in the RE–Co–Sn systems. Our explorations led to three new members in this system, namely,  $Y_7Co_6Sn_{23}$  and  $RE_5Co_6Sn_{18}$  (RE=Sc, Ho). Herein, we report their syntheses, crystal structures and chemical bonding.

## 2. Experimental section

### 2.1. Materials and instrumentation

All manipulations were performed inside an argon-filled glove-box with moisture level below 1 ppm. The metals used were Y, Sc, Ho blocks (RuiKe National Engineering Research Center of Rare Earth Metallurgy and Function Materials, Inner Mongolia, China, 99.9%), cobalt powder (Tianjin Fuchen Chemical Reagent Company, China, 99.99%), and tin granules (Acros, 99.999%). Elemental analyses for RE, Co, and Sn were performed on a JSM–6700F scanning electron microscope equipped with an energy dispersive X-ray spectroscope (EDS, Oxford INCA). Data were acquired with an accelerating voltage of 20 kV and SEM of 40°. X-ray powder diffraction patterns were collected on an X'Pert-Pro diffractometer using  $Cu K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The generator voltage was 45 kV and the tube current was 40 mA.

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## 2.2. Preparation of $Y_7Co_6Sn_{23}$

Single crystals of  $Y_7Co_6Sn_{23}$  were initially obtained by the solid-state reactions of the corresponding pure elements in a molar ratio of 1:1:7 (Y:Co:Sn), and the large excess of tin metal was used as the metal flux as reported by other groups [28]. The mixture was loaded into a tantalum tube, which was subsequently arc-welded under an argon atmosphere and sealed into an evacuated quartz tube ( $\sim 10^{-4}$  Torr). The quartz tube was put into a high-temperature furnace and allowed to react at 950 °C for 7 days, and then it was allowed to cool (0.1 °C/min) to room temperature. Single crystals of  $Y_7Co_6Sn_{23}$  (gray in color and prism in shape) were obtained and selected for structure determination. Microprobe analysis on several single crystals of  $Y_7Co_6Sn_{23}$  indicated the presence of Y, Co and Sn in a molar ratio of 6.8(1):6.1(5):23.4(2), which is in good agreement with the result from single-crystal X-ray diffraction study.  $Y_7Co_6Sn_{23}$  is stable in air for a few weeks. After proper structural analyses, attempts were made to prepare single phase product of  $Y_7Co_6Sn_{23}$  by reactions of the stoichiometric mixtures of the pure metals in Tb tubes at 980 °C for 3 days, and annealed at 600 °C for 15 days. X-ray powder diffraction studies revealed  $Y_7Co_6Sn_{23}$  ( $\sim 60\%$ ) as the major phase with some unidentified impurity phases. Attempts to synthesize the scandium analog of  $Y_7Co_6Sn_{23}$  were tried but unsuccessful.

## 2.3. Preparation of $RE_5Co_6Sn_{18}$ (RE = Sc, Ho)

Single crystals of  $Sc_5Co_6Sn_{18}$  were initially obtained from a mixture of Sc, Co, and Sn in a molar ratio of 7:6:23 at 980 °C in our attempts to prepare the analog of  $Y_7Co_6Sn_{23}$ . The samples were allowed to react at 980 °C for 7 days, and then annealed at 650 °C for 9 days. Afterward, it was allowed to cool at a rate of 0.1 °C/min to room temperature. Several prism-shaped single crystals of  $Sc_5Co_6Sn_{18}$  could easily be selected from reaction products and used for structure determination. Using of Ho instead of Sc led to  $Ho_5Co_6Sn_{18}$ . Microprobe analysis on clean surfaces of prism-shaped crystals of  $RE_5Co_6Sn_{18}$  gave approximate RE:Co:Sn molar ratio of 5.1(2):6.1(3):18.3(1) for  $Sc_5Co_6Sn_{18}$  and 4.9(6):6.2(3):18.4(5) for  $Ho_5Co_6Sn_{18}$ , respectively, which were consistent with the results derived from the single-crystal X-ray diffraction refinements. These compounds were also stable in air over several weeks. Subsequently, the reactions were carried out in a stoichiometric of the metals in our efforts to prepare single phases of these compounds. The samples were heated at 980 °C for 3 days, and annealing at different temperatures (600, 650, 700, 750 °C, respectively, for each individual reactions) for 20 days. However, X-ray powder patterns of the resultant products revealed the presence of impurity phases such as  $HoCoSn$  and other unidentified compounds. A lot of attempts to separate these ternary phases were tried but failed.

## 2.4. Crystal structure determination

Single crystals of the title compounds were selected from the bulk reaction products and sealed into thin-walled glass capillaries within the glove-box. Data collection for all compounds were performed on a Rigaku Mercury CCD (CCD stands for charge-Coupled Device, Mo-K $\alpha$  radiation, graphite monochromator) at 293(2) K. All data sets were corrected for Lorentz factor, polarization, air absorption and absorp-

**Table 2**

Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $Y_7Co_6Sn_{23}$  and  $RE_5Co_6Sn_{18}$  (RE = Sc, Ho).

Atom	Wyckoff site	x	y	z	$U(\text{eq})^a$
<b><math>Y_7Co_6Sn_{23}</math></b>					
Y(1)	1b	0	0	1/2	8(1)
Y(2)	6i	0.5219(1)	0.4781(1)	0.1934(1)	5(1)
Co(1)	6i	0.3357(1)	0.1679(1)	0.6982(1)	4(1)
Sn(1)	1a	0	0	0	9(1)
Sn(2)	6i	0.2344(1)	0.1172(1)	0.2245(1)	6(1)
Sn(3)	6h	0.3475(1)	0	1/2	7(1)
Sn(4)	6i	0.2185(1)	0.4371(1)	0.0463(1)	6(1)
Sn(5)	2d	1/3	2/3	0.3196(1)	5(1)
Sn(6)	2d	1/3	2/3	0.6124(1)	6(1)
<b><math>Sc_5Co_6Sn_{18}</math></b>					
Sc(1)	8b	1/2	3/4	1/8	18(1)
Sc(2)	32g	0.3673(1)	0.1180(1)	0.0584(1)	6(1)
Co(1)	32g	0.4991(1)	0.4935(1)	0.1248(1)	5(1)
Co(2)	16d	1/2	1/4	0.0030(1)	5(1)
Sn(1)	16f	0.1734(1)	0.4234(1)	1/8	13(1)
Sn(2)	32g	0.5039(1)	0.5773(1)	0.2113(1)	10(1)
Sn(3)	32g	0.4966(1)	0.5761(1)	0.0385(1)	12(1)
Sn(4)	16f	0.3264(1)	0.5764(1)	1/8	11(1)
Sn(5)	32g	0.4107(1)	0.3388(1)	0.0804(1)	7(1)
Sn(6)	16e	0.7186(1)	1/2	1/4	16(1)
<b><math>Ho_5Co_6Sn_{18}</math></b>					
Ho(1)	8b	1/2	3/4	1/8	10(1)
Ho(2)	32g	0.3633(1)	0.1173(1)	0.0569(1)	4(1)
Co(1)	32g	0.5007(1)	0.4951(1)	0.1248(1)	3(1)
Co(2)	16d	1/2	1/4	0.0019(1)	3(1)
Sn(1)	16f	0.1743(1)	0.4243(1)	1/8	10(1)
Sn(2)	32g	0.5077(1)	0.5779(1)	0.2110(1)	8(1)
Sn(3)	32g	0.4959(1)	0.5760(1)	0.0388(1)	11(1)
Sn(4)	16f	0.3282(1)	0.5782(1)	1/8	11(1)
Sn(5)	32g	0.4114(1)	0.3401(1)	0.0802(1)	7(1)
Sn(6)	16e	0.7094(1)	1/2	1/4	24(1)

<sup>a</sup>  $U(\text{eq})$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

tion due to variations in the path length through the detector faceplate. Absorption corrections based on multi-scan method were also applied [29].

All structures were solved by using direct methods (SHELXTL) and refined by least-squares methods with atomic coordinates and anisotropic thermal parameters [30]. The space groups of  $Y_7Co_6Sn_{23}$  and  $RE_5Co_6Sn_{18}$  (RE = Sc, Ho) were determined to be  $P-3m1$  (No. 164) and  $I4_1/acd$  (No. 142), respectively, on the basis of systematic absences,  $E$ -value statistics, and the satisfactory refinements for the structures. The

**Table 1**

Crystal data and structure refinements for  $Y_7Co_6Sn_{23}$  and  $RE_5Co_6Sn_{18}$  (RE = Sc, Ho).

	$Y_7Co_6Sn_{23}$	$Sc_5Co_6Sn_{18}$	$Ho_5Co_6Sn_{18}$
Empirical formula	$Y_7Co_6Sn_{23}$	$Sc_5Co_6Sn_{18}$	$Ho_5Co_6Sn_{18}$
Formula weight	3705.82	2714.80	3314.65
Space group	$P-3m1$ (No. 164)	$I4_1/acd$ (No. 142)	$I4_1/acd$ (No. 142)
$a$ (Å)	9.6618(3)	13.344(2)	13.5681(4)
$c$ (Å)	9.8618(5)	26.619(6)	27.072(1)
$V$ (Å <sup>3</sup> )	797.27(5)	4739.8(1)	4983.8(3)
$Z$	1	8	8
$D_{\text{calcd}}$ (g cm <sup>-3</sup> )	7.72	7.61	8.84
Temp, K	293(2)	293(2)	293(2)
$\mu$ (mm <sup>-1</sup> )	33.2	23.9	37.2
$F(000)$	1585	9336	11176
Crystal size (mm <sup>3</sup> )	0.10 × 0.02 × 0.02	0.12 × 0.03 × 0.03	0.15 × 0.05 × 0.02
Color and habit	Gray, Prism	Gray, Prism	Gray, Prism
Reflections collected	5324	16889	17723
Independent reflections	724	1368	1434
Reflections ( $I > 2(I)$ ) <sup>a</sup>	682	1235	1254
Data/restraints/parameters	724/0/41	1368/0/70	1434/0/70
GOF on F <sup>2</sup>	1.113	1.063	1.078
$R_1$ , $wR_2$ ( $I > 2(I)$ ) <sup>a</sup>	0.0244/0.0550	0.0214/0.0532	0.0397/0.0943
$R_1$ , $wR_2$ (all data)	0.0286/0.0565	0.0242/0.0549	0.0454/0.0988
Extinction coefficient	0.0075(2)	0.000210(7)	0.000081(6)
Largest diff. peak and hole (e Å <sup>-3</sup> )	4.38 (1.21 Å from the Sn(6) atom) and -2.88 (0.10 Å from the Sn(6) atom)	1.59 (1.04 Å from the Sc(2) atom) and -1.70 (0.51 Å from the Sn(1) atom)	7.32 (0.00 Å from the Ho(1) atom) and -4.63 (0.67 Å from the Ho(1) atom)

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / \sum w(F_o)^2 \}^{1/2}$ .

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