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Crystal structure of the $TbZnSn_2$ and TbZnSn ternary compounds

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ABSTRACT

The crystal structures of the $TbZnSn_2$ and TbZnSn compounds were determined by X-ray single crystal diffraction. The $TbZnSn_2$ compound crystallizes with the $HfCuSi_2$ structure type (space group $P4/nmm$) and TbZnSn crystallizes with the YPtAs structure type (space group $P6_3/mmc$).

1. Introduction

During a systematic investigation of the Tb–Zn–Sn ternary phase diagram two new ternary compounds were found. The ternary compounds with the same structure as $TbZnSn_2$ ($HfCuSi_2$-type) are formed in the R–Cu–As and R–Ag–Sb (were R = rare-earth elements and uranium) systems [1–3]. The equiatomic compound RZnSn were investigated with R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu, Sc and Y and are described in Ref. [4]. The crystal structure for the GdZnSn and YZnSn compounds was determined by single crystal method and for the samples with La, Ce, Pr, Nd and Sm the Rietveld method for powder patterns was used. For the samples with Dy–Lu only the lattice constants are reported [4]. All these compounds belong to the YPtAs structure type. Demchenko and Bodak [5] also reported the crystal structure of NdZnSn to be isotypical with $CaIn_2$-type.

In this paper we report our results on the synthesis and crystal structure refinement by single crystal method for the $TbZnSn_2$ and TbZnSn ternary compounds.

2. Experimental details

2.1. Synthesis and phase analysis

Terbium, zinc and tin, all with nominal purities ~99.9 wt%, were used as starting elements. A few alloys of nominal composition $Tb_{25}Zn_{25}Sn_{50}$, $Tb_{33.3}Zn_{33.3}Sn_{66.7}$ and $Tb_{37}Zn_{26}Sn_{37}$ were prepared by melting of the stoichiometric amounts of the constituent metals in the resistance furnace. The alloys were prepared in a few steps. In the first step the powders of the pure elements were pressed into pellets and enclosed in evacuated silica ampoules which then were placed in a resistance furnace with a thermocouple controller. The ampoules were heated at 873 K for 4 days, at 1073 K for next 4 days and finally half an hour at 1148 K. After that the ingots were annealed at 873 K for 24 days. Irregularly shaped single crystals, exhibiting metallic luster, were isolated by mechanical fragmentation from the alloys.

2.2. Structure analysis and refinement

Single crystals data for $TbZnSn_2$ and TbZnSn were collected at room temperature on the four-circle diffractometer Xcalibur Oxford Diffraction with a CCD detector (graphite monochromatized Mo Kα radiation). Scans were taken in the ω mode. The crystal structures of both compounds were successfully solved by direct methods and refined using SHELX-97 package programs [6,7].

The analysis of systematic absences and the statistical test of the distribution of the E-values [8] suggested that both structures are centrosymmetric. The structure solution and refinement were also performed in the non-centrosymmetric groups. The results clearly indicate that $TbZnSn_2$ and TbZnSn crystallize in the centrosymmetric space groups $P4/nmm$ and $P6_3/mmc$, respectively.

3. Results and discussion

3.1. $TbZnSn_2$

Small irregularly shaped single crystal was selected out from the alloy with the nominal composition $Tb_{25}Zn_{25}Sn_{50}$. This single crystal is stable in air over the long period of time and has metallic luster. Table 1 lists the dimensions of the crystal, details of data collection and the results of structure refinement. Atomic parame-

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Table 1
Crystallographic data for the $TbZnSn_2$ and TbZnSn single crystals and experimental details of the structure determination.

Empirical formula	$TbZnSn_2$	TbZnSn
Structure type	$HfCuSi_2$	YPtAs
Formula weight (g/mol)	262.99	283.00
Space group	*P*4/*nmm* (No. 129)	$P6_3/mmc$ (No. 194)
Pearson symbol	tP8	hP12
Crystal dimensions (mm^3)	$0.14 \times 0.13 \times 0.04$	$0.17 \times 0.11 \times 0.02$
Unit cell dimensions		
a, Å	4.3365(1)	4.4799(6)
c, Å	9.8754(5)	15.816(3)
V, $Å^3$	185.71(1)	274.89(8)
Z	2	4
Calculated density (D_{calc}, $g\,sm^{-3}$)	8.256	8.287
Absorption coefficient (μ, mm^{-1})	38.210	42.737
Scan mode	ω	ω
Theta range for data collection (°)	4.13–26.35	2.58–27.30
F(0 0 0)	390	580
Range in *h k l*	$-2 \le h \le 5$, $-5 \le k \le 3$, $-12 \le l \le 12$	$-2 \le h \le 2$, $-5 \le k \le 5$, $0 \le l \le 20$
Total no. of reflections	1154	1170
Independent reflections	145 (R_{int} = 0.0279)	173 (R_{int} = 0.0571)
Reflections with $I > 2\sigma(I)$	138 (R_{sigma} = 0.0141)	153 (R_{sigma} = 0.0210)
Weighting scheme	$1/[\sigma(F_0)^2 + (0.0168 \times P)^2 + 8.1318 \times P]$	$1/[\sigma(F_0)^2 + (0.1000 \times P)^2 + 0.001 \times P]$
Data/parameters	145/12	153/10
Goodness-of-fit on F^2	1.184	1.217
Final *R* indices	R_1 = 0.0250	R_1 = 0.0169
$[I > 2\sigma(I)]$	wR_2 = 0.0605	wR_2 = 0.0564
R indices (all data)	R_1 = 0.0266	R_1 = 0.0287
	wR_2 = 0.0617	wR_2 = 0.0683
Extinction coefficient	0.0270(19)	0.0016(10)
Largest diff. peak and hole	5.176 and -2.657 e/$Å^3$	1.181 and -1.269 e/$Å^3$

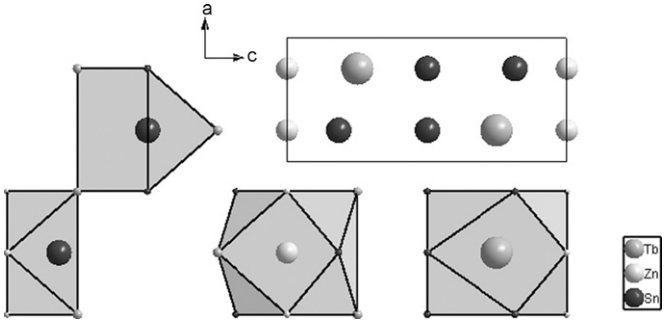

Fig. 1. Crystal structure projected on the *xz* plane and coordination polyhedra of the atoms in the $TbZnSn_2$ structure.

ters and anisotropic thermal displacement parameters are given in Table 2. The projection of the unit cell of $TbZnSn_2$ on the *xz* plane together with the coordination polyhedra for all atoms is shown in Fig. 1. This compound crystallizes with the $HfCuSi_2$-type of structure [9] and can be described as a "filled" variant of the PbFCl-type which in turn is an ordered superstructure to Cu_2Sb-type (Fig. 2).

Both Tb and Zn atoms are surrounded by 12 neighbour atoms forming deformed cuboctahedra [$TbZn_4Sn_8$] and [$ZnTb_4Sn_4Zn_4$]. The characteristic polyhedra of Sn atoms are tetragonal antiprism [$Sn_1Tb_4Zn_4$] and double anti-trigonal prism [$Sn_1Tb_4Sn_4$]. Interatomic distances in the $TbZnSn_2$ structure are collected in Table 3.

3.2. TbZnSn

According to the X-ray analysis the equiatomic compound TbZnSn was identified as an YPtAs-type cell [10]. The good quality single crystal of this compound was isolated by mechanical fragmentation from the $Tb_{33.3}Zn_{33.3}Sn_{33.3}$ and investigated by Xcalibur Oxford Diffraction diffractometer. The crystal shape, details of data collection and structure refinement are given in Table 1.

Atomic coordinates and thermal displacement parameters are listed in Table 2. The lattice parameters of TbZnSn are in good agreement with those reported by Manfrinetti and Pani [4]. The unit cell projection of TbZnSn is shown in Fig. 3. All interatomic distances

Table 2
Atomic coordinates and thermal displacement parameters ($\times 10^3$ $Å^2$) for the $TbZnSn_2$ and TbZnSn single crystals.

Atom	Site	*x*/*a*	*y*/*b*	z/*c*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}
$TbZnSn_2$									
Tb	2c	1/4	1/4	0.7494(1)	9.5(4)	8.5(5)	8.5(5)	11.5(6)	0
Zn	2a	3/4	1/4	0	21.1(7)	22(1)	22(1)	18(1)	0
Sn_1	2b	3/4	1/4	1/2	13.7(5)	12.7(6)	12.7(6)	15.7(8)	0
Sn_2	2c	1/4	1/4	0.1843(2)	20.5(6)	9.5(6)	9.5(6)	42(1)	0
TbZnSn									
Tb_1	2a	0	0	0	8.5(5)	8.1(7)	8.1(7)	9.2(7)	4.0(3)
Tb_2	2b	0	0	1/4	9.3(5)	9.4(7)	9.4(7)	9.1(6)	4.7(4)
Zn	4f	1/3	2/3	0.1581(1)	23.7(7)	21.9(7)	21.9(7)	27(2)	10.9(3)
Sn	4f	1/3	2/3	0.6139(1)	13.0(4)	12.5(4)	12.5(4)	14(1)	6.3(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $U_{ij} = -2\pi^2[(h^2a^*)^2U_{11} + \cdots + 2hka^*b^*U_{12}]$. $U_{13} = U_{23} = 0$.