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On the crystal structure of the compound $Tb_{0.83}Zn_{0.14}Sn_{2.86}$

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The ternary compound $Tb_{0.83}Zn_{0.14}Sn_{2.86}$ was observed for the first time. The X-ray single crystal method was used to determine the crystal structure. The new stannide crystallizes in a new structure type, which is a derivative of $AuCu_3$ (space group *Pmm*2, *a* = 4.332(3) Å, *b* = 4.427(3) Å, *c* = 5.479(4) Å). The structural relationship between $Tb_{0.83}Zn_{0.14}Sn_{2.86}$ and other structure types with small unit cells and close-packed structures is discussed.

Structure type / Terbium / Zinc / Tin / Ternary compound

Introduction

Recently, intermetallic compounds containing rare earth, transition metals and *p*-elements (such as Al, Sn *etc*.) have gained particular interest among researchers because of their useful properties. These predetermine their versatile application mainly as hydrogen storage materials. Systematic investigation of the Tb–Zn–Sn ternary system in the full concentration range was carried out in [1-4]. In the course of our studies we determined the crystal structures of three new ternary compounds from single crystal diffraction data: $TbZnSn_2$ [1], $Tb_{13}ZnSn_{13}$ [2], and $TbZn_xSn_{2-x}$ [3], confirmed the existence of one known compound TbZnSn [1,5] and constructed the isothermal section of the phase diagram at 600°C [4]. A single crystal of the new ternary compound $Tb_{0.83}Zn_{0.14}Sn_{2.86}$ was found in a non-equilibrium alloy with nominal composition $TbZnSn_2$ during an investigation of the tin-rich corner of the ternary system. In the beginning it was not clear whether it was a binary [6] or a ternary phase, as the refinement of binary and ternary structure models gave close agreement factors. Moreover, at the time of the study the Tb–Sn binary system was not well established in the region 25-33 at.% Tb. A later study of the tin-rich side of the Tb–Sn binary system [7] allowed determining the crystal structure of the high-temperature modification of Tb_3Sn_7, but the title compound was not detected in binary alloys at temperatures above 300°C. Further investigations of the tin-rich region of the ternary system Tb–Zn–Sn indicated formation of small amounts of the title compound in an alloy with composition $TbZn_2Sn_7$ and confirmed the existence of $Tb_{0.83}Zn_{0.14}Sn_{2.86}$.

Experimental

The alloy of composition $TbZnSn_2$, where the title compound was observed for the first time, was made by arc melting, using pure metals as starting components (Tb 99.9 wt.%, Zn 99.99 wt.%, Sn 99.999 wt.%). Further attempts were made in order to find the compound both in binary and ternary alloys, in the Sn-rich regions of the Tb–Sn and Tb–Zn–Sn systems. Different methods of synthesis were applied: i) arc melting, ii) sintering of pellets, made of stoichiometric amounts of metal powders, in evacuated silica ampoules, and iii) melting in evacuated Ta containers in an induction furnace (Hüttinger Elektronik, Freiburg, Typ TIG 2.5/300). The pellets made of powders of pure metals were heated in several steps at different temperatures, in order to achieve homogeneity and reaction completion.

The samples were submitted to different thermal treatments, depending on the method of synthesis:

- annealed at 300°C, 600°C, 700°C, 800°C in evacuated quartz ampoules for 30 days, quenched in water (ii and iii-a).
- heated from room temperature to 1150°C in 1 h, held for 2 h, cooled in 1.5 h from 1150 to 700°C, cooled to room temperature by switching off the furnace (iii-b).

Some of the samples were investigated as-cast. The compositions, details of synthesis, thermal treatment and phase compositions of the samples are summarized in Table 1. Several samples with the same compositions were synthesized by different methods.

Table 1 Nominal compositions, synthesis, thermal treatment and phase compositions of the samples.

Sample (nominal composition)	Synthesis		Final annealing		Phases	
	method	T_{max}, °C	T, °C	time, days		
N93II_Tb0.83Zn0.14Sn2.86	sintering	875	600	30	major	Sn, $TbSn_3$ cub[a]
					minor	αTb_3Sn_7, βTb_3Sn_7, $TbZn_xSn_{2-x}$
N58_Tb2Zn1Sn7	arc melting	?	as-cast	-	major	Sn, αTb_3Sn_7, βTb_3Sn_7, $TbZn_xSn_{2-x}$, $Tb_{0.83}Zn_{0.14}Sn_{2.86}$
N59III_TbZn2Sn7_cu	melting in sealed Ta-containers	1150	700	quenching	major	Sn, αTb_3Sn_7, βTb_3Sn_7, $Tb_{0.83}Zn_{0.14}Sn_{2.86}$
					minor	$TbZn_3$, traces TbZn, traces $TbZn_xSn_{2-x}$,
N59II_Tb1Zn2Sn7	sintering	875	600	30	major	$TbSn_3$ cub, Sn
					minor	αTb_3Sn_7, βTb_3Sn_7, $Tb_{0.83}Zn_{0.14}Sn_{2.86}$, $TbZn_xSn_{2-x}$
N76II_Tb23.8Zn4.8Sn71.4	sintering	875	600	30	major	$TbSn_3$ cub, Sn
					minor	αTb_3Sn_7, βTb_3Sn_7, $Tb_{0.83}Zn_{0.14}Sn_{2.86}$, $TbZn_xSn_{2-x}$
N76III_Tb23.8Zn4.8Sn71.4_cu(Ta)	melting in sealed Ta-containers	1150	700	quenching	major	βTb_3Sn_7, Sn
					minor	traces $TbZn_xSn_{2-x}$, traces $TbSn_3$ cub, traces αTb_3Sn_7, ?$Tb_{0.83}Zn_{0.14}Sn_{2.86}$
N77III_Tb3Sn74(Ta)_cu	sintering	1150	700	quenching	major	Sn, αTb_3Sn_7
					minor	$TbSn_2$, βTb_3Sn_7
N33II_TbSn3_300	sintering	450	300	30	major	$TbSn_3$ *Amm*2[b]
					minor	Sn
N96II_Tb3Sn7_300	melting in sealed Ta-containers	450	300	30	major	$TbSn_3$ *Amm*2
					minor	Sn, αTb_3Sn_7
TbSn3_700	melting in sealed Ta-containers	1200	700	30	major	αTb_3Sn_7
					minor	Sn
TbSn3_800	melting in sealed Ta-containers	1200	800	30	major	βTb_3Sn_7
					minor	Sn

[a] Cubic high-pressure modification of the $TbSn_3$ compound [8,9], structure type $AuCu_3$, space group *Pm*-3*m*, can be stabilized by Zn, hereafter referred to as $TbSn_3$ cub.

[b] Ambient pressure modification of the compound $TbSn_3$, structure type $GdSn_{2.75}$, space group A*mm*2 [10], hereafter referred to as $TbSn_3$ *Amm*2.

X-ray diffraction data were collected using an XCALIBUR (Oxford Diffraction, Sapphire2 CCD detector, Mo *K*α) diffractometer for single-crystal and Stoe STADI P (Cu *K*α), DRON-2.0M (Fe *K*α) diffractometers for powder data. The structure of $Tb_{0.83}Zn_{0.14}Sn_{2.86}$ was solved by direct methods using SHELXS-97 programs [11]; further refinement of the crystal structure was carried out using SHELXL-97 programs [12].

Results and discussion

A single crystal of the title compound was found in a non-equilibrium alloy with nominal composition $TbZnSn_2$, made by arc melting. Subsequently series of samples were made in order to confirm the existence of the compound. It was found in ternary Tb–Zn–Sn alloys, but not in binary Tb–Sn alloys, which indicates that the compound contains a third component – zinc.

In the beginning of the structural investigation we considered a binary model as a first approximation. The refinement of both binary and ternary structure models with mixed Zn/Sn occupation of the sites gave similar agreement factors. Further investigation of the binary Tb–Sn system confirmed that the title compound is ternary.

Investigation of the sample N76II_Tb23.8Zn4.8Sn71.4, with the ratio Tb:Sn = 1:3 and small excess of zinc, did not show significant amounts of the title compound, but only the cubic, high-pressure modification of the $TbSn_3$ compound [8,9] ($TbSn_3$ cub). Partial replacement of tin atoms by smaller zinc atoms in this phase leads to compression of the structure and its stabilization at ambient pressure.

The Tb:Zn,Sn ratio of the title compound was found to deviate from 1:3, since the refinement of the occupation of the terbium site considering vacancies gave lower agreement factors, and in the region with Tb:Zn,Sn ratio equal to 1:3 only the $TbSn_3$ cub phase was observed. We considered mixed occupation of this site by Tb/Zn or Tb/Sn as highly improbable based on crystallographic considerations, since, usually, rare-earth metals do not mix with zinc or tin atoms. Known exceptions are compounds with channels, like $Tb_{13}Zn_{\sim 58}$ [13], or derivatives of the structure types Th_2Zn_{17} and Th_2Ni_{17}.

The largest amount of $Tb_{0.83}Zn_{0.14}Sn_{2.86}$ was found in the sample N59_IIITbZn2Sn7_cu, made by melting in a sealed Ta-container. The samples made by arc melting, or by melting in a sealed Ta-container, contained larger amounts of the title compound than those made by sintering metal powders. Usually, the title compound was accompanied by $TbSn_3$ cub. This observation, together with the structural relationship and the close compositions, may indicate that, either the two phases are in equilibrium, or they form one from another.

The compound $Tb_{0.83}Zn_{0.14}Sn_{2.86}$ is the first representative of a new, disordered structure type, which is closely related to $AuCu_3$. The final model of the structure is presented in Tables 2 and 3, and Fig. 1.

At first glance, the structure type Ag_3Sb [14] seems to be closely related to the structure of the new compound because it has the same space group and Pearson symbol, and the same Wyckoff positions are occupied. But Ag_3Sb and $Tb_{0.83}Zn_{0.14}Sn_{2.86}$ cannot be considered to be isotypic, because the structures have different cell parameter ratios and atom coordinates, and consequently different coordination polyhedra. The structure type Ag_3Sb is a distorted derivative of Mg with close-packed layers in *h* stacking, and the coordination polyhedra are distorted anticuboctahedra, whereas $AuCu_3$ has close-packed

Table 2 Crystallographic data of the compound $Tb_{0.83}Zn_{0.14}Sn_{2.86}$ and details of the structure determination.

Empirical formula	$Tb_{0.83}Zn_{0.14}Sn_{2.86}$
Structure type	New
Space group	*Pmm*2 (No. 25)
Pearson symbol (Pearson code)	*oP*4 (*oP*3.83)
Unit cell dimensions:	
a, Å	4.332(3)
b, Å	4.427(3)
c, Å	5.479(4)
V, $Å^3$	105.1(1)
Z	1
Calculated density (D_x, g/cm^3)	7.594
Absorption coefficient (μ, mm^{-1})	31.154
Data collection mode	ω
Theta range for data collection, °	0.833-26.00
F(000)	201.1
Reflection index range	$-5 \leq h \leq 3$, $-4 \leq k \leq 5$, $-5 \leq l \leq 6$
Total no. reflections	394
Independent reflections	176 (R_{int} = 0.0431)
Reflections with $I > 2\sigma(I)$	114 (R_σ = 0.0348)
Data/parameters	176 / 21
Goodness-of-fit on F^2	1.20
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0464 wR_2 = 0.1298
Final *R* indices (all data)	R_1 = 0.0769 wR_2 = 0.1550
Largest diff. peak and hole	2.04 and -2.62 e/$Å^3$

Table 3 Atom coordinates of $Tb_{0.86}Zn_{0.14}Sn_{2.86}$.

Atom	Wyckoff	*x*	*y*	*z*	$U_{eq,}$ Å^2	Occupation
Tb1	1*d*	½	½	0.200(1)	0.040(6)	0.83(2)
Sn2	1*c*	½	0	0.7187(9)	0.025(3)	0.92(3)
Zn2	1*c*	½	0	0.7187(9)	0.025(3)	0.08(3)
Sn3	1*b*	0	½	0.634(3)	0.025(4)	0.94(3)
Zn3	1*b*	0	½	0.634(3)	0.025(4)	0.06(3)
Sn4	1*a*	0	0	0.134(3)	0.027(4)	1

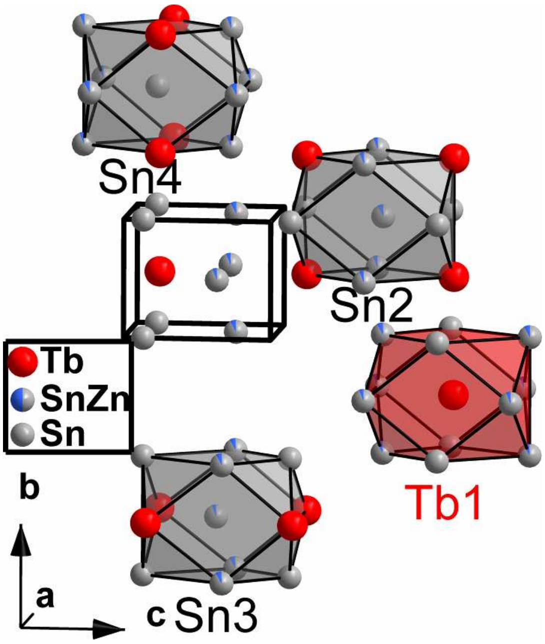

Fig. 1 Unit cell content and coordination polyhedra in $Tb_{0.83}Zn_{0.14}Sn_{2.86}$.

layers in *c* stacking and the coordination polyhedra are cuboctahedra.

A chain of transformations of related structure types containing four atoms per unit cell may be considered, starting from $AuCu_3$: $AuCu_3$-$SrPb_3$-$Tb_{0.83}Zn_{0.14}Sn_{2.86}$-$Ag_3Sb$-$Cu_3Ge$ (Table 4, Fig. 2). The relationship between them can be described as a gradual increase of the cell parameter ratios with simultaneous shift of the atoms. It should be noted that the part of covalent bonding increases from $AuCu_3$ (Au and Cu are metals) to Cu_3Ge (while Ge is a non-metal), which is in agreement with the decrease of symmetry. The transformations are discussed in detail below.

$AuCu_3$-$SrPb_3$: Increase of one of the cell parameters with respect to the other two causes loss of the three-fold axes, and the symmetry becomes tetragonal. For $SrPb_3$ the *c*/*a* ratio is not large enough to cause significant changes of the coordination polyhedra, which remain cubooctahedra, expanded in the *c* direction.

$SrPb_3$-$Tb_{0.83}Zn_{0.14}Sn_{2.86}$: The structure of $Tb_{0.83}Zn_{0.14}Sn_{2.86}$ can be obtained from $SrPb_3$ by shifting the Sn sites with partial substitution by Zn closer to each other. The Sn atoms in Wyckoff position 1*a* move out of the *xy* plane containing the Tb atoms. The Sn/Zn atoms in Wyckoff position 1*b* move in the same direction, and those in Wyckoff position 1*c* in the opposite direction (see Fig. 2). The shift is such that the four-fold axis is lost. A significant increase of the *c*/*a* ratio is observed, but the *b*-parameter increases very little. The coordination polyhedra of all of the atoms are distorted cubooctahedra with pairs of atoms shifted above and below the faces of the cubooctahedra (see Fig. 1).

$Tb_{0.83}Zn_{0.14}Sn_{2.86}$-$Ag_3Sb$: The transition from $Tb_{0.83}Zn_{0.14}Sn_{2.86}$ to Ag_3Sb does not affect the overall symmetry, since the two structure types are isopointal. But the Ag atoms are shifted much more than the Sn atoms in $Tb_{0.83}Zn_{0.14}Sn_{2.86}$. The *c*/*a* and *b*/*a* ratios are much higher than in $Tb_{0.83}Zn_{0.14}Sn_{2.86}$, which changes the coordination polyhedra from distorted cubooctahedra to distorted anticubooctahedra. In addition, the unit cell becomes orthohexagonal ($c/a = 1.733 \approx \sqrt{3}$). The coordination polyhedra are almost regular anticubooctahedra for the atoms in Wyckoff positions 1*a* and 1*d* and distorted analogues with pairs of shifted atoms dividing square faces into two triangles.

Ag_3Sb-Cu_3Ge: The orthorhombic structure of Ag_3Sb transforms into the monoclinic structure of Cu_3Ge by a small decrease of one of the interreticular angles. The monoclinic angle $\beta = 89.63°$ is very close to 90° but the symmetry is clearly monoclinic. The c/a ratio increases a little, and the b/a ratio decreases a little, in comparison with Ag_3Sb. The coordination polyhedra look like ordinary anticubooctahedra, but with some angular distortion caused by the monoclinic symmetry.

Table 4 Structure types containing 4 atoms in the unit cell and (distorted) close-packed layers.

$AuCu_3$ cubic [15]	$SrPb_3$ tetragonal [16]	$Tb_{0.83}Zn_{0.14}Sn_{2.86}$ orthorhombic (this work)	Ag_3Sb orthorhombic [14]	Cu_3Ge monoclinic [17,18]
Space group: *Pm*-3*m*	Space group: *P*4/*mmm*	Space group: *Pmm*2	Space group: *Pmm*2	Space group: $P2_1$, $P2_1/m$ or $P2_1/c$
				$\alpha = 89.63°$
$a = 3.75$ Å	$a = 4.955$ Å	$a = 4.332(3)$ Å	$a = 2.979$ Å	$a = 2.633$ Å
	$b = 4.955$ Å	$b = 4.427(3)$ Å	$b = 4.813$ Å	$b = 4.203$ Å
	$c = 5.025$ Å	$c = 5.479(4)$ Å	$c = 5.215$ Å	$c = 4.553$ Å
$c/a = 1$	$c/a = 1.014$	$c/a = 1.265$	$c/a = 1.751$	$c/a = 1.729$
$b/a = 1$	$b/a = 1$	$b/a = 1.022$	$b/a = 1.616$	$b/a = 1.596$

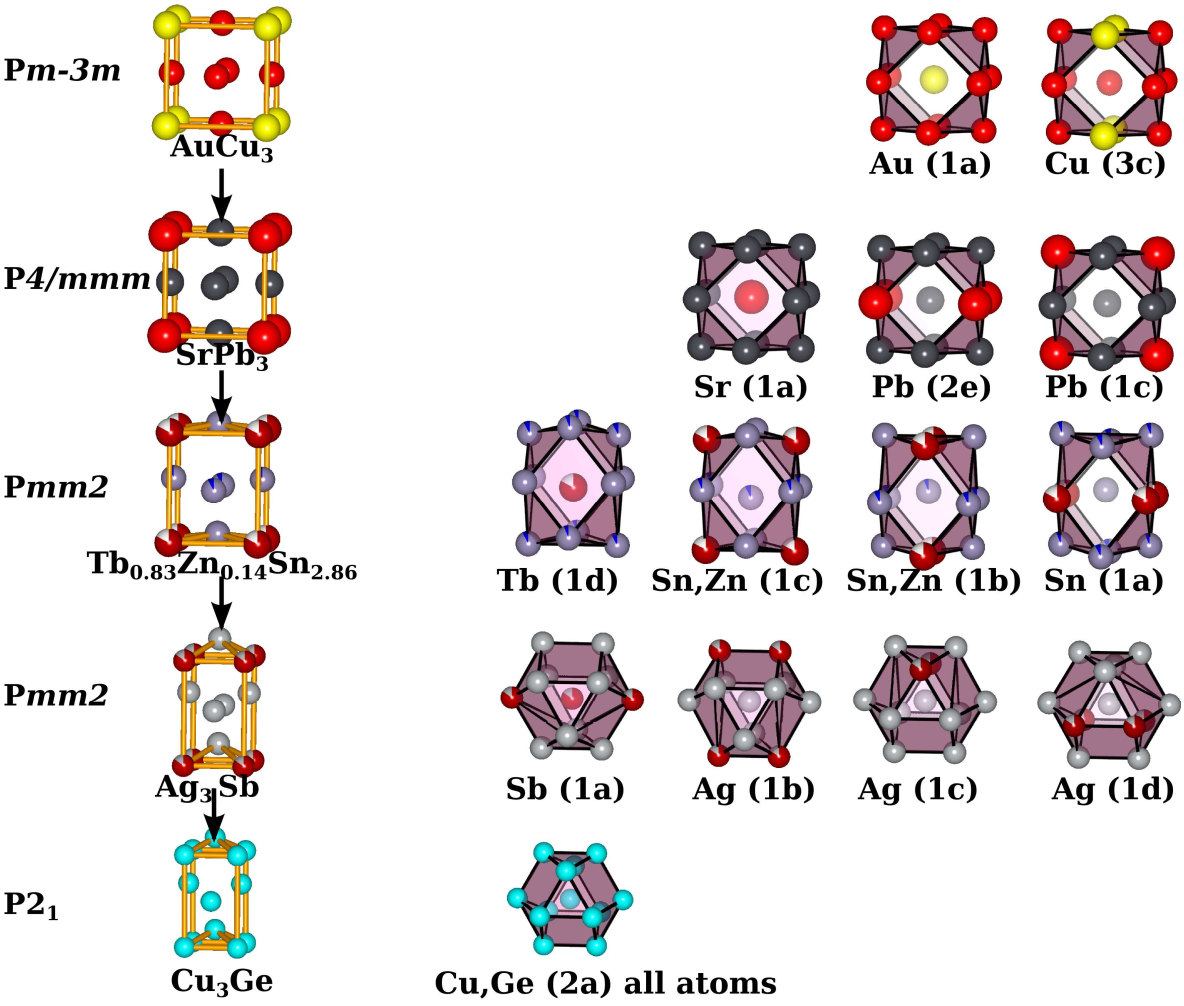

Fig. 2 Structure fragments and coordination polyhedra in structure types, derived from $AuCu_3$, with stoichiometry close to 1:3, containing 4 atoms in the unit cell and (distorted) close-packed layers.

Distorted cubooctahedra, with a shape close to that of the coordination polyhedra in the structure of $Tb_{0.83}Zn_{0.14}Sn_{2.86}$, are observed in the compounds βTb_3Sn_7, $TbSn_2$, $TbZn_xSn_{2-x}$, $TbSn_3$ cub, and $TbSn_3$ *Amm*2 [3,7-10,19].

Conclusion

A new compound, $Tb_{0.83}Zn_{0.14}Sn_{2.86}$, was found in ternary Tb–Zn–Sn alloys. The structure of the title compound adopts a new structure type, which is closely related to the $AuCu_3$ structure type. A chain of transformations of related structure types with small unit cells is proposed: $AuCu_3$ → $SrPb_3$ → $Tb_{0.83}Zn_{0.14}Sn_{2.86}$ → Ag_3Sb → Cu_3Ge. These structures can be obtained by gradual deformation and loss of symmetry from cubic to tetragonal, orthorhombic and finally monoclinic.

The way of formation of the title compound is still not clear since it was obtained only as a minor phase accompanying the Zn-stabilized high-pressure modification of $TbSn_3$. The reasons of this could be the high stability of the latter, together with the close compositions of the phases.

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