

Tb₁₃ZnSn₁₃: A novel intergrowth structure type

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The crystal structure of the new Tb₁₃ZnSn₁₃ compound (space group *I4/mmm*, $a = 11.599(2)$ Å, $c = 27.247(5)$ Å) was determined by X-ray single crystal diffraction. The composition was confirmed by EDX analysis. The compound crystallizes in its own structure type, which can be built from fragments that are related to the U₃Si₂, CsCl, PtHg₂, α-Po, and InBi structure types.

Intermetallics / Crystal chemistry of intermetallics / Diffraction / Structure type / Terbium / Zinc / Tin

1. Introduction

Little literature data is available at present about ternary systems formed by rare-earth elements, zinc and tin. For the Tb–Zn–Sn system, no information on the ternary phase diagram is available; however, the existence and crystal structures of some ternary compounds have been reported. The equiatomic compound TbZnSn was investigated and is described in [1,2]. Isostructural *RZnSn* compounds also form with $R = \text{La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Lu, Sc, and Y}$. The *RZnSn* compounds crystallize with the YPtAs structure type (space group *P6₃/mmm*). We have previously [2] reported also the crystal structure of the TbZnSn₂ compound, which crystallizes with the HfCuSi₂ structure type (space group *P4/nmm*). In this paper we report our results on the synthesis and crystal structure of the new Tb₁₃ZnSn₁₃ compound.

The Tb₁₃ZnSn₁₃ compound was found during a systematic investigation of the Tb–Zn–Sn ternary system while trying to prepare an inclusion phase Tb₅Zn_xSn₃, based on the binary compound Tb₅Sn₃. The first sample, with nominal composition Tb₅Zn₂Sn₃, was made by arc-melting. It suffered a large loss of mass and had a very complicated diffraction pattern. X-ray phase analysis showed that this sample was non-equilibrium, and consisted of multiple phases including some unknown one(s). Based on this evidence, we proceeded with the preparation of Tb₅Zn_xSn₃ phases by a different technique.

2. Experimental

2.1. Synthesis and phase analysis

An alloy with the nominal composition Tb₅ZnSn₃ was prepared by melting stoichiometric amounts of the constituent metals in a sealed Ta-container in a high-frequency furnace. Terbium, zinc and tin, all with nominal purities ~99.9 wt.%, were used as starting elements. The sample was first heated in the HF-furnace (Hüttinger Elektronik, Freiburg, Typ TIG 2.5/300) under flowing argon up to approximately 1000°C and held at that temperature for 1.5 hours. The temperature was controlled by a Sensor Therm Metis MS06 pyrometer with an accuracy of ±5 K. After the melting procedure the sample was slowly cooled to approximately 700°C and was finally quenched by switching off the power to the furnace. After cooling to room temperature, the grey samples could easily be separated from the tantalum crucibles. No reaction of the samples with the crucible material could be detected. Good-quality single crystals of Tb₁₃ZnSn₁₃ were selected from the annealed samples by mechanical fragmentation.

2.2. Structure analysis and refinement

Single crystal diffraction data for Tb₁₃ZnSn₁₃ were collected at room temperature on a Stoe IPDS-IIT image plate diffractometer with graphite monochromatized Mo K_α (0.71073 Å) radiation in the oscillation mode. Numerical absorption corrections were applied (X-Shape/X-Red).

Table 1 Crystallographic data of the Tb₁₃ZnSn₁₃ compound and experimental details of the structure determination.

Empirical formula	Tb ₁₃ ZnSn ₁₃
Structure type	New
Space group	<i>I4/mmm</i> (No. 139)
Pearson symbol	<i>tI150</i>
Unit cell dimensions:	
<i>a</i> , Å	11.599(2)
<i>c</i> , Å	27.247(5)
<i>V</i> , Å ³	3667(1)
<i>Z</i>	5.5
Calculated density (<i>D</i> _{calc} , g/cm ⁻³)	8.575
Theta range for data collection	3.82-27.50
Absorption coefficient (<i>μ</i> , mm ⁻¹)	44.05
Data collection mode	ω
<i>F</i> (000)	7858
Range in <i>h k l</i>	-15 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 15, -35 ≤ <i>l</i> ≤ 35
Total no. reflections	35207, rejected 4756
Independent reflections	1263 (<i>R</i> _{int} = 0.0777)
Reflections with <i>I</i> > 2σ(<i>I</i>)	1178 (<i>R</i> _{sigma} = 0.0193)
Goodness-of-fit on <i>F</i> ²	1.428
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0371 <i>wR</i> ₂ = 0.0482
Final <i>R</i> indices (all data)	<i>R</i> ₁ = 0.043 <i>wR</i> ₂ = 0.0493
Extinction coefficient	0.000036
Data / parameters	1263 / 78
Largest diff. peak and hole	3.432 and -3.610 e/Å ³

The crystal structure was successfully solved by direct methods and refined using SHELX-97 package programs [3,4].

The analysis of systematic absences and a statistical test of the distribution of the E-values suggested that the structure is centrosymmetric [5]. The results indicate that Tb₁₃ZnSn₁₃ crystallizes in the centrosymmetric space group *I4/mmm*.

2.3. SEM-EDX characterization

After the X-ray diffraction, the single crystal was analyzed with a JEOL SEM 5900LV scanning electron microscope. No impurity elements heavier than sodium were observed. The results of the EDX analysis are in good agreement with the composition resulting from the XRD data refinement.

3. Results and discussion

While trying to prepare an inclusion phase Tb₅Zn₅Sn₃ we found a new compound, Tb₁₃ZnSn₁₃, which crystallizes in a new structure type. Unit cell parameters, atomic coordinates and details of the refinement are given in Table 1. The crystal structure of Tb₁₃ZnSn₁₃ and a possible mechanism for its formation are given in Fig. 1 (projection of the cell in the middle of the picture), atomic parameters are given

in Table 2, and anisotropic displacement parameters of the atoms are given in Table 3.

There are two groups of split positions in Tb₁₃ZnSn₁₃: **Zn1-Zn2-Sn7** and **Zn3-Tb6-Tb7**. One group of split positions may contain simultaneously only zinc atoms in **Zn2** position or zinc atoms in **Zn1** position and a tin atom between them in **Sn7** position. In the same way, one group may contain simultaneously zinc atoms in **Zn3** position near terbium in **Tb7** position or only **Tb6** atoms. The occupation coefficients of the **Sn7** and **Zn1** positions are close and these positions can be occupied simultaneously. The occupation coefficients of the **Zn3** and **Tb7** positions are almost equal and the sums **Zn3+Tb6** and **Tb6+Tb7** are close to unity. The structure of Tb₁₃ZnSn₁₃ can be obtained considering insertion of zinc atoms into a hypothetical binary structure with chemical composition Tb_{1.04}Sn. Zinc atoms have much smaller radius than terbium and tin atoms and different electronic structure so they cannot substitute for terbium and tin atoms and only insertion is possible. If the **Sn7** position is occupied, then zinc atoms occupy **Zn1** positions near it, otherwise **Zn2** positions are occupied. Atoms in **Zn3** position displace terbium atoms. This position is partially occupied so we observe splitting of the nearby terbium position. The **Tb6** position is occupied when the **Zn3** position is empty. Filling of the **Zn3** position

Table 2 Atomic coordinates for the Tb₁₃ZnSn₁₃ compound.

Atom	Wyckoff	G	x/a	y/b	z/c	$U_{eq}, \text{\AA}^2$
Tb1	8i	1	0.23854(8)	0	0	0.0086(2)
Tb2	16n	1	1/2	0.23781(6)	0.06283(2)	0.0088(2)
Tb3	16n	1	1/2	0.14895(6)	0.19084(2)	0.0113(2)
Tb4	16m	1	0.18084(4)	0.18084(4)	0.11510(2)	0.0098(2)
Tb5	8f	1	1/4	1/4	1/4	0.0113(2)
Sn1	4c	1	1/2	0	0	0.0078(4)
Sn2	16n	1	0.25957(9)	0	0.20196(3)	0.0109(2)
Sn3	16n	1	0.37470(8)	0	0.10185(3)	0.0080(2)
Sn4	16m	1	0.36119(6)	0.36119(6)	0.15260(3)	0.0115(2)
Sn5	8h	1	0.26671(8)	0.26671(8)	0	0.0097(3)
Sn6	4e	1	0	0	0.06595(8)	0.0143(5)
Zn1	4e	0.70	1/2	1/2	0.0959(2)	0.017(1)
Zn2	4e	0.30	1/2	1/2	0.0612(3)	0.017(1)
Sn7	2b	0.70	1/2	1/2	0	0.017(1)
Zn3	4e	0.25	0	0	0.1599(5)	0.022(5)
Tb6	4e	0.75	0	0	0.2479(2)	0.0133(7)
Tb7	4e	0.24	0	0	0.2662(4)	0.0133(7)

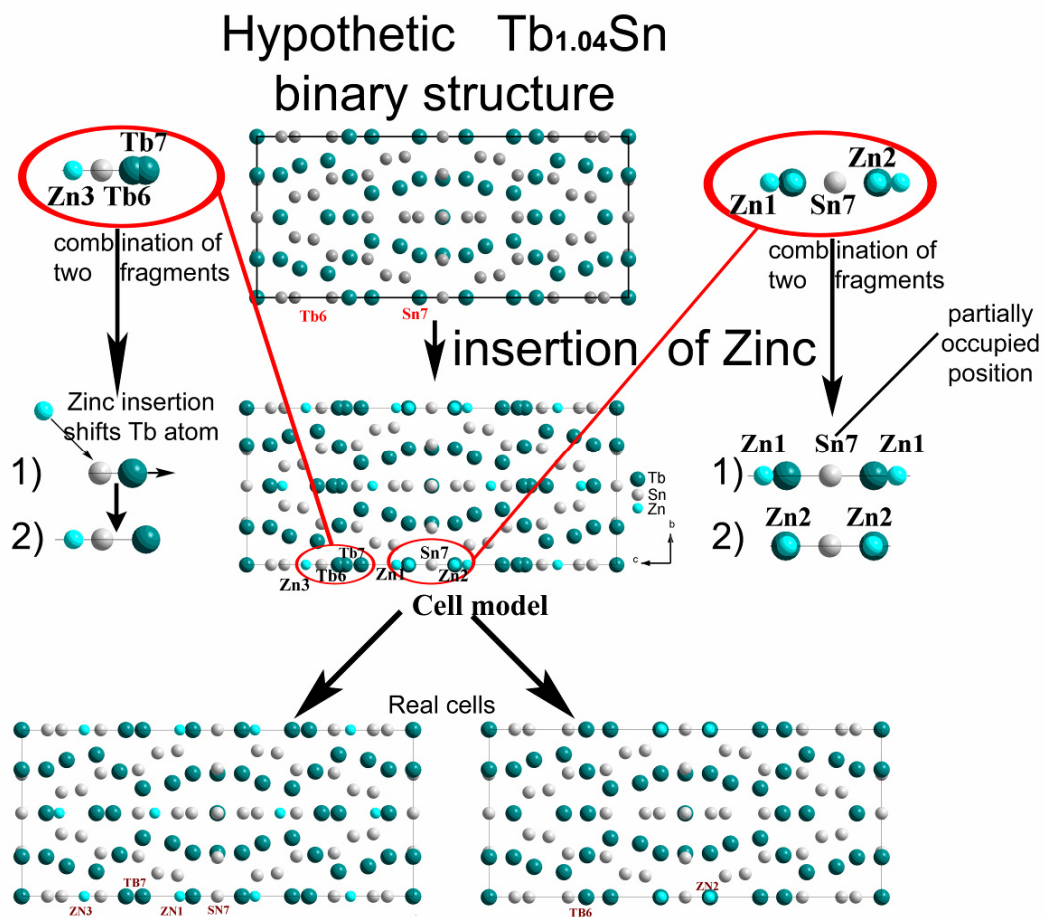
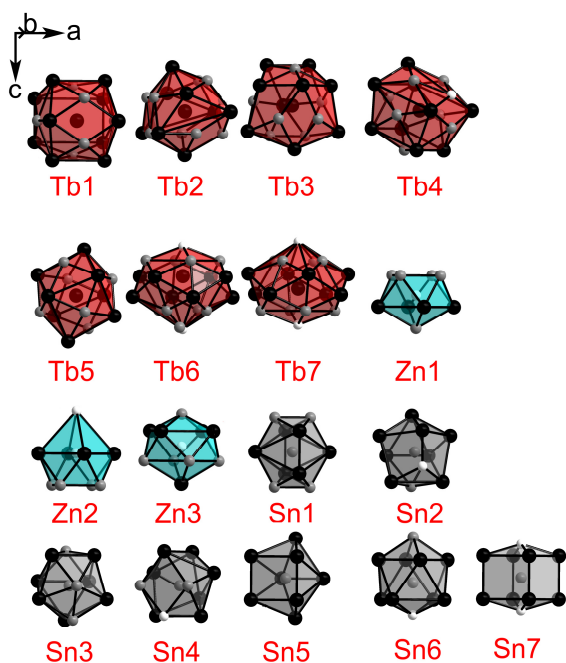
**Fig. 1** Crystal structure of the Tb₁₃ZnSn₁₃ compound and supposed mechanism of its formation.

Table 3 Anisotropic displacement parameters (Å²) of atoms in the Tb₁₃ZnSn₁₃ compound.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tb1	0.0076(4)	0.0088(4)	0.0093(4)	0	0	0
Tb2	0.0094(3)	0.0095(3)	0.0075(3)	0	0	-0.0004(2)
Tb3	0.0128(3)	0.0109(3)	0.0103(3)	0	0	0.0003(2)
Tb4	0.0095(2)	0.0095(2)	0.0105(3)	0.0028(3)	-0.0007(2)	-0.0007(2)
Tb5	0.0113(3)	0.0113(3)	0.0114(4)	0.0016(4)	0.0003(3)	0.0003(3)
Sn1	0.0069(9)	0.0100(9)	0.0068(8)	0	0	0
Sn2	0.0146(5)	0.0101(5)	0.0077(4)	0	0.0017(4)	0
Sn3	0.0065(4)	0.0086(4)	0.0090(4)	0	0.0002(3)	0
Sn4	0.0110(3)	0.0110(3)	0.0132(4)	0.0029(4)	0.0002(3)	0.0002(3)
Sn5	0.0089(4)	0.0089(4)	0.0111(6)	0.0016(5)	0	0
Sn6	0.0084(6)	0.0084(6)	0.027(1)	0	0	0

**Fig. 2** Coordination polyhedra of atoms in Tb₁₃ZnSn₁₃ compound.

displaces the nearby terbium atom from **Tb6** position to **Tb7**.

The metallic radii of the constituting elements are as follows: terbium 1.760 Å, zinc 1.330 Å and tin 1.400 Å. Selected interatomic distances are given in **Table 4**. The interatomic distances between the positions **Zn3-Tb6**, **Zn1-Zn2** and **Tb6-Tb7** are much less than the sums of the corresponding atomic radii so these pairs of positions cannot be occupied simultaneously. The interatomic distance between **Tb7** and **Zn3** positions is slightly shorter than the sum of the corresponding atomic radii. The composition determined from the structural refinement is identical to EDX data within experimental errors (see **Table 5**). Large experimental errors in the latter data are observed because a standard-free EDX technique was employed. The Tb₁₃ZnSn₁₃ stoichiometry was adopted as the closest integer ratio of the elements that describes the chemical composition of the compound.

The coordination polyhedra of the atoms in the Tb₁₃ZnSn₁₃ compound are shown in **Fig. 2**. The largest, Tb atoms are enclosed in 16-vertex polyhedra (**Tb1** and **Tb3**), 17-vertex polyhedra (**Tb2** and **Tb4**) and 18-vertex polyhedra (**Tb6** and **Tb7**). The **Tb5** atom is enclosed in a distorted rhombododecahedron (CN=14). The **Zn1** and **Zn2** atoms are characterized by monocapped tetragonal antiprisms (CN=9) and **Zn3** by a deformed bicapped tetragonal antiprism (CN=10). Atom **Sn5** is surrounded by 8 neighbors forming a trigonal prism with two additional atoms (CN=8). The remaining Sn atoms have distorted bicapped tetragonal prismatic coordination with CN=10. The shortest interatomic distances (**Table 4**) are in the ranges typical for intermetallic compounds.

The structure can be treated as packing of two different fragments: type **A** and type **B** (see **Fig. 3**).

Type **A** fragments are 24-vertex clusters with composition [Tb₂₈Zn_{0.54}Sn₂₄] around the void between **Sn6** atoms. The first coordination sphere has radius 4.35 Å and is a distorted rhombododecahedron. The second coordination sphere has radius 6.7 Å; it has 18 rectangular and 8 triangular faces. These clusters are connected by four faces into flat layers. Neighboring clusters are shifted by (½ ½ ½) with respect to each other.

Type **B** fragments are made of four octahedra around **Tb5** atoms ($R_{\max} = 3.3$ Å) and eight distorted square pyramids around **Tb3** atoms ($R_{\max} = 3.3$ Å) sharing faces. The **Tb3** atoms are situated close to the basis of the pyramids. The layers made of type **A** and type **B** fragments do not fill space completely. The major part of the split positions is situated in holes in the layers (see **Fig. 3**). Positions **Tb6** and **Tb7** are inside type **B** layers and **Zn1**, **Zn2** and **Sn7** positions are inside type **A** layers. Only **Zn3** positions are inside the 24-vertex clusters. Each unit cell contains two type **A** clusters and two type **B** fragments. In other words, the 24-vertex clusters may be structure-forming elements, type **B** fragments are linkers and voids between all these fragments are filled by atoms in split positions. It should be noted that the atoms in type **B** layers (linkers) and in split positions (spacers) have slightly higher isotropic displacements than the other ones.

Table 4 Selected interatomic distances.

Atom1	Atom2	d_{12} , Å	Atom1	Atom2	d_{12} , Å	
Tb1	1Sn1	3.033(1)		2Tb4	3.2916(9)	
	2Sn5	3.111(1)		2Tb3	3.295(1)	
	2Sn3	3.193(1)		1Tb7	3.483(6)	
	2Sn6	3.299(2)		2Sn2	4.258(1)	
	4Tb4	3.8319(7)	Sn3	1Sn3	2.907(2)	
	2Tb1	3.913(1)		1Sn2	3.037(2)	
	4Tb2	4.4426(9)		2Tb4	3.0962(9)	
Tb2	1Zn2	3.0415(8)	1Sn1	3.133(1)		
	1Zn1	3.172(2)	1Tb1	3.193(1)		
	2Sn5	3.2195(9)	2Tb2	3.2941(8)		
	1Sn1	3.2464(8)	2Tb3	3.313(1)		
	2Sn4	3.259(1)	2Sn5	4.341(1)		
	2Sn3	3.2941(8)	2Sn4	4.4146(9)		
	1Tb2	3.424(1)	1Sn6	4.455(1)		
	1Sn7	3.4899(8)	Sn4	1Zn1	2.752(3)	
	1Tb3	3.637(1)		2Tb3	3.121(1)	
	2Tb4	4.0211(7)		1Tb4	3.1299(9)	
	2Tb2	4.3009(8)		1Tb7	3.175(8)	
	2Tb1	4.4426(9)		2Sn4	3.220(1)	
				1Tb5	3.2202(9)	
		2Tb2		3.259(1)		
Tb3	1Sn2	3.108(1)	1Zn2	3.374(6)		
	2Sn4	3.121(1)	1Tb6	3.540(3)		
	2Sn2	3.295(1)	2Sn3	4.4146(9)		
	2Sn3	3.313(1)	1Sn5	4.437(1)		
	1Tb3	3.455(1)	Sn5	2Tb1	3.111(2)	
	2Tb5	3.5186(5)		4Tb2	3.220(1)	
	1Tb2	3.637(1)		2Tb4	3.4379(8)	
	2Tb3	4.0451(9)		1Sn7	3.827(1)	
	1Tb7	4.237(3)		2Sn1	4.110(1)	
	2Tb4	4.2544(7)		2Zn2	4.174(4)	
	1Tb6	4.401(2)		4Sn3	4.341(1)	
	Tb4	2Sn3	3.0962(9)	2Sn4	4.437(1)	
		1Sn4	3.1299(9)	Sn6	1Zn3	2.56(2)
1Zn3		3.208(5)	4Tb4		3.255(1)	
1Sn6		3.255(1)	4Tb1		3.299(1)	
2Sn2		3.2916(9)	1Sn6		3.594(3)	
1Sn5		3.4379(8)	4Sn3		4.4549(8)	
2Tb1		3.8319(7)	Zn1^a		1Zn2	0.95(1)
1Tb5		3.8467(8)			1Sn7	2.61(6)
2Tb2		4.0211(7)		4Sn4	2.752(3)	
2Tb4		4.1952(9)		4Tb2	3.172(2)	
2Tb3		4.2544(7)	1Tb7	3.76(1)		
Tb5	4Sn2	3.1835(5)	1Tb6	4.255(7)		
	2Sn4	3.2202(9)	1Zn2	4.28(1)		
	4Tb3	3.5186(7)	Zn2	1Zn1	0.95(1)	
	2Tb4	3.8467(8)		1Sn7	1.668(8)	
	2Tb6	4.1013(4)		4Tb2	3.0415(4)	
	2Tb7	4.125(1)		1Zn2	3.34(1)	
Sn1	2Tb1	3.033(1)	4Sn4	3.374(6)		
	4Sn3	3.133(1)	4Sn5	4.174(4)		
	4Tb2	3.2464(8)	1Zn1	4.28(1)		
	4Sn5	4.110(1)	Sn7	2Zn2	1.668(8)	
Sn2	1Sn3	3.037(2)		2Zn1	2.613(6)	
	1Tb3	3.108(1)		8Tb2	3.4899(8)	
	2Tb5	3.1835(5)		4Sn5	3.827(1)	
	1Zn3	3.222(5)				
	1Tb6	3.261(2)				

Table 4 Selected interatomic distances (continued).

Atom1	Atom2	$d_{12}, \text{\AA}$
Zn3	1Tb6	2.40(2)
	1Sn6	2.56(2)
	1Tb7	2.90(2)
	4Tb4	3.208(5)
	4Sn2	3.222(5)
Tb6	1Tb7	0.50(1)
	1Zn3	2.40(2)
	4Sn2	3.261(2)
	4Sn4	3.54(3)
	4Tb5	4.1013(4)
	1Zn1	4.255(7)
	4Tb3	4.401(2)
Tb7	1Tb6	0.50(1)
	1Zn3	2.90(2)
	4Sn4	3.17 (8)
	4Sn2	3.48(6)
	1Zn1	3.76(1)
	4Tb5	4.125(1)
	4Tb3	4.237(3)

^a Interatomic distances between atoms in split positions are given in bold face.

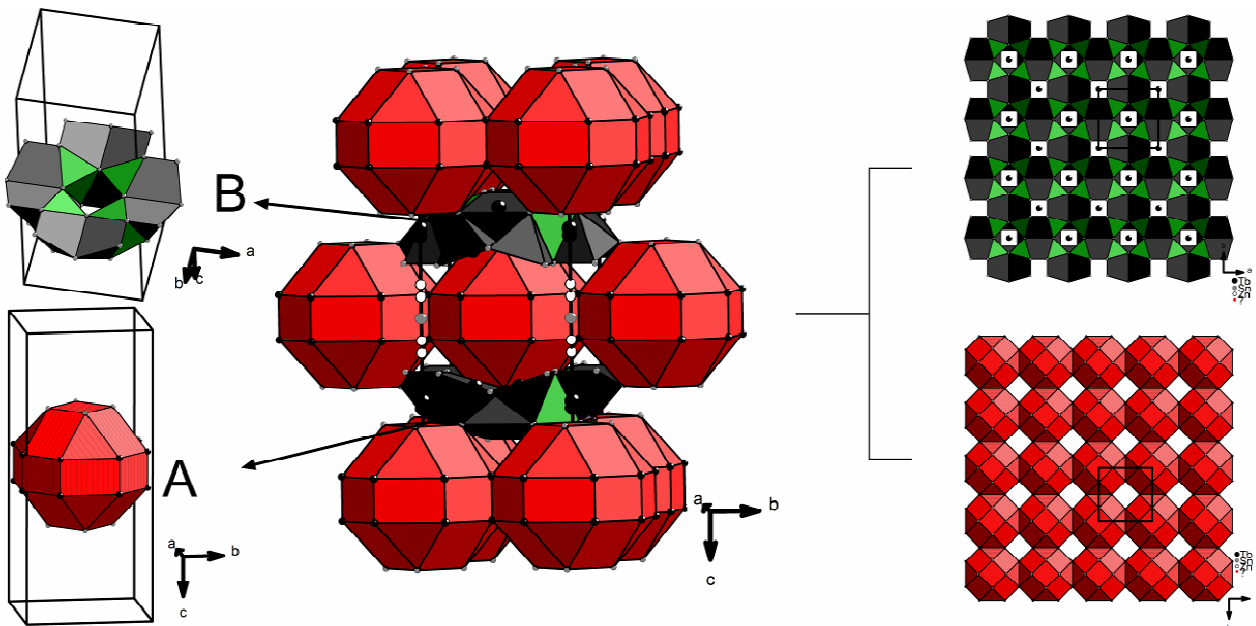
Another way to describe this structure type is to analyze the networks perpendicular to the longest cell parameter. There are four different networks, shown in Fig. 4, making twelve layers. The stacking sequence in the structure is **ABCDC'B'A'B'C'D'CB**.

Type **A'**, **B'**, **C'**, and **D'** networks are the same as **A**, **B**, **C**, and **D** but shifted by $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$.

Type **A** is a flat network at $z = 0.00$, which is formed of fragments of the α -Po [6] structure type. It consists of isolated square groups of terbium atoms and a subnet made of tin atoms. Its symbol is $8^2 4^2 + 8^1 4^2 + 4^4$.

Type **B** is a corrugated network ($z = 0.06-0.12$), which accommodates the majority of the terbium atoms. Type **B** network has fragments of three structure types: CsCl [7], α -Vlir [8], and U_3Si_2 [9]. The U_3Si_2 fragments are centered by zinc atoms. Larger terbium atoms surround smaller tin and zinc atoms and the fragment is defined here as CsCl type. The terbium atom framework can be described by the symbol $6^2 4^1 3^1 + 6^1 4^1 3^2$.

Type **C** is a corrugated network ($z = 0.15-0.20$), which has the symbol $12^2 3^1 + 12^1 4^1 3^2$. It consists of fragments of the PtHg₂ structure type [10]. Each of these fragments is connected to four other fragments forming dodecagonal crowns centered by zinc atoms.

**Fig. 3** Packing of clusters in the Tb₁₃ZnSn₁₃ compound.**Table 5** Composition of the Tb₁₃ZnSn₁₃ compound obtained from structure determination and EDX.

	Tb, at. %	Zn, at. %	Sn, at. %
Alloy composition	55.55	11.11	33.34
Structure determination	48.85	3.709	47.44
EDX	48±10	3.12±3.64	49±9

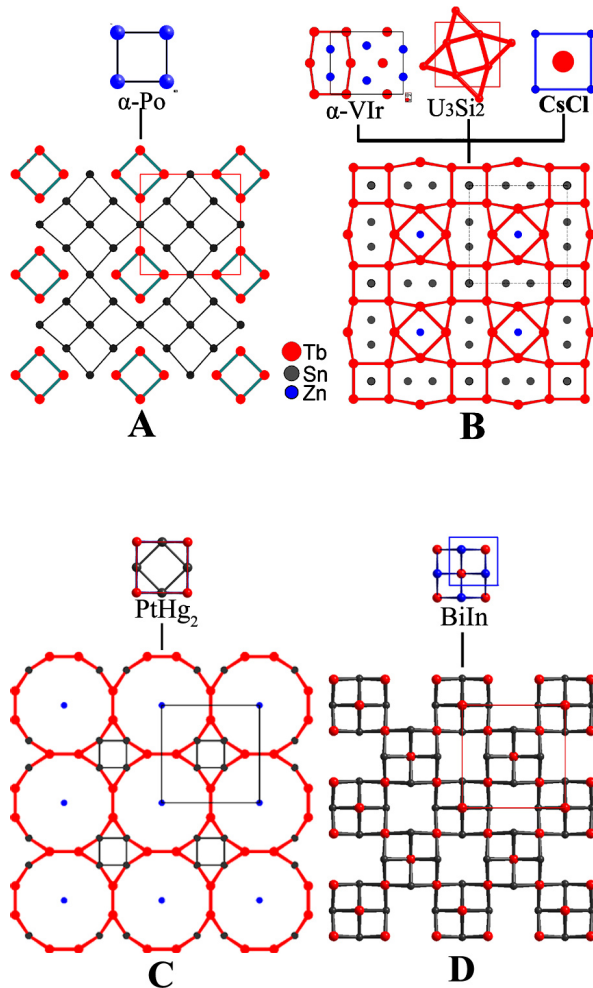


Fig. 4 Networks in the $Tb_{13}ZnSn_{13}$ compound and related fragments.

Type **A** network: $z = 0.00$.

Type **B** network: $z = 0.06-0.12$.

Type **C** network: $z = 0.15-0.20$.

Type **D** network: $z = 0.20-0.30$.

Type **D** is a corrugated network ($z = 0.20-0.30$), which consists of fragments of the BiIn structure type [11]. The fragments share atoms and the symbol of the framework is $8^2 4^2 + 4^4$.

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