

## Pentaterbium lithium tristannide, Tb<sub>5</sub>LiSn<sub>3</sub>

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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{Tb-Sn}) = 0.001$  Å;  $R$  factor = 0.021;  $wR$  factor = 0.066; data-to-parameter ratio = 15.4.

The new ternary phase pentaterbium lithium tristannide, Tb<sub>5</sub>LiSn<sub>3</sub>, crystallizes in the hexagonal Hf<sub>5</sub>CuSn<sub>3</sub> structure type, which is a 'filled' version of the binary RE<sub>5</sub>Sn<sub>3</sub> phases (Mn<sub>5</sub>Si<sub>3</sub>-type) (RE is rare earth). The asymmetric unit contains two Tb sites (site symmetries 3.2 and  $m2m$ ), one Li site (site symmetry  $\bar{3}m$ ) and one Sn site (site symmetry  $m2m$ ). The 14-vertex Frank–Kasper polyhedra are typical for Li and Tb atoms. The environment of the Sn atom is a pseudo-Frank–Kasper polyhedron with a coordination number of 13 for the tin atom. One of the Tb atoms is enclosed in a 17-vertex polyhedron. The metallic type of bonding was indicated by an analysis of the interatomic distances.

### Related literature

For the Hf<sub>5</sub>CuSn<sub>3</sub> structure type, see: Rieger & Parthé (1965). For related structures, see: Pavlyuk & Bodak (1992a,b); Pavlyuk *et al.* (1989, 1991, 1993). For the magnetic properties of related compounds, see: Tran *et al.* (2008).

### Experimental

#### Crystal data

Tb<sub>5</sub>LiSn<sub>3</sub>  $M_r = 1157.72$

Hexagonal,  $P6_3/mcm$

$a = 9.0122$  (14) Å

$c = 6.5744$  (13) Å

$V = 462.4$  (2) Å<sup>3</sup>

$Z = 2$

Mo  $K\alpha$  radiation

$\mu = 45.56$  mm<sup>-1</sup>

$T = 293$  K

$0.07 \times 0.05 \times 0.03$  mm

#### Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer

Absorption correction: analytical

(*CrysAlis RED*; Oxford

Diffraction, 2008)

$T_{\min} = 0.322$ ,  $T_{\max} = 0.657$

1907 measured reflections

216 independent reflections

207 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.066$

$S = 1.33$

216 reflections

14 parameters

$\Delta\rho_{\text{max}} = 1.08$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -1.47$  e Å<sup>-3</sup>

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FF2031).

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**supplementary materials**

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## Pentaterbium lithium tristannide, Tb<sub>5</sub>LiSn<sub>3</sub>

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### Comment

The RE<sub>5</sub>TM<sub>3</sub> (RE - rare earth, T - Cu, Ag and M - Sn, Pb) ternary stannides crystallize in a hexagonal Hf<sub>5</sub>CuSn<sub>3</sub> (superstructure to Ti<sub>5</sub>Ga<sub>4</sub>-type) with space group *P6<sub>3</sub>/mcm* (Rieger and Parthé, 1965). These intermetallic compounds are characterized by two different sites for the RE atoms located at *4 d* and *6 g*, respectively. The Sn or Pb atoms are located at the next *6 g* site and the transition atoms occupy *2 b* site. The RE<sub>5</sub>TM<sub>3</sub> intermetallics are 'filled' version of the binary RE<sub>5</sub>M<sub>3</sub> phases which crystallize in Mn<sub>5</sub>Si<sub>3</sub> structure type. It is also possible, that the transition metals fill the octahedral voids.

For the Ce based compounds, Ce<sub>5</sub>TM<sub>3</sub>, investigated by (Tran *et al.*, 2008) are found multiple magnetic phase transitions at low temperatures and discussed the role of *f*-*spd* hybridization on the evolution of heavy-fermion behaviour.

We detected the new ternary compound during the systematic study of ternary alloys of Tb—Li—Sn system from the concentration region with low content of lithium. The powder diffraction pattern of this compound is similar to the powder pattern of the RE<sub>5</sub>Sn<sub>3</sub> (RE - rare-earth metals) binary phases, but has some differences. So we decided to further study this phase using single-crystal method. Obtained single-crystal data show that the title compound crystallizes with the hexagonal space group *P6<sub>3</sub>/mcm* as a Hf<sub>5</sub>CuSn<sub>3</sub> type. The projection of the unit cell and coordination polyhedra of the atoms are shown in Fig. 1. The distribution of tin and lithium atoms in three-dimensional-nets consisted of Tb atoms are shown in Fig. 2.

The number of neighbouring atoms correlates well with the dimensions of the central atoms. The Tb atoms are enclosed in 14- and 17-vertex polyhedra. The coordination polyhedron of the Sn atom is pseudo Frank-Kasper polyhedron with CN=13. Lithium atom is surrounded by 14 neighbours atoms in the form of 14-vertex Frank-Kasper polyhedron. The shortest interatomic distances in the title compound are in the typical for intermetallic compounds ranges and indicate metallic type of bonding.

In the title compound lithium atoms occupy the same crystallographic position that the atoms of transition metal in the original structure type. The same was observed previously when we studied RELiSn<sub>2</sub> compounds with the CeNiSi<sub>2</sub> structure type (Pavlyuk *et al.*, 1989), RELiGe with the ZrNiAl type (Pavlyuk *et al.*, 1991 and Pavlyuk & Bodak, 1992*a*), RE<sub>3</sub>Li<sub>2</sub>Ge<sub>3</sub> with Hf<sub>3</sub>Ni<sub>2</sub>Si<sub>3</sub> type (Pavlyuk & Bodak, 1992*b*), solid solutions RLi<sub>x</sub>Cu<sub>2-x</sub>Si<sub>2</sub> and RLi<sub>x</sub>Cu<sub>2-x</sub>Ge<sub>2</sub> (Pavlyuk *et al.*, 1993).

### Experimental

Terbium, lithium and tin, all with a nominal purity more than 99.9 wt. %, were used as starting elements. First, the pieces of the pure metals with a stoichiometry Tb<sub>5</sub>Li<sub>10</sub>Sn<sub>35</sub> were pressed into pellet, enclosed in tantalum crucible and placed in a resistance furnace with a thermocouple controller. Heating rate from room temperature to 670 K was equal 5 K per minute. At this temperature the alloy was held over 2 d and then the temperature was increased from 670 to 1070 K over 1 h. Then the alloy was annealed at this temperature for 8 h and slowly cooled down to room temperature. After the melting

and annealing procedures, the total weight loss was less than 2%. Small good quality single-crystal of the title compound was isolated from alloy.

## Figures

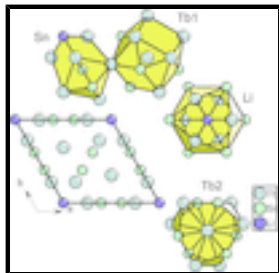


Fig. 1. The projection of the unit cell and coordination polyhedra of the atoms.

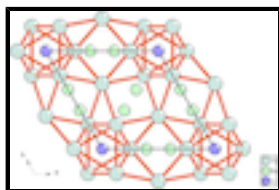


Fig. 2. The distribution of tin and lithium atoms in three-dimensional-nets consisted of Tb atoms.

## Pentaterybium lithium tristannide

### Crystal data

Tb<sub>5</sub>LiSn<sub>3</sub>

$M_r = 1157.72$

Hexagonal,  $P6_3/mcm$

Hall symbol: -P 6c 2

$a = 9.0122 (14) \text{ \AA}$

$c = 6.5744 (13) \text{ \AA}$

$V = 462.4 (2) \text{ \AA}^3$

$Z = 2$

$F(000) = 956$

$D_x = 8.315 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1907 reflections

$\theta = 2.6\text{--}27.4^\circ$

$\mu = 45.56 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism, metallic dark grey

$0.07 \times 0.05 \times 0.03 \text{ mm}$

### Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer

Radiation source: fine-focus sealed tube graphite

Detector resolution: 0 pixels  $\text{mm}^{-1}$

$\omega$  scans

Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)

$T_{\min} = 0.322$ ,  $T_{\max} = 0.657$

1907 measured reflections

216 independent reflections

207 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 27.4^\circ$ ,  $\theta_{\min} = 2.6^\circ$

$h = -11 \rightarrow 11$

$k = -11 \rightarrow 11$

$l = 0 \rightarrow 8$

Refinement

Refinement on $F^2$	0 restraints
Least-squares matrix: full	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.021$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.066$	$w = 1/[\sigma^2(F_o^2) + (0.0268P)^2 + 3.977P]$
$S = 1.33$	where $P = (F_o^2 + 2F_c^2)/3$
216 reflections	$(\Delta/\sigma)_{\max} < 0.001$
14 parameters	$\Delta\rho_{\max} = 1.08 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -1.47 \text{ e } \text{\AA}^{-3}$

Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Tb1	0.25088 (10)	0.0000	0.2500	0.0479 (3)
Tb2	0.3333	0.6667	0.0000	0.0535 (3)
Sn3	0.60694 (14)	0.0000	0.2500	0.0493 (4)
Li4	0.0000	0.0000	0.0000	0.055 (13)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Tb1	0.0478 (4)	0.0481 (5)	0.0479 (5)	0.0241 (3)	0.000	0.000
Tb2	0.0536 (4)	0.0536 (4)	0.0532 (6)	0.0268 (2)	0.000	0.000
Sn3	0.0491 (5)	0.0493 (7)	0.0496 (6)	0.0247 (4)	0.000	0.000
Li4	0.07 (2)	0.07 (2)	0.03 (2)	0.033 (11)	0.000	0.000

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Tb1—Li4	2.7952 (8)	Tb2—Tb1 <sup>xiii</sup>	3.8093 (7)
Tb1—Li4 <sup>i</sup>	2.7952 (8)	Tb2—Tb1 <sup>xi</sup>	3.8093 (7)
Tb1—Sn3 <sup>ii</sup>	3.1066 (11)	Tb2—Tb1 <sup>xiii</sup>	3.8093 (8)
Tb1—Sn3 <sup>iii</sup>	3.1066 (11)	Tb2—Tb1 <sup>ix</sup>	3.8093 (7)

## supplementary materials

Tb1—Sn3	3.2090 (16)	Sn3—Tb1 <sup>xvii</sup>	3.1066 (11)
Tb1—Sn3 <sup>iv</sup>	3.5281 (8)	Sn3—Tb1 <sup>xviii</sup>	3.1066 (11)
Tb1—Sn3 <sup>v</sup>	3.5281 (8)	Sn3—Tb2 <sup>vii</sup>	3.2247 (6)
Tb1—Tb2 <sup>vi</sup>	3.8093 (7)	Sn3—Tb2 <sup>vi</sup>	3.2247 (6)
Tb1—Tb2 <sup>vii</sup>	3.8093 (7)	Sn3—Tb2 <sup>ix</sup>	3.2247 (6)
Tb1—Tb2 <sup>viii</sup>	3.8093 (7)	Sn3—Tb2 <sup>viii</sup>	3.2247 (6)
Tb1—Tb2 <sup>ix</sup>	3.8093 (7)	Sn3—Tb1 <sup>iv</sup>	3.5281 (8)
Tb1—Tb1 <sup>x</sup>	3.9161 (17)	Sn3—Tb1 <sup>v</sup>	3.5281 (8)
Tb2—Sn3 <sup>xi</sup>	3.2247 (6)	Li4—Tb1 <sup>xix</sup>	2.7952 (8)
Tb2—Sn3 <sup>xii</sup>	3.2247 (6)	Li4—Tb1 <sup>xx</sup>	2.7952 (8)
Tb2—Sn3 <sup>xiii</sup>	3.2247 (6)	Li4—Tb1 <sup>xiii</sup>	2.7952 (8)
Tb2—Sn3 <sup>ix</sup>	3.2247 (6)	Li4—Tb1 <sup>x</sup>	2.7952 (8)
Tb2—Sn3 <sup>xiv</sup>	3.2247 (6)	Li4—Tb1 <sup>xiv</sup>	2.7952 (8)
Tb2—Sn3 <sup>iii</sup>	3.2247 (6)	Li4—Li4 <sup>i</sup>	3.2872 (6)
Tb2—Tb2 <sup>xv</sup>	3.2872 (6)	Li4—Li4 <sup>xxi</sup>	3.2872 (6)
Tb2—Tb2 <sup>xvi</sup>	3.2872 (6)		
Li4—Tb1—Li4 <sup>i</sup>	72.03 (3)	Sn3 <sup>xiv</sup> —Tb2—Tb1 <sup>xii</sup>	144.94 (2)
Li4—Tb1—Sn3 <sup>ii</sup>	82.67 (2)	Sn3 <sup>iii</sup> —Tb2—Tb1 <sup>xii</sup>	123.785 (13)
Li4 <sup>i</sup> —Tb1—Sn3 <sup>ii</sup>	82.67 (2)	Tb2 <sup>xv</sup> —Tb2—Tb1 <sup>xii</sup>	64.439 (7)
Li4—Tb1—Sn3 <sup>iii</sup>	82.67 (2)	Tb2 <sup>xvi</sup> —Tb2—Tb1 <sup>xii</sup>	115.561 (7)
Li4 <sup>i</sup> —Tb1—Sn3 <sup>iii</sup>	82.67 (2)	Sn3 <sup>xi</sup> —Tb2—Tb1 <sup>xi</sup>	53.50 (2)
Sn3 <sup>ii</sup> —Tb1—Sn3 <sup>iii</sup>	161.86 (5)	Sn3 <sup>xii</sup> —Tb2—Tb1 <sup>xi</sup>	110.39 (2)
Li4—Tb1—Sn3	143.985 (13)	Sn3 <sup>xiii</sup> —Tb2—Tb1 <sup>xi</sup>	59.520 (16)
Li4 <sup>i</sup> —Tb1—Sn3	143.985 (13)	Sn3 <sup>ix</sup> —Tb2—Tb1 <sup>xi</sup>	51.60 (2)
Sn3 <sup>ii</sup> —Tb1—Sn3	99.07 (2)	Sn3 <sup>xiv</sup> —Tb2—Tb1 <sup>xi</sup>	123.785 (13)
Sn3 <sup>iii</sup> —Tb1—Sn3	99.07 (2)	Sn3 <sup>iii</sup> —Tb2—Tb1 <sup>xi</sup>	144.94 (2)
Li4—Tb1—Sn3 <sup>iv</sup>	147.31 (3)	Tb2 <sup>xv</sup> —Tb2—Tb1 <sup>xi</sup>	115.561 (7)
Li4 <sup>i</sup> —Tb1—Sn3 <sup>iv</sup>	75.28 (2)	Tb2 <sup>xvi</sup> —Tb2—Tb1 <sup>xi</sup>	64.439 (7)
Sn3 <sup>ii</sup> —Tb1—Sn3 <sup>iv</sup>	93.283 (5)	Tb1 <sup>xii</sup> —Tb2—Tb1 <sup>xi</sup>	63.16 (2)
Sn3 <sup>iii</sup> —Tb1—Sn3 <sup>iv</sup>	93.283 (5)	Sn3 <sup>xi</sup> —Tb2—Tb1 <sup>xiii</sup>	59.520 (16)
Sn3—Tb1—Sn3 <sup>iv</sup>	68.70 (3)	Sn3 <sup>xii</sup> —Tb2—Tb1 <sup>xiii</sup>	123.785 (13)
Li4—Tb1—Sn3 <sup>v</sup>	75.28 (2)	Sn3 <sup>xiii</sup> —Tb2—Tb1 <sup>xiii</sup>	53.50 (2)
Li4 <sup>i</sup> —Tb1—Sn3 <sup>v</sup>	147.31 (3)	Sn3 <sup>ix</sup> —Tb2—Tb1 <sup>xiii</sup>	144.94 (2)
Sn3 <sup>ii</sup> —Tb1—Sn3 <sup>v</sup>	93.283 (5)	Sn3 <sup>xiv</sup> —Tb2—Tb1 <sup>xiii</sup>	110.39 (2)
Sn3 <sup>iii</sup> —Tb1—Sn3 <sup>v</sup>	93.283 (5)	Sn3 <sup>iii</sup> —Tb2—Tb1 <sup>xiii</sup>	51.60 (2)
Sn3—Tb1—Sn3 <sup>v</sup>	68.70 (3)	Tb2 <sup>xv</sup> —Tb2—Tb1 <sup>xiii</sup>	64.439 (7)
Sn3 <sup>iv</sup> —Tb1—Sn3 <sup>v</sup>	137.41 (5)	Tb2 <sup>xvi</sup> —Tb2—Tb1 <sup>xiii</sup>	115.561 (7)
Li4—Tb1—Tb2 <sup>vi</sup>	102.887 (9)	Tb1 <sup>xii</sup> —Tb2—Tb1 <sup>xiii</sup>	102.753 (8)
Li4 <sup>i</sup> —Tb1—Tb2 <sup>vi</sup>	136.924 (8)	Tb1 <sup>xi</sup> —Tb2—Tb1 <sup>xiii</sup>	93.848 (16)
Sn3 <sup>ii</sup> —Tb1—Tb2 <sup>vi</sup>	54.444 (14)	Sn3 <sup>xi</sup> —Tb2—Tb1 <sup>ix</sup>	123.785 (13)

Sn3 <sup>iii</sup> —Tb1—Tb2 <sup>vi</sup>	140.12 (2)	Sn3 <sup>xii</sup> —Tb2—Tb1 <sup>ix</sup>	59.520 (16)
Sn3—Tb1—Tb2 <sup>vi</sup>	53.886 (12)	Sn3 <sup>xiii</sup> —Tb2—Tb1 <sup>ix</sup>	144.94 (2)
Sn3 <sup>iv</sup> —Tb1—Tb2 <sup>vi</sup>	100.83 (2)	Sn3 <sup>ix</sup> —Tb2—Tb1 <sup>ix</sup>	53.50 (2)
Sn3 <sup>v</sup> —Tb1—Tb2 <sup>vi</sup>	51.970 (13)	Sn3 <sup>xiv</sup> —Tb2—Tb1 <sup>ix</sup>	51.60 (2)
Li4—Tb1—Tb2 <sup>vii</sup>	136.924 (8)	Sn3 <sup>iii</sup> —Tb2—Tb1 <sup>ix</sup>	110.39 (2)
Li4 <sup>i</sup> —Tb1—Tb2 <sup>vii</sup>	102.887 (9)	Tb2 <sup>xv</sup> —Tb2—Tb1 <sup>ix</sup>	115.561 (7)
Sn3 <sup>ii</sup> —Tb1—Tb2 <sup>vii</sup>	140.12 (2)	Tb2 <sup>xvi</sup> —Tb2—Tb1 <sup>ix</sup>	64.439 (7)
Sn3 <sup>iii</sup> —Tb1—Tb2 <sup>vii</sup>	54.444 (14)	Tb1 <sup>xii</sup> —Tb2—Tb1 <sup>ix</sup>	93.848 (16)
Sn3—Tb1—Tb2 <sup>vii</sup>	53.886 (12)	Tb1 <sup>xi</sup> —Tb2—Tb1 <sup>ix</sup>	102.753 (8)
Sn3 <sup>iv</sup> —Tb1—Tb2 <sup>vii</sup>	51.970 (13)	Tb1 <sup>xiii</sup> —Tb2—Tb1 <sup>ix</sup>	160.55 (2)
Sn3 <sup>v</sup> —Tb1—Tb2 <sup>vii</sup>	100.83 (2)	Tb1 <sup>xvii</sup> —Sn3—Tb1 <sup>xviii</sup>	78.14 (5)
Tb2 <sup>vi</sup> —Tb1—Tb2 <sup>vii</sup>	107.77 (2)	Tb1 <sup>xvii</sup> —Sn3—Tb1	140.93 (2)
Li4—Tb1—Tb2 <sup>viii</sup>	136.924 (8)	Tb1 <sup>xviii</sup> —Sn3—Tb1	140.93 (2)
Li4 <sup>i</sup> —Tb1—Tb2 <sup>viii</sup>	102.887 (9)	Tb1 <sup>xvii</sup> —Sn3—Tb2 <sup>vii</sup>	73.951 (16)
Sn3 <sup>ii</sup> —Tb1—Tb2 <sup>viii</sup>	54.444 (14)	Tb1 <sup>xviii</sup> —Sn3—Tb2 <sup>vii</sup>	137.78 (3)
Sn3 <sup>iii</sup> —Tb1—Tb2 <sup>viii</sup>	140.12 (2)	Tb1—Sn3—Tb2 <sup>vii</sup>	72.61 (2)
Sn3—Tb1—Tb2 <sup>viii</sup>	53.886 (12)	Tb1 <sup>xvii</sup> —Sn3—Tb2 <sup>vi</sup>	137.78 (3)
Sn3 <sup>iv</sup> —Tb1—Tb2 <sup>viii</sup>	51.970 (13)	Tb1 <sup>xviii</sup> —Sn3—Tb2 <sup>vi</sup>	73.951 (16)
Sn3 <sup>v</sup> —Tb1—Tb2 <sup>viii</sup>	100.83 (2)	Tb1—Sn3—Tb2 <sup>vi</sup>	72.61 (2)
Tb2 <sup>vi</sup> —Tb1—Tb2 <sup>viii</sup>	51.122 (14)	Tb2 <sup>vii</sup> —Sn3—Tb2 <sup>vi</sup>	145.22 (4)
Tb2 <sup>vii</sup> —Tb1—Tb2 <sup>viii</sup>	86.152 (16)	Tb1 <sup>xvii</sup> —Sn3—Tb2 <sup>ix</sup>	73.951 (16)
Li4—Tb1—Tb2 <sup>ix</sup>	102.887 (9)	Tb1 <sup>xviii</sup> —Sn3—Tb2 <sup>ix</sup>	137.78 (3)
Li4 <sup>i</sup> —Tb1—Tb2 <sup>ix</sup>	136.924 (8)	Tb1—Sn3—Tb2 <sup>ix</sup>	72.61 (2)
Sn3 <sup>ii</sup> —Tb1—Tb2 <sup>ix</sup>	140.12 (2)	Tb2 <sup>vii</sup> —Sn3—Tb2 <sup>ix</sup>	61.287 (15)
Sn3 <sup>iii</sup> —Tb1—Tb2 <sup>ix</sup>	54.444 (14)	Tb2 <sup>vi</sup> —Sn3—Tb2 <sup>ix</sup>	107.56 (2)
Sn3—Tb1—Tb2 <sup>ix</sup>	53.886 (12)	Tb1 <sup>xvii</sup> —Sn3—Tb2 <sup>viii</sup>	137.78 (3)
Sn3 <sup>iv</sup> —Tb1—Tb2 <sup>ix</sup>	100.83 (2)	Tb1 <sup>xviii</sup> —Sn3—Tb2 <sup>viii</sup>	73.951 (16)
Sn3 <sup>v</sup> —Tb1—Tb2 <sup>ix</sup>	51.970 (13)	Tb1—Sn3—Tb2 <sup>viii</sup>	72.61 (2)
Tb2 <sup>vi</sup> —Tb1—Tb2 <sup>ix</sup>	86.152 (16)	Tb2 <sup>vii</sup> —Sn3—Tb2 <sup>viii</sup>	107.56 (2)
Tb2 <sup>vii</sup> —Tb1—Tb2 <sup>ix</sup>	51.122 (14)	Tb2 <sup>vi</sup> —Sn3—Tb2 <sup>viii</sup>	61.287 (15)
Tb2 <sup>viii</sup> —Tb1—Tb2 <sup>ix</sup>	107.77 (2)	Tb2 <sup>ix</sup> —Sn3—Tb2 <sup>viii</sup>	145.22 (4)
Li4—Tb1—Tb1 <sup>x</sup>	45.533 (9)	Tb1 <sup>xvii</sup> —Sn3—Tb1 <sup>iv</sup>	73.62 (2)
Li4 <sup>i</sup> —Tb1—Tb1 <sup>x</sup>	45.533 (9)	Tb1 <sup>xviii</sup> —Sn3—Tb1 <sup>iv</sup>	73.62 (2)
Sn3 <sup>ii</sup> —Tb1—Tb1 <sup>x</sup>	50.93 (2)	Tb1—Sn3—Tb1 <sup>iv</sup>	111.30 (3)
Sn3 <sup>iii</sup> —Tb1—Tb1 <sup>x</sup>	110.93 (2)	Tb2 <sup>vii</sup> —Sn3—Tb1 <sup>iv</sup>	68.510 (11)
Sn3—Tb1—Tb1 <sup>x</sup>	150.0	Tb2 <sup>vi</sup> —Sn3—Tb1 <sup>iv</sup>	125.693 (6)
Sn3 <sup>iv</sup> —Tb1—Tb1 <sup>x</sup>	108.33 (2)	Tb2 <sup>ix</sup> —Sn3—Tb1 <sup>iv</sup>	125.693 (6)
Sn3 <sup>v</sup> —Tb1—Tb1 <sup>x</sup>	108.33 (2)	Tb2 <sup>viii</sup> —Sn3—Tb1 <sup>iv</sup>	68.510 (11)
Tb2 <sup>vi</sup> —Tb1—Tb1 <sup>x</sup>	99.726 (11)	Tb1 <sup>xvii</sup> —Sn3—Tb1 <sup>v</sup>	73.62 (2)
Tb2 <sup>vii</sup> —Tb1—Tb1 <sup>x</sup>	148.420 (11)	Tb1 <sup>xviii</sup> —Sn3—Tb1 <sup>v</sup>	73.62 (2)
Tb2 <sup>viii</sup> —Tb1—Tb1 <sup>x</sup>	99.726 (11)	Tb1—Sn3—Tb1 <sup>v</sup>	111.30 (3)

## supplementary materials

Tb2 <sup>ix</sup> —Tb1—Tb1 <sup>x</sup>	148.420 (11)	Tb2 <sup>vii</sup> —Sn3—Tb1 <sup>v</sup>	125.693 (6)
Sn3 <sup>xi</sup> —Tb2—Sn3 <sup>xii</sup>	163.38 (4)	Tb2 <sup>vi</sup> —Sn3—Tb1 <sup>v</sup>	68.510 (11)
Sn3 <sup>xi</sup> —Tb2—Sn3 <sup>xiii</sup>	72.44 (2)	Tb2 <sup>ix</sup> —Sn3—Tb1 <sup>v</sup>	68.510 (11)
Sn3 <sup>xii</sup> —Tb2—Sn3 <sup>xiii</sup>	96.334 (10)	Tb2 <sup>viii</sup> —Sn3—Tb1 <sup>v</sup>	125.693 (6)
Sn3 <sup>xi</sup> —Tb2—Sn3 <sup>ix</sup>	96.334 (10)	Tb1 <sup>iv</sup> —Sn3—Tb1 <sup>v</sup>	137.41 (5)
Sn3 <sup>xii</sup> —Tb2—Sn3 <sup>ix</sup>	72.44 (2)	Tb1 <sup>xix</sup> —Li4—Tb1 <sup>xx</sup>	88.933 (19)
Sn3 <sup>xiii</sup> —Tb2—Sn3 <sup>ix</sup>	97.06 (4)	Tb1 <sup>xix</sup> —Li4—Tb1	91.067 (19)
Sn3 <sup>xi</sup> —Tb2—Sn3 <sup>xiv</sup>	96.334 (10)	Tb1 <sup>xx</sup> —Li4—Tb1	180.0
Sn3 <sup>xii</sup> —Tb2—Sn3 <sup>xiv</sup>	97.06 (4)	Tb1 <sup>xix</sup> —Li4—Tb1 <sup>xiii</sup>	180.0
Sn3 <sup>xiii</sup> —Tb2—Sn3 <sup>xiv</sup>	163.38 (4)	Tb1 <sup>xx</sup> —Li4—Tb1 <sup>xiii</sup>	91.067 (19)
Sn3 <sup>ix</sup> —Tb2—Sn3 <sup>xiv</sup>	96.334 (10)	Tb1—Li4—Tb1 <sup>xiii</sup>	88.933 (19)
Sn3 <sup>xi</sup> —Tb2—Sn3 <sup>iii</sup>	97.06 (4)	Tb1 <sup>xix</sup> —Li4—Tb1 <sup>x</sup>	91.067 (19)
Sn3 <sup>xii</sup> —Tb2—Sn3 <sup>iii</sup>	96.334 (10)	Tb1 <sup>xx</sup> —Li4—Tb1 <sup>x</sup>	91.067 (19)
Sn3 <sup>xiii</sup> —Tb2—Sn3 <sup>iii</sup>	96.334 (10)	Tb1—Li4—Tb1 <sup>x</sup>	88.933 (19)
Sn3 <sup>ix</sup> —Tb2—Sn3 <sup>iii</sup>	163.38 (4)	Tb1 <sup>xiii</sup> —Li4—Tb1 <sup>x</sup>	88.933 (19)
Sn3 <sup>xiv</sup> —Tb2—Sn3 <sup>iii</sup>	72.44 (2)	Tb1 <sup>xix</sup> —Li4—Tb1 <sup>xiv</sup>	88.933 (19)
Sn3 <sup>xi</sup> —Tb2—Tb2 <sup>xv</sup>	120.643 (7)	Tb1 <sup>xx</sup> —Li4—Tb1 <sup>xiv</sup>	88.933 (19)
Sn3 <sup>xii</sup> —Tb2—Tb2 <sup>xv</sup>	59.357 (8)	Tb1—Li4—Tb1 <sup>xiv</sup>	91.067 (19)
Sn3 <sup>xiii</sup> —Tb2—Tb2 <sup>xv</sup>	59.357 (7)	Tb1 <sup>xiii</sup> —Li4—Tb1 <sup>xiv</sup>	91.067 (19)
Sn3 <sup>ix</sup> —Tb2—Tb2 <sup>xv</sup>	120.643 (8)	Tb1 <sup>x</sup> —Li4—Tb1 <sup>xiv</sup>	180.00 (7)
Sn3 <sup>xiv</sup> —Tb2—Tb2 <sup>xv</sup>	120.643 (7)	Tb1 <sup>xix</sup> —Li4—Li4 <sup>i</sup>	126.015 (13)
Sn3 <sup>iii</sup> —Tb2—Tb2 <sup>xv</sup>	59.357 (7)	Tb1 <sup>xx</sup> —Li4—Li4 <sup>i</sup>	126.015 (13)
Sn3 <sup>xi</sup> —Tb2—Tb2 <sup>xvi</sup>	59.357 (7)	Tb1—Li4—Li4 <sup>i</sup>	53.985 (13)
Sn3 <sup>xii</sup> —Tb2—Tb2 <sup>xvi</sup>	120.643 (7)	Tb1 <sup>xiii</sup> —Li4—Li4 <sup>i</sup>	53.985 (13)
Sn3 <sup>xiii</sup> —Tb2—Tb2 <sup>xvi</sup>	120.643 (8)	Tb1 <sup>x</sup> —Li4—Li4 <sup>i</sup>	53.985 (13)
Sn3 <sup>ix</sup> —Tb2—Tb2 <sup>xvi</sup>	59.357 (8)	Tb1 <sup>xiv</sup> —Li4—Li4 <sup>i</sup>	126.015 (13)
Sn3 <sup>xiv</sup> —Tb2—Tb2 <sup>xvi</sup>	59.357 (7)	Tb1 <sup>xix</sup> —Li4—Li4 <sup>xxi</sup>	53.985 (13)
Sn3 <sup>iii</sup> —Tb2—Tb2 <sup>xvi</sup>	120.643 (7)	Tb1 <sup>xx</sup> —Li4—Li4 <sup>xxi</sup>	53.985 (13)
Tb2 <sup>xv</sup> —Tb2—Tb2 <sup>xvi</sup>	180.0	Tb1—Li4—Li4 <sup>xxi</sup>	126.015 (13)
Sn3 <sup>xi</sup> —Tb2—Tb1 <sup>xii</sup>	110.39 (2)	Tb1 <sup>xiii</sup> —Li4—Li4 <sup>xxi</sup>	126.015 (13)
Sn3 <sup>xii</sup> —Tb2—Tb1 <sup>xii</sup>	53.50 (2)	Tb1 <sup>x</sup> —Li4—Li4 <sup>xxi</sup>	126.015 (13)
Sn3 <sup>xiii</sup> —Tb2—Tb1 <sup>xii</sup>	51.60 (2)	Tb1 <sup>xiv</sup> —Li4—Li4 <sup>xxi</sup>	53.985 (13)
Sn3 <sup>ix</sup> —Tb2—Tb1 <sup>xii</sup>	59.520 (16)	Li4 <sup>i</sup> —Li4—Li4 <sup>xxi</sup>	180.0

Symmetry codes: (i)  $-x, -y, z+1/2$ ; (ii)  $-y, x-y-1, z$ ; (iii)  $-x+y+1, -x+1, z$ ; (iv)  $-x+1, -y, -z+1$ ; (v)  $-x+1, -y, -z$ ; (vi)  $x, y-1, z$ ; (vii)  $-x+1, -y+1, z+1/2$ ; (viii)  $x, y-1, -z+1/2$ ; (ix)  $-x+1, -y+1, -z$ ; (x)  $-x+y, -x, z$ ; (xi)  $y, -x+y+1, -z$ ; (xii)  $x, y+1, z$ ; (xiii)  $-y, x-y, z$ ; (xiv)  $x-y, x, -z$ ; (xv)  $x, y, -z+1/2$ ; (xvi)  $x, y, -z-1/2$ ; (xvii)  $-y+1, x-y, z$ ; (xviii)  $-x+y+1, -x, z$ ; (xix)  $y, -x+y, -z$ ; (xx)  $-x, -y, -z$ ; (xxi)  $-x, -y, z-1/2$ .



Fig. 1

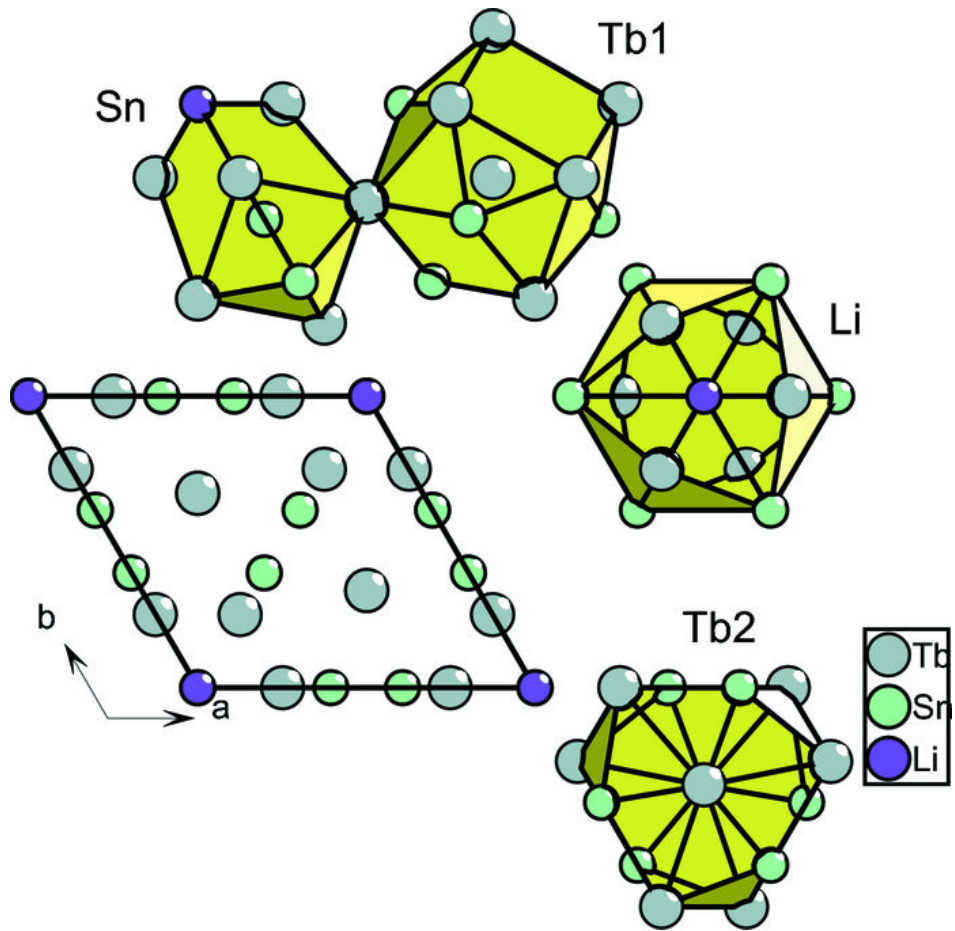


Fig. 2

