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Crystal and electronic structures of $TbCo_{0.29}Li_{0.05}Sn_2$ and $TbCu_{0.25}Li_{0.09}Sn_2$

Abstract

The new quaternary stannides, $TbCo_{0.29}Li_{0.05}Sn_2$ and $TbCu_{0.25}Li_{0.09}Sn_2$ crystallizes in the orthorhombic $CeNiSi_2$ structure type with space group Cmcm. The four independent *4c* atom positions (m2m site symmetry), three are fully occupied by individual atoms (two by Sn and one by Tb atoms) and the fourth is occupied by Li and transition metals Co or Cu atoms with a statistical distribution. The Tb coordination polyhedron is a 21-vertex pseudo-Frank–Kasper polyhedron. One Sn atom is enclosed in a tricapped trigonal prism, the second Sn atom is in a cuboctahedron and the statistically distributed (Li,Co or Cu) site is in a tetragonal antiprism with one added atom. Electronic structure calculations were used for the elucidation of reasons for and the ability of mutual substitution of lithium and transition metals. Positive charge density was observed around the rare earth atom and the Li and transition metal atoms, the negative charge density in the proximity of the Sn atoms.

Keywords: rare earths phases; crystal structure; electronic structure; X-ray diffraction

Introduction

During the systematic investigation of alloys of the Tb-Li-Sn, Tb-Co-Sn and Tb-Cu-Sn ternary systems the ternary compounds with the corresponding compositions $TbLiSn_2$[1] $TbCo_{0.25}Sn_2$[2] and $TbCu_{0.12}Sn_2$[3] were found. According to the X-ray data, all these phases crystallizes with orthorhombic symmetry (space group *Cmcm*, $CeNiSi_2$ structure type). Structural studies of the four-component alloys from $TbLiSn_2$–$TbZnSn_2$ sections indicate the existence of $TbLi_{1-x}Zn_xSn_2$ limited solid solution.[4] In the ternary $TbLiSn_2$ compound lithium atoms occupy the same crystallographic position that the atoms of transition metal in the original $CeNiSi_2$ structure type. The same was observed previously when we studied RELiGe phases (where RE – rare earth elements) with the ZrNiAl type[5] and $RE_3Li_2Ge_3$ germanides with $Hf_3Ni_2Si_3$ type.[6] X-ray single-crystal study showed that the $TbLi_{1-x}Zn_xSn_2$ solid solution formed by the partial substitution of lithium atoms by zinc atoms in *4c* site. The ability of lithium atoms to substitute the atoms of transition metals we observed previously studying solid solutions $RELi_xCu_{2-x}Si_2$ and $RELi_xCu_{2-x}Ge_2$.[7]

Experimental

Terbium, lithium, cobalt, cooper and zinc 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 $Tb_{25}Li_{10}Co_{15}Sn_{50}$ and $Tb_{25}Li_{10}Co_{15}Sn_{50}$ were pressed into pellets, enclosed in a tantalum crucible and placed in a resistance furnace with a thermocouple controller. The sample was heated to 670 K at a rate of 10 K/min, maintained over a period of 62 h and then temperature was increased to 1070 K over a period of 15 h. The alloy was annealed at 670 K for 120 h and cooled slowly to room temperature. Small, good quality plate-like single crystals of the title compounds were isolated from an alloys by mechanical fragmentation.

Single crystal X-ray diffraction (XRD) data of $TbCo_{0.29}Li_{0.05}Sn_2$ and $TbCu_{1-x}Li_xSn_2$ crystals were collected at room temperature by using a four-circle diffractometer (Xcalibur Oxford Diffraction) with a CCD detector (graphite monochromatized MoKa radiation). Scans were taken in the u mode, the analytical absorption corrections were made by CrysalisRed.[8] The systematic absences analysis for the both compounds data set indicated as possible space groups Cmc21 (№ 36), C2cm (№ 40) and Cmcm (№ 63). The adequate structural model was deduced from an automatic interpretation of direct methods with SHELX-97 package programs[9] in the centrosymmetric Cmcm space group; no missed higher crystallographic symmetry in the tested model was found by ADDSYM algorithm implemented in PLATON.[10] Final difference Fourier syntheses were flat and revealed no significant residual peaks. The crystal structure of $TbCo_{0.29}Li_{0.05}Sn_2$ and $TbCu_{0.25}Li_{0.09}Sn_2$ were successfully solved by direct methods. The statistical test of the distribution of the E values[11] suggested that the structure is centrosymmetric with probability 91 %.

The electronic structure calculations using TB-LMTO-ASA[12] program package were performed for the elucidation of reasons of the formation of solid solutions and the ability to mutual substitution of lithium and transition metals. The ordered model of $TbLiSn_2$, $TbCo(Cu)Sn_2$ ternary phases with $CeNiSi_2$ structure type were analyzed.

Results and discussion

The single-crystal X-ray data reported here show that the title compounds crystallizes in a $CeNiSi_2$ structure type in the orthorhombic space group *Cmcm*. The structures has four crystallographically distinct atoms, all of which occupy special equivalent positions. The Li position (Wyckoff sites *4c*) showed displacement parameters considerably smaller than it should be for the lithium, suggesting that this position is partially occupied by the heavier transition metals (Co or Cu) atom. The refinement of the occupancy of this statistically mixed position showed, that it contains of Li and of Co(or Cu) statistical mixture of atoms. The projection of the unit cell and coordination polyhedra of the atoms are shown in Figure 1. The Tb atoms (Wyckoff position *4c*, site symmetry m2m) are surrounded by 21-vertex pseudo-Frank–Kasper polyhedron. The coordination polyhedra of one Sn atom is enclosed in a tricapped trigonal prism, the second Sn atom is in a cuboctahedron and the statistically distributed (Li,Co or Cu) site is in a tetragonal antiprism with one added atom (Fig. 1).
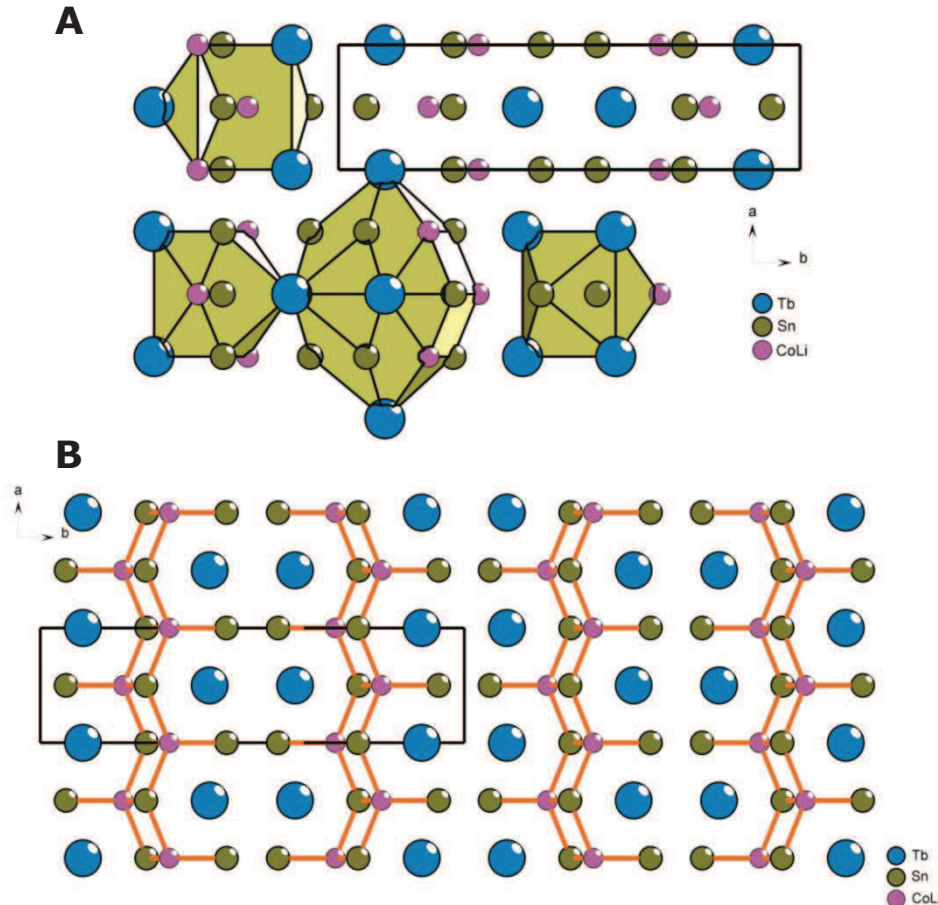
Figure 1. Unit cell and coordination polyhedra of atoms for (A): TbCo$_{0.29}$Li$_{0.05}$Sn$_2$ and (B): Co(Li)-Sn atomic nets.

The electronic structures of the title compounds were calculated using the tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic spheres approximation, using the experimental crystallographic data reported here. The exchange and correlation were interpreted in the local density approximation. The Tb, Co, Cu and Li atoms donate their electrons to the Sn atoms. Therefore, positive charge density can be observed around the rare earth, transitions and Li atoms, and negative charge density is present around the Sn atoms (Fig. 2). The isosurfaces of the ELF around the Sn atom types are shown in Figure 3.

The dominant type of bonding in this compound is metallic. The total and partial densities of states (DOS) for TbCuSn$_2$, TbCoSn$_2$ and TbLiSn$_2$ (Fig. 4a, 4b and 4c, respectively) in the region below Fermi level (EF) exhibit significant mixing between the Tb and Sn sites in all phases. The region above EF consists mostly of Tb *5d*-orbitals and Sn *p*-orbitals. The Sn *s*-type states and Co and Cu *d*-states are mainly close to the lower va-

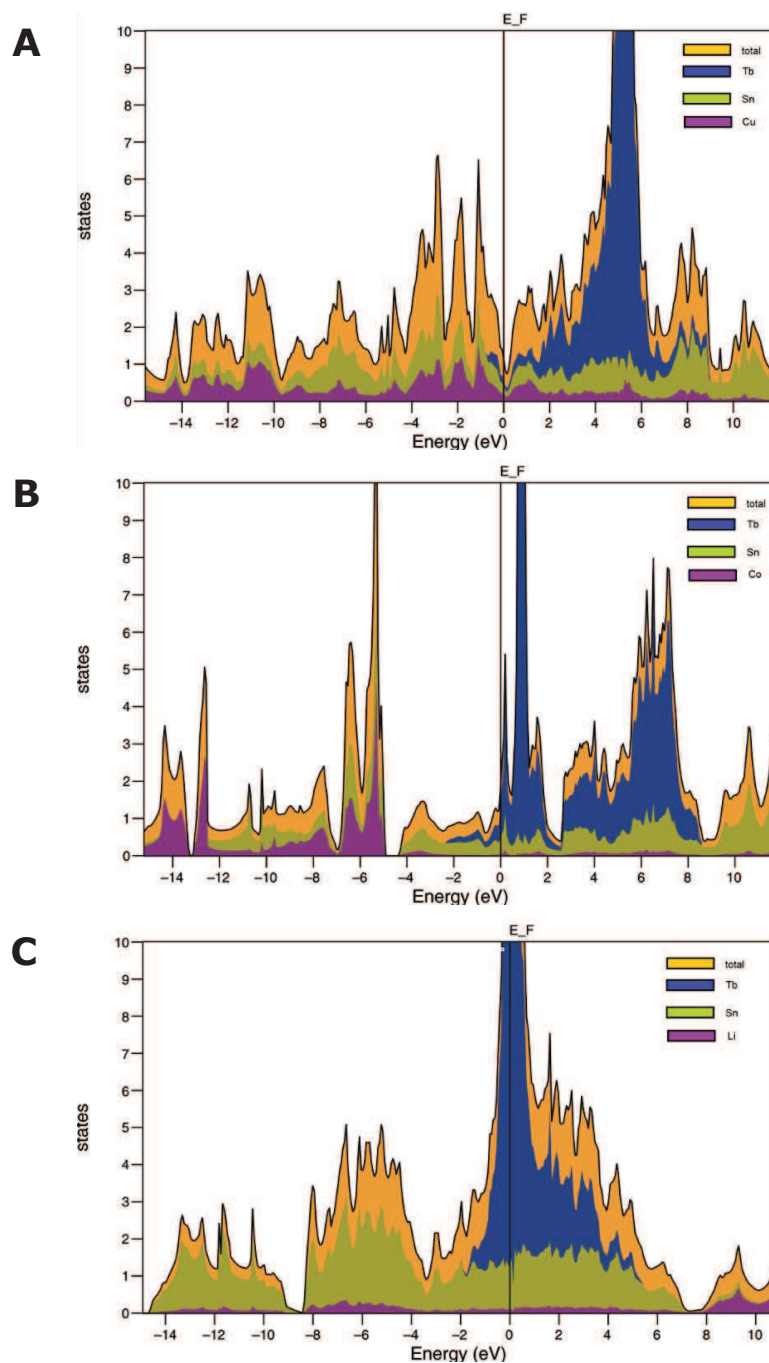lence band (from -15.0 eV to < -5.5 eV). The higher occupation number of electronic states at the Fermi level for TbLiSn$_2$ indicates a more metallic behaviour.
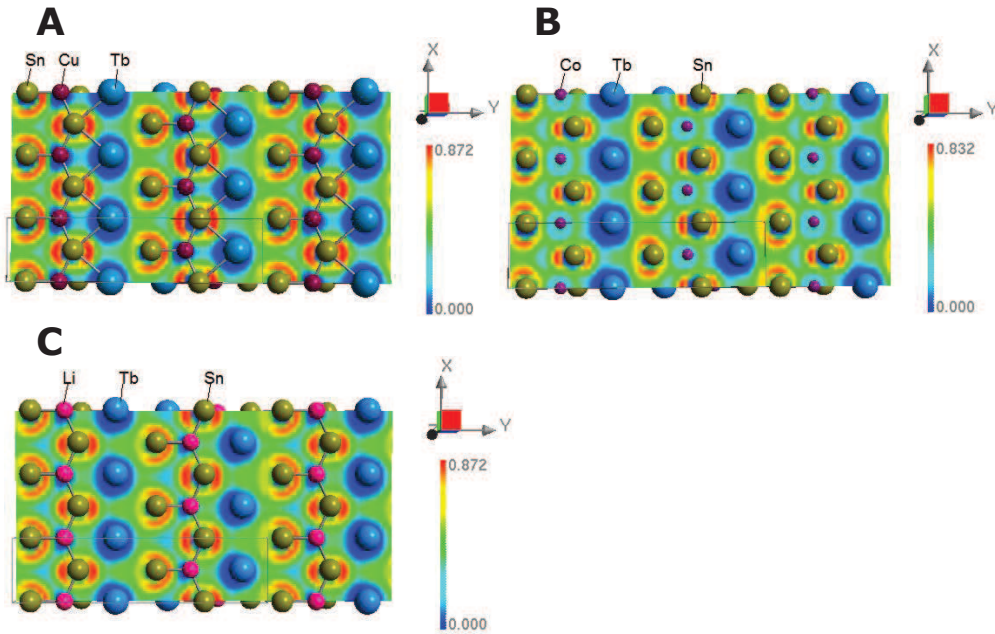
Figure 2. The electron localization function (ELF) for ordered structure models of (A): TbCuSn$_2$, (B): TbCoSn$_2$, and (C): TbLiSn$_2$.
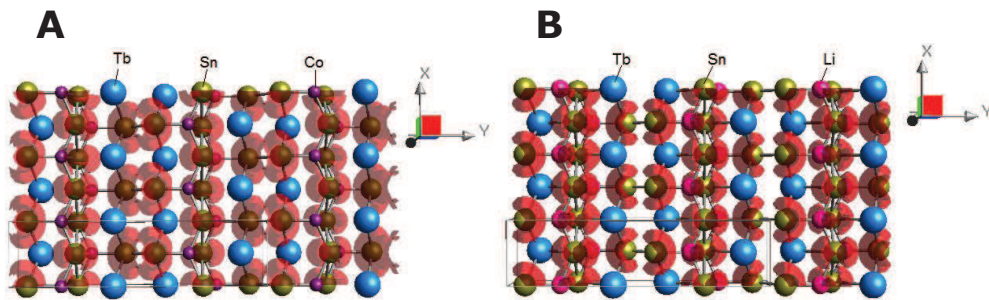
Figure 3. Isosurfaces of the ELF around the atoms for (A): TbCoSn$_2$ and (B): TbLiSn$_2$.

Figure 4. The total and partial density of states (DOS) for (A): TbCuSn$_2$, (B): TbCoSn$_2$, and (C): TbLiSn$_2$.

Table 1. Crystal data and structure refinement.

Empirical formula	$TbCo_{0.29}Li_{0.05}Sn_2$	$TbCu_{0.25}Li_{0.09}Sn_2$
Formula weight	413.67	412.76
Temperature	$T = 293$ K	$T = 293$ K
Wavelength	MoKa, 0.71073 nm	MoKa, 0.71073 nm
Crystal system, space group	orthorhombic, Cmcm (63)	orthorhombic, Cmcm (63)
Unit cell dimensions	$a = 4.4425$ (7) Å $b = 16.463$ (3) Å $c = 4.3898$ (7) Å	$a = 4.4300$ (13) Å $b = 16.414$ (5) Å $c = 4.3769$ (14) Å
Volume	321.05 (9) Å^3	318.3 (1) Å^3
Calculated density	8.558 g/cm^3	8.614 g/cm^3
Absorption coefficient	24.76 mm^{-1}	21.87 mm^{-1}
F(000)	487	391
Theta range for data collection	$\theta_{max} = 27.5°$, $\theta_{min} = 4.8°$	$\theta_{max} = 27.5°$, $\theta_{min} = 4.8°$
Index ranges	$-5<=h<=5$, $-21<=k<=16$, $-5<=l<=5$	$5<=h<=5$, $-21<=k<=17$, $-4<=l<=5$
Reflections collected/unique	1100/233	1042/229
Refinement method	Refinement on F^2 Least-squares matrix: full	Refinement on F^2 Least-squares matrix: full
Data/parameters	233/17	229/18
Goodness of fit on F^2	1.23	1.27
$R[F^2 > 2\sigma(F^2)]$	0.025	0.055
$wR(F^2)$	0.061	0.132
Extinction coefficient	0.0041 (4)	0.0002 (4)
Largest diff. peak and hole	2.03 and -2.26 eA^{-3}	4.53 and -2.42 eA^{-3}

Table 2. Fractional atomic coordinates and displacement parameters for $TbCo_{0.29}Li_{0.05}Sn_2$ and $TbCu_{0.25}Li_{0.09}Sn_2$ (Å^2).

Atom	Site	x/a	y/b	z/c	U_{iso}*/U_{eq}	Occ. (< 1)
			$TbCo_{0.29}Li_{0.05}Sn_2$			
Tb1	*4c*	0.0000	0.10091 (5)	0.2500	0.0144 (4)	
Sn1	*4c*	0.0000	0.43898 (10)	0.2500	0.0264 (5)	
Sn2	*4c*	0.0000	0.74923 (8)	0.2500	0.0250 (5)	
Co1	*4c*	0.0000	0.3040 (5)	0.2500	0.018 (3)*	0.292 (12)
Li1	*4c*	0.0000	0.3040 (5)	0.2500	0.018 (3)*	0.04
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tb1	0.0154 (5)	0.0126 (5)	0.0152 (6)	0.000	0.000	0.000

Table 2. (cont.).

Atom	Site	x/a	y/b	z/c	U_{iso}*/U_{eq}	Occ. (< 1)
Sn1	0.0139 (8)	0.0528 (14)	0.0126 (9)	0.000	0.000	0.000
Sn2	0.0181 (8)	0.0349 (12)	0.0220 (10)	0.000	0.000	0.000
TbCu$_{0.25}$Li$_{0.09}$Sn$_2$						
Tb1	*4c*	0.0000	0.10081 (10)	0.2500	0.0200 (7)	
Sn1	*4c*	0.0000	0.4392 (2)	0.2500	0.0356 (10)	
Sn2	*4c*	0.0000	0.7490 (2)	0.2500	0.0380 (10)	
Co1	*4c*	0.0000	0.3044 (9)	0.2500	0.024 (5)*	0.30 (2)
Li1	*4c*	0.0000	0.3044 (9)	0.2500	0.024 (5)*	0.03
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tb1	0.0186 (10)	0.0259 (11)	0.0156 (9)	0.000	0.000	0.000
Sn1	0.0156 (16)	0.081 (3)	0.0107 (13)	0.000	0.000	0.000
Sn2	0.0282 (18)	0.055 (2)	0.0312 (17)	0.000	0.000	0.000

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

Table 3. Geometric parameters (Å°) for TbCo$_{0.29}$Li$_{0.05}$Sn$_2$.

Tb1—Sn1[i]	3.1910 (5)	Sn2—Li1[viii]	2.363 (3)
Tb1—Sn1[ii]	3.1910 (5)	Sn2—Co1[viii]	2.363 (3)
Tb1—Sn1[iii]	3.1910 (5)	Sn2—Li1[vii]	2.363 (3)
Tb1—Sn1[iv]	3.1910 (5)	Sn2—Co1[vii]	2.363 (3)
Tb1—Sn2[v]	3.3009 (12)	Sn2—Li1[ix]	2.397 (3)
Tb1—Sn2[vi]	3.3009 (12)	Sn2—Co1[ix]	2.397 (3)
Tb1—Sn2[vii]	3.3022 (13)	Sn2—Li1[x]	2.397 (3)
Tb1—Sn2[viii]	3.3022 (13)	Sn2—Co1[x]	2.397 (3)
Tb1—Co1	3.343 (8)	Sn2—Sn2[xi]	3.1228 (4)
Tb1—Sn1[vi]	3.4699 (14)	Sn2—Sn2[xii]	3.1228 (4)
Tb1—Sn1[v]	3.4699 (14)	Sn2—Sn2[xiii]	3.1228 (3)
Sn1—Co1	2.222 (8)	Sn2—Sn2[xiv]	3.1228 (3)
Sn1—Sn1[vii]	2.976 (2)	Co1—Sn2[viii]	2.363 (3)
Sn1—Sn1[viii]	2.976 (2)	Co1—Sn2[vii]	2.363 (3)
Sn1—Tb1[i]	3.1910 (5)	Co1—Sn2[vi]	2.397 (3)
Sn1—Tb1[ii]	3.1910 (5)	Co1—Sn2[v]	2.397 (3)
Sn1—Tb1[iv]	3.1910 (5)	Co1—Tb1[ii]	3.493 (4)
Sn1—Tb1[iii]	3.1910 (5)	Co1—Tb1[i]	3.493 (4)

Table 3. (cont.).

Sn1—Tb1^{ix}	3.4699 (14)	Co1—Tb1^{iii}	3.493 (4)
Sn1—Tb1^{x}	3.4699 (14)	Co1—Tb1^{iv}	3.493 (4)

Symmetry codes: (i) $-x-1/2, -y+1/2, -z$; (ii) $-x+1/2, -y+1/2, -z+1$; (iii) $-x-1/2, -y+1/2, -z+1$; (iv) $-x+1/2, -y+1/2, -z$; (v) $x+1/2, y-1/2, z$; (vi) $x-1/2, y-1/2, z$; (vii) $-x, -y+1, -z+1$; (viii) $-x, -y+1, -z$; (ix) $x+1/2, y+1/2, z$; (x) $x-1/2, y+1/2, z$; (xi) $-x+1/2, -y+3/2, -z+1$; (xii) $-x-1/2, -y+3/2, -z$; (xiii) $-x+1/2, -y+3/2, -z$; (xiv) $-x-1/2, -y+3/2, -z+1$.

Table 4. Geometric parameters (Å°) for TbCu$_{0.25}$Li$_{0.09}$Sn$_2$.

Tb1—Sn1^{i}	3.1824 (11)	Sn2—Li1^{viii}	2.357 (6)
Tb1—Sn1^{ii}	3.1824 (11)	Sn2—Cu1^{viii}	2.357 (6)
Tb1—Sn1^{iii}	3.1824 (11)	Sn2—Li1^{vii}	2.357 (6)
Tb1—Sn1^{iv}	3.1824 (11)	Sn2—Cu1^{vii}	2.357 (6)
Tb1—Sn2^{v}	3.290 (3)	Sn2—Li1^{ix}	2.394 (6)
Tb1—Sn2^{vi}	3.290 (3)	Sn2—Cu1^{ix}	2.394 (6)
Tb1—Sn2^{vii}	3.297 (3)	Sn2—Li1^{x}	2.394 (6)
Tb1—Sn2^{viii}	3.297 (3)	Sn2—Cu1^{x}	2.394 (6)
Tb1—Cu1	3.341 (15)	Sn2—Sn2^{xi}	3.1139 (7)
Tb1—Sn1^{vi}	3.455 (3)	Sn2—Sn2^{xii}	3.1139 (7)
Tb1—Sn1^{v}	3.455 (3)	Sn2—Sn2^{xiii}	3.1139 (7)
Sn1—Cu1	2.214 (15)	Sn2—Sn2^{xiv}	3.1139 (7)
Sn1—Sn1^{vii}	2.961 (5)	Cu1—Sn2^{viii}	2.357 (6)
Sn1—Sn1^{viii}	2.961 (5)	Cu1—Sn2^{vii}	2.357 (6)
Sn1—Tb1^{i}	3.1824 (11)	Cu1—Sn2^{vi}	2.394 (6)
Sn1—Tb1^{ii}	3.1824 (11)	Cu1—Sn2^{v}	2.394 (6)
Sn1—Tb1^{iv}	3.1824 (11)	Cu1—Tb1^{ii}	3.481 (7)
Sn1—Tb1^{iii}	3.1824 (11)	Cu1—Tb1^{i}	3.481 (7)
Sn1—Tb1^{ix}	3.455 (3)	Cu1—Tb1^{iii}	3.481 (7)
Sn1—Tb1^{x}	3.455 (3)	Cu1—Tb1^{iv}	3.481 (7)

Symmetry codes: (i) $-x-1/2, -y+1/2, -z$; (ii) $-x+1/2, -y+1/2, -z+1$; (iii) $-x-1/2, -y+1/2, -z+1$; (iv) $-x+1/2, -y+1/2, -z$; (v) $x+1/2, y-1/2, z$; (vi) $x-1/2, y-1/2, z$; (vii) $-x, -y+1, -z+1$; (viii) $-x, -y+1, -z$; (ix) $x+1/2, y+1/2, z$; (x) $x-1/2, y+1/2, z$; (xi) $-x+1/2, -y+3/2, -z+1$; (xii) $-x-1/2, -y+3/2, -z$; (xiii) $-x+1/2, -y+3/2, -z$; (xiv) $-x-1/2, -y+3/2, -z+1$.

Conclusions

The two novel TbCo$_{0.29}$Li$_{0.05}$Sn$_2$ and TbCu$_{0.25}$Li$_{0.09}$Sn$_2$ quaternary phases were synthesized and their crystal structures solved from single crystal X-ray data. Both struc-

tures crystallizes in the orthorhombic CeNiSi$_2$ structure type with space group Cmcm. The lithium atoms form a statistical mixtures with cobalt or cooper atoms in *4c* site. On the basis of crystallographic analysis and LMTO electronic structure calculations, these phases have been interpreted as ∞[Li(Co or Cu)−Sn]$^{\delta-}$ polyanionic frameworks balanced by Tb cations. The Tb atoms do not simply act as electron donors but are strongly involved in the overall bonding by polar Tb−Sn interactions. The negatively charged networks of the two compounds consist of topologically similar structural blocks made up of Li(Co or Cu)−Sn contacts but joined.

References:

[1] V. Pavlyuk, O. Bodak, V. Pecharskii, R. Skolozdra, E. Gladyshevskii, *Inorg. Mater.*, **1989**, *25*, 962-965.

[2] A. Gil, B. Pene, E. Wawrzynska, J. Hernandez Velasco, A. Szytula, A. Zygmunt, *J. Alloys Compd.*, **2004**, *365*, 31-34.

[3] M. Francois, G. Venturini, B. Malaman, B. Roques, *J. Less-Common Met.*, **1990**, *160*, 197-213.

[4] A. Stetskiv, I. Tarasiuk, B. Rożdżyńska-Kiełbik, I. Oshchapovsky, V. Pavlyuk, *Acta Crystallogr. E.*, **2012**, *E68*, i1.

[5] V. Pavlyuk, O. Bodak, V. Bruskov, *Dopov. Akad. Nauk Ukr.*, **1991**, *1*, 112-114.

[6] V. Pavlyuk, O. Bodak, *Akad. Nauk SSSR Izvest. Metally*, **1992**, *6*, 207-210.

[7] V. Pavlyuk, O. Bodak, D. Kevorkov, *Dopov. Akad. Nauk Ukr.*, **1993**, *9*, 84-87.

[8] *CrysalisRed*, *Version 1.171.29.2*, *CCD data reduction GUI*, Oxford Diffraction Poland Sp, **2005**.

[9] G.M. Sheldrick, *SHELXL–97*, *Program for crystal structure refinement*, *SHELXS–97*, *Program for the solution of crystal structures*, University of Göttingen, Germany, **1997**.

[10] A.L. Spek, *PLATON*, *A multipurpose crystallographic tool*, Utrecht University, Netherlands, **2002**.

[11] L.J. Farrugia, *WinGX*, *Suite for small-molecule single-crystal crystallography*, *J. Appl. Cryst.*, **1999**, *32*, 837-838.

[12] K. Andersen, Z. Povlovska, O. Jepsen, *Phys. Rev. B*, **1986**, *34*, 51-53.