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Crystal and electronic structures of new intermetallic compounds $\text{Tb}_{0.87}\text{Na}_{0.13}\text{Zn}_{0.37}\text{Sn}_2$ and $\text{Tb}_{0.85}\text{Mg}_{0.15}\text{Zn}_{0.40}\text{Sn}_2$

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The new quaternary distannides, $\text{Tb}_{0.87}\text{Na}_{0.13}\text{Zn}_{0.37}\text{Sn}_2$ and $\text{Tb}_{0.85}\text{Mg}_{0.15}\text{Zn}_{0.40}\text{Sn}_2$, crystallizes in the orthorhombic CeNiSi_2 structure type with space group $Cmcm$ and Pearson symbol $oS16$. All atoms occupied four independent $4c$ Wyckoff sites ($m2m$ site symmetry). Two are fully occupied by Sn atoms, and one by a statistical mixture of Tb/Na or Tb/Mg atoms, and the fourth $4c$ site is partially occupied by Zn atoms. Electronic structure calculations were used for the elucidation of the reasons for and the ability of mutual substitution of Tb by Mg or Na atoms. Calculations of the electronic structure were used to elucidate the causes and ability of the interchange of Tb by Mg or Na atoms. Minima of the electron localization function were observed around Tb/Na/Mg atoms, and maxima were observed near Sn atoms. Replacing Tb with Na or Mg does not lead to significant changes in the electron localization function.

Keywords: intermetallics, crystal structure, electronic structure, chemical bond.

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Introduction

Rare earth metals (*RE*) today play a key role in high-tech industries, which makes them a strategically important raw material [1]. Their study, both of the metals themselves and of their alloys and compounds, is of great theoretical and practical importance. This is because REM-based materials have unique and valuable properties that enable broad application in modern technologies. Current research on intermetallic systems, including rare-earth metals, *d*-elements, and tin (Sn), is in the preliminary stage. We currently have limited information regarding the isothermal cross-sections of phase diagrams. Most available scientific papers focus on discovering new ternary compounds and analyzing their crystalline structures in detail [2-6].

On the other hand, the study of four-component systems, which, in addition to *RE*, *d*-elements and tin, also include alkali metals (Li, Na, K) and Mg, is currently practically absent in the scientific literature. In particular,

the article [7] reports on the construction of part of the phase equilibrium diagrams at 400 °C for a number of lithium-containing quaternary systems RE-T-Li-Sn (T as the *d*-element was used Co and Ni). Electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) established the formation of both individual quaternary compounds (e.g., $\text{TmLi}_2\text{Co}_6\text{Sn}_{20}$ [8], $\text{Ce}_2\text{Li}_{0.39}\text{Ni}_{1.61}\text{Si}_2$ [9]) and substitutional solid solutions based on various ternary phases (e.g., $\text{RELi}_x\text{T}_{1-x}\text{Sn}_2$ [5, 6] and others). Due to the high chemical activity of sodium and potassium alloys, systematic studies of ternary and quaternary systems containing them are extremely difficult.

Phase equilibria in the ternary system Tb-Zn-Sn were presented in [10] and are based on the study of 94 binary and ternary samples annealed at 600 °C and studied by X-ray phase, X-ray structural and, partially, local X-ray spectral analysis. At the annealing temperature, seven ternary compounds are formed in the system: TbZnSn , TbZnSn_2 , $\sim\text{TbZn}_3\text{Sn}$, $\text{TbZn}_{2-x}\text{Sn}_x$, $\text{Tb}_{13}\text{ZnSn}_{13}$ [11],

$TbZn_xSn_{2-x}$, $Tb_{0.83}Zn_{0.14}Sn_{2.86}$ [12]. The regions of homogeneity of the ternary compounds $TbZn_xSn_{2-x}$ and $TbZn_{2-x}Sn_x$ are small. At an isoconcentrate of 33.3 at. % Tb, concentration polymorphism of the $TbZn_{2-x}Sn_x$ phase is observed: a solid solution with $x = 0-0.30$ when changing the Sn content turns into a ternary compound with $x = 0.5-0.76$. In addition, the formation of substitutional solid solutions based on binary phases Tb_2Zn_{17} , $TbZn$ and $TbZn_2$ is observed.

Due to the complexity of synthesis and laboratory experiments, alloys of the Tb-Na-Sn system are studied only occasionally in the region of minimum sodium content. In particular, the publication [13] reports the formation of the $Tb_{1-x}Na_xSn_2$ compound ($x = 0.1$), which is characterized by orthorhombic syngony and isostructural phases with Gd, Ho, Dy, Er, Tm.

The addition of active elements such as Mg or Zn to RE-containing alloys enables the formation of intermetallics with new structures, some of which exhibit improved hydrogen sorption properties [14-16].

I. Experimental

The study samples, each weighing 1 gram, were synthesized from high-purity metals. In particular, the following were used: Tb - purity of at least 99.8% by weight; Na - purity 99.97 % by weight; Mg, Zn and Sn - purity 99.99% by weight.

For the synthesis of alloys, pieces of pure metals with the required component ratios were pressed into tablets. After that, they were placed in a tantalum crucible, which was sealed in an inert medium, then placed in a resistance furnace equipped with a temperature controller. Heating occurred gradually: from room temperature to 400 °C, the oven heated up at a rate of 5 °C per minute. The alloys were kept at this temperature for two days. After that, the temperature was increased from 400 °C to 800 °C for one hour. The resulting samples were annealed at a temperature of 400 °C for another eight hours. For heat treatment, a muffle furnace MP-60 with automatic temperature control was used, which ensured an accuracy of ± 5 °C. Annealed alloys were hardened in cold oil. Homogeneity and equilibrium were monitored by radiographic and microstructural analyses. The alloys were stored under a layer of inert oil that had been pre-purified and dehydrated.

The X-ray methods, the single crystal method (SC-XRD), and the powder method (PXRD) were used. The complete primary determination of the crystal structure – including the establishment of space groups, the calculation of atomic coordinates, the anisotropic displacement parameters, and the precise refinement of the population factors of the mixed Tb/M positions and the deficient Zn lattice – was performed exclusively using the data of the Single-Crystal X-ray Diffraction experiment (SC-XRD). Powder X-ray diffraction (PXRD) was used as an independent method to estimate the phase purity of a bulk sample and confirm that the single crystal selected for data collection fully represents the entire synthesized alloy.

The phase composition of the obtained alloys was investigated by X-ray diffraction on a Rigaku Miniflex D-

600 powder diffractometer using Cu $K\alpha$ -radiation. Considering the chemical activity of individual alloys, the powder was placed in a capillary. The atomic ratios of elements in each phase were confirmed using EDS with a Tescan Vega 3 LMU scanning electron microscope equipped with an Oxford Si-detector X-Max N60 LTE detector. In EDS analysis, the measurement error is 1 at. % for the element to be defined.

To identify the phases, the diffractograms of the studied samples were compared with theoretical ones based on data on pure components and known compounds in the respective binary and ternary systems (using the programs LATCON [17] and PowderCell [18]). The WinCSD software package [19] was used to calculate and index diffractograms and to determine crystal lattice parameters. The crystal structure was also determined by powder diffraction using the FullProf program [20].

By examining four-component alloys of the Tb-Na-Zn-Sn and Tb-Mg-Zn-Sn systems, specifically samples $Tb_{25}Na_5Zn_{10}Sn_{60}$ and $Tb_{25}Mg_5Zn_{10}Sn_{60}$, we obtained single crystals in the form of irregularly shaped wafers. At the first stage of the experiment, using the Laue and Weissenberg methods, it was found that the crystal has an orthorhombic symmetry (using the RGNS-2 chamber and Cu K-radiation) [21]. Experimental intensity arrays for the second phase of the studies were obtained using Oxford Diffraction's Xcalibur automatic diffractometer. This device used a Sapphire2 CCD detector and an ENHANCE radiation source (Mo $K\alpha$ -radiation, graphite monochromator, ω -scan method). The DIFABS program [22] was used to correct absorption, while ABSEN [23] was used to select spatial groups.

To determine the structure, direct methods of the SHELX-97 program complex [24] were employed, which enabled the assignment of the space group to *Cmcm*. The results of experimental studies and the clarification of the structure of the identified compounds with the CeNiSi₂ type structure, obtained by the single-crystal method, are shown in Table 1.

II. Results and discussion

The new quaternary phases $Tb_{0.87}Na_{0.13}Zn_{0.37}Sn_2$ and $Tb_{0.85}Mg_{0.15}Zn_{0.40}Sn_2$ were detected in the region of Sn-rich alloys from Tb-Na-Zn-Sn and Tb-Mg-Zn-Sn systems. Scanning electron microscopy (Figure 1) studies showed that both alloys consist predominantly of the quaternary phase, with minor amounts (< 5 vol.%) of a dark intergranular phase observed along the grain boundaries. The compositions of both quaternary phases are very similar, according to EDS data are $Tb_{0.87(1)}Na_{0.13(6)}Zn_{0.36(2)}Sn_{2.01(1)}$ and $Tb_{0.85(1)}Mg_{0.15(9)}Zn_{0.40(2)}Sn_{2.00(1)}$. Instead, the compositions of the intergranular phases are different at each point, indicating that it is not an individual compound. The X-ray powder diffraction patterns show that both alloys contain isostructural phases (Figure 2).

For a detailed study of the crystal structures, single-crystal X-ray diffraction was used, as both alloys provided high-quality crystals. Intensity data were collected using a four-circle Xcalibur automatic diffractometer. The best structural model was deduced from the automatic

interpretation of direct methods using the SHELXS-97 [24] software package and in the centrosymmetric space group $Cmcm$. Both isostructural compounds crystallizes in $CeNiSi_2$ structure type. The results of experimental studies and refinements of the crystal structures of the identified compounds obtained by the single-crystal method are given in Table 1.

Refinements of the position occupancy indicate that the terbium atoms are partially replaced by sodium or magnesium atoms. Another feature of both structures is

the partial occupancy of one $4c$ site by zinc atoms.

Table 2 shows the crystallographic coordinates and isotropic temperature parameters of the atoms for the intermetallics studied. Information on the anisotropic parameters of thermal displacements of these atoms is contained in Table 3.

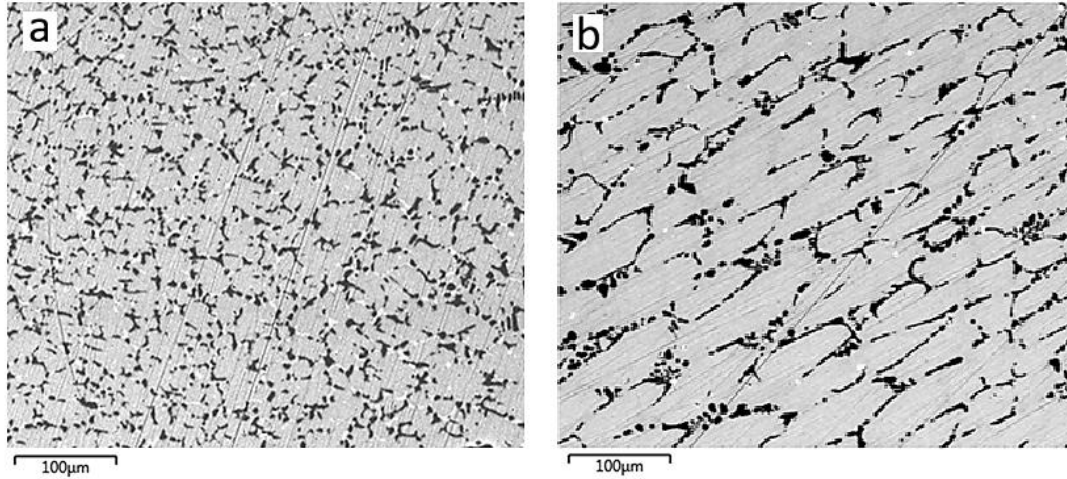


Fig. 1. SEM image (BSE mode) of the microstructure of the alloys of composition $Tb_{0.87}Na_{0.13}Zn_{0.37}Sn_2$ (a) and $Tb_{0.85}Mg_{0.15}Zn_{0.40}Sn_2$ (b). For both samples, the grey phase (orthorhombic quaternary compound) and the dark phase (intergranular material).

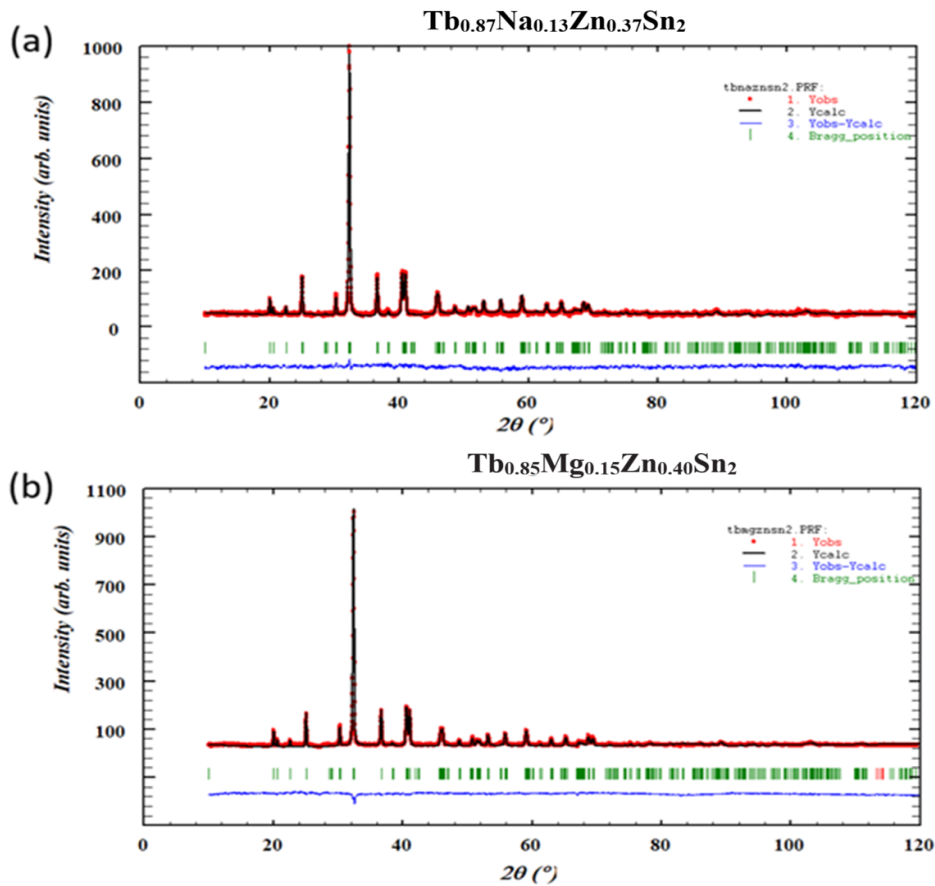


Fig. 2. Experimental and refined XRD patterns for the $Tb_{0.87}Na_{0.13}Zn_{0.37}Sn_2$ (a) and $Tb_{0.85}Mg_{0.15}Zn_{0.40}Sn_2$ (b). Observed (red circles), calculated (dark line) and difference (bottom blue line) diffraction patterns. Vertical bars indicate the Bragg positions of the corresponding quaternary orthorhombic phase.

Table 1.

Details of the experiment and results of refinement of the structure by the single crystal method for
 $Tb_{0.87}Na_{0.13}Zn_{0.37}Sn_2$ and $Tb_{0.85}Mg_{0.15}Zn_{0.40}Sn_2$

Empirical formula	$Tb_{0.87}Na_{0.13}Zn_{0.37}Sn_2$	$Tb_{0.85}Mg_{0.15}Zn_{0.40}Sn_2$
Composition from EDS	$Tb_{0.87(1)}Na_{0.13(6)}Zn_{0.36(2)}Sn_{2.01(1)}$	$Tb_{0.85(1)}Mg_{0.15(9)}Zn_{0.41(2)}Sn_{1.99(1)}$
Structural type	CeNiSi ₂	CeNiSi ₂
Molar mass (g/mol)	412.76	402.31
Temperature	T = 293 K	T = 293 K
Scan type	ω	ω
Radiation / (Å)	MoK α / 0.71073	MoK α / 0.71073
Symmetry, space group	orthorhombic, <i>Cmcm</i> (63)	orthorhombic, <i>Cmcm</i> (63)
Unit cell dimensions, (Å):	$a = 4.4504(3)$ $b = 17.698(8)$ $c = 4.3984(2)$	$a = 4.4415(6)$ $b = 17.687(2)$ $c = 4.3914(5)$
Cell volume, (Å ³)	346.43(1)	344.97(7)
Coefficient of absorption, (μ , mm ⁻¹)	36.82	35.98
θ range for data collection, (°)	4.61÷27.95	3.50÷27.00
Range in $h\ k\ l$	$-5 \leq h \leq 5$, $-19 \leq k \leq 23$, $-5 \leq l \leq 5$	$-5 \leq h \leq 5$, $-22 \leq k \leq 22$, $-5 \leq l \leq 5$
Collected/unique reflexes	1142/281	1276/292
Data/Parameters	281/18	292/18
Goodness-of-fit on F^2	1.25	1.19
$R[F^2 > 2\sigma(F^2)]$	0.034	0.041
$wR(F^2)$	0.062	0.074
$\Delta\rho_{fin}$ (max/min), e/Å ³	1.53 / -2.02	1.13 / -1.09

Table 2.

Atomic coordinates and parameters of thermal displacements of atoms

Atom	Sites	x/a	y/b	z/c	U_{iso}^*/U_{eq}	G
$Tb_{0.87}Na_{0.13}Zn_{0.37}Sn_2$						
Tb	4c	0	0.10094(2)	1/4	0.0189(7)	0.87(2)
Na	4c	0	0.10094(2)	1/4	0.0189(7)	0.13(2)
Sn1	4c	0	0.4387(1)	1/4	0.0196(5)	1
Sn2	4c	0	0.7494(1)	1/4	0.0203(4)	1
Zn	4c	0	0.3052(7)	1/4	0.028(6)	0.37(1)
$Tb_{0.85}Mg_{0.15}Zn_{0.40}Sn_2$						
Tb	4c	0	0.10089(3)	1/4	0.0190(6)	0.85(3)
Mg	4c	0	0.10089(3)	1/4	0.0190(6)	0.15(5)
Sn1	4c	0	0.4384(1)	1/4	0.0195(4)	1
Sn2	4c	0	0.7496(1)	1/4	0.0201(3)	1
Zn	4c	0	0.3056(5)	1/4	0.029(7)	0.40(2)

Table 3.

Anisotropic parameters of thermal displacements of atoms

Atom	$Tb_{0.87}Na_{0.13}Zn_{0.37}Sn_2$			$Tb_{0.85}Mg_{0.15}Zn_{0.40}Sn_2$		
	U_{11}	U_{22}	U_{33}	U_{11}	U_{22}	U_{33}
Tb	0.0199(6)	0.0239(8)	0.0179 (9)	0.0201(5)	0.0241(7)	0.0182 (7)
Na(Mg)	0.0199(6)	0.0239(8)	0.0179 (9)	0.0201(5)	0.0241(7)	0.0182 (7)
Sn1	0.0198(5)	0.031(6)	0.0147(3)	0.0196(6)	0.035(5)	0.0151(4)
Sn2	0.0282(3)	0.045 (7)	0.0212 (7)	0.0279(4)	0.048 (5)	0.0215 (8)
Zn	0.0252(4)	0.035 (6)	0.0165 (3)	0.0249(5)	0.039 (7)	0.0168 (4)

$$U_{12}=U_{13}U_{23} = 0$$

The projection of the unit cell and coordination polyhedra of the atoms is shown in Fig. 3. The coordination polyhedra of (Tb/Na/Mg) atoms are the 21-vertex polyhedron. The Sn1 has a coordination polyhedron as a 9-vertex tricapped trigonal prism, and the Sn2 has a coordination polyhedron named as a 12-vertex cuboctahedron. The zinc atoms are enclosed in a 9-vertex

tetragonal antiprism with one added atom.

In this work, the electronic structure was investigated using the TB-LMTO-ASA program package [25].

The specific parameters for our calculations in the TB-LMTO-ASA program were as follows: the calculations were carried out in the framework of local state density (LDA) using the exchange-correlation

potential parameterized by von Barth and Hedin; for integration over the Brillouin zone (k-points), the total grid was 4096 k-points for the full Brillouin zone, which after reduction gave 657 (16x16x16) irreducible *ks*-points for self-consistent iterations using the standard tetrahedron method.

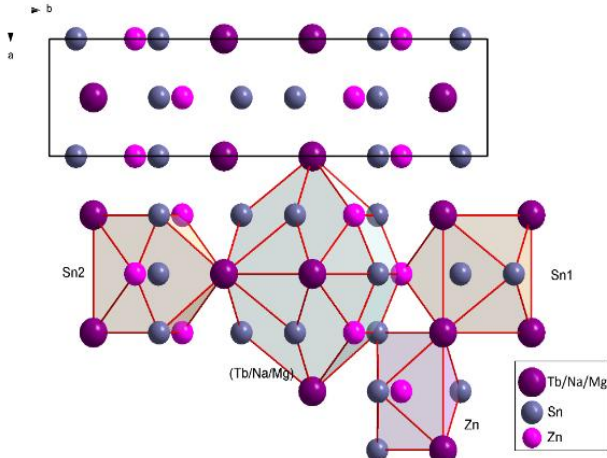


Fig. 3. Unit cell and coordination polyhedra for atoms of the quaternary orthorhombic phase.

The ASA approximation and the basic set of radii of the Wigner-Seitz spheres (atomic spheres) were automatically optimized to minimize the interstitial volume, provided that the overlap of the atomic spheres remained below the 16 % threshold. The valence baseset included the states Tb(6s, 6p, 5d), Zn(4s, 4p, 3d), and Sn(5s, 5p), with the higher empty shells being accounted for using the *downfolding* procedure. before the appearance of false highly localized peaks directly at the Fermi level), the 4f-electrons of terbium atoms were treated as backbone electrons (*open-core treatment*). Their population was recorded as 4f⁸ according to Hund's rules for the Tb³⁺ ion, which excluded them from the ensemble of valence bands.

The TB-LMTO-ASA framework inherently relies on strict translational symmetry and space groups, which prevents the direct implementation of true statistical disorder or partial occupancies. Constructing massive supercells to simultaneously mimic both Zn deficiency and Tb/M mixing within the Atomic Sphere Approximation (ASA) leads to severe geometric violations and unphysical overlap between atomic and empty spheres, thereby destroying the self-consistency of the ASA method. Consequently, the fully ordered structures TbZnSn₂, MgZnSn₂ and NaZnSn₂ have been explicitly redefined in the text as idealized boundary models. Their calculations serve as a necessary baseline for understanding the fundamental chemical bonding and the individual electronic contributions of Na, Mg, Tb, and the fully filled Zn framework to the overall Density of States (DOS) and Crystal Orbital Hamilton Population (COHP) data.

The electronic-structure calculation data indicate that the ELF maps show near-zero values in the regions surrounding the Tb, Na/Mg, and Zn atomic sites, confirming their highly electropositive character. Concurrently, the ELF maxima localized around the Sn

sites are interpreted as direct evidence of partial covalent interactions within the tin-containing framework. The maximum value of the electron localization function around tin atoms for the TbZnSn₂ structure is ELF = 0.832 (Fig. 4a). In the MgZnSn₂ structural model, ELF = 0.814 (Fig. 4b), and for NaZnSn₂, ELF = 0.807 (Fig. 4c). The closeness of these values for all models indicates that the replacement of Tb by Na or Mg does not lead to significant changes in the electron localization function, i.e. the structure remains stable. Taking into account also the closeness of the effective radius of Tb ($r_a = 1.75$ Å), Na ($r_a = 1.80$ Å), and Mg ($r_a = 1.60$ Å) atoms in intermetallic compounds, it can be concluded that nothing prevents their mutual substitution.

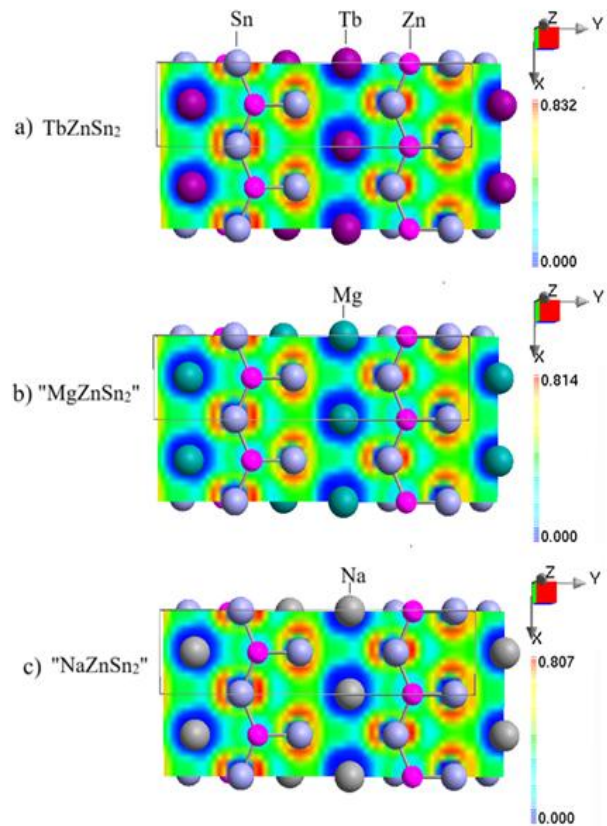


Fig. 4. The electron localization function (ELF) for ordered ternary compound TbZnSn₂ (a) and hypothetical structures MgZnSn₂ (b) and NaZnSn₂ (c) from LMTO calculations.

The total and partial densities of states (DOS) for TbZnSn₂ are shown in Fig. 5. The Fermi level (EF) lies within a continuous DOS region with a significant density of states, indicating a tendency towards metallic character of bonding for TbZnSn₂, however, the final determination of the type of conductivity (metallic, semimetallic, or degenerate semiconductor) requires systematic experimental measurements of resistivity and the Seebeck coefficient. The chemical bonding analysed from integrated crystal orbital Hamilton populations (iCOHP) exhibits strong Zn-Sn1 ($d = 2.3892$ Å and $-iCOHP = 1.237$ eV) and Zn-Sn2 ($d = 2.3923$ Å and $-iCOHP = 1.194$ eV) interactions. A slightly weaker interaction is observed between Tb-Sn1 atoms, with $d = 3.0821$ Å and $-iCOHP = 0.619$ eV.

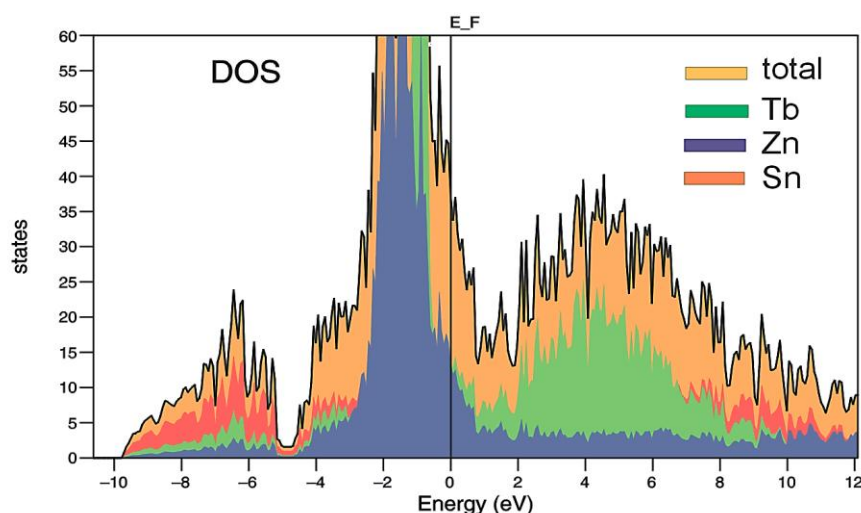


Fig. 5. The density of states (DOS) for for ordered ternary compound $TbZnSn_2$ from LMTO calculations.

Conclusions

Two new quaternary phases, $Tb_{0.87}Na_{0.13}Zn_{0.37}Sn_2$ and $Tb_{0.85}Mg_{0.15}Zn_{0.40}Sn_2$, were synthesized and their crystal and electronic structures were estimated. Both quaternary distannide crystallize in the orthorhombic $Cmcm$ structure type with space group $Cmcm$. It is established that the mechanism of formation of these phases is the partial substitution of terbium atoms by sodium and magnesium. It is also established that zinc atoms do not completely fill the crystallographic position 4c. Thus, the studied compounds are largely disordered. Calculation of the electronic structure allowed us to estimate the strength of the bonds between the atoms and determine that the strongest interaction is between tin and zinc atoms.

The results of theoretical calculations indicate a tendency towards metallic conductivity in both phases. However, the final determination of the type of

conductivity (metallic, semimetallic, or degenerate semiconductor) requires systematic experimental measurements of resistivity and the Seebeck coefficient on well-compacted single-phase samples over a wide temperature range, which is the goal of our future work.

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Кристалічні та електронні структури нових інтерметалічних сполук Tb_{0.87}Na_{0.13}Zn_{0.37}Sn₂ та Tb_{0.85}Mg_{0.15}Zn_{0.40}Sn₂

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Нові тетрарні дистаніди, Tb_{0.87}Na_{0.13}Zn_{0.37}Sn₂ та Tb_{0.85}Mg_{0.15}Zn_{0.40}Sn₂, кристалізуються в ромбічному структурному типі CeNiSi₂ з просторовою групою *Smc* і символом Пірсона oS16. Усі атоми займають чотири незалежні положення Вайкоффа 4c (симетрія положень *m2m*). Два положення повністю зайняті атомами Sn, а одне – статистичною сумішшю атомів Tb/Na або Tb/Mg.), а четверте положення 4c частково зайняте атомами цинку. Обчислення електронної структури використовувалися для з'ясування причин і здатності взаємозаміни Tb атомами Mg або Na. Мінімуми функції електронної локалізації спостерігалася навколо атомів Tb/Na/Mg, а максимуми – поблизу атомів Sn. Заміна тербію на Na або Mg не призводить до суттєвих змін у функції локалізації електронів.

Ключові слова: інтерметаліди, кристалічна структура, електронна структура хімічний зв'язок.