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The first quaternary intermetallide with $Sc_3Ce_2Si_4$-type structure

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The crystal structure of $Tm_2Ta_3Ge_{2.67}Si_{1.33}$ was solved and refined from X-ray single-crystal diffraction data. It is isotypic to $Sc_3Ce_2Si_4$: Pearson symbol *oP*36, space group *Pnma*, $a = 6.848(2)$, $b = 13.299(5)$, $c = 7.032(3)$ Å, $Z = 4$; $R = 0.0329$, $wR = 0.0817$ (for 608 independent reflections with $F > 2\sigma(F)$ and 50 variables). The structure of the new quaternary compound is partly disordered and characterized by statistic distribution of the smaller atoms, Ge and Si, which form pairs with the shortest distances 2.677(3) and 2.561(4) Å. The structure of $Tm_2Ta_3Ge_{2.67}Si_{1.33}$ can be described as a stacking of slabs along the crystallographic direction [010]. The slabs are formed by Ta-centered rhombic dodecahedra and are connected *via* common faces.

Germanium / Silicon / Tantalum / Thulium / X-ray single crystal diffraction / Crystal structure

Introduction

46 representatives of the orthorhombic structure type $Sc_3Ce_2Si_4$ (Pearson symbol *oP*36, space group *Pnma* [1]) are known so far, according to Pearson's Crystal Data [2]. This structure is formed in ternary systems with silicon: Sc–{La-Nd, Sm, Gd-Tm}–Si; Y–Ce–Si, Nb–{Sc, U}–Si; Mo–{Sc, Lu, Hf}–Si, W–Sc–Si, and germanium: Ca–{La, Ce}–Ge; Sc–{La-Nd, Sm, Gd}–Ge; Mo–Sc–Ge, Ti–{Gd-Tm, Lu}–Ge; V–Sc–Ge; Y–Ce–Ge; Zr–Ta–Ge; Nb–{Y, Gd-Lu}–Ge (the order of the chemical elements in the systems corresponds to the order of the chemical elements in the formula of the structure type $Sc_3Ce_2Si_4$). Almost half of these compounds, 22 compounds, are Sc-containing compounds. In the structures of the compounds with rare-earth metals, the Sc atoms occupy the sites of Sc in the prototype, whereas in the compounds with other *d*-elements (Nb, Mo, W, V) the Sc atoms occupy the site of Ce in the prototype. In [3] the crystal structures of the compounds $Nb_3R_2Ge_4$ (R = Y, Gd-Er, Lu) were assigned to the closely related structure type $Zr_2Nb_3Ge_4$ ($[NbZr_2]Nb_2Ge_4$) [4]. The ternary types $Sc_3Ce_2Si_4$ and $Zr_2Nb_3Ge_4$ are ordered substitution derivatives of the binary type Gd_5Si_4 [5], which is a branch of the type Sm_5Ge_4 [6].

In this work we present the results of a structural investigation of the first representative of the $Sc_3Ce_2Si_4$-type found in a quaternary system, Ta–Tm–Si–Ge.

Experimental

A sample of nominal composition $Tm_{33.3}Ge_{61.7}Si_5$ was synthesized from high-purity elements (Tm ≥ 99.83, Ge ≥ 99.999, and Si ≥ 99.999 wt.%) by arc melting in a water-cooled copper crucible with a tungsten electrode under a purified argon atmosphere (using Ti as a getter). The weight loss during the preparation of the alloy was less than 0.5 % of the total mass, which was 1 g. The sample was annealed at 600°C in a quartz ampoule under vacuum for one month and subsequently quenched in cold water. Single crystals were grown in a high-frequency furnace. The alloy, placed in a tantalum tube, was heated to a light orange color (until a flash was observed), kept for 30 minutes at this temperature, and then slowly (1 K/min) cooled.

Search and selection of a single crystal were carried out using a Leica 420i electron microscope. For further research, the single crystal was glued onto a glass capillary and tested for 5 min on a single-crystal diffractometer Oxford Diffraction Xcalibur 3, Sapphire 3 CCD Detector (Mo *K*α radiation). The obtained diffraction pattern was analyzed using the CrysAlis computer program package [7], which allows evaluating the quality of the single crystal and the parameters of the unit cell. Possible space groups were determined from an analysis of the systematic extinctions. The crystal structure was solved by direct methods and subsequent least-squares refinements were carried out with the SHELX-97 [8] program package. The chemical composition of the single crystal was checked by means of energy-dispersive

X-ray analysis, using a scanning electron microscope JEOL SEM 5900LV. The structure drawings were made with the program ATOMS [9].

Results and discussion

A preliminary analysis of the diffraction data showed that the investigated crystal belongs to the orthorhombic system. The final refinement was performed in the anisotropic approximation in space group *Pnma* and led to the composition $Tm_2Ta_3Ge_{2.67(5)}Si_{1.33(5)}$, which agrees well with the results of the EDX analysis of the crystal (see Table 1). Details of the data collection and final structure refinement are given in Table 2. The new quaternary compound, $Tm_2Ta_3Ge_{2.67}Si_{1.33}$, crystallizes with a $Sc_3Ce_2Si_4$-type structure: the Tm atoms occupy the positions of the Ce atoms (Wyckoff position 8*d* of the space group *Pnma*), the Ta atoms occupy the positions of the Sc atoms (8*d* and 4*c*), whereas the Ge and Si atoms statistically occupy the positions of the Si atoms (8*d*, 4*c*, and 4*c*). Two of the three sites occupied by the statistical mixture Ge/Si are mainly occupied by Ge atoms, more than 70 %. The refined atomic coordinates, site occupancies, and displacement parameters for $Tm_2Ta_3Ge_{2.67}Si_{1.33}$ are listed in Table 3 and Table 4. The positional parameters were standardized with the program STRUCTURE TIDY [10]. The interatomic distances within the coordination polyhedra are listed in Table 5. The shortest distances are observed between Ge/Si atoms of the sites *M*1, *M*2 and *M*3: $\delta_{M1\text{-}M1}$ = 2.677(3), $\delta_{M2\text{-}M3}$ = 2.561(4) Å. A projection of the structure $Tm_2Ta_3Ge_{2.67}Si_{1.33}$ along the crystallographic direction [100] is presented in Fig. 1.

In the structure of $Tm_2Ta_3Ge_{2.67}Si_{1.33}$, the Tm atoms have the largest coordination polyhedra, which can be described as a pentagonal prism consisting of one Tm, four Ta, and five Ge/Si atoms, and eight additional atoms of different kinds. The Ta atoms are situated in slightly smaller polyhedra: 16-vertex Frank-Kasper polyhedra (site Ta1) and rhombic dodecahedra (Ta2). In the case of site Ta1, the coordination polyhedron consists of five Tm, five Ta and six Ge/Si atoms, whereas the composition of the dodecahedron is $Tm_4Ta_4M_6$. The Ge and Si atoms center trigonal prisms of compositions Tm_3Ta_3 (*M*1), Tm_2Ta_4 (*M*2) and Tm_4Ta_2 (*M*3). All of the prisms are three-capped; in the case of sites *M*2 and *M*3 by one Ge/Si and two Ta atoms, in the case of site *M*1 by atoms of the three/four elements (Tm, Ta, Ge/Si).

Table 1 Results of the EDX analysis of the single crystal used in the experiment.

Element	Content (at.%)	Accuracy of the analysis (at.%)
Tm	21.87	± 2.7
Ta	31.65	± 2.1
Ge	30.59	± 3.6
Si	15.89	± 3.9

Table 2 Crystal data and details of the data collection and final refinement for $Tm_2Ta_3Ge_{2.67}Si_{1.33}$.

Composition from refinement	$Tm_2Ta_3Ge_{2.67}Si_{1.33}$
Molar mass M (g mol^{-1})	1111.66
Space group	*Pnma*
Cell parameters a, b, c (Å), V (Å^3)	6.848(2), 13.299(5), 7.032(3), 640.4(4)
Formula units per unit cell Z	4
Density D_x (Mg m^{-3})	11.530
Absorption coefficient μ (mm^{-1})	90.866
Radiation, wavelength (Å)	Mo $K\alpha$, 0.71073
Number of reflections for cell parameters	608
Temperature for data collection (K)	293(2)
Crystal color	gray, metallic
Collection mode	ω oscillation scans
Number of measured / independent reflections	18679 / 767
Number of reflections with $F > 2\sigma(F)$	608
R_{int}	0.0736
Range of h, k, l	$-8 \le h \le 8$, $-17 \le k \le 17$, $-9 \le l \le 9$
Refinement on	F^2
Reliability factors R, wR (for $F>2\sigma(F)$)	0.0407 (0.0329), 0.0840 (0.0817)
Goodness of fit S	1.126
Number of refined parameters	50
Weighting scheme	$w = 1/[(\sigma F_o)^2 + (0.0527P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
Extinction coefficient	0.00045(8)
Residual electron density $\Delta\rho_{max}$ / $\Delta\rho_{min}$ (e Å^{-3})	3.472 / -3.393

Table 3 Atom coordinates and site occupancies for $Tm_2Ta_3Ge_{2.67(5)}Si_{1.33(5)}$: structure type $Sc_3Ce_2Si_4$, *oP*36, *Pnma*, *a* = 6.848(2), *b* = 13.299(5), *c* = 7.032(3) Å.

Site	Wyckoff position	*x*	*y*	*z*	Occupancy
Tm	8*d*	0.99647(8)	0.59509(5)	0.17285(9)	1
Ta1	8*d*	0.34034(8)	0.12638(4)	0.17317(8)	1
Ta2	4*c*	0.16699(11)	¼	0.48903(11)	1
Ge1	8*d*	0.1748(2)	0.04066(13)	0.4637(2)	0.771(12)
Si1	8*d*	0.1748(2)	0.04066(13)	0.4637(2)	0.229(12)
Ge2	4*c*	0.0411(5)	¼	0.1199(5)	0.391(16)
Si2	4*c*	0.0411(5)	¼	0.1199(5)	0.609(16)
Ge3	4*c*	0.3045(3)	¼	0.8615(4)	0.733(15)
Si3	4*c*	0.3045(3)	¼	0.8615(4)	0.267(15)

Table 4 Equivalent and anisotropic displacement parameters ($Å^2$) for $Tm_2Ta_3Ge_{2.67}Si_{1.33}$.

Site	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tm	0.0047(2)	0.0059(3)	0.0029(3)	0.0054(4)	0.0001(2)	-0.0001(2)	0.0003(2)
Ta1	0.0042(2)	0.0060(3)	0.0011(3)	0.0054(3)	-0.0003(2)	0.0000(2)	0.0002(2)
Ta2	0.0038(2)	0.0044(4)	0.0019(4)	0.0050(4)	0.000	-0.0002(3)	0.000
Ge1	0.0044(6)	0.0046(9)	0.0019(9)	0.0067(10)	-0.0017(7)	0.0014(6)	0.0001(6)
Si1	0.0044(6)	0.0046(9)	0.0019(9)	0.0067(10)	-0.0017(7)	0.0014(6)	0.0001(6)
Ge2	0.0051(11)	0.0088(18)	0.0022(18)	0.0042(18)	0.000	-0.0015(13)	0.000
Si2	0.0051(11)	0.0088(18)	0.0022(18)	0.0042(18)	0.000	-0.0015(13)	0.000
Ge3	0.0044(8)	0.0052(13)	0.0023(13)	0.0058(13)	0.000	-0.0008(10)	0.000
Si3	0.0044(8)	0.0052(13)	0.0023(13)	0.0058(13)	0.000	-0.0008(10)	0.000

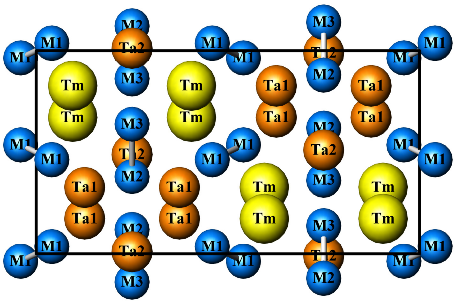


Fig. 1 Projection of the structure of $Tm_2Ta_3Ge_{2.67}Si_{1.33}$ along [100] emphasizing the pairs of *M* (Ge/Si) atoms.

The structure of $Tm_2Ta_3Ge_{2.67}Si_{1.33}$ can be represented as a stacking of layers of rhombic dodecahedra along the crystallographic direction [010]. Within the layers, the dodecahedra are connected *via* common faces (Fig. 2).

The structure type $Sc_3Ce_2Si_4$ is a ternary substitution derivative of the binary structure types Sm_5Ge_4 [6] and Gd_5Si_4 [5], where two of the three sites occupied by rare-earth atoms in the binary types (Wyckoff positions 8*d* and 4*c* of space group *Pnma*) are occupied by Sc atoms and the last one (8*d*) by Ce atoms. The structure type Gd_5Si_4 is closely related to the type Sm_5Ge_4 and is sometimes considered as a branch of the latter [6]. In Gd_5Si_4 and $Sc_3Ce_2Si_4$ all of the Si atoms form pairs (δ(Si1-Si1) = 2.48 and 2.54 Å, δ(Si2-Si3) = 2.48 and 2.61 Å, respectively, site names standardized) [11]. In Sm_5Ge_4 significantly longer distances occur within the Ge1-Ge1 pairs (3.71 Å) than within the Ge2-Ge3 pairs (2.66 Å).

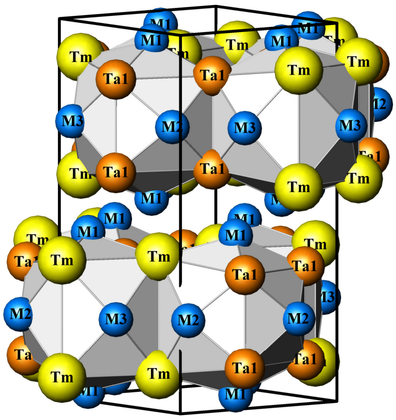


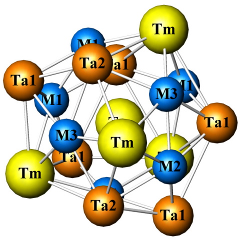
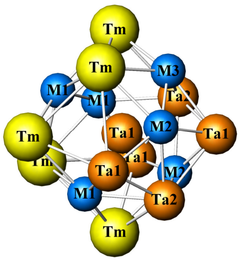
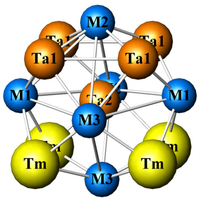
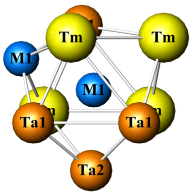
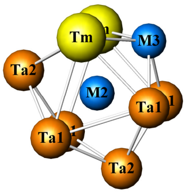
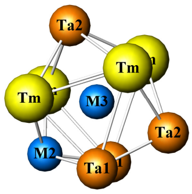
Fig. 2 Stacking of rhombic dodecahedra in the structure of $Tm_2Ta_3Ge_{2.67}Si_{1.33}$.

In the case of the compound $Tm_2Ta_3Ge_{2.67}Si_{1.33}$, synthesized here, the *M*1-*M*1 distances (2.60 Å) are only slightly longer than the *M*2-*M*3 distances (2.56 Å), and both must be considered to present partly covalent character. A disordered arrangement of the Ge and Si atoms was observed, however, the Si atoms show a preference for site *M*2.

Conclusions

The $Tm_2Ta_3Ge_{2.67}Si_{1.33}$ compound is the first quaternary intermetallide found to crystallize with a $Sc_3Ce_2Si_4$-type structure. The structure is disordered in relation to the Ge and Si atoms. It belongs to a family of structures with trigonal prismatic coordination of

Table 5 Interatomic distances and coordination polyhedra in $Tm_2Ta_3Ge_{2.67}Si_{1.33}$.

Atoms		δ (Å)	
Tm	- *M*1	2.785(2)	
	- *M*3	2.804(2)	
	- *M*1	2.904(2)	
	- *M*2	2.923(3)	
	- *M*3	2.924(2)	
	- *M*1	2.989(2)	
	- *M*1	3.006(2)	
	- Ta2	3.339(2)	
	- Ta2	3.351(2)	
	- Ta1	3.315(2)	
	- Ta1	3.378(2)	
	- Tm	3.508(3)	
	- 2Tm	3.592(3)	
	- Ta1	3.711(2)	
	- Ta1	3.715(2)	
	- Ta1	3.771(2)	
	- Tm	4.120(3)	
Ta1	- *M*2	2.590(3)	
	- *M*1	2.599(2)	
	- *M*2	2.654(3)	
	- *M*1	2.668(2)	
	- *M*1	2.734(2)	
	- *M*3	2.751(2)	
	- Ta2	3.001(2)	
	- Ta2	3.007(2)	
	- Ta1	3.288(2)	
	- Tm	3.315(2)	
	- Tm	3.378(2)	
	- 2Ta1	3.590(2)	
	- Tm	3.711(2)	
	- Tm	3.715(2)	
	- Tm	3.771(2)	
Ta2	- *M*2	2.674(3)	
	- *M*3	2.696(3)	
	- *M*2	2.735(4)	
	- *M*3	2.783(3)	
	- 2*M*1	2.790(2)	
	- 2Ta1	3.001(2)	
	- 2Ta1	3.007(2)	
	- 2Tm	3.339(2)	
	- 2Tm	3.351(2)	
*M*1	- Ta1	2.599(2)	
	- Ta1	2.668(2)	
	- *M*1	2.677(3)	
	- Ta1	2.734(2)	
	- Tm	2.785(2)	
	- Ta2	2.790(2)	
	- Tm	2.904(2)	
	- Tm	2.989(2)	
	- Tm	3.006(2)	
*M*2	- *M*3	2.561(4)	
	- 2Ta1	2.590(3)	
	- 2Ta1	2.654(3)	
	- Ta2	2.674(3)	
	- Ta2	2.735(4)	
	- 2Tm	2.924(3)	
*M*3	- *M*2	2.561(4)	
	- Ta2	2.696(3)	
	- 2Ta1	2.751(2)	
	- Ta2	2.783(3)	
	- 2Tm	2.804(2)	
	- 2Tm	2.924(2)	

the smaller atoms (Ge and Si), whereas the coordination polyhedra of the Tm and Ta atoms (two sites for the latter) are larger and correspond to 18-, and 16-, and 14-vertex polyhedra. The structure can be viewed as a stacking of layers, formed by interconnected Ta-centered 14-vertex polyhedra (rhombic dodecahedra), along the crystallographic direction [010].

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