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New compounds with $Sc_2Re_3Si_4$-type structure in the systems *R*–{Zr,Hf}–Ge

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Fifteen $Sc_2Re_3Si_4$-type (Pearson symbol *tP*36, space group $P4_12_12$) compounds, $Y_2\{Zr,Hf\}_3Ge_4$, $Gd_2\{Zr,Hf\}_3Ge_4$, $Tb_2\{Zr,Hf\}_3Ge_4$, $Dy_2\{Zr,Hf\}_3Ge_4$, $Ho_2Hf_3Ge_4$, $Er_2\{Zr,Hf\}_3Ge_4$, $Tm_2\{Zr,Hf\}_3Ge_4$, and $Lu_2\{Zr,Hf\}_3Ge_4$, were synthesized and characterized by means of X-ray diffraction and energy-dispersive analyses. The crystal structures of two alloys in the Tm-Zr-Ge and Ho-Hf-Ge systems ($Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$, $a = 7.3457(5)$, $c = 13.388(1)$ Å; $Ho_{1.38(8)}Hf_{3.62(8)}Ge_4$, $a = 7.3139(6)$, $c = 13.3550(13)$ Å) were refined by the Rietveld method on X-ray powder diffraction data. In both structures one of the atom sites was found to be occupied by a statistical mixture of rare-earth metal and Zr (Hf) atoms.

Rare-earth metals / Zirconium / Hafnium / Germanium / X-ray powder diffraction / Crystal structure

Introduction

The interest in intermetallic compounds of rare-earth metals (*R*) with Si and/or Ge in the ratio *R*:(Si,Ge) = 5:4 has rapidly grown since the discovery of a giant magnetocaloric effect near room temperature in the compound $Gd_5Si_2Ge_2$ [1]. Analysis of literature data [2] on the crystal structures of ternary compounds in the systems *R*–{Ti,Zr,Hf}–{Si,Ge} revealed the existence of a series of compounds with stoichiometry $R_2T_3M_4$. Crystallographic data for the ternary compounds $R_2T_3M_4$ in the systems *R*–{Ti,Zr,Hf}–{Si,Ge} are summarized in Table 1. The crystal structures of the listed ternary phases belong to two structure types: $Sc_2Re_3Si_4$ (*tP*36, $P4_12_12$) [11] and $Ce_2Sc_3Si_4$ (*oP*36, *Pnma*) [12], which are ternary ordered variants of the binary structure types Zr_5Si_4 (*tP*36, $P4_12_12$) [13] and Gd_5Si_4 (*oP*36, *Pnma*) [14], respectively. The latter type, where all the Si atoms are engaged in Si-Si dimers, is a branch of the structure type Sm_5Ge_4 (*oP*36, *Pnma*) [15].

Looking at the binary systems, it may be noted that Ti_5Ge_4 and Hf_5Ge_4 both adopt the Sm_5Ge_4 type, whereas Zr_5Ge_4 prefers the Zr_5Si_4 type. The latter type has been reported for the three corresponding silicides, but Ti_5Si_4 was found to be polymorphic, the room temperature modification crystallizing with a Gd_5Si_4-type structure. Orthorhombic Sm_5Ge_4- or Gd_5Si_4-type structures have been reported for all binary R_5Si_4 and R_5Ge_4 compounds with *R* = Y, Gd-Lu, except for Lu_5Si_4, Tm_5Si_4, and Lu_5Ge_4.

The crystal structures of the ternary silicides in Table 1 belong to the tetragonal structure type $Sc_2Re_3Si_4$, whereas those of the ternary germanides, except $Gd_3Zr_2Ge_4$, belong to the orthorhombic structure type $Ce_2Sc_3Si_4$. In some cases, *e.g.* for $Gd_{1.9}Ti_3Si_4$, $Gd_{1.94}Ti_3Ge_4$, $Tb_{1.98}Ti_3Ge_4$, $Dy_{1.94}Ti_3Ge_4$, $Ho_{1.92}Ti_3Ge_4$, and $Er_{1.82}Ti_3Ge_4$, complete structure refinements considered vacancies on the sites occupied by the rare-earth metal atoms, leading to *R*-deficient chemical formulas. Partial Dy/Ti disorder was refined for $Dy_3Ti_2Si_4$ [4]. A certain homogeneity range was found for the $Ce_2Sc_3Si_4$-type phase in the Tb–Ti–Ge system at 1070 K [10], $Tb_{1.35-2}Ti_{3.65-3}Ge_4$, where the phase was observed in equilibrium with the binary compound Tb_5Ge_4 (Sm_5Ge_4 type). $Gd_3Hf_2Si_4$ and $Gd_3Zr_2Ge_4$ [6] were found to be part of extended substitutional solid solutions based on the Zr_5Si_4-type binary compounds, $Gd_xHf_{5-x}Si_4$, x = 0-4.3, and $Gd_xZr_{5-x}Ge_4$, x = 0-3.23, respectively. In both systems, a solid solution with the orthorhombic Gd_5Si_4 type (or its branch Sm_5Ge_4) was observed on the Gd-rich side.

The aim of this work was to search for new ternary compounds of composition $R_2T_3Ge_4$ in the systems *R*–{Zr,Hf}–Ge with heavy rare-earth metals, and determine their crystal structures.

Experimental

18 alloys of nominal composition $R_{22.2}T_{33.3}Ge_{44.5}$ (*R* = Y, Gd-Lu, *T* = Zr, Hf) were prepared from high-

Table 1 Crystallographic data for the ternary compounds $R_2T_3M_4$ in the systems R–{Ti,Zr,Hf}–{Si,Ge}.

Compound	Structure type	Pearson symbol	Space group	Cell parameters, Å			Reference
				a	*b*	*c*	
$Gd_{1.9}Ti_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	6.997	–	12.878	[3]
$Tb_2Ti_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.006	–	12.875	[4]
$Tb_2Ti_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.014	–	12.898	[5]
$Dy_2Ti_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	6.977	–	12.814	[3,5]
$Ho_2Ti_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	6.970	–	12.793	[3]
$Er_2Ti_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	6.964	–	12.776	[3]
$Er_2Ti_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	6.985	–	12.809	[4]
$Lu_2Ti_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	6.980	–	12.775	[4]
$Dy_2Zr_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.236	–	13.249	[4]
$Ho_2Zr_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.208	–	13.200	[4]
$Er_2Zr_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.229	–	13.249	[4]
$Tm_2Zr_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.222	–	13.920	[4]
$Lu_2Zr_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.225	–	13.205	[4]
$Gd_{1.4}Hf_{3.6}Si_4$ [a]	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.247	–	13.242	[6]
$Tb_2Hf_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.2057		13.199	[7]
$Dy_2Hf_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.200	–	13.187	[4]
$Ho_2Hf_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.170	–	13.087	[4]
$Er_2Hf_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.170	–	13.096	[4]
$Tm_2Hf_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.198	–	13.15	[4]
$Lu_2Hf_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.190	–	13.120	[4]
$Gd_{1.94}Ti_3Ge_4$	$Ce_2Sc_3Si_4$	*oP*36	*Pnma*	7.042	13.494	7.186	[8]
$Gd_2Ti_3Ge_4$	$Ce_2Sc_3Si_4$	*oP*36	*Pnma*	7.044	13.494	7.187	[9]
$Tb_{1.98}Ti_3Ge_4$	$Ce_2Sc_3Si_4$	*oP*36	*Pnma*	7.019	13.457	7.156	[8]
$Tb_2Ti_3Ge_4$ [b]	$Ce_2Sc_3Si_4$	*oP*36	*Pnma*	7.019	13.457	7.156	[10]
$Dy_{1.94}Ti_3Ge_4$	$Ce_2Sc_3Si_4$	*oP*36	*Pnma*	6.987	13.409	7.122	[8]
$Ho_{1.92}Ti_3Ge_4$	$Ce_2Sc_3Si_4$	*oP*36	*Pnma*	6.981	13.399	7.117	[8]
$Er_{1.82}Ti_3Ge_4$	$Ce_2Sc_3Si_4$	*oP*36	*Pnma*	6.962	13.367	7.099	[8]
$Gd_{1.77}Zr_{3.23}Ge_4$ [c]	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	7.4131	–	13.602	[6]

[a] solid solution $Gd_xHf_{5-x}Si_4$ (x = 0-4.3); [b] solid solution $Tb_xTi_{5-x}Ge_4$ (x = 3-3.65); [c] solid solution $Gd_xZr_{5-x}Ge_4$ (x = 0-3.23).

purity metals ($R \geq 99.85$ mass%, $Zr \geq 99.89$ mass%, $Hf \geq 99.9$ mass%, $Ge \geq 99.999$ mass%) by arc-melting in a water-cooled copper cruicible with a tungsten electrode under purified argon using Ti as a getter. The ingots were annealed in evacuated quartz ampoules in a VULKAN A-550 muffle furnace and subsequently quenched in cold water. The samples containing Zr were held at 600°C for 45 days, and those containing Hf at 900°C for 120 days. The alloys had metallic luster and were stable in the air.

Phase analysis was performed based on X-ray powder diffraction patterns collected at room temperature on diffractometers of the models DRON-2.0M (Fe $K\alpha$ radiation, $\lambda = 1.9374$ Å) and Panalytical X'Pert (Cu $K\alpha_1$ radiation, $\lambda = 1.5406$ Å). The profile and structural parameters were refined by the Rietveld method on data collected on the Panalytical X'Pert diffractometer in the angular range 10-115° 2θ, using the program package FullProf Suite [16]. TYPIX database [17] was used to identify the prototypes and standardize the structural parameters.

The chemical compositions of the individual phases were checked by energy-dispersive X-ray analysis, which was performed on polished surfaces, using a REMMA-102-02 electron microscope equipped with an EDX detector.

Results and discussion

All the synthesized samples were multiphase but the main phase was a ternary phase crystallizing with one of the $R_2T_3Ge_4$ structure types. Additional phases were the binary compounds RGe_{2-x} with AlB_2-type structure (*hP*3, *P*6/*mmm*) or R_5Ge_3 (T_5Ge_3) with Mn_5Si_3-type structure (*hP*16, $P6_3/mmc$). This can be explained by the high stability of these phases, and even long-time annealing (120 days) did not allow obtaining single-phase alloys. In the diffraction patterns of some of the samples, peaks that did not belong to any of the known binary compounds were observed. This may indicate the formation of still unknown compounds in the investigated systems. The X-ray phase and structural analysis of the alloys indicated the formation of 15 compounds with $Sc_2Re_3Si_4$-

type structure: $Y_2\{Zr,Hf\}_3Ge_4$, $Gd_2\{Zr,Hf\}_3Ge_4$, $Tb_2\{Zr,Hf\}_3Ge_4$, $Dy_2\{Zr,Hf\}_3Ge_4$, $Ho_2Hf_3Ge_4$, $Er_2\{Zr,Hf\}_3Ge_4$, $Tm_2\{Zr,Hf\}_3Ge_4$, $Lu_2\{Zr,Hf\}_3Ge_4$ (Table 2). The cell parameters of the Zr-containing compounds are larger than those of the isotypic compounds with Hf, due to the larger size of the Zr atoms. It may be noted that all the rare-earth titanium germanides $R_2Ti_3Ge_4$ reported up to date crystallize with the orthorhombic structure type $Ce_2Sc_3Si_4$ (see Table 1).

The results of the energy-dispersive X-ray analysis, performed on selected samples, are given in Table 3, where the phases observed in the samples and their compositions are listed. Photographs of polished surfaces of the samples $Tb_{22.2}Zr_{33.3}Ge_{44.5}$, $Dy_{22.2}Zr_{33.3}Ge_{44.5}$, $Ho_{22.2}Zr_{33.3}Ge_{44.5}$, $Tb_{22.2}Hf_{33.3}Ge_{44.5}$, $Dy_{22.2}Hf_{33.3}Ge_{44.5}$ and $Ho_{22.2}Hf_{33.3}Ge_{44.5}$ are shown in Fig. 1.

Crystal structure refinements, including the refinement of the positional coordinates, isotropic displacement parameters and site occupancies, were performed using X-ray powder diffraction data collected on polycrystalline samples of composition $Tm_{22.2}Zr_{33.3}Ge_{44.5}$ and $Ho_{22.2}Hf_{33.3}Ge_{44.5}$. The former contained two phases: the new ternary compound $Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$ and the binary compound Tm_2Ge_3 (own structure type); the latter three phases: the expected ternary compound ($Ho_{1.38(8)}Hf_{3.62(8)}Ge_4$), and the binary compounds Hf_5Ge_3 (structure type Mn_5Si_3) and $HoGe_{1.5}$ (AlB_2). For the secondary phases only the scale factors and cell parameters were refined, while the profile parameters were constrained to be equal to the profile parameters of the main phase.

As starting model for the refinement of the structural parameters of the new ternary compounds, the atom coordinates in the structure of the prototype $Sc_2Re_3Si_4$ were chosen. The structure type $Sc_2Re_3Si_4$ is a ternary variant of the binary structure type Zr_5Si_4 with an ordered distribution of Sc and Re atoms: one site in Wyckoff position 8*b* is occupied by Sc atoms, whereas a second site in 8*b* and the site in 4*a* are occupied by Re atoms. The crystallographic parameters of the individual phases are listed in Table 4. Experimental and calculated X-ray powder diffraction patterns and the differences between them for the samples of nominal composition $Tm_{22.2}Zr_{33.3}Ge_{44.5}$ and $Ho_{22.2}Hf_{33.3}Ge_{44.5}$ are shown in Fig. 2.

The crystal structures of the ternary compounds $Tm_2Zr_3Ge_4$ and $Ho_2Hf_3Ge_4$ belong to the structure type $Sc_2Re_3Si_4$ (*tP*36, $P4_12_12$): $a = 7.3457(5)$, $c = 13.388(1)$ Å for the Tm-containing phase ($R_B = 0.0362$), and $a = 7.3139(6)$, $c = 13.3550(13)$ Å for the Ho-containing phase ($R_B = 0.0415$). Accurate refinement of the occupancy parameters revealed partial disorder on one of the sites in Wyckoff position

Table 2 Cell parameters of $R_2T_3Ge_4$ compounds with $Sc_2Re_3Si_4$-type structure (*tP*36, $P4_12_12$).

Compound	*a*, Å	*c*, Å	Compound	*a*, Å	*c*, Å
$Y_2Zr_3Ge_4$	7.380(3)	13.47(1)	$Y_2Hf_3Ge_4$	7.322(3)	13.371(7)
$Gd_2Zr_3Ge_4$	7.406(1)	13.542(3)	$Gd_2Hf_3Ge_4$	7.351(1)	13.474(3)
$Tb_2Zr_3Ge_4$	7.397(1)	13.501(3)	$Tb_2Hf_3Ge_4$	7.361(1)	13.466(2)
$Dy_2Zr_3Ge_4$	7.417(3)	13.547(7)	$Dy_2Hf_3Ge_4$	7.331(2)	13.402(6)
			$Ho_2Hf_3Ge_4$ [b]	7.3139(6)	13.3550(13)
$Er_2Zr_3Ge_4$	7.378(4)	13.419(7)	$Er_2Hf_3Ge_4$	7.330(4)	13.354(9)
$Tm_2Zr_3Ge_4$ [a]	7.3457(5)	13.388(1)	$Tm_2Hf_3Ge_4$	7.317(1)	13.355(3)
$Lu_2Zr_3Ge_4$	7.337(6)	13.38(1)	$Lu_2Hf_3Ge_4$	7.298(2)	13.247(4)

[a] refined composition $Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$; [b] refined composition $Ho_{1.38(8)}Hf_{3.62(8)}Ge_4$.

Table 3 Results of the energy-dispersive X-ray analysis of the samples $Tb_{22.2}\{Hf,Zr\}_{33.3}Ge_{44.5}$, $Dy_{22.2}\{Hf,Zr\}_{33.3}Ge_{44.5}$, and $Ho_{22.2}\{Hf,Zr\}_{33.3}Ge_{44.5}$.

Sample composition	Phase content (chemical composition)
$Tb_{22.2}Hf_{33.3}Ge_{44.5}$	$Tb_2Hf_3Ge_4$ ($Tb_{12.1}Hf_{47.4}Ge_{40.5}$) Hf_5Ge_3 ($Tb_{8.9}Hf_{55.2}Ge_{35.9}$) *X* ($Tb_{38.1}Hf_{28.4}Ge_{33.5}$)
$Dy_{22.2}Hf_{33.3}Ge_{44.5}$	$Dy_2Hf_3Ge_4$ ($Tb_{15.2}Hf_{43.0}Ge_{41.8}$)
$Ho_{22.2}Hf_{33.3}Ge_{44.5}$	$Ho_2Hf_3Ge_4$ ($Ho_{14.0}Hf_{44.0}Ge_{42.0}$) Hf_5Ge_3 ($Ho_{4.1}Hf_{60.2}Ge_{35.7}$) $HoGe_{1.5}$ ($Ho_{37.5}Hf_{2.5}Ge_{60.0}$)
$Tb_{22.2}Zr_{33.3}Ge_{44.5}$	$Tb_2Zr_3Ge_4$ ($Tb_{9.6}Zr_{51.5}Ge_{38.9}$)
$Dy_{22.2}Zr_{33.3}Ge_{44.5}$	$Dy_2Hf_3Ge_4$ ($Dy_{21.1}Zr_{40.5}Ge_{38.4}$) (Dy,Zr)Ge ($Dy_{12.0}Zr_{53.5}Ge_{34.5}$)
$Ho_{22.2}Zr_{33.3}Ge_{44.5}$	$Ho_2Zr_3Ge_4$ ($Ho_{13.8}Zr_{56.7}Ge_{29.5}$)

8*b*, which was found to be occupied by a statistical mixture of Tm and Zr, or Ho and Hf atoms. The refined compositions were $Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$ ($(Tm_{0.44(2)}Zr_{0.56(2)})_2Zr_3Ge_4$) and $Ho_{1.38(8)}Hf_{3.62(8)}Ge_4$ ($(Ho_{0.69(4)}Hf_{0.31(4)})_2Hf_3Ge_4$). The refined atom coordinates, site occupancies and displacement parameters in the structures of the compounds $Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$ and $Ho_{1.38(8)}Hf_{3.62(8)}Ge_4$ are given in Table 5, and interatomic distances are listed in Table 6. The existence of sites with mixed occupancy supports the idea that the compounds reported here may have significant homogeneity ranges. This has already been confirmed for $Gd_xZr_{5-x}Ge_4$ [6], where the homogeneity range was found to include the binary compound Zr_5Ge_4. The study of the site preference within the solid solution, which concluded in preferential substitution of Gd atoms on one of the sites in Wyckoff position 8*b*, is in agreement with the refinements presented here. Further substitution by Gd showed no preference for one or the other of the two remaining Zr sites. It may be noted that the sample of nominal composition $Gd_2Zr_3Ge_4$ in [6] was also not single-phase and the refined composition of the single crystal picked up from the sample was $Gd_{1,77(3)}Zr_{3.23(3)}Ge_4$. A comparison of the cell parameters indicates that the composition of the sample used here is probably closer to the ideal composition $Gd_2Zr_3Ge_4$.

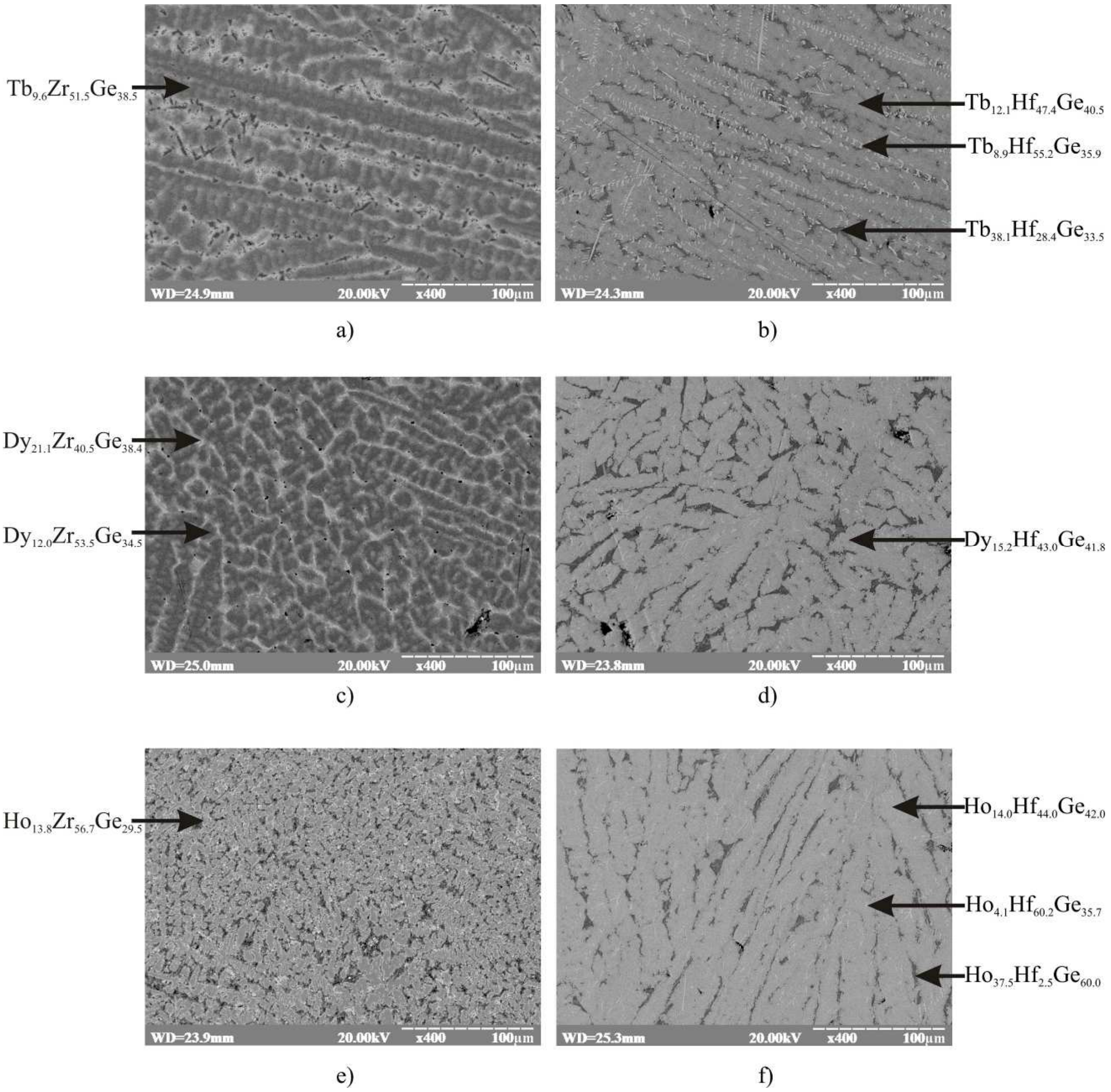


Fig. 1 Photographs of the polished surfaces in back-scattered X-rays of the samples $Tb_{22.2}Zr_{33.3}Ge_{44.5}$ (a), $Tb_{22.2}Hf_{33.3}Ge_{44.5}$ (b), $Dy_{22.2}Zr_{33.3}Ge_{44.5}$ (c), $Dy_{22.2}Hf_{33.3}Ge_{44.5}$ (d), $Ho_{22.2}Zr_{33.3}Ge_{44.5}$ (e), and $Ho_{22.2}Hf_{33.3}Ge_{44.5}$ (f).

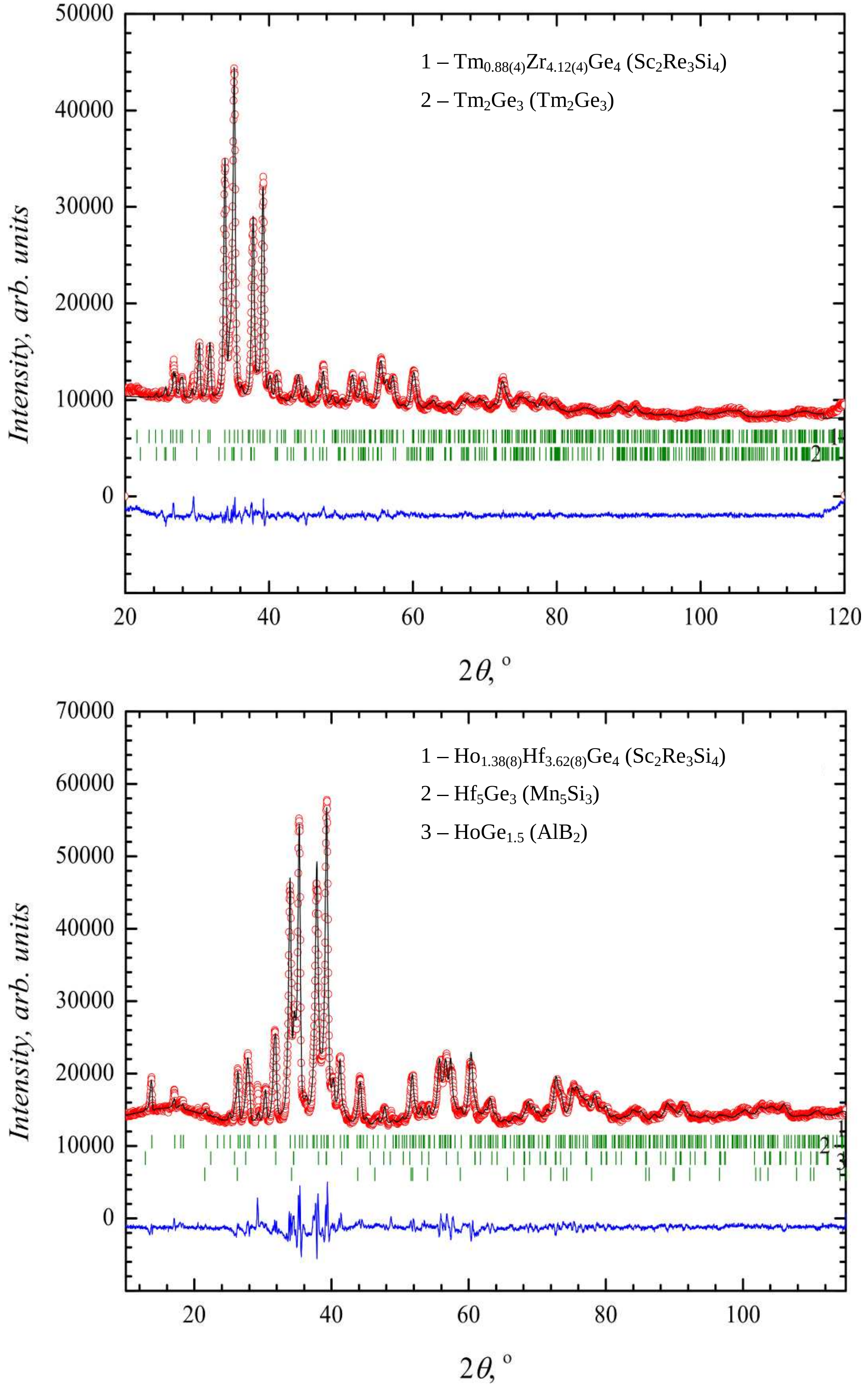


Fig. 2 Experimental (circles), calculated (continuous lines) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns (Cu $K\alpha_1$-radiation) of the samples $Tm_{22.2}Zr_{33.3}Ge_{44.5}$ ($R_p = 0.0144$, $R_{wp} = 0.0201$) and $Ho_{22.2}Hf_{33.3}Ge_{44.5}$ ($R_p = 0.0210$, $R_{wp} = 0.0308$). Vertical bars indicate the positions of the reflections of the individual phases.

Table 4 Crystallographic data for the individual phases in the samples $Tm_{22.2}Zr_{33.3}Ge_{44.5}$ and $Ho_{22.2}Hf_{33.3}Ge_{44.5}$.

Sample	$Tm_{22.2}Zr_{33.3}Ge_{44.5}$		$Ho_{22.2}Hf_{33.3}Ge_{44.5}$		
Phase	$Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$	Tm_2Ge_3	$Ho_{1.38(8)}Hf_{3.62(8)}Ge_4$	Hf_5Ge_3	$HoGe_{1.5}$
Content, mass%	89.1(2)	10.9(2)	90.8(9)	8.2(2)	1.0(2)
Structure type	$Sc_2Re_3Si_4$	Tm_2Ge_3	$Sc_2Re_3Si_4$	Mn_5Si_3	AlB_2
Pearson symbol	*tP*36	*mS*20	*tP*36	*hP*16	*hP*3
Space group	$P4_12_12$	$C2/c$	$P4_12_12$	$P6_3/mcm$	$P6/mmm$
Cell parameters: *a*, Å	7.3457(5)	8.933(2)	7.3139(6)	7.947(3)	3.919(2)
b, Å	–	6.607(1)	–	–	–
c, Å	13.388(1)	7.721(1)	13.3550(13)	5.612(3)	4.128(4)
β, °	–	116.013(9)	–	–	–

Table 5 Atomic coordinates, site occupancies and isotropic displacement parameters for the $Sc_2Re_3Si_4$-type (*tP*36, $P4_12_12$) compounds $Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$ and $Ho_{1.38(8)}Hf_{3.62(8)}Ge_4$.

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
$Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$ (a = 7.3457(5), c = 13.388(1) Å, R_B = 0.0362)					
R (0.44(2)Tm + 0.56(2)Zr)	8*b*	-0.0048(7)	0.3447(7)	0.2184(2)	0.51(8)
Zr1	8*b*	0.1572(7)	-0.0070(7)	0.3767(7)	0.95(7)
Zr2	4*a*	0.172(1)	0.172(1)	0	0.95(7)
Ge1	8*b*	0.291(1)	0.046(1)	0.1821(3)	0.77(8)
Ge2	8*b*	0.360(1)	0.307(1)	0.3196(5)	0.77(8)
$Ho_{1.38(8)}Hf_{3.62(8)}Ge_4$ (a = 7.3139(6), c = 13.3550(13) Å, R_B = 0.0415)					
R (0.69(4)Ho + 0.31(4)Hf)	8*b*	-0.0040(8)	0.339(8)	0.2211(3)	0.68(9)
Hf1	8*b*	0.159(5)	-0.003(6)	0.3723(6)	0.57(8)
Hf2	4*a*	0.1703(9)	0.1703(9)	0	0.59(9)
Ge1	8*b*	0.293(1)	0.033(1)	0.1768(6)	1.1(2)
Ge2	8*b*	0.358(2)	0.290(2)	0.3192(7)	1.0(2)

A projection of the unit cell of the ternary compound $Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$ along the crystallographic direction [100] and the coordination polyhedra of the atoms are shown in Fig. 3. The polyhedra in the structure of $Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$ derive from those in the parent structure type $Sc_2Re_3Si_4$. The sites *R* occupied by a statistical mixture of Tm and Zr atoms (*R* = 0.44(2)Tm + 0.56(2)Zr) are surrounded by 18-vertex polyhedra $RZr_8Ge_7R_3$, which can be described as pentagonal prisms with eight capping atoms in the equatorial plane. The coordination polyhedra for the Zr atoms occupying the sites in Wyckoff positions 8*b* and 4*a*, are 16- and 14-vertex Frank-Kasper polyhedra, $Zr1Ge_6R_6Zr_4$ and $Zr2Ge_6R_4Zr_4$, respectively. The polyhedra $Zr2Ge_6R_4Zr_4$ can be described as deformed rhombic dodecahedra (R_4Zr_4 cubes with six Ge atoms above the faces). The coordination polyhedra around the Ge atoms are tricapped trigonal prisms of composition $Ge1R_3Zr_5Ge$ and $Ge2R_4Zr_4Ge$.

The structures of $Ce_2Sc_3Si_4$ and $Sc_2Re_3Si_4$ are closely related and are built up from similar units *i.e.* layers of $ScCe_4Sc_4Si_6$ and $ReSc_4Re_4Si_6$ rhombic dodecahedra, respectively (Fig. 4). In the structure of $Ce_2Sc_3Si_4$ these Sc-centered polyhedra are connected *via* common faces within the layers and through Si-Si bonds in the perpendicular direction. In the structure of $Sc_2Re_3Si_4$ similar polyhedra, centered by Re atoms are connected *via* common faces and vertexes, forming a 3D-framework.

Conclusions

The crystal structures of the 15 compounds reported here: $Y_2\{Zr,Hf\}_3Ge_4$, $Gd_2\{Zr,Hf\}_3Ge_4$, $Tb_2\{Zr,Hf\}_3Ge_4$, $Dy_2\{Zr,Hf\}_3Ge_4$, $Ho_2Hf_3Ge_4$, $Er_2\{Zr,Hf\}_3Ge_4$, $Tm_2\{Zr,Hf\}_3Ge_4$, and $Lu_2\{Zr,Hf\}_3Ge_4$, belong to the structure type $Sc_2Re_3Si_4$ (Pearson symbol *tP*36, space group $P4_12_12$). Least-squares refinements of the structural parameters of two of them, revealed off-stoichiometric compositions, $Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$ and $Ho_{1.38(8)}Hf_{3.62(8)}Ge_4$. The site occupied by Sc in the structure type, was here found to contain a statistical mixture of rare-earth metal and Zr or Hf atoms, which points to the probable existence of significant homogeneity ranges for all these compounds. The structure type $Sc_2Re_3Si_4$ is built up of Re-centered rhombic dodecahedra of composition $Sc_4Re_4Si_6$, which are connected *via* common faces and vertexes to form a 3D-framework.

Table 6 Interatomic distances (δ) and coordination numbers (CN) in the structures of $Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$ and $Ho_{1.38(8)}Hf_{3.62(8)}Ge_4$ (standard deviation < 0.05 Å).

$Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$					$Ho_{1.38(8)}Hf_{3.62(8)}Ge_4$			
Atoms		δ, Å	Atoms	δ, Å	Atoms	δ, Å	Atoms	δ, Å
R (CN = 18)	– 1 Ge2	2.86	– 1 Zr2	3.45	– 1 Ge1	2.88	– 1 Hf1	3.45
	– 1 Ge1	2.94	– 1 Zr1	3.56	– 1 Ge2	2.91	– 1 Hf2	3.46
	– 1 Ge1	2.99	– 1 R	3.65	– 1 Ge2	2.98	– 1 R	3.55
	– 1 Ge2	3.02	– 2 R	3.71	– 1 Ge1	3.02	– 2 R	3.73
	– 1 Ge2	3.13	– 1 Zr1	3.86	– 1 Ge2	3.09	– 1 Hf1	3.85
	– 1 Ge1	3.14	– 1 Zr1	3.86	– 1 Ge2	3.12	– 1 Hf1	3.88
	– 1 Ge2	3.21	– 1 Zr1	3.89	– 1 Ge1	3.17	– 1 Hf1	3.88
	– 1 Zr1	3.44	– 1 Zr1	3.92	– 1 Hf1	3.43	– 1 Hf1	3.89
	– 1 Zr2	3.44			– 1 Hf2	3.44		
Hf1 / Zr1 (CN = 16)	– 1 Ge1	2.68	– 1 R	3.44	– 1 Ge1	2.63	– 1 R	3.43
	– 1 Ge2	2.73	– 1 R	3.56	– 1 Ge2	2.69	– 1 R	3.45
	– 1 Ge1	2.74	– 1 Zr1	3.72	– 1 Ge1	2.80	– 1 Hf1	3.64
	– 1 Ge2	2.77	– 1 Zr1	3.73	– 1 Ge1	2.80	– 1 Hf1	3.80
	– 1 Ge1	2.81	– 1 R	3.86	– 1 Ge2	2.81	– 1 R	3.85
	– 1 Ge2	2.85	– 1 R	3.86	– 1 Ge2	2.84	– 1 R	3.88
	– 1 Zr2	3.16	– 1 R	3.88	– 1 Hf2	3.15	– 1 R	3.88
	– 1 Zr2	3.17	– 1 R	3.92	– 1 Hf2	3.19	– 1 R	3.89
Hf2 / Zr2 (CN = 14)	– 2 Ge1	2.75	– 2 Zr1	3.17	– 2 Ge1	2.72	– 2 Hf1	3.19
	– 2 Ge2	2.85	– 2 R	3.44	– 2 Ge1	2.84	– 2 R	3.44
	– 2 Ge1	2.90	– 2 R	3.44	– 2 Ge2	2.94	– 2 R	3.46
	– 2 Zr1	3.16			– 2 Hf1	3.15		
Ge1 (CN = 9)	– 1 Zr1	2.68	– 1 Zr2	2.91	– 1 Hf1	2.63	– 1 Hf2	2.84
	– 1 Ge2	2.71	– 1 R	2.94	– 1 Ge2	2.72	– 1 R	2.88
	– 1 Zr1	2.74	– 1 R	2.99	– 1 Hf2	2.72	– 1 R	3.02
	– 1 Zr2	2.75	– 1 R	3.14	– 1 Hf1	2.80	– 1 R	3.17
	– 1 Zr1	2.81			– 1 Hf1	2.80		
Ge2 (CN = 9)	– 1 Ge1	2.71	– 1 R	2.86	– 1 Hf1	2.69	– 1 Hf2	2.94
	– 1 Zr1	2.73	– 1 R	3.02	– 1 Ge1	2.72	– 1 R	2.98
	– 1 Zr1	2.77	– 1 R	3.13	– 1 Hf1	2.81	– 1 R	3.09
	– 1 Zr2	2.85	– 1 R	3.21	– 1 Hf1	2.84	– 1 R	3.12
	– 1 Zr1	2.85			– 1 R	2.91		

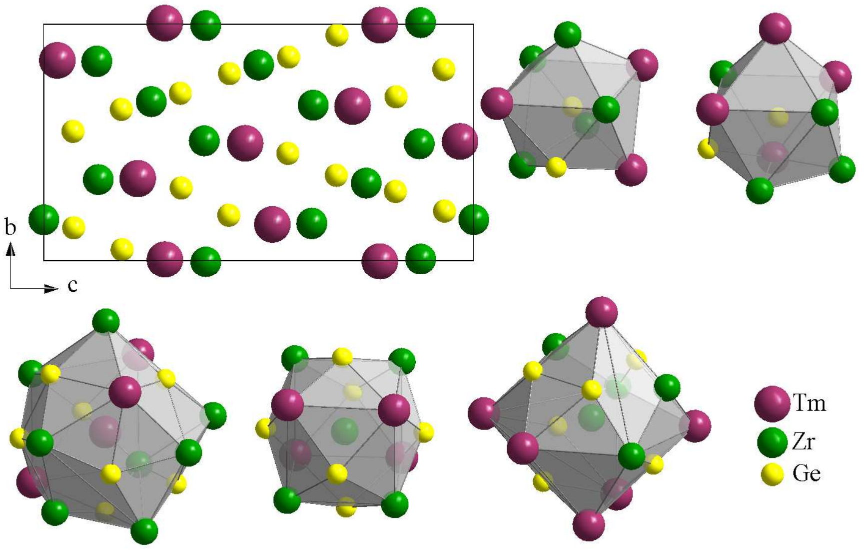
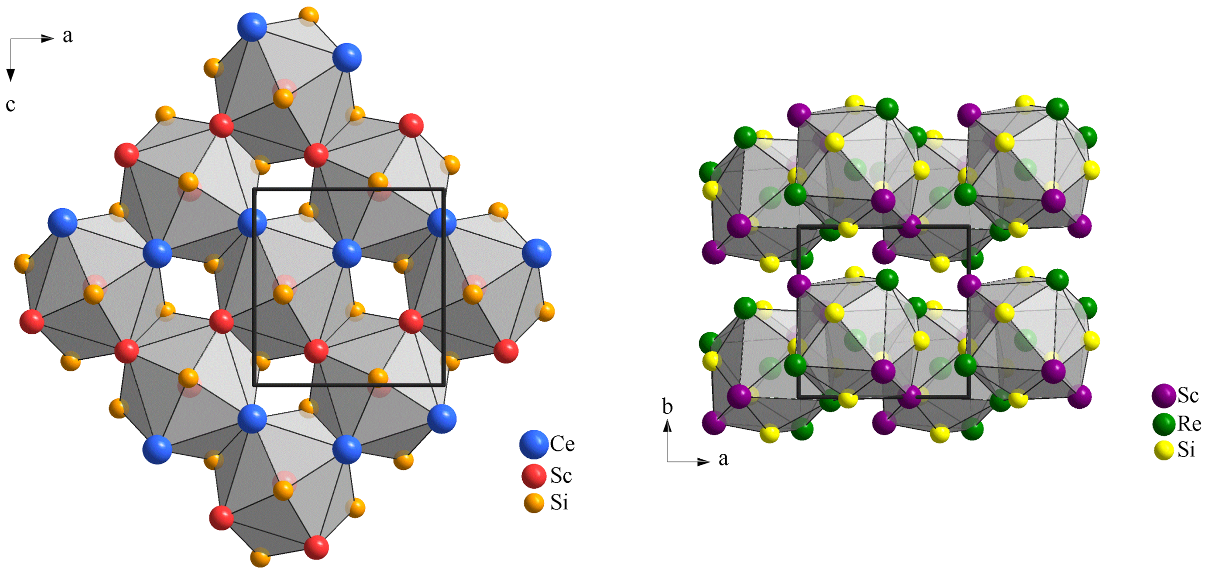


Fig. 3 Projection of the unit cell of the structure of $Tm_{0.88(4)}Zr_{4.12(4)}Ge_4$ onto the *bc* plane and coordination polyhedra of the atoms.



$Ce_2Sc_3Si_4$ $Sc_2Re_3Si_4$

Fig. 4 Layers of rhombic dodecahedra of compositions $Ce_4Sc_4Si_6$ and $Sc_4Re_4Si_6$ (centered by Sc and Re atoms, respectively) in the structure types $Ce_2Sc_3Si_4$ and $Sc_2Re_3Si_4$, respectively.

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