

## $R_{2-x}Ti_{3+x}Ge_4$ compounds in the $R-Ti-Ge$ ( $R = Gd-Lu$ ) systems

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The existence of five  $R_{2-x}Ti_{3+x}Ge_4$  compounds ( $R = Gd, Tb, Dy, Ho, Er$ ) was confirmed at 600°C and two new compounds,  $Tm_{1.79(2)}Ti_{3.21(2)}Ge_4$  and  $Lu_{1.74(2)}Ti_{3.26(2)}Ge_4$ , were found. No  $\sim R_2Ti_3Ge_4$  compound was observed for Yb. All the compounds crystallize with partly ordered variants of the structure type  $Sm_5Ge_4$  (Pearson symbol  $oP36$ , space group  $Pnma$ ). On going from gadolinium to lutetium, the unit-cell parameters are reduced, due to the lanthanide contraction, but also due to the fact that the refined composition becomes richer in Ti. One of the metal-atom sites located between the structural slabs was found to be fully occupied by titanium, whereas the other one is mainly or fully occupied by the rare-earth metal. The site located inside the slabs (rhombic dodecahedral coordination) is preferentially occupied by Ti.

### Rare-earth metals / Titanium / Germanides / Crystal structure

#### 1. Introduction

A number of  $\sim R_2T_3X_4$  compounds, where  $R$  is a heavy rare-earth metal,  $T$  is a IVB group element, and  $X$  is a IVA group element, form in the systems {Gd,Tb,Dy,Ho,Er,Tm,Yb,Lu}–{Ti,Zr,Hf}–{Si,Ge} [1-10]. Their crystal structures belong to two different structure types:  $Sc_2Re_3Si_4$  [11], which is an ordered derivative of the binary  $Zr_3Si_4$  type [12] (Pearson symbol  $tP36$ , space group  $P4_12_12$ ), and  $Ce_2Sc_3Si_4$  [13], which is an ordered derivative of the binary  $Sm_5Ge_4$  type [14] ( $oP36$ ,  $Pnma$ ). The  $R_5X_4$  compounds with  $Sm_5Ge_4$  structure type and their derivatives are unique magnetocaloric materials [15], and their representatives with gadolinium can be used as magnetic refrigerators already at relatively acceptable temperatures. A moderate magnetocaloric effect was found for the  $R_2Ti_3Ge_4$  compounds with  $R = Gd, Tb, Er$  [16].

It was surprising to see that the series of isotopic germanides with titanium ended with erbium. We decided to look for more representatives of the structure type  $Sm_5Ge_4$ , and in this work we present the results of structural studies of ternary  $\sim R_2Ti_3Ge_4$  compounds in the  $R-Ti-Ge$  ( $R = Gd-Lu$ ) systems.

#### 2. Experimental

Samples of composition  $R_{22.2}Ti_{33.3}Ge_{44.5}$  ( $R = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu$ ) were prepared by arc-melting the elements under a purified argon atmosphere. Elements of

the following purities were used:  $R > 99.85\%$ ,  $Ti > 99.93\%$ , and  $Ge > 99.999\%$ . The weight loss during the melting did not exceed 1%. The alloys were annealed at 600°C for 1500 h in evacuated quartz ampoules, and subsequently quenched in cold water.

The crystal structures were refined on X-ray powder diffraction patterns collected with a Panalytical X'Pert diffractometer (Cu  $K\alpha$  radiation), using the FullProf Suite software [17].

#### 3. Results

The phase and structural analysis of the alloys revealed the formation of seven ternary compounds: the existence of five compounds  $\sim R_2Ti_3Ge_4$  ( $R = Gd, Tb, Dy, Ho, Er$ ) was confirmed at 600°C and two new compounds, with slightly lower rare-earth content,  $Tm_{2-x}Ti_{3+x}Ge_4$  and  $Lu_{2-x}Ti_{3+x}Ge_4$ , were found (Table 1). For all the samples the reflections of the main phase could be indexed using the model of the  $Sm_5Ge_4$  type, but minor amounts of impurity phases were each time detected. Small additional peaks belonging to not identified phases were observed on the diffraction patterns of the samples with Dy and Lu.

The results of the refinements of the structures of the two new compounds (refined composition  $Tm_{1.79(2)}Ti_{3.21(2)}Ge_4$  and  $Lu_{1.74(2)}Ti_{3.26(2)}Ge_4$ , respectively) are presented in Table 2.  $\sim R_2Ti_3Ge_4$  compounds were obtained for all of the selected rare earths ( $R = Gd-Lu$ ), except for Yb. The unit-cell parameters gradually

**Table 1** Phase analysis of  $R_{2.2}Ti_{33.3}Ge_{44.5}$  alloys and unit-cell parameters of the  $\sim R_2Ti_3Ge_4$  compounds.

Sample	Refined composition (additional phases [type])	Unit-cell parameters (nm)			Reference
		<i>a</i>	<i>b</i>	<i>c</i>	
Gd <sub>22.2</sub> Ti <sub>33.3</sub> Ge <sub>44.5</sub>	Gd <sub>2.17(3)</sub> Ti <sub>2.83(3)</sub> Ge <sub>4</sub> (9 wt.% GdGe <sub>1.5</sub> [AlB <sub>2</sub> ], 6 wt.% GdGe [TII])	0.70301(5)	1.3468(1)	0.71730(6)	this work
	Gd <sub>1.94</sub> Ti <sub>3</sub> Ge <sub>4</sub> /Gd <sub>2</sub> Ti <sub>3</sub> Ge <sub>4</sub>	0.7042(1)	1.3494(2)	0.7186(1) <sup>a</sup>	[2,3]
	Gd <sub>2</sub> Ti <sub>3</sub> Ge <sub>4</sub>	0.7044(1)	1.3494(3)	0.7187(2) <sup>a</sup>	[4]
Tb <sub>22.2</sub> Ti <sub>33.3</sub> Ge <sub>44.5</sub>	Tb <sub>2.08(3)</sub> Ti <sub>2.92(3)</sub> Ge <sub>4</sub> (13 wt.% Ti <sub>5</sub> Ge <sub>3</sub> [Mn <sub>5</sub> Si <sub>3</sub> ], 2 wt.% TbGe <sub>1.5</sub> [AlB <sub>2</sub> ])	0.70180(5)	1.3469(1)	0.71614(6)	this work
	Tb <sub>1.98</sub> Ti <sub>3</sub> Ge <sub>4</sub>	0.7019(1)	1.3457(2)	0.7156(1)	[2]
	Tb <sub>1.98</sub> Ti <sub>3.02</sub> Ge <sub>4</sub> - Tb <sub>1.35</sub> Ti <sub>3.65</sub> Ge <sub>4</sub>	0.7019(1)- 0.6889(5)	1.3457(2)- 1.332(1)	0.7156(1)- 0.755(1) <sup>a</sup>	[5]
	Tb <sub>2</sub> Ti <sub>3</sub> Ge <sub>4</sub>	0.7016(1)	1.3455(2)	0.7157(1) <sup>a</sup>	[3]
	Tb <sub>2</sub> Ti <sub>3</sub> Ge <sub>4</sub>	0.70042(6)	1.34341(12)	0.71444(6) <sup>a</sup>	[6]
	Tb <sub>2</sub> Ti <sub>3</sub> Ge <sub>4</sub> (6 wt.% TbGe [TII], 5 wt.% Ti <sub>5</sub> Ge <sub>3</sub> [Mn <sub>5</sub> Si <sub>3</sub> ])	0.70142(6)	1.3451(1)	0.71535(7)	[7]
Dy <sub>22.2</sub> Ti <sub>33.3</sub> Ge <sub>44.5</sub>	Dy <sub>2.13(3)</sub> Ti <sub>2.87(3)</sub> Ge <sub>4</sub> (trace amounts of X <sup>b</sup> )	0.7021(5)	1.346(1)	0.7153(6)	this work
	Dy <sub>1.94</sub> Ti <sub>3</sub> Ge <sub>4</sub> /Dy <sub>2</sub> Ti <sub>3</sub> Ge <sub>4</sub>	0.6987(1)	1.3409(2)	0.7122(1) <sup>a</sup>	[2,3]
Ho <sub>22.2</sub> Ti <sub>33.3</sub> Ge <sub>44.5</sub>	Ho <sub>2.22(1)</sub> Ti <sub>2.78(1)</sub> Ge <sub>4</sub> (7 wt.% HoGe <sub>1.5</sub> [AlB <sub>2</sub> ], 2 wt.% HoGe <sub>1.7</sub> [α-ThSi <sub>2</sub> ])	0.69539(5)	1.3354(1)	0.70899(6)	this work
	Ho <sub>1.92</sub> Ti <sub>3</sub> Ge <sub>4</sub> /Ho <sub>2</sub> Ti <sub>3</sub> Ge <sub>4</sub>	0.6981(1)	1.3399(2)	0.7117(1) <sup>a</sup>	[2,3]
Er <sub>22.2</sub> Ti <sub>33.3</sub> Ge <sub>44.5</sub>	Er <sub>1.96(2)</sub> Ti <sub>3.04(2)</sub> Ge <sub>4</sub> (13 wt.% ErGe <sub>1.5</sub> [AlB <sub>2</sub> ])	0.69631(5)	1.3377(1)	0.71035(6)	this work
	Er <sub>1.82</sub> Ti <sub>3</sub> Ge <sub>4</sub> /Er <sub>2</sub> Ti <sub>3</sub> Ge <sub>4</sub>	0.6962(1)	1.3367(2)	0.7099(1) <sup>a</sup>	[2,3]
Tm <sub>22.2</sub> Ti <sub>33.3</sub> Ge <sub>44.5</sub>	Tm <sub>1.79(2)</sub> Ti <sub>3.21(2)</sub> Ge <sub>4</sub> (4 wt.% Tm <sub>2</sub> Ge <sub>3</sub> [Tm <sub>2</sub> Ge <sub>3</sub> ])	0.69287(4)	1.33090(8)	0.70624(4)	this work
Lu <sub>22.2</sub> Ti <sub>33.3</sub> Ge <sub>44.5</sub>	Lu <sub>1.74(2)</sub> Ti <sub>3.26(2)</sub> Ge <sub>4</sub> (trace amounts of X <sup>b</sup> )	0.69200(3)	1.33005(7)	0.70576(4)	this work

<sup>a</sup> sample annealed at 1070 K; <sup>b</sup> not identified phase

**Table 2** Atomic coordinates  $x$ ,  $y$ ,  $z$  (Wyckoff position) and isotropic displacement parameters  $B$  (nm<sup>2</sup>) for Tm<sub>2-x</sub>Ti<sub>3+x</sub>Ge<sub>4</sub> and Lu<sub>2-x</sub>Ti<sub>3+x</sub>Ge<sub>4</sub>.

		Tm <sub>1.79(2)</sub> Ti <sub>3.21(2)</sub> Ge <sub>4</sub>				Lu <sub>1.74(2)</sub> Ti <sub>3.26(2)</sub> Ge <sub>4</sub>				
		Pearson symbol <i>oP36</i> , space group <i>Pnma</i> , $a = 0.69287(4)$ , $b = 1.33090(8)$ , $c = 0.70624(4)$ nm				Pearson symbol <i>oP36</i> , space group <i>Pnma</i> , $a = 0.69200(3)$ , $b = 1.33005(7)$ , $c = 0.70576(4)$ nm				
Site	WP	$x$	$y$	$z$	$B \cdot 10^2$	$x$	$y$	$z$	$B \cdot 10^2$	
M1	8 <i>d</i>	0.0020(6)	0.09320(17)	0.6723(3)	2.38(5)	0.0011(6)	0.0944(2)	0.6722(3)	1.12(4)	
Ge1	8 <i>d</i>	0.1762(9)	0.0445(3)	0.0442(7)	2.96(8)	0.1777(9)	0.0423(3)	0.0451(9)	1.71(9)	
M2	8 <i>d</i>	0.3473(9)	0.1255(4)	0.3278(10)	2.9(2)	0.3489(9)	0.1288(4)	0.3307(11)	1.7(2)	
Ge2	4 <i>c</i>	0.0437(12)	¼	0.3726(9)	2.96(8)	0.049(1)	¼	0.3717(9)	1.71(9)	
M3	4 <i>c</i>	0.1810(18)	¼	0.0154(12)	4.3(3)	0.184(2)	¼	0.0129(14)	1.6(3)	
Ge3	4 <i>c</i>	0.3217(10)	¼	0.6313(11)	2.96(8)	0.321(1)	¼	0.6304(12)	1.71(9)	
					$M1 = 0.86(1)\text{Tm} + 0.14(1)\text{Ti}$ , $M2 = \text{Ti}$ , $M3 = 0.93(1)\text{Ti} + 0.07(1)\text{Tm}$	$M1 = 0.87(1)\text{Lu} + 0.13(1)\text{Ti}$ , $M2 = \text{Ti}$ , $M3 = \text{Ti}$				
					$R_B = 0.116$ , $R_p = 0.023$ , $R_{wp} = 0.032$	$R_B = 0.108$ , $R_p = 0.022$ , $R_{wp} = 0.033$				

decrease throughout the rare-earth metal series, as expected for lanthanide contraction (see Table 1).

The structure type Sm<sub>5</sub>Ge<sub>4</sub> contains three crystallographic sites occupied by the metal atoms.

Two of them are located between the [Sm<sub>5</sub>Ge<sub>4</sub>] slabs usually considered in this structure type ( $M1$  and  $M2$  in Wyckoff position 8*d*), and the third one at the center of the slabs ( $M3$  in Wyckoff position 4*c*).

Yao and Mozharivskiy [10] studied the substitution of Zr for Gd in  $Gd_5Ge_4$  ( $Gd_{5-x}Zr_xGe_4$ ,  $x = 0-1.5$ ) and observed a clear site preference of the Zr atoms in increasing order  $M1 < M2 < M3$ , which they explained both by size factors and electronic considerations. Complete refinements of isotypic ternary  $R_{5-x}Ti_xGe_4$  compounds near the composition 2:3:4 in general report fully ordered structures with site  $M1$  occupied by the rare-earth metal and sites  $M2$  and  $M3$  by the transition metal [4,5,7]. In [2] a similar atom distribution is reported, but up to 8% vacancies were found on the rare-earth metal site.

The refinements of the crystal structures of the  $\sim R_2Ti_3Ge_4$  compounds in the present investigation showed partly disordered distribution of  $R$  and Ti atoms over two sites ( $M1$  and  $M3$ ), while site  $M2$  was found to be fully occupied by Ti atoms. The refined site occupancies are given in Table 3. The  $R$  atoms dominate in the statistical mixture that occupies site  $M1$ , and in the holmium compound, which shows the highest  $R/Ti$  ratio, this site is exclusively occupied by Ho atoms. On site  $M3$ , a gradual increase of the Ti content is observed, and the position is fully occupied by Ti atoms in the lutetium compound, which shows a clearly off-stoichiometric, Ti-rich composition.

The anomalies observed on the dependence of the unit-cell parameters on the atomic number of the rare-earth metal atom are in rough agreement with the variations of the  $R/Ti$  ratio in the refined composition. For  $R = \text{Gd-Ho}$  the refined formula can be written as  $R_{2+x}Ti_{3-x}Ge_4$ , whereas for the remaining metals  $R_{2-x}Ti_{3+x}Ge_4$  is more appropriate. Thus, interplay between two effects should be taken into account, *i.e.* the variations of the effective radius of the ( $R/Ti$ ) statistical mixture and a redistribution of  $R$  and Ti atoms in the structure. We can also not exclude the existence of a certain homogeneity range for the  $\sim R_2Ti_3Ge_4$  compounds, the extension of which may depend on the atomic number of the rare-earth metal. Morozkin *et al.* [5] investigated the phase equilibria at 1070 K in the system Tb-Ti-Ge and observed a homogeneity range of some 7 at.% on the Ti-rich side of the stoichiometric composition 2:3:4 (see Table 1). However, a similar investigation of the Gd-Ti-Ge system at the same temperature revealed no significant homogeneity range [4].

Vacancies on the rare-earth sites were reported in [2] (see Table 1). A few years later, the same unit-cell parameters were reported for the stoichiometric composition, which seems to indicate that the deviations were not considered to be significant (standard uncertainty not published). Our refinements showed mixed occupancies, rather than vacancies, in all of the compounds. It may be noted that the highest amount of vacancies, and consequently the lowest  $R/Ti$  ratio, was reported for Er (Tm and Lu were not investigated), for which a significant decrease of the rare-earth content was also observed in the present work.

**Table 3** Refined occupancies of sites  $M1$  and  $M3$  ( $M2 = \text{Ti}$ ) and total  $R/Ti$  ratio in  $\sim R_2Ti_3Ge_4$  compounds.

$R$	$M1$	$M3$	$R/Ti$
Gd	0.93(1)Gd+0.07(1)Ti	0.72(1)Ti+0.28(1)Gd	2.17/2.83
Tb	0.91(1)Tb+0.09(1)Ti	0.74(1)Ti+0.26(1)Tb	2.08/2.92
Dy	0.95(4)Dy+0.05(4)Ti	0.73(5)Ti+0.27(5)Dy	2.13/2.87
Ho	1Ho	0.78(1)Ti+0.22(1)Ho	2.22/2.78
Er	0.89(1)Er+0.11(1)Ti	0.82(1)Ti+0.18(1)Er	1.96/3.04
Tm	0.86(1)Tm+0.14(1)Ti	0.93(1)Ti+0.07(1)Tm	1.79/3.21
Lu	0.87(1)Lu+0.13(1)Ti	1Ti	1.74/3.26

The absence of an ytterbium compound in the series may be attributed to the particular electronic configuration of ytterbium, which readily exhibits oxidation state +2. It may be noted that binary  $R_5Ge_4$  compounds with  $Sm_5Ge_4$ -type structures are known for all these rare-earths, including Yb [1].

#### 4. Discussion

Several ternary variants of the  $Sm_5Ge_4$  structure type, with complete or partial substitution of the atoms on particular sites, may be distinguished [18] (Table 4). The Zr atoms in the ternary ordered derivative  $Zr_2Nb_3Ge_4$  [19] exclusively occupy site  $M2$ , whereas the Sc atoms in  $Ce_2Sc_3Si_4$  [13] occupy sites  $M2$  and  $M3$ .  $Na_2Sr_3P_4$  [20] exhibits a partly ordered atom arrangement with Na on site  $M3$ , Sr on site  $M1$  and mixed occupation Na/Sr of site  $M2$ . The latter type should rather be considered as a derivative of the closely related structure type  $Gd_5Si_4$  [21], since all the P atoms form  $P_2$  dumbbells. In the structure of  $Tm_{2-x}Ti_{3+x}Ge_4$  the following Ge-Ge distances were found: 0.265 nm (Ge2-Ge3) and 0.278 nm (Ge1-Ge1). In this aspect, the structure represents an intermediate between the  $Sm_5Ge_4$  type, where half of the Ge atoms form pairs ( $d(\text{Ge-Ge}) = 0.266$  and 0.370 nm), and the  $Gd_5Si_4$  branch, where all the Si atoms form dumbbells (0.248 nm for the corresponding Si-Si distances). The significantly reduced difference between the two Ge-Ge distances may justify the assignment of the ordered structure type  $Ce_2Sc_3Si_4$  (0.260 and 0.254 nm) to the  $\sim R_2Ti_3Ge_4$  compounds studied here.

Another difference between the structure types  $Sm_5Ge_4$  and  $Gd_5Si_4$  is the coordination environment of the Sm and Gd atoms occupying the site  $M1$ . For the  $Sm_5Ge_4$  type, the coordination number is usually 16 or 17, while it is 18 for the  $Gd_5Si_4$  type. In all of the compounds investigated here, the coordination number of site  $M1$  is 17.

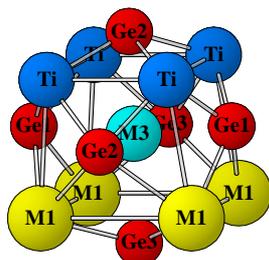
The shortest  $M$ -Ge distances in  $Tm_{1.79(2)}Ti_{3.21(2)}Ge_4$  occur for the site  $M2$  (0.256 nm), which is occupied exclusively by Ti, whereas no  $M$ -Ge distances shorter than 0.280 nm are observed for the site  $M1$ , which exhibits the highest rare-earth content, in agreement with the smaller atomic radius of Ti. A gradual decrease of the content of  $R$  atoms was observed for

**Table 4** Distribution of the metal atoms in the structure type  $\text{Sm}_5\text{Ge}_4$  and some of its derivatives [16], and in the structures of two of the  $R_{2-x}Ti_{3+x}Ge_4$  compounds investigated here ( $R = \text{Ho, Lu}$ ).

Site ( $x, y, z$ ) <sup>a</sup>	$\text{Sm}_5\text{Ge}_4$	$\text{Gd}_5\text{Si}_4$	$\text{Zr}_2\text{Nb}_3\text{Ge}_4$	$\text{Ce}_2\text{Sc}_3\text{Si}_4$	$\text{Na}_2\text{Sr}_3\text{P}_4$	$\text{Ho}_{2.22}\text{Ti}_{2.78}\text{Ge}_4$	$\text{Lu}_{1.74}\text{Ti}_{3.26}\text{Ge}_4$
$M1 (0.025, 0.100, 0.678)$	Sm	Gd	Nb	Ce	Sr	Ho	Lu/Ti
$M2 (0.380, 0.116, 0.339)$	Sm	Gd	Zr	Sc	Na/Sr	Ti	Ti
$M3 (0.212, 1/4, 0.002)$	Sm	Gd	Nb	Sc	Na	Ti/Ho	Ti

<sup>a</sup> approximate atom coordinates for  $\text{Sm}_5\text{Ge}_4$  [14]

the site  $M3$ , until the site was fully occupied by titanium atoms in the compound with lutetium. The coordination environment of the atoms occupying this position is presented on Fig. 1. The pseudo-cubes surrounding these atoms are formed by a slightly deformed square of atoms of the statistical mixture  $M1$  ( $R/\text{Ti}$ ) (or Ho atoms in the Ho-compound) and a square of Ti atoms from the site  $M2$ . With increasing atomic number of the rare-earth metal, the size of the square formed by the  $M1$  atoms is reduced and the atoms come closer to the atom inside the polyhedron, reducing the degree of deformation of the rhombic dodecahedron. As the size of the  $R$  atom decreases, the space inside the polyhedron decreases too and the situation becomes more favorable for the smaller titanium atoms. Finally, in the compound with lutetium, both sites  $M2$  and  $M3$  are fully occupied by Ti.

**Fig. 1** Rhombic dodecahedron surrounding site  $M3$  in the  $R_{2-x}Ti_{3+x}Ge_4$  compounds.

## Conclusions

The compounds of approximate composition  $R_3Ti_2Ge_4$ , where  $R = \text{Gd-Tm, Lu}$ , form partly ordered structures derived from the structure type  $\text{Sm}_5\text{Ge}_4$ , which may be assigned to the ternary ordered structure type  $\text{Ce}_2\text{Sc}_3\text{Si}_4$ . Off-stoichiometry was particularly pronounced for the smallest rare earths Er, Tm, and Lu.

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