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Phase equilibria in the Tb–Ti–Ge system at 1070 K

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Abstract

Physico-chemical analysis techniques, including X-ray phase analysis, electron probe X-ray analysis, differential thermal analysis and metallographic analysis were employed in constructing the isothermal section of the Tb–Ti–Ge system at 1070 K. The formation of the following ternary intermetallic compounds were detected in the Tb–Ti–Ge system at 1070 K: TbTiGe (high-temperature modification of CeFeSi structure type, space group *P*4/*nmm*, a=0.4050(2) nm, c=0.7652(3) nm: low-temperature modification of La_2Sb structure type, space group *I*4/*mmm*, a=0.4053(2) nm, c=1.5293(3) nm) and $Tb_{22...15}Ti_{34...41}Ge_{44}$ (Sm_5Ge_4 structure type, space group *Pnma*, a=0.7019(1)...0.6889(5) nm, b=1.3457(2)...1.332(1) nm, c=0.7156(1)...0.755(1) nm). The $TbGe_{3.5}$ compound belongs to the $ThGe_2$ structure type (space group *Cmmm*, a=2.0738(4) nm, b=0.4043(1) nm, c=0.3914(1) nm). The high-temperature modification of the Th_2Ge_3 compounds belongs to the $ThSi_2$ structure type (space group $I4_1/amd$, a=0.4061(2) nm, c=1.372(1) nm).

Keywords: Rare earth compounds; Ternary system; Phase diagram; Germanides; Structure type

1. Introduction

The interaction between the components in the Ti–Ge and Tb–Ge binary system have been studied in detail in Refs. [1–11] (Table 1). The TbTiGe ternary compound belongs to the CeFeSi structure type [12] and has a Néel point of T_N=288 K (Θ_p=248 K, μ_{eff}=9.4 μB) [13].

2. Experimental detail

The present study was carried out on about 20 alloys (Fig. 1). The mass of each sample was 1 g. The alloys were made in an electric arc furnace under an argon atmosphere using non-consumable tungsten electrode and a water-cooled copper tray. Germanium, terbium and titanium (purity of each component ≥99.99%) were used as starting components. Titanium was used as a getter during the melting process. The alloys were remelted twice in order to achieve complete fusion and homogeneous composition. The melted alloys were subjected to an anneal in evacuated quartz ampoules containing titanium chips as a getter. The ampoules were placed in a resistance furnace. The alloys were annealed at 1070 K for 2 weeks. The samples were quenched from 1070 K in ice-cold water. The phase equilibria in the Tb–Ti–Ge system were determined using X-ray phase analysis, electron probe X-ray analysis and metallography analysis. X-ray data were obtained on a diffractometer DRON-3.0 (Cu Kα radiation, 2Θ=20–70°, step 0.05°, for 5 s per step). The diffractograms obtained were identified by means of calculated patterns using the CSD-programs [16], the Rietan-program [17] and MRIA program [18] in the isotropic approximation. A ‘Camebax’ microanalyser was employed to perform local X-ray spectral analyses of the samples. A ‘Neophot’ microscope was employed for metallograhic inspections (×250, ×500). The high temperature differential thermal analysis was carried out on an VDTA-8M2 (Institute of metallophysic of the Ukraine). The samples were heated in helium (10^5 Pa) twice in order to achieve an accurate value of the melting temperature. The heating rate was kept constant for all samples (80 K min^{-1}). The investigation was carried out with a ZrO_2-crucible. The temperature was measured with a W–W

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Table 1
Crystallographic data and temperature of the phase transition of compounds in the binary systems Ti–Ge and Tb–Ge

	Compound	Space group	Structure type	*a* (nm)	*b* (nm)	*c* (nm)	*T**, K	Refs.
1	Ti^a	$P6_3/mmc$	Mg	0.29511	–	0.46843	1155	[1]
	Ti	$Im3m$	W	0.33065	–	–	**1933**	
2	Ti$_5$Ge$_3^a$	$P6_3/mcm$	Mn$_5$Si$_3$	0.7537	–	0.5223	**2253**	[2,3]
3	Ti$_6$Ge$_5^a$	$Ibam$	Ti$_6$Ge$_5$	1.6915	0.7954	0.5233	**1923**	[2,3]
4	TiGe$_2^a$	$Fddd$	TiSi$_2$	0.8864	0.5030	0.8594	**1348**	[2,3]
5	Ge^a	$Fd3m$	C	0.565754	–	–	**1211**	[1]
6	TbGe$_{3\pm x}$	...	...	...	...	...		[4]
	TbGe$_{3.5}^a$	$Cmmm$	ThGe$_2$	2.0738(4)	0.4043(1)	0.3914(1)		**
7	TbGe$_2^a$	*ortho.*	...	...	...	...		[6]
8	Tb$_2$Ge$_3^a$	$P6/mmm$	AlB$_2$	0.395	–	0.416		[3,5]
	Tb$_2$(Ti$_{0.08}$Ge$_{0.92}$)$_3^a$	$P6/mmm$	AlB$_2$	0.394(1)	–	0.429(1)		**
	Tb$_2$Ge3	$I4_1/amd$	ThSi$_2$	0.4061(2)	–	1.372(1)		**
9	TbGe^a	$Cmcm$	CrB	0.4300	1.0717	0.3950		[7,9,10]
10	Tb$_{11}$Ge$_{10}$	$I4/mmm$	Ho$_{11}$Ge$_{10}$	1.089	–	1.649		[7]
11	Tb$_5$Ge$_4^a$	$Pnma$	Sm$_5$Ge$_4$	0.7613	1.4633	0.7691		[3,8]
12	Tb$_5$Ge$_3^a$	$P6_3/mcm$	Mn$_5$Si$_3$	0.8495	–	0.6351		[3,11]
13	Tb	$Cmcm$	o	0.359	0.626	0.571	220	[1]
	Tb^a	$P6_3/mmc$	Mg	0.3601	–	0.56936	1590	[1]
	Tb	$Im3m$	W	0.402	–		**1629**	[1]

*The temperatures of listed refer to a phase transition (normal font) or to the melting temperature (bold font).
**The data of the present investigation.
[a] Compound detected in the isothermal section at 1070 K.

(20% Re) thermo-couple. As reference we used the melting temperature of Cu (1356 K) and the phase transitions temperatures of Fe (1041, 1183, 1663, 1812 K). The purity of all standard metals was 99.999at. %. The accuracy of the temperature measurements was ±5 K.

3. Results and discussion

The results obtained were used in the construction of the isothermal section of the Tb–Ti–Ge system at 1070 K, presented in Fig. 2. We use the data of Ref. [14,15] of the Gd–Ge binary system for estimating the temperatures of the phase transitions of the binary compounds in the Tb–Ge system.

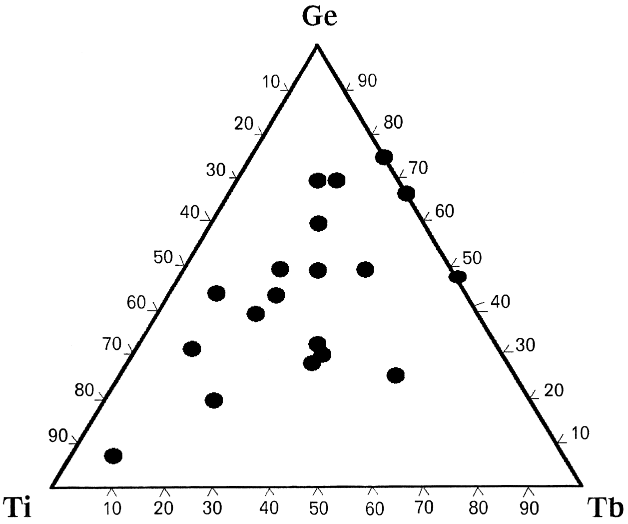

Fig. 1. The composition of the samples of the Tb–Ti–Ge system.

It was found that the system contains extended regions of ternary solid solution based on AlB$_2$ type Tb$_2$Ge$_3$ (~5 at. % Ti) and Tb$_2$Ti$_3$Ge$_4$ (Tb$_{22...15}$Ti$_{34...41}$Ge$_{44}$) (Tables 1 and 2). The solubility of the other rare earth compounds is about 1–2 at. % Ti. The compounds of the Ti–Ge system do not show any remarkable solubility.

The TbGe$_{3.5}$ compound belongs to the ThGe$_2$ structure type (space group *Cmmm*). We found that the high temperature phase of Tb$_2$Ge$_3$ belongs to the ThSi$_2$ structure type. We did not not detect the Tb$_{11}$Ge$_{10}$ compound at 1070 K.

The TbTiGe and Tb$_2$Ti$_3$Ge$_4$ (Tb$_{22...15}$Ti$_{34...41}$Ge$_{44}$) ternary intermetallic compounds were found in the Tb–Ti–Ge system at 1070 K (Table 2). The Tb$_2$Ti$_3$Ge$_4$ compound belongs to the Sm$_5$Ge$_4$ structure type. The TbTiGe compound has a high-temperature (HT) modification of the CeFeSi structure type and the low temperature (LT) modification of the La$_2$Sb structure type with a doubled lattice parameter *c*. The HT modification forms when quenching from the liquid during electric arc furnace melting. Annealing at 1070 K led to the formation of the LT modification which is accompanied by a small decrease of c/a ($2c/a$). The values $c/a=1.8894$ ($2c/a=3.7788$) were obtained for the CeFeSi structure type and $c/a=3.7733$ for the La$_2$Sb structure type. However, a large amount of the HT modification was present in the TbTiGe alloy. The HT and LT modifications of the TbTiGe

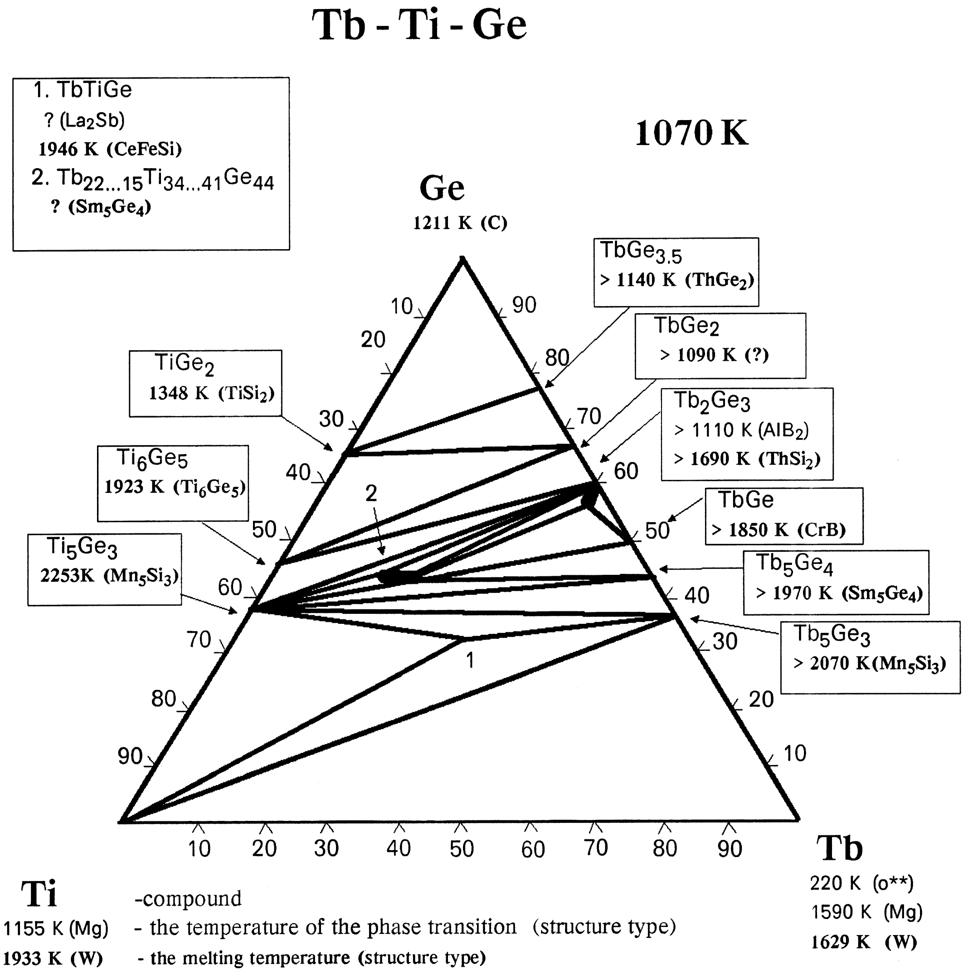

Fig. 2. Isothermal section of the Tb–Ti–Ge system at 1070 K and decomposition temperatures of the structures of the elements, binary and ternary compounds.

compound are coherent phases. Probably, the transition of the HT modification to the LT modification is kinetically limited. Atomic position parameters for $TbGe_{3.5}$, $Tb_2Ti_3Ge_4$ and TbTiGe compounds are listed in Table 3.

In Table 4 the step by step approximate scheme of the phase transitions in the Tb–Ti–Ge system is shown. The estimated data of the phase transition Tb_2Ge_3 ($ThSi_2$ structure type)$\rightarrow$$Tb_2Ge_3$ (AlB_2 structure type) is near the temperature of the investigated isothermal section. This is the reason why we detected the Tb_2Ge_3 ($ThSi_2$) and Tb_2Ge_3 (AlB_2) in our investigation.

4. Conclusion

We have investigated the isothermal section of the Tb–Ti–Ge system and can assume that the {Gd, Dy–Lu}–Ti–Ge systems have similar isothermal sections.

Table 2
Crystallographic data of the ternary compounds in the Tb–Ti–Ge system obtained in the present investigation the melting temperatures of TbTiGe is 1946 K (see Table 4)

	Compound	Space group	Structure type	*a* (nm)	*b* (nm)	*c* (nm)	*V* (nm^3)
1	TbTiGe[a]	*I4/mmm*	La_2Sb	0.4053(2)	–	1.5293(3)	0.25122
	TbTiGe	*P4/nmm*	CeFeSi	0.4050(2)	–	0.7652(1)	0.12551
2	$Tb_{22...15}$	*Pnma*	Sm_5Ge_4	0.7019(1)	1.3457(2)	0.7156(1)	0.67592
	$Ti_{34...41}Ge_44$[a]			0.6889(5)	1.332(1)	0.755(1)	0.69280

[a] Compounds detected in the isothermal section at 1070 K.

Table 3
Atomic position parameters for $TbGe_{3.5}$ ($ThGe_2$ structure type), TbTiGe (CeFeSi and La_2Sb structure types) and $Tb_2Ti_3Ge_4$ (Sm_5Ge_4 structure type)

Atom	Type position	Symmetry	x/a	y/b	z/c	Occupation factor
(a) TbGe3.5 (R_F=9.4%)						
Tb	4(g)	2*mm*	0.113(3)	0	0	0.57
Ge1	2(b)	*mmm*	1/2	0	0	1.00
Ge2	2(d)	*mmm*	0	0	1/2	1.00
Ge3	4(h)	2*mm*	0.349(3)	0	1/2	1.00
(b) TbTiGe (R_F=6.7%)						
Tb	2(c)	4*mm*	1/4	1/4	0.659	1.00
Ti	2(a)	4*m*2	3/4	1/4	0	1.00
Ge	2(c)	4*mm*	1/4	1/4	0.276	1.00
(c) TbTiGe (R_p=9.4% R_b=16.0% R_e=12.5% χ^2=0.82)						
Tb	4(e)	4*mm*	0	0	0.325(1)	1.00
Ti	4(c)	*mmm*	0	1/2	0	1.00
Ge	4(e)	4*mm*	0	0	0.127(3)	1.00
(d) $Tb_2Ti_3Ge_4$ (R_F=4.1%)						
Tb	8(d)	1	0.003(5)	0.090(2)	0.834(3)	1.00
Ti1	4(c)	*m*	0.323(3)	1/4	0.017(6)	1.00
Ti2	8(d)	1	0.158(4)	0.120(3)	0.312(4)	1.00
Ge1	4(c)	*m*	0.170(6)	1/4	0.619(6)	1.00
Ge2	4(c)	*m*	0.981(6)	1/4	0.127(5)	1.00
Ge3	8(d)	1	0.165(6)	0.954(7)	0.537(6)	1.00

Table 4
The approximate scheme of the phase transition in the Tb–Ti–Ge system

T (K)	Phase transitions
2253	Ti(L)+Ge(L)=Ti_5Ge_3(Mn_5Si_3)
>2070	Tb(L)+Ge(L)=Tb_5Ge_3(Mn_5Si_3)
>1970	Tb_5Ge_3(Mn_5Si_3)+(Tb,Ge)(L)=Tb_5Ge_4(Sm_5Ge_4)
...	?Tb_5Ge_4(Sm_5Ge_4)+Ti_5Ge_3(Mn_5Si_3)+(Tb,Ti,Ge)(L)=$Tb_2Ti_3Ge_4$(Sm_5Ge_4)
1946	Ti_5Ge_3(Mn_5Si_3)+Tb_5Ge_3(Mn_5Si_3)+(Tb,Ti)(L)=TbTiGe(CeFeSi)
1933	Ti(L)→Ti(W)
1923	Ti_5Ge_3(Mn_5Si_3)+(Ti,Ge)(L)=Ti_6Ge_5(Ti_6Ge_5)
>1850	Tb_5Ge_4(Sm_5Ge_4)+(Tb,Ge)(L)=TbGe(CrB)
>1690	?TbGe(CrB)+(Tb,Ge)(L)=Tb_2Ge_3($ThSi_2$)
1629	Tb(L)→Tb(W)
1590	Tb(W)→Tb(Mg)
1348	Ti_6Ge_5(Ti_6Ge_5)+(Ti,Ge)(L)=$TiGe_2$($TiSi_2$)
1211	Ge(L)→Ge(C)
1155	Ti(W)→Ti(Mg)
>1140	?Tb_2Ge_3($ThSi_2$)+(Tb,Ge)(L)=$TbGe_{3.5}$($ThGe_2$)
>1110	Tb_2Ge_3($ThSi_2$)→Tb_2Ge_3(AlB_2)
>1090	?Tb_2Ge_3(AlB_2)+Ge(C)=$TbGe_2$(*ortho*)
	?TbTiGe(CeFeSi)→TbTiGe(La_2Sb)

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