Phase equilibria in the Gd–Sc–Si and Tb–Sc–Si systems at 1100 K

A.V. Morozkin[a,*], R. Welter[b]

[a]Department of Chemistry, Moscow Lomonosov State University, Leninskie Gory, GSP-3, Moscow 119899, Russia
[b]Laboratoire DECMET, UMR 7513, Institut Le Bel, Universite Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France

Abstract

Phase equilibria in the system {Gd, Tb}–Sc–Si were investigated by X-ray powder diffraction and the isothermal cross-sections at 1100 K were obtained. The following ternary compounds have been confirmed: GdScSi (CeScSi-type, $I4/mmm$, $a=0.4235(1)$ and $c=1.5446(2)$ nm), $Gd_2Sc_3Si_4$ ($Ce_2Sc_3Si_4$-type, $Pnma$, $a=0.7099(2)$, $b=1.4018(4)$ and $c=0.7416(2)$ nm) and $Tb_2Sc_3Si_4$ ($Ce_2Sc_3Si_4$-type, $Pnma$, $a=0.7080(1)$, $b=1.3976(3)$ and $c=0.7394(1)$ nm). The CrB-type ternary compounds $Gd_{0.4}Sc_{0.6}Si$ ($a=0.4155(1)$, $b=1.0278(2)$ and $c=0.3757(1)$ nm) and $Tb_{0.4}Sc_{0.6}Si$ ($a=0.4135(1)$, $b=1.0233(2)$ and $c=0.3741(1)$ nm) were found. It is obvious, that they belong to the extended regions of the ScSi-based solid solutions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rare earth alloys; X-ray diffraction; Phase diagram

1. Introduction

The interaction between the components in the Gd–Si, Tb–Si, Sc–Si, Gd–Sc and Tb–Sc binary systems has been studied in Refs. [1–3]. The series of well-known Mn_5Si_3-, Sm_5Ge_4-, FeB-, AlB_2-, $ThSi_2$- and $GdSi_2$-type compounds form in the Gd–Si and Tb–Si systems. Only the CrB-type and AlB_2-type compounds form in the Sc–Si system (Table 1).

Continuous Mg-type solid solutions form in the Gd–Sc and Tb–Sc systems at 1100 K [3]. The GdScSi (CeScSi-type structure), $Gd_2Sc_3Si_4$ and $Tb_2Sc_3Si_4$ ($Ce_2Sc_3Si_4$-type) ternary compounds have been studied in Refs. [4,5] (Table 2). The $Ce_2Sc_3Si_4$-type compounds are ordered solid solutions based on the Sm_5Ge_4-type R_5Si_4 compounds (R=Gd, Tb), where R substitutes for Sc. The CeScSi-type compound forms in the Gd–Sc–Si systems, but does not form in the Tb–Sc–Si systems.

The aim of the present study is an investigation of the phase equilibria in the latter systems including a search for new ternary rare-earth compounds.

2. Experimental detail

The alloys were made in an electric arc furnace under an argon atmosphere using a non-consumable tungsten electrode and a water-cooled copper tray. Silicon, gadolinium, terbium and scandium (purity of each component≥ 99.98%) were used as starting components. Titanium was used as an O_2 getter during the melting process. The alloys were re-melted three times 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 an O_2 getter. The ampoules were placed in a resistance furnace. The alloys were annealed at 1100 K for 2 weeks. The samples were quenched from 1100 K in ice-cold water. The phase equilibria in the Gd–Sc–Si and Tb–Sc–Si systems were determined from X-ray phase analysis (powder and single crystal investigations) and metallographic analysis. Powder X-ray data were obtained on a DRON-3.0 diffractometer (Cu Kα radiation, $2\Theta=20–70°$, step 0.05°, for 5 s/step).

The powder X-ray diffractograms obtained were identified by means of calculated patterns using the Rietan-program [6,7] in the isotropic approximation.

A single crystal of the $Tb_{0.4}Sc_{0.6}Si$ compound was extracted from the as-cast ingot of nominal composition $Tb_{25}Sc_{25}Si_{50}$. It was mounted on a Nonius Kappa-CCD

*Corresponding author. Fax: +7-095-932-8846.
E-mail address: morozkin@general.chem.msu.ru (A.V. Morozkin).

Table 1
Crystallographic data of compounds in the binary Gd–Si, Tb–Si and Sc–Si systems

No.	Compound	Space group	Structure type	a (nm)	b (nm)	c (nm)	R_F (%)	Refs.
1.	Si	$Fd3m$	C	0.54307				[1,2]
2.	Sc (LT)	$P6_3/mmc$	Mg	0.3309		0.5273		[1,2]
	Sc (HT)	$Im3m$	W					[1,2]
3.	Gd (LT)	$P6_3/mmc$	Mg	0.3636		0.57826		[1,2]
	Gd (HT)	$Im3m$	W	0.405				[1,2]
4.	Tb (LT)	$Cmcm$	U	0.359	0.626	0.5715		[1,2]
	Tb	$P6_3/mmc$	Mg	0.3601		0.56936		[1,2]
	Tb (HT)	$Im3m$	W	0.402				[1,2]
5.	Sc_5Si_3	$P6_3/mcm$	Mn_5Si_3	0.7861		0.5812		[2,3]
6.	ScSi	$Cmcm$	CrB	0.3958	0.9882	0.3659		[2,3]
7.	$ScSi_{1.67}$	$P6/mmm$	AlB_2	0.366		0.387		[2,3]
8.	Gd_5Si_3	$P6_3/mcm$	Mn_5Si_3	0.851		0.639		[2,3]
	Gd_5Si_3	$P6_3/mcm$	Mn_5Si_3	0.8488(1)		0.6368(1)	4.0	This work
9.	Gd_5Si_4	$Pnma$	Sm_5Ge_4	0.74738	1.4724	0.77362		[2,3]
10.	GdSi	$Pnma$	FeB	0.800	0.385	0.573		[2,3]
11.	$GdSi_{1.67}$	$P6/mmm$	AlB_2	0.3877		0.4172		[2,3]
12.	$GdSi_2$ (HT)	$I4_1/amd$	$ThSi_2$	0.410		1.361		[2,3]
	$GdSi_2$ (LT)	$Imma$	$GdSi_2$	0.409	0.401	1.344		[2,3]
13.	Tb_5Si_3	$P6_3/mcm$	Mn_5Si_3	0.842		0.629		[2,3]
	Tb_5Si_3	$P6_3/mcm$	Mn_5Si_3	0.8424(2)		0.6292(1)	4.5	This work
14.	Tb_5Si_4	$Pnma$	Sm_5Ge_4	0.741	1.458	0.769		[2,3]
15.	TbSi	$Pnma$	FeB	0.797	0.382	0.569		[2,3]
16.	$TbSi_{1.5}$	$P6/mmm$	AlB_2	0.3847		0.4146		[2,3]
17.	$TbSi_2$ (HT)	$I4_1/amd$	$ThSi_2$	0.405		1.340		[2,3]
	$TbSi_2$ (LT)	$Imma$	$GdSi_2$	0.407	0.398	1.337		[2,3]

area detector diffractometer (Mo Kα, λ=0.71073 Å). The conditions of data ollection (Denzo software [8,9]), structure refinements and refined atomic coordinates are gathered in Tables 3 and 4. The cell parameters were determined from reflections taken from one set of ten frames (1.0° steps in phi angle), each at 20 s exposure. The refinements were conducted using the SHELX software [10]. The absorption corrections were made using the SORTAV software from multi-scan symmetry-related measurements [11]. The corresponding *.cif and *.fcf files can be obtained from the authors (welter@chimie.u-strasbg.fr) on request.

A 'Neophot' microscop was employed for metallographic inspections (×250, ×500).

3. Results and discussion

The results obtained were used in the construction of the isothermal cross-sections of the Gd–Sc–Si and Tb–Sc–Si systems at 1100 K, presented in Figs. 1 and 2.

The ternary compounds GdScSi, $Gd_2Sc_3Si_4$, $Tb_2Sc_3Si_4$ have been confirmed. The CrB-type ternary compounds $Gd_{0.4}Sc_{0.6}Si$ and $Tb_{0.4}Sc_{0.6}Si$ were found (Tables 2). The refined cell parameters and atomic coordinates for the $Tb_{0.4}Sc_{0.6}Si$ compounds are given in Tables 3 and 4. Possibly $Gd_{0.4}Sc_{0.6}Si$ and $Tb_{0.4}Sc_{0.6}Si$ belong to the extended ScSi (CrB-type) solid solution regions. However, the atomic radii of Gd, Tb markedly differ from the atomic radius of Sc (R_{Gd}=0.1802, R_{Tb}=0.1782 and R_{Sc}=0.1606

Table 2
Crystallographic data of compounds in the ternary Gd–Sc–Si and Tb–Sc–Si systems at 1100 K

No.	Compound	Space group	Structure type	a (nm)	b (nm)	c (nm)	R_F (%)	Refs.
1.	GdScSi	$I4/mmm$	CeScSi	0.4234		1.5443		[4]
	GdScSi	$I4/mmm$	CeScSi	0.4235(1)		1.5446(2)	3.1	This work
2.	$Gd_2Sc_3Si_4$	$Pnma$	$Ce_2Sc_3Si_4$	0.7092	1.4012	0.7412		[5]
	$Gd_2Sc_3Si_4$	$Pnma$	$Ce_2Sc_3Si_4$	0.7099(2)	1.4018(4)	0.7416(2)	3.6	This work
3.	$Tb_2Sc_3Si_4$	$Pnma$	$Ce_2Sc_3Si_4$	0.7078	1.3982	0.7395		[5]
	$Tb_2Sc_3Si_4$	$Pnma$	$Ce_2Sc_3Si_4$	0.7080(1)	1.3976(3)	0.7394(1)	4.0	This work
4.	$Gd_{0.4}Sc_{0.6}Si$	$Cmcm$	CrB	0.4155(1)	1.0278(2)	0.3757(1)	4.5	This work
5.	$Tb_{0.4}Sc_{0.6}Si$	$Cmcm$	CrB	0.4135(1)	1.0233(2)	0.3741(1)	4.5	This work
6.	$Gd_{2.5}Sc_{2.5}Si_3$	$P6_3/mcm$	Mn_5Si_3	0.8224(3)		0.6086(2)	3.8	This work
7.	$Tb_{2.5}Sc_{2.5}Si_3$	$P6_3/mcm$	Mn_5Si_3	0.8184(2)		0.6044(2)	4.2	This work
8.	~$(Gd_{0.9}Sc_{0.1})Si_{1.67}$	$P6/mmm$	AlB_2	0.3846(2)		0.4135(1)	4.4	This work
9.	~$(Tb_{0.9}Sc_{0.1})Si_{1.5}$	$P6/mmm$	AlB_2	0.3806(1)		0.4090(1)	4.8	This work

Table 3
Crystallographic data and data collection ($T = 293(5)$ K) of the compound $Tb_{0.4}Sc_{0.6}Si$

Average crystal diameter (m)	5×10^{-4}
Cell parameters refined from	959 reflections
a (Å)	4.156(1)
b (Å)	10.275(1)
c (Å)	3.761(1)
V (Å^3)	160.61(6)
Space group	$Cmcm$
θ limits	1.50–45.16
Calculated density (g cm^{-3})	4.90
μ (mm^{-1})	20.438
Recorded reflections	1400
Unique reflections	391
Refined ($F > 4\sigma(F)$)	363
R_{int} (%)	6
h	$0 \rightarrow 8$
k	$0 \rightarrow 20$
l	$0 \rightarrow 7$

Fig. 1. Isothermal cross-section of the Gd–Sc–Si system at 1100 K.

nm [1]), and the type structure-type of GdSi and TbSi (FeB) differs from the structure type of ScSi (CrB).

The $Gd_{5-x}Sc_xSi_3$ and $Tb_{5-x}Sc_xSi_3$ ($x = 0 \ldots 5$) solid solutions with the Mn_5Si_3-type structure form in the Gd–Sc–Si and Tb–Sc–Si systems. The cell parameters of these solid solutions for $x = 0$, 2.5 and 5 are given in Tables 1 and 2. The cell parameters Mn_5Si_3-type solutions correspond to the well-known Vegard law [12]: for $Tb_{2.5}Sc_{2.5}Si_3$ $a = 0.8184$ and $c = 0.6044$ nm, compared to $(a_{Tb_5Si_3} + a_{Sc_5Si_3})/2 = 0.81425$ nm and $(c_{Tb_5Si_3} + c_{Sc_5Si_3})/2 = 0.6052$ nm.

It was found, that the systems contain extended solid solution regions for the AlB_2-type $GdSi_{1.67}$ and $TbSi_{1.5}$ binary compounds (Table 2). R substitutes for Sc up to about the $(Gd_{0.9}Sc_{0.1})Si_{1.67}$ and $(Tb_{0.9}Sc_{0.1})Si_{1.5}$ compositions.

The ternary compounds in the Gd–Sc–Si and Tb–Sc–Si systems form solution regions for the Sm_5Ge_4-type R_5Si_4 binary compounds ($Ce_2Sc_3Si_4$-type $R_2Sc_3Si_4$ compounds) and for the CrB-type ScSi binary compound (CrB-type $R_{0.4}Sc_{0.6}Si$ compounds). Formally, the CeScSi-type

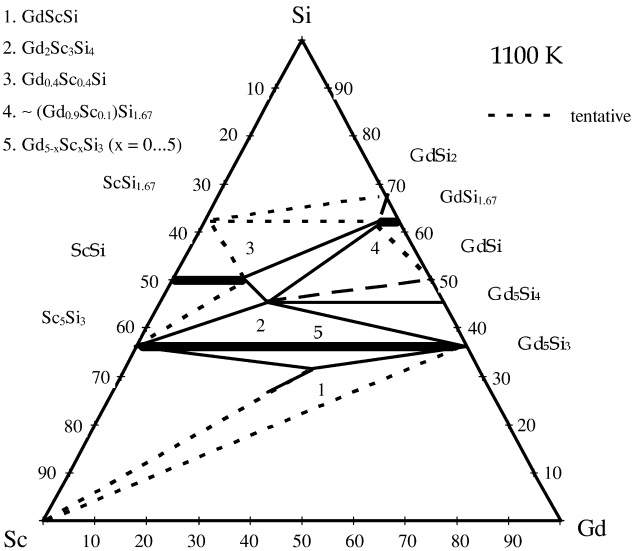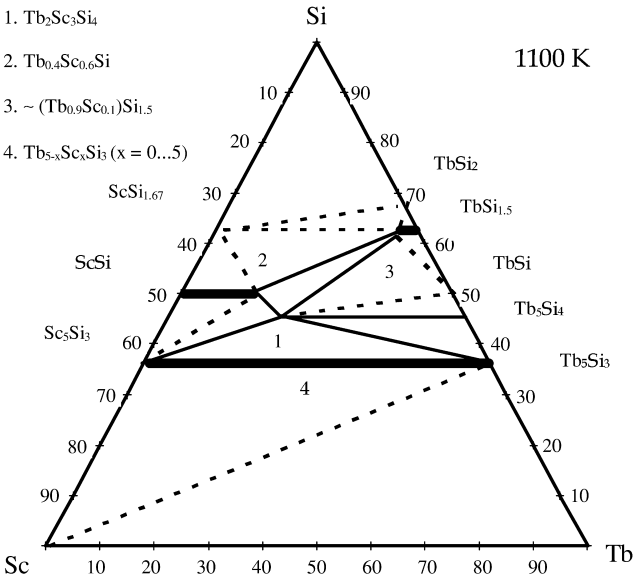Fig. 2. Isothermal cross-section of the Tb–Sc–Si system at 1100 K.

Table 4
Refinement and refined atomic coordinates of the compound $Tb_{0.4}Sc_{0.6}Si$

Number of parameters	11
$R [F^2 > 2\sigma(F^2)]$ (%)	5.55
$R [F^2]$ (%)	5.71
$wR [F^2]$ (%)	14.97
Goodness of fit	1.071
T_{min} (mm)	0.046
T_{max} (mm)	0.062

Atom	Type of position	x/a	y/a	z/a	Occupation factor	B_{eq} (Å^2)
Tb	4(c)	0	0.14136(4)	0.25	0.4(1)	0.87(16)
Sc	4(c)	0	0.14136(4)	0.25	0.6(1)	0.40(16)
Si	4(c)	0	0.42170(20)	0.25	1.0	1.33(5)

GdScSi compound forms from the Mn_5Si_3-type $Gd_{2.5}Sc_{2.5}Si_{3-x}$ solid solution at $x \rightarrow 0.5$ with strong changes of the initial unit cell.

4. Conclusions

We have confirmed the known ternary compounds and found new CrB-type $R_{0.4}Sc_{0.6}Si$ compounds in the Gd–Sc–Si and Tb–Sc–Si isothermal cross-sections. However, it is necessary to investigate the $R_xSc_{1-x}Si$ ($x = 0 \ldots 0.4$) solid solution region in more detail before reaching a final decision concerning the $R_{0.4}Sc_{0.6}Si$ compounds.

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