Crystal structure of the compounds $R\text{Fe}_4\text{Si}_2$ (R = Dy, Tm)

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The crystal structures of the compounds $R\text{Fe}_4\text{Si}_2$ (R = Dy, Tm) were determined from X-ray single-crystal (CAD-4T diffractometer, Mo $K\alpha$ radiation) and powder (HZG-4a diffractometer, Fe $K\alpha$ radiation) diffraction data. The compounds crystallize with the ZrFe_4Si_2 structure type, space group $P4_2/mnm$, Pearson symbol tP14; a = 7.1691(8), c = 3.780(1) Å, R_F = 0.0197, R_w = 0.0186 for DyFe_4Si_2 and a = 7.1235(3), c = 3.7847(2) Å, R_B = 0.0777 for TmFe_4Si_2. Both compounds are stoichiometric with an ordered distribution of the atoms.

Introduction

According to a literature survey of the R–Fe–Si systems, compounds crystallizing with the tetragonal ZrFe_4Si_2 structure type (space group $P4_2/mnm$, Pearson symbol tP14) [1] are formed with yttrium [2,3], terbium [4], dysprosium [2,5], holmium [2,6], erbium [2], thulium [2,7], and lutetium [2]. However, while, according to [3,4], the compounds with R = Y, Tb have the composition $R\text{Fe}_4\text{Si}_2$, other references report the off-stoichiometric composition $R\text{Fe}_{4.48}\text{Si}_{1.52}$ for the compounds with R = Y, Dy, Ho, Er, Tm, Lu. The crystal structure of the terbium compound has been refined from X-ray single-crystal data [4], whereas for the other compounds only lattice parameters have been reported so far.

Compounds with the ZrFe_4Si_2 structure type exist also in several R–Fe–Ge systems (R = Y [8,9], Dy [8,10,11], Ho [8,12,13], Er [8,14-16], Tm [8,15], Yb [17,18], Lu [8]). Differently from the silicides, they are all reported to be stoichiometric. The crystal structures have been refined from X-ray single-crystal diffraction data for the erbium compound and from X-ray or neutron powder diffraction data for the yttrium, dysprosium, holmium, erbium, thulium, and ytterbium compounds.

The aim of the present work was a more thorough investigation of the crystal structures of the compounds DyFe_4Si_2 (single-crystal diffraction) and TmFe_4Si_2 (powder diffraction).
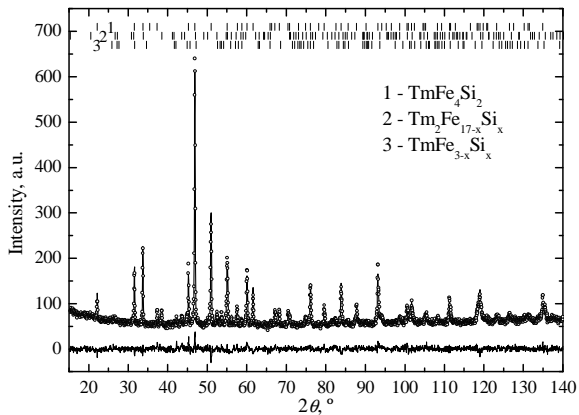
Experimental details

Alloys of ~2 g were synthesized from chemical elements of high purity (rare-earth metals 99.8 wt.%, iron 99.99 wt.%, silicon 99.9999 wt.%) by arc melting under an atmosphere of purified (Ti getter) argon. The alloys were remelted twice to ensure homogeneity. The composition of the samples was controlled by comparing the mass of the obtained alloy with the total mass of the initial load. The weight losses did not exceed 2% after melting. The samples were annealed at 800ºC under vacuum in quartz ampoules for 350 hours and subsequently quenched in cold water.

A single crystal suitable for X-ray structure studies of the compound DyFe_4Si_2 was selected from an alloy of nominal composition $\text{Dy}_{14}\text{Fe}_{57}\text{Si}_{29}$. The first stage of the investigation by Laue and rotation methods (RKV-86 camera, Mo K radiation) indicated tetragonal symmetry and yielded approximate values of the lattice parameters. X-ray diffraction data were collected on a CAD-4T diffractometer (Mo $K\alpha$ radiation). Experimental details and crystallographic parameters obtained using the WinCSD software package [17] are given in Table 1.

The crystal structure of the compound TmFe_4Si_2 was determined by X-ray powder diffraction from data collected on a HZG-4a diffractometer (Fe $K\alpha$ radiation) for an alloy of nominal composition $\text{Tm}_{15}\text{Fe}_{60}\text{Si}_{25}$. Experimental details and parameters from the structure refinement by the Rietveld method using the DBWS-9807 program [18] are given in

Table 2. Fig. 1 shows the powder diffraction pattern. The sample contained three phases; besides the main phase TmFe$_4$Si$_2$ (79%), minor amounts of the Tm$_2$Fe$_{17-x}$Si$_x$ (18%) and TmFe$_{3-x}$Si$_x$ (3%) phases were observed.

Fig. 1 Observed (dots), calculated (line) and difference (bottom) X-ray diffraction patterns for the alloy Tm$_{15}$Fe$_{60}$Si$_{25}$ (Fe $K\alpha$ radiation). Vertical bars indicate peak positions of the three identified phases.

Table 1 Experimental details and crystallographic data for DyFe$_4$Si$_2$.

Refined composition	DyFe$_4$Si$_2$
Formula weight, M_r	442.06
Structure type	ZrFe$_4$Si$_2$
Pearson symbol	tP14
Space group	$P4_2/mnm$ (#136)
Unit-cell parameters: a, Å	7.1691(8)
c, Å	3.780(1)
Cell volume V, Å^3	194.3(1)
Formula units per cell Z	2
Density D_X, g cm^{-3}	7.555
Absorption coefficient μ, mm^{-1}	34.932
Crystal size, mm	0.10×0.05×0.01
Maximal 2θ, °	79.97
Number of measured reflections	1437
Number of independent reflections ($F > 4\sigma(F)$)	360
Number of refined parameters	14
Reliability factors: R_F	0.0197
R_w	0.0186
S	1.030

Results and discussion

The crystal structure of the compound DyFe$_4$Si$_2$ was refined in the space group $P4_2/mnm$ as belonging to the ZrFe$_4$Si$_2$ structure type [1]. The composition of the single crystal showed no significant deviation from stoichiometric DyFe$_4$Si$_2$. This is in contradiction with the literature data available for the dysprosium compound, but in agreement with the data reported for

the terbium compound [4]. The lattice parameter a is slightly larger than the value reported for the composition DyFe$_{4.48}$Si$_{1.52}$ (a = 7.122, c = 3.784 Å [2]). Atomic coordinates, equivalent and anisotropic displacement parameters for the DyFe$_4$Si$_2$ compound are listed in Table 3. A projection of the unit cell along [0 0 1] and the coordination polyhedra of the atoms are shown in Fig. 2.

Table 2 Experimental details and crystallographic data for TmFe$_4$Si$_2$ (alloy Tm$_{15}$Fe$_{60}$Si$_{25}$).

Refined composition		TmFe$_4$Si$_2$
Formula weight, M_r		448.49
Structure type		ZrFe$_4$Si$_2$
Pearson symbol		tP14
Space group		$P4_2/mnm$ (#136)
Unit-cell parameters:	a, Å	7.1235(3)
	c, Å	3.7847(2)
Cell volume V, Å^3		192.05(1)
Formula units per cell Z		2
Density D_X, g cm^{-3}		7.758
Range 2θ, °		15-140
Number of refined parameters		16
FWHM parameters:	U	0.036(7)
	V	-0.01(1)
	W	0.029(4)
Mixing parameter η		0.70(3)
Asymmetry parameter C_M		-0.19(2)
Texture parameter G [axis]		1.066(5) [0 0 1]
Reliability factors:	R_B	0.0777
	R_p	0.0497
	R_{wp}	0.0635
	S	0.52

Table 3 Atomic coordinates and displacement parameters (Å^2) for DyFe$_4$Si$_2$ (tP14, $P4_2/mnm$, a = 7.1691(8), c = 3.780(1) Å).

Site	Wyckoff position	x	y	z	B_{eq}
Dy	2a	0	0	0	0.430(5)
Fe	8i	0.14982(9)	0.58764(8)	0	0.49(1)
Si	4f	0.2821(2)	0.2821(2)	0	0.52(2)

Site	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Dy	0.418(8)	0.418(8)	0.45(1)	0.014(9)	0	0
Fe	0.48(2)	0.55(2)	0.43(2)	0.04(1)	0	0
Si	0.56(3)	0.56(3)	0.44(5)	0.04(4)	0	0

* $B_{eq} = 1/3[B_{11}a^{*2}a^2 + ... 2B_{23}b^*c^*bc\cos\alpha]$.

In the structure of the DyFe$_4$Si$_2$ compound, the silicon atoms occupy the centres of trigonal prisms of composition Fe$_4$Dy$_2$. The prisms form columns running along the crystallographic direction [0 0 1] by sharing triangular faces. The columns are linked two by two via common Dy-Dy prism edges. The

coordination polyhedra of the Si atoms contain in addition two Fe atoms and one Dy atom, which cap the rectangular faces of the prism. The coordination polyhedra of the Fe atoms are slightly deformed cuboctahedra of composition $\mathrm{Si_3Fe_6Dy_3}$, whereas the coordination polyhedra of the Dy atoms are hexagonal prisms of composition $\mathrm{Si_4Fe_8}$ (Si atoms in *para*-positions) with an additional atom (2Si + 4Fe + 2Dy) capping each face.
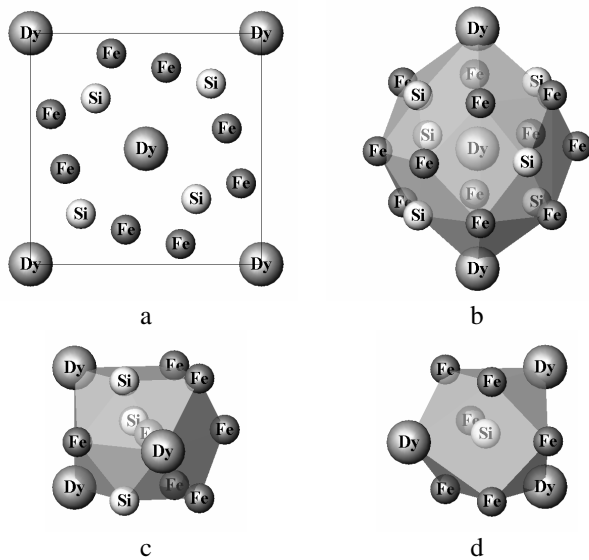
Fig. 2 Projection of the unit cell of $\mathrm{DyFe_4Si_2}$ along [0 0 1] (a) and coordination polyhedra of the atoms: [$\underline{\mathrm{Dy}}\mathrm{Si_6Fe_{12}Dy_2}$] (b), [$\underline{\mathrm{Fe}}\mathrm{Si_3Fe_6Dy_3}$] (c), and [$\underline{\mathrm{Si}}\mathrm{Fe_6Dy_3}$] (d).

Our studies show that the compound with Tm is also stoichiometric and crystallizes with the $\mathrm{ZrFe_4Si_2}$ structure type like the $\mathrm{DyFe_4Si_2}$ compound. The lattice parameter a is slightly larger, as compared with the value reported for the composition $\mathrm{TmFe_{4.48}Si_{1.52}}$ (a = 7.065, c = 3.777 Å [2]). Atomic coordinates and isotropic displacement parameters for the $\mathrm{TmFe_4Si_2}$ compound are listed in Table 4.

Table 4 Atomic coordinates and displacement parameters (Å^2) for $\mathrm{TmFe_4Si_2}$ ($tP14$, $P4_2/mnm$, a = 7.1235(3), c = 3.7847(2) Å).

Site	Wyckoff position	x	y	z	B_{iso}
Tm	2a	0	0	0	0.38(6)
Fe	8i	0.1511(6)	0.5859(6)	0	0.5(1)
Si	4f	0.281(1)	0.281(1)	0	0.7(2)

The unit-cell volumes of the compounds crystallizing with the $\mathrm{ZrFe_4Si_2}$ structure type in the R–Fe–Si systems according to various references are plotted in Fig. 3. The non-stoichiometric compounds ($R\mathrm{Fe_{4.48}Si_{1.52}}$) contain a higher amount of iron and part of the Fe atoms form a statistical mixture with the Si atoms in the Wyckoff position 4f. Hence, the larger values of the unit-cell volume observed for the stoichiometric $R\mathrm{Fe_4Si_2}$ compounds compared with those otained for the non-stoichiometric composition can be explained by the larger radius of the Si atoms (1.32 Å) with respect to Fe (1.26 Å). We cannot exclude that the compounds crystallizing with the structure type $\mathrm{ZrFe_4Si_2}$ in the systems R–Fe–Si have a certain homogeneity range.
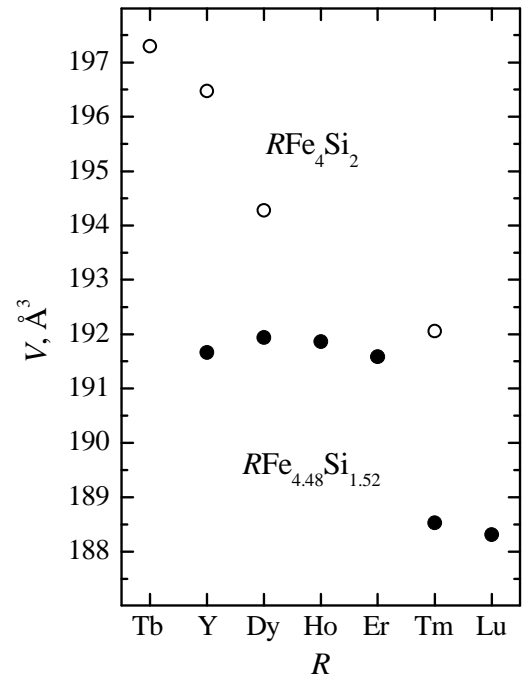
Fig. 3 Unit-cell volume for $R\mathrm{Fe_4Si_2}$ (open circles; R = Y [3], Tb [4], Dy and Tm from this work) and $R\mathrm{Fe_{4.48}Si_{1.52}}$ (filled circles; R = Y, Dy-Tm, Lu [2]) compounds with $\mathrm{ZrFe_4Si_2}$-type structure.

Conclusions

The crystal structure refinements carried out for the compounds $\mathrm{DyFe_4Si_2}$ and $\mathrm{TmFe_4Si_2}$ show that, at 800ºC, these compounds are stoichiometric with an ordered atom distribution. Similar results have earlier been obtained for the isotypic terbium-containing compound. The unit-cell volume is consistently larger for the compounds $R\mathrm{Fe_4Si_2}$ than reported for the composition $R\mathrm{Fe_{4.48}Si_{1.52}}$.

Acknowledgements

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