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NON-STOICHIOMETRY OF GdFe₂Si₂: A SINGLE CRYSTAL STUDY

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The title compound was prepared from the elements by arc-melting under argon followed by annealing in silica tubes at 800 °C for one month. The crystal structure of GdFe₂Si₂ was investigated by means of X-ray study of two single crystals, as well as powder X-ray diffraction phase and structural analyses and energy dispersive X-ray spectroscopy of four polycrystal samples. GdFe₂Si₂ crystallizes in the CeGa₂Al₂ structure type, space group I4/mmm, a = 3.938(1), c = 10.080(3) Å, Z = 2, R1 = 0.024, wR2 = 0.039 for 78 unique reflections with I₀ > 2σ(I₀) and 9 parameters. For the compound with smaller unit cell volume the Fe position is not fully occupied and the refinement results for a composition GdFe_{1.92}Si₂ is in agreement with the data of chemical analysis: space group I4/mmm, a = 3.9467(7), c = 9.710(2) Å, Z = 2, R1 = 0.031, wR2 = 0.063 for 102 unique reflections with I₀ > 2σ(I₀) and 10 parameters. Narrow homogeneity range GdFe_{2-x}Si₂ (0 ≤ x ≤ 0.08) for the compound was detected.

Keywords: ternary silicides, rare earth metals, single crystal, crystal structure.

1. Introduction

Numerous ternary compounds with the composition RT₂Si₂ (R = rare earth, T = transition element) have been reported during the last decades. They crystallize in the body-centered tetragonal crystal structure of the CeGa₂Al₂ type with space group I4/mmm. The first representatives of this structure type, CeGa₂Al₂, CeBe_{1.2}Al_{2.8}, and CeCuAl₃, were reported by Zarechnyuk et al. in 1964 [1]. Ban and Sikirica in 1965 reported the same crystal structure for ThCr₂Si₂ and several other compounds containing transition metals [2]. In the literature the first (CeGa₂Al₂) and the second (ThCr₂Si₂) representatives were used for denomination of this structure type of intermetallic compounds. We use the earlier reported representative for denomination of this structure type in the text.

CeGa₂Al₂ is an ordered ternary variant of the binary BaAl₄ tetragonal structure type [3], obtained by replacing two crystallographic Al sites 4d and 4e, by Ga and Al atoms, respectively. The largest Ce atoms occupy 2a site. The presence of two different crystallographic sites 4d and 4e with coordination numbers of 12 and 9, respectively, results in various ternary RT₂X₂ (R = rare earth, actinide, Ca, Sr, p-element; T = d-element; X = p-element) compounds adopting the CeGa₂Al₂ structure type. Rieger and Parthe [4] reported on synthesis of above 90 RT₂X₂ (R = Ca, Sr, rare earth, actinide; T =

Mn→Cu; $X = \text{Si, Ge}$) ternaries crystallizing in CeGa_2Al_2 type of structure. A number of rare earth d -transition element silicides and germanides RT_2X_2 were reported also in [5–6]. For all ternaries there was reported constant composition of 1:2:2. To our knowledge Gd and Y are the only rare earths for which Fe containing silicides with slightly non-stoichiometric $\text{GdFe}_{1.95}\text{Si}_{2.05}$ [6] and $\text{YFe}_{2-\delta}\text{Si}_2$ ($\delta = 0.2$) [7] compositions were obtained. However, the stoichiometric 1:2:2 samples for these ternaries were reported as well [4–5, 8–11]. The lattice parameters obtained from powder XRD data are the only crystal structure characteristics of GdFe_2Si_2 and $\text{GdFe}_{1.95}\text{Si}_{2.05}$ reported in [4–6, 8–11]. These data are presented in Table 1. The literature data indicated that GdFe_2Si_2 may have a narrow homogeneity range. Another indication of this may be slightly different values of the antiferromagnetic ordering temperature (Neel temperature) $T_N = 7$ K reported for $\text{GdFe}_{1.95}\text{Si}_{2.05}$ [6] and $T_N = 8$ K for GdFe_2Si_2 [12].

In the course of systematic studies of the Gd–Fe–Si system we have obtained new phases. Among them is a new ternary silicide $\text{GdFe}_{1-x}\text{Si}_2$ ($x = 0.32$) has been synthesized from the elements by arc-melting. It crystallizes in space group $Cmmm$ and represents a TbFeSi_2 -type structure. The Fe position is not fully occupied and the structure refinement results in a composition $\text{GdFe}_{0.68}\text{Si}_2$ in agreement with a chemical analysis [13].

Table 1

Literature data for lattice parameters for GdFe_2Si_2 (polycrystal powder XRD data) compared with our data

a , Å	c , Å	V , Å ³	Homogenizing procedure	Reference
3.940(6)	9.974(10)	154.83	900 °C, 100 h	[4]
3.940	9.974	154.83		[5]
3.940(5)	9.974(5)	154.83		[8]
3.932	9.971	154.16	900 °C, 8 d	[9]
3.94	10.03	155.70		[10]
3.936(1)	9.971(4)	154.48	800 °C, one week	[11]
3.94*	10.00*	155.24	800 °C, several weeks	$\text{GdFe}_{1.95}\text{Si}_{2.05}$ [6]
3.943(1)	9.890(3)	153.76	800 °C, one month	Our data
3.937(1)	10.009(3)	155.14	800 °C, one month	Our data

*deducted from a plot

The lattice parameters of GdFe_2Si_2 observed in our XRD powder data (see Table 1) as well as presented in the literature [4–6, 8–11] indicate some structural discrepancies. A closer single crystal study of the GeFe_2Si_2 compound became the subject of the present report.

2. Experimental

2.1. Synthesis

Polycrystalline samples of different compositions $\text{Gd}_{10}\text{Fe}_{40}\text{Si}_{50}$, $\text{Gd}_{15}\text{Fe}_{45}\text{Si}_{40}$, $\text{Gd}_{25}\text{Fe}_{35}\text{Si}_{45}$ and $\text{Gd}_{25}\text{Fe}_{35}\text{Si}_{40}$ were prepared from the commercially available pure elements: gadolinium metal with a claimed purity of 99.99 at.%, Alfa-Aesar, Johnson Matthey Company, sublimed bulk pieces; silicon as powder, purity >99.99 at.%, H. C. Starck, Germany; iron powder, purity 99.98 at.%, Fluka Chemicals. Suitable amounts of powders and freshly filed chips of the rare earth metal were mixed together and pressed into pellets. Arc-melting of the samples (1.00 g each) was performed on a water-cooled copper hearth under a purified argon atmosphere with Ti as the getter. To ensure homogeneity, the samples were turned over and re-melted two times. Weight losses were

generally smaller than 0.5%. For further heat treatments, the pellets were wrapped in tantalum foil, sealed in evacuated quartz tubes, annealed at $T = 800$ °C for 1 month and subsequently quenched by submerging the tubes in cold water. Single crystals of the gadolinium iron silicide, having a metallic luster and being unreactive towards air, were isolated by crushing the solidified samples.

2.2. Microprobe analysis

For metallographic inspection and for complementary qualitative phase analysis, energy dispersive X-ray spectroscopy (EDX) was employed. The samples were embedded in Wood's metal (melting point of 75°C, Fluka Chemie, Switzerland). The embedded samples were polished on a nylon cloth using chromium oxide (Bühler Isomet) with grain sizes 1–5 μm . Quantitative and qualitative composition analyses of the polished samples were performed by energy-dispersive X-ray spectroscopy (EDX) on a scanning electron microscope TESCAN 5130 MM with an Oxford Si-detector. From the EDX analysis of the annealed samples the different compositions were deduced and they are presented in Table 2. Standard deviations estimated to be about 1.0 at.%. The surface of the phases in the Gd–Fe–Si system appeared to be quite stable in air. Metallographic investigation, X-ray powder diffraction and EPMA analyses revealed the compound GdFe_{2-x}Si₂ ($0 \leq x \leq 0.8$) to be in phase equilibria with Gd₂Fe₃Si₅ [14], Gd₂FeSi₂ [15], GdSi [16], FeSi [17] and Fe₃Si [18] (Fig. 1).

Table 2

Characteristics of the phase equilibria with participation of GdFe₂Si₂ in the Gd–Fe–Si system at 800 °C

Alloy composition	Phases ^a	EDX ^a	Lattice parameters ^b
Gd ₁₀ Fe ₄₀ Si ₅₀	GdFe ₂ Si ₂ +FeSi	Gd ₂₀ Fe ₃₈ Si ₄₂ +Fe ₅₀ Si ₅₀	$a = 3.943(1)$ $c = 9.890(3)$
Gd ₁₅ Fe ₄₅ Si ₄₀	GdFe ₂ Si ₂ +Fe ₃ Si	Gd ₂₁ Fe ₄₂ Si ₃₇ +Fe ₇₆ Si ₂₄	$a = 3.937(1)$ $c = 10.009(3)$
Gd ₂₂ Fe ₃₃ Si ₄₅	GdFe ₂ Si ₂ +Gd ₃ Fe ₂ Si ₅	Gd ₂₁ Fe ₄₁ Si ₃₈ +Gd ₂₈ Fe ₂₁ Si ₅₁	$a = 3.934(2)$ $c = 9.936(3)$
Gd ₂₅ Fe ₃₅ Si ₄₀	GdFe ₂ Si ₂ +Gd ₂ FeSi ₂ +GdSi	Gd ₂₁ Fe ₃₉ Si ₄₀ +Gd ₄₁ Fe ₂₁ Si ₃₈ +Gd ₅₁ Si ₄₉	$a = 3.938(1)$ $c = 9.980(2)$

^aPhases detected by XRD and SEM/EDX analyses

^bXRD powder data refined for GdFe₂Si₂

3. Results and Discussion

The primary tool for phase and structural analysis was powder X-ray diffraction (XRD) performed on a DRON-2.0M (FeK _{α} -radiation) and STOE STADI P (MoK _{α} -radiation) and handled with program packages STOE WinXPOW [19] and WinCSD [20]. The unit cell parameters were refined with the help of the WinCSD program package. The indexing of the X-ray powder patterns was ensured through intensity calculations taking the atomic positions determined from the single crystal investigation. The unit cell parameters refined from X-ray powder data are presented in Table 2.

Small and irregularly platelet-shaped single crystals for X-ray investigation were selected from two crushed annealed samples of Gd₁₀Fe₄₀Si₅₀ and Gd₂₂Fe₃₃Si₄₅. X-ray diffraction data for GdFe₂Si₂ and GdFe_{1.92}Si₂ single crystals were collected at room temperature on a Stoe IPDS II image plate diffractometer with monochromatized MoK α

radiation in oscillation mode. The lattice parameters for GdFe_2Si_2 were determined from 879 reflections in the region $9.09\text{--}58.29^\circ 2\theta$ and for $\text{GdFe}_{1.92}\text{Si}_2$ were determined from 1588 reflections in the region $8.17\text{--}64.02^\circ 2\theta$. All relevant details concerning the data collection are listed in Table 3. Some difference between the lattice parameters refined from single crystal and powder X-ray diffraction data are quite usual. After X-ray data collection on a Stoe IPDS II image plate diffractometer, EDX analysis of the single crystal reveal the composition, which is in good agreement with the results obtained from bulk samples presented in Table 2, and the small difference indicates the surface irregularities of single crystal shape.

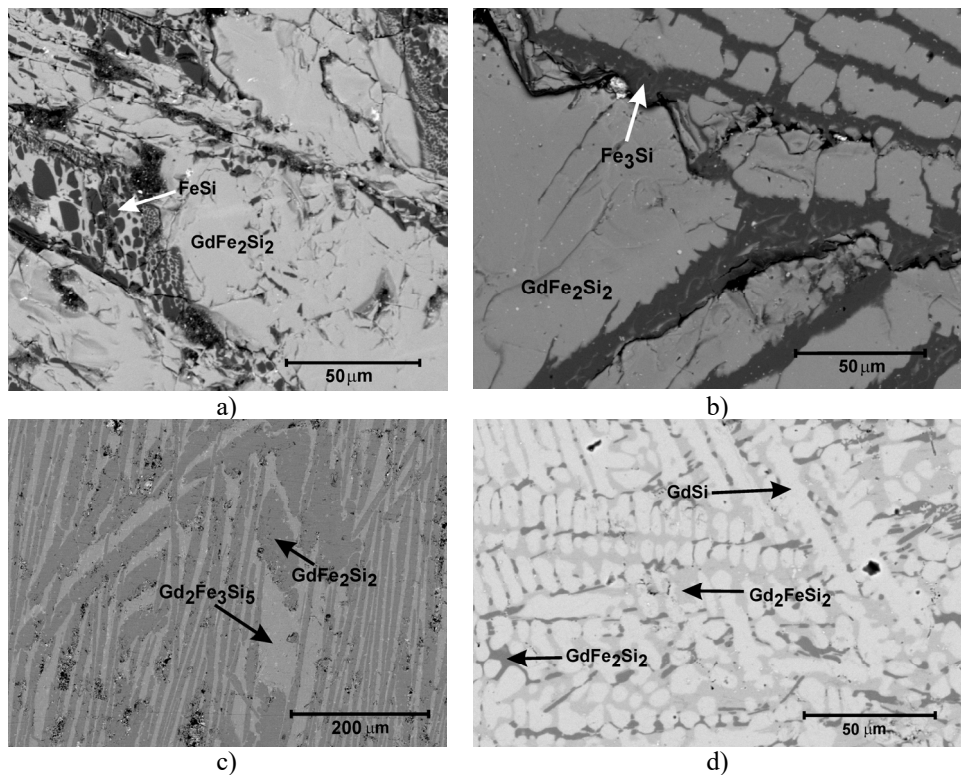


Fig. 1. Backscattered electron image of the annealed bulk samples with nominal atomic composition: a) $\text{Gd}_{10}\text{Fe}_{40}\text{Si}_{50}$, b) $\text{Gd}_{15}\text{Fe}_{45}\text{Si}_{40}$, c) $\text{Gd}_{22}\text{Fe}_{33}\text{Si}_{45}$, d) $\text{Gd}_{25}\text{Fe}_{35}\text{Si}_{40}$.

The unit cell parameters and extinction rules suggested $I4/mmm$ as the most appropriate space group. The starting atomic parameters derived *via* direct methods using the program SIR 97 [21] were subsequently refined with the program SHELXL-97 [22] (full-matrix least-squares on F^2) with anisotropic atomic displacements for the terbium atoms. Only three different atomic coordinates were obtained in $2a$, $4b$ and $4e$ Wyckoff positions equivalent to those of CeGa_2Al_2 structure type [1]. First the Gd, Fe and Si atoms were appointed in $2a$, $4b$ and $4e$ sites, according to CeGa_2Al_2 structure, respectively. Refinement

of the crystal structure with SHELXL program in anisotropic approximation of atomic displacement for the compound with larger unit cell converged well. The final difference Fourier map of GdFe₂Si₂ was flat, and the refinement of the occupancy factors (G) gave no evidence for partial occupations. Contrary to the previously crystal structure with full occupation for all atoms, the X-ray single crystal investigation for the compound with small unit cell shows the elevated values for atomic displacement parameters for the Fe atoms, there is significant residual electron density peak in difference Fourier close to the Gd atom ($4.9 \text{ e}^{-}\text{\AA}^{-3}$; 0.7 \AA). Refinement occupancy (G) for the $4d$ site resulted in $G = 0.96(1)$. The atomic coordinates and displacement parameters for both single crystals are given in Table 4 and selected interatomic distances are reported in Table 5.

Table 3

Single crystal and structure refinement data for GdFe ₂ Si ₂ and GdFe _{1.92(1)} Si ₂		
Empirical formula	GdFe ₂ Si ₂	GdFe _{1.92(1)} Si ₂
Crystal system	Tetragonal	Tetragonal
Space group	$I4/mmm$ (No. 139)	$I4/mmm$
Pearson symbol, Z	$tI10, 2$	$tI10, 2$
Lattice parameters		
$a, \text{\AA}$	3.938(1)	3.9467(7)
$c, \text{\AA}$	10.080(3)	9.710(2)
Unit cell volume, \AA^3	156.32(1)	155.31(6)
Calculated density, g/cm^3	6.908	6.952
Absorption coefficient, $1/\text{cm}$	30.58	30.77
Crystal size, mm^3	$0.11 \times 0.03 \times 0.06$	$0.15 \times 0.008 \times 0.06$
Radiation and wavelength, \AA	MoK α , 0.71073	MoK α , 0.71073
Diffractometer	STOE IPDS II	STOE IPDS II
Refined parameters	9	10
Refinement	F^2	F^2
$2\theta_{\text{max}}$ and $(\sin\theta/\lambda)_{\text{max}}$	58.32, 0.685	63.34, 0.738
h, k, l	$-4 < h < 5$	$-5 < h < 5$
	$-5 < k < 5$	$-5 < k < 5$
	$-13 < l < 13$	$-14 < l < 14$
Collected reflections	749	926
Independent reflections	84 ($R_{\text{int}} = 0.12$)	102 ($R_{\text{int}} = 0.11$)
Reflections with $I_o \geq 2\sigma(I_o)$	78 ($R_\sigma = 0.050$)	102 ($R_\sigma = 0.052$)
Final R_1 indices (R_1 all data)	0.024 (0.033) ^{a)}	0.031 (0.032) ^{a)}
Weighted wR_2 factor (wR_2 all data)	0.039 (0.045) ^{b)}	0.063 (0.062) ^{c)}
Goodness-of-fit on F^2 :	1.21	1.24
Extinction coefficient:	0.012(3)	0.040(7)
Largest diff. peak and hole, $\text{e}^{-}\text{\AA}^{-3}$	3.0/-2.4	4.0/-2.3

$$^a) R_1(F) = [\Sigma(|F_o| - |F_c|)] / \Sigma F_o$$

$$^b) wR_2(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}; [w^{-1} = \sigma^2(F_o)^2 + P], \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

$$^c) wR_2(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}; [w^{-1} = \sigma^2(F_o)^2 + (0.0261)^2 + 0.00P], \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

The 3D representation of the GdFe₂Si₂ structure is shown in Figure 2. Coordination polyhedron (CP) of the largest Gd atom in the structure is 22-vertex polyhedron [GdGd₄Fe₈Si₁₀] with 12 quadrangular and 24 triangular faces. The closest neighbors of Gd are 10 Si atoms ($d = 3.060(2) \text{ \AA}$) (see Table 5). The Gd–Fe distances are $3.198(2) \text{ \AA}$ long. Coordination number (CN) of Fe atoms is 12, CP is distorted cubooctahedron [FeGd₄Fe₄Si₄]. Fe–Si distances $2.333(2) \text{ \AA}$ are decreased (for about 4 %) compared with

the sum of Fe and Si atomic radii ($1.26 + 1.17 = 2.43 \text{ \AA}$) while Fe–Fe distances $2.785(1) \text{ \AA}$ are larger. The closest neighbors of Si atom are 4 Gd and 4 Fe metal atoms forming tetragonal antiprism. An additional Si atom centers square face of antiprism formed by 4 Gd atoms. Thus, CP of Si atom is $[\text{SiGd}_4\text{Fe}_4\text{Si}_1]$, CN is 9, Si–Si distance is $2.535(8) \text{ \AA}$. In the crystal structure of $\text{GdFe}_{1.92}\text{Si}_2$ all atoms have the same CPs and CNs and other characteristics as those presented for GdFe_2Si_2 (see Table 5).

Table 4

Atomic coordinates and displacement parameters ^a (\AA^2) for GdFe_2Si_2 and $\text{GdFe}_{1.92}\text{Si}_2$ single crystals								
Atom	Site	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$	U_{11}	U_{22}	U_{33}
GdFe_2Si_2								
Gd	$2a$	0	0	0	0.0088(6)	0.0068(6)	0.0068(6)	0.0128(8)
Fe	$4d$	0	1/2	1/4	0.0097(6)	0.0084(8)	0.0084(8)	0.012(1)
Si	$4e$	0	0	0.3743(4)	0.0109(8)	0.008(1)	0.008(1)	0.016(2)
$\text{GdFe}_{1.92}\text{Si}_2$								
Gd	$2a$	0	0	0	0.0059(5)	0.0043(5)	0.0043(5)	0.0092(6)
Fe ^b	$4d$	0	1/2	1/4	0.0058(7)	0.0056(8)	0.0056(8)	0.006(1)
Si	$4e$	0	0	0.3748(3)	0.0069(6)	0.0060(8)	0.0060(8)	0.009(2)

$${}^a U_{23} = U_{13} = U_{12} = 0.$$

$${}^b G = 0.96(1)$$

As it is seen from Fig. 3 the structure of $\text{GdFe}_{2-x}\text{Si}_2$ can be presented as built of layers of $[\text{SiGd}_4\text{Fe}_4]$ antiprisms rotated and shifted relative to each other, superimposed along $[001]$ direction. In this case each upper prism is in contact with four lower ones.

Table 5

Interatomic distances (\AA) for GdFe_2Si_2 and $\text{GdFe}_{1.92}\text{Si}_2$		
Atoms	GdFe_2Si_2	$\text{GdFe}_{1.92}\text{Si}_2$
Gd – 10 Si	3.060(2)	3.057(1)
8 Fe	3.198(2)	3.1793(4)
4 Gd	3.938(1)	3.947(1)
Fe – 4 Si	2.334(2)	2.333(2)
4 Fe	2.785(1)	2.7907(5)
4 Gd	3.198(2)	3.1793(4)
Si – 4 Fe	2.333(2)	2.333(2)
Si	2.535(8)	2.497(6)
4 Gd	3.059(2)	3.057(1)

A number of CeGa_2Al_2 type structures exhibit incomplete occupancy of the $4d$ or $4e$ sites. Non-stoichiometry was consistently observed in $\text{RCO}_{2-\delta}\text{As}_2$ structures ($\text{R} = \text{Ca}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$). In lanthanide containing structures, the concentration of Co vacancies (δ) increases with the increase of the lanthanide atomic number, i.e., $\delta = 0.09, 0.17, 0.22$ and 0.29 for $\text{R} = \text{La}, \text{Ce}, \text{Pr},$ and Nd , respectively [23]. The similar deficiency of Ni atoms was observed in a number of isostructural pnictides, for some of which a homogeneity range was defined, e.g., $\text{YNi}_{1.66-1.78}\text{P}_2$ [24], $\text{CeNi}_{1.72-1.88}\text{P}_2$, $\text{PrNi}_{1.47-1.97}\text{P}_2$ [25–28], $\text{EuNi}_{1.88}\text{As}_{1.92}$ [29], and $\text{SrNi}_{1.72-1.85}\text{Sb}_2$ [30]. The Ni deficiency in the case of pnictides as Fe deficiency in the crystal structure of silicides could be caused by the necessity to

stabilize the electronic structure by removing some atoms with the excess of valence electrons [25].

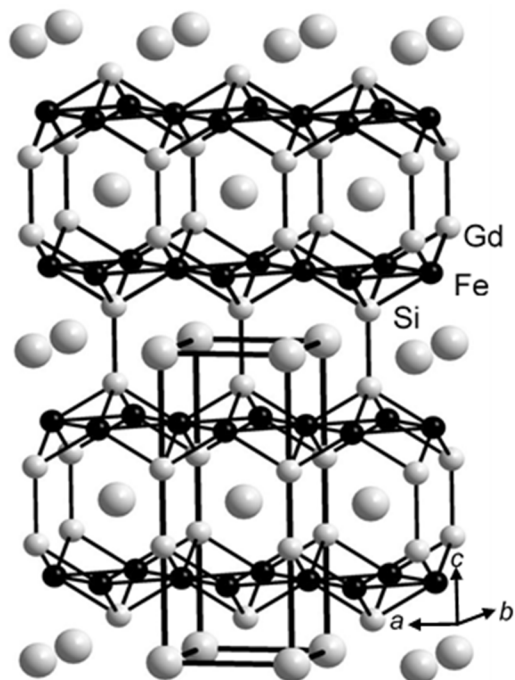


Fig. 2. Perspective view of the crystal structure of $\text{GdFe}_{2-x}\text{Si}_2$.

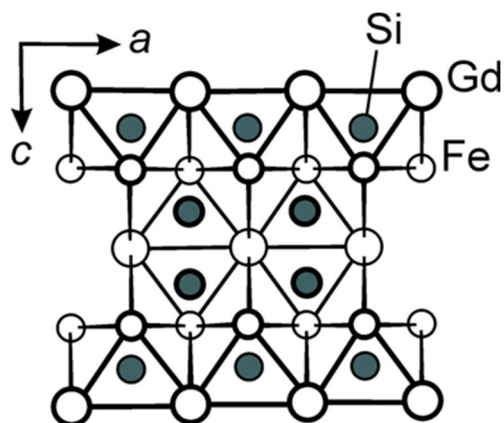


Fig. 3. Stacking of layers of tetragonal antiprisms $[\text{SiGd}_4\text{Fe}_4]$ in the structure of $\text{GdFe}_{2-x}\text{Si}_2$ in the projection along $[010]$.

4. Conclusion

In summary, the non-stoichiometry of GdFe_2Si_2 has been investigated by means of X-ray single crystal, powder X-ray diffraction phase and structural analyses and by energy dispersive X-ray spectroscopy. The unit cell parameters at room temperature were refined from X-ray single crystal and powder X-ray diffraction data pointing to narrow homogeneity range of the compound at 800°C , $\text{GdFe}_{2-x}\text{Si}_2$ ($0 \leq x \leq 0.08$). In the crystal structure of $\text{GdFe}_{1.92}\text{Si}_2$ the Fe position $4d$ is not fully occupied ($G = 0.96(1)$) and the results of structure refinement are in agreement with a chemical analysis. $\text{GdFe}_{2-x}\text{Si}_2$ ($0 \leq x \leq 0.08$) crystallizes in CeGa_2Al_2 structure type, Pearson symbol, $tI10$, space group $I4/mmm$, lattice parameters $a = 3.938(1)$, $c = 10.080(3)$ Å for GdFe_2Si_2 and $a = 3.9467(7)$, $c = 9.710(2)$ Å for $\text{GdFe}_{1.92}\text{Si}_2$.

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РЕЗЮМЕ

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ДОСЛІДЖЕННЯ НЕСТЕХІОМЕТРИЧНОСТІ СПОЛУКИ $GdFe_2Si_2$ МЕТОДОМ МОНОКРИСТАЛУ

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Тернарний силіцид $GdFe_2Si_2$ синтезовано електродуговою плавкою чистих компонентів в атмосфері очищеного аргону з наступним відпалом зразків при 800 °С упродовж одного місяця. Кристалічну структуру сполуки вивчено X-променевими методами монокристалу (монокристали складів $GdFe_2Si_2$ та $GdFe_{1,92}Si_2$), порошку та енергодисперсійною X-променевою спектроскопією. $GdFe_2Si_2$ кристалізується у структурному типі $CeGa_2Al_2$, символ Пірсона $tI10$, просторова група $I4/mmm$, $a = 3,938(1)$, $c = 10,080(3)$ Å, $Z = 2$, $R1 = 0,024$, $wR2 = 0,039$ для 78 рефлексів з $I_o > 2\sigma(I_o)$ та 9 уточнених параметрів. Для ізоструктурного монокристалу $GdFe_{1,92}Si_2$ з параметрами ґратки $a = 3,9467(7)$, $c = 9,710(2)$ Å, $Z = 2$, $R1 = 0,031$, $wR2 = 0,063$ для 102 рефлексів із $I_o > 2\sigma(I_o)$ та 10 уточнених параметрів положення атомів Fe 4d, 0 1/2 1/4 заповнене не повністю ($G = 0,96(1)$). Його склад підтверджено результатами енергодисперсійної X-променевої спектроскопії. Встановлена область гомогенності сполуки при 800 °С описується формулою $GdFe_{2-x}Si_2$ ($0 \leq x \leq 0,08$). Координаційні числа атомів Gd, Fe та Si становлять 22, 12 та 9. Координаційний многогранник найменших атомів Si у структурі сполуки – тетрагональна антипризма з додатковим атомом Si напроти чотирикутної грані, утвореної чотирма атомами Gd, [SiGd₄Fe₄Si]. У структурі сполуки скорочені віддалі Fe–Si (на ~4 %), а інші віддалі – рівні або більші за суму атомних радіусів відповідних атомів.

Ключові слова: тернарні силіциди, рідкісноземельні метали, монокристал, кристалічна структура.

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