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A ternary compound with α-$ThSi_2$-type structure in the system Dy–Ge–Si

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A new ternary compound $DyGeSi_{0.75}$ was found in the system Dy–Ge–Si. The crystal structure of the compound was determined by X-ray powder diffraction (Fe *Kα* radiation). The refined composition was $DyGe_{1.02(2)}Si_{0.73(2)}$ and the structure type α-$ThSi_2$, space group $I4_1/amd$, Pearson symbol *tI*12, $a = 4.052(3)$, $c = 13.6207(10)$ Å, $V = 221.78(3)$ Å^3, $R_B = 0.1011$.

Rare earth / Germanium / Silicon / X-ray powder diffraction / Crystal structure

1. Introduction

Literature data are available on the ternary systems *R*–Ge–Si, where *R* = La, Ce, Pr, Sm, Y, Gd, Er, and Tm. Ternary compounds are absent along the isoconcentrate 33.3 at.% *R* in the systems {La, Ce, Pr, Sm, Gd}–Ge–Si, but solid solutions of various extents are formed based on the binary silicides and germanides. Solid solutions $R(Ge,Si)_{2-x}$ with Ge/Si vacancies (homogeneity ranges of up to 4 at.% *R*) are formed based on binary rare-earth silicides and germanides [1-8]. A continuous transition between the α-$ThSi_2$ and α-$GdSi_2$ structure types takes place within the solid solutions $R(Ge,Si)_{2-x}$. The transition α-$GdSi_2$-type ↔ α-$ThSi_2$-type proceeds *via* a two-phase region for the lanthanum and cerium germanides, whereas in the systems with Pr, Sm, and Gd, the transition between these two structures is continuous and no two-phase region appears.

In the system Y–Ge–Si [6] two ternary compounds were found along the isoconcentrate 33.3 at.% Y: $YGe_{0.2}Si_{1.8}$ (α-$ThSi_2$ structure type) and $YGe_{0.6}Si_{1.4}$ (α-$GdSi_2$ structure type). The crystal structures of these compounds were determined by powder diffraction. The ternary compound ~ErGeSi is situated slightly off the isoconcentrate 33.3 at.% Er [9-11]. A structure refinement carried out on a polycrystalline sample (annealed at 600°C) indicated an orthorhombic structure of the structure type α-$GdSi_2$ ($ErGe_{0.79}Si_{0.88}$, space group *Imma*, $a = 3.9830(6)$, $b = 3.9786(6)$, $c = 13.4808(8)$ Å), whereas a refinement performed on a single crystal (single crystal extracted from the alloy after a special thermal treatment) indicated a tetragonal structure of the α-$ThSi_2$-type ($ErGe_{0.70}Si_{0.82}$, space group $I4_1/amd$, $a = 3.9710(6)$, $c = 13.451(3)$ Å). The compound crystallizing with the structure type α-$GdSi_2$ has a certain homogeneity region, $ErGe_{1.00-0.73}Si_{0.67-0.94}$. In the system Tm–Ge–Si a single-phase region exists in the Ge-rich region of the isoconcentrate ~33.3 at.% Tm [11,12], a solid solution of Si in the compound $TmGe_{1.83}$.

Continuous solid solutions are formed along the isoconcentrates 40 at.% *R*, except for the systems with Sm, Er, and Tm. It should be noted that on dissolving silicon in binary germanides and germanium in silicides, solid solutions with constant rare earth content are formed, *i.e.* mutual substitution of atoms of silicon and germanium occurs. Continuous solid solutions are formed between isotypic silicides and germanides and phase transitions without two-phase regions are observed in certain cases.

The existence of the ternary compound $DyGeSi_{0.75}$ was revealed while studying the system Dy–Ge–Si at 600°C. In this work, we report on the refinement of the crystal structure of this compound.

2. Materials and experimental methods

The existence of a new ternary compound $DyGeSi_{0.75}$ was revealed while studying the system Dy–Ge–Si at 600°C along the intersection 33.3 at.% Dy. Samples with a mass of 0.7-1.0 g were synthesized by arc-melting elements of high purity (content of the main component > 99.7 mass%). The batch was melted in an arc furnace with a tungsten electrode in a copper water-cooled crucible under argon atmosphere (99.998 vol.% Ar), additionally purified by a Ti getter under a pressure of 1.0×10^5 Pa. The weight loss after melting did not exceed 1 mass% of the initial mass. The alloys were sealed in quartz ampoules and annealed at 600°C for 720 h. The annealed samples were quenched into cold water without breaking the ampoules.

Phase analysis of the samples was performed using X-ray powder patterns obtained on a DRON-4.07 diffractometer (Fe $K\alpha$-radiation, 2θ scanning range 30-90°, 2θ step 0.05°, scanning time 3-5 s per point). The samples were fixed in the form of a paste of fine powder ground in inert oil on the surface of a quartz cuvette. The obtained experimental X-ray patterns were compared with patterns calculated for the pure components, known binary and ternary compounds (PowderCell program [13]). A full-profile refinement of the crystal structure of $DyGeSi_{0.75}$ was performed by the Rietveld method [14] using DBWS-9807 software [15].

3. Results and discussion

The phase analysis revealed a new compound in the polycrystalline sample of composition $Dy_{33.3}Ge_{50.0}Si_{16.7}$. The sample contained two phases: the ternary compound $DyGeSi_{0.75}$ (87(4) mass%) and the binary solid solution Ge-Si at the composition $Ge_{0.75}Si_{0.25}$ (13(4) mass%). The positions and intensities of the peaks belonging to the ternary phase indicated the α-$ThSi_2$ structure type. The refinement of the crystal structure by the Rietveld method confirmed the structure type. The compound is characterized by vacancies on the site occupied by Si and Ge atoms and has a certain homogeneity range (below 10 at.%) along the dysprosium isoconcentrate. The lattice parameters were a = 4.052(3), c = 13.6207(10) Å for the phase in the alloy $Dy_{33.3}Ge_{50.0}Si_{16.7}$, and a = 4.0269(5), c = 13.5804(19) Å for the alloy $Dy_{33.3}Ge_{40.0}Si_{26.7}$. The refined chemical formula, $DyGe_{1.02(2)}Si_{0.73(2)}$, hereafter approximated to $DyGeSi_{0.75}$, corresponds to the composition $Dy_{36.5}Ge_{37.0}Si_{26.5}$ when expressed in at.%. Experimental and calculated X-ray patterns of the alloy $Dy_{33.3}Ge_{50.0}Si_{16.7}$ are shown on Fig. 1.

Some results of the refinement of the crystal structure of the compound $DyGeSi_{0.75}$ are presented in Table 1, the atomic coordinates in Table 2. The interatomic distances are given in Table 3.

A single site (Wyckoff position 8*e*) occupied by the smaller atoms is present in the structure type α-$ThSi_2$, so the Ge and Si atoms form a statistical mixture 0.509(12)Ge + 0.366(12)Si, including 12.5 % vacancies. Tentative refinements using the models of α-$GdSi_2$ (space group *Imma*), LaPtSi (space group $I4_1md$) or $CeGe_{0.66}Si_{0.92}$ (space group I-4m2) with two crystallographic sites available to accommodate Ge atoms, Si atoms and vacancies, did not indicate any significant ordering. The stacking of trigonal prisms in the structure of the compound $DyGeSi_{0.75}$ is shown on Fig. 2.

Table 1 Experimental conditions and crystallographic parameters for the structures of the phases in the alloy $Dy_{33.3}Ge_{50.0}Si_{16.7}$.

Refined composition	$DyGe_{1.02(2)}Si_{0.73(2)}$	$Ge_{0.75(4)}Si_{0.25(4)}$
Content, mass%	87(4)	13(4)
Structure type	α-$ThSi_2$	C (diamond)
Pearson symbol	*tI*12	*cF*8
Space group	$I4_1/amd$	Fd-3m
Lattice parameters, Å	a = 4.052(3) c = 13.6207(10)	a = 5.5676(11)
Volume V, $Å^3$	221.78(3)	172.59(6)
Number of formula units Z	4	8
Density D_X, g/cm^3	7.696	4.727
Diffractometer	DRON-4.07	
Radiation, wavelength λ, Å	Fe $K\alpha$, 1.93735	
Scanning method	θ-2θ	
Range 2θ, °	30-120	
Scan step, °	0.05	
Software	DBWS-9807	
Peak width parameters U, V, W	0.18(3), -0.12(4), 0.136(12)	
Shape parameter η	0.34(2)	
Peak asymmetry parameter C_M	-0.11(3)	
Preferred orientation parameter [direction]	G = 0.962(3) [001] (for $DyGeSi_{0.75}$)	
Reliability factors	R_p = 0.0318, R_{wp} = 0.0437, R_B = 0.1011 (for $DyGeSi_{0.75}$)	
Number of refined parameters	15	

Table 2 Atomic coordinates, displacement parameters and occupancy factors in the structure of the compound $DyGeSi_{0.75}$ (space group $I4_1/amd$, origin choice 2).

Atom	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2	Occ.
Dy	4*a*	0	¾	⅛	0.69(6)	1
Ge	8*e*	0	¼	0.2939(2)	0.7	0.509(12)
Si	8*e*	0	¼	0.2939(2)	0.7	0.366(12)

Table 3 Computed interatomic distances (±0.005 Å) in the structure of the compound $DyGeSi_{0.75}$.

Atoms		*δ*, Å	Atoms		*δ*, Å
Dy	- 12 Ge/Si	3.060	Ge/Si	- 1 Ge/Si	2.209
	- 4 Dy	3.958		- 2 Ge/Si	2.345
	- 4 Dy	4.035		- 6 Dy	3.060

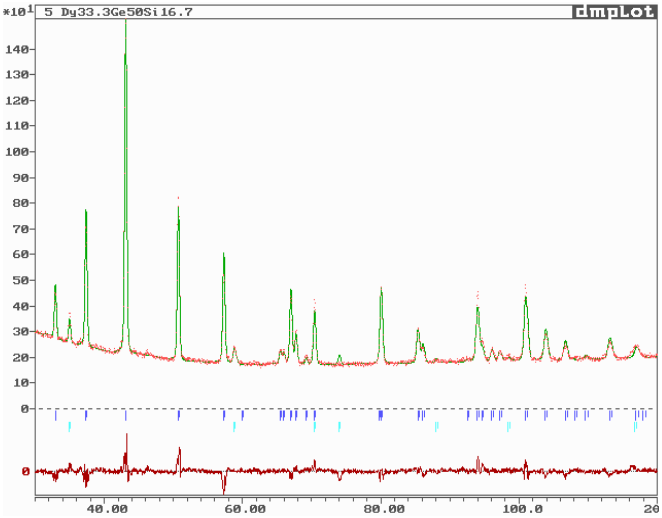

Fig. 1 Observed (points), calculated (line) and difference (bottom) patterns of the alloy $Dy_{33.3}Ge_{50.0}Si_{16.7}$; vertical bars indicate the positions of the reflections for the phases $DyGeSi_{0.75}$ and $Ge_{0.75}Si_{0.25}$.

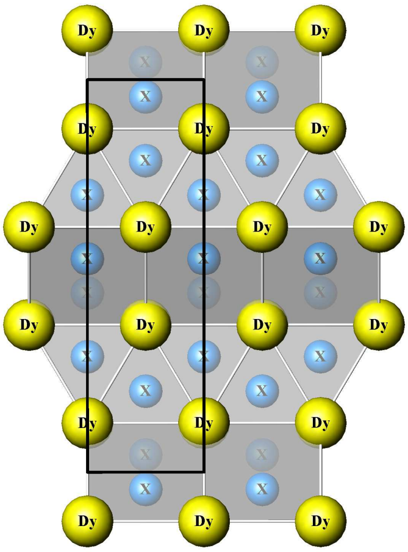

Fig. 2 Stacking of trigonal prisms in the structure of the compound $DyGeSi_{0.75}$ (X = 51% Ge, 37% Si, 12% vacancies).

The ternary compounds formed in the ternary systems {Y, Dy, Er, Tm}–Si–Ge near the intersection 33.3 at.% of the *R*-component crystallize with the structure types α-$ThSi_2$ and α-$GdSi_2$ derived from the AlB_2 type *via* certain relationships. In the AlB_2-type structure, the atoms of the rare-earth elements are located at the vertexes of trigonal prisms, which fill the space completely, while the atoms of Si or Ge are at the centers of the prisms. In the α-$ThSi_2$-type structure, the layers of trigonal prisms are rotated with respect to each other by 90°. The structure type α-$GdSi_2$ differs from α-$ThSi_2$ by splitting of the single Si site into two sites. The small orthorhombic deformation results in changes of the symmetry of the coordination polyhedra. The structure types AlB_2, on the one hand, and α-$ThSi_2$ and α-$GdSi_2$ on the other hand, differ from each other by the network formed by the atoms of Si (or Ge) bonded by covalent bonds. In the structures of the AlB_2-type these atoms form planar, graphite-like nets, while in the α-$ThSi_2$ and α-$GdSi_2$ types they form a three-dimensional framework (Fig. 3).

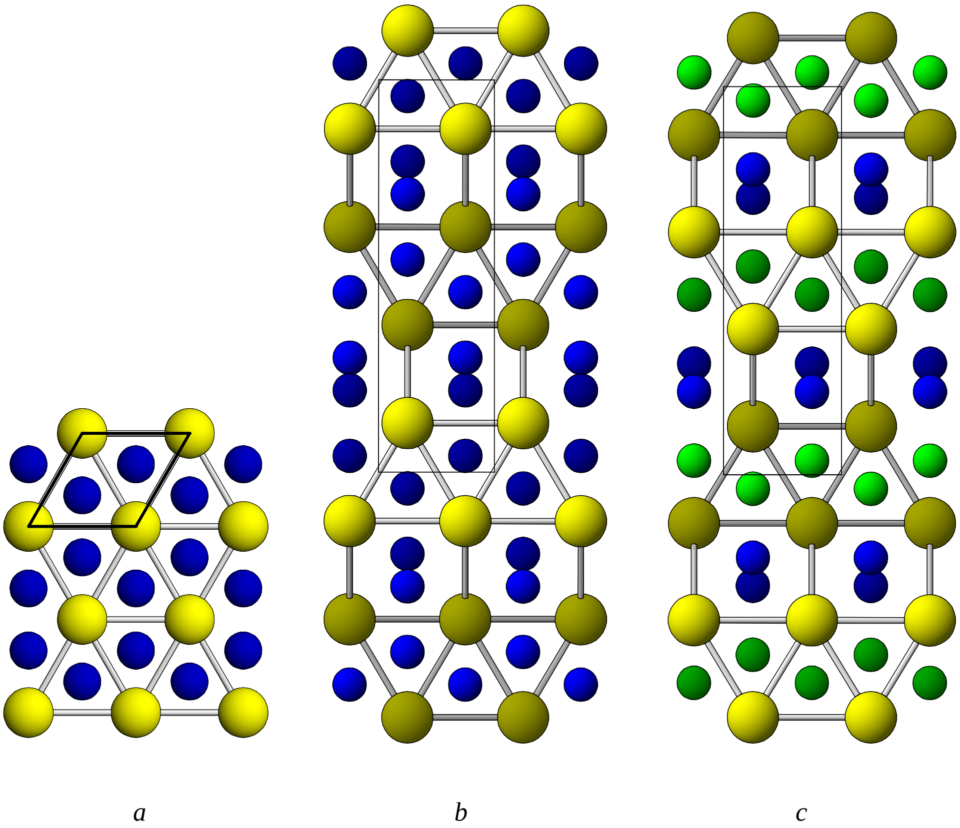
a *b* *c*

Fig. 3 Projections of the crystal structures of the types AlB_2 along [001] (*a*), α-$ThSi_2$ along [100] (*b*) and α-$GdSi_2$ along [100] (*c*).

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