Crystal structure of the ternary compound DyGa$_{0.5-0.4}$Ge$_{1.3-1.4}$

Taras DELENKO[1], Yaroslav TOKAYCHUK[1]*, Roman GLADYSHEVSKII[1]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv,*
Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
* *Corresponding author. Tel.: +380-32-2394506; e-mail: yaroslav.tokaychuk@lnu.edu.ua*

A new ternary intermetallic compound, DyGa$_{0.5-0.4}$Ge$_{1.3-1.4}$, was synthesized and its crystal structure was determined by X-ray powder diffraction (structure type Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$, Pearson symbol *oI*16, space group *Imma*, *a* = 4.0641(3)-4.0709(3), *b* = 4.0870(3)-4.0845(3), *c* = 13.888(11)-13.8426(9) Å, *Z* = 4). The structure type Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$ is closely related to the structure type GdSi$_{1.4}$, and belongs to the family of structures with trigonal-prismatic coordination of the smallest atoms.

Dysprosium / Gallium / Germanium / X-ray powder diffraction / Crystal structure

Introduction

The formation and crystal structures of seven ternary compounds have been reported in the system Dy–Ga–Ge. The compounds have constant or variable compositions and form in the concentration range 22.2-37.5 at.% Dy: Dy$_2$Ga$_{1.8}$Ge$_{5.2}$ (structure type Sm$_2$(Ga$_{0.26}$Ge$_{0.74}$)$_7$, Pearson symbol *oS*80, space group *Cmce*) [1], DyGa$_{2.92-2.52}$Ge$_{0.08-0.48}$ (Mg$_3$In, *hR*48, *R*-3*m*) [2], DyGa$_{2.32-2.20}$Ge$_{0.68-0.80}$ (PuAl$_3$, *hP*24, *P*6$_3$/*mmc*) [2], DyGa$_{1.4}$Ge$_{0.6}$ (α-ThSi$_2$, *tI*12, *I*4$_1$/*amd*) [3], Dy$_4$Ga$_{1.4}$Ge$_{5.6}$ (Er$_4$(Ga$_{0.19}$Ge$_{0.81}$)$_7$, *hP*11, *P*-6*m*2) [4], Dy$_3$Ga$_{3.5}$Ge$_{1.5}$ (Tm$_3$Ga$_5$, *oP*32, *Pnma*) [5], and Dy$_3$Ga$_{2.8-2.4}$Ge$_{2.2-2.6}$ (Pu$_3$Pd$_5$, *oS*32, *Cmcm*) [5]. The crystal structures were determined by X-ray powder diffraction and the positions of the *p*-element atoms were assumed to be occupied by statistical mixtures of Ga and Ge atoms. The Ga-rich Mg$_3$In- and PuAl$_3$-type phases belong to the family of close-packed structures and are characterized by cuboctahedral and anticuboctahedral coordination of the atoms. In the structure of the Ge-rich compound Dy$_2$Ga$_{2.23-1.24}$Ge$_{4.77-5.76}$ the *p*-element atoms have square antiprismatic and trigonal prismatic coordination, and form a three-dimensional framework. The α-ThSi$_2$-type phase exhibits trigonal-prismatic coordination of the Ga/Ge atoms, which also here form a three-dimensional network. The structure type Er$_4$(Ga$_{0.19}$Ge$_{0.81}$)$_7$, to which the crystal structure of the compound Dy$_4$Ga$_{1.4}$Ge$_{5.6}$ belongs, is a vacancy-ordered derivative of the structure type AlB$_2$. Consequently, the *p*-element atoms have trigonal-prismatic coordination and form planar nets, stacked in the crystallographic direction [001] of the hexagonal lattice. The structures of the two ternary compounds with the highest Dy content (37.5 at.%), Dy$_3$Ga$_{3.5}$Ge$_{1.5}$ and Dy$_3$Ga$_{2.8-2.4}$Ge$_{2.2-2.6}$, are characterized by trigonal-prismatic and icosahedral coordination of the Ga/Ge atoms, which form isolated, empty square pyramids, interpreted as *arachno*-clusters of the Wade type. In the structures of all of the ternary compounds, except the close-packed structures, a tendency towards the formation of covalent bonds between *p*-element atoms in three-dimensional frameworks, planar nets or isolated clusters was deduced by analyzing the interatomic distances.

The aim of the present work was the refinement of the crystal structure of the new ternary compound DyGa$_{0.5-0.4}$Ge$_{1.3-1.4}$, which was found during a systematic investigation of the phase equilibria in the ternary system Dy–Ga–Ge at 600°C. It is the third representative of the structure type Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$ (*oI*16, *Imma*) identified in *R*–Ga–Ge systems [6], after YGa$_{0.7}$Ge$_{1.0}$ [7] and GdGa$_{0.48}$Ge$_{1.22}$ [8].

Experimental

Alloys were synthesized from high-purity metals (Dy ≥ 99.9 wt.%, Ga ≥ 99.99 wt.%, Ge ≥ 99.999 wt.%) by arc-melting in a water-cooled copper crucible with a tungsten electrode under a purified argon atmosphere, using Ti as a getter. To achieve high efficiency of the interaction between the components and homogeneity, the samples were

remelted twice. After the synthesis, the alloys were wrapped into tantalum foil, sealed in quartz ampoules under vacuum, and annealed at 600°C for 720 h. Finally, the ampoules with the samples were rapidly quenched into cold water. The weight losses did not exceed 1 wt.% of the total mass, which was approximately 1 g for each alloy.

Phase analysis was performed using X-ray powder diffraction patterns collected on a diffractometer DRON-2.0M (Fe $K\alpha$-radiaton), and the WinXPOW program package [9]. It revealed the presence of a new ternary compound in the samples of nominal compositions Dy$_{35}$Ga$_{25-10}$Ge$_{40-55}$. The positions and intensities of the diffraction peaks of the new compound and the similarity with the X-ray powder diffraction patterns calculated for YGa$_{0.7}$Ge$_{1.0}$ [7] and GdGa$_{0.48}$Ge$_{1.22}$ [8] indicated possible formation of the structure type Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$, whereas the slight difference between cell parameters in different samples indicated the existence of a certain homogeneity range. Two-phase samples of nominal compositions Dy$_{35}$Ga$_{20}$Ge$_{45}$ and Dy$_{35}$Ga$_{15}$Ge$_{50}$ with different admixture phases were used for the refinement of the crystallographic parameters.

The compositions of the phases in the samples Dy$_{35}$Ga$_{20}$Ge$_{45}$ and Dy$_{35}$Ga$_{15}$Ge$_{50}$ were established by local energy-dispersive X-ray (EDX) spectral analysis performed on a raster electron microscope REMMA-102-02 equipped with a spectrometer EDAR. Secondary electron images of polished surfaces of the samples are shown in Fig. 1; phase compositions are listed in Table 1.

X-ray powder diffraction patterns were obtained at room temperature on a diffractometer STOE Stadi P equipped with a linear position-sensitive detector (Cu $K\alpha_1$-radiation, angular range $6° \leq 2\theta \leq 110°$, step 0.015°).

The crystal structure of the title compound was refined by the Rietveld method using the FullProf Suite program package [10], starting from the atom coordinates of the structure type Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$ [7]. The admixture phases, PuAl$_3$-type DyGa$_{2.32}$Ge$_{0.68}$ (*hP*24, *P6$_3$/mmc*, a = 6.0977(6), c = 14.3216(8) Å; 12.9(2) wt.% in the alloy Dy$_{35}$Ga$_{20}$Ge$_{45}$), and Cu$_3$Au-type DyGa$_{1.6}$Ge$_{1.4}$ (*cP*4, *Pm*-3*m*, a = 4.2658(4) Å; 7.4(1) wt.% in the alloy Dy$_{35}$Ga$_{15}$Ge$_{50}$) were modeled with individual scale factors and cell parameters, while the profile parameters were constrained to be the same as for the main phase. The Cu$_3$Au-type phase is a new ternary compound, which exists at 600°C in the system Dy–Ga–Ge [11]. The similarity of the atomic scattering factors of Ga and Ge prevents their distinguishing by X-ray diffraction, thus, any Ga/Ge position was assumed to be occupied by a statistical mixture of Ga and Ge atoms in ratios given by the compositions obtained by energy-dispersive X-ray spectroscopy. The backgrounds were defined using the Fourier filtering technique. Experimental, calculated, and difference X-ray powder diffraction patterns are presented in Fig. 2; experimental details and crystallographic data for the main phases in the alloys Dy$_{35}$Ga$_{20}$Ge$_{45}$ and Dy$_{35}$Ga$_{15}$Ge$_{50}$ are listed in Table 2.
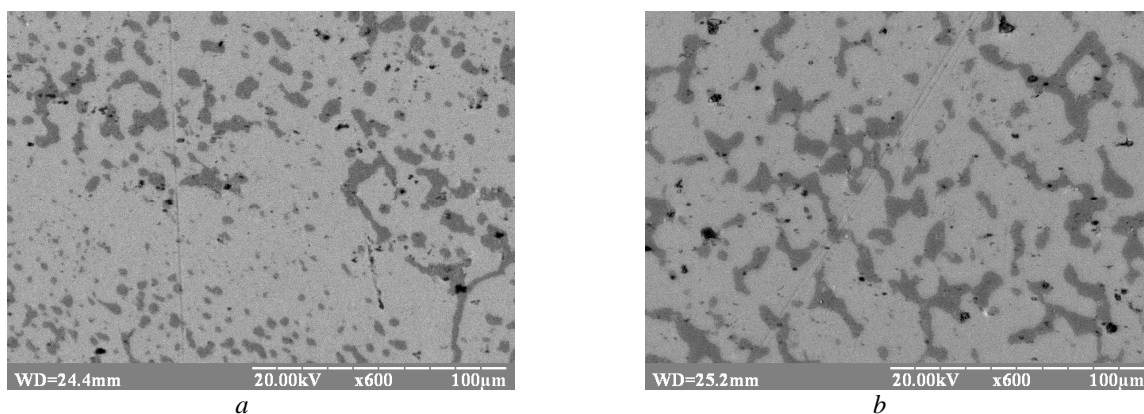
Fig. 1 Secondary electron images of polished surfaces of the samples Dy$_{35}$Ga$_{20}$Ge$_{45}$ (*a*) and Dy$_{35}$Ga$_{15}$Ge$_{50}$ (*b*). Black spots correspond to pores in the samples.

Table 1 Compositions of the phases in the alloys Dy$_{35}$Ga$_{20}$Ge$_{45}$ and Dy$_{35}$Ga$_{15}$Ge$_{50}$ from EDX analysis (formulas standardized to 1 Dy atom).

Nominal composition of the alloy	Dy$_{35}$Ga$_{20}$Ge$_{45}$	Dy$_{35}$Ga$_{15}$Ge$_{50}$
Gray phase (main)	Dy$_{36(2)}$Ga$_{18(2)}$Ge$_{46(2)}$ (DyGa$_{0.50(6)}$Ge$_{1.28(6)}$)	Dy$_{36(1)}$Ga$_{14(1)}$Ge$_{50(1)}$ (DyGa$_{0.39(3)}$Ge$_{1.39(3)}$)
Dark phase	Dy$_{25(2)}$Ga$_{58(2)}$Ge$_{17(2)}$ (DyGa$_{2.32(8)}$Ge$_{0.68(8)}$)	Dy$_{25(1)}$Ga$_{40(1)}$Ge$_{35(1)}$ (DyGa$_{1.60(4)}$Ge$_{1.40(4)}$)
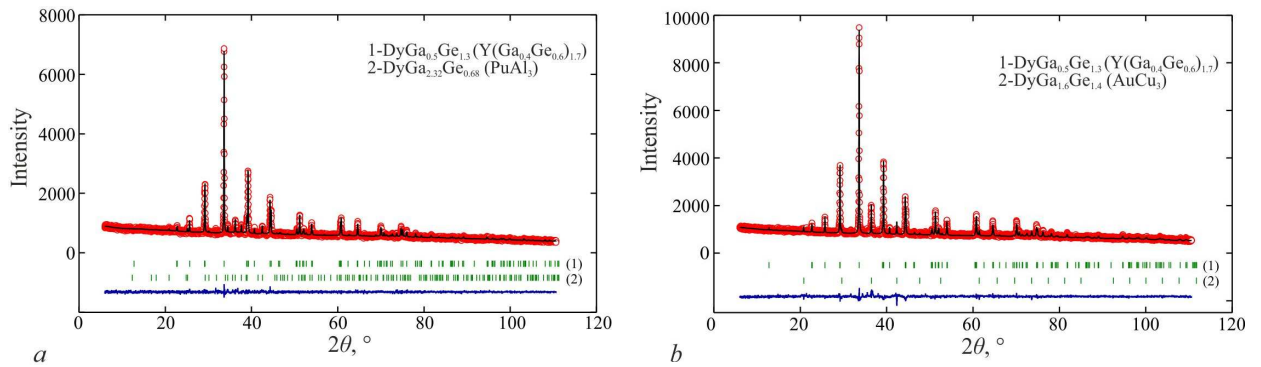
Fig. 2 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the samples (*a*) Dy$_{35}$Ga$_{20}$Ge$_{45}$ and (*b*) Dy$_{35}$Ga$_{15}$Ge$_{50}$ (Cu $K\alpha_1$-radiation). Vertical bars indicate the positions of reflections of the individual phases.

Table 2 Experimental details and crystallographic data for the Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$-type phase in the samples Dy$_{35}$Ga$_{20}$Ge$_{45}$ and Dy$_{35}$Ga$_{15}$Ge$_{50}$.

| Nominal composition of the alloy		Dy$_{35}$Ga$_{20}$Ge$_{45}$	Dy$_{35}$Ga$_{15}$Ge$_{50}$
Phase composition		DyGa$_{0.5}$Ge$_{1.3}$	DyGa$_{0.4}$Ge$_{1.4}$
Content, mass %		92.6(9)	87.1(9)
Structure type		Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$	
Pearson symbol		*oI*16	
Space group		*Imma*	
Cell parameters:	*a*, Å	4.0709(3)	4.0641(3)
	b, Å	4.0845(3)	4.0870(3)
	c, Å	13.8426(9)	13.888(11)
Cell volume *V*, Å^3		230.168(3)	230.675(3)
Formula units per unit cell *Z*		4	
Density D_X, g cm^{-3}		8.410	8.451
Preferred orientation: value / [direction]		0.911(5) / [110]	0.915(6) / [110]
Reliability factors:	R_B	0.0775	0.0749
	R_F	0.0536	0.0485
Profile parameters	*U*	-0.0112(5)	-0.0063(6)
	V	0.0338(5)	0.0287(6)
	W	0.0027(12)	0.0041(13)
Shape parameter η		0.698(6)	0.655(12)
Asymmetry parameters *P*1, *P*2		0.062(9), 0.0182(16)	0.091(9), 0.0298(18)
Reliability factors:	R_p	0.0302	0.0323
	R_{wp}	0.382	0.0409
	χ^2	1.30	1.05

Results and discussion

The crystal structure of the ternary compound of variable composition Dy(Ga,Ge)$_{1.8}$ belongs to the orthorhombic structure type Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$. Atom coordinates and isotropic displacement parameters for DyGa$_{0.5}$Ge$_{1.3}$ and DyGa$_{0.4}$Ge$_{1.4}$ are given in Table 3. The structure is characterized by one site for the Dy atoms and by two sites for the statistical mixture of Ga and Ge atoms. The main feature of the structure is the local positional disorder of the *p*-element atoms, modeled by a split position 8*i*, occupied by 41 and 39 % in DyGa$_{0.5}$Ge$_{1.3}$ and DyGa$_{0.4}$Ge$_{1.4}$, respectively,

instead of one 4-fold site. The refined separations between the neighboring positions are 0.811(10) and 0.854(11) Å in DyGa$_{0.5}$Ge$_{1.3}$ and DyGa$_{0.4}$Ge$_{1.4}$, respectively. It should be noted that the occupancy of site *M*2 cannot exceed 50 %.

The content of the unit cell and the coordination polyhedra of the atoms in the structure of DyGa$_{0.5}$Ge$_{1.3}$ are shown in Fig. 3. The Dy atoms center twenty-vertex pseudo Frank-Kasper polyhedra Dy*M*$_{12}$Dy$_8$. The coordination polyhedra of the smaller atoms are three-capped trigonal prisms $\underline{M}$1Dy$_6$*M*$_3$, $\underline{M}$2Dy$_6$*M*$_3$. The interatomic distances within the coordination polyhedra are summarized in Table 4.

Table 3 Atomic coordinates, site occupancies and isotropic displacement parameters for DyGa$_{0.5}$Ge$_{1.3}$ and DyGa$_{0.4}$Ge$_{1.4}$ (structure type Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$, Pearson symbol *oI*16, space group *Imma*).

Site	Wyckoff position	x	y	z	Occupancy	B_{iso}, Å^2
DyGa$_{0.5}$Ge$_{1.3}$ ($a = 4.0641(3)$, $b = 4.0870(3)$, $c = 13.888(11)$ Å, $M = 0.28$Ga $+ 0.72$Ge)
Dy	4*e*	0	¼	0.6236(2)	1	0.53(7)
*M*1	4*e*	0	¼	0.0519(4)	1	1.43(14)
*M*2	8*i*	0.099(18)	¼	0.2247(5)	0.41(6)	1.32(4)
DyGa$_{0.4}$Ge$_{1.4}$ ($a = 4.0709(3)$, $b = 4.0845(3)$, $c = 13.8426(9)$ Å, $M = 0.22$Ga $+ 0.78$Ge)
Dy	4*e*	0	¼	0.6236(2)	1	0.56(6)
*M*1	4*e*	0	¼	0.0512(4)	1	1.22(13)
*M*2	8*i*	0.105(18)	¼	0.2225(6)	0.39(6)	1.29(4)
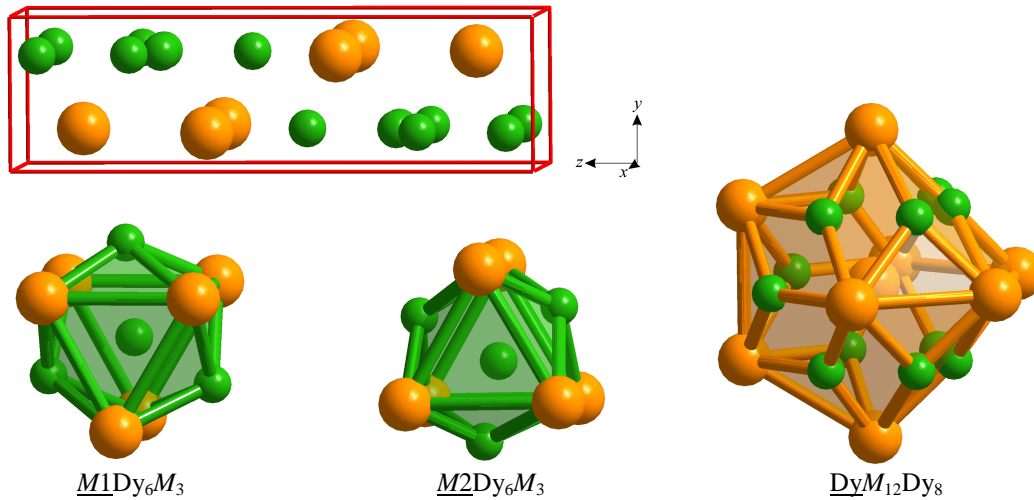
Fig. 3 Cell content and coordination polyhedra of the atoms in the structure of DyGa$_{0.5}$Ge$_{1.3}$.

Polyhedra labels: *M*1Dy$_6$*M*$_3$ *M*2Dy$_6$*M*$_3$ Dy*M*$_{12}$Dy$_8$

Table 4 Interatomic distances (δ) and coordination numbers (CN) in the structures of DyGa$_{0.5}$Ge$_{1.3}$ and DyGa$_{0.4}$Ge$_{1.4}$ (Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$, *oI*16, *Imma*).

| Atoms		δ, Å		CN
		DyGa$_{0.5}$Ge$_{1.3}$ [a]	DyGa$_{0.4}$Ge$_{1.4}$ [b]	
Dy	$-$ 2 *M*2	2.965(5)	2.938(6)	
	$-$ 4 *M*2	2.963(5) (*3.477(6)*) [c]	2.982(6) (*3.480(6)*) [c]	
	$-$ 4 *M*1	3.049(2)	3.053(2)	
	$-$ 2 *M*1	3.173(5)	3.162(5)	20
	$-$ 2 Dy	3.995(3)	3.985(3)	
	$-$ 2 Dy	4.056(3)	4.048(3)	
	$-$ 2 Dy	4.0641(3)	4.0709(3)	
	$-$ 2 Dy	4.0870(3)	4.0844(3)	
*M*1	$-$ 1 *M*2	2.434(9)	2.409(10)	
	$-$ 2 *M*1	2.501(5)	2.486(4)	9
	$-$ 4 Dy	3.049(2)	3.053(2)	
	$-$ 2 Dy	3.173(5)	3.162(5)	
*M*2	$-$ 2 *M*2	2.150(10) (*1.409(10), 2.929(10)*) [c]	2.173(11) (*1.405(11), 2.988(11)*) [c]	
	$-$ 1 *M*1	2.434(9)	2.409(10)	9
	$-$ 2 Dy	2.965(5)	2.938(6)	
	$-$ 4 Dy	2.963(5) (*3.477(6)*) [c]	2.982(6) (*3.480(6)*) [c]	

[a] $M = 0.28$Ga $+ 0.72$Ge; [b] $M = 0.22$Ga $+ 0.78$Ge; [c] alternative interatomic distances due to splitting of site *M*2 are indicated in italics.

The structure type Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$ (*oI*16, *Imma*) derives from the binary type GdSi$_{1.4}$ (*oI*12, *Imma*) [12] with the same space group and similar cell parameters but differs from it by the Wyckoff sequence due to splitting of one position 4*e* (in GdSi$_{1.4}$) into 8*i* (in Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$). The structure type GdSi$_{1.4}$ is an orthorhombically distorted variant of the structure type α-ThSi$_2$ [13]. These types belong to the large family of structures that have trigonal-prismatic coordination of the smallest atoms. One of the simplest structure types of this family is the binary type AlB$_2$ [14], which is represented in the system Dy–Ga–Ge by the binary dysprosium digallide [15] and the solid solution of substitution type based on it (DyGa$_{2-1.55}$Ge$_{0-0.45}$ at 600°C) [3]. In the structure type AlB$_2$ the trigonal prisms, formed by the larger atoms and centered by the smaller atoms, fill space by connecting bases along the crystallographic direction [001] and rectangular faces in the plane perpendicular to it. In the structure type α-ThSi$_2$, which is adopted in the system Dy–Ga–Ge at 600°C by the ternary compound DyGa$_{1.4}$Ge$_{0.6}$ [3], the 3-fold axes of the trigonal prisms in consecutive layers are rotated by 90°. Similar stacking of slightly deformed trigonal prisms is observed for the structure types GdSi$_{1.4}$ and Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$. The α-ThSi$_2$ type has also been reported for the high-temperature phase DyGe$_{1.67}$ (*a* = 4.047, *c* = 13.716 Å) [16], which does not exist at 600°C. However, later the structure type Y$_3$Ge$_5$, which is an ordered vacancy derivative of the type α-ThSi$_2$,

was assigned to this phase: *oF*64, *Fdd*2, *a* = 5.729, *b* = 17.190, *c* = 13.678 Å [17]. The structure type GdSi$_{1.4}$ is not represented in the system Dy–Ga–Ge at 600°C.

The small atoms in the AlB$_2$-type phase DyGa$_{2-1.55}$Ge$_{0-0.45}$ are relatively strongly bonded forming planar graphite-like nets: δ_{M-M} = 2.411 Å for DyGa$_{1.55}$Ge$_{0.45}$. In the α-ThSi$_2$-type ternary compound DyGa$_{1.4}$Ge$_{0.6}$ the Ga/Ge atoms form a three-dimensional network with the corresponding contact distances δ_{M-M} = 2.378 and 2.425 Å (Fig. 4*a*). In the structure of the ternary phase DyGa$_{0.5-0.4}$Ge$_{1.3-1.4}$ positional disorder was observed for one site of Ga/Ge atoms (Fig. 4*b*): atoms from site *M*2 "move" from the ideal positions, that in real structure would provoke breaking of the 3D network: δ_{M2-M2} = 2.150(10) or 2.929(10) Å for DyGa$_{0.5}$Ge$_{1.3}$; δ_{M2-M2} = 2.173(11) or 2.988(11) Å for DyGa$_{0.4}$Ge$_{1.4}$. Commensurate values for the corresponding distances were observed in the structures of the isotypic ternary compounds YGa$_{0.7}$Ge$_{1.0}$ (δ_{M2-M2} = 2.184 or 2.953 Å) [7] and GdGa$_{0.48}$Ge$_{1.22}$ (δ_{M2-M2} = 2.186 or 2.929 Å) [8]. This may be caused by selective replacement of less electronegative Ga atoms (element of group IIIA) by more electronegative Ge atoms (element of group IVA) in only one of the atom sites. Similar displacement disorder of *p*-element atoms was observed in the structure of the ternary compound Dy$_2$Ga$_{1.8}$Ge$_{5.2}$ [1].
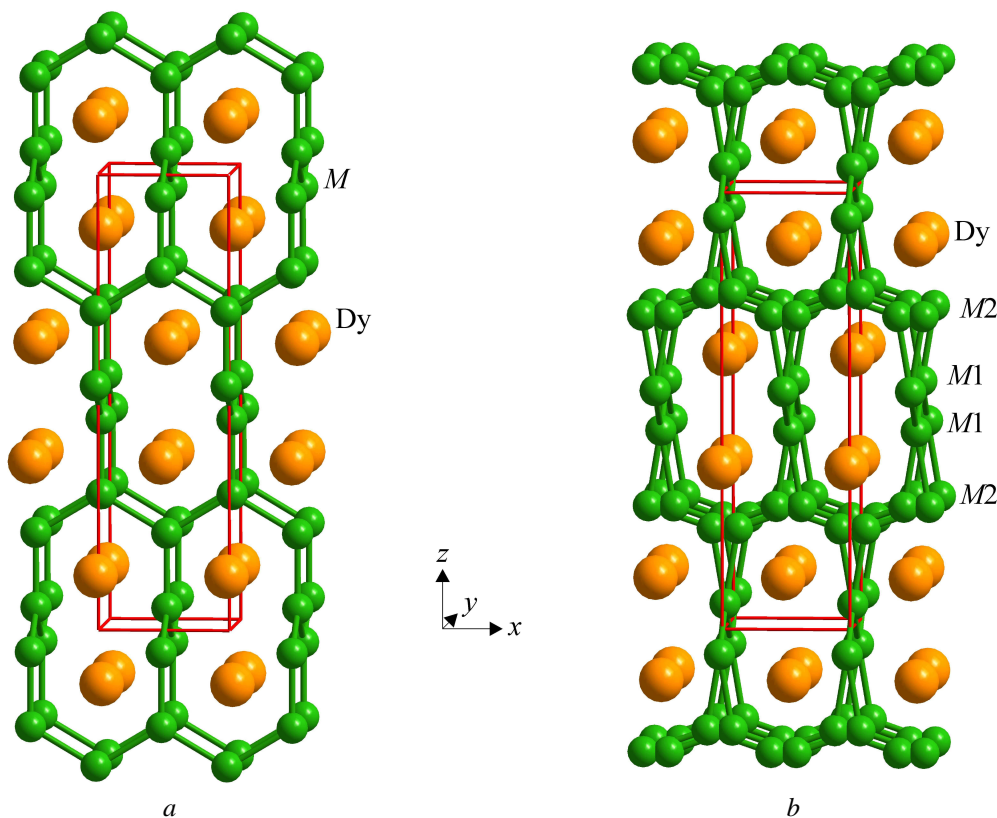
Fig. 4 Ga/Ge atom networks in the structures of the ternary compounds (*a*) DyGa$_{1.4}$Ge$_{0.6}$ and (*b*) DyGa$_{0.5}$Ge$_{1.3}$.

Conclusions

The new ternary compound DyGa$_{0.5-0.4}$Ge$_{1.3-1.4}$ was synthesized and its crystal structure was refined by Rietveld method from X-ray powder diffraction data. The structure belongs to the structure type Y(Ga$_{0.4}$Ge$_{0.6}$)$_{1.7}$, which is closely related to the structure type GdSi$_{1.4}$, and is a representative of the family of structures with trigonal-prismatic coordination of the smaller atoms. Ga/Ge atoms form relatively strong bonds within a three-dimensional network. Local displacement disorder of one site occupied by Ga/Ge atoms, presumably caused by electronic factor, was modeled by split positions.

Acknowledgment

References

[1] Ya. Tokaychuk, T. Delenko, R. Gladyshevskii, *Chem. Met. Alloys* 6 (2013) 220-224.

[2] T. Delenko, A. Horyn, Ya. Tokaychuk, R. Gladyshevskii, *Solid State Phenom.* 289 (2019) 53-58.

[3] Ya. Tokaychuk, T. Delenko, R. Gladyshevskii, *Visn. Lviv. Univ., Ser. Khim.* 55 (2014) 47-53.

[4] T. Delenko, Ya. Tokaychuk, R. Gladyshevskii // *Coll. Abstr. XIV Int. Conf. Cryst. Chem. Intermet. Compd.*, Lviv (2019). 105.

[5] T. Delenko, Ya. Tokaychuk, R. Gladyshevskii, *Visn. Lviv. Univ., Ser. Khim.* 60 (2019) 91-102.

[6] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, ASM International, Materials Park, OH, USA, Release 2018/19.

[7] V.Ya. Markiv, N.M. Belyavina, M.V. Speka, *J. Alloys Compd.* 285 (1999) 167-171.

[8] G. Venturini, A. Vernière, *J. Alloys Compd.* 305 (2000) 7-13.

[9] *WinXPow. Version 2.21*, Stoe & Cie GmbH, Darmstadt, 2007.

[10] J. Rodríguez-Carvajal, *Commission on Powder Diffraction (IUCr), Newsletter* 26 (2001) 12-19.

[11] T.O. Delenko, *Thesis*, Ivan Franko National University of Lviv, 2019.

[12] J.A. Perri, I. Binder, B. Post, *J. Phys. Chem.* 63 (1959) 616-619.

[13] G. Brauer, A. Mitius, *Z. Anorg. Allg. Chem.* 249 (1942) 325-339.

[14] W. Hoffmann, W. Jäniche, *Naturwissenschaften* 23 (1935) 851.

[15] S.E. Haszko, *Trans. Metall. Soc. AIME* 221 (1961) 201-204.

[16] K. Sekizawa, *J. Phys. Soc. Jpn.* 21 (1966) 1137-1142.

[17] P. Schobinger Papamantellos, D.B. De Mooij, K.H.J. Buschow, *J. Less-Common Met.* 163 (1990) 319-330.