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Crystal structure of $Dy_2Ga_{1.8}Ge_{5.2}$

Yaroslav TOKAYCHUK[1]*, Taras DELENKO[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: tokaychuk@mail.lviv.ua*

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A new ternary intermetallic compound, $Dy_2Ga_{1.8}Ge_{5.2}$, was synthesized and its crystal structure determined from X-ray powder diffraction data: structure type $Sm_2(Ga_{0.26}Ge_{0.74})_7$, Pearson symbol *oS*80-8, space group *Cmce*, *a* = 8.3284(6), *b* = 8.0320(6), *c* = 20.9167(15) Å, *Z* = 8. The structure type $Sm_2(Ga_{0.26}Ge_{0.74})_7$ is closely related to the type $Ce_2(Ga_{0.1}Ge_{0.9})_7$. Both types are vacancy derivatives of the structure type $SmNiGe_3$, which is a linear intergrowth of layers characteristic of the structure types $BaAl_4$, AlB_2, and α-Po. In the structure of $Dy_2Ga_{1.8}Ge_{5.2}$ every second square antiprism in the $BaAl_4$-type slabs is vacant and the Ga/Ge atoms centering the remaining antiprisms are subjected to displacement disorder modeled by a split site.

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

Introduction

The crystal structure of the ternary compound $Ce_2(Ga_{0.1}Ge_{0.9})_7$ (own structure type, Pearson symbol *oS*72, space group *Cmce*, *a* = 8.6373, *b* = 8.2697, *c* = 21.451 Å) was solved from X-ray single-crystal diffraction data in 1989 [1]. At 600°C this compound has a certain homogeneity range, which can be described by the formula $Ce_2Ga_{2.24\text{-}0.91}Ge_{4.76\text{-}6.09}$ [2]. Ternary compounds isotypic to $Ce_2(Ga_{0.1}Ge_{0.9})_7$ have been reported in other *R*–Ga–Ge systems (*R* = Y, Pr, Nd, Gd, Tb) [2-4]. Atomic coordinates were refined for $Y_2Ga_{0.34}Ge_{6.66}$ (*a* = 8.242, *b* = 7.964, *c* = 20.72 Å) [3] and $Tb_2Ga_{1.82}Ge_{5.18}$ (*a* = 8.2790, *b* = 7.9946, *c* = 20.787 Å) [4], whereas for the other compounds the structure type was assigned based on X-ray diffraction phase analysis. Later the crystal structure of the ternary compound $Sm_2Ga_{1.8\text{-}0.9}Ge_{5.2\text{-}6.1}$ was determined from X-ray powder diffraction data for the composition $Sm_2Ga_{1.8}Ge_{5.2}$ [5]. It defines a closely related structure type ($Sm_2(Ga_{0.26}Ge_{0.74})_7$, Pearson symbol *oS*80-8, space group *Cmce*, *a* = 8.4622, *b* = 8.1534, *c* = 21.1243 Å), which differs from the former by the splitting of one of the 8-fold sites occupied by Ga/Ge atoms in $Ce_2(Ga_{0.1}Ge_{0.9})_7$ into a site in Wyckoff position 16*g*.

The aim of the present work was to determine the crystal structure of the new ternary compound $Dy_2(Ga_xGe_{1-x})_7$, which was found during studies of the phase equilibria in the ternary system Dy–Ga–Ge at 600°C.

Experimental

An alloy of nominal composition $Dy_{22}Ga_{20}Ge_{58}$ was 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 under a purified argon atmosphere, using a tungsten electrode. To achieve good homogeneity, the sample was melted twice. After the synthesis the alloy was wrapped into tantalum foil, sealed in a quartz ampoule under vacuum and annealed at 600°C for 720 h. Finally the ampoule with the sample was quenched into cold water. The weight loss, which was controlled at all stages of the synthesis, did not exceed 1 % of the total mass, which was approximately 1 g.

Phase analysis was carried out using the WinXPOW program package [6] on an X-ray powder diffraction pattern recorded on a STOE Stadi P diffractometer equipped with a linear position-sensitive detector (Cu $K\alpha_1$-radiation, angular range $4° \leq 2\theta \leq 110°$, step 0.015°). The crystal structure of the ternary compound $Dy_2(Ga_xGe_{1-x})_7$ was refined by the Rietveld method as included in the FullProf Suite program package [7], starting from the atom coordinates of the structure type $Ce_2(Ga_{0.1}Ge_{0.9})_7$ [1]. Due to the similarity of the atomic scattering factors of Ga and Ge, the Ga/Ge positions were assumed to be occupied by a mixture of Ga and Ge atoms in the ratio given by the nominal composition. In spite of the relatively good profile fit obtained by using as model the structure type $Ce_2(Ga_{0.1}Ge_{0.9})_7$, the values of the isotropic displacement parameters suggested disorder on one of the six sites occupied by Ga/Ge atoms. Better values were obtained considering splitting of this site, initially located in Wyckoff position 8*f*, into a half-occupied site in Wyckoff position 16*g*. The resulting model corresponds to the structure type $Sm_2(Ga_{0.26}Ge_{0.74})_7$ [5]. The refined distance between neighboring positions of the split site was 0.57(2) Å. In the final cycles of the refinement an overall isotropic displacement parameter was refined for the positions occupied by Ga/Ge atoms. Small amounts (4.5 wt.% from the Rietveld refinement) of elementary Ge (structure type C (diamond), space group *Fd*-3*m*, $a = 5.6542(5)$ Å) were found in the $Dy_{22}Ga_{20}Ge_{58}$ sample, in agreement with the slight deviation from the Dy:(Ga,Ge) ratio 2:7. One scale factor and one cell parameter were refined for the admixture phase, while the profile parameters were constrained to be equal to those of the main phase. Finally, in total 33 parameters were allowed to vary: 2θ shift (with $\sin(2\theta)$ dependence sample transparency coefficient), two scale factors, four cell parameters, six profile parameters (pseudo-Voigt profile), 17 positional parameters, two atomic displacement parameters, and one texture parameter. The background was defined using a Fourier filtering technique. The fit between the experimental and calculated X-ray powder diffraction patterns for the sample of nominal composition $Dy_{22}Ga_{20}Ge_{58}$ is shown in Fig. 1. Experimental details and crystallographic data for the individual phases are listed in Table 1.

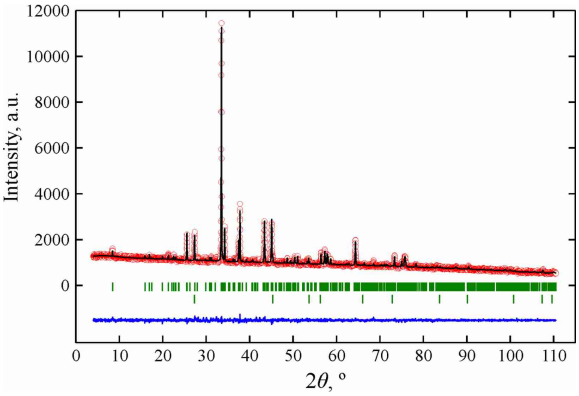


Fig. 1 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns for the sample $Dy_{22}Ga_{20}Ge_{58}$ (Cu $K\alpha_1$-radiation). Vertical bars indicate the positions of the reflections of $Dy_2Ga_{1.8}Ge_{5.2}$ and Ge.

Results and discussion

The crystal structure of the ternary compound $Dy_2Ga_{1.8}Ge_{5.2}$ belongs to the orthorhombic structure type $Sm_2(Ga_{0.26}Ge_{0.74})_7$. The positional coordinates and isotropic displacement parameters obtained from the Rietveld refinement are listed in Table 2. The structure contains one site occupied by Dy atoms and six sites occupied by Ga and Ge atoms.

Table 1 Experimental details and crystallographic data for the individual phases in the sample $Dy_{22}Ga_{20}Ge_{58}$.

Phase		$Dy_2Ga_{1.8}Ge_{5.2}$	Ge
Content, wt.%		95.5(10)	4.5(1)
Structure type		$Sm_2(Ga_{0.26}Ge_{0.74})_7$	C (diamond)
Pearson symbol		*oS*80-8	*cF*8
Space group		*Cmce* (#64)	*Fd*-3*m* (#227)
Cell parameters:	*a*, Å	8.3284(6)	5.6542(5)
	b, Å	8.0320(6)	–
	c, Å	20.9167(15)	–
Cell volume *V*, Å^3		1399.19(17)	180.77(3)
Number of formula units in the cell *Z*		8	8
Density D_X, g cm^{-3}		7.861	5.335
Preferred orientation: value / [direction]		0.898(6) / [110]	–
Reliability factors:	R_B	0.1050	0.0963
	R_F	0.1750	0.1040
Profile parameters	*U*	0.005(5)	
	V	0.014(5)	
	W	0.0063(10)	
Shape parameter		0.43(5)	
Asymmetry parameters		0.103(8), 0.0245(18)	
Reliability factors:	R_p	0.0276	
	R_{wp}	0.0358	
	χ^2	1.24	

As mentioned above, a peculiarity of the structure is the splitting of one of the Ga/Ge (M) sites. The small M atoms form an infinite three-dimensional framework containing layers of empty M_8 cubes and zigzag chains running along [010] (Fig. 2). The layers of cubes and the zigzag chains are interconnected along the crystallographic direction [001] *via* Ga/Ge atoms from the split site $M1$. One of the faces of the M_8 cubes is enlarged and rather rhomb-like. Site $M1$ is split along the longer diagonal of this face, tending to achieve a four-bonded state instead of the five-bonded one in the idealized ordered structure. For the ternary compound $Sm_2Ga_{1.8}Ge_{5.2}$, the following model was proposed for the distribution of the Ga and Ge atoms: the M_8 cubes are formed by Ge atoms, while site $M1$ contains large amounts of Ga, which stabilize the M_{8+1} fragments [5].

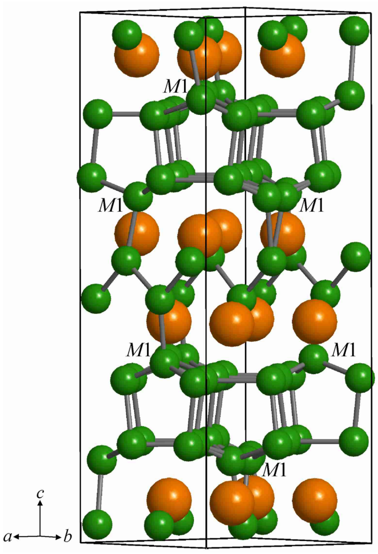


Fig. 2 Unit cell content of the compound $Dy_2Ga_{1.8}Ge_{5.2}$, emphasizing the Ga/Ge framework.

Selected interatomic distances, coordination numbers and coordination polyhedra in the structure of $Dy_2Ga_{1.8}Ge_{5.2}$ are presented in Table. 3. The polyhedra around the Dy atoms have 18 vertexes ($\underline{Dy}M_{12}Dy_6$) and can be described as pentagonal prisms M_{10} with two additional M and six additional Dy atoms. The M sites have coordination numbers 8 ($M2$, $M3$, $M5$, $M6$) and 9 ($M1$, $M4$). The corresponding polyhedra are: a square antiprism Dy_4M_4 with one additional M atom for $M1$, trigonal prisms Dy_2M_4 with two additional M atoms for $M2$, $M5$, and $M6$, a trigonal prism Dy_6 with two additional M atoms for $M3$, and a trigonal prism Dy_6 with three additional M atoms for $M4$. Like for $Sm_2Ga_{1.8}Ge_{5.2}$, as a consequence of the splitting of site $M1$ the distances to the two neighboring $M2$ atoms have considerably different lengths (2.32 and 2.85 Å for Sm, 2.17 and 2.70 Å for Dy). The coordination polyhedron of site $M4$ is similar to the polyhedra of the Ga/Ge sites in the structures of the recently reported AlB_2- and α-$ThSi_2$-type phases in the system Dy–Ga–Ge at 600°C, namely $DyGa_{2\text{-}1.55}Ge_{0\text{-}0.45}$ and $DyGa_{1.4}Ge_{0.6}$ [8]. It is difficult to draw any conclusions concerning possible ordering of Ga and Ge atoms from the analysis of the structure, but it seems reasonable to believe that Ga is mainly concentrated on site $M1$, as suggested for $Sm_2Ga_{1.8}Ge_{5.2}$ in [5].

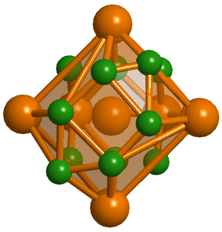
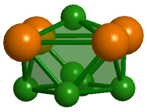
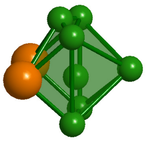
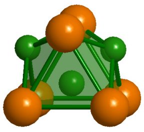
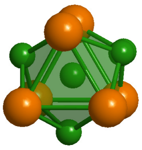
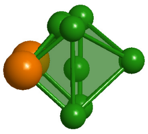
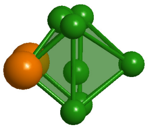
The structure types $Sm_2(Ga_{0.26}Ge_{0.74})_7$ and $Ce_2(Ga_{0.1}Ge_{0.9})_7$ are vacancy derivatives of the structure type $SmNiGe_3$ (*oS*20, *Cmmm*, $a = 4.102$, $b = 21.657$, $c = 4.092$ Å) [9]. The latter belongs to a homologous series of structures formed by linear intergrowth of slabs characteristic of the simple structure types $BaAl_4$, AlB_2, and α-Po [5,10,11]. The defect $BaAl_4$-type slabs in $Dy_2Ga_{1.8}Ge_{5.2}$ contain $M1$-centered square antiprisms alternating with empty square antiprisms. The AlB_2-type fragments are formed by trigonal prisms of Dy atoms centered by Ga/Ge atoms from site $M4$, and the α-Po-type fragments are made from empty M_8 cubes. The ordered arrangement of vacancies in the $BaAl_4$-type slabs results in doubling of the two short translation periods as compared with the structure of $SmNiGe_3$. The intergrowth of slabs along [001] of the pseudo-tetragonal cell in $Dy_2Ga_{1.8}Ge_{5.2}$ is shown in Fig. 3. A monoclinic vacancy derivative of $SmNiGe_3$, which also forms in ternary *R*–Ga–Ge systems [12], was first refined on La_2AlGe_6 (*mS*36, *C*2/*m*, $a = 8.373$, $b = 8.833$, $c = 10.887$ Å, $\beta = 101.34°$) [13]. It is interesting that three of the closely related structure types mentioned above, namely $Ce_2(Ga_{0.1}Ge_{0.9})_7$, $SmNiGe_3$, and La_2AlGe_6, were found to coexist at the same temperature (600°C) in the system Y–Ga–Ge [3].

Table 2 Positional coordinates and isotropic displacement parameters for the compound $Dy_2Ga_{1.8}Ge_{5.2}$ (structure type $Sm_2(Ga_{0.26}Ge_{0.74})_7$, *oS*80-8, *Cmce*).

Site	Wyckoff position	x	y	z	B_{iso}, Å^2
Dy	16*g*	0.2504(6)	0.3721(19)	0.08098(10)	0.42(8)
$M1^{a,b}$	16*g*	0.0341(17)	0.1158(19)	0.1522(6)	1.95(10)
$M2^{a}$	16*g*	0.2758(9)	0.119(2)	0.1908(2)	1.95(10)
$M3^{a}$	8*f*	0	0.128(3)	0.4602(8)	1.95(10)
$M4^{a}$	8*f*	0	0.132(2)	0.0335(8)	1.95(10))
$M5^{a}$	8*f*	0	0.352(2)	0.3054(8)	1.95(10)
$M6^{a}$	8*f*	0	0.385(3)	0.1880(7)	1.95(10)

[a] $M = 0.26Ga + 0.74Ge$; [b] Occ. = 0.5.

Table 3 Interatomic distances (δ), coordination numbers (CN), and coordination polyhedra in the structure of the compound $\mathrm{Dy_2Ga_{1.8}Ge_{5.2}}$ (structure type $\mathrm{Sm_2(Ga_{0.26}Ge_{0.74})_7}$, *oS*80-8, *Cmce*).

Atoms [a]	δ, Å	CN	Polyhedron
Dy – 1 $M1$	2.945(16) (*3.411(16)*) [b]	18	 $\underline{\mathrm{Dy}}M_{12}\mathrm{Dy}_6$
– 1 $M3$	2.985(18)		
– 1 $M4$	3.008(14)		
– 1 $M2$	3.043(13)		
– 1 $M3$	3.051(19)		
– 1 $M6$	3.061(12)		
– 1 $M2$	3.072(14)		
– 1 $M4$	3.110(14)		
– 1 $M1$	3.114(17) (*3.474(16)*) [b]		
– 1 $M5$	3.161(13)		
– 1 $M4$	3.171(14)		
– 1 $M3$	3.276(14)		
– 1 Dy	3.915(8)		
– 1 Dy	3.962(8)		
– 2 Dy	4.02(15)		
– 1 Dy	4.157(8)		
– 1 Dy	4.171(8)		
$M1$ – 1 $M2$	2.169(16)	9	 $\underline{M1}\mathrm{Dy}_4M_5$
– 1 $M5$	2.31(2)		
– 1 $M6$	2.31(3)		
– 1 $M4$	2.50(2)		
– 1 $M2$	2.704(16)		
– 1 Dy	2.945(16)		
– 1 Dy	3.114(17)		
– 1 Dy	3.411(16)		
– 1 Dy	3.474(16)		
$M2$ – 1 $M1$	2.169(16) (*2.704(16)*) [b]	8	 $\underline{M2}\mathrm{Dy}_2M_6$
– 1 $M2$	2.515(9)		
– 1 $M5$	2.634(17)		
– 1 $M6$	2.65(2)		
– 1 Dy	3.043(13)		
– 1 Dy	3.072(14)		
– 1 $M6$	3.14(2)		
– 1 $M5$	3.145(17)		
$M3$ – 1 $M4$	2.463(3)	8	 $\underline{M3}\mathrm{Dy}_6M_2$
– 1 $M3$	2.65(3)		
– 2 Dy	2.985(18)		
– 2 Dy	3.051(19)		
– 2 Dy	3.276(14)		
$M4$ – 1 $M3$	2.463(3)	9	 $\underline{M4}\mathrm{Dy}_6M_3$
– 1 $M1$	2.50(2)		
– 1 $M4$	2.54(2)		
– 2 Dy	3.008(14)		
– 2 Dy	3.110(14)		
– 2 Dy	3.171(14)		
$M5$ – 1 $M1$	2.31(2)	8	 $\underline{M5}\mathrm{Dy}_2M_6$
– 1 $M6$	2.47(2)		
– 2 $M2$	2.634(17)		
– 2 $M2$	3.145(17)		
– 2 Dy	3.161(13)		
$M6$ – 1 $M1$	2.31(3)	8	 $\underline{M6}\mathrm{Dy}_2M_6$
– 1 $M5$	2.47(2)		
– 2 $M2$	2.65(2)		
– 2 Dy	3.061(12)		
– 2 $M2$	3.14(2)		

[a] M = 0.26Ga + 0.74Ge, [b] alternative interatomic distances due to splitting of site $M1$ are indicated in italics.

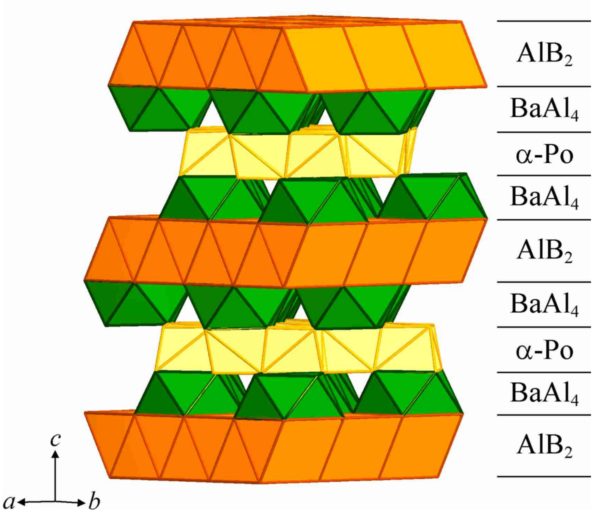


Fig. 3 Intergrowth of AlB_2-, α-Po-, and defect $BaAl_4$-type slabs along [001] in the structure of $Dy_2Ga_{1.8}Ge_{5.2}$.

Conclusions

The structure of the new ternary compound $Dy_2Ga_{1.8}Ge_{5.2}$ was refined by the Rietveld method from X-ray powder diffraction data. The structure belongs to the structure type $Sm_2(Ga_{0.26}Ge_{0.74})_7$, which differs from the closely related type $Ce_2(Ga_{0.1}Ge_{0.9})_7$ by the splitting of one of the sites occupied by Ga/Ge atoms. Both structure types may be considered as intergrowths of layers derived from the simple structure types $BaAl_4$, AlB_2, and α-Po.

Acknowledgements

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