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Crystal structure of the ternary compound $Dy_3Ga_{2.54}Sn_{2.46}$

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The crystal structure of the new ternary compound $Dy_3Ga_{2.54(5)}Sn_{2.46(5)}$ belongs to the Pu_3Pd_5 structure type (Pearson symbol *oS*32, space group *Cmcm*, *a* = 9.7300(3), *b* = 7.7081(2), *c* = 9.7925(3) Å). The atoms of the *p*-elements are distributed over three Wyckoff positions with a tendency towards ordering: two sites for Ga and one site for Sn (ideal composition $Dy_3Ga_3Sn_2$). They form isolated empty square-pyramidal clusters. The structure can also be decomposed into two kinds of layer. At *z* ≈ 0 and *z* ≈ ½ Dy (site Dy1) and Ga (site *M*2 = 0.81(3)Ga2 + 0.19(3)Sn2) atoms form slightly puckered deformed NaCl-type layers. At *z* = ¼ and *z* = ¾ Dy (site Dy2), Ga (*M*3 = 0.74(3)Ga3 + 0.26(3)Sn3) and Sn (*M*1 = 0.09(4)Ga1 + 0.91(4)Sn1) atoms form flat deformed $LiFeO_2$-type layers (the $LiFeO_2$ type is a ternary ordered derivative of the binary NaCl type). The structure type Pu_3Pd_5 belongs to the family of deformation variants of the structure type Rh_5Ge_3.

Dysprosium / Gallium / Tin / Intermetallic compound / X-ray powder diffraction / Crystal structure

Introduction

The structure type Pu_3Pd_5 (Pearson symbol *oS*32, space group *Cmcm*) [1] is adopted by binary compounds with alkaline-earth or rare-earth metals and *p*-elements of groups III and IV (In, Tl, Sn, Pb), Zr_3Rh_5, Zr_3Ga_5, U_3Ga_5, Th_3Tl_5, and Eu_3Ge_5 [2]. 18 ternary phases crystallizing with Pu_3Pd_5-type structures are divided into two groups: structures with statistical distribution of larger atoms (Pu sites, 5 representatives) and structures with statistical distribution of smaller atoms (Pd sites, 13 representatives). The latter compounds were found in the systems of Ba with *p*-elements of groups III and IV (Ga, In, Si, Ge, Sn, Pb) [3], La_3CuSn_4 [4], $Er_3Ga_{2.21}Ge_{2.79}$ [5] and $Sm_3Ga_{0.80\text{-}2.48}Sn_{4.20\text{-}2.52}$ [6]. For the latter compound a partially ordered distribution of Sn and Ga atoms over three crystallographic positions and an evolution of the structure as a function of the Ga content were reported. It was shown that the structure remains partially ordered within the whole homogeneity range of the compound.

During an investigation of the phase diagram of the ternary system Dy–Ga–Sn at 600ºC we identified a new ternary compound of variable composition $Dy_3Ga_{3.00\text{-}2.54}Sn_{2.00\text{-}2.46}$ crystallizing with a Pu_3Pd_5-type structure [7]. The present article reports its crystal structure and some crystal chemical peculiarities.

Experimental

Alloys of nominal compositions $Dy_{37.5}Ga_{42.5\text{-}27.5}Sn_{20\text{-}35}$ were synthesized from the pure elements (99.95 % Dy, 99.99 % Ga, 99.90 % Sn) by arc melting in a water-cooled copper hearth under Ti-gettered argon atmosphere. To achieve high homogeneity of the samples, the alloys were melted twice. The ingots were annealed at 600ºC in quartz ampoules under vacuum for 720 h and subsequently quenched in cold water. The weight losses during the preparation of the samples were less than 0.5 % of the total mass, which was 1 g for each alloy. X-ray phase analysis was carried out using X-ray powder diffraction patterns collected at room temperature on a diffractometer DRON-2.0M (Fe *K*α-radiation, angular range $20^o \le 2\theta \le 120^o$, step 0.05º). The samples contained the new ternary phase with admixtures of the known binary compounds $DyGa_2$ (structure type AlB_2, Pearson symbol *hP*3, space group *P*6/*mmm*) [8] and $DySn_2$ ($ZrSi_2$, *oS*12, *Cmcm*) [9]. The positions and intensities of the reflections of the new compound and the similarity of the collected X-ray powder diffraction patterns to the X-ray powder diffraction patterns of $Sm_3Ga_{0.80\text{-}2.48}Sn_{4.20\text{-}2.52}$ [6] indicated possible realization of the structure type Pu_3Pd_5. The crystal structure was refined by the Rietveld method for a sample of nominal composition $Dy_{37.5}Ga_{32}Sn_{30.5}$ using

an X-ray powder diffraction pattern collected at room temperature on a powder diffractometer Stoe Stadi P (Cu $K\alpha_1$-radiation, angular range $10^o \le 2\theta \le 110^o$, step 0.015º). Refinement of the profile and structural parameters was performed using the FullProf Suite package [10]. The atomic coordinates of $Sm_3Ga_{1.89}Sn_{3.11}$ reported in [6] were used as a starting model for the new compound. The binary phases $DyGa_2$ and $DySn_2$ were identified as admixtures in the sample (21.9(3) and 17.1(2) wt.%, respectively). They were modeled with individual scale factors, unit cell and preferred orientation parameters, while the profile parameters were constrained to be the same for all phases. For the main phase the following parameters were refined: scale factor, three cell parameters, six profile parameters (pseudo-Voigt profile), seven positional, three displacement and three occupational parameters. Isotropic displacement parameters for the three positions of the *p*-elements were refined by one parameter. In total 32 parameters were included in the final cycles of the refinement. The background was defined using the Fourier filtering technique. Experimental, calculated and difference X-ray powder diffraction patterns are presented in Fig. 1; experimental details and crystallographic data for the individual phases in the alloy $Dy_{37.5}Ga_{32}Sn_{30.5}$ are listed in Table 1.

Results and discussion

The atomic coordinates, site occupancies and isotropic displacement parameters for the structure of the ternary compound are listed in Table 2. The structure is partially ordered and belongs to the orthorhombic structure type Pu_3Pd_5, refined composition $Dy_3Ga_{2.54(5)}Sn_{2.46(5)}$. All three positions of the *p*-element atoms are occupied by statistical mixtures of Ga and Sn atoms. However, the position 8*g* is occupied mainly by Sn atoms, whereas the positions 8*f* and 4*c* are preferentially occupied by Ga atoms. A similar tendency for the ordering of Ga and Sn atoms was observed for the ternary compound $Sm_3Ga_{0.80-2.48}Sn_{4.20-2.52}$ [6]: the 8*g* position remained occupied almost exclusively by Sn atoms within the whole homogeneity range, whereas gradual replacement of Sn atoms by Ga atoms was observed in the two other positions. The homogeneity range of the ternary compound extends up to 6 at.% Ga/Sn, as estimated from the X-ray phase analysis of the samples from the line 37.5 at.% Dy with different contents of Ga and Sn.

Interatomic distances, coordination numbers and coordination polyhedra of the atoms in the structure of $Dy_3Ga_{2.54}Sn_{2.46}$ are presented in Table 3. The Dy atoms center distorted tetragonal prisms with two or

Table 1 Experimental details and crystallographic data for the individual phases in the alloy $Dy_{37.5}Ga_{32}Sn_{30.5}$.

Compound		$Dy_3Ga_{2.54(5)}Sn_{2.46(5)}$	$DyGa_2$	$DySn_2$
Abundance, %		61.9(10)	22.0(3)	17.1(2)
Structure type		Pu_3Pd_5	AlB_2	$ZrSi_2$
Pearson symbol		*oS*32	*hP*3	*oS*12
Space group		*Cmcm*	*P*6/*mmm*	*Cmcm*
Formula units per cell *Z*		4	1	4
Unit-cell parameters:	*a*, Å	9.7300(3)	4.2092(7)	4.3915(7)
	b, Å	7.7081(2)	–	16.220(3)
	c, Å	9.7925(3)	4.0698(7)	4.2962(7)
Cell volume *V*, Å^3		734.44(4)	62.445(17)	306.02(9)
Density D_x, g cm^{-3}		8.655	8.032	8.683
Preferred orientation parameter [direction]		–	0.9832(13)[110]	0.799(15) [101]
Diffractometer			Stoe Stadi P	
Radiation type, wavelength λ, Å			Cu $K\alpha_1$, 1.54060	
Scanning mode			$\theta/2\theta$	
Range of 2θ, º			6.0-106.8	
Step size, º			0.015	
Profile parameters *U*, *V*, *W*			0.044(14), 0.032(12), 0.001(2)	
Mixing parameter			0.665(13)	
Asymmetry parameters			-0.016(9), -0.004(2)	
Reliability factors:	R_B	0.0558	0.0345	0.0586
	R_F	0.0671	0.0323	0.0851
	R_p[a]		0.0314	
	R_{wp}[a]		0.0406	
	χ^2		1.21	

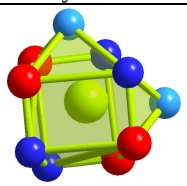
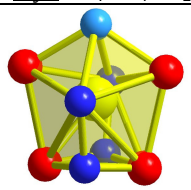
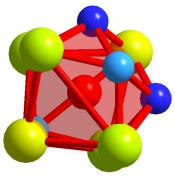
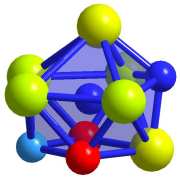
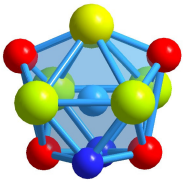
[a] Not corrected for background.

Table 2 Atomic coordinates, isotropic displacement and occupancy parameters for $Dy_3Ga_{2.54}Sn_{2.46}$.

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Dy1	8*e*	0.1968(5)	0	0	0.52(16)
Dy2	4*c*	0	0.6404(10)	1/4	0.7(2)
*M*1	8*g*	0.2067(6)	0.2934(7)	1/4	1.0(2)
*M*2	8*f*	0	0.3198(14)	0.0488(7)	1.0(2)
*M*3	4*c*	0	0.0258(18)	1/4	1.0(2)

*M*1 = 0.09(4)Ga1 + 0.91(4)Sn1; *M*2 = 0.81(3)Ga2 + 0.19(3)Sn2; *M*3 = 0.74(3)Ga3 + 0.26(3)Sn3.

Table 3 Interatomic distances (δ), coordination numbers (CN) and coordination polyhedra of the atoms in the structure of $Dy_3Ga_{2.54}Sn_{2.46}$.

Atoms		δ, Å	CN	Polyhedron
Dy1	– 2 *M*1	3.068(4)	10	 Dy1$M1_4M2_4M3_2$
	– 2 *M*3	3.114(3)		
	– 2 *M*2	3.159(9)		
	– 2 *M*2	3.296(6)		
	– 2 *M*1	3.334(4)		
Dy2	– 2 *M*2	2.942(8)	9	 Dy2$M1_4M2_4M3$
	– 1 *M*3	2.971(16)		
	– 2 *M*1	3.088(7)		
	– 2 *M*2	3.160(11)		
	– 2 *M*1	3.346(9)		
*M*1	– 2 *M*2	2.823(7)	10	 *M*1$Dy1_4Dy2_2M2_2M3_2$
	– 1 *M*3	2.881(12)		
	– 2 Dy1	3.068(4)		
	– 1 Dy2	3.088(7)		
	– 2 Dy1	3.334(4)		
	– 1 Dy2	3.346(9)		
	– 1 *M*3	3.369(9)		
*M*2	– 2 *M*1	2.823(7)	10	 *M*1$Dy1_4Dy2_2M1_2M2M3$
	– 1 *M*2	2.938(15)		
	– 1 Dy2	2.942(8)		
	– 1 *M*3	3.003(14)		
	– 2 Dy1	3.158(9)		
	– 1 Dy2	3.160(11)		
	– 2 Dy1	3.296(6)		
*M*3	– 2 *M*1	2.881(12)	11	 *M*1$Dy1_4Dy2M1_4M2_2$
	– 1 Dy2	2.971(16)		
	– 2 *M*2	3.003(14)		
	– 4 Dy1	3.114(3)		
	– 2 *M*1	3.369(9)		

one additional atoms: Dy1$M1_4M2_4M3_2$ and Dy2$M1_4M2_4M3$. The coordination polyhedra around the Ga and Sn atoms can be described as tetragonal prisms with two additional atoms, *M*1$Dy1_4Dy2_2M2_2M3_2$, and tetragonal antiprisms with two or three additional atoms: *M*1$Dy1_4Dy2_2M1_2M2M3$ and *M*1$Dy1_4Dy2M1_4M2_2$. The Ga and Sn atoms form square pyramids of composition $M1_2M2_2M3$ (Fig. 2), which can be interpreted as arachno-clusters of the Wade type [11]. Complete ordering of Ga and Sn atoms would result in clusters of composition Sn_2Ga_3 and absence of contact distances between Sn atoms. The interatomic distances in the basal planes of the pyramids ($\delta_{M1\text{-}M2}$ = 2.823(7) Å) are the shortest distances in the structure.

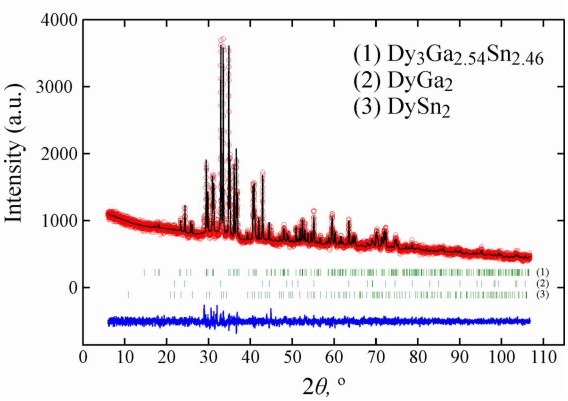


Fig. 1 Experimental (points), calculated (continuous line) and difference (continuous line at the bottom of the picture) diffractogram of the sample of composition $Dy_{37.5}Ga_{32}Sn_{30.5}$ (Cu $K\alpha_1$-radiation). Vertical lines show the positions of the reflections of the ternary compound $Dy_3Ga_{2.54}Sn_{2.46}$, $DyGa_2$, and $DySn_2$.

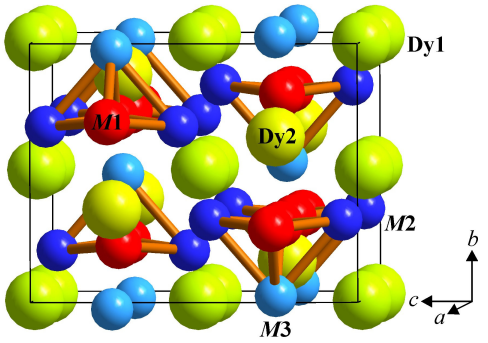


Fig. 2 Content of the unit cell and square pyramidal arachno-type clusters in the structure of $Dy_3Ga_{2.54}Sn_{2.46}$.

The structure of the ternary compound $Dy_3Ga_{2.54}Sn_{2.46}$ can be decomposed into two kinds of slab stacked along the crystallographic direction [001] (Fig. 3a). Slab ***A*** (at z ≈ 0 and z ≈ ½, related through the mirror plane) is a puckered layer of atoms from sites Dy1 and *M*2, arranged as in the structure type NaCl [12] (Fig. 3b). The flat layer ***B*** (at z = ¼ and ¾, mapped by a 2_1 screw axis), formed by atoms of sites Dy2, *M*1 and *M*3, can be described as an ordered substitutional derivative of the layer ***A*** and corresponds to a distorted layer of the tetragonal structure type $LiFeO_2$ [13] (Fig. 3c), which is an ordered derivative of the cubic structure type NaCl. Layer ***B*** can also be described as an infinite net of *p*-element atoms forming empty triangles and hexagons filled by Dy atoms (Fig. 3d). Such a description relates the structure of the ternary compound $Dy_3Ga_{2.54}Sn_{2.46}$ to the family of deformation variants of the structure type Rh_5Ge_3 [14]. The main feature of the structures of Rh_5Ge_3, Yb_5Sb_3 [15], U_3S_5 [16], Yb_5Bi_3 [17], Tm_3Ga_5 [18] and Pu_3Pd_5 [1] is a framework of interconnected infinite columns of filled trigonal prisms (Fig. 4) [19]. The prisms share triangular faces and edges with neighboring prisms, forming a three-dimensional network with large deformed hexagonal channels. These channels can be considered as columns of face-sharing hexagonal

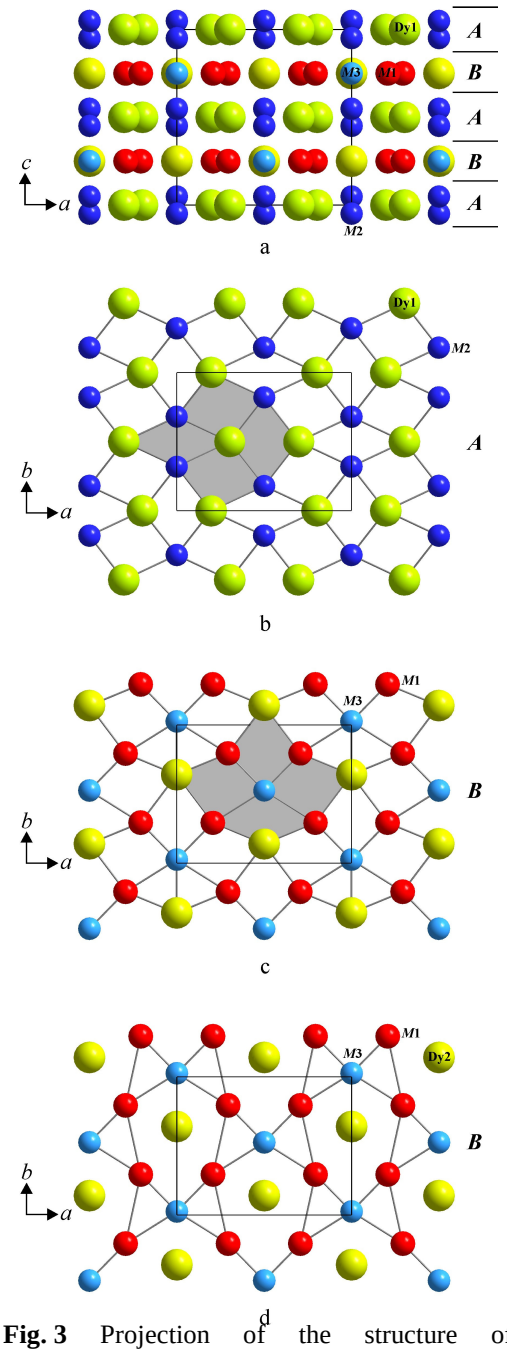


Fig. 3 Projection of the structure of $Dy_3Ga_{2.54}Sn_{2.46}$ along [001] and stacking of two kinds of slab, ***A*** and ***B*** (a); the puckered slab ***A***, a distorted NaCl-type layer (b); the flat layer ***B***, a distorted $LiFeO_2$-type layer (c); layer ***B*** seen as an infinite net of empty triangles and Dy-filled hexagons (d).

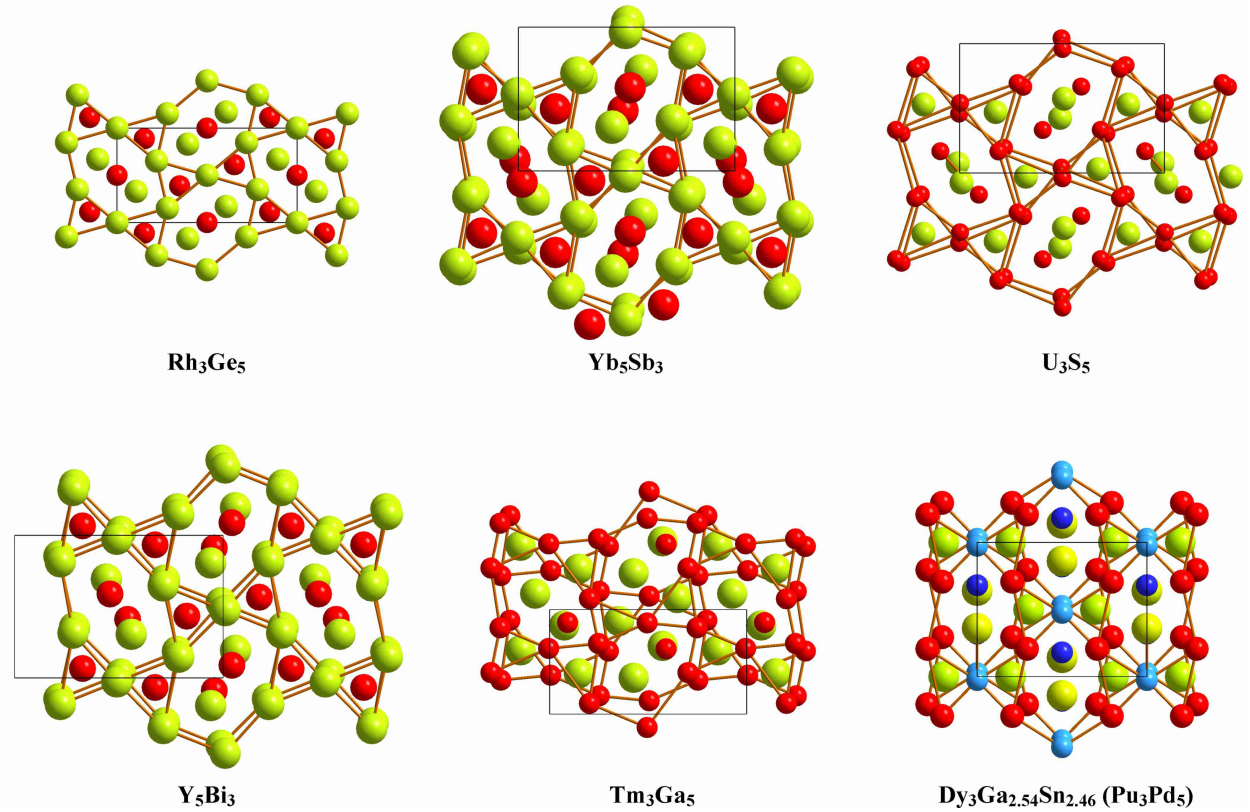


Fig. 4 Projections of the structures of Rh_3Ge_5 and $Dy_3Ga_{2.54}Sn_{2.46}$ along [001], and of Yb_5Sb_3, U_3S_5, Y_5Bi_3, and Tm_3Ga_5 along [100].

prisms. Inside each hexagonal prism there are two atoms in the central plane and one atom at the center of each hexagonal base plane of the prisms. In the structure of Rh_3Ge_5 the elongated hexagons form a parquet-like patchwork, which can also be found in all of the derivative structures. Yb_5Sb_3 and Y_5Bi_3 are distorted variants of the Rh_3Ge_5 type, U_3S_5 represents an antitype to the Yb_5Sb_3 type; the closely related structure types Tm_3Ga_5 and Pu_3Pd_5 are distorted variants of Yb_5Sb_3. It should be noted that in the system Dy–Ga–Sn the latter two structure types coexist at 600ºC, represented by the binary gallide Dy_3Ga_5 (structure type Tm_3Ga_5) and the ternary phase $Dy_3Ga_{3.00\text{-}2.54}Sn_{2.00\text{-}2.46}$ (partially ordered Pu_3Pd_5-type structure).

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