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The $BaAl_4$ structure and its derivatives from the R-Zn-Ga systems

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Abstract. Seven new ternary $RZn_{1+x}Ga_{3-x}$ (R = Ce, Pr, Nd, Sm, Ho and Er) and $Ce_5Zn_2Ga_{17}$ phases are synthesized for the first time. Their crystal structures are solved on basis of X-ray powder diffraction data. The above mentioned compounds belong to the $BaAl_4$ (space group *I*4/*mmm*) and Rb_5Hg_{19} (space group *I*4/*m*) structure types. Details of the structure of the $Ce_5Zn_2Ga_{17}$ compound and relationship with $RZn_{2-x}Ga_{2+x}$ ($BaAl_4$ type) and $R_3Zn_{8-x}Ga_{3+x}$ (La_3Al_{11} type) are briefly discussed.

Introduction

The rare earths-transition metal-gallium systems have been intensively investigated in recent years with respect to their phase relations, crystal structures and magnetic and transport properties [1-4]. However, among them, the R-Zn-Ga systems were poorly studied: the phase diagram, crystal structure and physical properties of the compounds from the Yb-Zn-Ga system were reported in [5-7]; structural and magnetic studies on the $RZn_{2-x}Ga_{2+x}$ (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Yb) phases, with $BaAl_4$ and/or $CaCu_{0.15}Ga_{3.85}$ structure types, can be found in [8-11]; identification of the new intermediate phases with the $CeCu_2$, $CaIn_2$, $CeCd_2$ and AlB_2 structure types from the RGa_2-RZn_2 (R = Y, La, Ce, Pr, Sm, Eu, Gd, Dy, Er, Tm) cross-section are published in [12,13]; structural studies on the new representatives with $BaAl_4$ ($RZn_{2-x}Ga_{2+x}$, R = Y, Gd, Tb, Dy), La_3Al_{11} ($R_3Zn_{8-x}Ga_{3+x}$, R = Dy, Ho, Er, Tm, Lu) and $BaHg_{11}$ ($RZn_{9-x}Ga_{2+x}$, R = Y, Gd, Tb, Dy, Ho, Er, Tm) structure types are given in [14,15]; investigations on the YZn_xGa_{1-x} alloys are reported in [16]; single crystal studies of the defected $La_{5-x}Zn_{1.5}Ga_{1.5}$ phase with W_5Si_3 are shown in [17]. Herein, we present data on the crystal structure of other new ternary phases from the R-Zn-Ga systems.

Experimental details

Metals with nominal purities > 99.95 wt. % (rare earth ingots, Zn spheres and Ga pieces) were used as starting materials. The samples, with a total weight 0.5-1.0 g, were prepared by heating the elements under vacuum at T > 900°C inside quartz ampoules, followed by annealing at 400°C for 1-3 months and quenched by submerging the quartz tubes into cold water.

X-ray phase and structural analysis were performed using a PANalitical X'Pert Pro diffractometer (Cu Kα-radiation). The scans were taken in the $\theta/2\theta$ mode with the following parameters: 2θ region 15-120º; step scan 0.03º; counting time per step 15-20 s. The lattice parameters were obtained by least-squares fitting using the Latcon program [18]. The FullProf [19] program was used for Rietveld refinements. Pseudo-Voigt profile shape function was used. The background was refined with a polynomial function.

Results and discussion

Six new ternary phases, with $BaAl_4$ structure type, were identified in the annealed alloys with the $CeZnGa_3$, $RZn_{1.5}Ga_{2.5}$ (R = Ce, Pr, Nd, Sm and Ho) and $ErZn_{1.75}Ga_{2.25}$ compositions. Their calculated lattice parameters, as well as atom coordinates and thermal parameters are given in Table 1. The formation of $R_3Zn_{8-x}Ga_{3+x}$ ($0.5 < x < 4$) phases with La_3Al_{11} structure type was also confirmed in the annealed alloys. As examples, X-ray diffractograms of $SmZn_{1.5}Ga_{2.5}$ and $Er_3Zn_4Ga_7$ are shown in Fig. 1*a* and 1*b*, respectively. The relation between the structures of R-Zn-Ga phases with $BaAl_4$ and La_3Al_{11} structure types was discussed in [14,15].

Table 1. Crystallographic data for $RZn_{2-x}Ga_{2+x}$ phases ($BaAl_4$-type structure, *I4/mmm*, $Z = 2$)

Phase	$CeZn_{1.5}Ga_{2.5}$	$PrZn_{1.5}Ga_{2.5}$	$NdZn_{1.5}Ga_{2.5}$	$SmZn_{1.5}Ga_{2.5}$	$HoZn_{1.5}Ga_{2.5}$	$ErZn_{1.75}Ga_{2.25}$
Lattice parameters:						
a (Å)	4.2758(1)	4.2421(2)	4.2171(1)	4.1764(1)	4.0973(3)	4.0817(2)
c (Å)	10.6680(3)	10.6865(5)	10.7134(3)	10.7534(3)	10.8177(9)	10.8443(5)
V (Å^3)	195.03(1)	192.31(1)	190.52(1)	187.56(1)	181.61(3)	180.72(2)
Reliability factors:						
R_B, R_F (%)	5.28, 4.44	6.03, 3.57	5.85, 4.63	7.70, 5.27	7.20, 4.53	7.38, 5.89
R_p, R_{wp} (%)	8.84, 11.6	10.7, 13.9	9.71, 12.7	10.2, 13.5	14.0, 18.0	11.8, 15.9
Atom coordinates and thermal parameters:						
R (0 0 0),	1Ce	1Pr	1Nd	1Sm	1Ho	1Er
B_{iso} (Å^2)	1.12(4)	0.92(4)	0.95(3)	0.94(4)	1.30(15)	0.98(6)
M1(0 ½ ¼),	1M	1M	1M	1M	1M	1M
B_{iso} (Å^2)	1.16(5)	1.52(6)	1.38(5)	1.26(5)	1.52(16)	0.89(7)
M2 (0 0 *z*),	1M	1M	1M	1M	1M	1M
B_{iso} (Å^2)	0.38483(15)	0.38578(17)	0.38624(15)	0.38635(18)	0.3889(4)	0.3906(3)
	0.84(5)	0.84(5)	0.84(4)	0.90(5)	0.90(11)	1.17(8)
Mixture M	3/8Zn+5/8Ga	3/8Zn+5/8Ga	3/8Zn+5/8Ga	3/8Zn+5/8Ga	3/8Zn+5/8Ga	7/16Zn+9/16Ga

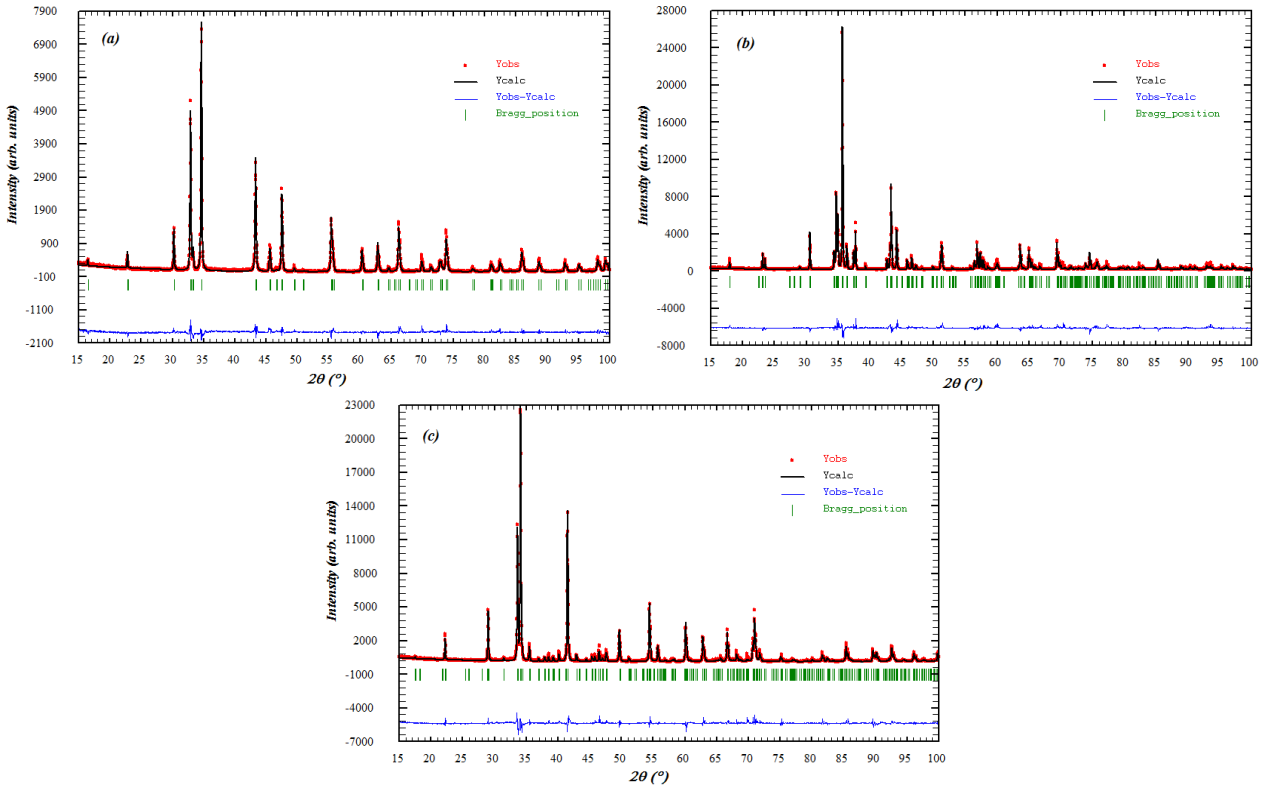


Fig.1 X-ray diffraction patterns of $SmZn_{1.5}Ga_{2.5}$ (*a*), $Er_3Zn_4Ga_7$ (*b*) and $Ce_5Zn_2Ga_{17}$ (*c*).

X-ray analysis of ~$Ce_{20}Zn_{10}Ga_{70}$ as-prepared alloys at 1000°C indicated the existence of a new compound and monophasic samples were obtained for the $Ce_{20.8}Zn_{8.4}Ga_{70.8}$ ($Ce_5Zn_2Ga_{17}$) composition. XRD data was successfully indexed within a tetragonal unit cell, and taking into account stoichiometry, symmetry and two possible space groups (*I4/m* or $I\bar{4}$), the Rb_5Hg_{19} structure type was chosen as a model for the crystal structure refinement. Results of such refinement can be seen in Fig. 1*c*. Atoms parameters as well as interatomic distances are given in Tables 2 and 3. The shortest interatomic distances are in the good agreement with the sum of the atomic radii of pure metals. Due to the small difference between Zn and Ga scattering factors, statistical mixture of these elements was presented as M = 0.10Zn + 0.90Ga. Ce atoms occupy the Rb sites, while small atoms M (Zn and Ga) are distributed over the Hg positions. It should be noted that the final XRD refinement indicates a partial occupation of the 2*a*, 4*d* and 16*i* Wyckoff positions. Similar tendency was also observed for other gallides, $R_5Ag_{2-x}Ga_{17-y}$ (R = Gd, Tb), with Rb_5Hg_{19} structure type [20].

Table 2. Atom coordinates and isotropic displacement parameters of $Ce_5Zn_2Ga_{17}$ (Rb_5Hg_{19}-type structure, *I*4/*m*, *Z* = 2), with lattice parameters *a* = 9.7240(2) Å, *c* = 10.1108(3) Å, *V* = 956.03(4) Å^3.

Atom	Site	*x*	*y*	*z*	B_{iso} (Å^2)	Occ.
Ce1	2*b*	0	0	½	1.0(2)	1Ce
Ce2	8*h*	0.3074(3)	0.1057(4)	0	0.9(1)	1Ce
M1	2*a*	0	0	0	0.9(4)	0.78M
M2	4*d*	0	½	¼	0.8(3)	0.91M
M3	16*i*	0.2053(6)	0.3963(7)	0.1248(3)	0.9(1)	0.94M
M4	16*i*	0.0869(5)	0.1788(4)	0.2297(4)	0.8(1)	1M

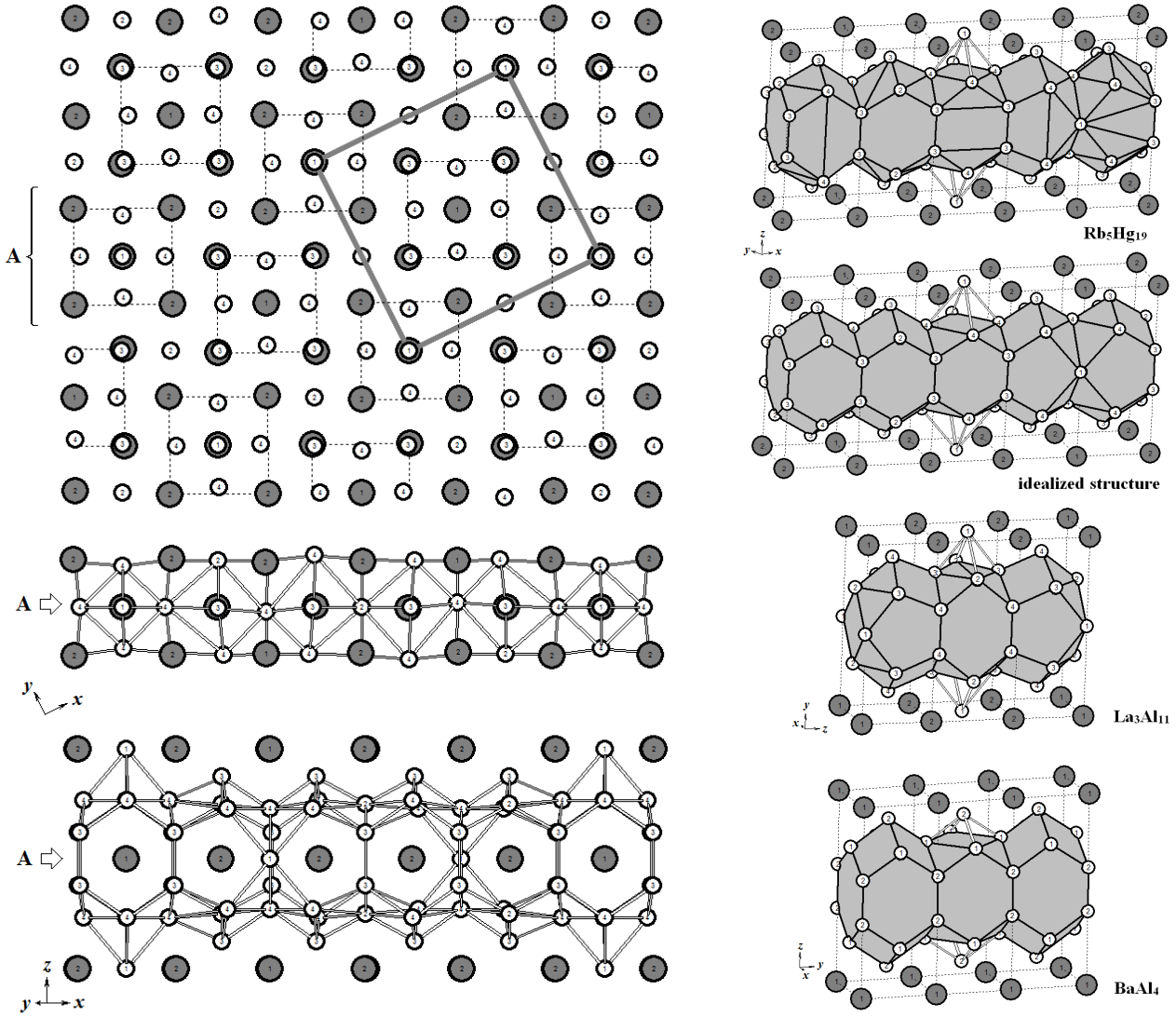
R_B = 8.54%, R_F = 6.48%, R_p = 10.3 %, M = 0.10Zn + 0.90Ga

Table 3. Interatomic distances and coordination number of the atoms in the $Ce_5Zn_2Ga_{17}$.

Atoms	*d* (Å) / CN	Atoms	*d* (Å) / CN	Atoms	*d* (Å) / CN
Ce1-	16	M2-	8	M1-	12
-8M3	3.290(6)	-4M3	2.570(5)	-8M4	3.022(4)
-8M4	3.348(4)	-4Ce2	3.310(2)	-4Ce2	3.161(3)
Ce2-	13	M3-	9	M4-	9
-1M1	3.161(3)	-1M3	2.524(4)	-1M3	2.604(7)
-2M4	3.235(5)	-1M2	2.570(5)	-1M3	2.621(7)
-2M4	3.240(5)	-1M4	2.604(7)	-1M3	2.631(7)
-2M3	3.250(7)	-1M4	2.621(7)	-2M4	2.734(6)
-2M3	3.291(7)	-1M4	2.631(7)	-1M1	3.022(4)
-2M2	3.310(2)	-1Ce2	3.250(7)	-1Ce2	3.235(5)
-2M3	3.389(7)	-1Ce1	3.290(6)	-1Ce2	3.240(5)
		-1Ce2	3.291(7)	-1Ce1	3.348(4)
		-1Ce2	3.389(7)		

Projection of the $Ce_5Zn_2Ga_{17}$ structure on the *XY* plane is shown in the top of Fig. 2*a*. Unit cell is marked by bold dark lines. This phase can be seen as an intergrown structure of the two types of internal and/or external deformed $BaAl_4$-like unit cells (slabs) along *z* axis. Here, the tetragonal $BaAl_4$ subcells with a_0 = 4.267 Å and c_0 = 10.111 Å are shown by dotted squares. Calculated "a_0" of deformed $BaAl_4$ subcell vary between 4.273 and 4.267 Å. The sharp angle ∠Ce2 is equal to 87.3°. Similar to the $RZn_{2-x}Ga_{2-x}$ phases with $BaAl_4$ type, the small M (Zn and Ga) atoms form a three-dimensional network in the structure of $Ce_5Zn_2Ga_{17}$. Part of these nets is shown in the centre and bottom part of Fig. 2*a*. Surroundings of the Ce and M (Zn and Ga) atoms are also similar to the $BaAl_4$ type phases.

Fig. 2*b* shows the relationship between the $BaAl_4$, La_3Al_{11} and Rb_5Hg_{19} structures of the R-Zn-Ga phases. The last two structures can be interpreted as a defected variant of the $BaAl_4$ structure type, where the collapsing of part of the small atoms is observed. The general formula A_nB_{4n-m} can be used to describe such structures, with *n* - number of the $BaAl_4$ subcell (with lattice constants a_0 and c_0) and *m* - pair of collapsing atoms (2 → 1). Transformations of above mentioned structure are following: $(LaAl_4)_3 = La_3Al_{12} \rightarrow La_3Al_{11}$ (*n* = 3, *m* = 1; $a \sim a_0$, $b \sim c_0$, $c \sim 3a_0$) and $(RbHg_4)_5 = Rb_5Hg_{20} \rightarrow Rb_5Hg_{19}$ (*n* = 5, *m* = 1; $a \sim \sqrt{5}a_0$, $c \sim c_0$). A more detailed description of the Rb_5Hg_{19} type can be found in [21].



(*a*) (*b*)

Fig. 2 Projection of $Ce_5Zn_2Ga_{17}$ on *XY* plane and three-dimensional [ZnGa] network (*a*) (dark filled circles represent Ce atoms; Zn and Ga atoms are represented by white balls). Relationship between $BaAl_4$, La_3Al_{11} and Rb_5Hg_{19} structure types (*b*).

Conclusions

Seven new phases, namely, $RZn_{1+x}Ga_{3-x}$ (R = Ce, Pr, Nd, Sm, Ho and Er) and $Ce_5Zn_2Ga_{17}$, were identified by means of X-ray diffraction. They belong to the known structure types $BaAl_4$ and Rb_5Hg_{19}, respectively. Crystal structures of the title compounds were fully investigated. The coordination of the atoms, interatomic distances and relation with other structures of the $Ce_5Zn_2Ga_{17}$ compound were discussed. The available data on the R-M-X (R - rare earth, M - Zn and Cd, X - Al and Ga) systems point to the possibility of existence of new compounds of the above cited structure types in the yet unexplored systems.

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