ISSN 2078-5615. Вісник Львівського університету. Серія хімічна. 2015. Випуск 56. Ч. 1. С. 80–86
Visnyk of the Lviv University. Series Chemistry. 2015. Issue 56. Pt. 1. P. 80–86

УДК 546.736.681

THE CRYSTAL STRUCTURE OF THE TERNARY Yb$M_{0.15}$Ga$_{3.85}$ (M = Cu AND Ag) PHASES

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Ternary gallides, Yb$M_{0.15}$Ga$_{3.85}$ (M = Cu and Ag), have been prepared by arc–melting of the metals and annealed at 400 °C. Their crystal structure has been investigated by means of powder X–ray diffraction analysis. The phases belong to the monoclinic partial ordered CaCu$_{0.15}$Ga$_{3.85}$ structure type (space group *C2/m*, Pearson symbol *mC*10, Z = 2). Structural peculiarities, coordination and interactions of the atoms in the investigated compounds have been briefly discussed.

Key words: Ytterbium compounds, Ternary gallides, X–ray diffraction, Crystal structure.

The existence of the ternary intermetallic gallides, namely, ~Yb$M_{0.15}$Ga$_{3.85}$ (M = Cu, Ag and Au), were first reported by Grin et al. [1]. They indicated that these phases belong to the CaCu$_{0.15}$Ga$_{3.85}$ structure type, a monoclinically distorted BaAl$_4$ structure type. The Yb$M_{0.15}$Ga$_{3.85}$ intermetallics with M = Ag and Au were further confirmed to exist by Gumeniuk [2] during systematic investigation of the phase diagram of the Yb–Ag–Ga and Yb–Au–Ga systems at 600 °C. In both cases, the authors presented only lattice parameters without structural refinements performed. The Yb–Cu–Ga system was studied by Shevchenko and Markiv [3] in the range of 0–33.3 at.% Yb at 500 °C. No ternary YbCu$_{0.15}$Ga$_{3.85}$ phase was revealed. In present paper we report on the synthesis of the title phases at 400 °C and the results of their crystal structure investigation.

Starting materials for the synthesis of the Yb–M–Ga alloys were ytterbium ingots (R > 99.9 wt.%), copper, silver and gold plate (99.99 wt.%), and gallium pieces (99.999 wt.%). Samples with a total weight of 1 g were prepared by arc–melting buttons in a water–cooled copper crucible with a tungsten electrode under a purified argon atmosphere using Ti as a getter. The products were turned over and re–melted two times in order to ensure homogeneity. Ball–like alloys were further sealed in evacuated quartz tubes under vacuum and annealed at 400 °C for one month. After that, the samples were quenched by submerging the quartz tubes in ice–cold water.

The polycrystalline products were crushed, powdered in an agate mortar, and examined by X–ray powder diffraction. X–ray structural studies were performed using a PANalytical X'Pert Pro diffractometer (Cu Kα radiation). The scans were taken in the θ/2θ mode with the following parameters: 2θ region 15–100°; step scan 0.03°; counting time per step 25 s. The theoretical powder patterns were calculated with the help of the PowderCell program [4]. Data treatment and structure solution were performed using the JANA2006 program [5]. The FullProf [6] program was used for the Rietveld refinements. A pseudo–Voigt profile shape function was used. The background was refined with a polynomial function.

The single phase samples of the Yb–*M*–Ga alloys have been obtained. Diffraction angles and peaks intensities were evaluated from the total diffraction profiles. The unit cell parameters of the monoclinic symmetry were determined by means of automatic indexing and refined of least squares according to the diffraction angles for 121 ($YbCu_{0.15}Ga_{3.85}$) and 123 ($YbAg_{0.15}Ga_{3.85}$) reflections, respectively. From the systematic absences in the experimental sets, three possible space groups were found, *C2/m*, *C2* and *Cm*. The $YbM_{0.15}Ga_{3.85}$ structures were successfully solved in the *C2/m* space group, and three independent atomic positions were obtained. The ytterbium atoms occupy the 2*a* sites, while the copper/silver and gallium atoms are situated in two 4*i* sites. Large differences between scattering factors of the Ag and Ga atoms allowed the refinement of the occupation coefficients in the structure of the $YbAg_{0.15}Ga_{3.85}$ phase. It was found that only one of 4*i* sites is filled by the Ag/Ga mixture (*M*). No refinement of the occupation coefficients for the Cu/Ga site positions was performed for the $YbCu_{0.15}Ga_{3.85}$ phase. In the last step of the refinement the statistical mixture *M* of the Cu and Ga atoms was fixed, presented as 7.5% Cu + 92.5% Ga and suggested occupying the same site as in the silver–containing phase. The final values of atomic coordinates, occupation and thermal displacement coefficients are listed in Table 1. Interatomic distances are given in Table 2. Results of the Rietveld profile refinement of the $YbM_{0.15}Ga_{3.85}$ phases are presented in Fig. 1.

Table 1

Atomic and thermal parameters in the structure of the $YbM_{0.15}Ga_{3.85}$ phases

Atom	Site	*x*	*y*	*z*	B_{iso} (Å^2)	Occupation G
$YbCu_{0.15}Ga_{3.85}$						
Yb	2*a*	0	0	0	0.97(5)	2Yb
Ga	4*i*	0.3860(2)	0	0.4124(6)	0.88(7)	4Ga
M	4*i*	0.7474(2)	0	0.2231(6)	1.00(7)	0.3(–)Cu + 3.7(–)Ga
Lattice parameters:						
a = 11.47913(26), *b* = 4.22421(9), *c* = 4.33648(10) Å, *β* = 110.5886(13)°.						
Reliability factors: R_B = 6.75 %, R_F = 4.38 %, R_p = 7.96 %, R_{wp} = 10.4 %.						
$YbAg_{0.15}Ga_{3.85}$						
Yb	2*a*	0	0	0	0.91(5)	2Yb
Ga	4*i*	0.3860(2)	0	0.4081(7)	0.86(7)	4Ga
M	4*i*	0.7472(3)	0	0.2294(6)	0.78(7)	0.30(3)Ag + 3.70(3)Ga
Lattice parameters:						
a = 11.50945(34), *b* = 4.26518(13), *c* = 4.34358(13) Å, *β* =110.8747(16)°.						
Reliability factors: R_B = 4.90 %, R_F = 3.57 %, R_p = 8.52 %, R_{wp} = 11.3 %.						

The structure of the $YbM_{0.15}Ga_{3.85}$ (*M* = Cu and Ag) phases (Fig. 2, left) is a new partially ordered version of the $CaCu_{0.15}Ga_{3.85}$ structure type [1] and isopointal with the $CaCu_2Sn_2$ structure [7]. Here, ytterbium sites build a slightly monoclinically distorted body–cantered tetragonal subcell (with $\beta \sim 91.5°$ in the setting of *I*2/*m* space group), which

reminds of the well known $BaAl_4$ structure type (Fig. 2, right). The $[Cu_{0.15}Ga_{3.85}]$ and $[Ag_{0.15}Ga_{3.85}]$ networks in the structures however are also distorted, when compared with the aluminium network of the $BaAl_4$ type. Within this network the *M* (Cu/Ga or Ag/Ga) atoms form squares faced by pure gallium atoms.

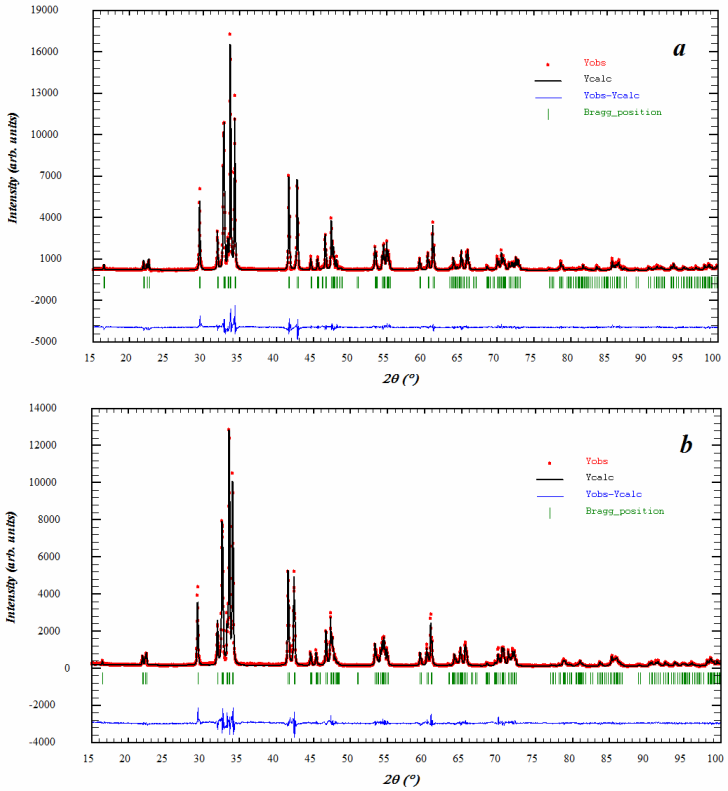
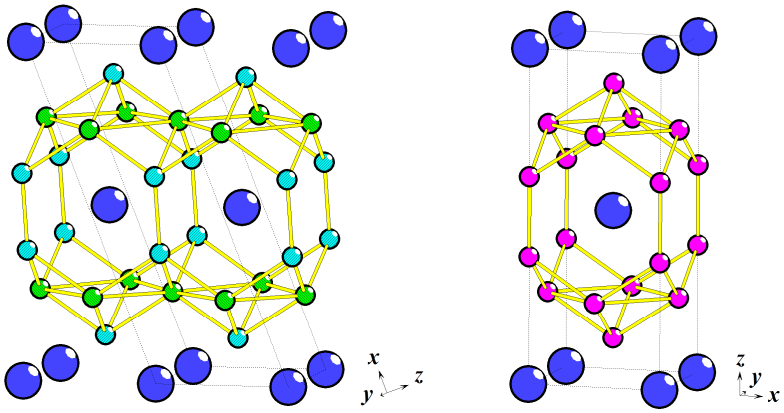


Fig. 1. Rietveld refinement of the samples $YbCu_{0.15}Ga_{3.85}$ (*a*) and $YbAg_{0.15}Ga_{3.85}$ (*b*).

Table 2

Interatomic distances of the atoms in the $YbM_{0.15}Ga_{3.85}$ phases

Atoms		$d_{M=Cu}$ (Å)	$d_{M=Ag}$ (Å)	Atoms		$d_{M=Cu}$ (Å)	$d_{M=Ag}$ (Å)
Yb:	4Ga	3.213(2)	3.237(3)	*M*:	1Ga	2.558(4)	2.559(5)
	4Ga	3.319(2)	3.327(3)		2Ga	2.598(2)	2.611(2)
	2*M*	3.364(3)	3.395(4)		1Ga	2.640(4)	2.644(5)
	4*M*	3.396(2)	3.408(3)		2*M*	2.879(3)	2.935(3)
	2*M*	3.590(4)	3.568(6)		2*M*	3.183(3)	3.158(3)
					1Yb	3.364(3)	3.395(4)
Ga:	1Ga	2.455(3)	2.456(3)		2Yb	3.396(2)	3.408(3)
	1*M*	2.558(4)	2.559(5)		1Yb	3.590(4)	3.568(6)
	2*M*	2.598(2)	2.611(2)				
	1*M*	2.640(4)	2.644(5)				
	2Yb	3.213(2)	3.237(3)				
	2Yb	3.319(2)	3.327(3)				



a *b*

Fig. 2. The crystal structure of the Yb$M_{0.15}$Ga$_{3.85}$ phases (*a*). The three–dimensional [$M_{0.15}$Ga$_{3.85}$] is outlined. Big blue circles are the Yb atoms, small green left hatching and cyan right hatching ones are the *M* (Cu/Ga or Ag/Ga) and Ga atoms, respectively.
The $BaAl_4$ structure type (*b*). Big blue circles are the Ba atoms, and small violet ones are the Al atoms. (Color figures are available in the electronic edition of the journal).

Surroundings of the Yb atoms in the form of truncated square prism are composed by eight *M* and eight Ga atoms. Shortest Yb–*M* distances (3.21–3.33 Å) are close to the sum of the atomic radii, $r_{Yb} + r_{Ag/Cu/Ga}$ [8]. The Yb atoms are well separated from each other ($d_{Yb–Yb}$ ~ 4.30 Å) showing weakly bonding. Tetragonal antiprisms (Yb$_4M_4$) with an additional vertex (Ga) in front of the basic face are coordination polyhedra for the Ga atoms. The *M* mixtures are located inside strongly distorted cubooctahedra, Yb$_4M_4$Ga$_4$. The shortest distances can be seen between Ga–Ga (~ 2.46 Å) and *M*–Ga (2.56–2.64 Å) atoms indication on strong interactions. That is in contrast to the *M*–*M* pairs. The *M*–*M* distances (~ 2.90 Å) are longer than the sum of the atomic radii of the respective atoms [8].

The structure of the above mentioned phases belong to a large family of the $A(BC)_4$ compounds [9] which are derived from the well known $BaAl_4$ structure type [10]. Most of these structures ($BaAl_4$, $BaCu_2Sb_2$, $BaMg_2Sn_2$, $BaNiSn_3$, $BaNi_2Si_2$, $CaGa_4$, $CaBe_2Ge_2$, $CaCu_{0.15}Ga_{3.85}$, $CaCu_2Sn_2$, $CeAl_2Ga_2$, $CeCu_{2–x}In_{2–y}$, $CeNi_{2.36}Sb_{1.64}$, $CePt_{0.95}Ga_{3.05}$, $LaPd_{0.58}Pt_{1.42}Ge_2$, $LaPt_2Ge_2$ etc.) are discussed in some review articles [11–13]. In the meantime further new structure types ($BaHg_{2.1}Ga_{1.9}$, $BaNi_2Ge_2$, $CeNi_{2.33}As_{1.67}$ (=$Ce_3Ni_7As_5$), $CePt_2Al_2$, Ce_2SbO_2, $DyCu_{0.5}Ga_{3.5}$, $EuPt_2Ga_2$, $GdCu_3Ga$, $LaNi_{0.5}Al_{3.5}$ (=La_2NiAl_7), $LaZn_4$, $SmCu_{1.07}As_{0.85}P_{1.15}$, $SrMgIn_3$, $SrRh_2As_2$ and $SrPd_2Bi_2$) of this family have been reported in the literature [14–27]. All these structures are related by a group–subgroup scheme [28, 29] and represented for the first time in Fig. 3. It should be note that the $CeCu_{2–x}In_{2–y}$, Ce_2SbO_2, $DyCu_{0.5}Ga_{3.5}$, $GdCu_3Ga$ and $SmCu_{1.07}As_{0.85}P_{1.15}$ structures have defected positions of the atoms. Modulated structures are suggested for the $DyCu_{0.5}Ga_{3.5}$ and $EuPt_2Ga_2$ phases. Mixing of the *B* and *C* atoms in the $A(BC)_4$ structures are observed for the $CaCu_{0.15}Ga_{3.85}$, $CeNi_{2.36}Sb_{1.64}$, $CePt_{0.95}Ga_{3.05}$, $LaPd_{0.58}Pt_{1.42}Ge_2$, $BaHg_{2.1}Ga_{1.9}$, $DyCu_{0.5}Ga_{3.5}$ and $SmCu_{1.07}As_{0.85}P_{1.15}$ ones. Other structures have an ordered distribution of the atoms. Detailed descriptions and relations among the structures related to the $BaAl_4$ structure type will be given in our further paper.

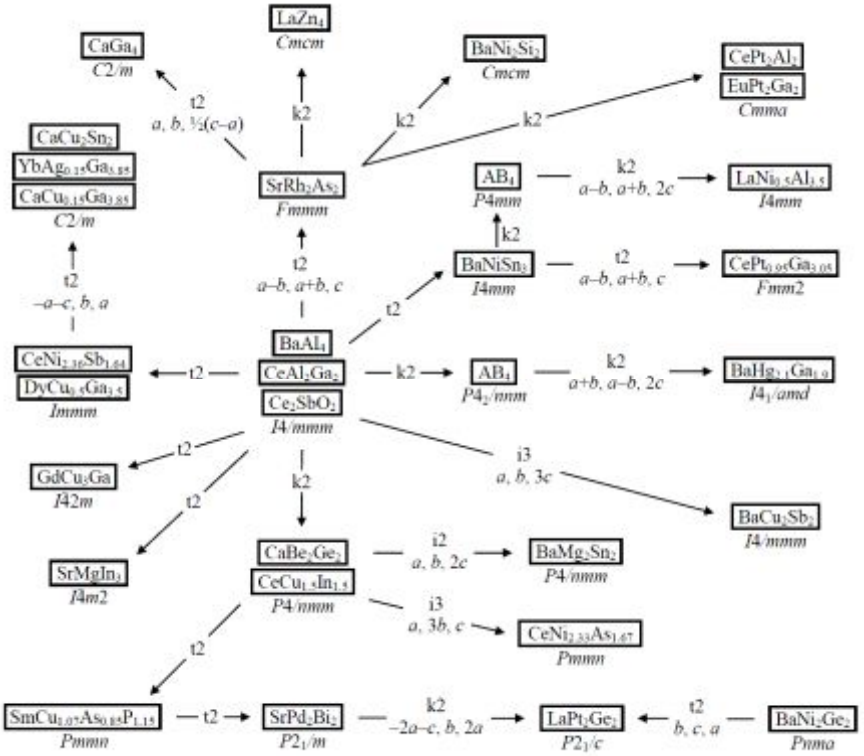


Fig. 3. Group–subgroup relationship in the *Bärnighausen* formalism for some $BaAl_4$ superstructures. The indices of the *translationengleiche* (t), *klassengleiche* (k), and *isomorphic* (i) transitions, as well as the unit cell transformations are given.

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КРИСТАЛІЧНА СТРУКТУРА ТЕРНАРНИХ ФАЗ $YbM_{0.15}Ga_{3.85}$ (*M* = Cu та Ag)

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Тернарні галіди $YbM_{0,15}Ga_{3,85}$ (*M* = Cu та Ag) синтезовано методом дугового плавлення з подальшим відпалом при 400 °C. Рентгенівським дифракційним методом порошку визначено їхню кристалічну структуру. Досліджувані фази мають моноклінну частково впорядковану структуру типу $CaCu_{0,15}Ga_{3,85}$ (просторова група *C*2/*m*, символ Пірсона *oC*10, *Z* = 2). Коротко проаналізовано структурні особливості сполук.

Ключові слова: сполуки ітербію, тернарні галіди, рентгенівська дифракція, кристалічна структура.

Стаття надійшла до редколегії 17.09.2014
Прийнята до друку 30.12.2014