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$BaAl_4$-type structure derivatives in the Ga-rich part of the Y–Cu–Ga system

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ABSTRACT

The crystal structures of seven Ga-rich compounds that exist in the Y–Cu–Ga system were studied by the X-ray single-crystal and powder diffraction methods. The crystal structures of six phases were shown to be constructed from the orthorhombic distorted $BaAl_4$-like fragments by multiplication of its *a* and *b* lattice constants. These compounds are: 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$ (modified $BaAl_4$-type structure, 1×1 multiplication), 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$ and 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$ (own type structure, 3×3), 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$ (own, 9×9), 5-$Y_3Cu_4Ga_7$ and 6-$Y_{3.21}Cu_{3.09}Ga_{7.70}$ (La_3Al_{11}, 3×1), 7-$YCuGa_2$ (own, 3×3).

1. Introduction

The isothermal section (500 °C) of the Y–Cu–Ga phase diagram was investigated in Refs. [1,2]. Five intermediate compounds were found to exist at the Ga-rich region (20–25 at.% Y, 50–70 at.% Ga). As regards the positions of the diffraction peaks with the highest intensities, the crystal structures of these 5 compounds are closely related [2]. Without any calculations we assumed [2] that the crystal structure of the 1-$YCu_{1.3-1.2}Ga_{2.7-2.8}$ compound belongs to the $BaAl_4$-type ($a = 0.4089–0.4094$ nm, $c = 1.044–1.053$ nm). As to 2-$YCu_{1.15}Ga_{2.85}$, 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$ and 4-$YCu_{0.8}Ga_{3.2}$ compounds, the main reflections of their diffraction patterns were indexed well within an orthorhombically distorted $BaAl_4$-type unit cell with somewhat different *b/a* and *c/a* ratios [2]. The crystal structure of the 5-$Y_3Cu_4Ga_7$ compound was studied in Ref. [3] by the single-crystal method (La_3Al_{11}-type structure ($a = 1.23673$ nm, $b = 0.41867$ nm, $c = 0.93794$ nm). Therefore, the 5-$Y_3Cu_4Ga_7$ is the one among other Ga-rich compounds, for which the crystal structures were completely determined. The crystal structure of the 7-$Y_{23}Cu_{27}Ga_{50}$ compound, found in Ref. [1], was not determined yet.

Moreover, previous investigations have shown that the $RECu_xGa_{4-x}$ ternary phases with $BaAl_4$-type structure (tetragonal, $1 \times 1 \times 1$ multiplicity) exist also in the other RE–Cu–Ga systems, namely, in RE = La, Ce, Pr, Nd, Sm with $x \approx 1.4–1.7$ [2–6]; RE = Eu with $x \approx 0.2–1.1$ [2]; RE = Gd with $x \approx 1.0–1.7$ [2,4]; RE = Tb, Dy with $x \approx 1.3$ [2] and RE = Yb with $x \approx 0.3–1.0$ [2,7]. Besides the mentioned above phases, the isostructural 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$ compounds have been detected in the {Ho, Er, Tm, Lu}–Cu–Ga systems. The $RE_3Cu_xGa_{11-x}$ phases of the La_3Al_{11}-type (orthorhombic, $3 \times 1 \times 1$ multiplicity) [2] are formed in the {Dy, Ho, Er, Tm, Yb, Lu}–Cu–Ga systems. A set of YAl_xGa_{4-x} (orthorhombic, $4 \times 3 \times 1$, $4 \times 2 \times 1$, $3 \times 2 \times 1$, $2 \times 2 \times 1$, $2 \times 1 \times 1$ multiplicity) phases [8], La_2NiAl_7 (tetragonal, $\sqrt{2}x\sqrt{2}x\,2$) [9] and $REPt_{2.12}Sb_{1.75}$ (RE = La, Ce, Pr, tetragonal, $2\sqrt{2}x\,2\sqrt{2}x\,2$) [10] could be specially mentioned among the other compounds derived from the $BaAl_4$ type with the multiplication of lattice parameters.

Here we present the results of the structural determinations of the Ga-rich compounds, which exist in the Y–Cu–Ga system at 500 °C.

2. Experimental

A set of the Y–Cu–Ga alloys (55 alloys in all) containing 20.0, 20.5, 21.0, 21.4, 23.0 and 25 at.% Y, 50–75 at.% Ga was prepared by the arc melting of yttrium (99.8 wt.%), gallium (99.999 wt.%) and electrolytic copper (99.99 wt.%) under purified argon atmosphere. The ingots were remelted several times in order to ensure perfect homogeneity. After arc melting the samples were wrapped in molybdenum foil, sealed in evacuated quartz tubes, and annealed at 500 °C for 150 h with subsequent quenching in cold water.

The X-ray powder diffraction data were collected with a DRON-3 automatic diffractometer (CuKα radiation) [11]. The diffraction patterns were obtained in a discrete mode under the following scanning parameters: observation range $2\theta = (10–120)^\circ$, step scan 0.03°, counting time per step 3–5 s. The peak positions and integral intensities of the observed reflections were determined using full profile analysis. After removal of the $CuK\alpha_2$ components the diffraction profiles were fitted using the Lorentz function. The peak positions and integral intensities have been calculated with accuracy $\pm(0.001–0.005)^\circ$ and ±(5–10)%, respectively.

In order to determine phase compositions and crystal structures of the alloys we used the original software program packages with special banks for the X-ray

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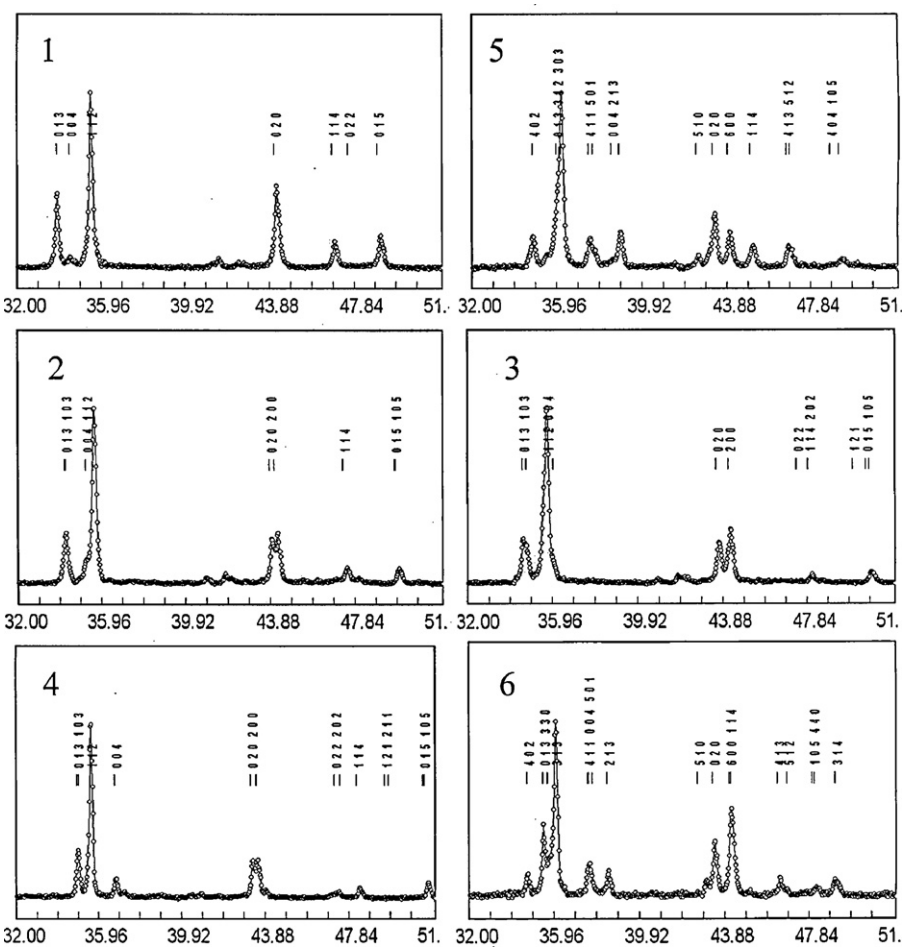

Fig. 1. Parts of the diffraction patterns for the investigated compounds: 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$, 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$, 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$, 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$, 5-$Y_3Cu_4Ga_7$ and 6-$Y_{3.21}Cu_{3.09}Ga_{7.70}$ (CuKα radiation).

diffraction data and for the crystal structures of intermetallic and inorganic compounds [11].

Plate-shaped crystals of the investigated compounds were mechanically extracted from the holes of a single-phase ingots (weight 10 g), which have been slowly cooled in a furnace from the melt during 24 h. These crystals were checked and oriented by the Laue photographs. The lattice constants were determined from the rotating-crystal X-ray photographs and then refined from the powder diffraction data using a least-squares method. The determinations of the systematic extinction for each crystal were carried out on a complete set of the layer-line photographs, obtained by the means of the de Jong-Bouman techniques. Tests of the suggested structural models and structural parameters refinement were carried out by the powder diffraction data using original software complex [11].

3. Results and discussion

All reflections of the diffraction pattern for the 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$ compound (Fig. 1) were indexed well within a tetragonal unit cell ($a = 0.40986(4)$ nm, $c = 1.0411(1)$ nm). Taking into account the phase composition of alloys, this phase contains ~20.3 at.% Y and 52–55 at.% Ga. Its Laue photographs revealed the tetragonal symmetry (*4/mmm*) with the 4-fold axis oriented perpendicularly to the well-developed crystal face. The results of the layer-line photographs indexing (zero-, first-, second -and third-layers, obtained at the crystal rotation around *c*-direction (Fig. 2) as well as zero- and first-layers around *a*-direction) lead to the *I4/mmm* space group. So, the $BaAl_4$-type structure was taken as a trial model for the further structure determination of the 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$ compound by a powder diffraction method. A comparison of the observed and calculated intensities showed a satisfactory agreement within the selected structural model. However, better results were obtained for the model of the modified $BaAl_4$-type structure, in which Cu/Ga atoms partially occupy an additional *2d* position (Table 1). The occupancy of the *2d* position is rather small and is accompanied by the occurrence of the vacant *2a* and *4e* positions, occupied by Y and Cu/Ga atoms, respectively (Table 1) (thereof, compound contains 20.3 at.% Y). Thus, the crystal structure of the 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$ compound can be derived from the $BaAl_4$-type structure by means of low-size atom implantations into its basic planes.

As regard to the positions of the diffraction peaks, the diffraction patterns for the 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$, 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$ and 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$ phases (Fig. 1) are mutually similar. Moreover, these patterns are also similar to the pattern for the 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$ compound, however *h00, h0l* and *hkl* reflections are spitted into two components. So, the main reflections of the patterns for the 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$, 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$ and 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$ compounds can be indexed well within the orthorhombically distorted $BaAl_4$-type unit cell ($a \approx 0.410$–0.411 nm, $b \approx 0.412$–0.418 nm, $c \approx 1.02$–0.98 nm) with somewhat different *b/a* and *c/a* ratios. For this reason the common trial model, which is orthorhombically distorted structure of the 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$ one, was proposed for these three compounds (Table 2). One can see that the observed and calculated intensities for such structural model are in a good agreement. Moreover, one can conclude that the yttrium atoms fill completely *2a* position in the structures of the 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$, 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$ and 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$ compounds (Table 2) in contrast to

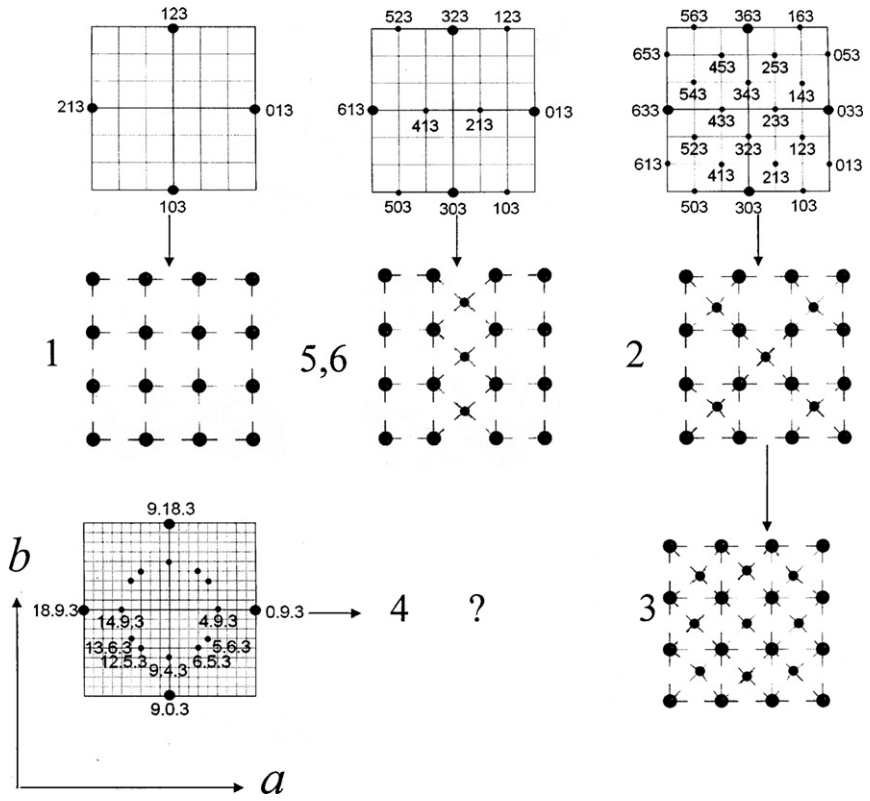

Fig. 2. Indexing of the third-layers of the de Jong-Bouman photographs (crystals rotation around *c*-direction) and the basic planes ($Z = 0$) (yttrium atoms – large circles, Cu/Ga atoms – small circles): 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$, 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$, 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$, 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$, 5-$Y_3Cu_4Ga_7$, 6-$Y_{3.21}Cu_{3.09}Ga_{7.70}$ and 7-$YCuGa_2$ compounds.

Table 1
Crystal data for 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$ compound (modified $BaAl_4$-type structure).

Atom	Site	Site occ.	*x*	*y*	*z*
Y	*2a*	0.97(1)	0	0	0
Me(1)	*4e*	0.86(1)	0	0	0.3861(6)
Me(2)	*4d*	1.00(1)	0	0.5	0.25
Me(3)	*2b*	0.08(1)	0.5	0.5	0
Space group			*I4/mmm* (no. 139)		
Lattice constants, *a*, *c*, nm			0.40986(4); 1.0411(1)		
Independent reflections			36		
Total isotropic *B* factor, nm^2			$B = 3.06(1) \times 10^{-2}$		
Calculated yttrium content			20.3 at%		
Me			0.34 Cu + 0.66 Ga		
Reliability factor			$R_W = 0.043$		

Table 2
Crystal data for 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$, 3-$Y_{1.05}Cu_{1.0}Ga_{2.95}$ and 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$ compounds, refined on their sublattices (orthorhombically distorted $BaAl_4$-type structure).

Atom	Site	2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$		3-$Y_{1.05}Cu_{1.0}Ga_{2.95}$		4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$	
		Site occ.	z[a]	Site occ.	z[a]	Site occ.	z[a]
Y	*2a*	1.00(1)	0	1.00(1)	0	1.00(1)	0
Me(1)	*4i*	0.75(1)	0.3812(6)	0.78(1)	0.3725(6)	0.66(1)	0.3815(7)
Me(2)	*4j*	1.00(1)	0.2501(2)	1.00(1)	0.269(1)	1.00(1)	0.249(1)
Me(3)	*2c*	0.32(1)	0	0.44(1)	0	0.31(1)	0
Space group		*Immm* (no. 71)					
Lattice constants, *a*, *b*, *c*, nm		0.41011(9); 0.41215(9); 1.0206(9)		0.4090(1); 0.4142(1); 0.9961(2)		0.4154(1); 0.41806(5); 0.9787(1)	
Independent reflections		58		54		56	
Total isotropic *B* factor, nm^2		$B = 4.59(7) \times 10^{-2}$		$B = 3.77(1) \times 10^{-2}$		$B = 3.91(1) \times 10^{-2}$	
Calculated yttrium content		20.7 at.%		21.0 at.%		21.6 at.%	
Me		0.29 Cu + 0.71 Ga		0.25 Cu + 0.75 Ga		0.17 Cu + 0.83 Ga	
Reliability factor		$R_W = 0.043$		$R_W = 0.036$		$R_W = 0.046$	

[a] *x* and *y* coordinates are the same that *x* and *y* ones for 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$ compound.

Table 3
Crystal data for 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$ and 3-$Y_{1.05}Cu_{1.0}Ga_{2.95}$ compounds ($Y_{1.04}Cu_{1.12}Ga_{2.84}$-type structure).

Atom	Site	2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$				3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$			
		Site occ.	*x*	*y*	*z*	Site occ.	*x*	*y*	*z*
Y(1)	*2a*	1.00(1)	0	0	0	1.00(1)	0	0	0
Y(2)	*4e*	1.00(1)	0.333	0	0	1.00(1)	0.333	0	0
Y(3)	*4g*	1.00(1)	0	0.333	0	1.00(1)	0	0.333	0
Y(4)	*8n*	1.00(1)	0.332(1)	0.332(1)	0	1.00(1)	0.336(1)	0.336(1)	0
Me(1)	*2c*	1.00(1)	0	0	0.5	1.00(1)	0	0	0.5
Me(2)	*16o*	1.00(1)	0.333	0.339(1)	0.3808(3)	1.00(1)	0.331(2)	0.331(1)	0.3737(3)
Me(3)	*8m*	1.00(1)	0.167(3)	0	0.25	1.00(1)	0.167(1)	0	0.25
Me(4)	*8l*	1.00(1)	0	0.185(1)	0.25	1.00(1)	0	0.169(1)	0.25
Me(5)	*4j*	1.00(1)	0.5	0	0.25	1.00(1)	0.5	0	0.25
Me(6)	*16o*	1.00(1)	0.170(2)	0.333	0.25	1.00(1)	0.166(1)	0.333	0.25
Me(7)	*8l*	1.00(1)	0	0.333	0.3808(3)	1.00(1)	0	0.331(1)	0.3737(3)
Me(8)	*8n*	0.52(1)	0.190(2)	0.190(2)	0	0.25(2)	0.157(4)	0.157(4)	0
Me(9)	*8m*	0.25(1)	0.33(1)	0	0.3808(3)	0.25(1)	0.334(3)	0	0.3737(3)
Me(10)	*4h*	0.12(3)	0.5	0.190(4)	0	0.25(3)	0.5	0.157(4)	0
Me(11)	*4f*	–	–	–	–	0.34(21)	0.158(4)	0.5	0
Space group		*Immm* (no. 71)							
Lattice constants, *a*, *b*, *c*, nm		1.2311(6); 1.2366(2); 1.0206(9)				1.2269(2); 1.2426(2); 0.9961(2)			
Independent reflections		249				235			
Total isotropic *B* factor, nm^2		$B = 4.64(3) \times 10^{-2}$				$B = 3.69(5) \times 10^{-2}$			
Calculated yttrium content		20.7 at.%				21.0 at.%			
Me		0.29 Cu + 0.71 Ga				0.25 Cu + 0.75 Ga			
Reliability factor		$R_W = 0.069$				$R_W = 0.068$			

Table 4
Crystal data for 5-$Y_3Cu_4Ga_7$ and 6-$Y_{3.21}Cu_{3.09}Ga_{7.70}$ compounds (La_3Al_{11}-type structure).

Atom	Site	5-$Y_3Cu_4Ga_7$				6-$Y_{3.21}Cu_{3.09}Ga_{7.70}$			
		Site occ.	*x*	*y*	*z*	Site occ.	*x*	*y*	*z*
Y(1)	*2a*	1.00(1)	0	0	0	1.00(1)	0	0	0
Y(2)	*4e*	1.00(1)	0.3043(4)	0	0	1.00(1)	0.3136(6)	0	0
Me(1)	*8m*	1.00(1)	0.3479(5)	0	0.3629(6)	1.00(1)	0.3564(6)	0	0.3680(5)
Me(2)	*2c*	0.91(1)	0.5	0.5	0	0.82(1)	0.5	0.5	0
Me(3)	*8m*	1.00(1)	0.1396(5)	0	0.2795(5)	1.00(1)	0.1664(8)	0	0.2619(5)
Me(4)	*4j*	1.00(1)	0	0.5	0.6924(9)	0.59(1)	0	0.5	0.6647(9)
Space group		*Immm* (no. 71)							
Lattice constants, *a*, *b*, *c*, nm		1.2354(3); 0.4183(1); 0.9326(3)			1.2290(6); 0.4168(2); 0.9560(5)				
Independent reflections		112			87				
Total isotropic *B* factor, nm^2		$B = 3.29(6) \times 10^{-2}$			$B = 3.42(6) \times 10^{-2}$				
Calculated yttrium content		21.6 at.%			22.9 at.%				
Me		0.36 Cu + 0.64 Ga			0.30 Cu + 0.70 Ga				
Reliability factor		$R_W = 0.051$			$R_W = 0.051$				

Table 5
Crystal data for 7-$YCuGa_2$ compound (own type structure).

Atom	Site[a]	Site occ.	*x*	*y*	*z*
Y(1)	*2a*	1.00(1)	0	0	0
Y(2)	*4e*	1.00(1)	0.341(1)	0	0
Y(3)	*4i*	1.00(1)	0	0	0.300(1)
Y(4)	*8m*	1.00(1)	0.341(1)	0	0.300(1)
Y(5)	*2d*	1.00(1)	0.5	0	0.5
Y(6)	*4j*	1.00(1)	0	0.5	0.25
Me(1)	*16o*	1.00(1)	0.378(3)	0.298(2)	0.382(2)
Me(2)	*8l*	1.00(1)	0	0.315(3)	0.180(2)
Me(3)	*8m*	1.00(1)	0.180(2)	0	0.180(2)
Me(4)	*4j*	1.00(1)	0.5	0	0.220(3)
Me(5)	*4f*	1.00(1)	0.180(2)	0.5	0
Me(6)	*4h*	1.00(1)	0.5	0.290(3)	0
Me(7)	*16o*	0.87(2)	0.180(2)	0.180(2)	0.319(3)
Me(8)	*16o*	0.87(2)	0.152(3)	0.289(2)	0.354(2)
Space group			*I2/m* (*Immm*, in fact)		
Lattice constants *a*, *b*, *c*, nm, ∠γ, grad			1.2642(3); 0.9568(2); 1.2369(4); 90.55(2)		
Independent reflections			245		
Total isotropic *B* factor, nm^2			$B = 3.96(1) \times 10^{-2}$		
Calculated yttrium content			25.0 at.%		
Me			0.33 Cu + 0.67 Ga		
Reliability factor			$R_W = 0.083$		

[a] For this model equivalent positions are the same as for *Immm* space group.

the partial occupation of *2a* position by yttrium atoms in the 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$ compound (Table 1).

The Laue photographs for the 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$, 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$ and 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$ crystals revealed an orthorhombic symmetry (*mmm*). Zero- and first-layers of the de Jong-Bouman photographs, obtained at the rotation of these crystals about *c*-direction, were mutually similar and also similar to the appropriate layer-lines photographs of the 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$ crystal. However, the *third* layers, obtained at the rotation of these crystals around *c*-direction, were peculiar for each of these crystals (Fig. 2). Arrangements of the intense reflexes on all these layer-lines photographs were similar to those of the $BaAl_4$-type structure (a major radius circles). Except these intense reflections, the photographs include also the weak additional reflexes (a small radius circles). These additional reflexes are placed as inserting nodes (Fig. 2). Taking these inserting nodes into account, the crystal structures of the 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$ and 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$ compounds reveal $3 \times 3 \times 1$ multiplies of their lattice subcells as well as the crystal structure of the 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$ compound reveals $9 \times 9 \times 1$ multiplies of its lattice subcell.

In consideration of the systematic extinction (an absence of the $h+k+l=2n+1$ reflections on the de Jong-Bouman photographs) (Fig. 2) and the symmetry of the Laue photographs (*mmm*), the possible space group for 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$, 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$ and 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$ compounds is *Immm*. So, the structural models for the 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$ and 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$ compounds (with 3 multiplications of their lattice subcells) were considered within the framework of this space group (*Immm*) (Table 3). Here we have assumed that the modified $BaAl_4$-type fragments (in fact the crystal structure of the 1-$Y_{1.02}Cu_{1.35}Ga_{2.63}$ compound) form the basis of these phases. The comparison of the observed and calculated intensities for both structural models shows a good agreement.

However, the calculation results (Table 3) demonstrate that crystal structures of the 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$ and 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$ compounds display different arrangements of the additional Cu/Ga atoms within their basic plane with $Z=0$ (Fig. 2). So, there are only five partially filled positions in the crystal structure of the 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$ compound, while in the crystal structure of the 3-$Y_{1.05}Cu_{1.00}Ga_{2.95}$ compound additional Cu/Ga atoms partially occupy all nine positions (Fig. 2).

The unit cell of the 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$ compound is very big (more than 800 atoms per unit cell). Therefore it was impossible to determine its crystal structure by the X-ray powder diffraction. However, certain speculations, concerning atomic arrangement in the basic plane ($Z=0$) of the structure of the 4-$Y_{1.08}Cu_{0.72}Ga_{3.20}$ compound, could originate from the geometry of the de Jong-Bouman photograph. So, in the case of 9 times multiplication of *a* and *b* sublattice constants the arrangement of the additional Cu/Ga atoms is similar to the arrangement of the additional reflections on this photograph (Fig. 2).

As a result of the previous single-crystal investigation [3], it was shown that the crystal structure of the 5-$Y_3Cu_4Ga_7$ compound belongs to the La_3Al_{11}-type, in which yttrium, copper and gallium atoms completely filled corresponding positions. The results of the present X-ray powder diffraction investigation (Table 4) reveal the partial occupation of 2*d* position by Cu/Ga atoms in this structure.

The X-ray study of the alloys with 21.4–23 at.% Y displayed the existence of the novel 6-$Y_{3.21}Cu_{3.09}Ga_{7.70}$ compound (54–57 at.% Ga), that was not detected earlier. The powder diffraction pattern for such compound is similar to that for the 5-$Y_3Cu_4Ga_7$ one (Fig. 1). However, at 500 °C both of these compounds are strongly individual. The crystal structure of the 6-$Y_{3.21}Cu_{3.09}Ga_{7.70}$ complex also belongs to the La_3Al_{11}-type with the partial occupations of the *2c* and *4j* positions (Table 4).

Table 6
Crystallographic data of the Ga-rich ternary compounds.

Compound	*Me* content, at.%			Structure type	Space group	Multiplicity of the subcell	Lattice constants, nm		
	Y	Cu	Ga				*a*	*b*	*c*
1-$Y_{1.02}Cu_{1.38-1.23}Ga_{2.60-2.75}$	20.40	27.60–24.60	52.00–55.00	$BaAl_4$[a]	*I4/mmm*	$1 \times 1 \times 1$	0.40986(5)–0.40989(6)	–	1.0411(2)–1.0528(2)
2-$Y_{1.04}Cu_{1.16-1.12}Ga_{2.80-2.84}$	20.80	23.20–22.20	56.00–57.00	Own	*Immm*	$3 \times 3 \times 1$	1.2303(1)–1.2305(1)	1.2365(2)–1.2366(2)	1.02305(7)–1.02062(4)
3-$Y_{1.05}Cu_{1.00-0.90}Ga_{2.95-3.05}$	21.00	20.00–18.00	59.00–61.00	Own	*Immm*	$3 \times 3 \times 1$	1.2268(2)–1.2300(1)	1.2426(2)–1.2565(2)	0.9984(5)–0.9985(6)
4-$Y_{1.08}Cu_{0.57-0.17}Ga_{3.35-3.75}$	21.60	11.40–3.40	67.00–75.00	Own	*Immm*	$9 \times 9 \times 1$	3.7282(8)–3.7605(9)	3.7517(9)–3.7694(8)	0.9823(7)–0.9682(5)
5-$Y_{3.02}Cu_{3.98}Ga_{7.00}$	21.57	28.43	50.00	La_3Al_{11}	*Immm*	$3 \times 1 \times 1$	1.2354(3)	0.4183(1)	0.9326(3)
6-$Y_{3.23}Cu_{3.21-2.93}Ga_{7.56-7.84}$	23.07	22.93–20.93	54.00–56.00	La_3Al_{11}	*Immm*	$3 \times 1 \times 1$	1.2290(6)–1.2286(7)	0.4168(1)–0.4130(6)	0.9560(5)–0.9680(6)
7-YCuGa$_2$	25.00	25.00	50.00	Own	*I2/m*	$3 \times 3 \times 1$	1.2369(4)	1.2642(3)	0.9568(2)
								$\angle\alpha = 90.55°$	

[a] Modified $BaAl_4$-type structure.

All efforts to obtain the single crystals of the 7-$YCuGa_2$ compound were unsuccessful. So, the further determination of its crystal structure has been carried out by a powder method. The X-ray diffraction pattern of the 7-$YCuGa_2$ compound can be indexed well within a monoclinic lattice constants $a = 1.2642(3)$ nm, $b = 0.9568(2)$ nm, $c = 1.2369(4)$ nm, $\angle\gamma = 90.55(2)^\circ$ (subcell lattice constants: $a = 0.4214$ nm, $b = 0.9568$ nm, $c = 0.4123$ nm, $\angle\gamma = 90.55^\circ$). Taking into account the systematic extinction, the possible space group is *I2/m*. So, as regard to the similarity of the diffraction patterns of the 5-$Y_3Cu_4Ga_7$ and 7-$YCuGa_2$ compounds as well as to the values of their lattice constants, one can assume that the basis of the structure of the 7-$YCuGa_2$ complex is also formed by the $BaAl_4$-type structure (La_3Al_{11}) fragments. Moreover, to simplify the trial model calculations we supposed that in the *I2/m* space group all atomic coordinates with *x*, *y*, *z* and *x*, −*y*, *z* are mutually related (i.e. equivalent positions correspond in fact to the *Immm* space group). The results of the refinement of this trial model, which led to a good correspondence of the observed and calculated intensities, are listed in Table 5. However, it should be noted that the obtained structure of the 7-$YCuGa_2$ compound needs to be refined by the single-crystal technique, since certain limitations were imposed on the atomic coordinates.

So, the obtained results show that tetragonal 1-$Y_{1.02}Cu_{1.38}Ga_{2.60}$ phase is the parent structure for a series of the Ga-rich compounds containing 20–25 at.% Y. If the crystal structure of the 1-$Y_{1.02}Cu_{1.38}Ga_{2.60}$ compound is accepted as the basic one (multiplication of the lattice constants is $1 \times 1 \times 1$), the crystal structures of all other ones could be derived from the parent structure by multiplication of their *a* and *b* lattice subcells. We consider two subseries for these compounds, namely, $Y_{1+x}(Cu,Ga)_{4-x}$ and $Y_{3+x}(Cu,Ga)_{11-x}$.

The first of them ($Y_{1+x}(Cu,Ga)_{4-x}$ subseries) exhibits the steady increasing multiplication of the *a* and *b* sublattice constants from 1×1 (for the 1-$Y_{1.02}Cu_{1.38-1.18}Ga_{2.60-2.80}$ phase) to 3×3 (for the 2-$Y_{1.04}Cu_{1.12}Ga_{2.84}$ and 3-$Y_{1.05}Cu_{1.00-0.90}Ga_{2.95-3.05}$ phases) and, finally, to 9×9 (for the 4-$Y_{1.08}Cu_{0.57-0.17}Ga_{3.35-3.75}$ phase). The yttrium content also increases gradually from 20 to 22 at.% upon increasing Ga-content. Some fragments of the basic yttrium planes of these compounds occur to be partially (to 50%) centered by Cu/Ga atoms.

The second one ($Y_{3+x}(Cu.Ga)_{11-x}$ subseries) reveals the 3×1 multiplicity of the *a* and *b* lattice subcells for both 5-$Y_3Cu_4Ga_7$ and 6-$Y_{3.21}Cu_{3.09}Ga_{7.70}$ compounds. Cu/Ga atoms take place in the center of about one-third of the basic yttrium plane fragments. The compositions of these two compounds shift to the higher yttrium content (from 21.5 to 23 at.% Y).

Crystallographically independent yttrium atoms in the 1–6 compounds form a similar body-centered atomic arrangements (tetragonal or orthorhombically distorted), resembling the $BaAl_4$-type structure. However, the arrangements of Cu/Ga atoms in each of these compounds are somewhat peculiar. Each Cu/Ga atom, placed in basic yttrium planes, is a result of the replacement of a couple of Cu/Ga atoms, placing directly above and below this atom. Couple of Cu/Ga atoms in the $Y_{3+x}(Cu,Ga)_{11-x}$ series compounds is completely replaced by one Cu/Ga atom, whereas similar replacement in the $Y_{1+x}(Cu,Ga)_{4-x}$ series compounds is rather stochastic. So, as regard to the main structure arrangement, the reported compounds are shown to be closely related and derived from the $BaAl_4$-type structure.

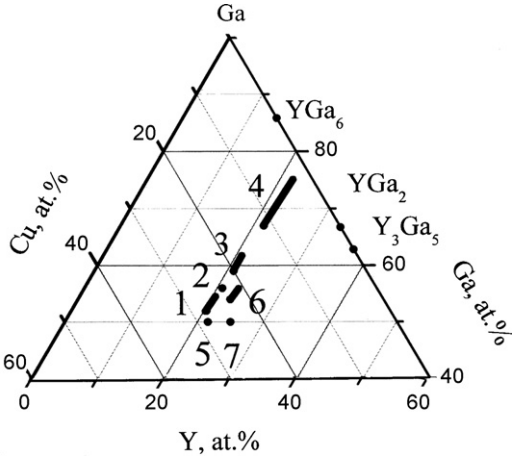

Fig. 3. Plots of the phase compositions in the Ga-rich part of the Y–Cu–Ga system at 500 °C.

In a conclusion, the performed investigation exhibits the existence of 7 ternary compounds in the Ga-rich part of the Y–Cu–Ga system at 500 °C (Table 6). The X-ray crystal structure study reveals that the compositions of complexes gradually shift to the higher yttrium content with increasing Ga-content (Fig. 3). Such changing of the Y-content is caused by an increasing of the atomic vacancies in the Cu/Ga positions. Previously we have revealed the similar effect for the series of the $CaCu_5$-type structure derivatives [12], which exist in the Cu-rich part of the Y–Cu–Ga system.

As a whole the highest amount of ternary compounds, which crystal structures were shown to be constructed from the orthorhombic distorted $BaAl_4$-like fragments by multiplication of its *a* and *b* lattice constants *concurrently* exist in the investigated part of the Y–Cu–Ga equilibrium diagram.

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