Compounds $Ln_5(Ag, Ga)_{19-x}$ (Ln = Gd, Tb) – Defective Partially Ordered Representatives of the Rb_5Hg_{19} Structure Type

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New compounds $Ln_5(Ag, Ga)_{19-x}$ (Ln = Gd, Tb) have been found to crystallise with the Rb_5Hg_{19} structure type (space group $I4/m$). The crystal structures were refined for $Gd_5Ag_{1.8}Ga_{15}$ and $Tb_5Ag_2Ga_{15.6}$ from X-ray powder data: $a = 9.4635(1)$, $c = 9.8638(2)$ Å, $R_I = 0.093$ and $a = 9.4313(1)$, $c = 9.8491(2)$ Å, $R_I = 0.085$, respectively. Some positions in the crystal structures of new the compounds are occupied partially.

Key words: Crystal Structure, Ternary Gallides

Introduction

During an investigation of the Tb-Ag-Ga system at 873 K a new gallide with the composition $\sim TbAg_{0.5}Ga_{3.5}$ has been found [1]. Its crystal structure was not established because of the absence of a single crystal with suitable size. Proceeding from the compound's composition one can assume that its structure might be closely related to the $BaAl_4$-type. Such a hypothesis is supported by the presence in the related Yb-Ag-Ga system, at 20 – 22 at. % of rare-earth metal content, of a ternary gallide with $BaAl_4$ type [2], and also two gallides with $CaCu_{0.15}Ga_{3.85}$ [3] and La_3Al_{11} [4] type structures, which are derivatives of the $BaAl_4$ type. In the Gd-Ag-Ga system a new ternary gallide with the approximate composition $GdAg_{0.5}Ga_{3.5}$ was also discovered. Its powder diffraction pattern was very similar to that of $TbAg_{0.5}Ga_{3.5}$. To establish the crystal structure of these new ternary gallides we used the atomic parameters established for the Rb_5Hg_{19} structure type [5], which is also related to the $BaAl_4$ type. If lattice parameters in the $BaAl_4$ structure are equal to a_0 and c_0, then in the Rb_5Hg_{19} type they will have values of about $a \approx 2a_0$ and $c \approx c_0$. All our assumptions have been confirmed experimentally (see Tables 1 and 2).

Table 1. Crystallographic data of the compounds $Ln_5(Ag, Ga)_{19-x}$.

	Compound	
Parameters	$Gd_5Ag_{1.8}Ga_{15}$	$Tb_5Ag_2Ga_{15.6}$
Structure type	Rb_5Hg_{19}	Rb_5Hg_{19}
Space group	$I4/m$	$I4/m$
Lattice parameters (Å)		
a	9.4635(1)	9.4313(1)
c	9.8638(2)	9.8491(2)
Cell volume (Å^3)	883.38(4)	876.07(4)
Calculated density (g/cm^3)	7.63(4)	7.93(4)
Number of atoms in cell	43.7	45.06
$2\theta°$-Range	3 – 98	3 – 98
Number of free parameters	20	20
R_I/R_P	0.093/0.162	0.085/0.154

Experimental Section

The samples were prepared by arc-melting of mixtures of the elemental components (Gd 99.5 wt.% pure, Tb 99.5 wt.% pure, Ag 99.995 wt.%, and Ga 99.95 wt.%) in a purified argon atmosphere. All alloys were then sealed in evacuated quartz ampoules and homogenized at 873 K for 720 h. Then the alloys were quenched in cold water without breaking the ampoules.

Phase analysis was carried out using powder diffraction patterns collected using the $\theta - 2\theta$ scan technique with a step width of 0.05° in 2θ ($2\theta_{max} = 90°$) and an exposition time of 12 s for each step (DRON-3M diffractometer, Cu-K_α-radiation). Diffraction data for the crystal structure determination were obtained on a Huber image plate Guinier camera G 670 in a 2θ-range of 3 – 100° (exposition time 6×15 min, Cu-K_{α_1}-radiation). All calculations were performed using the CSD software [6].

Table 2. Structural data of $Ln_5(Ag, Ga)_{19-x}$ compounds (Ln = Gd, Tb).

Atoms	WP	Coordinates *x*	*y*	*z*	B_{iso}	Minimal δ (Å)	CN
$Gd_5Ag_{1.8}Ga_{15}$							
2Gd1	2(*a*)	0	0	1/2	0.4(1)	-8Ga2 - 3.164(4)	20
8Gd2	8(*h*)	0.1068(3)	0.3132(2)	0	0.58(7)	-2Ga2 - 3.045(5)	19
2.92(4)Ga1	4(*d*)	0	1/2	1/4	0.57(1)	-4Ga2 - 2.478(4)	12
12.78(8)Ga2	16(*i*)	0.9077(5)	0.7050(4)	0.6214(3)	1.5(1)	**-1Ga2 - 2.391(4)**	9
T1(0.28(4)Ga+1.72(4)Ag)	2(*b*)	0	0	0	0.8(1)	-8T2 - 2.927(3)	12
T2(14.1(1)Ga+1.9(1)Ag)	16(*i*)	0.1835(3)	0.0868(4)	0.2239(2)	0.83(9)	-1Ga2 - 2.520(5)	12
$Tb_5Ag_2Ga_{15.6}$							
2Tb1	2(*a*)	0	0	1/2	0.31(9)	-8Ga2 - 3.182(4)	20
8Tb2	8(*h*)	0.1064(3)	0.3153(2)	0	0.66(7)	-2Ga2 - 3.001(4)	19
2Ag	2(*b*)	0	0	0	0.7(1)	-8T - 2.920(2)	12
2.88(4)Ga1	4(*d*)	0	1/2	1/4	2.0(1)	-4Ga2 - 2.440(4)	12
14.18(4)Ga2	16(*i*)	0.9084(5)	0.7009(4)	0.6209(2)	2.0(1)	**-1Ga2 - 2.382(3)**	9
T(14.08(4)Ga+1.92(4)Ag)	16(*i*)	0.1819(3)	0.0886(3)	0.2244(2)	0.85(6)	-1Ga2 - 2.537(4)	12

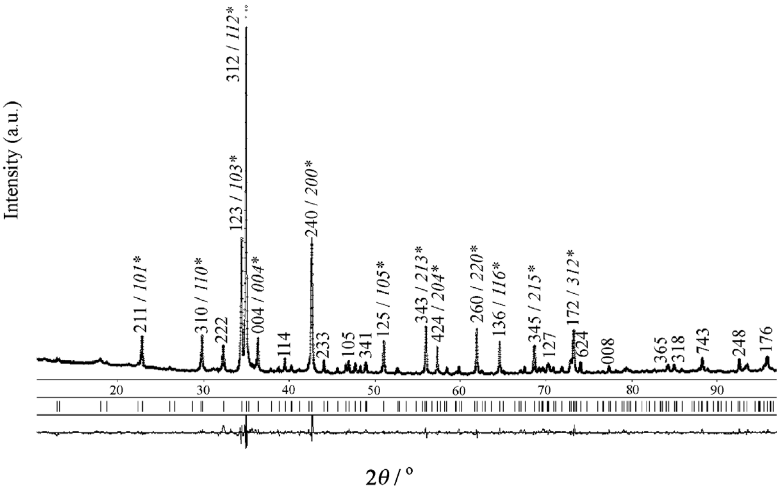

Fig. 1. Experimental and calculated profiles of $Gd_5Ag_{1.8}Ga_{15}$ (Rb_5Hg_{19} type). Indexes which belong to the $BaAl_4$ type subcell are marked by asterics. The position of the Bragg reflections are marked by vertical lines. The lowest line corresponds to the difference $I_o - I_c$.

Results and Discussion

Crystal structure of $Gd_5Ag_{1.8}Ga_{15}$

The most intense reflections of the powder patterns of the ternary gallides with the composition $\sim GdAg_{0.5}Ga_{3.5}$ were indexed with a tetragonal unit cell with lattice parameters $a = 4.2262(3)$ and $c = 9.853(1)$ Å (see Fig. 1). However, a large number of unindexed reflections, which did not belong to other known binary or ternary phases in the Gd-Ag-Ga system, indicated that the crystal structure of the new compound is more complicated than the $BaAl_4$ type. All additional reflections were very well indexed in a tetragonal unit cell with the lattice parameters shown in Table 1, where *a* is doubled with respect to $BaAl_4$ type. An analysis of systematic absences of reflections showed two possible space groups: $I4/m$ or $I\bar{4}$. The values of unit cell parameters as well as the symmetry of the ternary compound $\sim GdAg_{0.5}Ga_{3.5}$ allowed us

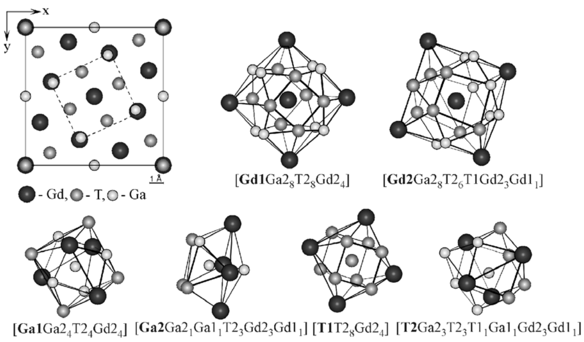

Fig. 2. *xy* projection and coordination polyhedra in the crystal structure of $Gd_5Ag_{1.8}Ga_{15}$. The $BaAl_4$ type subcell is marked by dotted lines.

to choose the Rb_5Hg_{19} type as a model for crystal structure refinement. Atomic coordinates, the type of atom distribution and the displacement parameters (see Table 2) correspond to the final *R*-values given in Table 1. The minimum interatomic distances (Table 2)

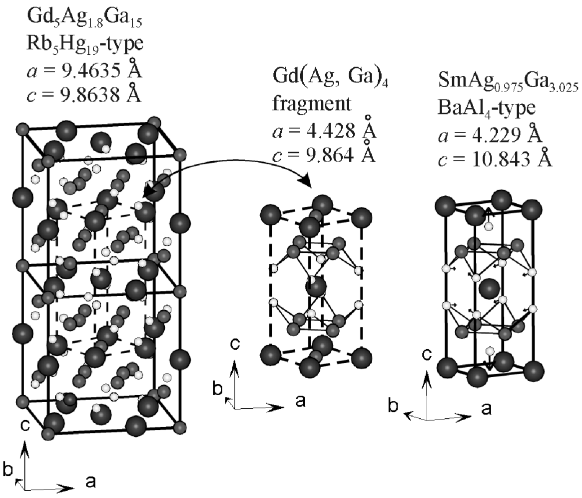

Fig. 3. The relationship between the Rb_5Hg_{19} and $BaAl_4$ types. The $BaAl_4$ type subcell in the crystal structure of $Gd_5Ag_{1.8}Ga_{15}$ is marked by dotted lines.

in the structure of the new compound are in the good agreement with the sum of the atomic radii of the elements [7]. Wyckoff positions $4(d)$ and $16(i)$ are partially occupied by Ga atoms; therefore this compound is a defective, partially ordered representative of the Rb_5Hg_{19} type.

The *xy* projection of the crystal structure of $Gd_5Ag_{1.8}Ga_{15}$ and the coordination polyhedra of all atoms are shown in Fig. 2. The Gd1 and Gd2 atoms are localized in the centers of 20- and 19-vertices polyhedra, which are very similar to the 22-vertices polyhedra of the $BaAl_4$ structure. The Ga2 atoms center tetragonal antiprisms with an additional atom (CN = 9), while the T1-atoms are in the centers of hexahedra formed by T1-atoms, four edges of which are centred by Gd atoms. Such coordination polyhedra demonstrate a close relationship between the Rb_5Hg_{19} and $BaAl_4$ types. The relationship of these two types was studied in detail in [5] and [8].

The doubled unit cell of $Gd_5Ag_{1.8}Ga_{15}$, as well as a fragment of the $BaAl_4$ type structure, are shown in Fig. 3. The fragment is very similar to the structure of $SmAg_{0.975}Ga_{3.025}$ ($BaAl_4$-type) [9]. In this structure directions of the atoms' displacement, which leads to the formation of the corresponding fragment of $Gd_5Ag_{1.8}Ga_{15}$, are marked by arrows. Such similarities of the $SmAg_{0.975}Ga_{3.025}$ and $Gd_5Ag_{1.8}Ga_{15}$ structures shows once again the close relationship between Rb_5Hg_{19} and $BaAl_4$.

Crystal structure of the $Tb_5Ag_2Ga_{15.6}$

Crystallographic data of $Tb_5Ag_2Ga_{15.6}$ are presented in Table 1. The atomic parameters given in Table 2 correspond to the final values of $R_I = 0.085$ and $R_P = 0.154$. The $4(d)$ and $16(i)$ positions are partially occupied, similar to $Gd_5Ag_{1.8}Ga_{15}$. However, the statistical mixtures of Ag and Ga atoms occur in the former structure only for one Wyckoff position. Thus this compound is also a defective, partially ordered representative of the Rb_5Hg_{19} type. The minimum interatomic distances correlate very well with the sum of atomic radii of the elements [7].

Thus, both ternary gallides are defective, partially ordered variants of the Rb_5Hg_{19} type structure. Compounds with such a structure are found in the *Ln*-Ag-Ga systems for the first time. However, the tendency towards formation of defective structures in the Ga-rich region of ternary systems is not exceptional. For example, the structures of $LaNi_{1-x}Ga_6$ [10], $CeAg_{1.25}Ga_{4.25}$ [11], $YbGa_5$ [12], and some others, are related to the $BaAl_4$ type and also contain partially occupied positions.

The structures of $Tb_5Ag_2Ga_{15.6}$ and $Gd_5Ag_{1.8}Ga_{15}$ belong to the family of structures with an Archimedian cube coordination for the Ga-atoms [13]. This fact confirms once again that the formation of compounds with icosahedral coordination of smaller atoms (Ag, Ga) is not typical for the *Ln*-Ag-Ga systems, and this is the main difference between the *Ln*-Ag-Ga and *Ln*-Ag-Al systems.

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