Compounds Ln₅(Ag, Ga)₁₉₋ₓ (Ln = Gd, Tb) – Defective Partially Ordered Representatives of the Rb₅Hg₁₉ Structure Type

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New compounds Ln₅(Ag, Ga)₁₉₋ₓ (Ln = Gd, Tb) have been found to crystallise with the Rb₅Hg₁₉ structure type (space group I₄/m). The crystal structures were refined for Gd₅Ag₁₋₇Ga₁₅ and Tb₅Ag₂Ga₁₅₋₆ 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 ~TbAg₀.₅Ga₃.₅ 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 BaAl₄-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 BaAl₄ type [2], and also two gallides with CaCu₀.₁₅Ga₃.₈₅ [3] and La₃Al₁₁ [4] type structures, which are derivatives of the BaAl₄ type. In the Gd-Ag-Ga system a new ternary gallide with the approximate composition GdAg₀.₅Ga₃.₅ was also discovered. Its powder diffraction pattern was very similar to that of TbAg₀.₅Ga₃.₅. To establish the crystal structure of these new ternary gallides we used the atomic parameters established for the Rb₅Hg₁₉ structure type [5], which is also related to the BaAl₄ type. If lattice parameters in the BaAl₄ structure are equal to \(a₀\) and \(c₀\), then in the Rb₅Hg₁₉ type they will have values of about \(a ≈ 2a₀\) and \(c ≈ c₀\). All our assumptions have been confirmed experimentally (see Tables 1 and 2).

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.% pure, and Ga 99.95 wt.% pure) 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 \(θ – 2θ\) scan technique with a step width of 0.05° in \(2θ (2θ_{max} = 90°)\) and an exposition time of 12 s for each step (DRON-3M diffractometer, Cu-Kα₁-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 x 15 min, Cu-Kα₂-radiation). All calculations were performed using the CSD software [6].

Table 1. Crystallographic data of the compounds Ln₅(Ag, Ga)₁₉₋ₓ

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Compound</th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
<th>(V) (Å³)</th>
<th>(d_0) (Å)</th>
<th>(c_0) (Å)</th>
<th>(2θ_{max}) (°)</th>
</tr>
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<tbody>
<tr>
<td>Structure type</td>
<td>Rs₂Hg₁₉</td>
<td>9.4635(1)</td>
<td>9.4313(1)</td>
<td>883.38(4)</td>
<td>7.63(4)</td>
<td>7.93(4)</td>
<td>90</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td>Rs₂Hg₁₉</td>
<td>9.8638(2)</td>
<td>9.8491(2)</td>
<td>876.07(4)</td>
<td>7.63(4)</td>
<td>7.93(4)</td>
<td>90</td>
</tr>
<tr>
<td>Cell volume</td>
<td>Rs₂Hg₁₉</td>
<td>883.38(4)</td>
<td>876.07(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated density</td>
<td>Rs₂Hg₁₉</td>
<td>7.63(4)</td>
<td>7.93(4)</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Number of atoms in</td>
<td>Rs₂Hg₁₉</td>
<td>43.7</td>
<td>45.06</td>
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<td></td>
<td></td>
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<tr>
<td>2θ°-Range</td>
<td>Rs₂Hg₁₉</td>
<td>3 – 98</td>
<td>3 – 98</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of free parameters</td>
<td>Rs₂Hg₁₉</td>
<td>20</td>
<td>20</td>
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### Results and Discussion

**Crystal structure of Gd₅Ag₁₈Ga₁₅**

The most intense reflections of the powder patterns of the ternary gallides with the composition \( \sim \text{GdAg}_0.₅\text{Ga}_3.₅ \) were indexed with a tetragonal unit cell with lattice parameters \( a = 4.2262(3) \) and \( c = 9.853(1) \) \( \text{Å} \) (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 BaAl₄ 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 BaAl₄ type. An analysis of systematic absences of reflections showed two possible space groups: \( I4/m \) or \( I4 \). The values of unit cell parameters as well as the symmetry of the ternary compound \( \sim \text{GdAg}_0.₅\text{Ga}_3.₅ \) allowed us to choose the Rb₅Hg₁₉ 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)
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 Rb5Hg19 type.

The xy projection of the crystal structure of Gd5Ag1.8Ga15 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 BaAl4 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 Rb5Hg19 and BaAl4 types. The relationship of these two types was studied in detail in [5] and [8].

The doubled unit cell of Gd5Ag1.8Ga15, as well as a fragment of the BaAl4 type structure, are shown in Fig. 3. The relationship between the Rb5Hg19 and BaAl4 types. The BaAl4 type subcell in the crystal structure of Gd5Ag1.8Ga15 is marked by dotted lines.

The crystal structure of the Tb5Ag2Ga15.6

Crystallographic data of Tb5Ag2Ga15.6 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 Gd5Ag1.8Ga15. 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 Rb5Hg19 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 Rb5Hg19 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 LaNi1-xGa6 [10], CeAg1.25Ga4.25 [11], YbGa5 [12], and some others, are related to the BaAl4 type and also contain partially occupied positions.

The structures of Tb5Ag2Ga15.6 and Gd5Ag1.8Ga15 belong to the family of structures with an Archimedean 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.


Fig. 3. The fragment is very similar to the structure of SmAg0.975Ga3.025 (BaAl4-type) [9]. In this structure directions of the atoms’ displacement, which leads to the formation of the corresponding fragment of Gd5Ag1.8Ga15, are marked by arrows. Such similarities of the SmAg0.975Ga3.025 and Gd5Ag1.8Ga15 structures shows once again the close relationship between Rb5Hg19 and BaAl4.