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Неорганічна хімія

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ISOTHERMAL SECTION OF PHASE DIAGRAMS OF THE Gd–Ag–In AND Y–Ag–In SYSTEMS AT 870 K

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The phase equilibria in the Gd–Ag–In and Y–Ag–In systems at 870 K have been studied in the whole concentration range using X-ray powder and single crystal diffraction and EDX analysis. The isothermal sections of {Gd, Y}–Ag–In phase diagrams at this temperature have been constructed. In both systems, the existence of the following compounds has been confirmed: *RE*Ag_2In (the $MnCu_2Al$-type structure) and *RE*$(Ag,In)_2$ (the $CaIn_2$-type structure). The homogeneity ranges of the ternary phases with the $CaIn_2$ structure type range from 27.5 to 40.0 at. % of In for Gd-containing compound and from 37.0 to 48.0 at. % of In for Y-containing compound. The existence of solid solutions based on *RE*Ag (the CsCl-type structure) binary compounds up to 30 and 28 at. % of In and *RE*In_3 (the $AuCu_3$-type structure) binary compounds up to 11 and 18 at. % of Ag in the systems with Gd and Y respectively has been found. The new *RE*$Ag_{3.5}In_{2.5}$ compounds were found in the {Gd, Y}–Ag–In systems. The crystal structure of $GdAg_{3.5}In_{2.5}$ was determined based on X-ray single crystal data: $YbAg_2In_4$-type, *Im*-3, $Z = 24$, $a = 15.217(2)$ Å, $R1 = 0.0453$).

Key words: intermetallic compounds, indium, phase equilibria, crystal structure.

Compounds of the systems of rare earths with silver and indium have attracted significant interest during the last decades due to their crystal chemistry and physical properties [1]. The investigations of these systems started with the studies of the crystal structure and magnetic properties of the solid solutions *RE*Ag–*RE*In (*RE* = rare earths) [2–7].

Ternary Heysler-type phases *RE*Ag_2In (*RE* = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm) have been found by authors of [8–9] and the results of the measurements of magnetic and electrical properties of those compounds have been reported. It has been confirmed by X-ray and neutron diffraction experiments [10] that $TbAg_2In$ and $DyAg_2In$ compounds are Heysler-type phases with the ordered arrangement of all atoms. For Tb-containing compound magnetic ordering at 8.3 K was observed and for Dy-containing compound magnetic ordering has not been observed up to 1.6 K.

The ternary compounds *RE*(Ag,In)$_2$ with CaIn$_2$ structure type have been found in the systems *RE*-Ag-In, where *RE* = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu [11]. Ratio Ag:In = 1:3 for compound with Ce has been established. The Tb_2AgIn_3 compound crystallizes with the CaIn$_2$ type and orders antiferromagnetically at 42 K [12, 13].

The crystal structure of $YbAg_2In_4$ [14] has been investigated by single crystal X-ray diffraction. The electrical properties of this compound were reported in the same paper. The structure is characterized by silver atoms partially occupying split-positions and it is closely related to the structures of the binary intermetallics YCd_6 [15] and $YbCd_6$ [16]. The isotypic compounds with *RE*$Ag_{3.5}In_{2.5}$ composition have been found later in the systems where *RE* = Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu [17]. Recently, we have investigated the crystal structures of the compounds with Tb and Dy in detail using X-ray single crystal diffraction data and for Dy-containing compound additionally X-ray synchrotron powder diffraction and found that they form at compositions close to $TbAg_3In_3$ [18] and $DyAg_3In_3$ [19] and also characterized by split positions of silver atoms. *bcc*-Type phases $RE_{16}Ag_{42}In_{42}$ (*RE* = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) which are possibly isostructural with *RE*Cd_6 have been investigated by authors of [20] and the structures of those compounds have been described as 1/1 Yb–Cd type approximants in [21]. Magnetic properties of the 1/1 approximant $Ag_{50}In_{36}Gd_{14}$ and the icosahedral Ag–In–Gd quasicrystal were investigated by authors of [22-25] and for the Ag–In–Yb alloys in [26-29]. *RE*$Ag_{5.4}In_{6.6}$ (*RE* = La, Ce, Pr, Nd, Sm, Eu, Yb) compounds with $ThMn_{12}$ type of structure have been reported in [30] and their magnetic and electrical properties were reported in [31].

In spite of considerable interest to alloys of *RE*–Ag–In systems their phase diagrams have been constructed only for {Tb, Dy}–Ag–In systems at 870 K [32]. The purpose of this work is the investigation of interaction of components in the {Gd, Y}–Ag–In ternary systems and the construction of the isothermal sections of their phase diagrams in the whole concentration ranges at 870 K.

The literature data on the crystallographic parameters of the compounds of the {Gd, Y}–Ag–In systems are listed in Table 1.

The binary {Gd, Y}–Ag [33-35], {Gd, Y}–In [36-38] and Ag–In [39, 40] systems, which limit the {Gd, Y}–Ag–In ternary systems have been well studied and their phase diagrams over the whole concentration ranges have been constructed.

41 and 33 ternary alloys have been prepared in Gd–Ag–In and Y–Ag–In systems, respectively, by arc-melting of the pure metals (Gd, 99.9 %; Y, 99.9 %; Ag, 99.9 %; and In, 99.999 %) under an argon atmosphere. The argon was purified before by melting titanium sponge. To ensure homogeneity, the alloys were re-melted twice. The samples were annealed at 870 K for 1 month in evacuated and sealed quartz tubes and subsequently quenched in cold water. The weight losses during the samples preparations were less than 0.5 wt. %. Phase analysis, crystal structure determination and refinement were carried out using X-ray powder diffraction data collected on diffractometers DRON-2.0 (Fe *K*α radiation), HZG-4a (Cu *K*α radiation) and by Debye–Scherrer technique (RKD-57.3 camera on URS-55 apparatuses, Cr *K* radiation). The profile and structural parameters were refined by the Rietveld method using the program DBWS-9807 [41]. The crystal structure of the $GdAg_{3.5}In_{2.5}$ compound was determined on the basis of single crystal X-ray data (KM-4 diffractometer with CCD detector, Mo *K*α radiation). The crystal structure was solved by direct methods and refined using the SHELXS-86 [42] and SHELXL-97 programs [43].

A polished sample of the $Gd_{10}Ag_{55}In_{45}$ alloy (Fig. 1) was analyzed by EDX measurements using a LEICA 420 I scanning electron microscope with GdF_3, elemental silver and indium arsenide as standards. No impurity elements were detected. The analyses of light grey phase (15±1 at. % Gd : 47±1 at. % Ag : 38±1 at. % In) showed more precise composition of new compound.

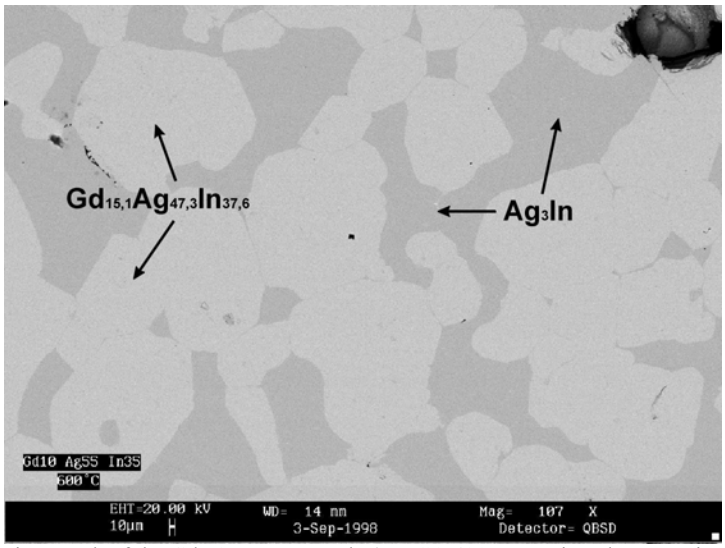

Fig. 1. Micrograph of the $Gd_{10}Ag_{55}In_{35}$ sample (LEICA 420 I scanning electron microscope).

During the investigation of the isothermal sections of the phase diagrams of the ternary Gd–Ag–In and Y–Ag–In systems at 870 K, the existence of the following binary compounds have been confirmed: *RE*Ag (structure type CsCl), *RE*Ag_2 ($MoSi_2$), $RE_{14}Ag_{51}$ ($Gd_{14}Ag_{51}$), *RE*In_3 ($AuCu_3$), RE_3In_5 (Pu_3Pd_5), *RE*In (CsCl), RE_5In_3 (W_5Si_3), RE_2In (Ni_2In) where *RE* is Gd and Y and Ag_3In (ζ) (Cu_3Au).

The phase compositions of the ternary alloys and the phase equilibria in the {Gd, Y}–Ag–In systems at 870 K are shown in Fig. 2 and Fig. 3. In both systems the same number of ternary compounds is formed and similar phase fields are found, only binary compounds *RE*Ag and *RE*In_3 form the solid solutions and ternary compounds with $CaIn_2$-type have homogeneity regions. The consistency of the cell parameters for $GdAg_{3.5}In_{2.5}$ and $YAg_{3.5}In_{2.5}$ compounds in different alloys indicate constant compositions of those compounds. Similar statement is valid for $GdAg_2In$ and YAg_2In Heysler-type phases. Refined values of the cell parameters are close to the parameters described in literature (Table 1).

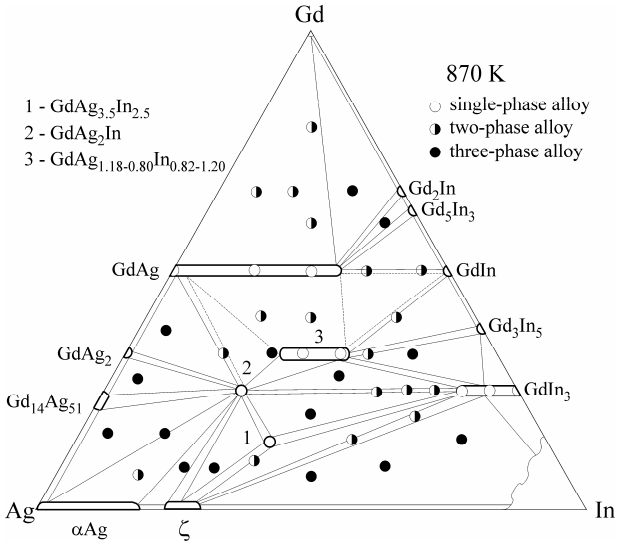

Fig. 2. Chemical and phase composition of samples and isothermal section of the Gd–Ag–In system at 870 K.

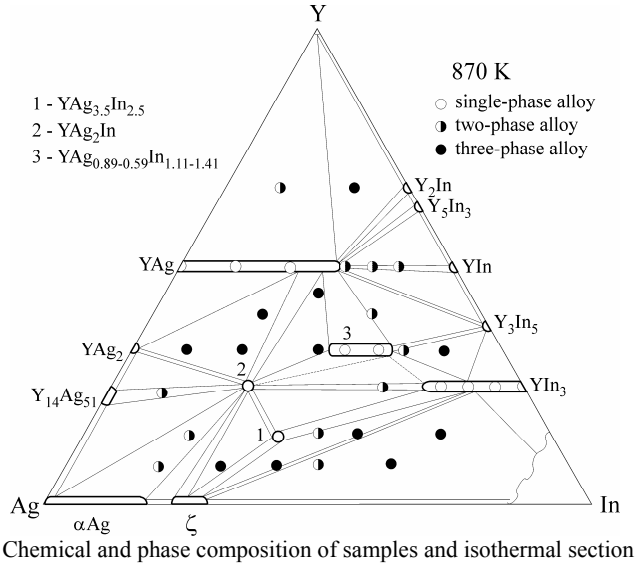

Fig. 3. Chemical and phase composition of samples and isothermal section of the Y–Ag–In system at 870 K.

Table 1

Crystallographic parameters for the ternary compounds in the {Gd, Y}–Ag–In systems

Compound	Structure type	Pearson symbol	Space group	Cell parameters, Å		*Ref.*
				a	*c*	
$GdAg_{3.5}In_{2.5}$	$YbAg_2In_4$	*cI*168	*Im*-3	15.217(2)	–	*
$GdAg_2In$	$MnCu_2Al$	*cF*16	*Fm*-3*m*	6.965	–	8
$GdAg_2In$	$MnCu_2Al$	*cF*16	*Fm*-3*m*	6.971(2)	–	*
Gd_2AgIn_3	$CaIn_2$	*hP*6	$P6_3/mmc$	4.802	7.323	11
$GdAg_{1.17-0.80}In_{0.83-1.20}$	$CaIn_2$	*hP*6	$P6_3/mmc$	4.820(1)-4.823(2)	7.038(1)-7.261(4)	*
$GdAg_{1-x}In_x$ (x=0.6-1)	-	-	*Tetr.*	3.742-3.830	3.711-3.640	4
$GdAg_{1-x}In_x$ (x=0-0.5)	CsCl	*cP*2	*Pm*-3*m*	3.660-3.718	–	4
$GdAg_{1-x}In_x$ (x=0-0.6)	CsCl	*cP*2	*Pm*-3*m*	3.648(2)-3.729(2)	–	*
$GdAg_xIn_{3-x}$ (x=0-0.44)	$AuCu_3$	*cP*4	*Pm*-3*m*	4.6011(9)-4.5600(7)	–	*
$YAg_{3.5}In_{2.5}$	$YbAg_2In_4$	*cI*168	*Im*-3	15.167(2)	–	*
YAg_2In	$MnCu_2Al$	*cF*16	*Fm*-3*m*	6.914	–	8
YAg_2In	$MnCu_2Al$	*cF*16	*Fm*-3*m*	6.923(1)	–	*
Y_2AgIn_3	$CaIn_2$	*hP*6	$P6_3/mmc$	4.749	7.330	11
$YAg_{0.89-0.56}In_{1.11-1.44}$	$CaIn_2$	*hP*6	$P6_3/mmc$	4.746(9)-4.778(2)	7.320(2)-7.356(2)	*
$YAg_{1-x}In_x$ (x=0-0.56)	CsCl	*cP*2	*Pm*-3*m*	3.612(1)-3.991(1)	–	*
YAg_xIn_{3-x} (x=0-0.72)	$AuCu_3$	*cP*4	*Pm*-3*m*	4.590(2)-4.536(1)	–	*

* – this work.

According to the phase diagrams, the binary GdAg and YAg compounds dissolve up to 30 and 28 at. % of indium, respectively. The limits of the solid solutions have been established by changes of the cell parameters of the phases of the *RE*Ag–*RE*In section (Fig. 4). The cell parameters increase with the increase of indium content within the solid solutions (a = 3.648(2)-3.729(2) Å for $GdAg_{1-0.40}In_{0-0.60}$ and a = 3.612(1)–3.691(1) Å for $YAg_{1-0.44}In_{0-0.56}$), what can be explained by bigger effective radius of the In atoms comparing to the size of the Ag atoms. The composition $GdAg_{0.5}In_{0.5}$, described in the literature [4-6], is the part of this solid solution.

$GdIn_3$ and YIn_3 compounds with the $AuCu_3$ structure type dissolve up to 11 and 18 at. % of Ag, respectively. The limits of the solid solution have been also established by the changes of the cell parameters of the phases of the section $REAg_3$–$REIn_3$ (Fig. 4). The cell parameters decrease with the increase of silver content within the solid solutions (a = 4.6011(9)-4.5600(7) Å for $GdAg_{0-0.44}In_{3-2.56}$ and a = 4.590(2)-4.536(1) Å for $YAg_{0-0.72}In_{3-2.28}$), what can be explained, as in the previous case, by bigger effective radius of the In atoms comparing to the size of the Ag atoms. It is necessarily to mention that in the case of the solid solution with CsCl-type the cell parameter changes in agreement with Vegard's rule, but for the solid solution with $AuCu_3$-type a negative deviation occurs.

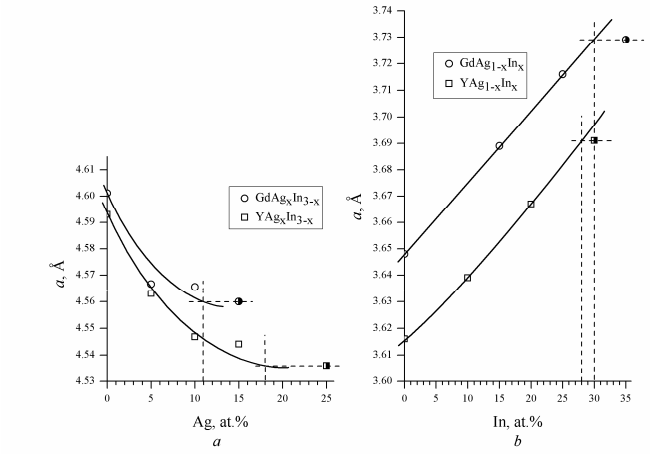

Fig. 4. The dependence of the lattice parameters in the solid solutions $RE\text{Ag}_x\text{In}_{3-x}$ on the content of Ag (*a*) and $RE\text{Ag}_{1-x}\text{In}_x$ on the content of In (*b*), *RE* = Gd, Y.

The compounds $RE(\text{Ag,In})_2$ formed at constant *RE* content 33.3 at. % *RE* are characterized by certain homogeneity range assuming Ag/In atoms substitutions (Fig. 5). The homogeneity ranges for Gd-containing phase ranges from 27.5 to 40 at. % of In and for Y-containing phase ranges from 37 to 48 at. % of In. The cell parameters within the homogeneity ranges are a = 4.820(1)-4.823(2) Å, c = 7.038(1)-7.261(4) Å for $\text{GdAg}_{1.17\text{-}0.80}\text{In}_{0.83\text{-}1.20}$ and a = 4.746(9)-4.778(2) Å, c = 7.320(2)-7.356(2) Å for $\text{YAg}_{0.89\text{-}0.56}\text{In}_{1.11\text{-}1.44}$, respectively (Fig. 5).

During the investigation of the Gd–Ag–In system at 870 K, a single crystal of irregular shape was selected mechanically from the $\text{Gd}_{15}\text{Ag}_{47}\text{In}_{38}$ sample. Some details of the data collection and refinement parameters are listed in Table 2. The atomic coordinates and anisotropic displacement parameters are given in Table 3.

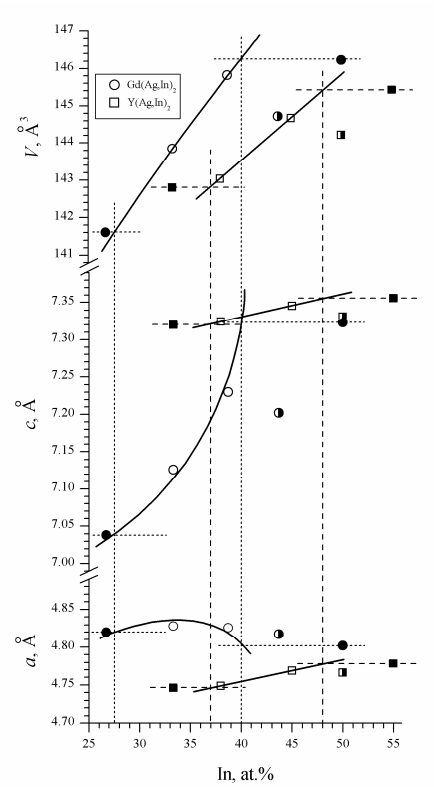

Fig. 5. The dependence of the lattice parameters on the content of In in the solid solutions based on $Gd(Ag,In)_2$ and $Y(Ag,In)_2$ ternary compounds.

The crystal structure refinement revealed that a new compound crystallizes with the $YbAg_2In_4$-type (space group *Im*-3) [14]. Due to different occupation of silver atoms in the sites 16*f* and 24*g* and replacements of In atoms for Ag atoms in the sites 12*e* and 24*g*, a new composition $GdAg_{3,5}In_{2,5}$ is realized. Isotypic compounds with Tb and Dy have slightly different compositions $TbAg_3In_3$ [18] and $DyAg_{3.010}In_3$ (or $DyAg_{2.853}In_3$) [19]. One more representative was found based on the X-ray powder data also in the yttrium system (Table 1). The basic structure motif of these compounds has been considered in detail in the mentioned papers [14, 18, 19].

Table 2

Crystal data and structure refinements for $GdAg_{3.5}In_{2.5}$

Compound	$GdAg_{3.5}In_{2.5}$
Molar weight, g/mol	609.00
Structure type	$YbAg_2In_4$
Pearson symbol	*cI*168
Space group	*Im*-3 (№ 204)
Z	24
Cell parameter, Å	15.217(2)
Volume, Å^3	3532.6(2)
Density (calculated), g/cm^3	8.036
Crystal (alloy) colour	metallic dark grey
Diffractometer	KM-4, CCD
X-ray radiation, Å	Mo Kα, 0.71069
θ range,°	4.0–28.0
Index range	±19, -20 < *k* < +15, ±19
Total number of reflections	9670
Independent reflections	739 (R_{int} = 0.0904)
Reflections with $I > 4\sigma(I)$	738(R_{sigma} = 0.0313)
Absorption coefficient, μ/mm^{-1}	28.50
Extinction coefficient	0.00009(2)
Refinement method	Full-matrix least-squares on F^2
*R*1 [$I > 4\sigma(I)$]	0.0453
wR_2 [$I > 4\sigma(I)$]	0.0997
Goodness-of-fit on F^2	1.247
Peak and hole (e/Å^3)	3.76 and -1.80

Table 3

Atomic coordinates and atomic displacement parameters for $GdAg_{3.5}In_{2.5}$

Atom	Wyckoff position	G	*x/a*	*y/b*	*z/c*	U_{eq}, Å^2
Gd	24*g*	1	0	0.18600(7)	0.30300(7)	0.0145(3)
Ag1	16*f*	0.939(8)	0.1630(3)	0.1630(3)	0.1630(3)	0.030(2)
Ag2	16*f*	0.102(8)	0.133(2)	0.133(2)	0.133(2)	0.023(10)
Ag3	24*g*	0.92(4)	0	0.2437(16)	0.0929(6)	0.027(3)
Ag4	24*g*	0.08(4)	0	0.212(8)	0.080(4)	0.020(9)
Ag5	48*h*	0.163(8)	0.0902(7)	0.0283(19)	0.0679(16)	0.115(19)
Ag6	12*e*	1	0.19343(14)	0	1/2	0.0165(5)
Ag7	24*g*	1	0	0.4024(1)	0.3472(1)	0.0173(4)
In1	12*d*	1	0.41011(16)	0	0	0.0284(6)
In2	48*h*	1	0.20272(8)	0.11744(8)	0.33945(8)	0.0248(4)
Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Gd	0.0129(5)	0.0153(5)	0.0154(5)	-0.001(4)	0	0
Ag1	0.0300(17)	0.0300(17)	0.0300(17)	0.0138(16)	0.0138(16)	0.0138(16)
Ag2	0.023(10)	0.023(10)	0.023(10)	0.002(9)	0.002(9)	0.002(9)
Ag3	0.016(1)	0.047(7)	0.018(2)	0.007(3)	0	0
Ag4	0.025(13)	0.015(27)	0.021(13)	-0.009(15)	0	0
Ag5	0.028(5)	0.25(2)	0.071(9)	-0.10(2)	-0.006(6)	-0.039(12)
Ag6	0.0121(10)	0.0128(10)	0.0245(11)	0	0	0
Ag7	0.0186(7)	0.0169(8)	0.0165(7)	0.0014(6)	0	0
In1	0.0194(11)	0.0472(16)	0.0186(11)	0	0	0
In2	0.0205(6)	0.0337(7)	0.0205(6)	-0.0069(5)	-0.0031(4)	0.0074(5)

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ІЗОТЕРМІЧНИЙ ПЕРЕРІЗ ДІАГРАМ СТАНУ СИСТЕМ Gd–Ag–In ТА Y–Ag–In ПРИ 870 K

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Методами рентгенівського та мікроструктурного аналізів досліджені фазові рівноваги в системах Gd–Ag–In та Y–Ag–In у повному концентраційному інтервалі при 870 K та побудовані ізотермічні перерізи діаграм стану. В обох системах підтверджено існування сполук REAg$_2$In (структурний тип MnCu$_2$Al) та RE(Ag,In)$_2$ (структурний тип CaIn$_2$). За зміною періодів комірки визначено області гомогенності фаз із структурою типу CaIn$_2$: від 27.5 до 40.0 ат. % In для сполуки з гадолінієм та від 37.0 до 48.0 ат. % In для сполуки з ітрієм. Виявлено існування твердих розчинів на основі бінарних сполук REAg (структурний тип CsCl) до 30 та 28 ат. % In та REIn$_3$ (структурний тип AuCu$_3$) до 11 та 18 ат. % Ag для систем з Gd та Y відповідно. Під час досліджень визначено існування нових сполук складу REAg$_{3.5}$In$_{2.5}$. Методом монокристалу уточнено кристалічну структуру сполуки GdAg$_{3.5}$In$_{2.5}$: структурний тип YbAg$_2$In$_4$, просторовагрупа Im-3, Z = 24, a = 15.217(2) Å, R1 = 0.0453.

Ключові слова: інтерметаліди, індій, фазові рівноваги, кристалічна структура.

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