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Phase equilibria and crystal structure of the ternary compounds of the La–Ag–Ga system in the region up to 50.0 at.% of La

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Phase diagrams of the La–Ag–Ga system at 500°C (La content 0-50.0 at.%) and 300°C (La content 0-33.3 at.%) have been built using X-ray structure and phase analysis. The existence of the ternary gallide $LaAg_{1.0-0.5}Ga_{3.0-3.5}$ ($BaAl_4$-type) has been confirmed and the atomic coordinates, displacement parameters and site occupancies have been determined. A new ternary compound, $La(Ag_{0.51}Ga_{0.49})_{11}$ with $BaHg_{11}$-type structure (space group $Pm\bar{3}m$, a = 0.87619(1) nm, wR_p = 0.072), has been discovered at 300°C.

La–Ag–Ga alloys / Phase equilibria / Ternary intermetallic compounds / Crystal structure / X-ray diffraction

1. Introduction

Phase diagrams have been built (entirely or partially) for the RE–Ag–Ga systems where RE = Y [1], Ce [2], Tb [3], the Ce–Ag–Ga system being investigated only in the Ga-rich region. Other RE–Ag–Ga systems have been studied only with the purpose of discovering new ternary gallides of certain structure types: $BaAl_4$, La_3Al_{11}, β-$YbAgGa_2$, $CaIn_2$, KHg_2. None of the discovered ternary gallides contains more than 33.3 at.% of the rare earth element (RE).

A compound with variable composition $LaAg_{0.55-0.675}Ga_{3.45-3.325}$ and $BaAl_4$-type structure (a = 0.4375-0.4356, c = 1.0655-1.0729 nm) is known in the La–Ag–Ga system [4]. Taking into consideration that all the ternary compounds in the RE–Ag–Ga systems form at a RE content of up to 33.3 at.%, we carried out investigations of the La–Ag–Ga system in this region. Since in the RE–Ag–Ga systems the character of the phase equilibria varies with temperature, the experiment was carried out at two temperatures: 500°C and 300°C.

2. Experimental

Samples for the investigation were prepared by arc melting of elements with the following purity: La (99.5 wt.%), Ag (99.95 wt.%), Ga (99.99 wt.%) in purified argon atmosphere. The alloys were annealed in evacuated quartz ampoules at 500°C for 600-900 hours or at 300°C for 1200 hours and then quenched in cold water without breaking the ampoules. Samples with high Ga content were placed in molybdenum crucibles. Phase analysis was carried out using either X-ray powder diffraction patterns obtained by the Debye-Scherrer technique with nonfiltered Cr-K radiation in cameras of 57.3 mm diameter, or X-ray powder diffraction patterns recorded on a DRON-3M diffractometer in the continuous mode (Cu-$K\alpha$ radiation) using the θ-2θ scan technique with steps of 0.02° ($2\theta_{max}$ = 120°) and exposure time of 5-30 s at every point. All calculations were performed using CSD [5] and PC-GSAS [6] software.

3. Binary systems

According to the phase diagram of the La–Ag system, two compounds with point composition: $LaAg_5$ (exists in two modifications with the temperature of polymorphic transformation being ~540°C) and $LaAg_2$ form peritectically. The compounds $La_{14}Ag_{51}$ and LaAg form congruently and the former has a certain homogeneity region [7].

A generalized version of the phase diagram of the La–Ga system shows the existence of five compounds, one of which, $LaGa_2$, forms congruently at 1450°C and has a wide homogeneity region (18-33 at.% La). $LaGa_6$ forms peritectically at 477°C. The other compounds that exist in the system are beyond the investigated region [9].

In the Ag–Ga system a compound with 27-32 at.% of Ga forms peritectically at 609°C.

Table 1 Crystallographic data of the compounds in the binary systems La–Ag, La–Ga and Ag–Ga.

Compounds	Space group	Structure type	Lattice parameters, nm			Ref.
			a	*b*	*c*	
α-$LaAg_5$	$P6_3/mmc$	$MgZn_2$	0.55690	–	0.90775	[7]
$LaAg_5$	$F\bar{4}3m$	$AuBe_5$	0.796	–	–	[8]
$La_{14}Ag_{51}$	$P6/m$	$Gd_{14}Ag_{51}$	1.2955	–	0.9525	[7]
			1.2935(3)		0.9523(4)	*
$LaAg_2$	*Imma*	KHg_2	0.4825	0.7287	0.8196	[7]
			0.4832(3)	0.7285(5)	0.8204(5)	*
LaAg	$Pm\bar{3}m$	CsCl	0.378-0.380	–	–	[7]
			0.3811(7)			*
$LaGa_6$	$P4/nbm$	$PuGa_6$	0.6101	–	0.7696	[12]
$LaGa_{2+x}$	$P6/mmm$	AlB_2	0.4324	–	0.4410	[12]
			0.4317(1)		0.4418(2)	*
ζ-Ag_2Ga(H)	$P6_3/mmc$	Mg	0.28869	–	0.46753	[13]
ζ'-Ag_2Ga(L)	$P\bar{6}2m$	Mg_2In	0.77460	–	0.28704	[13]
			0.7763(2)		0.2881(2)	*
AgGa	$Pm\bar{3}m$	CsCl	0.3171	–	–	[11]

* our results

Table 2 Crystallographic data of some La–Ag–Ga ternary alloys annealed at 500°C.

Composition, at.%			Phase analysis	Lattice parameters, nm		
La	Ag	Ga		*a*	*b*	*c*
10	45	45	$La(Ag,Ga)_4$	0.4383(3)	–	1.0612(7)
			Ag_2Ga	0.7764(5)	–	0.2872(3)
20	10	70	$La(Ag,Ga)_4$	0.43817(1)	–	1.06104(5)
20	15	65	$La(Ag,Ga)_4$	0.43517(3)	–	1.0738(1)
20	20	60	$La(Ag,Ga)_4$	0.43543(1)	–	1.07734(1)
25	50	25	$La(Ag,Ga)_4$	0.4348(1)	–	1.0765(1)
			$La(Ag,Ga)_2$	0.492(1)	0.721(1)	0.813(3)
33.3	6	60.7	$La(Ga,Ag)_2$	0.43158(7)	–	0.4423(1)
33.3	20	46.7	$La(Ag,Ga)_2$	0.4721(4)	0.7298(5)	0.8107(6)
			$La(Ga,Ag)_2$	0.43161(6)	–	0.4426(2)
33.3	30.7	36	$La(Ag,Ga)_2$	0.4723(2)	0.7302(4)	0.8112(5)
33.3	35.7	31	$La(Ag,Ga)_2$	0.4753(4)	0.7312(2)	0.8107(3)
33.3	48.7	18	$La(Ag,Ga)_2$	0.4822(2)	0.7349(2)	0.8143(2)
33.3	56.7	10	$La(Ag,Ga)_2$	0.4795(5)	0.7435(8)	0.8113(8)

The compound undergoes a polymorphic transformation at 432°C. Another compound, AgGa, forms peritectically at 302°C. The maximum solubility of Ga in Ag is ~18 at.% at 380°C and decreases down to 11.8 at.% Ga at 200°C [10,11].

Summarized data on the crystal structure of the binary compounds in the systems that bound the investigated La–Ag–Ga system (Ag–$LaAg_2$–$LaGa_2$–Ga region) are shown in Table 1. Existence of the compound AgGa was not confirmed at the investigated temperatures.

4. Results and discussion

4.1 Phase equilibria

The phase diagram of the investigated part of the La–Ag–Ga system is shown in Fig. 1(a,b). At 500°C we found a considerable solid solution based on the $LaAg_2$ compound, which reaches the composition of $LaAg_{1.05}Ga_{0.95}$. Lattice parameters of some typical samples containing the solid solution $LaAg_{2-x}Ga_x$ are shown in Table 2. The solubility of gallium in the LaAg compound does not exceed ~22 at.%. The composition limit of the solid solution is defined as $LaAg_{0.56}Ga_{0.44}$ (a = 0.3792(5) nm). The unit cell volume of the solid solution decreases with increasing substitution of Ga for Ag, which is in agreement with the atomic dimensions of the two elements. The other binary compounds do not dissolve noticeable amounts of the third element.

The ternary gallide $La(Ag,Ga)_4$ has a homogeneity region ($LaAg_{1.0-0.5}Ga_{3.0-3.5}$) that agrees well with previously obtained data [4]. At 500°C the compound $La(Ag,Ga)_4$ is in equilibrium with all the binary

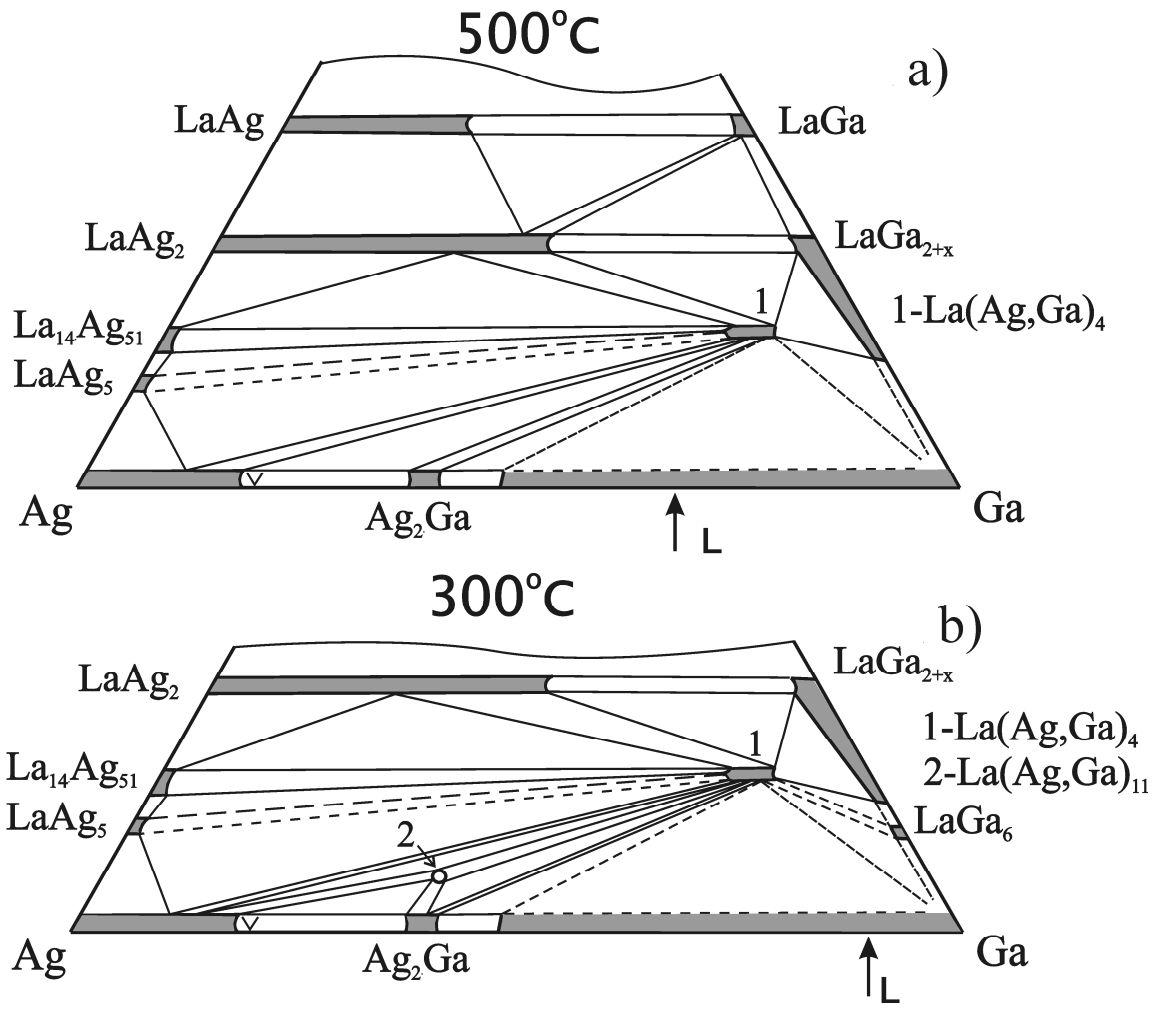

Fig. 1 Part of the phase diagram isothermal section of the of the La–Ag–Ga system at 300°C and 500°C.

compounds of the investigated part of the system (Fig. 1(a)), which may indicate its congruent formation.

Phase analysis of the Ga-rich part of the system at 300°C (Fig. 1(b)) revealed that, with the decrease of temperature, one more compound, $La(Ag,Ga)_{11}$ with a cubic structure of the $BaHg_{11}$-type (a = 0.87649(2) nm) and a small homogeneity region, forms.

4.2 Crystal structure of $La(Ag_{0.18}Ga_{0.82})_4$

It is known that the $La(Ag,Ga)_4$ compound has a $BaAl_4$-type structure [4]. A refinement of the atomic coordinates and distribution of the atoms in the structure was carried out. These data are shown in Table 3, and the interatomic distances in the structure are shown in Table 4.

The $BaAl_4$-type belongs to the class of structures with tetragonal-antiprismatic coordination of the smallest atoms. In the structure of $La(Ag,Ga)_4$ these atoms are Ga. The tetragonal antiprisms are formed by La atoms and a statistical mixture of smaller atoms (Ag+Ga). The interatomic distances in the structure are close to the sum of the atomic radii: r_{La} = 0.1877 nm, r_{Ga} = 0.139 nm, r_{Ag} = 0.1444 nm [14]. Slight shortening of the interatomic distances between Ga atoms in 4(*e*) position (10 %) can indicate the appearance of partially covalent interaction between these atoms. In the structure of $La(Ag,Ga)_4$ one can observe partial ordering of Ag and Ga atoms, since only Ga atoms center antiprisms, forming Ga_2 pairs.

4.3 Crystal structure of the new compound $La(Ag_{0.51}Ga_{0.49})_{11}$

The compound $La(Ag_{0.51}Ga_{0.49})_{11}$ was detected only in samples that were annealed at 300°C: It has a point composition with almost equal amounts of Ag and Ga. The structure of the compound belongs to the $BaHg_{11}$-type. The conditions under which the structure was determined, atomic coordinates and the distribution of the atoms are shown in Table 5, and the interatomic distances in Table 6.

The $BaHg_{11}$-type belongs to the class of structures with coordination polyhedra (CP) similar to the 10-vertex polyhedron characteristic of the $MnAl_6$-type (T2 atoms) [15]. The deformed icosahedron in the structure of $La(Ag_{0.51}Ga_{0.49})_{11}$ corresponds to the position 8(*g*). Such coordination is typical for

Table 3 Refinement of the crystal structure of $La(Ag_{0.18}Ga_{0.82})_4$.

Composition		$La(Ag_{0.18}Ga_{0.82})_4$			
Structure type		$BaAl_4$			
Space group		*I*4/*mmm* (No. 139)			
Lattice parameters, nm		*a* = 0.43824(1),			
		c = 1.06099(4)			
Cell volume, nm^3		0.20377(2)			
Number of atoms in cell		10			
Calculated density, g/cm^3		7.256(1)			
Radiation, nm		Cu-*K*α, 0.154185			
Mode of refinement		Full-profile (CSD)			
$2\theta_{max}$, °		120			
Scale factor		0.6797(8)			
R		$R_I = 0.055$, $R_p = 0.095$			
Atoms	WP	*x*	*y*	*z*	$B_{iso}\cdot10^2$, nm^2
La	2(*a*)	0	0	0	0.48(5)
T1(2.56(3)Ga+1.44(3)Ag)	4(*d*)	0	1/2	1/4	0.56(5)
Ga	4(*e*)	0	0	0.3834(3)	0.85(8)

Table 4 Interatomic distances (δ) for $La(Ag_{0.18}Ga_{0.82})_4$.

Atoms		δ, nm
La	-8 Ga	0.3337(1)
	-8 T1	0.3440(1)
T1	-4 Ga	0.2609(2)
	-4 T1	0.3099(1)
	-4 La	0.3440(1)
Ga	-1 Ga	0.2474(5)
	-4 T1	0.2609(2)
	-4 La	0.3337(1)

Table 5 Refinement of the crystal structure of new ternary compound $La(Ag_{0.51}Ga_{0.49})_{11}$.

Composition		$La(Ag_{0.51}Ga_{0.49})_{11}$			
Structure type		$BaHg_{11}$			
Space group		$Pm\bar{3}m$ (No. 221)			
Lattice parameter, nm		*a* = 0.87649(1)			
Cell volume, nm^3		0.6734(1)			
Number of atoms in cell		36			
Calculated density, g/cm^3		8.293(1)			
Radiation, nm		Cu-*K*α, 0.154185			
Mode of refinement		Full-profile (PC-GSAS)			
$2\theta_{max}$, °		120			
Scale factor		2.9542			
R		$wR_p = 0.072$, $R_p = 0.056$			
Atoms	WP	*x*	*y*	*z*	$B_{iso}\cdot10^2$, nm^2
La	3(*d*)	1/2	0	0	0.51(2)
T1(0.37(2)Ag+0.63(2)Ga)	1(*b*)	1/2	1/2	1/2	0.51(3)
Ag	8(*g*)	0.1755(2)	*x*	*x*	0.99(3)
T2(0.83(3)Ag+11.17(3)Ga)	12(*i*)	0	0.3490(3)	*y*	0.69(3)
T3(7.71(3)Ag+4.29(3)Ga)	12(*j*)	1/2	0.2671(3)	*y*	0.58(3)

Table 6 Interatomic distances (δ) for $La(Ag_{0.51}Ga_{0.49})_{11}$.

Atoms		δ, nm
La	-4 T3	0.3311(3)
	-8 T2	0.3333(3)
	-8 Ag	0.3581(2)
T1	-12 T3	0.2887(3)
Ag	-3 T2	0.2644(3)
	-3 T3	0.3062(2)
	-3 Ag	0.3076(3)
	-3 La	0.3581(4)
T2	-2 Ag	0.2644(3)
	-2 T2	0.2647(4)
	-4 T3	0.2783(3)
	-2 La	0.3333(3)
T3	-4 T2	0.2783(3)
	-1 T1	0.2887(3)
	-4 T3	0.2887(3)
	-2 Ag	0.3062(2)
	-1 La	0.3311(3)

transition metal, Cu, and Ag atoms in compounds with rare earth elements. In the investigated structure this position is the only one, which is occupied solely by Ag atoms, whereas the other positions are occupied by a statistical mixture of Ag and Ga atoms.

The interatomic distances in the structure $La(Ag_{0.51}Ga_{0.49})_{11}$ are close to the sum of the atomic radii of the components (Table 6).

5. Discussion

Our investigation gives an opportunity to compare the interaction of the components in the La–Ag–{Al, Ga, In} systems. The common feature for these systems is that all the ternary compounds form at a relatively small amount of La (0-50 at.%). The solubility of Al and Ga in the binary compound $LaAg_2$ is almost the same: $LaAg_2$ dissolves Al up to the composition $LaAg_{0,96}Al_{1,04}$ [8]. Six ternary compounds form in the La–Ag–Al system, while only two in the La–Ag–Ga system; only the compounds $La(Ag,Al)_4$ and $La(Ag,Ga)_4$ belong to the same, $BaAl_4$-type. All the other ternary intermetallics in the La–Ag–Al system belong to structure types, which are characterized by icosahedral coordination of the smaller atoms: $BaCd_{11}$, Th_2Ni_{17}, Th_2Zn_{17}, $CaCu_5$ and $PuNi_3$ [8]. Icosahedral coordination is common for compounds, the components of which are typical metals. In the La–Ag–Ga system compounds with icosahedral coordination do not exist. In the La–Ag–In system the number of compounds increases again to five ($ThMn_{12}$, $MnCu_2Al$, $CaIn_2$, CsCl, and La_4Ag_3In structure types). And again there is a structure type with icosahedral coordination ($ThMn_{12}$-type) [15].

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