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Isothermal Section of Phase Diagram of Lu–Ge–In Ternary System at 870 K

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The isothermal section of the Lu–Ge–In phase diagram at 870 K over the whole concentration range has been constructed using X-ray phase analysis. Only $LuGe_{1-x}In_x$ (x = 0.035) compound (CrB-structure type, space group *Cmcm*, a = 4.1582(1), b = 10.4616(4), c = 3.8664(1) Å) is formed in the ternary system. The Lu_5Ge_3 compound dissolves up to 10 at. % of indium along the isoconcentration of lutetium 62.5 at. %.

Key words: Lu–Ge–In alloys, isothermal section, phase diagram, X-ray powder diffraction

Earlier we investigated phase equilibria in the Lu–Si–In [1], Y–Ge–In [2] and Sm–{Si,Ge}–In [3] ternary systems. In this paper we present the results of the interaction of the components in the Lu–Ge–In system at 870 K as the continuation of [1–3]. Information on the Ge–In, Lu–Ge and Lu–In binary systems is available in [4–10].

There are no intermediate phases in the Ge–In system [4]. The main feature of its phase diagram is an eutectic reaction, which occurs at 429.3 K and concentration ~99.99 at. % of In. The Lu–Ge phase diagram is given in [5]. There are six compounds in the system: Lu_5Ge_3, Lu_5Ge_4, $Lu_{11}Ge_{10}$, Lu_4Ge_5, $LuGe_{1.5}$ and $LuGe_{1.8}$. The crystal structures of the Lu_4Ge_5 and $LuGe_{1.5}$ compounds were unknown. Information about the compound of the Lu_3Ge_4 composition has been reported later [6]. The phase diagram of the Lu–In system given in [7] contains five intermediate phases: Lu_2In, Lu_5In_3, LuIn, Lu_3In_5 and $LuIn_3$. Later the crystal structure of the Lu_5In_4, LuIn, Lu_3In_5 and $LuIn_2$ binary compounds was investigated [8] and in [9] the own variant of Lu–In phase diagram is given. The existence of the Lu_2In, Lu_5In_3, Lu_5In_4, LuIn, Lu_3In_5, $LuIn_2$ and $LuIn_3$ compounds is reported [9]. The Lu_5In_3 and Lu_5In_4 compounds, that have close crystal structures, form the solid solution Lu_5In_{3+x}, where $0 \le x \le 1$. Crystallographic data for all the binary compounds are given in Table 1.

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Table 1. Crystallographic data for binary phases in the Lu–Ge–In system.

Compound	Structure type	Space group	Cell parameters, Å			Ref.
			a	b	c	
Lu_5Ge_3	Mn_5Si_3	*F6₃/mcm*	8.214		6.157	5
Lu_5Ge_4	Sm_5Ge_4	*Pnma*	7.46	14.29	7.46	5
$Lu_{11}Ge_{10}$	$Ho_{11}Ge_{10}$	*I4/mmm*	10.668		15.880	5
Lu_4Ge_5			unknown			5
Lu_3Ge_4	Er_3Ge_4	*Cmcm*	3.968	10.438	14.040	6
$LuGe_{1.5}$	AlB_2	*P6/mmm*	3.83		4.05	10
$LuGe_{1.8}$	$ZrSi_2$	*Cmcm*	3.987	15.558	3.851	5
Lu_2In	Ni_2In	*P6₃/mmc*	5.237		6.568	7
Lu_5In_3	Mn_5Si_3	*F6₃/mcm*	8.801		6.485	7
Lu_5In_4	Ti_5Ga_4	*F6₃/mcm*	9.001		6.539	8
LuIn	AuCu	*P4/mmm*	4.597		4.928	8
Lu_3In_5	Tm_3Ga_5	*Pnma*	12.045	10.201	6.332	8
$LuIn_2$	$ZrGa_2$	*Cmmm*	4.529	13.923	4.562	8
$LuIn_3$	$AuCu_3$	*Pm* $\bar{3}$*m*	4.544			7

EXPERIMENTAL

14 binary and 60 ternary samples were prepared by arc melting of pure components (lutetium 99.83%, germanium 99.99% and indium 99.999%) under an argon atmosphere (sponge Ti was used as getter). The chemical composition of the alloys was checked by weight losses. All prepared alloys were annealed at 870 K for 700 h in evacuated quartz tubes and quenched in cold water. Phase analysis was carried out using X-ray powder diffraction. RKD-57.3 cameras (Debye-Scherrer technique with non-filtered CrK-radiation), DRON-2.0 (FeK_α-radiation, silicon as internal standard) and HZG-4a (CuK_α-radiation) powder diffractometers were used for data collection.

RESULTS AND DISCUSSION

The isothermal section of the Lu–Ge–In phase diagram at 870 K has been constructed (Fig. 1). The existence of the binary compounds: Lu_5Ge_3, Lu_5Ge_4, $Lu_{11}Ge_{10}$, Lu_3Ge_4, $LuGe_{1.5}$, $LuGe_{1.8}$, Lu_2In, Lu_5In_3, LuIn, Lu_3In_5 and $LuIn_3$ has been confirmed at 870 K. The existence of the Lu_4Ge_5 [5], Lu_5In_4 [8] compounds and the solid solution Lu_5In_{3+x}, where $0 \le x \le 1$ [9] was not observed by us. A Lu_5Ge_3 based solid solution has been established. The compound dissolves up to 10 at. % of indium (28 mole % of Lu_5In_3). The composition of the solid solution can be described as $Lu_5Ge_{3-x}In_x$, where $0 \le x \le 0.8$. The solubility of indium in the Lu_5Ge_3 compound is accompanied by an increase of the unit cell parameters: a = 8.216(4)–8.273(4) and c = 6.158(3)–6.227(6) Å (Fig. 2). The values of the unit cell parameters deviate from the dashed lines that connect the cell parameters of the pure Lu_5Ge_3 and Lu_5In_3 compounds. At the same time the Lu_5In_3 compound, which is isostructural to Lu_5Ge_3, does not solve germanium.

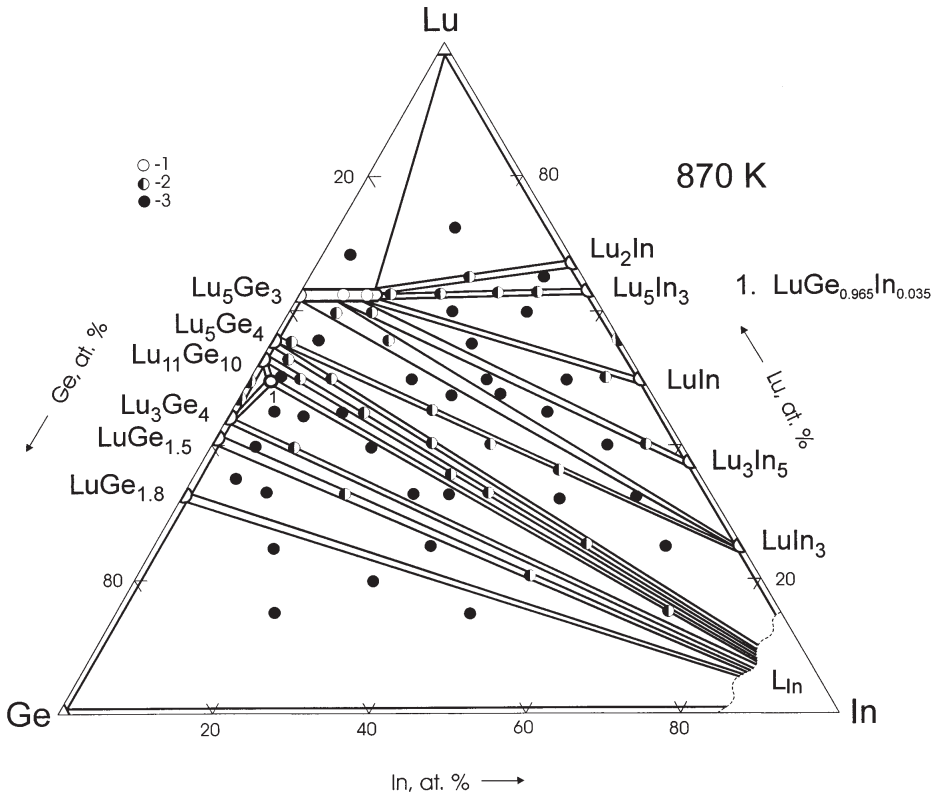

Figure 1. Isothermal section of the Lu–Ge–In phase diagram at 870 K (1 – single-phase, 2 – two-phase and 3 – three-phase alloys).

In the region adjacent to the $Lu_{11}Ge_{10}$ and Lu_3Ge_4 compounds a ternary compound with unknown crystal structure has been revealed. The sample of $Lu_{0.40}Ge_{0.40}In_{0.20}$ composition was the most pure, but it contained small additions of the Lu_3Ge_4 and In phases. X-ray powder data have been collected using HZG-4a diffractometer, CuK_α-radiation, $15 \le 2\Theta \le 110°$, step scan mode with a step size of 0.05°and counting time of 10 s per data point.

According to [10] all the heavy rare-earth metals form monogermanides of the CrB-type structure. Only for Yb and Lu the existence of such binary compounds is still unknown. We have not revealed the existence of the compound with such a structure in the binary alloys, but we supposed the forming of the compound in the ternary region to be the result of stabilization by In. Therefore, the CrB crystal structure (space group *Cmcm*, oC8, unit cell parameters for TmGe are: a = 4.185, b = 10.524, c = 3.885 Å [10]) has been chosen as model for the calculations. The structure determination has been performed using the Rietveld Analysis Program DBWS-9411 PC [11]. The results of the calculation confirm our suppositions. The atomic and thermal

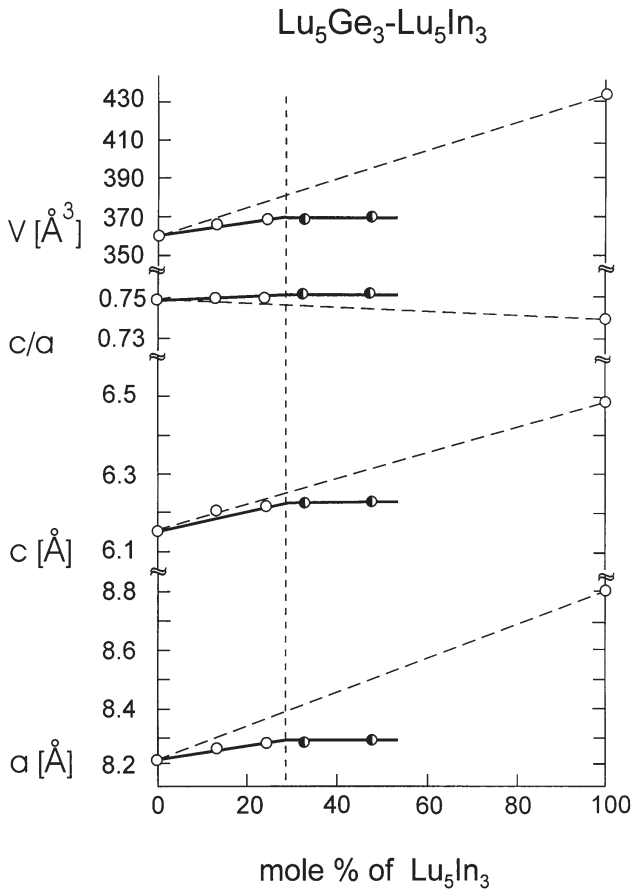

Figure 2. Unit cell parameters of the $Lu_5Ge_{3-x}In_x$ ($0 \le x \le 0.8$) solid solution.

parameters refined to $R_P = 0.0279$, $R_{WP} = 0.0367$ ($R_I = 0.0817$ and $R_F = 0.0716$ for the phase with CrB type structure) are given in Table 2. The refined values of the unit cell parameters are: a = 4.1582(1), b = 10.4616(4), c = 3.8664(1) Å. The composition of the compound can be described as $LuGe_{1-x}In_x$, where x = 0.035.

Table 2. Atomic and thermal parameters of the $LuGe_{1-x}In_x$, x = 0.035.

Atom	Wyckoff position	x/a	y/b	z/c	B, Å^2
Lu	4(c)	0	0.1396(2)	1/4	1.32(5)
M	4(c)	0	0.4113(3)	1/4	1.63(10)

M = 3.86(3) Ge + 0.14(4) In.

The isothermal section of the Lu–Ge–In system in the range of small concentration of lutetium is characterized by phase equilibria between In and germanides of Lu. This indicates that germanium rich lutetium germanides are more thermodynamically stable than its indium rich indides. This fact can also prove the higher stability of two-phase alloys In–$LuGe_{1.8}$ than that of Ge–$LuIn_3$ or three phase alloys In–$LuGe_{1.8}$–Ge than that of Ge–$LuIn_3$–In.

The phase equilibria in the Lu–Ge–In system are very close to those in the Lu–Si–In system [1]. In both systems the Lu_5Si_3 and Lu_5Ge_3 based solid solutions are observed. But in the investigated system, the Lu_5In_3 compound does not solve the third component, as it takes place in the Lu–Si–In system. These features are common for all the investigated R–Ge–In (R – rare earth element) systems [2,3].

The {Sm,Y}–Ge–In systems in the range of small concentrations of rare earth elements are very close to Lu–Ge–In system, but they differ from it by the formation of the compounds R_2Ge_2In (Mo_2FeB_2 structure type) and $R_{11}Ge_4In_6$ (the derivative of $Ho_{11}Ge_{10}$ type).

In the Lu–Si–In and Sm–Si–In systems no ternary compounds have been revealed and the character of the phase equilibria is more simple than that in the Lu–Ge–In system.

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