Conference Paper

# Lanthanum Activity in La–U–Ga–X Systems (X = Al or In)

**Raguzina E.V., Maltsev D.S., and Volkovich V.A.**

Department of Rare Metals and Nanomaterials, Institute of Physics and Technology, Ural Federal University, Ekaterinburg, 620002, Russia 620002

## Abstract

Lanthanum activity was determined for the first time in La–U–Ga–X (X = Al or In) alloys. Ga–In and Ga–Al alloys were taken in the eutectic composition (21.8 wt.% In and 1.6 wt.% Al, respectively). Measurements were performed between 573 and 1073 K employing the e.m.f. method.

**Keywords:** Lanthanum; Uranium; Gallium-Indium Eutectic; Gallium-Aluminium Eutectic; Activity; Thermodynamics.

Corresponding Author:
Maltsev D.S.
d.s.maltsev@gmail.com

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## 1. Introduction

Liquid metallic alloys have a considerable potential for application in pyrochemical technologies of spent nuclear fuel (SNF) reprocessing as working media for separating fissile materials and selective extraction of fission products. Thus, studying the behavior, physical-chemical and thermodynamic properties of SNF elements in the salt and liquid metal media is important from both, fundamental and practical points of view, for developing and optimizing technological stages of pyrochemical SNF reprocessing.

Basic thermodynamic properties, i.e. activity, activity coefficient and solubility, of lanthanum in Ga-In and Ga–Al alloys of various composition were reported in a number of recent works [1–5]. It was shown that the thermodynamic properties of lanthanum depended on the metal phase composition and temperature. Another question having an interest from the technological point of view is the possible effect of uranium content in the alloy on the thermodynamic properties of fission products (for example, lanthanum).

Metallic lanthanum has two modifications (α, β) in the solid state. To enable the comparison of the available information, the data reported must be brought to the

same standard state. In the present study β - lanthanum and super cooled liquid lanthanum were chosen as the standard states. The aim of the present work was determining thermodynamic activity of lanthanum in pseudo-quaternary La–U–(Ga–In)$_{eut}$ and La–U–(Ga–Al)$_{eut}$ alloys.

## 2. Experimental

The electromotive force (e.m.f.) method was chosen in the present work for studying lanthanum behavior in the liquid alloys. The measurements were performed between 573 and 1073 K. To determine lanthanum activity, the EMF of the following galvanic cell was measured:

$$(-)\ \text{La–In}\ |\ (\text{LiCl–KCl–CsCl}) + \text{LaCl}_3\ |\ (\text{La–U–Me}) + \text{LaMe}_x\ (+), \quad (1)$$

where Me is the low melting metal (Ga, In, Al, Ga-In or Ga-Al eutetctic). Lanthanum metal noticeably reacts with alkali chloride based melts containing dissolved lanthanum(III) chloride and therefore cannot be reliably employed as the reference electrode. In this work L-LaIn$_3$ alloy (where L is liquid La-In alloy) was used as the reference electrode because the potential of La-In alloy relative to metallic lanthanum is known [6] and its temperature dependence is described by the following equation:

$$E = 802.3 - 263.0 \cdot 10^{-3} \cdot T,\ mV \quad (2)$$

To relate the potentials of the two phase liquid metal reference electrode (L+LaIn$_3$) of the galvanic cell (1) to the potential of metallic lanthanum, the experimental e.m.f. of the galvanic cell (1) was corrected on the value of the electromotive force calculated using equation (2).

Low melting ternary LiCl-KCl-CsCl eutectic (57.5 mol. % LiCl and 16.5 mol. % KCl, m.p. 536 K) was used as the solvent salt. Individual alkali metal chlorides (of purity 99.5% and above) were dried under vacuum at 773-873 K for several hours, then melted and dry hydrogen chloride was bubbled through the melt for approximately three hours to remove trace water and convert oxide impurities to the corresponding chlorides. The salt mixtures containing La(III) chloride (around 1-3 wt.% lanthanum), were prepared by chlorination of lanthanum oxide (99.9 % purity) in the chloride eutectic using chlorine and hydrogen chloride as chlorinating agents. Gallium-indium and gallium-aluminum alloys of the eutectic compositions (21.8 wt.% In, 1.6 wt. % Al, respectively [7]) were prepared by fusing individual metals (Ga of 99.9999 % purity, In of 99.9995 % and Al of 99.999 %) in an argon filled dry box MBraun Unilab

1200/780. Quaternary La-U-Ga-Me (Me = In or Al) alloys were obtained by adding metallic uranium and lanthanum to the Ga-Me (Me = In, Al) eutectic.

Experiments were carried out in the inert glovebox with high purity argon atmosphere equipped with the furnace in the experimental cell schematically shown in Fig.1.

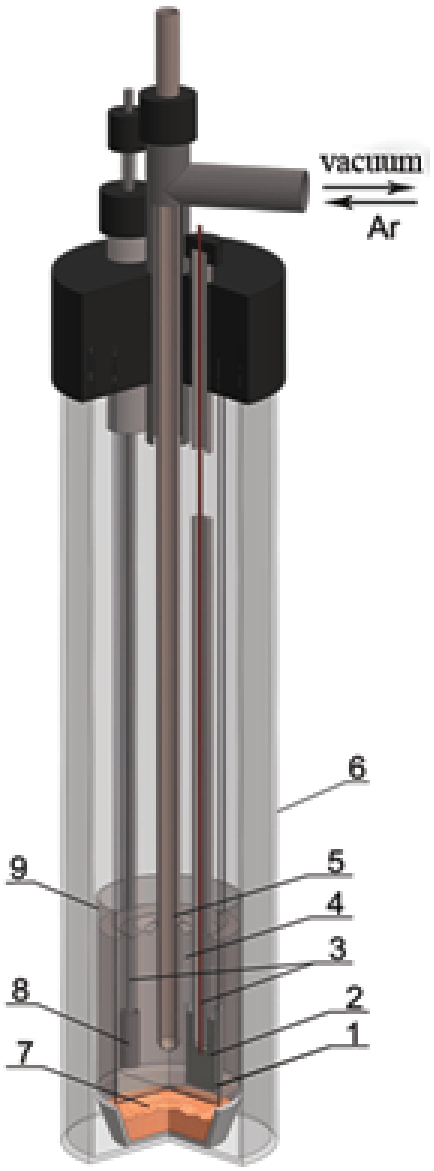


**Figure** 1: Experimental cell for e.m.f. measurements. 1 – small beryllium oxide crucible; 2 – liquid alloy; 3 – current conductors; 4 – molten salt electrolyte; 5 – beryllium oxide thermocouple sheath; 6 – silica cell; 7 – zirconium turnings; 8 – reference electrode; 9 – large beryllium oxide crucible.

The cell was assembled in the glovebox with argon atmosphere. The potentials of the liquid alloys were measured using True RMS Multimeter ABM-4081. At fixed temperature the potentials were considered as stationary if they neither exhibited a tendency to monotonous change nor changed by more than by 0.1-0.5 mV over an

hour. The potentials were normally measured starting from the highest temperature. The cell was then cooled in steps of ca. 50 degrees and the potentials measured over selected temperature interval. The melt temperature was measured by a K-type thermocouple (Omega Engineering, Inc.) dipped into the salt melt and protected by a beryllium oxide sheath.

After completing the measurements the cell was allowed to cool and the quenched salt was dissolved in cold distilled water. The liquid alloys were washed with water and ethanol and dried at room temperature.

Beta-lanthanum and super cooled liquid lanthanum were taken as the reference states when lanthanum activity was determined. To account for lanthanum phase transformations the following correction was added to the experimentally measured electrode potentials:

$$\Delta E = -\left(\frac{R \cdot T}{n \cdot F}\right) \cdot lna_o, \tag{3}$$

where $a_0$ is lanthanum activity at the working temperature relative to β-lanthanum or liquid lanthanum. The value of $lna_0$ was calculated from the known thermodynamic parameters of lanthanum phase transitions [6; 8]. For example, activity of α-La relative to β-La can be calculated from the following expression:

$$R \cdot lna_o = \frac{\Delta H_\alpha}{T_\alpha \cdot T} \cdot \left(T_\alpha - T\right), \tag{4}$$

where ΔHα and Tα are the enthalpy change and temperature of the α→β transition.

## 3. Results and Discussion

Lanthanum activity in the liquid metal was determined from the results of measuring e.m.f. of heterogeneous alloys saturated with lanthanum and uranium.

### 3.1. Activity of lanthanum in La-U-(Ga-In)$_{eut}$ alloy

Experimental temperature dependence of e.m.f. of the cell (1) containing two-phase La-U-Ga-In alloy is presented in Fig. 2. In the temperature range studied the *E = f(T)* dependence was linear and could be described by following equation:

$$E = 1.02 - 3.89 \cdot 10^{-4} \cdot T,\ V \tag{5}$$

X-ray powder diffraction analysis of samples of two-phase La-U-(Ga-In)$_{eut}$ alloys cooled to room temperature, Fig. 3, showed that these samples contained $LaGa_6$, $LaGa_3$

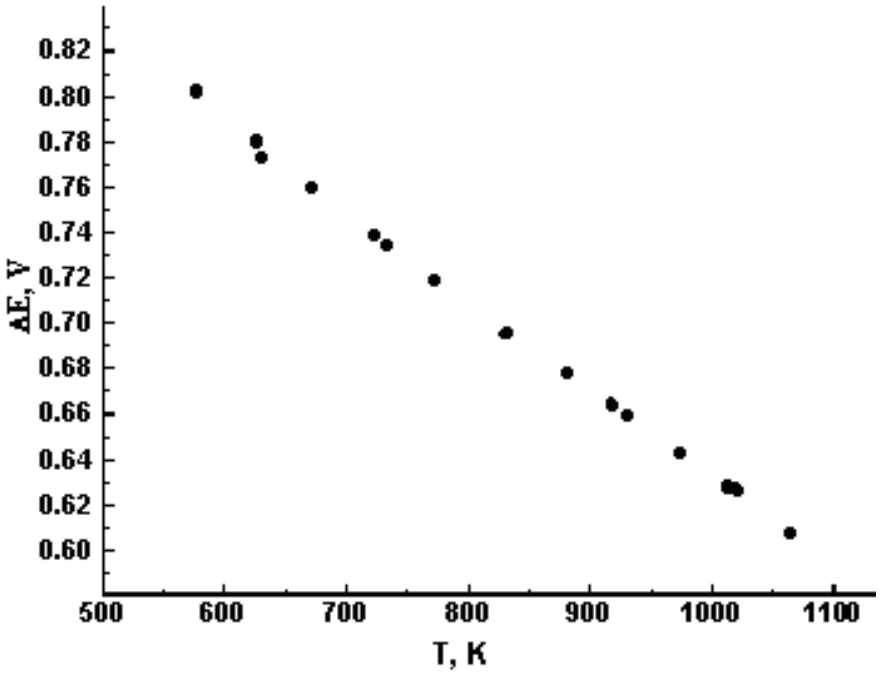


**Figure** 2: The effect of temperature on e.m.f. of La-U-(Ga-In)$_{eut}$ alloys saturated with lanthanum and uranium. Reference electrode – (L+LaIn$_3$) alloy. Lanthanum concentration in the metallic phase in various samples was 0.1-10 mol. % (depending on temperature).

and $UGa_3$ intermetallic compounds. $LaGa_6$ was the major crystalline phase in the sample. Since the peak positions in the diffraction pattern corresponded exactly to those for Ga contained intermetallic compounds it can be concluded that no indium entered the crystal lattice. No peaks that could be attributed to uranium or gallium were observed.

Activity of β-La and super cooled liquid lanthanum in the La-U-(Ga-In)$_{eut}$ alloys were calculated from the measured EMF values and at 573-1073 K they are described by the following equations:

$$lga_{\beta-La(U-Ga-In)} = 5.97 - 1.55 \cdot 10^4 \cdot T^{-1} \quad (6)$$

$$lga_{l-La(U-Ga-In)} = 6.39 - 1.60 \cdot 10^4 \cdot T^{-1} \quad (7)$$

Comparison of β-lanthanum activity in La-U-(Ga-In)$_{eut}$, La-Ga, La-In and La-(Ga-In)$_{eut}$ alloys, Fig. 4, showed that lanthanum activity in the alloys contained uranium was essentially identical to the activity of lanthanum in liquid alloys without uranium presence. There was a good agreement of La activity values in La-U-(Ga-In)$_{eut}$, La-Ga and La-(Ga-In)$_{eut}$ alloys. This again indicates that the same intermetallic phases, i.e., $LaGa_3$ and $LaGa_6$, were present in the equilibrium with the liquid phase in alloys of lanthanum with U-Ga-In, Ga-In and Ga. Partial thermodynamic functions of β-La in La-U-(Ga-In)$_{eut}$ alloy were calculated and the results are presented in Table 1.

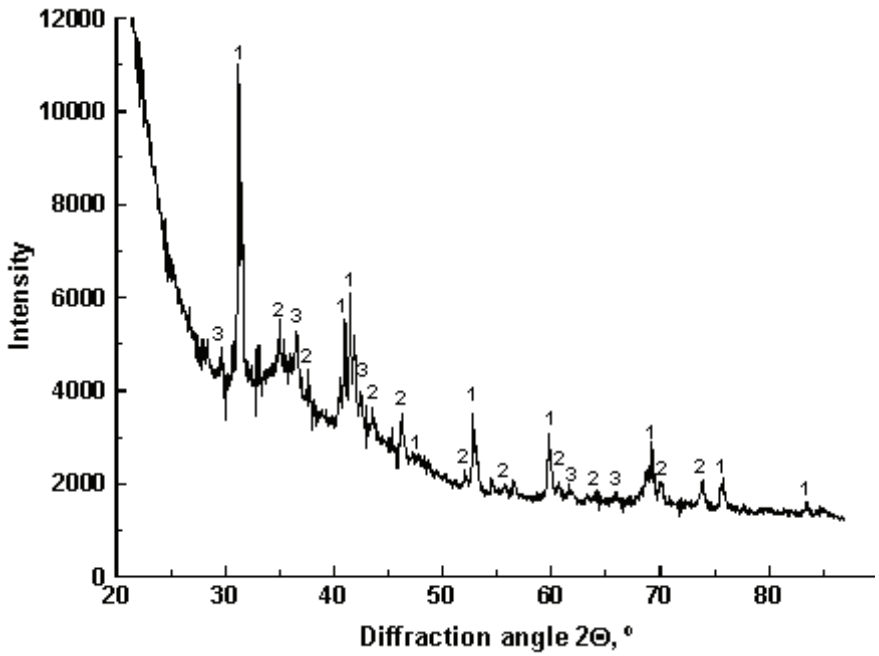


**Figure** 3: X-ray diffraction pattern of intermetallic compounds formed in La-U-(Ga-In)$_{eut}$ alloy cooled to room temperature. Phases: $Ga_6La$ (1); $Ga_3La$ (2); and $Ga_3U$ (3).

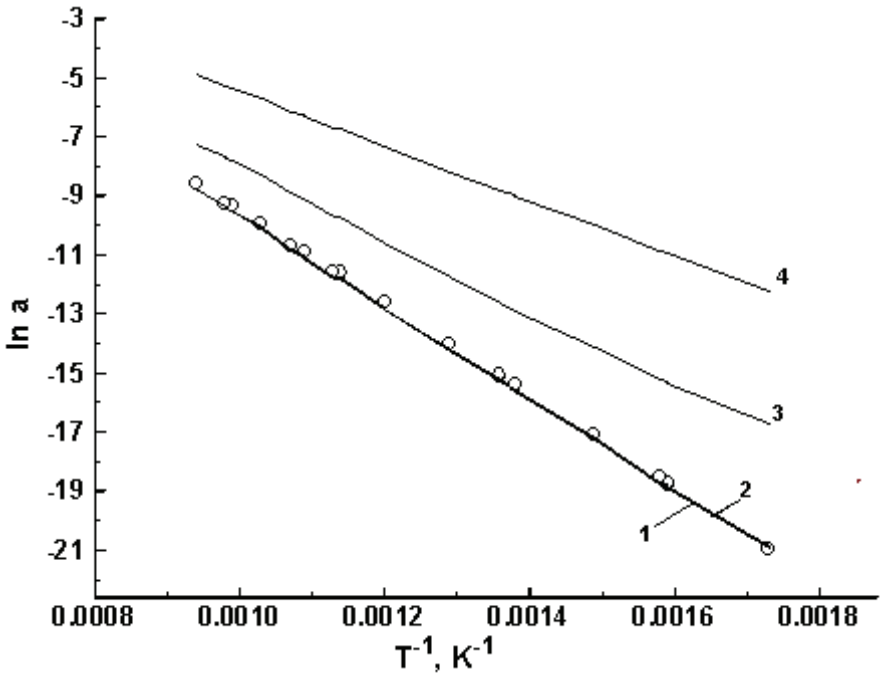


**Figure** 4: Activity of β-lanthanum in La-U-(Ga-In)$_{eut}$, La-Ga, La-In and La-(Ga-In)$_{eut}$ alloys. Symbols are the present study. Lines are the literature data: 1 – La-Ga [6], 2 – La-(Ga-In)$_{eut}$ [2], 3 – La-In [6], 4 – U-(Ga-In)$_{eut}$ [9].

Table 1: Partial thermodynamic functions of β-La in saturated alloys with gallium, indium, $(Ga\text{-}In)_{eut}$ and $U\text{-}(Ga\text{-}In)_{eut}$ (partial molar excess Gibbs free energy calculated at 1050 K).

| System | $-\Delta\overline{H}_U$, kJ/mol | $-\Delta\overline{S}_U$, J/mol·K | $-\Delta\overline{G}_U$, kJ/mol | $\Delta T$, K | Reference |
|---|---|---|---|---|---|
| Ga-La | 294.6 | 108.3 | 186.3 | 633-993 | [11] |
| | 299.1 | 103.0 | 196.1 | 675-975 | [12] |
| In-La | 232.2 | 76.1 | 156.1 | 633-993 | [11] |
| | 226.7 | 69.8 | 156.9 | 725-975 | [13] |
| | 225.7 | 64.3 | 161.4 | 953-1083 | [14] |
| Ga-In-U-La | 295.6 | 112.6 | 177.3 | 573-1073 | present work |

## 3.2. Activity of lanthanum in La-U-$(Ga\text{-}Al)_{eut}$ alloy

Experimental temperature dependence of e.m.f. of the cell (1) containing two-phase La-U-Ga-Al alloy is presented in Fig. 5.

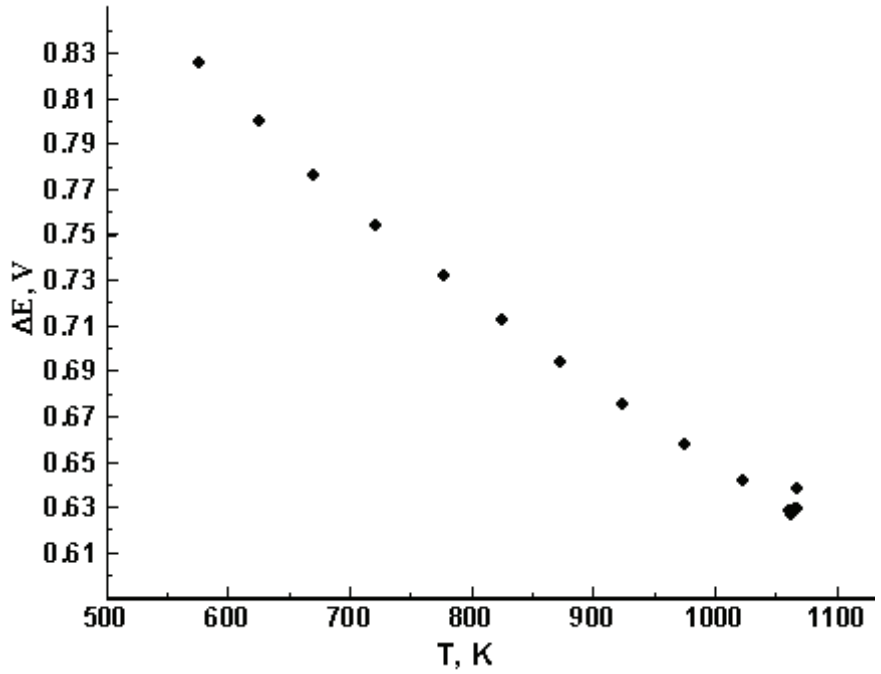


**Figure** 5: The effect of temperature on e.m.f. of La-U-$(Ga\text{-}Al)_{eut}$ alloys saturated with lanthanum and uranium. Reference electrode – $(L+LaIn_3)$ alloy. Lanthanum concentration in the metallic phase in various samples was 0.1-10 mol. % (depending on temperature).

In the temperature range studied the *E = f(T)* dependence was linear and could be adequately described by the following equation:

$$E = 1.09 - 4.25 \cdot 10^{-4} \cdot T,\ V \tag{8}$$

X-ray diffraction analysis of samples of two-phase La-U-(Ga-Al)$_{eut}$ alloys cooled to room temperature, Fig. 6, showed that these samples contained $LaGa_3$, $LaGa_6$, $UGa_3$ intermetallic compounds. $UGa_3$ was the major crystalline phase in the samples.

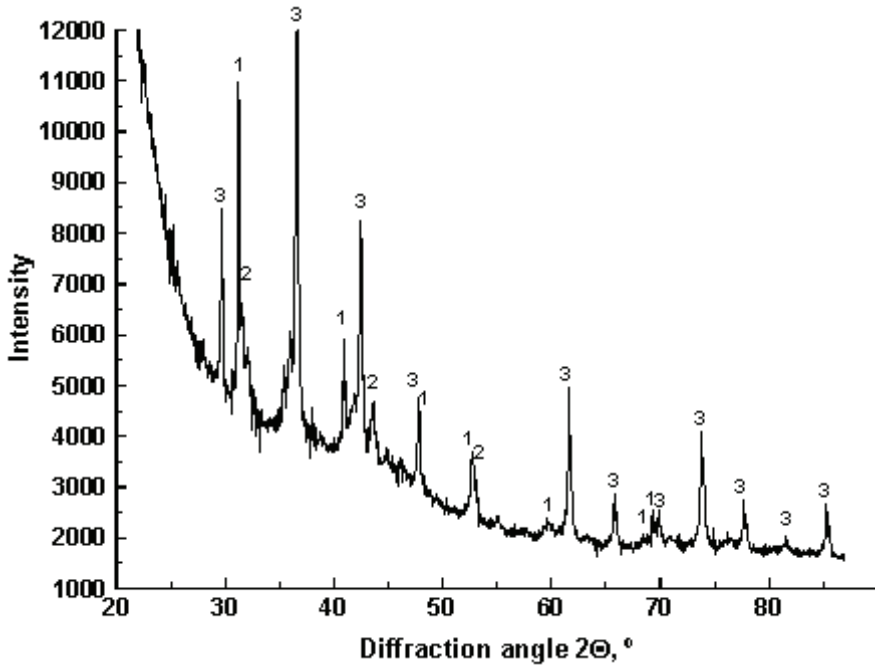


**Figure** 6: X-ray diffraction pattern of intermetallic compounds formed in La-U-(Ga-Al)$_{eut}$ alloy cooled to room temperature. Phases: $Ga_6La$ (1); $Ga_3La$ (2); and $Ga_3U$ (3).

Activity of β-La and super cooled liquid lanthanum in the La-U-(Ga-Al)$_{eut}$ alloys were also calculated from the measured e.m.f. values and at 573-1073 K they are described by the following equations:

$$lga_{\beta-La(U-Ga-Al)} = 6.07 - 1.59 \cdot 10^4 \cdot T^{-1} \quad (9)$$

$$lga_{l-La(U-Ga-Al)} = 6.48 - 1.63 \cdot 10^4 \cdot T^{-1} \quad (10)$$

Comparison of β-lanthanum activity in La-U-(Ga-Al)$_{eut}$, La-Ga, La-Al and La-(Ga-Al)$_{eut}$ alloys, Fig. 7, showed that lanthanum activity in the alloys contained uranium was identical to the activity of lanthanum in the liquid alloys without uranium and were in a good agreement with literature data for La-Ga and La-Ga-Al alloys. This again indicated that the same intermetallic phases, i.e., $LaGa_3$, $LaGa_6$, were present in the equilibrium with the liquid phase in alloys of lanthanum with U-Ga-In. Partial thermodynamic functions of β-La in La-U-(Ga-Al)$_{eut}$ alloy were calculated and presented in Table 2.

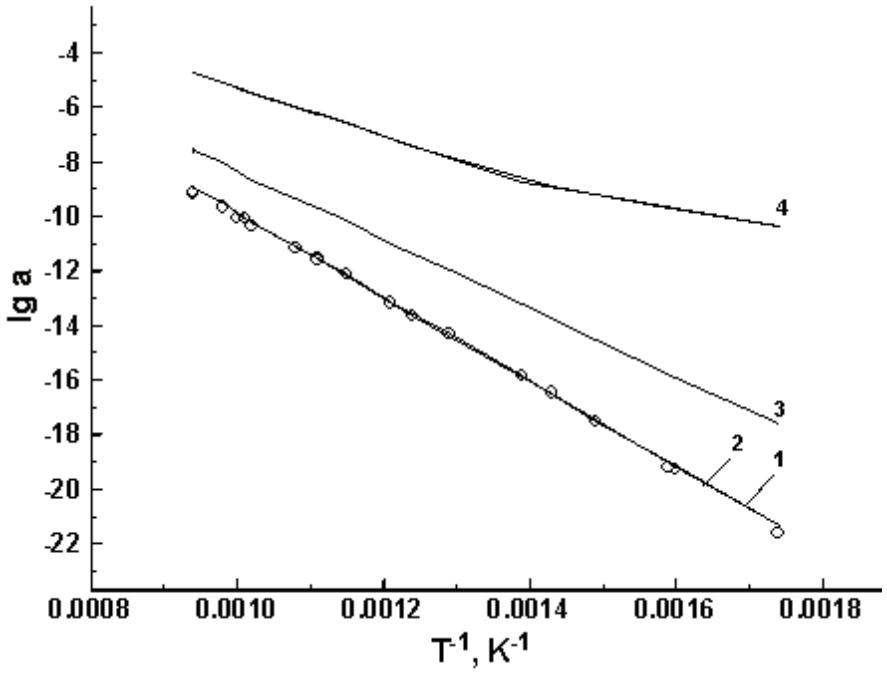


**Figure** 7: Activity of β-lanthanum in La-U-(Ga-Al)$_{eut}$, La-Ga, La-Al and La-(Ga-Al)$_{eut}$ alloys. Symbols are present study. Lines are literature data: 1 – La–Ga [6], 2 – La-(Ga-Al)$_{eut}$ [4], 3 – La–Al [6], 4 – U–(Ga–Al)$_{eut}$ [10].

Table 2: Partial thermodynamic functions of β-La in saturated alloys with aluminium and U-(Ga-Al)$_{eut}$ (partial molar excess Gibbs free energy calculated at 1050 K).

| System | $-\Delta\overline{H}_U$, kJ/mol | $-\Delta\overline{S}_U$, J/mol·K | $-\Delta\overline{G}_U$, kJ/mol | $\Delta T$, K | Reference |
|---|---|---|---|---|---|
| Al-La | 241.6 | 81.8 | 159.8 | 1000-1150 | [15] |
| | 253.6 | 81.4 | 172.2 | 673-873 | [16] |
| (Ga-Al)$_{eut}$-U-La | 314.4 | 123.0 | 185.2 | 573-1073 | present work |

## 4. Conclusions

Partial thermodynamic functions of lanthanum, as well as lanthanum activity were determined for the first time in Ga-In and Ga-Al eutectic alloys contained uranium and lanthanum over 500 degrees range (between 573 and 1073 K).

Activity of lanthanum in alloys with the U-(Ga-In)$_{eut}$ and U-(Ga-Al)$_{eut}$ were close to those in alloys with gallium and Ga-In or Ga-Al eutectic alloys due to formation of the same intermetallic compounds, i.e., $LaGa_6$ and $LaGa_3$, in both systems. It was found that uranium has no influence on lanthanum activity in La-U-Ga-In and La-U-Ga-Al alloys.

## Acknowledgements

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