

Short communication

## Liquid–liquid equilibrium in the lithium–lanthanum system

Rashid A. Khairulin<sup>a,\*</sup>, Anastasiya A. Belozerova<sup>b</sup>, Rasul N. Abdullaev<sup>c</sup>, Sergei V. Stankus<sup>a</sup><sup>a</sup> Institute of Thermophysics, Siberian Branch of the Russian Academy of Sciences, Lavrentyev Avenue 1, 630090 Novosibirsk, Russia<sup>b</sup> Institute of Metallurgy, Ural Division of the Russian Academy of Sciences, Amundsen Street 101, 620016 Ekaterinburg, Russia<sup>c</sup> Novosibirsk State University, Pirogov Street 2, 630090 Novosibirsk, Russia

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## ABSTRACT

The boundaries of the liquid–liquid immiscibility region on the phase diagram of the Li–La system have been determined by the gamma-ray attenuation technique. At the monotectic temperature (1118 K), the miscibility gap ranges from 0.25 to 92.9 at.% La. As the temperature increases, the solubility of the liquid metals in each other rises slightly.

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## 1. Introduction

Phase diagrams of the “alkali metal – rare-earth metal” systems have hardly been explored. We found only one experimental work (Ganiev et al. [1]), in which the systems Li–La, Li–Ce, Li–Nd, Li–Pr, and Li–Sm were investigated. Ganiev et al. [1] applied the method of differential thermal analysis, and only one composition (50 at.%) of each system was analysed. Using some criteria and empirical formulas from Refs. [2,3], Ganiev et al. supposed that there is a liquid–liquid immiscibility region on the phase diagrams of these systems. In particular, according to the estimates, for the Li–La system the miscibility gap ranges from ~10 to 38.2 at.% La at the monotectic temperature  $T_M = 733$  K. Based on the results of Ref. [1], Okamoto [4] drew a phase diagram of the Li–La system that has been published in some reference books and online databases (see, for example, [5,6]). The aim of the present work is to refine the phase diagram of the lithium–lanthanum system.

## 2. Experimental details

Experimental study of liquid–liquid equilibria in the lithium–lanthanum system was performed by a gamma-ray attenuation technique. In comparison with a thermal analysis, the gamma-ray attenuation technique has some advantages, which

include the possibility of carrying out measurements at small heating/cooling rates (including zero), controlling the homogeneity of the sample, and considerable reduction of the number of required samples. Previously we had successfully applied this method to determine immiscibility regions in a number of binary systems undergoing two-melt phase separation [7–9]. The measurements were carried out with a gamma-densitometer, which has been described in detail elsewhere [10]. An ampoule containing the caesium-137 isotope, which has an activity of  $1.5 \cdot 10^{11}$  Bq and quantum energy of 662 keV, was used as the gamma-ray source. In the course of the experiment, a cell with two-phase melt moves in a vertical direction with respect to the axis of a gamma-quanta beam, which allows us to measure the height dependence of the intensity of the radiation transmitted through the liquid sample. The law of radiation attenuation in a binary melt with components A and B may be written as [9]:

$$\frac{S_A X(x) + S_B [(1 - X(x))]}{V[X(x)]} = \frac{1}{d} \ln \left[ \frac{J_0}{J(x)} \right], \quad (1)$$

where  $x$  is the coordinate (height of the beam passage with respect to the crucible bottom);  $J(x)$  and  $J_0$  are the intensities of the radiation after passage through the crucible with and without the sample, respectively;  $d$  is the gamma-ray attenuation length (the inner diameter of the crucible corrected for beam diameter);  $X(x)$  and  $V[X(x)]$  are the atomic concentration of the component A and the molar volume of the melt at the site of the beam passage, respectively; and  $S_i$  ( $i = A, B$ ) are the gamma-ray attenuation cross-sections of the components. With knowledge of the concentration

\* Corresponding author.

E-mail address: [kra@itp.nsc.ru](mailto:kra@itp.nsc.ru) (R.A. Khairulin).

**Table 1**  
Specification of chemical samples.

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
lithium	JSC “Novosibirsk Chemical Concentrates Plant”	0.9995	none	–	–
lanthanum	JSC “Uralredmet”	0.998	none	–	–

dependence of the molar volume,  $V(X)$ , Eq. (1) enables the concentration at the site of the beam passage to be determined. Moving the crucible in a vertical direction, we can determine the distribution of the components through the height of the melt column  $X(x)$ , and for a segregated system, we can find the compositions of the liquid phases in equilibrium with each other. The  $V(X)$  dependence of monotectic and eutectic systems deviates very slightly (by no more than 1–2%) from the additivity rule for ideal solutions [7–9,11,12]. In this connection, we used the following relation for the temperature and concentration dependence of the molar volume for the liquid alloy:

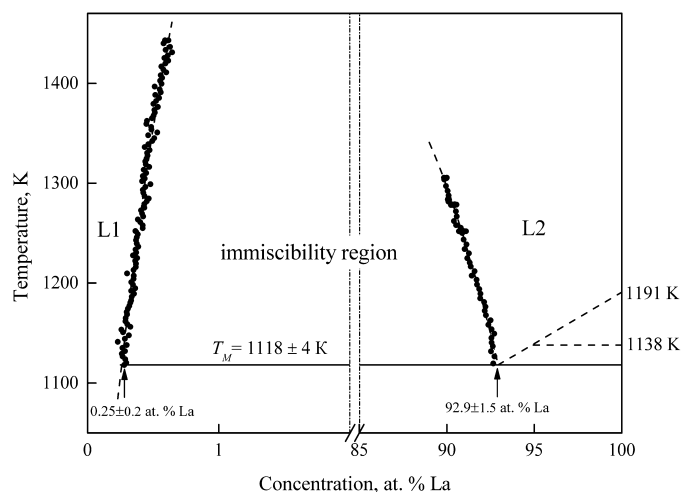
$$V(X, T) = V_{\text{La}}(T) \cdot X + V_{\text{Li}}(T) \cdot (1 - X). \quad (2)$$

Here,  $T$  is the temperature;  $V_{\text{La}}$  and  $V_{\text{Li}}$  are molar volumes of the system components. The data on the volumetric properties of liquid lanthanum and lithium are taken from Refs. [13,14]. According to our estimate, the additional error in determining the concentration associated with the approximate nature of Eq. (2) is 0.001–0.5 at.-%.

Measuring cells for the samples were made of tantalum. This metal is practically insoluble in the liquid lithium and lanthanum [5,6]. The tantalum was of “TVCh–1” grade according to Russian Technical Standard TU95.2817–2002 (99.9 mass% pure). The cell contained a cylindrical crucible, which was 60 mm high with an internal diameter of 38 mm, and a cap with a thin-walled protective sleeve for the immersion thermocouple (Type K). The uncertainty in the absolute temperature measurement was no more than  $\pm 4$  K, and the relative temperature was accurate to at least  $\pm 0.5$  K. The samples were prepared from lanthanum and natural lithium of 99.8 and 99.95 mass% purity, respectively (Table 1). To remove dissolved gases and volatile impurities, lanthanum was annealed at 900 K under a vacuum of  $10^{-3}$  Pa. The gamma-ray attenuation cross-sections of the components were measured on solid samples of La and Li with accurately metered geometric dimensions by the procedure described in Ref. [15]. The density of the metals at room temperature needed for the calculations of the  $S$  values was determined by the Archimedean method. Silicone oil was used as the reference liquid. The uncertainty of the attenuation cross-sections is estimated to be within  $\pm 0.1\%$ .

The samples were prepared in a glove box filled with high purity argon (99.992 vol.%). The surfaces of the metal ingots were cleaned of oxide and nitride films. The weights of the lithium and lanthanum pieces needed for the calculations of the mean compositions of the alloys were determined using an electronic analytical balance with an accuracy of 2–3 mg. The samples contained 24 at.% La, which is approximately equal to the mid-range of the miscibility gap according to the data of Ganiev et al. [1]. A composite sample was placed into the cell. The cell was installed in the furnace of the gamma-densitometer and the latter was evacuated and filled with pure argon up to 0.1 MPa.

The first experiments were carried out with an unsealed cell. They revealed that solid lanthanum did not interact with liquid lithium to any appreciable extent up to 1000 K. Since the saturated vapour pressure of lithium increases rapidly at higher temperatures, the second cell was sealed by arc welding in the argon glove box. In the next experiments, the sample was heated above the melting point of lanthanum (1191 K [4]) up to 1450 K. At this temperature, an attempt was made to homogenize the liquid sample by shaking the cell. However, gamma-raying of the melt at different heights had shown that the sample remained non-homogeneous,



**Fig. 1.** The liquid–liquid immiscibility region on the phase diagram of the Li–La system. The points are experimental data. The melting temperature and the solid–solid phase transition temperature of lanthanum are taken from Ref. [4].

with a clear boundary between two liquid phases. To determine the compositions of the phases in equilibrium with each other as functions of the temperature, the gamma-ray attenuation in the two-phase melt (above and below the interphase boundary) was measured during the course of cooling. The computer-based system of data collection recorded the gammagram (temperature and height dependence of the radiation intensity), the thermogram (time dependence of the sample temperature), and the analogue of the DTA thermogram (the temperature dependence of the temperature difference between the sample and the furnace). The rate of cooling was no more than 1 K/min. At some temperatures, the measurements were carried out after long isothermal holding times (15–20 min). We found no significant differences between the results of the stationary and dynamic measurements, that is, the phase equilibrium in the sample had time to be established at these cooling rates. The study of liquid–liquid phase equilibria was conducted down to the monotectic temperature. The monotectic temperature was directly measured by the heat effect on the thermogram, accompanying the beginning of the monotectic reaction (decomposition of the La-rich liquid phase into Li-rich liquid phase and La-rich solid phase).

### 3. Results and discussion

The experimentally determined parts of the liquid–liquid coexistence curve on the  $T$ – $X$  diagram of the Li–La system are presented in Fig. 1 and Table 2. To construct the smoothed temperature dependences of the compositions of the liquid phases in equilibrium with each other, the raw data for the Li-rich and La-rich phases were fitted with second-degree polynomials. The smoothed data are tabulated in Table 3. According to our data, the monotectic temperature is equal to 1118 K, which is 385 K higher than the  $T_M$  value given in Ref. [1]. At the monotectic temperature, the miscibility gap ranges from practically pure lithium to  $\approx 93$  at.% La, which is also very different from the published data. As the temperature increases, the maximum mutual solubility of the liquid metals in each other rises slightly. In particular, the solubility of La

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