



# Mixing enthalpy of liquid Ga–Li–Zn alloys

S. Terlicka\*, A. Dębski

Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25, Reymonta Street 30-059 Kraków, Poland



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## ABSTRACT

The integral molar mixing enthalpies of liquid Ga–Li–Zn alloys were determined by drop calorimetry and with the use of the Setaram MHTC 96 Line Evo calorimeter.

The measurements for this ternary system were taken at four temperatures and six different alloy compositions: at 993 K the  $(\text{Ga}_{0.90}\text{Li}_{0.10})_{1-x}\text{Zn}_x$  and the  $(\text{Ga}_{0.75}\text{Li}_{0.25})_{1-x}\text{Zn}_x$ , at 1044 K the  $(\text{Ga}_{0.60}\text{Li}_{0.40})_{1-x}\text{Zn}_x$ , the  $(\text{Ga}_{0.50}\text{Li}_{0.50})_{1-x}\text{Zn}_x$ , the  $(\text{Ga}_{0.40}\text{Li}_{0.60})_{1-x}\text{Zn}_x$ , at 891 K and 1018 K the  $(\text{Ga}_{0.25}\text{Li}_{0.75})_{1-x}\text{Zn}_x$ . This study has begun the experimental measurements of the Ga–Li–Zn system and shows a comparison of previous literature data for binary Ga–Li system.

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## 1. Introduction

In the last several years a rapidly growing interest of ecological sources and lead-free soldering materials for new electronic appliances and eco-technologies industry was observed. The Li-based alloys are promising for the new environmentally friendly energy storage materials such as electrodes for Li-ion batteries [1,2]. However the alloys based on lithium are not well known. This is probably due to very high reactivity of lithium with the oxygen, nitrogen, and water vapour contained in the air, which poses problems during thermodynamic studies of alloys with lithium.

The gallium alloys are desirable because of their low melting points and good wetting properties. Addition of gallium improves the soldering adhesives, oxidation resistance and also decreases the melting temperature of alloys. The gallium based multicomponent alloys varieties are applied in semiconducting industry [3–5].

The Ga–Li–Zn alloys could be used as potential lead-free solder materials or as electrodes in newly generated rechargeable batteries; however, available literature data for this ternary system are extremely limited.

### 1.1. Ga–Li system

The thermodynamic studies of the Ga–Li system were started in 1956, by Schneider and Hilmer [6], who measured the enthalpy of fusion of the LiGa phase with the use of drop calorimetry technique. Later Thummel and Klemm [7] determined the existence of three intermetallic phases ( $\text{GaLi}$ ,  $\text{Ga}_2\text{Li}$  and  $\text{GaLi}_2$  (or  $\text{Ga}_4\text{Li}_9$ )), by using the thermal analysis and proposed first phase diagram for this binary system. They also presented the lattice parameters of the GaLi phase. In 1973, Yatsenko et al. [8] found two new phases:  $\text{Ga}_4\text{Li}$  and  $\text{Ga}_2\text{Li}_3$  by means of differential thermal analysis. In the same year, Yatsenko et al. [9] measured the activity of lithium in the liquid Ga–Li system at 1023 K, by using the electromotive force measurements. Later, Buchmanov and Yatsenko [10] measured the heat of fusion of the intermetallic GaLi phase by means of differential scanning calorimetric technique. Wen and Huggins [11] examined electrochemically the properties for the Ga–Li liquid and solid solutions in the concentration range between 0.1 and 72 at. % of Li at 688 K. Then, the authors [11] measured the diffusion chemical coefficient in the GaLi intermetallic phase at 688 K. In 1991, Sangster and Pelton [12], evaluated the Ga–Li phase diagram and proposed new one with the six intermetallic phases determined in the available literature:  $\text{Ga}_{14}\text{Li}_3$ ,  $\text{Ga}_2\text{Li}_7$ , GaLi,  $\text{Ga}_4\text{Li}_5$ ,  $\text{Ga}_2\text{Li}_3$  and  $\text{GaLi}_2$  and two eutectics. Later, Okamoto [13] presented another phase diagram with two additional phases:  $\text{Ga}_8\text{Li}_3$ ,  $\text{Ga}_9\text{Li}$ , which were determined by Tillard-Charbonnel and Belin [14] with the use of the X-ray diffraction and the DTA study. In 2003, Yuan et al.

\* Corresponding author. Tel.: +48 122952814.

E-mail address: [s.terlicka@mim.pl](mailto:s.terlicka@mim.pl) (S. Terlicka).

[15] developed the phase diagram and created a complete set of optimized modelled parameters which they used for the calculation of the Ga–Li phase diagram. In 2006, Okamoto [16], once again presented the Ga–Li phase diagram and demonstrated disagreement in the liquidus line calculated by Yuan et al. [15]. Finally in 2015 Dębski et al. [17] presented the mixing enthalpy of liquid Ga–Li alloys by means of drop calorimetry in three temperatures at 873 K, 992 K and at 1039 K in the entire concentration range.

### 1.2. Ga–Zn

The liquidus line of the Ga–Zn system has been experimentally described by several authors with the use of various methods [18–23]. The phase diagram was modelled and calculated by Kubaschewski et al. [24,25], Akhkubekov et al. [26] and Dudkiewicz et al. [27] and it was based on available literature data. The Ga–Zn system has an eutectic point at 3.87 at. % Zn at temperature of c.a. 298 K. The equilibrium phases of this system are: the liquid, the hexagonal (Zn) terminal solid solution, with a maximum solubility of 2.36 at. % Ga at 533 K and the orthorhombic (Ga) solid solution, with a maximum solubility of 0.8 at. % Zn at 293 K. The solidus was determined by Davis [28] in 1965, with the use of X-ray diffraction method. Thermodynamic properties were measured by many authors, with the use of electromotive force method (EMF) [29–34], vapour pressure studies [35], calorimetric measurements [36,37]. The calculated and experimental data are in a good agreement. The complete thermodynamic description for Ga–Zn system was published by Hultgren [38] and later by Dudkiewicz et al. [27].

### 1.3. Li–Zn system

The determination of liquidus and solidus lines of the Li–Zn system, for the concentration range of 60–100 at. % Zn by using thermal analysis [39], started the experimental studies of this binary system. In 1933, Grube and Vosskühler [40], and in 1934, Baroni [41], found two intermetallic phases:  $\text{Li}_2\text{Zn}_3$  and  $\text{LiZn}_4$ , (both stoichiometric) with the use of the thermal and X-ray analyses. Moreover, they also noticed the presence of three high temperature phases:  $\beta\text{Li}_2\text{Zn}_3$ ,  $\beta\text{Li}_2\text{Zn}_5$  and  $\beta\text{LiZn}_4$ , two infinitely diluted solid solutions:  $\beta\text{Li}$  and  $\text{Zn}$ , as well as five intermetallic phases existing at room temperature:  $\text{LiZn}$ ,  $\alpha\text{Li}_2\text{Zn}_3$ ,  $\text{LiZn}_2$ ,  $\alpha\text{Li}_2\text{Zn}_5$  and  $\alpha\text{LiZn}_4$ .

Then, in 1935, Zintl and Schneider [42] and later, in 1976, Schonemann and Schuster [43] confirmed the existence of the intermetallic phases mentioned above. Farrar and King [44] measured the solubility of Li in Zn at 423 K. The lithium activity in liquid alloys was determined for the concentration range between 70.37 and 99.26 at. % Zn at 773 K by Hoshino et al. [45], by Moser et al. [46] in the whole concentration range at 803–833 K, and also by Gąsior and Moser [47] in the concentration range between 0.12 and 0.975 at. % Zn at 733–850 K. All the results of the activity of Li in liquid alloys were tally with each other. In 1989, Moser et al. [48] presented the mixing enthalpies of liquid Li–Zn alloys in the whole concentration range at three temperatures: 816, 818 and 820 K with the use of calorimetric methods. Pelton [49], and Liang et al. [50] optimized the phase diagram of the Li–Zn system. Finally, Dębski and Gąsior [51] presented the mixing enthalpies of liquid Li–Zn, which agreed with previous literature data, and for the first time, they experimentally measured the enthalpies of formation of  $\beta$ -phases from this system.

### 1.4. Ga–Li–Zn

There is a lack of thermodynamic data in the literature for the Ga–Li–Zn system. Taking into account the lack of thermodynamic

**Table 1**  
Materials applied in this study.

Chemical name	Source	Final purity [wt. %]
Gallium	Alfa Aesar	99.999
Lithium	Alfa Aesar	99.9
Zinc	Alfa Aesar	99.999
Argon	Air Products	99.9999

data in the Ga–Li–Zn system, the authors initiated calorimetric investigations of this system. In the present paper, the results of mixing enthalpies of the liquid Ga–Li–Zn alloys were presented by means of drop calorimetry method.

## 2. Materials and methods

The integral molar mixing enthalpy of liquid Ga–Li–Zn alloys were measured with the use of pure, metallic gallium, lithium and zinc (Table 1). For calorimetric studies the Setaram MHTC 96 Line Evo calorimeter was used. All the calorimetric measurements were carried out with the protective argon atmosphere, so before running each experiment and before the pieces of the sample (Ga, Li or Zn) were dropped into the calorimeter, the apparatus was evacuated with a turbo molecular pump several times and then flushed with high purity argon. For the calorimetric study, tungsten crucibles with protective alumina tube were used. At the beginning of all measurements, the calorimeter was calibrated with pieces of gallium. In the case of the pieces of lithium used in experiments, the prepared pieces of lithium were closed inside the glove box with high purity argon in a calorimetric antechamber. Then, the antechamber was removed from the glove box and connected with the calorimeter. The voltage signal from the thermopile was registered in a digital form by the computer with the use of the commercial Calisto software.

The drop calorimetric technique used for determination of the integral molar mixing enthalpies is well established in available literature [52,53]. The research of the liquid alloys from the Ga–Li–Zn system, was started by direct measurements of the mixing enthalpies of liquid Ga–Li alloys, whose concentrations were initial values for the tested alloys from the ternary system. Then to the binary Ga–Li system the appropriate amounts of zinc were dropped. The measurements of the liquid Ga–Li–Zn system were done at four temperatures: 891 K, 993 K, 1018 K and 1044 K in six different alloy compositions, which are shown in Fig. 1.

## 3. Results and discussions

The integral enthalpies of mixing ( $\Delta H_m$ ) of the Ga–Li–Zn liquid solutions were calculated based on the following equations:

$$H_{\text{DISS-X}} = (\Delta H_{\text{Signal}} \cdot K) - (H_X^{T_D \rightarrow T_M} \cdot n_X) \quad (1)$$

$$K = \frac{H_X^{T_D \rightarrow T_M} \cdot n_X}{\Delta H_{\text{Calibration}}} \quad (2)$$

$$\Delta H_m = \frac{\sum H_{\text{DISS-X}}}{n_{\text{Ga}} + n_{\text{Li}} + n_{\text{Zn}}} \quad (3)$$

where,  $\Delta H_{\text{Signal}}$  is the heat effect of each dropped metal (Ga, Li or Zn) which equalled the added drop enthalpy;  $K$  is the calorimeter constant;  $T_D$  is the drop temperature;  $T_M$  is the calorimeter temperature of the respective measurement in Kelvin;  $H_X^{T_D \rightarrow T_M}$  is the enthalpy of the pure metals (Ga, Li or Zn), which was obtained from Pandat 2014 (Pan.SGTE database based on the original SGTE v4.4 database);  $n_X$  ( $n_{\text{Ga}}$ ,  $n_{\text{Li}}$ ,  $n_{\text{Zn}}$ ) are the number of moles of gallium,

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