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CALORIMETRIC MEASUREMENTS OF Ga-Li SYSTEM BY DIRECT REACTION METHOD

The direct reaction calorimetric method was used for the determination of the formation enthalpy of alloys which concentrations correspond to the: Ga_7Li_2, Ga_9Li_5, GaLi, Ga_4Li_5, Ga_2Li_3, and $GaLi_2$ intermetallic phases. The obtained experimental values of the formation enthalpy were: −18.1 ±0.8 kJ/mol at., −26.5 ±0.3 kJ/mol at., −34.7 ±0.3 kJ/mol at., −33.5 ±0.5 kJ/mol at., −32.8 ±0.3 kJ/mol at. and −24.6 ±1.4 kJ/mol at., respectively. After the calorimetric measurements, all the samples were checked by way of X-ray diffraction investigations to confirm the structure of the measured alloys. All the measured values of the formation enthalpy of the Ga-Li alloys were compared with literature data and the data calculated with use of the Miedema model.

Keywords: Gallium-lithium system; Ga-Li; calorimetry; thermochemistry

1. Introduction

Currently, a hugely important issue is a more effective storage of energy. The most popular Li-Ion batteries are the key for portable electronic devices. However, scientists are still searching for alternative materials which offer better usable parameters.

Lithium gallium alloys are promising anode materials for rechargeable batteries. For example, one of the phases from the Ga-Li system, the $GaLi_2$ phase, has the theoretical capacity around 750 mAhg^{-1} [1], that is about twice as high as the theoretical capacity of graphite, which is the most commonly used negative electrode in Li-ion batteries [2]. It could also be used as semiconductor materials for electronics.

The first experimental investigation of the Ga-Li system began in 1956, when Schneider and Hilmer [3] measured the enthalpy of fusion of the LiGa phase with the use of the drop calorimetry technique. In 1970, Thümmel and Klemm [4] confirmed the existence of three intermetallic phases: GaLi, Ga_2Li and $GaLi_2$ (or Ga_4Li_9), by means of thermal analysis and proposed the first Ga-Li phase diagram. Moreover, they measured the lattice parameters for the GaLi phase by way of using X-ray analysis. Yatsenko et al. [5], in 1973, found two additional phases: Ga_4Li and Ga_2Li_3, with the use of differential thermal analysis. In the same year, Yatsenko et al. [6] measured the lithium activity in the liquid Ga-Li system at 1023 K by an electromotive force measurement of the concentration cells with liquid lithium as the reference electrode. In 1981, Buchmanov and Yatsenko [7] determined the heat of fusion of the intermetallic GaLi phase with the use of the differential scanning calorimetric technique. Wen and Huggins [8] published the electrochemical properties of the Ga-Li liquid and solid solutions in the concentration range

between 0.1 and 72 at. % of Li at 688 K, obtained by way of using an (Al)+LiAl two-phase electrode as the reference one. The temperature dependence of the EMF for the two-phase $(Ga)_l$+$(GaLi)_s$ alloys with the overall composition of 40 at. % Li was determined to be between 653 and 848 K. Then, the authors [8] measured the diffusion chemical coefficient in the GaLi intermetallic phase at 688 K. In 1991, Sangster and Pelton [9], based on the available literature data, evaluated the Ga-Li phase diagram with the six following intermetallic phases: $Ga_{14}Li_3$, Ga_7Li_2, GaLi, Ga_4Li_5, Ga_2Li_3 and $GaLi_2$ and two eutectics.

In 1999, another phase diagram with two new intermetallic phases: Ga_8Li_3, Ga_9Li_5, proposed by Tillard-Charbonnel and Belin [10], was published by Okamoto [11], who used the new values from the X-ray diffraction and the DTA study by Tillard-Charbonnel and Belin [10].

Yuan et al. [12], in 2003, conducted a critical evaluation of all the available data for the Ga-Li system and, for the first time, they elaborated a complete set of optimized modeled parameters, which they used for the calculation of the Ga-Li phase diagram. Once again, Okamoto, in 2006 [13], demonstrated the Ga-Li phase diagram which is presented in Fig. 1, and showed a disagreement with the liquidus lines calculated by Yuan et al. [12] and the available literature DTA data. Furthermore, the existence of the Ga_8Li_3 phase proposed by [10] should be confirmed.

Dębski et al. [14] presented the mixing enthalpy of the liquid Ga-Li alloys by means of drop calorimetry at three different temperatures, i.e. 873 K, 992 K and at 1039 K, in the entire concentration range.

Taking into account the lack of experimental studies concerning the formation enthalpy of the intermetallic phases from the Ga-Li system, the Institute of Metallurgy and Materials

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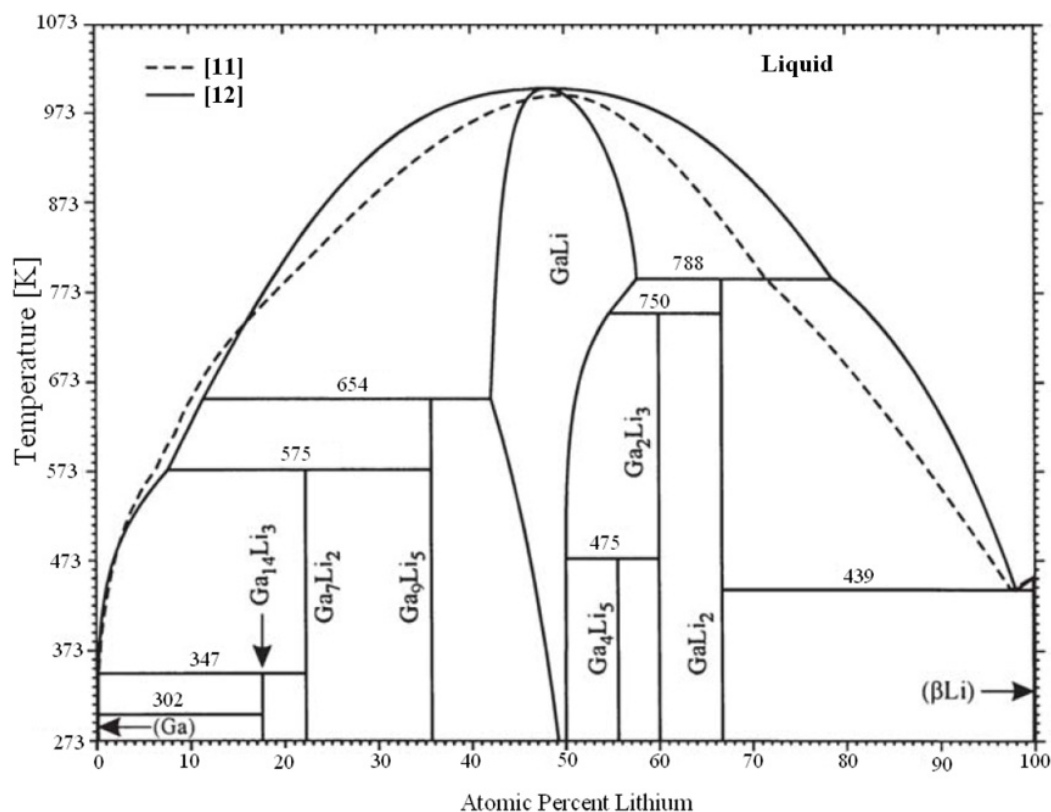
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Fig. 1. Phase diagram of the Ga-Li system [13] with literature data [11,12]

Science PAS, initiated calorimetric investigations. To describe the values of the formation enthalpy in the Ga-Li system two calorimetric methods were applied: the direct reaction method and solution calorimetry. This work compares the calorimetric results of the formation enthalpy of the Ga-Li alloys obtained by the direct reaction method with the data calculated by the Miedema model [15, 16] and by Yuan et al. [12].

2. Experimental

Calorimetric measurements were performed with use of the modified Setaram MHTC 96 Line evo calorimeter. The scheme of modified device is presented in Fig. 2.

To determine the formation enthalpy of the Ga-Li alloys, metallic gallium (ingot purity 99.999 mass. %, Alfa Aesar, stock # 10187) and lithium (rod 12.7 mm, purity 99.9 mass. % Alfa Aesar, stock # 10773) were used. All the calorimetric measurements were carried out with in the protective atmosphere of high purity argon (Air Products 99.9999 mass. %). For the calorimetric study, tungsten crucibles with protective alumina tube were used. Tungsten crucibles were used for measurements, because W does not form intermetallics with Ga and Li, and its mutual solubility with Ga and Li is extremely small. At the beginning of every series, the calorimeter was calibrated by means of pieces of gallium or lithium. In the case of the calibration with use of lithium, the prepared pieces were closed inside a glove-box with high purity argon (H_2O, N_2 and O_2 < 1 ppm) in a calorimetric antechamber (Fig. 3).
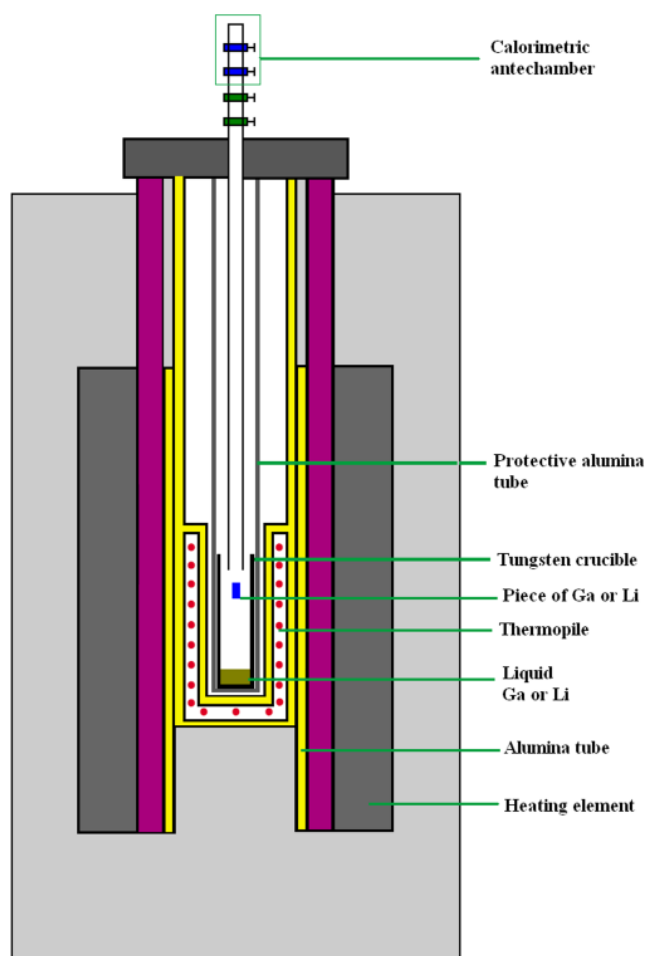

Fig. 2. The scheme of modified device.

Fig. 3. The calorimetric antechamber

The antechamber was removed from the glove-box and connected to the calorimeter. Before each experimental run and before the dropping of the pieces of Ga or Li samples into the calorimeter, the apparatus was evacuated with a turbo molecular pump several times and then flushed with high purity argon (Air Products 99.9999 mass. %).

The direct synthesis method is based on the measurement of the reaction energetic effect of the components (Ga, Li) at a fixed temperature. In the case of the Ga-Li system, the calculation procedure of the formation enthalpy is based on the following deduction: The synthesis of the compound is described by the following thermochemical reaction:

$$X_{Ga}Ga_{(T_R)} + X_{Li}Li_{(T_R)} = Ga_{X_{Ga}}Li_{X_{Li}(T)} + \Delta H^{ef} \qquad (1)$$
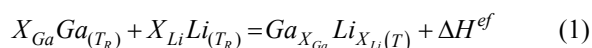
where: T_R designates the temperature of the components before the introduction into the reaction zone (crucible), T is the temperature at which the reaction goes on (crucible), and ΔH^{ef} is the reaction heat effect measured by the calorimeter.

In such a case, the formation enthalpy $\Delta_f H$ at temperature T is the difference between the determined reaction heat effect and the heat consumed by the components for the heating up from temperature T_R to temperature T and it is expressed according to the following equation:

$$\Delta_f H = \Delta H^{ef} - X_i \Delta H_i \qquad (2)$$

where: X_i is the mole fraction of the reacted components (Ga, Li) and ΔH_i is the enthalpy changes of gallium and lithium between temperatures T_R and T which was obtained from Pandat 2014 (Pan_SGTE database based on the original SGTE v4.4 database).

The time of an individual measurement was from 45 minutes (for the alloys whose concentrations correspond to the GaLi$_2$ and GaLi phases) to about 2.5 hours (for the alloy whose concentration correspond to the Ga$_7$Li$_2$ phase – Fig. 4), where the observed base line was constant and it showed the same level as the one at the beginning of the experiment. The formation of the Ga$_7$Li$_2$ intermetallic phase in the course of lithium solution in the liquid gallium is presented in Fig. 4. As it can be seen, it is a two-stage process. An exact explanation of what is forming at the time of the first exothermic reaction (first peak) is rather impossible without a high temperature X-ray study. However, one can suppose that, after dropping the lithium into the liquid gallium, the GaLi phase was the first to be formed. The second one may indicate, that the rest of the liquid phase in the sample has been changed into the solid phase.
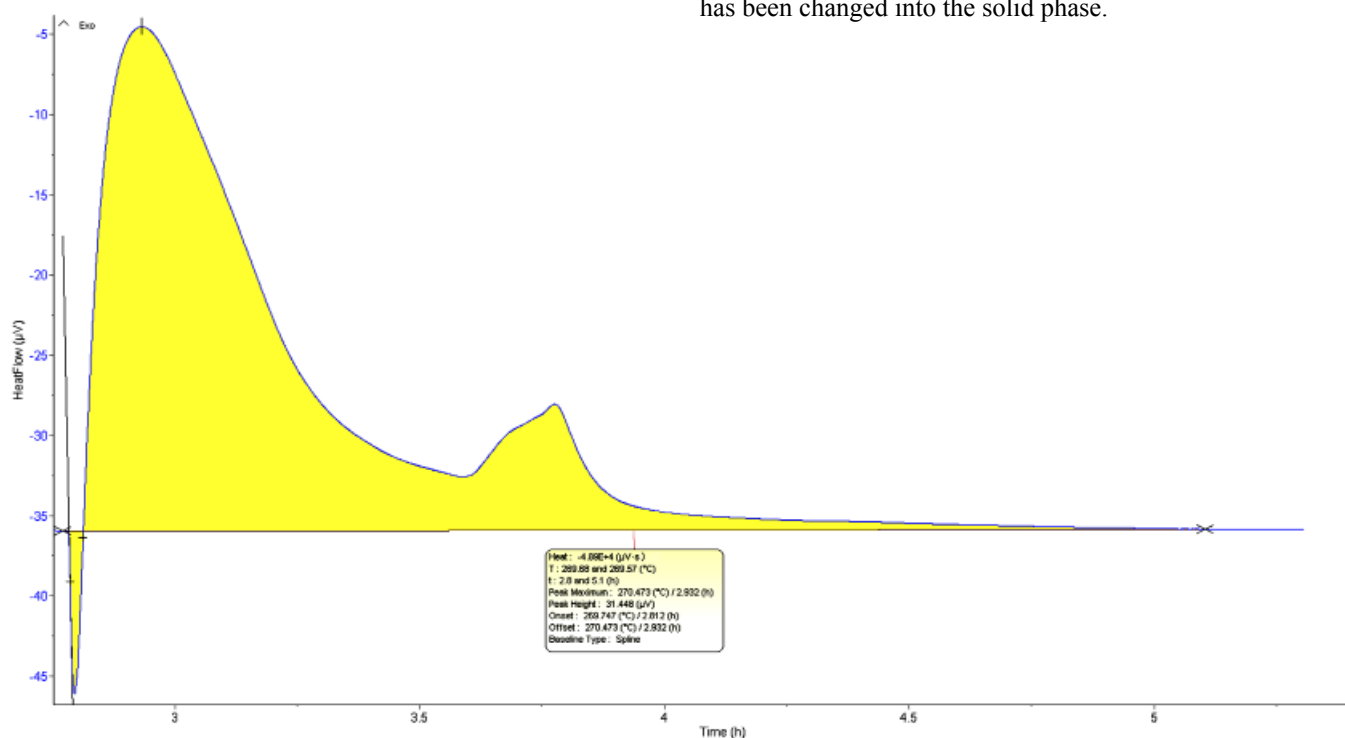

Fig. 4. Example of the heat effect for the alloy whose concentration correspond to the Ga$_7$Li$_2$ phase

3. Results and discussion

The experimental data of the formation enthalpy of the alloys whose concentrations correspond to the Ga_7Li_2, Ga_9Li_5, GaLi, Ga_4Li_5, Ga_2Li_3, and $GaLi_2$ intermetallic phases, together with the standard deviation and the average values, are presented in Table 1. For the verification of the applied direct reaction method, all the alloys obtained after the reaction were analyzed by the X-ray diffraction method with the use of the Philips PW 1710 (Co-Kα radiation) diffractometer. The analysis of the phases was performed with the use of the EVA software. The diffraction patterns of all the measured alloys are shown in Figs. 5-10.

TABLE 1

Heat effects ΔH^{ef} and formation enthalpies $\Delta_f H$ of Ga_7Li_2, Ga_9Li_5, GaLi, Ga_4Li_5, Ga_2Li_3, and $GaLi_2$ intermetallic phases. Reference state: Ga – liq, Li – liq

Alloys (Phases)	Temperature of reaction [K]	The enthalpy changes ΔH_i [kJ/mol]	No of sample	ΔH^{ef} [kJ/mol at.]	$\Delta_f H$ [kJ/mol at.]	Phases in the alloy according to XRD*
77.8 at. % of Ga (Ga₇Li₂)	$T = 542$	$\Delta H_{Ga} = 12.2723$ $\Delta H_{Li} = 9.85661$	1	−17.5	−19.6	PDF 04-017-5844 $Ga_{1.108}Li_{0.892}$ PDF 01-071-8546 $Ga_{14}Li_3$
			2	−16.8	−19.0	
			Average	−17.1	−19.3	
			Standard deviation	0.8	0.8	
64.3 at. % of Ga (Ga₉Li₅)	$T = 615$	$\Delta H_{Ga} = 14.2203$ $\Delta H_{Li} = 12.023$	1	−26.8	−31.1	PDF 04-001-3757 GaLi PDF 01-071-8546 $Ga_{14}Li_3$ PDF 00-001-1264 Li
			2	−27.1	−31.4	
			Average	−27.0	−31.2	
			Standard deviation	0.3	0.3	
50 at. % of Ga (GaLi)	$T = 891$	$\Delta H_{Ga} = 21.5102$ $\Delta H_{Li} = 20.0666$	1	−29.1	−39.1	PDF 04-001-3757 GaLi PDF 00-001-1264 Li PDF 01-089-2884 Ga
			2	−29.0	−39.0	
			Average	−29.0	−39.1	
			Standard deviation	0.3	0.3	
44.4 at. % of Ga (Ga₄Li₅)	$T = 463$	$\Delta H_{Ga} = 10.1454$ $\Delta H_{Li} = 7.48163$	1	−34.1	−38.6	PDF 04-001-3757 GaLi PDF 00-036-0934 $GaLi_2$ PDF 01-071-8546 $Ga_{14}Li_3$ PDF 01-089-2884 Ga
			2	−33.9	−38.4	
			Average	−34.0	−38.5	
			Standard deviation	0.5	0.5	
40 at. % of Ga (Ga₂Li₃)	$T = 727$	$\Delta H_{Ga} = 17.1889$ $\Delta H_{Li} = 15.309$	1	−30.0	−36.8	PDF 04-001-3757 GaLi PDF 00-036-0934 $GaLi_2$ PDF 00-036-0933 Ga_2Li_3
			2	−30.4	−37.3	
			Average	−30.2	−37.1	
			Standard deviation	0.3	0.3	
33.3 at. % of Ga (GaLi₂)	$T = 769$	$\Delta H_{Ga} = 18.2978$ $\Delta H_{Li} = 16.5323$	1	−23.0	−29.1	PDF 00-036-0934 $GaLi_2$ PDF 04-017-5844 $Ga_{1.108}Li_{0.892}$ PDF 01-071-8546 $Ga_{14}Li_3$ PDF 01-089-2884 Ga
			2	−21.0	−27.1	
			Average	−22.0	−28.1	
			Standard deviation	1.4	1.4	

* XRD results at room temperature after the calorimetric measurements.

As it can be seen, all the measured alloys showed the existence of other intermetallic phases in the measured sample. And so, these measurements cannot be treated as the measurements of the formation enthalpy of the intermetallic phases but as the formation enthalpy of the Ga-Li alloys. The XRD measurements performed for the alloys of the concentrations corresponding to those of the Ga_7Li_2 and Ga_9Li_5 phases did not confirm the occurrence of these phases, but they showed the presence mainly of the GaLi phase and a small amount of the $Ga_{14}Li_3$ phase. This means that the time of the calorimetric measurement up to the creation of the base line at the tested temperature was insufficient for the formation of the assumed intermetallic phases, and the obtained measurement value of the thermal effect is the resultant of the thermal effects of the formation of the GaLi and $Ga_{14}Li_3$ phases. For the alloys whose concentration corresponds to that of the GaLi and Ga_4Li_5 phases, the XRD tests confirmed the occurrence of mainly the GaLi phase as well as inclusions of other phases, which are of no particular significance for the measurement of the thermal effect of the GaLi phase. The obtained result of the formation enthalpy of the alloy whose concentration corresponds to that of the GaLi phase should be treated as the measurement result of the formation enthalpy of the GaLi phase. In the case of the measurement of the thermal effect of the alloy whose concentration corresponds to that of the Ga_4Li_5 phase, the obtained result of the formation enthalpy should not be treated as the result of the formation enthalpy of the Ga_4Li_5 phase, but rather as the limiting value of the formation enthalpy of the GaLi phase. The XRD results for the alloy whose concentration corresponds to that of the intermetallic Ga_2Li_3 phase confirmed the formation of this phase during the measurement, as well as of the neighboring phases, GaLi and $GaLi_2$. That is why the obtained result of the formation enthalpy can be close to the value of the formation enthalpy of the intermetallic Ga_2Li_3 phase. The X-ray phase analysis of the alloy whose concentration corresponds to that of
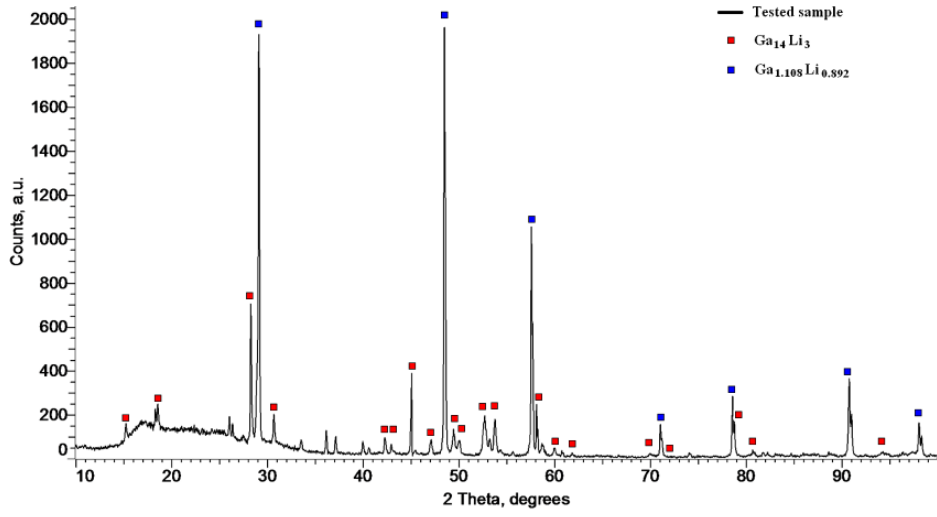
Fig. 5. Diffraction pattern of the Ga_7Li_2 sample after the reaction of Ga and Li in the measurement of the formation enthalpy by the direct reaction calorimetric method
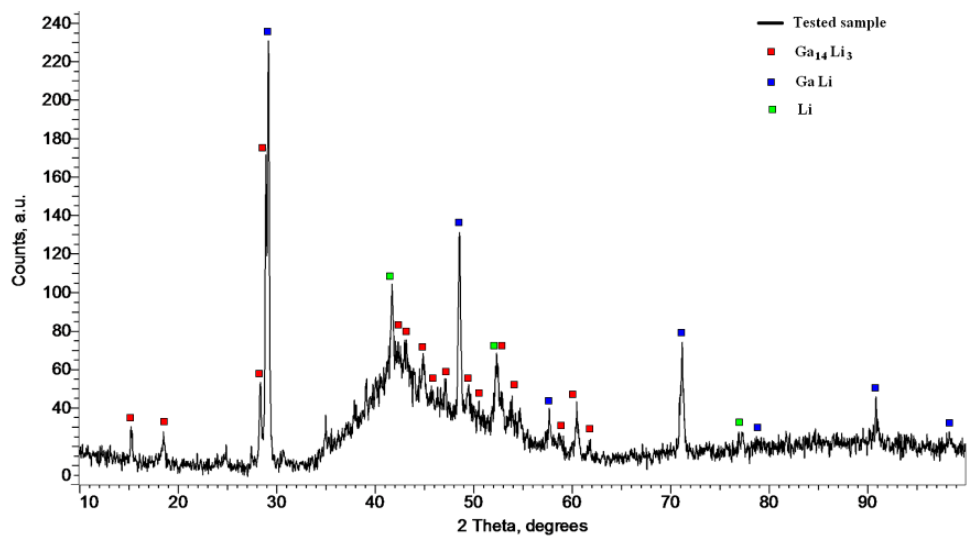

Fig. 6. Diffraction pattern of the Ga_9Li_5 sample after the reaction of Ga and Li in the measurement of the formation enthalpy by the direct reaction calorimetric method
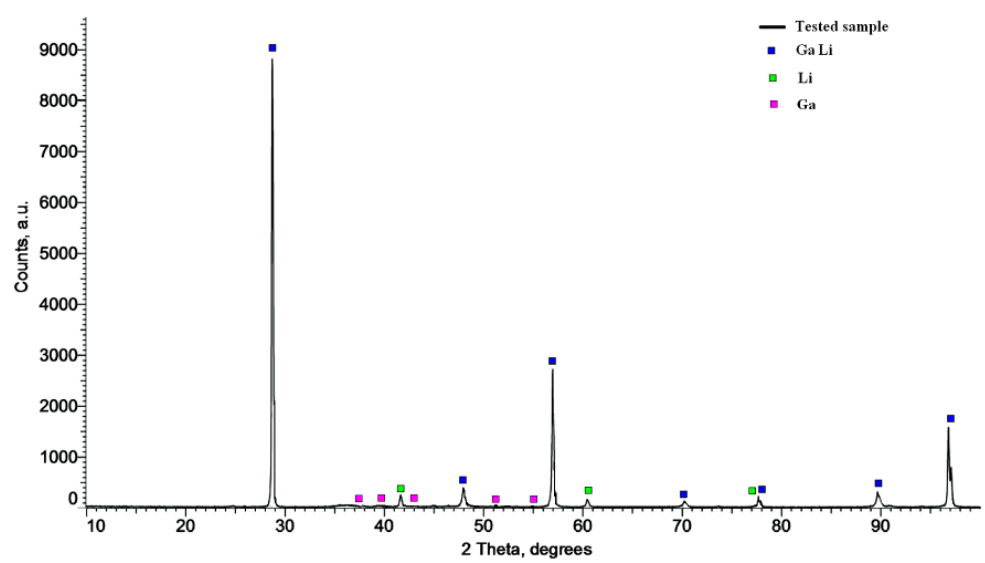

Fig. 7. Diffraction pattern of the GaLi sample after the reaction of Ga and Li in the measurement of the formation enthalpy by the direct reaction calorimetric method
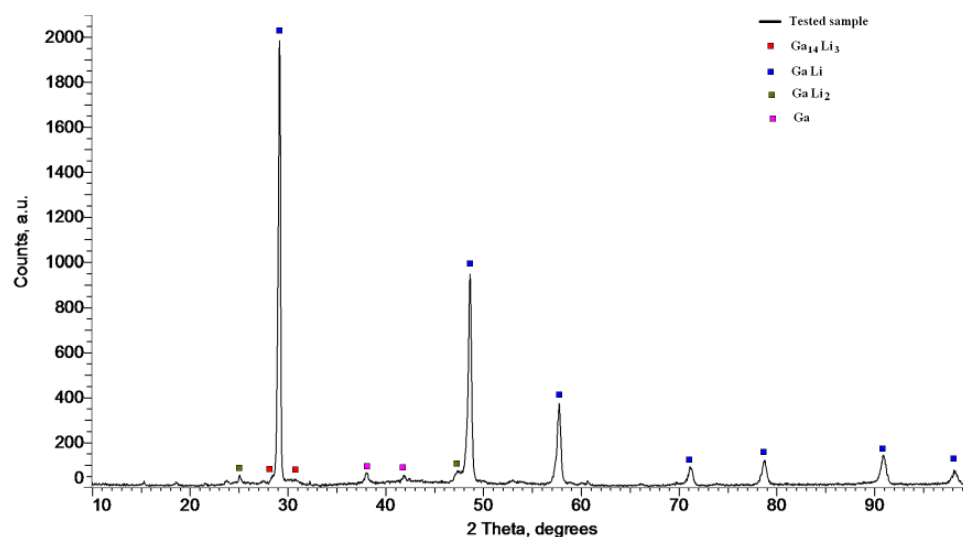
Fig. 8. Diffraction pattern of the Ga_4Li_5 sample after the reaction of Ga and Li in the measurement of the formation enthalpy by the direct reaction calorimetric method
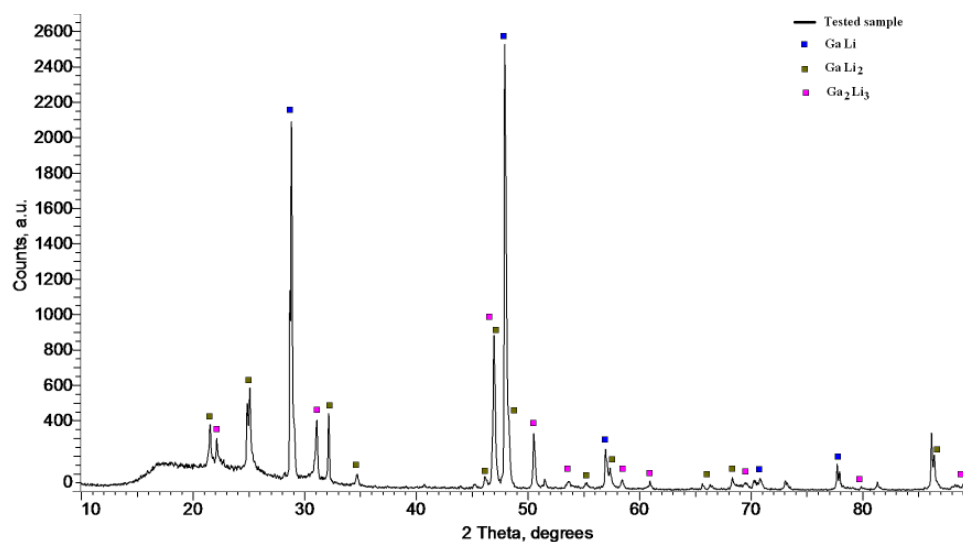

Fig. 9. Diffraction pattern of the Ga_2Li_3 sample after the reaction of Ga and Li in the measurement of the formation enthalpy by the direct reaction calorimetric method
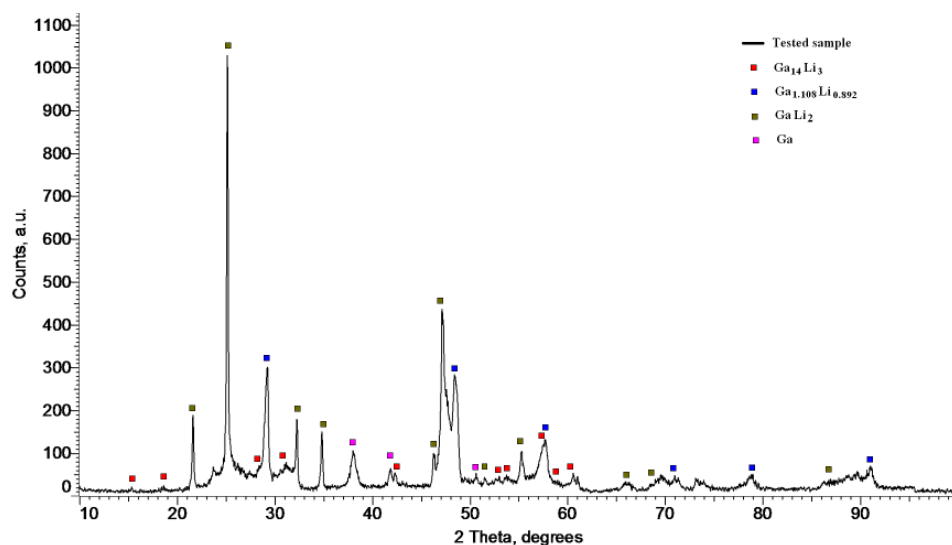

Fig. 10. Diffraction pattern of the $GaLi_2$ sample after the reaction of Ga and Li in the measurement of the formation enthalpy by the direct reaction calorimetric method

the GaLi$_2$ phase confirmed the formation of mostly this phase, as well as the GaLi phase and trace amounts of the Ga$_{14}$Li$_3$ phase and Ga. That is why the influence of the Ga$_{14}$Li$_3$ phase and Ga on the value of the measured thermal effect can be neglected, as opposed to the GaLi phase, which will raise the value of the measured thermal effect.

The obtained experimental data of the formation enthalpy of the alloys whose concentrations correspond to the Ga-Li intermetallic phases are shown in Table 2, together with the

data calculated by Yuan et al. [12], the data calculated by the Miedema model, which were obtained with the use of the Entall Miedema calculator [17] and DFT calculations [18]. Because, the obtained results of formation enthalpy for temperature range of 463-891 K do not vary significantly with the enthalpy of formation data calculated for 298 K, it may indicate lack of the temperature dependence of formation enthalpy of Ga-Li intermetallic phases. Taking into account this assumption, all data of formation enthalpy are presented in Fig. 11.

TABLE 2

The comparison of the experimental data of the formation enthalpy of the measured Ga-Li alloys, with the data calculated by Yuan et al. [12], the data calculated by the Miedema model [17] and DFT calculations [18]. Reference state: Ga- solid, Li- solid

| Alloys composition/phases	$\Delta_f H$ [kJ/mol at.]			
	This study Direct reaction calorimetry	Yuan et al. [12]	Miedema Model [17]	DFT calculations [18]
Ga$_{14}$Li$_3$		−13.999	−4.95	
77.8 at. % of Ga	−18.1 at T = 542 K		−6.25	−17.374 for Ga$_3$Li
Ga$_7$Li$_2$		−16.5		
64.3 at. % of Ga	−26.5 at T = 615 K		−9.88	
Ga$_9$Li$_5$		−23.5		
50 at. % of Ga	−34.7 at T = 891 K		−12.24	
GaLi		−30.609		−31.369
44.4 at. % of Ga	−33.5 at T = 463 K		−12.34	
Ga$_4$Li$_5$		−28.5		
40 at. % of Ga	−32.8 at T = 727 K		−12.02	
Ga$_2$Li$_3$		−25.48		−31.755
33.3 at. % of Ga	−24.6 at T = 769 K		−10.87	
GaLi$_2$		−21.3		−29.535
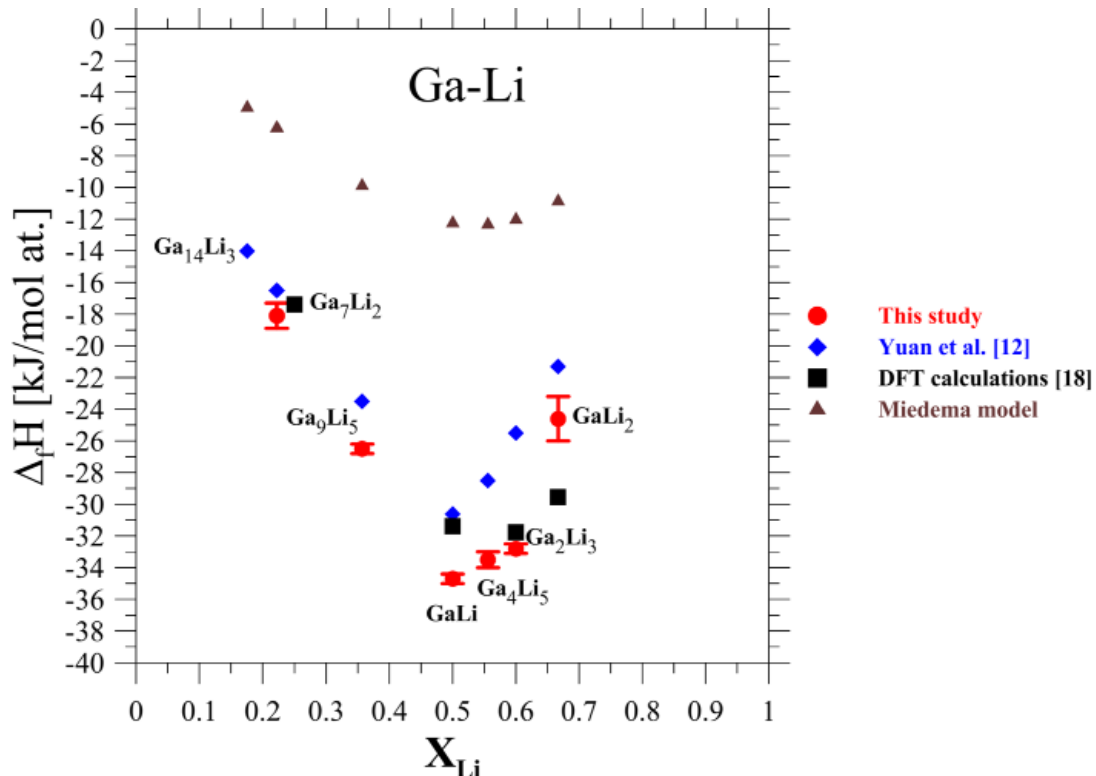
Fig. 11. The comparison of the experimental data of the formation enthalpy of the measured Ga-Li alloys, with the data calculated by Yuan et al. [12] and the data calculated by the Miedema model. Reference state: Ga- solid, Li- solid

As it can be seen in Fig. 11, the Miedema model gives values which are much less negative than those presented in this study. Taking into account the experimental errors, the XRD results, and the same reference state, the results of the present calorimetric measurements of the enthalpy of formation of the Ga-Li alloys are similar to the data of the formation enthalpy of the Ga-Li intermetallic phases calculated by Yuan et al. [12] and DFT studies [18].

4. Conclusion

In this paper, the formation enthalpies of the alloys whose concentrations correspond to the Ga_7Li_2, Ga_9Li_5, $GaLi$, Ga_4Li_5, Ga_2Li_3, and $GaLi_2$ intermetallic phases were measured by means of the direct reaction calorimetry. The correlation analysis of the formation enthalpy data for the Ga-Li intermetallic phases showed that those calculated by the Miedema model [15, 17] are much more exothermic than calculated data (presented by Yuan et al. [12] and DFT calculations) as well as the ones from this study. Taking into consideration the experimental problems indicated in this studies and the fact that the results of Yuan et al. [12] are one of the possible propositions of optimization, the last three sets of data could be thought of as comparable at this stage of investigations. Based on the X-ray diffraction analysis, it was found that, in the course of the direct synthesis, in the calorimetric experiments, the formation processes of the Ga-Li intermetallic phases were not completed, though the thermal calorimeter equilibrium was reached, and the measurement had to be terminated (constant value of the base line). It is obvious that more reliable data could be obtained by the solution calorimetry, in which the Ga-Li intermetallic phases are used for the solution in liquid metal. The phases should be produced and, before the calorimetric study, their structure must be confirmed by X-ray diffraction. Such experiments are planned to be conducted at our laboratory, as the next step in the investigations of the Ga-Li system.

REFERENCES

[1] J. Saint, M. Morcrette, D. Larcher, J.M. Tarascon, Solid State Ionics **176,** 189 (2005).

[2] G.A. Nazri, G. Pistoia, Lithium Batteries Science and Technology, Kluwer Academic Plenum: Boston, 2004.

[3] A. Schneider, O. Hilmer Z. Anorg. Allg. Chem. **286** (3-4), 97 (1956).

[4] R. Thümmel, W. Klemm, Z. Anorg. Allg. Chem. **376** (1), 44 (1970).

[5] S.P. Yatsenko, K.A. Chuntonov, S.I. Alyamovsky, E.N. Diyeva, Izv. Akad. Nauk SSSR Met. **1**, 185 (1973).

[6] S.P. Yatsenko, E.A. Saltykova, V.N. Diev, L.N. Rykova, Zh. Fiz. Khim. **47** (9), 2417 (1973).

[7] V.D. Bushmanov, S.P. Yatsenko. Zh. Fiz. Khim. **55** (11), 2951 (1981).

[8] C.J. Wen, R.A. Huggins, J. Electrochem. Soc. **128** (8), 1636 (1981).

[9] J. Sangster, A.D. Pelton, J. Phase Equilibria **12** (1), 33 (1991).

[10] M. Tillard-Charbonnel, C. Belin C.R. Acad. Sci. Paris **306**, 1161 (1988).

[11] H. Okamoto, J. Phase Equilib. **20** (1), 92 (1999).

[12] W.X. Yuan, W.J. Wang, Y.T. Song, X.L. Chen, Scri. Mater. **48**, 1053 (2003).

[13] H. Okamoto, J. Phase Equilib. Diff. **27** (2), 200 (2006).

[14] A. Dębski, W. Gąsior, R. Dębski, J. Chem. Thermodyn. **97**, 348 (2016).

[15] A.R. Miedema, J. Less-Common Met. **32**, 117 (1973).

[16] F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, Cohesion in Metals: Transition Metal Alloys (North-Holland, Amsterdam [etc], 1989).

[17] A. Dębski, R. Dębski, W. Gąsior, Arch. Metall. Mater. **59** (4), 1337 (2014).

[18] http://www.oqmd.org/materials/composition/Ga-Li.