

THERMODYNAMIC STUDY OF Ga–Sn AND Ga–Zn SYSTEMS USING QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS

D. Živković, D. Manasijević and Z. Živković*

University of Belgrade, Technical Faculty, VJ 12, 19210 Bor, Yugoslavia

(Received January 7, 2003; in revised form February 12, 2003)

Abstract

The results of quantitative differential thermal analysis application in thermodynamic investigation of two gallium-based binary systems, Ga–Sn and Ga–Zn, are presented in this paper. Integral molar enthalpies of mixing in liquid state, as well as the activities, activity coefficients, and other partial and integral molar quantities were determined at the temperatures of 1000, 1073 and 1200 K (for Ga–Sn system) and 723 K (for Ga–Zn system). Obtained results were compared with literature data and comparison showed good agreement. Also, phase diagrams for the investigated simple eutectic systems were confirmed based on DTA curves and compared with literature.

Keywords: binary systems, gallium alloys, Ga–Sn, Ga–Zn, thermodynamics

Introduction

Ga–Sn and Ga–Zn alloys belong to the group of systems, which present the constituents of different gallium-based multicomponent alloys applied in semiconducting industry. These two systems, characterized by low-melting eutectics, are well described in literature and there are a lot of references considering their phase diagrams [1–7] and thermodynamic properties [8–15].

Ga–Sn system [16] has an eutectic point at 8.5 at%Sn and temperature of 19°C, while maximum solubility of Ga in Sn-rich solid solution at 19°C is 7.1 at%Ga. Ga–Zn system [17] has an eutectic point at 3.7 at%Zn and temperature of 25°C. The hexagonal (Zn) terminal solid solution has a maximum solubility of 2.36 at%Ga at 260°C, while the orthorhombic (Ga) solid solution has a maximum solubility of 0.8 at%Zn at 20°C.

Considering the thermodynamics of Ga–Sn system, one of the first investigations was the work of Cohen, Howlett and Bever [8], who determined the heat of solution of Ga in liquid Sn. Later, Predel [9] defined the equilibrium conditions for this system by several experimental methods and calculated values of ΔG^M and ΔS^M for

* Author for correspondence: E-mail: jmm@eunet.yu

liquid alloys from the melt equilibria. Also, he determined the activity curve on the assumptions of a regular solution model and pointed out to moderately positive deviations from Raoult law at 513 K in the whole composition range. Pool and Lundin [10] measured partial molar heat of solution at infinite dilution of Ga in Sn at 750 K using tin solution calorimetry, while Danilin and Yatsenko [11] did EMF measurements and determined slight deviation from Raoult law at all compositions. In early seventies, Bros and Laffite [12] determined the enthalpy of formation of the liquid alloys at temperatures 400–750 K in the whole concentration range using microcalorimetry; Hultgren and coworkers presented the compilation of data published up to 1973 in their well known book [13], while Muggianu, Gambino and Bros [14] determined mixing enthalpies for Ga–Sn alloys. One of the latest work on Ga–Sn thermodynamics is presented by Katayama, Maki, Nakamo and Iida [15] in 1996, who performed EMF measurements with zirconia solid electrolyte and determined gallium and tin activities, as well as partial and integral molar Gibbs energies of mixing in the temperature interval 1000–1200 K.

Thermodynamics of Ga–Zn system is also well investigated by several different experimental methods. There are many results obtained using EMF measurements by: Genta, Fiorani and Valenti [18], Svirbley and Read [19], Gerasimenko, Zoitsev, Lozkhin and Morachevskii [20], Predel, Mohs and Rothacker [21], Ryabov and Sryvalin [22] and Moser [23]. Vapour pressure measurements were performed by Piacente, Desideri, Malaspina and Hallgass [24], while calorimetric measurements were done by Kleppa [25]. Also, there are some results obtained by thermodynamic calculations according to Lukas, Henig and Zimmermann [26] and Hajra and Mazumdar [27]. Complete thermodynamic data on Ga–Zn system are presented in [13] and in the work of Dutkiewicz *et al.* [28] in 1990.

Results of thermodynamic analysis of Ga–Sn and Ga–Zn alloys according to quantitative DTA are presented in this paper and compared with literature data, in order to evaluate the accuracy of this method in thermodynamic description of these binary systems.

Experimental

Quantitative differential thermal analysis [29–34] was used for experimental investigations presented in this paper. Commercial DTA apparatus could not be directly used for quantitative measurements of binary and ternary metal systems. For that reason, special DTA apparatus, adequate for these purposes, has been made [31]. The schematic presentation of this apparatus is shown in Fig. 1.

According to the experimental procedure, samples were prepared (Fig. 2) such that the required gallium mass was melted firstly at the bottom of a pyrex tube, within which a protective tube was fixed for the NiCr–Ni thermocouple. A tin or zinc (depending on a system investigated) ring of a corresponding mass was fixed to the same tube, in order to provide, after melting, an alloy of the required composition. In all cases two heatings were carried out [29, 30, 34].

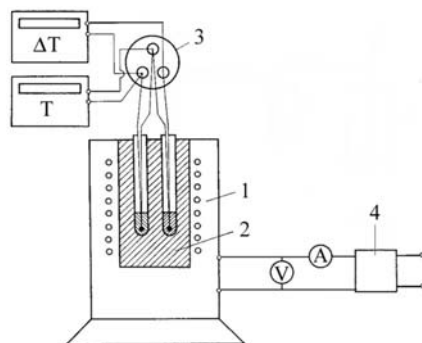


Fig. 1 Apparatus for quantitative DTA measurements; (1 – electric inductive furnace; 2 – Ni-block with pyrex tubes and NiCr–Ni thermocouples; 3 – thermostat; 4 – transformer with amperometer and voltmeter)

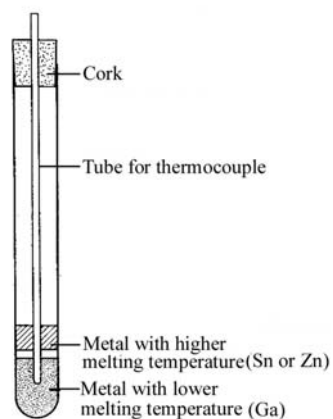


Fig. 2 Tube with a sample

Table 1 Composition and masses of the investigated Ga–Sn and Ga–Zn alloys

Sample	Ga–Sn		Ga–Zn		
	x_{Ga}	Mass/g	Sample	x_{Ga}	Mass/g
L1	1	2.9550	S1	1	1.7730
L2	0.95	3.0021	S2	0.9628	1.7838
L3	0.9258	3.0241	S3	0.8616	1.8139
L4	0.8	3.1332	S4	0.5890	1.9027
L5	0.6	3.2878	S5	0.3054	2.0086
L6	0.3	3.4852	S6	0.1978	2.0530
L7	0	3.6500	S7	0	2.1420

The experiments were done in an air atmosphere, with calcined alumina as reference material. Both tubes (with sample and reference material) are heated in the furnace according to an appropriate program, so T and DTA curves could be obtained. The heating rate in all cases was 10 K min^{-1} .

Metals (Ga, Sn and Zn) used in this work were of p.a. purity. The compositions of the investigated alloys in Ga–Sn and Ga–Zn systems are given in Table 1. The volume of samples was constant 0.5 and 0.3 cm^3 for Ga–Sn and Ga–Zn system, respectively.

Results and discussion

According to the theoretical principles of DTA application in quantitative calorimetric determination [29–34], the basic analytical expression of the quantitative DTA is given as

$$m\Delta H_T^0 = gK_s \int T dt \quad (1)$$

where are m – mass of the sample, ΔH_T^0 – reaction enthalpy, gK_s – calibration constant of the apparatus and $\int T dt$ – area of DTA peak.

The first and very important step in the application of this method is determination of the calibration constant, gK_s . By recording the relationship of the peak area and sample mass, for the pure metals and their eutectic, it is possible to determine the calibration constant of the apparatus, which represents the equivalence factor between endothermic or exothermic effects and the area of DTA peak. gK_s consists of two constants: g – geometric constant and K_s – heat conductivity of the sample. In order to eliminate the influence of the geometric constant, the sample volume is kept constant during the experiments. Also, Živković has shown [35] that there is a linear dependence of gK_s on conductivity coefficient and composition for eutectic binary systems, which offers a possibility for a simplified, direct determination of this very important constant based upon the given composition of the eutectic system investigated.

In the case of Ga–Sn and Ga–Zn systems, DTA curves for different masses of pure gallium, tin and zinc were recorded. Graphical representation of peak area dependence on mass, for all used metals, is given in Fig. 3. Calculated values of calibration constants for gallium, tin and zinc are given in Table 2, while linear dependencies of gK_s on molar content for both investigated systems are shown in Fig. 4.

The second step in the quantitative DTA is determination of the integral molar enthalpy of mixing. As mentioned earlier, prepared samples are heated twice. During the first heating, gallium melts at its melting point of 302.8 K , which is recorded as

Table 2 Values of calibration constants for gallium, tin and zinc

Metal	$gK_s/\text{J mm}^{-2}$
Gallium	0.11348
Tin	0.24207
Zinc	0.26604

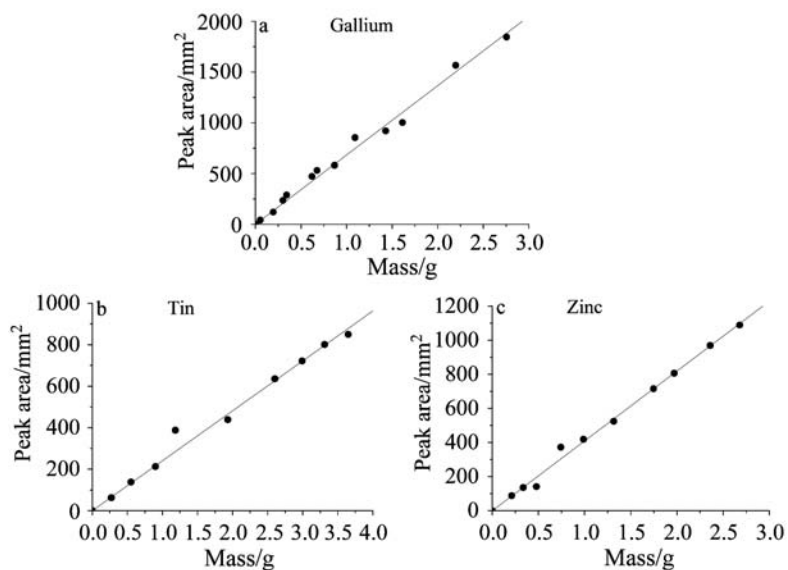


Fig. 3 Dependence of peak area on sample mass for pure metals: a – gallium, b – tin and c – zinc

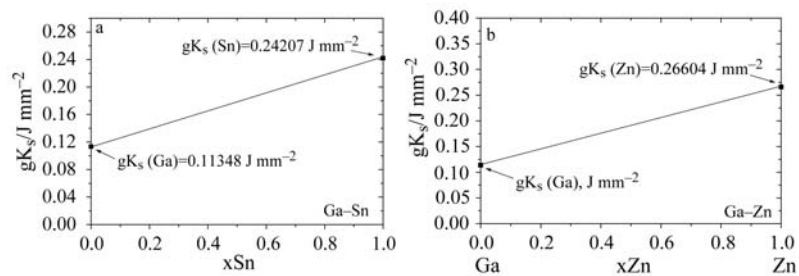


Fig. 4 Dependence of gK_s vs. molar content for a – Ga–Sn alloys and b – Ga–Zn alloys

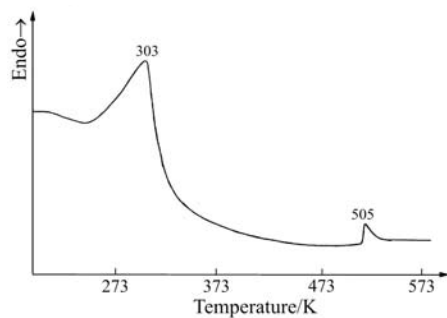


Fig. 5 Characteristic DTA curve for the first melting of sample L2 (Ga–Sn system)

the first peak at the obtained DTA curve. Further, as heating process goes on, second metal (tin or zinc – depending on the system investigated) melts at its melting temperature (505 and 693 K, respectively), and at the same time drops into the melted gallium, which is recorded by the second peak of the obtained DTA curve. Characteristic example of such DTA curve is shown in Fig. 5.

So, during the first melting (I), obtained DTA peak areas are proportional to the enthalpy of the first melting, which can be expressed in the case of Ga–M system ($M=Sn, Zn$) as:

$$\Delta H_I = x_{Ga} \Delta H_{f,Ga} + x_i \Delta H_{f,i} + \Delta H^M \quad (2)$$

where are $\Delta H_{f,i}$ – enthalpy of fusion for the component i ; x_i – molar content of component and ΔH^M – integral molar enthalpy of mixing in liquid state. The enthalpy of the first melting, ΔH_I , is determined based on the known peak areas and calibration constants for each alloy composition, according to Eq. (1). Values for integral molar enthalpy of mixing in liquid state, for both investigated gallium-based binary systems, are given in Table 3.

Table 3 Values of the integral molar enthalpies of mixing for investigated Ga–Sn and Ga–Zn alloys

Ga–Sn		Ga–Zn	
$\Delta H^M / \text{J mol}^{-1}$			
L1	0	S1	0
L2	95	S2	336
L3	306	S3	493
L4	673	S4	1368
L5	907	S5	1477
L6	723	S6	1255
L7	0	S7	0

Comparison between values for the integral molar enthalpies of mixing obtained for Ga–Sn and Ga–Zn alloys by quantitative DTA and literature data [12, 13, 35] and [13, 28], respectively, is presented graphically in Fig. 6.

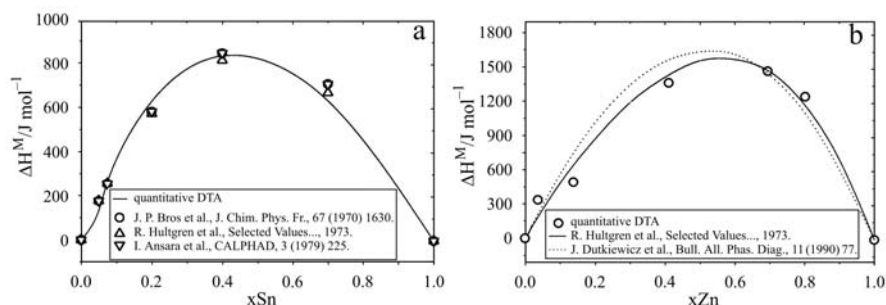


Fig. 6 Comparison of the values for ΔH^M obtained by quantitative DTA and literature data; a – Ga–Sn system and b – Ga–Zn system

It can be concluded that there is an excellent agreement between results obtained by quantitative DTA and literature data in the case of Ga–Sn alloys, where positive values for ΔH^M are noticed. The same positive trend is characteristic for the Ga–Zn alloys, but with higher values of the integral molar enthalpy of mixing and presented slight deviation between results of quantitative DTA and literature data.

Following the experimental procedure of the quantitative DTA, the second melting should be described. After the homogenization of alloy formed during the first melting, it solidifies up to the room temperature. Then, heating is repeated during the second melting (II). Phase transformations occurring in the solid-state, as well as the alloy melting, are recorded at DTA curve, so it can be used for the investigation of the phase diagram, typical for the chosen system. Temperatures for the eutectics and liquidus lines, in both systems, determined on the base of DTA curves for heating during the second melting show good agreement with phase diagrams of Ga–Sn and Ga–Zn systems, according to SGTE Phase Diagram Collection [16, 17], as presented in Fig. 7.

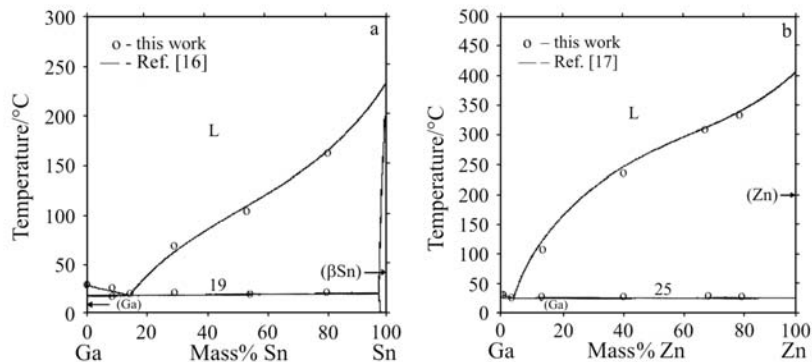


Fig. 7 Phase diagrams of a – Ga–Sn and b – Ga–Zn systems

And finally, the last step in the quantitative DTA thermodynamic analysis is determination of activities for both components in a binary system. In this case, regular solution model was applied in order to obtain characteristic partial and integral molar quantities, which means that [36]

$$\Delta H^M = \Delta G^{xs} \tag{3}$$

where ΔG^{xs} presents integral molar excess Gibbs energy. So, the problem was solved by fitting of ΔH^M vs. composition and further calculation of the partial molar excess Gibbs energies according to known relation

$$G_i^{xs} = \Delta G^{xs} + (1-x_i) \frac{\partial \Delta G^{xs}}{\partial x_i} \tag{4}$$

where G_i^{xs} presents partial molar excess Gibbs energy. Results obtained by such a calculation procedure, at the temperatures of 1000, 1073 and 1200 K for Ga–Sn system and at the temperature of 723 K for Ga–Zn system, are presented in Table 4. They in-

Table 4a Partial and integral molar quantities obtained by quantitative DTA; a – Ga–Sn system

x_{Ga}	a_{Ga}	a_{Sn}	γ_{Ga}	γ_{Sn}	G_{Ga}^{M}	G_{Sn}^{M}	$G_{\text{Ga}}^{\text{ss}}$	$G_{\text{Sn}}^{\text{ss}}$	ΔG^{M}	ΔG^{ss}
1000 K										
1	1	0	1	1	0	0	0	0	0	0
0.95	0.953	0.084	1.003	1.680	-400	-20593	26	4313	-1410	241
0.9258	0.936	0.118	1.011	1.590	-550	-17768	91	3857	-1827	371
0.8	0.822	0.289	1.027	1.445	-1630	-10320	226	3060	-3368	793
0.6	0.659	0.489	1.098	1.222	-3467	-5948	780	1670	-4459	1136
0.3	0.407	0.728	1.357	1.040	-7474	-2639	2536	326	-4090	989
0	0	1	1	1	0	0	0	0	0	0
1073 K										
1	1	0	1	1	0	0	0	0	0	0
0.95	0.952	0.081	1.002	1.620	-439	-22421	19	4303	-1538	233
0.9258	0.935	0.114	1.010	1.536	-600	-19372	88	3831	-1993	366
0.8	0.820	0.281	1.025	1.405	-1770	-11324	220	3033	-3681	783
0.6	0.655	0.483	1.092	1.208	-3775	-6492	782	1682	-4862	1142
0.3	0.399	0.726	1.330	1.037	-8196	-2857	2544	325	-4459	991
0	0	1	1	1	0	0	0	0	0	0

Table 4a Continued

x_{Ga}	a_{Ga}	a_{Zn}	γ_{Ga}	γ_{Zn}	G_{Ga}^{M}	G_{Zn}^{M}	$G_{\text{Ga}}^{\text{XS}}$	$G_{\text{Zn}}^{\text{XS}}$	ΔG^{M}	ΔG^{XS}
1200 K										
1	1	0	1	1	0	0	0	0	0	0
0.95	0.951	0.077	1.001	1.540	-501	-25580	10	4308	-1755	225
0.9258	0.934	0.109	1.009	1.469	-681	-22113	88	3837	-2271	366
0.8	0.818	0.271	1.023	1.355	-2004	-13026	222	3031	-4209	783
0.6	0.649	0.473	1.082	1.183	-4313	-7469	783	1672	-5576	1139
0.3	0.387	0.723	1.290	1.033	-9471	-3236	2541	323	-5107	988
0	0	1	1	1	0	0	0	0	0	0

Table 4b Partial and integral molar quantities obtained by quantitative DTA; b – Ga–Zn system

x_{Ga}	a_{Ga}	a_{Zn}	γ_{Ga}	γ_{Zn}	G_{Ga}^{M}	G_{Zn}^{M}	$G_{\text{Ga}}^{\text{XS}}$	$G_{\text{Zn}}^{\text{XS}}$	ΔG^{M}	ΔG^{XS}
1	1	0	1	1	0	0	0	0	0	0
0.9628	0.964	0.099	1.001	2.661	-220	-13901	7	5884	-729	226
0.8616	0.879	0.303	1.020	2.189	-775	-7177	120	4710	-1661	755
0.589	0.704	0.593	1.195	1.443	-2110	-3141	1072	2204	-2534	1537
0.3054	0.508	0.766	1.663	1.103	-4071	-1602	3059	588	-2356	1342
0.1978	0.389	0.836	1.967	1.042	-5675	-1077	4065	248	-1986	1003
0	0	1	1	1	0	0	0	0	0	0

clude activities, activity coefficients, partial and integral molar excess Gibbs energies and Gibbs energies of mixing,

Comparison was also made with literature, for both systems: activities for gallium and tin in Ga–Sn system, obtained by quantitative DTA, were compared with Ref. [15] (at the temperature of 1073 K), while activities for gallium and zinc in Ga–Zn system, obtained by quantitative DTA, were compared with Refs [13, 28] (at the temperature of 723 K). Comparative review, presented in Fig. 8, points out to a good mutual agreement between quantitative DTA results and literature, noticed in both investigated systems.

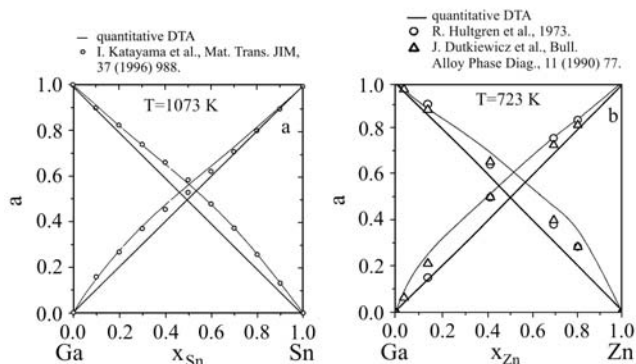


Fig. 8 Comparison between thermodynamic data obtained by quantitative DTA and literature data; a – a_{Ga} and a_{Sn} vs. molar content at 1073 K in Ga–Sn system; b – a_{Ga} and a_{Zn} vs. molar content at 723 K in Ga–Zn system

Presented application of quantitative DTA to gallium-based binary systems Ga–Sn and Ga–Zn and the comparison of such obtained results with literature show good results. Although DTA is mostly considered as a qualitative method (for some limitations, such as poor repeatability of the effects or causing troubles in interpretation), this method can be used as quantitative one, also. Investigations of different authors [29–34] show that control of experimental conditions (sample mass and granulation, mass and granulation of the reference material, heat conductivity, etc.), as well as a correct determination of the calibration constant, positively influence and contribute to the reproduction of the results, which has already been proved [37–39]. For that reason application of DTA as a quantitative method could be used as simple and accurate method in thermodynamic analysis of binary eutectic systems.

Conclusions

Results of the quantitative DTA application to gallium-based binary systems Ga–Sn and Ga–Zn are presented in this paper. Calibration constants were determined for alloys in the both systems, as well as the integral molar enthalpy of mixing and other partial and integral molar quantities (for Ga–Sn system at 1000–1200 K and for Ga–Zn system at 723 K). Phase diagrams of these systems were also confirmed based

on DTA curves for heating. Comparison of results obtained by this method with literature data show good mutual agreement in all cases.

* * *

The authors wish to express their gratitude to Prof. Jaroslav Šestak (Czech Republic), Prof. Iwao Katayama (Japan) and Dr. Leszek Zabdyr (Poland) for their help in the preparation of this work.

References

- 1 N. A. Puschin, S. Stepanovic and V. Stajic, *Z. Anorg. Allg. Chem.*, 20 (1932) 329.
- 2 B. Predel, M. Frebel and W. Gust, *J. Less-Comm. Metals*, 17 (1969) 391.
- 3 V. Valenti and M. Fiorani, *Gazz. Chim. Ital.*, 85 (1955) 103.
- 4 T. Heumann, B. Predel and M. B. Bever, *Z. Metallknd.*, 49 (1958) 90.
- 5 D. A. Davis, *J. Inst. Met.*, 93 (1965) 515.
- 6 S. Delcroix, A. Defrain and I. Epelboin, *J. Phys. Rad.*, 24 (1963) 17.
- 7 P. E. Shurai, W. N. Danilin, I. T. Sryvalin and A. G. Dolesov, *Izv. Akad. Nauk SSSR, Metal*, 5 (1974) 245.
- 8 J. B. Cohen, B. W. Howlett and M. B. Bever, *Trans. Met. Soc. AIME*, 221 (1961) 683.
- 9 B. Predel, *J. Less-Comm. Metals*, 7 (1964) 347.
- 10 M. J. Pool and C. E. Lundin, *Trans. Met. Soc. AIME*, 230 (1964) 587.
- 11 N. V. Danilin and S. P. Yatsenko, *Izv. Akad. Nauk SSSR, Metal*, 203 (1968) 207.
- 12 J. P. Bros and M. Laffite, *J. Chim. Phys. Fr.*, 67 (1970) 1636.
- 13 R. Hultgren, Selected values of thermodynamic properties of binary metal systems, ASM, Metals Park, Ohio 1973.
- 14 Y. M. Muggianu, M. Gambino and J. P. Bros, *J. Chim. Phys.*, 72 (1975) 83.
- 15 I. Katayama, K. Maki, M. Nakamo and T. Iida, *Mat. Trans. JIM*, 37 (1996) 988.
- 16 <http://www.met.kth.se/pd/element/Ga-Sn.html>.
- 17 <http://www.met.kth.se/pd/element/Ga-Zn.html>.
- 18 V. Genta, M. Fiorani and V. Valenti, *Gazz. Chim. Ital.*, 85 (1955) 103.
- 19 W. J. Svirbley and S. M. Read, *J. Phys. Chem.*, 66 (1962) 658.
- 20 L. N. Gerasimenko, V. A. Zoitsev, L. N. Lozkhin and A. G. Morachevskii, *Izv. V. U. Z. Tsvetn. Metall.*, 1 (1966) 46.
- 21 B. Predel, R. Mohs, and D. Rothacker, *J. Less-Comm. Met.*, 12 (1967) 483.
- 22 V. G. Ryabov and I. T. Sryvalin, *Izv. Akad. Nauk. SSSR, Met.*, 2 (1971) 78.
- 23 Z. Moser, *Metall. Trans.*, 4 (1973) 2399.
- 24 V. Piacente, A. Desideri, L. Malaspina and A. Hallgass, *Rev. Int. Hautes Temp. Refract.*, 10 (1973) 85.
- 25 O. J. Kleppa, *Acta. Metall.*, 6 (1958) 225.
- 26 H. L. Lukas, E. T. Henig and B. Zimmermann, *CALPHAD*, 1 (1977) 225.
- 27 J. P. Hajra and B. Mazumdar, *Metall. Trans.*, 22B (1991) 593.
- 28 J. Dutkiewicz, Z. Moser, L. Zabdyr, D. Gohil, T. G. Chart, I. Ansara and C. Girard, *Bull. Alloys Phase Diag.*, 11 (1990) 77.
- 29 B. Dobovisek and B. Straus, *RMZ*, 3 (1960) 273 (in Slovenian).
- 30 B. Dobovisek and A. Paulin, *RMZ*, 3 (1962) 229 (in Slovenian).
- 31 A. Rosina, N. Smajic and B. Dobovisek, *Microchim. Acta*, 4 (1967) 626.

- 32 B. Predel, I. Arpshofen and M. J. Pool, *Thermochim. Acta*, 22 (1978) 211.
- 33 Z. Živković, *Thermochim. Acta*, 44 (1981) 385.
- 34 Z. Živković and D. Živković, *Arch. Hutnictwa*, in print.
- 35 I. Ansara, J. P. Bros and M. Gambino, *CALPHAD*, 3 (1979) 225.
- 36 D. R. Gaskell, *Introduction to Metallurgical Thermodynamics*, McGraw-Hill, New York 1973.
- 37 Z. Živković, D. Živković and J. Šesták, *J. Thermal Anal.*, 43 (1995) 417.
- 38 D. Minic, D. Živković and Z. Živković, *Arch. Hutnictwa*, 46 (2001) 13.
- 39 Z. Živković, D. Živković and J. Šesták, *Min. Met. Quart.*, 42 (1995) 237.