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Comparative thermodynamic study of Ga–In–Sb system

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Abstract The results of comparative thermodynamic analysis of Ga–In–Sb system are presented in this paper. Investigations, carried out in the section from Ga corner with molar ratio of In:Sb equal to 1:1, were done experimentally, using Oelsen calorimetry at the temperature 873 K and analytically, applying different calculation methods—Toop and Muggianu, in the temperature interval from 873 to 1673 K. Excess molar Gibbs energies and activity of all components in specified temperature interval were calculated.

Keywords Ternary system Ga–In–Sb · Thermodynamic calculation · Oelsen calorimetry · Lead-free solders

Introduction

Materials based on ternary system Ga–In–Sb, and the constituent systems included in its composition, are widely used in electronic industry in the form of thin films in the production of various electronic devices. They also find application in the manufacture of semiconductor devices. Alloy $Ga_{1-x}In_xSb$ with $x \approx 0.2$ is used for microwave oscillators based on Gunn-effect [1]. This system belongs to the family of III–IV semiconductors of In–Ga–Al–Sb–As, with a wide range of applications, and for that reason Ga–In–Sb system was studied by many researchers, both experimental and theoretical way.

In examining and determining the phase diagram of Ga–In–Sb system had worked Blom and Plaskett [2], Antypas [3], Miki et al. [4], Gorshkov and Goryunova [5], Ufimtsev et al. [6], Woolley and Lees [7] and Joullié et al. [8], using thermal analysis method. Ansara et al. [9] determined the enthalpy of mixing in liquid state using calorimetry, while Vecher et al. [10] for the same purpose used a quantitative DTA, however, these two sets of results show significant discrepancies. Partial Gibbs energy of liquid gallium, using the EMF method, was measured by Aselage and Anderson [11] and Chang et al. [12]. Rugg et al. [13] and Mechkovskii et al. [14] have measured enthalpy of mixing for pseudo binary solid solution (Ga, In) Sb.

In the alloy system Ga–In–Sb activity of gallium in liquid state for $T = 1050$–1150 K, in the entire area of concentration, was determined by the Katayama et al. [15], using the EMF method with ZrO_2 as a solid electrolyte. Jianrong and Watson [16] have optimized phase diagram and thermodynamic properties of ternary system Ga–In–Sb, where they found the existence of the region with balance of three phases in the corner of antimony at temperatures from 768 to 860 K. Thermodynamic analysis of this system also was performed by Yu and Brebrick [17] using a Margules-type model for the liquid phase, and results showed that excess mixing entropy and enthalpy of mixing are quadratic function of temperature, while thermodynamic predicting of ternary system Ga–In–Sb using general solution model was presented in [18], following the procedure done in [19, 20].

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Experimental

The Oelsen's calorimetry method, described in Refs. [21–23], was used for the experimental thermodynamic analysis of a section in the ternary Ga–In–Sb system with a constant molar ratio of In:Sb = 1:1. According to the requirements of the utilized method, the total volume of all samples was constant—0.5 cm^3, while their compositions and masses are given in Table 1.

Used metals were of the analytical grade. The water equivalent for the calorimeter was determined by a standard method using dissolved Na_2CO_3 and its value was 4465 J/K. All experiments were carried out in air atmosphere. The samples were cooled in the furnace to the room temperature. Schematic representation of the used Oelsen calorimeter is given in Fig. 1. The calorimeter is composed of a Dewar flack with water, a stirrer and a thermometer. It also contains housing from copper sheet into which the iron holder with the sample is added, after it being heated in a separate oven to the initial temperature. The temperature of the sample is followed with NiCr–Ni thermocouple during cooling and simultaneously the temperature of the water is measured. The pair of values of a temperature measurement in the sample and in the water leads to a point on heat content curve.

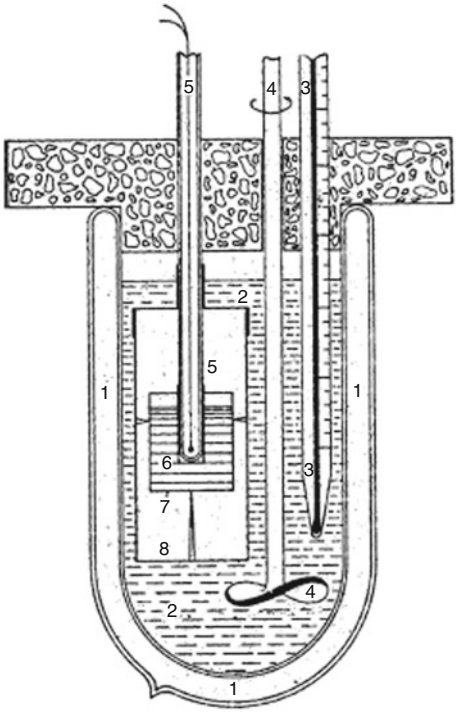

Fig. 1 Oesen calorimeter: *1* Dewar flask, *2* water, *3* Beckman thermometer, *4* stirrer, *5* NiCr–Ni thermocouple, *6* sample, *7* sample holder, *8* copper sheet, *9* thermal insulation

Theoretical fundamentals

There are many methods for calculating thermodynamic properties of ternary systems based on information about binary systems included in their composition [24–27]. For calculating thermodynamic properties of Ga–In–Sb system in this work two thermodynamic models were used: Toop [26] as asymmetric and Muggianu et al. [27] as symmetric model. The basic theoretical interpretations of mentioned models are given as follows:

(a) Toop model

$$\Delta G^{\mathrm{E}} = \frac{x_2}{1-x_1}\Delta G^{\mathrm{E}}_{12}(x_1;1-x_1) + \frac{x_3}{1-x_1}\Delta G^{\mathrm{E}}_{13}(x_1;1-x_1) + (x_2+x_3)\Delta G^{\mathrm{E}}_{23}\left(\frac{x_2}{x_2+x_3};\frac{x_3}{x_2+x_3}\right) \quad (1)$$

Table 1 Composition and masses of the investigated samples

Alloy	x_{Ga}	x_{In}	x_{Sb}	m_{Ga}/g	m_{In}/g	m_{Sb}/g
A1	0	0.5	0.5	0	1.69	1.793
A2	0.2	0.4	0.4	0.4372	1.4399	1.5277
A3	0.4	0.3	0.3	0.9353	1.1551	1.2255
A4	0.6	0.2	0.2	1.5079	0.8276	0.8781
A5	0.8	0.1	0.1	2.173	0.4472	0.4745

(b) Muggianu model

$$\Delta G^{\mathrm{E}} = \frac{4x_1x_2}{(1+x_1-x_2)(1+x_2-x_1)} \times \Delta G^{\mathrm{E}}_{12}\left(\frac{1+x_1-x_2}{2};\frac{1+x_2-x_1}{2}\right) + \frac{4x_2x_3}{(1+x_2-x_3)(1+x_3-x_2)} \times \Delta G^{\mathrm{E}}_{23}\left(\frac{1+x_2-x_3}{2};\frac{1+x_3-x_2}{2}\right) + \frac{4x_3x_1}{(1+x_3-x_1)(1+x_1-x_3)} \times \Delta G^{\mathrm{E}}_{31}\left(\frac{1+x_3-x_1}{2};\frac{1+x_1-x_3}{2}\right) \quad (2)$$

In all given equations, ΔG^{E} and $\Delta G^{\mathrm{E}}_{ij}$ correspond to the integral molar excess Gibbs energies for ternary and binary systems, respectively, while x_1, x_2, x_3 correspond to the mole fraction of components in investigated ternary system.

Basic thermodynamic data on the constituent binary subsystems Ga–In, In–Sb and Sb–Ga, needed for calculation of thermodynamic properties in the investigated Ga–In–Sb system, were taken in the form of Redlich–Kister parameters from Refs. [28, 29].

Results and discussion

Oelsen calorimetry

The calorimetric measurements and thermodynamic calculations were carried out in the Ga–InSb section of the ternary Ga–In–Sb system. Based on the cooling curves obtained by calorimetric measurements, according to the Oelsen procedure [21–23], temperature changes of the calorimeter were determined for all samples in the temperature range up to 873 K. According to this data, the enthalpy space diagram and enthalpy isotherm diagram were constructed and presented in Figs. 2 and 3, respectively. (It should be noted that in presented diagrams 1 K corresponds to the value of water equivalent.)

The basic equation in Oelsen thermodynamic analysis [21] is given as:

$$\frac{G_i^{\mathrm{M}}}{T} = \int_{1/T_0}^{1/T} H_{x,T}\,\mathrm{d}\left(\frac{1}{T}\right) = R\,\ln a_i \qquad (3)$$

where G_i^{M} is the partial molar Gibbs energy for component i, T_0 the starting temperature, T the final temperature, $H_{x,T}$ the enthalpy value measured in the Oelsen calorimeter for the temperature change from T_0 to T, R the gas constant and a_i is the activity of the component i. Further calculation in the thermodynamic analysis was done based on Eq. 3 and the results of the graphic planimetry [22], which enabled the determination of antimony activities, activity coefficients and partial molar quantities at 873 K. The results are given in Table 2.

Thermodynamic calculation

For the purpose of further calculation, basic thermodynamic information on the liquid phase of constitutive subsystems in the Ga–In–Sb system was taken from Refs.

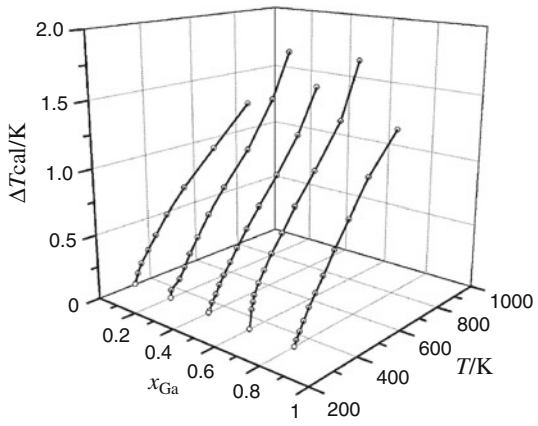

Fig. 2 Enthalpy space diagram

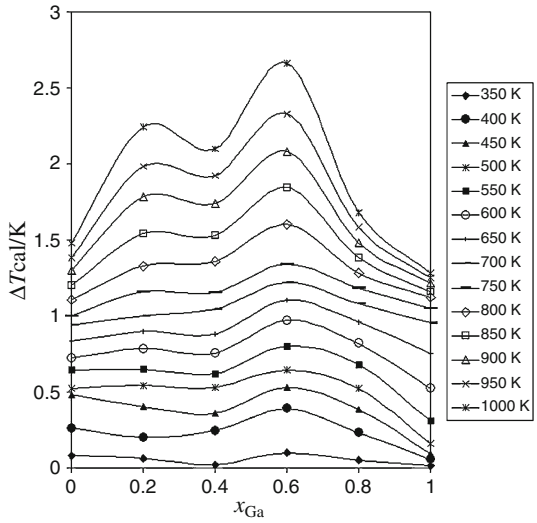

Fig. 3 The enthalpy isotherm diagram for the temperature interval 350–1000 K

Table 2 The results of the Oelsen quantitative thermodynamic analysis at temperature of 873 K/energies in J/mol

T/K	873 K			
x_{Ga}	a_{Ga}	γ_{Ga}	$G_{\mathrm{Ga}}^{\mathrm{M}}$	$G_{\mathrm{Ga}}^{\mathrm{E}}$
0	0	–	–	–
0.2	0.248	1.240	−10120.19	1561.30
0.4	0.417	1.042	−6353.68	296.87
0.6	0.607	1.012	−3623.45	84.19
0.8	0.806	1.008	−1565.37	54.23

[28, 29], and presented in the form of Redlich–Kister parameters in Table 3.

Ternary Ga–In–Sb system has been investigated in the section from Ga corner with molar ratio of In:Sb equal to 1:1

Partial thermodynamic quantities of gallium, indium and antimony are calculated according to the equations:

$$G_i^{\mathrm{E}} = G^{\mathrm{E}} + (1 - x_i)\left(\partial G^{\mathrm{E}}/\partial x_i\right) = RT\ln\gamma_i \qquad (4)$$

and

$$a_i = x_i\gamma_i \qquad (5)$$

All thermodynamic properties calculated in this work are related to the liquid phase.

Values of ΔG^{E} and activity, obtained by chosen thermodynamic models, are presented in Figs. 4 and 5.

Comparison of the results

The comparison of the results of Oelsen thermodynamic analysis, and thermodynamic calculation according Muggianu and Toop model at temperature of 873 K with results

Table 3 Redlich–Kister parameters for constitutive binary systems

System *ij*	L_{ij}^{0}/T	L_{ij}^{1}/T	L_{ij}^{2}/T
Ga–In [28]	$4450 + 1.19185T$	$0.0 + 0.25943T$	0
In–Sb [29]	$-25631.2 + 102.9324T - 13.45816T \ln T$	$-2115.4 - 1.31907T$	2908.9
Ga–Sb [29]	$-13953.8 + 71.07866T - 9.9232T \ln T$	$1722.9 - 1.92588T$	2128.3

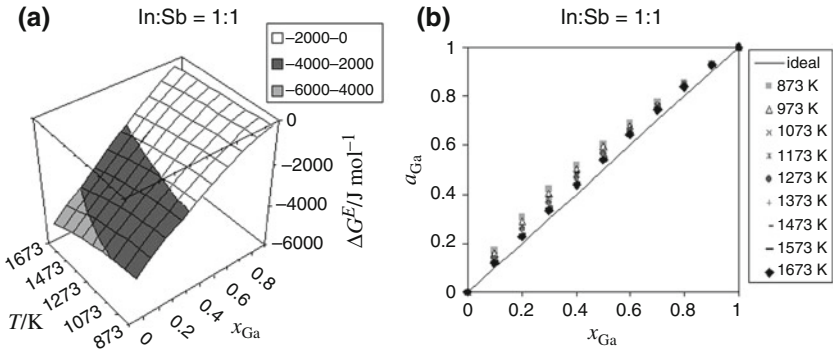

Fig. 4 The results of thermodynamic calculation according to Muggianu model in temperature range 873–1673 K for cross-section Ga–InSb

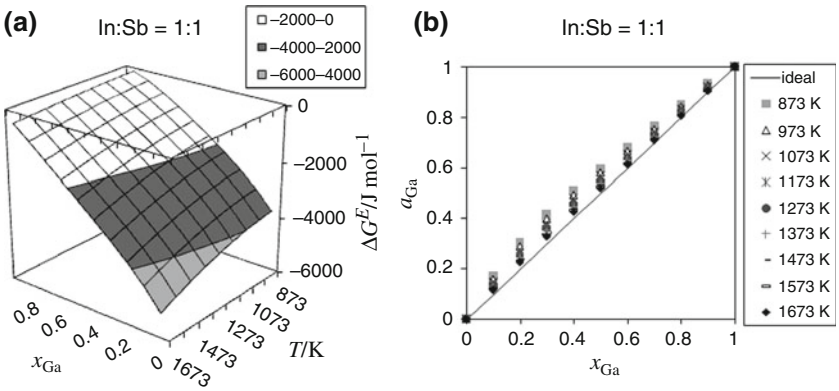

Fig. 5 The results of thermodynamic calculation according to Toop model in temperature range 873–1673 K for cross-section Ga–InSb

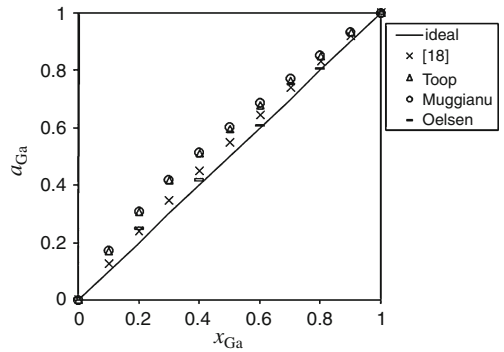

Fig. 6 Dependence of a_{Ga} from composition at 873 K, determined experimentally using Oelsen method and predicted according to Toop, Muggianu and general solution model [18]

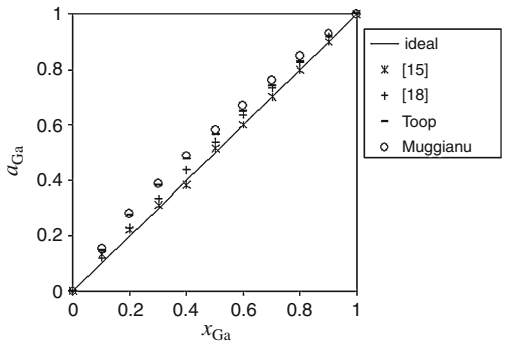

Fig. 7 Dependence of a_{Ga} from composition at 1073 K, predicted according to Toop and Muggianu compared with literature data [15, 18]

of general solution model [18] are given in Fig. 6. Also, comparison of obtained results for gallium activity values at 1073 K calculated by Muggianu model and Toop model with the data available in literature [18] and [15] is presented in Fig. 7.

It can be noticed that the agreement between experimental thermodynamic data of gallium activities, obtained by Oelsen calorimetry, and ones calculated by general solution model [18], shows better accordance comparing to Muggianu or Toop model. It indicates that investigated

system does not strictly belong to asymmetric or symmetric type of systems.

Also, the results of comparison with experimental data [15], shown in the Fig. 7, show good agreement with calculated data values.

Conclusions

Comparative thermodynamic analysis of Ga–InSb system was done experimentally using Oelsen calorimetry and by thermodynamic calculation, using general solution model, Muggianu model and Toop model. Results of the comparative analysis for the thermodynamic parameters showed good agreement between experimentally obtained and ones calculated by general solution model. Finally, the presented thermodynamic data for the Ga–In–Sb alloys could be useful for the further assessment of this system and its phase diagram as well as for completing description of these alloys.

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