

COMPARATIVE THERMODYNAMIC STUDY OF GaSb–Sn SYSTEM

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Abstract

The results of comparative thermodynamic study of GaSb–Sn system are presented in this paper. Calorimetric measurements according to Oelsen's method and EMF measurements with zirconia as solid electrolyte were used for experimental investigation, while Chou's general solution model, Toop, Kohler and Muggianu methods were used for predicting thermodynamic characteristics in this system. Also, phase diagram of this quasibinary system, determined by DTA and optical microscopy, is presented.

Keywords: Ga–Sb–Sn alloys, ternary systems, thermodynamics

Introduction

Many investigations were done in order to give the correct interpretation of the phenomena occurring in alloy systems containing semiconducting compounds. Thermodynamic study of these materials is important from scientific and technological point of view, since ternary and multicomponent systems are not completely experimentally investigated, although some of the binary systems have been studied extensively.

For their important industrial application in the solid-state electronic devices, GaSb-based ternary alloys with Bi, Ge, In, Sn, Te, S, have been the subject of an increasing attention in the semiconductor production [1–6]. Ternary system Ga–Sb–Sn is one of these systems.

There are a lot of literature data concerning the thermodynamics of its constituent binary systems Ga–Sb [7–13], Sb–Sn [14] and Sn–Ga [15–18]. But, there is only one reference on thermodynamics of ternary Ga–Sb–Sn system by Katayama and collaborators [19], in which activities of gallium, in liquid Ga–Sb–Sn alloys along three lines of constant molar ratio of Sb:Sn, were measured by EMF method using zirconia as solid electrolyte.

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Considering the phase equilibrium investigations, Osamura and Murakami [20] suggested the phase diagram of Ga–Sb–Sn ternary system, while Gerdes and Predel [21] researched quasibinary section GaSb–Sn in this system.

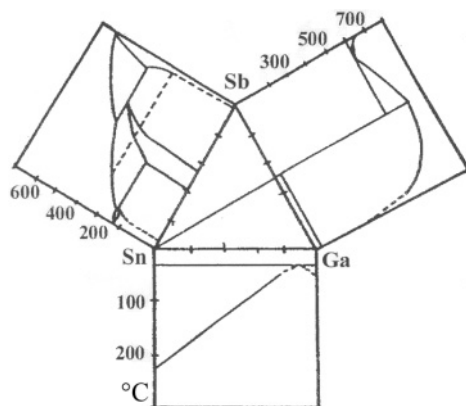


Fig. 1 Ternary system Ga–Sb–Sn with signed quasibinary section GaSb–Sn

In order to contribute to the better knowledge of the Ga–Sb–Sn system thermodynamics, the results of comparative thermodynamic analysis (experimental and thermodynamic predicting) and phase diagram investigations of the quasibinary section GaSb–Sn (shown in Fig. 1) are presented in this paper.

Experimental

Oelsen calorimetry and EMF measurements with zirconia as solid electrolyte has been performed in the experimental part of thermodynamic investigation in this paper, while DTA and optic microscopy were used for phase diagram determination.

All experiments were performed using metals Ga, Sb, Sn of p.a. purity.

Oelsen calorimetry

Measurements were carried out according to procedure described in [5, 22–24], in an air atmosphere. Water equivalent was determined by a standard method using dissolved Na_2CO_3 , and its value was 3870 J K^{-1} . Compositions and masses of the investigated alloys are presented in Table 1. Alloy volume was constant 0.1 cm^3 .

EMF measurements

EMF method with zirconia as solid electrolyte has been used. Experimental equipment and procedure is presented in [19]. EMFs of cell

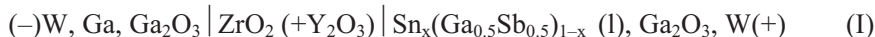


Table 1 Composition and masses of the investigated samples

| Alloy | x_{Sn} | x_{Ga} | x_{Sb} | Mass% Sn | Mass% Ga | Mass% Sb | Mass/g | m_{Sn} | m_{Ga} | m_{Sb} |
|-------|-----------------|-----------------|-----------------|----------|----------|----------|----------|-----------------|-----------------|-----------------|
| L0 | 0 | 0.5 | 0.5 | 0 | 36.41302 | 63.58698 | 0.637744 | 0 | 0.232222 | 0.405522 |
| L1 | 0.1 | 0.45 | 0.45 | 12.10746 | 32.00433 | 55.88822 | 0.647654 | 0.078414 | 0.207277 | 0.361962 |
| L2 | 0.2 | 0.4 | 0.4 | 23.66087 | 27.79738 | 48.54175 | 0.657402 | 0.155547 | 0.182741 | 0.319114 |
| L3 | 0.3 | 0.35 | 0.35 | 34.69741 | 23.77864 | 41.52395 | 0.666992 | 0.231429 | 0.158602 | 0.276961 |
| L4 | 0.4 | 0.3 | 0.3 | 45.25101 | 19.93576 | 34.81323 | 0.676427 | 0.30609 | 0.134851 | 0.235486 |
| L5 | 0.5 | 0.25 | 0.25 | 55.35269 | 16.25743 | 28.38988 | 0.685712 | 0.37956 | 0.111479 | 0.194673 |
| L6 | 0.6 | 0.2 | 0.2 | 65.03087 | 12.73332 | 22.23582 | 0.69485 | 0.451867 | 0.088477 | 0.154506 |
| L7 | 0.7 | 0.15 | 0.15 | 74.31163 | 9.353911 | 16.33446 | 0.703845 | 0.523038 | 0.065837 | 0.114969 |
| L8 | 0.8 | 0.1 | 0.1 | 83.21896 | 6.110483 | 10.67056 | 0.712699 | 0.593101 | 0.043549 | 0.076049 |
| L9 | 0.9 | 0.05 | 0.05 | 91.77496 | 2.994987 | 5.230058 | 0.721416 | 0.66208 | 0.021606 | 0.03773 |
| L10 | 1 | 0 | 0 | 100 | 0 | 0 | 0.73 | 0.73 | 0 | 0 |

were measured. Ga₂O₃ powder was added to the alloy electrode and referent electrode in a mass ratio 1:9. Zirconia solid electrolyte crucibles (0.92ZrO₂+0.08Y₂O₃), dimension 8×5×50 mm, were used. EMFs of cell and the cell temperature were measured with digital voltmeter (Multi Logging Meter AD-5311, A&D) with printer. Temperature was controlled using Pt–13RhPt thermocouple and a thermocontroller. All experiments were carried out under argon atmosphere. Compositions of the investigated alloys were as follows: $x_{\text{Sn}}=0, 0.052, 0.176, 0.335, 0.539, 0.7, 0.8, 0.9$.

Differential thermal analysis

A MOM Derivatograph, Hungary was used in the experimental work. DTA curves have been recorded at heating rate of 10°C min⁻¹ in an air atmosphere, while Al₂O₃ was used as a reference material during measurements. In this case, the following compositions of the investigated alloys were used: $x_{\text{Sn}}=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1$.

Optical microscopy

A Reichert MeF2 microscope was used. Solution of (8 mL H₂SO₄+2 g K₂Cr₂O₇) was used as etching reactant.

Theoretical principles

Different methods of thermodynamic predicting, such as Chou's general solution model [25], Toop [27], Kohler [28] and Muggianu model [29], were used for analytical determination of thermodynamic properties in Ga–Sb–Sn system.

The basic theoretical interpretations of these models are given:

Chou's general solution model [25, 26]

$$G^E = \Delta G_{12}^E \frac{X_1 X_2}{(X_1 + \xi_{12} X_3)(X_2 + (1 - \xi_{12}) X_3)} + \Delta G_{31}^E \frac{X_1 X_3}{(X_3 + \xi_{31} X_2)(X_1 + (1 - \xi_{31}) X_2)} + \Delta G_{23}^E \frac{X_3 X_2}{(X_2 + \xi_{23} X_1)(X_3 + (1 - \xi_{23}) X_1)} \quad (1)$$

where are $X_{1(12)} = x_1 + x_3 \xi_{12}$; $X_{3(31)} = x_3 + x_2 \xi_{31}$; $X_{2(23)} = x_2 + x_1 \xi_{23}$ and ξ_{ij} is the similarity coefficient.

Toop model [27]

$$G^E = \frac{x_2}{1-x_1} \Delta G_{12}^E(x_1; 1-x_1) + \frac{x_3}{1-x_1} \Delta G_{13}^E(x_1; 1-x_1) + (x_2 + x_3)^2 \Delta G_{23}^E \left(\frac{x_2}{x_2 + x_3}; \frac{x_3}{x_2 + x_3} \right) \quad (2)$$

Kohler model [28]

$$\begin{aligned}
 G^E = & (x_1+x_2)^2 \Delta G_{12}^E \left(\frac{x_1}{x_1+x_2}; \frac{x_2}{x_1+x_2} \right) + \\
 & + (x_2+x_3)^2 \Delta G_{23}^E \left(\frac{x_2}{x_2+x_3}; \frac{x_3}{x_2+x_3} \right) + \\
 & + (x_3+x_1)^2 \Delta G_{31}^E \left(\frac{x_3}{x_1+x_3}; \frac{x_1}{x_1+x_3} \right)
 \end{aligned} \quad (3)$$

Muggianu model [29]

$$\begin{aligned}
 G^E = & \frac{4x_1x_2}{(1+x_1-x_2)(1+x_2-x_1)} \Delta G_{12}^E \left(\frac{1+x_1-x_2}{2}; \frac{1+x_2-x_1}{2} \right) + \\
 & + \frac{4x_2x_3}{(1+x_2-x_3)(1+x_3-x_2)} \Delta G_{23}^E \left(\frac{1+x_2-x_3}{2}; \frac{1+x_3-x_2}{2} \right) + \\
 & + \frac{4x_3x_1}{(1+x_3-x_1)(1+x_1-x_3)} \Delta G_{31}^E \left(\frac{1+x_3-x_1}{2}; \frac{1+x_1-x_3}{2} \right)
 \end{aligned} \quad (4)$$

Hillert model [30]

$$G^E = \frac{x_2}{1-x_1} \Delta G_{12}^E(x_1; 1-x_1) + \frac{x_3}{1-x_1} \Delta G_{13}^E(x_1; 1-x_1) + \frac{x_2x_3}{v_{23}v_{32}} \Delta G_{23}^E(v_{23}; v_{32}) \quad (5)$$

where is $v_{ij} = 1/2(1+x_i-x_j)$.

In all given equations, G^E and ΔG_{ij}^E 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.

Results and discussion

Oelsen's calorimetry

Based on the cooling curves obtained by Oelsen's calorimetry, the temperature changes of the calorimeter used were determined for all samples in the investigated temperature interval 300–1100 K. That enabled the determination of the dependence of the calorimeter temperature change on the composition and temperature, and the construction of the enthalpy isotherm diagram for the investigated temperature interval 300–1100 K, presented in Fig. 2.

Following the basic equation in Oelsen's thermodynamic analysis [5, 22–24], in the case of investigated GaSb–Sn system given as

$$-\frac{G_{\text{Sn}}^{\text{M}}}{T} = \int_{1/T_0}^{1/T} H_{x,T} d\left(\frac{1}{T}\right) = -R \ln a_{\text{Sn}} \quad (6)$$

(where G_{Sn}^{M} – is the partial molar Gibbs energy for tin, T_0 – is the starting temperature, T – is the final temperature, $H_{x,T}$ – is the enthalpy value measured in the Oelsen calorimeter for the temperature change from T_0 to T , R – is the gas constant and a_{Sn} – is the activity of tin), further calculations in the thermodynamic analysis was done. Based on Eq. (5) and the results of graphic planimetry, the tangents were constructed for the calculation of $-R \ln a_{\text{Sn}}$ at temperatures 1000, 1050 and 1100 K, which enabled the determination of tin activities, activity coefficients and partial molar quantities. The results are given in Table 2.

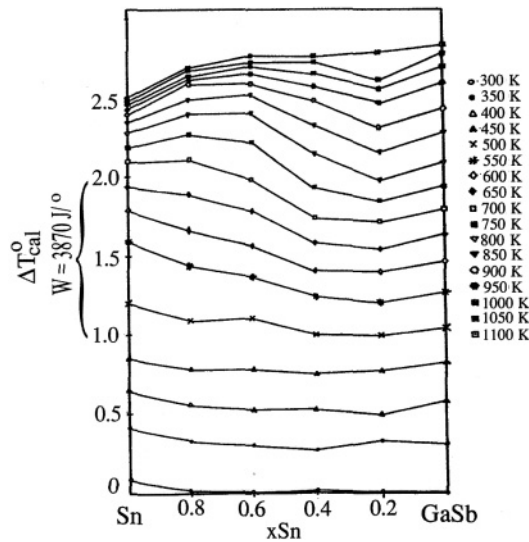


Fig. 2 The enthalpy isotherm diagram for the temperature interval 300–1100 K

Slight positive deviation from the ideal behavior can be noticed for tin activities in the whole composition range for all investigated temperatures, while a slight change of tin activities with temperature is present. Negative values for partial molar Gibbs energies of mixing and positive values for partial molar excess Gibbs energies are typical for all investigated alloys and complete temperature range.

EMF measurements with zirconia as solid electrolyte

After the cell temperature reached the desired value, it was held constant for ca 12 h, and then tungsten lead wire was dipped into the alloy electrode. Thereafter, it took about several tens of minutes to several hours to reach stable *EMF* of the cell. On changing the temperature, equilibration at a new temperature took a very short period of time. The tungsten lead wire could be used to stir the alloy electrode to confirm the equilibrium *EMF*.

Table 2 Results of the Oelsen's quantitative thermodynamic analysis at 1000, 1050 and 1100 K (energies in J mol⁻¹)

| <i>T</i> /K | | 1000 | | | | 1050 | | | | 1100 | | | |
|------------------------|------------------------|----------------------|----------------------------|----------------------------|------------------------|----------------------|----------------------------|----------------------------|------------------------|----------------------|----------------------------|----------------------------|--|
| <i>x</i> _{Sn} | <i>a</i> _{Sn} | γ_{Sn} | G_{Sn}^{M} | G_{Sn}^{E} | <i>a</i> _{Sn} | γ_{Sn} | G_{Sn}^{M} | G_{Sn}^{E} | <i>a</i> _{Sn} | γ_{Sn} | G_{Sn}^{M} | G_{Sn}^{E} | |
| 0.1 | 0.107 | 1.067 | -18581 | 539.17 | 0.105 | 1.048 | -19675 | 409.28 | 0.102 | 1.025 | -20877 | 225.82 | |
| 0.2 | 0.22 | 1.098 | -12588 | 777.28 | 0.212 | 1.059 | -13541 | 500.43 | 0.204 | 1.022 | -14538 | 199.02 | |
| 0.3 | 0.311 | 1.038 | -9710 | 310.08 | 0.308 | 1.025 | -10281 | 215.56 | 0.306 | 1.019 | -10830 | 172.13 | |
| 0.4 | 0.412 | 1.028 | -7372 | 229.59 | 0.413 | 1.033 | -7720 | 283.43 | 0.405 | 1.012 | -8266 | 109.09 | |
| 0.5 | 0.516 | 1.032 | -5501 | 261.88 | 0.513 | 1.026 | -5827 | 224.07 | 0.507 | 1.014 | -6212 | 127.15 | |
| 0.6 | 0.607 | 1.012 | -4151 | 99.174 | 0.618 | 1.03 | -4201 | 258.04 | 0.614 | 1.024 | -4461 | 216.9 | |
| 0.7 | 0.714 | 1.02 | -2801 | 164.64 | 0.71 | 1.014 | -2990 | 121.37 | 0.714 | 1.02 | -3081 | 181.1 | |
| 0.8 | 0.82 | 1.025 | -1650 | 205.29 | 0.805 | 1.007 | -1894 | 60.895 | 0.815 | 1.019 | -1871 | 172.13 | |
| 0.9 | 0.908 | 1.009 | -802.4 | 74.491 | 0.914 | 1.015 | -785 | 129.97 | 0.919 | 1.021 | -772.5 | 190.06 | |

Table 3 Temperature dependence of *EMF* of cell (I) and thermodynamic quantities of gallium obtained at 1000, 1050 and 1100 K in GaSb–Sn system

| x_{Sn} | E/mV | T/K | a_{Ga} | γ_{Ga} | $G_{\text{Ga}}^{\text{E}}/\text{J mol}^{-1}$ |
|-----------------|--|--------------|-----------------|----------------------|--|
| 0 | $-4.86+32.48 \cdot 10^{-3}T/\text{K} \pm 3.83$ | 1000 | 0.382 | 0.762 | -2236 |
| | | 1050 | 0.379 | 0.758 | -2414 |
| | | 1100 | 0.376 | 0.753 | -2599 |
| 0.052 | $7.58+22.69 \cdot 10^{-3}T/\text{K} \pm 3.10$ | 1000 | 0.348 | 0.753 | -2557 |
| | | 1050 | 0.353 | 0.745 | -2575 |
| | | 1100 | 0.357 | 0.753 | -2595 |
| 0.176 | $7.01+24.91 \cdot 10^{-3}T/\text{K} \pm 3.53$ | 1000 | 0.329 | 0.799 | -1870 |
| | | 1050 | 0.333 | 0.808 | -1863 |
| | | 1100 | 0.336 | 0.817 | -1854 |
| 0.335 | $9.81+24.73 \cdot 10^{-3}T/\text{K} \pm 3.19$ | 1000 | 0.300 | 0.902 | -859 |
| | | 1050 | 0.305 | 0.917 | -761 |
| | | 1100 | 0.310 | 0.930 | -660 |
| 0.539 | $-21.24+60.94 \cdot 10^{-3}T/\text{K} \pm 7.61$ | 1000 | 0.251 | 1.086 | 672 |
| | | 1050 | 0.242 | 1.048 | 404 |
| | | 1100 | 0.235 | 1.016 | 138 |
| 0.700 | $1.69+47.85 \cdot 10^{-3}T/\text{K} \pm 3.89$ | 1000 | 0.178 | 1.187 | 1427 |
| | | 1050 | 0.179 | 1.191 | 1523 |
| | | 1100 | 0.179 | 1.193 | 1616 |
| 0.800 | $-25.85+84.70 \cdot 10^{-3}T/\text{K} \pm 3.48$ | 1000 | 0.129 | 1.288 | 2103 |
| | | 1050 | 0.123 | 1.234 | 1833 |
| | | 1100 | 0.119 | 1.187 | 1565 |
| 0.900 | $-24.65+10.29 \cdot 10^{-3}T/\text{K} \pm 11.34$ | 1000 | 0.0655 | 1.311 | 2249 |
| | | 1050 | 0.0629 | 1.258 | 2003 |
| | | 1100 | 0.0606 | 1.212 | 1760 |

The experimental results are shown in Fig. 3. As all the data points distribute around a straight line for each composition, the relations between *EMF* (E mV) and temperature (T/K) are obtained by least-square regression analysis, and are listed in Table 3.

For tin concentrations higher than 0.335, gallium activities show negative deviation from Raoult law, while for lower tin concentrations, slight positive deviation of gallium activities from the ideal behavior is present.

Thermodynamic predicting

Basic thermodynamic data on the constituent binary subsystems Ga–Sb, Sb–Sn and Sn–Ga, needed for predicting of thermodynamic properties in the investigated GaSb–Sn system, are fitted to the Redlich–Kister presentation by Eq. (7):

$$\Delta G_{ij}^{\text{E}} = x_i x_j \sum (x_i - x_j)^{\nu} L_{ij}^{(\nu)}(T) \quad (7)$$

$$L_{ij}^{(\nu)}(T) = a_{ij}^{(\nu)} + b_{ij}^{(\nu)} T$$

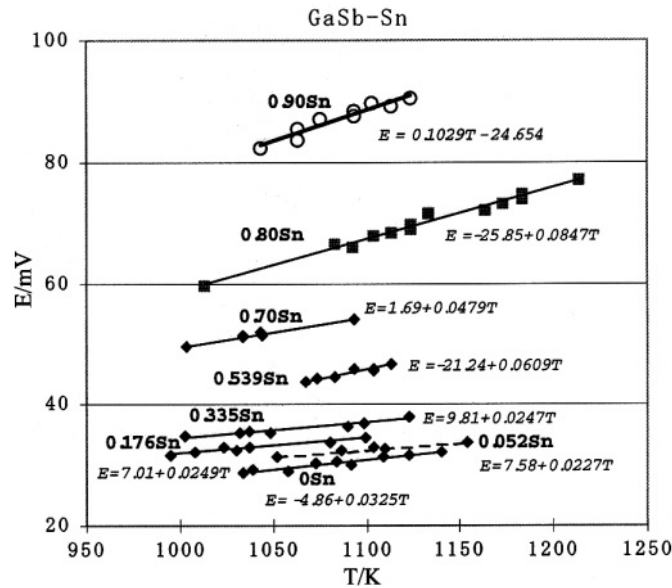


Fig. 3 Temperature dependence of the EMF of cell (I)

According to the experimental data in [7, 14, 15], ΔG_{ij}^E values were calculated in the temperature range of 1000–1200 K at intervals of 50 K. The fitting parameters were obtained and shown in Table 4, as well as similarity coefficients determined as important parameters in general solution model application.

Based on these starting data, calculations were carried out according to different predicting methods for all alloys in the investigated GaSb–Sn system at different temperatures of 1000, 1050 and 1100 K. The results of thermodynamic predictions, according to Chou’s general solution model [25, 26] and models of Toop [27], Kohler [28], Muggianu [29] and Hillert [30], are given in Table 5. Good mutual agreement could be noticed between the results of different applied thermodynamic predicting models.

Table 4 Redlich–Kister parameters for ΔG_{ij}^E and similarity coefficients for Ga–Sb, Sb–Sn and Sn–Ga systems

| System | ν | $a_{ij}^{(\nu)}$ | $b_{ij}^{(\nu)}$ | Temp. range/K | System | T/K | ξ_{ij} |
|--------|-------|------------------|------------------|---------------|--------|------|------------|
| Ga–Sb | 0 | –832.80 | –6.6885 | 1000–1200 | Ga–Sb | 1000 | 0.987 |
| | 1 | 5598.30 | –6.6301 | | | 1050 | 0.980 |
| | 2 | –120.56 | –1.1081 | | | 1100 | 0.972 |
| Sn–Ga | 0 | 16792 | –12.1380 | 1000–1200 | Sn–Ga | 1000 | 0.443 |
| | 1 | –15241 | 13.0650 | | | 1050 | 0.429 |
| | 2 | 5651.50 | –5.2132 | | | 1100 | 0.415 |
| Sb–Sn | 0 | –4855.5 | –1.6688 | 1000–1200 | Sb–Sn | 1000 | 0.016 |
| | 1 | 1092.70 | –1.1787 | | | 1050 | 0.026 |
| | 2 | 1752.80 | –0.7129 | | | 1100 | 0.039 |

Table 5 Integral molar excess Gibbs energies for GaSb–Sn system at 1000, 1050 and 1100 K calculated by different predicting methods (energies in J mol⁻¹)

| Alloy | Chou | Toop | Hillert | Kohler | Muggianu |
|-----------------|--------------------------------|--------|---------|--------|----------|
| 1000 K | | | | | |
| x_{Sn} | $\Delta G^E/\text{J mol}^{-1}$ | | | | |
| 0.1 | -1587 | -1613 | -1367 | -1658 | -1645 |
| 0.2 | -1344 | -1351 | -922 | -1407 | -1388 |
| 0.3 | -1135 | -1089 | -564 | -1137 | -1128 |
| 0.4 | -948 | -835 | -293 | -861 | -872 |
| 0.5 | -774 | -595 | -104 | -602 | -628 |
| 0.6 | -607 | -375 | 12 | -370 | -405 |
| 0.7 | -444 | -184 | 77 | -174 | -212 |
| 0.8 | -285 | -28 | 90 | -19 | -58 |
| 0.9 | -135 | 84 | 94 | 89 | 48 |
| 1050 K | | | | | |
| x_{Sn} | $\Delta G^E/\text{J mol}^{-1}$ | | | | |
| 0.1 | -1704 | -1722 | -1473 | -1741 | -1735 |
| 0.2 | -1474 | -1482 | -1048 | -1499 | -1488 |
| 0.3 | -1264 | -1239 | -707 | -1244 | -1239 |
| 0.4 | -1065 | -997 | -447 | -988 | -996 |
| 0.5 | -872 | -763 | -264 | -743 | -761 |
| 0.6 | -683 | -539 | -144 | -516 | -540 |
| 0.7 | -498 | -334 | -74 | -312 | -340 |
| 0.8 | -318 | -153 | -30 | -137 | -167 |
| 0.9 | -150 | -0.321 | 12 | 7 | -25 |
| 1100 K | | | | | |
| x_{Sn} | $\Delta G^E/\text{J mol}^{-1}$ | | | | |
| 0.1 | -1651 | -1830 | -1579 | -1825 | -1825 |
| 0.2 | -1539 | -1612 | -1174 | -1592 | -1587 |
| 0.3 | -1427 | -1388 | -849 | -1353 | -1352 |
| 0.4 | -1315 | -1159 | -601 | -1116 | -1119 |
| 0.5 | -1204 | -930 | -423 | -884 | -893 |
| 0.6 | -1092 | -704 | -301 | -661 | -675 |
| 0.7 | -980 | -485 | -218 | -451 | -468 |
| 0.8 | -868 | -277 | -151 | -255 | -275 |
| 0.9 | -757 | -85 | -71 | -75 | -99 |

Comparative thermodynamic study

In order to compare the results of the thermodynamic predicting with obtained experimental data at investigated temperatures, partial thermodynamic quantities for tin and gallium were derived according to well known expressions: $G_i^E = G^E + (1-x_i)(\partial G^E / \partial x_i) = RT \ln \gamma_i$ and $a_i = x_i \gamma_i$. The results of calculation, which include tin and gallium activities for the researched alloys, are shown in Table 6.

The graphic presentation of the comparison with experimental data, at temperature of 1000 K, is given in Fig. 4.

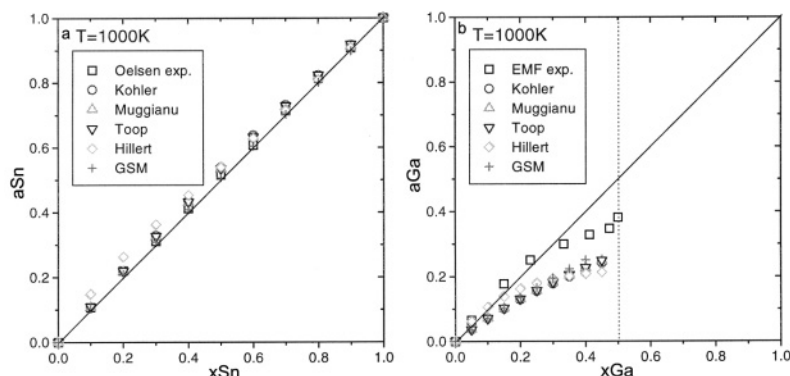


Fig. 4 Comparison between experimental and predicted results for the dependence a_{Sn} ; a – and a_{Ga} ; b – vs. molar content at 1000 K

Good agreement between experimental thermodynamic data on tin activities, obtained by Oelsen calorimetry and thermodynamic predicting, is noticed. Considering the thermodynamic behavior of gallium in the investigated alloys in Ga–Sb–Sn system, slight deviation of experimental data is shown, comparing to predicted thermodynamic values.

Phase diagram determination

The phase diagram of the Ga–Sb–Sn system was investigated based on the cooling curves obtained by the Oelsen's calorimetry, DTA results and the results of microstructure analysis.

DTA results are shown in Fig. 5, while characteristic microphotograph recorded by optical microscopy for the sample L6 (with $x_{Sn}=0.6$) is presented in Fig. 6.

Graphical representation of the obtained phase diagram for GaSb–Sn system, compared with literature data [20, 21], is given in Fig. 7.

The eutectic type of the phase diagram is noticed. The quasibinary hypoeutectic alloys, presented in the widest part of the investigated concentration range in the GaSb–Sn system, solidify with the primary crystallization of the intermetallic compound GaSb and the eutectic reaction /GaSb+Sn/ (dark phase). According to the results of optical microscopy, quantity of the primarily solidified GaSb crystals (light phase) increases by decreasing of tin concentration.

Table 6 The values for tin and gallium activities at investigated temperatures calculated from the predicted results

| Alloy | Chou | Toop | Hillert | Kohler | Muggianu | Chou | Toop | Hillert | Kohler | Muggianu |
|----------|----------|-------|---------|--------|----------|----------|-------|---------|--------|----------|
| 1000 K | | | | | | | | | | |
| x_{Sn} | a_{Sn} | | | | | a_{Ga} | | | | |
| 0.1 | 0.105 | 0.108 | 0.109 | 0.108 | 0.148 | 0.277 | 0.249 | 0.213 | 0.242 | 0.247 |
| 0.2 | 0.209 | 0.218 | 0.219 | 0.217 | 0.264 | 0.251 | 0.227 | 0.209 | 0.221 | 0.225 |
| 0.3 | 0.31 | 0.329 | 0.327 | 0.326 | 0.363 | 0.223 | 0.205 | 0.202 | 0.199 | 0.203 |
| 0.4 | 0.409 | 0.437 | 0.433 | 0.432 | 0.454 | 0.195 | 0.182 | 0.193 | 0.178 | 0.181 |
| 0.5 | 0.507 | 0.539 | 0.535 | 0.534 | 0.541 | 0.165 | 0.157 | 0.180 | 0.155 | 0.157 |
| 0.6 | 0.605 | 0.638 | 0.633 | 0.632 | 0.627 | 0.135 | 0.131 | 0.163 | 0.129 | 0.131 |
| 0.7 | 0.702 | 0.732 | 0.729 | 0.727 | 0.717 | 0.103 | 0.103 | 0.139 | 0.101 | 0.102 |
| 0.8 | 0.801 | 0.824 | 0.824 | 0.82 | 0.81 | 0.071 | 0.071 | 0.107 | 0.071 | 0.071 |
| 0.9 | 0.899 | 0.917 | 0.919 | 0.914 | 0.908 | 0.036 | 0.037 | 0.062 | 0.037 | 0.037 |
| 1050 K | | | | | | | | | | |
| x_{Sn} | a_{Sn} | | | | | a_{Ga} | | | | |
| 0.1 | 0.103 | 0.105 | 0.104 | 0.105 | 0.105 | 0.291 | 0.264 | 0.227 | 0.257 | 0.257 |
| 0.2 | 0.206 | 0.211 | 0.253 | 0.212 | 0.212 | 0.262 | 0.237 | 0.219 | 0.232 | 0.233 |
| 0.3 | 0.307 | 0.316 | 0.349 | 0.319 | 0.317 | 0.231 | 0.211 | 0.209 | 0.208 | 0.209 |
| 0.4 | 0.406 | 0.421 | 0.440 | 0.424 | 0.421 | 0.199 | 0.185 | 0.196 | 0.183 | 0.185 |
| 0.5 | 0.505 | 0.523 | 0.528 | 0.526 | 0.522 | 0.167 | 0.157 | 0.179 | 0.156 | 0.158 |
| 0.6 | 0.604 | 0.622 | 0.617 | 0.625 | 0.621 | 0.135 | 0.129 | 0.159 | 0.129 | 0.131 |
| 0.7 | 0.703 | 0.720 | 0.709 | 0.722 | 0.718 | 0.102 | 0.098 | 0.132 | 0.099 | 0.101 |
| 0.8 | 0.802 | 0.817 | 0.804 | 0.817 | 0.814 | 0.069 | 0.068 | 0.099 | 0.068 | 0.069 |
| 0.9 | 0.902 | 0.914 | 0.904 | 0.913 | 0.910 | 0.035 | 0.035 | 0.057 | 0.035 | 0.036 |

Table 6 Continued

| Alloy | Chou | Toop | Hillert | Kohler | Muggianu | Chou | Toop | Hillert | Kohler | Muggianu |
|-----------------|-----------------|-------|---------|--------|----------|-----------------|-------|---------|--------|----------|
| | 1100 K | | | | | | | | | |
| x_{Sn} | a_{Sn} | | | | | a_{Ga} | | | | |
| 0.1 | 0.102 | 0.101 | 0.134 | 0.103 | 0.103 | 0.287 | 0.278 | 0.240 | 0.272 | 0.272 |
| 0.2 | 0.203 | 0.204 | 0.243 | 0.207 | 0.207 | 0.256 | 0.248 | 0.229 | 0.243 | 0.244 |
| 0.3 | 0.304 | 0.307 | 0.338 | 0.310 | 0.309 | 0.225 | 0.218 | 0.215 | 0.215 | 0.216 |
| 0.4 | 0.404 | 0.409 | 0.429 | 0.413 | 0.411 | 0.193 | 0.188 | 0.198 | 0.187 | 0.188 |
| 0.5 | 0.504 | 0.512 | 0.517 | 0.514 | 0.512 | 0.162 | 0.157 | 0.178 | 0.158 | 0.159 |
| 0.6 | 0.604 | 0.612 | 0.608 | 0.614 | 0.617 | 0.129 | 0.127 | 0.155 | 0.128 | 0.129 |
| 0.7 | 0.704 | 0.712 | 0.701 | 0.713 | 0.710 | 0.098 | 0.096 | 0.126 | 0.098 | 0.098 |
| 0.8 | 0.804 | 0.811 | 0.798 | 0.811 | 0.808 | 0.065 | 0.064 | 0.093 | 0.066 | 0.067 |
| 0.9 | 0.903 | 0.909 | 0.899 | 0.909 | 0.907 | 0.033 | 0.032 | 0.052 | 0.033 | 0.034 |

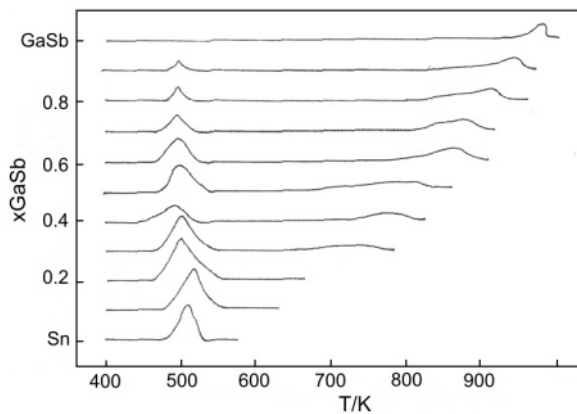


Fig. 5 DTA curves obtained for the investigated Ga–Sb–Sn alloys



Fig. 6 Characteristic microphotograph for sample L6 (magnification $\times 120$) (light phase – primary solidified GaSb crystals; dark phase – binary eutectics (GaSb–Sn))

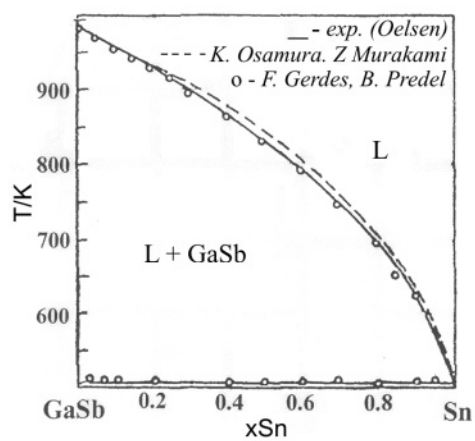


Fig. 7 Phase diagram of the GaSb–Sn system

Good agreement was noticed between results of experimental research, presented in this work, and literature data [20, 21].

Conclusions

The thermodynamic properties of the GaSb–Sn system were experimentally (Oelsen calorimetry, EMF measurements with zirconia as solid electrolyte) and analytically (thermodynamic predicting methods: Chou's general solution model, Toop, Kohler, Muggianu, Hillert) determined. The calculated results show agreement between data obtained by different models, as well as with experimental data. Phase diagram investigation confirmed good agreement between experimental research (DTA, optical microscopy) and literature data for the investigated Bi–GaSb system.

Obtained results could be useful in further interpretation of the phenomena occurring in the ternary Ga–Sb–Sn system and in the compilation of the thermodynamic studies of III–V compounds-related materials at high temperatures.

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