Comparative calculation of thermodynamic properties in Ga-In-Sb system

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In the paper are presented the results of comparative thermodynamic analysis of Ga-In-Sb ternary system. Investigation was carried out applying different calculating methods – Toop and Muggianu in sections from Ga, In and Sb corner, respectively, with following ratios 1:3 and 3:1 in the temperature interval from 873 K to 1673 K. Based on this, excess molar Gibbs energies and activity of all components in specified temperature interval were calculated.

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1. 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 Plaskett and Bloom [2], Antypas [3], Miki et al. [4], and Gorshkov and Goryunova [5], Ufimtsev et al. [6], Woolley and Lees [7] and Joullič et al. [8], using thermal analysis method. Ansari 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 pseudobinary 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 K 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.

Thermodynamic analysis of ternary system Ga-In-Sb, by means of general solution model, was performed by L. Gomidželović et al. [18]. Also, comparative thermodynamic analysis for ternary systems Ga-In-Sb and Sn-In-Sb was done using RKM model [19].

2. Theoretical fundamentals

There are many methods for calculating thermodynamic properties of ternary systems based on information about binary systems included in their composition. For calculating thermodynamic properties of Ga-In-Sb system in this work were used two different models: Toop [20] as asymmetric and Muggianu [21] as symmetric model. The basic theoretical interpretations of mentioned models are given as follows:

a) Toop model

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

b) Muggianu model

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

In all given equations, ΔG^E and ΔG^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 from Refs. [22-24].

3. Results and discussion

For the purpose of further calculation, basic thermodynamic information on the constitutive subsystems in the Ga-In-Sb system was taken from Refs. [22-24], and presented in the form of Redlich-Kister parameters in Table 1.

Table 1. Redlich-Kister parameters for constitutive binary systems.

System *ij*	$L^{o}_{ij}(T)$	$L^{1}_{ij}(T)$	$L^{2}_{ij}(T)$
Ga-In [22]	4450+1.19185*T*	0.0+0.25943*T*	0
In-Sb [23]	-25631.2+102.9324*T*-13.45816*T*ln*T*	-2115.4-1.31907*T*	2908.9
Ga-Sb [24]	-13953.8+71.07866*T*-9.9232*T*ln*T*	1722.9-1.92588*T*	2128.3

Ternary Ga-In-Sb system has been investigated in 6 sections (Fig. 1). Sections were taken from Ga, In and Sb corner, respectively, with ratios 1:3 and 3:1, and with molar content of 0-0.9 for the third component.

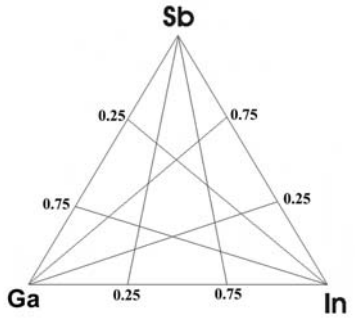

Fig. 1. Schematic diagram of the investigated concentration regions in ternary system Ga-In-Sb.

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

$$G_i^E = G^E + (1-x_i)(\partial G^E/\partial x_i) = RT\ln\gamma_i \quad (3)$$

and

$$a_i = x_i\gamma_i \quad (4).$$

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

Muggianu model

Values of ΔG^E and activity, obtained by Muggianu model, are presented in Figs. 2-4.

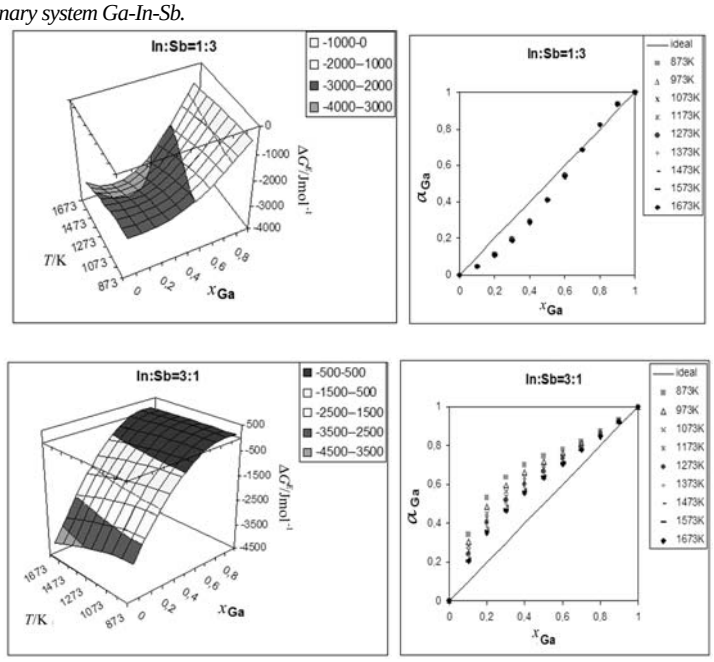

Fig. 2. Results of thermodynamic calculation according to Muggianu model in temperature range 873-1673K for investigated investigated cross-sections from gallium corner.

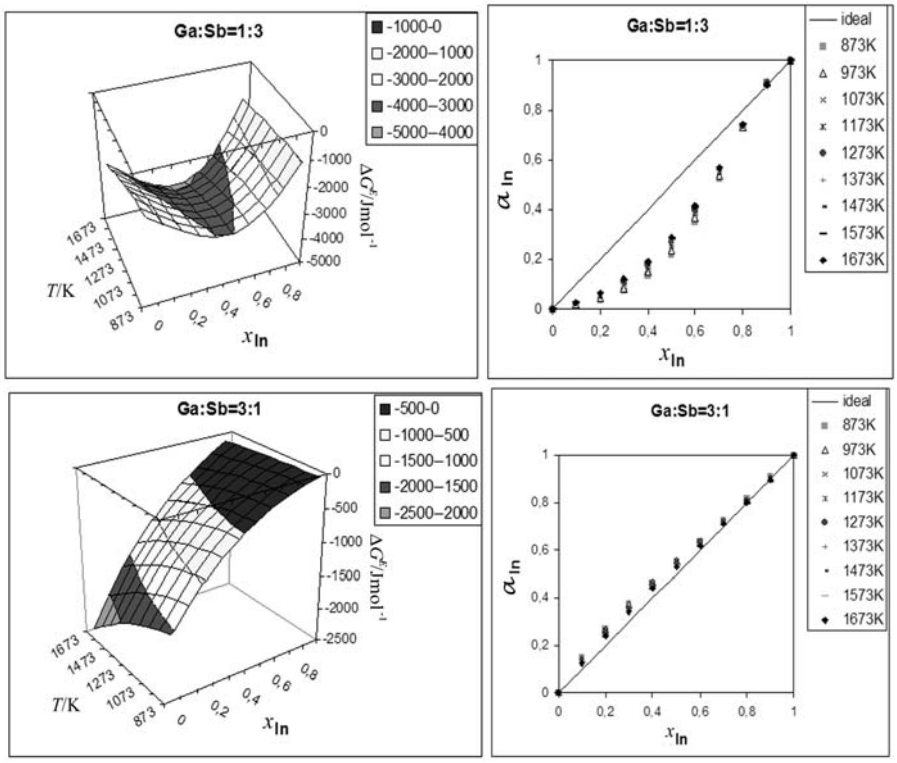

Fig. 3. Results of thermodynamic calculation according to Muggianu model in temperature range 873-1673K for investigated cross-sections from indium corner.

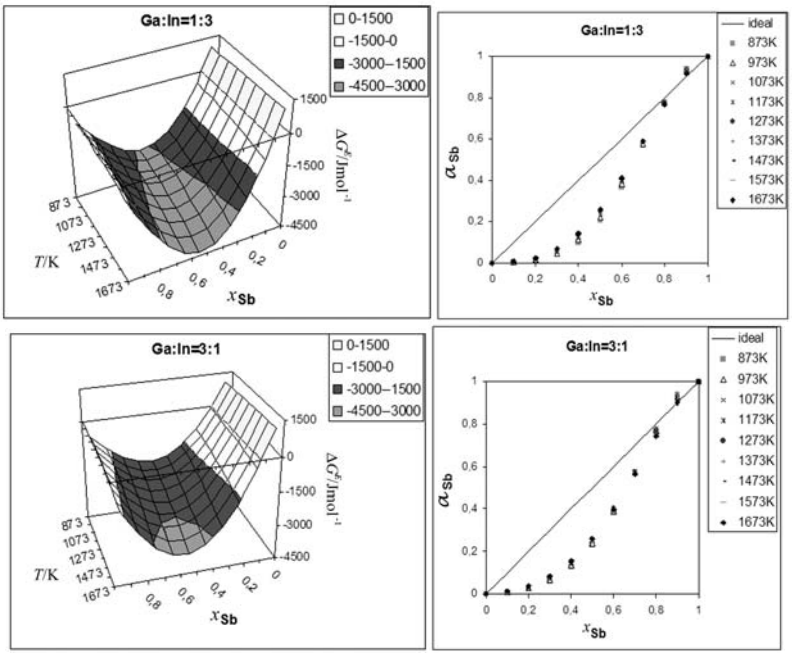

Fig. 4. Results of thermodynamic calculation according to Muggianu model in temperature range 873-1673K for investigated cross-sections from antimony corner.

Calculation of thermodynamic properties for ternary system Ga-In-Sb was performed using the Muggianu model. Values for excess integral Gibbs energy of investigated sections from the corner of gallium and indium are negative, with minimum values to -5 kJ/mol, while for the investigated section from the corner of

antimony Gibbs energy is within 1.5 kJ/mol to -4.5 kJ / mol.

Also, it was noticed that the value of indium activities show negative deviation from Rault's law for section Ga:Sb = 1:3, and for the section Ga:Sb = 3:1 activity of indium has slightly positive deviation from ideal conditions.

Gallium activity shows a positive deviation from the Rault's law for section In:Sb=3:1, but for the section In:Sb = 1:3 activity of gallium slightly negatively deviates from Rault's law up to $x_{Ga} = 0.8$.

With $x_{Sb} > 0.8$, the activity of antimony shows a positive deviation from Rault's law, which indicates that the high content of antimony in the alloy reduces the miscibility of alloy components.

Toop model

Values of ΔG^E and activity, obtained by Toop model, are presented in Figs. 5-7.

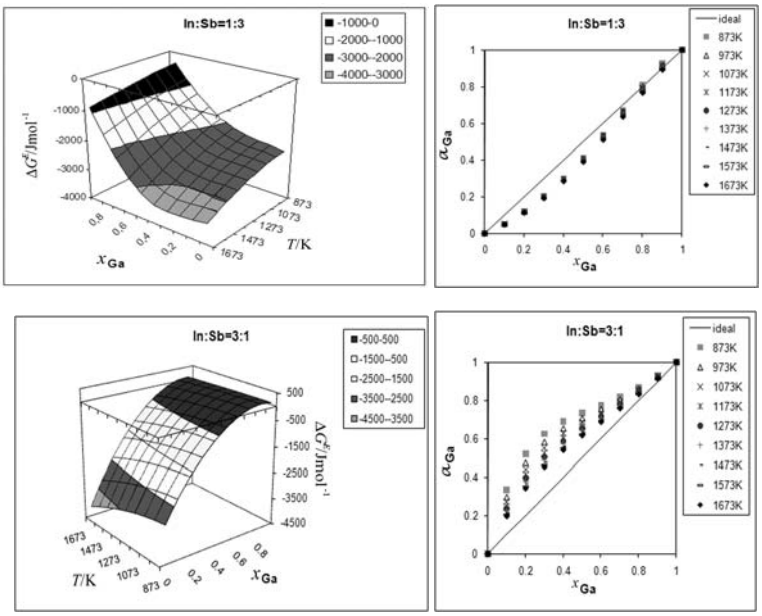

Fig. 5. Results of thermodynamic calculation according to Toop model in temperature range 873-1673K for investigated cross-sections from gallium corner.

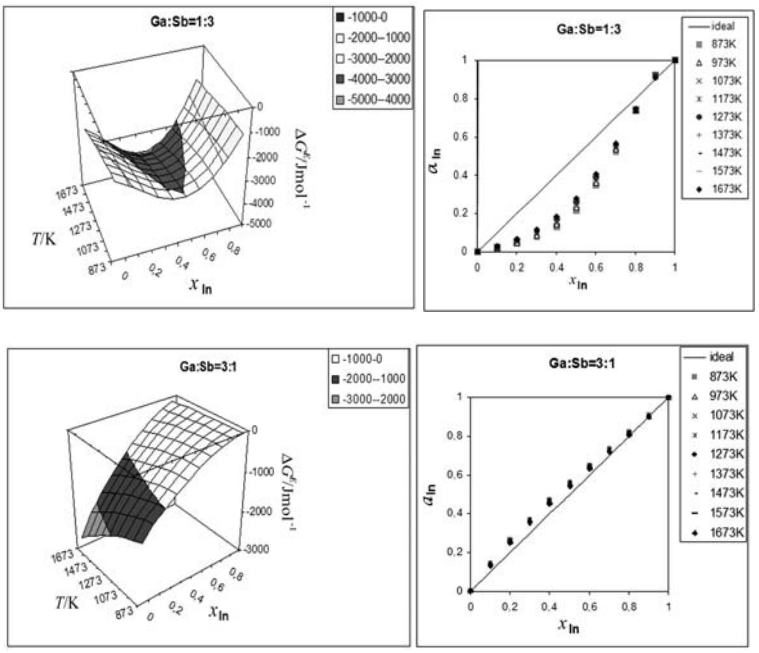

Fig. 6. Results of thermodynamic calculation according to Toop model in temperature range 873-1673K for investigated cross-sections from indium corner.

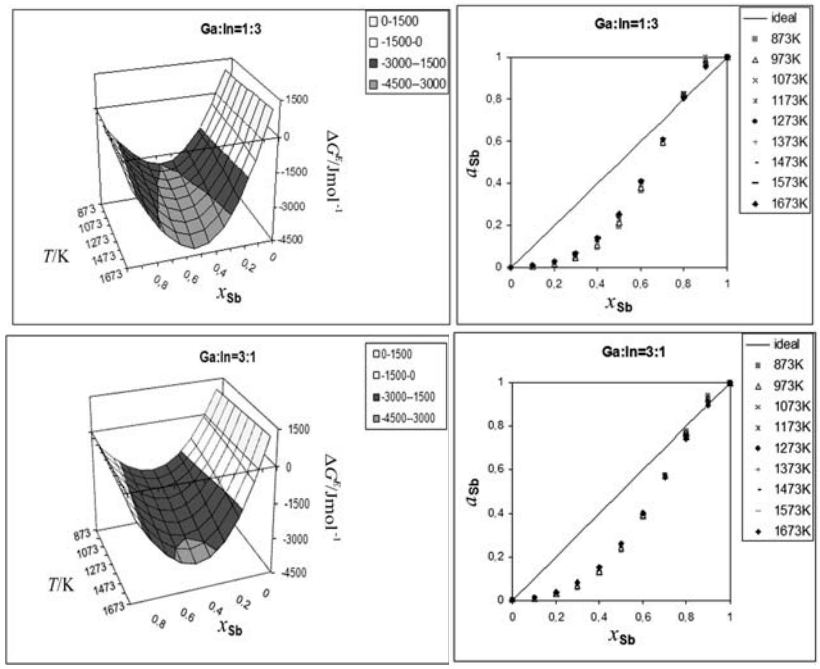

Fig. 7. Results of thermodynamic calculation according to Toop model in temperature range 873-1673K for investigated cross-sections from antimony corner.

Calculation of thermodynamic properties for ternary system Ga-In-Sb was performed using the Toop model. Values for excess integral Gibbs energy of the investigated sections from the corner of gallium and indium are negative, with minimum values of -5 kJ/mol, while for the investigated section from the corner of antimony Gibbs energy is within 1.5 kJ/mol to -4.5kJ / mol.

Also, it was noticed that the value of indium activities show negative deviation from Rault's law for section Ga:Sb=1:3, and for the section Ga: Sb = 3:1 activity of indium has slightly positive deviation from ideal conditions.

Gallium activity shows a positive deviation from the Rault's law for section In:Sb=3:1, but for the section In:Sb = 1:3 activity of gallium slightly negatively deviates from Rault's law up to $x_{Ga} = 0.8$.

With $x_{Sb} > 0.8$, the activity of antimony shows a positive deviation from Rault's law which indicates that the high content of antimony in the alloy reduces the miscibility of alloy components.

Comparison of the results

The 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, 19] is presented in Fig. 8.

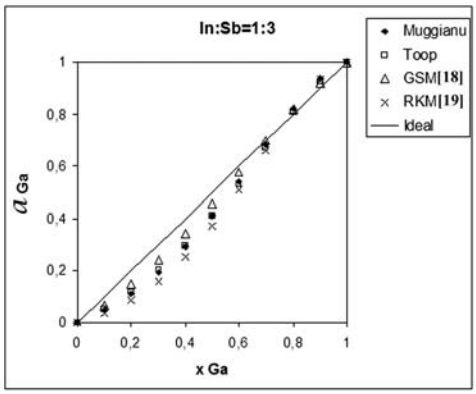

Fig. 8. Dependence of a_{Ga} from composition at 873K, predicted according to Toop and Muggianu models compared with literature data [18, 19].

4. Conclusion

Comparative thermodynamic analysis of Ga-InSb system was done using Muggianu and Toop model in the temperature interval from 873 K to 1673 K. Based on this, excess molar Gibbs energies and activity of all components were calculated. Results obtained in this work contribute to more complete knowledge of thermodynamic properties of Ga-In-Sb alloys.

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References

[1] A. Joullie, R. Aulombard, G. Bougnot, J. Cryst. Growth, **24/25**, 276 (1974).
[2] G. B. Blom, T. S. Plaskett, J. Electrochem. Soc., **118**(2), 1831 (1971).
[3] G. Antypas, J. Cryst. Growth, **16**, 181 (1972).
[4] H. Miki, K. Segawa, M. Otsubo, K. Shirahata, K. Fujibayashi, Japanese J. Appl. Phys., **17**(12), 2079 (1978).
[5] I. Y. Gorshkov, N. A. Goryunova, Zh. Neorg. Khim., **3**, 668 (1958).
[6] V. B. Ufimtsev, A. S. Timoshin, G. V. Kostin, Neorg. Met., **7**, 2029 (1971).
[7] J. C. Woolley, D. G. Lees, J. Less-Common Metals, **1**, 192 (1959).
[8] A. Joullič, R. Dedies, J. Chevrier, G. Bougnot, Revue de Physique Appliquěe, **9**, 455 (1974).
[9] I. Ansara, M. Gambino, J-P. Bros, J. Cryst. Growth, **32**, 101 (1976).
[10] A. A. Vecher, E. I. Voronova, L. A. Mechkovskii, A. S. Skoropanov, Zh. Neorg. Khim., **48**(4), 584 (1974).
[11] T. L. Aselage, T. J. Anderson, High Temp. Sci., **20**, 207 (1985).
[12] K. M. Chang, C. A. Coughanowr, T. J. Anderson, Chem. Eng. Commun., **38**, 275 (1985).
[13] B. C. Rugg, A. W. Bryant, N. J. Silk, B. B. Argent, Calphad, **19**(3), 389 (1995).
[14] L. A. Mechkovskii, A. A. Savitskii, V. F. Skums, A. A. Vecher, Zh. Neorg. Khim., **45**(8), 2016 (1971).
[15] I. Katayama, J-I. Nakayama, T. Ikura, T. Tanaka, Z. Kozuka, T. Iida, J. Non-Cryst. Solids **156-158**, 393 (1993).
[16] Y. Jianrong, A. Watson, Calphad, **18**(2), 165 (1994).
[17] T-C. Yu, R. B. Brebrick, Met. Mater. Trans. A, **25A**, 2331 (1994).
[18] L. Gomidželović, D. Živković, I. Mihajlović, Hem. Ind. **62**(3), 153 (2008) (in Serbian).
[19] L. Gomidželović, D. Živković, D. Manasijević, D. Minić, J. Univ. Chem. Technol. Metall., **45**(3), 221 (2010).
[20] G. W. Toop, Trans. Met. Soc. AIME, **233**, 850 (1965).
[21] Y. M. Muggianu, M. Gambino, J. P. Bross, J. Chimie Physique, **72**, 83 (1975).
[22] T. J. Anderson, I. Ansara, J. Phase Equilib. **12**(1), 64 (1991).
[23] A. T. Dinsdale, A. Kroupa, J. Vizdal, J. Vrestal, A. Watson, A. Zemanova, COST 531 Database for Lead-free Solders, Ver. 2.0, 2006, Unpublished Research.
[24] I. Ansara, C. Chatillon, H. L. Lukas, T. Nishizawa, H. Ohtani, K. Ishida, M. Hillert, B. Sundman, B. B. Argent, A. Watson, T. G. Chart, T. Anderson, Calphad **18**(2), 177 (1994).

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