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COMPARATIVE THERMODYNAMIC ANALYSIS OF THE Bi–$Ga_{0.1}Sb_{0.9}$ SECTION IN THE Bi–Ga–Sb SYSTEM

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Abstract

Results of the comparative thermodynamic analysis of the Bi–$Ga_{0.1}Sb_{0.9}$ section in the Bi–Ga–Sb system are given in this paper. Experimental calorimetric investigations were done according to Oelsen's method, while for the thermodynamic prediction Chou's general solution model was applied. Activities, activity coefficients, partial molar quantities for bismuth and integral molar quantities were obtained at a temperature of 1073 K. Based on obtained cooling curves, DTA and SEM results for the investigated samples, phase diagram of the investigated section is constructed and presented in this paper, too.

Keywords: alloy thermodynamics, Ga–Sb–Bi alloys, semiconducting materials, ternary systems, thermodynamic predicting models

Introduction

Many studies have been carried out on alloy systems containing semiconducting compounds, which are significant from both the scientific and practical point of view. One of them is Bi–Ga–Sb ternary system, which has an important industrial application in the solid state electronic devices [1].

Although there are a lot of references in the literature concerning the thermodynamic calculation of the constituent binary alloys: Ga–Sb [7–13], Bi–Sb [14–17] and Ga–Bi systems [1, 18–21], there are only a few thermodynamic data for the Bi–Ga–Sb system investigated here [1, 22]. One of them is reference on the Ga–Sb–Bi thermodynamics in the work of Katayama and collaborators [1], who performed the emf measurement of the electrochemical cell with zirconia as solid electrolyte to obtain the gallium activities at 1073 K. Also, the comparative approach to the thermodynamic predicting of gallium quantities in five sections of this system at a temperature of 1073 K, is recently presented in the work of ivković *et al*. [22].

Concerning that the thermodynamic data are not completed yet for the whole Bi–Ga–Sb system, results of the comparative thermodynamic investigations done in

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the Bi–$Ga_{0.1}Sb_{0.9}$ section are presented in this paper, in order to enable further interpretation of the phenomena occurring in this system.

Experimental

Oelsen's calorimetry was used for the experimental thermodynamic analysis of the investigated system. Descriptions of this experimental technique can be found in the Refs [23–25]. The water equivalent was determined by a standard method using dissolved Na_2CO_3, and for the calorimeter used it has a value of 3453 J K^{-1}.

The calorimetric measurements and thermodynamic calculations in the Bi–Ga–Sb system were carried out along the line of a constant mole ratio Ga:Sb=1:9, as is indicated in Fig. 1. The composition and masses of ten samples investigated are given in Table 1.

Table 1 Compositions of the investigated sample (masses in g)

Alloy	x_{Bi}	x_{Ga}	x_{Sb}	m_{Bi}	m_{Ga}	m_{Sb}	m_{tot}
A1	0	0.1	0.9	0	0.3965	6.2318	6.6283
A2	0.1	0.09	0.81	1.1638	0.3494	5.4918	7.0050
A3	0.2	0.08	0.72	2.2800	0.3043	5.0782	7.6625
A4	0.3	0.07	0.63	3.3517	0.2609	4.1005	7.7131
A5	0.4	0.06	0.54	4.3813	0.2193	3.4458	8.0464
A6	0.5	0.05	0.45	5.3712	0.1792	2.8162	8.3666
A7	0.6	0.04	0.36	6.3239	0.1407	2.2105	8.6751
A8	0.7	0.03	0.27	7.2412	0.1035	1.6271	8.9718
A9	0.8	0.02	0.18	8.1252	0.0678	1.0650	9.2580
A10	0.9	0.01	0.09	8.9775	0.0333	0.5230	9.5338

DTA-TG-DTG analyses were done on a Derivatograph 1500, MOM Budapest, while SEM analyses were performed on the electronic microscope Philips XL-300 with EDX.

The metals used were of analytical grade. All experiments were carried out in an air atmosphere.

Results and discussion

Oelsen's calorimetry

The temperature changes of the calorimeter used based on the cooling curves obtained by Oelsen's calorimetry, were determined for all samples in the investigated temperature interval 400–1100 K, which 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 400–1100 K, presented in Fig. 2.

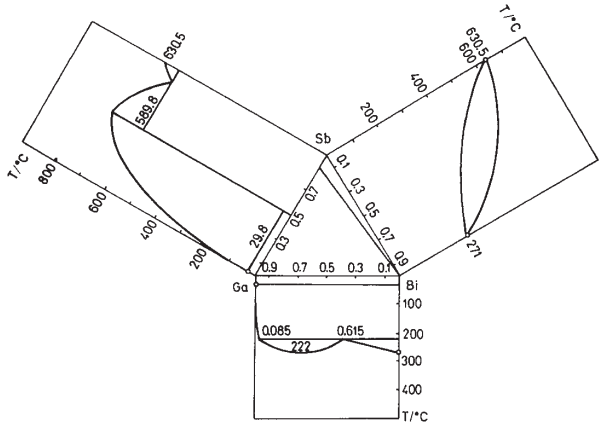

Fig. 1 Ternary system Bi–Ga–Sb with the indicated section $Bi–Ga_{0.1}Sb_{0.9}$

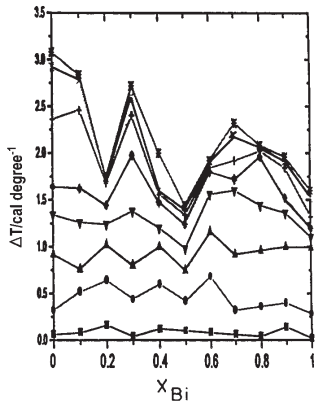

Fig. 2 Enthalpy isotherm diagram for the temperature interval 400–1100 K. ■ – 400 K, ● – 500 K, ▲ – 600 K, ▼ – 700 K, ◆ – 800 K, | – 900 K, x – 1000 K, ∗ – 1100 K

Following the basic equation in Oelsen's thermodynamic analysis [23–25] given as

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

where G_i^M – is the partial molar Gibbs energy for component i, 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_i – is the activity of the component i, further calculations in the thermodynamic analysis was done. Based on Eq. (1) and results of the graphic planimetry, the tangent was constructed for the calculation of $-R\ln a_{Bi}$ at 1073 K, which enabled the determination of bismuth activities, activity coefficients and partial molar quantities. The results are given in Table 2.

Table 2 Results of the Oelsen's quantitative thermodynamic analysis at 1073 K (energies in J mol^{-1})

Alloy	a_{Bi}	γ_{Bi}	G^{M}_{Bi}	G^{E}_{Bi}
A1	0	–	–	–
A2	0.165	1.650	–16074	4467
A3	0.260	1.300	–12017	2341
A4	0.364	1.213	–9016	1725
A5	0.486	1.215	–6437	1737
A6	0.575	1.150	–4937	1247
A7	0.596	0.993	–4647	–59
A8	0.649	0.927	–3857	–675
A9	0.786	0.983	–2148	–157
A10	0.866	0.962	–1283	–344

Positive deviation from Raoult's law can be noticed in the composition range up to $x_{Bi}\approx 0.6$, while for further increasing of the bismuth molar constant – negative deviation from the ideal behaviour is noticed.

General solution model

For Oelsen's calorimetry results are related only to bismuth, thermodynamic predicting according to Chou's general solution model [26] was applied in order to obtain the integral thermodynamic quantities in the investigated section of the ternary system Bi–Ga–Sb. This model breaks down the boundary between symmetrical and asymmetrical models, and has already been proved in some practical examples [26–28] as the correct and accurate model.

The basic equations of this model are given as follows:

$$G^{E}=x_1x_2[A^0_{12}+A^1_{12}(x_1-x_2)+A^2_{12}(x_1-x_2)^2]+x_2x_3[A^0_{23}+A^1_{23}(x_2-x_3)+ \\ +A^2_{23}(x_2-x_3)^2]+x_3x_1[A^0_{31}+A^1_{31}(x_3-x_1)+A^2_{31}(x_3-x_1)^2]+fx_1x_2x_3 \quad (2)$$

where A^0_{ij}, A^1_{ij}, A^2_{ij} are parameters for binary system '*ij*' independent of composition, only relying on temperature, which have been used in the regular type equation:

$$G^{E}_{ij}=X_iX_j[A^0_{ij}+A^1_{ij}(X_i-X_j)+A^2_{ij}(X_i-X_j)^2+...+A^n_{ij}(X_i-X_j)^2] \quad (3)$$

where X_i and X_j indicate the mole fraction of component '*i*' and '*j*' in '*ij*' binary system. The function *f* is the ternary interaction coefficient expressed by

$$f=(2\xi_{12}-1)\{A^2_{12}[(2\xi_{12}-1)x_3+2(x_1-x_2)]+A^1_{12}\}+ \\ +(2\xi_{23}-1)\{A^2_{23}[(2\xi_{23}-1)x_1+2(x_2-x_3)]+A^1_{23}\}+ \\ +(2\xi_{31}-1)\{A^2_{31}[(2\xi_{31}-1)x_2+2(x_3-x_1)]+A^1_{31}\} \quad (4)$$

where ξ_{ij} are the similarity coefficients defined η_i called the deviation sum of squares:

$$\xi_{ij} = \frac{\eta_i}{\eta_i + \eta_j} \tag{5}$$

where

$$\eta_I = \int_{x_i=0}^{x_i=1} (\Delta G_{12}^E - \Delta G_{13}^E)^2 \mathrm{d}X_1$$
$$\eta_{II} = \int_{x_i=0}^{x_i=1} (\Delta G_{21}^E - \Delta G_{23}^E)^2 \mathrm{d}X_2 \tag{6}$$
$$\eta_{III} = \int_{x_i=0}^{x_i=1} (\Delta G_{31}^E - \Delta G_{32}^E)^2 \mathrm{d}X_3$$

and

$$X_{1[12]} = x_1 + x_3\xi_{12}$$
$$X_{2[23]} = x_2 + x_1\xi_{23} \tag{7}$$
$$X_{3[31]} = x_3 + x_2\xi_{31}$$

In all given equations, G^E and G_{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.

Values for the integral molar excess Gibbs energies for the constituent binary systems Bi–Sb, Sb–Ga and Ga–Bi, available in the literature for the temperature of 1073 K [14], were used as the starting data for the calculation, and their binary parameters calculated by Eq. (3) are presented in Table 3. Also, similarity coefficients for three constituent binary systems, calculated by Eqs (5–7), are presented in the same Table.

Table 3 Binary parameters and similarity coefficients at 1073 K for systems Bi–Sb, Sb–Ga and Ga–Bi

Parameter	Ga–Sb	Sb–Bi	Bi–Ga
A_{ij}^0	–8414.89	–9111.98	8322.73
A_{ij}^1	–2079.99	–1135.14	551.75
A_{ij}^2	840.02	6906.7	–7464.84
A_{ij}^3	778.55	–5050.54	4361.18
ξ_{ij}	0.989	0.010	0.498

Thermodynamic prediction based on these data and according to Eqs (2), (4) was done for the selected alloys (Table 1) in the Bi–$Ga_{0.1}Sb_{0.9}$ section of the Bi–Ga–Sb system, and values of the integral molar excess Gibbs energies and ternary interaction coefficients were determined. In order to compare the experimental re-

sults with the predicted ones, partial thermodynamic quantities for bismuth were derived according to the following equation

$$G_{Bi}^{E}=G^{E}+(1-x_{Bi})\frac{\partial G^{E}}{\partial x_{Bi}} \quad (8)$$

The results of thermodynamic prediction, as well as the derived values for bismuth thermodynamic quantities, are shown in Table 4.

Table 4 Results of the thermodynamic predicting according to general solution model [26] (energies in J mol^{-1})

Alloy	f_{123}	ΔG^{E}	a_{Bi}	γ_{Bi}	G_{Bi}^{M}	G_{Bi}^{E}
A1	–13802	–595	0	/	/	/
A2	–10968	–1166	0.189	1.890	–14862	5679
A3	–8206	–1592	0.359	0.795	–9139	5219
A4	–5491	–1902	0.462	1.540	–6889	3852
A5	–2799	–2062	0.516	1.290	–5903	2272
A6	–106	–2017	0.553	1.106	–5285	899
A7	2614	–1727	0.596	0.993	–4617	–60
A8	5384	–1206	0.660	0.943	–3707	–525
A9	8228	–560	0.751	0.939	–2555	–564
A10	11170	–24	0.868	0.964	–1263	–323

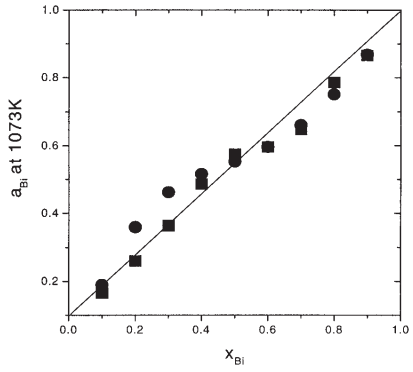

Fig. 3 Comparison between bismuth activities at 1073 K obtained experimentally and by prediction according to the general solution model. ■ – exp., ● – predicted

As it can be noticed, negative values for the integral molar excess Gibbs energies were obtained in the whole concentration range of the Bi–$Ga_{0.1}Sb_{0.9}$ section investigated. This indicates good miscibility between the constituent components and is in accordance with the neighbourhood of binary Bi–Sb and Ga–Sb systems, which also have negative binary integral molar excess Gibbs energies [14].

The comparison between the experimentally obtained and predicted partial bismuth thermodynamic quantities also shows good agreement, as in Fig. 3 for the example of bismuth activities at a temperature of 1073 K.

Phase diagram determination

DTA and SEM results, as well as the cooling curves obtained by Oelsen's calorimetry, were used for the determination of the Bi–$Ga_{0.1}Sb_{0.9}$ section phase diagram.

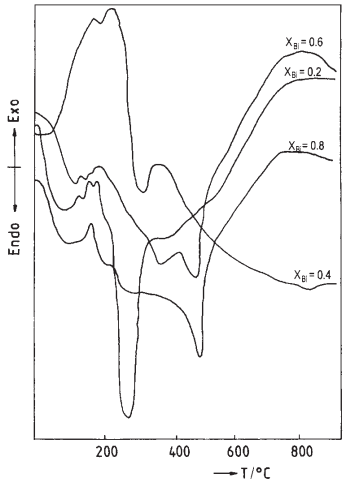

Fig. 4 DTA curves for samples with x_{Bi}=0.2, 0.4, 0.6 and 0.8 obtained at a heating rate of 10°C min^{-1} in an air atmosphere

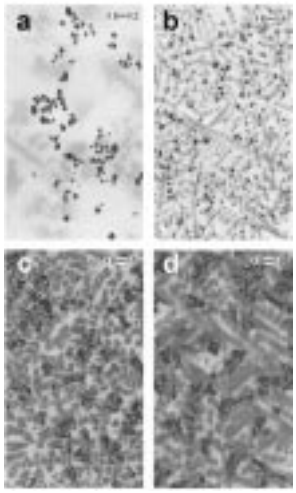

Fig. 5 SEM photographs for samples with a – x_{Bi}=0.2; b – 0.4; c – 0.6 and d – 0.8; (black phase – $Ga_{0.1}Sb_{0.9}$ eutectic; dark gray phase – Bi–Sb solid solution rich on Sb; light gray phase – Bi–Sb solid solution rich on Bi)

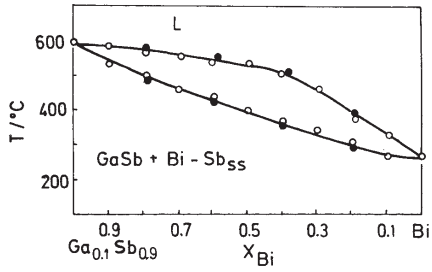

Fig. 6 Phase diagram of the investigated Bi–$Ga_{0.1}Sb_{0.9}$ section. o – cooling curves, • – DTA

Results obtained by DTA for alloys with x_{Bi}=0.2, 0.4, 0.6 and 0.8 are shown in Fig. 4, while SEM photographs of the same samples are presented in Fig. 5.

Based on these data, phase diagram for the Bi–$Ga_{0.1}Sb_{0.9}$ section in the ternary system Bi–Ga–Sb was constructed and presented in Fig. 6.

As it can be seen, the investigated section in the Bi–Ga–Sb system, which links bismuth corner with the $Ga_{0.1}Sb_{0.9}$ eutectic, shows great similarly with the binary Bi–Sb phase diagram and is in agreement with the literature data about the Bi–Ga–Sb phase diagram [29].

Conclusions

Comparative thermodynamic analysis of the Bi–$Ga_{0.1}Sb_{0.9}$ section in the Bi–Ga–Sb system was done based on the experimental calorimetric investigations according to Oelsen's method and thermodynamic prediction by Chou's general solution model. Values for the activities, activity coefficients, partial molar quantities for bismuth and integral molar quantities at a temperature of 1073 K were obtained and their comparison shows good agreement. Also, DTA and SEM results for the investigated samples, a based on the obtained cooling curves, a phase diagram of the investigated section is constructed and presented in this paper.

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