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THERMODYNAMIC ANALYSIS AND CHARACTERIZATION OF Ga–$GeSb_{0.855}$ SECTION IN Ga–Ge–Sb TERNARY SYSTEM

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Abstract

In this paper, Ga–$GeSb_{0.855}$ section in the ternary system Ga–Ge–Sb was studied using thermodynamic predicting methods by Muggianu and Toop, while characterization of the chosen alloys was done by DTA, X-ray and SEM-EDX method.

Keywords: Ga–Ge–Sb system, thermodynamics of alloys

Introduction

The invention of the first electronic device represented a revolutionary event which produces a completely new wave in the use and application of rare metals for making components in electronic devices and instruments [1]. Generally, rare metals such as gallium and germanium possess special characteristics, which are necessary for the further progress in electronics [2, 3]. These metals are used [4–8] in electro-techniques, radio-techniques and electronics, in electronic and optical devices and instruments as functional materials for diodes, transistors, conductors, correctors, in integrated circuits, optical cables, as well as in atomic and astrophysical investigations, atomic reactors, in laser technology, as sensors of neuron grids, in semiconductors industry, etc.

Considering their extensive application in almost all important branches and fields of techniques, it is very important to know the thermodynamic determination and description of gallium and germanium based systems completely.

One of them is the ternary Ga–Ge–Sb system. For its binary constitutive systems, there are a lot of thermodynamic data [10–13], while for the whole ternary system, there are just a few articles dealing with its thermodynamic behavior [14–17]. In the work of Katayama and coworkers [14], measurements of gallium activity in the temperature range from 1058–1236 K by EMF method with zirconia as solid electrolyte, are pre-

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sented, while Kostov and coworkers [15–17] gave comparative thermodynamic analysis of alloys done experimentally by Oelsen calorimetry and Chou and Hajra method.

Therefore, in this paper, the thermodynamic analysis of one section in Ga–Ge–Sb ternary system (Ga–$GeSb_{0.855}$) is done by Muggianu and Toop predicting models for ternaries and also the characterization of the chosen alloys is carried out by DTA, X-ray and SEM-EDX methods.

Experimental

The selected Ga–$GeSb_{0.855}$ section is presented as a line, which goes from gallium corner to eutectic in Ge–Sb binary system, that corresponds to $GeSb_{0.855}$ composition. The seven alloys with constant volume of 1 cm^3 are chosen from concentration area in the investigated selection. Chemical compositions are shown in Table 1.

DTA experiments are performed by derivatograph (MOM, Hungary) in air atmosphere and at a constant heating rate of 10°C min^{-1}. X-ray investigations are done by Roentgen apparatus (Siemens, Germany) with copper-anticathode and nickel-filters. SEM-EDX analysis is carried out by electronic microscope (Philips XL-300) with energetic dispersion spectrometer EDX.

Results and discussion

Thermodynamic analysis

The basic theoretical interpretations of the traditional predicting models are classified according to Hillert [9] into two categories: symmetrical and asymmetrical. In this paper one symmetrical – Muggianu, and one asymmetrical model – Toop, were used for thermodynamic analysis of Ga–$GeSb_{0.855}$ section in Ga–Ge–Sb ternary system. These models are given as follows:

Muggianu model

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

Toop model

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

Table 1 Alloy compositions of Ga–$GeSb_{0.855}$ section in Ga–Ge–Sb ternary system

No.	Composition/mass%			Mole composition			Mass/g			m_Σ/g
	Ga	Ge	Sb	x_{Ga}	x_{Ge}	x_{Sb}	Ga	Ge	Sb	
A1	0	9.20	90.80	0	0.145	0.855	0	0.6513	5.8621	6.5134
A2	13.24	8.48	78.28	0.20	0.123	0.677	0.8515	0.5452	5.0330	6.4297
A3	28.84	7.19	63.97	0.40	0.092	0.508	1.8246	0.4549	4.0464	6.3259
A4	33.50	6.50	60.00	0.452	0.084	0.464	2.1106	0.4095	3.7802	6.3003
A5	47.79	5.06	47.15	0.60	0.061	0.339	2.9691	0.3143	2.9294	6.2128
A6	70.96	2.86	26.18	0.80	0.031	0.169	4.3101	0.1739	1.5899	6.0739
A7	100	0	0	1	0	0	5.9100	0	0	5.9100

Table 2 Thermodynamic value for gallium in Ga–Ge–Sb ternary system (Ga–$GeSb_{0.855}$ section) at 1273 K obtained by Muggianu and Toop models

No.	Muggianu model					Toop model				
	a_{Ga}	γ_{Ga}	G^{xs}_{Ga}/ J mol^{-1}	G^{M}_{Ga}/ J mol^{-1}	ΔG^{xs}/ J mol^{-1}	a_{Ga}	γ_{Ga}	G^{xs}_{Ga}/ J mol^{-1}	G^{M}_{Ga}/ J mol^{-1}	ΔG^{xs}/ J mol^{-1}
A1	0	0	–	–	–2448	0	0	–	–	–2448
A2	0.119	0.593	–5525	–22559	–3054	0.114	0.572	–5908	–22942	–3150
A3	0.275	0.689	–3947	–13645	–3476	0.272	0.679	–4095	–13792	–3611
A4	0.328	0.725	–3404	–11808	–3496	0.325	0.718	–3502	–11906	–3629
A5	0.502	0.836	–1897	–7304	–3247	0.502	0.836	–1897	–7303	–3354
A6	0.767	0.959	–445	–2806	–2084	0.769	0.961	–419	–2781	–2126
A7	1	1	0	0	0	1	1	0	0	0

The excess free energies for the three binary systems Ga–Ge, Ge–Sb and Sb–Ga are taken from [10–12], respectively.

Based on these data and Eqs (1) and (2), calculation according to different predicting methods was done for the investigated alloys at a temperature of 1273 K. Results of Muggianu and Toop model are given in Table 2.

The obtained results are compared to results obtained by experimental Oelsen calorimetry and predicting methods of Chou and Hajra [15–17].

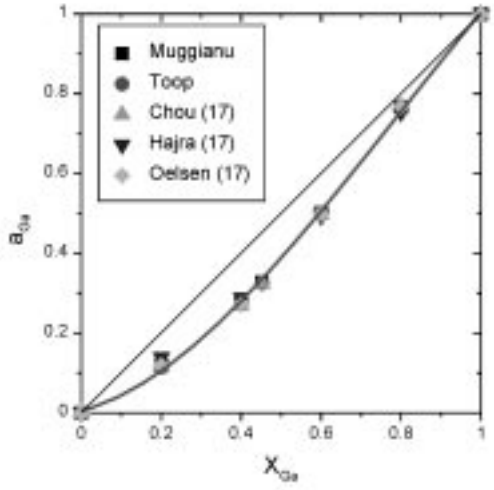

Fig. 1 Dependence of gallium activity *vs*. molar content obtained by different methods at 1273 K

Dependence of gallium activity upon molar content obtained by different methods in ternary system Ga–Ge–Sb for Ga–$GeSb_{0.855}$ section at 1273 K is shown in Fig. 1.

Characterization of obtained alloys

DTA method

Differential thermal analysis (DTA method) is used for the investigation of the investigated alloys in Ga–$GeSb_{0.855}$ section in Ga–Ge–Sb ternary system. The values of characteristic temperatures related to the maximum peak temperature on DTA curves of heating and cooling, are given in Table 3.

X-ray analysis

X-ray diffraction method is also used for the characterization of alloy compositions in Ga–$GeSb_{0.855}$ section in Ga–Ge–Sb ternary system. The obtained diffractograms of chosen alloys are shown in Fig. 2. The results of phase characterization by this method are given in Table 4.

Table 3 Values of characteristic temperatures corresponding to the maximum on DTA peaks

No.	Heating	Cooling
	Temperature/°C	
A2	510 625	455
A3	510 580 630	460 470 480 585
A4	500 605 645	465 480 600
A5	30 625	580
A6	30 570	525

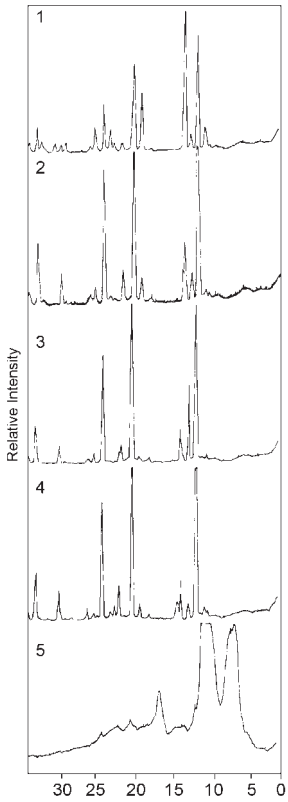

Fig. 2 X-ray diffractogram of investigated alloys (1 – A2, 2 – A3, 3 – A4, 4 – A5, 5 – A6)

Table 4 X-ray phase characterization

No.	A2		A3		A4		A5		A6	
Ref.	nm	element	nm	element	nm	element	nm	element	nm	element
1	1.354	Sb	1.357	Sb	1.360	Sb	1.360	Sb	1.839	$GaSb_{eut}$
2	1.392	$GaSb_{eut}$	1.392	$GaSb_{eut}$	1.392	$GaSb_{eut}$	1.392	$GaSb_{eut}$	2.000	
3	1.412	Ge	1.420	Ge	1.396	$GaSb_{eut}$	1.396	$GaSb_{eut}$	2.017	
4	1.430	Sb	1.519	$GaSb_{eut}$	1.519	$GaSb_{eut}$	1.450		2.145	$GaSb_{eut}$
5	1.484	Sb	1.548	Sb	1.553	Sb	1.519	$GaSb_{eut}$	2.435	
6	1.519	$GaSb_{eut}$	1.716	Ge	1.716	Ge	1.551		2.547	
7	1.546	$GaSb_{eut}$	1.756	Sb	1.717		1.595		2.690	
8	1.716	Ge	1.832	$GaSb_{eut}$	1.759	Sb	1.710	Ge	3.199	
9	1.753	Sb	1.895	Sb	1.832	$GaSb_{eut}$	1.759		3.366	
10	1.829	$GaSb_{eut}$	1.935	Sb	2.000		1.792	Ga	3.534	$GaSb_{eut}$
11	1.889	Sb	2.017	Ge	2.017	Ge	1.832	$GaSb_{eut}$		
12	1.935	Sb	2.148	$GaSb_{eut}$	2.043		1.912	Ga		
13	2.017	Ge	2.249	Sb	2.145	$GaSb_{eut}$	1.959	Ga		
14	2.145	$GaSb_{eut}$	2.482		2.247	Sb	2.000	Ge		
15	2.247	Sb	2.894		2.365		2.052			
16	2.405		2.950		2.397		2.150	$GaSb_{eut}$		
17	2.528		3.049	$GaSb_{eut}$	3.049	$GaSb_{eut}$	2.258	Ga		
18	3.095	Sb	3.099	Sb	3.095	Sb	2.410			
19	3.297	Ge	3.222		3.292	Ge	2.958	Ga		
20	3.524	$GaSb_{eut}$	3.292	Ge	3.524	$GaSb_{eut}$	3.049	$GaSb_{eut}$		

Table 4 Continued

No.	A2		A3		A4		A5		A6	
Ref.	nm	element	nm	element	nm	element	nm	element	nm	element
21	3.816	Sb	3.341		3.727	Sb	3.222			
22	3.978		3.524	$GaSb_{eut}$	3.978		3.292	Ge		
23			3.822	Sb			3.341			
24			3.971				3.524	$GaSb_{eut}$		
25			4.294				3.855	Ga		
26			4.471				3.978			
27			6.588							

SEM-EDX analysis

SEM-EDX analysis is carried out in order to confirm alloy compositions of Ga–$GeSb_{0.855}$ section in Ga–Ge–Sb ternary system. SEM photographs are shown in Fig. 3, and characteristic EDX curves for sample A4 are given in Fig. 4.

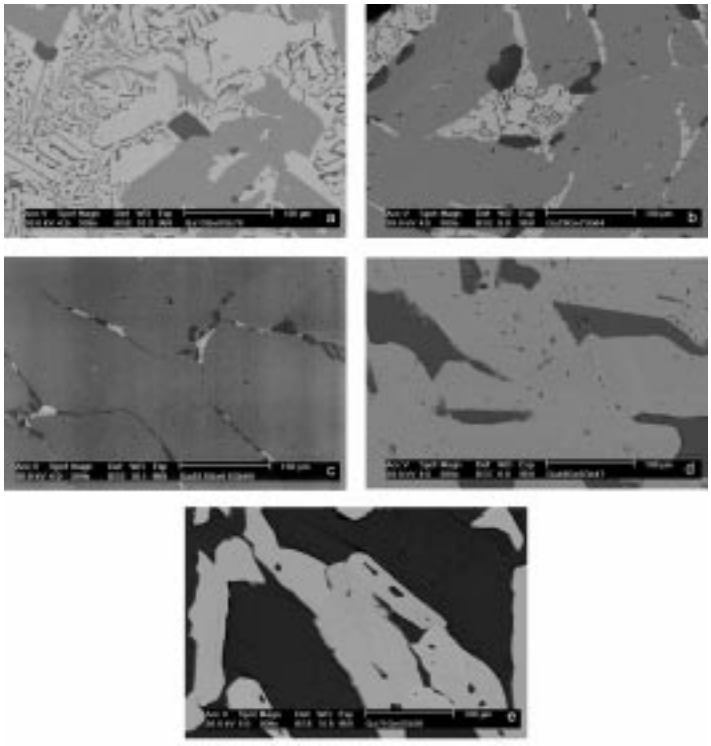

Fig. 3 SEM photographs of samples a – A2, b – A3, c – A4, d – A5, e – A6

According to the figures shown and SEM-EDX analysis of the investigated samples it can be concluded that the structure of the sample:

- A2 consists of primary crystals of germanium and antimony and eutectic (Ga+Sb),
- A3 consists of eutectic (Ga+Sb) and primary crystals of germanium and antimony,
- A4 consists of eutectic (Ga+Sb), as majority phase, and remnant crystals of germanium and antimony, with minor separation of gallium crystals,
- A5 consists of primary crystals of gallium and eutectic (Ga+Sb), and
- A6 consists of primary crystals of gallium and eutectic (Ga+Sb).

The obtained results by SEM-EDX investigations for characteristic compositions of Ga–$GeSb_{0.855}$ section completely determine and characterize the chosen alloys in Ga–Ge–Sb ternary system.

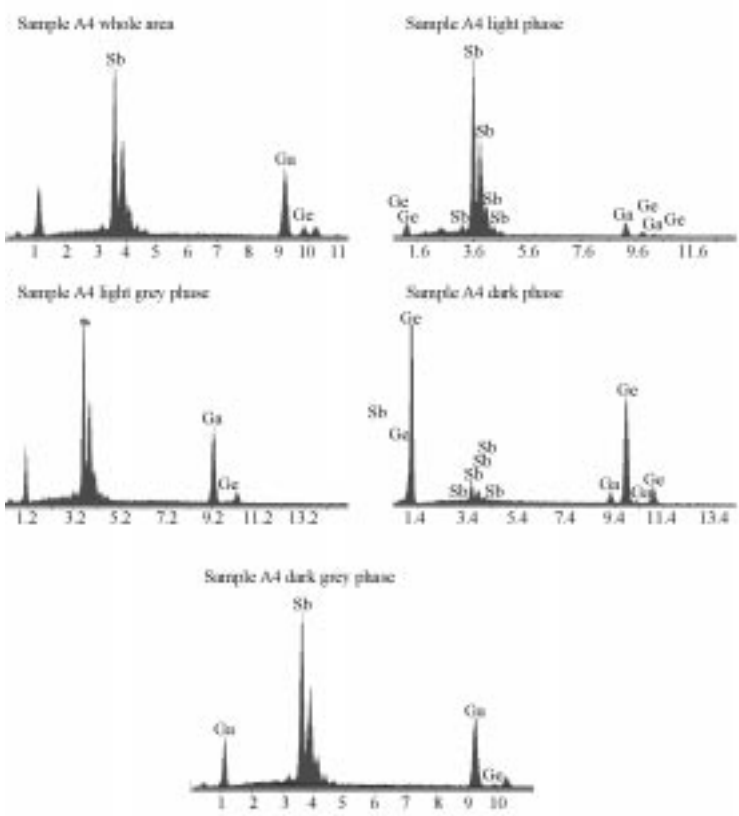

Fig. 4 EDX semi-quantitative analysis of sample A4

Discussion of obtained results

Thermodynamic values: activities, activity coefficients, and partial molar properties (excess Gibbs energy and Gibbs energy of mixing for gallium) in Ga–$GeSb_{0.855}$ section in ternary Ga–Ge–Sb system at 1273 K, are determined using thermodynamic predicting methods, by Muggianu and Toop models.

The calculated values for the activity of gallium show a negative deviation from Raoult's law in the whole concentration area. With x_{Ga} increasing, activity of gallium uniformly increases, which means that gallium is mixed well with other constituents in the investigated section. Negativity of the partial molar excess Gibbs energy and partial molar Gibbs energy of mixing for gallium decreases with increasing the molar content. If the negativity increases, there will be a stronger interaction between components. These confirm the conclusions about the thermodynamic behavior of the ternary system with respect to Raoult's law.

Also, the thermodynamic properties of the Ga–$GeSb_{0.855}$ section in ternary system Ga–Ge–Sb calculated by using Muggianu and Toop models were compared to results obtained by Chou and Hajra models as well as experimental Oelsen calorime-

try [17]. The obtained results show that data offered by Toop and Muggianu models are close to those predicted by Chou model and experimental Oelsen calorimetry.

It has to be mentioned here that the arrangement of three components to a triangle for an asymmetrical model is very important, because a wrong arrangement will lead to even worse results than a symmetrical model. In this example, the component gallium has been selected as a symmetric point. All of these are a result of human interference. But Chou's model automatically puts gallium in a symmetrical position without any human interference [17].

The similarity coefficients for three binaries, given by the Chou's model [17], indicate that Ga–Ge–Sb ternary system is regarded as an asymmetrical system. Because of that, the calculated results predicted by Toop could be taken as more correct than those from the Muggianu symmetrical model. Therefore, among all traditional models, the Toop model gives better results, the closest to Chou's results.

DTA, X-ray and SEM-EDX methods are used in order to confirm and characterize the chosen alloys of Ga–$GeSb_{0.855}$ section in Ga–Ge–Sb ternary system. The results obtained by the use of these methods, show a structure consisting of primary crystals of germanium and antimony and eutectic (Ga+Sb) for content from x_{Ga}=0 to x_{Ga}=0.452, for content from x_{Ga}=0.452 to x_{Ga}=1 while structure consists of primary crystals of gallium and eutectic (Ga+Sb).

Those results present a contribution to a better knowledge of this ternary system.

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