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THERMODYNAMIC ANALYSIS AND CHARACTERIZATION OF Ga-Ge-Sb ALLOYS AS MATERIALS FOR SEMICONDUCTOR APPLICATION

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ABSTRACT
Thermodynamic analysis and characterization of the investigated Ga-Ge-Sb alloys, which is of a practical importance in electric - semiconductors industry, are presented in this paper. Thermodynamic analysis are done by the used of experimental investigation technique of Oelsen calorimetry and different thermal analysis (DTA) and thermodynamic predicting methods, while characterizations are done by the used of SEM-EDX analysis. The experimental and calculated values are shown a good agreement as well as the obtained phase diagram of the investigated semiconductor alloys.
Keywords: thermodynamic, characterization, Ga-Ge-Sb alloys

1. INTORDUCTION

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 these Ga-Ge based systems is the ternary system Ga-Ge-Sb, which is of a practical interest in semiconducting industry.

2. EXPERIMENTAL PART

The seven alloys with constant volume of 1 cm^3 are chosen from concentration area in the investigated Ga-Ge-Sb alloys. Chemical compositions are shown in Table 1. Oelsen calorimetry was used for the experimental thermodynamic investigation in the ternary system Ga-Ge-Sb. Descriptions of this experimental technique were reported in [9-11].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.

3. RESULTS AND DISCUSSION

Based on the cooling curves obtained by rapid cooling of the investigated samples in Oelsen's calorimeter, the space diagram dependence of the temperature change of the calorimeter upon molar content and temperature is constructed. According to the temperature change of the calorimeter read from the constructed space diagram, the enthalpy diagrams shown in Fig.1 for the temperature interval 350-1300 K in ternary system Ga-Ge-Sb was obtained.

Table 1. Selected alloy compositions in Ga-Ge-Sb ternary system.

No.	Composition, mass%			Mole composition		
	Ga	Ge	Sb	x_{Ga}	x_{Ge}	x_{Sb}
A1	0	9,20	90,80	0	0,145	0,855
A2	13,24	8,48	78,28	0,20	0,123	0,677
A3	28,84	7,19	63,97	0,40	0,092	0,508
A4	33,50	6,50	60,00	0,452	0,084	0,464
A5	47,79	5,06	47,15	0,60	0,061	0,339
A6	70,96	2,86	26,18	0,80	0,031	0,169
A7	100	0	0	1	0	0

Table 2. Results of the Oelsen's quantitative thermodynamic analysis for the ternary system Ga-Ge-Sb at 1273 K.

No.	a_{Ga}	γ_{Ga}	G^{XS}_{Ga}	G^{M}_{Ga}
			$Jmol^{-1}$	
A1	0	-	-	-
A2	0,120	0,599	-5424	-22458
A3	0,272	0,680	-4079	-13776
A5	0,499	0,832	-1953	-7359
A6	0,767	0,958	-452	-2813
A7	1	1	0	0

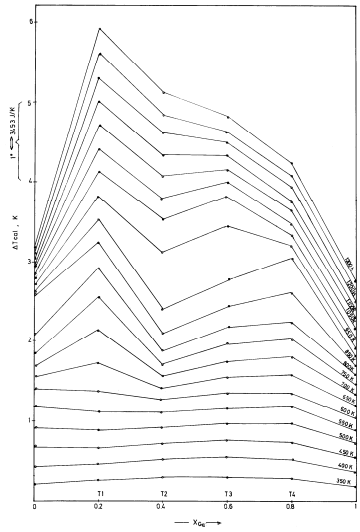

Figure 1. The enthalpy isotherm diagram for the temperature interval 350-1300 K in the ternary system Ga-Ge-Sb.

The results of the Oelsen's quantitative thermodynamic analysis, which include values for activities, activity coefficients, and partial molar Gibbs energy of mixing and partial molar Gibbs excess energy for gallium at 1273 K, for investigated ternary system Ga-Ge-Sb are given in Table 2.

The Chou's general solution model for predicting thermodynamic properties of a multicomponent system from binaries [12-14] has been used to predict thermodynamic properties of the investigated ternary system Ga-Ge-Sb. The method provided by Chou has been proved to be the most reasonable one in all aspects among other geometrical models. This model cannot only generalize various kinds of situations, break down the boundary between symmetrical and asymmetrical systems, but also can thoroughly rule out any human interference in the calculation process.

Hajra's method [15,16] has been also used to predict thermodynamic properties of the investigated ternary system Ga-Ge-Sb. Hajra's method for predicting the thermodynamic properties of ternary systems is based on the knowledge of the infinite dilution constants and interaction parameters for the constitutive binary systems. Although these parameters are originally intended to be useful in the interpretation of properties for dilute solutions, by this method the approach is extended to the

concentrated solutions. Hajra developed a ternary function based on the Maclaurin infinite series and subjected to different boundary conditions, which presents the summary of these series. It is thermodynamically consistent and capable of interpreting properties of the ternary systems.

Comparative analysis is done for thermodynamic properties of gallium, which are obtained by the following methods: experimental use of Oelsen's calorimetry, and predicting methods according to Chou and Hajra, at the investigated temperature 1273 K in the ternary system Ga-Ge-Sb are shown in Fig. 2 and Fig. 3.

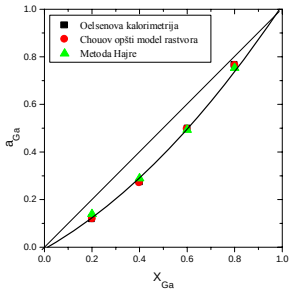

Figure 2. Activity vs. molar content of gallium in ternary system Ga-Ge-Sb at 1273 K obtained by experimental Oelsen's calorimetry, and predicting methods of Chou and Hajra.

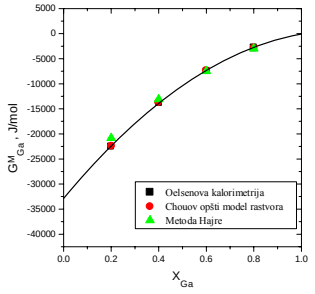

Figure 3. Partial molar excess Gibbs energy vs. molar content of gallium in ternary system Ga-Ge-Sb at 1273 K obtained by experimental Oelsen's calorimetry and predicting methods of Chou and Hajra.

Considering the results shown above, the following observations can be made. Results obtained by predicting methods of Chou and Hajra show good agreement with results obtained by experimental Oelsen calorimetry. Better agreement was noticed between experimental results and results obtained by Chou's method, than one obtained by Hajra's method application. Obtained negative deviation of a_{Ga} from Raoult's law indicates good miscibility in the investigated system. Also, a negative deviation from Raoult's law is noticed for antimony, while germanium showed a positive deviation from Raoult's law. This indicates better miscibility between gallium and antimony than germanium; i.e. antimony is more dissolved into gallium than germanium into gallium. The dependence of ΔG^{xs} and ΔG^{M} upon molar content shows minimum at $x_{Ga} \geq 0,6$ which pointed out the possible existence of the eutectic of this ternary system. The existence of the eutectic is proved by experimental DTA and SEM-EDX methods.

The results of characteristic temperatures related to the maximum peak temperature on DTA curves of heating and cooling, are shown in Table 3. SEM-EDX analysis is carried out for the investigated semiconductor alloys, and characteristic SEM photograph for the alloy A2 are shown in Figs.4. Obtained experimental results of DTA and SEM-EDX are used for phase diagram calculations in Ga-Ge-Sb ternary system. The obtained phase diagram is given in Fig. 5. The phase diagram of the investigated system is similar with the phase diagram of the binary system Ga-Ge, and it is a simple eutectic system.

4. CONCLUSION

The observations confirm the conclusions about the thermodynamic behavior of investigated ternary system Ga-Ge-Sb with respect to Raoult's law. Namely, it is noticed that negativity of the partial molar excess Gibbs energy and partial molar Gibbs energy of mixing for gallium decreases with increasing of molar content. If the negativity more increases, there will be a stronger interaction between components, considering the compound formed between gallium and antimony.

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

No.	Temperature, ^{0}C	
	Heating	Cooling
A2	510	455
	625	
A3	510	460
	580	470
	630	480
		585
A4	500	465
	605	480
	645	600
A5	30	580
	625	
A6	30	525
	570	

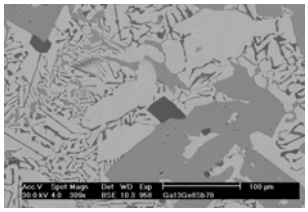

Figure 4. SEM of alloy A2.

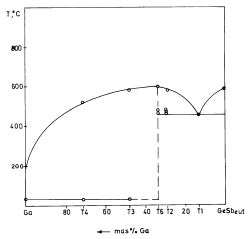

Figure 5. Phase diagram of Ga-GeSb$_{eut}$ system.

The obtained and shown thermodynamic data describe the investigated ternary system Ga-Ge-Sb completely thermodynamically at the investigated temperature of 1273 K. At the same time, those thermodynamic data presents a contribution to a better knowledge of this ternary system Ga-Ge-Sb, and also present the starting base for all further thermodynamic research.

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