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DTA THERMODYNAMIC BEHAVIOUR OF THE TERNARY SYSTEM Ga-Ge-Sb

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Abstract

Finding new types of materials, usually by modernizing classic materials by introducing and combining some of the new components within the already existing standard ones, based on improved and innovated classical materials, leads to the production of materials that are characterized by a complex of new features that enable a wide range of their practical applications.

It is widely known that rare metals such as gallium and germanium possess special features that are necessary for further progress in electronics. These materials are used in electrical engineering, radio engineering and electronics, in optical and electronic devices and instruments as functional materials for transistors, diodes, integral circuits, optical cables, conductors, rectifiers, etc. in atomic and astrophysical testing, aerospace industry, laser technology, sensors of neural networks, atomic reactors and the semiconductor industry.

Given the wide range of applications and use of these materials in almost all-important areas and techniques, there is a need for a more complete knowledge of the properties of not only these elements, but also the systems of which they are integral parts, from the aspect of their fuller description and thermodynamic determination.

Therefore, in this paper, research in the ternary system Ga-Ge-Sb will be presented in order to complete the thermodynamic description of the system. Its practical significance and application are mostly in the semiconductor industry, from the point of view of defining the thermodynamic quantities of the components constituting this system, as well as the results characterization of the thermodynamic behavior of the investigated alloys by DTA analysis of this system.

***Keywords**: ternary system Ga-Ge-Sb, DTA, thermodynamic*

1. INTRODUCTION

Gallium is element of the III group of the periodic table and represents elemental semiconductor element. It is often mixing with elements that belong to the V group of the periodic table especially with arsenic and form a lot number of compounds based on gallium arsenide, which is the materials used a lot in the laser technology, making CD and DVD devices, etc. [1] Also, a lot of compounds can be formed by combining III (Al, Ga, In) and V (Si, Ge, Sn) groups or II (Zn, Cd, Hg) and VI (S, Se, Te) groups of the periodic table and make combinations of elements that exhibit semiconductor properties. Some of those combinations and compounds possess special semiconductor properties and behavior's which enable their application and numerous branches of the electrical industry [2].

The knowledge of their special characteristics is necessary for the further progress in electronics and optoelectronics, because of their large use in optical and electronical devices as materials for semiconductors, transistors, optical cables, integrated circuits, power plants and space technologies [1,3]. Therefore, these materials and compounds are the subject of numerous investigations.

The phase equilibria in the systems Ga,Ge-Sb-Gd–Fe were investigated from Ivan Franko National University of Lviv in Ukraine [4] for the different content of elements at 500 ºC and the corresponding isothermal section of the phase diagram was constructed. The crystal structures of the few semiconductor compounds were refined.

Electrical and optical properties of Sb-rich nanoparticles for phase-change memory applications have been examined in Reference [5]. The results show that phase-change properties of Ge15Sb85 material still exist for nanoparticles of 8.0 nm size and Ge15Sb85 nanoparticles are a good candidate for phase-change memory applications in terms of long data retention time. The observed phase transition in Ge15Sb85 nanoparticles is promising for down scaling the size of phase change solid-state memory devices.

Chalcogenide glasses of $(GeSe4)_{1-x}Ga_x$ and $(GeSe5)_{1-x}Ga_x$ systems, with 5, 10, 15, 20 at % Ga were investigated as well as basic properties such as density, molar volume and compactness of the samples were calculated in Reference [6]. According to obtained properties and due to some unique optical and electrical phenomena, these materials are expected to be promising material in the IR optics, microelectronics.

Structural analysis of RF sputtered Ge-Sb-Se thin films by Raman and X-ray photoelectron spectroscopies are given in [7].

A phase diagram of the Ga–Ge–Sb ternary system was calculated by the CALPHAD approach, using only optimized thermodynamic parameters for the constitutive binary systems [8-13]. The CALPHAD method is based on constrained minimization of Gibbs energy for a given temperature, pressure and overall composition [14,15].

Considering the fact that the thermodynamic data for the Ga-Ge-Sb ternary system do not exist, the existing literature data mainly relate to the thermodynamic analysis of the binary systems as the constituents of the ternary system, which can also be concluded on the basis of the aforementioned literature review, there is a need for a complete thermodynamic determination of this ternary system as well as DTA analysis of the investigated ternary alloys in the aim to obtained thermodynamic values which after that will be used for calculation the phase diagram of the investigated ternary system.

2. EXPERIMENTAL

All experimental research whose results are presented in this paper, were carried out with pure metal gallium, germanium and antimony p.a. cleanliness. Weighed pieces of gallium, germanium and antimony were melted in the low-frequency induction furnace under argon inert gas atmosphere and cast in charcoal molds. First it was prepared pre-alloys: Ga-Ge and Ge-Sb, and after that from pre-alloys, the Ga-Ge-Sb alloys were made.

DTA experiments were performed on the Labsys EVO TG-DTA/DSC instrument (SETERAM). Experiments were carried out in an atmosphere of argon inert gas with pressure of 1,5 bar and in water cooling system. A constant heating rate was 5 ^{0}C/min.

3. RESULTS AND DISCUSSION

Six alloys of a certain composition and a constant volume of 1 cm^3 were selected from the concentration region of the Ga-Ge-Sb ternary system. The data of the selected alloys are given in Table 1.

DTA investigations of the selected alloys were performed at three different temperatures: 1073K, 1173K and 1273K. The activity, Gibbs energy of mixing and Gibbs excess energy for gallium were obtained. The diagram of dependence of the gallium activity from the composition at temperatures of 1073K, 1173K and 1273K is presented in Figure 1.

Table 1. Data of the selected alloys in Ga-Ge-Sb ternary system

Composition	%Ga	%Ge	%Sb
1	0	9.2	90.8
2	13.24	8.48	78.28
3	28.84	7.19	63.97
4	47.79	5.06	47.15
5	70.96	2.86	26.18
6	100	0	0

A negative deviation from Raoult's law was observed from the diagram. This indicates a good miscibility of the constituent components of the examined Ga-Ge-Sb ternary system and formation of alloys with good homogenous liquid alloys. The dependences of Gibbs energy of mixing and Gibbs excess energy from the compositions at temperatures 1073K, 1173K and 1273K are shown in Figures 2 and 3, respectively. The dependence of the integral Gibbs energy of mixing and the integral Gibbs excess energy in the Ga-Ge-Sb ternary system is shown in Figure 4.

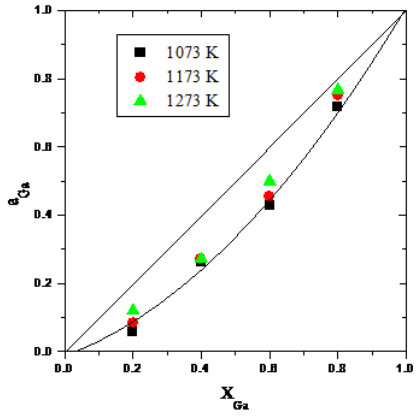

Figure 1. The dependence of gallium activity on the composition in the Ga-Ge-Sb ternary system at temperatures of 1073K, 1173K and 1273K

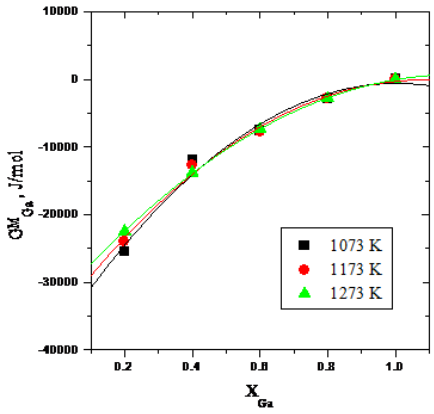

Figure 2. Dependence of Gibbs energy of mixing of gallium from the composition in the Ga-Ge-Sb ternary system at temperatures of 1073K, 1173K and 1273K

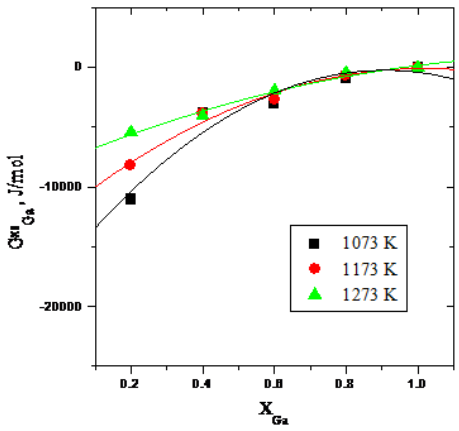

Figure 3. Dependence of Gibbs excess energy of gallium from the composition in the Ga-Ge-Sb ternary system at temperatures of 1073K, 1173K and 1273K

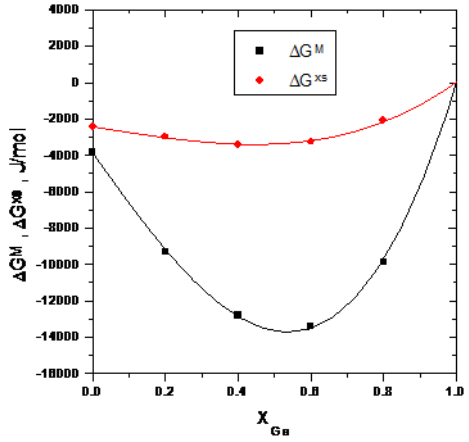

Figure 4. Dependence of integral molar Gibbs energy of mixing and excess energy in the Ga-Ge-Sb ternary system

A negative deviation from Raoult's law was observed, indicating good mixing of the component components in the Ga-Ge-Sb ternary system. Activity of gallium in the entire concentration range

are less than 1. With increasing gallium content, its activity is uniformly increasing at all investigated temperatures, which points to the fact that deviation from Raoult's law is less. Also, with increasing temperature for all investigated compositions, activity of gallium is increasing equally. The dependence of the partial Gibbs energy of mixing for gallium from the composition and temperature indicates that as the gallium content grows in the solution, the negativity of the given function increases with the temperature decreases. The obtained values of partial excess Gibbs energy for gallium, derived from known values for activity of gallium and confirm the conclusions about the behavior of this solution in relation to Raoult's law.

4. CONCLUSION

Obtained values for gallium activities show a negative deviation from Raoult's law throughout the concentration range. With the rise of mole content of gallium, activity of gallium increases uniformly. Dependence and compositions show a minimum in the composition $x_{Ga} \sim 0.4$, which corresponds to the eutecticum in the phase diagram of the Ga-Ge-Sb ternary system. Integral molar Gibbs excess energy along the whole area of the ternary system Ga-Ge-Sb has a negative value. The negativity of this function grows with gallium content. With the increase in the content of the components, the negativity of the function increases to $x_{Ga} = 0.2$, $x_{Ge} = 0.4$ and $x_{Sb} = 0.4$, and then decreases. It is noted that the minimum value is characteristic of the central part of the concentration triangle, and it can be expected that the mixing of the constituents in this part of the system is greatest.

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