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THERMAL ANALYSIS OF PHASE EQUILIBRIA IN THE MUTUAL SYSTEMS Ga,In//As,Sb AND Ga,La//O,S

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ABSTRACT

The liquidus surfaces of the Ga,In//As,Sb and Ga,La//O,S mutual systems have been determined on the basis of limited quantity of DTA measurements planned with the help of the equations with coordinated thermodynamic characteristics of solutions and individual phases including the parameters of component fusion.

INTRODUCTION

The compounds $A^{III}B^{V}$, $A_2^{III}B_3^{VI}$, $Ln_2B_3^{VI}$ and the solid solutions on their basis are characterized by the valuable semiconductor qualities /1,2/.However,phase diagrams of ternary mutual systems formed by the compounds mentioned above have been poorly studied.In particular,for Ga,In //As,Sb and Ga,La //O,S mutual systems only phase diagrams of the La_2SO_2 - Ga_2S_3 section /3,4/ and the temperature values of crystallization beginning are known for several compositions of solid solutions $Ga_xIn_{1-x}As_kSb_{1-k}$ /5/. Determination of phase diagram of Ga,In //As,Sb and Ga,La //O,S mutual systems only with DTA requires a large volume of experimental work.At present design methods of ternary diagram according to the data of boundary systems are in progress /6/.While using such design methods the number of experimental measurements being carried out in thermal analysis of the alloys of ternary multicomponent system is minimized.In the present work for planning the experiments according to DTA the thermodynamic method put forward in /7/ was used.

MEASURING METHODS

DTA of the samples was made using the derivatograph Q-1500 D at the heating rate equal to 15°/min.The investigation of the alloys was also carried out by the methods of X-ray diffraction and microstructural analyses.X-ray diffraction analysis was run using the diffractometer "DRON-2" in CuK_α emission with Ni-filter.Microstructural analysis was carried out using MBI-6.

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To determine liquidus surface of the La_2O_3-La_2S_3-Ga_2S_3 ternary system there have been studied the alloys of quasi-binary section $La_6Ga_{10/3}S_{14}$-La_2O_2S and non-quasi-binary sections Ga_2S_3 - $(La_2S_3)_{0,5}$ $(La_2O_3)_{0,5}$ and $La_6Ga_{10/3}S_{14}$-$(Ga_2S_3)_{0,75}$ $(La_2O_3)_{0,25}$ as well as the alloys of some compositions of previously studied quasi-binary systems Ga_2S_3-La_2O_2S /3,4/, La_2O_3-La_2S_3 /8/ and Ga_2S_3-La_2O_3 /9/. In the Ga,In//As,Sb system DTA was carried out only for five compositions: X=K=0,5; X=0,25, K=0,25; X=0,25, K=0,75; X=0,75, K=0,25; X=0,75, K=0,75. The alloys were synthesized by the ceramic ampoule method /9/ out of initial compounds.

RESULTS AND DISCUSSION

A ternary mutual system with a stable diagonal is called an irreversible, but without the stable diagonal - reversible. For determining the type of ternary mutual systems Ga,In//As,Sb and Ga,La//O,S it was carried out the thermodynamic analysis of the reactions

$$GaAs + InSb \rightleftarrows GaSb + InAs \qquad (1)$$

$$Ga_2O_3 + La_2S_3 \rightleftarrows La_2O_3 + Ga_2S_3 \qquad (2)$$

On the basis of thermodynamic functions of formation of $A^{III}B^{V}$ type compounds /10/ according to the Gibbs-Helmgolts equation for the reaction free energy in the temperature interval T=700-1000K it has been got

$$\Delta G \text{ (kJ/mol)} = 18,64 - 22,6\ 10^{-3}T \qquad (3).$$

It follows from (3) that in the temperature interval of T=700-1000K, ΔG value is sign varying. That is why it is admitted that the Ga,In//As,Sb system refers to the type of reversibly-mutual systems.

With the help of handbooks /11,12/ for the temperature dependence of the free energy of the reaction (2) it was got

$$\Delta G = -37,4-28,1\ 10^{-3}T - 12,6\ 10^{-3}(T-(298) \qquad (4)$$

(T=298 - 800K)

It follows from (4) that $\Delta G < 0$ in the temperature interval under consideration. Therefore, it can be supposed that in the Ga,La //O,S mutual system there is a stable diagonal La_2O_3 -Ga_2S_3. Thus, the mutual system Ga,La//O,S can be broken into two quasi-ternary ones: Ga_2S_3-La_2O_3-La_2S_3 and Ga_2S_3-Ga_2O_3-La_2O_3. As there is no information of phase diagram of the Ga_2O_3-La_2O_3 system in literature, in the present work the liguidus surface is determined only

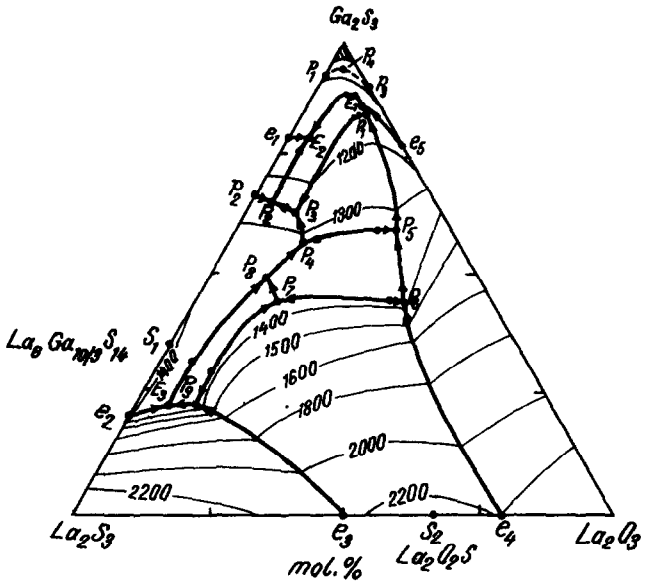

Fig. 1. Liquidus surface of the system La_2O_3-La_2S_3-Ga_2S_3

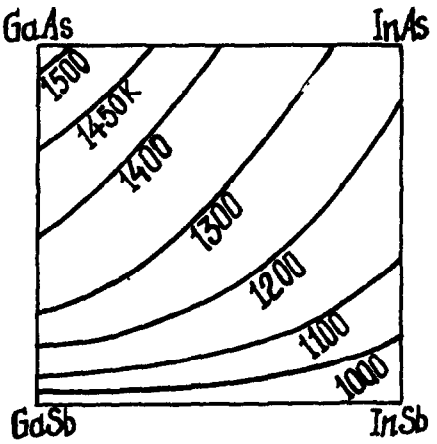

Fig. 2. Liquidus surface of the system Ga,In//As,Sb (calculation according to the eq.(5)).

for the quasi-ternary system Ga_2S_3-La_2S_3-La_2O_3 (Fig.1).To construct the liquidus surface of this quasi-ternary system together with the studied in this work sections it has been used known from /3,4/ the phase diagram of the Ga_2S_3-La_2O_2S section.The most ref-

ractory part of the liquidus-the surface of La_2O_3 compound crystallization is calculated according to the equation supposed in /7/. Quasi-binary systems InSb-GaSb, InAs-GaAs, GaAs-GaSb and InSb-InAs are characterized by the unlimited solubility in liquid and solid states /1/. Naturally, unlimited solubility will also take place in all the concentration range of reversibly-mutual system Ga, In// As, Sb. The liquidus surface of the similar systems is calculated according to the equation /7/

$$T\{(1-x)[(1-K)\Delta S_1^{fus} + K\Delta S_2^{fus}] + X[K\Delta S_3^{fus} + (1-K)\Delta S_4^{fus}] - R((1-x)[(1-K)\ln(1-K)(1-X) + K\ln K(1-X)] + x[K\ln KX + (1-K)\ln X(1-K)])\} = (1-X)[(1-K)\Delta H_1^{fus} + K\Delta H_2^{fus}] + X[K\Delta H_3^{fus} + (1-K)\Delta H_4^{fus}] - (1-K)D_{1-4} - KD_{2-3} - (1-X)D_{1-2} - XD_{3-4} \quad (5)$$

where X, K are equivalent fractions of In and As in liquid solution of composition $Ga_{1-x}In_xAs_kSb_{1-k}$; 1-GaSb; 2-GaAs; 3-InAs; 4-InSb; D_{i-j} is the difference of integral free energies of equilibrium liquid and solid solution mixing, that is calculated from the phase diagram of boundary quasi-binary systems. The values H_i^{fus} and S_i^{fus} are borrowed out of /10/. The difference in calculated and experimental values of liquidus temperature is within 10-15°. The results of calculation according to the eq.(5) are presented in Fig.2.

Thus, the present work shows that using the thermodynamic method one can minimize essentially the number of experiments according to DTA for determining the fusion diagram of ternary mutual systems.

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