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Thermodynamic modelling of liquidus in the system Li-Ga

D N Kamaev and A V Sharov

Kurgan state university, Kurgan, Russia

E-mail: Kamayev_DN@kgsu.ru

Abstract. On the basis of available experimental data of the state diagram Li-Ga system, thermodynamic simulation of liquidus in the system Li-Ga has been carried out with using of the model of subregular solutions. From the results of calculations energy parameters of mixture of system components in a melt have been determined and the temperature dependences of constants of melting of chemical compounds in the system have been found out. The developed calculated liquidus line of the system corresponds to the available experimental data of the state diagram. The results of the research allow determining the dependence of activities of components in melt on atomic per cent and can be used while growing monocrystals of gallium nitride in lithium flux.

1. Introduction

Gallium nitride has widespread application as a long-term semiconducting material for electronics industry, in particular for the production of white, blue and ultraviolet light-emitting diodes, lasers ultraviolet transducers, power and high frequency electronics. One of the ways of its monocrystal growth is in the interaction of nitrogen with gallium in the flux, having alkali metal and lithium can be used as one. In this case for the realization of this process the data on the thermodynamics of the diagram of state Li-Ga are necessary as one of the components, which are very few in the literature. On this basis the attempt of thermodynamic simulation of liquidus line of the given system has been made.

2. Methodic of modelling

State diagram of system Li-Ga (figure 1) [1] is plotted in the study [2] on the basis of optimization and generalization of given works [3-5]. The data of phase transformation in the system are presented in table 1. Modeling was carried out with the using of subregular theory [6]. From the point of view of this model the activity of flux compounds of binary system is expressed as

$$a_i = N_i e^{\frac{N_j^2 (N_i Q_{ij} + N_j Q_{ji})}{RT}},$$

where N is atomic per cent of a component in the solution (flux), Q is energies of compound mixing, R is a universal gas constant, T is temperature.

In this case in the view of common expression $\mu = \mu^0 + RT \ln a$ equations for the chemical potentials of first and the second components in the system can be written in the following way:



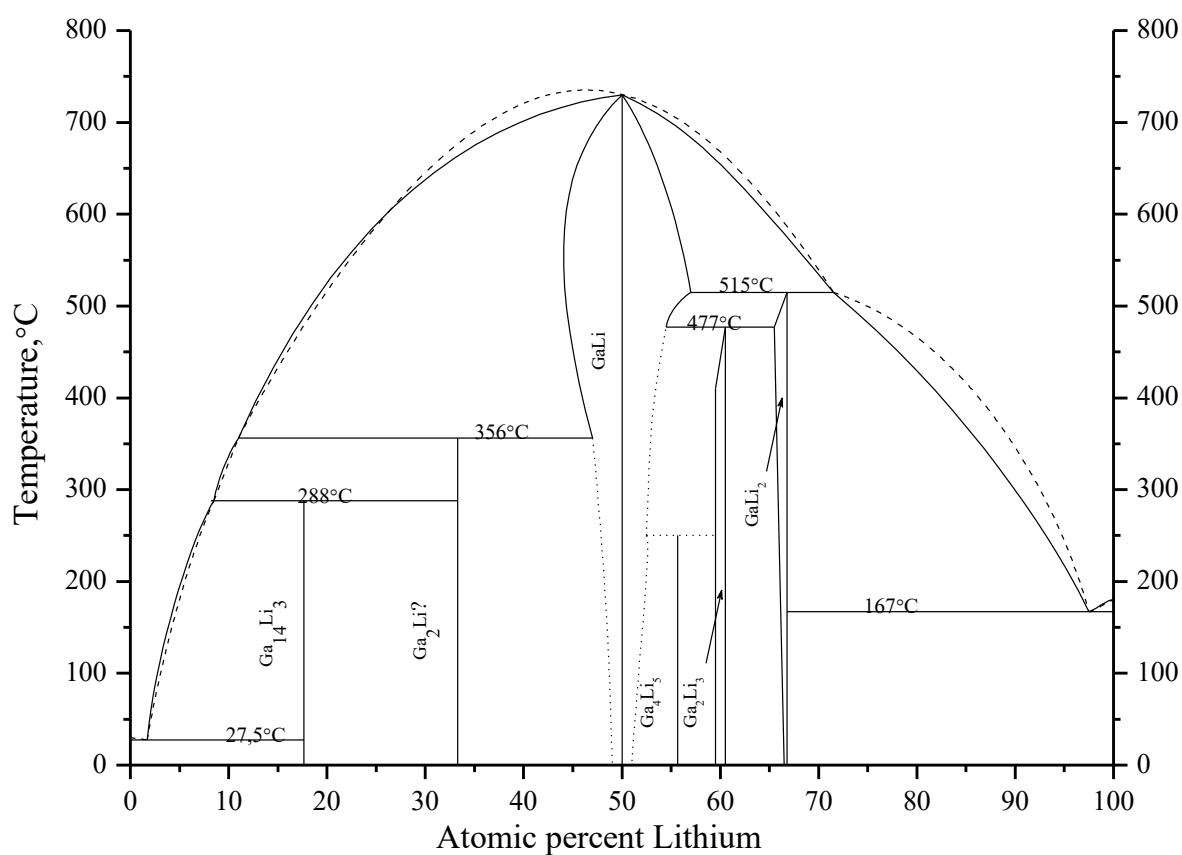


Figure 1. Diagram of the state of system Ga–Li: data [2] (*full line*), calculated data (*broken line*).

Table 1. Nonvariant points in system Li–Ga [2].

№	Type of change	Phases	Composition, at. % Li	Temperature, °C
1	Eutectic	Ga + Flux + Ga ₁₄ Li ₃	1.7	27.5
2	Peritectic	Flux + Ga ₁₄ Li ₃ + Ga ₂ Li	8	288
3	Peritectic	Flux + Ga ₂ Li + GaLi	11	356
4	Congruent melting	GaLi	50	730
5	Peritectic	GaLi + GaLi ₂ + flux	7.5	515
6	Eutectic	GaLi ₂ + flux + Li	97.5	167
7	Peritectoid transformation	GaLi + Ga ₂ Li ₃ + Ga ₄ Li ₅	-	-
8	Peritectoid transformation	GaLi + GaLi ₂ + Ga ₂ Li ₃	59	477

$$\mu_1 = \mu_1^0 + RT \ln x_1 + x_2^2 (x_1 Q_{12} + x_2 Q_{21})$$

$$\mu_2 = \mu_2^0 + RT \ln x_2 + x_1^2 (x_1 Q_{12} + x_2 Q_{21}),$$

where μ_1 and μ_2 are chemical potentials of the first and second components in the melt, μ_1^0, μ_2^0 are standard chemical potentials, x_1 and x_2 are atomic per cent of the components in the melt, Q_{12}, Q_{21} energies of compound mixing (energetic parameters of mixing). Index «1» refers to Ga, index «2» refers to Li.

$$\ln K = -\frac{A}{T} + B,$$

where K is an equilibrium constant, A and B are numerical coefficients, T is a temperature, and , in the view of the common equation $\mu = \mu^0 + RT \ln a$ is expressed with the use of the chosen model. The more detailed method is given in works [7, 8]. Reference data of melting enthalpy of pure compounds were taken from source [9].

For calculations the equations for equilibriums has been written in the fixed points. Fixed points 1–6 were taken from table 1. After recording all possible equilibriums the received equation system was solved and energetic parameters of compound mixing were found as well as values for coefficients A and B . Knowing all the necessary parameters, liquidus line was calculated, as a function of temperature from the composition.

3. Results

Values of energies of compound mixing are presented in table 2. The received calculated liquidus line corresponds to the experimental satisfactorily and is presented in picture 1.

Table 2. Energies of compound mixing in flux Li–Ga (J/mole).

Component	Ga	Li
Ga	0	2161
Li	–2722	0

Calculation values of coefficients A and B for constants of melting of chemical compounds in the system are presented in table 3.

Table 3. Calculation values of coefficients A and B for constants of melting of chemical compounds in system Li–Ga.

Compound	Melting temperature, °C	Melting character	$\ln K = -A/B + T$	
			A	B
Ga ₁₄ Li ₃	288	incongruent	1546	–4.906
Ga ₂ Li	356	incongruent	3676	–2.227
GaLi	730	congruent	1132	–0.275
GaLi ₂	515	incongruent	2344	0.912

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