

CALCULATIONS OF THERMAL FUNCTIONS OF GROUP-III NITRIDES

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The change of thermal functions ($\Delta H^0(T)$, $\Delta S^0(T)$, $\Delta G^0(T)$) and formation functions ($\Delta H_f^0(T)$, $\Delta G_f^0(T)$, $K_f(T)$) with temperature for gallium nitride and indium nitride have been formulated based on the reliable experimental data obtained by the use of the same equipment in one laboratory.

Keywords: formation functions, gallium nitride, indium nitride, thermal functions

Introduction

Nitride semiconductors of group-III are currently the main subject of investigations in many laboratories of high-developed electronics technology, because of their great importance and in electronic devices of high power generation. A few physical, structural and stability data were summarized in monographs [1, 2].

The most important from the semiconductors of the group-III nitrides that over a time of few recent decades have been played very radical role in research and development of the modern optoelectronics is crystalline gallium nitride GaN(cr). Many methods for formation of crystalline layers of these semiconductors have been elaborated [1–7] and in the literature one can find many experimental data concerning its thermal properties [8–15].

Indium is applicable in the direct-band-gap semiconductors InN, In_xGa_{1-x}N and In_xAl_{1-x}N and its electronic structures are described in many papers e.g. [16–19]. The vapor pressure data of InN have been given by Jones *et al.* [20] and the thermal data for indium nitride can be found in some papers [21–25].

Knowledge of the thermodynamic phase stabilities and phase diagrams is important for device application of the nitride semiconductors of group-III, since thermal degradation during device operation can be caused in part by thermal decomposition. The main problem concerning both GaN and InN experimental thermal data is concerned with the big discrepancy between data coming from different laboratories and measured by the use of different methods and apparatuses. Therefore consistent thermodynamic models describing thermal function of group-III nitrides combining all available thermal data are urgently needed for calculation of the missing properties. Below one can find such approach to deriva-

tion of the temperature dependence of the thermal and formation function of gallium and indium nitrides based on the consistent experimental data obtained in one laboratory.

The discrepancy between the thermal data of group-III nitrides obtained by the use of different samples, different methods and different equipment in different laboratories, causes that the comprehensive description of their thermodynamic properties is very difficult. That is why we decided to measure the basic thermal properties (heat of formation and heat capacity) of the same sample of gallium nitride and indium nitride using the same equipment in one laboratory.

Experimental

The samples of gallium nitride and indium nitride taken for the experiment [8, 25] were selected very carefully:

- the gallium nitride sample of monocrystalline in hexagonal wurzite structure received from High Pressure Research Center PAS (Warsaw, Poland) achieved the purity exceeded 99.99% (confirmed by X-ray diffraction) [8],
- because of the lack of high quality single-crystal samples, the properties of indium nitride have been measured for black powder sample of crystalline wurzite structure manufactured by Sigma-Aldrich (purity 99.99% based on trace metals). The X-ray diffraction pattern and thermal analysis show that the main impurity in the sample of indium nitride was pure In (the amount of In was finally calculated as 8.4%) [25]. For the experiment the samples were prepared in the same way under controlled nitrogen atmosphere in the glovebox ‘UNI lab’ from M. Braun GmbH (Gutensbergstr. 3, D-85748, Ger-

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many). The standard molar enthalpy of formation for both nitrides have been measured by the use of fluorine combustion calorimetry [23, 24]. It assumes the following values:

- for GaN: $\Delta_f H_m^0$ (298.15 K) = -163.7 ± 4.2 kJ mol⁻¹ [23],
- for InN: $\Delta_f H_m^0$ (298.15 K) = -146.5 ± 4.6 kJ mol⁻¹ [23, 24].

Heat capacity of crystalline gallium nitride GaN was determined by DSC method [26] using DuPont Thermal Analyst 2100, DSC 951 unit. The measurements were carried out in the temperature range 300–850 K at heating rate 5 K min⁻¹, in the atmosphere of dry, pure argon at flow rate 100 mL min⁻¹ [8]. The obtained results [8] allowed for determination of accurate (root mean square deviations: 0.22 J mol⁻¹ K⁻¹ – 0.55%) temperature (T) dependence of the heat capacity (the Leitner *et al.* equation [15]) of gallium nitride ($C_{p,\text{GaN}}^0$) which can be presented in the following form:

$$C_{p,\text{GaN}}^0 = 32960 + 0.162 \cdot 10^{-1} T + 2360170 T^{-2} - 775370000 T^{-3} \quad (1)$$

The measurements of indium nitride heat capacity were made according to the Calvet heat flux principle, widely used in calorimetry, which is distinguished by a heat transducer surrounding the sample whilst the majority of the DSC sensors are of the plate-type transducer. The surrounding transducer imparts great mattering accuracy on the DSC measurements and makes it independent of the properties of the crucible used and of the properties and flow-rate of the sweeping gas. In this case, based on the differential construction, the DSC calorimeter (the difference of heat flux between sample and reference is measured) was adopted to the solid material analysis [25]. In our investigations the continuous method of heat capacity C_p measurements was applied what allowed for a direct determination of C_p for any temperature. The heat capacity of the solid indium nitride was measured, using the Calvet TG-DSC 111 differential scanning microcalorimeter (Setaram, France), in the temperature between (314–978 K) [25].

As it was mentioned the sample of indium nitride was impure with the pure indium as the only important impurity (8.4%). That is why to have the proper values of heat capacity for indium nitride we had to recalculate the experimental data by subtracting, in the adequate proportion (8.4%), the heat capacity data of pure indium [25]. The obtained recalculated results [25] allowed for determination of very accurate (root mean square deviations: 0.019 J mol⁻¹ K⁻¹ – 0.046%) temperature (T) dependence of the heat capacity (the Leitner *et al.* equation [15]) of indium nitride ($C_{p,\text{InN}}^0$) which can be presented in the following form:

$$C_{p,\text{InN}}^0 = 41.400 + 0.499 \cdot 10^{-3} T - 135502 T^{-2} - 26169900 T^{-3} \quad (2)$$

Calculation

Thermodynamic data for condensed states are derived from either measured or estimated information. Having the accurate temperature dependent equation for heat capacity they are obtained normally by its appropriate integration. The normal relationships between the thermal functions are as follows:

$$H^0(T) = \int_0^T C_p^0(T) dT \quad (3)$$

$$S^0(T) = \int_0^T [C_p^0(T)/T] dT \quad (4)$$

$$[G^0(T) - H^0(298.15 \text{ K})]/T = -S^0(T) + [H^0(T) - H^0(298.15 \text{ K})]/T \quad (5)$$

where C_p^0 – standard molar heat capacity at constant pressure, H^0 – standard molar enthalpy, S^0 – standard molar entropy, G^0 – standard molar Gibbs energy, T – temperature (K).

So, in our case, assuming the Leitner *et al.* [15] equation, as the model equation, the temperature dependence of the heat content (Eq. (3)) can be derived by integration of Eq. (3) with respect to temperature and will have the following form:

- for GaN (Eq. (1)):

$$[H^0(T) - H^0(298.15 \text{ K})] = 32960T + 8.100 \cdot 10^{-3} T^2 - 2360 \cdot 10^6 T^{-1} + 3.877 \cdot 10^8 T^{-2} - 6.992 \cdot 10^3 \quad (6)$$

- for InN (Eq. (2)):

$$[H^0(T) - H^0(298.15 \text{ K})] = 41.400T + 0.250 \cdot 10^{-3} T^2 + 1.355 \cdot 10^5 T^{-1} + 1.309 \cdot 10^7 T^{-2} - 1.297 \cdot 10^4 \quad (7)$$

In the same way, we can calculate the standard entropy (Eq. (4)) and the standard Gibbs energy (Eq. (5)). They assume the following form for the investigated substance:

- for GaN (Eq. (1)):

$$[S^0(T) - S^0(298.15 \text{ K})] = 32.960 \ln T + 1.620 \cdot 10^{-2} T - 1.180 \cdot 10^6 T^{-2} + 2.584 \cdot 10^8 T^{-3} - 1.891 \cdot 10^2 \quad (8)$$

$$[G^0(T) - G^0(298.15 \text{ K})] = -32.960T \ln T - 8.100 \cdot 10^{-3} T^2 + 2.221 \cdot 10^2 T - 1.180 \cdot 10^6 T^{-1} + 1.293 \cdot 10^8 T^{-2} - 6.992 \cdot 10^3 \quad (9)$$

where:

$$G^0(298.15 \text{ K}) = H^0(298.15 \text{ K}) - 298.15 S^0(298.15 \text{ K}) \quad (10)$$

- for InN (Eq. (2)):

$$[S^0(T) - S^0(298.15 \text{ K})] = 41.400 \ln T + 4.990 \cdot 10^{-1} T + 6.775 \cdot 10^4 T^{-2} + 8.723 \cdot 10^6 T^{-3} - 3.852 \cdot 10^2 \quad (11)$$

$$[G^0(T) - G^0(298.15 \text{ K})] = -41.400 T \ln T - 2.500 \cdot 10^{-1} T^2 + 4.266 \cdot 10^2 T + 6.755 \cdot 10^4 T^{-1} + 4.367 \cdot 10^6 T^{-2} - 1.297 \cdot 10^4 \quad (12)$$

Having these expressions for temperature-dependent thermodynamic functions one can calculate the formation functions for GaN and InN. The formation functions consist of enthalpy of formation, Gibbs energy of formation and equilibrium constant of formation.

Enthalpies of formation at temperatures other than 298.15 K require knowledge of enthalpy of formation at 298.15 K and the enthalpies of the reference elements. The general equation for such calculation can be written as follows:

$$\Delta H_f^0(T) = \Delta H_f^0(298.15 \text{ K}) + [H^0(T) - H^0(298.15 \text{ K})]_{\text{compound}} + \sum [H^0(T) - H^0(298.15 \text{ K})]_{\text{elements}} \quad (13)$$

The Gibbs energy of formation can be calculated from the enthalpy of formation when the entropies of the elements are known, according to the following formula:

$$\Delta G_f^0(T) = \Delta H_f^0(T) - T[S^0(T)_{\text{compound}} - \sum S^0(T)_{\text{elements}}] \quad (14)$$

The equilibrium constant of formation K_f can be found from the following relation:

$$\Delta G_f^0(T) = -RT \ln K_f \quad (15)$$

In the case of investigated compounds we deal with three elements: gallium, indium and nitrogen. So, to calculate the formation functions both for GaN and InN we have to have the accurate temperature dependence of heat capacities for all those elements.

The temperature dependence of heat capacity for pure indium has been calculated previously [25] based on the data from Barin collection [27] and can be described by the following equations:

- solid phase:

$$C_p^0 = 15340 + 0.370 \cdot 10^{-1} T + 32481.2 T^{-2} \quad (16)$$

- liquid phase:

$$C_p^0 = 29.003 + 0.236 \cdot 10^{-4} T + 95271.7 T^{-2} \quad (17)$$

where C_p^0 – heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$), T – temperature (K).

In the case of left pure elements (gallium in solid and liquid phase and nitrogen in gas phase) the temperature dependence of heat capacity has been obtained from the experimental data [28]. The data have

been correlated by the following three different, most popular, polynomial equations:

- in the form proposed by Chen *et al.* [13]:

$$C_p^0 = C_1 + C_2 T + C_3 T^{-2} \quad (18)$$

- in the form proposed by Itagaki and Yamaguchi [14]:

$$C_p^0 = C_1 + C_2 T + C_3 T^{-2} + C_4 T^2 \quad (19)$$

- in the form proposed by Leitner *et al.* [15]:

$$C_p^0 = C_1 + C_2 T + C_3 T^{-2} + C_4 T^{-3} \quad (20)$$

where C_p^0 – heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$), T – temperature (K), $C_1 \dots C_4$ – adjustable parameters.

The minimization function (F) was defined as follows:

$$F = \min \sum_{i=1}^n (C_{p_i}^{\text{exp}} - C_{p_i}^{\text{cal}})^2 \quad (21)$$

where $C_{p_i}^{\text{exp}}$, $C_{p_i}^{\text{cal}}$ – the experimental and calculated heat capacities, respectively, n – the number of experimental data points.

For each equation the adjustable parameters were calculated using the Levenberg–Marquardt algorithm [29].

The results of correlation ($D(C_p)$ and $DR(C_p)$ – the absolute and relative root mean square deviations of heat capacity, respectively) as well as the obtained values of adjustable parameters are shown in Table 1.

$$D(C_p) = \left[\frac{\sum_{i=1}^n (C_{p_i}^{\text{exp}} - C_{p_i}^{\text{cal}})^2}{n-m} \right]^{0.5} \quad (22)$$

$$DR(C_p) = \left[\frac{\sum_{i=1}^n \left(\frac{C_{p_i}^{\text{exp}} - C_{p_i}^{\text{cal}}}{C_{p_i}^{\text{exp}}} \right)^2}{n-m} \right]^{0.5} \quad (23)$$

where $C_{p_i}^{\text{exp}}$, $C_{p_i}^{\text{cal}}$ – the experimental and calculated heat capacities, respectively, n – the number of experimental data points, m – the number of adjustable parameters.

The results of correlation of Ga heat capacities experimental data both for liquid and solid phase obtained by the use of the all three equations (Table 1) are much better than the level of the experimental accuracy (0.5%).

However, the best results of correlation for Ga data in solid phase have been obtained for the Leitner *et al.* [15] and the Itagaki and Yamaguchi [14] equations with four adjustable parameters (Table 1). In this case the ac-

Table 1 Results of correlation of the heat capacity experimental data of Ga and N₂

Equation	Correlation		
	$D(C_p)/J\ mol^{-1}\ K^{-1}$	$DR(C_p)/\%$	Adjustable parameters/ $J\ mol^{-1}$
Ga – liquid phase			
1) Chen <i>et al.</i> [13]	0.093	0.341	$C_1=26.078; C_2=0.227\cdot 10^{-3}$ $C_3=197093$
2) Itagaki and Yamaguchi [14]	0.085	0.320	$C_1=25.352; C_2=0.123\cdot 10^{-2}$ $C_3=247515; C_4=-0.320\cdot 10^{-6}$
3) Leitner <i>et al.</i> [15]	0.094	0.346	$C_1=26.042; C_2=0.246\cdot 10^{-3}$ $C_3=203870; C_4=-0.320\cdot 10^{-6}$
Ga – solid phase			
1) Chen <i>et al.</i> [13]	0.052	0.210	$C_1=21.670; C_2=0.165\cdot 10^{-1}$ $C_3=-48289$
2) Itagaki and Yamaguchi [14]	0.016	0.060	$C_1=27.817; C_2=-0.259\cdot 10^{-1}$ $C_3=-75047; C_4=0.764\cdot 10^{-4}$
3) Leitner <i>et al.</i> [15]	0.014	0.053	$C_1=16.218; C_2=0.294\cdot 10^{-1}$ $C_3=143512; C_4=-15028800$
N ₂ – gas phase			
1) Chen <i>et al.</i> [13]	1.109	3.427	$C_1=32.501; C_2=0.117\cdot 10^{-2}$ $C_3=-259851$
2) Itagaki and Yamaguchi [14]	0.650	1.870	$C_1=29.020; C_2=0.400\cdot 10^{-2}$ $C_3=-67747; C_4=-0.435\cdot 10^{-6}$
3) Leitner <i>et al.</i> [15]	0.706	2.194	$C_1=34.067; C_2=0.826\cdot 10^{-3}$ $C_3=-1408140; C_4=250009000$

curacy of correlation was more than three times better than for the Chen *et al.* [13] equation.

For the liquid phase of Ga the best results of correlation (Table 1), but only slightly better than others, have been obtained by the use of the Itagaki and Yamaguchi [14] equation.

That is why we have decided to use the Itagaki and Yamaguchi equation [14] for description of the heat capacities temperature dependence of pure Ga in our further calculations.

The results of correlation of N₂ heat capacities experimental data (gas phase) show the bigger discrepancy between the used equations. The best results have been obtained by the use of the Itagaki and Yamaguchi [14] equation which correlated the experimental data with accuracy almost twice better than the Chen *et al.* [13] equation and significantly better than the Leitner *et al.* [15] equation. Therefore this equation have been selected for further investigations.

So, finally the temperature dependence of heat capacity for the pure elements can be given by the following equations:

for Ga:

- solid phase:

$$C_p^0 = 27.817 - 0.259 \cdot 10^{-1} T - 75047 T^{-2} + 0.764 \cdot 10^{-4} T^2 \quad (24)$$

- liquid phase:

$$C_p^0 = 25.352 + 0.123 \cdot 10^{-2} T + 247515 T^{-2} - 0.320 \cdot 10^{-6} T^2 \quad (25)$$

for N₂ (gas phase):

$$C_p^0 = 29.020 + 0.400 \cdot 10^{-2} T - 67747 T^{-2} - 0.435 \cdot 10^{-6} T^2 \quad (26)$$

where C_p^0 – heat capacity ($J\ mol^{-1}\ K^{-1}$), T – temperature (K).

Since both gallium and indium form two phases (solid and liquid) in the investigation range (298–1000 K) to calculate the formation functions we need to know the value of the melting temperature and heat of fusion for those elements. These values (shown in Table 2) were taken from the Barin collection [27] for indium and the JANAF Tables [28] for gallium, respectively.

Table 2 Melting temperature and heat of fusion of the pure elements

Element	Melting temperature, T_m/K	Heat of fusion, $L_m/kJ\ mol^{-1}$
Gallium (Ga)	302.92	5.59±0.4
Indium (In)	429.76	3.26±0.3

Thus, the general equation for the enthalpy change for those elements can be written as follows:

$$H^0(T) - H^0(298.15) = \int_{298.15}^T C_p^0(T)_s dT + L_m + \int_{T_m}^T C_p^0(T)_l dT \quad (27)$$

where $C_p^0(T)_s$, $C_p^0(T)_l$ – temperature dependence of heat capacity in solid and liquid phase, respectively, T – temperature (K),

Introducing the Eqs (16) and (17) for indium and Eqs (24) and (25) for gallium into Eq. (27) we can calculate the enthalpy changes for those elements. They assume the following form:

- for indium:

$$H^0(T) - H^0(298.15) = -522698 - 95271T^{-1} + 29003T + 0.11810^{-4}T^2 \quad (28)$$

- for gallium:

$$H^0(T) - H^0(298.15) = -118780 - 247515T^{-1} + 25352T + 0.61510^{-3}T^2 - 0.10710^{-6}T^3 \quad (29)$$

For the third element, nitrogen, the change of enthalpy can be calculated after introducing Eq. (26) to Eq. (3) and it assumes the following form:

$$H^0(T) - H^0(298.15) = -9053.53 + 67747T^{-1} + 29020T + 0.20010^{-2}T^2 - 0.14310^{-6}T^3 \quad (30)$$

Now, introducing to Eq. (13) the measured values of heat of formation (gallium [23], indium [23, 24]) and equation for the change of enthalpy with temperature for nitrides (Eq. (6) for GaN, Eq. (7) for InN) and pure elements (Eq. (28) for Ga, Eq. (29) for In, Eq. (30) for N_2 – remembering that in nitrides there is only one atom of N_2) we can obtain the formulas for description of enthalpies of formation at temperatures other than 298.15 K. They assume the following forms:

- for GaN:

$$\Delta H_f^0(T) = -164977 + 3.87710^8 T^{-2} - 2146358.5T^{-1} - 6.902T - 0.16210^{-3}T^2 + 1.79210^{-7}T^3 \quad (31)$$

- for InN:

$$\Delta H_f^0(T) = -149716 + 1.30910^7 T^{-2} + 196898T^{-1} - 2.1132T - 0.77010^{-3}T^2 + 0.71510^{-7}T^3 \quad (32)$$

To calculate the other thermal function (Eqs (14) and (15)) we need to know the temperature dependence of the entropy both for the compounds and pure elements. The entropy for nitrogen can be obtained directly from Eq. (4) in the following way:

$$S^0(T) = S^0(298.15) + \int_{298.15}^T [C_p^0(T)/T] dT \quad (33)$$

and for gallium and indium (two phases (solid and liquid) in the investigation range) from the following equation:

$$S^0(T) = S^0(298.15) + \int_{298.15}^T [C_p^0(T)_s/T] dT + L_m/T + \int_{T_m}^T [C_p^0(T)_l/T] dT \quad (34)$$

where $S^0(298.15)$ – standard entropy at temperature $T=298.15$ K.

The standard entropy values at $T=298.15$ K for nitrogen and indium were taken from the Barin collection [27] and for gallium from the JANAF Tables [28]. They are given in Table 3.

Thus, introducing Eq. (26) into Eq. (33) the temperature dependence of entropy for nitrogen assumes the following form:

$$S^0(T) = 23.953 + 29.020 \ln T + 33873.5T^{-2} + 0.40010^{-2}T - 0.21810^{-6}T^2 \quad (35)$$

and introducing the Eqs (16) and (17) for indium and Eqs (24) and (25) for gallium into Eq. (34) we obtained the following equation for the temperature dependence of entropy of those elements:

- for Ga:

$$S^0(T) = -84.213 + 25.352 \ln T - 123757.3T^{-2} + 0.12310^{-2}T - 0.16010^{-6}T^2 \quad (36)$$

- for In:

$$S^0(T) = -99.825 + 29.003 \ln T - 47635.9T^{-2} + 0.23610^{-4}T \quad (37)$$

The temperature dependence of entropy for gallium nitride and indium nitride can be calculated directly from Eqs (8) and (11), respectively, if we know the values of their standard entropy at $T=298.15$ K. In the literature [12, 18, 21, 22, 30] there is a discrepancy between standard entropy values for those compounds. For our calculations we decided to use the values (Table 3) given by Unland *et al.* [30] and Onderka *et al.* [21] because they have been calculated in the consistent way by the same group both for GaN and InN. The calculation based on the assumption that at low temperature the heat capacity at constant pressure can be approximated by the Debye model for heat capacity at constant volume expressed by the following equation:

$$C_p^0(T) = 18R \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (38)$$

where R – the gas constant, Θ_D – the Debye temperature: $\Theta_D=654$ K [30] for GaN; $\Theta_D=674$ K [21] for InN.

Table 3 Standard entropy of the components and pure elements

Element	Temperature, T/K	Standard entropy, $S^0(T)/\text{J K}^{-1} \text{mol}^{-1}$
Gallium nitride (GaN)	298.15	30.000
Indium nitride (InN)	298.15	31.600
Gallium (Ga)	298.15	40.828
Indium (In)	298.15	57.823
Nitrogen (N ₂)	298.15	191.609

So, finally the equations describing their temperature dependence of entropy assume the following form:

- for GaN:

$$S^0(T) = -159.1 + 32.960 \ln T + 2.584 \cdot 10^8 T^{-3} - 1.180 \cdot 10^6 T^{-2} + 1.620 \cdot 10^{-2} T \quad (39)$$

- for InN:

$$S^0(T) = -353.9 + 41.400 \ln T + 8.723 \cdot 10^6 T^{-3} + 6.775 \cdot 10^4 T^{-2} + 4.990 \cdot 10^{-1} T \quad (40)$$

Now, introducing to the Eq. (14) the equation for temperature dependence of enthalpies of formation (Eq. (31) for GaN, Eq. (32) for InN) and equation for the change of entropy with temperature for nitrides (Eq. (39) for GaN, Eq. (40) for InN) and pure elements (Eq. (37) for Ga, Eq. (38) for In, Eq. (36) for N₂ – remembering that in nitrides there is only one atom of N₂) we can obtain the formulas for description of Gibbs energy of formation at temperatures other than 298.15 K. They assume the following forms:

- for GaN:

$$\Delta G_f^0(T) = -164977 + 6.902 T \ln T + 1.293 \cdot 10^8 T^{-2} - 1.073 \cdot 10^6 T^{-1} + 79.944 T - 1.320 \cdot 10^{-2} T^2 - 8.890 \cdot 10^{-8} T^3 \quad (41)$$

- for InN:

$$\Delta G_f^0(T) = -149716 + 2.113 T \ln T + 4.367 \cdot 10^6 T^{-2} - 9.745 \cdot 10^4 T^{-1} + 263.939 T - 0.498 T^2 - 1.470 \cdot 10^{-7} T^3 \quad (42)$$

The equilibrium constant of formation K_f can be found introducing Eqs (41) and (42) to Eq. (15) for GaN and InN, respectively. The temperature dependence of K_f assumes the following form:

- for GaN:

$$\ln K_f = -9.615 - 0.830 \ln T - 1.555 \cdot 10^7 T^{-3} + 1.291 \cdot 10^5 T^{-2} + 1.984 \cdot 10^4 T^{-1} + 1.588 \cdot 10^{-3} T + 1.069 \cdot 10^{-8} T^2 \quad (43)$$

- for InN:

$$\ln K_f = -31.745 - 0.254 \ln T - 5.252 \cdot 10^5 T^{-3} + 1.172 \cdot 10^4 T^{-2} + 1.801 \cdot 10^4 T^{-1} + 0.589 \cdot 10^{-3} T + 1.786 \cdot 10^{-8} T^2 \quad (44)$$

Conclusions

The change of thermal functions ($\Delta H^0(T)$, $\Delta S^0(T)$, $\Delta G^0(T)$) and formation functions ($\Delta H_f^0(T)$, $\Delta G_f^0(T)$, $K_f(T)$) with temperature for gallium nitride and indium nitride have been formulated based on the reliable data obtained by the use the same equipment in one laboratory.

The calculations needed auxiliary information concerning the heat capacity of pure elements forming the studied nitrides and their entropy at low temperature.

That is why we have correlated the selected experimental heat capacity data [27, 28] of the pure elements by the use of the three most popular equations used for this purpose [13–15]. The results of correlation of pure In were reported previously [25] and showed that the best approximation (accuracy on the experimental level) have been obtained by the use of the Chen *et al.* equation [13].

The results of correlation of Ga heat capacities experimental data both for liquid and solid phase obtained by the use of the all three equations (Table 1) are much better the level of the experimental accuracy (0.5%). However, the best results of correlation for Ga data in solid phase have been obtained both for the Leitner *et al.* [15] and the Itagaki and Yamaguchi [14] equations (Table 1). For the liquid phase of Ga the best results of correlation (Table 1), have been obtained by the use of the Itagaki and Yamaguchi [14] equation and this equation have been used for further consideration.

The results of correlation of N₂ heat capacities experimental data (gas phase) (Table 1) showed that the best results have been obtained by the use of the Itagaki and Yamaguchi [14] and this equation have been selected for further calculation. It is important to notice that in this case the accuracy of correlation was much poorer that in the case of pure Ga and In.

Finally, we got the set of consistent equations: the Chen *et al.* equation [13] for correlation of pure In, the Itagaki and Yamaguchi equation [14] for pure Ga and N₂ and the Leitner *et al.* equation [15] for GaN and InN, which adjustable parameters have been obtained by the use of the same mathematical procedure [29].

The values of the standard entropy at $T=298.15$ K for GaN and InN were taken from Unland *et al.* [30] and Onderka *et al.* [21] works because they have been calculated in the consistent way by the same group both for GaN an InN.

Based on the correlation equations and the standard entropy values both for pure elements and nitrides we have formulated the recommended temperature dependence for thermal ($\Delta H^0(T)$ – Eqs (6) and (7), $\Delta S^0(T)$ – Eqs (8) and (11), $\Delta G^0(T)$ – Eqs (9) and (12)) and formation functions ($\Delta H_f^0(T)$ – Eqs (31) and (32), $\Delta G_f^0(T)$ – Eqs (41) and (42), $K_f(T)$ – Eqs (43) and (44)) of gallium and indium nitrides.

It is worth noticing also that if we are interested in the use of other equations for temperature dependence of C_p and entropy values for the studied nitrides and their elements we can easily replace them in the proper formulas of the thermal function but we have to remember that in this case it is necessary to check their internal consistency.

List of symbols

$\Delta_f H_m^0$	standard enthalpy of formation, J mol ⁻¹
$\Delta_f G^0$	standard Gibbs energy of formation, J mol ⁻¹
C_p^0	standard molar heat capacity at constant pressure, J mol ⁻¹ K ⁻¹
H^0	standard molar enthalpy, J mol ⁻¹
S^0	standard molar entropy, J mol ⁻¹ K ⁻¹
G^0	standard molar Gibbs energy, J mol ⁻¹
T	temperature, K
K_f	equilibrium constant of formation
$C_1 \dots C_4$	adjustable parameters
$C_{p_i}^{\text{exp}}$	the experimental heat capacity for 'i' experimental point, J mol ⁻¹ K ⁻¹
$C_{p_i}^{\text{cal}}$	the calculated heat capacity for 'i' experimental point, J mol ⁻¹ K ⁻¹
n	the number of experimental data points
m	the number of adjustable parameters
$D(C_p), DR(C_p)$	the absolute and relative root mean square deviations of heat capacity, respectively
R	the gas constant
Θ_D	the Debye temperature, K

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