

THERMODYNAMIC ANALYSIS OF THE Ga-N SYSTEM

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ABSTRACT

The experimental thermochemical and phase diagram data for the Ga-N system have been critically assessed utilizing the CALPHAD (CALculation of PhAse Diagrams) method. A consistent thermodynamic description has been achieved through optimization of Gibbs energy expressions for the GaN compound and (Ga+N) melt, and by accounting for non-ideal behavior in the gas phase at high temperatures. The calculated phase diagram predicts that GaN sublimates incongruently, but can reach its maximum congruent melting temperature if a corresponding overpressure of nitrogen is maintained.

INTRODUCTION

Although significant progress has been made in the development of III-nitride optoelectronic and electronic devices, several challenges remain for the further advancement of gallium nitride processing technology. These challenges include the production of substrate quality bulk crystals and preventing thermal degradation during device processing or operation caused in part by dissociative sublimation and/or thermal decomposition of GaN. Knowledge of the pressure-temperature-composition phase diagram would be helpful in understanding such processes as thin film and bulk crystal growth, conventional and rapid thermal annealing, and contact formation. An experimental determination of the Ga-N system is time consuming and experimentally difficult given the high melting temperature of GaN and extremely high equilibrium nitrogen pressures encountered in this system (1). Thus, the assessment of the available thermochemical and phase diagram data using appropriate thermodynamic models and their interpolation and extrapolations is attractive.

This paper reports a thermodynamic analysis of the Ga-N system utilizing CALPHAD procedures for calculation of phase diagram and thermochemistry by using the BINGSS (2) and Thermo-Calc (3) software packages. Consistent model representations of all available thermodynamic properties in this system allowed calculation of reasonable estimates of missing properties, including the melting and sublimation temperatures of GaN, and the equilibrium nitrogen and gallium partial pressures in the system. The calculation results can further be used in optimizing growth processes.

EVALUATION OF EXPERIMENTAL DATA

Although there has been intense interest in GaN and related materials, very little information on the thermochemistry and phase equilibria in the Ga-N system has been published. The paucity of information is mainly associated with the high N_2 pressures at elevated temperature, and the controversial thermal behavior of GaN (4-12) resulting from the large kinetic barrier encountered for both the synthesis and decomposition of the compound (4,7,8,13-21). The experimental data (9,15,16,22-37), their uncertainties as assessed by the present authors, and the methods of investigation of phase equilibria are summarized in Tables I and II. Only data representing the three-phase equilibrium solid (GaN) + liquid (Ga-rich) + gas (mostly N_2) were used in the assessment. It was believed that measurements that did not involve a liquid phase were not likely to have been made at equilibrium. Also the results of kinetic studies on the growth and heat treatment of GaN (4,7,8,14,15,39-42) were not included in the thermodynamic assessment as they were assumed to have been collected at non-equilibrium conditions.

Thermochemical Data

Thermodynamic functions of pure condensed and gaseous gallium and of liquid nitrogen were taken from the SGTE databank (38). The Gibbs energies of the solid and liquid phases in the Ga-N system were assumed to be pressure independent, while at high pressures the gas phase was considered nonideal. Since the equilibrium partial pressure of Ga vapor in the system is much lower than the corresponding N_2 pressure (32), the gas mixture was assumed to be an ideal solution of non-ideal gases. The thermodynamic description of the nitrogen fugacity as a function of temperature and pressure was evaluated in (43,44). The most recent evaluation (44), implemented in the "Allprops" program (45), includes a fundamental equation explicit in the Helmholtz energy with 28 coefficients valid to $1 \cdot 10^4$ atm and 2000 K. The latter description has been extrapolated to $5 \cdot 10^4$ atm and 2800 K and adopted in the present work.

GaN is essentially a stoichiometric compound with narrow homogeneity range and therefore was treated as a line compound in the assessment. The wurtzite structure was taken as the only stable solid form (46). Although the metastable zincblende structure can be produced in thin films (47,48) and at high-pressure a NiAs-type modification is expected in Group III nitrides (49), these structures were not considered. The reported melting temperature of GaN is controversial and varies from 1973 to over 2573 K (16,28,31-33). It is experimentally difficult to maintain a high equilibrium pressure of nitrogen over GaN during thermal equilibration. An N_2 overpressure that was too low would lead to a loss of nitrogen and formation of gallium droplets on the surface of GaN (7,9,12,22,27,40,50,51). The Ga-rich liquidus temperature at the established N_2 partial pressure would then be the measured temperature, and necessarily below the compound melting temperature. Therefore the highest reported value of 2791 K (52) predicted from the semiempirical theory of electronegativity was pre-selected as the congruent melting temperature of GaN.

The specific heat C_p of GaN in the temperature range 298 to 1773 K was evaluated by (53). The expression is based on low temperature calorimetric measurements in the range of 5 to 300 K (36,37) and extrapolated to higher temperature. The expression adopted is:

$$C_p = 44.377 + 1.260 \cdot 10^{-2} \cdot T - 1.173 \cdot 10^6 / T^2 \quad (\text{J/mol} \cdot \text{K}) \quad [1]$$

The standard enthalpy of formation $\Delta_f^\circ H_{298}$ and absolute entropy $^\circ S_{298}$ determined by calorimetry and derived from partial pressure data are listed in Table II and vary considerably. The second law enthalpy and entropy values (27,31,32) estimated from high-pressure, high-temperature data reflect the derivative of the experimental data and therefore are prone to error. The combustion calorimetric values $\Delta_f^\circ H_{298} = -111.2$ kJ/mol (34) and $^\circ S_{298} = 36.5$ J/mol·K (36) were thus assigned a greater significance in the assessment.

Since the congruent melting temperature of GaN has not been reliably measured, the enthalpy and entropy of fusion are not known. Estimates (52) based on the two-band electronegativity theory yielded values of ΔS_m for InN as 43 J/mol·K, 67 J/mol·K for GaN, and 70 J/mol·K for AlN. In contrast, a comparison with similar III/V compounds (54) predicted much lower entropies of fusion for the Group III nitrides. The value for the AlN, for example, was suggested to be 23 J/mol·K. In the present assessment, the thermodynamic properties at the melting temperature were fitted and compared with the previously estimated values.

Temperature-Composition Phase Diagram

The T-x diagram of the Ga-N system is unknown. There are only four independent sets of measurements of the solubility of nitrogen in liquid gallium in the 1400 to 1850K temperature interval (24,27,30,31). The assessed Ga-rich liquidus curve and these data are shown in Figure 1(a). It is observed that three of data sets (24,27,30) show limited solubility, < 0.5% at N, in this temperature range, while one measurement (31) suggests that up to 1 % at. N can be dissolved in gallium at 1773 K. Based on the steep slope of the liquidus curve, the low solubility of nitrogen in other Group III metals, and comparison with the evaluated Al-N phase diagram (55), it is reasonable to expect the formation of a liquid miscibility gap on the Ga-rich side of the phase diagram. A liquid solution model was selected that was capable of predicting liquid phase immiscibility.

Pressure-Temperature Diagram

The values of the nitrogen partial pressure in equilibrium with (GaN + Ga-rich liquid) mixtures, corresponding to the Ga-rich liquidus on the T-x diagram, are summarized in Table I and shown in Figure 2. The highest temperature at which GaN is experimentally observed to remain stable is 2573 K at a nitrogen pressure of $6 \cdot 10^4$ atm (31). The results

of the most extensive high-pressure study (31) suggest that the temperature extrapolated N₂ pressure is approximately 4.5 · 10⁴ atm at the predicted melting temperature of 2791 K (30). Overall, the P(N₂) dataset shown in Figure 2 is consistent within the assessed experimental errors, except for one set of measurements (27). These data show a lower GaN decomposition temperature at a given N₂ pressure.

THERMODYNAMIC MODELS AND PARAMETER OPTIMIZATION

Solid GaN was treated as strictly stoichiometric in the assessment. Its Gibbs energy is referenced to the stable elemental references (H^{ser}). The enthalpy term H^{ser} is the sum of enthalpy values for gallium and nitrogen in their stable forms at 1 atm and 298 K, i.e., H^{ser} = °H_{Ga,298} + ½ °H_{N₂,298}. Combining the C_p expression [1] with the calorimetric values of Δ_f°H₂₉₈ = -111.2 kJ/mol (34) and °S₂₉₈ = 36.5 J/mol · K (36) gives the following expression:

$$G_{GaN} - H^{\text{ser}} = -128925 + 271.073 \cdot T - 44.377 \cdot T \cdot \ln T - 6.301 \cdot 10^{-3} \cdot T^2 + 5.8639 \cdot 10^5/T \text{ (J/mol)} \quad [2]$$

Only the first two terms in this expression were re-adjusted in the optimization procedure.

The (Ga+N) liquid phase was modeled as a disordered solution using a Redlich-Kister polynomial (56) to describe its excess Gibbs energy. The total Gibbs energy for the liquid is represented by the reference^(ref), ideal^(id), and excess^(ex) contributions in terms of one mole of atoms:

$$G^{\text{Liq}} = {}^{\text{ref}}G^{\text{Liq}} + {}^{\text{id}}G^{\text{Liq}} + {}^{\text{ex}}G^{\text{Liq}}, \quad [3]$$

where

$${}^{\text{ref}}G^{\text{Liq}} = x_{\text{Ga}} \cdot G_{\text{Ga}}^{\text{Liq}} + x_{\text{N}} \cdot G_{\text{N}}^{\text{Liq}}, \quad [3a]$$

$${}^{\text{id}}G^{\text{Liq}} = RT(x_{\text{Ga}} \ln x_{\text{Ga}} + x_{\text{N}} \ln x_{\text{N}}) \quad [3b]$$

$${}^{\text{ex}}G^{\text{Liq}} = x_{\text{Ga}} x_{\text{N}} \sum_j {}^jL_{\text{Ga,N}}^{\text{Liq}} (x_{\text{Ga}} - x_{\text{N}})^j, j = 0 \dots n \quad [3c]$$

In these expressions x_i is the atomic fraction of Ga or N and jL are adjustable model parameters with a temperature dependence given by ${}^jL_{\text{Ga,N}}^{\text{Liq}} = {}^j a + {}^j b \cdot T$.

Accounting for nonideal behavior of the gas phase and assuming that the vapor phase in equilibrium with the compound GaN is mostly the N₂ species, the partial molar Gibbs energy of nitrogen in the liquid mixture was arrived at by applying the Lewis-Randall rule (57):

$$G_N^{\text{Liq}}(P,T,x) = \frac{1}{2} G_{N_2}^{\text{V}}(1\text{atm},T) + RT \cdot \ln f_{N_2}^{\text{pure}}(P,T), \quad [4]$$

where $f_{N_2}^{\text{pure}}(P,T)$ is a fugacity of pure nitrogen gas.

Using equation [4], the experimental nitrogen vapor pressure data along the liquidus line have been introduced into the assessment in a form of $G_N^{\text{VLS}}(P_{N_2}^{\text{VLS}}, T^{\text{VLS}}, x^{\text{VLS}})$, where symbol $^{\text{VLS}}$ denotes conditions at the three-phase equilibrium. Values for $f_{N_2}^{\text{pure}}(P_{N_2}^{\text{VLS}}, T^{\text{VLS}})$ were calculated using the ‘‘Allprops’’ program (45). As an example of the magnitude of the deviation from ideal solution behavior, the fugacity $f_{N_2}^{\text{pure}}$ at the experimental pressure $P_{N_2}^{\text{VLS}} = 2.03 \cdot 10^4$ atm (31) and $T^{\text{VLS}} = 1912$ K is calculated to be $5.57 \cdot 10^5$ atm.

The CALPHAD procedure of obtaining a simultaneous quantitative fit to all available thermochemical and phase diagram data is described elsewhere (2,58). In the optimization process, each set of data from Tables I and II was assigned a certain weight based on the evaluated accuracy of the experimental method, the validity of the results, and the compatibility with other datasets. The thermodynamic functions for the liquid phase and for the GaN compound were optimized using the BINGSS software (2). The best overall fit to the experimental data was achieved with two coefficients for the excess Gibbs energy expression [3c]. The optimized coefficients are listed in Table III along with modified Gibbs energy expression for the compound GaN in which the first two coefficients were reassessed.

Table III. Optimized parameters for the Ga-N system.

Liquid: equation [3c]
${}^0L = -35811.5 + 21.74 \cdot T \quad {}^1L = 55558.6 - 7.68 \cdot T$ (J/mol K)
GaN: equation [2]
$G_{\text{GaN}} - H^{\text{ser}} = -134869 + 270.578 \cdot T - 44.377 \cdot T \cdot \ln T - 6.301 \cdot 10^{-3} \cdot T^2 + 5.864 \cdot 10^5/T$ (J/mol)

RESULTS AND DISCUSSION

The assessed model parameters listed in Table III were used to calculate the phase diagram and thermochemical properties of the Ga-N system. The calculated T-x and P-T projections of the P-T-x phase diagram are shown in Figures 1 and 2, and compared with the experimental data used in this assessment. Except for the Ga-rich eutectic region and the liquid miscibility gap in Figure 1, the calculated lines on these projections correspond to the three-phase equilibrium between GaN compound, liquid (melt), and vapor phase. For example, the temperature dependence of the N₂ and Ga partial pressures on P-T projection in Figure 2 corresponds to the three-phase equilibrium along the liquidus line on T-x projection in Figure 1; and conversely, the liquidus and solidus lines in Figure 1

represent phase relations and compositions at the equilibrium partial component pressures from Figure 2. For simplicity and since the equilibrium gas phase is essentially pure nitrogen, the vapor composition line is not indicated on T-x projection.

The calculated T-x diagram is similar to that of the Al-N system (55), and shows a steep liquidus on the Ga-rich side with an estimated maximum solubility of 7.3 % at. N at the monotectic temperature of 2791.4 K. The enlarged Ga-rich area in Figure 1(a) shows reasonable agreement between the calculated liquidus and the experimental solubility data, except for one measurement (31). The predicted liquid miscibility gap forms a dome with a maximum at 32 % at. N and 4278 K. The calculated congruent melting temperature at 2792 K is nearly identical to the predicted value (52) and is very close to the assessed monotectic temperature.

Figure 2 shows that the calculated equilibrium nitrogen partial pressure is large even on the Ga-rich side of the phase diagram. At the melting temperature of GaN the equilibrium N_2 pressure is calculated to be $4.85 \cdot 10^4$ atm and close to the estimated value $4.5 \cdot 10^4$ atm (30). The assessed nitrogen partial pressures corresponding to the (GaN + Ga-rich melt + gas) equilibrium compare well to the experimental data. The calculated gallium partial pressures for the three-phase equilibrium are 4 to 8 orders of magnitude lower than the corresponding nitrogen pressures and are not supported by any experimental measurements.

It is important to note that two the N_2 and Ga pressure loops shown in Figure 2, which define the pressure-temperature stability region for GaN, do not overlap at any temperature. This implies that the congruent sublimation reaction $GaN^s = Ga^v + \frac{1}{2}N_2^v$, for which the relation $P_{Ga} = 2P_{N_2}$ should hold, is not realized under equilibrium conditions. The incongruent sublimation of GaN is also demonstrated on the isobaric section of the P-T-x diagram, calculated at 1 atm of nitrogen (Figure 3). This figure shows that at standard conditions GaN sublimates incongruently by decomposing into a gas phase (essentially pure nitrogen) and a Ga-rich liquid at 1052 K which is well below its congruent melting temperature. Incongruent sublimation of GaN has to be accounted for in the analysis of thermal stability studies. The pressure dependence of GaN thermal stability as calculated from P-T projection is shown in Figure 4. It demonstrates that the overpressure of nitrogen should always be maintained during processing of GaN at high temperatures, when no kinetic barrier exists for its decomposition. The calculated thermodynamic instability of GaN is supported by the experimental evidence of GaN decomposition below 1073 to 1123 K in vacuum or in nitrogen at 1 atm (9,22,27). Further discussion on defining conditions of synthesis and thermal annealing of Group III nitrides, derived from calculated P-T-x diagrams of the III-N systems, will be presented in subsequent work.

Table IV shows the optimized thermochemical properties for the compound GaN. When compared with the experimental values from Table II, the assessed standard enthalpy of formation and absolute entropy at 298 K are much closer to the direct calorimetric determinations in (34) and (36), respectively, than to the values derived from partial pressure data (27,32).

Table IV. Calculated thermochemical properties for the GaN compound.

$\Delta_f^\circ H_{298}$ kJ/mol	$\Delta_f^\circ S_{298}$ J/mol·K	$^\circ S_{298}$ J/mol·K	T_m K	ΔS_m J/mol·K
-117.1	-99.5	37.0	2792	31.5

The calculated entropy of fusion is comparable with the predicted value of (54), in contrast to the much higher estimates of (52). The absence of experimental information on the enthalpy of mixing in the liquid, which would help in separating optimized Gibbs functions into enthalpy and entropy terms, makes it difficult to choose a reliable value for ΔS_m from an optimization based entirely on the phase diagram and vapor pressure data. Therefore, more experimental data on melt properties are needed to produce a reliable description of the liquid phase in this and other Group III - nitrogen systems.

CONCLUSION

A set of consistent thermodynamic data on phases and phase equilibria in the Ga-N system has been produced based on critically evaluated experimental data. The best description of the thermochemical and phase diagram data has been achieved with the Redlich-Kister polynomial for the liquid phase, a line compound model for GaN, and accounting for non-ideality in the gas phase with an equation of state for nitrogen.

The compound GaN is predicted to melt congruently at 2792 K provided a nitrogen pressure in excess of the equilibrium pressure $4.85 \cdot 10^4$ atm is maintained. The GaN sublimation behavior, as evaluated from the temperature dependence of component partial pressures, is likely to be incongruent in the entire temperature range of GaN existence. Its decomposition temperature at one atmospheric pressure of nitrogen is calculated to be 1052 K. This thermal instability of gallium nitride should be taken into account in annealing experiments at elevated temperatures.

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Table I Summary of experimental data for the three-phase equilibrium:
solid(GaN) + liquid(Ga-rich) + vapor(N₂)

Experimental methods	Temperature range, K	Nitrogen pressure range, atm	Assessed uncertainty, %		(Ref.)
			$\pm\Delta T$	$\pm\Delta P$	
Thermal treatment of GaN in N ₂ , NH ₃	1023-1343	0.83	1	20	9
Thermal treatment of GaN in vacuum	873-1273	10 ⁻⁵ - 1.0	1	20	15
Thermal treatment of GaN in N ₂ in high pressure autoclave	1873	700	1	5	16
Thermal treatment of GaN in N ₂	973-1073	1.0	1	1	22
Thermal treatment of GaN in vacuum	1373	~ 10 ⁻⁵	1	30	23
Formation of GaN from Ga ^l and NH ₃ ; decomposition of GaN in H ₂	1173-1423	6-600	1	20	24
Formation of GaN from Ga ^l and NH ₃	1173-1373	~100	1	20	25
Formation of GaN from Ga ^l and NH ₃	1273	~100	1	20	26
Thermal treatment of GaN in N ₂ in a high pressure vessel	1173-1523	10-7,000	0.5	20	27
Thermal treatment of GaN in N ₂ in a high pressure autoclave	1473-1853	not monitored	2	20	28-30
Growth of GaN from Ga-rich melt in N ₂ ; heat treatment of GaN in N ₂ in high pressure autoclave	1273-2573	100-60,000	1-10	5-15	31,32
Growth of GaN from Ga ^l and NH ₃ ; heat treatment of GaN in vacuum	1223	not monitored	1	-	33

Table II Experimental heat of formation and standard entropy of GaN at 298 K.

Experimental methods	T, K	$\Delta_f^\circ H_{298}$ kJ/mol	$\pm \Delta\Delta H$ kJ/mol	$^\circ S_{298}$ J/mol·K	$\pm \Delta S$ J/mol·K	(Ref)
Derived from P(T) curves	1173-1523	-152.1	15	-	-	27
Derived from P(T) curves	1273-2573	-152.2	15	19.24	4	31,32
Combustion of GaN in a bomb-calorimeter	1223-1373	-111.2*	5	-	-	34
Double comparison with AlN, AlSb and GaSb	298-1500	-104.3	20	36.4	6	35
C _p (T) measurements	5-300	-	-	36.5	3	36
C _p (T) measurements	55-300	-	-	36.9	3	37

*- re-calculated using data for Ga and Ga₂O₃ from (38).

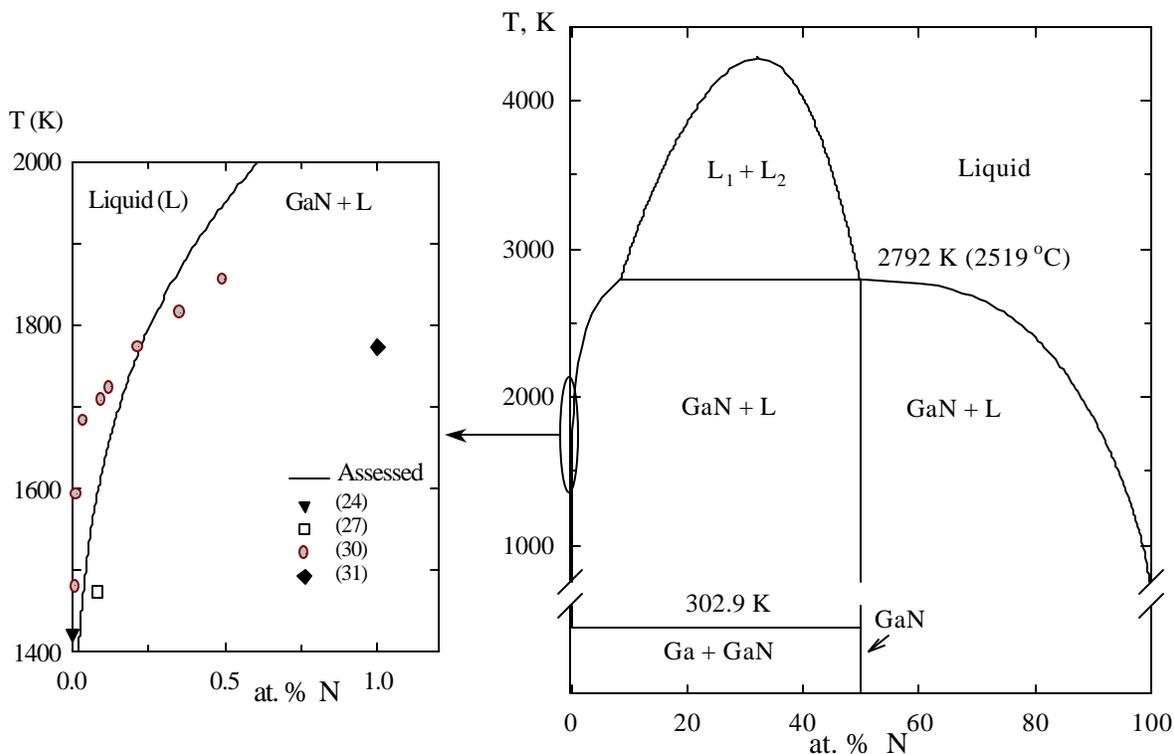


Fig. 1(a) Ga-rich liquidus in the Ga-N system.

Fig. 1(b) T-x projection of the Ga-N system calculated at equilibrium pressure of N_2 .

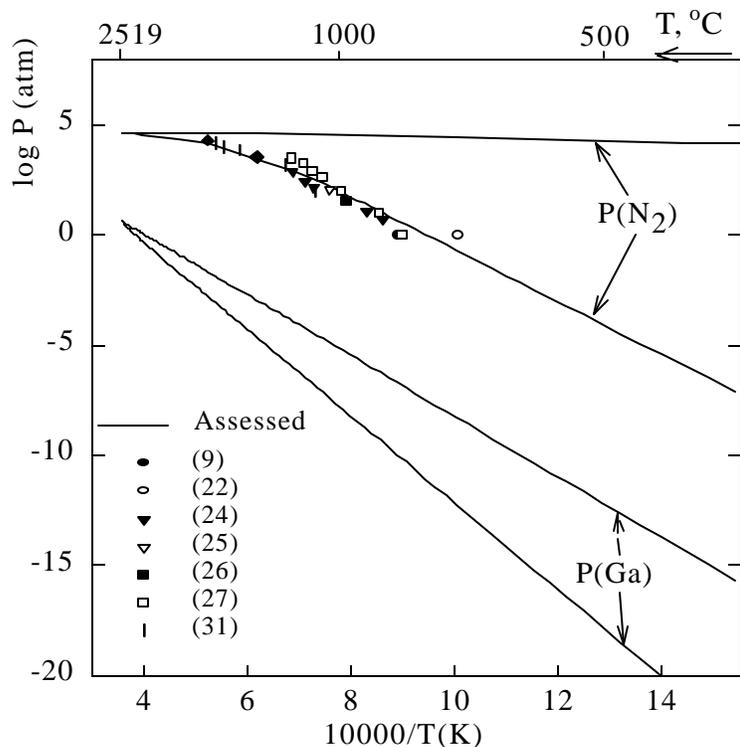


Fig. 2 P-T projection of the three-phase equilibrium GaN + liquid + gas. The area inside each envelope represents the two-phase equilibrium of GaN + gas and corresponds to GaN stability.

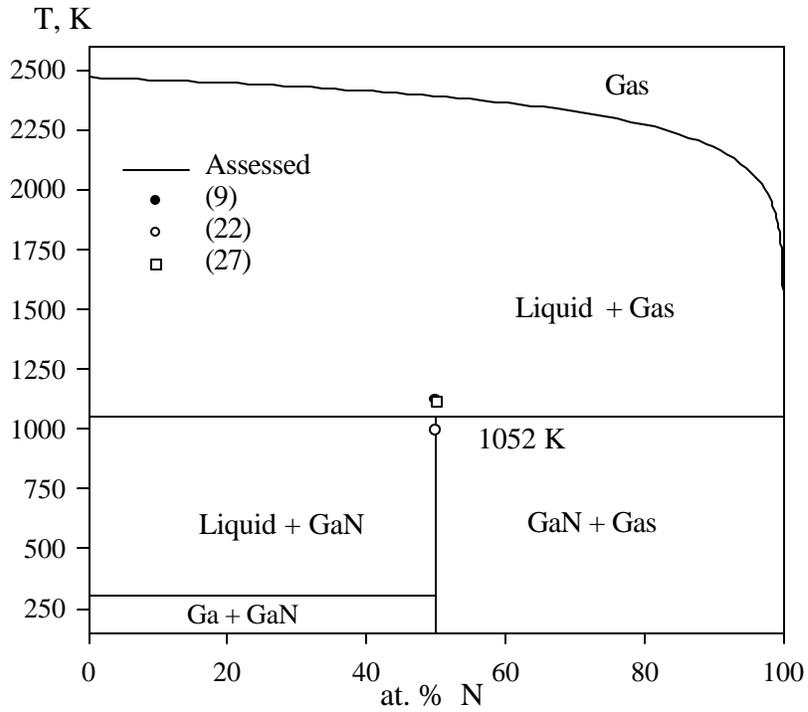


Fig. 3 Section of the P-T-x diagram at 1 atm pressure of N₂ : peritectic line at 1052 K indicates the upper stability limit of GaN above which GaN decomposes incongruently into liquid (Ga-rich) and gas (N₂)

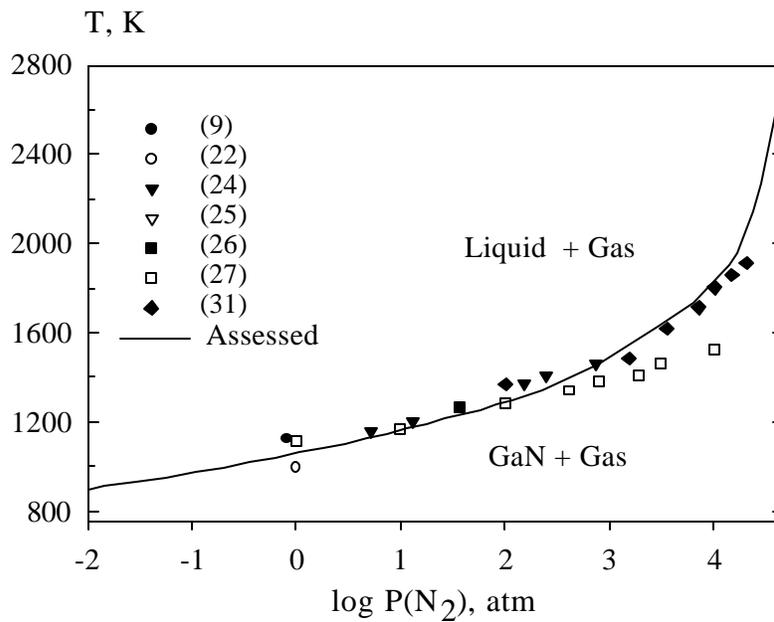


Fig. 4 Pressure dependence of the thermal stability of GaN, calculated from P-T projection in Fig. 2.