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Kinetics and mechanism of free-surface vaporization of groups IIA, IIIA and IVA nitrides analyzed thermogravimetrically by the third-law method

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Abstract

The purpose of this work was to re-measure the enthalpy $\Delta_r H^\circ_T$ of free-surface vaporization of hexagonal (h) Mg_3N_2, AlN, GaN, InN and Si_3N_4 and cubic (c) BN by the third-law method and by comparing them with the enthalpies calculated from thermodynamics to deduce the composition of primary products (bN and $c\mathrm{N}_2$) for the generalized decomposition reaction: $\mathrm{M}_a\mathrm{N}_{b+2c} \leftrightarrow a\mathrm{M} + b\mathrm{N} + c\mathrm{N}_2$. In addition to these nitrides, the literature data were used for the investigation of vaporization of h-Be_3N_2 and c-AlN and c-GaN. The relative standard deviation in determination of $\Delta_r H^\circ_T$ values is $\leq$1% and in determination of $b/(b+2c)$ ratio is better than 2–4%. As a result of this study, some important features in the decomposition mechanism of different nitrides were revealed: the identity in composition of primary products for h-Be_3N_2 and h-Mg_3N_2 ($b/(b+2c) = 0.75$) and h-AlN and h-GaN ($b/(b+2c) = 0.42$) and the release of only molecular nitrogen in cases of c-BN, c-AlN and c-GaN ($b/(b+2c) = 0$). The last feature that was observed earlier for cubic metal oxides [B.V. L'vov, V.L. Ugolkov, F.F. Grekov, Kinetics and mechanism of free-surface vaporization of zinc, cadmium and mercury oxides analyzed thermogravimetrically by the third-law method, Thermochim. Acta 411 (2004) 187–193.] supports the effect of crystal symmetry on the decomposition mechanism. The distance between the closest atoms (N—N) in a crystalline lattice has a secondary or no effect on the composition of primary products. These features might be useful for the development/improving of appropriate technologies (including nano-technologies) for production of solid materials by the chemical vapour deposition.

Keywords: Atomic nitrogen release; Effect of crystal symmetry; Free-surface vaporization of nitrides; Stoichiometry of reactions; Third-law method

1. Introduction

Over the past three decades, the development and commercialization of light-emitting diodes and semiconductor lasers operating in the infrared, red and green regions of the optical spectrum have generated much interest in materials capable of extending the operation of these devices into the blue and ultraviolet regions. The hexagonal nitrides such as AlN, GaN and InN are candidate materials for applications at such energies. Knowledge of conditions and mechanism of their decomposition is vital for film growth, processing of devices and high-temperature operation.

Besides, their decomposition mechanism is of considerable scientific interest. For most of nitrides, the evaporation coefficient is rather low in spite of their congruent vaporization that yields (with the exception of BN) only vapour species. Generally recognized explanation of this phenomenon is based on the difference between the low internuclear distance in the gaseous N_2 molecule (1.07 Å) and much larger distances (2.5–3.5 Å) between closest nitrogen atoms in a lattice of solid nitrides. As assumed, this should cause the difficulty in accommodating on the surface a gaseous molecule, which does not exist as a structural unit in the condensed phase. However, this explanation is now out of date. It has been shown that the so-called 'difficulty' in decomposition is actually related to the difference of composition of primary products from the equilibrium one

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[1]. In case of gaseous products, atomic species (e.g., O, S and N) are released in addition to equilibrium diatomic molecules (O_2, S_2 and N_2). From the recent analysis of crystal structure for 12 different oxides, which evaporate with releasing of molecular oxygen, and for 13 compounds, which evaporate with releasing of atomic oxygen, it was revealed that the first mechanism is observed for all oxides with the cubic crystal structure [2]. The minimum O–O distance for these oxides reaches 4 Å, which is much higher than the internuclear distance in O_2 molecule (1.21 Å). For all other compounds of different (from cubic) singony, the release of oxygen occurs in the form of free O atoms. Therefore, the distance between the closest atoms in a crystalline lattice has a secondary or no effect on the composition of primary products. A decisive role in this difference belongs to a local symmetry in the position of atoms in a crystal. For those oxides, where this symmetry is the highest and environment is close to isotropic, there is the molecular mechanism of dissociation. Oxygen atoms, which are in low-symmetrical positions, leave their sites without recombination.

It is of interest to extend these investigations to decomposition of other solid compounds, in particularly, of nitrides. Such studies have been performed in some of our previous works [1,3–5]. However, analysis of stoichiometry of decomposition reactions was based only on the literature data relating to determination of evaporation coefficients by the Knudsen (effusion) and Langmuir (free-surface) methods. The reliability of these data, especially in case of Langmuir measurements by the second-law method is rather low. As a result, the composition of nitrogen species deduced from these data varied in different publications. In particular, the content of atomic N species in primary nitrogen products reported in [1,4,5] were: 70, 75 and 50% for Be_3N_2; 60, 50 and 50% for h-AlN; 60, 50 and 50% for h-GaN.

The purpose of this work is to re-measure the enthalpy of free-surface vaporization of some available to us nitrides (Mg_3N_2, BN, AlN, GaN, InN and Si_3N_4) by the third-law method and by comparing them with the enthalpies calculated from thermodynamics to deduce the stoichiometry of appropriate vaporization reactions. In conclusion, a possible correlation between the stoichiometry and crystal structure of nitrides will be considered. It is expected that, as in many other cases [4,5], application of the third-law method to these measurements will significantly increase precision and accuracy of experimental results and, therefore, reliability of final conclusions.

2. Theoretical

2.1. Determination of the molar enthalpy of free-surface solid vaporization by the third-law method

In case of a solid compound R vaporized in vacuum into gaseous products A, B and C, that is

$$\mathrm{R\,(s)} \leftrightarrow a\mathrm{A\,(g)} + b\mathrm{B\,(g)} + c\mathrm{C\,(g)} \quad (1)$$

the maximum vapour flow J (in moles) in the absence of any diffusion limitations can be evaluated with the use of the Hertz–Langmuir equation that for simple vaporization of solids (e.g., metals) is expressed as

$$J = \frac{P}{(2\pi MRT)^{1/2}} \quad (2)$$

Here P is the equilibrium vapour pressure of material with the molar mass M at temperature T. To apply this equation to reaction (1), it is necessary to take into account the condition of congruent vaporization

$$\frac{J_\mathrm{A}}{a} = \frac{J_\mathrm{B}}{b} = \frac{J_\mathrm{C}}{c} \quad (3)$$

or

$$\frac{P_\mathrm{A}}{a(2\pi M_\mathrm{A} RT)^{1/2}} = \frac{P_\mathrm{B}}{b(2\pi M_\mathrm{B} RT)^{1/2}} = \frac{P_\mathrm{C}}{c(2\pi M_\mathrm{C} RT)^{1/2}} \quad (4)$$

The total maximum vapour flow J_Σ (in kg m^{-2} s^{-1}) in case of reaction (1) is equal to

$$J_\Sigma = M_\mathrm{A} J_\mathrm{A} + M_\mathrm{B} J_\mathrm{B} + M_\mathrm{C} J_\mathrm{C} = \frac{M_\mathrm{A} P_\mathrm{A}}{(2\pi M_\mathrm{A} RT)^{1/2}} + \frac{M_\mathrm{B} P_\mathrm{B}}{(2\pi M_\mathrm{B} RT)^{1/2}} + \frac{M_\mathrm{C} P_\mathrm{C}}{(2\pi M_\mathrm{C} RT)^{1/2}} \quad (5)$$

On substitution P_B and P_C values for P_A from Eq. (4), we obtain

$$J_\Sigma = \frac{M_\mathrm{R} P_\mathrm{A}}{a(2\pi M_\mathrm{A} RT)^{1/2}} \quad (6)$$

or

$$P_\mathrm{A}\,[\mathrm{bar}] = \frac{a(2\pi M_\mathrm{A} RT)^{1/2}}{\gamma M_\mathrm{R}} J_\Sigma \quad (7)$$

where M_R is the molar mass of reactant. The coefficient $\gamma = 10^5$ Pa bar^{-1} is the conversion factor from Pascal to bar used in the further thermodynamic calculations with participation of P_A.

The next step to determination of the molar enthalpy by the third-law method is related to the evaluation of the equilibrium constant of reaction (1) through the partial pressure P_A. Taking into account Eq. (4), we obtain

$$K_P = P_\mathrm{A}^a \times P_\mathrm{B}^b \times P_\mathrm{C}^c = \delta \times P_\mathrm{A}^\nu \quad (8)$$

where

$$\delta = \left(\frac{b}{a}\right)^b \left(\frac{c}{a}\right)^c \left(\frac{M_\mathrm{B}}{M_\mathrm{A}}\right)^{b/2} \left(\frac{M_\mathrm{C}}{M_\mathrm{A}}\right)^{c/2} \quad (9)$$

and

$$\nu = a + b + c \quad (10)$$

If we insert K_P value from Eq. (8) into the fundamental equation of chemical thermodynamics

$$\Delta_\mathrm{r} H_\mathrm{T}^\circ = T(\Delta_\mathrm{r} S_\mathrm{T}^\circ - R \ln K_P) \quad (11)$$

where $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{T}}$ and $\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{T}}$ are the enthalpy and entropy of reaction (1), we obtain

$$\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{T}} = T(\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{T}} - R\ln\delta - \nu R\ln P_{\mathrm{A}}) \qquad (12)$$

The molar value of enthalpy is equal to

$$\frac{\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{T}}}{\nu} = T\left(\frac{\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{T}}}{\nu} - \frac{R\ln\delta}{\nu} - R\ln P_{\mathrm{A}}\right) \qquad (13)$$

2.2. *Thermodynamic calculation of the reaction enthalpy and entropy*

The $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{T}}$ and $\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{T}}$ values for the reactions with known stoichiometry are calculated by the obvious equations:

$$\begin{aligned}\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{T}} &= a\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{T}}(\mathrm{A}) + b\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{T}}(\mathrm{B})\\ &\quad + c\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{T}}(\mathrm{C}) - \Delta H^{\circ}_{\mathrm{T}}(\mathrm{R})\end{aligned} \qquad (14)$$

and

$$\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{T}} = aS^{\circ}_{\mathrm{T}}(\mathrm{A}) + bS^{\circ}_{\mathrm{T}}(\mathrm{B}) + cS^{\circ}_{\mathrm{T}}(\mathrm{C}) - S^{\circ}_{\mathrm{T}}(\mathrm{R}) \qquad (15)$$

The magnitudes of thermodynamic functions (the standard enthalpies of formation $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{T}}$ and absolute values of entropy S°_{T}) for the components of decomposition reactions of nitrides at different temperatures are listed in Table 1.

3. Experimental

The experiments were carried out with a Netzsch STA 429 instrument on the TG and DSC measuring head. The actual measured quantities were the mass change of the sample per time unit, $\Delta m/\Delta t$, and the absolute crucible temperature. An open alumina crucible 5.7 mm inner diameter and 4.0 mm high was used as a sample container. The reacting materials were commercial high purity powders of Mg_3N_2 (99.5%), GaN (99.99%) and InN (99.99%) from Aldrich, Si_3N_4 (H-1) from Stark and AlN and BN of undefined origin. To prevent the ejection of powder from a crucible under violent evaporation, 1:1 mixtures of some nitrides (Mg_3N_2, GaN and InN) with high purity Al_2O_3 powder were used. A powder sample (5–30 mg) introduced into a crucible was leveled and pressed manually (about 1 kg mm^{-2}) into a flat pellet. The total (outer) surface area of pellet was calculated taking into account the crucible diameter and the thickness of pellet.

The sample chamber was evacuated to a residual pressures about 5×10^{-8} bar with the use of rotation and oil-diffusion pumps. All measurements have been conducted at continuous pumping under isothermal conditions. The heating rate of the sample from the room temperature to intermediate one (20 K lower than the desired temperature) was 20 K min^{-1} and from intermediate to the desired temperature was 2 K min^{-1}. At the beginning of each measuring cycle, the system was heated at the temperature chosen, usually for 10 min, to reach a constant rate of the decomposition.

Table 1
Thermodynamic functions [7–10] used in the calculations

Species	T (K)	State of aggregation	$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{T}}$ (kJ mol^{-1})	S°_{T} (J mol^{-1} K^{-1})
c-AlN	1300	s	−274.2	83.2
Al	1300	g	350.7	195.3
N_2	1300	g	31.5	236.8
N	1300	g	493.5	183.8
h-AlN	1700	s	−254.1	96.7
Al	1700	g	359.0	200.9
N_2	1700	g	45.5	246.2
N	1700	g	501.8	189.4
h-AlN	1800	s	−248.9	99.6
Al	1800	g	361.1	202.1
N_2	1800	g	48.9	248.2
N	1800	g	503.9	190.6
c-BN	1800	s	−187.5[a]	82.7
B	1800	g	596.3	190.7
Be_3N_2	1600	s	−436.5	215.4
Be	1600	g	357.3	171.1
N_2	1600	g	41.9	244.0
N	1600	g	499.7	188.1
c-GaN	900	s	−128.7[b]	86.5[b]
Ga	900	g	287.6	197.8
N_2	900	g	18.2	224.6
h-GaN	1200	s	−112.7[b]	101.9[b]
Ga	1200	g	294.6	204.5
N_2	1200	g	28.1	234.1
N	1200	g	491.4	182.1
h-GaN	1300	s	−107.1[b]	106.2[b]
Ga	1300	g	296.8	206.3
InN	1000	s	−90.6[a]	106.0[a]
In	1000	g	257.0	201.5
N_2	1000	g	21.5	228.1
N	1000	g	487.3	178.3
InN	1100	s	−84.5[a]	111.6[a]
In	1100	g	259.7	204.1
N_2	1100	g	24.8	231.2
N	1100	g	489.3	180.3
Mg_3N_2	1200	s	−353.8	246.0
Mg	1200	g	165.7	177.5
Mg_3N_2	1300	s	−340.8	256.3
Mg	1300	g	167.8	179.1
Si_3N_4	1700	s	−576.6	308.1
Si	1700	g	479.7	204.9

[a] From [7].
[b] From [10].

The absolute value of the decomposition rate, J_{Σ}, for powder samples was estimated using the method proposed in our previous work [6]. It consists in the evaluation of the absolute decomposition rate of a powder sample (reduced to the unit of the outer surface area of a pellet formed by the powder sample in a cylindrical crucible). The value received is lowered by the correction (empirical) factor and then used for the calculation of molar enthalpy by the third-law method. The value of this factor (2.8 ± 0.4), as was shown in [6], does not depend on the temperature, residual pressure of gas in the reactor, grain size and mass of a powder sample.

The changes of the mass and surface area of powders during measuring cycle were also taken into account. A decrease of the surface area, as was checked experimentally, was proportional to $(1-\alpha_m)^{2/3}$ where α_m is the decomposition degree by the time of measurement. (This dependence can be interpreted as a combined result of the reduction of number and size of particles in the process of decomposition.) Temperature was measured with Pt–Pt10% Rh thermocouple placed with its junction immediately below the crucible. Temperature variations in the process of mass-change measurements (usually, during 20–30 min) did not exceed ±0.2 K. A single measurement of the decomposition rate took entirely about 2–3 h.

4. Results and discussion

The experimental conditions and results of determination of the molar enthalpy for vaporization of Mg_3N_2, BN, AlN, GaN, InN and Si_3N_4 by the third-law method are presented in Table 2. The stoichiometry of reaction indicated in the first column was deduced on a basis of the best correlation between the $\Delta_r H_T^\circ/\nu$ value measured experimentally and that calculated for a given temperature from the thermodynamic data listed in Table 1. For illustration of the effect of stoichiometry on the experimental and theoretical $\Delta_r H_T^\circ$ values, we report in Table 3 the corresponding data for AlN. As can be seen, an increase of N species in primary products from 40 to 44% reduces the experimental value by 0.06% and increases the theoretical value by 1.1%. In case of Mg_3N_2, an increase of N species in primary products from 70 to 75% reduces the experimental value by 0.06% and increases the theoretical $\Delta_r H_T^\circ/\nu$ value by 2%. Therefore, taking into account that the relative standard deviation in determination of $\Delta_r H_T^\circ/\nu$ in all cases is ≤1%, the uncertainty in the deduced stoichiometry of reactions (reduced to the content of N species) cannot exceed 2–4%.

The experimental conditions and the results of our calculation by the third-law method of the molar enthalpy for vaporization of hexagonal Be_3N_2, Mg_3N_2, AlN, GaN, InN and Si_3N_4 and cubic BN, AlN and GaN based on the literature data [11–17] are presented in Table 4. It should be noted that all calculations of $\Delta_r H_T^\circ/\nu$ values in Tables 2 and 4 have been performed with Eq. (13), which in contrast with appropriate equations in our earlier works (with the exception of [18]) takes into account the congruent condition of decomposition in the form of additional term $(R \ln \delta)/\nu$. Its values for different nitrides are listed in Table 4. Use of this improved calculation scheme increases the $\Delta_r H_T^\circ/\nu$ values for some nitrides by 7–8 kJ mol^{-1}. This table contains also the $\Delta_r H_T^\circ/\nu$ values measured in original publications by the second-law method. The deduced $\Delta_r H_T^\circ/\nu$ values for Mg_3N_2, BN, AlN, GaN, InN and Si_3N_4 were taken from Table 2. For Be_3N_2, $\Delta_r H_T^\circ/\nu$ value was deduced from a comparison with the experimental value calculated by the third-law method from the literature data. The values of $\Delta_r H_T^\circ/\nu$ for cubic BN, AlN and GaN correspond to the equilibrium reactions with a release of only molecular nitrogen. Decomposition of c-BN deserves special consideration. This is the only nitride under investigation that decomposes with formation of a solid product (boron). Its decomposition can be described by the reaction,

$$\text{c-BN (s)} \leftrightarrow \text{B (g)} + 0.5\text{N}_2 \rightarrow \text{B (s)} + 0.5\text{N}_2 \qquad (16)$$

However, kinetics of c-BN decomposition is determined only by the first stage of reaction. The partial returning of the condensation energy to reactant can be neglected [5] because the equivalent pressure of B for reaction (16) at 1800 K is only one order of magnitude higher than the saturated pressure of metal. Nevertheless, the 2% difference in experimental and theoretical $\Delta_r H_T^\circ/\nu$ values for BN in Table 2 may be related to this approximation.

Table 5 summarizes both the averaged data obtained in this work (Table 2) and the results obtained from analysis of the literature (Table 4). Besides, Table 5 contains the data, which describe the crystal structure of nitrides: the system (singony), space group and N–N minimum distance [19,20]. There are some controversies in definition of the system for Mg_3N_2. In some reference books it is defined as cubic one. At the same time, Mitchell [21] observed for Mg_3N_2 two polymorphous transitions at 823 ± 3 and 1061 ± 5 K. The enthalpies of both transitions were very low. Our attempts to repeat these experiments allowed observing with some degree of certainty only the first transition at 823 K. Nevertheless, taking into account that Be_3N_2 and Ca_3N_2 possess the hexagonal system at high temperatures, we assigned to decomposing Mg_3N_2 the hexagonal system as well.

From analysis of the data listed in Tables 2–5, the following conclusions can be deduced.

1. Special attention must be given to the distinct difference in the decomposition of the cubic and hexagonal nitrides. All cubic nitrides decompose with a release of only molecular nitrogen and all hexagonal nitrides decompose with a release from 32 to 75% atomic nitrogen. The first part of this regularity is in a full agreement with the decomposition mechanism of oxides [2]. This is not the case for hexagonal nitrides. For all oxides and some double oxides ($MgSO_4$ and $BaSO_4$) with the different from cubic system (II, III, IIIa, IV and V), the release of oxygen occurs in the form of free atoms only but not as a mixture of O and O_2 [2].
2. The identical stoichiometry of decomposition reactions is observed for two pairs of nitrides of identical composition (Be_3N_2/Mg_3N_2 and AlN/GaN) in spite of great difference in their decomposition temperatures: 1600/1200 and 1800/1300 K. Apparently, the stoichiometry of decomposition is not dependent on the temperature. However, the stoichiometry of InN decomposition unexpectedly differs from that of AlN and GaN. The reason remains unclear.
3. No correlation between the stoichiometry and minimum N–N distance in crystals are observed. What is more, the

Table 2
Experimental conditions for nitride decomposition in vacuum ($n \times 10^{-8}$ bar) and the results of determination of the molar enthalpy by the third-law method (this work)

Deduced reaction	T (K)	m_0 (mg)	S_0 (mm^2)	α_m	S_m[a] (mm^2)	$(\Delta m/\Delta t)$ (µg s^{-1})	J_Σ[b] (kg m^{-2} s^{-1})	P_A (bar)	ν	$(\Delta S^\circ_T/\nu)$ (J mol^{-1} K^{-1})	$(\Delta_r H^\circ_T/\nu)$ (kJ mol^{-1})	
											Third law	Deduced
$Mg_3N_2 \leftrightarrow 3Mg(g) + 1.5N + 0.25N_2$	1261	10.2[c]	47.4	0.369	34.9	0.987	1.01×10^{-5}	1.17×10^{-7}	4.75	129.8	335.6	335.5
	1232	10.2[c]	47.4	0.206	40.6	0.540	4.75×10^{-6}	7.75×10^{-8}	4.75	130.0	332.3	335.6
	1201	9.8[c]	47.4	0.143	42.8	0.234	1.95×10^{-6}	3.14×10^{-8}	4.75	130.1	333.1	335.8
$BN \leftrightarrow B(g)_\downarrow + 0.5N_2$	1800	30.0	60.0	0.016	59.3	0.51	3.07×10^{-6}	5.63×10^{-8}[d]	1.5	154.7	526.1	538.8
	1799	30.0	60.0	0.013	59.5	0.43	2.59×10^{-6}	4.74×10^{-8}[d]	1.5	154.7	528.7	538.8
$AlN \leftrightarrow Al(g) + 0.42N + 0.29N_2$	1784	30.0	61.8	0.046	59.9	5.53	3.30×10^{-5}	4.06×10^{-7}	1.71	149.4	492.0	488.9
	1785	30.0	61.8	0.066	59.0	6.90	4.17×10^{-5}	5.13×10^{-7}	1.71	149.4	488.8	488.9
$GaN \leftrightarrow Ga(g) + 0.42N + 0.29N_2$	1268	10.0	50.6	0.070	48.2	1.49	1.10×10^{-5}	9.04×10^{-8}	1.71	144.4	361.4	363.1
	1256	5.0[c]	45.7	0.042	44.4	0.53	4.27×10^{-6}	3.51×10^{-8}	1.71	144.5	368.0	363.2
	1277	10.0[c]	50.5	0.20	43.6	2.09	1.71×10^{-5}	1.41×10^{-7}	1.71	144.4	359.3	363.0
	1257	10.1[c]	50.5	0.030	49.5	1.33	9.60×10^{-6}	6.52×10^{-8}	1.71	144.5	361.9	363.2
	1256	10.0[c]	50.5	0.037	49.2	1.35	9.80×10^{-6}	8.06×10^{-8}	1.71	144.5	359.4	363.2
	1266	5.0[c]	45.7	0.046	44.2	1.41	1.14×10^{-5}	9.37×10^{-8}	1.71	144.4	360.5	363.1
	1267	4.5[c]	45.7	0.046	44.2	1.20	9.69×10^{-6}	7.97×10^{-8}	1.71	144.4	362.5	363.1
$InN \leftrightarrow In(g) + 0.32N + 0.34N_2$	1028	10.0[c]	54.6	0.070	52.1	0.137	9.40×10^{-7}	5.93×10^{-9}	1.66	138.6	311.2	307.5
	1008	10.0[c]	54.6	0.040	53.2	0.131	8.79×10^{-7}	5.55×10^{-9}	1.66	138.7	305.8	307.7
	1009	10.0[c]	54.6	0.035	53.3	0.126	8.44×10^{-7}	5.33×10^{-9}	1.66	138.7	306.4	307.7
$\alpha,\beta\text{-}Si_3N_4 \leftrightarrow 3Si(g) + 1.8N + 1.1N_2$	1700	30.0	61.8	0.020	60.9	1.34	7.86×10^{-6}	8.41×10^{-8}	5.9	155.3	501.6	503.2
	1699	30.0	61.8	0.019	61.0	1.29	7.57×10^{-6}	8.10×10^{-8}	5.9	155.3	501.8	503.2

[a] The surface area by the time of measurement calculated by the equation $S_m = S_0(1 - \alpha_m)^{2/3}$.

[b] $J_\Sigma = (\Delta m/\Delta t)/(2.8 S_m)$.

[c] Diluted with Al_2O_3 in 1:1 ratio.

[d] Corresponds to the nitrogen pressure and calculated by the equation $P_{N_2} = J(2\pi M_{N_2} RT)^{1/2}(\gamma M_{N_2})^{-1}$.

Table 3
Effect of reaction stoichiometry on the experimental and calculated values of molar enthalpy

Deduced reaction	ν	$(\Delta S^\circ_T/\nu)$ (J mol^{-1} K^{-1})	$(R \ln \delta/\nu)$ (J mol^{-1} K^{-1})	$(\Delta H^\circ_T/\nu)$ (kJ mol^{-1})	
				Third law[a]	Deduced
$AlN \leftrightarrow Al(g) + 0.5N_2$	1.5	151.2	−1.87	488.3	423.1
$AlN \leftrightarrow Al(g) + 0.40N + 0.30N_2$	1.70	149.5	−4.02	489.1	486.1
$AlN \leftrightarrow Al(g) + 0.42N + 0.29N_2$	1.71	149.4	−4.04	488.9	488.9
$AlN \leftrightarrow Al(g) + 0.44N + 0.28N_2$	1.72	149.3	−4.05	488.8	491.6
$AlN \leftrightarrow Al(g) + N$	2.0	146.7	−1.36	479.3	557.1

[a] At $P_A = 5.1 \times 10^{-7}$ bar and $T = 1785$ K.

minimum N–N distance for InN (3.5 Å) is higher than that for AlN and GaN (3.1 Å) despite the lower content of free N atoms in the primary products of decomposition (32 and 42%, respectively). A generally recognized explanation of a low evaporation coefficients for nitrides [13], which is based on the difference between the low internuclear distance in the gaseous N_2 molecule (1.07 Å) and much larger distances (2.5–3.5 Å) between closest nitrogen atoms in a lattice of solid nitrides, is untrue.

4. From the data listed in Table 4 it can be seen that the values of $\Delta_r H^\circ_T/\nu$ obtained by the third-law method are more reliable than those obtained by the second-law method. In seven from ten instances, the data obtained by the second-law method are lower. The difference in $\Delta_r H^\circ_T/\nu$ for BN reaches 60%. We explain this systematic underestimation by the effect of self-cooling, which was especially significant for BN because of formation of a boron layer on the surface of BN and reduction of the effective value of emittance factor ε [5]. Even if we exclude this discrepancy (for BN) from consideration, the mean relative standard deviation between $\Delta_r H^\circ_T/\nu$ measured by the second-law and the deduced values will be equal to 13%. It is clear that the interpretation of stoichiometry on the basis of $\Delta_r H^\circ_T$ measured by the second-law method would be very unreliable. The correlation between $\Delta_r H^\circ_T/\nu$ measured by the third-law method and the deduced values for AlN, GaN, InN, Si_3N_4 and BN taken from Table 2 is much better. The relative standard deviation is only 2.6%. The value $\Delta_r H^\circ_T/\nu = 296$ kJ mol^{-1} for Mg_3N_2 calculated from the data in [12] is obviously underestimated. It follows from a comparison of this value with $\Delta_r H^\circ_T/\nu = 305$ kJ mol^{-1} measured in [12] for the Knudsen vaporization of Mg_3N_2. The value $\Delta_r H^\circ_T/\nu$ for the free-surface (Langmuir) vaporization cannot be less than the value measured under conditions close to the equilibrium.

Table 4
Experimental conditions for nitride decomposition and the results of our calculation of the molar enthalpy by the third-law method (based on the literature data)

Deduced reaction	Sample	T (K)	P_A (bar)	ν	$(R \ln \delta/\nu)$ (J mol^{-1} K^{-1})	$(\Delta S^\circ_T/\nu)$ (J mol^{-1} K^{-1})	$(\Delta H^\circ_T/\nu)$ (kJ mol^{-1})			Reference
							Second law	Third law	Deduced	
$Be_3N_2 \leftrightarrow 3Be(g) + 1.5N + 0.25N_2$	Pressed pellet	1600	1.5×10^{-9}[a]	4.75	−2.53	129.4	428	481	480.2	[11]
$Mg_3N_2 \leftrightarrow 3Mg(g) + 1.5N + 0.25N_2$	Pressed pellet	1200	1.3×10^{-6}	4.75	−3.60	130.1	238[b]	296	335.8	[12]
h-AlN $\leftrightarrow Al(g) + 0.42N + 0.29N_2$	Pressed pellet	1800	1.7×10^{-7}	1.71	−4.04	149.3	494[b]	509	488.8	[13]
h-GaN $\leftrightarrow Ga(g) + 0.42N + 0.29N_2$	MOCVD film	1300	1.0×10^{-7}	1.71	−5.80	143.9	379	369	362.8	[14]
h-GaN $\leftrightarrow Ga(g) + 0.42N + 0.29N_2$	Pressed pellet	1300	2.8×10^{-7}	1.71	−5.80	143.9	305	358	362.8	[15]
$InN \leftrightarrow In(g) + 0.32N + 0.34N_2$	Polycrystal film	1100	5.4×10^{-8}	1.66	−6.59	137.9	336	312	306.8	[14]
α,β-$Si_3N_4 \leftrightarrow 3Si(g) + 1.8N + 1.1N_2$	Powder	1713	2.9×10^{-7}	5.9	−4.29	155.2	480[b]	488	503.1	[16]
c-BN $\leftrightarrow B(g)_{\downarrow} + 0.5N_2$	Pressed pellet	1800	2.4×10^{-8}[c]	1.5	1.20[d]	154.7	329[b]	539	538.8	[13]
c-AlN $\leftrightarrow Al(g) + 0.5N_2$	MOCVD film	1300	1.2×10^{-8}	1.5	−1.87	153.7	414	399	427.1	[14]
c-GaN $\leftrightarrow Ga(g) + 0.5N_2$	MBE film	900	1.2×10^{-10}	1.5	−3.18	149.1	261	308	283.6	[17]

MOCVD: metal organic chemical vapour deposition; MBE: molecular beam epitaxy.

[a] P_A is reduced by a factor 2.8 to correct the porosity (18%) of pressed pellet.

[b] Calculated in this work on the basis of experimental data reported in original publications.

[c] Corresponds to the nitrogen pressure.

[d] Taking into account that $\delta = (a/b)^a (M_A/M_B)^{a/2}$.

Table 5
Decomposition mechanism of nitrides in vacuum versus their crystal structure (overall data)

Deduced reaction	$b/(b+2c)$[a] (%)	Sample	System	Space group	N–N minimum distance (Å)	T (K)	$(\Delta_r H^\circ_T/\nu)$ (kJ mol^{-1})			Reference
							Second law	Third law	Deduced	
$Be_3N_2 \leftrightarrow 3Be\,(g) + 1.5N + 0.25N_2$	75	Pressed pellet	III	194	2.84	1600	428	481	480	[11]
$Mg_3N_2 \leftrightarrow 3Mg\,(g) + 1.5N + 0.25N_2$	75	Pressed pellet	III[b]	194	3.29	1200	238	296	336	[12]
		Pellet				1231	350	334	336	This work
h-AlN $\leftrightarrow Al\,(g) + 0.42N + 0.29N_2$	42	Pressed pellet	III	186	3.07	1800	494[c]	509	489	[13]
		Pellet				1785	–	490	489	This work
h-GaN $\leftrightarrow Ga\,(g) + 0.42N + 0.29N_2$	42	MOCVD film	III	186	3.17	1300	379	369	363	[14]
		Pressed pellet				1300	305	358	363	[15]
		Pellet				1264	–	362	363	This work
$InN \leftrightarrow In\,(g) + 0.32N + 0.34N_2$	32	Polycrystal film	III	186	3.51	1100	336	312	307	[14]
		Pellet				1015	–	308	308	This work
α,β-$Si_3N_4 \leftrightarrow 3Si\,(g) + 1.8N + 1.1N_2$	45	Powder	III	159, 176	2.82, 2.79	1713	480[c]	488	503	[16]
		Pellet				1700	–	502	503	This work
c-BN $\leftrightarrow B\,(g)_{\downarrow} + 0.5N_2$	0	Pressed pellet	I	216	2.56	1800	329[c]	539	539	[13]
		Pellet				1800	–	527	539	This work
c-AlN $\leftrightarrow Al\,(g) + 0.5N_2$	0	MOCVD film	I	216	3.09	1300	414	399	427	[14]
c-GaN $\leftrightarrow Ga\,(g) + 0.5N_2$	0	MBE film	I	216	3.09	900	261	308	284	[17]

MOCVD: metal organic chemical vapour deposition; MBE: molecular beam epitaxy.

[a] Content of atomic nitrogen species in the reaction $M_aN_{b+2c} \leftrightarrow aM\,(g) + bN + cN_2$.

[b] Polymorphous transition from the cubic (α) to hexagonal (β) structure for Mg_3N_2 at 823 K has been observed in [21] and supported in this work.

[c] Calculated in this work on the basis of experimental data reported in original publications.

5. Conclusions

The application of the third-law method to investigation of kinetics of the congruent dissociative vaporization of metal nitrides has made it possible to interpret the composition of primary nitrogen products (bN and cN$_2$) with a precision, which is inaccessible for the second-law method. The relative standard deviation in determination of $\Delta_r H^\circ_T/\nu$ values is lower than 1% and in determination of $b/(b+2c)$ ratios is better than 2–4%. As a result, some important features in the decomposition mechanism of different nitrides were revealed: the identity in composition of products for hexagonal Be_3N_2 and Mg_3N_2 ($b/(b+2c) = 0.75$) and AlN and GaN ($b/(b+2c) = 0.42$) and the release of only molecular nitrogen in cases of cubic BN, AlN and GaN ($b/(b+2c) = 0$). The last feature was observed earlier [2] for cubic metal oxides and deserves further study in relation to the obvious effect of crystal symmetry on the decomposition mechanism. At the same time, the distance between the closest atoms (N–N) in a crystalline lattice has a secondary or no effect on the composition of primary products. These features might be important not only for fundamental studies of the effect of crystal structure on thermal stability of solids but also for the development of appropriate technologies (including nano-technologies) for production of solid materials by the chemical vapour deposition.

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