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Thermochemistry of $GaBO_3$ and phase equilibria in the Ga_2O_3–B_2O_3 system

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Abstract

Employing a Tian-Calvet-type calorimeter operating in the scanning mode at temperatures from 1120 to 1220 K, the enthalpy change, $\Delta_d H$, associated with the decomposition of $GaBO_3$ ($=1/2\beta\text{-}Ga_2O_3+1/2B_2O_3$(liq.)) and the corresponding decomposition temperature, T_d, were determined: $\Delta_d H=30.34\pm0.6$ kJ/mol, $T_d=1190\pm5$ K. Using the transposed-temperature-drop method the thermal enthalpy, $H(T)-H(295\text{ K})$, of $GaBO_3$ was measured as a function of temperature, T, in the region from 760 to 1610 K; the results obtained are

$$[H(T)-H(295\text{ K})]/(\text{J/mol}) = 104.8\cdot(T/\text{K}) - 31\,300 \quad (760\text{ K} < T < 1190\text{ K}),$$

$$[H(T)-H(295\text{ K})]/(\text{J/mol}) = 138.8\cdot(T/\text{K}) - 41\,480 \quad (1190\text{ K} < T < 1590\text{ K}).$$

On the basis of the experimental results, the enthalpy and entropy of formation, $\Delta_f H$ and $\Delta_f S$, respectively, of $GaBO_3$ from the component oxides were derived:

$$\Delta_f H = -30.34\text{ kJ/mol},\quad \Delta_f S = -25.50\text{ J/(K}\cdot\text{mol) at 1190 K},$$

$$\Delta_f H = -10.55\text{ kJ/mol},\quad \Delta_f S = -5.48\text{ J/(K}\cdot\text{mol) at 298 K}.$$

The enthalpy versus temperature curve shows, apart from a step associated with the decomposition of $GaBO_3$, a further step at 1593 K which is attributed to a monotectic equilibrium.

Keywords: Thermodynamics; Ga_2O_3–B_2O_3 System; Ga_2O_3

1. Introduction

The phase relations in the Ga_2O_3–B_2O_3 system have recently been investigated at temperatures up to1573 K [1]. The phase diagram resulting from these investigations exhibits solely one compound, $GaBO_3$, crystallizing in the calcite structure [2,3]. At higher temperatures the compound decomposes into $\beta\text{-}Ga_2O_3$ and (nearly) pure liquid B_2O_3 [1]. The temperature of the peritectic equilibrium $\beta\text{-}Ga_2O_3/GaBO_3/\text{liquid } B_2O_3$ has differently been reported (at 1191 K [1], near 1273 K [3]).

In the present work the thermochemical properties of $GaBO_3$ are investigated by high-temperature calorimetry, and the enthalpy and entropy of formation of $GaBO_3$ from the component oxides and the thermal enthalpy of $GaBO_3$ as a function of temperature, were determined; a monotectic equilibrium was found at 1593 K. The results obtained are required to establish a physico-chemical basis for GaAs single crystal growth by the liquid encapsulated Czochralski technique using liquid B_2O_3 as encapsulant [4].

2. Materials and experimental procedures

Using the chemicals $Ga(NO_3)_3\cdot9H_2O$ (purity, 99.9 mass%; J. Matthey, Karlsruhe) and H_3BO_3 (Merck, 'purest', Darmstadt) two batches, in the following designated 'A' and 'B', were prepared; each one containing the aforementioned substances in the molar ratio 1:2 and weighing about 20 g was thoroughly mixed and then slowly heated up in a platinum crucible. At temperatures around 800 K a liquid mixture formed which was, after homogenization, further heated up in order to expel the

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water content and the nitrous gases. The remaining solid material was annealed at 1083 K for 168 h; after this treatment it consisted of $GaBO_3$ and small amounts of B_2O_3 glass and β-Ga_2O_3. The glass was completely washed out using hot distilled water. The residue was dried and again annealed at 1083 K for 96 h. Examination of the material thus obtained by X-ray powder diffraction using Cu Kα radiation confirmed the presence of well-crystallized $GaBO_3$ and small amounts of β-Ga_2O_3.

The content of β-Ga_2O_3 in the batches A and B was determined through a gravimetric method: samples of about 0.5 g were separately annealed in a platinum crucible at 1370 K for 2 h; thus the $GaBO_3$ was decomposed. The material was quenched, and the B_2O_3 formed by decomposition was completely extracted using hot distilled water. The residue was dried and reweighed, and from the weight loss the amount of excess β-Ga_2O_3 was calculated: 0.16 mass% β-Ga_2O_3 was determined in batch A and 0.87 mass% in batch B.

While for the measurements of the decomposition enthalpy of $GaBO_3$ samples were made from both batch A and B, all samples for drop calorimetry were prepared from batch B.

The enthalpy of decomposition of $GaBO_3$ was measured in a Setaram twin microcalorimeter HT 1000 suitable for work up to 1250 K. This apparatus is similar to that used in previous work [5] at temperatures up to 1050 K. In these calorimeters the enthalpy effect generated in the active working cell is registered as a temporary thermal imbalance between this cell and the passive reference cell. The imbalance is measured by two 198 couple Pt/Pt-13Rh thermopiles which surround the calorimeter cells and are linked back to back to obtain a difference reading. The difference emf is amplified and digitized, and the signal is fed into a Hewlett-Packard 86B computer which, using a program written in HP-BASIC, determines the area of the calorimetric peak in the emf versus time diagram. The results are displayed on a monitor and plotted for documentation.

Before initiating an experiment, platinum crucibles were inserted into the calorimetric cells, the calorimeter was heated up to about 1120 K, and at that temperature a sample of about 50 mg encased in a 10-μm platinum foil was dropped into the working cell. When the temperature remained constant, the apparatus was heated up at a constant rate of 0.005 K/s. At temperatures in the vicinity of 1160 K, the first calibration was carried out by dropping, from room temperature (=295 K) into the working cell of the calorimeter, a platinum sphere; at 1180 K the decomposition of the $GaBO_3$ sample set in, and after the emf versus time curve had returned to the base line, a second calibration was performed.

The thermal enthalpy of $GaBO_3$ was determined at temperatures from 760 to 1610 K using the transposed-temperature-drop method. Measurements were performed in two different calorimeters: below 1000 K in the Setaram twin microcalorimeter HT 1000 and above 1000 K in the Setaram Multi-Detector High-Temperature Calorimeter which has been described in detail in a previous publication [6]. To initiate a measurement a sample of about 20 mg of $GaBO_3$ was placed in a small platinum capsule made from 10-μm platinum foil and dropped from room temperature (=295 K) into the working cell of the calorimeter maintained at the respective measurement temperature. In a typical experiment, a set of about eight measurements was carried out in air; thereby runs with $GaBO_3$ samples were alternated with calibration runs. Calibration was again performed using platinum spheres as described above.

3. Results and discussion

In order to exemplify the data obtained in measuring the enthalpy of decomposition (Table 1) contains the result from one experiment. Using the masses of the platinum spheres and the known enthalpy function of platinum [7] the calibration factor, relating the area under the calorimetric peak to the enthalpy effect involved, was calculated from the results obtained in the calibration drops. With the average value of the calibration factor, $f = 0.5422$ mJ/area units, the enthalpy effect associated with the decomposition of the respective $GaBO_3$ sample was computed.

A total of 10 experiments was executed; thereby part of the samples were prepared from batch A, others were made from batch B. From the results evaluated as described in Table 1, the enthalpy of decomposition of $GaBO_3$ related to the reaction,

$$GaBO_3 = \frac{1}{2}\beta - Ga_2O_3 + \frac{1}{2}B_2O_3(\text{liq.}), \qquad (1)$$

was determined. The individual data are listed in Table 2. The mean value of the enthalpy of decomposition, $\Delta_d H$, and the respective standard deviation read,

$$\Delta_d H = 30.34 \pm 0.6\ \text{kJ/mol} \qquad (2)$$

Table 1
Results from an experiment made for the determination of the enthalpy of decomposition of $GaBO_3$

No.	Mass of Pt (mg)	Area of calorimetric peak (arbitrary units)	Calibration factor (mJ/area units)
Calibration drops			
1	103.72	24 074.86	0.5359
2	108.52	26 338.52	0.5485

Mass of $GaBO_3$ (mg)	Area of calorimetric peak (arbitrary units)	Enthalpy effect observed (J)
Enthalpy of decomposition measurement		
50.22	21 605.76	11.715

Table 2
Enthalpy of decomposition, $\Delta_d H$, of GaBO

Batch	No.	$\Delta_g H$ (kJ/mol)
A	1	30.52
	2	29.81
	3	30.81
	4	30.11
	5	30.69
	6	30.71
B	1	29.4
	2	30.53
	3	31.15
	4	29.62

The corresponding decomposition temperature, T_d, was found at $T_d = 1190 \pm 5$ K. This temperature was graphically determined from the thermograms of the various measurements, see for example Fig. 1, by drawing in each case a tangent at the point of inflection on the ascending branch of the calorimetric peak and by prolonging the tangent up to the base line. The value obtained in this study is in good agreement with information from DTA measurements in which the decomposition was found to take place at 1191±8 K [1].

The data determined by transposed-temperature-drop calorimetry are shown in Table 3 and are represented in Figs. 2 and 3. In deriving these data from the experimental results corrections taking into account the β-Ga_2O_3 content of the $GaBO_3$ samples were made using the enthalpy function of β-Ga_2O_3 given in Ref. [7]. The line in Fig. 2 through the data points referring to solid $GaBO_3$ (below T_d) was obtained by linear regression; the equation reads,

$$[H(T) - H(295\,\mathrm{K})]/(\mathrm{J/mol}) = 104.8 \cdot (T/\mathrm{K}) - 31\,300 \tag{3}$$

Thus, the thermal capacity of $GaBO_3$ is

$$C_\mathrm{P} = 104.8\ \mathrm{J/(K \cdot mol)} \tag{4}$$

In the range from 1190 to 1593 K, Fig. 2, a mechanical mixture of β-Ga_2O_3 and liquid B_2O_2 exists. A linear fit of all the data points of this range (including the experimental zero at 295 K) gives

$$[H(T) - H(295\,\mathrm{K})]/(\mathrm{J/mol}) = 138.8 \cdot (T/\mathrm{K}) - 41\,480 \tag{5}$$

By taking the difference between the extrapolated line according to Eq. (3) and that according to Eq. (5) another value of the enthalpy of decomposition is obtained:

$$\Delta_d H = 30.2 \pm 0.5\ \mathrm{kJ/mol},$$

which is in full agreement with the value given by Eq. (2).

With respect to a further evaluation of the experimental results given above it is noted that, at the decomposition temperature of $GaBO_3$, the Ga_2O_3 content of the B_2O_3

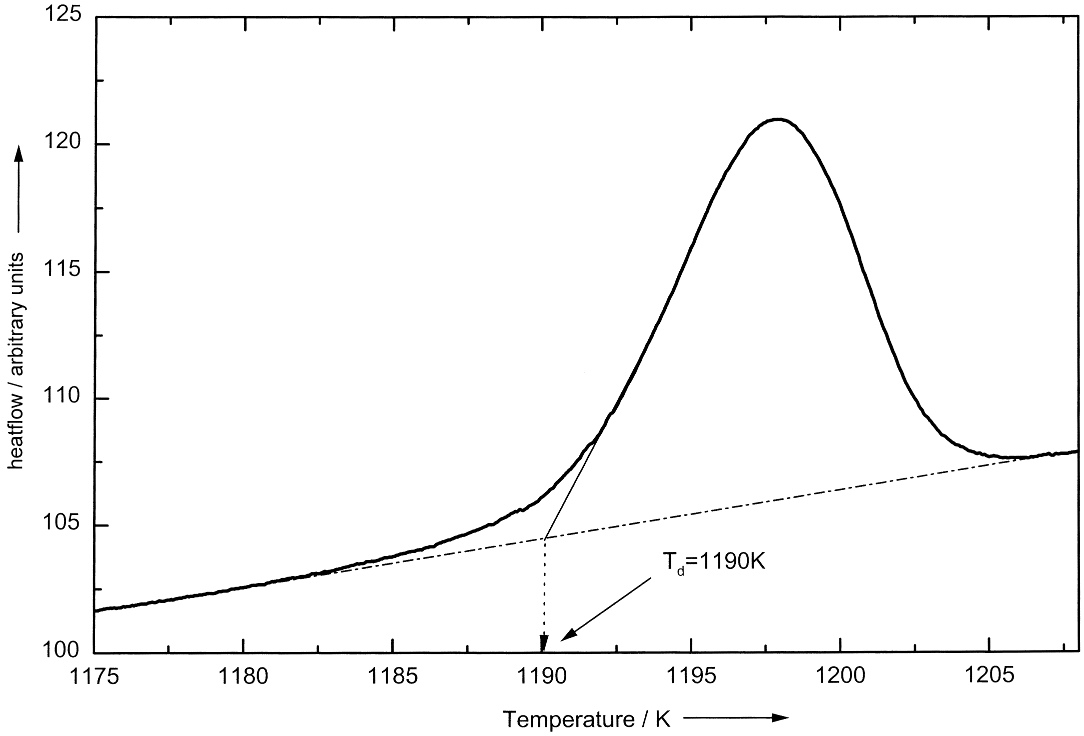

Fig. 1. Thermogram showing the calorimetric peak due to the decomposition of $GaBO_3$ and explaining the determination of the decomposition temperature, T_d.

Table 3
Thermal enthalpy, $H(T)$–$H(295\text{ K})$, of $GaBO_3$ as a function of temperature, T

T (K)	State at T	$H(T)-H(295\text{ K})^a$ (J/mol)
295	$GaBO_3$(sol)	0
759	$GaBO_3$(sol)	47 380±930 (5)
866	$GaBO_3$(sol)	59 500±2340 (6)
956	$GaBO_3$(sol)	67 710±2320 (6)
1057	$GaBO_3$(sol)	80 270±1360 (4)
1078	$GaBO_3$(sol)	81 750±1540 (7)
1088	$GaBO_3$(sol)	84 260±900 (3)
1105	$GaBO_3$(sol)	84 720±2340 (6)
1129	$GaBO_3$(sol)	86 140±2360 (6)
1138	$GaBO_3$(sol)	87 050±1470 (6)
1160	$GaBO_3$(sol)	91 280±2160 (4)
1178	$GaBO_3$(sol)	91 980±1600 (3)
1188	$GaBO_3$(sol)	92 620±2110 (5)
1209	B_2O_3(liq)+β-Ga_2O_3	124 280±10 270 (4)
1281	B_2O_3(liq)+β-Ga_2O_3	137 590±3010 (4)
1326	B_2O_3(liq)+β-Ga_2O_3	142 440±3430 (3)
1397	B_2O_3(liq)+β-Ga_2O_3	153 720±1460 (4)
1564	B_2O_3(liq)+β-Ga_2O_3	173 960±4060 (3)
1573	B_2O_3(liq)+β-Ga_2O_3	177 620±5070 (4)
1581	B_2O_3(liq)+β-Ga_2O_3	178 850±2130 (4)
1586	B_2O_3(liq)+β-Ga_2O_3	179 290±2130 (4)
1588	–	182 610±5240 (3)
1590	–	184 310±7290 (4)
1593	–	190 430±6230 (4)
1595	–	195 900±9680 (4)
1597	–	202 950±2580 (4)
1604	–	200 340±10 090 (4)
1608	–	202 390±5620 (4)

[a] Error is standard deviation from the mean; number in parentheses is number of measurements.

melt amounts to only 0.26 mol% [1], and therefore at this temperature the melt may be regarded as being a pure liquid. Thus, when at 1190 K reaction (1) proceeds from right to left the formation of $GaBO_3$ from its component oxides takes place. Consequently, the enthalpy of formation, $\Delta_f H$, of $GaBO_3$ is

$$\Delta_f H(1190\text{ K}) = -30.34\pm0.6\text{ kJ/mol} \tag{6}$$

The corresponding entropy of formation, $\Delta_f S$, of $GaBO_3$ can be obtained from the relation,

$$\Delta_f S = \frac{\Delta_f H}{T_d},$$

which gives,

$$\Delta_f S = -25.50\text{ J/mol} \tag{7}$$

Using the data from Eqs. (4), (6), and (7) the enthalpy and entropy of formation of $GaBO_3$ from its component oxides at 298 K were calculated:

$$\Delta_f H(298\text{ K}) = -10.55\text{ kJ/mol},$$
$$\Delta_f S(298\text{ K}) = -5.48\text{ J/(K}\cdot\text{mol)},$$

the respective thermochemical data required for β-Ga_2O_3 and solid B_2O_3 in this calculation were taken from thermochemical tables [7].

The stability range of β-Ga_2O_3 and liquid B_2O_3 is delimited at 1593 K by a step in the enthalpy curve (Fig. 3). This indicates the existence of a nonvariant three-phase equilibrium at the aforementioned temperature. Here, if

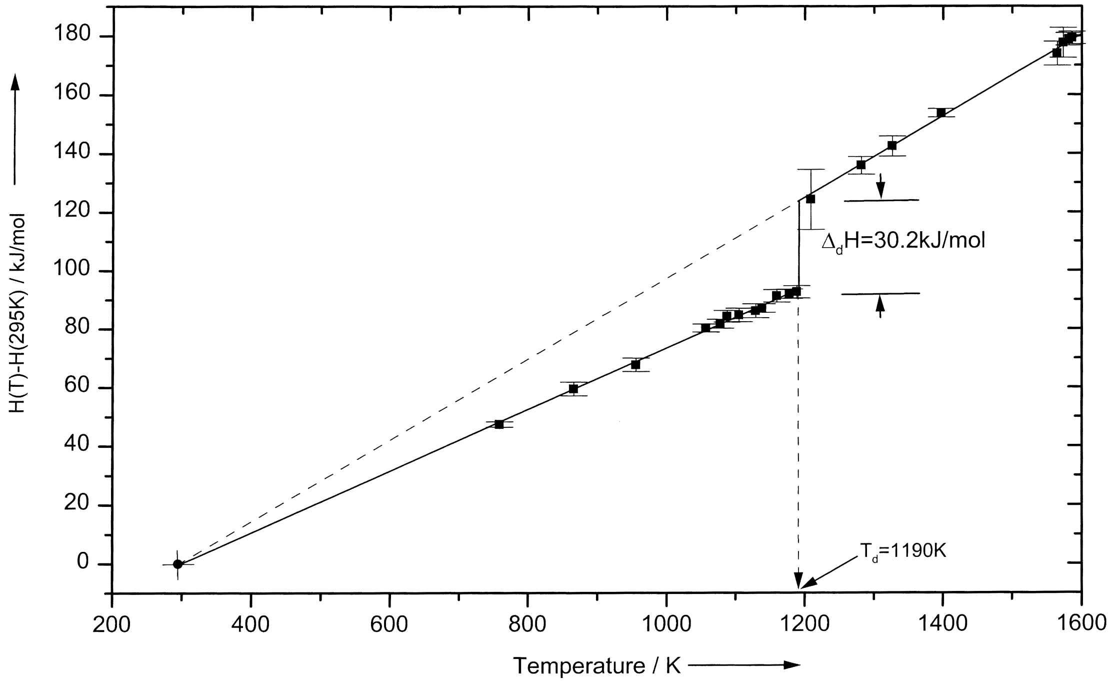

Fig. 2. Thermal enthalpy of $GaBO_3$ versus temperature; results from drop experiments in the temperature range from 760 to 1590 K.

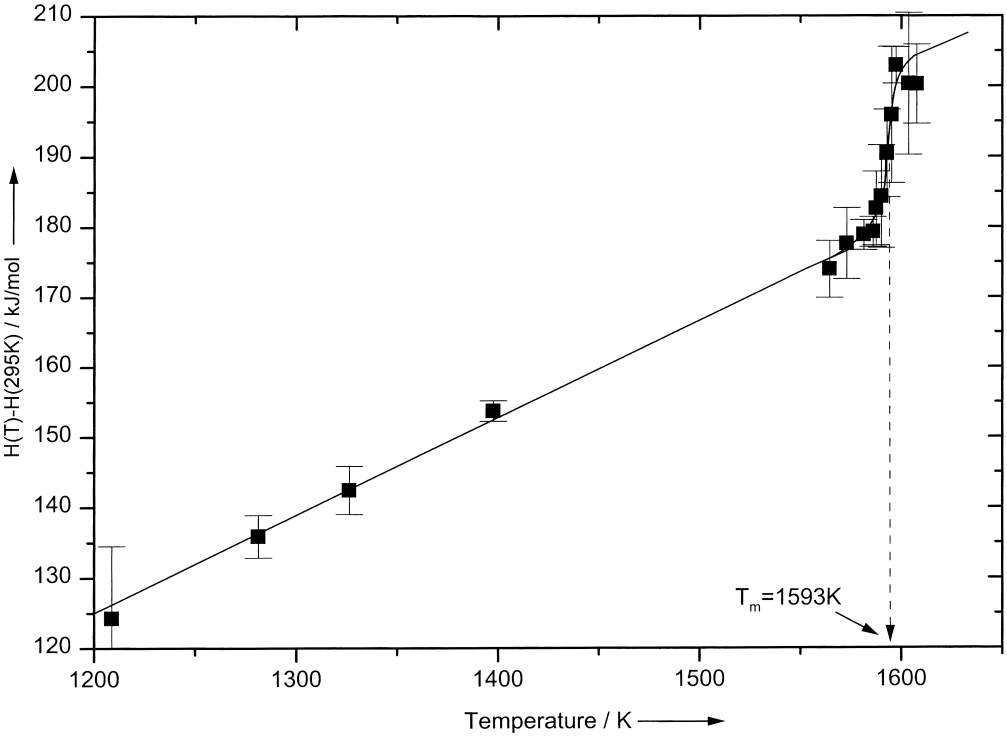

Fig. 3. Thermal enthalpy of $GaBO_3$ versus temperature; results from drop experiments in the temperature range from 1200 to 1610 K; monotectic temperature, T_m.

heat is fed to the pair of phases β-Ga_2O_3/liquid B_2O_3, these will react to form a third phase while either β-Ga_2O_3 or liquid B_2O_3 will disappear. Since at higher temperatures a solid phase does not exist, the third phase is expected to be a liquid. Thus, it appears that the three-phase equilibrium at 1593 K is monotectic. This finding has recently been corroborated by thermochemical calculation showing that a miscibility gap exists in the liquid state [8].

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