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# HEAT CAPACITY OF INDIUM NITRIDE

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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). The temperature dependence of the heat capacity can be presented in the following form: $C_p$=41.400+0.499·$10^{-3}T$–135502$T^{-2}$–26169900 $T^{-3}$.

***Keywords:*** *heat capacity, indium nitride*

## Introduction

Nitride semiconductors of group-III are currently experiencing a most exciting development. It is the main subject of investigations in many laboratories of high-developed electronics technology, because of their great importance in modern optoelectronic and in electronic devices of high power generation.

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. [1–4]. The vapor pressure data of InN have been given by Jones *et al*. [5]. Onderka *et al*. [6] presented the thermodynamics and phase stability in the In–N system. The heat capacity of solid InN have been measured by Krukowski *et al*. [3] using differential scanning calorimeter Setaram DSC 92 in the temperature between 153–300 K and Leitner *et al*. [7] in the temperature range of 305–390 K by the Calvet-type Setaram C-80 calorimeter. Our previous studies concerned the standard molar enthalpy of formation of InN ($\Delta_f H^0_m$(298.15 K)=–146.5+4.6 kJ mol$^{-1}$), which have been obtained by fluorine combustion calorimetry [8, 9]. Now we present results of the heat capacity $C_p$ of InN obtained by the use of the Calvet TG-DSC 111 differential scanning microcalorimeter (Setaram, France) in the temperature range between (314–978 K).

## Experimental

### Materials

Indium nitride black powder sample of crystalline wurtzite structure was manufactured by Sigma-Aldrich (purity 99.99% based on trace metals). Chemical analysis showed (in %) the mass of the following elements: In: 89.3±3, N: 9.86±0.16 and impurities: C: 0.22±0.02, and trace metals; Na: 51.6 ppm, Ca: 27.0 ppm, Fe: 21.8 ppm, Ga: 17.3 ppm, Te: 17.0 ppm, Sn: 8.4 ppm, Ag: 5.9 ppm, Mg: 5.9 ppm, Cr: 4.7 ppm; Ni: 1.7 ppm, Zn: 1.7 ppm. The X-ray diffraction pattern (made by Dr. Z. Kaszkur) and thermal analysis show that the most impurity in the sample of indium nitride was pure In (the amount of In was finally calculated as 8.4%).

### Methods

The measurements 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 difference of heat flux between sample and reference is measured) the DSC calorimeter was adopted to the solid material analysis.

The continuous method of heat capacities, $C_p$ measurements was applied in our investigations. This method allows for a direct determination of $C_p$ for any temperature. The precise determination of $C_p$ requires two identical tests under identical experimental conditions:

- the first measurement is carried out with two empty cells (blank measurement), prepared in the glove box, as well as samples
- the second measurement is carried out with sample *vs*. reference cell

The formula of $C_p$ determination is as follows:

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$$C_\mathrm{p}(T)=\frac{HF_\mathrm{sample}-HF_\mathrm{blank}}{\mathrm{sensitivity}(T)\mathrm{mass}_\mathrm{sample}\dfrac{\mathrm{d}T}{\mathrm{d}t}}$$

where $HF_\mathrm{sample}$ and $HF_\mathrm{blank}$ are the heat fluxes [mW] of sample and blank measurements, respectively.

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, Germany). The samples about 100 mg were placed in stainless steal crucibles of the total volume of 150 μL. The stainless steal cover was crimped with nickel seal with use of crimping press. The DSC measurements were made in the temperature range 314–978 K, with a temperature scan rate of 0.5 K $\mathrm{min}^{-1}$.

The measured, in such a way, values of heat capacities as a function of temperature are shown and Fig. 1.

As it was mentioned the sample of indium nitride was impure with the pure indium as the only important impurity (8.4%). It can be seen as a phase transition (solid–liquid) at 429.75 K in Fig. 1. That is why to have the proper values of heat capacities 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. The indium data have been taken from Barin [10] and correlated by the following equations:

- solid phase: $C_\mathrm{p}$=15.340+0.370·$10^{-1}T$+32481.2$T^2$
- liquid phase: $C_\mathrm{p}$=29.003+0.236·$10^{-4}T$+95271.7$T^2$

where $C_\mathrm{p}$ – heat capacity [J $\mathrm{mol}^{-1}$ $\mathrm{K}^{-1}$], $T$ – temperature [K].

The recalculated values of indium nitride heat capacity are plotted in Fig. 2 and their numerical values are given in Table 1.

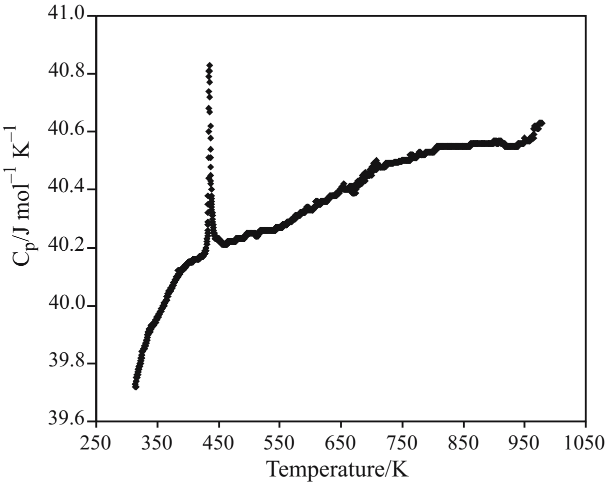

**Fig. 1** Experimental heat capacity of impure (8.4% In) InN

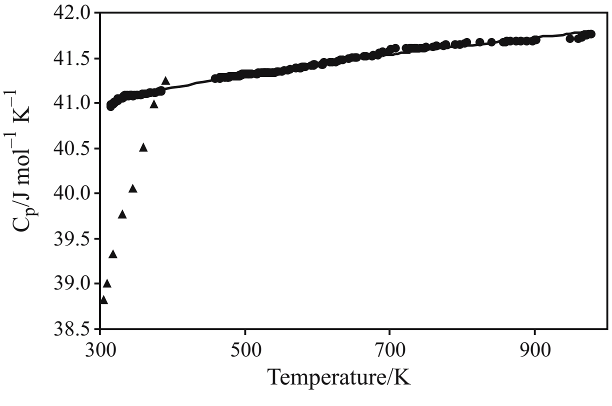

**Fig. 2** Comparison of the ● – experimental; — – Eg. 2 and the ▲ – literature data of InN heat capacity

## Calculation of heat capacity data

The experimental data have been correlated by three different polynomial equations describing the heat capacity in the solid phase:

- in the form proposed by Chen *et al.* [11]:

$$C_\mathrm{p}=C_1+C_2T+C_3T^{-2}$$

- in the form proposed by Itagaki and Yamaguchi [12]:

$$C_\mathrm{p}=C_1+C_2T+C_3T^{-2}+C_4T^2$$

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

$$C_\mathrm{p}=C_1+C_2T+C_3T^{-2}+C_4T^{-3}$$

The minimization function ($F$) was defined as follows:

$$F=\min\sum_{\mathrm{i}=1}^{\mathrm{n}}[C_{\mathrm{p\,i}}^{\mathrm{exp}}-C_{\mathrm{p\,i}}^{\mathrm{cal}}]^2$$

where $C_{\mathrm{p\,i}}^{\mathrm{exp}}$, $C_{\mathrm{p\,i}}^{\mathrm{cal}}$ – experimental and calculated heat capacities, respectively, $n$ – number of experimental data points. For each equation the adjustable parameters were calculated using the Levenberg–Marquardt algorithm [14].

The results of correlation ($D(C_\mathrm{p})$ and $DR(C_\mathrm{p})$ – absolute and relative root mean square deviations of heat capacity, respectively) as well as the obtained values of adjustable parameters are shown in Table 3.

$$D(C_\mathrm{p})=\left\{\frac{\sum_{\mathrm{i}=1}^{\mathrm{n}}[C_{\mathrm{p\,i}}^{\mathrm{exp}}-C_{\mathrm{p\,i}}^{\mathrm{cal}}]^2}{n-m}\right\}^{0.5}$$

$$DR(C_\mathrm{p})=\left\{\frac{\sum_{\mathrm{i}=1}^{\mathrm{n}}\left[\dfrac{C_{\mathrm{p\,i}}^{\mathrm{exp}}-C_{\mathrm{p\,i}}^{\mathrm{cal}}}{C_{\mathrm{p\,i}}^{\mathrm{exp}}}\right]^2}{n-m}\right\}^{0.5}$$

**Table 1** Recalculated experimental values of InN heat capacities

| $T$/K | $C_p$/J mol$^{-1}$ K$^{-1}$ | $T$/K | $C_p$/J mol$^{-1}$ K$^{-1}$ | $T$/K | $C_p$/J mol$^{-1}$ K$^{-1}$ | $T$/K | $C_p$/J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 313.93 | 40.97 | 476.07 | 41.28 | 521.02 | 41.34 | 667.69 | 41.51 |
| 315.21 | 40.98 | 476.95 | 41.28 | 523.38 | 41.34 | 674.55 | 41.53 |
| 317.02 | 40.99 | 477.34 | 41.29 | 524.96 | 41.34 | 677.15 | 41.54 |
| 317.92 | 41.00 | 478.43 | 41.30 | 526.20 | 41.34 | 683.48 | 41.54 |
| 319.08 | 41.00 | 479.07 | 41.30 | 527.10 | 41.34 | 684.84 | 41.56 |
| 320.11 | 41.01 | 480.13 | 41.30 | 527.74 | 41.34 | 689.10 | 41.57 |
| 321.30 | 41.02 | 480.82 | 41.30 | 528.71 | 41.34 | 697.68 | 41.57 |
| 322.64 | 41.02 | 481.24 | 41.30 | 530.11 | 41.34 | 700.70 | 41.59 |
| 323.71 | 41.03 | 481.88 | 41.30 | 530.78 | 41.34 | 707.92 | 41.60 |
| 324.09 | 41.05 | 482.57 | 41.30 | 531.65 | 41.34 | 722.54 | 41.61 |
| 327.05 | 41.05 | 482.96 | 41.30 | 532.72 | 41.34 | 726.65 | 41.61 |
| 329.23 | 41.05 | 483.61 | 41.30 | 534.28 | 41.34 | 729.01 | 41.61 |
| 331.21 | 41.06 | 484.27 | 41.30 | 537.05 | 41.34 | 730.78 | 41.61 |
| 332.27 | 41.07 | 484.71 | 41.30 | 537.23 | 41.34 | 733.41 | 41.61 |
| 333.11 | 41.07 | 485.38 | 41.30 | 538.83 | 41.34 | 735.31 | 41.61 |
| 333.99 | 41.08 | 486.07 | 41.30 | 540.74 | 41.34 | 736.42 | 41.61 |
| 334.64 | 41.09 | 486.67 | 41.30 | 543.32 | 41.35 | 740.75 | 41.61 |
| 336.39 | 41.09 | 487.08 | 41.30 | 545.51 | 41.35 | 743.77 | 41.61 |
| 338.99 | 41.09 | 487.74 | 41.30 | 549.82 | 41.35 | 746.18 | 41.62 |
| 340.01 | 41.09 | 488.39 | 41.30 | 553.95 | 41.36 | 748.12 | 41.62 |
| 341.73 | 41.09 | 489.02 | 41.30 | 559.34 | 41.36 | 749.55 | 41.62 |
| 344.12 | 41.09 | 489.47 | 41.30 | 562.39 | 41.37 | 758.89 | 41.62 |
| 345.42 | 41.09 | 490.09 | 41.30 | 569.47 | 41.38 | 763.18 | 41.64 |
| 347.35 | 41.09 | 490.75 | 41.30 | 570.38 | 41.39 | 774.25 | 41.64 |
| 349.50 | 41.09 | 491.39 | 41.30 | 575.13 | 41.40 | 777.33 | 41.65 |
| 351.89 | 41.09 | 492.05 | 41.30 | 576.04 | 41.40 | 790.26 | 41.65 |
| 354.27 | 41.10 | 492.46 | 41.31 | 577.10 | 41.40 | 795.84 | 41.65 |
| 356.68 | 41.10 | 493.14 | 41.31 | 578.62 | 41.40 | 802.64 | 41.66 |
| 358.80 | 41.10 | 493.77 | 41.31 | 579.91 | 41.40 | 806.50 | 41.68 |
| 361.18 | 41.10 | 494.43 | 41.31 | 581.17 | 41.40 | 823.77 | 41.68 |
| 363.31 | 41.11 | 495.11 | 41.31 | 583.55 | 41.41 | 839.58 | 41.68 |
| 365.34 | 41.11 | 495.74 | 41.31 | 591.07 | 41.42 | 856.24 | 41.68 |
| 367.22 | 41.11 | 495.95 | 41.32 | 593.49 | 41.42 | 859.88 | 41.68 |
| 368.95 | 41.12 | 496.80 | 41.32 | 594.34 | 41.43 | 860.92 | 41.69 |
| 374.33 | 41.12 | 497.87 | 41.32 | 596.28 | 41.43 | 866.30 | 41.69 |
| 376.48 | 41.12 | 498.94 | 41.32 | 605.16 | 41.43 | 873.54 | 41.69 |
| 381.24 | 41.13 | 499.85 | 41.32 | 606.66 | 41.43 | 881.03 | 41.69 |
| 383.82 | 41.13 | 500.92 | 41.32 | 608.59 | 41.46 | 888.80 | 41.69 |
| 384.04 | 41.14 | 501.77 | 41.32 | 617.04 | 41.46 | 896.85 | 41.69 |
| 458.81 | 41.27 | 502.89 | 41.32 | 619.86 | 41.46 | 899.28 | 41.70 |
| 464.15 | 41.27 | 503.75 | 41.32 | 624.87 | 41.46 | 900.60 | 41.70 |
| 464.80 | 41.28 | 504.83 | 41.32 | 627.64 | 41.47 | 948.90 | 41.71 |
| 465.02 | 41.28 | 505.90 | 41.32 | 631.30 | 41.48 | 958.95 | 41.71 |
| 466.56 | 41.28 | 506.98 | 41.32 | 635.00 | 41.48 | 964.29 | 41.72 |
| 468.93 | 41.28 | 507.83 | 41.32 | 642.34 | 41.49 | 965.13 | 41.75 |
| 470.85 | 41.28 | 508.94 | 41.32 | 647.74 | 41.50 | 966.21 | 41.76 |
| 471.94 | 41.28 | 514.72 | 41.32 | 651.24 | 41.50 | 970.12 | 41.76 |
| 473.68 | 41.28 | 515.87 | 41.32 | 652.27 | 41.51 | 973.36 | 41.77 |
| 474.56 | 41.28 | 516.95 | 41.32 | 654.55 | 41.51 | 977.79 | 41.77 |
| 475.41 | 41.28 | 518.22 | 41.34 | 663.73 | 41.51 | 978.05 | 41.77 |

**Table 2** Results of correlation of the heat capacity experimental data of InN

| | Correlation | | |
|---|---|---|---|
| Equation | $D(C_p)$/J mol$^{-1}$ K$^{-1}$ | $DR(C_p)$/% | Adjustable parameters/J mol$^{-1}$ |
| 1) Chen *et al.* [11] | 0.021 | 0.051 | $C_1$=41.014<br>$C_2$=0.825·10$^{-3}$<br>$C_3$= –26613.6 |
| 2) Itagaki and Yamaguchi [12] | 0.019 | 0.046 | $C_1$=40.274<br>$C_2$=0.260·10$^{-2}$<br>$C_3$=4201.48<br>$C_4$=–0.112·10$^{-5}$ |
| 3) Leitner *et al.* [13] | 0.019 | 0.046 | $C_1$=41.400<br>$C_2$=0.499·10$^{-3}$<br>$C_3$= –135502<br>$C_4$=–26169900 |

where $(C_p)_i^{\mathrm{exp}}$, $(C_p)_i^{\mathrm{cal}}$ – experimental and calculated heat capacities, respectively, $n$ – number of experimental data points, $m$ – the number of adjustable parameters.

The results of correlation of heat capacities experimental data (average error about 0.02 J mol$^{-1}$ K$^{-1}$–0.05%) obtained by the use of the all three equations are much better than the level of the experimental accuracy (0.5%).

The slightly better results of correlation have been obtained for the Leitner *et al.* [13] and the Itagaki and Yamaguchi [12] equations which have four adjustable parameters (Table 2). However the difference in correlation (0.002 J mol$^{-1}$ K$^{-1}$) compared to the Chen *et al.* [11] equation, with three adjustable parameters, is unimportant and is caused only by the higher number of adjustable parameters used for correlation.

The discrepancy between the correlation results and the experimental heat capacities data are plotted in Fig. 2.

## Conclusions

The experimental results differ from the estimated literature data [3, 6, 7, 10]. In the literature there is a lack of experimental data covering the whole temperature range of our investigation, so direct comparison is impossible.

The data of Leitner *et al.* [7] (Fig. 2) which cover only small range of our experiment differ significantly from our data but the difference is only in the shape of temperature dependence of $C_p$. The accuracy of our experiment was on the level of 0.5% what gives the maximum error for $C_p$ in the common (Leitner *et al.* [7] and our data) range of experiment about 2 J mol$^{-1}$ K$^{-1}$. So, taking this into account we cannot say that there is a discrepancy between these both experimental data sets.

Our experimental data have been measured in the wide temperature range, with the very precise method. The smooth shape of the measured heat capacities, very well correlated by the widely used $C_p$ correlation equations, seems to confirm the accuracy and applicability of the used method and allow us for its recommendation for measurement of heat capacities of the group-III nitrides.

All polynomial equations used for the correlation fit the heat capacities data with experimental accuracy (<0.5%). The results obtained for the four parametric equations [12, 13] differ only slightly from the results obtained for the three [11].

## Acknowledgements

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## List of symbols

| | |
|---|---|
| $C_p$ | heat capacity, J mol$^{-1}$ K$^{-1}$ |
| $HF_{\mathrm{sample}}$,<br>$HF_{\mathrm{blank}}$ | heat fluxes, mW of sample and blank measurements, respectively |
| $T$ | temperature, K |
| $C_1 \cdots C_4$ | adjustable parameters |
| $(C_p)_i^{\mathrm{exp}}$ | experimental heat capacity for $i$ experimental point, J mol$^{-1}$ K$^{-1}$ |
| $(C_p)_i^{\mathrm{cal}}$ | calculated heat capacity for $i$ experimental point, J mol$^{-1}$ K$^{-1}$ |
| $n$ | number of experimental data points |
| $m$ | number of adjustable parameters |

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