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# Thermodynamic Study of Zirconium and Hafnium Boranate - $Zr(BH_4)_4$ and $Hf(BH_4)_4$

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## 1. INTRODUCTION AND MOTIVATION

The storage of hydrogen in boranates may contribute to the energy transition from fossil fuels to renewable sources. Although $Zr(BH_4)_4$ and $Hf(BH_4)_4$ are well established precursors for the chemical vapor deposition of borides [1-4], reliable thermodynamic data for the assessment of their potential use in hydrogen storage applications especially regarding thermodynamic tuning remains scarce [5,6]. Additionally, some Zr and Hf containing compounds are catalysts for re-/dehydrogenation reactions of complex hydrides and thus the boranates are also of particular interest in that regard [7].

## 2. SYNTHESES BY SOLID STATE METATHESIS

$$MCl_4 + 4\ LiBH_4 \longrightarrow M(BH_4)_4 + 4\ LiCl \quad (M = Zr, Hf)\ [1]$$

The boranates were separated from the by-product by destillation as their boiling point is lower and their vapor pressure higher than the ones of LiCl [1,8].

## 3. INVESTIGATION OF THE MELTING AND DECOMPOSITION BEHAVIOUR

The fusion and decomposition of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ were investigated in the temperature ranges from 10 °C to 30 °C and 10 °C to 325 °C, respectively to determine the corresponding heats and temperatures (Fig. 1 and Tab. 1).

Tab. 1: Comparison of the determined melting and fusion temperatures with literature data.

| | $Zr(BH_4)_4$ | $Hf(BH_4)_4$ |
|---|---|---|
| $T_m$ [°C] | 28.7 [2,8]<br>28.5 [9]<br>31.85 [10]<br>27.94 this work | 29 [8,9]<br>28.43 this work |
| $T_{dec}$ [°C] | 81.85 [10]<br>100 [3]<br>72 [11]<br>126.85 [12]<br>130.27 this work | 100 [3]<br>200 [4]<br>136.44 this work |

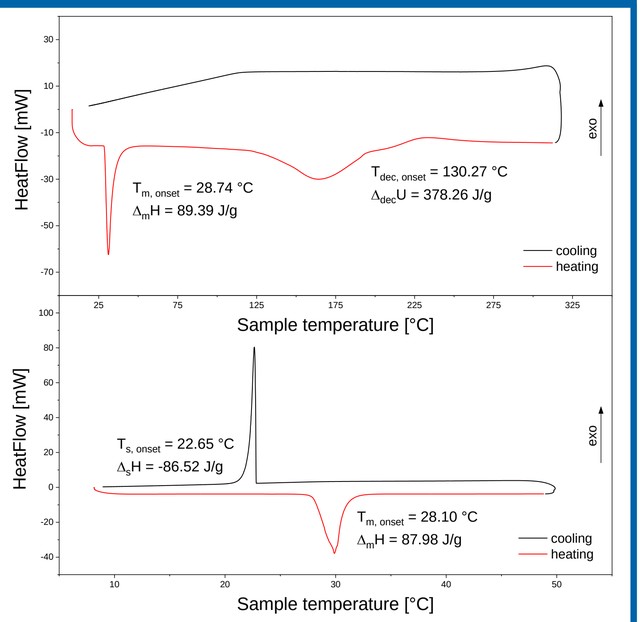


Fig. 1: DSC measurements of ca. 40 mg $Zr(BH_4)_4$ using a Setaram DSC-111.

## 4. HEAT CAPACITY MEASUREMENTS OF THE SOLID AND LIQUID PHASE

The heat capacites of the liquid and solid phase of both compounds were measured between 10 °C and 35 °C using closed steel crucibles (see Fig. 2). The coefficents of the linear heat capacity functions

$$C_P = A + B \cdot T$$

are given in Tab. 2. A constant heat capacity was assigned to the liquid phase of $Hf(BH_4)_4$ because only one data point could be measured due to a large melting event.

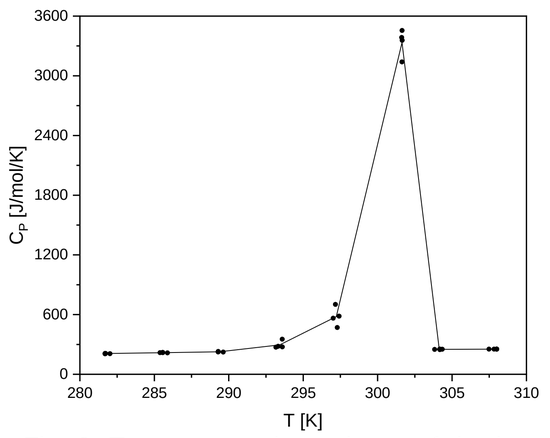


Fig. 2: Temperature dependency of the heat capacity of $Zr(BH_4)_4$ , measured with a sample of about 50 mg using a Setaram DSC-111.

Tab. 2: Coefficents of the heat capacity functions.

| | T range [K] | A [J mol$^{-1}$ K$^{-1}$] | B [J mol$^{-1}$ K$^{-2}$] |
|---|---|---|---|
| $Zr(BH_4)_4$ | 280 - 301<br>301 - 310 | -4.20E2<br>9.13E1 | 2.23E0<br>5.24E-1 |
| $Hf(BH_4)_4$ | 280 - 301<br>301 - 310 | -4.72E1<br>2.59E2 | 9.14E-1<br>/ |

The melting entropies and enthalpies were obtained by integration of the $C_P/T$ curves considering the respective temperatures (see Tab. 3).

## 5. STUDY OF THE DECOMPOSITION REACTIONS

The decomposed samples, obtained from the DSC measurements (Fig. 1), are amorphous towards X-rays. These samples were further investigated up to 650 °C using TG-DSC-MS measurements, which were performed under 1 bar argon atmosphere (see Fig. 3). Since the mass loss in the TG is accompanied by the evolution of hydrogen, we propose the investigated sample to contain $MH_2$. The powder X-ray diffractogram collected after the TG-DSC-MS measurement shows, that $MB_2$ is formed in the decomposition process (see Fig. 4).

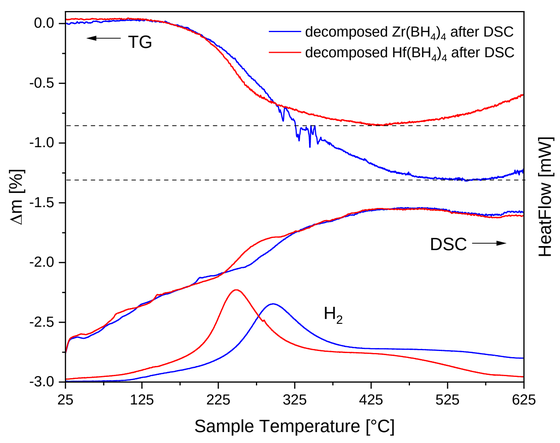


Fig. 3: TG-DSC-MS measurements of the samples obtained from the DSC investigations (section 4) using about 10 mg each, carried out on a Setaram Sensys.

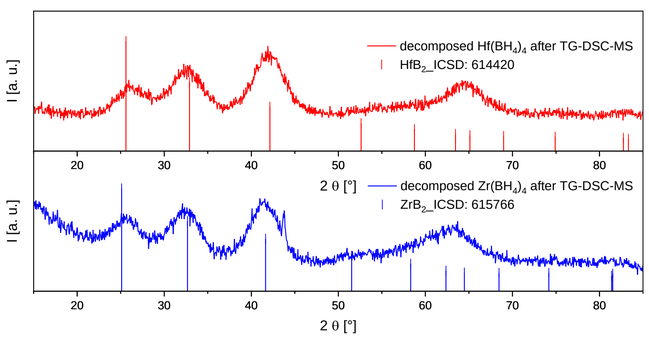


Fig. 4: Powder X-ray diffractograms of the samples after the TG-DSC-MS measurements. The reference patterns were taken from the ICSD.

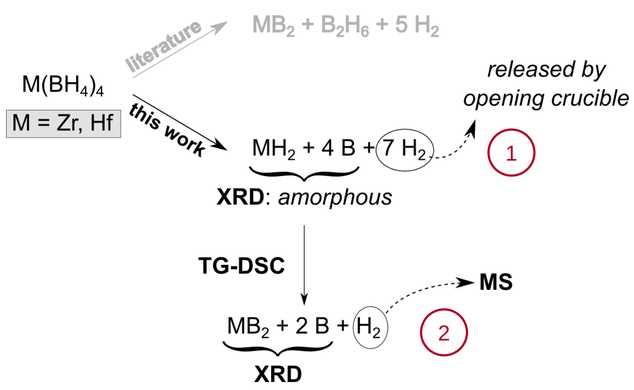


Fig. 5: Proposed decomposition reactions of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ identified by the mentioned techniques compared to the route reported in ref. [10,13].

The previously described results indicate, that the boranates dehydrogenate first into metal dihydrides, boron and hydrogen (reaction 1, Fig. 5). Then, the hydrides decompose and the borides are formed in the second step (reaction 2, Fig. 5). In contrast to the literature [10,13], we did not observe the evolution of diborane during the decomposition in the TG-DSC-MS measurement (grey reaction, see Fig. 5).

## 6. CALPHAD OPTIMISATION OF THERMODYNAMIC DATA

The enthalpies of formation of the boranates were calculated using the determined decompostion enthalpies and Hess‘ law. Their absolute entropies were computed by DFT. Using our phase change data and vapour pressure measurements from ref. [8], data were optimised based on the CalPhaD method (see Fig. 6). The full set of optimised data for both compounds is given in Tab 3.

Tab. 3: Optimised data for both compounds.

| | $Zr(BH_4)_4$ | $Hf(BH_4)_4$ |
|---|---|---|
| $\Delta_F H(298.15\ K)$ [kJ/mol] | -260.59 | -227.99 |
| $S(298.15\ K)$ [J/mol/K] | 228.4 | 212.7 |
| $T_m$ [°C] | 28.50 | 29.05 |
| $\Delta_m H$ [kJ/mol] | 12.6 | 10.0 |
| $\Delta_m S$ [kJ/mol] | 41.7 | 33.2 |
| $\Delta_v H(293.15\ K)$ [kJ/mol] | 35.7 | 40.3 |
| $\Delta_v S(293.15\ K)$ [kJ/mol] | 89.7 | 103.2 |
| $\Delta_{dec} H(T_{dec})$ [kJ/mol] | 80.42 | 99.46 |
| $T_{dec}$ [°C] | 130.4 | 136.4 |

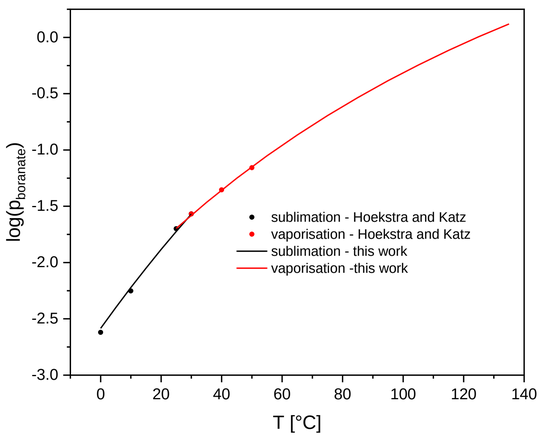


Fig. 6: Experimental vapour pressures, taken from Ref. [8] (dots), and the ones calculated by us using optimised data (lines) of $Zr(BH_4)_4$.

## 7. CONCLUSION

$Zr(BH_4)_4$ and $Hf(BH_4)_4$ were synthesised by solid state metathesis and characterised regarding their melting and decomposition heats, $C_P$ functions and enthalpies of formation using DSC measurements. TG-DSC-MS as well as XRD were employed to identify the decomposition reactions. The absolute entropies of the boranates were calculated by DFT. All data was optimised using the CalPhaD method. The assessment of the thermodynamic data reveals both boranates to not be suitable for reversible hydrogen storage themselves.

## 8. ACKNOWLEDGEMENT

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