Hydrogen storage properties of LiBH$_4$

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Abstract

Metal hydrides typically absorb 1–2 hydrogen atoms per metal atom and exhibit very large volumetric storage densities of up to 150 kg H$_2$ m^{-3} (e.g. Mg$_2$FeH$_6$). However, due to the large atomic mass of the transition metals the gravimetric hydrogen density is limited to less than 5 mass%. Light weight group 3 metals, e.g. Al, B, are able to bind four hydrogen atoms and form together with an alkali metal an ionic or at least partially covalent compound. These compounds are rather stable and often desorb the hydrogen only above their melting temperature. LiBH$_4$ has a gravimetric hydrogen density of 18.5 mass% and a volumetric hydrogen density of 121 kg H$_2$ m^{-3}. The compound was first synthesized by Schlesinger and Brown [*J. Am. Chem. Soc.* 62 (1940) 3429] in an organic solvent. According to the work of Stasinevich and Egorenko [*Russian J. Inorg. Chem.* 13(3) (1968) 341] hydrogen desorbs from LiBH$_4$ at temperatures greater than 470 °C. We have successfully identified the low temperature structure of LiBH$_4$: orthorhombic, space group *Pnma* (#62), the unit cell contains four molecules and has the dimensions $a = 7.1730$ Å, $b = 4.4340$ Å, $c = 6.7976$ Å at 25 °C. A slight hydrogen desorption was observed during the structure transformation around 100 °C and the major hydrogen desorption (13.5 mass%) starts at approximately 200 °C when SiO$_2$-powder is added to the LiBH$_4$ sample.
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1. Introduction

Metal hydrides exhibit appreciable volumetric hydrogen densities which reach 150 kg H$_2$ m^{-3} (Mg$_2$FeH$_6$) more than double the density of liquid hydrogen. The maximum known hydrogen to metal atomic ratio is 4.5 *H/M* in complex hydrides, e.g. BaReH$_9$ [1]. However, the gravimetric hydrogen density in metal hydrides which remain metallic upon hydrogen absorption is less than 3 mass% and in those which become semiconductive or even insulating is less than 8 mass% (MgH$_2$) [2] (Table 1). Using the maximum hydrogen to metal ratio of 4.5 as a limitation, a potential hydride can only exceed the 8 mass% if it consists only of elements with an average molecular mass of less than 51.8 g mol^{-1} (Cr).

The group one, two and three light metals, e.g. Li, Be, Na, Mg, B, Al, build a large variety of metal–hydrogen complexes. They are especially interesting because of their light weight and the number of hydrogen atoms per metal atom, which is in many cases *H/M* = 2. The hydrogen in the complex hydrides is located in the corners of a tetraeder with boron or aluminum in the center. The negative charge of the anion, [BH$_4$]$^-$ and [AlH$_4$]$^-$ is compensated by a cation e.g. Li or Na. The hydride complexes of borane, the tetrahydroborates M(BH$_4$), and of alane, the tetrahydroaluminate M(AlH$_4$) are interesting storage materials, however, they were known to be stable and decompose only at elevated temperatures and often above the melting point of the complex.

Bogdanovi and Schwickardi [3] presented in 1996 for the first time adsorption and desorption pressure–concentration isotherms of catalyzed NaAlH$_4$ at temperatures of 180 and 210 °C. The isotherms exhibit an absence of hysteresis and a nearly horizontal pressure plateau. Furthermore, the catalyzed system reversibly absorbed and desorbed hydrogen up to 4.2 mass% and the mechanism of the two-step reaction was described. A more detailed study of the NaAlH$_4$ with an improved catalyst was published in 2000 by Bogdanovic et al. [4]. A desorption hydrogen pressure of 2 bar at 60 °C was found and the enthalpies for the dissociation reaction were determined to be 37 and 47

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Table 1
Physical properties of selected complex hydrides: M, molecular mass; ρ, gravimetric density; T_m, melting point; $T_{dec.}$, decomposition temperature; x, the gravimetric hydrogen density

Formula	M (g mol^{-1})	ρ (g cm^{-3})	T_m (°C)	$T_{dec.}$ (°C)	x (mass%)	Ref.
LiBH$_4$	21.784	0.66	268	380	18.4	[6]
NaBH$_4$	37.83	1.074	505	400	10.6	[25]
LiAlH$_4$	37.95	0.917	>125	125	9.5	[25]
KBH$_4$	53.94	1.178	585	500	7.4	[25]
NaAlH$_4$	54.0	1.27	178	210	7.4	[4]
Mg$_2$NiH$_4$	111.3	2.72		280	3.6	[2]
Mg$_2$FeH$_6$	110.5	2.72		320	5.4	[1]
Mg$_3$MnH$_7$	134.9	2.30		280	5.2	[1]
BaReH$_9$	332.5	4.86		<100	2.7	[1]

kJ mol^{-1} for the first dissociation step of Ti-doped NaAlH$_4$: $3\text{NaAlH}_4 \rightarrow \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2$ (3.7 wt.% H) and the second $\text{Na}_3\text{AlH}_6 \rightarrow 3\text{NaH} + \text{Al} + 3/2\,\text{H}_2$ (3.0 wt.% H), respectively. Therefore, the equilibrium hydrogen pressure at room temperature is approximately 1 bar. Furthermore, the reaction is reversible, a complete conversion to product was achieved at 270 °C under 175 bar hydrogen pressure in 2–3 h [5].

The first report of a pure alkali metal tetrahydroboride appeared in 1940 by Schlesinger and Brown [6] who synthesized the lithium tetrahydroboride (lithium-borohydride) (LiBH$_4$) by the reaction of ethyl lithium with diborane (B$_2$H$_6$). The direct reaction of the corresponding metal with diborane in etheral solvents under suitable conditions produces high yields of the tetrahydroborides [7] $2\text{MH} + \text{B}_2\text{H}_6 \rightarrow 2\text{MBH}_4$ where M = Li, Na, K, etc. Direct synthesis from the metal, boron and hydrogen at 550–700 °C and 30–150 bar H$_2$ has been reported to yield the lithium salt, and it has been claimed that such a method is generally applicable to group IA and IIA metals [8]. The reaction involving either the metal or the metal hydride, or the metal together with triethylborane in an inert hydrocarbon has formed the basis of a patent M + B + $2\text{H}_2 \rightarrow \text{MBH}_4$, where M = Li, Na, K, etc.

Lithium tetrahydroboride is a salt-like, hydroscopic, crystalline material with a reported melting point at 275 °C [6] or 278 °C and densities 0.681 or 0.66 g cm^{-3} at 25 °C. At 0 °C, its vapor pressure is much less than 10^{-5} mbar, and the salt neither decomposes nor sublimes. The heat of formation of the compound has been measured [9], and the heat capacity was determined from 15 to 303 K. The usual thermodynamic functions have been tabulated for 15 to 300 K and 0 to 2000 K (for a hypothetical solid). At 298.15 K the values are as follows: $\Delta H_f = -194.44$ kJ mol^{-1}, $\Delta F_f = -128.96$ kJ mol^{-1}, $S^0 = 75.91$ J K^{-1} mol^{-1}, $c_p = 82.60$ J K^{-1} mol^{-1}.

The stability of metal tetrahydroborides has also been discussed in relation to their percentage ionic character, and those compounds with less ionic character than diborane are expected to be highly unstable [10]. Steric effects have also been suggested to be important in some compounds [11,12]. The special feature exhibited by the covalent metal hydroborides is that the hydroboride group is bonded to the metal atom by bridging hydrogen atoms similar to the bonding in diborane, which may be regarded as the simplest of the so called 'electron-deficient' molecules. Such molecules possess fewer electrons than those apparently required to fill all the bonding orbitals, based on the criterion that a normal bonding orbital involving two atoms contains two electrons. The molecular orbital bonding scheme for diborane has been discussed extensively [12].

Fedneva et al. [13] investigated LiBH$_4$ by means of thermal analysis (DTA). The thermogram of LiBH$_4$ showed three endothermic effects: at 108–112, 268–286, and 483–492 °C. The endothermic effect at 108–112 °C is reversible and corresponds to polymorphic transformation of LiBH$_4$. The second peak at 268–286 °C corresponds to the fusion of LiBH$_4$. The fusion is accompanied by a slight decomposition, which liberates approximately 2% of the hydrogen in the compound. The main evolution of gas starts at 380 °C and liberates 80% of the hydrogen in LiBH$_4$. The reason for the small effect at 483–492 °C is according to the authors uncertain. However, it coincides with the liberation of 50% of the hydrogen.

Stasinevich and Egorenko [14] investigated the alkali metal tetrahydroborides by means of thermal analysis in hydrogen at pressures up to 10 bar. The decomposition of the compounds can proceed in one of the following directions: $\text{MBH}_4 \rightarrow \text{M} + \text{B} + 2\text{H}_2$ or $\text{MBH}_4 \rightarrow \text{MH} + \text{B} + 3/2\text{H}_2$. The thermal decomposition, at least in the early stages, is reversible, as is shown by the decomposition temperature being higher in the presence of hydrogen than in the vacuum or inert gas [15,16] and also by the existence [16,17] of a rapid isotopic exchange between tetrahydroboride and deuterium at $T > 350$ °C. The decomposition temperature obtained for various hydrogen pressures lead to the following enthalpy and entropy for LiBH$_4$: $\Delta H_f = -177$ kJ mol^{-1}, $S^0 = 238$ J K^{-1}:

$$\log(p) = 12.47 - \frac{9265}{T}$$

with p in bar.

The change in free energy (isobaric) for the formation of

the alkali metal tetrahydroborides from the elements have been published [18,19]:

$$LiBH_4 \rightarrow Li + B + 2H_2$$
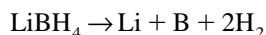
$$\Delta G_T = -194.2 + 0.219T \text{ kJ mol}^{-1}$$

$$LiBH_4 \rightarrow LiH + B + 3/2H_2$$

$$\Delta G_T = -103.4 + 0.150T \text{ kJ mol}^{-1}$$

The lattice energy of the crystalline compound is estimated from heats of formation to be 779 kJ mol^{-1} [20].

The stability of metal hydrides can be changed by partial substitution of the consisting elements. Due to the delocalized electrons in metals substituted elements influence the overall stability of the interstitial hydrogen atoms. The electrons in ionic compounds are strongly localized, therefore, other routes have to be developed to destabilize the complex hydrides.

In this paper we report about the result of the structure investigation by means of synchrotron powder diffraction. The hydrogen desorption properties of pure LiBH$_4$ were investigated in detail and a catalyst was found which allowed to lower the hydrogen liberation temperature to approximately 200 °C.

2. Experimental

The compounds were purchased from Fluka Chemie AG in Switzerland (Sigma–Aldrich Fine Chemicals) [21]: lithium borohydride (LiBH$_4$) No. 62460 (pract.=95% gas-volumetric). The samples were handled solely in the argon glove box. The LiBH$_4$ powder was transferred to the Mark-tubes with an inner diameter of 1 mm in the argon glove box and sealed on top with putty and later on the tubes where closed by melting the glass in a gas flame. The structure at room temperature was investigated by means of synchrotron radiation at the Swiss Light Source (SLS) with a high-resolution powder diffractometer (Debye–Scherrer geometry). The photon energy was set to 8.15 eV ($\lambda = 1.52$ Å), 2θ step was 0.003°C and time/step was set to 2 s. The diffraction pattern was fitted by means of the Fullprof program [26] applying a pseudo-Voight profile function.

The desorption experiments were carried out in a stainless steel cylinder. Approximately 200 to 300 mg of LiBH$_4$ was used for each desorption experiment. The desorbed gas was measured by means of a mass flow controller (Brooks instruments, 5850E, max. flow 5 standard cm^3 min^{-1}), with a maximum full scale error of 1%.

3. Results and discussion

The structure of LiBH$_4$ is orthorhombic in agreement with Harris and Meibohm [22]. The unit cell contains four molecules and has the dimensions $a = 7.1730$ Å, $b = 4.4340$ Å, $c = 6.7976$ Å at 25 °C. The calculated density of LiBH$_4$ is 0.669 g cm^{-3} (Fig. 1). The arrangement of lithium and tetrahydroboride ions satisfies the space group *Pnma* (#62). Each Li$^+$ ion is surrounded by four [BH$_4$]$^-$-ions in a tetrahedral configuration. The [BH$_4$] tetrahedrons are strongly deformed, two hydrogen atoms are at a bond length of $d(B-H) = 1.30$ Å, one at $d(B-H) = 1.28$ Å and one at $d(B-H) = 1.44$ Å. Table 2 summarizes the refinement parameters, which were determined using a starting parameter set from Soulié et al. [23]. Pistorius [24] investigated the phase diagram of LiBH$_4$ over a large temperature and pressure range and found a structural transition from the orthorhombic phase at low temperature

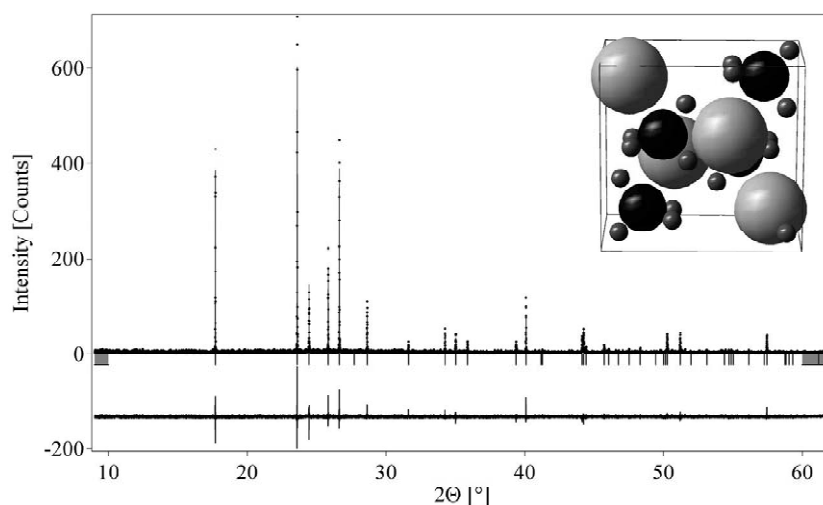Fig. 1. Synchrotron powder diffraction spectrum (Debye–Scherrer) of polycrystalline LiBH$_4$. The inset shows a drawing of the orthorhombic unit cell containing four LiBH$_4$, the size of the atoms corresponds to 25% of their covalent radii.

Table 2
Refinement [26] results for the orthorhombic $LiBH_4$ at room temperature ($T = 298$ K) from synchrotron powder diffraction data

Atom	Site	Symmetry	x/a	y/b	z/c	Biso [Å]
Li	4(c)	m	0.146(1)	0.25	0.099(2)	6.5(4)
B	4(c)	m	0.306(1)	0.25	0.415(1)	1.8(3)
H1	4(c)	m	0.934(4)	0.25	0.954(5)	1.0(6)
H2	4(c)	m	0.424(4)	0.25	0.243(5)	1.0
H3	8(d)	l	0.153(3)	0.104(4)	0.453(3)	1.0

Space group *Pnma* (#62), $a = 7.1730(1)$ Å, $b = 4.4340(1)$ Å, $c = 6.7976(1)$ Å, $V = 216.20$ Å^3, $Z = 4$, $\rho = 0.669(2)$ g cm^{-3}, $R_{Bragg} = 6.94\%$, $R_{wp} = 7.68\%$ and $\chi^2 = 0.58$.

to a tetragonal phase around 105 °C. However, the structural transition around 100 °C is accompanied by a hydrogen desorption and therefore not only the structure but also the composition changes slightly. The thermal desorption spectra of pure $LiBH_4$ shown in Fig. 2a exhibits a slight hydrogen desorption between 100 and 200 °C of 0.3 mass% or approximately 1.5% of the total hydrogen content of the compound which is in good agreement with the observation of Fedneva et al. [13]. The fusion was observed around 270 °C without liberation of hydrogen. At 320 °C the first significant hydrogen desorption peak starts and liberates an additional 1 mass% of hydrogen. This first desorption goes over to a second desorption peak starting at 400 °C and reaches its maximum around 500 °C. The integrated amount of hydrogen desorbed up to a temperature of 600 °C is 9 mass%, which corresponds exactly to half of the hydrogen in the starting compound. The end product has the nominal composition '$LiBH_2$'. The thermal desorption spectra of $LiBH_4$ mixed with SiO_2-powder (25:75 mass%) shown in Fig. 2b exhibits also three hydrogen desorption features, however the desorption starts at lower temperatures and 9 mass% of hydrogen is liberated below 400 °C. The first hydrogen desorption peak

starts already at 200 °C and the second hydrogen desorption peak starts at 453 °C and is very sharp. The SiO_2-powder catalyzes the decomposition reaction of $LiBH_4$ and lowers the temperature for all three hydrogen desorption features. Furthermore, the pure $LiBH_4$ sample only exhibits significant desorption above 400 °C in the second hydrogen desorption peak while the first hydrogen desorption peak starting at 200 °C is the dominant peak of the catalyzed sample.

The decomposition reaction of the catalyzed $LiBH_4$ can be schematically described as follows:

1. $LiBH_4 \rightarrow LiBH_{4-\epsilon} + \epsilon/2H_2$: structural transition at $T = 108$ °C.
2. $LiBH_{4-\epsilon} \rightarrow \text{'}LiBH_2\text{'} + (1 - \epsilon/2) \cdot H_2$: first hydrogen peak starting at $T = 200$ °C.
3. $\text{'}LiBH_2\text{'} \rightarrow LiH + B + 1/2H_2$: second hydrogen peak starting at $T = 453$ °C.

The compound $LiBH_2$ is in parentheses, since such a compound is not known yet. However, the desorption of 9 mass% points to this composition. Furthermore, Fedneva et al. [13] and Stasinev and Egorenko [14] observed a
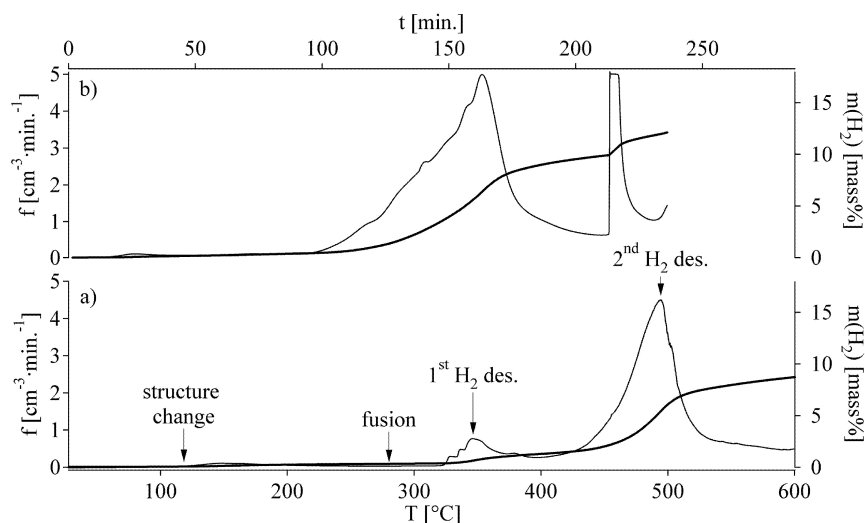

Fig. 2. Thermal desorption spectra of $LiBH_4$. The sample was heated after evacuation at room temperature with a heating rate of 2 K min^{-1}. The gas flow was measured as a function of time and the desorbed hydrogen was computed from the integrated gas flow. (a) Pure $LiBH_4$ and (b) $LiBH_4$ mixed with SiO_2 as catalyst.
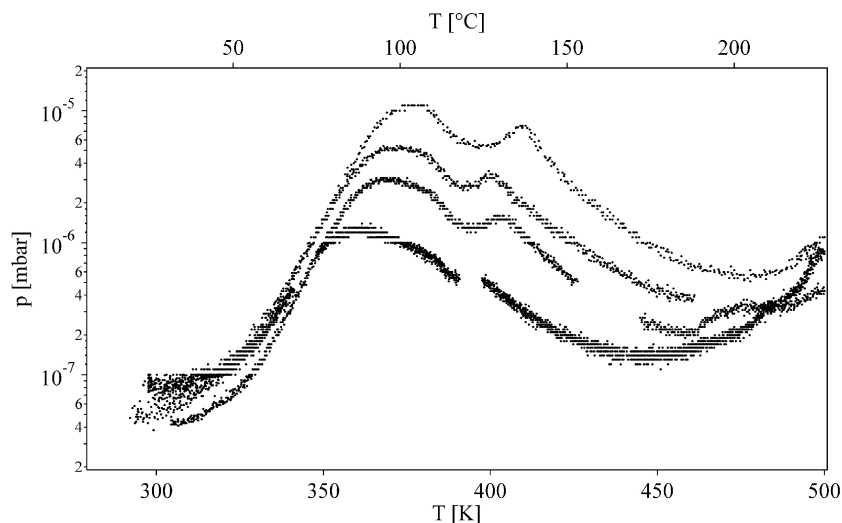
Fig. 3. Hydrogen partial pressure measured by means of a mass spectrometer in the UHV chamber for the hydrogen desorption peak during the structural transformation of $LiBH_4$ around 100 °C for various heating rates.

endothermal effect at the composition 'LiBH$_2$'. Thermal desorption spectroscopy with different heating rates was applied in order to determine the activation energy of the slight hydrogen desorption process around 100 °C (Fig. 3). The logarithm of the ratio of the heating rate divided by the square of the peak temperature is a linear function of the inverse temperature if the hydrogen desorption is a first order reaction (Fig. 4). The computed activation energy is $E_A = 156 \pm 20$ kJ mol^{-1}. The temperature of the major hydrogen desorption peaks strongly depends on the heating rate as shown in Fig. 5. At low heating rates of 0.5 and 1 K min^{-1} three distinct desorption peaks were observed. The peak maxima correspond to 0.33, 1.0 and 2.0 mol H per mol LiBH$_4$. This indicates that the hydrogen desorption reaction is divided into at least three steps with inter-

mediate products. The maximum amount of desorbed hydrogen is limited to 13.5 mass% due to the formation of lithiumhydride (LiH) which is stable up to 900 °C [25].

4. Conclusion

We have investigated the structure and the thermal hydrogen desorption process of LiBH$_4$. It was found that the compound liberates hydrogen in different reaction steps and temperature regimes. The low temperature desorption from the orthorhombic phase liberates only a small amount (0.3 mass%) of hydrogen. The high temperature phase liberates up to 13.5 mass% of hydrogen (3 mol H per LiBH$_4$). 4.5 mass% of the hydrogen remain as LiH in the
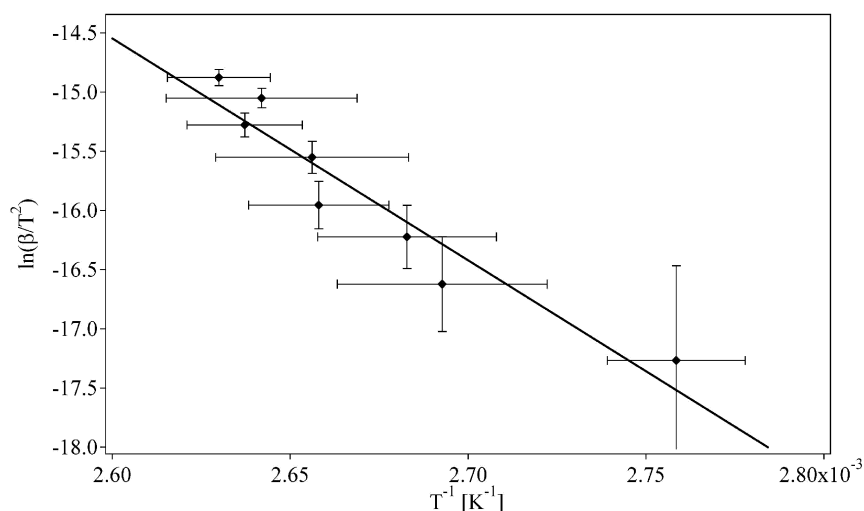

Fig. 4. Plot of the logarithm of the ratio of the heating rate divided by the square of the temperature where the peak maximum was detected versus the inverse temperature. The slope of the fitted line corresponds to the activation energy for the reaction, $E_A = 156 \pm 20$ kJ mol^{-1}.
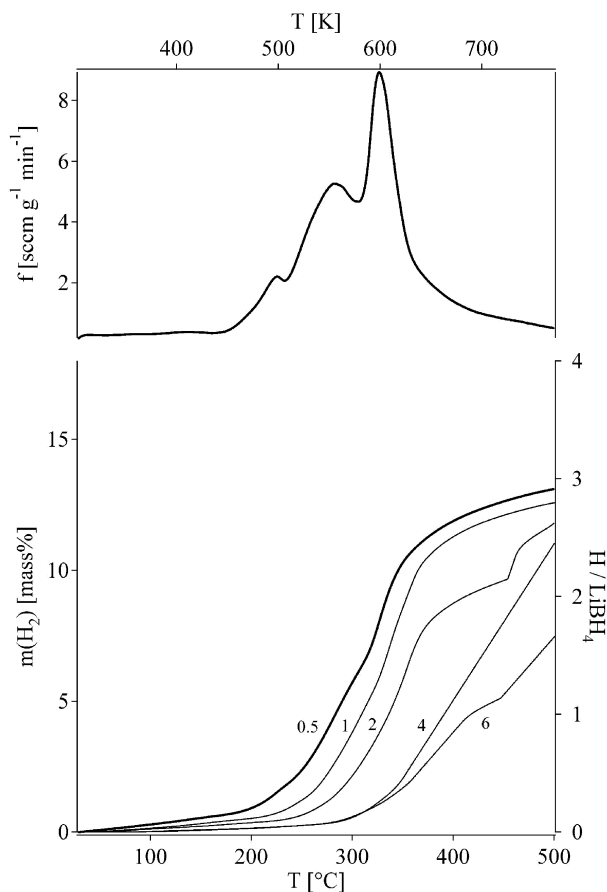
Fig. 5. Desorbed amount of hydrogen as a function of temperature for various heating rates, numbers indicate the heating rate in K min^{-1} on bottom and the hydrogen desorption flow as a function of temperature for a heating rate of 0.5 K min^{-1} on top. The sample was LiBH$_4$ (28 mass%) mixed with SiO$_2$-powder.

decomposition product. All attempts to synthesize LiBH$_4$ from the elements at elevated conditions up to 650 °C and 150 bar H$_2$ pressure failed up to now.

Acknowledgements

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