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Analysis of the decomposition gases from α and β - $\text{Cd}(\text{BH}_4)_2$ synthesized by temperature controlled mechanical milling

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ABSTRACT

We present a comprehensive study on the controlled phase synthesis and thermal decomposition of $\text{Cd}(\text{BH}_2)_4$, a material for solid state hydrogen storage obtained via the metathesis reaction of LiBH_4 with CdCl_2 . By adjusting the stoichiometry of the reactants and controlling the mechanical milling vial temperature, we have isolated the tetragonal ($P4_2mn$) low temperature phase and the cubic ($Pn-3m$) high temperature phase of the cadmium borohydride. $\text{Cd}(\text{BH}_2)_4$ has a low thermodynamic stability and decomposes with fast kinetic at 348 K, when heated at $1 \text{ K}\cdot\text{min}^{-1}$ against a backpressure of 1 bar H_2 . A semi-quantitative analysis reveals that the decomposition gases are composed of 1:1 $\text{H}_2+\text{B}_2\text{H}_6$ and that only Cd remains as solid crystalline phase.

KEYWORDS

Energy storage materials, metal hydride, mechanochemical processing, diborane.

1. Introduction

Since the first application of tetrahydroborate as possible solid material for hydrogen storage, historically LiBH_4 [1], all the efforts have focused in the reduction of the temperature of the

hydrogen release and on the enhancement of the kinetics and reversibility for their hydrogenation and dehydrogenation cycles. Destabilization of LiBH_4 can be achieved by the use of composite systems like $2\text{LiBH}_4\text{-MgH}_2$ [2–4], $6\text{LiBH}_4\text{-CaH}_2$ [3,5] or by adding metal like Al [3,4,6] where the effects are to stabilize the products of the decomposition by forming the corresponding borides (MgB_2 , CaB_6 , AlB_2 ,...) and thus decrease the decomposition temperatures. Other systems have also been investigated, for example $\text{LiBH}_4\text{-LiNH}_2$ [7] or $\text{LiNH}_2\text{-MgH}_2\text{-LiBH}_4$ [8] and in those cases new quaternary hydrides with the composition of $\text{Li}_4\text{BN}_3\text{H}_{10}$ [9] are formed and exhibit lower decomposition temperatures.

The thermodynamic stability of the ionic borohydrides is closely anti-correlated with the Pauling electronegativity of the metal cations [10–12], and according to this principle double-cation borohydrides $\text{M}_x\text{Li}_y(\text{BH}_4)_z$, have been synthesized to adjust the decomposition temperatures. Partial substitution of Li^+ by others cations aim also at retain the gravimetric hydrogen content as high as possible. For example $\text{LiZr}(\text{BH}_4)_5$, $\text{Li}_2\text{Zr}(\text{BH}_4)_6$, $\text{LiK}(\text{BH}_4)_2$, $\text{Al}_3\text{Li}_4(\text{BH}_4)_{13}$ and $\text{LiSc}(\text{BH}_4)_4$ [11,13–15] have been synthesized and most of them exhibit thermodynamic stabilities in between those of $\text{M}(\text{BH}_4)_z$ and LiBH_4 . Nevertheless, none of them meet the desired low thermodynamic stability and furthermore it has been shown that concurrently to hydrogen diborane is also released during their thermal decomposition.

The paper presents a comprehensive analysis of the structure and the decomposition of crystalline solvent free cadmium tetrahydroborate obtained by ball milling. Cadmium was chosen for its large Pauling electronegativity ($\chi_p = 1.69$), and thus the expected low thermodynamic stability cadmium based borohydride together with the claimed successful synthesis of lithium-cadmium tetrahydroborate ($\text{Li}_2\text{Cd}(\text{BH}_4)_3$) by wet chemistry methods [16].

2. Experimental

All the commercial chemical compounds were used as received powders without further purification. All sample storage and handling were performed in an inert gas (Ar) glove-box ($\text{H}_2\text{O} <$

0.1 ppm, $O_2 < 0.1$ ppm). $LiBH_4$ (Sigma-Aldrich no. 62460, 95.0%) and $CdCl_2$ (Sigma-Aldrich no. 202908-10G 99.99%) were mixed in the molar ratios 1:1 and 2:1 and then ball milled in a high energy mill, Pulverisette P6, from Fritsch. Typically 2 g of powder were ball milled under argon atmosphere in a 250 ml stainless steel vial containing 25 tungsten carbide balls of 8 mm in diameter giving a ball to powder ration of $\sim 158:2$. Two strategies were adopted to reduce the increase of the temperature in the vial during the milling. The first strategy was to program 5 min. breaks after every 2 min. of milling (the samples prepared this way are denoted HM, standing for hot milled samples). The second strategy was, using the same stepped program, to cool down the milling vial prior to the milling and during the breaks by sinking it into a bath of liquid nitrogen (the samples prepared this way are denoted CM, standing for cold milled samples). The rotation speed was set to 650 rpm or 450 rpm and the typical milling time to 24 - 30 min, not including the breaks. The milling vial was equipped with a GTM II lid, a Fritsch component allowing the measure of the average temperature and gas pressure in the vial during the milling. For the HM samples the temperatures reached at maximum 308 K and for the CM samples the milling temperatures were around 253 K.

The amount of gases released during the thermal decomposition (TD) of the samples was measured in a Sievert's type system under 1 of H_2 . The Sievert's reactor was heated with a ramp of 1 K/min in a Carbolite furnace from room temperature up to 523 K. About 0.5 to 1 g of sample were used. A valve on the reactor prevented the powder from being exposed to air during transportation from the glove-box to the Sievert's system. The minimum operation time between the end of the milling and the start of the TD was 20 minutes.

Powder diffraction X-Ray (PXRD) pattern were recorded on a BRUKER D8 (40 kV, 40 mA, Cu radiation $K_{\alpha} = 1.542 \text{ \AA}$). To avoid contact with air or moisture a polyethylene film covered the samples. It gave rise to a broad peak at around 21° in 2θ , together with one weak peak from the sample holder itself at 43.5° . These peaks were excluded from the patterns during the Rietveld refinements.

Mass spectrometry measurements (MS), using an OmniStar (GSD 320) mass spectrometer, were performed on the gases released from the samples during thermal decomposition and on the gas contained in the vial after the milling process.

The possible phase transition temperatures of the new synthesized compounds were determined by differential scanning calorimetry (DSC), using a Netzsch DSC 200 F3 calorimeter.

3. Results and discussions

3.1. Molar ratio 2:1

The diffraction patterns of the powders obtained after cold and hot milling of the 2:1 mixture ($2\text{LiBH}_4 + \text{CdCl}_2$) are displayed in figures 1 and 2. For both samples no CdCl_2 was detected. For the CM-sample two phases were identified: a low temperature polymorph of the cadmium borohydride, denoted here as $\alpha\text{-Cd}(\text{BH}_4)_2$, and LiCl . Thus, the controlled phase synthesis used herein allows to isolate the $\alpha\text{-Cd}(\text{BH}_4)_2$ polymorph, enabling a good identification of its crystal structure from X-ray diffraction. For the HM-sample, the two main identified phases are a high temperature polymorph of the cadmium borohydride, denoted here as $\beta\text{-Cd}(\text{BH}_4)_2$ and LiCl and while containing small amount of Cd and $\alpha\text{-Cd}(\text{BH}_4)_2$, the diffraction pattern provides good data to identify the $\beta\text{-Cd}(\text{BH}_4)_2$ crystal structure. The $\alpha\text{-Cd}(\text{BH}_4)_2$ crystallizes in the tetragonal system, space group $\text{P4}_2\text{nm}$. It is isostructural to the high isostatic pressure tetragonal $\delta\text{-Mg}(\text{BH}_4)_2$ phase.[17][18]. It has one of the highest volumetric hydrogen density (122 g H_2/L at ambient conditions against 93 for LiBH_4 and 126 for $\text{Be}(\text{BH}_4)_2$). The $\beta\text{-Cd}(\text{BH}_4)_2$ crystallizes in the cubic system, space group $\text{Pn}\bar{3}\text{m}$, antitype structure of Cu_2O [18]. It has an even higher volumetric hydrogen density (131 g H_2/L). The proposed data for the crystallographic structures (see Table 1) come from the Rietveld refinement of the X-ray diffraction patterns of figures 1 and 2. The hydrogen atoms are omitted. The Rietveld refinements show good agreement with the experimental data. Neutron data and high resolution X-ray diffraction data would be required to accurately and fully describe the two structures. The quantitative phase analysis gave the following phase composition: CM-sample ~ 30 mol% $\alpha\text{-Cd}(\text{BH}_4)_2$, ~ 70 mol%

LiCl, HM-sample β -Cd(BH₄)₂ ~ 25 mol% , ~ 72 mol% LiCl, ~ 2.5 mol% α -Cd(BH₄)₂ and ~ 0.5 mol% Cd.

From these results, it is possible to state unambiguously that ball-milling of the 2:1 mixture of LiBH₄ and CdCl₂ promote the following metathesis reaction:



To investigate the existence of other possible cadmium-lithium tetrahydroborate phases / stoichiometry, syntheses using LiBH₄ rich mixtures (4LiBH₄+CdCl₂) were also performed. It led to the same results as for the 2:1 with the formation of Cd(BH₄)₂ and LiCl, leaving 2.LiBH₄ as unreacted. Furthermore it was found that any excess of LiBH₄ prevents the formation of unwanted by-product (see section 3.2.).

The control of the temperature within the milling vial has a dramatic effect. With hot milling the low temperature polymorph exists only in small amount and the yield of the reaction is lowered by the thermal decomposition of the cadmium borohydride as proved by the presence of Cd (see the paragraph 3.3. on the thermal decomposition). With cold milling a higher yield is obtained and no thermal decomposition occurs.

3.2. *Molar ratio 1:1*

In continuation of the investigation of other possible cadmium-lithium tetrahydroborate phases / stoichiometry, syntheses using 1:1 mixtures (LiBH₄+CdCl₂) were also performed. A diffraction pattern of the powder obtained after hot milling of this ratio is displayed in figure 3. No reflections from LiBH₄ are detected but small amount of un-reacted CdCl₂ is found. The β -Cd(BH₄)₂ peaks are identified together with these of Cd and LiCl. Furthermore, a phase not present in the 2:1 ball-milled powder is present and could be identified as Li₂CdCl₄. The diffraction pattern shows broader peaks than those of the 2:1 ratio. This is an indication of the poor crystallinity, the presence of defects in the crystallites and/or the small crystallite sizes of the different phases and could originate from the thermal decomposition of the hydride during the milling. While the peak positions are properly fitted

during the Rietveld refinement, their shapes together with the background are difficult to model and thus the refinement is of poor quality. It doesn't allow conducting an accurate quantitative phase analysis. Nevertheless, it can be stated unambiguously that ball-milling of the 1:1 mixture of LiBH₄ and CdCl₂ promote the following metathesis reaction:



The comparison of the reactions (1) and (2) established after the examination of the products obtained from the milling of the 2:1 and 1:1 mixtures indicates that the reaction of CdCl₂ with LiBH₄ is favourable over the reaction of CdCl₂ with LiCl. It is only when all LiBH₄ has been consumed that CdCl₂ reacts with LiCl to form Li₂CdCl₄. If LiBH₄ is in excess then Li₂CdCl₄ doesn't form. A mass spectrometry analysis of the gasses contained in the milling vial revealed the only presences of H₂ and Ar (from the glove-boxe). The hydrogen can be produced during the substitution of Li by Cd or by thermal decomposition of the new Cd(BH₄)₂ phase. The amount of H₂ presents in the vial correspond to roughly 2 wt% of the hydrogen content of the 2:1 mixture introduced in the vial. This is in agreement with the results obtained from the monitoring of the evolution of the pressure in the milling vial.

3.3. *Thermal decomposition*

A comprehensive analysis of the thermal decomposition products have been conducted by combining mass spectrometry measurements, to analyse the chemical composition of the released gases, a Sievert's type system, to monitor the kinetics and amount of gas released and X-ray diffraction to analyse the crystalline phases present in the remaining powder after thermal treatment.

In figure 4 are plotted the evolution of the number of moles of gas released by 1g of the samples previously described during their thermal decomposition from room temperature to 523 K. The largest amount of gas released is found for the CM-2:1 sample, the lowest for the HM-1:1 sample. This is in agreement with the results presented above and the different composition of the samples; for the 2:1 ratio the yield of the reaction (eq.1) is larger for the CM sample and the 1:1 ratio contains

evidently less hydrogen than the 2:1 mixtures. Furthermore the HM-samples undergo thermal decomposition during the milling. The decomposition temperature are much lower than for LiBH_4 , 373 K and 348 K for the 1:1 and 2:1 ratios respectively, to be compared with 523 K [6]. There is no difference, except for the amount of gas released, in the shape of the curves for the (2:1) CM and HM samples. The releases occur in one step in a temperature range <10 K, thus one should note here the rather fast decomposition kinetics. The 1:1 curve shows first a slightly slower release of gas (starting at ~ 373 K) and a second, with a lower amount released in between 388-405 K. This suggests that either the decomposition of one compound occurs in two steps or that two different compounds decompose. This latter hypothesis seems unlikely to occur since only one containing hydrogen phase was identified in the diffraction data. It is not clear why the thermal decomposition for the 1:1 HM sample occurs at a temperature 25 K higher than for the 2:1 samples. One possible explanation could be that the heat provided to the powder is used at first to complete the reaction between the unreacted CdCl_2 and LiCl resulting in the formation of Li_2CdCl_4 and the “delayed” hydrogen desorption. Indeed the temperature is not directly measured in the powder but as the temperature of the sample holder.

Mass spectrometry measurements were performed on the gases released by the different samples during their thermal decomposition under dynamical vacuum. Figure 5 displays an example of the typical results here obtained for the 2:1 HM-sample. The decomposition temperatures are in agreement with those observed from the TD measurements as well as the number of the decomposition events. Only H_2 and B_2H_6 were found to compose the released gases, no traces of Cl_2 or HCl for example. One should note that H_2 is detected slightly before B_2H_6 as a result of the mass separation occurring during the pumping of the gases through the capillary down to the detector.

The diffraction patterns, taken after the thermal decomposition revealed that the only crystalline phases detectable after the decomposition of $\text{Cd}(\text{BH}_4)_2$ is Cd. Of course every possible by-products

of the synthesis are present in the decomposition products, as for example LiCl or Li₂CdCl₄. (See figure 6 for the decomposition products of 2:1 CM-sample).

The ratios of the experimentally obtained amount of gases over the theoretical amounts of hydrogen or hydrogen + diborane that could be released from the samples during their thermal decomposition are plotted in figure 7. The results clearly indicate, in agreement with the mass spectrometry measurements that the gases are composed of 1:1, H₂+B₂H₆ whatever synthesis conditions, CM or HM have been used. The ratio for 1:1 H₂+B₂H₆ is closed to the theoretical value 1 while if only H₂ is supposed to be released then the ratio is about 0.5. This is to date the first semi-quantitative analysis giving a 1:1, H₂+B₂H₆ composition for the gas released during the complete decomposition of a tetrahydroborate, in a study the same composition was given for LiZn₂(BH₄)₅ but only during its first decomposition step [19].

Thus it is clear, while rather unfortunate, that cadmium borohydride will decompose, at a rather low temperature ($T_d \sim 348$ K) and fast kinetics, following the reaction:



At this point it is of course rather clear that this reaction will hinder any possible reversibility if the material as to be use as solid state hydrogen storage media.

3.4. DSC measurements

In figure 8 the DSC curves for the 2:1 CM and HM-samples are plotted. The samples were first cooled down from room temperature to 253 K and then heated up to 328 K at rates of ± 2 K/min. During the cooling the signal of the HM sample, composed mainly of the β -Cd(BH₄)₂ shows an exothermic event (from 281 to 289 K, maximum at ~ 285 K) that could be attributed to the phase transition from the β to the α polymorph. This event was not found for the CM sample. During the heating the signals for both samples show one clear endothermic event, in between 313 to 325 K with a minimum at ~ 316 K. This event must correspond to the phase transition from the α low temperature tetragonal (P 42 nm) structure to the cubic (P $n\bar{3}m$), β high temperature polymorph.

4. Discussion

Dry ball milling of $n\text{LiBH}_4:m\text{CdCl}_2$ promotes the synthesis of $\text{Cd}(\text{BH}_4)_2$ and it is established that depending on the stoichiometry, an unwanted byproduct, Li_2CdCl_4 , can form if $m/n > 0.5$ or unreacted LiBH_4 can be found if $m/n < 0.5$. No Li-Cd containing tetrahydroborate were synthesized and one could speculate that the energy of mechanical ball-milling is too large to synthesize the bication compound. Reduced milling speed, from 650 to 450 rpm and control of the temperature into the vial didn't change the elemental composition of the end product.

However, the control of the temperature and the right stoichiometry have enable us to isolate two different polymorphs of the cadmium tetrahydroborate. For an apparent temperature of ~ 253 K in the milling vial, the tetragonal ($P4_2nm$) structure was synthesized, while for an apparent temperature of 308 K, the tetrahydroborate adopted a cubic ($Pn-3m$), structure. DSC measurements revealed that the transition temperature from the low temperature to the high temperature polymorph is around 316 K.

The thermal decomposition exhibits very fast kinetics and occurs at low temperature ($T_d \sim 348$ K). This value follows the quadratic correlation between the decomposition temperatures and the Pauling electronegativity of the cation as described by Nakamori et al. [10] for $\text{M}(\text{BH}_4)_n$ where $\text{M} = \text{Na}, \text{Li}, \text{Mg}, \text{Sc}, \text{Zr}$ and Zn . In figure 9 have been plotted T_d versus χ_p for the data taken from [10] completed with the value obtained in this study. The experimental data have been fitted using the following expression:

$$T_d = F_1 (\chi_p - F_2)^2 \quad (4)$$

where $F_1 = 175.914$ and $F_2 = 3.11$ are dimensionless fitting parameters.

The simple model of equ. 4 is supported by the following simple analysis. Pauling [20] pointed out that the energy, $E(A-B)$ of heteratomic bonds is related to the difference between the electron-attracting abilities of A and B by the relation:

$$\chi_A - \chi_B \propto \{ E(A - B) - [E(A - A) + E(B - B)] / 2 \}^{1/2} \quad (5)$$

where the second term can be approximately calculated from the heat of formation (ΔH_f) in the case of MX_n , X being an anion, thus giving:

$$\chi_A - \chi_B \propto (-\Delta H_f/n)^{1/2} \quad (5)$$

Then using the well-known Van't Hoff equation one obtained the expression of equ. 4. where F_2 can be viewed as the electron attracting ability of the BH_4^- anion and F_1 contains the entropy values of the decomposition considered in a first order approximation as constant for all compounds and due to the release of the gases, the contribution from the crystalline phases formed as product being here neglected (but not negligible in reality).

The release of gaseous B_2H_6 has previously been observed for borohydride decomposing at temperatures below 250 °C [21] and our semi-quantitative analysis gives a 1:1 $\text{H}_2+\text{B}_2\text{H}_6$ composition for $\text{Cd}(\text{BH}_4)_2$. Attempts to use additives to catalyze the splitting of diborane were not successful [19], probably because of the deactivation of the additives covered by boron [22] and until now no solution has been proposed. The difficulty resides in the rather strong B-H bond to be broken.

5. Conclusions

We have presented a comprehensive study on the controlled phase synthesis and the decomposition of $\text{Cd}(\text{BH}_2)_4$, a potential material for solid state hydrogen storage. It emphasizes the importance of the control of the synthesis parameters. With simple control of the temperature during the milling and with stoichiometric adjustments, we have been able to isolate and characterize two polymorphs of the cadmium borohydride. The semi-quantitative analysis conducted on the decomposition gases have permitted to clearly identify and quantify the decomposition gases, composed of 1:1 $\text{H}_2+\text{B}_2\text{H}_6$. The temperature of decomposition is found to follow the quadratic correlation between the decomposition temperatures and the Pauling electronegativity of the cation for borohydrides of general formulae: $\text{M}(\text{BH}_4)_n$.

Acknowledgments

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Figures

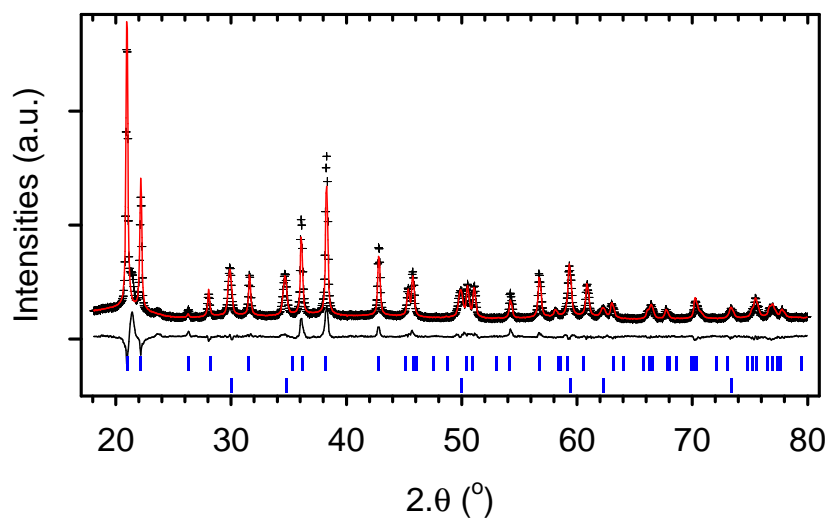


Fig. 1. PXD pattern of 2:1 CM-sample. The dots are the experimental points, the line is the refined pattern based on the Rietveld method, the bottom line is the difference between the experimental and the refined pattern ($R_{wp} = 8.7\%$). The ticks are the position of the Bragg peaks- upper line: α - $\text{Cd}(\text{BH}_4)_2$, lower line LiCl.

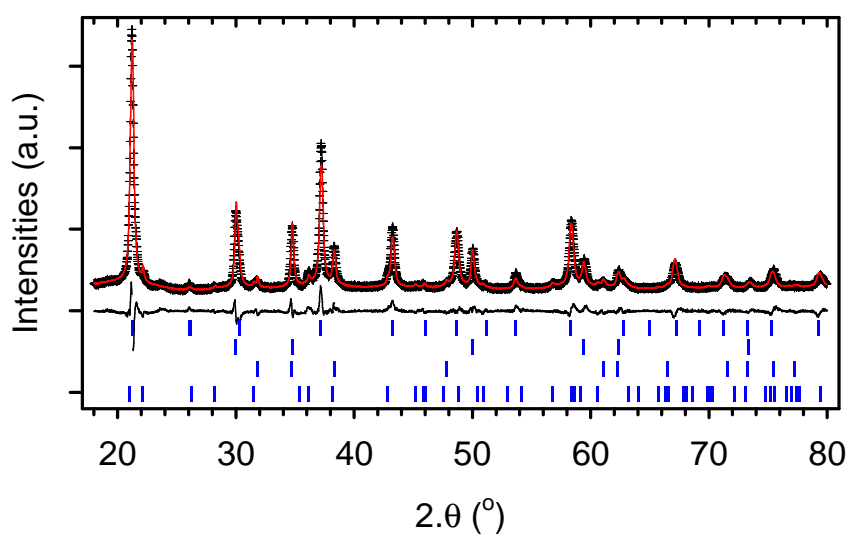


Fig. 2. The PXD pattern of 2:1 HM-sample. The dots are the experimental points, the line is the refined pattern based on the Rietveld method, the bottom line is the difference between the experimental and the refined pattern ($R_{wp} = 6.1\%$). The ticks are the position of the Bragg peaks - 1st line: β - $\text{Cd}(\text{BH}_4)_2$, 2nd line: LiCl , 3rd line: Cd , 4th α - $\text{Cd}(\text{BH}_4)_2$.

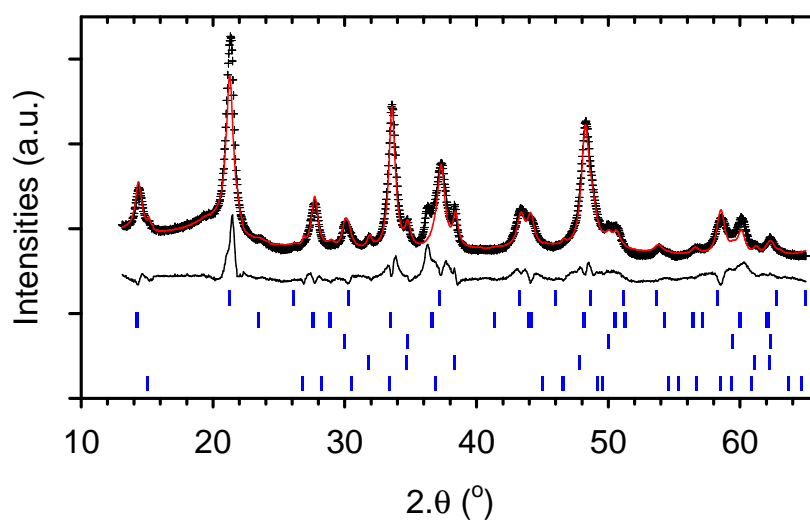


Fig. 3. The PXD pattern of 1:1 HM-sample. The dots are the experimental points, the line is the refined pattern based on the Rietveld method, the bottom line is the difference between the experimental and the refined pattern ($R_{wp} = 10\%$). The ticks are the position of the Bragg peaks - 1st line: β - $\text{Cd}(\text{BH}_4)_2$, 2nd line: Li_2CdCl_4 , 3rd line: LiCl , 4th line: Cd , 5th line: CdCl_2 .

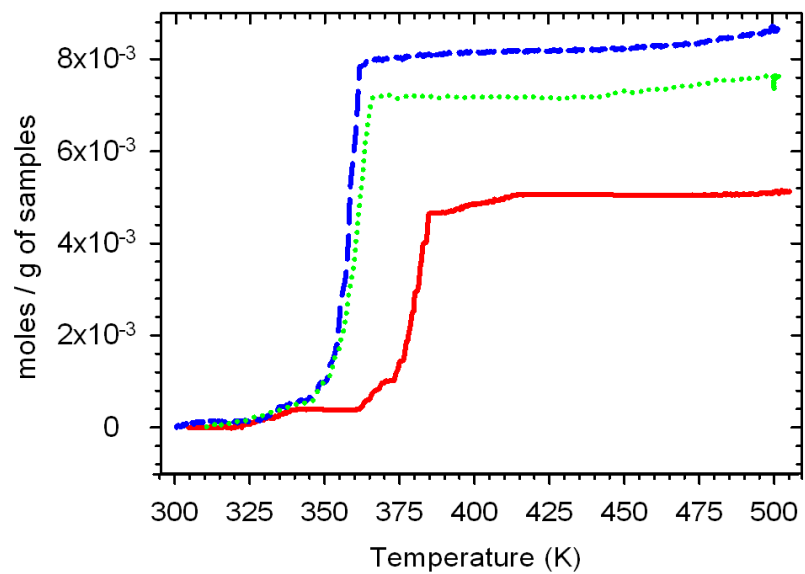


Fig. 4. Number of moles of gas released during the thermal decomposition of the (—) 1:1 HM-sample, (---) 2:1 CM-sample and (.....) 2:1 HM-samples.

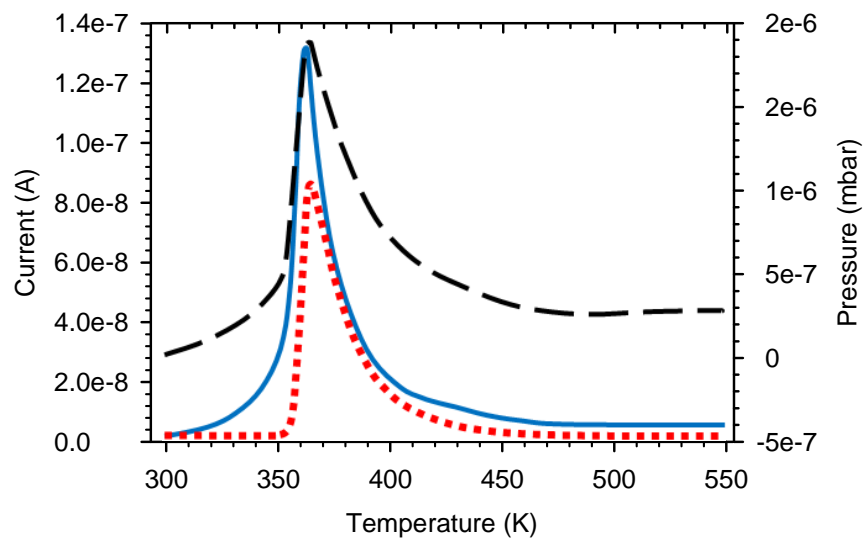


Fig. 5. Mass spectrometry measurement performed on the gases released during the thermal decomposition under dynamical vacuum of the HM-2:1 sample. (---) pressure evolution, (—) H₂ signal, (· · · · ·) B₂H₆ signal.

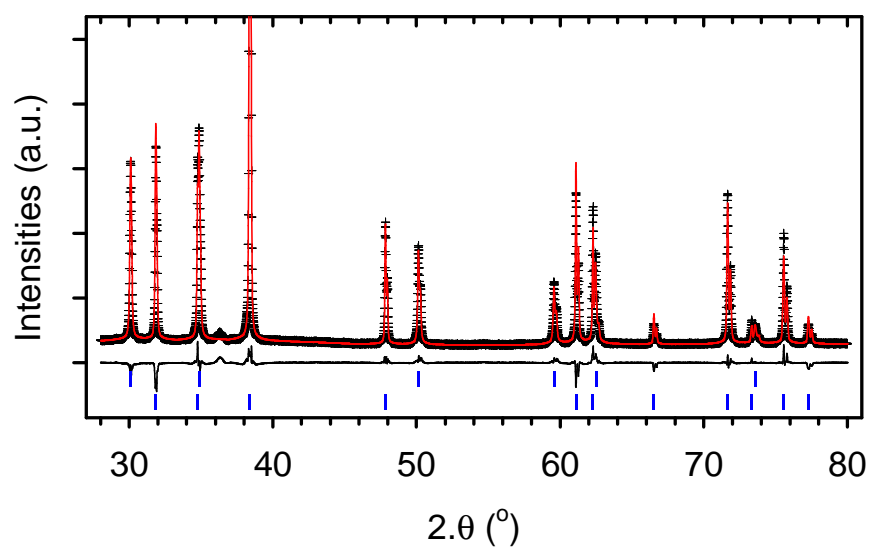


Fig. 6. The PXD pattern of the 2:1 CM-sample after its thermal decomposition up to 503 K. The dots are the experimental points, the line is the refined pattern based on the Rietveld method, the bottom line is the difference between the experimental and the refined pattern. The ticks are the position of the Bragg peaks - 1st line: LiCl, 2nd line: Cd.

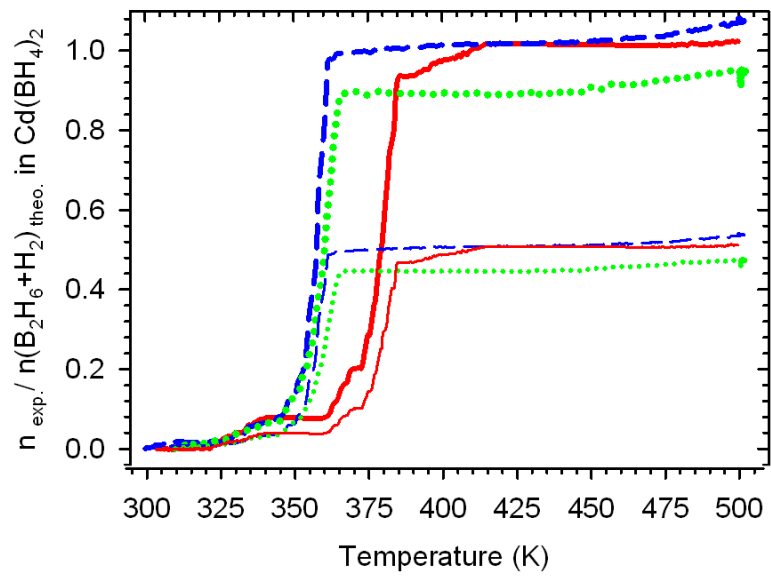


Fig. 7. Ratio of the number of moles of gas released during the thermal decomposition of the (—) 1:1 HM-sample, (— —) 2:1 CM-sample and (·····) 2:1 HM-samples over the theoretical number of moles of H₂ or H₂+B₂H₆ that could be released from Cd(BH₄)₂. Thick lines: $n_{\text{exp}}/n_{\text{H}_2+\text{B}_2\text{H}_6}$. Thin lines: $n_{\text{exp}}/n_{\text{H}_2}$.

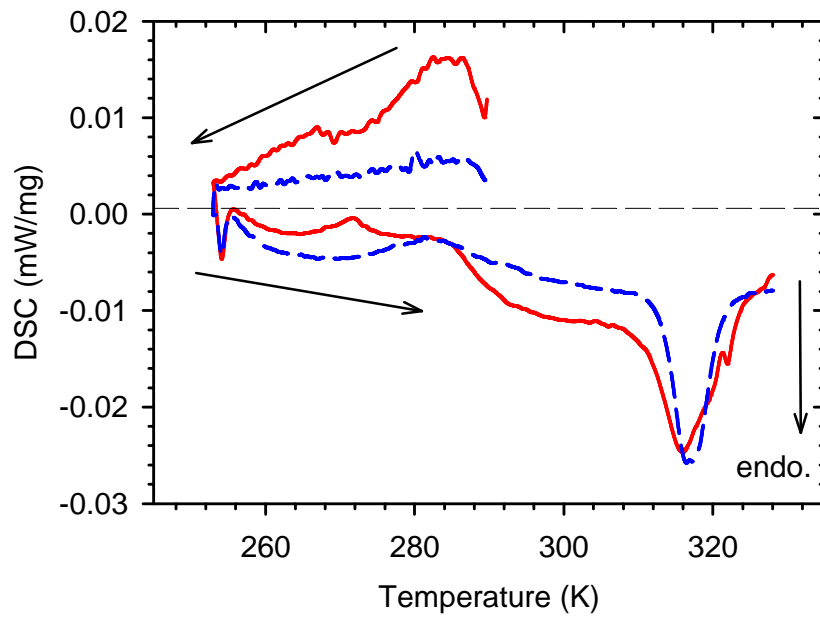


Fig. 8. DSC curves for the (—) 2:1 HM-sample and (- -) 2:1 CM-sample. The samples were first cooled down from room temperature to 253 K (right to left arrow, upper part) and then heated to 328 K (left to right arrow, lower part) at a rate of ± 2 K/min. The negative heat flow is endothermic.

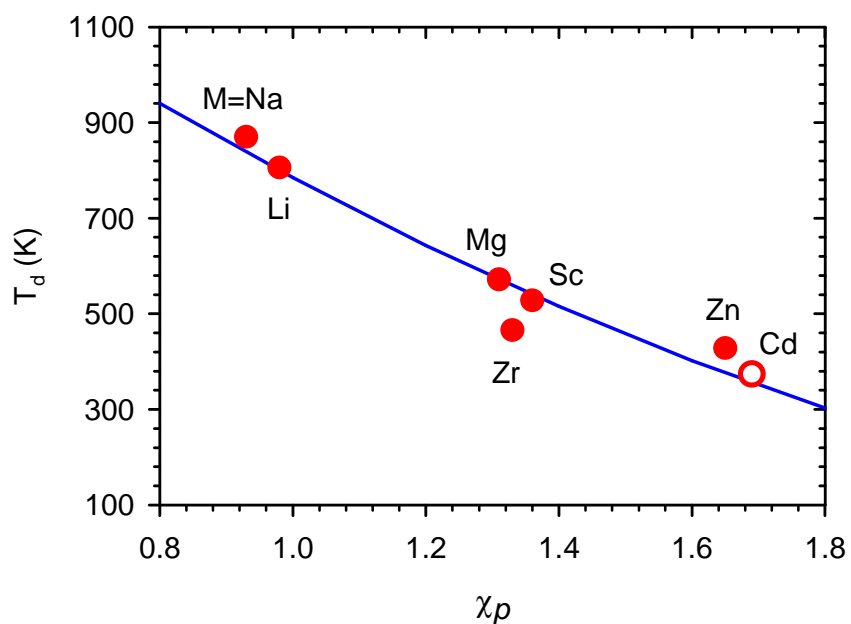


Fig. 9. The desorption temperatures, T_d of $M(\text{BH}_4)_2$, as a function of the cation M Pauling electronegativity χ_p . The filled circles are plotted using the experimental desorption temperatures published in [10], the empty circle is from this study. The blue line is a least square fit of the points ($Td = A.(\chi_p-B)^2$, A and B fitting parameters – see section 4.)

Table 1. Structural data, without the hydrogen atomic parameters, for the two Cd(BH₄)₂ polymorphs.

Phase	Space group	Cell parameters	Atom	Atomic parameters				
				Oxid.	Wyckoff pos.	x/a	y/b	z/c
α -Cd(BH ₄) ₂	$P4_2nm$	a = b = 5.64	Cd	-2	2a	0	0	0
		c = 6.33	B	1	4c	1/4	1/4	1/4
β -Cd(BH ₄) ₂	$Pn\bar{3}m$	a = b = c	Cd	-2	2a	1/4	1/4	1/4
		5.89	B	1	4b	0	0	0