Y(BD₄)₃, an efficient store of deuterium, and impact of isotope effects on its thermal decomposition

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Y(BD₄)₃, which stores as much as 16.6 wt.% and 252 kg/m³ D, has been synthesized via high-energy disk milling. The thermal decomposition of Y(BD₄)₃ has been investigated using thermogravimetric and calorimetric analyses combined with the spectroscopic evolved gas analysis. Two major endothermic events corresponding to thermal decomposition could be distinguished in the DSC profile up to 400 °C at ca. 231 and 285 °C, preceded by a phase transition (at ca. 198 °C) from the low-temperature Pa-3 form to a high-temperature polymorph of Y(BD₄)₃ (F-43c). The high-temperature phase forming at the onset of thermal decomposition may be prepared quantitatively by heating of the low-temperature phase to ca. 216 °C followed by rapid quenching.

Effects of isotope H→D substitution on various properties of yttrium borohydride have been analyzed. Y(BD₄)₃ constitutes a very efficient low-temperature source of deuterium gas on the laboratory scale.

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1. Introduction

Metal borodeuterides (borohydrides) rank among the most intensely investigated deuterium (respectively, hydrogen) storage materials [1–4] as they contain significantly larger amount of D (H) in comparison to corresponding metal binary deuterides (hydrides) (e.g. LiD – 22.5 (12.7) wt.% vs. LiBD₄ – 31.2 (18.5) wt.%, MgD₂ – 14.2 (7.7) wt.% vs. MgBD₄₂ – 26.0 (14.9) wt.%). Metal borodeuterides also contain large amounts of deuterium in terms of volumetric density: LiD 207 kg/m³ vs. LiBD₄ 246 kg/m³, MgD₂ 224 kg/m³ vs. MgBD₄₂ 294 kg/m³, Y(BD₄)₃ 252 kg/m³, which exceed by far that for liquid D₂, 162 kg/m³. These combined features render borodeuterides the very attractive class of materials for solid state storage of deuterium, in terms of volumetric D content superior to LiD, which has been utilized during the Manhattan project.

Recently, numerous metal borohydrides have been synthesized in a solvent-free form and characterized with respect to hydrogen storage properties; these are LiBH₄ [5–8], Mg[BH₄]₂ [9–11], the crystallographic structure of which has been solved very recently [12], Ca(BH₄)₂ [13,14], "Sc(BH₄)₃" [15] (later shown to be in fact LiSc[BH₄]₃ [16], and others [17]. All these materials suffer from too large thermodynamic stability and concomitantly too high temperatures of thermal decomposition with evolution of H₂. High-temperature and high-pressure forms for many of these compounds have also been studied aiming at their thermodynamic destabilization [18–21]. Some of these phases are metastable at ambient conditions upon temperature–quenching or decompression, e.g. for Mg(BH₄)₂ the high-pressure and high-temperature phases are metastable at ambient conditions [12,22] while for Ca(BH₄)₂ the high pressure phase is metastable at room temperature [14,23].

In our recent work we have reported successful preparation of solvent-free Y(BH₄)₃ [24]. This H-rich material has proved to exhibit unusually low temperature of thermal decomposition (ca. 160 °C onset value, 223 °C at DSC peak for 1 K/min scan). Thermal stability of Y(BH₄)₃ is thus much lower than those for homologous borohydrides of di- and mono-valent cations of ionic radius similar to that of tri-valent yttrium (R/Y³⁺) [26] cubic = 1.16Å; Ca(BH₄)₂ (320 °C, R(Ca²⁺) cubic = 1.26Å), and NaBH₄ (485 °C, R(Na⁺) cubic = 1.32Å); this is obviously due to increased positive charge density and concomitant enhanced electron-acceptor properties [25] of a triply-charged cationic center as compared to other two species.

Although studies for H-rich materials are prevalent in the literature [25], yet their deuterated analogs received much less attention. In particular, isotope effects of H→D substitution on many important physicochemical properties are largely unknown. Since deuterium is the most important stable isotope tracer, and important nuclear fuel for fusion reactor, we have now decided to study an efficient deuterium store, Y(BD₄)₃ as an extension of our previous investigations for the non-deuterated analog [24]. We are interested in the impact of isotopic substitution on various properties of this novel material [26] and especially in its thermal decomposition. The volumetric content of deuterium in Y(BD₄)₃ (252 kg/m³) is very large and it even
slightly exceeds that for LiBD₄ (246 kg/m³). Y(BD₄)₃ could thus be applied as an efficient low-temperature source of deuterium in the laboratory, a powerful deuterium-introducing agent in organic chemistry, a compound with ‘chemically-precompressed’ deuterium [27,28] for the purpose of high-pressure metallization or even superconductivity within deuterium sublattice [29] as well as for model studies of cold and muon-catalyzed nuclear fusion.

If one considers the deuteride materials as a part of fusion materials, there are a number of requirements to address, not only a large amount of deuterium storage but also ease of deuterium absorption and release, stability of the material for repeated use, possible effects of isotopic and other impurities.

2. Experimental procedures

2.1. Synthesis

2.1.1. Substrates

All substrates were fine quality anhydrous chemicals from Sigma–Aldrich (LiBD₄ > 95%, NaBD₄ > 98% D. YCl₃ + 99.9% on metal basis). To avoid hydrolysis all reactions were performed (and all samples were stored) in an inert gas (Ar) atmosphere of the MBRAUN Labmaster DP glovebox (<0.1 ppm O₂,<0.1 ppm H₂O).

2.1.2. Dry (mechanochemical) synthesis from MBDA and YX₃

For mechanochemical synthesis the vibrating mill (Testchem) and chromium steel bowl and disk were used. Substrates, YCl₃ and MBDA (M = Li, Na) were mixed in ca 1:3 M ratio (with a 5% excess of MBDA) and milled for 30–60 min in Ar atmosphere. Milling periods of 3–5 min were altered with 2–5 min rests to avoid thermal decomposition of the products. Temperature of the milling bowl did not exceed 40 °C as measured by pyrometer. The product contains only the LiCl by-product, according to reaction equation:

\[ \text{YCl}_3 + 3\text{LiBD}_4 \rightarrow \text{Y(BD}_4\text{)}_3 + 3\text{LiCl} \]  

(1)

2.1.3. Preparation of the HT phase

To quench the high-temperature phase of Y(BD₄)₃ the samples of low-temperature phase (together with LiCl as a dead mass) were slowly heated to a selected temperature (at 1 K/min) and then rapidly cooled (at 40–50 K/min) via a liquid N₂ cooling system of the TGA oven.

2.2. Methods

2.2.1. Infrared spectroscopy

Infrared absorption spectra of all solid products were measured using Vertex 80v FT–IR spectrometer (Bruker). Anhydrous KBr was used as a pellet material.

2.2.2. Raman spectroscopy

Raman scattering spectra of all solid products sealed inside 1 mm quartz capillaries were measured using dispersive T64000 Raman spectrometer (Jobin Yvon–SpeX, 647.1 and 514.5 nm, holographic gratings) equipped with an optical microscope BX40 (Olympus, 50 mm lense).

2.2.3. X-ray diffraction

Solid products sealed inside the 1 mm or 0.3 mm quartz capillaries were investigated by X-ray powder diffraction using the D8 Discover diffractometer from Bruker (a parallel beam; the Cu Kα1 and Cu Kα2 intensity ratio of ca. 2:1).

2.2.4. X-ray diffraction analysis

Powder X-ray diffraction patterns (XRDs) were processed in Materials Studio 4.2 from Accelrys. The X-Cell program [30] has been used for indexing and determination of systematic absences.

2.2.5. Thermal decomposition

Thermal decomposition of samples was investigated with a thermogravimetric (TGA) analyzer and differential scanning calorimeter (DSC) combined in a simultaneous thermal analyzer STA 409 PG (Netzsch) at a constant Ar (99.999%) flow of 50 ml/min. Simultaneously the evolved gas analysis (EGA) was carried out with a quadrupole mass spectrometer QMS 403 C (Pfeiffer Vacuum) and a vacuum Infrared spectrometer Vertex 80v (Bruker). The spectrometers were connected to the TGA/DSC device by quartz capillary and Teflon® tube, respectively. Both transfer lines were preheated to 200 °C to avoid condensation of low-boiling volatiles. Samples were placed inside Al₂O₃ crucibles with cover and were heated at various rates (1, 5 or 10 K/min).

3. Results and discussion

Similarly to yttrium borohydride [24,31], yttrium borodeuteride has been synthesized mechanochemically in the reaction which leads to a mixture of Y(BD₄)₃ and LiCl, via high-energy disk milling of YCl₃ and LiBD₄ Eq. (1). The product has been characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. Mechanochemical synthesis using NaBH₄ instead of LiBH₄ was unsuccessful: the side product, NaCl, was imperceptible in XRD pattern (Fig. 1), and peaks originating from Y(BD₄)₃ could not be detected. The only phase observed in XRD pattern was NaBH₄. Its broad reflectance of low intensity indicate that this substrate is dispersed and forms very small crystallites. Use of YF₃ precursor instead of YCl₃ does not yield the desired product, either [24].

Y(BD₄)₃ and LiCl form a mechanically-inseparable phase containing 52.6 wt.% of Y(BD₄)₃ and 47.4% of LiCl (Fig. 2). This mixture stores 9.18% of deuterium by weight; pure Y(BD₄)₃ would contain as much as 16.6 wt.% D.

3.1. Crystal structure and vibrational spectra of Y(BD₄)₃

The crystal structure of Y(BD₄)₃ solved by Sato et al. [31] is presented in Fig. 3. Yttrium borodeuteride adopts a primitive cubic structure, with a = 10.771 Å in a space group Pa-3 (No. 205). The BH₄⁻ anions are located approximately in the middle of the edges of a distorted cube formed by Y³⁺ cations; every Y³⁺ cation is coordinated by six BH₄⁻ ions in an approximately octahedral fashion. The B–Y–B angles are equal to 160.3° (axial) and 78.2–104.1°.

Fig. 1. The powder diffractogram of YCl₃ and NaBD₄ mixture milled for 32 min. All broad peaks seen can be assigned small grain substrate, NaBD₄; rest of the sample is amorphous.
(adjacent B atoms) with Y–B and Y–D distances of 2.66–2.80 Å and 2.23–2.38 Å, respectively.

The FTIR spectrum of Y(BD₄)₃ (Fig. 4) shows two major bands originating from B–D stretching, one at 1714 cm⁻¹ (vs) and another at 1884 cm⁻¹ (w) with two shoulders at 1788 cm⁻¹ and 1631 cm⁻¹, as well as a strong band at 920 cm⁻¹ coming from D–B–D bending vibrations, with two shoulders at ca. 852 cm⁻¹ and 999 cm⁻¹. Raman spectrum (Fig. 5) is predominated by a very strong doublet at 1647 cm⁻¹ (BD stretching modes) and it also shows weaker bands at 958 cm⁻¹ (m) and 818 cm⁻¹ (broad, DBD bending modes). In both FTIR and Raman spectra of Y(BD₄)₃ weak bands appear in the region typical of ν(B–H) and δ(H–B–H) modes; this is partly due to an incomplete isotope substitution in commercial LiBD₄ used by us for preparation of the Y(BD₄)₃ samples and also due to slight molar excess of LiB(D/H)₄ used for synthesis.

The vibrational spectra of Y(BH₄)₃ differ markedly from those of Y(BD₄)₃. The most intense peaks in the FTIR spectrum are at 2304 cm⁻¹ (vs), 2274 cm⁻¹ (s) and 2387 cm⁻¹ (sh) (ν(B–H) region) and at 1212 cm⁻¹ (vs) and 1128 cm⁻¹ (s) (δ(H–B–H) region). Raman spectrum of Y(BH₄)₃ shows distinct features at 2317 cm⁻¹ (vs) and 2204 cm⁻¹ (s) with a shoulder at 2300 cm⁻¹ (BD stretching modes) and it also shows weaker bands at 1350 cm⁻¹ (m) and 1149 cm⁻¹ (w) (HBH bending modes). The redshift of the major IR and Raman bands upon the H?D isotope substitution is by the factor of 1.32–1.41, in fair agreement with the approximate value of √2 expected from the reduced mass increase.

3.2. Thermal decomposition of Y(BD₄)₃

Thermal decomposition process of Y(BD₄)₃/3 LiCl mixture has been investigated with the TGA/DSC/EGA analyzer. It is commonly assumed that LiCl (melting without decomposition at 605 °C) does not influence significantly the decomposition process of borohydrides [16,17]. The TGA, the first TGA derivative (DTG) and DSC profiles of thermal decomposition of the mixture of Y(BD₄)₃ and LiCl at the heating rate of 10 K/min are shown in the Fig. 6. The thermal decomposition is a complex process, where two major endothermic steps can be distinguished up to 400 °C. The onset of mass loss is around 165 °C, the temperatures at the main DSC peaks are ca. 231 °C and 285 °C. These values are slightly higher, or equal to those measured for Y(BH₄)₃ (160, 230 and 279 °C, respectively).

The first major step, from 165 to 266 °C (as measured from the onset point to the valley between two DSC peaks, with the integrated heat transfer of ca.*196.2 J/g which corresponds to

![Fig. 2. The powder diffractogram of YCl₃ and LiBD₄ mixture milled for 40 min. All unmarked peaks originate from Y(BD₄)₃, in the structure first solved by Sato et al. [31]. The background has been removed.](image)

![Fig. 4. The FTIR spectra of synthesized Y(BD₄)₃ (up) and Y(BH₄)₃ (bottom).](image)

![Fig. 5. Raman spectra of Y(BD₄)₃ (top) and Y(BH₄)₃ (bottom) excited with 514.5 nm and 647.1 nm laser lines, respectively.](image)
+54.3 kJ/mol Y(BD4)3, is characterized by a rather small mass loss of ca. 2.1%. This is equivalent to about 2.9 D atoms per molecule of Y(BD4)3; a solid product has a nominal composition of ca. YB3D9. This endothermic event is complex as it covers in fact three overlapping endothermic processes, which could be distinguished at a slower heating rate of 1 K/min (Fig. 7). Similarly as for yttrium borohydride, the lowest-temperature part of the first endothermic DSC peak (temperature range of 165–205 °C) corresponds to a very small mass loss (ca. 1 wt.% at 1 K/min), which suggests that a phase transition is taking place around ca. 190 °C, only slightly overlapped with thermal decomposition. The high-temperature form of Y(BD4)3, first observed by us [24] and later studied independently by two groups [32,33], will be briefly discussed in Section 3.4 of this paper and analyzed in extenso in a separate contribution [34].

During the second major endothermic step of thermal decomposition (266–400 °C at 10 K/min) about 4.9% mass is lost, corresponding to additional 6.7 D atoms. The heat transfer connected to the second decomposition step is about +249.7 J/g (+69.1 kJ/mol Y). Thus, a total of 7.0% mass is lost below 400 °C, which is an equivalent to 9.6 D atoms released; note that 12.0 D atoms per formula unit are expected for the full thermal decomposition of Y(BD4)3; a solid product has a nominal composition of ca. YB3D9. This endothermic event is complex as it covers in fact three overlapping endothermic processes, which could be distinguished at a slower heating rate of 1 K/min (Fig. 7). Similarly as for yttrium borohydride, the lowest-temperature part of the first endothermic DSC peak (temperature range of 165–205 °C) corresponds to a very small mass loss (ca. 1 wt.% at 1 K/min), which suggests that a phase transition is taking place around ca. 190 °C, only slightly overlapped with thermal decomposition. The high-temperature form of Y(BD4)3, first observed by us [24] and later studied independently by two groups [32,33], will be briefly discussed in Section 3.4 of this paper and analyzed in extenso in a separate contribution [34].

The heating rate has dramatic effects on the DSC profile of Y(BD4)3, similar to its non-deuterated analog [24]. (i) First, as mentioned above, the first major endothermic peak (231 °C at 10 K/min) reveals its more complex structure by splitting in two distinct peaks at 1 K/min (192 °C and 228 °C). The associated integrated heat transfer changes considerably from +196.2 J/g (10 K/min) to +130.7 J/g (1 K/min). These changes suggest that initial stages of thermal decomposition of Y(BD4)3 progress along at least two independent reaction pathways of considerably different kinetics and thermodynamics. Unfortunately, it is difficult to immediately suggest any chemical reaction equations since none of these pathways leads to detectable amounts of crystalline products. Given small amount of D2 gas evolved, it is sensible to assume that complex M–B–D intermediates (D:B < 4) are formed, similar to those detected during thermal decomposition of Ca(BH4)2 [35]. (ii) The second major step of thermal decomposition is also affected by the heating rate, its main DSC peak being downshifted appreciably from 285 °C to ca. 248 °C and the associated heat transfer being changed from +249.7 J/g to +338.8 J/g. This indicates that the kinetics of the second step of decomposition is also rather slow.

3.3. Purity of D2 gas evolved during thermal decomposition

The time-resolved mass spectra and the FTIR spectra of gases evolved during the thermal decomposition are shown in Fig. 8a. Evolved gas analysis (EGA) shows that released D2 gas is only slightly contaminated. The vast majority of ion current comes from D2 ions. The percent of D isotope in all hydrogen present in gaseous products has been estimated at ca. 95% while assuming that the ionisation cross-sections of D2, DH and H2 are identical. This is in fair agreement with the nominal D content in commercial LiBD4 (98% D) used for preparation of Y(BD4)3. According to the time-resolved mass spectra, almost pure D2 is released at the initial stages of the thermal decomposition (165–225 °C) with the mass loss corresponding to 1 D atom per formula unit. At the latter stage of decomposition (225–270 °C), perceptible ion currents coming from the ions of M/Z: 34, 30, 31, 29, 33 are observed, which correspond to B2D6 and the products of its decay. In the FTIR spectrum of the gaseous thermal decomposition products measured at this decomposition stage (Fig. 8b), four broad bands appear in the range of wavenumbers typical of the bending and stretching B–D vibrations [36–38] (at 900–1050 cm−1, 1125–1290 cm−1, around 1400 cm−1 and 1795–2025 cm−1, Fig. 3b). A weak band at ca. 1400 cm−1...
2580 cm\(^{-1}\) apparently originates from traces of \(^1\)H in the sample (vB–H).

Majority of D\(_2\) is evolved in the temperature range 270–320 °C. A detectable maximum of ion current has been observed in this range for the ion of M/Z = 42 corresponding to ArD\(^+\) cation. The FTIR spectra of gases evolved in this temperature range show very low signal to noise ratio and have low intensity; the B\(_2\)\(\text{D}_{\text{m}}\) impurities of the deuterium released, are hardly detectable (Fig. 9). This can be understood if one recollects that majority of boron hydrides and deuterides are thermodynamically unstable species, which undergo facile thermal decomposition at elevated temperatures. It is also important to notice that peaks originating from various volatile atomic chlorine, BCl\(_3\), B\(_n\)D\(_m\)Cl\(_{\text{in}}\), or their dimers, could not be observed in the time-resolved MS spectra, which suggests that LiCl is indeed an inert phase and it does not influence thermal decomposition of Y(BD\(_4\))\(_3\).

3.4. High-temperature (HT) polymorphic form of Y(BD\(_4\))\(_3\)

Similarly to high-temperature Y(BH\(_4\))\(_3\) [24], a new crystalline HT–Y(BD\(_4\))\(_3\) phase could be prepared by heating the starting material (Y(BD\(_4\))\(_3\) in mixture with LiCl) up to the temperatures of ca. 200–220 °C and fast cooling down to the room temperature (at ca. 50 K/min). The new phase appears close to 200 °C and it becomes the only Y-containing phase observed in the powder XRD measurement of a sample prepared by heating the starting material up to 216 °C (at the heating rate of 1 K/min, Fig. 10). The peaks of the new phase could be indexed leading to several solutions with good figure of merit. The best solutions obtained were cubic cell vectors with a = 5.50 Å (V = 166.6 Å\(^3\)) and 11.01 Å (V = 1333 Å\(^3\)), with extinction classes of P2\(_3\) and F-43c, respectively. According to the Infomatica and PDF2 ICCD databases, none of the known compounds, containing the elements present in the sample (Y, B, Cl, Li, H), adopts such unit cell. Since formation of this new phase is associated with a minor mass loss of the samples (ca. 1 wt.%), and the expected molar volume of the best P2\(_3\) solution is only 4.8% larger than that of the low-temperature phase of Y(BD\(_4\))\(_3\) (159.4 Å\(^3\)), it may be safely assumed that one deals with a genuine high-temperature polymorph of Y(BD\(_4\))\(_3\). Additional support for the HT form of Y(BD\(_4\))\(_3\) comes from the quantum–mechanical DFT calculations, which show absence of imaginary phonon modes for this phase. The results of our experimental and computational studies on the above mentioned structure, described recently by two other groups [32,33], will be published in a separate contribution [34].

3.5. Y(BD\(_4\))\(_3\) vs. Y(BH\(_4\))\(_3\): summary of isotope effects

The H→D isotopic substitution is related to a huge relative change of atomic mass (an increase by 100%) and thus it is thought to be source of the largest among isotope effects achievable via any isotopic exchange in the periodic table (except for H→T one). Indeed, selected properties of isotopically substituted dihydrogen molecules differ considerably depending on of the type of their atomic constituents (Table 1).

In view of these differences, it is natural to expect that selected properties of H- and D-rich compounds i.e. hydrides and deuterides, will also differ considerably from one another. In particular, thermal decomposition of both classes of compounds should be considerably affected. There are two major reasons for that: (i) isotope effects are supposed to influence heat effects of thermal decomposition mostly via a non-vanishing contributions from element–H(D) and H–H (D–D) zero-point energy (ZPE); (ii) temperature of thermal decomposition should be also affected since in the first approximation temperature of thermal decomposition (at thermodynamic limit) equals \(\Delta H/\Delta S\), where \(\Delta H\) and \(\Delta S\) are, respectively, enthalpy and entropy changes at the thermal decomposition. While entropy of \(\text{H}_2\) is only 90% that of \(\text{D}_2\) gas.

As recent computational studies have shown [39–41] the zero-point energy corrections largely cancel out both at temperature- and pressure-induced phase transitions as well as at during chemical reactions (such as thermal decomposition) of various hydrides, such as LiBH\(_4\) [39], LiAlH\(_4\) [40], or NaAlH\(_4\) [41]. Nevertheless, for certain reactions the non-compensated ZPE correction may sometimes exceed 0.1 eV per one evolved \(\text{H}_2\) molecule [39,41]. In addition, correction related to the specific heat and entropy terms (strongly affecting the process of thermal decomposition) may also be quite large. Specifically, entropy of a substrate hydride in the solid state (largely dependent on its low-energy phonons) is affected by H/D isotope substitution to a comparable degree as the entropies of the reaction products in the solid state [41]. In consequence, entropy of the decomposition reaction is predominantly governed by entropy of the solely gaseous product, \(\text{H}_2\) (or \(\text{D}_2\)), so it must be strongly isotope–dependent.

It is thus interesting to learn to what extent isotope effects affect structure, properties and process of thermal decomposition of Y(BH\(_4\))\(_3\) compound containing as much as 75 M % H. The impact of the H→D substitution has been summarized in Table 2.

As expected, the lattice constants and the unit cell volumes of both low- and high-temperature forms of Y(BH\(_4\))\(_3\) are rather weakly affected by isotopic substitution. Surprisingly, the effect has different sign for both forms: deuteration decreases the unit cell vector for the low-T form but increases it for the high-T form. The temperatures of the phase transition and of both steps of thermal decomposition are also weakly affected by deuteration. On the other hand, heats of the phase transition and of both steps of thermal decomposition are very sensitive to isotope effects, the values for deuterated compound being larger by up to 72% from those

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**Fig. 9.** The FTIR spectrum of the gaseous thermal decomposition products of Y(BD\(_4\))\(_3\) at ca. 280 °C. No bands of significant intensity can be observed in the BD stretching region (1800–2000 cm\(^{-1}\)). Therefore, the bands marked as ** and ** could not originate from DBD bending modes; they probably originate from X–OH bending modes of unknown impurities.

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**Fig. 10.** The powder diffractogram of the high-temperature phase of Y(BD\(_4\))\(_3\) obtained at 216 °C from the low-temperature phase, together with LiCl by-product. The background has been removed.
measured for non-deuterated one. This result suggests that increased heat of the phase transition/decomposition reaction is partly compensated by entropy increase of the evolved gas, thus leading to similar values of characteristic temperatures.

### 3.6. Remaining issue

Reversibility of \( \text{H}_2 \) (or \( \text{D}_2 \)) desorption/absorption is an important practical issue for hydrogen storage materials. The previous thermodynamic considerations (based on results shown later in Table 2) indicate possibility of achieving partial reversibility of \( \text{H}_2 \) evolution due to a nice balance of enthalpic and entropic effects. The heat associated with the first large DSC peak, \( Q_{\text{DSC}_1} \), of 51.3 kJ/mol, is comparable to the entropy effect at room temperature of 1.25 mol of \( \text{H}_2 \) and 1.25 mol of \( \text{D}_2 \) gas evolved during thermal decomposition.

### 4. Conclusions

We have obtained \( \text{Y(BD}_4\text{)}_3 \) in a mixture with \( \text{LiCl} \) via short high-energy disk milling of the \( \text{LiBD}_4 \) and \( \text{YCl}_3 \) precursors, similarly to non-deuterated \( \text{Y(BH}_4\text{)}_3 \) synthesized recently [24,31]. Slow and moderately endothermic decomposition of \( \text{Y(BD}_4\text{)}_3 \) starts above 165 °C (10 K/min) with a significant acceleration of deuterium evolution above 200 °C. Simultaneously, a very weakly endothermic reaction is noticed at this stage, 1.25 TS \( \text{H}_2 \rangle \text{mol} = 48.7 \text{kJ/mol.} \)

Impact of isotopic H→D substitution on thermal decomposition of yttrium borohydride is revealed mainly in the increased heat of the phase transition (preceding the decomposition) and heat of the second step of thermal decomposition but not in the associated characteristic temperatures of these events.

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### References


### Table 1

Selected properties of \( \text{H}_2 \) molecule in its ground \( \chi \left( ^1 \Sigma \right) \) state, which are influenced by isotopic substitutions (source of numerical data from Ref. [37] unless stated otherwise).

<table>
<thead>
<tr>
<th>Property</th>
<th>( \text{H}_2 )</th>
<th>( \text{HD} )</th>
<th>Change (%)</th>
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<td>10.83(1)</td>
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<td>( V_{\text{TR}} ) (cm(^{-1}))</td>
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<td>( V_{\text{TR}} ) (Å)</td>
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<td>( V_{\text{TR}} ) (cm(^{-1}))</td>
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<td>( \Delta H_{\text{TR}} ) (kJ/mol)</td>
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<td>165</td>
<td>1.2</td>
</tr>
<tr>
<td>( \Delta T_{\text{TR}} ) (°C)</td>
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<td>198</td>
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</tr>
<tr>
<td>( \Delta T_{\text{DSC}_1} ) (°C)</td>
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<td>231</td>
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<td>( \Delta T_{\text{DSC}_2} ) (°C)</td>
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<tr>
<td>( T_{\text{IR}, \text{max}} ) (cm(^{-1}))</td>
<td>2317, 2204</td>
<td>1716, 1604</td>
<td>-26.0, -27.0</td>
</tr>
</tbody>
</table>

\( a_{\text{TR}} \) The measured heat values do not correspond precisely to reaction enthalpy since experiment is conducted in the Ar gas flow and not in \( \text{H}_2/\text{D}_2 \) gas at 1 atm.

\( b \) Values calculated for characteristic temperatures in the Kelvin scale.