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FT-IR spectra of inorganic borohydrides



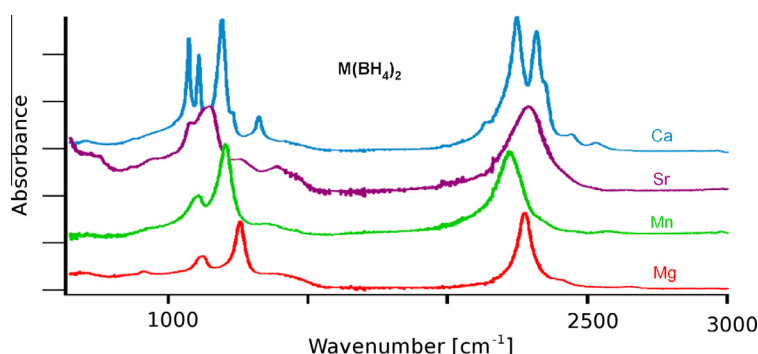
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HIGHLIGHTS

- A collection of FTIR spectra of borohydrides and deuterides is presented.
- All spectra are available digitally for the research community.
- This database is a new tool in the field of potential hydrogen storage materials.
- This database will be continuously extended.

GRAPHICAL ABSTRACT



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ABSTRACT

Inorganic compounds with BH_4^- ions are the subject of many recent investigations in the context of potential hydrogen storage materials. In this work, Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectra of a series of reference and research compounds (including deuterated samples) are collected and made available to the research community.

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Introduction

Compounds with a high gravimetric hydrogen content attract a lot of research interest as potential hydrogen storage materials [1,2]. Among these compounds are the borohydrides and, over the last 5 years, many new compounds have been prepared and characterized [3–6]. In the course of our investigations in this field, we have obtained many vibrational spectra of borohydrides. The application of the IR [7] and Raman [8] spectroscopies in the structural studies of borohydrides gives an important contribution in the understanding of the local structure and symmetry of the

BH_4^- ions in the crystals [7]; in the IR region, in fact, the bending and stretching modes of the BH_4^- group are detected. There have been several reviews presenting vibrational spectra of these compounds previously (e.g. Refs. [9,10]), and a collection of Inelastic Neutron Scattering data can also be found [11]. The hydrolysis of borohydrides leads to borates for which literature data are also available (see for example [12]). In the course of the synthesis of new borohydrides or during the studies of their thermal decomposition, it is of interest to have a set of reference spectra to assist the identification of the products formed. The aim of this work is to present and make available a collection of ATR-FTIR spectra in this field. The detailed discussion with respect to the assignment of specific features can be found in the above mentioned review papers as well as in the original publications [13–26]. The use of the ATR technique was chosen as it appeared that the KBr pellet technique is not suitable for several compounds

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(e.g. LiBH_4 and $\text{Ca}(\text{BH}_4)_2$ [17]). Further, this method allows to load the sample under controlled atmosphere in the glove box, avoiding, then, the exposure of the borohydrides to humidity. The collection of spectra presented here will be continuously extended as new samples will be available [27].

Experimental

All the spectra were recorded at ambient temperature using a Specac Golden Gate Diamond ATR setup in a Biorad Excalibur FT-IR instrument with a nominal resolutions of 1 or 2 cm^{-1} . When necessary, the signals of the water vapor and the carbon dioxide were subtracted manually. All the samples were loaded in a nitrogen-filled glove box. For each compound, the best experimental spectrum available (for the purest compound) was kept for this spectral collection. Besides the commercial samples (see Table 1), all other borohydrides were prepared either by metathesis, ball milling or other methods as specified in the corresponding original literature [3]. The synthesis of $(\text{CH}_3)_4\text{N} \cdot \text{BH}_4$ was reported in [28,29], together with IR data as part of its characterization. $\text{Sr}(\text{BH}_4)_2$ was prepared by reacting SrH_2 with Et_3NBH_3 , similarly to the

preparation of $\text{Mg}(\text{BH}_4)_2$ [3]; the α -phase of $\text{Ca}(\text{BH}_4)_2$ was obtained by drying $\text{Ca}(\text{BH}_4)_2 \cdot \text{THF}$.

Results and discussion

Table 1 summarizes all the spectra contained currently in the data collection with their filenames as appearing in the supplementary data-files and the references (if applicable) of the publications for which these spectra were measured. This collection also contains the spectra of some partially and fully deuterated borohydrides. Spectra of some hydrides (Ca, Sr, Y) are also included for comparisons; the IR spectra of these compounds have been studied in detail previously [30–32]. The spectral region analyzed (typically $600\text{--}3000\text{ cm}^{-1}$) corresponds to the BH_4^- bending ($1000\text{--}1500\text{ cm}^{-1}$) and to the B–H stretching modes ($2000\text{--}2500\text{ cm}^{-1}$).

Alkali borohydrides

Fig. 1 presents the IR spectra of the alkali borohydrides: Harvey and McQuaker [33,34] have studied previously the IR and Raman spectra of MBH_4 and MBD_4 ($M = \text{Li, Na, K}$). For LiBH_4 , time resolved IR spectra have been presented recently [35]. With the exception of LiBH_4 , all the other compounds are face-centered cubic with a tetrahedral BH_4^- ion. According to the selection rules, for a tetrahedral system, there are only two IR active modes, one bending and one stretching mode, both with T_2 symmetry. The additional bands observed around 2300 cm^{-1} are caused by strong Fermi resonances. It is interesting to note that the relative intensities of these bands change for the corresponding deuterides (Fig. 2). These intensity changes can be quantitatively understood using anharmonic DFT calculations [36]. For LiBH_4 , a significant splitting of the bending mode reflects the lowering of the symmetry of the BH_4^- ion in this crystal. Interestingly, the stretching vibrations remain well centered around 2300 cm^{-1} . This is also the case for the bimetallic compound $\text{LiK}(\text{BH}_4)_2$. Note that this compound (prepared by ball milling of LiBH_4 and KBH_4 in a ratio of 2:1 [37]) also contains an excess of LiBH_4 .

Table 1

List of the borohydrides whom IR spectra are included in the data collection. For each compound, the filename and the reference from where the IR spectrum was taken (when available) are shown. For the commercial samples, the supplier and nominal purity are indicated.

Borohydride	Filename	Reference and remarks
LiBH_4	LiBH4.txt	Sigma Aldrich (>90%)
NaBH_4	NaBH4.txt	[13]
KBH_4	KBH4.txt	[13]
RbBH_4	RbBH4.txt	[13]
CsBH_4	CsBH4.txt	[13]
$(\text{CH}_3)_4\text{N} \cdot \text{BH}_4$	Me4NBH4.txt	Sigma Aldrich (95%)
LiBD_4	LiBD4.txt	[3]
NaBD_4	NaBD4.txt	[13]
KBD_4	KBD4.txt	[13]
RbBD_4	RbBD4.txt	[13]
CsBD_4	CsBD4.txt	[13]
NaBH_4 solution	NaBH4_solution.txt	[14]
$\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$	NaBH4_2H2O.txt	[14]
NaBHD_3	NaBD3H.txt	[15]
$\alpha\text{-Mg}(\text{BH}_4)_2$	MgBH4_2_alpha.txt	[16]
$\alpha\text{-Ca}(\text{BH}_4)_2$	CaBH4_2_alpha.txt	[17]
$\beta\text{-Ca}(\text{BH}_4)_2$	CaBH4_2_beta.txt	[17]
$\text{Mn}(\text{BH}_4)_2$	MnBH4_2.txt	[18]
$\alpha\text{-Mg}(\text{BD}_4)_2$	MgBD4_2.txt	[19]
$\text{Ca}(\text{BH}_4)_2 \cdot \text{THF}$	CaBH4_2_THF.txt	
$\text{Ca}(\text{BD}_4)_2$	CaBD4_2.txt	[19]
$\text{Mg}(\text{BH}_3\text{D})_2$	MgBH3D_2.txt	
$\text{Mg}(\text{BHD}_3)_2$	MgBHD3_2.txt	
$\text{Ca}(\text{BH}_3\text{D})_2$	CaBH3D_2.txt	
$\text{Ca}(\text{BHD}_3)_2$	CaBD3H_2.txt	
$\text{Sr}(\text{BH}_4)_2$	SrBH4_2.txt	Contains SrH_2 .
$\text{Y}(\text{BH}_4)_3$	YBH4_3.txt	Contains YH_3 .
$\text{LiSc}(\text{BH}_4)_4$	LiScBH4_4.txt	[20]
$\text{NaSc}(\text{BH}_4)_4$	NaScBH4_4.txt	[21]
$\text{KSc}(\text{BH}_4)_4$	KScBH4_4.txt	[22]
$\text{LiZn}_2(\text{BH}_4)_5$	LiZn2BH4_5.txt	[23]
$\text{NaZn}_2(\text{BH}_4)_5$	NaZn2BH4_5.txt	[23]
$\text{NaN}(\text{BH}_4)_3$	NaNBH4_3.txt	[23]
$\text{Al}_3\text{Li}_4(\text{BH}_4)_{13}$	Li4Al3BH4_13.txt	[24]
$\text{NaAl}(\text{BH}_4)_x\text{Cl}_{4-x}$	NaAlClxBH4_y.txt	[25]
$\text{K}_2\text{Mg}(\text{BH}_4)_4$	K2MgBH4_4.txt	[26]
$\text{K}_2\text{Mn}(\text{BH}_4)_4$	K2MnBH4_4.txt	[26]
$\text{K}_3\text{Mg}(\text{BH}_4)_5$	K3MgBH4_5.txt	[26]
$\text{LiK}(\text{BH}_4)_2$	LiKBH4_2.txt	Contains LiBH_4 .
$\text{LiRb}(\text{BH}_4)_2$	LiRbBH4_2.txt	
CaH_2	CaH2.txt	Sigma Aldrich (>97%)
SrH_2	SrH2.txt	Cerac (99%)
YH_3	YH3.txt	Absco materials (99%)

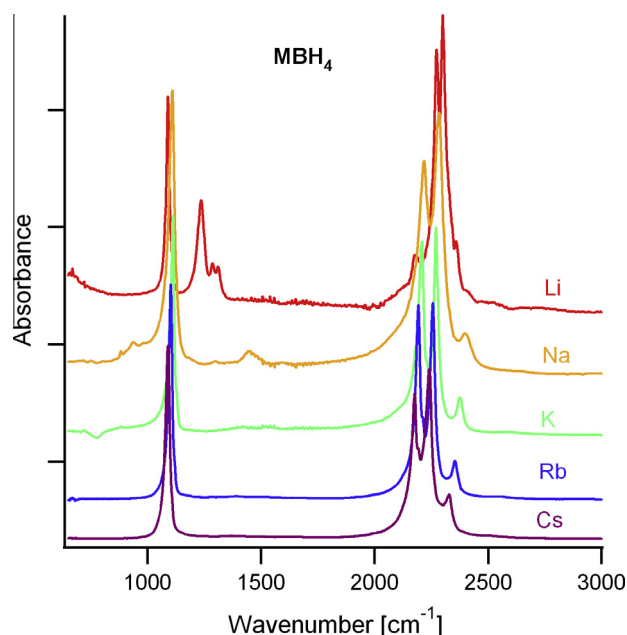


Fig. 1. IR spectra of MBH_4 , $M = \text{Li, Na, K, Rb, Cs}$. For Na, K, Rb, CsBH_4 the spectra are taken from Ref. [13].

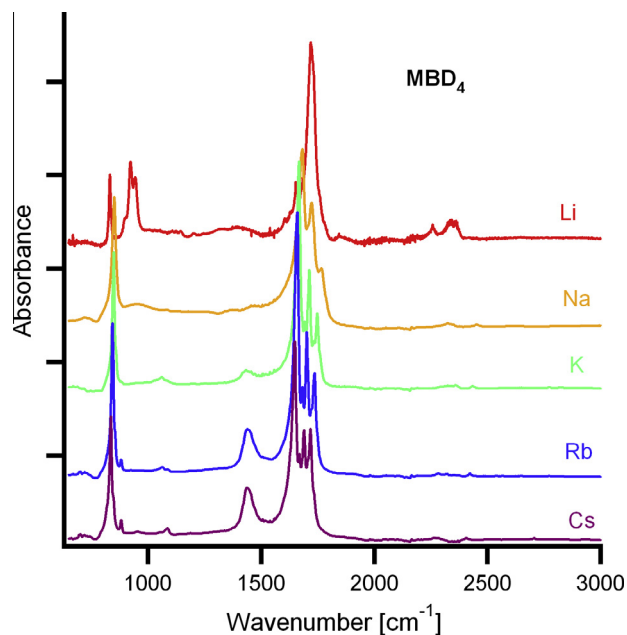


Fig. 2. IR spectra of MBD_4 , $M = \text{Li, Na, K, Rb, Cs}$. For Na, K, Rb and CsBD_4 , the spectra are taken from Ref. [13]. The LiBD_4 sample contains some LiBD_3H , as seen by the presence of the B–H stretching mode at about 2300 cm^{-1} .

$M(\text{BH}_4)_2$ and $M(\text{BD}_4)_2$ with $M = \text{Mg, Mn, Ca}$ and Sr

Fig. 3 combines the spectra of $M(\text{BH}_4)_2$ with $M = \text{Mg, Mn, Ca}$ (α -phase) and Sr . The sample of $\text{Sr}(\text{BH}_4)_2$ contains some unreacted SrH_2 , which contributes to a weak band below 1000 cm^{-1} . The preparation and crystal structure of $\text{Sr}(\text{BH}_4)_2$ has been reported recently [38]. The Raman spectrum of this compound [38] shows similar broad band as the IR spectrum reported here. The spectra of $\text{Mn}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$ are quite similar [39], like those of

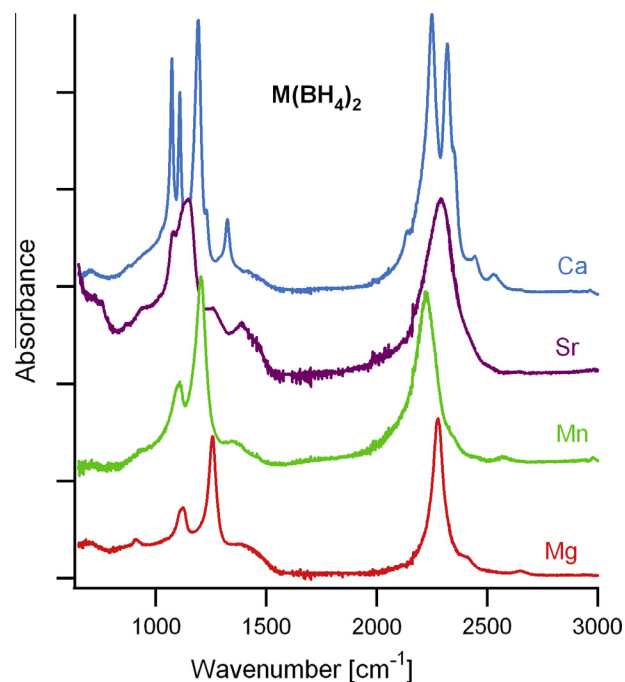


Fig. 3. IR spectra of $M(\text{BH}_4)_2$, $M = \text{Mg, Mn, Ca, Sr}$. For $\text{Ca}(\text{BH}_4)_2$ the α -phase is shown. The spectra of Mg, Mn and α - $\text{Ca}(\text{BH}_4)_2$ are taken from [16,18,17], respectively.

$\text{K}_2\text{M}(\text{BH}_4)_4$ with $M = \text{Mn}$ and Mg [26] (see Fig. 7). The IR spectra of $\text{Mg}(\text{BH}_4)_2$ are only slightly different for different polymorphs [40]. It is interesting to note that for $M = \text{Ca}$ [17], there are many sharp deformation bands for both α and β phases between 1000 and 1400 cm^{-1} , while, for the other compounds, the bands are broader. IR frequencies for $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ have been reported previously [41].

The database contains also the spectra of selectively labeled $M(\text{BD}_3\text{H})_2$ and $M(\text{BH}_3\text{D})_2$ ($M = \text{Ca, Mg}$) prepared similarly as NaBD_3H [15].

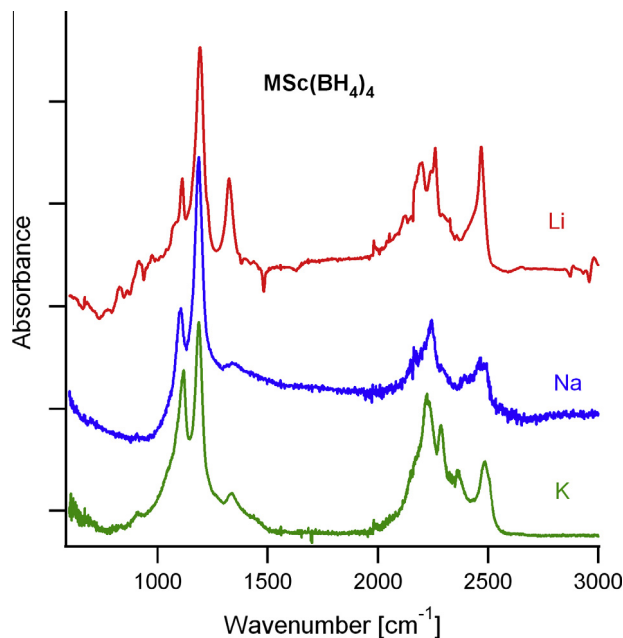


Fig. 4. IR spectra of $\text{MSc}(\text{BH}_4)_4$, $M = \text{Li}$ [20], Na [21], K [22].

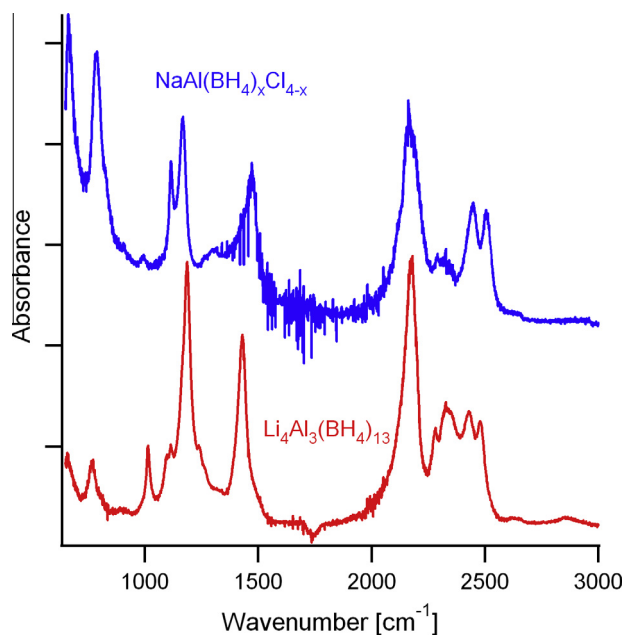


Fig. 5. IR spectra of $\text{Li}_4\text{Al}_3(\text{BH}_4)_{13}$ [24] and $\text{NaAl}(\text{BH}_4)_x\text{Cl}_{4-x}$, obtained by ball milling of NaBH_4 and AlCl_3 in a 1:1 ratio [25].

Bimetallic borohydrides

Fig. 4 collects the spectra of $MSc(BH_4)_4$ ($M = Li, Na, K$) [20–22], while Fig. 5 presents spectra of compounds with Al [24,25]. In both cases, an ion $M(X)_4^-$ ($M = Al, Sc, X = BH_4^-, Cl^-$) is formed. The spectra of these ions may be compared with those of neutral $M(BH_4)_4$ compounds such as $Zr(BH_4)_4$ which has been studied theoretically and experimentally [42]. In the case of $M = Sc$, the BH_4^- groups present a tridentate binding towards the central Sc atom, while for Al the binding is bidentate. A signature of this bidentate coordination is the relatively strong band appearing around 1400 cm^{-1} , seen also in the compounds with Zn [23]

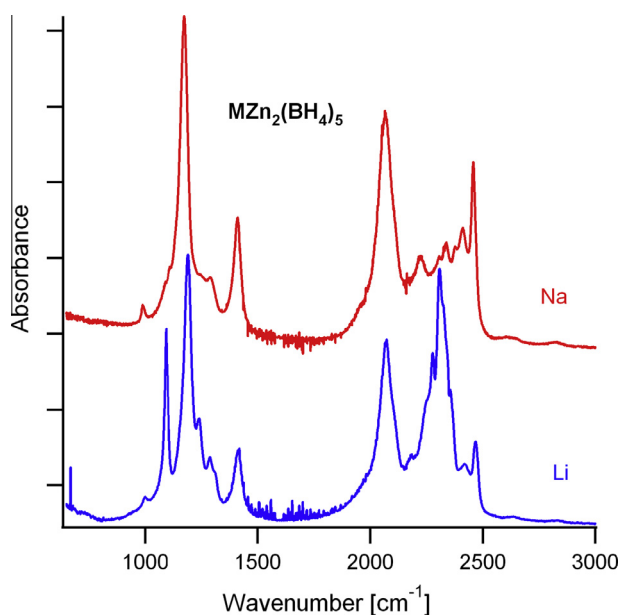


Fig. 6. IR spectra of $MZn_2(BH_4)_5$, $M = Li, Na$. The Li compound contains unreacted $LiBH_4$. The spectra are taken from Ref. [23].

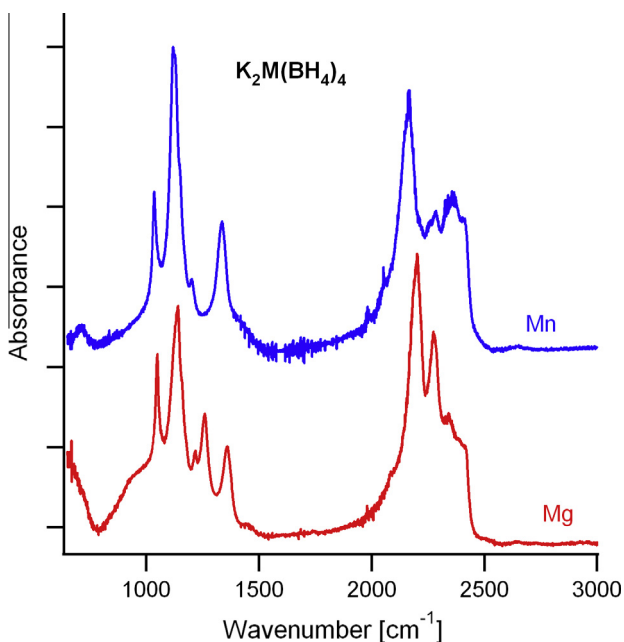


Fig. 7. IR spectra of $K_2M(BH_4)_4$, $M = Mg, Mn$. The spectra are taken from Ref. [26].

(Fig. 6) Mg and Mn [26] in Fig. 7. Other spectroscopic studies on the mixed cation borohydrides with Zn can be found in Ref. [43].

All the spectra shown in Figs. 4–7 also reveal an important splitting of the B–H stretching modes, which reflects a significant difference of the B–H bond lengths between hydrogen atoms located between the central metal and the boron atom and those on the outside. For example, in the case of $LiSc(BH_4)_4$, a DFT calculation for the isolated $Sc(BH_4)_4^-$ ion yielded three B–H bond lengths of 1.24 Å and one of 1.21 Å for each BH_4^- group [20]. This appears to be a common feature for complex ions formed in the solid. It is interesting to observe that for $Y(BH_4)_3$ this splitting does not appear. The IR spectra obtained by Jaroń and Grochala [44] show for the deuterated sample two bands around 2250 and 2300 cm^{-1} corresponding to the B–H stretches, in agreement with the theoretical DFT results [45]. The weak band appearing close to 2550 cm^{-1} results probably from a Fermi resonance.

It should be noted that, for Mn and Mg, it is possible to observe either the formation of complex ions (when another metal such as K is present), or an ionic network with BH_4^- ions connecting the divalent metal ions.

Conclusions

The collection of spectra of borohydrides presented here shows that several families of compounds (e.g. $M(BH_4)_2$) present some similar features which may be useful for the future study of new compounds. Further, during the thermal decomposition of bimetallic borohydrides, it is possible that starting compounds are formed again, as seen in the case of $LiK(BH_4)_2$ (unpublished results).

This database will be extended to other borohydrides, such as $B_{12}H_{12}^-$, to assist further investigations of decomposition reactions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2014.02.130>.

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