Unstable Borohydrides

Screening of Metal Borohydrides by Mechanochemistry and Diffraction**

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Research into energy materials is of utmost importance regarding for example energy harvesting and energy storage. Novel materials with new functional properties often form the backbone in emerging energy technologies. Therefore, experimental screening approaches are needed to discover and investigate novel materials. Mechanochemical synthesis combined with characterization using time-resolved in situ synchrotron radiation powder X-ray diffraction (SR-PXD) at variable temperature (VT) and pressures provide simultaneous unprecedented information about material composition, structure, and properties, such as chemical reactions and thermal decomposition pathways.[1–3] We illustrate the efficiency and versatility of this approach by studying a series of novel cadmium-based metal borohydrides.

During the past decade, a number of monometallic borohydrides, such as $Mg(BH_4)_2$ and $Ca(BH_4)_2$, have been characterized in great detail and are now available commercially.[4–7] In the past few years we have witnessed a significant increase in the number of novel borohydrides combining different metals, filling the gap between the stable alkali and the unstable transition metal borohydrides.[2,5–8] Bonding in metal borohydrides can in general be ionic, partly covalent, or a combination of both, resulting in complex structures. In bimetallic borohydrides, metal atoms of the more electronegative elements and BH_4 groups form partly covalent

complex anions, such as $[Zn_2(BH_4)_5]^-$ and $[Sc(BH_4)_4]^-$. The complex anions combine with alkali metal cations, forming for example $Li[Zn_2(BH_4)_5]$, $Na[Zn_2(BH_4)_5]$, $Li[Sc(BH_4)_4]$, and $Na[Sc(BH_4)_4]$ in the solid state.[2,6,9–15] Realization of the two bonding modes allows the composition and properties of this emerging group of hydrides to be tuned, and an empirical relation is established between the decomposition temperature and the electronegativity of the complex-forming metal.[6,16–18] The most electronegative element incorporated into borohydrides to date is zinc; its compounds show decomposition temperatures as low as 100°C.[13–15] Our aim is to extend this series to more electronegative elements, such as cadmium, forming less stable metal borohydrides with anticipated decomposition temperatures below 100°C.

The information on cadmium borohydrides is sparse, and their structures have not previously been reported.[19] Herein, the existence of alkali-metal (M = Li, Na or K) cadmium borohydrides is screened by mechanochemical treatment (ball milling) of MBH_4 and $CdCl_2$ in various ratios and the resulting materials are characterized by time-resolved in situ VT SR-PXD studies. A three-parameter space is mapped: composition (M = Li, Na, K), reactant ratio (1:1, 2:1, 3:1, and 4:1), and temperature. Products obtained by mechanochemical synthesis often contain several compounds, which tend to hamper their identification using PXD (Table 1).

Diffraction data measured at variable temperature provide a powerful approach and allows grouping diffraction peaks according to their behavior, that is, by peak intensity change or peak shift owing to decomposition, melting, or a chemical reaction in the sample. Each group of reflections can be associated with a known compound or used for indexing and structure solution. Fine temperature resolution allows selecting two patterns collected at relatively similar temperatures and differing only by the presence of an unknown compound. The Rietveld refinement profile of the pattern containing known compounds can be subtracted from the other pattern providing a difference plot, which can be used for indexing and structure solution of the unknown compound. We refer to this approach as "decomposition-aided indexing and structure solution".[2]

The screening of MBH_4-$CdCl_2$ (M = Li, Na or K) for novel compounds is performed by high-energy ball milling of the compositions MBH_4:$CdCl_2$ (1:1, 2:1, 3:1, and 4:1). Each sample was investigated by in situ VT SR-PXD. All observed diffracted intensities in the 875 collected PXD patterns are accounted for by ten known compounds and four new cadmium-based borohydrides presented herein. Table 1 provides a list of compounds observed in the as-synthesized samples at room temperature. Sequential Rietveld refine-

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Table 1: Reactant composition and synthetic products obtained by ball milling.[a]

Reactants	Molar ratios	Ball-milling products
$LiBH_4$-$CdCl_2$	1:1, 2:1	β-$Cd(BH_4)_2$, LiCl, Li_2CdCl_4, (α-$Cd(BH_4)_2$)
$LiBH_4$-$CdCl_2$	3:1, 4:1	α-$Cd(BH_4)_2$, LiCl
$NaBH_4$-$CdCl_2$	1:1	β-$Cd(BH_4)_2$, Na_2CdCl_4, Na_6CdCl_8, (α-$Cd(BH_4)_2$)
$NaBH_4$-$CdCl_2$	2:1	β-$Cd(BH_4)_2$, NaCl, Na_6CdCl_8, (α-$Cd(BH_4)_2$)
$NaBH_4$-$CdCl_2$	3:1, 4:1	α-$Cd(BH_4)_2$, NaCl, Na_6CdCl_8, (β-$Cd(BH_4)_2$)
KBH_4-$CdCl_2$	1:1	α-$Cd(BH_4)_2$, $KCd(BH_4)_3$, $K_2Cd(BH_4)_4$, $KCdCl_3$
KBH_4-$CdCl_2$	2:1, 3:1, 4:1	$K_2Cd(BH_4)_4$, $KCdCl_3$

[a] Compounds in parentheses are only present in minor amounts.

ment of in situ VT SR-PXD data provides detailed insight into the often complex variation in sample composition and decomposition pathways, thus providing a unique platform for creating synergy between synthesis and characterization of novel materials.

Figure 1 illustrates the application of decomposition-aided indexing and structure solution to determine the structure of two novel compounds in the KBH_4-$CdCl_2$ system, namely $KCd(BH_4)_3$ and $K_2Cd(BH_4)_4$, identified from the same VT diffraction data series. The difference plots used for indexing and structure solution (for details, see the Supporting Information) compare well to the calculated patterns for the pure phases. Thus, decomposition-aided indexing and structure solution allows for a thorough characterization of samples containing more than one unknown compound, provided they decompose at different temperatures.

Figure 2 shows crystal structures of four new compounds, α-$Cd(BH_4)_2$, β-$Cd(BH_4)_2$, $KCd(BH_4)_3$, and $K_2Cd(BH_4)_4$, solved by direct space algorithms in the program FOX.[20] The tetragonal species α-$Cd(BH_4)_2$ is a low-temperature polymorph ($T < \approx 55\,°C$), derived from the cubic high-temperature β-$Cd(BH_4)_2$. Each structure (Figure 2 a,b) contains two identical three-dimensional interpenetrated frameworks with Cd tetrahedrally coordinated to four BH_4^- units and each BH_4^- linearly connected to two Cd. β-$Cd(BH_4)_2$ is a Cu_2O antitype with B and Cd on the positions of Cu and O, respectively. This structure type has been previously discussed as a possible high-symmetry polymorph of $Mg(BH_4)_2$.[21] The tetragonal α-phase is the distortion variant of the cubic β-phase and is isostructural to the high-pressure δ-polymorph of $Mg(BH_4)_2$.[4] This structural topology clearly indicates directionality in the Cd-BH_4 interaction within the two framework structures.

$K_2Cd(BH_4)_4$ contains discrete tetrahedral $[Cd(BH_4)_4]^{2-}$ anions and eight-coordinated K^+ cations associated with the anions by weak K−BH_4 interactions (Figure 2 c). The average K−B distance is 0.89 Å longer than the average Cd−B distance, which is more than twice the difference in ionic radii of K^+ (1.38 Å) and Cd^{2+} (0.95 Å), underlining the presence of complex $[Cd(BH_4)_4]^{2-}$ anion and K^+ cations. This partitioning is further supported by the fact that $K_2Cd(BH_4)_4$ is a monoclinic distortion of the β-K_2SO_4 structure type. A similar correspondence exists between $KSc(BH_4)_4$, containing discrete $[Sc(BH_4)_4]^-$ anions,[12] and the $BaSO_4$ structure type.

The fourth new compound, $KCd(BH_4)_3$, is an intermediate between the framework structures, α-$Cd(BH_4)_2$ and β-$Cd(BH_4)_2$, and the structure containing complex anions, $K_2Cd(BH_4)_4$. It consists of a three-dimensional polymeric anion, $[\{Cd(BH_4)_3\}_n]^{n-}$ built from corner-sharing $Cd(BH_4)_4$ tetrahedra and $Cd(BH_4)_6$ octahedra (Figure 2 d). Most of the BH_4 units are linearly coordinated to the metal atoms, while some act as a terminal ligand, causing a distortion of the $Cd(BH_4)_4$ tetrahedra (Supporting Information, Table S7). The $[\{Cd(BH_4)_3\}_n]^{n-}$ anion is counterbalanced by two crystallographically independent K^+ cations, having octahedral and saddle-like coordination by BH_4 units. The Cd−B distance is shorter than K−B by almost the difference in Cd and K radii, indicating that the [{Cd-
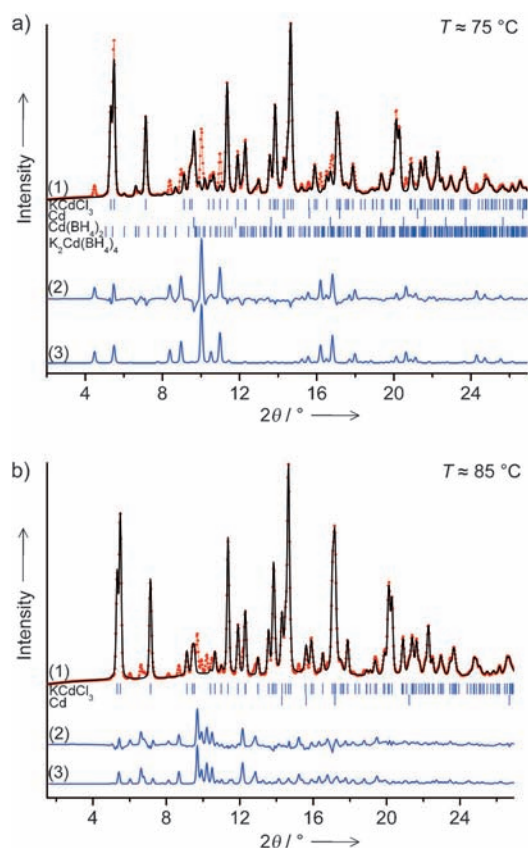

Figure 1. SR-PXD data measured for the KBH_4-$CdCl_2$ (1:1) sample at a) about 75 °C and b) about 85 °C, used for indexing and ab initio structure determination of $KCd(BH_4)_3$ and $K_2Cd(BH_4)_4$, respectively. The curves show 1) observed data (Y_{obs}, red curve) and Rietveld refinement profile (Y_{calc}, black curve) of structurally characterized compounds; 2) difference plot $Y_{obs}-Y_{calc}$ showing a contribution from the phase that decomposed; 3) calculated PXD pattern Y_{calc} of the new structure after its solution and Rietveld refinement. Close similarity can be observed between curves (2) and (3), thus allowing the successful analysis of the data in (2).
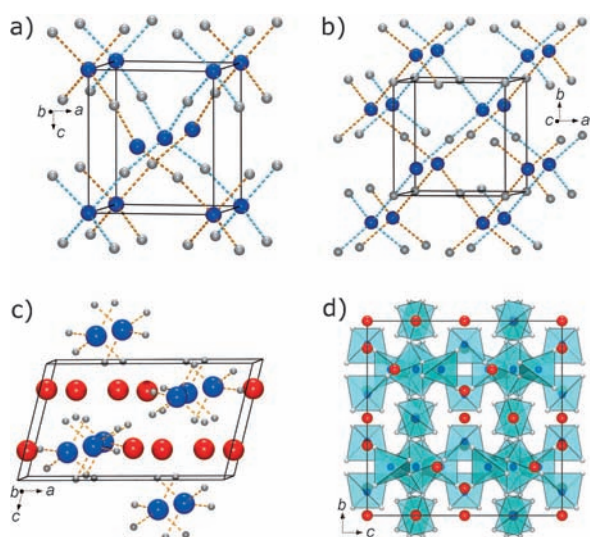
Figure 2. Crystal structures of a) α-Cd(BH$_4$)$_2$, b) β-Cd(BH$_4$)$_2$, c) K$_2$Cd-(BH$_4$)$_4$, and d) KCd(BH$_4$)$_3$. Hydrogen atoms are omitted for clarity; Cd—B connectivity is shown by broken lines or by coordination polyhedra. The two interpenetrated 3D frameworks in (a) and (b) are highlighted in blue and light-brown. Cd blue, K red, B light gray.
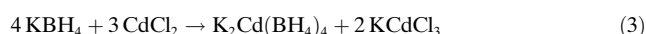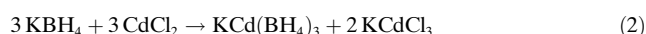
(BH$_4$)$_3$}$_n$]$^{n-}$ anion is not as discrete as [Cd(BH$_4$)$_4$]$^{2-}$ in K$_2$Cd(BH$_4$)$_4$.

The samples LiBH$_4$-CdCl$_2$ and NaBH$_4$-CdCl$_2$ contain α- and β-Cd(BH$_4$)$_2$ with a preference for the low-temperature α-Cd(BH$_4$)$_2$ polymorph at higher alkali borohydride content. This might be due to more pronounced contribution to sample heating from the exothermic formation of ternary chlorides for the cadmium-rich samples, which show a preference for formation of β-Cd(BH$_4$)$_2$. For the 3:1 and 4:1 LiBH$_4$-CdCl$_2$ mixtures, the simplest metathesis reaction pathway is observed:

$$2\,LiBH_4 + CdCl_2 \rightarrow Cd(BH_4)_2 + 2\,LiCl \qquad (1)$$
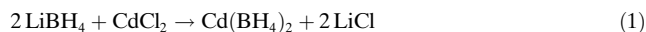
A similar reaction path leads to a formation of the α- and β-polymorphs of Y(BH$_4$)$_3$.[22,23]

The KBH$_4$-CdCl$_2$ samples yield K$_2$Cd(BH$_4$)$_4$ for KBH$_4$ rich samples, that is, molar ratios ≥ 2:1, whereas the 1:1 composition provides three different borohydrides α-Cd-(BH$_4$)$_2$, KCd(BH$_4$)$_3$, and K$_2$Cd(BH$_4$)$_4$. Furthermore, most of the samples (see Table 1) contain ternary chlorides: Li$_2$CdCl$_4$, Na$_2$CdCl$_4$, Na$_6$CdCl$_8$, and KCdCl$_3$. These salts are formed by side reactions between cadmium chloride and the alkali chlorides formed in metathesis reactions similar to reaction (1). Thus, formation of the ternary chlorides lowers the yield of metal borohydrides. The overall formation reactions of potassium-cadmium-borohydrides are as follows:

$$3\,KBH_4 + 3\,CdCl_2 \rightarrow KCd(BH_4)_3 + 2\,KCdCl_3 \qquad (2)$$

$$4\,KBH_4 + 3\,CdCl_2 \rightarrow K_2Cd(BH_4)_4 + 2\,KCdCl_3 \qquad (3)$$

In general, the more CdCl$_2$-rich samples tend to provide higher amounts of ternary chlorides; for example, for LiBH$_4$:CdCl$_2$ ≥ 3:1 no Li$_2$CdCl$_4$ is formed and for

NaBH$_4$:CdCl$_2$ ≥ 2:1 only Na$_6$CdCl$_8$ and no Na$_2$CdCl$_4$ is formed. Simultaneous formation of ternary chloride salts and metal borohydrides has previously been observed, for example, during formation of NaZn$_2$(BH$_4$)$_5$, NaZn(BH$_4$)$_3$, NaSc(BH$_4$)$_4$, and KSc(BH$_4$)$_4$.[11–14]

All the cadmium-based borohydrides show low thermal stability. Their decomposition temperatures exhibit the following trend: β-Cd(BH$_4$)$_2$ (ca. 75°C) < KCd(BH$_4$)$_3$ (ca. 80°C) < K$_2$Cd(BH$_4$)$_4$ (ca. 85°C). The low-temperature polymorph α-Cd(BH$_4$)$_2$ transforms to β-Cd(BH$_4$)$_2$ by a first-order phase transition at about 55°C (Figure 3). β-Cd(BH$_4$)$_2$ decomposes at about 75°C to metallic cadmium and possibly hydrogen and borane gasses according to reaction (4). The observed (TGA) and calculated mass loss for this reaction are 10.5 and 13.1 wt%, respectively (see the Supporting Information).[19]

$$\beta\text{-}Cd(BH_4)_2(s) \rightarrow Cd(s) + B_2H_6(g) + H_2(g) \qquad (4)$$
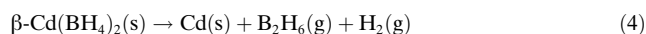
KCd(BH$_4$)$_3$ and K$_2$Cd(BH$_4$)$_4$ show more complex decomposition pathways involving two-step segregation of cadmium:

$$2\,KCd(BH_4)_3(s) \rightarrow K_2Cd(BH_4)_4(s) + Cd(s) + B_2H_6(g) + H_2(g) \qquad (5)$$

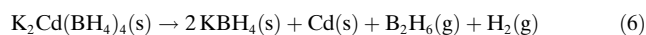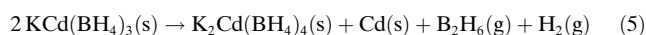$$K_2Cd(BH_4)_4(s) \rightarrow 2\,KBH_4(s) + Cd(s) + B_2H_6(g) + H_2(g) \qquad (6)$$
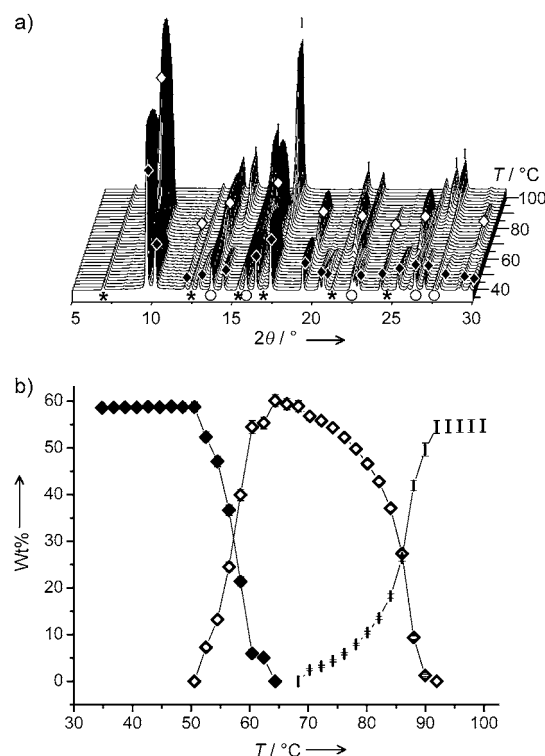
Figure 3. a) In situ SR-PXD data for the 4:1 LiBH$_4$-CdCl$_2$ sample measured from room temperature to 100°C, $\Delta T/\Delta t = 1$°C min^{-1} and $\lambda = 0.709595$ Å. b) Weight fractions of α-Cd(BH$_4$)$_2$, β-Cd(BH$_4$)$_2$, and Cd extracted from the Rietveld refinement. The polymorphic phase transition and the decomposition reactions are followed as a function of temperature. ◆ α-Cd(BH$_4$)$_2$, ◇ β-Cd(BH$_4$)$_2$, | Cd, ○ LiCl, ⋆ CdCl$_2$.

$KCd(BH_4)_3$ transforms into $K_2Cd(BH_4)_4$ and presumably to β-$Cd(BH_4)_2$, at about 80°C. The latter readily decomposes at this temperature. The reactions (5) and (6) are in excellent agreement with sample compositions extracted from in situ diffraction data as a function of temperature. This agrees with the fact that all Cd in β-$Cd(BH_4)_2$ and half of that in $KCd(BH_4)_3$ is reduced into metallic Cd, while the other half of the Cd contained in $KCd(BH_4)_3$ is retained in $K_2Cd(BH_4)_4$. Above about 85°C, $K_2Cd(BH_4)_4$ decomposes with formation of KBH_4 and metallic Cd. Formation of intermediate transition metal borohydride and its immediate reduction to the metal with evolution of borane gases and hydrogen has also been observed for the alkali-metal zinc borohydrides.[13,24]

Furthermore, a series of reduction and addition reactions involving the ternary chloride salts are observed at elevated temperatures. In the reduction reactions, Cd^{2+} in the ternary chlorides is reduced to the metal by an alkali borohydride. Na_6CdCl_8 reacts with $NaBH_4$ at 60–90°C in $NaBH_4$-$CdCl_2$ (2:1, 3:1, and 4:1) samples, while $KCdCl_3$ reacts with KBH_4 at about 140°C in all KBH_4-$CdCl_2$ samples according to reactions (7) and (8), respectively. No changes occur for Li_2CdCl_4 formed in the $LiBH_4$-$CdCl_2$ (1:1 and 2:1) samples.

$$Na_6CdCl_8(s) + 2\,NaBH_4(s) \rightarrow$$
$$8\,NaCl(s) + Cd(s) + B_2H_6(g) + H_2(g) \qquad (7)$$

$$KCdCl_3(s) + 2\,KBH_4(s) \rightarrow$$
$$3\,KCl(s) + Cd(s) + B_2H_6(g) + H_2(g) \qquad (8)$$
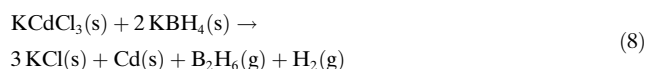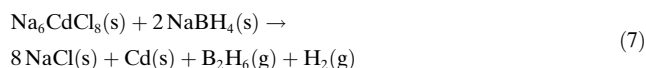
Addition reactions between ternary and binary chlorides result in other ternary chlorides. In this way, KCl formed in reaction (8) is readily consumed in reaction (9), which occur at about 140°C; that is, reactions (8) and (9) are coupled. Reaction (10) proceeds over a wide temperature range from 20 to 160°C, with the highest rate at 60–90°C.

$$KCdCl_3 + 3\,KCl \rightarrow K_4CdCl_6 \qquad (9)$$

$$Na_6CdCl_8 + 2\,CdCl_2 \rightarrow 3\,Na_2CdCl_4 \qquad (10)$$

In summary, we have demonstrated a combined approach for the search and characterization of novel complex hydrides. It consists of sequential screening various reactant compositions and ratios by mechanochemical synthesis followed by VT diffraction studies of the reaction products. The use of multiple powder patterns allows for solving structures of two or more new compounds present in the same sample, by the method we refer to as "decomposition-aided indexing and structure solution".[2] We anticipate that this approach is generally applicable to a variety of other complex systems and illustrate it by the characterization of structure and thermal properties of four novel cadmium-based borohydrides. These compounds posses interesting framework structures (α- and β-$Cd(BH_4)_2$) and polymeric and isolated complex anions, $[\{Cd(BH_4)_3\}_n]^{n-}$ and $[Cd(BH_4)_4]^{2-}$, charge-balanced by K^+ cations. The synergy between mechanochemical synthesis and in situ SR-PXD allows information to be obtained on structural, chemical, and physical properties of the hydrides.

Their stability varies in the range $Cd(BH_4)_2 < KCd(BH_4)_3 < K_2Cd(BH_4)_4$, showing the stabilizing effect of charge transfer from the alkali-metal atoms to the complex anions. The decomposition temperatures, 75–85°C, of the cadmium-based borohydrides are lower than for any other known solid borohydride, following the recently established relation with the electronegativity of the complex-forming element.[5] Finally, we have demonstrated that temperature-induced reaction pathways can be thoroughly elucidated. They involve phase transition, coupled reactions of borohydride decomposition, formation of ternary chlorides, and their reaction with the excess reactants and with the decomposition products. The systems containing the heavier alkali metal (potassium) show larger number of cadmium-based borohydrides, ternary chlorides, and more complex set of thermally induced reactions. Thus, this approach provides new knowledge on a new series of metal borohydrides and an efficient way for a sequential synthetic screening and characterization of complex materials.

Experimental Section

The materials were prepared from MBH_4 (M = Li, Na, K) and $CdCl_2$ by ball milling in argon atmosphere. Simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed at a heating rate of 10°Cmin^{-1} from RT to 300°C (helium atmosphere, corundum crucibles).

The samples were investigated by SR-PXD at beamline BM01A at the European Synchrotron Radiation Facility or at beamline I711 of the synchrotron MAX II. MAR345 IP and MAR165 CCD detectors and monochromatic X-ray wavelengths were used. Four new crystal structures of Cd-based borohydrides were determined by decomposition-aided indexing and structure solution in direct space. The structures were refined by the Rietveld method. Crystallographic details and agreement factors: α-$Cd(BH_4)_2$: $P4nm$, $a = 5.62948(15)$, $c = 6.3285(3)$ Å, $Z = 2$ (R_{wp} (not corrected for background) = 5.25%, R_p (corrected for background) = 9.01% and R_{Bragg} = 4.85%). β-$Cd(BH_4)_2$: $Pn\bar{3}m$, $a = 5.8949(5)$ Å, $Z = 2$ (R_{wp} = 7.66%, R_p = 11.2%, and R_{Bragg} = 4.52%). $KCd(BH_4)_3$: $Ia\bar{3}$, $a = 17.9353(5)$ Å, $Z = 32$ (R_{wp} = 2.29%, R_p = 2.91%, and R_{Bragg} = 1.91%). $K_2Cd(BH_4)_4$: $P2_1/n$, $a = 13.6992(9)$, $b = 9.7268(6)$, $c = 7.9585(6)$ Å, $\beta = 104.259(3)°$, $Z = 4$ (R_{wp} = 2.27%, R_p = 3.52%, and R_{Bragg} = 3.49%). More details are given in the Supporting Information.

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