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Mixed-cation manganese borohydride synthesized by ball-milling KBH$_4$ and MnCl$_2$ for hydrogen storage

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**Abstract**

In this work, a mixed-cation borohydride (K$_2$Mn(BH$_4$)$_4$) with P2$_1$/n structure was successfully synthesized by mechanochemical milling of the 2KBH$_4$ e MnCl$_2$ sample under argon. The structural and thermal decomposition properties of the borohydride compounds were investigated using XRD, Raman spectroscopy, FTIR, TGA-MS and DSC. Apart from K$_2$Mn(BH$_4$)$_4$, the KMnCl$_3$ and unreacted KBH$_4$ compounds were present in the milled 2KBH$_4$ e MnCl$_2$. The two mass loss regions were observed for the milled sample: one was from 100 to 160 $^\circ$C with a 1.6 ± 0.1 wt% loss (a release of majority hydrogen and trace diborane), which was associated with the decomposition of K$_2$Mn(BH$_4$)$_4$ to form KBH$_4$, boron, and finely dispersed manganese; the other was from 165 to 260 $^\circ$C with a 1.9 ± 0.1 wt% loss (only hydrogen release), which was due to the reaction of KBH$_4$ with KMnCl$_3$ to give KCl, boron, finely dispersed manganese. Simultaneously, the formed KCl could dissolve in KBH$_4$ to yield a K(BH$_4$)$_x$Cl$_{1-x}$ solid solution, and also react with KMnCl$_3$ to form a new compound K$_4$MnCl$_6$.

**1. Introduction**

Borohydrides formed from transition metals with electronegativities between 1.2 and 1.6 are expected to be promising candidates for hydrogen storage [1,2]. Manganese borohydride (Mn(BH$_4$)$_2$) has a theoretical hydrogen content of 9.5 wt% with a thermal decomposition temperature between 130 and 180 $^\circ$C [2]. Mechanochemical synthesis (ball milling) has successfully been used to synthesize Mn(BH$_4$)$_2$ via a metathesis reaction between lithium borohydride (LiBH$_4$) and manganese chloride (MnCl$_2$) [2–4]. The composition and decomposition properties of resulting materials from ball-milling technique highly depend on the precursors. Although Mn(BH$_4$)$_2$ was also formed through ball milling of NaBH$_4$ with MnCl$_2$ (under optimized conditions), the resulting material (under comparable milling conditions) was poorly crystalline [5] and the formed NaCl, unlike LiBH$_4$ as a precursor, where LiCl as one of resulting products was formed through a complete metathesis reaction [4], subsequently reacted with the remaining NaBH$_4$ and MnCl$_2$ to produce a solid solution of NaCl$_x$(BH$_4$)$_{1-x}$ and an amorphous Na–Mn–(BH$_4$)–Cl phases [5]. These preparations involved a complete or incomplete ion exchange reaction between alkali borohydrides and manganese chloride.

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To obtain borohydride complexes with improved thermodynamic properties, one approach is to prepare mixed-cation borohydrides by thermodynamic tuning, which allows the borohydride-based compounds to be synthesized selectively. Combining appropriate cations has been an effective method for adjusting the thermodynamic stability of borohydrides so as to have decomposition temperatures within the desired range for hydrogen storage applications. Several examples, such as LiK(BH4)2, ZrLi(BH4)4, ZrLi2(BH4)6, LiSc(BH4)4, and NaZn2(BH4)5, have been reported so far [6-9].

For modifying the thermodynamic properties of borohydrides, the mixed-anion borohydrides through the anion substitution between halide anions (F-, Cl-, Br-, I-) in alkaline or alkaline earth salts and BH4- in metal borohydride structure have been prepared. Dissolution of ACl into ABH4 (A = Li, Na or K), forming solid solutions such as Na(BH4),0.3Cl2 [10] and Li(BH4),0.3Cl2 [11,12], has been observed through ball-milling and annealing of ball-milling and annealing of ABH4-ACl mixture. The formation of the solid solutions may alter the decomposition pathways, the structural flexibility and reactivity of ABH4. Therefore, the mixed-ion borohydrides might play an important role in the modification of the thermal decomposition of borohydride compounds.

The bimetallic borohydrides K2M(BH4)4 (M = Mg or Mn) and K2Mg(BH4)5 have been recently synthesized by Schouwink et al. through mechanochemical ball-milling of the reactants KBH4 with M(BH4)2 in different molar ratios, where Mn(BH4)2 was firstly prepared by the metathesis reaction between LiBH4 and MnCl2 in ether [13]. An in-depth crystallographic and spectroscopic characterization revealed that K2M(BH4)4 crystallized as a distorted K2SO4-type structure in space group P21/n. Schouwink et al. also reported that although K2Mn(BH4)4 was formed by ball milling of 4KBH4-3MnCl2, its structural features were not identical to those of the chlorine-free synthesis, due to the severe peak overlap and the temperature dependent interplay of two polymorphs of the ternary chloride KMnCl3 [13].

The aims of this study are to extend the results from the milled KBH4-MnCl2 sample to the ternary borohydride (K-Mn-BH4) system and to provide insight into the decomposition mechanism(s) in detail within the milled multiple polymorphs so as to facilitate the development of reversible hydrogen sorption reaction pathways. The milled 2KBH4-MnCl2 sample is investigated by X-ray diffraction (XRD), vibrational spectroscopy (Raman and FTIR), thermal analysis (TGA-MS and DSC).

2. Experimental method

2.1. Materials and synthetic method

Potassium borohydride (KBH4, >98%) and anhydrous manganese chloride (MnCl2, 99.999%) were obtained from Sigma−Aldrich Company Ltd. All the materials and prepared samples were stored and handled in an argon (99.99% purity) filled glovebox (MBrAn Labstar). The levels of water and oxygen in the glovebox were kept below 0.1 ppm and the hydrogen level was less than 0.1%.

A 6 g mixture of KBH4 and MnCl2 in 2:1 molar ratios was put in a stainless steel milling bowl (250 ml) and sealed under argon with a lid using a Viton O-ring. The mass ratio of the stainless steel balls (14 mm diameter) to powder was approximately 32:1. At room temperature, the mixture was milled using a Retsch PM400 Planetary Ball Mill at 175 rpm. In order to reduce the amount of heat generated, milling was carried out in 36 × 10 min durations separated by 10 min rest intervals, giving total milling times of 360 min.

2.2. XRD characterization

The crystal properties of milled samples were investigated using a Bruker D8 Advance X-ray Diffractometer with Cu Kα radiation (λ = 0.154 nm). An Anton Parr XRF900 high-temperature sample cell was used to measure the temperature dependent properties of samples heated at 2 °C/min under 3 bar He flowing at 100 ml/min.

TOPAS software supplied by Bruker AXS [14], jEdit obtained from Durham University website managed by Prof. John Evans [15] and Crystallographic Information Files (.cif) from the Chemical Crystal Database [16], were used for the analysis of the polymorphs present in the XRD pattern of prepared samples.

2.3. Raman and IR analysis

Raman spectra were obtained using a Renshaw inVia Raman Microscope with Ar ion laser power (2 mW, 488 nm). A microscope objective was used to focus the laser beam onto the sample with a spot-diameter of about 50 μm. The Raman scattered light ranged between 100 and 4000 cm⁻¹ was collected using a 2400 grooves/mm grating. The spectral resolution was 2–4 cm⁻¹. The number of scans was optimized for each sample to obtain high intensity and well-resolved Raman spectra. In an Ar glovebox, the sample was loaded into an Instruc HCS621V sample cell stage, preventing contact between the sample and the air. The temperature-dependent Raman spectra were measured by heating sample at 2 °C/min in 1 bar Ar flowing at 100 ml/min.

IR spectroscopic measurements were performed with a Nicolet 8700 Fourier Transform Infrared (FTIR) spectrometer using an attenuated total reflectance (ATR) attachment that allowed inert loading of samples. The spectrometer was purged with high-purity nitrogen for 30 min prior to measurements in order to try to minimize the carbon dioxide and water level within the spectrometer. The spectral resolution was 4 cm⁻¹, and a spectral range of 500–4000 cm⁻¹ was selected. For FTIR measurements, the powder samples were pressed onto the crystal (of the ‘Golden Gate’) with a calibrated torque and sealed in the sample holding cell in the glovebox.

2.4. Thermal analysis

The thermal decomposition behaviour of the milled mixtures was investigated by thermogravimetric analysis (TGA, Netzsch TG209) with the exhaust gas analysed by mass spectrometry (MS, Hiden Analytical HAL IV). Approximately 10–15 mg of sample was placed in an aluminium oxide crucible and covered with a lid. The sample was heated from 30 to
Accordingly, the synthetic process of ball milling of the K$_2$Mn(BH$_4$)$_4$ with a space group of $P2_1/n$ (No. 14) was performed on a pre-weighed sample of approximately 10 mg in an Al crucible heated from 30 to 500 °C. A temperature ramp rate of 2 °C/min and 4 bar argon flowing at 100 ml/min were used for all the measurements. Before the sample measurement, a baseline was conducted using an empty Al pan under the same conditions as the sample measurement to reduce the effect of background on the sample measurement.

Differential scanning calorimetry (DSC, Netzsch DSC204HP) was performed on a pre-weighed sample of KBH$_4$ with heating rate of 2 °C/min under 1.5 bar argon at 2495 cm$^{-1}$, and a combination band at 2380 cm$^{-1}$ [20]. After ball milling of KBH$_4$ with MnCl$_2$, the intensity of the strongest band at 2305 cm$^{-1}$ for KBH$_4$ decreases dramatically with no significant change in Raman frequency. The superposition of two overtones at 2175 and 2206 cm$^{-1}$, as well as doublet bands at 2380 and 2408 cm$^{-1}$ are observed in the milled 2KBH$_4$–MnCl$_2$ sample. An overtone for KBH$_4$ at 2495 cm$^{-1}$ is not present in the milled 2KBH$_4$–MnCl$_2$ sample. In addition to the bending modes at 1248 and 1118 cm$^{-1}$ in both milled KBH$_4$ and 2KBH$_4$–MnCl$_2$ samples, the two new vibration modes at 1342 and 1035 cm$^{-1}$ are observed only for the milled 2KBH$_4$–MnCl$_2$ sample. These results indicate that the Raman spectrum of the milled 2KBH$_4$–MnCl$_2$ sample is associated with two separate borohydride environments: one from excess KBH$_4$ and the other from the newly formed K$_2$Mn(BH$_4$)$_4$. An overtone for MnCl$_2$ at 190 cm$^{-1}$ is not present in the milled 2KBH$_4$–MnCl$_2$ sample. As a reference.

3. Results and discussion

3.1. XRD of the milled material

Powder XRD was performed on the milled 2KBH$_4$–MnCl$_2$ sample, as shown in Fig. 1. There are three major polymorphs, identified as orthorhombic K$_2$MnCl$_3$(o) ($a = 8.79(4)$ Å, $b = 3.88(5)$ Å, $c = 14.42(2)$ Å) [17], cubic KBH$_4$ ($a = 6.715(6)$ Å) and K$_2$Mn(BH$_4$)$_4$ with a space group of $P2_1/n$ ($a = 8.1347(5)$ Å, $b = 9.860(6)$ Å, $c = 12.768(8)$ Å, $\beta = 100.530(6)^\circ$) [13]. The structure of the K$_2$Mn(BH$_4$)$_4$ compound was reported by Schouwink et al. [13], who used synchrotron radiation powder X-ray diffraction (SR-PXD) to identify the structure of K$_2$Mn(BH$_4$)$_4$. A mixed-cation borohydride KSc(BH$_4$)$_4$ and mixed-anion and -cation borohydride compound KZn(BH$_4$)$_2$Cl$_2$ have also been prepared through ball milling of both KBH$_4$ with ScCl$_3$ and KBH$_4$ with ZnCl$_2$ respectively [18,19]. Accordingly, the synthetic process of ball milling of the KBH$_4$–MnCl$_2$ sample with 2:1 molar ratio can be proposed via Equation (1), giving excess KBH$_4$ in the milled sample:

$$4\text{KBH}_4 + 3\text{MnCl}_2 \rightarrow 2\text{KMnCl}_3(o) + \text{K}_2\text{Mn(BH}_4)_4$$

(1)

3.2. Spectroscopic properties of the milled sample

Raman spectra of milled samples of 2KBH$_4$–MnCl$_2$ and KBH$_4$ are shown in Fig. 2. In the B–H stretching region, the spectrum of KBH$_4$ consists of strong band at 2305 cm$^{-1}$, overtones located at 2183, 2210 and 2495 cm$^{-1}$, and a combination band at 2380 cm$^{-1}$ [20]. After ball milling of KBH$_4$ with MnCl$_2$, the intensity of the strongest band at 2305 cm$^{-1}$ for KBH$_4$ decreases dramatically with no significant change in Raman frequency. The superposition of two overtones at 2175 and 2206 cm$^{-1}$, as well as doublet bands at 2380 and 2408 cm$^{-1}$ are observed in the milled 2KBH$_4$–MnCl$_2$ sample. An overtone for KBH$_4$ at 2495 cm$^{-1}$ is not present in the milled 2KBH$_4$–MnCl$_2$ sample. In addition to the bending modes at 1248 and 1118 cm$^{-1}$ in both milled KBH$_4$ and 2KBH$_4$–MnCl$_2$ samples, the two new vibration modes at 1342 and 1035 cm$^{-1}$ are observed only for the milled 2KBH$_4$–MnCl$_2$ sample. These results indicate that the Raman spectrum of the milled 2KBH$_4$–MnCl$_2$ sample is associated with two separate borohydride environments: one from excess KBH$_4$ and the other from the newly formed K$_2$Mn(BH$_4$)$_4$. An overtone for MnCl$_2$ at 190 cm$^{-1}$ is not present in the milled 2KBH$_4$–MnCl$_2$ sample. As a reference.

Fig. 2 – Raman spectra of the milled 2KBH$_4$–MnCl$_2$, measured at RT and −190 °C (with 360-min milled KBH$_4$ at −190 °C, as a reference).
1118, 2210, 2282 and 2273 cm\(^{-1}\), are related to excess KBH\(_4\) in spite of a slight shifting in peak position compared to the pure KBH\(_4\). The other five vibration modes, located at 1038, 1204, 1342, 2174 and 2428 cm\(^{-1}\), are associated with K\(_2\)Mn(BH\(_4\))\(_4\).

The combination of vibration spectroscopy and XRD results confirms that the K\(_2\)Mn(BH\(_4\))\(_4\) borohydride complex is formed through ball milling of 2KBH\(_4\)–MnCl\(_2\) with excess KBH\(_4\) according to Equation (1).

### 3.3 Thermal decomposition

Fig. 4 shows TGA profiles of the milled 2KBH\(_4\)–MnCl\(_2\) samples coupled with mass spectra. The two main mass loss regions are observed for the milled samples: one is from 100 to 160 °C with a mass loss of 1.6 ± 0.1 wt%, which is associated with the decomposition of the formed K\(_2\)Mn(BH\(_4\))\(_4\) compound; the other is from 165 to 260 °C with a mass loss of 1.9 ± 0.1 wt%, which is possibly due to the decomposition of KBH\(_4\) within the mixture. The mass losses in the two regions are accompanied by the release of hydrogen. A trace amount of diborane is detected by MS during the first decomposition process of the milled 2KBH\(_4\)–MnCl\(_2\) sample. The first hydrogen evolution is observed at 135 °C for the milled 2KBH\(_4\)–MnCl\(_2\). The second hydrogen release around 165–260 °C seems to have large doublets at 210 and 230 °C for the milled sample, suggesting that a multi-step decomposition process occurs.

DSC profiles of the milled 2KBH\(_4\)–MnCl\(_2\) samples show that on heating from room temperature to 500 °C, there are several major endothermic and exothermic reactions as shown in Fig. 5: exothermic peaks at 115 °C and endothermic peaks at 129, 203, 214, 231, and 451 °C. DSC results in conjunction with mass spectrometry suggest that the endothermic DSC peak at 129 °C is due to the decomposition of the K\(_2\)Mn(BH\(_4\))\(_4\) compound, accompanied by hydrogen evolution with a trace amount of diborane. The peaks at 203, 214 and 231 °C are associated with the second multi-step decomposition reaction within the mixture by desorbing hydrogen, which is consistent with TGA results. The exothermic peaks before the decomposition at 115 °C are not accompanied by the release of hydrogen, possibly due to the dissociation of K\(_2\)Mn(BH\(_4\))\(_4\) to form new polymorphs. The sharp endothermic peak at 451 °C can be related to a phase change in one of the final decomposition products.

### 3.4 Decomposition behaviour

Fig. 6 shows in-situ XRD patterns of the milled 2KBH\(_4\)–MnCl\(_2\) sample in the temperature range of 30–500 °C. At room temperature, the XRD pattern indicates the presence of KMnCl\(_3\), K\(_2\)Mn(BH\(_4\))\(_4\) and KBH\(_4\). Upon heating, the very weak diffraction peaks corresponding to K\(_2\)Mn(BH\(_4\))\(_4\) at 16.7 and 22.1° 2θ disappear above 120 °C, due to decomposition of the K\(_2\)Mn(BH\(_4\))\(_4\) complex. This corresponds to the endothermic DSC peaks at around 129 °C and TGA mass losses between 100 and 158 °C with hydrogen and diborane evolution. Simultaneously, an increase in the intensity of the diffraction peaks for KBH\(_4\) occurs between 100 and 160 °C, suggesting that the K\(_2\)Mn(BH\(_4\))\(_4\) compound decomposes to form KBH\(_4\). Schouwink et al. also found that the decomposition of the K\(_2\)Mn(BH\(_4\))\(_4\) compound resulted in the formation of KBH\(_4\) and a further new polymorph with weak XRD reflections which has been identified as KMn(BH\(_4\))\(_3\) (however, the XRD data was not clear enough to allow the accurate crystal structure to be solved) [13]. Although the KBH\(_4\) compound is formed during the...
decomposition of $K_2Mn(BH_4)_4$ in this study, peaks for $KMn(BH_4)_3$ are not observed in the in-situ XRD pattern (Fig. 6). However, an exothermic peak at 115 °C in the DSC profile may be related to the decomposition of $K_2Mn(BH_4)_4$ to form $KBH_4$ and $KMn(BH_4)_3$.

On the other hand, the lattice parameter ($a$) of $KBH_4$ linearly increases from room temperature to 150 °C (due to thermal expansion) then tends to constant between 150 and 170 °C, thereafter the lattice parameter ($a$) of $KBH_4$ reduces (Fig. 7). This result indicates that a proportion of the $BH_4^-$ ions within $KBH_4$ are substituted by $Cl^-$ ions from 150 °C to form a $BH_4^-$-rich $K(BH_4)_{1-x}Cl_x$ solid solution. The formation of the $KBH_4$ compound has also been observed during the decomposition of $KSc(BH_4)_4$ prepared by Cerný et al. [18]. They reported that no $Cl^-$ ions substitution in $KBH_4$ was observed from room temperature to 220 °C, however, a significant substitution occurred at 220 °C–320 °C.

On further heating, the diffraction peaks of $KBH_4$ gradually broaden in width, decrease in intensity and shift in peak position. Simultaneously, the reflections of $K MnCl_3$ reduce and new diffraction peaks at 14.6, 25.3, 31.2, 33.0 and 34.8° are observed, possibly due to $K_4MnCl_6$. With continued heating, the X-ray reflections of $K(BH_4)_{1-x}Cl_x$ slowly approach the diffraction positions of KCl-type, suggesting more $Cl^-$ substituting for $BH_4^-$. All the diffraction peaks disappear completely other than those of KCl above 450 °C. These results suggest that between 165 and 260 °C, three processes occur: the ternary chloride $K MnCl_3$ reacts with $KBH_4$ to produce KCl and possible finely dispersed manganese, boron or borane species (accompanied by hydrogen evolution in multiple steps); some of the produced KCl dissolve in $KBH_4$ to form a $K(BH_4)_{1-x}Cl_x$ and some of the produced KCl react with $KMnCl_3$ to form $K_4MnCl_6$. These results are reasonably in agreement with the two mass loss steps in the TGA profile and several DSC peaks between 170 and 250 °C.

In addition to the reflections of KCl above 450 °C, the diffraction peaks due to the $K_4MnCl_6$ compound are absent, most likely due to the decomposition and melting of $K_4MnCl_6$ at this temperature [23], which corresponds to a significant endothermic DSC peak at 451 °C.

The thermal decomposition of $K_2Mn(BH_4)_4$ in this study is very similar to that of $KSc(BH_4)_4$ prepared by ball milling of $KBH_4$ and $ScCl_3$ [18]. In both cases, $KBH_4$ is formed during the first decomposition of the complex borohydrides with the concurrent release of hydrogen. The $KBH_4$ then reacts with $K-Mn(Sc)-Cl$, resulting in a second hydrogen evolution and the formation of KCl. The formed KCl compound then subsequently dissolves in the remaining $KBH_4$ to give a $K(BH_4)_{1-x}Cl_x$ solid solution.

Fig. 8 shows in-situ Raman spectra of the milled $2KBH_4-MnCl_2$ sample during heating. A decrease in intensity for each $B-H$ vibration mode is observed with increasing temperature. On heating sample to 120 °C, the external vibrations, the stretching mode at 2408 cm$^{-1}$ and the bending bands at 1342 and 1035 cm$^{-1}$ disappear, which corresponds to the decomposition of the formed mixed-ions compound $K_2Mn(BH_4)_4$. At 120 °C, there are still $B-H$ stretching bands at 2175, 2205, 2306 and 2380 cm$^{-1}$, as well as a bending band at 1248 cm$^{-1}$, which are all associated with the unreacted $KBH_4$ compound. These observations agree with the in-situ XRD results (Fig. 6).
Fig. 9 shows the FTIR spectra of the milled 2KBH₄–MnCl₂ sample heated to 150, 250 and 450 °C then cooled to room temperature. The milled sample heated to 150 °C indicates that five modes at 1038, 1204, 1342, 2174 and 2373 cm⁻¹ disappear due to the decomposition of KₓMn(BH₄)ₓ; and four B–H bands at 1118, 2210, 2282 and 2373 cm⁻¹ corresponding to KBH₄, and vibration modes at 1246 and 1365 cm⁻¹ due to B–B bonding are observed. On further heating to 250 °C, a significant shifting of the four B–H bands from KBH₄ are observed, which corresponds to the dissolution of KBH₄ in KCl to form a K(BH₄)₁ₓClₓ solid solution. This observation is consistent with the in-situ XRD patterns, where the reflections for KBH₄ slowly approach those of KCl. Apart from the B–H bands due to K(BH₄)₁ₓClₓ solid solution and the B–B bands at 928, 1263 and 1346 cm⁻¹ for the decomposed sample at 250 °C, there is a very weak vibration mode at 2478 cm⁻¹, which is possibly due to the reaction of K(BH₄)₁ₓClₓ with ternary chloride to form a borane species (KₓB₁₂H₁₂), however, very weak bands owing to KBH₄, or K(BH₄)₁ₓClₓ, or K₂B₁₂H₁₂ [24], are not observed.

A borane compound is not observed in the in-situ XRD pattern (perhaps owing to a small relative proportion and/or lack of crystallinity), however, it is suggested that, due to the DSC profiles with several endothermic peaks between 170 and 260 °C and the mass spectra of the milled sample with a multi-step hydrogen release, the intermediate compounds may be formed during the thermal decomposition process. The decomposed sample at 450 °C shows that there are no B–H bands owing to KBH₄, or K(BH₄)₁ₓClₓ, however, very weak vibration modes at 1075 and 2470 cm⁻¹ corresponding to broad bands at 925, 1239 and 1351 cm⁻¹ associated with B–B bonding are present.

Although there are no Raman vibration modes observed for the milled 2KBH₄–MnCl₂ samples decomposed respectively at 150, 250 and 450 °C, after being exposed to air at room temperature, these samples exhibit a shark peak at 641 cm⁻¹ (Fig. 10), which is believed to be due to the vibrational mode for a manganese oxide [25]. This result indirectly implies that finely dispersed manganese is formed during the decomposition of milled 2KBH₄–MnCl₂ sample.

Therefore, through the combination of thermal analysis, in-situ XRD measurement, Raman and IR spectrometry, the first thermal decomposition of the milled 2KBH₄–MnCl₂ sample between 100 and 160 °C can be described in Equation (2):

$$K_xMn(BH_4)_x \rightarrow 2KBH_4 + Mn + 12/7B + 1/7B_2H_6 + 25/7H_2$$

where the theoretical mass loss (1.58 wt%) in the mixture is consistent with the experimental data (1.6 wt%).

In the second thermal decomposition between 165 and 260 °C, there are several reactions taking place simultaneously: the reaction of KBH₄ with ternary chloride to release hydrogen and to form KCl, boron, finely dispersed manganese and possibly small amounts of higher borane species (Equation (3)) with the theoretical mass loss of 1.96 wt% in the mixture, which is consistent with the experimental data (1.9 wt%); the dissolution of KBH₄ in KCl to form the solid solution as described in Equation (4); and the transformation of ternary chloride as shown in Equation (5).

$$2KMnCl_3 \rightarrow 4KBH_4 \rightarrow 6KCl + 2Mn + (4 - 2y/z)B + 7H_2$$

$$xKCl + (1 - x)KBH_4 \rightarrow K(BH_4)_{1-x}Cl_x$$

$$K_xMnCl_3 \rightarrow 3KCl + K_xMnCl_6$$

4. Conclusions

For the milled 2KBH₄–MnCl₂ sample, unlike ABH₄(A = Li and Na) as precursors, there are no distinct X-ray reflections associated with the Mn[BH₄]ₓ compound. Characterization of the milled materials shows mixed-ion borohydride KₓMn(BH₄)ₓ, ternary chloride KMnCl₃ and unreacted KBH₄ polymorphs. The KₓMn(BH₄)ₓ compound has XRD reflections consistent with the P2₁/n structure proposed by Schouwink et al. [13].
The mixed 2KBH₄–MnCl₂ sample shows a two-step decomposition behaviour. The first between 100 and 160 °C is associated with the decomposition of KₓMn(BH₄)ₓ to form KBH₄, boron, finely dispersed manganese, as well as the release of hydrogen and trace diborane with a mass loss of 1.6 ± 0.1 wt%. The second between 165 and 260 °C shows several reactions taking place simultaneously: the reaction of KBH₄ (or KCl) with manganese to release hydrogen with a mass loss of 1.9 ± 0.1 wt% and to form KCl, boron, finely dispersed manganese and possibly small amounts of higher borane species; the dissolution of KCl in KBH₄ to form a KClₓ(BH₄)₁₋ₓ solid solution phase; and the transformation of ternary chloride from KMnCl₃ to KₓMnCl₂.

The decomposition properties of Mn-based borohydrides highly depend on their composition and nature. The mixed-ion borohydride (KₓMn(BH₄)ₓ) from the mixed 2KBH₄–MnCl₂ sample exhibits a lower decomposition temperature than that of the mixed 2LiBH₄–MnCl₂ sample [4], thus the combination of appropriate cations is a potential method for adjusting the thermodynamic stability of borohydrides so as to have decomposition temperatures within the desired range for hydrogen storage applications.

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