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## Investigation of $\text{MBH}_4\text{—VCl}_2$ , $\text{M} = \text{Li, Na or K}$

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### ABSTRACT

Systematic investigations of  $\text{MBH}_4\text{—VCl}_2$ ,  $\text{M} = \text{Li, Na, or K}$ , 2:1 or 3:1, samples prepared by mechano-chemistry and different milling time in order to gain insight in the phase stability and search for novel borohydrides. The samples were investigated using powder X-ray diffraction and Raman spectroscopy. Subsequently, the samples were exposed to heat treatment and investigated by *in-situ* synchrotron radiation powder X-ray diffraction (SR-PXD). These studies reveal formation of numerous compounds during decomposition of the samples, which contrasts with previous investigations. In several cases the formed compounds were in a less well-crystalline state, which did not allow identification. One of the unidentified compounds was observed both in the  $\text{LiBH}_4\text{—VCl}_2$  and  $\text{NaBH}_4\text{—VCl}_2$  systems and appeared to decompose at  $T \sim 190^\circ\text{C}$  and is assumed to be a new vanadium borohydride. Crystalline  $\text{Li}_2\text{VCl}_4$  was observed, but a major fraction of the decomposition products appeared to be amorphous. The  $\text{KBH}_4\text{—VCl}_2$  system revealed formation of well-crystalline solid solutions of  $\text{K}(\text{BH}_4)_{1-x}\text{Cl}_x$ .

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## 1. Introduction

Light element borohydrides have received significant attention due to extremely high hydrogen contents, which is attractive for solid-state hydrogen storage for mobile application [1–3]. A drawback for many metal borohydrides is their high stability and high hydrogen release temperatures. Second, borohydrides often have relatively slow kinetics for hydrogen release and in particular hydrogen uptake reactions [3–5].

It is well established that the hydrogen desorption temperature  $T_d$  of  $\text{M}(\text{BH}_4)_n$  correlates with the Pauling electronegativity,  $\chi_p$  of the metal  $\text{M}$  and  $T_d$  decreases with increasing values of  $\chi_p$

[6]. On the other hand, for  $\chi_p > \sim 1.6$  the metal coordinating to the borohydride may be reduced and borane gasses are released in addition to hydrogen [7,8]. Moreover, the higher the oxidation state of the metal, the higher the tendency for a reduction of the metal, which leads to release of borane gasses, e.g. the system  $\text{LiBH}_4\text{—VCl}_3$  releases a mixture of diborane and hydrogen during mechano-chemical treatment [9]. In fact, prolonged ball milling of  $2\text{LiBH}_4\text{—VCl}_3\text{—LiH}$  is presented as a new route for production of  $\text{VB}_2$  nanoparticles [10].

Despite the high thermal stability, lithium and sodium borohydrides are still among the most investigated hydrogen storage materials due to the prolific properties of reactive

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hydride composites, e.g. the system  $\text{LiBH}_4\text{-MgH}_2$  [11–15]. Furthermore, a range of other additives has been investigated recently with the aim to discover a catalyst that could possibly improve the kinetics [3]. There are a large number of potential destabilizing agents, and in the following we focus on metal chlorides. Recently, it was indicated that an effective additive for  $\text{LiBH}_4$  is the mixture of  $0.2 \text{ MgCl}_2 + 0.1 \text{ TiCl}_3$  [3,16]. Although, other investigations suggest that the molecular borohydride  $\text{Ti}(\text{BH}_4)_3$  may form in the system  $\text{LiBH}_4\text{-MgCl}_2\text{-TiCl}_3$  and evaporate, decompose and lead to loss of diborane and decreasing reversible hydrogen storage capacity [17].

According to the calculated energy of decomposition vanadium(II) borohydride,  $\text{V}(\text{BH}_4)_2$  is stable at room temperature in contrast to  $\text{Ti}(\text{BH}_4)_3$  [18]. However, there is still no clear experimental evidence for formation of  $\text{V}(\text{BH}_4)_2$ . On the other hand, vanadium(III) borohydride,  $\text{V}(\text{BH}_4)_3$  appeared to form by mechanochemical treatment (with cooling) of  $\text{NaBH}_4\text{-VCl}_3$ . The existence of  $\text{V}(\text{BH}_4)_3$  was based on infrared spectroscopy and no structural data is yet available. However, it is interesting that only hydrogen was released from this sample at  $T < 250 \text{ }^\circ\text{C}$  [19]. The complexes of vanadium(III) borohydride,  $\text{V}(\text{BH}_4)_3(\text{PMe}_3)_2$  and  $[\text{V}(\text{BH}_4)_2(\text{PMe}_3)_2]_2\text{O}$ , remain as the only fully structurally investigated compounds [20]. Furthermore, vanadium hydride is one out of very few binary hydrides to release and absorb hydrogen at moderate conditions. This has prompted the present investigation, which tends to include a larger range of sample compositions in order to map the possible formation of new vanadium borohydrides. We investigated the reactions in the  $\text{MBH}_4\text{-VCl}_2$ ,  $M = \text{Li, Na or K}$  systems, facilitated by mechanochemical and heat treatment observed by combined *ex-situ* and *in-situ* synchrotron radiation powder X-ray diffraction (SR-PXD) and Raman spectroscopy that allowed us to gain some insight in the reactions and the complex chemistry that occur.

## 2. Experimental

### 2.1. Sample preparation

The mechanochemical synthesis was performed under argon atmosphere using tungsten carbide (WC) hard alloy vessel (80 mL) and balls (10 mm diameter) in a Fritsch P4 planetary mill [21].  $\text{MBH}_4\text{-VCl}_2$  mixture ( $\sim 1.0 \text{ g}$ ) in the appropriate molar ratios 2:1 or 3:1 was prepared for one time. Commercially available chemicals were used: lithium borohydride ( $\text{LiBH}_4$ , 95%, Aldrich), sodium borohydride ( $\text{NaBH}_4$ , 98.5%, Aldrich), potassium borohydride ( $\text{KBH}_4$ , 98.5%, Aldrich) and anhydrous vanadium(II) chloride ( $\text{VCl}_2$ , 85%, Aldrich). Vanadium(II) chloride is air sensitive and is oxidized to vanadium(III) oxochloride ( $\text{VOCl}$ ) upon exposure to the atmosphere.

A special milling scheme was applied in order to prevent heating of the sample and decomposition of less stable borohydrides, i.e. 2 min milling time, 2 min pause, 30–60 repetitions. The sample-to-ball weight ratio was 1:32. The speed of the main disk was fixed at 200 rpm, and the planets' speed was  $\sim 560 \text{ rpm}$ .

Synthesized samples are denoted S1 to S14 and listed in Table 1. All handling and manipulation of the chemicals was

**Table 1 – Composition of the  $\text{MBH}_4\text{-VCl}_2$  samples prepared mechanochemically.**

Notation	Materials	Molar ratio	Composition (mol%)		Ball milling time (min)
			$\text{MBH}_4$	$\text{VCl}_2$	
S1	$\text{LiBH}_4\text{-VCl}_2$	2:1	66.7	33.3	60
S2	$\text{LiBH}_4\text{-VCl}_2$	2:1	66.7	33.3	90
S3	$\text{LiBH}_4\text{-VCl}_2$	2:1	66.7	33.3	120
S4	$\text{LiBH}_4\text{-VCl}_2$	3:1	75.0	25.0	60
S5	$\text{NaBH}_4\text{-VCl}_2$	2:1	66.7	33.3	60
S6	$\text{NaBH}_4\text{-VCl}_2$	2:1	66.7	33.3	90
S7	$\text{NaBH}_4\text{-VCl}_2$	2:1	66.7	33.3	120
S8	$\text{NaBH}_4\text{-VCl}_2$	3:1	75.0	25.0	60
S9	$\text{KBH}_4\text{-VCl}_2$	2:1	66.7	33.3	60
S10	$\text{KBH}_4\text{-VCl}_2$	2:1	66.7	33.3	90
S11	$\text{KBH}_4\text{-VCl}_2$	2:1	66.7	33.3	120
S12	$\text{KBH}_4\text{-VCl}_2$	3:1	75.0	25.0	60
S13	$\text{KBH}_4\text{-VCl}_2$	3:1	75.0	25.0	90
S14	$\text{KBH}_4\text{-VCl}_2$	3:1	75.0	25.0	120

carried out under argon atmosphere in an MBraun Unilab glove box with a recirculation gas purification system and gas/humidity sensors. Oxygen and water levels were kept below 1 ppm during all operations.

### 2.2. Synchrotron radiation powder X-ray diffraction (SR-PXD)

Details of the interactions during reactive milling and subsequent heating of  $\text{MBH}_4\text{-VCl}_2$ ,  $M = \text{Li, Na or K}$ , were obtained by *ex-situ* and *in-situ* SR-PXD experiments. Data were collected at the beamline BM01A of the Swiss-Norwegian Beam Lines (SNBL), European Synchrotron Radiation Facility (ESRF), Grenoble, France and at beamline I711 at the synchrotron MAX II, MAX-lab, Lund, Sweden.

At ESRF data were recorded using a MAR345 image plate detector. The selected wavelengths were 0.696713 and 0.739505 Å. The X-ray exposure time was 30 s per powder diffraction pattern. The samples were mounted in glass capillaries (0.5 mm outer diameter) in an argon-filled glove box and sealed with glue during a short air-exposure. The samples were typically heated from RT to 420 or 500 °C depending on sample composition with a heating rate of 2.5–5 °C/min.

At MAX-lab data were collected using Oxford Diffraction Titan CCD detector [22]. The samples were mounted in sapphire single crystal tubes ( $\text{Al}_2\text{O}_3$ , o.d. 1.09 mm, i.d. 0.79 mm) in an argon-filled glove box ( $p(\text{O}_2, \text{H}_2\text{O}) < 1 \text{ ppm}$ ) [23]. The sample holder was specially developed for studies of gas/solid reactions and allows hydrogen pressures up to 20 MPa and inert conditions without air exposure [24]. The selected wavelength was 0.9892 Å. The X-ray exposure time was 30 s per PXD pattern. The samples were heated from RT to 500 °C with a heating rate of 10 °C/min.

All obtained raw images were transformed to 2D-powder patterns using the FIT2D program [25], which was also used for calibration using a standard NIST  $\text{LaB}_6$  sample. Data analysis was performed by Rietveld refinement of selected PXD patterns using the full profile fitting program Fullprof [26]. The backgrounds were described by linear interpolation

between selected points, while pseudo-Voigt profile functions were used to fit the diffraction peaks. In general unit cell parameters, zero shift, profile parameters and the overall temperature factors,  $B_{ov}$  were refined. For the modelling of the  $K(BH_4)_{1-x}Cl_x$  solid solutions, Cl was introduced on the position of B in  $KBH_4$  and the occupancies of Cl, B and H were refined. The overall occupancy of Cl and  $BH_4$  was constrained to one.

### 2.3. Raman spectroscopy

Raman spectroscopic measurements were performed on selected samples using a Thermo Scientific DXR Raman Microscope. The excitation laser had a power of  $\sim 6$  mW and a wavelength of  $\lambda = 532$  nm. The samples were packed under Ar atmosphere in 0.5 mm glass capillaries (o.d. 0.5 mm).

## 3. Results and discussion

### 3.1. Mechano-chemical treatment of $LiBH_4-VCl_2$ system

Fig. 1 compares SR-PXD patterns of  $LiBH_4-VCl_2$  mixtures subjected to ball milling as a function of milling time (60, 90, and 120 min) and components ratio (2:1 or 3:1). The SR-PXD data reveal the presence of several chlorides, LiCl,  $Li_2VCl_4$  and VOCl besides the reactants  $VCl_2$  and  $LiBH_4$ , which suggests that several reactions have occurred during mechano-chemical treatment. Rietveld refinements of the SR-PXD data for samples S1 and S4 (2:1 and 3:1 ratios, respectively, ball-milled for 60 min) show remaining  $LiBH_4$ , whereas  $VCl_2$  is observed only for S1. Moreover, for the two samples an unidentified peak at  $d = 5.39$  Å is observed (although, rather weak in sample S4). The compound giving rise to this peak is denoted 1.

Increasing the milling time (sample S2 and S3) leads to a significant reduction in the number and intensity of recorded reflections in the SR-PXD patterns. The data for sample S2 (2:1, 90 min BM) show diffraction from  $Li_2VCl_4$ , LiCl, VOCl and trace

amounts of 1, while the reactants were completely consumed in the reaction. Diffraction peaks from  $Li_2VCl_4$  decrease in intensity along with increase of LiCl intensity for S2, corresponding to a LiCl: $Li_2VCl_4$  weight ratio of 3:1 determined by Rietveld refinement. A minor decrease in diffracted intensity from VOCl is also observed. Mechano-chemical treatment for 120 min (sample S3) further decreases the diffracted intensity from  $Li_2VCl_4$  and VOCl and increases the intensity of LiCl leading to a LiCl: $Li_2VCl_4$  weight ratio of 9:1. Furthermore, 1 becomes weaker in the SR-PXD profile of S3.

In general, it may be speculated that lithium chloride is formed in a metathesis reaction between the reactants  $LiBH_4$  and  $VCl_2$ , possibly also forming a new vanadium borohydride. The latter may be observed as the reflection denoted 1. The amount of 1 decreases with prolonged BM, possibly due to decomposition or amorphization. Formation of vanadium borohydride in a similar metathesis reaction was previously suggested from FTIR data [19]. The data also suggest that full consumption of  $VCl_2$  during ball milling requires excess  $LiBH_4$  (S4) or prolonged ball milling (>60 min). The ternary chloride,  $Li_2VCl_4$ , may form in an addition reaction between LiCl and  $VCl_2$ , in analogy to e.g.  $Na_2ZnCl_4$  or  $Na_3ScCl_6$  formed during synthesis of  $NaZn(BH_4)_3$  or  $NaSc(BH_4)_4$  [7,27]. Ternary chlorides may react upon further mechanochemical treatment with remaining alkali metal borohydrides [7,27]. Therefore,  $Li_2VCl_4$  may react with remaining amorphous lithium borohydride forming more lithium chloride (lithium borohydride is previously observed to become amorphous by BM [28]). Vanadium oxychloride VOCl may form due to oxygen contamination of the sample [29].

### 3.2. Thermal treatment of $LiBH_4-VCl_2$

Changes in structure and composition for the samples S1, S3 and S4 during thermal treatment are studied by *in-situ* SR-PXD technique (the data are shown in Figs. 2–4, respectively). Fig. 2 shows the data for sample S1 heated from RT to 420 °C. At

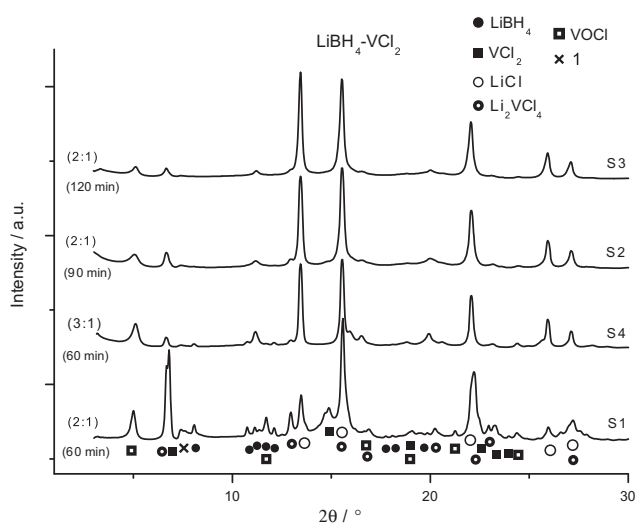


Fig. 1 – SR-PXD data for ball-milled samples S1-S3 of  $LiBH_4-VCl_2$  (2:1) and S4 of  $LiBH_4-VCl_2$  (3:1) measured at RT ( $\lambda = 0.696713$  Å, BM01A, ESRF).

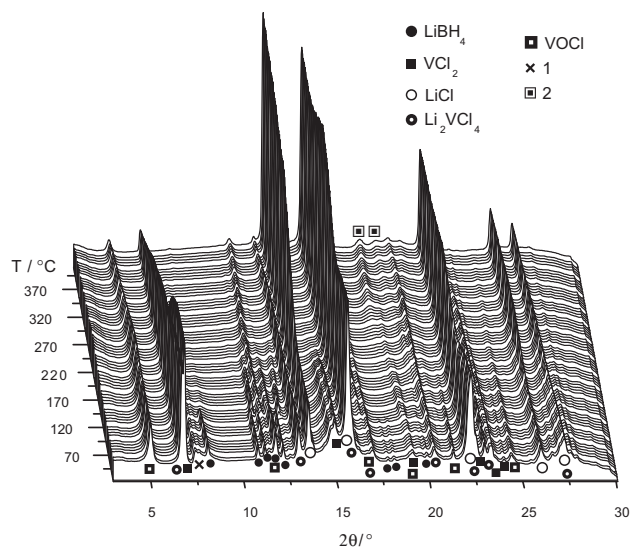
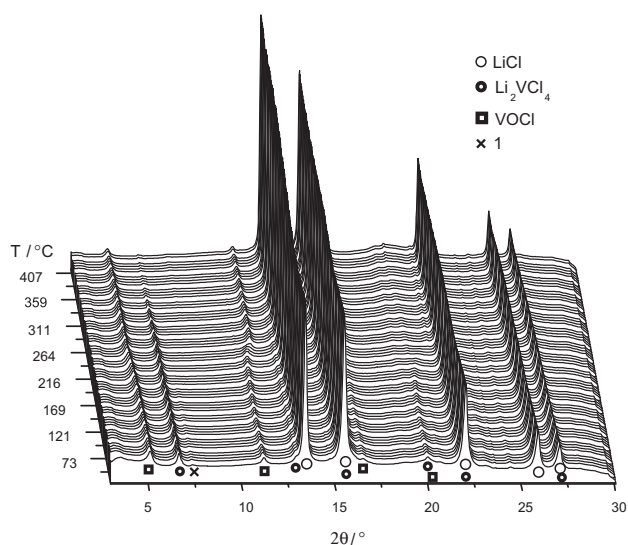
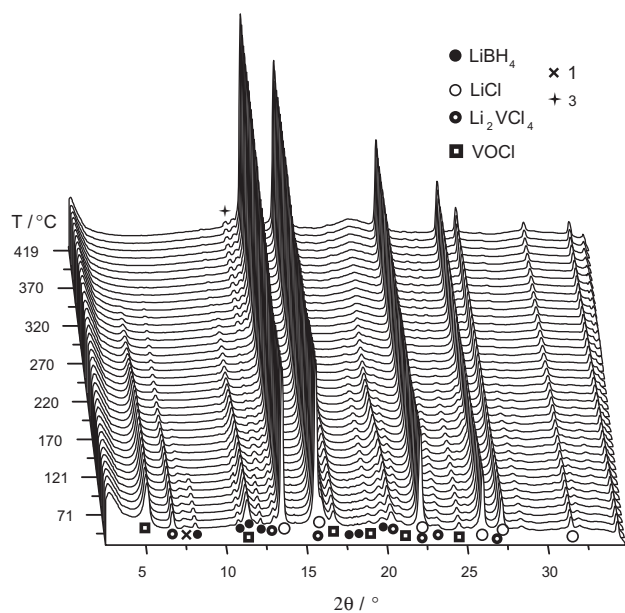


Fig. 2 – *In-situ* SR-PXD data for the ball-milled sample of  $LiBH_4-VCl_2$  (S1, 2:1) heated from RT to 420 °C,  $\Delta T/\Delta t = 2.5$  °C/min ( $\lambda = 0.696713$  Å, BM01A, ESRF).



**Fig. 3** – In-situ SR-PXD data for the ball-milled sample of  $\text{LiBH}_4\text{-VCl}_2$  (S3, 2:1) heated from RT to, 410 °C,  $\Delta T/\Delta t = 2.5$  °C/min ( $\lambda = 0.696713$  Å, BM01A, ESRF).

110 °C, orthorhombic *o*- $\text{LiBH}_4$  undergoes a polymorphic transition to the hexagonal modification, *h*- $\text{LiBH}_4$  [5,24]. The Bragg peak from 1, which may be a new vanadium borohydride, disappears at ca. 190 °C. The weight ratio between  $\text{VCl}_2$  and  $\text{Li}_2\text{VCl}_4$  is constant from RT to  $T < 170$  °C, while the relative amount of  $\text{Li}_2\text{VCl}_4$  gradually increases at higher temperatures. At  $T \sim 220$  °C, vanadium chloride reflections disappear simultaneously with decreasing intensity from *h*- $\text{LiBH}_4$ . The latter changes also occur simultaneously with increasing intensity from LiCl.

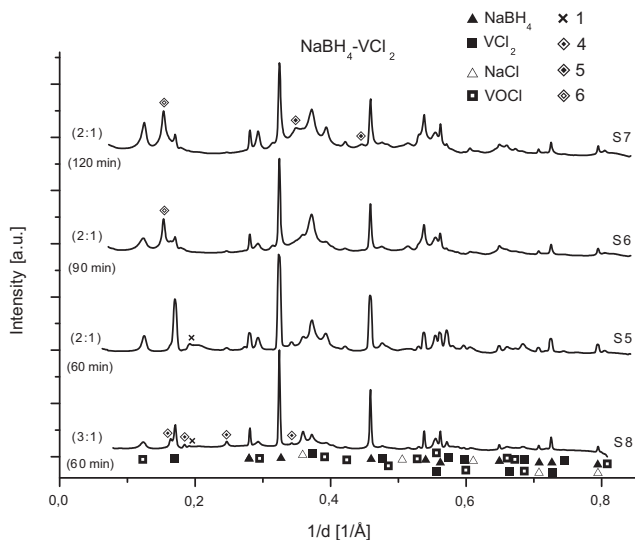


**Fig. 4** – In-situ SR-PXD data for the ball-milled sample of  $\text{LiBH}_4\text{-VCl}_2$  (S4, 3:1) heated from RT to, 420 °C,  $\Delta T/\Delta t = 5$  °C/min ( $\lambda = 0.696713$  Å, BM01A, ESRF).

The obtained data (Fig. 2) provide evidence that thermally induced reactions occur during the heating above 170 °C. Further thermal treatment leads to a gradual decrease of the amount of  $\text{Li}_2\text{VCl}_4$  phase along with the increase of LiCl quantity in the reaction product. This finding is in agreement with results obtained during increasing ball milling time (see Fig. 1). Hexagonal  $\text{LiBH}_4$  commences to melt at ca. 270 °C. Two diffuse reflections denoted 2 appear when *h*- $\text{LiBH}_4$  peaks disappear at temperatures above 300 °C. The reflections denoted 2 may correspond to  $\text{V}_2\text{H}$  with peak positions slightly shifted towards larger  $2\theta$  Bragg angles possibly due to a lower than expected hydrogen content [30]. This is supported by another similar in-situ SR-PXD experiment of  $\text{LiBH}_4\text{-VCl}_2$  (S1, 2:1) conducted in hydrogen atmosphere,  $p(\text{H}_2) = 10$  bar, which reveals stronger diffraction from  $\text{V}_2\text{H}$  (2). Temperature-induced decomposition of metal borohydrides may lead to the formation of the hydrides of the corresponding metals [6,31,32], while  $\text{V}_2\text{H}$  was experimentally obtained by isothermal desorption of ball-milled  $\text{LiBH}_4\text{-V}$  (2:1) mixture at 1 bar  $\text{H}_2$  back-pressure [33]. The in-situ SR-PXD data for sample  $\text{LiBH}_4\text{-VCl}_2$  (S3, 2:1) shown in Fig. 3, further support that  $\text{Li}_2\text{VCl}_4$  finally transforms to LiCl in the studied system. During heating from RT to 410 °C, S3 reveals similar thermal behaviour as observed for S1. At 410 °C, the sample S3 consists mainly of LiCl with a smaller amount of  $\text{Li}_2\text{VCl}_4$  and VOCl. Vanadium(III) oxychloride, VOCl, appears not to participate in hydrogen release and uptake reactions (see Figs. 2 and 3). For the  $\text{LiBH}_4\text{-VCl}_2$  (S4, 3:1) sample with excess of  $\text{LiBH}_4$ , in-situ SR-PXD data, see Fig. 4, show the *o*- to *h*- $\text{LiBH}_4$  polymorphic transformation at 110 °C and melting of *h*- $\text{LiBH}_4$  at ca. 270 °C. The unidentified reflection from 1 disappears at ca. 190 °C in accord with investigations of samples S1 and S3 (see Figs. 2 and 3). This decomposition temperature is similar to that for the decomposition of  $\text{Y}(\text{BH}_4)_3$  ( $\sim 190$  °C), which further supports the suggestion that 1 may be a new vanadium borohydride [28]. The diffracted intensity from  $\text{Li}_2\text{VCl}_4$  and VOCl starts to decrease in the same temperature range as the melting of  $\text{LiBH}_4$  and vanishes at 340 °C, possibly due to a reaction with excess  $\text{LiBH}_4$ . Clearly, the thermal stability of VOCl is lower for sample S4 as compared to samples S1, S2 and S3 whereas it is similar for  $\text{Li}_2\text{VCl}_4$  in all four samples. Moreover, unidentified peaks denoted 3 appear at 280 °C for S4. 3 may be formed in a reaction between VOCl and molten  $\text{LiBH}_4$ . Crystalline vanadium or boron is not detected in any of the samples S1 to S4 suggesting existence of amorphous material in these samples. In fact, in a similar in-situ SR-PXD experiment of  $\text{LiBH}_4\text{-VCl}_2$  (S1, 2:1) conducted in hydrogen atmosphere,  $p(\text{H}_2) = 10$  bar, a broad Bragg diffraction peak at  $d \sim 2$  Å was observed, which coincides with the strongest diffraction peak from  $\text{VB}_2$  [10,34].

### 3.3. Mechanochemical treatment of $\text{NaBH}_4\text{-VCl}_2$ system

SR-PXD data measured at RT for ball-milled samples of  $\text{NaBH}_4\text{-VCl}_2$  (sample S5 – S8) are shown in Fig. 5. Clearly, there is unreacted  $\text{VCl}_2$  and  $\text{NaBH}_4$  in all samples and only minor amounts of NaCl present. In contrast, for the samples S1 to S4 limited amounts of  $\text{LiBH}_4$  are observed but significant amounts of LiCl. This observation tends to suggest that the system  $\text{NaBH}_4\text{-VCl}_2$  is less reactive as compared to

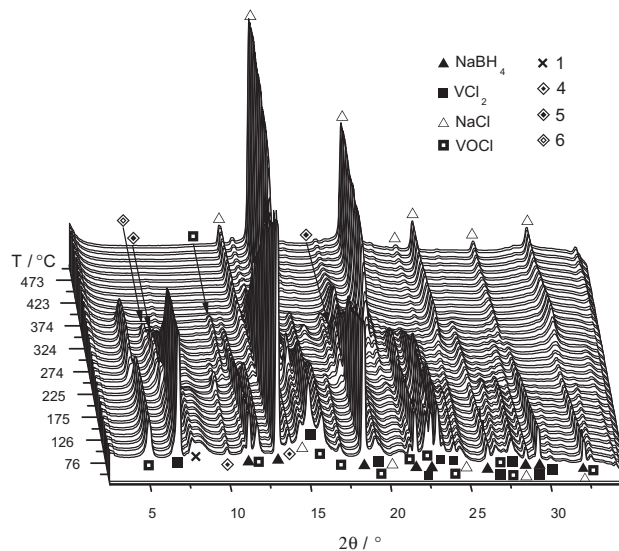


**Fig. 5** – SR-PXD data for ball-milled samples S5–S7 of  $\text{NaBH}_4\text{--VCl}_2$  (2:1) and S8 of  $\text{NaBH}_4\text{--VCl}_2$  (3:1) measured at RT ( $\lambda = 0.696713 \text{ \AA}$  for S5–S7,  $\lambda = 0.739505 \text{ \AA}$  for S8, BM01A, ESRF).

$\text{LiBH}_4\text{--VCl}_2$ . Rietveld refinement of PXD data measured for sample  $\text{NaBH}_4\text{--VCl}_2$  (S5, 2:1) and (S8, 3:1) reveals the presence of  $\text{NaBH}_4$ ,  $\text{VCl}_2$ ,  $\text{NaCl}$  and  $\text{VOCl}$ . Additionally, Bragg peaks from an unidentified compound denoted 4 were detected as well as a peak similar to 1 observed in the  $\text{LiBH}_4\text{--VCl}_2$  system. The presence of the unidentified 1 also in samples synthesized using  $\text{NaBH}_4$  further supports that 1 might be a new vanadium borohydride. 1 is only observed after 60 min of milling. Previous investigations of the system  $\text{NaBH}_4\text{--VCl}_3$  (3:1) suggest formation of  $\text{V}(\text{BH}_4)_3$  based on IR data [19]. Increasing the ball milling time to 90 or 120 min (S6 and S7) produce an unidentified reflection denoted 6 and ball milling for 120 min (S7) produce another unidentified reflection denoted 5. Some of the unidentified reflections 4, 5 and/or 6 may correspond to ternary sodium vanadium chlorides in analogy to  $\text{Li}_2\text{VCl}_4$ . Significant amounts of reactants remained in the sample after 120 min BM, while the amount of  $\text{NaCl}$  increases insignificantly.

### 3.4. Thermal treatment of $\text{NaBH}_4\text{--VCl}_2$ system

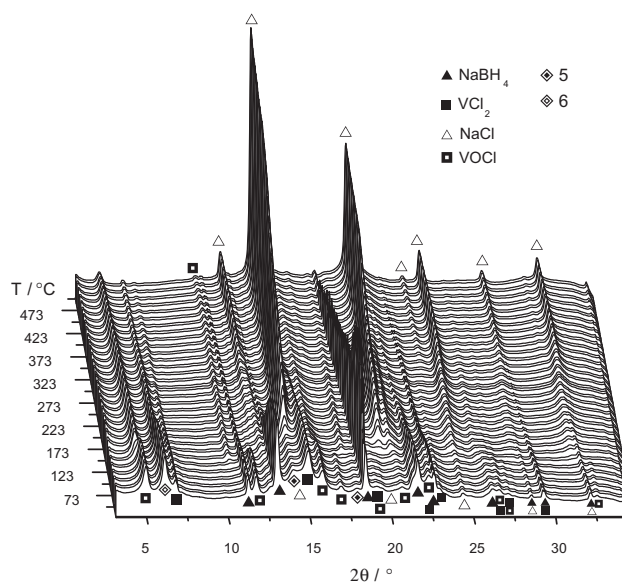
Figs. 6–8 illustrates *in-situ* SR-PXD data for S5, S7 and S8, respectively. Numerous thermally induced reactions occur in the temperature range RT to  $500 \text{ }^\circ\text{C}$  for sample S5, see Fig. 6. The Bragg peak from 1 vanishes at  $\sim 175 \text{ }^\circ\text{C}$ . Another unidentified compound, 4, formed during milling and has decreasing diffracted intensity  $T > 190 \text{ }^\circ\text{C}$  simultaneously with the onset of formation of 5 for S5. A shift in Bragg peaks position of  $\text{VOCl}$  is observed at ca.  $205 \text{ }^\circ\text{C}$ . 4 completely disappears at ca.  $250 \text{ }^\circ\text{C}$  while 5 disappears from the patterns at ca.  $300 \text{ }^\circ\text{C}$  and 6 is observed in the temperature range  $290\text{--}330 \text{ }^\circ\text{C}$ . Bragg peaks from vanadium chloride  $\text{VCl}_2$  and  $\text{NaBH}_4$  vanish at ca.  $315 \text{ }^\circ\text{C}$  possibly due to a chemical reaction followed by increasing intensity of  $\text{NaCl}$ .  $\text{VOCl}$  disappears at  $\sim 350 \text{ }^\circ\text{C}$  and at  $500 \text{ }^\circ\text{C}$  the sample consists of  $\text{NaCl}$  and  $\text{NaBH}_4$ .



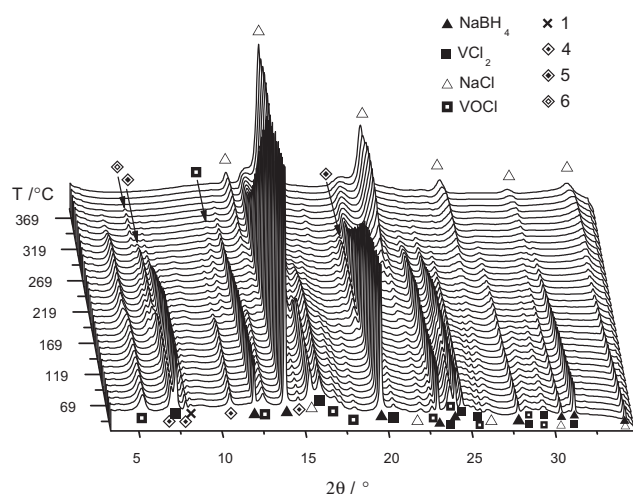
**Fig. 6** – *In-situ* SR-PXD data for the ball-milled sample of  $\text{NaBH}_4\text{--VCl}_2$  (S5, 2:1) heated from RT to,  $500 \text{ }^\circ\text{C}$ ,  $\Delta T/\Delta t = 2.5 \text{ }^\circ\text{C}/\text{min}$  ( $\lambda = 0.696713 \text{ \AA}$ , BM01A, ESRF).

In sample  $\text{NaBH}_4\text{--VCl}_2$  (S7, 2:1)  $\text{VOCl}$  shows a minor shift towards smaller  $2\theta$  angles already  $\sim 105 \text{ }^\circ\text{C}$  but remains in the sample until the end of the experiment. The diffracted intensity from the reactants decreases at  $225 \text{ }^\circ\text{C}$  simultaneously with a significant increase in the amount of  $\text{NaCl}$ . At the end of the experiment, at  $500 \text{ }^\circ\text{C}$  significant amounts of  $\text{NaCl}$  and  $\text{VOCl}$  remain in the sample along with smaller amounts of 6 and  $\text{NaBH}_4$ .

Thermal events observed using *in-situ* SR-PXD for sample  $\text{NaBH}_4\text{--VCl}_2$  (S8, 3:1) with excess of  $\text{NaBH}_4$  and ball milled for 60 min (see Fig. 8) appear to be somewhat similar to that observed for sample S5 (Fig. 6). Compound 1, which may be a



**Fig. 7** – *In-situ* SR-PXD data for the ball-milled sample of  $\text{NaBH}_4\text{--VCl}_2$  (S7, 2:1) heated from RT to,  $500 \text{ }^\circ\text{C}$ ,  $\Delta T/\Delta t = 2.5 \text{ }^\circ\text{C}/\text{min}$  ( $\lambda = 0.696713 \text{ \AA}$ , BM01A, ESRF).



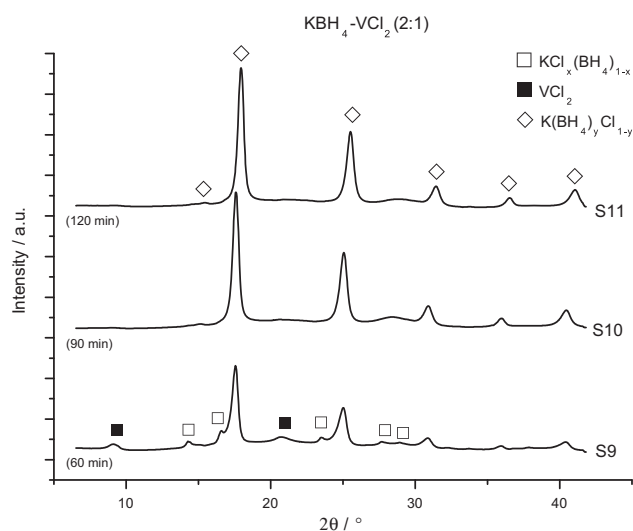
**Fig. 8** – In-situ SR-PXD data for the ball-milled sample of  $\text{NaBH}_4\text{--VCl}_2$  (S8, 3:1) heated from RT to, 380 °C,  $\Delta T/\Delta t = 5$  °C/min ( $\lambda = 0.739505$  Å, BM01A, ESRF).

vanadium borohydride, disappears again at ca. 190 °C. However, 6 is formed at  $\sim 140$  °C and decomposed at ca. 360 °C. 4 is formed during BM and diffraction decreases and vanishes at 260 °C possibly correlated with formation of 5, which is observed in the temperature range  $\sim 150\text{--}300$  °C. The peak positions for VOCl are shifted at ca. 170 °C and they vanish at ca. 350 °C.

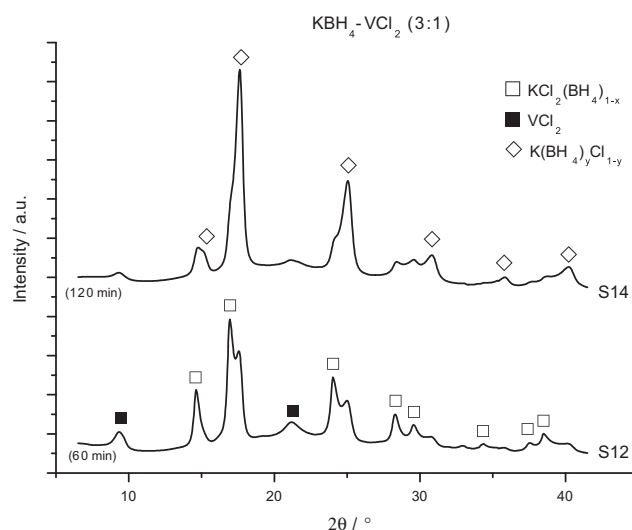
Consumption of the reactants  $\text{NaBH}_4$  and  $\text{VCl}_2$  and gradual increasing diffracted intensity from NaCl are observed at  $T > 230$  °C. Sample S8 consists of NaCl and minor amounts of  $\text{NaBH}_4$  at the end of the experiment at 380 °C.

### 3.5. Mechanochemical treatment of $\text{KBH}_4\text{--VCl}_2$ system

Details of the reaction between  $\text{KBH}_4$  and  $\text{VCl}_2$  during ball milling are shown in Figs. 9 and 10. Fig. 9 compares SR-PXD



**Fig. 9** – SR-PXD data for ball-milled samples of  $\text{KBH}_4\text{--VCl}_2$  (2:1) measured at RT ( $\lambda = 0.9892$  Å, I711, MAX-lab).



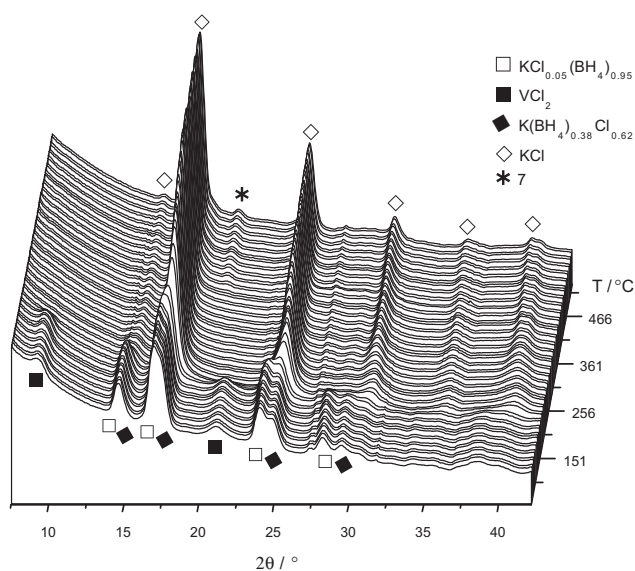
**Fig. 10** – SR-PXD data for ball-milled samples of  $\text{KBH}_4\text{--VCl}_2$  (3:1) measured at RT ( $\lambda = 0.9892$  Å, I711, MAX-lab).

patterns from  $\text{KBH}_4\text{--VCl}_2$  samples S9, S10 and S11 (2:1) ball milled for 60, 90, and 120 min, respectively. Rietveld refinement reveals a sample composition of  $\text{KCl}_{0.99}(\text{BH}_4)_{0.01}$ ,  $\text{K}(\text{BH}_4)_{0.95}\text{Cl}_{0.05}$  and unreacted  $\text{VCl}_2$  after short BM (S9, 60 min). Two solid solutions form due to dissolution of small amounts of  $\text{KBH}_4$  in KCl and small amounts of KCl in  $\text{KBH}_4$ . With increasing milling time the anion substitution reaction continues and the two solid solutions merge into one, which is observed as a shift of peak positions corresponding to  $\text{K}(\text{BH}_4)_y\text{Cl}_{1-y}$  and disappearance of  $\text{KCl}_x(\text{BH}_4)_{1-x}$  peaks. Furthermore, the amount of  $\text{KBH}_4$  in the sample decreases due to a reaction with  $\text{VCl}_2$ , which produces stoichiometric KCl after 120 min BM while all vanadium chloride and potassium borohydride has been consumed.

Fig. 10 illustrates the SR-PXD profiles of S12 and S14 samples (3:1 ratio) subjected to 60 and 120 min of ball milling, respectively. Rietveld refinement reveals that S12 is composed of  $\text{K}(\text{BH}_4)_{0.95}\text{Cl}_{0.05}$ ,  $\text{KCl}_{0.62}(\text{BH}_4)_{0.38}$  and  $\text{VCl}_2$ . Further ball milling for 120 min (S14) produces a solid solution with composition  $\text{KCl}_{0.69}(\text{BH}_4)_{0.31}$  and another  $\text{K}(\text{BH}_4)_{0.88}\text{Cl}_{0.12}$  along with minor amounts of remaining  $\text{VCl}_2$ . Samples S9 to S14 contain lower amounts of vanadium(III) oxochloride not detectable in the SR-PXD data obtained using the sapphire cell and a lower X-ray flux as compared to that used for measurements of the SR-PXD data for samples S1 to S8. Moreover, samples of  $\text{KBH}_4\text{--VCl}_2$  (S9 to S14) were synthesized first using more 'fresh'  $\text{VCl}_2$  containing less VOCl in comparison with that used for preparation of samples S1 to S8.

### 3.6. Thermal treatment of $\text{KBH}_4\text{--VCl}_2$ system

Fig. 11 shows in-situ SR-PXD data for sample  $\text{KBH}_4\text{--VCl}_2$  (S12, 2:1) heated from RT to 500 °C. The composition of the sample remains constant in the temperature range RT to 180 °C, where a reaction initiates. Peaks corresponding to  $\text{K}(\text{BH}_4)_{0.95}\text{Cl}_{0.05}$  and  $\text{VCl}_2$  vanish and those from  $\text{KCl}_{0.62}(\text{BH}_4)_{0.38}$  shift towards larger  $2\theta$  angles. Potassium chloride dissolves in



**Fig. 11** – In-situ SR-PXD data for the ball-milled sample of  $\text{KBH}_4\text{-VCl}_2$  (S12, 3:1) heated from RT to, 500 °C,  $\Delta T/\Delta t = 10$  °C/min ( $\lambda = 0.9892$  Å, I711, MAX-lab).

the solid solution  $\text{KCl}_{0.62}(\text{BH}_4)_{0.38}$  visible as increasing diffracted intensity observed until 195 °C, where the reaction rate decreases and the composition is stabilized. In the temperature range 400–500 °C only diffraction from KCl along with an unidentified Bragg peak at  $d = 2.86$  Å, denoted 7, is observed. The obtained results for thermal treatment are in accord with studies of the  $\text{KBH}_4\text{-ScCl}_3$  system [35].

### 3.7. Raman spectroscopy

The ball-milled mixtures and pure  $\text{VCl}_2$  are black powders and the quality of their Raman spectra is relatively poor compared to the spectra of  $\text{LiBH}_4$  or  $\text{NaBH}_4$ , which are white powders. Likewise, the broad feature around  $1080\text{ cm}^{-1}$  generated by the capillary does not seem to appear in other Raman spectra. No characteristic bands of the reactants are observed in any of the samples and it confirms that the reaction has been completed (at least on the surface) even at the short milling time. The synthesized samples show similar Raman profiles with a number of characteristic bands, e.g. at ca.  $430\text{--}460\text{ cm}^{-1}$ , which may correspond to metal-boron stretching mode previously reported for  $\text{M-B}$  ( $\text{M} = \text{Sc}, \text{Y}, \text{Zn}$ ) in [35–37]. The Raman peak observed around  $1100$  to  $1400\text{ cm}^{-1}$  could be attributed to B–H bending mode [9,37], but some similar bands may also suggest the presence of ternary chlorides  $\text{MV}_x\text{Cl}_y$ , ( $\text{M} = \text{Li}, \text{Na}$ ), which is supported by the SR-PXD data. The prominent thermal background at higher wavenumbers does not allow to distinguish peaks from possible vanadium borohydride [6].

## 4. Conclusions

Reactions in the  $\text{MBH}_4\text{-VCl}_2$ ,  $\text{M} = \text{Li}, \text{Na}$  and  $\text{K}$  system are highly complex depending on the details of sample preparation and desorption conditions. In-situ SR-PXD allows

investigation of crystalline compounds to reveal the formation of some phases different from previously described compounds. Compound 1 was observed in  $\text{LiBH}_4\text{-VCl}_2$  and  $\text{NaBH}_4\text{-VCl}_2$  samples and maybe a new vanadium borohydride in agreement with the low decomposition temperature,  $T_{\text{dec}} \sim 190$  °C. Moderate stability and low degree of crystallinity may in part be assumed to follow the previously proposed trend that transition metal borohydrides mainly form for electron configurations  $d^0$ ,  $d^5$  or  $d^{10}$ . At the same time neither crystalline boron nor vanadium were observed after mechanochemical and thermal treatments. These observations tend to suggest that vanadium ions in 1 are not reduced to the metallic state, which would also release borane gasses. Therefore, vanadium borohydride remains as a possible hydrogen storage system. The unidentified compounds 4, 5 and 6, observed during ball milling of  $\text{NaBH}_4$  and  $\text{VCl}_2$  might be ternary sodium vanadium chlorides with different stoichiometry. This contrasts with the solid solutions of  $\text{K}(\text{BH}_4)_{1-x}\text{Cl}_x$  observed for the  $\text{KBH}_4\text{-VCl}_2$ . The complexity and reactivity in the system  $\text{MBH}_4\text{-VCl}_2$  decrease with increasing cation size of the alkali metal in the series  $\text{Li}, \text{Na} > \text{K}$ .

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