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Flux-assisted single crystal growth and heteroepitaxy of perovskite-type mixed-metal borohydrides

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Structural investigations on mixed-metal borohydrides have been the subject of powder diffraction since the discovery that hydrogen-release temperatures can be tailored by more electronegative metals. The lack of producing suitable samples for single crystal X-ray diffraction has defined powder diffraction as the choice of method, which, however, is less sensitive to structural details of the compounds in question. Here we show how to overcome this limitation by developing a flux-assisted single crystal growth procedure to lower the melting point of mixed-metal compounds that are thermally unstable and usually decompose either before melting or are unstable in the melt. We prove the validity of this principle on a member of the recently reported perovskite-type class of borohydrides and show that the defined approach is easily generalized. Interesting structural details are revealed that stand in contrast with results obtained on samples produced by mechano-chemistry. The differences in lattice instabilities are discussed and put into context with discovered epitaxial relationships between rocksalt-type $A\mathrm{BH}_4$ and perovskite-type $A\mathrm{Ca(BH_4)_3}$ (A = alkaline metal). In this context, the preliminary results provide a valuable scheme that can be made use of when physical deposition of metal borohydrides reaches its working stage.

Introduction

Throughout the past ten years metal borohydrides have become a large family of materials, that has attracted interest in a range of energy-related fields, both as potential hydrogen storage materials,[1] owed to their high hydrogen content, and as solid electrolytes, where the mobility of cations such as Li^+ or Na^+,[2] but also Mg^{2+},[3] is promoted by structural dynamics specific to the tetrahydroborate anion BH_4, such as the paddle wheel effect.[4] Recently, reports on luminescence have suggested their utility as solid state phosphors.[5,6] Such a diversity in physical properties is owed to quite a pronounced structural flexibility of metal borohydrides, ranging from close packed compounds to nano-porous gas hosts.[7] The structural characterization has been at the front line of all investigations on these systems, and the method of choice has usually been that of X-ray powder diffraction, due to its tremendous flexibility and speed of data collection as opposed to neutron diffraction. However, structural details, such as the orientation of the BH_4 group and hence the atomic position of hydrogen, are not accessible by X-ray powder diffraction. At the same time, it is these details that are both crucial for an accurate theoretical treatment and dictate the physical properties desired in these systems. Hence, while the real working materials for such applications will likely be polycrystalline, the quality of information obtained from structural studies on such samples is nevertheless far from optimal.

Single crystal samples, on the other hand, would not only provide a superior description of the crystal structure, but also allow overcoming the problem of powder averaging during the measurement of highly anisotropic physical properties. Both lattice and molecular vibrations, which play a fundamental role in the thermal stability of the respective materials,[8] are subject to space group symmetry and hence anisotropic. Also physical properties such as ionic mobility are directional mechanisms, which correlate well to structural details.

In the metal borohydrides community, the synthetic method of choice is commonly based on mechano-chemistry (ball-milling).[9,10] Next to suffering from significant size- and strain-broadening in diffraction patterns, the produced powders are often highly reactive and can contain multiple thermodynamically metastable phases. An accurate description of the crystal structure in such cases is very difficult to obtain, if possible at all. Moreover, the mechano-chemical approach entails out-of-equilibrium conditions. The development of hydrogen-storage systems, for instance, however requires knowledge on the equilibrium structure. It is thus essential to provide information as accurate as possible for both theoretical and experimental exploration and the design of novel systems. These briefly addressed points all present serious obstacles for the accurate structural description of novel compounds.

To minimize such issues, significant efforts have been invested into wet-chemistry based methods by many different groups, including our own.[7,11] However, unfavourable thermodynamics prevents single phase yields of mixed-metal compounds both from simple addition reactions in wet chemistry as well as ball-milling.

A major challenge has been posed in the recent past to modify metathesis reactions between a borohydride and halide precursor, commonly employed in the synthesis of mixed-metal borohydrides, resulting in the presence of binary or ternary halides in the product, the so-called “dead mass” problem. Separation is impossible due to the solvation of borohydride single and double salts and the purification of ball-milled samples is additionally hindered by the mechanical formation of composite grains of various different phases, essentially halides and borohydrides.[12] Though it has previously been suggested that intergrowth may occur between grains of different crystalline phases, entailing major complications in wet-chemistry separation processes, such an intergrowth has not been experimentally confirmed. Very recently, this challenge has been solved by Jarón *et al.* in a solvent-mediated approach using bulky organic cations and weakly coordinating anions.[13] Presenting a major progress, this has provided a means of producing single phase pure dual-cation metal borohydrides for the first time. Still, this does not solve powder-related issues during structural investigation, as the outlined approach results in fine-grained poly-crystalline samples.

Crystal structure solutions on polycrystalline borohydrides (and in general) can be partially[14-16] incorrect, and have sometimes been corrected later on. In α-$Mg(BH_4)_2$, for instance, additional symmetry elements were missed due to the projection of three- onto one-dimensional reciprocal space implied by powder averaging.[14]

Structural information may be maximized by diffraction methods to obtain structural models which are then refined by solid state DFT calculations.[17-19] Such a “refinement” process however takes place at absolute zero temperature and is thus fundamentally biased in some cases.

All of the above mentioned issues could be minimized or eliminated by producing single crystal samples. However, no report on a mixed-metal borohydride single crystal is found in the literature. Few single crystal studies are available for mono-metallic compounds where additionally powder diffraction structures have been re-visited and corrected.[15,20-25] The phonon dispersion was measured for $NaBH_4$ on crystals of up to 2 mm size.[26] Such investigations are of fundamental importance since physical properties but also interatomic interactions crucial to hydrogen release mechanisms are reflected in the lattice dynamics of a material.

Given the limitations for single crystal growth imposed by wet-chemistry methods as outlined above, it is worth considering solid state syntheses, followed by crystal growth from the melt.

Such an approach also implies limitations that need to be taken into consideration at this point. Mixed-metal double-salt borohydrides tend to melt incongruently, dissociate into their reactants, or decompose into more stable products accompanied by the evolution of gases. The latter event often competes with the solid-liquid transition itself, i.e. occurs during or very shortly after melting.

Our attempts to stabilize the desired materials in the liquid phase at temperatures above their melting point, using high-gas pressures ($p(H_2)$ = 100 bar) or high physical pressure, have been partially successful, but are both impractical and hard to re-produce. It is therefore desirable to lower the melting point of the material at ambient pressure.

This is commonly achieved by means of a flux, whose melting point is considerably lower and whose chemistry is inert with respect to the compound system, and of course, stable in the liquid phase. Under these constraints, it is not possible to recur to monometallic borohydrides, all of them releasing gases in close vicinity of the liquidus, i.e. shortly below or above.[27]

Very recently, a survey was conducted on different eutectic borohydride systems under the aspect of hydrogen release kinetics and ionic conductivity.[27] Some of the reported systems melt tens or even hundreds of degrees before releasing gases, lending themselves to the implementation as a solvent.

Herein, we describe a flux-assisted crystal growth procedure, choosing as solvent the eutectic system $0.62LiBH_4 – 0.38NaBH_4$, whose eutectic point is located at 488 K.[27]

In the first part we perform a case study using this eutectic on the double-salt $KCa(BH_4)_3$ and present the first single crystal structural investigation of a mixed-metal borohydride. Recently reported, $KCa(BH_4)_3$ is a member of a large family of new perovskite-type metal borohydrides, that host various physical properties, including luminescence and hydrogen storage, as well as unusual weak interactions, which are responsible for the formation of large superstructures.[6]

In the second part, we highlight the importance of single crystal studies by discussing relevant differences between the lattice-type specific lattice instabilities occurring in (i) $KCa(BH_4)_3$ obtained from flux-melting and (ii), $KCa(BH_4)_3$ obtained by mechano-chemistry. These differences suggest epitaxial intergrowth at the grain-interfaces generated by the stresses arising during high-energy ball milling.

Not only does this comparison emphasize the utility of a single-crystal growth procedure to study equilibrium structures but it also suggests interesting prospects related to strain-engineering.

The proposed growth-procedure is suggested to be generalizable given the large number of binary eutectic borohydride systems.

Experimental

Sample preparation

All sample handling was performed in inert Argon atmosphere. The preparation for crystal growth experiments consisted in preparing $KCa(BH_4)_3$ by mechano-chemistry in a Fritsch Pulverisette P7 ball mill, where 60 repetitions of 2 min each were performed at 600 rpm, interrupted by cooling breaks of 5 min. The nominal composition was chosen as $KBH_4 : Ca(BH_4)_2$

1:1, where the precursors where used as purchased from Sigma-Aldrich. The resulting powder was mixed in different molar ratios with the chosen eutectic mixture, as of now called the solvent. These mixtures corresponded to volume excess of sample (molar ratio solvent:sample 1:1), volume excess of solvent (9:1) and identical volumes (8.6:1.4).

Thermal Analysis

Thermal analysis was carried out on all samples to localize the melting point of each ball-milled $KCa(BH_4)_3$ as well as of the mixtures solvent : $KCa(BH_4)_3$. Differential scanning calorimetry (DSC) and thermogravimetry (TGA) were performed with a Netzsch 404 F3 Pegasus apparatus under nitrogen flow.

Crystal growth experiments

In a second step, a pellet was pressed of the mixture solvent-$KCa(BH_4)_3$ of diameter 0.5 mm, placed in an alumina crucible and sealed by welding in stainless steel tubes in an argon-filled glove box. The alumina crucible was covered with alumina wool, to allow for crystal separation from the melt by turning the stainless steel tubes upside down inside the furnace using a home built system. All crystal growth experiments were performed in a muffle furnace calibrated for operating at low temperatures (between 300 and 700 K).

Powder X-ray Diffraction

To survey synthetic efforts powder diffraction was performed on all samples prior to the crystal growth experiment and after it, with an Empyrean PANalytical laboratory powder diffractometer. *In-situ* powder diffraction as a function of temperature to monitor the evolution of ball-milled and wet-chemistry obtained samples, discussed in the second part, was performed at the Swiss Norwegian Beamlines of the European Synchrotron Radiation Facility (Grenoble, France) at a wavelength of 0.8277 Å, and using borosilicate glass capillaries of 0.5 mm diameter.

Single Crystal X-ray Diffraction

Single crystal X-ray diffraction was performed on selected crystal platelets of 50×50 μm. The crystal structure at 180 K was measured *in-house* on an Oxford Diffraction SuperNova equipped with a dual micro-source and a CCD-camera. Data acquisition was done using Cu K-alpha radiation, the temperature was controlled with the cryojet.

At 250 K the crystal structure was solved using data collected at the Swiss Norwegian Beamlines of ESRF (Grenoble, France). The wavelength of this experiment was 0.8193 Å and the temperature controlled by the Oxford cryostream. Due to air sensitivity single crystal samples were mounted on the goniometer head in Fomblin@Y oil.

In both cases crystal structures were solved with the charge flipping method implemented in Olex2.[28] Refinements were performed with the Shelx code[29] treating BH_4 tetrahedra as semi-rigid bodies during refinement.

Crystal data:

$KCa(BH_4)_3$ at $T = 180$ K, orthorhombic, space group $P2_12_12$, $a = 7.8755(14)$, $b = 7.8505(15)$, $c = 5.5546(11)$ Å, $V = 343.42(11)$ Å^3, $Z = 2$, $R_{\text{int}} = 0.065$ $R_1 = 0.09$, w$R_2 = 0.17$ for 392 independent reflections with $I > 2\sigma(I)$, 38 refined parameters using 3 restraints, GoF = 1.002.

$KCa(BH_4)_3$ at $T = 250$ K, orthorhombic, space group $Pbcm$, $a = 7.9090(3)$, $b = 7.9712(4)$. $c = 22.1827(14)$ Å, $V = 1398.48(12)$ Å^3, Z = 8, $R_{\text{int}} = 0.36$, $R_1 = 0.082$, w$R_2 = 0.20$ for 734 independent reflections with $I > 2\sigma(I)$, 77 refined parameters using 1 restraint, GoF = 1.093.

Results and Discussion

Flux assisted single-crystal growth of $KCa(BH_4)_3$

Different aspects need to be considered when choosing the optimum eutectic system amongst the reported ones. Firstly, many of the reported systems decompose during or within a very small temperature interval of melting, which does not provide a sufficiently large T-range to temper and crystallize. Secondly, the phase diagrams of binary borohydride systems are often very rich.[19] It is crucial to verify the chemical inertia of the components constituting the eutectic with respect to the other precursors, KBH_4 and $Ca(BH_4)_2$. In the case of the presently employed eutectic $0.62LiBH_4$-$0.38NaBH_4$ four binary phase diagrams need to be considered. Both the systems $LiBH_4$-$Ca(BH_4)_2$[30] and $NaBH_4$-$Ca(BH_4)_2$[27] do not form stable mixed-metal phases. While KBH_4-$Ca(BH_4)_2$ contains a line phase representing the target material $KCa(BH_4)_3$, an issue arises with a reported stable phase $LiK(BH_4)_2$[31] in the remaining binary system $LiBH_4$-KBH_4. This is not a major complication, the crystal structure of $LiK(BH_4)_2$ being known and its presence thus easily recognized from a powder diffraction measurement on the products retrieved from crystallization attempts. Additionally, we have studied the $LiBH_4$-KBH_4 system quite well recently and have no reason to expect further stable phases.

To evaluate the relative stabilities of the concerned mono-metallic phases and in particular of the mixed-metal compounds (double salts) $LiK(BH_4)_2$ and $KCa(BH_4)_3$, a mixture $LiBH_4$-$Ca(BH_4)_2$-KBH_4, of nominal molar ratio 1:1:1, was prepared by mechano-chemistry to determine the resulting phase composition, a Rietveld plot is provided in the Supplementary Information (Supplementary Fig. 1). Perovskite-type $KCa(BH_4)_3$ is relatively more stable compared to $LiK(BH_4)_2$, the latter not being formed at all during ball-milling. $LiBH_4$ is not visible as Bragg peaks and likely has been mechano-chemically amorphized. Hence, $LiK(BH_4)_2$ does not form in the presence of $Ca(BH_4)_2$ in the ternary borohydride system Li-Ca-K. The lattice constants of $KCa(BH_4)_3$ are identical within errors as compared to those reported previously,[6] which underlines the stability of this structure and further allows us to exclude any dissolution of monovalent Li^+ or Na^+, both being components of the eutectic solvent system, on the potassium site of $KCa(BH_4)_3$. In summary, this analysis suggests that during flux-assisted growth or recrystallization $KCa(BH_4)_3$ will be the only double salt that is formed due to its superior stability and hence, the eutectic 0.62$LiBH_4$-0.38$NaBH_4$ is well suited for crystallisation attempts.

The procedure of finding the appropriate eutectic to crystallize double-cation borohydride salts may therefore be summarized as the following: (1) Identify decomposition and/or melting of target compound. (2) Find eutectic borohydride system with its eutectic temperature considerably below the events found in (1) and with a sufficiently large temperature interval between melting and gas release. (3) Scan the different binary phase diagrams defined by the components of eutectic and target compound by mechano-chemistry, identifying further stable mixed-metal compounds. If the target compound only is formed or in major yield, the chemistry of the eutectic system can be considered as appropriate. We do not consider it necessary to scan ternary possible systems, since triple-cation salts are rather unstable with respect to their decomposition to double-salts.

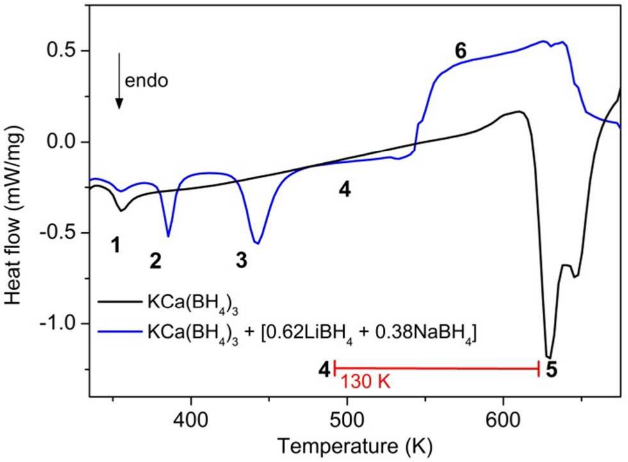

Fig 1 Differential scanning calorimetry of samples containing $KCa(BH_4)_3$ and a mixture of the eutectic composition 0.62$LiBH_4$ – 0.38$NaBH_4$: $KCa(BH_4)_3$ 8.6:1.4.

The melting point of $KCa(BH_4)_3$ is located at 618 K and labelled as endothermic event **5** in Fig. 1. The doublet peak shape arises from melting/decomposition of the perovskite at the liquidus, followed by melting of the KBH_4 precursor. The eutectic temperature (onset) of 0.62$LiBH_4$ – 0.38$NaBH_4$ is reported at 488 K. In principle this provides a sufficiently large temperature window of 130 K to avoid the decomposition and melt the perovskite in the solvent. The thermal events **1-4** and **6** labelled in Fig.1 correspond to the polymorphic transformations of **1** $KCa(BH_4)_3$ at approx. 350 K and **2** $LiBH_4$ at 389 K, melting **4** of the mixture eutectic : $KCa(BH_4)_3$ and decomposition of the eutectic **6**. The latter involves various exothermic chemical reactions leading to higher borane decomposition products.[32] Event **3** could not be identified. It is located at temperatures that agree well with the α→β transition of $Ca(BH_4)_2$, however this compound is not detected in the diffraction pattern.

Initial discrepancies that were noted between the reported eutectic temperature of 488 K of the eutectic composition 0.62$LiBH_4$ – 0.38$NaBH_4$ and the melting points determined in this study motivated us to visually follow the melting behaviour of (i) a mixed solvent-$KCa(BH_4)_3$ pellet and (ii) a hybrid pellet where both solvent and $KCa(BH_4)_3$ are compressed separately, i.e. where the pellet contains two different chemical compositions.

From a series of photographs shown in Supplementary Fig. 2 it can be seen that in the hybrid pellet the onset of melting of the solvent proceeds from the interface solvent-$KCa(BH_4)_3$ outwards, starting at 503 K, 25 K higher than the reported eutectic temperature. It can furthermore be seen that, as expected from its melting point of 618 K, the $KCa(BH_4)_3$ component of the hybrid pellet is stable up to high temperatures.

The fact that expansion (cracking), i.e. the onset of eutectic melting, starts at the interface suggests that the sample $KCa(BH_4)_3$ is acting on the solvent. This is likely due to remnant KBH_4 stemming from the mechano-chemical synthesis of $KCa(BH_4)_3$. Reactions producing mixed-metal borohydrides are always incomplete, as stated above, due to unfavourable thermodynamics. Crystalline KBH_4 can be identified in ball-milled samples by X-ray diffraction (Supplementary Fig. 1). Such unreacted precursors could increase the eutectic from a binary to a ternary, altering its melting temperature of the eutectic composition. Indeed, such a ternary eutectic system between $LiBH_4$-$NaBH_4$-KBH_4 has been reported,[27] its melting point lying 65 K above that of the Li-Na eutectic.

It should be noted here, that a visual inspection before determining the growth temperature of single crystal growth is advisable, similar to what is performed here. Borohydrides behave very differently from other systems during melting, being accompanied by foaming or bubbling for instance.[27,33,34] Visual inspection can be very useful to separate different changes undergone by the sample. The photographs taken at different temperatures shown in Fig. 2 evidence these processes in a pellet where the molar ratio flux : $KCa(BH_4)_3$ is 8.6:1.4, which corresponds to identical volume fractions. It can be seen that melting/frothing occurs above 510 K, which is in good agreement with differential scanning calorimetry (DSC) shown in Fig. 1.

According to the previous reports[27] the onset of gas release in the eutectic 0.62$LiBH_4$ – 0.38$NaBH_4$ is located around 570-580 K and is manifested as a broad exothermic process in thermal analysis (Fig. 1). Crystallisation attempts of $KCa(BH_4)_3$ at the upper stability of the eutectic liquid phase at 573 K still contain traces of the decomposition of $KCa(BH_4)_3$, manifested in a relatively higher phase yield of KBH_4 compared to the unheated mixture, which was determined from laboratory powder diffraction on the educts and products.

At 573 K, 45 K below the endothermic thermal event associated with melting/decomposition of $KCa(BH_4)_3$, the compound's decomposition/dissociation thus still competes with its melting. $Ca(BH_4)_2$ is not visible in the diffraction pattern. It is likely that it has been amorphized during decomposition of $KCa(BH_4)_3$.

Fig. 2 Images of a mixed pellet of molar composition solvent : $KCa(BH_4)_3$ 8.6:1.4 at different temperatures.

The reported weight losses arising due to the decomposition of $Ca(BH_4)_2$ at approximately 620 K and 770 K[35] are present in thermal analyses on the different mixtures, indicating that $KCa(BH_4)_3$ dissociates to KBH_4 and $Ca(BH_4)_2$.

Following the crystallization attempts this way with powder diffraction allowed us to determine the ideal working temperature at 513 K. after the onset of melting **4** reported in Fig. 1. Visually it is seen from Fig. 2 that the mixed powder is melting at this temperature, and X-ray diffraction on the resulting powder shows that $KCa(BH_4)_3$ is still 100 % stable at these temperatures. Hence, the single crystals analysed in the following were grown at a temperature of 513 K.

Single Crystal X-ray Diffraction: Crystal structure of $KCa(BH_4)_3$ at 180 and 250 K

The crystal structure of $KCa(BH_4)_3$ was solved for two different low-temperature polymorphs at 180 and 250 K, without determining the transition temperature.

The higher *R*-factor and goodness of fit of the 180 K model is due to lesser data quality in the laboratory experiment. This is mainly owed to reflection overlap with a second phase, $NaBH_4$, which had crystallized in the same grain, and could not be mechanically separated. This, however, does not influence the results concerning the determined space group.

At 180 K, the stable equilibrium polymorph of perovskite-type $KCa(BH_4)_3$ has space group symmetry $P2_12_12$, a low-symmetric two-fold supercell to the basic primitive cubic perovskite unit cell $Pm\text{-}3m$. The resulting structural model is shown in Fig. 3a, hydrogen atoms have been omitted for clarity. It can be seen that the displacement parameters of boron atoms are highly anisotropic, their main amplitude parallel to the *c* axis for equatorial ones and within the a-b plane (perpendicular to *c*) for axial ones. Both these displacements are indicative of a lattice instability that may occur due to octahedral tilts, which are absent along *c* in the 180 K polymorph. At 250 K this octahedral rotation is stabilized, leading to a quadruple cell in *c*-direction, of which the space group symmetry is *Pbcm*, and which is visible in the reciprocal space reconstruction in planes *hkl*, *h* = odd (Fig. 2c). A commensurate modulation can furthermore be identified by means of the K atoms in green in Fig. 2b, visible on a sinusoidal modulation of the orientation of displacement ellipsoids.

This polymorphic transformation is noteworthy, given that the large superstructure is stabilized in the high temperature polymorph. Such behaviour is highly unusual for the perovskite-type and derived lattices, where octahedral rotation and polar displacement instabilities are usually generated at low temperatures, often being explained by the soft mode concept.

We have previously attributed the appearance of unexpected low symmetry high-temperature polymorphs in metal borohydride-perovskites to the presence of structural dynamics and weak interactions, such as di-hydrogen contacts.[6] The present finding of the modulation in the 8-fold supercell of $KCa(BH_4)_3$ at 250 K are in perfect agreement with the postulated trend that perovskite-type metal borohydrides can violate the intuitive temperature behaviour of perovskite-crystal symmetries, i.e. symmetry-increase with temperature.

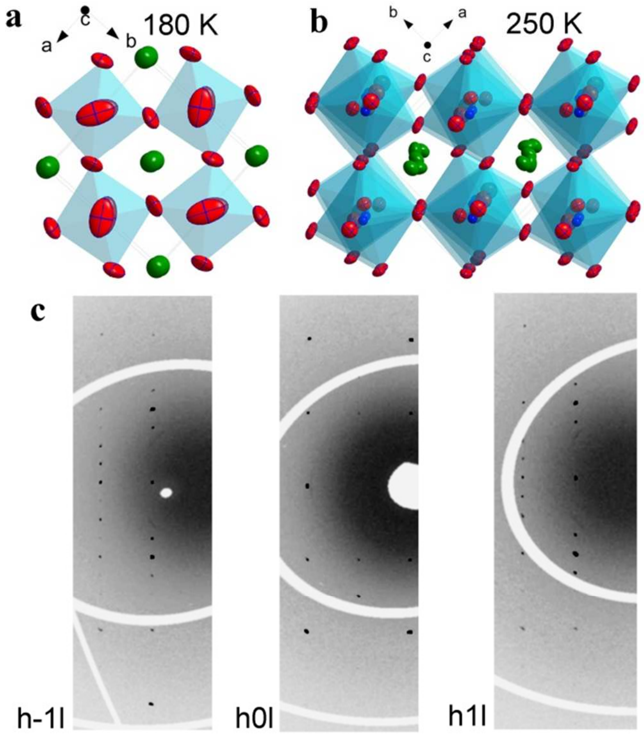

Fig. 3 **a**, Crystal structures solved at 180 K ($P2_12_12$) and **b**, 250 K (*Pbcm*). Reciprocal space reconstructions showing the quadruple cell of the 250 K structure are shown in **c**.

Generally spoken, it is noteworthy that the crystals do not crack nor develop domain structures in spite of at least two polymorphic transformations necessarily occurring between the

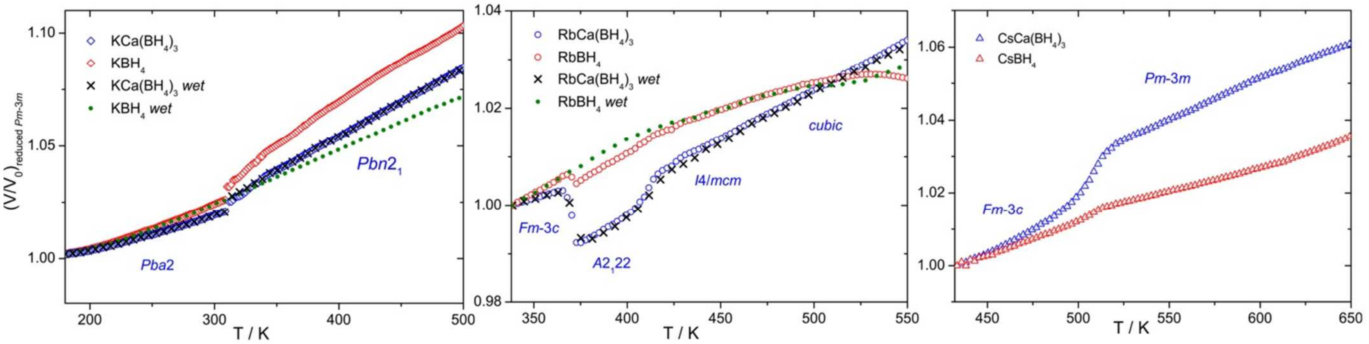

Fig. 4 Temperature dependency of normalized unit cell volume for ball milled samples of KCa(BH_4)$_3$, RbCa(BH_4)$_3$ and CsCa(BH_4)$_3$ (left to right). For comparison the volume evolution is given also for samples obtained from growth from a solution of $RbBH_4$ and Ca(BH_4)$_2$ in DMS, for the former two cases.

applied crystallisation temperature of 513 K and the lowest measurement temperature of 180 K. This may be owed to the low symmetry of the *HT*-phase, providing lesser tendency for domain formation due to the absence of crystallographically equivalent directions relating the *HT*- and the *LT*-phases.

In-situ Powder X-ray Diffraction: Epitaxial intergrowth

In-situ temperature dependent powder diffraction was performed to follow the unit-cell evolution of ball milled samples *A*Ca(BH_4)$_3$ across different polymorphic transformations at high temperatures. The space group symmetries of the involved polymorphs were recently reported[6] and the details concerning the mechanism controlling these transitions are not subject of this article. However, the unit cell expansion shall be used to point out interesting differences between samples grown by the flux method, i.e. in equilibrium, and those produced by mechano-chemistry. The unit cell expansion as a function of temperature of three samples *A*Ca(BH_4)$_3$ (*A* = K, Rb, Cs) is shown in Fig. 4. It is worth noting, and discussed below, that the low temperature phase transformation described above for single crystal KCa(BH_4)$_3$ does not occur in ball-milled powder samples.

Two further features are worth emphasizing, (1) in all ball-milled samples the temperature-induced unit cell volume anomaly of *A*Ca(BH_4)$_3$ (open symbols in Fig. 4) is followed across structural phase transitions by the unreacted precursor *A*BH_4, and (2), this is not the case for the precursors used in wet chemistry. It should be noted that all alkaline metal borohydrides have been thoroughly investigated and undergo no phase transitions at the respective temperatures (verified by the present data) corresponding to the lattice discontinuities in Fig. 4. Such a behaviour points towards an intergrowth mechanism between rocksalt- and perovskite-type borohydrides.

Epitaxial relationships occur on surfaces, usually between a substrate and a second phase to be deposited. Epitaxy is actively applied for growth of thin films or bulk semiconductors, epitaxial relationships moreover present the basis of strain-engineering in oxide perovskite-type heterostructures.[36,37]

A similar process is suggested here, which is discussed in the following. The findings outlined in the previous section and shown in Fig. 4 allow us to draw one conclusion: both perovskite-type *A*Ca(BH_4)$_3$ and rocksalt-type *A*BH_4 must be mechano-chemically epitaxially intergrown. In other words, the precursor *A*BH_4 is serving as a substrate for the metal borohydride perovskite. We have not found a similar relationship experimentally reported in the literature. However, the building principle of the Ruddlesden-Popper phases presents the materials realization of this situation, where two-dimensional perovskite-type slabs alternate with rocksalt-type layers. The lattice constraints imposed by the suggested epitaxy are also reflected in the lattice parameters of the rocksalt-type precursor *A*BH_4. Both KBH_4 and $RbBH_4$ are constrained to slightly smaller dimensions, the room temperature lattice parameters being a = 6.7205(3) and 7.0185(2) Å as compared to the reported values of 6.7306(1) and 7.0293(1) Å.[38] The values of precursors for the wet chemistry samples on the other hand, are in perfect agreement with the latter, 6.7302(1) and 7.0289(1), respectively. In contrast, the unit cell volume of $CsBH_4$ is slightly larger than the reported value of a = 7.4286(4) vs. 7.4098(2).[38] Despite these lattice strains the space group symmetry of *Fm*-3*m* is maintained in *A*BH_4.

Such epitaxial constraints however provide a due explanation for space group discrepancies between single crystals grown at equilibrium conditions and samples prepared by mechano-chemistry. The single crystal structure of KCa(BH4)3 at 180 K was solved in space group $P2_12_12$. The crystal structure of the same compound at identical temperature in ball milled samples is *Pba*2. Static solid state calculations on KCa(BH_4)$_3$ in our very recent study[6] suggested that $P2_12_12$ is the ground state of KCa(BH_4)$_3$.

The present findings are in quite good agreement with the theoretical structure, since the equilibrium structure of single crystal KCa(BH_4)$_3$ corresponds to this ground state. Hence, the polymorph *Pba*2 may be strain-stabilized by mechano-chemical substrating to KBH_4 due to ball-milling, explaining also the absence of any transformation below room temperature in ball milled samples.

Conclusions

Flux-assisted single crystal growth has been demonstrated on perovskite-type $KCa(BH_4)_3$, providing the first single-crystal specimen of a mixed-metal borohydride of suitable size for diffraction experiments and structural characterization. The described procedure which makes use of a eutectic system $0.62LiBH_4$-$0.38NaBH_4$, which is inert with respect to the target compound $KCa(BH_4)_3$, is generalizable thanks to the large and increasing number of eutectic borohydride systems that is known. Such an approach contrasts the commonly performed mechano-chemical one in that it provides thermodynamic equilibrium. This is impressively demonstrated on the basis of comparing single crystal structures to those obtained on ball-milled powders, where metastable phases are strain-stabilized mechano-chemically by generating epitaxial intergrowth between perovskite-type ACa$(BH_4)_3$ and rocksalt-type ABH_4, which may be considered a substrate in this process.

Such discovered relationships will readily come to use when physical deposition methods have been optimized for metal borohydrides, which are currently being developed and evaluated.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [Rietveld plot, photographs of synthesis, details of different mixtures used for synthesis]. See DOI: 10.1039/b000000x/

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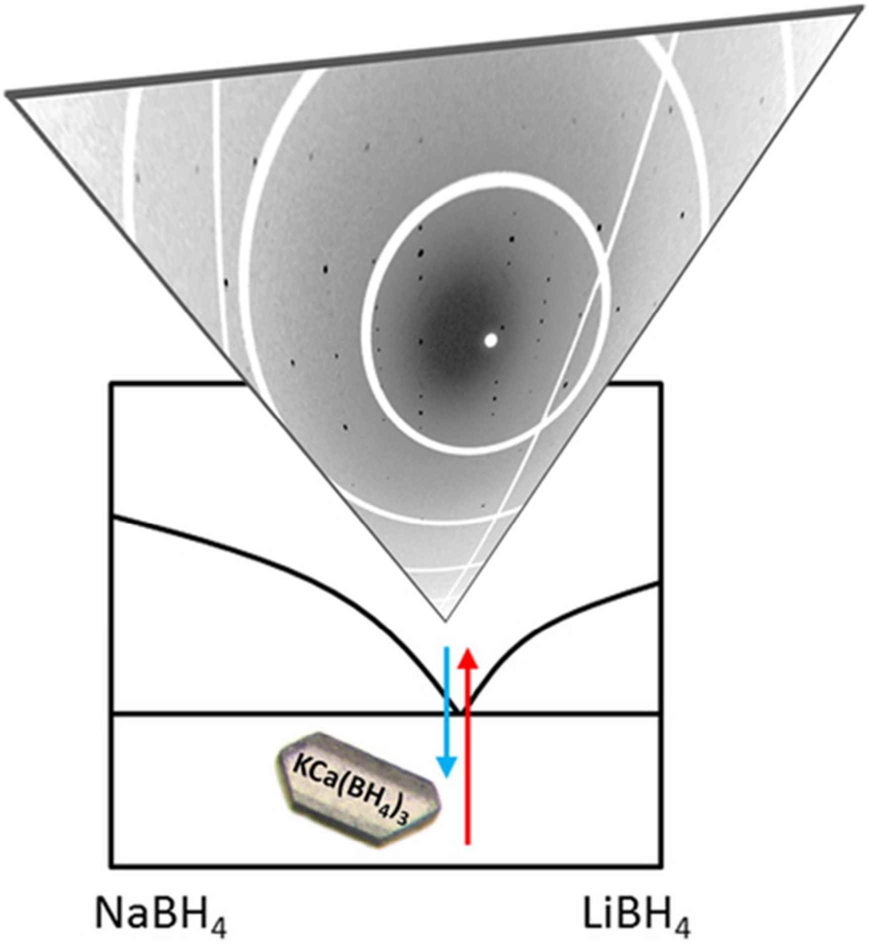

Single crystals of mixed-metal perovskite-type borohydride $KCa(BH_4)_3$ are prepared by an easily generalized flux melting procedure based on eutectic borohydride systems.
39x40mm (300 x 300 DPI)