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Halide substitution in Ca(BH₄)₂

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Halide substitution in Ca(BH₄)₂ has been investigated in ball milled mixtures of Ca(BH₄)₂ and CaX₂ (X = F, Cl, Br) with different molar ratios. In-situ synchrotron radiation powder X-ray diffraction measurements of Ca(BH₄)₂ + CaCl₂ with 1:0.5, 1:1 and 1:2 molar ratios reveal that no substitution of Cl⁻ for BH₄⁻ occurs from the ball milling process. However, substitution readily occurs after the transitions from α - to β -Ca(BH₄)₂ and from orthorhombic to tetragonal CaCl₂ upon heating above ~250 °C, which is evident from both contraction of the unit cell and changes in the relative Bragg peak intensities, in agreement with theoretical calculations. Rietveld analyses of the obtained β -Ca((BH₄)_{1-x}Cl_x)₂ solid solutions indicate compositions from x = 0 to 0.6, depending on the amount of CaCl₂ in the parent mixtures. β -Ca((BH₄)_{0.5}Cl_{0.5})₂ was investigated by differential scanning calorimetry and has a slightly higher decomposition temperature compared to pure Ca(BH₄)₂. No substitution with CaF₂ or CaBr₂ is observed.

Introduction

The efforts to find fuels that are non-polluting and not contributing to the greenhouse effect is on-going. Hydrogen is a clean energy carrier, releasing only water when used in fuel cells. Hydrogen is a gas with low boiling point and consequently the challenge for hydrogen to become a widely used energy carrier is an efficient storage system. It is possible to store hydrogen gas under pressure, but a safer and much more compact way is to store hydrogen chemically bonded in solid compounds.¹ The storage material should have both high gravimetric and volumetric hydrogen content, good cycling ability and fast hydrogen sorption kinetics. NaAlH₄ with titanium-based additives was the first complex metal hydrides to be considered for hydrogen storage², but the practical gravimetric hydrogen storage capacity is less than 4.5 wt%.³ Metal borohydrides have high gravimetric hydrogen density and are thus of interest as hydrogen storage materials.^{4, 5} Ca(BH₄)₂ can theoretically store up to 11.6 wt% hydrogen and the volumetric hydrogen content is 108 g H/L. DFT calculation estimates an equilibrium H₂ pressure of 1 bar at temperatures below 100 °C,⁶ which is ideal for hydrogen storage for mobile applications. Experimentally, however, the dehydrogenation process occurs between 360 and 500 °C.⁶⁻⁸ The hydrogen sorption is partially reversible at 90 bar and temperatures from 350 to 420 °C.⁷ Ca(BH₄)₂ is generally observed to decompose to CaB₆ and CaH₂, according to the reaction 3Ca(BH₄)₂ → CaB₆ + 2CaH₂ + 10H₂, but the process is complicated and several intermediate phases are involved.⁹⁻¹²

The observed dehydrogenation temperature is too high for practical purposes,¹ thus the stability has to be reduced for Ca(BH₄)₂ to become an effective energy carrier. Brinks *et al.*

have shown that the stability of Na₃AlH₆ can be considerably changed by partly substituting hydrogen with fluorine.¹³ Several studies have shown that heavier halides can substitute BH₄⁻ in borohydrides, e.g. Cl⁻, Br⁻, and I⁻ substitution in LiBH₄,¹⁴⁻¹⁶ and Cl⁻ substitution in NaBH₄,¹⁷ Mg(BH₄)₂¹⁸ and Ca(BH₄)₂.^{19, 20} Recently, three new compounds have been reported in the Ca(BH₄)₂-CaI₂ system.²¹ F⁻ is reported to substitute H⁻ in NaBH₄²² and KBH₄.²³

Several structural modifications of Ca(BH₄)₂ have been described in the literature.^{6, 24-30} α -Ca(BH₄)₂ (orthorhombic, space group *F2dd*) is the stable polymorph at room temperature.^{25, 31} It transforms to tetragonal α' -Ca(BH₄)₂ through a second-order transformation around 220 °C and further completely to β -Ca(BH₄)₂ upon heating above 300 °C.²⁵ The β -phase crystallizes with tetragonal symmetry first described in space group *P4₂/m*²⁶ and later revised to *P-4*.^{25, 29, 32, 33} γ -Ca(BH₄)₂ is sometimes formed at room temperature. This phase is metastable and crystallizes in the orthorhombic space group *Pbca*.^{10, 31}

The purpose of this work is to study possible substitution of F⁻, Cl⁻ and Br⁻ in Ca(BH₄)₂. The most likely substitute for hydrogen is fluorine, because of the similarity in size. On the other hand, the BH₄⁻ ion has similar size (2.05 Å) to both the Cl⁻ ion (1.81 Å) and the Br⁻ ion (1.96 Å). These halides might therefore substitute the whole BH₄⁻ group.

Experimental and theoretical methods

Preparation of Ca(BH₄)₂ + CaX₂ samples

Ca(BH₄)₂·2THF (purchased from Sigma Aldrich) was dried in vacuum ($p \approx 1 \cdot 10^{-1}$ mbar) at 160 °C for 24 hours to remove the THF adducts, which yielded a mixture of the α and β polymorphs

of Ca(BH₄)₂ after cooling to ambient temperature. The calcium halides, CaX₂, X = F, Br (Aldrich, purity: 99.99%, 99.98%, respectively) and X = Cl (Alfa Aesar, purity: 99.9%) were used as purchased.

The solvent-free Ca(BH₄)₂ was mixed with CaX₂ in molar ratios of 1:0.5 (X = F, Cl), 1:1 (X = Cl, Br) or 1:2 (X = Cl) and ball milled for 2 hours (2 min milling, 2 min pause, times 60) under argon atmosphere with a ball-to-powder ratio of approximately 30:1 using tungsten carbide bowl (15 mL) and balls (10 mm) in a Fritsch Pulverisette P4. The bowl was sealed with a lid and a polymer O-ring.

All handling of the materials was done in purified Ar atmosphere (< 1 ppm O₂ and H₂O) in an MBraun glove box.

In situ Synchrotron Radiation Powder X-ray Diffraction

In situ synchrotron radiation powder X-ray diffraction (SR-PXD) was performed at beamline BM01A at the Swiss-Norwegian Beamlines (SNBL) at European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A MAR345 image plate detector was used and the samples were packed in boronglass capillaries (0.5 mm) and connected to a vacuum pump. The X-ray exposure time for each measurement was 30 s and the readout time was 90 seconds, thus a complete SR-PXD diagram was collected every second minute. The wavelengths used were $\lambda = 0.703511 \text{ \AA}$. The wavelength and detector geometry were calibrated with LaB₆ as an external standard. Different heating rates were used, 3 K/min was used for all Ca(BH₄)₂ + CaCl₂ samples, 2 and 3 K/min were used for other samples.

One-dimensional diffraction patterns were obtained by integrating the 2D images using the Fit2D program.³⁴ Data analyses were performed using the Rietveld method in the FullProf suite.³⁵ The background was interpolated between manually selected points and the Bragg peaks were modeled by a pseudo-Voigt function with 3 refinable parameters.

Thermal Analysis

Differential scanning calorimetry (DSC) was performed with a Netzsch STA449C Jupiter instrument at heating rates of 10 K/min in a flow of He (50 mL/min). The samples were contained in Al₂O₃ crucibles with tiny holes in the lid to prevent pressure build-up during desorption of gases.

Computational Details

The calculations were performed applying the periodic quantum-mechanical software CRYSTAL09 within the Density Functional Theory, PBE functional. The CRYSTAL code utilizes localized

Gaussian functions to describe electrons. Ca was described by a 86-511d21G all-electron basis set³⁶; B by a 6-21G(d) basis set ($\alpha_{\text{sp}} = 0.124 \text{ bohr}^{-2}$ for the most diffuse shell exponent and $\alpha_{\text{pol}} = 0.800 \text{ bohr}^{-2}$ for polarization); H by a 31G(p) ($\alpha_{\text{sp}} = 0.1613 \text{ bohr}^{-2}$ for the most diffuse shell exponent and $\alpha_{\text{pol}} = 1.1 \text{ bohr}^{-2}$ for polarization),³⁷ F by a 7-311G(d),³⁸ Cl by a 86-311G with an additional d orbital ($\alpha_{\text{sp}} = 0.125 \text{ bohr}^{-2}$ for the most diffuse shell exponent and $\alpha_{\text{d}} = 0.750 \text{ bohr}^{-2}$)³⁹ and Br by a 6-311G(d) ($\alpha_{\text{d}} = 0.154 \text{ bohr}^{-2}$ for the most diffuse shell exponent and $\alpha_{\text{pol}} = 0.451 \text{ bohr}^{-2}$ for polarization).⁴⁰ Grimme correction was also considered to take the dispersive contributions into account in all the calculations for geometry optimization and energetic description.⁴¹ Phonons at Γ point in the harmonic approximation were computed to derive the thermodynamic functions by diagonalizing the associated mass-weighted Hessian matrix.⁴²

Results and Discussion

The Ca(BH₄)₂-CaF₂ system

For Ca(BH₄)₂-CaF₂ with molar ratio 1:0.5, the four phases α -, β -, and γ -Ca(BH₄)₂ and CaF₂ are observed in the diffraction pattern of the as-milled sample. The amount of CaF₂, compared to the amount of Ca(BH₄)₂ calculated from the SR-PXD data, indicates that no F-substitution had occurred. During heating, the phase transformation from the α - to the β -modification is observed between 160 and 220 °C, in addition to the changes in unit cell parameters due to the thermal expansion. The intensities corresponding to the Bragg peaks from CaF₂ do not decrease and there were no significant changes in the relative intensities of the Bragg peaks from Ca(BH₄)₂. This indicates that there is no fluorine substitution neither in the α nor in the β polymorph of Ca(BH₄)₂.

The Ca(BH₄)₂-CaCl₂ system

After ball milling Ca(BH₄)₂ and CaCl₂ in the molar ratios 1:0.5, 1:1 and 1:2, α -Ca(BH₄)₂ is the most prominent Ca(BH₄)₂ polymorph, but a residue of the β -phase is also observed by SR-PXD. CaCl₂ is observed in its stable modification (space group *Pnmm*), but it is also present in two other modifications with space groups *Pbcn*⁴³ and *Pbca*⁴⁴ in the milled Ca(BH₄)₂-CaCl₂ samples. The latter is a high pressure CaCl₂ polymorph formed from the *Pbcn* phase during milling. Some additional peaks from minor impurity phases are also observed, but they have been disregarded in the Rietveld refinements.

Table 1 Crystallographic parameters for pure and chloride containing Ca(BH₄)₂ compounds at different temperatures

Compound	Crystal System	Space group	a/Å	b/Å	c/Å	V/Å ³	T/°C
α -Ca(BH ₄) ₂ ²⁹	Orthorhombic	<i>F2dd</i>	8.745	13.105	7.495	858.95	RT
α -Ca(BH ₄) ₂ [*]	Orthorhombic	<i>F2dd</i>	8.755(6)	13.143(6)	7.532(5)	867(1)	40
β -Ca(BH ₄) ₂ ²⁵	Tetragonal	<i>P-4</i>	6.9189(1)		4.3471(1)	208.1	RT
β -Ca(BH ₄) ₂ ³²	Tetragonal	<i>P-4</i>	6.9509(5)		4.3688(3)	211.1(2)	160
β -Ca(BH ₄) ₂ ⁴⁵	Tetragonal	<i>P-4</i>	7.005(5)		4.414(7)	216.6(4)	350
β -Ca((BH ₄) _{0.7} Cl _{0.3}) ₂ [*]	Tetragonal	<i>P-4</i>	6.7725(6)		4.3074(6)	197.6(1)	350
β -Ca((BH ₄) _{0.5} Cl _{0.5}) ₂ [*]	Tetragonal	<i>P-4</i>	6.673(4)		4.268(2)	190.0(2)	350
β -Ca((BH ₄) _{0.4} Cl _{0.6}) ₂ [*]	Tetragonal	<i>P-4</i>	6.542(3)		4.214(2)	180.3(1)	350

^{*} This work

The sample Ca(BH₄)₂-CaCl₂ 1:1 was studied with SR-PXD

during heating up to 360 °C, and the results are shown in Figure

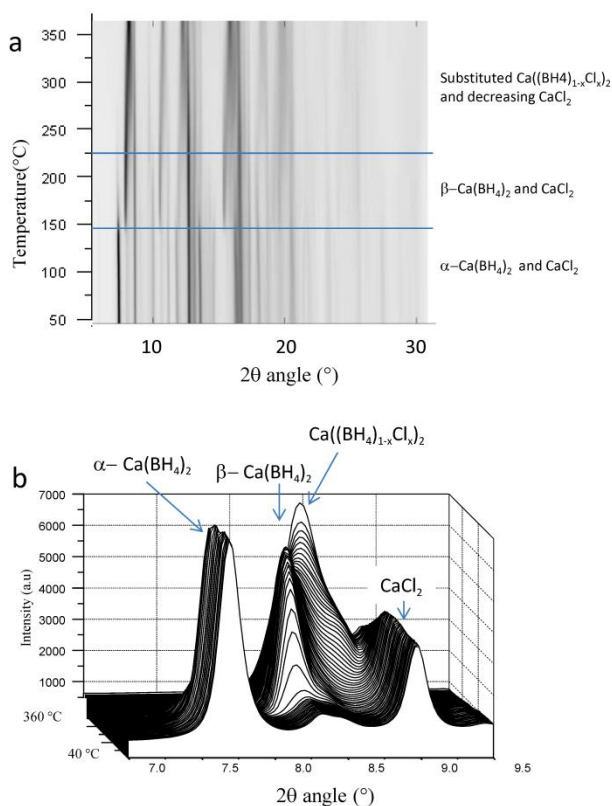


Fig. 1 In situ SR-PXD measured for $\text{Ca}(\text{BH}_4)_2 + \text{CaCl}_2$ in molar ratio 1:1, heating rate 3 K/min. The temperature increases from 40 to 360 °C. (a) gives a plot of the evolution of Bragg peak intensities. (b) 3D plot of selected 2θ area. $\lambda = 0.703511 \text{ \AA}$

1. Rietveld refinement of the SR-PXD data collected at about 40 °C gives $\alpha\text{-Ca}(\text{BH}_4)_2$ (36 wt%), CaCl_2 *Pnmm* (20 wt%) and CaCl_2 *Pbca* (33 wt%) as the main components, with minor amounts of $\beta\text{-Ca}(\text{BH}_4)_2$ (2 wt%) and CaCl_2 *Pbcn* (7 wt%). $\text{Ca}(\text{BH}_4)_2$ and CaCl_2 in 1:1 molar ratio corresponds to a mass ratio of 39:61. This is close to the refined values when summing all the $\text{Ca}(\text{BH}_4)_2$ phases and CaCl_2 phases: 38 wt% and 62 wt%, respectively. This indicates that most of the sample is crystalline and also that no reaction between the compounds has occurred during ball milling. The refined unit cell parameters for $\alpha\text{-Ca}(\text{BH}_4)_2$ at 40 °C are: $a = 8.755(6) \text{ \AA}$, $b = 13.143(6) \text{ \AA}$ and $c = 7.532(5) \text{ \AA}$. These are in good agreement with literature values (see Table 1) and the relative intensities of the Bragg peaks from $\alpha\text{-Ca}(\text{BH}_4)_2$ fits well with published crystal structure data²⁹, thus supporting that no substitution has taken place at this temperature. Substitution would be evident as a decrease in the unit cell size and marked changes in the relative intensities due to the smaller size and higher X-ray scattering cross section for Cl^- compared to BH_4^- .

The phase transformation from $\alpha\text{-Ca}(\text{BH}_4)_2$ to $\beta\text{-Ca}(\text{BH}_4)_2$ takes place in the temperature range 150–200 °C, see Figure 1. At about 260 °C a shoulder starts to appear on the high angle side of the $\beta\text{-Ca}(\text{BH}_4)_2$ peaks. Upon further heating, the diffraction peaks from the β -polymorph is gradually shifted to higher scattering angle, indicating contraction of the unit cell. This is in agreement with substitution of BH_4^- with the smaller Cl^- . The following reaction seems to take place:

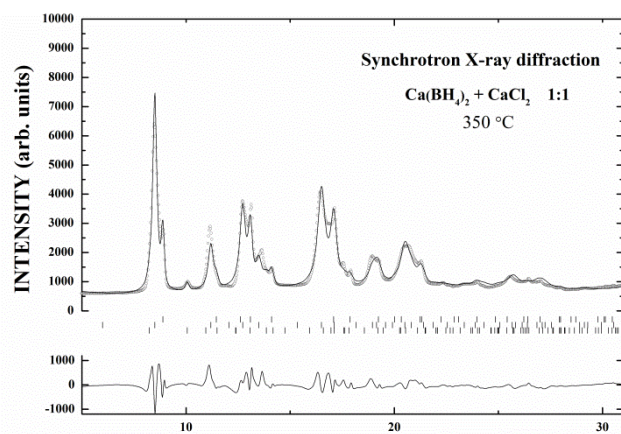


Fig. 2 Rietveld refinement for SR-PXD data of ball milled $\text{Ca}(\text{BH}_4)_2$ and CaCl_2 in molar ratio 1:1 at 350 °C. Three phases are refined CaCl_2 *P4₂/mnm* (top tick marks), substituted $\beta\text{-Ca}((\text{BH}_4)_{1-x}\text{Cl}_x)_2$ with $x = 0.5$ (middle) and CaCl_2 *Pbcn* (bottom tick marks). Experimental data are shown as dots, and the calculated profile is a solid line. The bottom line shows the difference plot. $\lambda = 0.703511 \text{ \AA}$.

$\beta\text{-Ca}(\text{BH}_4)_2 + x \text{CaCl}_2 \rightarrow (1+x) \beta\text{-Ca}((\text{BH}_4)_{1-x}\text{Cl}_x)_2$

Furthermore, from the Rietveld refinement the relative intensities of the peaks for the proposed $\beta\text{-Ca}((\text{BH}_4)_{1-x}\text{Cl}_x)_2$ do not match the diffraction pattern for pure $\beta\text{-Ca}(\text{BH}_4)_2$. Exchanging some of the BH_4^- with Cl^- in the Rietveld refinement of $\beta\text{-Ca}(\text{BH}_4)_2$, results in a better fit to the observed data. Figure 2 shows the refinement for substituted $\text{Ca}((\text{BH}_4)_{1-x}\text{Cl}_x)_2$ giving $x = 0.53(3)$ at 350 °C.

The onset of chloride substitution in $\beta\text{-Ca}(\text{BH}_4)_2$ follows shortly after the reported phase transformation temperature of CaCl_2 from the orthorhombic *Pnmm* phase to a tetragonal phase described in space group *P4₂/mnm* at 235 °C.⁴⁶ The transition is of the second-order and proceeds by contraction of the *a*-axis and expansion of the *b*-axis in the orthorhombic phase until they become identical at the phase transition temperature. It is interesting to note that this high-temperature phase of CaCl_2 (HT- CaCl_2) can be regarded as isostructural to $\beta\text{-Ca}(\text{BH}_4)_2$ if the non-spherical symmetry of BH_4^- is disregarded. The difference in space group, *P4₂/mnm* vs *P-4*, is due to the tetrahedral symmetry of the BH_4^- anion compared to spherical symmetry of Cl^- . The phase transformation of CaCl_2 induce only subtle changes in the diffraction pattern which are not directly observable in the present data, due to extensive peak overlap with $\text{Ca}(\text{BH}_4)_2$. However, HT- CaCl_2 was used in Rietveld refinements of data collected above the transition temperature, resulting in good fits to the data.

For the sample with molar ratio 1:1, the refinements show that there is still 15 wt% of CaCl_2 left in the sample at 350 °C, suggesting that the substituted fraction x in $\text{Ca}(\text{BH}_4)_2$ must be somewhat smaller than 0.5. Specifically, calculation of the degree of substitution from the weight fractions of the different phases gives $x = 0.45(5)$. For the 1:2 and 1:0.5 samples at 350 °C, the Rietveld refinements of anion site occupancies give compositions $x = 0.81(1)$ and $x = 0.46(2)$, respectively. From the refined phase fractions x should be 0.60(6) for the 1:2 sample and 0.30(3) for the 1:0.5 sample. Thus, the refined ratios of the BH_4^- and Cl^- in the three substituted phases all overestimate the amounts of Cl^- compared to the nominal compositions. This could be due to the high anisotropy of BH_4^- , making it difficult to determine exact

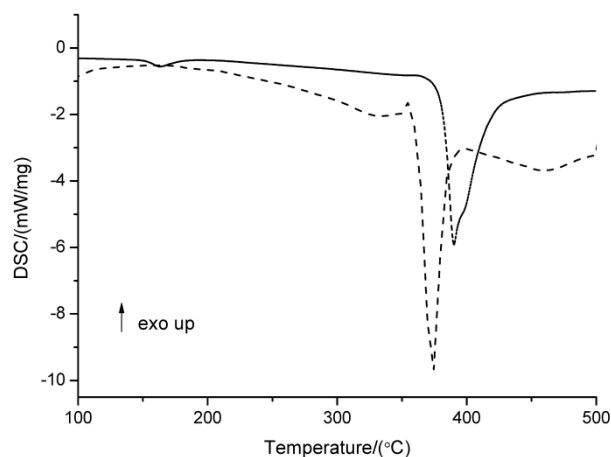


Fig. 3 DSC data for $\text{Ca}(\text{BH}_4)_2$ (dashed) and $\text{Ca}(\text{BH}_4)_2\text{-CaCl}_2$ (1:1) (solid) with heating rate 10K/min.

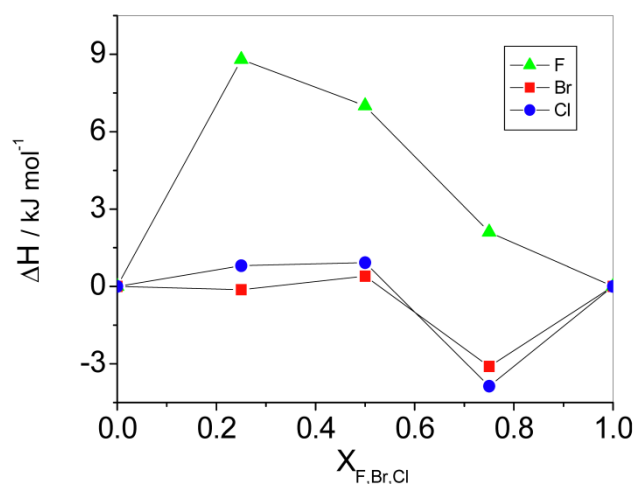


Fig. 4 Computed enthalpy of mixing for solid solution of beta calcium borohydride, where BH_4^- units have been progressively substituted by BF_4^- , Cl^- and Br^- . All values are per formula unit.

positions of the H atoms and, consequently, making refinement less stable. The compositions estimated from the phase fractions, i.e. from the ratio of unreacted CaCl_2 and substituted $\text{Ca}(\text{BH}_4)_2$, are deemed to be more reliable. Hence, the compositions of the three substituted phases are given with one decimal precision as $\text{Ca}((\text{BH}_4)_{0.5}\text{Cl}_{0.5})_2$ ($x=0.5$), $\text{Ca}((\text{BH}_4)_{0.4}\text{Cl}_{0.6})_2$ ($x=0.6$) and $\text{Ca}((\text{BH}_4)_{0.7}\text{Cl}_{0.3})_2$ ($x=0.3$) for the samples 1:1, 1:2 and 1:0.5, respectively.

Table 1 shows significant contraction in unit cell dimensions for all Cl-substituted $\beta\text{-Ca}(\text{BH}_4)_2$ sample. The changes are anisotropic with larger changes in the a-axis than the c-axis. This is can be explained by a greater difference in the a-axis than the c-axis between pure $\beta\text{-Ca}(\text{BH}_4)_2$ ($a=7.0\text{ \AA}$, $c=4.4\text{ \AA}$ at 350°C) and HT- CaCl_2 ($a=6.4\text{ \AA}$, $c=4.2\text{ \AA}$ at 350°C)⁴⁶. The changes in unit cell parameters are approximately proportional to the amount of Cl substitution into the lattice, in agreement with Vegard's law.⁴⁷

DSC measurements were performed for pure $\text{Ca}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2\text{-CaCl}_2$ ball milled in molar ratio 1:1, respectively, see Figure 3. For the pure $\text{Ca}(\text{BH}_4)_2$, there is a sharp endothermic peak in the DSC data at about 370°C . This is consistent with release of hydrogen from $\text{Ca}(\text{BH}_4)_2$. The same feature is seen in the 1:1 $\text{Ca}(\text{BH}_4)_2\text{-CaCl}_2$ sample, but the temperature of the event is increased to 390°C , indicating a slight stabilization of the Cl-containing compound. SR-PXD data show that CaHCl is a decomposition product. This is in agreement with our recent report that the $\text{Ca}(\text{BH}_4)_2\text{-CaI}_2$ decompose to CaHI ²¹. No other crystalline decomposition products are observed in the present study.

The $\text{Ca}(\text{BH}_4)_2\text{-CaBr}_2$ system

$\text{Ca}(\text{BH}_4)_2$ and CaBr_2 were ball milled in the molar ratio 1:1. CaBr_2 ($V=196\text{ \AA}^3$) is isostructural with the $Pnmm$ modification of CaCl_2 (168 \AA^3). When the $\text{Ca}(\text{BH}_4)_2\text{-CaBr}_2$ sample is heated, the SR-PXD data shows the transformation from $\alpha\text{-}$ to $\beta\text{-Ca}(\text{BH}_4)_2$ in the temperature range $150\text{-}200^\circ\text{C}$. There are no significant changes in unit cell parameters beside thermal expansion, no change in relative intensities of the $\beta\text{-Ca}(\text{BH}_4)_2$ diffraction peaks and the intensities of the CaBr_2 peaks do not decrease. This indicates that no appreciable amount of Br^- is substituted into $\text{Ca}(\text{BH}_4)_2$, which is confirmed with Rietveld

refinement showing a good fit without any substitution. The lack of substitution can be explained by the high transition temperature of the transition from $Pnmm$ to $P4_2/mnm$ for CaBr_2 , which occurs at 553°C .⁴⁶ Thus, $\text{Ca}(\text{BH}_4)_2$ and CaBr_2 do not have any isostructural relationship in the investigated temperature range, which makes substitution less favorable.

The in situ SR-PXD measurement shows that CaHBr is a decomposition product of the 1:1 $\text{Ca}(\text{BH}_4)_2 + \text{CaBr}_2$ mixture above 360°C . No other crystalline decomposition products are observed.

DSC measured on the 1:1 ratio of $\text{Ca}(\text{BH}_4)_2\text{-CaBr}_2$ (not shown) reveal an increase in decomposition temperature which is comparable to that observed for the Cl-substituted sample, even though Br substitution is not taking place. This observation indicates that changed reaction paths, evident from the decomposition products CaHCl and CaHBr , could have a larger impact on the decomposition temperature than the actual halide substitution.

Theoretical calculations

Theoretical modelling has been used to estimate the solubility of F^- , Cl^- and Br^- into $\beta\text{-Ca}(\text{BH}_4)_2$. A single unit cell of $\beta\text{-Ca}(\text{BH}_4)_2$ with the $P-4$ symmetry has been considered, and the four BH_4^- units have been progressively substituted by a halide in the case of Cl^- and Br^- , while F substituted H-atoms rather than whole BH_4^- groups. Since the unit cell of the pure $\beta\text{-Ca}(\text{BH}_4)_2$ ($\text{Ca}_4\text{B}_4\text{H}_{16}$) contains 16 H-atoms, a very large number of symmetry-non-equivalent configurations should be considered for single H-to-F substitutions in the BH_4^- units. So, F-substitution has been conducted following the same procedure described for orthorhombic LiBH_4 ,⁴⁸ where a "locality principle" was established. It simply states that the lowest energy is obtained when all four H-atoms are substituted by F-atoms in the BH_4^- units. As a consequence, only BF_4^- to BH_4^- unit substitutions have been considered. A single substitution corresponds to a fraction $x=0.25$, two substitutions to $x=0.50$ and, finally, three substitution to $x=0.75$. It has to be noticed that for $x=0.5$, two possible configurations are possible. In this case, the solution with the lowest energy was considered. The results, expressed in

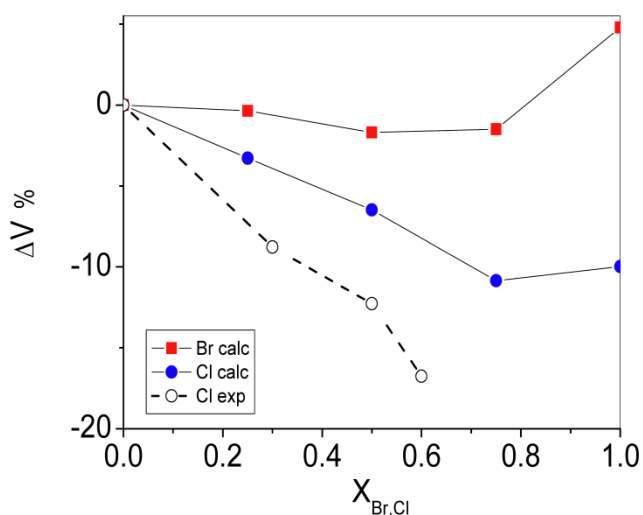


Fig. 5 Variations of the unit cell volume for solid solution of $\beta\text{-Ca}(\text{BH}_4)_2$, where BH_4^- units have been progressively substituted by Cl^- (circles) and Br^- (squares). Continuous lines (computed), dashed line (experimental).

terms of enthalpy of mixing as a function of composition, are reported in Figure 4.

It is clear that BF_4^- substitution leads to a significant positive enthalpy of mixing, suggesting strong immiscibility. On the other hand, both Cl^- and Br^- substitutions appear more favorable, giving an enthalpy of mixing close to zero. As shown in Figure 4, the enthalpy of mixing in the case of $x=0.75$ gives a negative value around -3 kJ mol^{-1} per formula unit for both Cl^- and Br^- substitutions. The two cases are however very different with respect to variation of the unit cell volume, as shown in Figure 5, where the calculated volume variation of the unit cell is shown as a function of halide substitution. A decrease in volume is indeed computed for Cl^- substitution, in line with the experimental trend. Calculations suggest that a maximum volume change occurs at $x=0.75$. Calculated values are underestimated, with respect to experimental results, by a few percent points, due to systematic errors of the adopted functionals and basis set or to neglecting temperature effects in the calculations. Calculated volume variations for Br^- substitution are much smaller in comparison to those obtained for Cl^- substitution, giving an almost constant volume as a function of composition. This behavior can be easily rationalized on the basis of the ionic radius of Br^- , which is much closer to BH_4^- than Cl^- . In turn, the significant volume decrease for the Cl^- substituted structures forces the BH_4 group to rotate in such a way that the H-H intermolecular repulsive contacts are minimized. This effect does not occur for the Br^- substituted structures, as the volume change is minor compared to pure $\text{Ca}(\text{BH}_4)_2$ and, consequently, the BH_4 groups maintain their pristine orientation. The computed structural data (not reported here for brevity) shows that the unit cell contraction for $x=0.5 \text{ Cl}^-$ is anisotropic (see Table S1 in Supplementary Information) with larger change in a - than c -axis, in agreement with the experiments (see Table 1).

In order to estimate the solubility of Cl^- and Br^- in $\beta\text{-Ca}(\text{BH}_4)_2$ from mixtures with the corresponding halides, thermodynamics of CaCl_2 and CaBr_2 compounds have to be considered. For both CaCl_2 and CaBr_2 , the most stable structure at $T = 25 \text{ }^\circ\text{C}$ has the $Pnmm$ symmetry. To estimate the effect of halide substitution, the

free energy of CaCl_2 and CaBr_2 structures have been computed considering, as a reference, the high-temperature structures, crystallizing with the $P4_2/mnm$ symmetry.⁴⁶ In order to be coherent, the thermodynamic data have been recalculated considering the two structures within the $P-4$ symmetry (subgroup of $P4_2/mnm$) of the reference $\beta\text{-Ca}(\text{BH}_4)_2$ structure, obtaining very similar results (see Tables S1 and S2 in Supplementary Information). The predicted structures of the two high temperature phases are in good agreement with the experimental data, as shown in Table S2 in Supplementary Information. Calculations at $T = 25 \text{ }^\circ\text{C}$ on CaCl_2 give $\Delta H = -6.8 \text{ kJ mol}^{-1}$ per formula unit and $\Delta S = 0.5 \text{ J mol}^{-1} \text{ K}^{-1}$ per formula unit, respectively, for the phase transition from the $P4_2/mnm$ to the $Pnmm$ structure. Calculations on CaBr_2 led to a lower enthalpy change, corresponding to a value of $\Delta H = -3.0 \text{ kJ mol}^{-1}$ per formula unit, but a much higher entropy change, equal to $\Delta S = -5.3 \text{ J mol}^{-1} \text{ K}^{-1}$ per formula unit. This large variation of entropy for CaBr_2 compared to CaCl_2 may result from the fact that very low vibrational frequencies, which dominate the entropy value, are much smaller for CaBr_2 than for CaCl_2 , due to the higher mass of Br . The calculated values of enthalpy and entropy should imply a phase transition from orthorhombic ($Pnmm$) to tetragonal ($P4_2/mnm$) symmetry at about $297 \text{ }^\circ\text{C}$ for CaBr_2 , underestimated with respect to the experimental transition temperature of $553 \text{ }^\circ\text{C}$. On the contrary, a higher stability of $Pnmm$ with respect to the $P4_2/mnm$ structure is predicted at all temperatures for the CaCl_2 crystal.

According to thermodynamic calculations, a similar behavior is expected for Br^- and Cl^- substituted solid solutions. In particular, considering ideal entropy of mixing, a negative free energy of mixing is expected at about $350 \text{ }^\circ\text{C}$. In this case, because of the low value of the enthalpy of mixing calculated for $x=0.5$, a two-phase equilibrium between Cl -poor, i.e. $\text{Ca}[(\text{BH}_4)_{0.75}\text{Cl}_{0.25}]_2$, and Cl -rich, i.e. $\text{Ca}[(\text{BH}_4)_{0.25}\text{Cl}_{0.75}]_2$, solid solutions should occur for $0.25 < x < 0.75$. This trend suggests a specific stability of terminal solid solutions, likely because of a combination of geometric and electronic effects. Similar trend is estimated for Br substitutions. On the other hand, the presence of CaCl_2 and CaBr_2 (i.e. $x=1$) in their stable structures could also limit the formation of halide-rich solid solutions. In addition, the calculated closer stability of the $P4_2/mnm$ structure with respect to the $Pnmm$ for CaBr_2 compared to CaCl_2 would suggest an easier solubility. The reasons for the disagreement between the calculations and experimental findings are not clear. It could be that kinetic effects, related to ionic size, play a crucial role during experiments. The discrepancies could also be due to uncertainties in the calculations, as the absence of the predicted $Pnmm$ to $P4_2/mnm$ phase transformation for CaBr_2 in the experimentally explored temperature range, can hinder the predicted solubility. It is worth noting that a stabilization of $\beta\text{-Ca}[(\text{BH}_4)_{1-x}\text{Cl}_x]_2$ solid solutions with respect to pure $\beta\text{-Ca}(\text{BH}_4)_2$ reduces the driving force for the transformation into dehydrogenated products, and thus possibly increasing the dehydrogenation temperature, as observed experimentally (see Figure 3).

The concept of anion substitution in borohydrides remains not fully explored, however, some trends in the structural chemistry are revealed from this work and the literature. For substitution of borohydrides with the heavier halides, (i) the solid containing the

smaller anion, e.g. CaCl_2 , tends to dissolve into the compound containing the larger anion, $\beta\text{-Ca}(\text{BH}_4)_2$, and the structure of the latter tends to be preserved in the obtained solid solution. This trend can be interpreted as an increase in the lattice energy due to the clearly observed decrease in the unit cell volume, which may create an internal 'chemical pressure'.⁴⁹ (ii) some polymorphs of metal borohydrides are more prone to perform anion substitution, than others, e.g. $\beta\text{-Ca}(\text{BH}_4)_2$ and not $\alpha\text{-Ca}(\text{BH}_4)_2$ as shown here. (iii) This work also high-light that isomorphism may be more important to facilitate anion substitution as compared to similarities in anion radii. This explains that CaBr_2 did not dissolve in $\text{Ca}(\text{BH}_4)_2$, despite the fact that $r(\text{BH}_4^-) \sim r(\text{Br}^-)$. In fact, in some cases anion substitution may occur in both compounds, which is previously observed for the systems, $\text{LiBH}_4\text{-LiBr}$, $\text{LiBH}_4\text{-LiI}$ and $\text{NaBH}_4\text{-NaCl}$ systems, possibly due to the fact that $\beta\text{-LiBr}$, $\beta\text{-LiI}$ and h-LiBH_4 as well as NaBH_4 and NaCl are isostructural.⁵⁰⁻⁵³

Conclusions

Possible halide substitutions in $\text{Ca}(\text{BH}_4)_2$ have been investigated by experimental and theoretical (ab-initio) methods. For mixtures with CaX_2 , $\text{X} = \text{F}$, Cl and Br , substitution is only observed for CaCl_2 , and no substitution with CaF_2 and CaBr_2 was found.

The absence of solid solubility in the $\text{Ca}(\text{BH}_4)_2 - \text{CaF}_2$ system is rationalized by a positive calculated enthalpy of mixing. Substitution with Cl^- is only observed into the β -modification of $\text{Ca}(\text{BH}_4)_2$ after heating the ball milled sample above 250°C which is above the orthorhombic-to-tetragonal phase transformation temperature for CaCl_2 , while no substitution is observed in $\alpha\text{-Ca}(\text{BH}_4)_2$. This is explained by the isostructural relationship between $\beta\text{-Ca}(\text{BH}_4)_2$ and the tetragonal high-temperature modification of CaCl_2 . The resulting phase $\text{Ca}(\text{BH}_4)_{1-x}\text{Cl}_x$ has been observed with x from 0 to 0.6, depending on the $\text{Ca}(\text{BH}_4)_2\text{:CaCl}_2$ ratio in the initial mixture. However, it is possible that there is full solubility between the two phases due to their isostructural relationship. The decomposition temperature of $\beta\text{-Ca}((\text{BH}_4)_{0.5}\text{Cl}_{0.5})_2$ was found to be slightly increased compared to pure $\text{Ca}(\text{BH}_4)_2$, likely due to a reduction of driving force for the dehydrogenation reaction. Br^- substitution in $\beta\text{-Ca}(\text{BH}_4)_2$ is predicted by theoretical calculations, but it is not observed experimentally. This is explained by the lack of orthorhombic-to-tetragonal phase transition in the experimental temperature range even though it is predicted by the calculations.

Notes

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† Electronic Supplementary Information (ESI) available: Unit cell parameters and volumes of $\text{Ca}(\text{BH}_4)_2$ with different levels of Cl or Br substitution calculated from DFT; unit cell parameters and volumes of CaCl_2 and CaBr_2 in space groups $Pnmm$ and $P4_2/mnm$ calculated from DFT. See DOI: 10.1039/b000000x/

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References

1. L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353-358.
2. B. Bogdanovic and M. Schwickardi, *J. Alloys Compd.*, 1997, **253-254**, 1-9.
3. J. M. Bellosta von Colbe, O. Metz, G. A. Lozano, P. K. Pranza, H. W. Schmitz, F. Beckmann, A. Schreyer and T. D. Klassen, M. , *Int. J. Hydrogen Energy*, 2012, **37**, 2807-2811.
4. H.-W. Li, Y. Yan, A. Orimo S. Züttel and C. M. Jensen, *Energies*, 2012, **4**, 185-214.
5. L. H. Rude, T. K. Nielsen, D. B. Ravnsbæk, U. Bösenberg, M. B. Ley, B. Richter, L. M. Arnbjerg, M. Dornheim, Y. Filinchuk, F. Besenbacher and T. R. Jensen, *Physica Status Solidi A*, 2011, **208**, 1754-1773.
6. K. Miwa, M. Aoki, T. Noritake, N. Ohba, Y. Nakamori, S. Towata, A. Züttel and S. Orimo, *Phys. Rev. B*, 2006, **74**.
7. J.-H. Kim, S.-A. Jin, J.-H. Shim and Y. W. Cho, *Scripta Materialia*, 2008, **58**, 481-483.
8. E. Rønnebro and E. H. Majzoub, *J. Phys. Chem. B*, 2007, **111**, 12045-12047.
9. Y. Kim, S.-J. Hwang, J.-H. Shim, Y.-S. Lee, H. N. Han and Y. W. Cho, *J. Phys. Chem. C*, 2012, **116**, 4330-4334.
10. M. D. Riktor, M. H. Sørby, K. Chlopek, M. Fichtner, F. Buchter, A. Züttel and B. C. Hauback, *J. Mater. Chem.*, 2007, **17**, 4939-4942.
11. M. D. Riktor, Y. Filinchuk, P. Vajeeston, E. G. Bardaji, M. Fichtner, H. Fjellvag, M. H. Sørby and B. C. Hauback, *J. Mater. Chem.*, 2009, **21**, 7188-7193.
12. I. Llamas-Jansa, O. Friedrichs, M. Fichtner, E. G. Bardaji, A. Züttel and B. C. Hauback, *J. Phys. Chem. C*, 2012, **116**, 13472-13479.
13. H. W. Brinks, A. Fossdal and B. C. Hauback, *J. Phys. Chem. C*, 2008, **112**, 5658-5661.
14. H. Maekawa, M. Matsuo, H. Takamura, M. Ando, Y. Noda, T. Karahashi and S. I. Orimo, *J. Am. Chem. Soc.*, 2009, **131**, 894-895.
15. L. Mosegaard, B. Møller, J. E. Jørgensen, Y. Filinchuk, Y. Cerenius, J. C. Hanson, E. Dimasi, F. Besenbacher and T. R. Jensen, *J. Phys. Chem. C*, 2008, **112**, 1299-1303.
16. L. M. Arnbjerg, D. B. Ravnsbæk, Y. Filinchuk, R. T. Vang, Y. Cerenius, F. Besenbacher, J. E. Jørgensen, H. J. Jakobsen and T. R. Jensen, *Chem. Mater.*, 2009, **21**, 5772-5782.
17. J. E. Olsen, M. H. Sørby and B. C. Hauback, *J. Alloys Compd.*, 2011, **509**, L228-L231.
18. S. Hino, J. E. Fonnelp, M. Corno, O. Zavorotynska, A. Damin, B. Richter, M. Baricco, T. R. Jensen, M. H. Sørby and B. C. Hauback, *J. Phys. Chem. C*, 2012, **116**, 12482-12488.

19. C. Rongeat, I. Lindemann, A. Borgschulte, L. Schultz and O. Gutfleisch, *Int. J. Hydrogen Energy*, 2011, **36**, 247-253.
20. J. Y. Lee, Y. S. Lee, J. Y. Suh, J. H. Shim and Y. W. Cho, *J. Alloys Compd.*, 2010, **506**, 721-727.
21. L. H. Rude, Y. Filinchuk, M. H. Sørby, B. C. Hauback, F. Besenbacher and T. R. Jensen, *J. Phys. Chem. C*, 2011, **115**, 7768-7777.
22. L. H. Rude, U. Filsø, V. D'Anna, A. Spyratou, B. Richter, S. Hino, O. Zavorotynska, M. Baricco, M. H. Sørby, B. C. Hauback, H. Hagemann, F. Besenbacher, J. Skibsted and T. R. Jensen, *Phys. Chem. Chem. Phys.*, 2013, **15**, 18185-18194.
23. R. H. Heyn, I. Saldan, M. H. Sørby, C. Frommen, B. Arstad, A. M. Bougza, H. Fjellvag and B. C. Hauback, *Phys. Chem. Chem. Phys.*, 2013, **15**, 11226-11230.
24. Y. Filinchuk, D. Chernyshov and V. Dmitriev, *Z. Krist.*, 2008, **223**, 649-659.
25. Y. Filinchuk, E. Rønnebro and D. Chandra, *Acta Mater.*, 2009, **57**, 732-738.
26. F. Buchter, Z. Lodziana, A. Remhof, O. Friedrichs, A. Borgschulte, P. Mauron, A. Zuttel, D. Sheptyakov, G. Barkhordarian, R. Bormann, K. Chlopek, M. Fichtner, M. Sørby, M. Riktor, B. Hauback and S. Orimo, *J. Phys. Chem. B*, 2008, **112**, 8042-8048.
27. M. Aoki, K. Miwa, T. Noritake, N. Ohba, M. Matsumoto, H. W. Li, Y. Nakamori, S. Towata and S. Orimo, *Applied Physics a-Materials Science & Processing*, 2008, **92**, 601-605.
28. G. Barkhordarian, T. R. Jensen, S. Doppiu, U. Bosenberg, A. Borgschulte, R. Gremaud, Y. Cerenius, M. Dornheim, T. Klassen and R. Bormann, *J. Phys. Chem. C*, 2008, **112**, 2743-2749.
29. Y. S. Lee, Y. Kim, Y. W. Cho, D. Shapiro, C. Wolverton and V. Ozolins, *Phys. Rev. B*, 2009, **79**.
30. F. Buchter, Z. Lodziana, A. Remhof, O. Friedrichs, A. Borgschulte, P. Mauron, A. Zuttel, D. Sheptyakov, L. Palatinus, K. Chlopek, M. Fichtner, G. Barkhordarian, R. Bormann and B. C. Hauback, *J. Phys. Chem. C*, 2009, **113**, 17223-17230.
31. T. Noritake, M. Aoki, M. Matsumoto, K. Miwa, S. Towata, H. W. Li and S. Orimo, *J. Alloys Compd.*, 2010, **491**, 57-62.
32. T. J. Frankcombe, *J. Phys. Chem. C*, 2010, **114**, 9503-9509.
33. E. H. Majzoub and E. Rønnebro, *J. Phys. Chem. C*, 2009, **113**, 3352-3358.
34. A. P. Hammersley. Internal Report ESRF-98-HA01T, 1998
35. J. Rodríguez-Carvajal, *Physica B*, 1993, **192**, 55.
36. L. Valenzano, F. J. Torres, D. Klaus, F. Pascale, C. M. Zicovich-Wilson and R. Dovesi, *Z. Phys. Chemie-Int. J. Res. Phys. Chem. Chem. Phys.*, 2006, **220**, 893-912.
37. R. Dovesi, C. Ermondi, E. Ferrero, C. Pisani and C. Roetti, *Phys. Rev. B*, 1984, **29**, 3591-3600.
38. R. Nada, C. R. A. Catlow, C. Pisani and R. Orlando, *Model. Simul. Mater. Sci. Eng.*, 1993, **1**, 165-187.
39. E. Apra, M. Causa, M. Prencipe, R. Dovesi and V. R. Saunders, *J. Phys.-Condes. Matter*, 1993, **5**, 2969-2976.
40. L. A. Curtiss, M. P. McGrath, J. P. Blaudeau, N. E. Davis, R. C. Binning and L. Radom, *J. Chem. Phys.*, 1995, **103**, 6104-6113.
41. S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787-1799.
42. F. Pascale, C. M. Zicovich-Wilson, F. L. Gejo, B. Civalleri, R. Orlando and R. Dovesi, *J. Comput. Chem.*, 2004, **25**, 888-897.
43. P. E. Tomaszewski, *Phase Transitions*, 1992, **38**, 127-220.
44. M. Olejak-Chodan and H. A. Eick, *J. Solid State Chem.*, 1987, **69**, 274-279.
45. M. Riktor, personal communication, 2012
46. C. J. Howard, B. J. Kennedy and C. Curfs, *Phys. Rev. B*, 2005, **72**.
47. L. Vegard, *Zeitschrift Fur Physik*, 1921, **5**, 17-26.
48. M. Corno, E. Pinatel, P. Ugliengo and M. Baricco, *J. Alloys Compd.*, 2011, **509**, S679-S683.
49. V. D'Anna, L. M. L. Daku, H. Hagemann and F. Kubel, *Phys. Rev. B*, 2010, **82**, 11.
50. J. E. Olsen, M. H. Sørby and B. C. Hauback, *J. Alloys Compd.*, 2011, **509**, L228-L231.
51. L. H. Rude, O. Zavorotynska, L. M. Arnbjerg, D. B. Ravnsbæk, R. A. Malmkjaer, H. Grove, B. C. Hauback, M. Baricco, Y. Filinchuk, F. Besenbacher and T. R. Jensen, *Int. J. Hydrogen Energy*, 2011, **36**, 15664-15672.
52. L. H. Rude, E. Groppo, L. M. Arnbjerg, D. B. Ravnsbæk, R. A. Malmkjaer, Y. Filinchuk, M. Baricco, F. Besenbacher and T. R. Jensen, *J. Alloys Compd.*, 2011, **509**, 8299-8305.
53. D. B. Ravnsbæk, L. H. Rude and T. R. Jensen, *J. Solid State Chem.*, 2011, **184**, 1858-1866.