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ARTICLE

# Structural Distortion in Perovskite Type $KCaH_{3-x}F_x$ ($0.54 \leq x \leq 3$)

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*Dedicated to Prof. Dr. Hans-Jörg Deiseroth on the Occasion of his 75th Birthday*

**Abstract**. Representatives of the solid solution series $KCaH_{3-x}F_x$ were synthesized by solid state reactions from binary metal hydrides and fluorides. Crystal structures were analyzed by Rietveld refinement based on X-ray powder diffraction. The degree of substitution was determined by refinement of site occupancy factors as well as elemental analysis for hydrogen. Three sections of $x$ in $KCaH_{3-x}F_x$ can be distinguished. For $x < 0.54$ no hydride fluoride exists, i.e. there is no hydride of the composition $KCaH_3$ and the solid solution starts only at $x = 0.54$. The tetragonal $SrTiO_3$ type structure with partial ordering of hydrogen and fluorine atoms is found for $0.54 \leq x \leq 1.7$. Both anion positions show mixed occupation with some preference of hydrogen atoms for 8*h* and fluorine atoms for 4*a* sites (*I*4/*mcm*, $SrTiO_3$ type). For fluorine-rich compounds a solid solution with orthorhombic $GdFeO_3$ type structure (*Pnma*) and a perfectly statistical distribution of hydrogen and fluorine atoms is found ($1.8 \leq x \leq 3$). Interatomic distances resulting from the structure refinements are in the range of typical K–H, K–F, Ca–H, and Ca–F distances for mainly ionic compounds.

## Introduction

The cubic perovskite type is one of the basic structure types in structural chemistry. Its large structural family with many distortion and substitutional derivatives[1] comprises many inorganic solids, with numerous examples especially for oxides and halides. Many representatives show interesting chemical and physical properties and are thus of importance for various applications. Examples are ferroelectrics and multiferroics,[2–4] solar cell materials,[5] nonlinear optical materials,[6] or luminescent materials,[7,8] just to name a few.

As compared to oxides and halides, perovskite type hydrides are less numerous and less well investigated, which is due on one hand to the necessity of neutron diffraction for the location of hydrogen in many cases and on the other hand to their considerable sensitivity to air and moisture. Nevertheless, they constitute a substantial body of the known metal hydride crystal structures and thus comprise an important subsection of this class of compounds. Chemical bonding within perovskite related metal hydrides varies considerably with ionic compounds such as $LiMH_3$ (inverse perovskite, $M$ = Sr, Ba, Eu)[9] and defect variants such as $EuMg_2H_6$,[10] and metallic hydrides with perovskite ($SrPdH_3$, $EuPdH_3$) or *anti*-perovskite type structure such as $MPd_3H_{1-x}$ ($x \leq 1$; $M$ = Mg, In, Tl, Sn, Pb, Mn).[11] $K_2PtCl_6$-type related structures like $M^{II}FeH_6$, $M^{II}RuH_6$, $M^{II}CoH_5$, $M^{II}IrH_5$, $M^{II}NiH_4$, and $M^{II}PdH_4$ ($M^{II}$ = Ca, Sr, Ba, Eu, Yb) are also related to the cubic perovskite type as vacancy derivatives and are classified as coordination compounds with 18-electron hydridometalate complexes with covalent and ionic bonding for hydrogen atoms.[12–15]

The cubic perovskite type is an attractive host for luminescence materials. These require a large bandgap, i.e. only ionic hydrides may be considered suitable. The hydride ligand offers the possibility to greatly influence the $4f^7$–$4f^6 5d$ transition of $Eu^{II}$-activated phosphors. Due to its extreme polarizability, tendency for more covalent bond character and its strong ligand field, the hydride ion enormously affects the energetic position of *d* levels. The bary center of the excited state is located at lower energies in comparison to phosphors containing harder anions with weaker ligand fields. Furthermore, the crystal field strength increases the splitting of the 5d state. Both effects yield in a strong redshift of emission in comparison with analogous fluoride compounds.[8]

Solid solutions between hydrides and fluorides thus offer excellent opportunities for tuning emission wavelengths of $Eu^{II}$-doped host materials. Since the exact coordination of europium atoms in such hosts is of importance, we have reinvestigated the crystal structure of potential host materials with distorted perovskite type. The well-known hydride-fluoride analogy[9] states that ionic metal hydrides and fluorides often exhibit the same crystal structure type or at least similar structures. This offers the opportunity for substitutional hydride-fluoride solid solutions, a concept, which has already been exploited.[16,17] Hydride fluorides of the composition $KCaH_{3-x}F_x$ ($x$ = 1, 1.5, 2, 2.5) have been reported to crystallize in the orthorhombic $GdFeO_3$ type,[18–20] similar to $NaMgH_{3-x}F_x$.[17,21,22] In contrast to the latter, the hydride boundary phase $KCaH_3$ does not seem to exist and has been investigated so far by theoretical calculations only.[23] They

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predict an orthorhombic $GdFeO_3$ type structure and suggests that preparation of $KCaH_3$ from KH and $CaH_2$ is not likely to be successful.[23] By determination of the standard enthalpies of formation by calorimetry, it was shown that the thermodynamic stability decreases upon increasing hydrogen content.[20] Some questions about the symmetry of the members of this solid solution series and the anion distribution in $KCaH_{3-x}F_x$ remain as well as the exact boundary for the hydrogen richest compounds. Therefore, we have reinvestigated the series $KCaH_{3-x}F_x$ and characterized chemical composition and crystal structure.

## Results and Discussion

Members of the solid solution series $KCaH_{3-x}F_x$ were synthesized via solid state reactions of binary hydrides and fluorides under inert conditions. The colorless powders were analyzed by X-ray powder diffraction and structures were refined by the Rietveld method. For all compounds with $0.54 \leq x$ solid solutions $KCaH_{3-x}F_x$ were found with a few percent of calcium oxide and unreacted starting materials as secondary phases (for details see Experimental Section and Supporting Information.).

The orthorhombic $GdFeO_3$ type[18,19] was used as starting model for Rietveld refinements. The cell parameters *a*, *b*, and *c* show a continuous decrease with increasing fluorine content *x*. This observation is expected as ionic hydrides usually have larger unit cells in comparison to their corresponding isostructural fluorides.[9] The parameters *a* and *c* converge for decreasing *x* giving rise to the assumption that representatives with high hydrogen content might crystallize in a tetragonal space group. Therefore, several structure types with tetragonal space groups were tested as models for the Rietveld refinements. Within the family of perovskite related structures six common structure types have a tetragonal space group (*P*4/*mmm*, *P*4/*mbm*, *I*4/*mcm*, *I*4/*mmm*, *P*4*mm*, *I*4/*m*[1]). Rietveld refinements show satisfactory agreement only for the tetragonal $SrTiO_3$ type with space group *I*4/*mcm*. For *x* up to 1.73 the refinements confirm the tetragonal $SrTiO_3$ structure type, while for *x* higher than 1.73 the refinements show better *R* values in the $GdFeO_3$ structure type and a splitting of reflections becomes apparent (Figure 1).

Three experiments aimed to synthesize phases with $x = 0.3$, 0.39, and 0.5. Crystal structure refinements resulted in similar lattice parameters, the formula $KCaH_{0.54}F_{2.46}$ and considerable amounts of hydride secondary phases in all three cases. The series $KCaH_{3-x}F_x$ thus seems to have a phase boundary at $x = 0.54$. Accordingly, structure and properties of the hypothetical compound $KCaH_3$ have been determined so far from theoretical calculations only.[23]

The exact hydride and fluoride content was determined by two independent methods. In Rietveld refinements, hydrogen and fluorine atoms were placed on the same crystallographic sites with the constraint of occ(F) + occ(H) = 1. Refinement of occupation factors does thus not only allow to calculate the substitutional degree *x* in $KCaH_{3-x}F_x$, but also gives information on the hydride-fluoride order within the anionic positions, i.e. preferred crystallographic sites for hydrogen and fluorine atoms (vide infra). For most compounds, location or refinement of occupational parameters for hydrogen atoms in crystal structures requires neutron diffraction.[24] In case of the solid solution series $KCaH_{3-x}F_x$, however, this is not necessary, because hydrogen positions are well determined by fluorine positions. Since calcium with only twenty electrons is the electron richest atom and 60 % of all atoms in $KCaF_3$ are fluorine, the atomic form factor of fluorine atoms for X-rays contributes considerably to the X-ray diffraction pattern, i.e. occupation factors can be determined with good accuracy from XRPD patterns and Rietveld analysis in this case. The hydrogen content of samples was also determined by elemental analyses (CHN, Table 1).

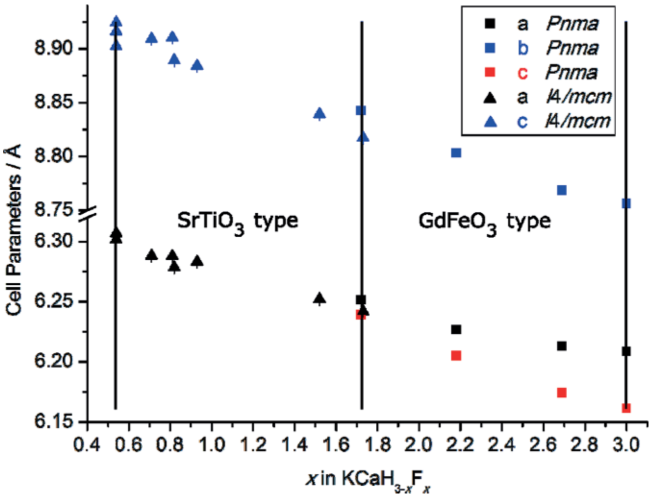

**Figure 1.** Unit cell parameters in $KCaH_{3-x}F_x$ (*x* determined by Rietveld refinement on X-ray diffraction patterns, see Table 1).

The comparison of the two analysis methods requires taking into account the content of secondary phases. Considering the uncertainty of the CHN analysis for small hydrogen contents values from elemental analysis are in good agreement with those from crystal structure refinements (Table 1).

Three sections within the series $KCaH_{3-x}F_x$ may be distinguished: no compound for $x < 0.54$, a solid solution with tetragonal $SrTiO_3$ type structure for $0.54 \leq x \leq 1.7$ and a solid solution with orthorhombic $GdFeO_3$ type structure for $1.8 \leq x \leq 3$.

For $1.8 \leq x \leq 3$, the solid solution series $KCaH_{3-x}F_x$ crystallizes with the orthorhombic $GdFeO_3$ type structure. In comparison to the cubic perovskite aristotype the $Ca^{2+}$ surrounding corner connected octahedra are distorted and tilted by angles of 156.7° to 163.8°. The $K^+$ surrounding polyhedra are strongly distorted compared to the ideal cuboctahedra, as well (Figure 2). The refined atomic position parameters agree with those from previous investigations.[19] Interatomic angles and polyhedral distortions are similar to related crystal structures of this type, for example $KCaF_3$.[25] Interatomic distances resulting from the structure refinements are in the range of typical ionic hydrides and fluorides.[16,26]

**Table 1.** Comparison of hydrogen content in potassium calcium hydride fluorides from XRPD based Rietveld refinements and elemental analyses; hydrogen content by XRPD accounts for secondary phases and is thus directly comparable to hydrogen content by elemental analysis; entries in *italics: orthorhombic $GdFeO_3$ type*, other entries: tetragonal $SrTiO_3$ type.

| Phase | Secondary phases content /wt % | Hydrogen content in sample by XRPD /wt % | Hydrogen content in sample by elemental analysis /wt % |
|---|---|---|---|
| *$KCaH_{0.31}F_{2.69}$* | 6 % CaO<br>4 % KF | *0.22* | *0.03* |
| *$KCaH_{0.82}F_{2.18}$* | 6 % CaO | *0.64* | *0.37* |
| $KCaH_{1.27}F_{1.73}$ | 9 % CaO<br>2 % KH | 1.06 | 1.11 |
| *$KCaH_{1.28}F_{1.72}$* | 7 %CaO<br>2 % $CaF_2$ | *1.00* | *1.09* |
| $KCaH_{1.48}F_{1.52}$ | 16 % CaO | 1.14 | 1.07 |
| $KCaH_{2.07}F_{0.93}$ | 11 % CaO<br>2 %KH | 1.89 | 1.65 |
| $KCaH_{2.16}F_{0.84}$ | 6 % CaO | 2.11 | 1.53 |
| $KCaH_{2.18}F_{0.82}$ | 3 % CaO<br>3 % $CaF_2$ | 2.13 | 1.42 |
| $KCaH_{2.29}F_{0.71}$ | 7 %CaO | 2.43 | 2.14 |
| $KCaH_{2.46}F_{0.54}$ | 17 %CaO<br>9 %$CaH_2$ | 2.43 | 2.01 |
| $KCaH_{2.46}F_{0.54}$ | 11 %CaO<br>10 %KH<br>6 %$CaH_2$ | 2.51 | 2.48 |
| $KCaH_{2.46}F_{0.54}$ | 17 % CaO<br>23 % KH<br>15 % $CaH_2$ | 2.51 | 2.38 |

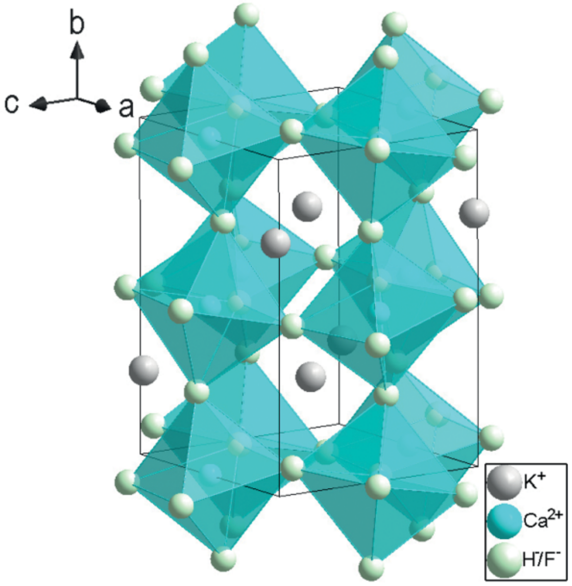

**Figure 2.** Crystal structure of $KCaH_{0.82}F_{2.18}$ in the orthorhombic $GdFeO_3$ type structure (space group type *Pnma*); interatomic distances / Å and angles / °: K–H1/F1: 2.815(5) – 3.409(5), K–H2/F2: 2.647(4) – 3.688(4), Ca–H1/F1: 2.228(1), Ca–H2/F2: 2.236(3)–2.275(4), Ca–H1/F1–Ca: 162.00(18), H1/F1–Ca–H1/F1: 180, H2/F2–Ca–H2/F2: 88.68(12), 91.32(12), Ca–H2/F2–Ca: 154.04(17), F1/H1–F2/H2–F1/H1: 103.77(10), 75.40(8).

Phases with higher hydrogen content crystallize in the tetragonal $SrTiO_3$ structure type (space group *I*4/*mcm*, no. 140). This is in contrast to earlier studies, where an orthorhombic structure had been derived for the whole range of solid solutions although a progressive shifting of the anions with increasing hydrogen proportion towards a less tilted octahedral network was already identified.[18,19] Cuboctahedra and octahedra are distorted and twisted by angles of 20.7° to 34.7°. These torsion angles are much higher than in tetragonal $SrTiO_3$ with 3.6°.[27] Interatomic K–H, K–F, Ca–H, and Ca–F distances are comparable to other typical ionic hydrides and fluorides[16,26] (Figure 3).

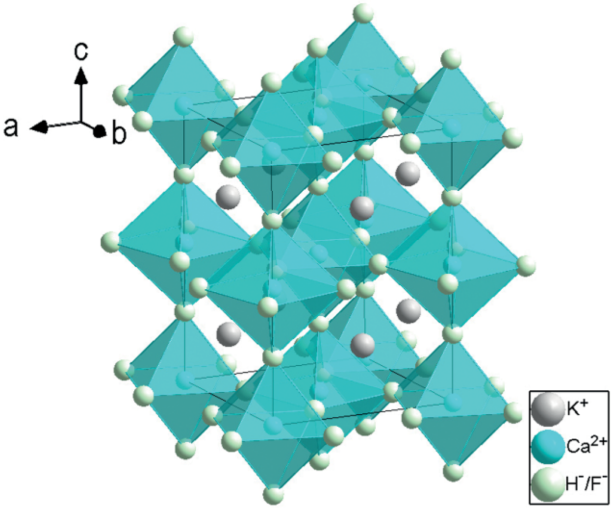

**Figure 3.** Crystal structure of $KCaH_{2.18}F_{0.82}$ in tetragonal $SrTiO_3$ type structure (space group type *I*4/*mcm*); interatomic distances / Å and angles / °: K–H1/F1: 3.139(0), K–H2/F2: 2.764(4)– 3.572(5), Ca–H1/F1: 2.222(0), Ca–H2/F2: 2.293(7), Ca–H1/F1–Ca: 180, H1/F1–Ca–H1/F1: 180, H2/F2–Ca–H2/F2: 90, Ca–H2/F2–Ca: 150.90(33), F1/H1–F2/H2–F1/H1: 88.07(17).

No hydrogen-fluorine ordering, i.e. perfect statistical distribution over both crystallographic anion sites, is observed for fluorine-rich compounds with $GdFeO_3$ type. This is in agreement with earlier investigations[18–20] and in analogy to similar solid solution series like $NaMgH_{3-x}F_x$.[17] For hydrogen-rich compounds with tetragonal $SrTiO_3$ type structure a partial ordering of hydrogen and fluorine atoms is found ($0.54 \leq x \leq 1.7$). Both anion positions show mixed occupation, but with some preference of hydrogen atoms for 8*h* and fluorine atoms for 4*a* sites, e.g. occ(H1, 4*a*) = 0.250(9) and occ(H2, 8*h*) = 0.616(6) in $KCaH_{1.48}F_{1.52}$ with occ(H) + occ(F) = 1 for each position (*I*4/*mcm*, $SrTiO_3$ type, see Supporting Information).

Calculating the Goldtschmidt tolerance factor *t* is a common method to predict structural deviation from the cubic perovskite type structure.[28] Based on the crystal radii determined by *Shannon*[29] the factor for $KCaF_3$ is $t = 0.90$ in agreement with a non-cubic (orthorhombic $GdFeO_3$ type) perovskite type crystal structure. For increasing fluoride substitution by hydride ions, the tolerance factor *t* is expected to decrease, since ionic radius of a hydride radius is usually slightly larger than that of a fluoride ion. However, due to the extremely large polarizability of the hydride anion, its ionic radius is not a constant,[30] which is why no value for the tolerance factor *t* is given here for hydride containing compounds. Temperature and pressure dependent phase transitions between tetragonal and orthorhombic perovskites are numerous, for example $CaTiO_3$ undergoing a transition from room temperature orthorhombic (*Pnma*) to tetragonal (*I*4/*mcm*) structure at 1373 K followed by a further transition to cubic ($Pm\bar{3}m$) at 1523 K.[31] An according change from tetragonal to orthorhombic perovskite type structure as a function of composition in a solid solution series is known for cation substitution. Increasing the barium content *x* in $Sr_{1-x}Ba_xZrO_3$ changes the crystal structure from orthorhombic (*Pnma*) to orthorhombic (*Imma*) to tetragonal and finally to cubic perovskite type.[32] To the best of our knowledge, no switching between tetragonal and orthorhombic perovskite type structures by compositional changes of anions in solid solution series was reported as yet. The solid solution series $KCaH_{3-x}F_x$ ($0.54 \leq x \leq 3$) might be the first such example.

## Experimental Section

**Sample Preparation:** Starting materials were KF (abcr, 99 %), $CaF_2$ (Alfa Aesar, 99.5 %), KH (Sigma Aldrich) and Ca (Alfa Aesar, 99.5 %). KF and $CaF_2$ were dried at 483 K in air prior to use. Due to air and moisture sensitivity of the hydrides, all samples were handled in an argon-filled glove box. $CaH_2$ was synthesized by hydrogenation of Ca at 400 °C and 60 bar hydrogen gas pressure in an autoclave made of V4A steel. Mixed anionic hydride fluorides were synthesized by grinding stoichiometric ratios of the reactants in an agate mortar regarding the desired sum formula. The mixtures were pressed into pellets and heated at 500 °C and 60 bar hydrogen gas pressure in an autoclave made of Inconel alloy (Böhler L718V) for 96 h. The obtained white samples were ground and analyzed by X-ray diffraction.

**X-ray Powder Diffraction:** X-ray powder diffraction data were collected on a Huber G670 Guinier diffractometer with Cu-$K_{\alpha1}$ radiation in the range $4° \leq 2\theta \leq 100°$. Samples were enclosed between kapton® foils in apiezon® grease. Crystal structures were refined using the software TOPAS V.5.0.[33] Structure parameters to be refined were cell parameters, atomic positions, thermal displacements and occupancy factors. Thermal parameters were constrained to be the same for all anions (H and F atoms). Occupation factors were constrained to sum up to fully occupied sites 4*c* and 8*d*.

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD-1950921, CSD-1950922, CSD-1950923, CSD-1950924, CSD-1950925, CSD-1950926, CSD-1950927, CSD-1950928, CSD-1950929, CSD-1950930, CSD-1950931.

**Elemental Analysis:** The hydrogen content of the hydrides was determined by elemental analysis with a VARIO EL (Elementar Analysensysteme GmbH, Hanau, Germany) microanalyzer using the carrier gas-hot extraction method in triplicate repetition.

**Supporting Information** (see footnote on the first page of this article):

Crystal structures of $KCaH_{3-x}F_x$ ($0.54 \leq x \leq 3$) based on X-ray powder diffraction (XRPD) and Rietveld refinements

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**Keywords:** Metal hydride; Metal fluoride; X-ray diffraction; Rietveld refinement; Perovskite

## References

[1] O. Bock, U. Müller, *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 594–606.
[2] S. Krohns, P. Lunkenheimer, *Phys. Sci. Rev.* **2019**, *4*, 20190015.
[3] T. Walther, U. Straube, R. Köferstein, S. G. Ebbinghaus, *J. Mater. Chem. C* **2016**, *4*, 4792–4799.
[4] S. Dong, J.-M. Liu, *Mod. Phys. Lett. B* **2012**, *26*, 1230004.
[5] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050–6051.
[6] S. A. Veldhuis, P. P. Boix, N. Yantara, M. Li, T. C. Sum, N. Mathews, S. G. Mhaisalkar, *Adv. Mater.* **2016**, *28*, 6804–6834.
[7] Z. Song, J. Zhao, Q. Liu, *Inorg. Chem. Front.* **2019**, *6*, 2969–3011.
[8] N. Kunkel, T. Wylezich, *Z. Anorg. Allg. Chem.* **2019**, *645*, 137–145.
[9] C. E. Messer, *J. Solid State Chem.* **1970**, *2*, 144–155.
[10] H. Kohlmann, F. Gingl, T. Hansen, K. Yvon, *Angew. Chem.* **1999**,*111*, 2145–2147; *Angew. Chem. Int. Ed.* **1999**, *38*, 2029–2032.
[11] A. Götze, H. Kohlmann, in: *Elsevier Reference Module in Chemistry, Molecular Sciences and Chemical Engineering* (Ed.: J. Reedijk) Waltham, MA: Elsevier, **2017**.
[12] R. O. Moyer Jr., B. J. Burnim, R. Lindsay, *J. Solid State Chem.* **1996**, *121*, 56–60.
[13] K. Yvon, in: *Encyclopedia of Materials: Science and Technology* (Eds.: K. H. J. Buschow, R. W. Cahn, M. C. Flemings, B. Ilschner, E. J. Kramer, S. Mahajan), Elsevier, Amsterdam, **2004**, 1–9.
[14] H. Kohlmann, R. O. Moyer Jr., T. Hansen, K. Yvon, *J. Solid State Chem.* **2003**, *174*, 35–43.
[15] H. Kohlmann, *Z. Kristallogr.* **2009**, *224*, 454–460.

[16] T. Wylezich, S. Welinski, M. Hoelzel, P. Goldner, N. Kunkel, *J. Mater. Chem. C* **2018**, *6*, 13006–13012.
[17] C. Pflug, A. Franz, H. Kohlmann, *J. Solid State Chem.* **2018**, *258*, 391–396.
[18] J.-P. Soulié, A. Bouamrane, *Phys. Chem. News* **2002**, *5*, 82–86.
[19] J.-P. Soulié, J.-P. Laval, A. Bouamrane, *Solid State Sci.* **2003**, *5*, 273–276.
[20] A. Bouamrane, J.-P. Soulie, J. P. Bastide, *Thermochim. Acta* **2001**, *375*, 81–84.
[21] A. Bouamrane, J. P. Laval, J.-P. Soulie, J. P. Bastide, *Mater. Res. Bull.* **2000**, *35*, 545–549.
[22] N. Kunkel, A. Meijerink, M. Springborg, H. Kohlmann, *J. Mater. Chem. C* **2014**, *2*, 4799–4804.
[23] P. Vajeeston, P. Ravindran, H. Fjellvåg, *J. Chem. Phys.* **2010**, *132*, 114504.
[24] K. Yvon, *Locating Hydrogen in Metal Hydrides by X-ray and Neutron Diffraction*, in *Neutron Scattering from Hydrogen in Materials* (Ed.: A. Furrer), World Scientific, Singapore, **1994**, 84–96.
[25] K. S. Knight, C. N. W. Darlington, I. G. Wood, *Powder Diffr.* **2005**, *20*, 7–13.
[26] J.-F. Brice, A. Courtois, J. Aubry, *J. Solid State Chem.* **1978**, *24*, 381–387.
[27] J. M. Kiat, T. Roisnel, *J. Phys.: Condens. Matter* **1996**, *8*, 3471–3475.
[28] V. M. Goldschmidt, *Naturwissenschaften* **1926**, *14*, 477–485.
[29] R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr., Theor. Gen. Crystallogr.* **1976**, *32*, 751–767.
[30] W. Bronger, *Z. Anorg. Allg. Chem.* **1996**, *622*, 9–16.
[31] S. A. T. Redfern, *J. Phys.: Condens. Matter* **1996**, *8*, 8267–8275.
[32] L. Li, B. J. Kennedy, Y. Kubota, K. Kato, R. F. Garrett, *J. Mater. Chem.* **2004**, *14*, 263–273.
[33] Bruker AXS (2014) TOPAS V5: General profile and structure analysis software for powder diffraction data – User's Manual, Bruker AXS, Karlsruhe.

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