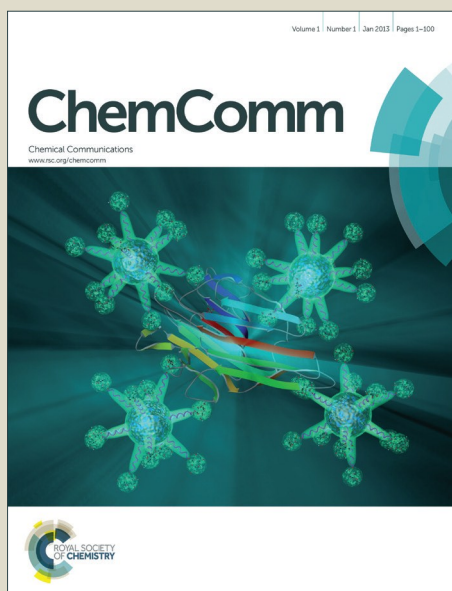


ChemComm

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: A. Santoru, C. Pistidda, M. H. Sørby, M. R. Chierotti, S. Garroni, E. Pinatel, F. Karimi, H. Cao, N. Bergemann, T. T. Le, J. Puzkiel, R. Gobetto, M. Baricco, B. C. Hauback, T. Klassen and M. Dornheim, *Chem. Commun.*, 2016, DOI: 10.1039/C6CC05777B.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

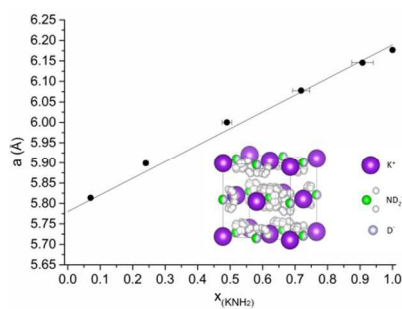
Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Table of Contents

The addition of KH to KNH_2 provides the first metal amide – hydride solid solution by either mechanochemical or thermal input.



KNH₂ - KH: a metal amide - hydride solid solution

Antonio Santoru^{*[a, b]}, Claudio Pistidda^[a], Magnus H. Sørby^[c], Michele R. Chierotti^[b], Sebastiano Garroni^[d], Eugenio Pinatel^[b], Fahim Karimi^[a], Hujun Cao^[a], Nils Bergemann^[a], Thi T. Le^[a], Julián Puzskiel^[a, e], Roberto Gobetto^[b], Marcello Baricco^[b], Bjørn C. Hauback^[c], Thomas Klassen^[a] and Martin Dornheim^[a]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

We report for the first time the formation of a metal amide-hydride solid solution. The dissolution of KH into KNH₂ leads to an anionic substitution, which decreases the interaction among NH₂⁻ ions. The rotational properties of the high temperature polymorphs of KNH₂ are thereby retained down to room temperature.

The amides of alkaline and alkaline-earth metals were discovered and independently investigated by J. L. Gay-Lussac and H. Davy in the early 19th century^{1, 2}. Further studies on their properties were performed towards the end of the same century, most systematically from A. W. Titherley³. The determination of their crystal structures was possible only after the 1930s with the studies of Juza et al.,⁴⁻¹⁰ later continued by Jacobs et al.^{11, 12}

At that time this class of compounds was mostly used for organic synthesis. However, more recently, metal amides – metal hydrides mixtures have been proven to be suitable for reversible hydrogen storage.¹³ Furthermore, metal amides – metal borohydrides systems are regarded as potential solid state ionic conductors.¹⁴

The structural and thermal properties of light-weight amides prepared by reaction of metal hydrides with ammonia have been systematically examined by *in situ* diffraction experiments.¹⁵ While the reaction mechanism and products reported in previous studies were confirmed for the amides of lithium and sodium,¹⁶⁻¹⁸ the formation of new K-N-H based intermediates was suggested for potassium amide. The same

intermediates were proven to play a role in the desorption reactions of the K-Mg-N-H system.¹⁹ These intermediates are isolated here in the KNH₂-KH system and, to the best of our knowledge, identified as the first metal amide-hydride solid solution.

The crystal structures of pristine potassium amide and potassium hydride have already been investigated by X-ray and neutron diffraction.^{7, 8, 12, 20-22} Potassium hydride is known to crystallize in a cubic rock-salt type structure with space group (s.g.) *Fm* $\bar{3}$ *m* and no polymorph changes are expected in the temperature range from room temperature (RT) to 390 °C.²¹ For potassium amide, the stable polymorph at RT is monoclinic with s.g. *P2*₁/*m*.⁷ Upon heating this phase transforms into a tetragonal structure with in *P4/nmm* at 54 °C.¹² The latter phase is stable only in a narrow temperature range; and already above 75 °C the stability of a cubic phase (*Fm* $\bar{3}$ *m*) prevails.^{12, 20, 22} An increase of symmetry is therefore reached with the two phase transitions at higher temperature. The explanation of the symmetry changes resides in the increasingly high orientational disorder of the amide anions, as proven by powder neutron diffraction (PND), quasielastic incoherent neutron scattering and orientation-dependent deuterium spin lattice relaxation.^{20, 23, 24} If the maximum temperature upon heating is kept below the decomposition temperature of KNH₂ (ca. 340 °C), the two phase transitions and the associated rotational dynamics should be reversible on cooling.

This is in agreement with the present *in situ* synchrotron radiation powder X-ray diffraction experiment (SR-PXD) on KNH₂ (ESI). When a 0.5 KNH₂ + 0.5 KH mixture was investigated, the expected phase transformations of KNH₂ took place, but the interaction of KNH₂ and KH in the temperature range between 100 °C and 270 °C led to the formation of a new cubic structure (Figure 1 a).[†]

PND at 270 °C of a potassium deuteramide - potassium deuteride mixture confirmed the presence of a single cubic phase at this temperature (Figure 1 b).[‡]

^a Nanotechnology Department, Helmholtz-Zentrum Geesthacht Max-Planck Straße 1, 21502, Geesthacht, Germany

^b Department of Chemistry and NIS centre, University of Torino, V. Giuria 7, 10125, Torino, Italy

^c Physics Department, Institute for Energy Technology (IFE), P.O. Box 40, NO-2027 Kjeller, Norway

^d Department of Chemistry and Pharmacy, University of Sassari, V. Vienna 2, 07100, Sassari, Italy

^e Department of Physicochemistry of Materials, Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) y Centro Atómico Bariloche, Av. Bustillo km 9500, San Carlos de Bariloche, CP 8400, Argentina

Electronic Supplementary Information (ESI) available: powder X-ray and neutron diffractograms, Rietveld refinements, thermal decomposition, experimental details. See DOI: 10.1039/x0xx00000x

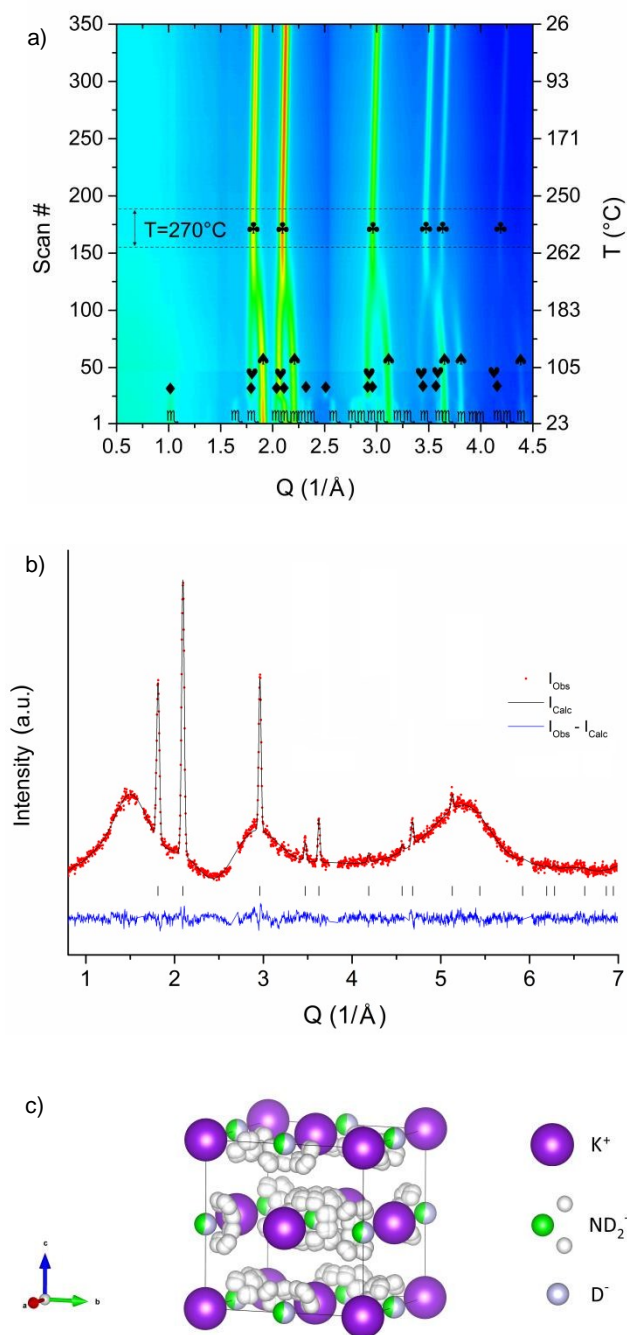


Figure 1. a) *In situ* SR-PXD experiment on the 0.5 KNH₂ + 0.5 KH sample. \square = KNH₂ (P21/m), \blacklozenge = KNH₂ (P4/nmm), \blacktriangledown = KNH₂ (Fm $\bar{3}$ m), \blacktriangle = KH (Fm $\bar{3}$ m), \clubsuit = new phase (Fm $\bar{3}$ m). b) PND pattern of the nominal 0.5 KND₂ + 0.5 KD mixture annealed up to 270 °C and kept in isothermal condition during the data collection. Rwp(%) = 2.8 (corrected for background). The wavy background was originated from the quartz sample holder (see Supporting Information). c) Structural model of the cubic phase (s.g. Fm $\bar{3}$ m) of composition K(ND₂)_{0.46}D_{0.54} obtained after the Rietveld refinement, taking into account the anionic substitution at the position (0.5 0.5 0.5) and the orientational disorder of amide anions.

The structure was solved assuming an ionic crystal with unaltered positions for the potassium cations and partially occupied sites at the original positions of amide and hydride anions. Indeed the formation of a solid solution is highly favorable due to the structural similarities between the two

cubic polymorphs of KNH₂ and KH (same space group, same cation, same charge for the anions, similar lattice constants).

The local symmetry of the deuteramide groups is compatible with the s.g. Fm $\bar{3}$ m only assuming rotational dynamics and orientational disorder. In this case the restrictions imposed from both the s.g. and rigid amide groups resulted in partially occupied sites (multiplicity = 192) for the deuterium atoms of each amide group (Figure 1 c).

The final Rietveld refinement^{25, 26} of the PND pattern (Figure 1 b) confirmed the structural model, i.e. the formation of a potassium amide-hydride solid solution. To the best of our knowledge, no similar cases have been reported so far for other alkaline metal amides-metal hydrides mixtures.

The similarity of chemical environment between the starting materials and the x KNH₂ + (1 - x) KH samples at different compositions (x = 0.1, 0.5, 0.9) after annealing was verified by ¹H magic angle spinning solid-state NMR (MAS SSNMR), see Figure 2.5

No significant shifts are observed while the integral values perfectly reflect the composition of the solid solution. Furthermore, the same T₁ ¹H value (46 s) for both signals supports the formation of a solid solution since it indicates that spin diffusion is active. This is only possible if they belong to the same phase or in the case of homogeneous samples on a nanometer scale.²⁷ Direct evidence of the solid solution formation is provided by the ¹H double-quantum (DQ) MAS SSNMR experiment (Figure 2 b). Indeed, the observed DQ correlation between the KNH₂ (-3.2 ppm) and KH (4.8 ppm) signals implies that they are in close spatial proximity each other (less than 5 Å). This is only possible if they are intimately related as in a solid solution.^{28, 29} Similar correlation, although much weaker, is observed for the sample before annealing (Supporting Information), which can be explained with the formation of a small fraction of solid solution due to the fast rotation and slightly increased temperature during the NMR experiment.

The effect of the starting composition of the mixtures on the final structure was studied by means of *in situ* SR-PXD. A linear relationship was found between the unit cell parameter of the cubic phase at T = 270 °C and the molar fraction of amide anions (Figure 3 and Table 1) as expected from Vegard's law.³⁰ This indicates volumes of mixing close to zero and, therefore, an almost ideal behavior for the solid solution ($\Delta H_{\text{mix}} \approx 0$).

It is noteworthy that, for the compositions x = 0.1, 0.3, 0.5, 0.7, the structure did not change during the cooling process down to RT, except for the thermal contraction of the unit cell volume (more details in Table 1 and in Supporting Information).

It appears that the addition of potassium hydride can stabilize the cubic geometry, which retains the rotation of the amide anions even at RT. A similar behavior was previously reported for the sodium borohydride - sodium chloride systems, at different temperature (T = - 81 °C).³¹ *Ex situ* PXD of annealed samples (x = 0.3, 0.5, 0.7, 0.9) collected with a Bragg Brentano diffractometer proves the coexistence of at least two different cubic structures. The composition x = 0.1, however, presented unchanged cubic phase (see Supporting Information). At the

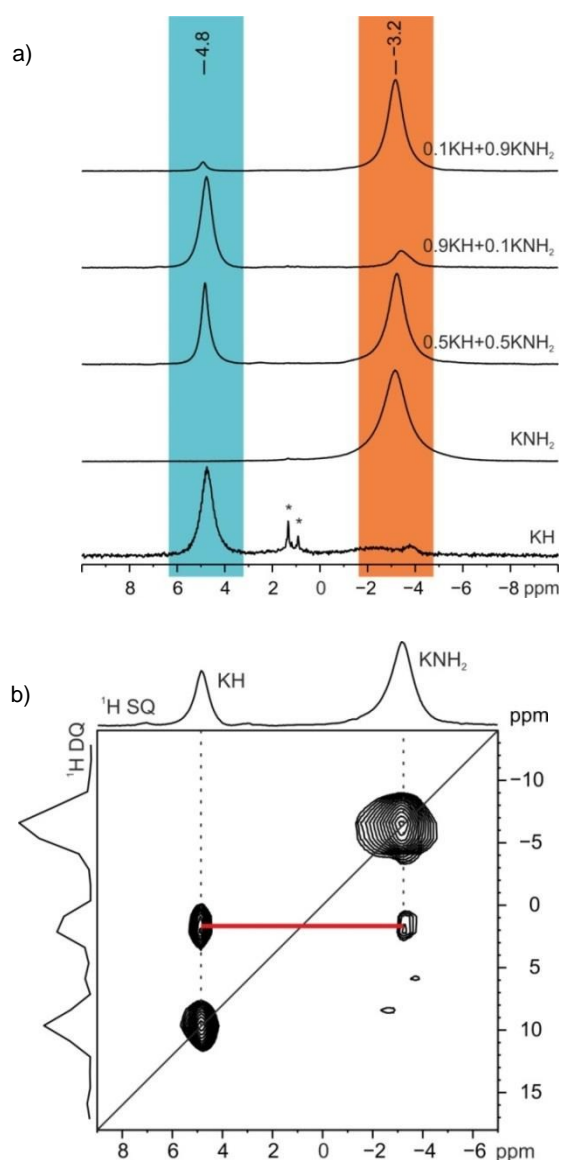


Figure 2. a) ^1H (400.23 MHz) MAS SSNMR spectra of starting reagents and $x\text{KNH}_2 + (1-x)\text{KH}$ samples at different composition ($x = 0.1, 0.5, 0.9$) after annealing recorded with a spinning speed of 32 kHz. Asterisks denote impurities. b) 2D ^1H (400.23 MHz) DQ MAS SSNMR spectrum of the $\text{KNH}_2 + \text{KH}$ ($x = 0.5$) after annealing recorded with a spinning speed of 32 kHz. The red line highlights the DQ correlation between the KH and KNH_2 signal.

composition $x = 0.9$, coexistence of the cubic and monoclinic phases was found. These results suggest the presence of a two phase field at RT. Nevertheless, even in the cases where phase segregation occurred, both cubic structures were proven to be unchanged even after several months, hence a complete transformation back to the pure monoclinic phase of KNH_2 and cubic phase of KH did not occur.

Noteworthy, the same structures are formed simply by mechanochemical treatments of the starting reactants. In some cases ($x = 0.1, 0.3$ and 0.9) manual grinding is enough to promote the formation of detectable amounts of $\text{K}(\text{NH}_2)_x\text{H}_{(1-x)}$ solid solution. These species are therefore easily formed and are expected to be possibly identified as reaction products or

intermediates in future studies of amide-based systems containing potassium.

DOI: 10.1039/C6CC05777B

Table 1. Structural details of the $\text{K}(\text{NH}_2)_x\text{H}_{(1-x)}$ phase at different compositions

x [a]	x [b]	$a / \text{\AA}$ [c]	α / K^{-1} [d]	$a / \text{\AA}$ [e]
0	0	5.74934(14)	3.19(2)E-05	5.70390(14)
0.1	0.070(5)	5,81372(13)	5.30(1)E-05	5.73769(13)
0.3	0.240(8)	5,8989(2)	5.88(2)E-05	5.8134(2)
0.5	0.490(14)	6.0003 (2)	6.32(1)E-05	5.9060(2)
0.7	0.72(3)	6,07768(12)	6.83(1)E-05	5.98320(12)
0.9	0.91(3)	6,14553(14)	6.83(2)E-05	6.04230(14)
1	1	6,17667(8)	7.38(1)E-05	6.06473 (8)

[a] Nominal composition and [b] Refined composition (molar fraction) of KNH_2 [c] Refined cell parameters at 270 °C [d] Calculated linear thermal expansion coefficients [e] Calculated cell parameters at 20 °C. Estimated standard deviations are given in parentheses.

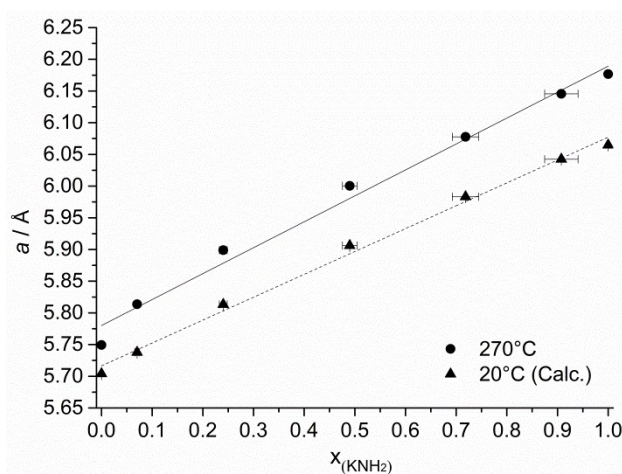


Figure 3. Unit cell parameters (dots) obtained by *in situ* SR-PXD experiments in isothermal conditions ($T = 270\text{ °C}$) as a function of the potassium amide content and corresponding linear fit (continuous line). The values for $T = 20\text{ °C}$ (triangles) were calculated using the thermal expansion coefficient of each phase and then fitted (dotted line). The error bars for molar fractions and cell parameters were calculated considering the errors of the Rietveld process.

To the best of our knowledge, amide/hydride solid solutions were not reported so far. In this sense, the chemistry of the K-based amide/hydride system is interestingly peculiar and differs substantially from the one of the other alkaline metal amides/hydrides.

The research leading to these results has received funding from the European Marie Curie Actions under ECOSTORE grant agreement no. 607040. The help of the beamline scientists Francisco Martinez Casado, Dorthe Haase, Olivier Balmes, (MAX-lab – Lund, Sweden), Martin Etter and Jozef Bednarcik (DESY – Hamburg, Germany) is thankfully acknowledged. A.S. thanks the research groups of Turin University, Sassari University and IFE for the fruitful discussion and Dr. Klaus Taube, coordinator of the ECOSTORE project, for providing the essential networking opportunities.

Notes and references

† The *in situ* SR-PXD experiments were performed at the diffraction beamline I711, MAX Lab (Lund, Sweden) and at the diffraction beamline P02, DESY (Hamburg,

Germany) (monochromatic beams of $\lambda \approx 0.99 \text{ \AA}$ and $\approx 0.2 \text{ \AA}$ were employed respectively). The in situ cells and the procedure used are described elsewhere.^{19,32} \ddagger PND was performed at the PUS instrument at the JEEP II reactor at IFE, Norway.³³ Neutrons with $\lambda = 1.5539 \text{ \AA}$ were provided by a focussing Ge(511) monochromator at 90° take-off angle. Data was collected in the range $2\theta = 10\text{--}130^\circ$ ($\Delta 2\theta = 0.05^\circ$) by 2 detector banks each with 7 vertically stacked position sensitive detectors. The sample was contained in an argon-filled quartz tube with 6 mm diameter placed inside an in-house built furnace. The structure solution was carried out using the software "FOX"³⁴. The Rietveld refinement was performed by means of the software GSAS³⁵ and the EXPGUI graphic interface³⁶.

\S Solid-state NMR experiments were run on a Bruker AVANCE II 400 instrument operating at 400.23 MHz for ^1H and equipped with a 2.5 mm probe. The ^1H MAS spectra were acquired at the spinning speed of 32 kHz with the DEPTH sequence ($\pi/2 - \pi - \pi$) for the suppression of the probe background signal ($^1\text{H } 90^\circ = 2.5 \mu\text{s}$; scans = 16; relaxation delay = 53 s). 2D ^1H DQ MAS experiments were performed at 32 kHz with the back-to-back (BABA) recoupling pulse sequence with excitation times of one rotor period ($^1\text{H } 90^\circ = 2.5 \mu\text{s}$; 32 scans; t_1 increments = 46; relaxation delay = 53 s). ^1H scale was calibrated with adamantane (^1H signal at 1.87 ppm) as external standards.

- J. L. Gay and L. J. Thenard, *Journal*, 1809, **32**, 23-39.
- H. Davy, *Philosophical Transactions of the Royal Society of London*, 1808, **98**, 333-370.
- A. W. Titherley, *Journal of the Chemical Society, Transactions*, 1894, **65**, 504-522.
- R. Juza, *Angewandte Chemie*, 1964, **76**, 290-300.
- R. Juza, *Zeitschrift für anorganische und allgemeine Chemie*, 1937, **231**, 121-135.
- R. Juza, K. Fasold and C. Haeberle, *Zeitschrift für anorganische und allgemeine Chemie*, 1937, **234**, 75-85.
- R. Juza, H. Jacobs and W. Klose, *Zeitschrift für anorganische und allgemeine Chemie*, 1965, **338**, 171-178.
- R. Juza and H. Liedtke, *Zeitschrift für anorganische und allgemeine Chemie*, 1957, **290**, 205-208.
- R. Juza and K. Opp, *Zeitschrift für anorganische und allgemeine Chemie*, 1951, **266**, 313-324.
- R. Juza, H. H. Weber and K. Opp, *Zeitschrift für anorganische und allgemeine Chemie*, 1956, **284**, 73-82.
- H. Jacobs, *Zeitschrift für anorganische und allgemeine Chemie*, 1971, **382**, 97-109.
- H. Jacobs and E. Von Osten, *Zeitschrift für Naturforschung*, 1976, **31**, 385-386.
- P. Chen, Z. Xiong, J. Luo, J. Lin and K. L. Tan, *Nature*, 2002, **420**, 302-304.
- M. Matsuo, A. Remhof, P. Martelli, R. Caputo, M. Ernst, Y. Miura, T. Sato, H. Oguchi, H. Maekawa, H. Takamura, A. Borgschulte, A. Züttel and S.-i. Orimo, *Journal of the American Chemical Society*, 2009, **131**, 16389-16391.
- C. Pistidda, A. Santoru, S. Garroni, N. Bergemann, A. Rzeszutec, C. Horstmann, D. Thomas, T. Klassen and M. Dornheim, *The Journal of Physical Chemistry C*, 2015, **119**, 934-943.
- W. I. F. David, M. O. Jones, D. H. Gregory, C. M. Jewell, S. R. Johnson, A. Walton and P. P. Edwards, *Journal of the American Chemical Society*, 2007, **129**, 1594-1601.
- J. W. Makepeace, M. O. Jones, S. K. Callear, P. P. Edwards and W. I. F. David, *Physical Chemistry Chemical Physics*, 2014, **16**, 4061-4070.
- H. Yamamoto, H. Miyaoka, S. Hino, H. Nakanishi, T. Ichikawa and Y. Kojima, *International Journal of Hydrogen Energy*, 2009, **34**, 9760-9764.
- A. Santoru, S. Garroni, C. Pistidda, C. Milanese, A. Girella, A. Marini, E. Masolo, A. Valentoni, N. Bergemann, T. T. Le, H. Cao, D. Haase, O. Balmes, K. Taube, G. Mulas, S. Enzo, T. Klassen and M. Dornheim, *Physical Chemistry Chemical Physics*, 2016, **18**, 3910-3920.
- M. Müller, J. Senker, B. Asmussen, W. Press, H. Jacobs, W. Kockelmann, H. M. Mayer and R. M. Ibberson, *The Journal of chemical physics*, 1997, **107**, 2363-2373.
- V. G. Kuznetsov and M. M. Shkrabkina, *J Struct Chem*, **3**, 532-537.
- M. Müller, B. Asmussen, W. Press, J. Senker, H. Jacobs, H. Büttner, W. Kockelmann and R. M. Ibberson, *Physica B: Condensed Matter*, 1997, **234-236**, 45-47.
- M. Müller, B. Asmussen, W. Press, J. Senker, H. Jacobs, H. Büttner and H. Schober, *The Journal of chemical physics*, 1998, **109**, 3559-3567.
- J. Senker, *Solid State Nuclear Magnetic Resonance*, 2004, **26**, 22-35.
- H. M. Rietveld, *Journal*, 1967, **22**, 151-152.
- H. M. Rietveld, *Journal*, 1969, **2**, 65-71.
- K. Gaglioti, M. R. Chierotti, F. Grifasi, R. Gobetto, U. J. Griesser, D. Hasa and D. Voinovich, *CrystEngComm*, 2014, **16**, 8252-8262.
- D. Braga, L. Chelazzi, F. Grepioni, E. Dichiarante, M. R. Chierotti and R. Gobetto, *Crystal Growth & Design*, 2013, **13**, 2564-2572.
- M. R. Chierotti and R. Gobetto, *CrystEngComm*, 2013, **15**, 8599-8612.
- L. Vegard, *Zeitschrift für Physik*, **5**, 17-26.
- J. E. Olsen, P. Karen, M. H. Sørby and B. C. Hauback, *Journal of Alloys and Compounds*, 2014, **587**, 374-379.
- U. Bösenberg, C. Pistidda, M. Tolkiehn, N. Busch, I. Saldan, K. Suarez-Alcantara, A. Arendarska, T. Klassen and M. Dornheim, *International Journal of Hydrogen Energy*, 2014, **39**, 9899-9903.
- B. C. Hauback, H. Fjellvåg, O. Steinsvoll, K. Johansson, O. T. Buset and J. Jørgensen, *Journal of Neutron Research*, **8**, 215-232.
- V. Favre-Nicolin and R. Cerny, *Journal of Applied Crystallography*, 2002, **35**, 734-743.
- A. C. L. a. R. B. V. Dreele, *Los Alamos National Laboratory Report LAUR 86-748*, 2000.
- B. Toby, *Journal of Applied Crystallography*, 2001, **34**, 210-213.