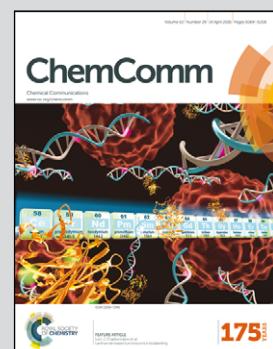


Showcasing research by Dr Martin Dornheim and Coworkers/  
The Institute of Materials Research, Materials Technology,  
Helmholtz-Zentrum Geesthacht, Germany

New synthesis route for ternary transition metal amides as well  
as ultrafast amide–hydride hydrogen storage materials

Ternary transition-metal amides were synthesized on large scale  
for the first time by mechanochemical reaction without applying  
high temperatures, high pressures or long reaction times. This  
opens up the possibility to obtain novel hydrogen storage  
materials and important transition-metal nitrides.

### As featured in:



See Hujun Cao et al.,  
*Chem. Commun.*, 2016, **52**, 5100.



Cite this: *Chem. Commun.*, 2016, 52, 5100

Received 25th January 2016,  
 Accepted 29th February 2016

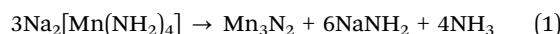
DOI: 10.1039/c6cc00719h

[www.rsc.org/chemcomm](http://www.rsc.org/chemcomm)

**K<sub>2</sub>[Mn(NH<sub>2</sub>)<sub>4</sub>] and K<sub>2</sub>[Zn(NH<sub>2</sub>)<sub>4</sub>] were successfully synthesized via a mechanochemical method. The mixture of K<sub>2</sub>[Mn(NH<sub>2</sub>)<sub>4</sub>] and LiH showed excellent rehydrogenation properties. In fact, after dehydrogenation K<sub>2</sub>[Mn(NH<sub>2</sub>)<sub>4</sub>]-8LiH fully rehydrogenates within 60 seconds at ca. 230 °C and 5 MPa of H<sub>2</sub>. This is one of the fastest rehydrogenation rates in amide–hydride systems known to date. This work also shows a strategy for the synthesis of transition metal nitrides by decomposition of the mixtures of M[M'(NH<sub>2</sub>)<sub>n</sub>] (where M is an alkali or alkaline earth metal and M' is a transition metal) and metal hydrides.**

Transition metal nitrides attract increasing attention owing to their interesting physical and chemical properties (*e.g.* optical, magnetic, electrical, mechanical and catalytic properties).<sup>1</sup> Zn<sub>3</sub>N<sub>2</sub> powder was first synthesized by Juza and Hahn in 1940.<sup>2a</sup> This material is a promising candidate for optoelectronic applications because of its high electron mobility and high electrical conductivity.<sup>2</sup> Manganese nitrides (*i.e.* Mn<sub>4</sub>N, Mn<sub>3</sub>N<sub>2</sub>, Mn<sub>6</sub>N<sub>5</sub>, and Mn<sub>2</sub>N), are well known for their phase-dependent magnetic properties.<sup>3</sup> Apart from the binary transition metal nitrides, the development of ternary transition metal nitrides have attracted considerable attention due to their various properties.<sup>4</sup> In the past decades, a lot of ternary transition metal nitrides have been explored such as Ca[NiN], Sr[NiN], Li<sub>7</sub>[MnN<sub>4</sub>], Li<sub>7</sub>[VN<sub>4</sub>] and Li[ZnN].<sup>4</sup> Owing to N<sub>2</sub> having extremely strong covalent bonds and therefore high stability, it is very difficult to employ it to synthesize nitrogen containing materials (*i.e.* transition

metal nitrides). Usually the synthesis conditions for transition metal nitrides vary remarkably.<sup>5</sup> The lighter 3d-transition metals are thermodynamically more stable than the heavier ones. To synthesize nitrides of Ti to Ni from the elements, often high temperatures and high pressures are favorable, for example, Ni<sub>3</sub>N was synthesized by use of supercritical nitrogen at ~1800 K and 10 000 MPa.<sup>6</sup> However, such reaction conditions are challenging for large-scale synthesis and practical applications. The use of NH<sub>3</sub> instead of N<sub>2</sub> allows a considerable reduction of reaction times, pressures and temperatures. Ammonothermal synthesis, using supercritical NH<sub>3</sub>, gives access to synthesize some transition metal nitrides like Mn<sub>4</sub>N, Mn<sub>3</sub>N<sub>2</sub>, Fe<sub>4</sub>–Ni<sub>x</sub>N, Ni<sub>3</sub>N and Cu<sub>3</sub>N.<sup>7</sup> Using this method very well crystallized powder, or even single crystals of transition metal nitrides like EuN and Mn<sub>3</sub>N<sub>2</sub> can be obtained, the formation process still needs high pressures, high temperatures and long reaction times.<sup>8</sup> Usually, ternary transition metal amides (M[M'(NH<sub>2</sub>)<sub>n</sub>]) are synthesized by ammonothermal method, and they are important intermediates for synthesis of transition metal nitrides. For example, Mn<sub>3</sub>N<sub>2</sub> was obtained by decomposition of Na<sub>2</sub>[Mn(NH<sub>2</sub>)<sub>4</sub>] (reaction (1)). However, Na<sub>2</sub>[Mn(NH<sub>2</sub>)<sub>4</sub>] was synthesized by reaction of MnI<sub>2</sub> and NaNH<sub>2</sub> at 673–873 K and 600 MPa of NH<sub>3</sub> for more than 30 days (reaction (2)).<sup>9</sup>



M[M'(NH<sub>2</sub>)<sub>n</sub>] compounds contain NH<sub>2</sub><sup>–</sup> group like alkali/alkaline earth metal amides which are excellent candidates for hydrogen storage.<sup>10</sup> M[M'(NH<sub>2</sub>)<sub>n</sub>] compounds also contain transition metals and most of transition metals have some “catalytic effect” on hydrogen dissociation.<sup>11</sup> Using M[M'(NH<sub>2</sub>)<sub>n</sub>] as a hydrogen storage media might be an important step towards the development of new hydrogen storage systems with novel hydrogen sorption properties. In addition, some metal nitrides are easily obtained by dehydrogenation of amide–hydride mixtures. For example, LiNH<sub>2</sub>-2LiH converts to Li<sub>3</sub>N after dehydrogenation.<sup>10c</sup> This could be a viable method to rapidly and conveniently obtain ternary and/or

<sup>a</sup> Institute of Materials Research, Materials Technology, Helmholtz-Zentrum Geesthacht GmbH, Max-Planck-Straße 1, D-21502 Geesthacht, Schleswig-Holstein, Germany. E-mail: [hujun.cao@hzg.de](mailto:hujun.cao@hzg.de); Fax: +49 04152/87-2625; Tel: +49 04152/87-2643

<sup>b</sup> Institute of Inorganic Chemistry, University Stuttgart, Pfaffenwaldring 55, Stuttgart 70569, Germany

<sup>c</sup> Dalian National Laboratory for Clean Energy Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

† Electronic supplementary information (ESI) available: Experimental procedures; TG-DTA curves of monoclinic K<sub>2</sub>[Zn(NH<sub>2</sub>)<sub>4</sub>]; TG-DTA-MS curves and de/re-hydrogenation curves of the as ball milled K<sub>2</sub>[Mn(NH<sub>2</sub>)<sub>4</sub>]-8LiH sample. See DOI: 10.1039/c6cc00719h



quaternary transition metal nitrides by decomposing mixtures of  $M'[M'(NH_2)_n]$  and metal hydrides under mild temperature and gas pressure conditions.

Various mechanochemical reactions have been developed for synthesis of intermetallics, alloy compounds, nanocrystalline powders, magnetic materials, ceramic powders, hydrogen storage materials and catalytic materials.<sup>12</sup> That is because mechanochemical synthesis methods offer several advantages over traditional processing routes. These advantages include low-temperature, solid state reactions, fewer processing steps, ease to scale-up and consequently, lower costs for material production.

In this work, for the first time  $K_2[Mn(NH_2)_4]$  and  $K_2[Zn(NH_2)_4]$  were synthesized by mechanochemical reaction.  $K_2[Mn(NH_2)_4]$ -8LiH mixture showed excellent hydrogen absorption properties. In addition, an excellent material for electrode application (*i.e.*  $Li_2[MnN_4]$ ) was obtained by dehydrogenation of  $K_2[Mn(NH_2)_4]$ -8LiH.

The formula of  $K_2[Zn(NH_2)_4]$  was proposed for the product of the reaction between a zinc salt and  $KNH_2$  in liquid  $NH_3$  by Juza in 1937.<sup>13</sup> Prior to this, it was first synthesized by Fitzgerald in 1907, when crystals were grown from  $Zn/Zn(NH_2)_2$  in a solution of  $KNH_2$  in liquid  $NH_3$  at ambient temperature.<sup>14</sup> In 1969, Brisseau and Rouxel found that  $K_2[Zn(NH_2)_4]$  is a triclinic unit cell. More detailed unit cell parameters with  $a = 6.730(1)$  Å,  $b = 7.438(1)$  Å,  $c = 8.019(2)$  Å,  $\alpha = 72.03(2)^\circ$ ,  $\beta = 84.45(2)^\circ$ , and  $\gamma = 63.82(1)^\circ$  were determined until 1997.<sup>15</sup> Monoclinic  $K_2[Mn(NH_2)_4]$  was first synthesized in 1975 by Drew *et al.* with the same method as for  $K_2[Zn(NH_2)_4]$ .<sup>16</sup> In 2013, a new monoclinic  $K_2[Zn(NH_2)_4]$ , which is isotypic to  $K_2[Mn(NH_2)_4]$  was obtained by Richter *et al.* using an ammonothermal synthesis method under 720 K and 249 MPa pressures of ammonia for *ca.* 7 days.<sup>17</sup> For this work,  $K_2[Zn(NH_2)_4]$  (triclinic) and  $K_2[Mn(NH_2)_4]$  were synthesized under moderate conditions by ball milling K and Zn/Mn in a molar ratio of 2:1 at 0.7 MPa of  $NH_3$  for 12 h. The characterization was carried out by high resolution X-ray diffraction experiments (Hard X-ray diffraction beamline – P02, PETRA III, Hamburg). Based on the Rietveld analysis results,  $K_2[Zn(NH_2)_4]$  (triclinic) and  $K_2[Mn(NH_2)_4]$  were obtained with high purities (Fig. 1). According to the Rietveld refinements, *ca.*  $4.6 \pm 0.2$  wt% of unreacted Mn was found in the

$K_2[Mn(NH_2)_4]$  sample. This is most likely due to the fact that a fraction of metallic manganese was adhered on areas of the walls of the milling vial were only few collisions took place. However the results indicate that  $K_2[Zn(NH_2)_4]$  (triclinic) and  $K_2[Mn(NH_2)_4]$  were synthesized by ball milling metallic manganese/zinc with potassium under moderate conditions without use of high pressures, high temperatures and long reaction times. However, the unit cell parameters of the mechanochemically synthesized  $K_2[Zn(NH_2)_4]$  (triclinic) and  $K_2[Mn(NH_2)_4]$  differ slightly from the values reported in literatures (Table S1, ESI†).<sup>15,16</sup> These differences maybe attribute to the different synthesis methods and measurement uncertainties.

Thermogravimetry (TG) combined with differential thermal analysis (DTA) was employed to investigate the thermal decomposition process of the as-prepared triclinic  $K_2[Zn(NH_2)_4]$  and  $K_2[Mn(NH_2)_4]$  (Fig. 2). After heating to *ca.* 500 °C, the weight losses of both  $K_2[Zn(NH_2)_4]$  and  $K_2[Mn(NH_2)_4]$  were about 35 wt% in the TG curves. However, the thermal decomposition process of  $K_2[Mn(NH_2)_4]$  is very different from that of  $K_2[Zn(NH_2)_4]$ . Based on the weight losses, *ca.* 2 equiv.  $NH_3$  were released from  $K_2[Mn(NH_2)_4]$  and  $K_2[Zn(NH_2)_4]$  at *ca.* 360 and 420 °C, respectively.

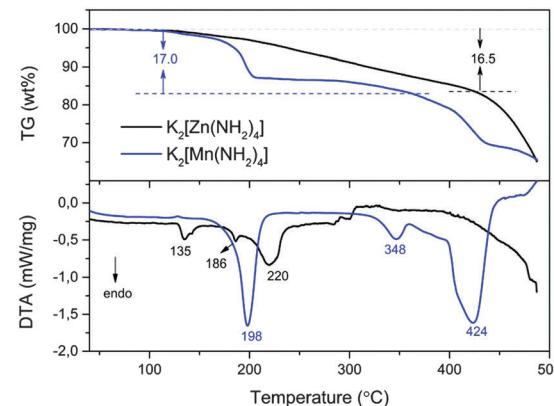


Fig. 2 TG-DTA curves of the as-synthesized triclinic  $K_2[Zn(NH_2)_4]$  and  $K_2[Mn(NH_2)_4]$ , heating from 30 °C to 500 °C with a heating rate of 5 °C min<sup>-1</sup>.

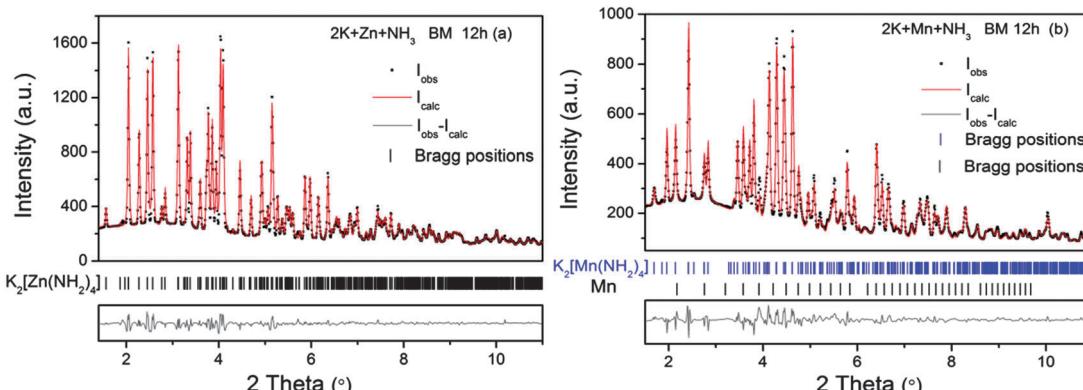


Fig. 1 High resolution powder X-ray diffraction patterns (black dots) and Rietveld refinements (red line) of the as-synthesized triclinic  $K_2[Zn(NH_2)_4]$  – (a) and  $K_2[Mn(NH_2)_4]$  – (b). Bragg reflections for each phase are indicated by the tick marks. The bottom line represents the difference curve ( $I_{\text{obs}} - I_{\text{calc}}$ ). Weighted  $R$ -factors as low as  $R_w$  (%) = 6.83 and  $R_w$  (%) = 6.35 were obtained for (a) and (b) respectively.



In addition, there was no evidence of weight losses for  $K_2[Mn(NH_2)_4]$  in the temperature range between 200 and 300 °C, meaning that a relatively stable compound could be formed at this point. DTA measurements show that both  $K_2[Mn(NH_2)_4]$  and  $K_2[Zn(NH_2)_4]$  decompose in a multi-steps reaction. The  $K_2[Mn(NH_2)_4]$  decomposition process can be clearly divided into three steps upon heating from 30 to 500 °C. For  $K_2[Zn(NH_2)_4]$  three separate thermal events at 135, 186 and 220 °C can be observed clearly, which correlate well with the results of Richter *et al.*<sup>17</sup> The first signal at 135 °C can be attributed to the phase transition from triclinic to monoclinic. After heating to *ca.* 420 °C, mechanochemically synthesized  $K_2[Zn(NH_2)_4]$  and ammonothermally synthesized  $K_2[Zn(NH_2)_4]$  undergo similar weight losses (16.5 wt% and 16.4 wt% respectively), meaning that the purities of these two materials are extremely close to each other's (Fig. S1, ESI†).

Recently, we found that the mixture of  $K_2[Zn(NH_2)_4]$  and 8LiH is a good hydrogen storage material due to its excellent hydrogen absorption properties.<sup>18</sup> Here the hydrogen sorption properties of  $K_2[Mn(NH_2)_4]$ -8LiH were studied and compared with the reference material  $LiNH_2$ -2LiH. The results of this investigation are summarized in Fig. S2 (ESI†) and Fig. 3. Fig. S2 (ESI†) shows that  $K_2[Mn(NH_2)_4]$ -8LiH decomposes in the temperature range between room temperature to 500 °C in 3 steps. Most of the hydrogen together with an almost undetectable amount of ammonia were released during the first two decomposition steps. Fig. 3 summarizes the volumetric de/re-hydrogenation properties (HERA, Quebec, Canada) of  $K_2[Mn(NH_2)_4]$ -8LiH and the reference material  $LiNH_2$ -2LiH. The results show that after heating to 400 °C *ca.* 4.2 and 4.3 wt% of hydrogen were released from  $K_2[Mn(NH_2)_4]$ -8LiH and  $LiNH_2$ -2LiH, respectively. Interestingly, the onset decomposition temperature of  $K_2[Mn(NH_2)_4]$ -8LiH is about 60 °C lower than that of the  $LiNH_2$ -2LiH sample. Noteworthy, from the inset in Fig. 3, it is known that most of hydrogen (~60% of the total capacity) can be hydrogenated by  $K_2[Mn(NH_2)_4]$ -8LiH sample during the time from 3990 to 4053 s (at which time the

temperature is close to ~230 °C), however, less than 2% of hydrogen was absorbed by the reference  $LiNH_2$ -2LiH during the same time. The rehydrogenation rate of  $K_2[Mn(NH_2)_4]$ -8LiH is one of the fastest absorption reaction rates known for amide-hydride systems.

It is known that  $LiNH_2$ -2LiH converts into  $Li_3N$  upon dehydrogenation to 500 °C, which shows a high reactivity towards most nitrides.<sup>10c</sup> Thus; the decomposition of such amide-hydride systems is a strategy to obtain transition metal nitrides.  $Li_7[MnN_4]$ , due to its high specific gravimetric capacity, in excess of 300 mAh g<sup>-1</sup> and excellent retention is a good candidate as a cathode material.<sup>19</sup> Usually,  $Li_7[MnN_4]$  is synthesized by heating the mixture of  $Li_3N$  and Mn under  $N_2$  at high temperature (> 700 °C) for long time (> 24 h).<sup>4c,20</sup> In this work,  $Li_7[MnN_4]$  is synthesized by dehydrogenation of  $K_2Mn(NH_2)_4$ -8LiH below 500 °C within 100 min. However,  $Li_7[MnN_4]$  is formed together with K and  $Mn_4N$  and unknown compounds (Fig. 4).

In summary,  $K_2[Mn(NH_2)_4]$  and  $K_2[Zn(NH_2)_4]$  were synthesized for the first time by mechanochemical reaction. These phases are extremely promising both as hydrogen storage materials and as intermediates toward the formation of transition metal nitrides. With the method described in this work,  $M[M'(NH_2)_n]$  can be synthesized in large-scale under mild temperatures, without the need of applying high gas pressures and long reaction times. After mixing  $K_2[Mn(NH_2)_4]$  with 8LiH, it released 4.2 wt% of  $H_2$  below 400 °C. Compared to the reference  $LiNH_2$ -2LiH,  $K_2[Mn(NH_2)_4]$ -8LiH showed improved de/re-hydrogenation performance. The dehydrogenated  $K_2[Mn(NH_2)_4]$ -8LiH sample can be rehydrogenated within 60 seconds at *ca.* 230 °C and 5 MPa of  $H_2$  with a rehydrogenation rate of *ca.* 3 wt% per min, which is one of the fastest rehydrogenation rates measured in amide-hydride systems. Moreover, this study has shown evidence of binary and ternary transition metal nitrides formation upon dehydrogenation of the mixtures of  $M[M'(NH_2)_n]$  and metal hydrides.

Financial support by the Helmholtz-Chinese Academy of Science Joint Research Group "RevHy"- "Study on the synthesis,

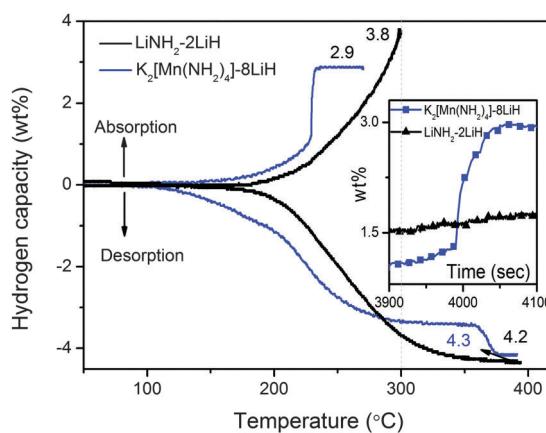


Fig. 3 De/re-hydrogenation curves of the as ball milled  $K_2[Mn(NH_2)_4]$ -8LiH sample, heating from room temperature to 400 °C at a ramping rate of 3 °C min<sup>-1</sup> under vacuum for dehydrogenation, heating from room temperature to 300 °C at a heating rate of 3 °C min<sup>-1</sup> and 5 MPa of  $H_2$  for re-hydrogenation. Inset is the re-hydrogenation curve of as ball milled  $K_2[Mn(NH_2)_4]$ -8LiH and  $LiNH_2$ -2LiH samples under different absorption time.

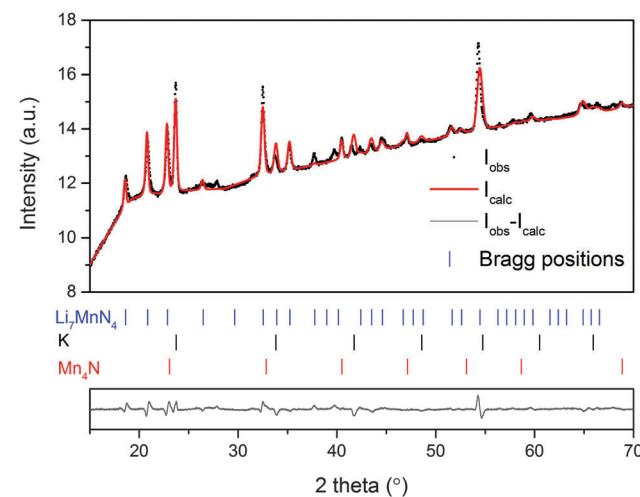


Fig. 4 Rietveld analysis for the X-ray powder diffraction pattern of the as ball milled  $K_2[Mn(NH_2)_4]$ -8LiH sample after thermal desorption to 500 °C in TG, (small black dots),  $R_w$  (%) = 1.26322.



structures and performance of complex hydrides systems for Reversible high capacity Hydrogen storage at low temperatures", Marie Curie Initial Training Network "ECOSTORE - Novel Complex Metal Hydrides for Efficient and Compact Storage of Renewable Energy as Hydrogen and Electricity" (grant 607040) is thankfully acknowledged.

We thank Dr Bednarcik Jozef and Dr Martin Etter for their kind helps on the high resolution X-ray diffraction experiments.

## Notes and references

- (a) D. S. Bem and H. C. Z. Loyer, *J. Solid State Chem.*, 1993, **104**, 467; (b) M. Nishijima, N. Tadokoro, Y. Takeda, N. Imanishi and O. Yamamoto, *J. Electrochem. Soc.*, 1994, **141**, 2966; (c) M. Nishijima, T. Kagohashi, M. Imanishi, Y. Takeda, O. Yamamoto and S. Kondo, *Solid State Ionics*, 1996, **83**, 107; (d) M. Nishijima, T. Kagohashi, Y. Takeda, M. Imanishi and O. Yamamoto, *J. Power Sources*, 1997, **68**, 510; (e) G. Hitoki, A. Ishikawa, T. Takata, J. N. Kondo, M. Hara and K. Domen, *Chem. Lett.*, 2002, 736; (f) J. L. Tirado, *Mater. Sci. Eng., R*, 2003, **40**, 103; (g) D. J. Ham and J. S. Lee, *Energies*, 2009, **2**, 873; (h) B. Cao, G. M. Veith, J. C. Neufeld, R. R. Adzic and P. G. Khalifah, *J. Am. Chem. Soc.*, 2013, **135**, 19186; (i) M.-S. Balogun, W. Qiu, W. Wang, P. Fang, X. Lu and Y. Tong, *J. Mater. Chem. A*, 2015, **3**, 1364; (j) S. Dong, X. Chen, X. Zhang and G. Cui, *Coord. Chem. Rev.*, 2013, **257**, 1946; (k) J. Guo, F. Chang, P. Wang, D. Hu, P. Yu, G. Wu, Z. Xiong and P. Chen, *ACS Catal.*, 2015, **5**, 2708; (l) R. S. Ningthoujam and N. S. Gajbhiye, *Prog. Mater. Sci.*, 2015, **70**, 50.
- (a) R. Juza and H. Hahn, *Z. Anorg. Allg. Chem.*, 1940, **244**, 125; (b) M. Futsuhara, K. Yoshioka and O. Takai, *Thin Solid Films*, 1998, **322**, 274; (c) R. Long, Y. Dai, L. Yu, M. Guo and B. Huang, *J. Phys. Chem. B*, 2007, **111**, 3379; (d) S.-H. Yoo, A. Walsh, D. O. Scanlon and A. Soon, *RSC Adv.*, 2014, **4**, 3306.
- (a) W. R. L. Lambrecht, M. Prikhodko and M. S. Miao, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **68**, 174411; (b) A. Janotti, S.-H. Wei and L. Bellaiche, *Appl. Phys. Lett.*, 2003, **82**, 766; (c) K. Suzuki, T. Kaneko, H. Yoshida, Y. Obi, H. Fujimori and H. Morita, *J. Alloys Compd.*, 2000, **306**, 66; (d) H. Jacobs and C. Stüve, *J. Less-Common Met.*, 1984, **96**, 323.
- (a) R. Juza, E. Anschütz and H. Puff, *Angew. Chem.*, 1959, **71**, 161; (b) R. Niewa, F. J. DiSalvo, D. K. Yang, D. B. Zax, H. Luo and W. B. Yelon, *J. Alloys Compd.*, 1998, **266**, 32; (c) R. Juza, K. Langer and K. Von Benda, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 360; (d) T. M. M. Richter, N. S. A. Alt, E. Schlücker and R. Niewa, *Z. Anorg. Allg. Chem.*, 2015, **641**, 1016.
- (a) E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H.-k. Mao and R. J. Hemley, *Nat. Mater.*, 2004, **3**, 294; (b) T. Hashimoto, F. Wu, J. S. Speck and S. Nakamura, *Nat. Mater.*, 2007, **6**, 568; (c) F. Rivadulla, M. Banobre-Lopez, C. X. Quintela, A. Pineiro, V. Pardo, D. Baldomir, M. A. Lopez-Quintela, J. Rivas, C. A. Ramos, H. Salva, J.-S. Zhou and J. B. Goodenough, *Nat. Mater.*, 2009, **8**, 947; (d) S. T. Oyama, *The Chemistry of Transition Metal Carbides and Nitrides*, Springer, 1995.
- M. Hasegawa and T. Yagi, *J. Alloys Compd.*, 2005, **403**, 131.
- (a) M. Zajac, J. Gosk, E. Grzanka, S. Stelmakh, M. Palczewska, A. Wysmolek, K. Korona, M. Kamińska and A. Twardowski, *J. Alloys Compd.*, 2008, **456**, 324; (b) H. Jacobs, D. Rechenbach and U. Zachwieja, *J. Alloys Compd.*, 1995, **227**, 10; (c) A. Leineweber, H. Jacobs and S. Hull, *Inorg. Chem.*, 2001, **40**, 5818; (d) T. M. M. Richter and R. Niewa, *Inorganics*, 2014, **2**, 29.
- H. Jacobs and U. Fink, *Z. Anorg. Allg. Chem.*, 1978, **438**, 151.
- (a) G. Kreiner and H. Jacobs, *J. Alloys Compd.*, 1992, **183**, 345; (b) B. Fröhling and H. Jacobs, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1108.
- (a) H. Cao, Y. Zhang, J. Wang, Z. Xiong, G. Wu and P. Chen, *Prog. Nat. Sci.*, 2012, **22**, 550; (b) P. Chen and M. Zhu, *Mater. Today*, 2008, **11**, 36; (c) P. Chen, Z. Xiong, J. Luo, J. Lin and K. L. Tan, *Nature*, 2002, **420**, 302.
- M. Pozzo and D. Alfè, *Int. J. Hydrogen Energy*, 2009, **34**, 1922.
- (a) A.-L. Chaudhary, D. A. Sheppard, M. Paskevicius, M. Saunders and C. Buckley, *RSC Adv.*, 2014, **42**, 21979; (b) J. Huot, D. B. Ravnsbaek, J. Zhang, F. Cuevas, M. Latroche and T. R. Jensen, *Prog. Mater. Sci.*, 2013, **58**, 30; (c) H. Y. Leng, T. Ichikawa, S. Hino, N. Hanada, S. Isobe and H. Fujii, *J. Power Sources*, 2006, **156**, 166; (d) C. Xu, S. De, A. M. Balu, M. Ojeda and R. Luque, *Chem. Commun.*, 2015, **51**, 6698; (e) P. G. McCormick, T. Tsuzuki, J. S. Robinson and J. Ding, *Adv. Mater.*, 2001, **13**, 1008; (f) B. D. Stojanovic, *J. Mater. Process. Technol.*, 2003, **143-144**, 78; (g) V. Sepelak, A. Duvel, M. Wilkering, K.-D. Becker and P. Heitjans, *Chem. Soc. Rev.*, 2013, **42**, 7507.
- R. Juza, *Z. Anorg. Allg. Chem.*, 1937, **231**, 121.
- F. F. Fitzgerald, *J. Am. Chem. Soc.*, 1907, **29**, 656.
- (a) L. Brisseau, J. Rouxel and C. R. Hebd, *C. R. Acad. Sci.*, 1969, **268**, 2308; (b) B. Fröhling and H. Jacobs, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1103.
- M. Drew, L. Guémás, P. Chevalier, P. Palvadeau and J. Rouxel, *Rev. Chim. Miner.*, 1975, **12**, 419.
- T. M. M. Richter, S. Zhang and R. Niewa, *Z. Kristallogr. - Cryst. Mater.*, 2013, **228**, 351.
- H. Cao, T. M. M. Richter, C. Pistidda, A. L. Chaudhary, A. Santoru, G. Gizer, R. Niewa, P. Chen, T. Klassen and M. Dornheim, *ChemSusChem*, 2015, **22**, 3777.
- (a) L. Ji, Z. Lin, M. Alcoutlaibi and X. Zhang, *Energy Environ. Sci.*, 2011, **4**, 2682; (b) J. Cabana, C. M. Ionica-Bousquet, C. P. Grey and M. R. Palacín, *Electrochem. Commun.*, 2010, **12**, 315.
- R. Niewa and F. J. DiSalvo, *Chem. Mater.*, 1998, **10**, 2733.

