

## Application 2040



### **Structural characterization of Sr(11BD4)2·2ND3 by powder neutron diffraction**

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Ammonia, NH<sub>3</sub>, is catalytically split to N<sub>2</sub> and H<sub>2</sub> and is a candidate for on-board hydrogen storage as a result of its high hydrogen content (17.3 wt%) and the ability to store 30 % more energy per volume than liquid hydrogen. However, due to the toxicity of NH<sub>3</sub> there are substantial safety issues that hamper widespread utilization. Ammonia reacts with metal borohydrides owing to formation of dihydrogen bonds and/or coordination to the metal producing metal borohydride ammoniates, M(BH<sub>4</sub>)<sub>m</sub>·nNH<sub>3</sub>. This is a newer class of materials, which has been studied for hydrogen storage purposes since 2009. The fact that the properties of metal borohydride ammoniates are somewhat tunable makes them highly interesting; the amount of NH<sub>3</sub> content, the strength of the dihydrogen bond and the electronegativity of the metal strongly influence the decomposition temperature and mechanism. Metal borohydrides with low electronegativity are destabilized by ammoniate formation while those with higher electronegativity are stabilized [1].

We recently published the synthesis and crystal structure of Sr(BH<sub>4</sub>)<sub>2</sub> [2], and have now synthesized the corresponding ammoniate. The unit cell is indexed in a tetragonal cell from powder X-ray diffraction data, and based on initial thermal analysis and the volume of the unit cell, the composition is likely Sr(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>. Since Cl<sup>-</sup> and BH<sub>4</sub><sup>-</sup> have similar size and same charge, metal borohydride ammoniates and metal chloride ammoniates are often isostructural, e.g. Mg(NH<sub>3</sub>)<sub>6</sub>Cl<sub>2</sub> and Mg(NH<sub>3</sub>)<sub>6</sub>(BH<sub>4</sub>)<sub>2</sub>. However, the ammoniate of SrCl<sub>2</sub> that are used for ammonia storage contains 8 NH<sub>3</sub> molecules, Sr(NH<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub>. We speculate that the difference between the ammoniates of SrCl<sub>2</sub> and Sr(BH<sub>4</sub>)<sub>2</sub> may be a consequence of strong dihydrogen bonds, Hδ<sup>+</sup>...δ<sup>-</sup>H, between H on NH<sub>3</sub> and BH<sub>4</sub>, respectively. Furthermore, the evaluation of the dihydrogen bonds may be used to understand why some metal borohydride ammoniates release NH<sub>3</sub>, while others release H<sub>2</sub> from dihydrogen elimination.

We propose to investigate the novel Sr(11BD4)<sub>2</sub>·2ND<sub>3</sub> in order to solve the crystal structure and obtain precise H positions by combined powder neutron diffraction and powder X-ray diffraction.

## References

- [1] L.H. Jepsen, M.B. Ley, T. R. Jensen et al., Boron-nitrogen based hydrides and reactive composites for hydrogen storage, *Mater Today*. 10.1016/j.mattod.2014.02.015.
- [2] D.B. Ravnsbæk, E.A. Nickels, T. R. Jensen et al., Novel alkali earth borohydride  $\text{Sr}(\text{BH}_4)_2$  and borohydride-chloride  $\text{Sr}(\text{BH}_4)\text{Cl}$ , *Inorg. Chem.* 52 (2013) 10877–10885