

# Destabilization of light borohydrides by pressure, temperature and by reaction with water

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Light borohydrides are considered as promising energy storage systems. However, they are not yet regarded as practical materials for hydrogen storage due to the excessive stability. Their destabilization can be achieved by varying thermodynamic parameters such as temperature and pressure or via chemical reaction, such as hydrolysis.

To address the temperature-induced changes in  $\text{LiBH}_4$  and  $\text{NaBH}_4$ , their structures have been studied for the first time by synchrotron diffraction on single crystals. This allowed us to unambiguously determine the symmetry and structure of the phases, in particular detect and quantify the disorder of the  $\text{BH}_4$  anions. The temperature evolution of the structures was studied by powder diffraction, which revealed lattice anharmonicity and shed light on microscopic mechanisms of the phase transitions. We show that B-H distances and H-B-H angles can be accurately determined even from powder X-ray diffraction data using area detectors. A correction of the apparent B-H distances is proposed. The  $\text{BH}_4$  tetrahedra are undistorted in all known ambient pressure phases.

Our studies of  $\text{LiBH}_4$  and  $\text{NaBH}_4$  in diamond anvil cells [1,2] showed that their high-pressure phases have structures different from those predicted by theory. The new *Ama2* structure of  $\text{LiBH}_4$  reveals a novel coordination of the  $\text{BH}_4$  anion by Li atoms, and exceptionally short B-H...H-B distances of 1.9 Å at 2.4 GPa. The DFT-optimized structure indicates the deformation of the  $\text{BH}_4$  unit, which is likely to decrease an activation barrier for hydrogen desorption. This phase may show more favourable hydrogen storage properties than pure  $\text{LiBH}_4$  if stabilized by chemical substitution at ambient pressure.

X-ray diffraction on single crystals of  $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$  showed [3] that the  $\text{BH}_4$  anion is undistorted, despite short observed dihydrogen O-H<sup>δ+</sup>...<sup>δ-</sup>H-B bonds (1.77-1.95 Å). *In-situ* powder diffraction demonstrated that the hydrate does not directly release hydrogen – it decomposes at 314K into  $\text{NaBH}_4$  and  $\text{H}_2\text{O}$ , the latter two compounds then react, releasing hydrogen. For the first time, the intermediate phases in the reaction of  $\text{LiBH}_4$  with water have been identified. The dihydrogen bond lengths and enthalpies of formation were evaluated from the DFT calculations starting from the experimentally determined structures. The shortest H<sup>δ+</sup>...<sup>δ-</sup>H bond in the first intermediate phase, the hydrate of  $\text{LiBH}_4$ , is only 1.63 Å (!) long, indicating possible instability towards hydrogen desorption. The second intermediate phase is the precipitate that accounts for the incomplete hydrolysis of  $\text{LiBH}_4$ . The results are of significant fundamental and practical interest.

## References

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