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Li-disorder in the hydrogen storage material $\text{LiCe}(\text{BH}_4)_3\text{Cl}$ and detailed investigation of hydrogen positions

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Borohydrides have received considerable interest as hydrogen storage materials due to their very high gravimetric hydrogen densities (e.g. 18.1 w% H in LiBH_4). However, their practical applications are hampered by several issues, most notably sluggish kinetics on rehydrogenation.

Recently, a new class of borohydrides with the general composition $\text{LiRE}(\text{BH}_4)_3\text{Cl}$ (RE= La, Ce, Gd) has been discovered [1-3]. These materials have fair hydrogen capacity despite the presence of rare earth elements (e.g. 5.3 wt% H in $\text{LiCe}(\text{BH}_4)_3\text{Cl}$). Interestingly, this novel class of materials has been shown to exhibit high Li-ion conductivity even at ambient temperature [2-3]. This is highly interesting since it can be the key to fast reaction rates in the solid state and novel classes of combined hydrogen storage and ion conducting materials.

Two different structural models have been proposed for $\text{LiCe}(\text{BH}_4)_3\text{Cl}$, which differ in the distribution of Li-ions. One reports Li in fully occupied sites, indicating a high degree of order [1], while other reports Li distributed over several partly ordered sites, thus indicating a higher degree of disorder [2]. The uncertainty in the Li-distribution in the material is due to the fact that both reports are based on powder X-ray diffraction, and Li is a very weak X-ray scatterer due to its low atomic number. Furthermore, the hydrogen positions unknown, which will also be addressed in the proposed investigation.

Knowledge about the Li-ion distribution is crucial for a fundamental understanding of the mechanism of Li-ion conduction and its influence on the reaction kinetics. If the Li-ion disorder is confirmed at ambient temperature, it will also shed light on the diffusion mechanism to investigate if the disorder is retained at low temperature (e.g. around 10 K). Such knowledge can be obtained by powder neutron diffraction (PND) since Li has a better contrast compared to the other elements involved with neutrons compared to X-rays. Moreover, neutron diffraction will give precise information about the hydrogen positions which are impossible to determine with confidence from PXD. The PND experiment is challenging, though, due to several problematic elements in the material: Hydrogen has a strong incoherent scattering cross section for neutrons while boron and lithium have strong and intermediate absorption cross section for neutrons, respectively.

To overcome these problems a triple isotope enriched sample has been made: ${}^7\text{-LiCe}({}^{11}\text{-BD}_4)_3\text{Cl}$ and the sample purity and quality was investigated by in-house PXD. The use of the isotopes ${}^7\text{-Li}$ and ${}^{11}\text{-B}$ rather than the natural elements greatly reduce the neutron absorption of the sample. The use of D instead of H gives much less incoherent neutron scattering resulting in data with much less noise.

To conclude, the proposed PND experiment can give very valuable detailed structural information about both Li and H (D) positions in $\text{LiCe}(\text{BH}_4)_3\text{Cl}$, which is not possible to obtain by other techniques. We have obtained a suitable sample for a PND experiment by triple isotope substitution. We therefore apply to H2FC for use of the powder neutron diffractometer PUS in the JEEP II infrastructure to investigate the material, both at ambient and low temperature (~ 10 K).

We hope, that the new structural insight will allow rational design of novel combined hydrogen storage and Li-ion conducting materials in the future.