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Several bi- and tri- metallic borohydride systems were studied:

$LiBH_4$: $K(Rb,Cs)BH_4$: $Mg(BH_4)_2$

Novel trimetallic framework borohydride $LiKMg(BH_4)_4$ is formed in system with potassium. Systems with rubidium and caesium show formation of other phases that are not yet fully identified. Orthorhombic structure of $LiKMg(BH_4)_4$ is built from $[LiMg(BH_4)_4]^-$ sheets showing a disorder between Li and Mg. Various ordered models were prepared and optimized by DFT calculations and the correct symmetry of the locally ordered crystal was identified. When heated $LiKMg(BH_4)_4$ reacts with residual KBH_4 according to the reaction

$$2\ LiKMg(BH_4)_4 + KBH_4 \rightarrow Li_2K_3Mg_2(BH_4)_9$$

resulting in polymerisation to double sheets. The in-situ Raman setup available at SNBL was important to resolve this reaction and exclude various other potential models of the system behaviour. The manuscript with the results is currently being prepared.

$LiBH_4$: $RbBH_4$

Inspired by the compound $LiK(BH_4)_2$ showing the decomposition temperature between those of $LiBH_4$ and KBH_4, we have investigated other ball milled mixtures of alkali metal borohydrides. In the system Li-Rb two new compounds $Li_2Rb(BH_4)_3$ and $LiRb(BH_4)_2$ were found, the second one having RT and HT (> 410 K) phases. Their decomposition temperatures are lower than that of starting binary alkali metal borohydrides. The RT phase of $LiRb(BH_4)_2$ contains a square 4-fold coordination of Li, for the first time observed among borohydrides. On the other side $Li_2Rb(BH_4)_3$, a lithium rich compound, contains tetrahedraly coordinated lithium ordered in helical chains along the hexagonal c-axis, a promising structural feature for Li-conductivity. Publication with these results is being prepared. Also

Li-Cs system shows a great variety of different phases as concluded from the temperature depended synchrotron powder diffraction data which are currently analysed.

$KBH_4/RbBH_4 : CrCl_3$

Our approach of studying the crystal chemistry of transition metals in borohydrides by synthesising bimetallic compounds instead of the pure binary transition metal borohydrides (unstable) is proving to be the right way. A phase $KTi(BH_4)_4$ was discovered during an earlier beamtime at SNBL, the above mentioned system is proving to provide new borohydride phases also. The results are still being analysed.

Perovskite borohydrides

This project was opened at SNBL with the discovery of $KMn(BH_4)_3$ that was published in 2012. A total of 6 perovskite systems and substitution variants were studied during this beamtime to establish systematic trends of symmetry, formability and stability. It is an ongoing project at SNBL, the first manuscript has been written and will be submitted soon.

$Mg(BH_4)_2(NH_3BH_3)_2$

A novel compound, $Mg(BH_4)_2(NH_3BH_3)_2$ has been synthesized from different solid state reactions between $Mg(BH_4)_2$ and NH_3BH_3. $Mg(BH_4)_2(NH_3BH_3)_2$ contains 17.4 wt% H_2 and 20 H atoms pr. magnesium metal. From T-ramping the decomposition temperature was determined to be below 100 °C. From the data obtained at SNBL we were able to index the unit cell and then combined with data obtained at Diamond, Oxford in September, we were finally able to solve the structure. It crystallizes in an orthorhombic unit cell with space group symmetry $P2_12_12_1$ and contains dihydrogen bondings, which are now studied by DFT calculations. One manuscript is in progress.

$(Na,K,Rb,Cs)BH_4 : Sr(BH_4)_2$

Strontium borohydride remains a less studied metal borohydride compared to well known materials as $Mg(BH_4)_2$ and $Ca(BH_4)_2$. New synthesis methods have made production of pure strontium borohydride possible. Several systems containing $NaBH_4$, KBH_4, $RbBH_4$ and $CsBH_4$ alongside $Sr(BH_4)_2$ were studied using *in situ* SR-PXD at SNBL. Several new phases have been discovered and structural analysis is in progress.

Mixed metal borohydrides $Y(BH_4)_3$

A new project was started with bimetallic borohydrides, i.e. $Y(BH_4)_3$−MBH_4, M = Li, Na, Rb and Cs, using salt-free and metal hydride free $Y(BH_4)_3$. This is the first study of mixed metal borohydride system using completely pure $Y(BH_4)_3$. $Y(BH_4)_3$ was produced using a new synthesis method developed at Aarhus University, Denmark. The solvent used for purification of $Y(BH_4)_3$ forms a novel solvent containing structure, and the structure was solved from data collected at SNBL. New compounds were obtained in mixtures containing of $RbBH_4/CsBH_4$ and $Y(BH_4)_3$. This project form the basis for further research conducted in a following beam time at SNBL in November 2012. The salt-free $Y(BH_4)_3$ synthesised at Aarhus Univ. also allowed synthesis of novel trimetallic mixtures using $Y(BH_4)_3$, which was also further studied. One manuscript will be submitted about high-pressure studies of $Y(BH_4)_3$ and solvent mediate synthesis of $Y(BH_4)_3$ containing data from experiments conducted at SNBL.