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| | Experiment title: Synthesis and structural characterization of novel metal borohydrides for hydrogen storage and lithium batteries. | Experiment number: 01-02-970 |
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Several bimetallic systems prepared by mechanosynthesis were studied. The systems which show formation of novel bimetallic borohydrides are:

KBH₄ : ZnCl₂ [1]

Three novel potassium-zinc borohydrides/chlorides are described. $\text{KZn}(\text{BH}_4)_3$ and $\text{K}_2\text{Zn}(\text{BH}_4)_x\text{Cl}_{4-x}$ form in ball milled $\text{KBH}_4:\text{ZnCl}_2$ mixtures with molar ratios ranging from 1.5:1 up to 3:1. On the other hand, $\text{K}_3\text{Zn}(\text{BH}_4)_x\text{Cl}_{5-x}$ forms only in the 2:1 mixture after longer milling times. The new compounds have been studied by a combination of *in situ* synchrotron powder diffraction, thermal analysis, Raman spectroscopy and DFT calculations. Rhombohedral $\text{KZn}(\text{BH}_4)_3$ contains an anionic complex $[\text{Zn}(\text{BH}_4)_3]^-$ with D_3 (32) symmetry, located inside a rhombohedron K_8 . $\text{KZn}(\text{BH}_4)_3$ contains 8.1 wt% of hydrogen and decomposes at ~385 K with a release of hydrogen and diborane similar to other Zn-based bimetallic borohydrides like $M\text{Zn}_2(\text{BH}_4)_5$ ($M=\text{Li}, \text{Na}$) and $\text{NaZn}(\text{BH}_4)_3$. The decomposition temperature is much lower than for KBH_4 . Monoclinic $\text{K}_2\text{Zn}(\text{BH}_4)_x\text{Cl}_{4-x}$ contains a tetrahedral complex anion $[\text{Zn}(\text{BH}_4)_x\text{Cl}_{4-x}]^{2-}$ located inside an Edshammar polyhedron (pentacapped trigonal prism) K_{11} . The compound is a monoclinically distorted variant of the paraelectric orthorhombic *ht*-phase of K_2ZnCl_4 (structure type K_2SO_4). $\text{K}_2\text{Zn}(\text{BH}_4)_x\text{Cl}_{4-x}$ releases BH_4 starting from 395 K, forming Zn and KBH_4 . As the reaction proceeds and x decreases, the monoclinic distortion of $\text{K}_2\text{Zn}(\text{BH}_4)_x\text{Cl}_{4-x}$ diminishes and the structure transforms at 445 K into the orthorhombic *ht*-phase of K_2ZnCl_4 . Tetragonal $\text{K}_3\text{Zn}(\text{BH}_4)_x\text{Cl}_{5-x}$ is a substitutional and deformation variant of the tetragonal ($I4/mcm$) Cs_3CoCl_5 structure type possibly with the space group $P4_2/nm$. $\text{K}_3\text{Zn}(\text{BH}_4)_x\text{Cl}_{5-x}$ decomposes nearly at the same

temperature as $\text{KZn}(\text{BH}_4)_3$, *i.e.* at ~ 400 K with a formation of $\text{K}_2\text{Zn}(\text{BH}_4)_x\text{Cl}_{4-x}$ and KBH_4 , indicating that the compound is an adduct of the two latter compounds.

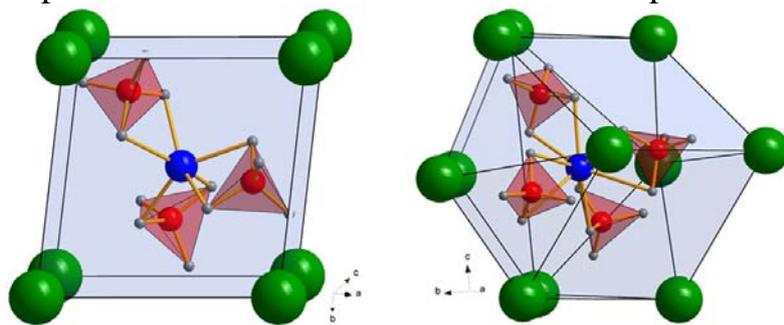


Figure 1: Triangular anionic complex $[\text{Zn}(\text{BH}_4)_3]^-$ located in a deformed alkali metal cage K_8 in the crystal structure of $\text{KZn}(\text{BH}_4)_3$ (left) and tetrahedral anionic complex $[\text{Zn}(\text{BH}_4)\text{Cl}_4]^{2-}$ located in Edshammar polyhedron (pentacapped trigonal prism) K_{11} (right).

KBH_4 : $\text{Mg}(\text{BH}_4)_2$ and KBH_4 : $\text{Mn}(\text{BH}_4)_2$ [2]

Four novel bi-metallic borohydrides have been discovered $\text{K}_2\text{M}(\text{BH}_4)_4$ ($M = \text{Mg}$ or Mn), $\text{K}_3\text{Mg}(\text{BH}_4)_5$, $\text{KMn}(\text{BH}_4)_3$, and are carefully investigated structurally as well as regarding their decomposition reaction mechanism by means of in-situ synchrotron radiation powder X-ray diffraction (SR-PXD), vibrational spectroscopies (Raman and IR), thermal analysis (TGA and DTA) and ab initio density functional theory (DFT) calculations. Mechano chemical synthesis (ball-milling) using the reactants KBH_4 , $\alpha\text{-Mg}(\text{BH}_4)_2$ and $\alpha\text{-Mn}(\text{BH}_4)_2$ ensures chlorine free reaction products. A detailed structural analysis reveals significant similarities as well as surprising differences among the two isomorphs $\text{K}_2\text{M}(\text{BH}_4)_4$, most importantly concerning the extent to which the complex anion $[\text{M}(\text{BH}_4)_4]^{2-}$ is isolated in the structure. Anisotropic thermal expansion and an increase in symmetry at high temperatures in $\text{K}_3\text{Mg}(\text{BH}_4)_5$ is ascribed to the motion of BH_4 groups inducing hydrogen repulsive effects, the dynamics of $\text{K}_3\text{Mg}(\text{BH}_4)_5$ are investigated. Decomposition in the manganese system proceeds via the formation of $\text{KMn}(\text{BH}_4)_3$, the first perovskite type borohydride reported up to date.

LiBH_4 : KBH_4 : $\text{Mg}(\text{BH}_4)_2$

Formation of a novel framework borohydride $\text{LiKMg}(\text{BH}_4)_4$ is observed. Its orthorhombic structure was verified by DFT calculations, and studied IR and Raman spectroscopies. The high temperature decomposition/phase transition is currently studied by in-situ synchrotron radiation powder diffraction, IR and mass spectroscopies, and by TG and DSC.

LiBH_4 : $\text{M}(\text{BH}_4)_2$: ZnCl_2 ($M = \text{Mg}, \text{Mn}$)

Formation of a first trimetallic borohydride $\text{Li}(\text{Li}_2\text{M})\text{Zn}_5(\text{BH}_4)_{15}$ ($M = \text{Mg}, \text{Mn}$) is observed. Its hexagonal structure was verified by DFT calculations. As part of lithium is loosely located in octahedral coordination, the ionic Li^+ conductivity is currently studied by impedance spectroscopy.

(1) Cerny R., Ravnsbæk D., Schouwink P., Filinchuk Ya., Penin N., Teyssier J., Smrcok L. and Jensen T.R. *J. Phys. Chem. C*, 116(2012)1563-1571.

(2) Schouwink P., D'Anna V., Ley M.B., Lawson Daku L.M., Richter B., Jensen T.R., Hagemann H. and Cerny R. *J. Phys. Chem. C*, submitted.