



Experiment title:

Garnet-type and spinel-type metal borohydrides as superionic conductors.

Experiment number:

01-02-1022

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Shifts: 12	Local contact(s): Dr. V. Diadkin	<i>Received at ESRF:</i>

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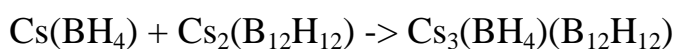
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Different ball-milled mixtures were studied:

LiBH₄ : KBH₄ (or RbBH₄ or CsBH₄) : Y(BH₄)₃

These trimetallic systems were aimed for preparation of **garnet-like borohydride** containing lithium on disordered tetrahedral site. The double-perovskite Li(Rb,Cs)₂Y(BH₄)₆ was observed among many other novel phases instead. Few additional samples were, i.e. several binary system, and starting products suspected of the NaBH₄ contamination. Now the project is closed, and a publication is under preparation.

Formation of an unknown compound was observed as a thermal decomposition product of nearly all ball-milled mixtures. The compound has formed in a broad range of starting ratios, and has shown high thermal stability. It was finally characterized as alkali metal borohydride containing icosahedral closoborane anion B₁₂H₁₂²⁻, and having anti-perovskite structure type (Figure 1). We have prepared the Cs-analog by ball-milling according to the reaction



The compound is an analogous of A₃H(B₁₂H₁₂) (A=K, Rb, Cs, NH₄, H = Cl, Br, I) [1,2]. Its high-temperature cubic anti-perovskite structure transforms below 300°C to a monoclinic phase, and decomposes at ~ 550°C.

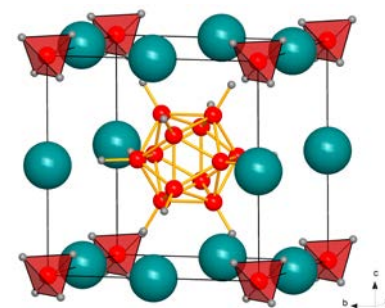


Figure 1: Anti-perovskite type borohydride A₃(BH₄)(B₁₂H₁₂) (A=Rb, Cs). A green-blue, BH₄ and B red.

Perovskite-borohydrides

Within the continuation of our perovskite-borohydride project following compounds were studied by T-ramping of as ball-milled mixtures:

$\text{NH}_4\text{Cl} : \text{LiBH}_4 : \text{Ca}(\text{BH}_4)_2$

Formation of a hydrogen rich perovskite-borohydride (15.6 wt.% of hydrogen) $(\text{NH}_4)\text{Ca}(\text{BH}_4)_3$ (Figure 2) was observed in ball-milled mixtures $\text{NH}_4\text{Cl} + \text{LiBH}_4 + \text{Ca}(\text{BH}_4)_2$. Lithium borohydride apparently does not participate in the formation of a new compound but acts as a source of borohydride in the synthesis. The presence of both *protic* (NH_4^+) and *hydridic* (BH_4^-) hydrogen in the same compound is known to *promote H_2 molecule release*, on the other side the presence of the metal cation such as Ca^{2+} will stabilize the otherwise too unstable hydrogen rich ammonium borohydride NH_4BH_4 according to the inversed relation between the *stability* and *cation electronegativity*.

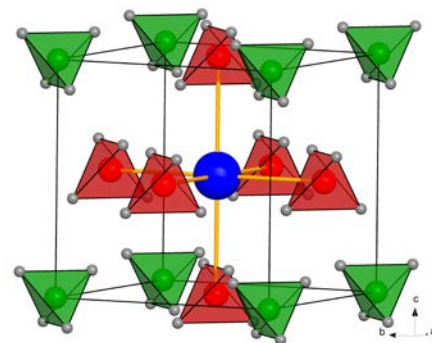


Figure 2: Perovskite type borohydride $(\text{NH}_4)\text{Ca}(\text{BH}_4)_3$. Ca blue, BH_4 red, NH_4 green

$\text{RbCa}(\text{BH}_4)_3$, $\text{RbCa}_{0.5}\text{Mg}_{0.5}(\text{BH}_4)_3$, $\text{KCa}(\text{BH}_4)_3$, $\text{CsMn}(\text{BH}_4)_3$, $\text{CsPb}(\text{BH}_4)_3$, $\text{CsSn}(\text{BH}_4)_3$, $(\text{CH}_3\text{NH}_3)\text{Ca}(\text{BH}_4)_3$, $\text{CsEu(II)}(\text{BH}_4)_3$, $\text{Rb}_2\text{Eu(III)}(\text{BH}_4)_6$. In addition to perovskite-type borohydride phosphors we studied the binary compounds $\text{Eu}(\text{BH}_4)_2$ and $\text{Eu}(\text{BH}_4)_3$. Eu^{3+} is not particularly stable in the reducing BH_4^- environment, which makes it useless for luminescence. We have begun to understand the concepts behind borohydride perovskites from past experiments and the present one at SNBL and are now searching for applications.

Other systems

Few other light-metal hydride systems were studied: ball-milled mixtures of azolates and complex hydrides, samples in $(\text{Li}, \text{Na}, \text{Ca})\text{BH}_4\text{-Al}(\text{BH}_4)_3$ systems, Li- and K- based hydrazinidoboranes, single-crystal structures of some alkali-metal imidazolates (3 new structures obtained). Other powder diffraction data are being analysed.

Ammoniates of $\text{Mn}(\text{BH}_4)_2$, $\text{Mn}(\text{BH}_4)_2 \cdot x\text{NH}_3$ ($x = 2, 3, 6$)

$\text{Mn}(\text{BH}_4)_2$ reacts with dry ammonia gas to form a new compound $\text{Mn}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, which crystallizes is structural to $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$. Mechanochemical mixtures of $\text{Mn}(\text{BH}_4)_2 \cdot 6\text{NH}_3\text{-Mn}(\text{BH}_4)_2$ (4:2, 3:3 and 2:4) were prepared in attempts to modify the coordination number of NH_3 . Sample $\text{Mn}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ is isostructural to $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$. The structural analysis of the mixture of $\text{Mn}(\text{BH}_4)_2 \cdot 6\text{NH}_3\text{-Mn}(\text{BH}_4)_2$ (3:3) is in progress.

Thermal decomposition of NaNH_2 .

From T-ramping of NaNH_2 and NaNH_2 added small amount of NaOH a new crystalline compound (indexed in a tetragonal cell) is observed from a reaction between the starting materials. This lowers the melting point for the sample from 200 to 162 °C. Further analysis is in progress.

[1] O.A. Kanaeva et al. *Rus. J. Inorg. Chem.* 1990, **35**, 1421-1422. [2] I. Tiritiris et al. *Z. Naturforsch.* 2005, **60b**, 627-639.