FunHy Newsletter

Who and where?

Jakob B. Grinderslev, Kasper T. Møller, Martin Bremholm and Torben R. Jensen has recently published the article *Trends in Synthesis, Crystal Structure, and Thermal and Magnetic Properties of Rare-Earth Metal Borohydrides* in Inorganic Chemistry (DOI: https://doi.org/10.1021/acs.inorgchem.8b03258)

Why?

Comprehensive search for potential solid-state hydrogen storage materials, also within boron-containing compounds, has exposed several new materials exhibiting properties suitable for other applications, *e.g.* heat storage and batteries. The rare-earth metal borohydrides investigated here may possess other interesting properties, *e.g.* luminescence has been observed of solvates $RE(BH_4)_2(THF)_2$, *RE* = Eu and Yb, and in the perovskite-type metal borohydride $CsEu(BH_4)_3$. Additionally, $Gd(BH_4)_3$ and the potassium and caesium-derivatives have been investigated for their potential use for magnetic refrigeration. Furthermore, several rare-earth borohydride derivatives, *e.g.* $RE(BH_4)_x$-*n*THF, have been widely investigated as reducing agents or catalysts within organic and polymer chemistry. Little research has been conducted on the pure $RE(BH_4)_x$, and are thus investigated here.

How?

To investigate the rare-earth metal borohydrides, a comprehensive amount of synthesis for the complete series of rare-earths were performed. Synthesis, crystal structures, thermal and magnetic properties of the complete series of halide-free rare-earth (*RE*) metal borohydrides are presented in the article. Fifteen new metal borohydride structures are reported. The trends in crystal structures, thermal behavior, and magnetic properties for the entire series of $RE(BH_4)_x$ are compared and discussed. The $RE(BH_4)_x$ possess a very rich crystal chemistry, dependent on the oxidation state and the ionic size of the rare-earth ion. Due to the lanthanide contraction, there is a significant decrease in the volume of the RE^{3+}-ion with increasing atomic number, which correlates linearly with the unit cell volume of the α- and β-$RE(BH_4)_3$ polymorphs and the solvated

complexes α-RE$(BH_4)_3$·$S(CH_3)_2$. The thermal analysis reveals a one-step decomposition pathway in the temperature range from 247 to 277 °C for all *RE*$(BH_4)_3$, except Lu$(BH_4)_3$, which follows a three-step decomposition pathway. In contrast, the *RE*$(BH_4)_2$ decompose at higher temperatures in the range 306 to 390 °C, due to lower charge density on the rare-earth ion. The *RE*$(BH_4)_3$ show increasing stability with increasing Pauling electronegativity, which contradicts other main group and transition metal borohydrides. The majority of the compounds follow Curie-Weiss paramagnetic behaviour down to 3 K with weak antiferromagnetic interactions and magnetic moments in accord with that of isolated 4f ions. Some of the *RE*$(BH_4)_x$ display varying degrees of temperature-dependent magnetic moments due to low-lying excited stated induced by crystal field effects. Additionally, a weak antiferromagnetic ordering is observed in Gd$(BH_4)_3$, indicating superexchange through a borohydride group.

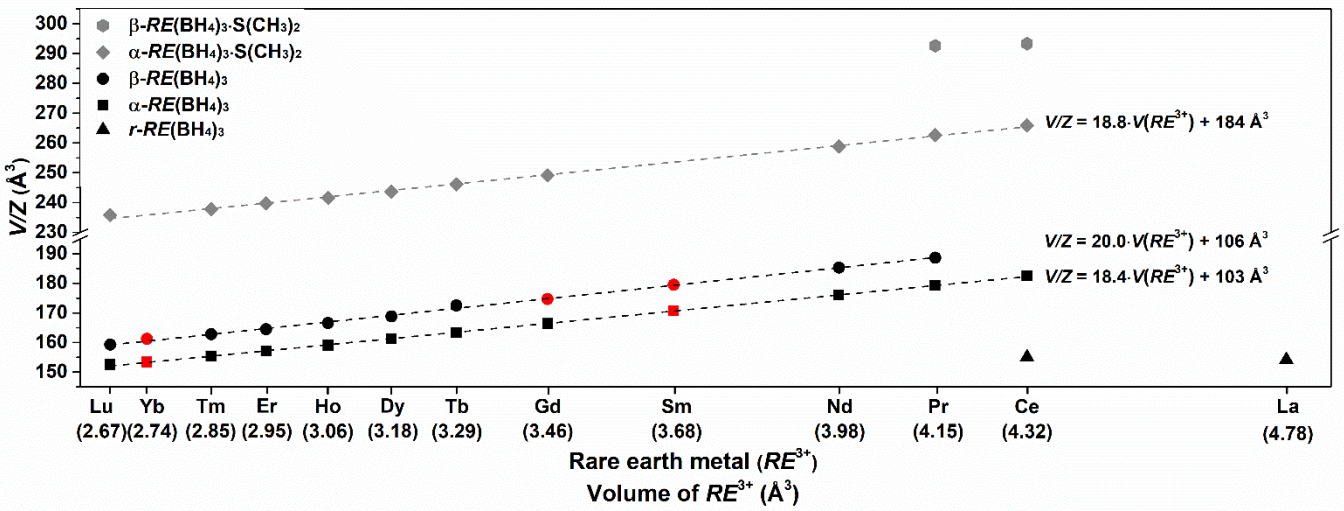

Figure 1. The volume per formula unit (*V/Z*) at room temperature is shown as a function of the volume of the RE^{3+}-ion for the *RE*$(BH_4)_3$ and *RE*$(BH_4)_3$·$S(CH_3)_2$. The *RE*$(BH_4)_3$ crystallise in three different crystal structures, the *r*-*RE*$(BH_4)_3$ (*R-3c*), the α-*RE*$(BH_4)_3$ (*Pa-3*) and the β-*RE*$(BH_4)_3$ (*Fm-3c*) structure type. *RE* = Sm and Yb and β-Gd$(BH_4)_3$ are obtained from literature values. The *RE*$(BH_4)_3$·$S(CH_3)_2$ crystallise in two different crystal structures, α- and β-*RE*$(BH_4)_3$·$S(CH_3)_2$ ($P2_1/c$). A linear trend line is shown for α-/β-*RE*$(BH_4)_3$ and α-*RE*$(BH_4)_3$·$S(CH_3)_2$.

FunHy webpage: http://inano.au.dk/about/research-groups/nano-energy-materials/projects/neutrons-for-multi-functional-hydrides-funhy/