	Experiment title: Framework and molecular metal borohydrides: high pressure studes assisted by metal oxides analogy.	**Experiment number**: 01-02-1023
Beamline: BM01-A	**Date of experiment**: from: June 12 to: June 15, 2013	**Date of report**: 15 September 2014
Shifts: 12	**Local contact(s)**: Dr. V. Dmitriev	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*P. Schouwink, Laboratoire de Cristallographie, Genève, Switzerland

*N. Tumanov, Université de Louvain, Belgium

This proposal was designed at evaluating the pressure impact on a new series of up to date over 30 metal borohydride materials crystallizing with the perovskite type structure [1]. The perovskite ABX_3 structure type is built of an octahedral framework where the vacancies are filled with large countercations. Orbital-induced effects aside, the instabilities in this structure type are dominated by the behaviour of phonons. In the case of $AB(BH_4)_3$ we have found that very interesting interactions take place between the phonons molecular vibrations B-H of the tetrahydroborate anion.

These interactions cause the stabilization of large superstructures in the high-temperature polymorphs. The present experiments compare the impact of a vacant and filled *A*-site on the pressure stability of the octahedral framework (figure 1) in ReO_3-type and perovskite-type metal borohydrides. The materials are extremely soft with bulk moduli around 25-30 GPa. This means that the lanthanide luminescence studied in a new related family of perovskite-type borohydride solid state phosphors [1] should show a strong pressure-dependency, which can provide useful pressure standards in the low pressure regime. For compounds with 100 % vacancies on the *A*-site it was found that the *HP*-phase phase transformations are not reversible, in contrast to the well-known transition reported for metal oxides of the ReO_3-type. We expect this to be related to *HP*-induced lattice instabilities that have their origin in weak interactions and the tetrahedral geometry of the BH_4^- anion, both features entirely unknown for metal oxide perovskites, and which are discussed in detail in [1].

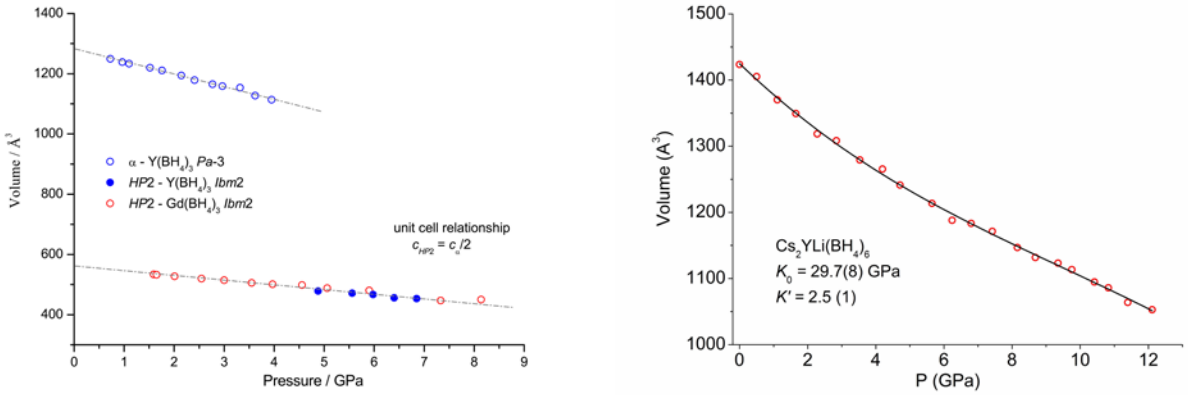

Figure 1. Left: Compressibility of a model-system double perovskite-type metal borohydride. The bulk modulus was determined from a fitted 3rd order Birch-Murnaghan EoS. **Right:** Compressibility and first-order phase transition of ReO_3-type metal borohydrides $Y(BH_4)_3$ and $Gd(BH_4)_3$, dotted lines are eye-guides.

High pressure polymorphism of $Mn(BH_4)_2$ was also studied during this experiment. Two samples of $Mn(BH_4)_2$ were used with LiCl impurity and with $NaBH_4$ impurity. We found that $Mn(BH_4)_2$ behaves similarly in both experiments, undergoing two phase transitions: the first phase transition occurs at approximately the same pressure for both experiments, whereas the pressure value for the second phase transition lies in a wider range. As will be discussed below, we suggest the impurity to be responsible for such behavior. The first phase transition $Mn(BH_4)_2$ experiences in the range of 0.5-2.0 GPa, which goes with a coexistence of two phases: the initial phase and the emerged high-pressure phase. The second phase transition occurs between 8.5 and 11.5 GPa, only with a slight change in the diffraction pattern; but appearance of new superstructure peaks allowed us to identify the second high-pressure phase. The structure determination revealed that that the first high-pressure phase of $Mn(BH_4)_2$ is isostructural to a high-pressure phase of $Mg(BH_4)_2$, *i.e.*, δ-$Mg(BH_4)_2$. This new phase, which we named δ-$Mn(BH_4)_2$ by analogy with δ-$Mg(BH_4)_2$, was refined in $P4_2nm$, by using crystal structure of δ-$Mg(BH_4)_2$ as an initial model (replacing Mg for Mn atom). The structure of α-$Mn(BH_4)_2$ is characterized by a significant amount of empty space; during the first phase transition, which is the first-order transition, α-$Mn(BH_4)_2$ collapses, losing 17% of volume, and rearranges into δ-$Mn(BH_4)_2$. As its Mg analog, δ-$Mn(BH_4)_2$ consists of two interpenetrated $Mn(BH_4)_2$ frameworks, similar to the Cu_2O structure, showing no empty voids in the structure and has a volumetric density of hydrogen of 125 g H_2/L at a pressure of 1 GPa. The second phase to δ'-$Mn(BH_4)_2$ transition in both experiments occurs near 8.5-11.5 GPa and results in a few additional new peaks in the diffraction pattern that indicate a superstructure, emerging mostly due to the ordering of hydrogen atoms. Structure of δ'-$Mn(BH_4)_2$ is very similar to the first high-pressure phase and is comprised of two interpenetrated $Mn(BH_4)_2$ frameworks as well, with the ordering of hydrogen atoms being more pronounced. The latter is the reason for a larger unit cell and the appearance of new superstructure peaks.

[1] P. Schouwink, M. B. Ley, A. Tissot, H. Hagemann,T. R. Jensen, L'. Smrčok, R. Černý, Nature Comm., *submitted*.