ESRF	**Experiment title:** From transition metal borohydrides towards bimetallic borohydrides.	**Experiment number**: 01-02-933
Beamline: BM01-A	**Date of experiment**: from: Nov 29 to: Dec 1, 2010	**Date of report**:
Shifts: 6	**Local contact(s)**: Dr.D.Chernyshov	*Received at ESRF:*

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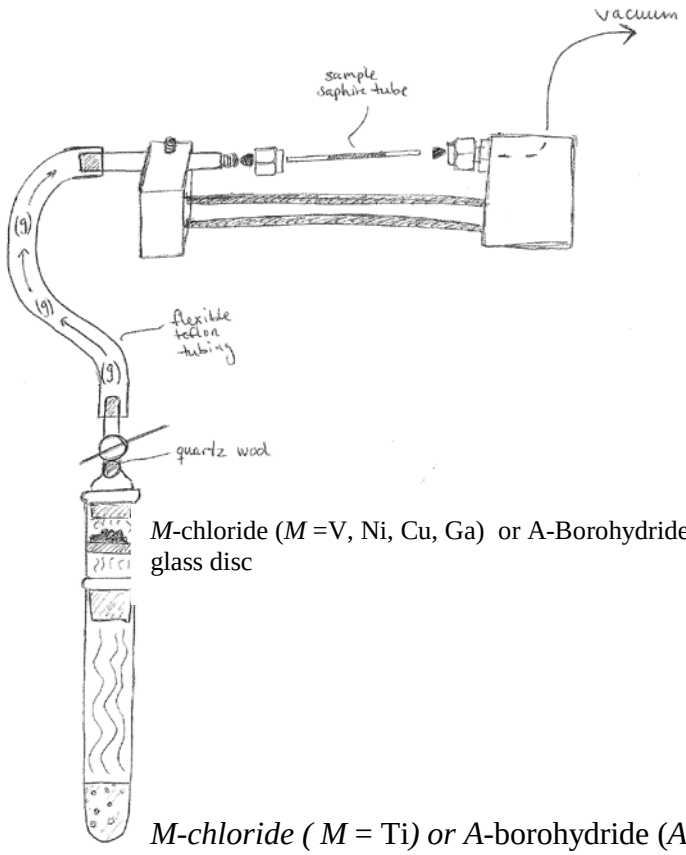
The aim of a first part of the project was in-situ synthesis and crystallization of unstable transition metal borohydrides. For diffraction data collection we have used the MAR345 detector at the BM01A beamline. The synchrotron powder patterns were collected in the capillary set-up.

To trap the unstable 3*d*-metal borohydrides we have used a small glass reaction apparatus prepared by us, which was mounted on a goniometric head of the MAR345 diffractometer (see the drawing below). The apparatus has a reservoir for liquid 3*d*-metal chlorides or aluminium borohydride, and a sintered glass disc for solid 3*d*-metal chlorides or alkali borohydrides. The reservoir and glass disc were filled at approx. -20 C (using a cold plate) in the local glove box available at the SNBL. Then it was brought to the experimental hutch and fixed on the goniometric head of the MAR345 diffractometer, and afterwards heated up (max. to 373 K) to complete the exchange reaction. Volatile 3*d*-metal borohydride formed by the exchange reaction were condensed into crystalline matter in the sapphire tube exposed to the X-ray beam. The tube was cooled using a Cryostream. The whole system of the small glass reaction apparatus was flushed with argon prior to measurements and pumped by the primary vacuum pump during the experiment. The apparatus is designed for application of both high and low pressure (10^{-3} – 100 bar), which have been tested during numerous experiments at the synchrotron MAXlab in Sweden.

Following systems were tried:

$TiCl_4$ (l) + $LiBH_4$ (s), $Al(BH_4)_3$ (l, tol) + $TiCl_3$ (s), $Al(BH_4)_3$ (l, tol) + VCl_2 (s), $Al(BH_4)_3$ (l, tol) + $GaCl_3$ (s) $Al(BH_4)_3$ (l, tol) + $FeCl_3$ (s), $Al(BH_4)_3$ (l, tol) + $CuCl_2$ (s), $Al(BH_4)_3$ (l, tol) + $NiCl_2$ (s). Only vanadium

containing system has shown diffraction pattern of a new unknown phase, the data are currently being analyzed.



In the second part of the project we have measured the T-ramps of the ball-milled mixtures $RbBH_4$+$ScCl_3$ and $CsBH_4$+$ScCl_3$ in the ratios 2:1, 3:1, 4:1 and 4:3. The aim was to study the formation of a bimetallic alkali-metal scandium borohydrides like $LiSc(BH_4)_4$ [1], $NaSc(BH_4)_4$ [2] and $KSc(BH_4)_4$ [3]. We have observed the formation of bimetallic borohydrides-chlorides $A_3Sc(BH_4Cl)_6$, $A_3Sc_2(BH_4Cl)_9$ (*A*=Rb, Cs) derived from known structures of bimetallic chlorides. Peaks of unknown phases, probably $ASc(BH_4Cl)_4$ (*A*=Rb, Cs), were observed and tentatively indexed in monoclinic cells, but due to low yield of these phases the structure solution was unsuccessful. The phases decompose at ~ 400 K.

(1) Hagemann, H.; Longhini, M.; Kaminski, J.W.; Wesolowski, T.A.; Černý, R.; Penin, N.; Sorby, M.H.; Hauback, B.C.; Severa, G.; Jensen, C.M. *J. Phys. Chem. A* **2008**, *112*, 7551-7555.
(2) Černý, R.; Severa, G.; Ravnsbæk, D.; Filinchuk, Y.; D'Anna, V.; Hagemann, H.; Haase, D.; Jensen, C.M.; Jensen, T.R. *J. Phys. Chem. C* **2010**, *114*, 1357-1364.
(3) Černý, R.; Ravnsbæk, D.; Severa, G.; Filinchuk, Y.; D'Anna, V.; Hagemann, H.; Haase, D.; Skibsted, J.; Jensen, C.M.; Jensen, T.R. *J. Phys. Chem. C* **2010**, *114*, 19540-19549.