Preliminary report
STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE – high resolution experiments 01-01-618

B. C. Hauback, H. W. Brinks, D. Blanchard, A. Fossdal, A. Istad Lem
Department of physics, Institute for Energy Technology, P. O. Box 40, NO-2027 Kjeller, Norway

The high-resolution experiments (BM01B) were carried out on the following samples:

(a) Doped $NaAlH_4$ (6 samples)
(b) Doped $LiAlD_4$ (17 samples)
(c) $Mg(AlH_4)_2$
(d) $ZrCr_2D_4$
(e) $Zr_2NiD_{4.7}$
(f) $BaMgNiD_4$

The samples were in 0.3 or 0.5 mm boron-glass capillaries. The wavelength was 0.49956 Å.

The analyses of most of the data are not finished at the moment, but some preliminary results are given here.

$NaAlH_4$ and $LiAlD_4$ samples:

We did more detailed follow-up studies of two earlier publications based on data from SNBL. The main idea is to find how the additives work in alanates; they clearly improve the kinetics, but there is now information of the chemical state of the additive. By adding e.g. $TiCl_3$ to $NaAlH_4$, from the presence of NaCl and Al in the sample afterwards there has been a reaction between the additive and $NaAlH_4$, but no traces of any Ti containing phase or any solid-solution of Ti in the $NaAlH_4$ phase.

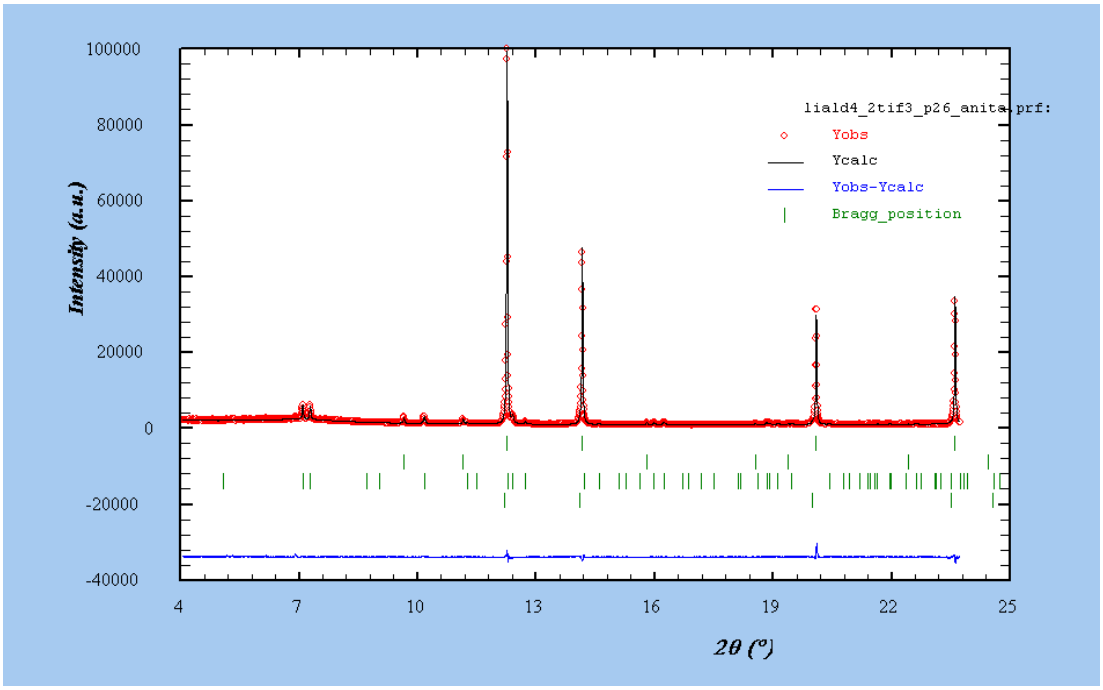
At this experiment we tried with higher additive concentration in the search for Ti, in particular in the cycled samples of $NaAlH_4$. Again, no Ti compound was seen directly after ball milling. On the other hand, evidencies of an Al-Ti phase after cycling was seen more clearly with 10 mol% compared to 2 mol% of Ti additive.

For $LiAlD_4$ we also tried with larger VCl_3 amounts added by ball milling, and we are here able to observe some unreacted VCl_3, but no other vanadium-containing phases were seen after ball milling. Samples heated to 270°C furthermore do not show any traces of vanadium – even with 15 mol% VCl_3 in the original sample.

Samples with additives added to Li_3AlD_6 (and measured at SNBL) are also under investigation.

$LiAlD_4$ with TiF_3 additives react completely during ball milling with no traces of neither Ti nor F. NaF was expected with analogy to the findings of NaCl in the VCl_3 doped samples. The samples are not stable towards desorption in glove box, evidenced by samples which contained $LiAlD_4$ + Li_3AlD_6 + Al six months before, now were nearly completely desorbed to LiD + Al.

In the figure below, $LiAlD_4$ + 2 mol% TiF_3 which has been stored for 5 months, containing Al, LiD, Li_3AlD_6 and trace amounts of LiCl (from impurities in $LiAlD_4$):



$Mg(AlH_4)_2$

Data were collected at both room temperature and 110 K (using nitrogen cooler). These data are used in combination with powder neutron diffraction data, and a publication will be submitted within a few weeks.

$ZrCr_2D_4$

This system has been studied by powder neutron diffraction focusing on determination of local order. However, data below about 200K shows ordering, and there are some indications that the previously published structure is not correct. The SNBL-data at 110K will be used to clarify this point. Refinements are in progress.

$Zr_2NiD_{4.7}$

We have worked intense on this system for a long time. The saturated hydride, $Zr_2NiD_{4.7}$ shows several superstructure reflections indicating lowered symmetry. However, it has until now been impossible to determine the correct unit cell and space group. The purpose of this experiment was to collect data with extremely good statistics to find even very weak superstructure reflections. In particular reflections at low angles are important. The analysis of the data is in progress.

$BaMgNiD_4$

This is a new interesting Mg-based complex hydride. Powder neutron diffraction data suggest lowering of the symmetry compared to standard X-ray data, but the possible splitting of

reflections are very weak. High-resolution synchrotron data are therefore required to sort out this problem.