

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.


Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Novel Complex Transition Metal Hydrides Containing Group VI Metals: Synthesis and Observation at Extreme Conditions Using LVP at Beamline ID06	Experiment number: CH-4899
Beamline: ID06-LVP	Date of experiment: from: 21/09/16 to: 27/09/16	Date of report: 27/02/2017
Shifts: 18	Local contact(s): Wilson A. Crichton	<i>Received at ESRF:</i>
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Report:

During experiment CH4899 at ID06-LVP we have explored formation pathways and structures of complex hydrides in the ternary systems A-T-H (M=alkali/alkali earth metal, T = group VI-XI element) under extreme pressure and temperature in situ. Complex metal hydrides containing TH_n^{0-} homoleptic complex units are an important and actively studied class of compounds, and are of high interest for both applied and fundamental chemistry [1]. Applying pressures in a GPa range is a promising route for synthesizing novel complex metal hydrides due to the considerably increased oxidative potential of hydrogen at extreme p,T [2]. For a long time A_mTH_n were considered to be restricted to Group VII-XII elements, until it was shown that a compound Mg_3CrH_8 can be formed in a multianvil press on heating at 5 GPa [3]. Therefore our primary focus was on T = Cr, W (group VI). Using Large Volume Press at ID06 has allowed obtaining important information during synthesis of A_mTH_n (T=Cr, W), as well as revealing a new, yet unreported compound in the Cr-containing system.

An additional exploratory study was performed on A-T-H systems where T belongs to group VIII-XI. These systems have a potential to yield new complex hydride structures due to increase in oxidation state of T-metal ions. As a result, detailed diffraction information was collected during the synthesis of five different A_mTH_n . In one of the systems containing an alkali metal as a counterion a new unquenchable compound has been observed. A high pressure assembly for hydrogenation experiments in a Large Volume Press has been adapted specifically for CH4899 and has shown a high rate of success and stability during pressurizing and heating. The allocated 18 shifts were efficiently used with the total of 9 experiments performed.

Technical aspects

All the samples and sample capsules for CH-4899 were prepared and handled in the glove box at the ESRF chemistry lab. The NaCl capsules (3mm OD, 2mm ID) served as sample containers, as they can be sealed very tightly and are not permeable to hydrogen. Each container was made of NaCl oven-dried at 600 °C during 10 days by pressing a pellet of appropriate length and later drilling a 2 mm hole in it, leaving ~0.5 mm

thick bottom. The samples were prepared as compact 2 mm OD, 1.5 mm thick pellets pressed from stoichiometric mixtures of the alkali or alkali earth metal hydride and a transition metal powder. The sample pellet was loaded inside the NaCl capsule along with two hydrogen source pellets surrounding it. Ammonia borane (NH_3BH_3) was chosen as a hydrogen source. NH_3BH_3 dehydrogenation behaviour at high p, T is well studied, and it is known to release H_2 rapidly and irreversibly in two steps, yielding inert BN-like product [4]. Sample capsules were sealed by adding extra NaCl to an open end and re-pressurizing. Extracted capsules could be handled safely outside glove box.

All the runs were performed using a 14/8 2-stage high pressure assembly with an octahedral pressure medium (Cr_2O_3 -doped MgO). Each sample capsule was loaded into a 14 mm-OEL octahedron along with a carbon foil furnace (4.5 mm OD, 3.5 mm ID), a BN sleeve (3.5 mm OD, 3 mm ID) and two 3.5 mm OD ZrO_2 pistons. Two X-ray transparent SiBCN windows were inserted in the octahedra along the beam direction. Octahedron was then positioned between eight 8 mm TEL gasketed tungsten carbide anvils. The MgO insertions were placed in the gaskets along the beam direction. Using MgO proved beneficial for studying complex metal hydrides since clean low angle range can be observed (where characteristic peaks for A_mTH_n normally appear). The outer side of the tungsten carbide cubes was insulated with mica sheets. In order to perform the heating copper foil was attached outside the cubes adjacent to the carbon furnace.

Samples were typically pressurized to 5 GPa and subsequently heated using Delta Elektronika SM6000 power supply by regulating the voltage. Diffraction patterns were collected in angle-dispersive mode ($\lambda=0.22542 \text{ \AA}$) during compression (32 sec/pattern) and heating (3.2 sec/pattern) using a pixelated 1D detector from Detection Technology. Using salt sample containers was advantageous since pressure and temperature could be estimated in situ using the NaCl equation of state. During the second step of hydrogen evolution from ammonia borane ($\sim 300^\circ\text{C}$ at 5 GPa) the samples were allowed to dwell for ~ 30 min. The final temperature and heating duration resulted from the kinetics of target compounds formation as well as their temperature-dependent behaviour, but mostly ranged between $600\text{--}900^\circ\text{C}$ and 1-4 hours.

Results

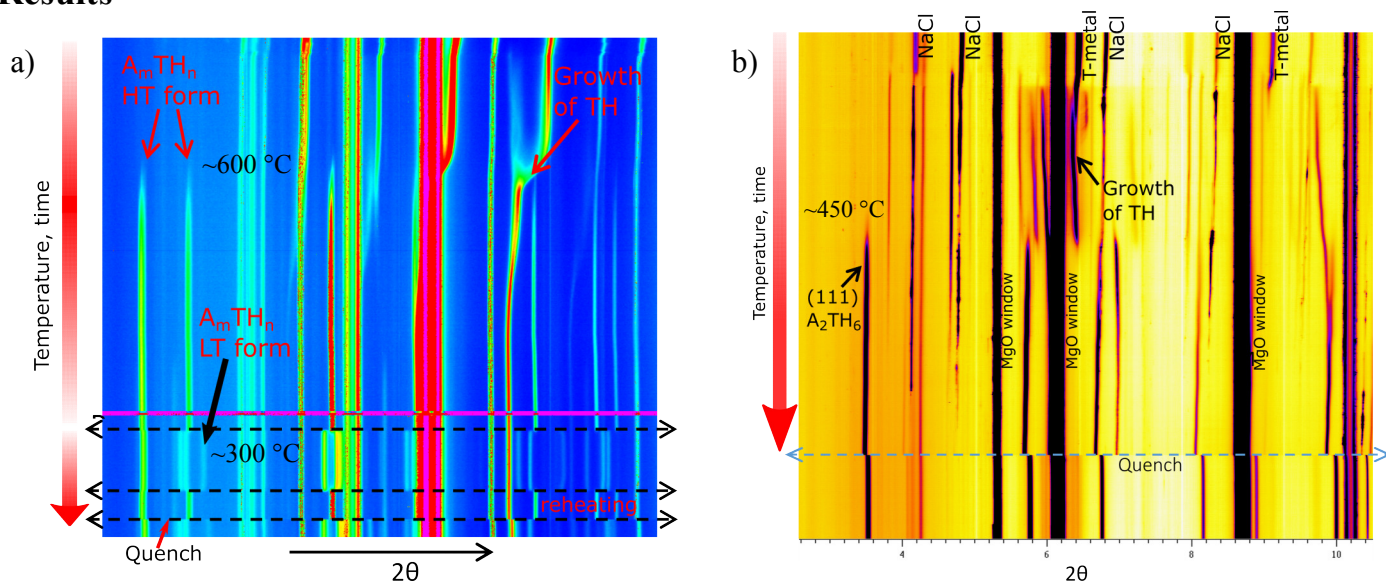


Figure 1. (a) Diffraction data following formation of a novel A_mTH_n containing group X metal. Arrows mark the transitions between high- and low-temperature form. (b) Example of time-resolved data collected during synthesis of previously known A_2TH_6 compound with Fm-3m structure.

Using the ID06-LVP was essential for the CH4899, as the experimental setup for hydrogenation described above in combination with stable heating in $600\text{--}900^\circ\text{C}$ range is not feasible with DACs. The limitations encountered during the study were exclusively sample-related. The formation of complex metal hydrides A_mTH_n was observed in all the systems, except for those containing tungsten and copper. Interestingly, A_mTH_n growth was preceded by that of an interstitial transition metal hydride TH_x ($x \sim 1$) as intermediate phase whose formation typically coincided with the second step of hydrogen release from the ammonia borane source. For $T = \text{W, Cu}$ no interstitial transition metal hydride was observed. The direct temperature estimation from NaCl cell parameters appeared to be limited to $\sim 700^\circ\text{C}$, as above this temperature salt starts to recrystallize and grow rather large grains, making accurate determination of reflection positions

challenging. Nevertheless, it worked sufficiently well as majority of the complex hydrides have shown growth below this temperature.

Interestingly, the Cr-containing system has revealed growth of a novel compound forming $>850\text{ }^{\circ}\text{C}$. The compound was recovered at ambient conditions and its PXRD pattern acquired at ID22 was indexed in monoclinic crystal system. Following the formation of this complex in situ was highly important due to its stability only in a particular temperature range, while decreasing the temperature yielded an already reported hydride. Another new $A_m\text{TH}_n$ complex was revealed in a system containing group X metal and an alkali metal hydride. This complex hydride would form around $600\text{ }^{\circ}\text{C}$ displaying cubic symmetry while instantly but reversibly changing to an orthorhombic low temperature form on cooling (Fig. 1a). However, this complex appeared unquenchable to room p,T , making in situ diffraction study a unique way to observe it. The obtained data on both new compounds was successfully reproduced later during in-house research at ID06-LVP. Other complex hydrides synthesized during the study corresponded to already published structures, yet the diffraction data following their formation is important and represents well the stability and performance of the employed setup (fig 1b). Developing a different, scaled-down hydrogenation setup to reach pressures above 10 GPa would be the next step in searching for the new complex metal hydrides in these systems.

Data evaluation is currently in progress. A number of samples have been studied ex-situ by PXRD, and some are planned to be probed with Raman spectroscopy. Overall three papers are going to be published using the results from CH4899.

References

- [1] Bronger, W. *J. All. Comp.* 229 (1995), 1–9.
- [2] Bronger, W., Auffermann, G. *Z. Anorg. Allg. Chem.* 621 (1995) 1318.
- [3] Takagi et al. *Angew. Chem. Int. Ed.* 54 (2015), 5650 –5653.
- [4] Nylen et al. *J.Chem. Phys.* 131 (2009), 104506.