# Experimental report

16/02/2016

**Proposal:** **7-03-148** **Council:** 4/2015

**Title:** Nature of hydride-ion mobility in peculiar perovskite oxyhydrides

**Research area:** Materials

**This proposal is a new proposal**

**Main proposer:** **Maths KARLSSON**

**Experimental team:** Carin OSTERBERG

**Local contacts:** Bernhard FRICK
Monica JIMENEZ RUIZ

**Samples:** BaTiO3-xHx (x = 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6)

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| IN16B | 9 | 5 | 20/11/2015 | 25/11/2015 |
| IN1 LAG | 4 | 4 | | |

## Abstract:

This proposal request 9 days on IN16B as well as 4 days on IN1-LaGrange to investigate the nature of hydride-ion diffusion and vibrational properties in the novel class of perovskite type oxyhydrides, BaTiO3-xHx (x = 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6) as a function of both temperature and hydride-ion concentration (x). The specific questions are rather obvious: (i) what is the features/mechanism of hydride-ion dynamics and vibrational properties in perovskite oxyhydrides and how does it depend on temperature and hydride-ion concentration?, (ii) how is the mechanism of hydride-ion conduction related to proton dynamics in classic proton conducting perovskite type oxide analogous?, and (iii) what can be learned towards a fundamental understanding of H dynamics - now stretching from protic to hydridic species - in perovskite materials?

# Nature of hydride-ion mobility in peculiar perovskite oxyhydrides
# Experiment 7-03-148

## 1. Scientific background

This proposal concerned QENS experiments to investigate hydrogen dynamics in the recently discovered oxyhydrides $A\mathrm{TiO}_{3-x}\mathrm{H}_x$ ($A$ = Ba, Sr, Ca, $x < 0.6$) [1]. In contrast to the majority of materials in the perovskite family, which are hydrated and acceptor doped (e.g. $\mathrm{BaTi}_{1-x}\mathrm{In}_x\mathrm{O}_3\mathrm{H}_x$) and where the hydrogen atoms are of protonic character ($\mathrm{H}^+$), the hydrogen in oxyhydrides is of hydridic nature ($\mathrm{H}^-$). Only a handful of oxyhydrides have been reported and the oxyhydrides $A\mathrm{TiO}_{3-x}\mathrm{H}_x$, are the first ones based on the perovskite structure. Representing a solid solution, $\mathrm{O}^{2-}$ and $\mathrm{H}^-$ ions form commonly the octahedral environment around Ti, which now is in a mixed IV/III oxidation state [1]. In contrast with most other oxyhydrides the systems $A\mathrm{TiO}_{3-x}\mathrm{H}_x$ are stable in air and water. Further, they are stable at elevated temperatures up to ca. 400 °C above which hydrogen is released [1]. This observation leads to the conclusion that the hydride species in $A\mathrm{TiO}_{3-x}\mathrm{H}_x$ have to be mobile. This finding is highly exciting because it implies that the perovskite structural framework can accommodate both, cation (proton) and anion (hydride) conduction. In particular, interesting diffusion mechanisms specific to hydride-ions may be at play and the development of a detailed understanding of such can help providing new input into hydrogen dynamics in perovskite structures - now stretching from protic to hydridic hydrogen species.

On the basis of the scientific background as described above, we wanted to investigate the mechanistic aspects of hydride-ion mobility in the novel class of perovskite oxyhydrides, using QENS. Building further on our promising results from a previous QENS study on IN16B (2 days in December 2014) on $\mathrm{BaTiO}_{2.6}\mathrm{H}_{0.4}$, we wanted to do a systematic investigation, on the six samples $\mathrm{BaTiO}_{3-x}\mathrm{H}_x$ (x = 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6). In particular, we wanted to investigate the Q- and T-dependence of the QENS spectra, with the aim to determine the geometry and activation energy of the proton dynamics present, as well as to determine how it depends on the concentration of hydride ions ($x$).

## 2. Experiment

Aluminium sample holders were used with an outer diameter of 22 mm and a height of 62 mm. Three different samples were used in the experiment; $\mathrm{BaTiO}_{2.4}\mathrm{H}_{0.6}$ and $\mathrm{BaTiO}_{2.8}\mathrm{H}_{0.2}$, which were prepared using $\mathrm{NaBH}_4$ as one of the starting reactants, and, differently, $\mathrm{BaTiO}_{2.6}\mathrm{H}_{0.4}$, which was prepared using $\mathrm{CaH}_2$ as one of the starting reactants. One should note that the latter sample was used in our previous experiment on IN16B (experiment 7-03-137, December 2014). Customized made inserts were used in the sample holders in order to get the appropriate sample thickness for each sample to avoid multiple scattering; 1.8 mm for $\mathrm{BaTiO}_{2.4}\mathrm{H}_{0.6}$, 2.6 mm for $\mathrm{BaTiO}_{2.8}\mathrm{H}_{0.2}$ and 2 mm for $\mathrm{BaTiO}_{2.6}\mathrm{H}_{0.4}$. All three sample holders were only loosely tightened so that the samples were exposed to vacuum during the measurements. Fixed window scans (FWSs) were measured from 2 K to 550 K at 1 K/min for all three samples, including data collection at 0 μeV (elastic intensity) and at 2 μeV (quasielastic intensity), respectively. The elastic peak (0 μeV) was measured for 30 seconds and the quasielastic peak (2 μeV) was measured for 2 minutes. Additionally, FWS measuring at 0 and 1 μeV was also preformed on $\mathrm{BaTiO}_{2.6}\mathrm{H}_{0.4}$ with a temperature ramp of 1 K/min and also going from 2 K to 550 K. QENS data was then collected, on $\mathrm{BaTiO}_{2.4}\mathrm{H}_{0.6}$ with the Doppler set to 4.5 m/s, at 2 K (resolution), 250 K and 400 K for 2 hours and, 300 K and 350 K for 3 hours. QENS was also measured on $\mathrm{BaTiO}_{2.6}\mathrm{H}_{0.4}$ with the same settings at 380 K for 1 h, at 2 K (resolution), 300K, 320 K, 350 K and 450 K for 2 h and, 200 K, 250 K, 270 K, 300 K, 320 K and 350 K for 4 h. Furthermore, at the same settings, an empty can and a vanadium standard were measured at 2 K for 4 h and 1.5 h, respectively, for background correction and to normalize the measured intensity against the detector efficiency. The ILL software LAMP was used for plotting and data analysis.

## 3. Preliminary results and and analysis

During the course of the measurements, we found that the scattering intensity of the two $\mathrm{BaTiO}_{2.4}\mathrm{H}_{0.6}$ and $\mathrm{BaTiO}_{2.8}\mathrm{H}_{0.2}$ samples (prepared using $\mathrm{NaBH}_4$) was unexpectedly low, which we interpreted due to residual boron in these materials. For this purpose, we instead focused our measurements on the third sample, $\mathrm{BaTiO}_{2.6}\mathrm{H}_{0.4}$, which, differently, showed higher intensity, however not as high as in our previous experiment, *cf.* Figure 1. We interpreted the lowering in quasielastic signal due to a loss of hydrogen in the sample between the two experiments, but importantly the temperature dependence of the intensity [Figure 1(b)] shows essentially the same features. Further analysis of the data is ongoing.

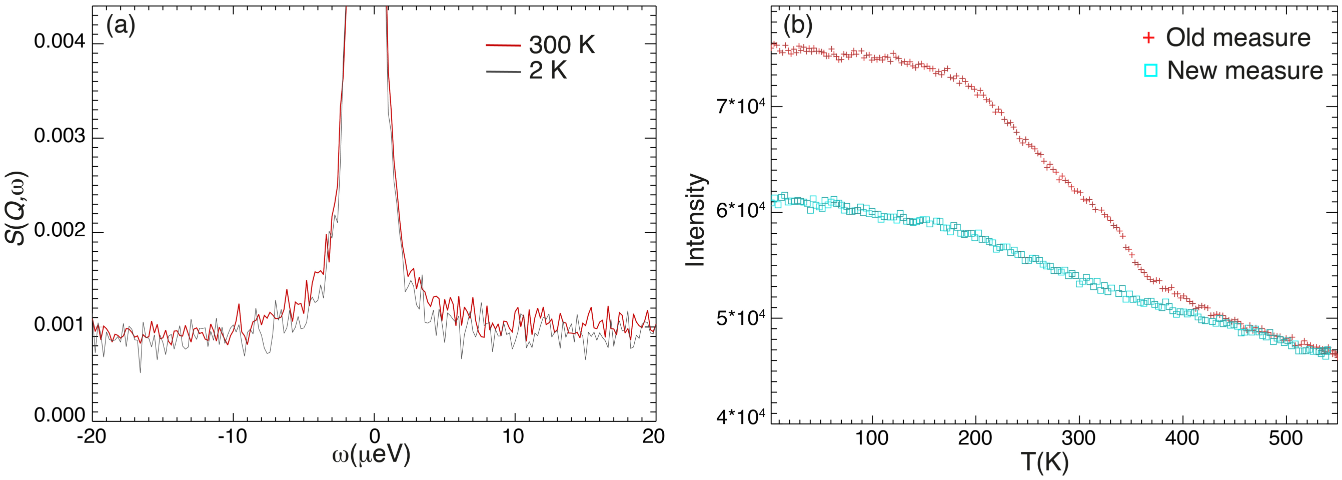

Figure 1(a), the QENS spectrum of the old sample, $BaTiO_{2.6}H_{0.4}$ at 2 and 300 K, respectively; Q = 1.3 Å$^{-1}$. (b) FWS of $BaTiO_{2.6}H_{0.4}$ upon heating from from 2 K to 550 K. The old measurement (red) is from Dec 2014 compared to the new measurement (teal). Both curves have been normalized to the values at the highest temperature.

## References

[1] Y. Kobayashi *et al.*, *Nature Mater*. **11** (2012) 507.
[2] C. Österberg, R. Nedumkandathil, U. Häussermann, M. Tyagi, C. M. Brown, M. Karlsson, *In manuscript.*