Experimental report

16/02/2016

Proposal: **7-03-137** **Council:** 10/2014

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

Research area: Materials

This proposal is a new proposal

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Samples: BaTiO2.9H0.1
BaTiO2.6H0.4

Instrument	Requested days	Allocated days	From	To
IN16B	8	2	15/12/2014	17/12/2014
IN6	4	4		
IN11	7	7	30/07/2015	06/08/2015

Abstract:

This proposal requests 8 days on IN16B, 7 days on IN11-C, and 4 days on IN6, to investigate the mechanistic aspects (relaxation times, activation energies, and spatial geometry) of hydride-ion mobility in a novel class of perovskite type oxyhydrides. Our investigations will focus on two sample compositions, BaTiO2.6H0.4 and BaTiO.2.9H0.1, and build on a recent (test) experiment at the backscattering spectrometer (HFBS) of the NCNR. Salient questions are: (i) what is the mechanism of H- dynamics in BaTiO3-xHx (x = 0.1 and 0.4) and how does it depend on the level of incorporated hydrogen (x)?, (ii) how is the mechanism of H- conduction related to H+ dynamics in classic perovskite type proton conductors?, and (iii) what can be learned towards a fundamental understanding of H transport in perovskite materials?

Nature of hydride-ion mobility in peculiar perovskite oxyhydrides
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1. Scientific background

This proposal concerned QENS experiments to investigate hydrogen dynamics in the novel class of hydride-ion conducting perovskites of chemical formula $A\text{TiO}_{3-x}\text{H}_x$ (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. $\text{BaTi}_{1-x}\text{In}_x\text{O}_3\text{H}_x$) and where the hydrogen atoms are of protonic character (H^+), the hydrogen in oxyhydrides is of hydridic nature (H^-). Only a handful of oxyhydrides have been reported and the oxyhydrides $A\text{TiO}_{3-x}\text{H}_x$, are the first ones based on the perovskite structure. Representing a solid solution, O^{2-} and H^- ions form commonly the octahedral environment around Ti, which now is in a mixed IV/III oxidation state. In contrast with most other oxyhydrides the systems $A\text{TiO}_{3-x}\text{H}_x$ are stable in air up to ca. 400 °C above which hydrogen is released. This observation leads to the conclusion that the hydride species in $A\text{TiO}_{3-x}\text{H}_x$ 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. 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

An aluminium sample holder was used with a diameter of 22 mm and a height of 62 mm. A lid of steel was closely tightened against the aluminium sample holder, in order to make a tight cell. The samples were contained in an aluminium foil that was shaped into a cylinder in order to make an annulus cell. This gave the total sample thickness, exposed to the beam, of 3mm. The only sample measured was $\text{BaTiO}_{2.6}\text{H}_{0.4}$. A fixed window scan (FWS) was measured from 200 K to 2 K and then again during heating to 550 K. The Doppler was set so that the FWS measurements were measured at 0 μeV and at 2 μeV, respectively, in order to collect continuous data from both the elastic peak and from the quasielastic region. The elastic peak (0 μeV) was measured for 30 seconds and the quasielastic peak (2 μeV) was measured for 2 minutes. QENS data was then collected with the Doppler set to 4.5 m/s at 2 K (used as resolution function), 150 K, 300 K and 225 K for 2 hours, 420 K and 480 K for 3 hours, and 250 K, 330 K (measurements of an empty cell) + 330 K and 360 K for 4 hours. LAMP was used to plot and analyse the data.

3. Preliminary results

Figure 1(a) shows the FWS of the elastic and quasielastic intensity upon heating. Most noticeable is the increase of QENS between 250 K and 450 K, which corresponds to a simultaneous decrease of the elastic intensity in this temperature interval, suggesting that we are sensitive to the H dynamics in the material, which is further emphasized by the significant quasielastic intensity at 300 K as shown in Figure 1(b). In particular, the non-linear behaviour of the temperature dependence of the quasielastic intensity suggests the presence of more than one type of H motion. Further analysis, particularly in terms of the Q-dependence of the observed dynamics, is ongoing and will be compared to data obtained from complementary investigations.

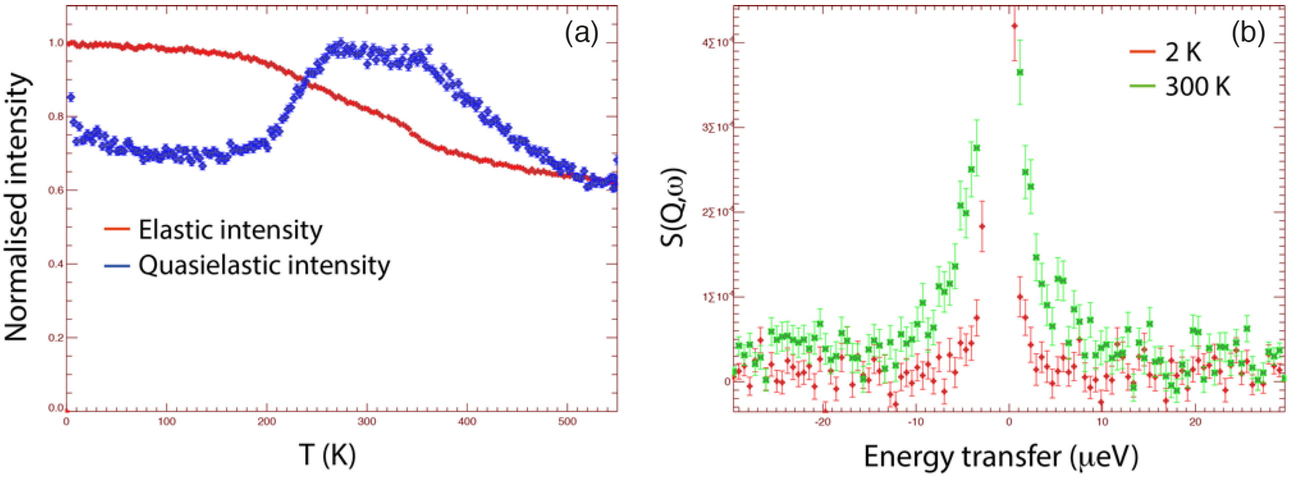

Figure 1(a) FWS of $BaTiO_{2.6}H_{0.4}$. The red curve shows the elastic intensity, whereas the blue curve shows the intensity of a position off the elastic peak (in the quasielastic region). Both curves are normalized to 1, but the blue curve has been multiplied by a factor of ~100 for easier comparison. (b) QENS spectra measured at 2 K and 300 K, respectively; Q = 0.19 $Å^{-1}$.

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.*