H2. PROTON CONDUCTION IN YTTRIUM DOPED BARIUM CERATE

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One of the major challenges in the development of hydrogen fuel cells remains the choice of electrolyte. Severe demands exist on a number of its properties including very high ionic and very low electronic conductivity, high thermal and chemical stability and durability. Yttrium doped barium cerate (BCY) meets many of the above requirements. It has been studied intensively since the first observation of its high proton conductivity at elevated temperatures (> 600°C) [1]. Barium cerate has a perovskite-type structure, in which substitutions of Ce^{4+} by Y^{3+} cause the formation of oxygen vacancies. The doped material is hygroscopic, it absorbs water dissociatively resulting in the formation of hydroxyl groups (see Figure 1). At temperatures above 400-500°C, hydrogen atoms in the structure become mobile, leading to proton conductivity (20% yttrium doping necessary for optimal conductivity). While the ultimate interest is the macroscopic motion of H atoms under an applied electric field, the understating of the mechanism itself requires the knowledge of the local proton environment. It is studied here using a combination of inelastic and quasi-elastic neutron scattering, taking advantage of the complementary techniques available on pulsed (IPNS, ANL) and continuous (LLB, Saclay) neutron sources. The experimental data are to be complemented with microscopic simulation at a later stage.
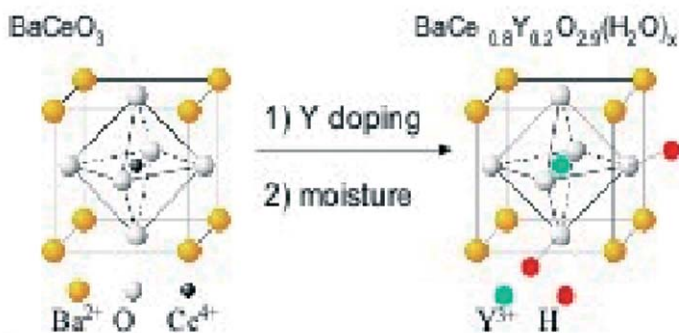
In recent neutron diffraction experiments, the structural phase transitions of the underlying perovskite network, as a function of temperature and water uptake, have been highlighted as a crucial factor determining the behaviour of H atoms [2]. A monoclinic (I2/m) phase has been identified as a phase accommodating the H atoms in the structure at room temperature. Furthermore, our measurements on the QENS spectrometer at IPNS, providing concurrent structural and dynamic information, give evidence for a link between the disappearance of the monoclinic (I2/m) phase at around 400 °C and a change in the proton dynamics as indicated by the mean-squared displacement determined from the Debye-Waller factor (see Figure 2).
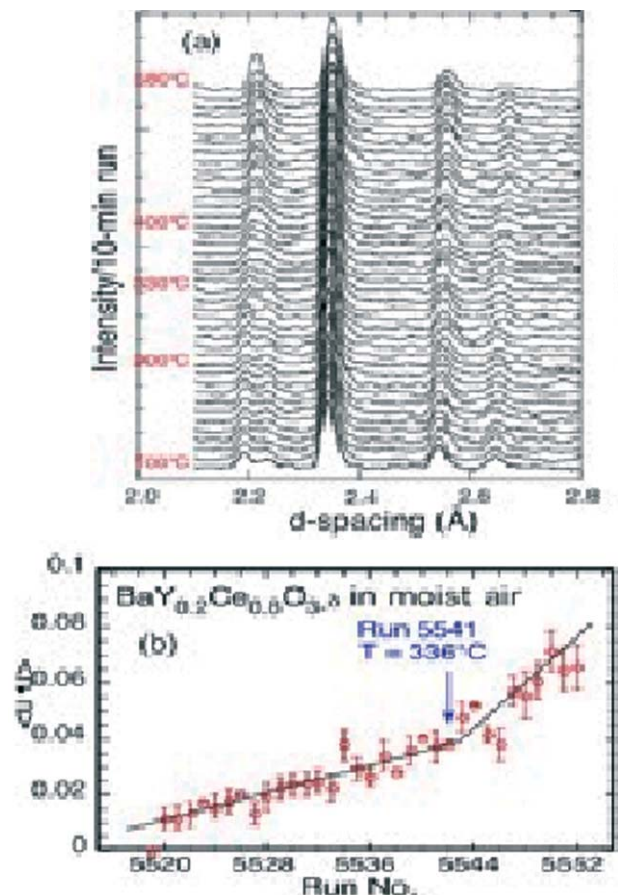

Figure 1: Idealised (cubic) structure of barium cerate and its yttrium-doped counterpart containing hydroxyl (OH) groups.

Figure 2: Concurrent data collection of the diffraction patterns of BCY and the hydrogen atom mean-square displacements (QENS spectrometer, IPNS).
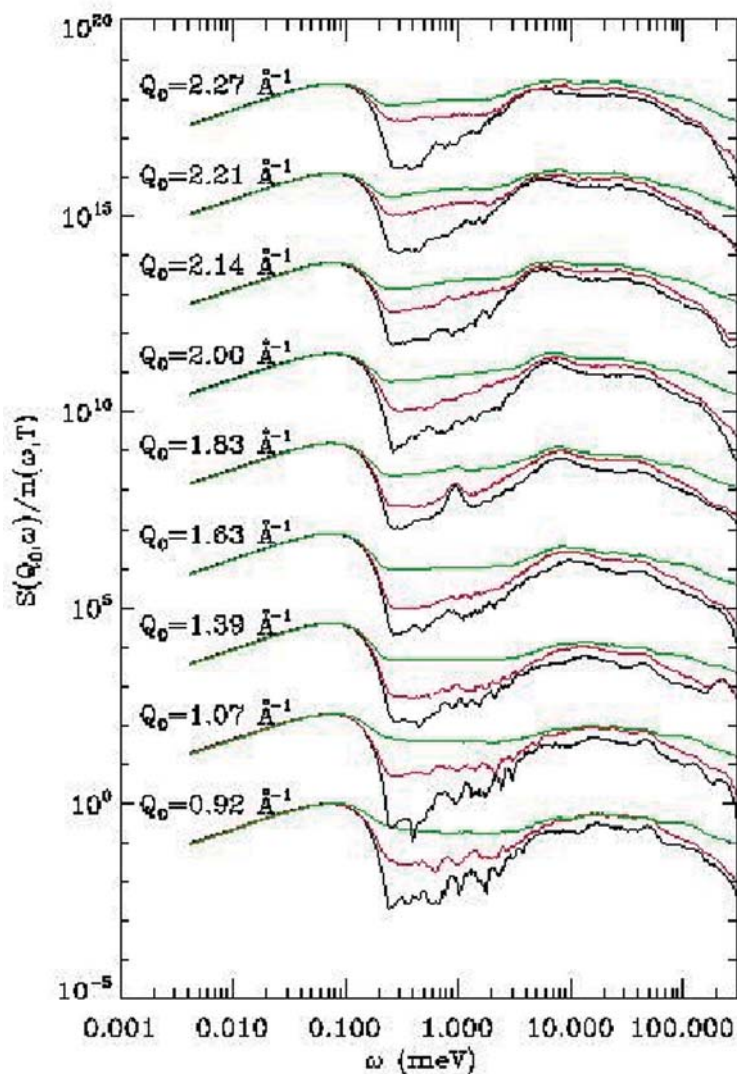
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Figure 3: Susceptibility representation of low-resolution quasi-elastic data (650ºC, MIBEMOL) on wet BCY (green), dry BCY (red), background (=quartz tube, black).

We are currently complementing the existing quasi-elastic neutron data with more detailed measurements, at varying resolutions, to elucidate the Q-dependence of the observed hydrogen motion.

Using a flow-cell set-up, allowing in-situ hydration and dehydration of the BCY system, we have collected both low- and high-resolution data, at the MIBEMOL spectrometer (LLB, resolution (FWHM) of 150 μeV) and IRIS spectrometer (ISIS, resolution (FWHM) of 18 μeV) respectively.

Susceptibility representation of the low-resolution data (Figure 3), indicates increased signal in the region 0.3-2 meV upon hydration of the BCY sample as well as around 100 meV. The observed quasi-elastic broadening is reproduced well using a trans-rotational model, giving rise to a narrow and broad component. In agreement with previous quasi-elastic neutron scattering studies, the Q-independent rotational broadening is of the order of 1-2 meV (HWHM). However, in the Q range studied (0.8 - 3.0 Å-1), the translational broadening shows rather a weak Q dependence. Data in a lower Q region are probably necessary in order to determine the corresponding diffusion coefficient.

Aside from quasi-elastic spectrometers, the pulse-source HRMECS spectrometer (IPNS, ANL) provides a very wide dynamic range (up to E=600 meV in energy transfer over a large Q-range). High-energy transfers are essential to probe the phonon and local modes involving hydrogen and the surrounding heavier atoms. Experimental phonon density of states of BCY is to be used as a check in the choice of inter-atomic force fields, the key parts of any microscopic model of the system.

[1] H. Iwahara *et al*, Solid State Ionics **77** (1995) p.289.

[2] K. Takeuchi *et al.*, Solid State Ionics **138** (2000) p.63.