Experimental report

07/09/2015

Proposal: **7-03-130** **Council:** 4/2014

Title: Fundamentals of proton self diffusion in proton conducting perovskitetype oxides

Research area: Materials

This proposal is a continuation of 7-03-124

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Samples: BaZr0.9M0.1O3H0.1 (M = Y and Sc)

Instrument	Requested days	Allocated days	From	To
IN11	11	10	28/08/2014	07/09/2014

Abstract:

This continuation proposal requests 11 days on IN11 to investigate the role of dopant atoms on the mechanistic aspects of local proton dynamics in proton conducting perovskite type oxides of relevance for the development of intermediate temperature fuel cells. More specifically, we aim to investigate the important Q dependence of a local dynamical process observed in our previous experiment in order to elucidate its nature with respect to spatial geometry and how it is affected by the type of dopant atom (M) in the two materials BaZr0.9M0.1O3H0.1 (M = Y and Sc). In addition, we propose to measure on one un-protonated sample (BaZr0.9Y0.1O2.95) in order to confirm that the observed relaxational decays of the intermediate scattering function of the hydrated samples are due to the protons.

Fundamentals of proton self-diffusion in proton conducting perovskite type oxides

1. Background

Hydrated acceptor doped perovskite type oxides (e.g. Y-doped $BaZrO_3$) are considered promising materials to be used as proton conducting electrolytes in various environmental friendly devices, such as next generation intermediate-temperature (~100—500 ˚C) fuel cells, hydrogen pumps, steam electrolysers, and in hydrogen sensors [1–3]. The acceptor doping creates an oxygen-deficient structure [4]. Protons can be introduced into this structure by exposure to humid conditions at elevated temperatures, then the water molecules dissociate into hydroxide ions, which fill the oxygen vacancies, and protons, which bond to lattice oxygens [4]. The protons are not stuck to any particular oxygen but they are rather free to move from one oxygen to another, resulting in a high proton conductivity of these materials (10^{-6}-10^{-2} S cm^{-1} in the temperature range 100—500 ˚C) [1]. Two elementary steps govern the proton conduction mechanism on a local scale: proton transfer between neighbouring oxygens and reorientational motion of the hydroxyl group in between such transfers, and a series of such jumps and reorientations is believed to lead to proton diffusion on a longer length-scale [1]. However, the details about what chemical and physical factors that influence these motions and in which way (i.e. the effects of dopant atoms, local chemistry and structure, symmetry reduction and proton defect interactions) are still not clear, and represent a crucial knowledge in order to develop a thorough understanding for how to tailor new materials with desired proton conductivity for technological applications [4].

2. Experiment

In this neutron spin-echo (NSE) experiment, we investigated the proton self-diffusion in the hydrated proton conducting perovskites $BaZr_{0.9}Y_{0.1}O_3H_{0.1}$ and $BaZr_{0.9}Sc_{0.1}O_3H_{0.1}$, hereafter referred to as 10Y:BZO and 10Sc:BZO, respectively. The measurements were performed on the IN11C spectrometer using a incident neutron beam with an effective average wavelength of 5.5 Å, which gives access to a dynamical range of 5 ps —1.3 ns, and with the 30˚ wide-angle detector centred at 50˚, which gives access to a Q range of 0.7—1.2 Å^{-1}. The powder samples were loaded in cylindrical Al cells with a diameter of 10 mm. Spectra were measured at 2 K, 249 K, 421 K, 454 K, 500 K, 528 K, and 546 K for 10Y:BZO, and at 2 K, 299 K, 373 K, 453 K, 491 K, and 546 K for 10Sc:BZO. The spectra were measured for 8 h (249—528 K) and 16 h (2 K and 546 K), respectively, and the 2 K spectra were used as resolution functions in the data analysis, since at this low temperature all diffusional dynamics can be expected to be frozen-in. All spectra were measured upon heating. To increase the statistics of the data, the spectra measured at 249—528 K were, after normalization with the resolution function, summed over the whole Q-range, thus giving an average Q-value of 0.96 Å^{-1}. For the longest measurements, as performed at 546 K, the spectra were grouped into three Q-values, 0.77, 0.99, and 1.17Å^{-1}.

3. Preliminary results and data analysis

In Fig. 1 is shown the I(Q,t) at Q = 0.96 Å^{-1}, as a function of temperature, for both materials. Considering first the Y-doped material [Fig. 1(a)], we observe that at the lowest temperature (249 K), the I(Q,t) is essentially flat, meaning that materials are not characterized by proton dynamics occurring on the accessible time and Q-range at this temperature. For higher temperatures (421—546 K), however, the I(Q,t) decays significantly and systematically more and more with increasing temperature. This suggests, we observe proton dynamics and that the dynamics is thermally activated. Note, however, that due to the limited range of the NSE time-window, we are unable to observe the full decay of I(Q,t), even for the highest temperature. This means that either the dynamics is too slow to be observable within the probed NSE time-window, or that there is a certain fraction of immobile protons in the material, which contributes to a background and thereby effectively increasing the level to which the I(Q,t) should eventually decay to in the long-time limit of the particular dynamical processes, or there is a combination of the two. A more detailed analysis of the scattering functions, shows that an analytical approximation is challenging. Generally, the I(Q,t)s show a rather monotonic decay with no distinguished profile. Best agreement was achieved with a stretch exponential function (although with parameters of low reliability), pointing towards a distribution of different time-scales for the protons due to a structurally locally (very) distorted perovskite lattice. Further analysis of the data is ongoing. In particular, the IN11 data is now being complemented by data obtained in a subsequent experiment on the time-of-flight spectrometer IN5, on the very same samples.

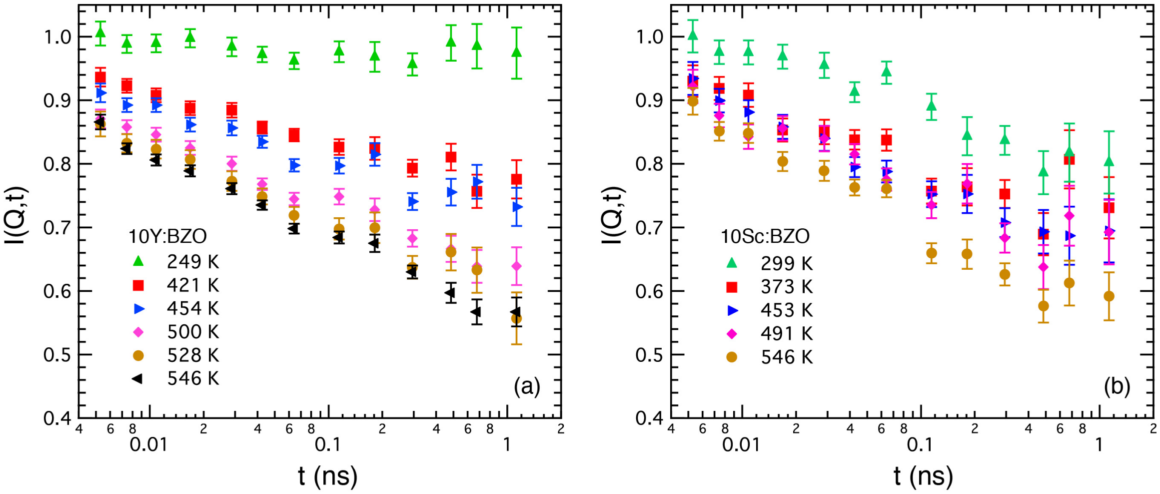

Fig. 1. Temperature dependence of the normalized intermediate scattering functions, I(Q,t), at Q = 0.96˚A^{-1}, for (a) 10Y:BZO and (b) 10Sc:BZO.

References

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