Experimental Report

16/01/2014

Proposal: **7-03-124** **Council:** 10/2012

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

This proposal is a new proposal

Researh Area: Materials

Main proposer: **KARLSSON Maths**

Experimental Team: KARLSSON Maths

Local Contact: FOUQUET Peter

Samples: BaZr0.95Y0.05O3H0.05
BaZr0.95Sc0.05O3H0.05
BaZr0.9Sc0.1O3H0.1

Instrument	Req. Days	All. Days	From	To
IN11	13	12	02/05/2013	13/05/2013

Abstract:

This proposal requests 13 days on the IN11 spin-echo spectrometer to investigate the role of type (M) and concentration (x) of dopant atoms on the proton self-diffusion, on an intermediate length-scale, in proton conducting perovskite type oxides of the form BaZr1-xMxO3Hx. In particular, we aim to elucidate one of the biggest questions in the field of proton conducting oxides, namely if the dopant atoms act as well localized trapping centers for the proton diffusion or if they tend to affect the proton diffusion in a much more non-local way by altering the activation energies for proton migration over the whole perovskite lattice. To resolve this issue is not easy, but we have the experience in relation to QENS studies on proton conducting oxides as well as the theoretical tools to take on this challenge. It is our firm belief that the new insights into the mechanistic aspects of proton self-diffusion in proton conducting oxides will be of huge interest for the solid-state-ionics community and particularly for those working on proton conducting oxides. It may be noted that this proposal is part of an ILL PhD thesis to commence in early 2013.

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Karlsson, Koza, Noferini, Wahnström

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 $BaZr_{0.9}Y_{0.1}O_3H_{0.1}$, $BaZr_{0.9}Sc_{0.1}O_3H_{0.1}$ and $BaZr_{0.95}Sc_{0.05}O_3H_{0.05}$, hereafter referred to as 10Y:BZO, 10Sc:BZO and 5Sc: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—1.3 $Å^{-1}$. For 10Y:BZO we also measured with the detector centred at 20˚, and with the use of 8 Å neutrons, but these measurements were severely intensity limited and therefore it was not possible to extract any significant result from this data. The powder samples were loaded in cylindrical Al cells with a diameter of 10 mm. The resulting scattering, considering full protonation and an average density of the material of 2.5 g/cm^2, is in the range ~10—15%. For 10Y:BZO, we collected spectra at 250 K, 396 K, 435 K, 482 K, 528 K, 563 K; for 10Sc:BZO at 250 K, 319 K, 357 K, 397 K, 435 K, 482 K, 527 K, 563 K, and for 5Sc:BZO at 319 K, 397 K, 482 K and 563 K. Moreover, for each sample we collected spectra at 2 K which were used as resolution functions (I(Q,0)), assuming that all diffusional motions of the protons are *frozen-in* at these low temperatures and the scattering of the samples is purely elastic in the NSE time window. We thus obtained the normalised intermediate scattering function I(Q,t)/I(Q,0). Due to poor statistics, it was not possible to observe any Q-dependence, therefore we decided to sum all the spectra collected at different Q-values in the range 0.7—1.3 Å.

3. Results

Figure 1 shows some of the I(Q,t)s for 10Y:BZO and 10Sc:BZO for the resulting "average" Q-value of 1 $Å^{-1}$ and temperatures in the range 250—563 K. The data have been fitted (solid lines in figure 1) using the expression:

$$\frac{I(Q,t)}{I(Q,0)} = p + a \exp\left(-\frac{t}{\tau}\right), \qquad (1)$$

where p is the plateau, a is the amplitude and τ is a characteristic relaxation time of the observed dynamics. Although all parameters were free to vary with temperatures, we found a relaxation time (30 ps for 10Y:BZO and 80 ps for 10Sc:BZO) independent of temperature, therefore it was set to constants values in the fitting procedure.. Moreover, the plateau (p) at long time-scales was calculated as the average value of the data in the range t= 0.13—1.3 ns for 10Y:BZO and t= 0.18—1.3 ns for 10Sc:BZO, and kept fixed or used as initial guess in the fitting procedure. One may note that the single exponential behaviour and the value of the relaxation time are in agreement with the NSE measurements performed on 10In:BZO [5].

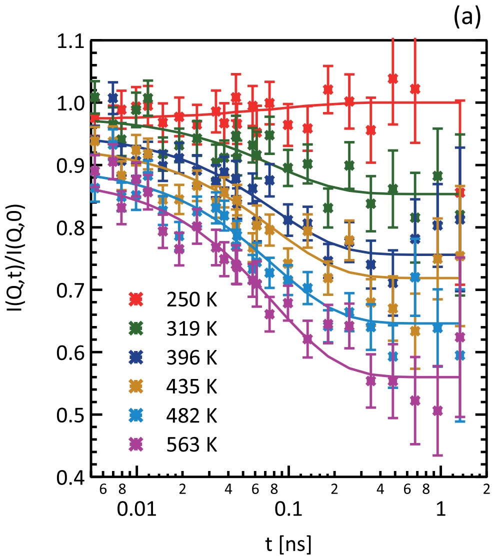

Figure 1. I(Q,t)/I(Q,0) for BaZr$_{0.9}$Sc$_{0.1}$O$_3$H$_{0.1}$ (10Sc:BZO) (a) and BaZr$_{0.9}$Y$_{0.1}$O$_3$H$_{0.1}$ (10Y:BZO) (b). Solid lines represent fits according to equation 1.

Using the values obtained from the fitting procedure and the relative weights of the coherent and incoherent contributions (indicated respectively as *coh* and *inc*) from the polarization analysis (Figure 2), and assuming no coherent dynamics in our experimental window, we calculated the incoherent mobile fraction (*MF*), i.e. the fraction of protons that contribute to the relaxational decay (= perform the observed motion):

$$MF = \frac{a}{a+p-\frac{coh}{coh-\frac{1}{3}inc}}. \qquad (2)$$

Figure 3 shows the fitting parameters *p* and *a* as a function of the temperature for both samples (up left) and the calculated values of the mobile and immobile fractions (down right).

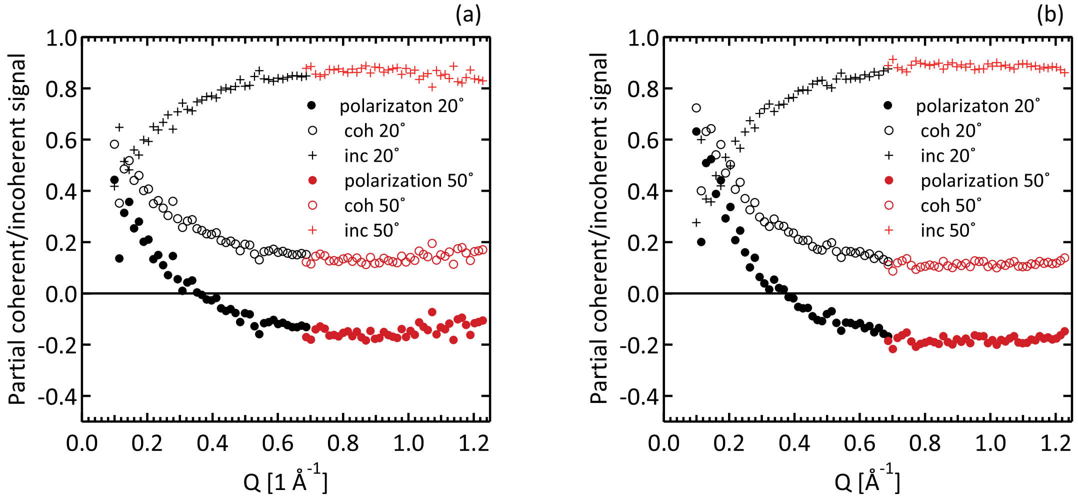

Figure 2. (a): polarization analysis of BaZr$_{0.9}$Sc$_{0.1}$O$_3$H$_{0.1}$ (10Sc:BZO) (a) and BaZr$_{0.9}$Y$_{0.1}$O$_3$H$_{0.1}$ (10Y:BZO) (b).

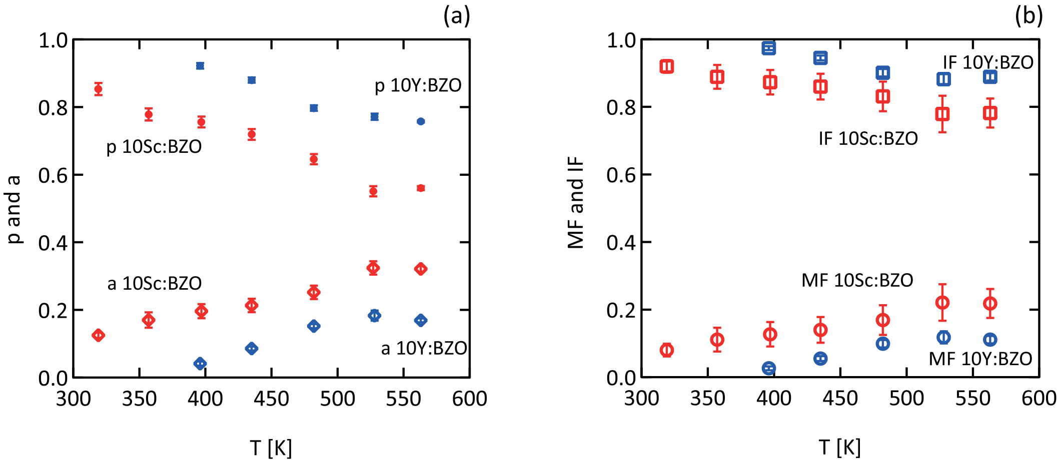

Figure 3. *T*-dependence of the fitting parameters *a* and *p* from equation 1 (a) and incoherent mobile and immobile fractions, respectively indicated as MF and IF (b).

The mobile fractions are significantly larger for the Sc-doped sample. It was also possible to extract an activation energy associated to the mobile fractions, which is about 200 meV and 63 meV respectively for 10Y:BZO and 10Sc:BZO. We note that these values are of the same order of the ones that can be extracted from the intensity of the quasielastic peak of an experiment we performed at the IN6 time of flight spectrometer at ILL on the same materials [6]. The assumption of no coherent dynamics in the experimental time window is made on the fact that the oxygen diffusion occurs at considerable slower time scales than proton diffusion at the investigated temperature [7]. Nevertheless a tilting motion of the oxygen octahedra, due to a dynamical disorder in the lattice, could occur, as suggested by theory and experimental evidences [8], may be associated to the observed relaxation decay.

4. Conclusions

From these results, a significant role of the type of dopant atom on the fraction of mobile protons, the associated activation energy and the relaxation time is suggested. Moreover, the observed dynamics seems to be a localized motion, but further investigations and comparisons with calculation results are needed to clearly understand this dynamics. Additionally, in order to be able to observe the full relaxational decay of I(Q,t), related to the long-range proton self-diffusion, it would be necessary to extend the measureable Fourier time range, and/or increase the temperature. Moreover, in order to make a clear attribution of the dynamics to protons and/or the oxygen octahedral, a measurement on an unprotonated sample would be required. Further data analysis is in progress.

References

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