Experimental report

25/09/2022

Proposal:	**7-03-206**	**Council:**	4/2021

Title: Hydride-ion jump-diffusion dynamics in the oxyhydride BaTiO2.9H0.1

Research area: Materials

This proposal is a new proposal

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Samples: BaTiO2.9H0.1

Instrument	Requested days	Allocated days	From	To
IN5	3	3	08/10/2021	11/10/2021
IN16B	2	2	02/10/2021	04/10/2021

Abstract:

This proposal requests 2 days on IN16 and 3 days on IN5 to investigate the diffusional dynamics of hydride-ions in the novel perovskite type oxyhydride BaTiO2.9H0.1. Perovskite type oxyhydrides are an emerging class of materials that may find diverse applications, ranging from catalysis, topochemical synthesis to solid state ionics, but the mechanism of hydride-ion transport is at present unclear. Of specific concern here, we, with this proposal, want to consolidate, or disprove, an earlier QENS study that indicates that the hydride-ion dynamics can be described by a jump-diffusion mechanism with the jump-diffusion pathway changing from a low-temperature to a high-temperature behaviour. Dynamics data form computer simulations, which will help in the evaluation of the neutron data.

Hydride-ion jump-diffusion dynamics in the oxyhydrides $BaTiO_{2.9}H_{0.1}$ and $SrTiO_{2.8}H_{0.1}$

1 Introduction

Perovskite type oxyhydrides, $ATiO_{3-x}H_x$, A = Ca, Sr, and Ba, with $x < 0.6$ [3], are a novel class of hydride-ion (H^-) conducting materials that may find diverse applications in the fields of catalysis, topochemical synthesis, and electrochemistry, but fundamental questions surrounding the mechanism of hydride-ion conductivity remain to be answered.

The current understanding of the hydride-ion dynamics in these materials is primarily based on our results from a quasielastic neutron scattering (QENS) experiment of oxyhydride of several compositions [1]. A key result for this experiment was the observation of a strongly temperature dependent hydride-ion dynamics on the picosecond to nanosecond timescale. At relatively low temperatures (225–250 K), the hydride-ions were found to perform jumps between neighboring oxide-ion vacancies of the perovskite lattice and with a mean residence time of ~ 0.1 ns. At higher temperatures (400 – 700 K), the hydride-ions were instead found to perform jumps between next-nearest neighboring oxide-ion vacancies, with a mean residence time of ~ 10 ps. Crucially, these dynamics are notably faster than oxide-ion diffusion in perovskite type oxides (ca. 10 ns at 700 K) [2], suggesting that the hydride-ion diffusion does not rely on the mobility of oxide-ion vacancies but rather on the availability of (static) vacant oxide-ion sites close to the hydride-ions. In this study, we attempt to confirm the presumed transport mechanism with two new compositions, namely $BaTiO_{2.88}H_{0.12}\square_0$ and $SrTiO_{2.81}H_{0.13}\square_{0.06}$, by performing QENS measurement on two instruments probing respectively the two timescale observed previously. This allows us to investigate the potential crossover from a low-temperature to a high-temperature regime.

2 Experimental details

Approximately 5 g of powder sample $BaTiO_{2.88}H_{0.12}\square_0$ (BTOH) and $SrTiO_{2.81}H_{0.13}\square_{0.06}$ (STOH) were filled into standard aluminum cells (hollow cylinders of 15mm in outer-diameter and 12mm in inner-diameter, with 3 cm in height exposed to the beam), unsealed to keep the material in contact with a low pressure helium exchange gas (~ 100 mbar).

The QENS measurements were performed on the backscattering spectrometer IN16B in the "high-flux" position with the Si(111) unpolished analyzers. This yielded a full width at half maximum (FWHM) of the resolution function of ~ 0.75 μeV and an accessible momentum transfer (Q) $0.1 - 1.8$ Å^{-1}.

First, fixed elastic/inelastic window scans (E/IFWS) were performed upon heating and cooling from base—5 K—to high temperature—450 K. QENS measurements were subsequently performed over the complete dynamic range of ± 30 μeV with a measuring time of 3h per spectrum, with $225 < T < 325$ K for BTOH and $300 < T < 500$ K for STOH. An additional measurement of BTOH at 2 K was used as a resolution function.

Secondly, the samples were measured with the time-of-flight (TOF) spectrometer IN5. It was operated with 5 Å wavelength neutrons yielding an instrumental resolution of 80 μeV (FWHM) and an accessible Q-range $0.2 - 2.3$ Å^{-1}. A measure of STOH at 2 K was taken as the resolution function.

After an initial heating to 450 K for cleaning the sample from potential organic phases of impurity, short TOF spectra (5 mins) were acquired under cooling. QENS spectra were then measured by TOF acquisitions of 1h at $100 < T < 550$ K for BTOH and $50 < T < 550$ K for STOH. Additional measures of a vanadium sample and an empty container were also acquired.

The data was reduced and analyzed within Mantid. Empty cell subtraction, detector calibration and masking were included in the reduction procedure.

3 Results and discussion

IN16B

Despite the absence of clear intensity drop in the EFWS, QENS spectra of BTOH were acquired over a small temperature range (225 – 325 K), where measurements had already been performed with IN16B on a similar sample [1]. Because of the absence of broadening of the elastic peak in BTOH (see Figure 1), spectra for STOH were acquired at higher temperature (300, 400, 500 K). None of the sample revealed a clearly identifiable QENS signal, whatever the temperature. Figure 1 shows the spectra measured at 325 K on BTOH and 500 K on STOH

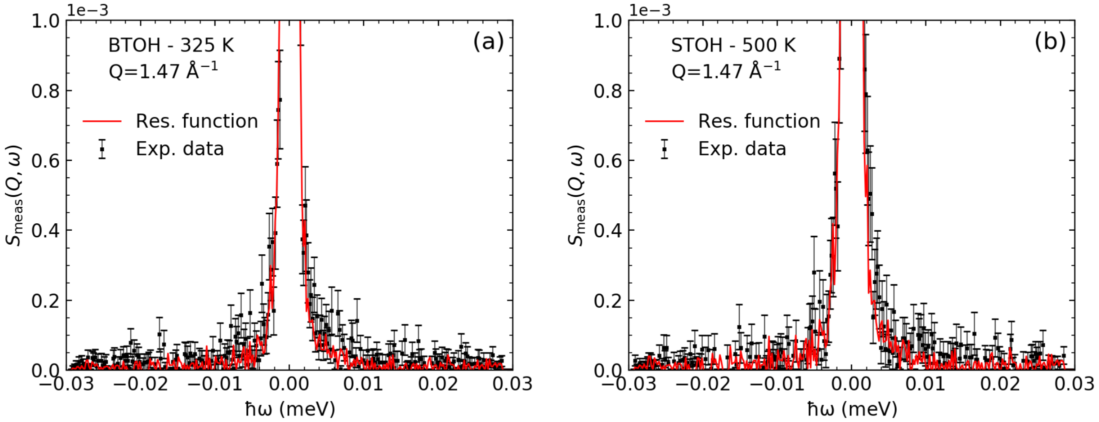

Figure 1: Selected QENS spectra at $Q = 1.47$ Å^{-1} of (a) BTOH at 325 K and (b) STOH at 500 K as measured, together with the scaled resolution function.

at $Q = 1.69$ Å^{-1} together with the resolution function, scaled to fit the data: $S_{\mathrm{meas}}(Q,\omega) = A(Q)R(Q,\omega)$, with $R(Q,\omega) = S_{\mathrm{meas}}^{\mathrm{BTOH@2K}}(Q,\omega)$.

IN5

A selected QENS spectrum of BTOH at 300 K, $Q = 1.45$ Å^{-1}, together with fitting components is shown in Figure 2a. A model of the dynamical structure factor that does not include a Lorentzian component is sufficient to satisfactorily describe the data at 300 K. Therefore, we conclude that BTOH does not show a QENS signal within the time window of IN5, at room temperature. Since the oxygen vacancies concentration is negligible in this sample, this result is in line with our assumption that H^{-} diffusion relies on the existence of percolation pathways of oxygen vacancies.

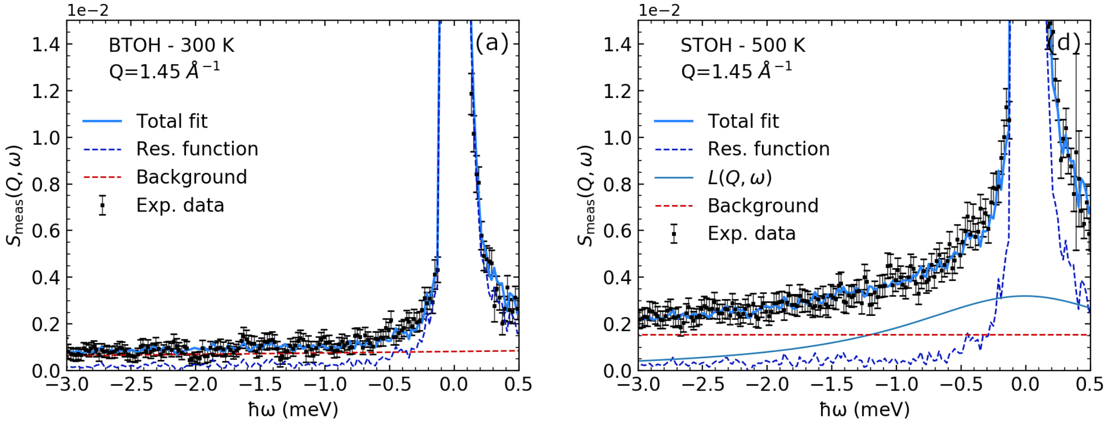

Figure 2: Measured dynamical structure factor at $Q = 1.45$ Å^{-1}, for (a) BTOH at 300 K, and (d) STOH at 500 K, together with fitting components.

Figure 2d shows a spectrum of STOH at 500 K together with fitting components. A clear broadening is visible over the temperature range $100 - 500$ K, and persists at 50 K even if very subtle in intensity. Analysis of the width of the Lorentzian, Γ, shows that Γ does not vary with Q until 450 K. For higher temperatures, it shows an increasing tendency with Q, but still questionable regarding the uncertainty values. As a result, the data was fitted with a global Γ, independent of Q, without loosing in fit quality. Note that enforcing a Q-independent Γ is to model a localized process, instead of long-range diffusion. In addition, the amplitude of the Lorentzian component is found to depend strongly on Q, which is in line with a scenario of localized motions.

Γ clearly shows a temperature dependence, and has rather high energy values, corresponding to fast dynamics with characteristic relaxation times in the range $0.6 - 2.6$ ps, which is much faster than previously observed

($\sim$ 0.1 ns at 300 K [1]). More interestingly, we report dynamics at very low temperature, 50 K. This observation raises several interrogations about the possible existence of H^- diffusive motions at such low temperatures, but the very low intensity and the large uncertainties that go along with this data do not allow us to interpret it in terms of microscopic mechanism. Above 150 K, the quasi-elastic broadening follows an Arrhenius trend, and let us assume that these dynamics are thermally activated.

In an attempt to model the geometry of H^- motions, the data was fitted with a 2-sites jump model, yielding jump distances of $d \approx 2.2$ Å until 300 K, followed by an increasing tendency reaching $d \approx 3.2$ Å at 550 K. Interestingly, the distance separating two nearest neighboring oxygen sites, $d_{O-O} \approx 2.8$ Å, lies within this range.

To conclude, the experimental observations of QENS over 150 K in STOH are in line with the presumed mechanism of H^- hopping between two nearest oxygen vacancies, but the physical interpretation of the low temperature behavior and the geometry of the H^- motions require further investigations and need to be confirmed.

References

[1] Eklöf-Österberg, C., Nedumkandathil, R., Häussermann, U., Jaworski, A., Pell, A. J., Tyagi, M., Jalarvo, N. H., Frick, B., Faraone, A., and Karlsson, M. Dynamics of hydride ions in metal hydride-reduced batio3 samples investigated with quasielastic neutron scattering. *The Journal of Physical Chemistry C 123*, 4 (2019), 2019–2030.

[2] Kessel, M., De Souza, R. A., and Martin, M. Oxygen diffusion in single crystal barium titanate. *Phys. Chem. Chem. Phys. 17* (2015), 12587–12597.

[3] Kobayashi, Y., Hernandez, O., Sakaguchi, T., Yajima, T., Roisnel, T., Tsujimoto, Y., Morita, M., Noda, Y., Mogami, Y., Kitada, A., Ohkura, M., Hosokawa, S., Li, Z., Hayashi, K., Kusano, Y., Kim, J., Tsuji, N., Fujiwara, A., Matsushita, Y., and Kageyama, H. An oxyhydride of batio3 exhibiting hydride exchange and electronic conductivity. *Nature materials 11* (04 2012), 507–11.