Experimental report

15/07/2021

Proposal: 7-03-196 **Council:** 10/2020

Title: Oxide ion and proton dynamics in Ba7Nb4MoO20 solid electrolyte

Research area: Materials

This proposal is a new proposal

Main proposer: Bettina SCHWAIGHOFER

Experimental team: Bettina SCHWAIGHOFER

Local contacts: Markus APPEL
Michael Marek KOZA

Samples: Ba7Nb4MoO20

Instrument	Requested days	Allocated days	From	To
IN16B	4	2	28/05/2021	30/05/2021
IN5	4	0		

Abstract:

Dual oxide ion and proton conductors have been proposed as promising materials for application in solid oxide fuel cells (SOFCs). Fluorite-type yttria-stabilized zirconia (YSZ) is currently the most commonly used electrolyte in SOFCs, leading to high operating temperatures (800 - 1000 °C), precluding their more widespread use. Recently, the high oxide ion and proton conductivity of 4.0 mS cm-1 at 510 °C in humidified air has been reported in Ba7Nb4MoO20, a cation deficient hexagonal perovskite derivative. The conductivity of this novel ionic conductor is considerably higher than that of YSZ. With the conductivity measurements confirming long-range dynamics in Ba7Nb4MoO20, we propose to perform variable-temperature inelastic and quasi-elastic neutron scattering experiments on this dual oxide ion and proton conductor in dry and humidified air. This should enable us to separate and individually characterise the dynamics directly related to oxide ion and proton conduction. We request 4 days of IN16B beam time and 4 days of IN5 beam time to carry out variable-temperature inelastic/quasi-elastic neutron scattering experiments on Ba7Nb4MoO20.

Oxide ion and proton dynamics in $Ba_7Nb_4MoO_{20}$ solid electrolyte

Background and context

Oxide ion and proton conducting materials have recently become a focus of research due to their application as electrolyte in solid oxide fuel cells (SOFCs) and proton ceramic fuel cells (PCFCs). Fluorite-type yttria-stabilized zirconia (YSZ) is currently the most commonly used electrolyte in SOFCs, leading to high operating temperatures (800 – 1000 °C), precluding their more widespread use. A key factor for the advancement of the rational design of SOFCs is the development and characterisation of new electrolyte materials which support a high ionic conductivity at reduced temperatures. Dual oxide ion and proton conductors have been proposed as a new type of electrolyte for intermediate temperature SOFCs. Recently, high oxide ion and proton conductivity, as well as chemical and electrical stability have been reported in $Ba_7Nb_4MoO_{20}$.[1] These interesting and exploitable properties are linked to the distinct disordered crystal structure of this hexagonal perovskite derivative. The discovery of dual ion conductivity in a new class of materials is exciting as it provides significant opportunities for improving the properties by chemical modifications, which, in turn, requires an in-depth understanding of structure-property relationships; for $Ba_7Nb_4MoO_{20}$ material, such insight is currently very limited.

Purpose of the experiment and expected outcomes

Using variable temperature quasielastic neutron scattering, we should be able to observe and individually characterise the diffusion of oxide ions (using dry air) and protons (using humidified air). The expected outcomes of the experiment, which will be analysed in conjunction with the results of the *ab initio* molecular dynamics simulations, were:

- To observe the diffusional dynamics and its evolution with temperature,
- To separate and individually characterise oxide ion and proton dynamics,
- To determine the relevant quantitative parameters for migration of both oxide ions and protons (activation energy, jump rates),

Experiment

We measured $Ba_7Nb_4MoO_{20}$ in a furnace to access the temperatures where long range proton and oxide ion diffusion sets in. An incident neutron wavelength of 6.271 Å and an energy resolution of 0.75 μeV were used to attempt accessing nanosecond dynamics in $Ba_7Nb_4MoO_{20}$. Measurements were performed in humidified N_2 and under vacuum. The energy transfer window used for all QENS measurements was ±7 μeV.

For the measurements performed under vacuum, 5.3 g of sample was placed in a Nb sample holder of diameter 8 mm, filling approximately 4 cm of it. During heating to 950 °C, elastic fixed window scans (EFWS, 2 min) and inelastic fixed window scans (IFWS, 10 min, 2 μeV) were collected in 25 °C steps and at 950 °C a QENS measurements was performed with a total data collection time of 5 h. The sample was then cooled to 50 °C while again collecting EFWS (1 min) and IFWS (5 min, 2 μeV). At 50 °C, QENS data were collected for 3 h. For the measurement in humid air, approximately 11 g of sample were placed in a stainless-steel sample holder of diameter 10 mm. N_2 was bubbled through distilled water and blown on the sample via a thin metal capillary in the steel tube. Initially, RT scans were performed to obtain QENS data (5 h). The sample was heated to 500 °C during which EFWS (2 min) and IFWS (10 min, 2 μeV) were collected in 25 °C steps. During heating QENS measurements were performed at 350 °C, 425 °C and 500 °C for 6 h per temperature. The sample was then cooled to 225 °C collecting EFWS (2 min) and IFWS (10 min, 2 μeV) in 25 °C steps to collect QENS data at 225 °C for 6 h, and after further cooling at 175 °C for 4 h. Data were also collected at RT on the empty tube (QENS: 4 h; EFWS: 2 min; IFWS 10 min, 2μeV) and on a vanadium standard (QENS: 30 min) to allow for the necessary corrections to be completed.

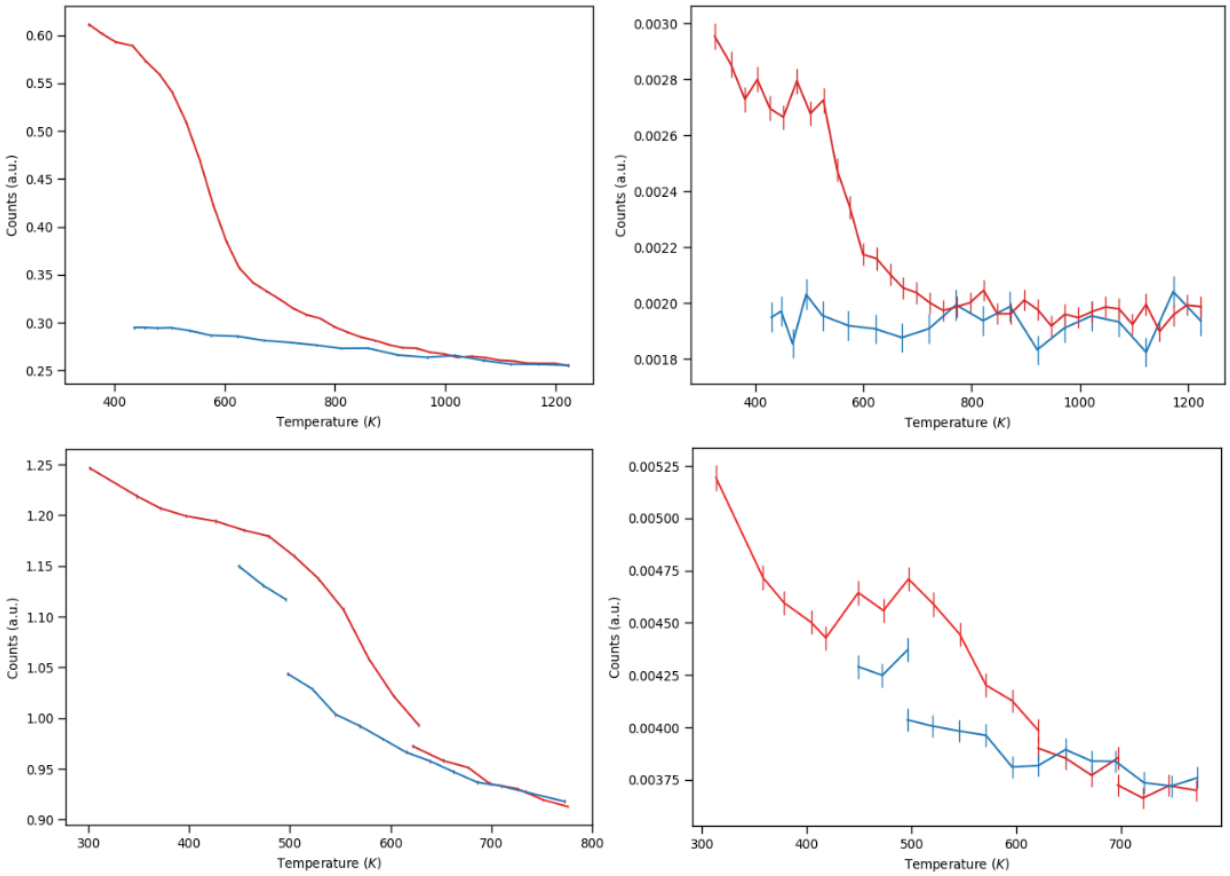

Figure 1. Elastic fixed window scans (left) and Inelastic fixed window scans (right) in vacuum (top) and humid N2(bottom). Data collected on heating are shown in red, and on cooling in blue. Gaps in curves are caused by QENS measurements performed for several hours between the fixed window scans during which some intensity is gained (if water is reabsorbed on cooling) or lost (if water is lost).

References

1. Fop, S.; McCombie, K. S.; Wildman, E. J.; Skakle, J.M. S.; Irvine, J. T. S.; Connor, P. A.; Savaniu, C.; Ritter, C.; Mclaughlin, A. C., High oxide ion and proton conductivity in a disordered hexagonal perovskite. Nature Materials **2020**,19, 752-757