Experimental report

06/01/2021

Proposal: 7-03-183

Council: 4/2019

Title: Oxide ion dynamics in Ba3NbMoO8.5 solid electrolyte

Research area: Materials

This proposal is a new proposal

Main proposer: Ivana EVANS

Experimental team: Miguel Angel GONZALEZ
Andrea PIOVANO
Bettina SCHWAIGHOFER
Chloe FULLER

Local contacts: Michael Marek KOZA
Markus APPEL

Samples: Ba3NbMoO8.5

Instrument	Requested days	Allocated days	From	To
IN16B	4	4	10/02/2020	14/02/2020
IN5	3	3	14/02/2020	17/02/2020

Abstract:

Oxide ion conductors have been a focus of research due to their application as electrolyte 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, high oxide ion conductivity has been reported in Ba3NbMoO8.5 a hybrid of the 9R perovskite polytype (A3B2O9) and the palmierite (A3B2O8). With the conductivity measurements confirming long-range dynamics in Ba3MoNbO8.5, we propose to perform variable-temperature inelastic (INS)/quasi-elastic (QENS) neutron scattering experiments on this oxide ion conductor, to observe the dynamics directly related to ionic conduction. We request 4 days of IN16B beam time and 3 days of IN5 beam time to carry out variable-temperature inelastic/quasi-elastic neutron scattering experiments on Ba3MoNbO8.5

Experiment 7-03-183: Oxide ion dynamics in $Ba_3NbMoO_{8.5}$ solid electrolyte

Background and context

Oxide ion conductors have been a focus of research due to their application as electrolyte 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, high oxide ion conductivity has been reported in $Ba_3NbMO_{8.5}$ (M = Mo, W). The significance of this finding is that this interesting and exploitable property has been observed for the first time in a particular structural family - a hybrid of the 9R perovskite polytype ($A_3B_2O_9$) and the palmierite ($A_3B_2O_8$).[1]The materials are pure oxide ion conductors under standard conditions with a conductivity of ~2×10^{-3} S cm^{-1} at 600 °C.[1]

The discovery of oxide ion conductivity in a new and compositionally/structurally flexible 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 $Ba_3NbMoO_{8.5}$ material, such insight is currently very limited.

Purpose of the experiment and expected outcomes

With the conductivity measurements confirming long-range dynamics in $Ba_3MoNbO_{8.5}$ and our extensive neutron and simulation experience with oxide ion conductors, we propose to perform variable-temperature inelastic (INS)/quasi-elastic (QENS) neutron scattering experiments on this hybrid hexagonal perovskite - palmierite based oxide ion conductor, to observe the dynamics directly related to ionic conduction. In particular, we should be able to observe the diffusion of oxide ions in the QENS part and the modification of the vibrational density of states (vDOS) as a function of the evolution of defects.

Based on our experience with oxide ion conductors with similar building blocks, we'd like to probe dynamics directly related to the ionic conduction from the picosecond to the nanosecond time scale. Given that the scattering cross section of oxygen is almost entirely coherent, we will use a large (10 g) sample.

Since the material displays a structural rearrangement between 300 and 400 ^{o}C, we propose to collect data below this change, through it and after it, at sufficiently high temperatures that the rearrangement is complete and the dynamics are vigorous.

The expected outcomes of the experiment, which will be analysed in conjunction with the results of the ab-initio molecular dynamics simulations, are:

- To observe the diffusional dynamics and its evolution with temperature,
- To determine the relevant quantitative parameters (activation energy, jump rates),
- To determine and interpret the modifications in the vDOS as a function of the temperature-dependent defect evolution and structural rearrangements.

Experiments

We measured $Ba_3NbMO_{8.5}$ sample in a furnace to access the temperature range where dynamics set in. A stainless-steel tube was used to avoid the potential loss of oxygen under vacuum.

We collected QENS data on IN16B backscattering instrument to access dynamics on the ns timescale. We first ran elastic fixed window scans (30 second/point) on heating from 150°C to 800 °C using a heating rate of 10 °C min^{-1}. Following that, elastic (60 second/point) and inelastic fixed window scans (3 minutes/point, 2 µeV offset) were recorded on cooling to 150 °C and again on heating to 800 °C, using a heating rate of 1.8 °C min^{-1}. QENS measurements were collected at 800 °C and 400 °C with an energy transfer window of ±15 µeV and a data collection time of 4 h at each temperature. During cooling (1.2 °C min^{-1}), elastic (60 second/point) and inelastic fixed window scans (10 minutes/point, 5 µeV offset) were collected. Data were also collected on the empty tube and a vanadium standard in order to perform the necessary corrections.

Due to unexpected decomposition of the sample during the repeated heating to 800 °C and the 4 h QENS measurement at 800 °C, no trends indicating the presence of a measurable QENS signal could be observed in the fixed window scans, and no broadening of the elastic peak is apparent in the QENS data.

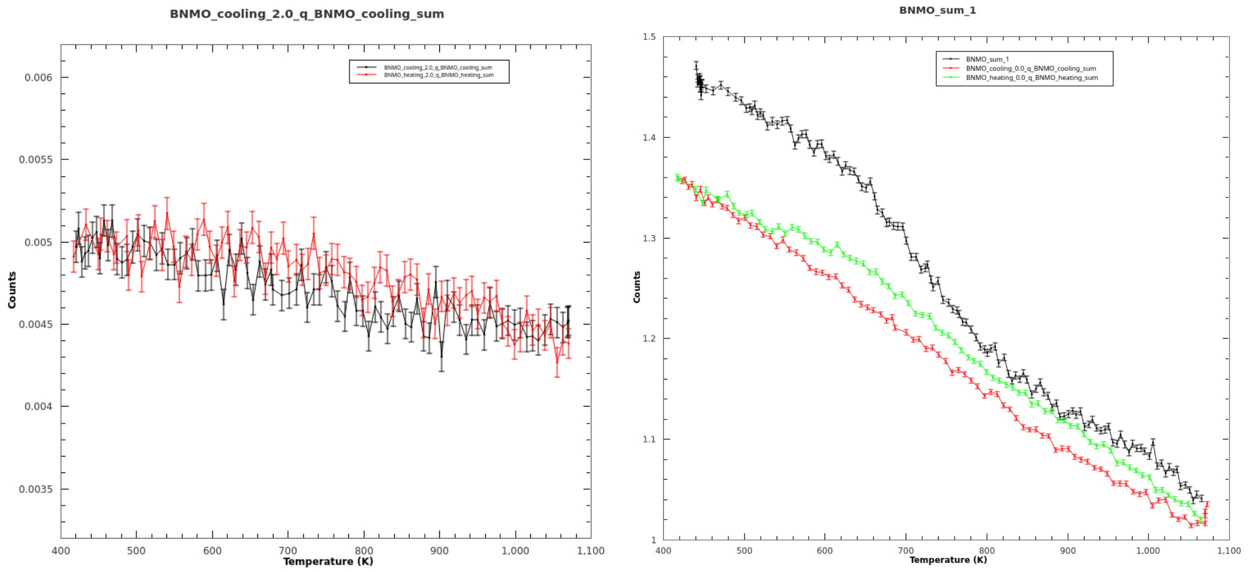

Figure 1 Inelastic (left) and elastic (right) fixed window scans summed over all detectors measured on IN16B on $Ba_3NbMoO_{8.5}$.

In addition, we collected INS and QENS data on IN5 using a wavelength of 4.8 Å and a fresh sample of $Ba_3NbMoO_{8.5}$. On heating from 200 °C to 600 °C, measurements were taken every 16.7 °C (24 points, 5 minutes/ point, 1 minute stabilisation), and 30 minutes measurements were recorded at 200 °C and 400 °C. At 600 °C the sample was measured for 5 hours (30 x 10 minutes). On cooling to 200 °C, 24 5-minute measurements were recorded similarly to the measurements collected during heating. At 400 °C and 200 °C the sample was measured for 2 hours (4 x 30 minutes) each.

Diffraction data showed that decomposition of the sample could be avoided, but no QENS signal was observed.

References

1. Fop, S.; Skakle, J. M. S.; McLaughlin, A. C.; Connor, P. A.; Irvine, J. T. S.; Smith, R. I.; Wildman, E. J., Oxide Ion Conductivity in the Hexagonal Perovskite Derivative $Ba_3MoNbO_{8.5}$. *Journal of the American Chemical Society* **2016,** 138, (51), 16764-16769.