# Experimental report

30/08/2016

**Proposal:** 7-03-151 **Council:** 4/2016

**Title:** Direct Observation of Oxide Ion Conduction

**Research area:** Chemistry

**This proposal is a continuation of 7-03-139**


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**Samples:** Na0.5Bi0.5TiO3
Bi0.913V0.087O1.587
Na0.5Bi0.49Ti0.98Mg0.02O2.965
La1.54Sr0.46Ga3O7.27

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| IN16B | 6 | 4 | 03/06/2016 | 07/06/2016 |


## Abstract:

Oxide ion conductors are key components in a number of technologically important applications, including solid oxide fuel cells (SOFCs), where they act as electrolytes transporting O2- to react with a fuel in the direct conversion of chemical to electrical energy. Better understanding of how the structures of such materials lead to high oxide ion conductivity will lead to more efficient fuel cells with lower operating temperatures. This would have significant technological and environmental impact.
Using IN16b we have successfully investigated oxygen diffusion in La2Mo2O9 and have measured a QENS signal indicating oxygen dynamics in bismuth vanadate. In this proposal we request beam time on IN16b to complete our study of bismuth vanadate as well as investigate three new materials which are good candidates for intermediate temperature oxide ion conduction. IN16b is required to directly observe oxygen dynamics on the nanosecond timescales which are associated with long range diffusion and can be confronted with macroscopic, conductivity measurements. Ab initio molecular dynamics simulations are being performed on these materials to give detailed insight into diffusion mechanisms.

# Direct Observation of Oxide Ion Conduction – Experimental Report

Oxide ion conductors are key components in a number of technologically important applications, including oxygen sensors and pumps, membranes for oxygen separation and solid oxide fuel cells (SOFCs). In the latter case, they act as electrolytes transporting $O^{2-}$ to react with a fuel such as $H_2$ in the direct conversion of chemical to electrical energy. Better understanding of how the structures of such materials lead to high oxide ion conductivity will lead to more efficient fuel cells with lower operating temperatures. This would have significant technological and environmental impact.

A key factor for the advancement of the rational design of SOFC materials is the nature of oxide ion transport in the solid state, especially in structurally complex oxides, in which the mechanisms of $O_2$ transport are more complex involving flexible O environments and variable coordination polyhedra.

## Samples

In this experiment the sample studied was a powder of $Bi_{0.913}V_{0.087}O_{1.587}$. This is known to be a very good oxide ion conductor and had shown QENS signal indicating dynamics in initial measurements during a previous experiment on IN16b (experiment 07-03-139). The µeV energy resolution of IN16b shows that dynamics occur over a nanosecond timescale and this experiment was carried out to further probe these processes.

## Data Collection

Having carried out an elastic scan in our previous IN16b experiment as well as three QENS scans at varying temperatures, we carried out further QENS scans at 9 temperatures in a range from 200 °C to 500 °C in an energy window of ±10 µeV in order to optimise the counting rate (figure 1, some temperatures omitted for clarity). In addition to this, four scans were measured with an energy window of the ±30 µeV in order to check that the background level was the same at all temperatures and consistent with the resolution and empty sample cell measurements (figure 2).

## Results

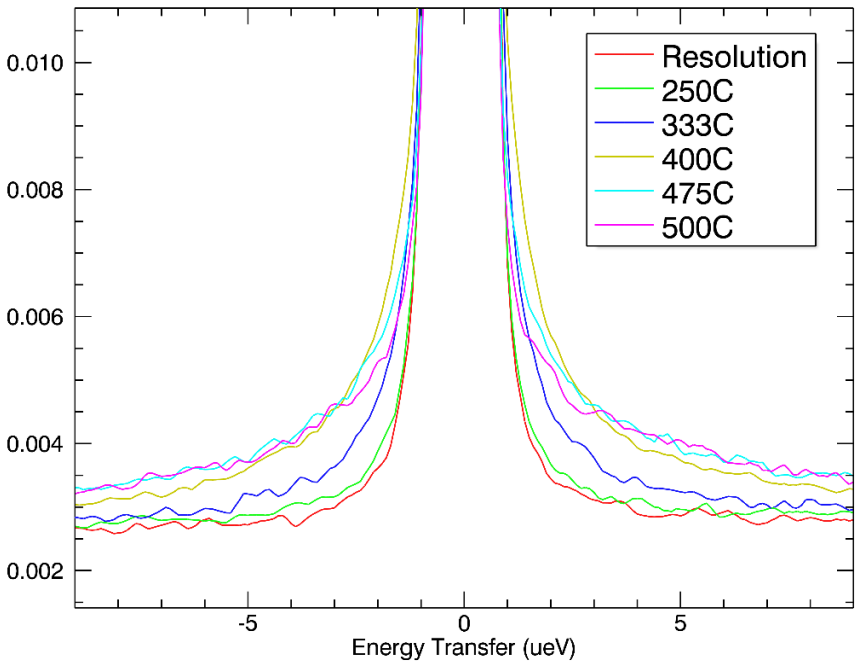


**Figure 1:** QENS spectra recorded at a range of temperatures for $Bi_{0.913}V_{0.087}O_{1.587}$ with an energy window of ±10 µeV

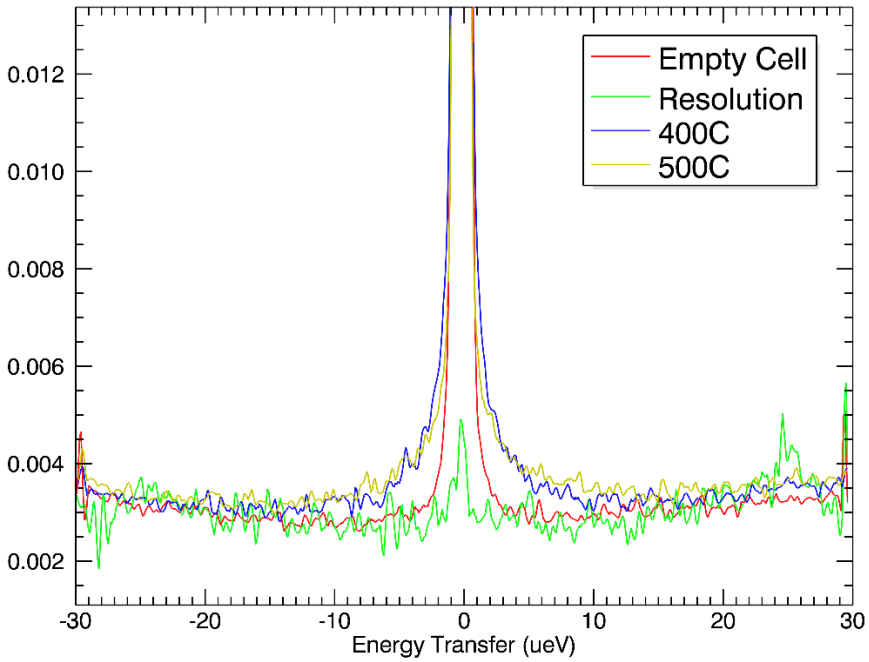


**Figure 2:** QENS spectra recorded at a range of temperatures for $Bi_{0.913}V_{0.087}O_{1.587}$ with an energy window of ±30 μeV

Figure 1 show that there is a clear QENS signal visible at this resolution that broadens as temperature increases. From figure 2 it can be seen that these spectra do indeed fall to the background level at higher energy transfer range and can be accurately fitted with a single Lorentzian. An activation energy has been extracted from the temperature dependence of the spectral width which is consistent with macroscopic conductivity measurements.

Ab initio (DFT) molecular dynamics are being performed and analysed to understand the diffusion mechanism. A single dynamical process is observed on IN16b and IN6 (ps timescale) whereas, initially, a fast, local process (rotation of metal-oxide polyhedral) and a slower, long-range process were expected. Simulations seem to indicate that both local and long-range processes involve vacancy hopping around and between metal sites which occur on a similar timescale. The Q-dependence of the QENS signal is being investigated to confirm this model.