Experimental report

18/12/2015

Proposal: 7-03-139 **Council:** 10/2014

Title: Direct observation of oxygen ion conduction

Research area: Chemistry

This proposal is a resubmission of 7-03-133

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Samples: La2Mo2O9
Sr2Fe2O5
Bi26Mo10O69
Bi10VO17

Instrument	Requested days	Allocated days	From	To
IN16B	6	5	31/10/2015	05/11/2015

Abstract:

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 O2- to react with a fuel such as H2 in the direct conversion of chemical to electrical energy. Better understanding of why such materials show this unusual behaviour will lead to new oxide ion conductors and more efficient fuel cells operating at lower 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 than conventional vacancy-hopping. In this proposal we request IN16b beam time to extend successful time-of-flight measurements to the time domain of longer range, translational diffusion, which is the microscopic ionic conduction process.

Direct Observation of Oxide Ion Conduction – Experimental Report

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Samples

A total of four samples were studied in this experiment $La_2Mo_2O_9$, $Bi_{0.913}V_{0.087}O_{1.587}$, $Bi_{26}Mo_{10}O_{69}$ and $Sr_2Fe_2O_5$. Each of these is known to be an oxide ion conductor and has shown a QENS signal indicating dynamics in previous experiments on TOF instruments. The μeV energy resolution of IN16b allows dynamics that occur over a nanosecond timescale to be probed meaning that longer range oxygen diffusion can be observed than that which occurs on the picosecond timescales probed in these earlier experiments.

Data Collection

For each of the four samples, elastic scans were first carried out to investigate the variation in elastic intensity with temperature (see Figure 1). A range of temperatures were then chosen and QENS measurements were carried out over the energy transfer range, limited to ±10 μeV in order to optimise the counting rate.

Results

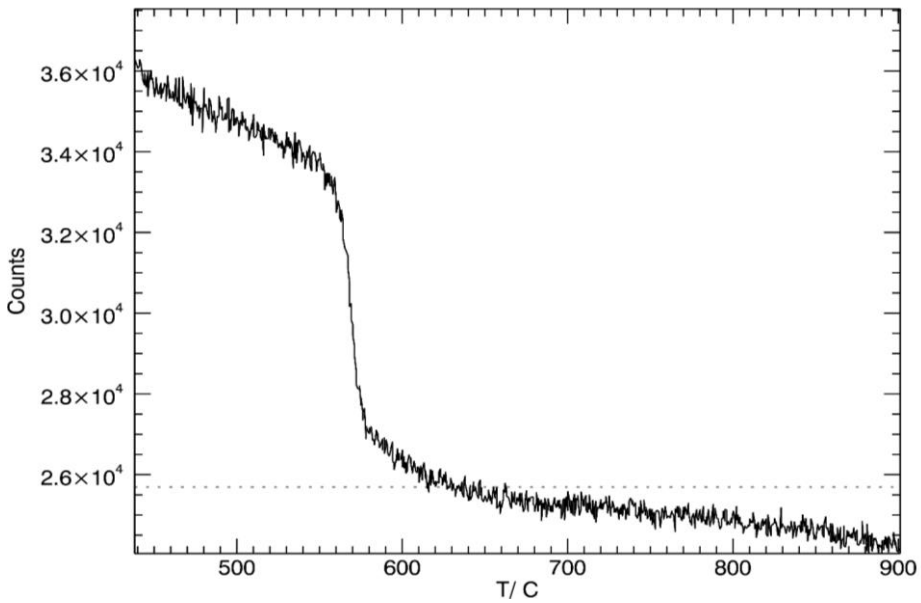

Figure 1: Intensity of the elastic peak plotted against temperature for $La_2Mo_2O_9$

The variation in elastic intensity with temperature for $La_2Mo_2O_9$ shows a large drop of roughly 25 % between 560-580 °C, this coincides with a known phase transition that causes the conduction to dramatically increase. The loss in elastic intensity is due to the onset of dynamics.

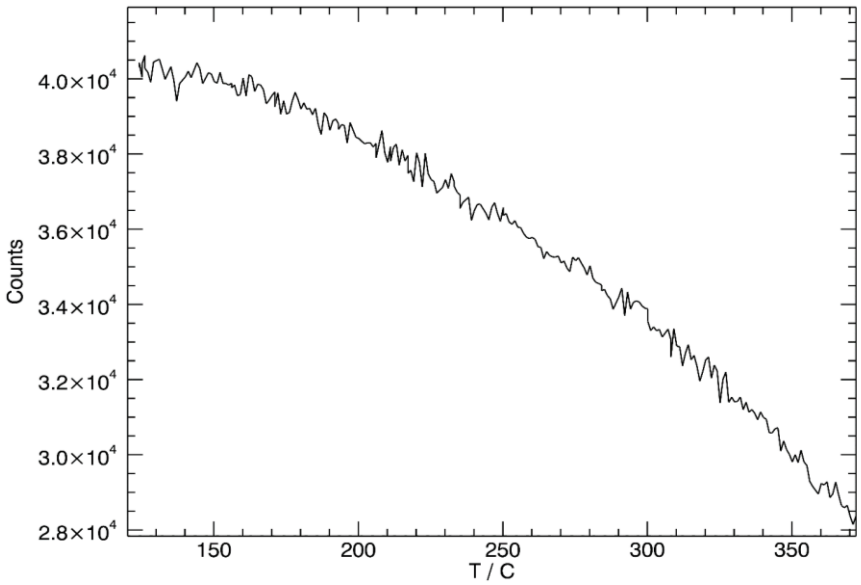

Figure 2: Intensity of the elastic peak plotted against temperature for $Bi_{0.913}V_{0.087}O_{1.587}$

The $Bi_{0.913}V_{0.087}O_{1.587}$ does not show such a drastic drop as no phase transition occurs at these temperatures. However, the decrease in intensity is much faster than the linear section of the $La_2Mo_2O_9$ figure perhaps indicating lower frequency dynamics in $Bi_{0.913}V_{0.087}O_{1.587}$. The remaining two samples showed small linear decreases over the entire temperature range.

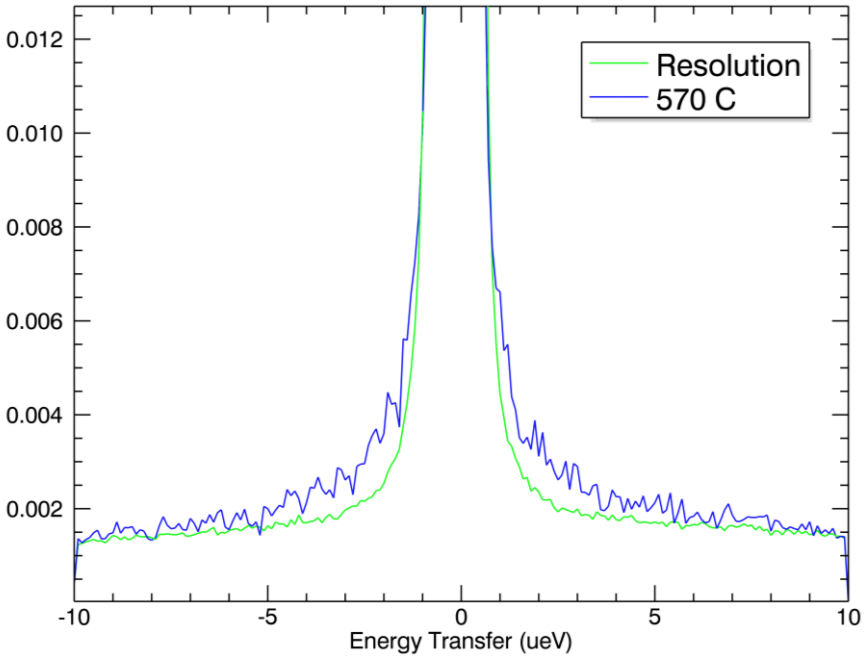

Figure 3: A QENS spectrum recorded at 570 C for $La_2Mo_2O_9$.

The $La_2Mo_2O_9$ and $Bi_{0.913}V_{0.087}O_{1.587}$ both showed QENS signals indicating that at these temperatures dynamics do occur on the nanosecond timescale. For the $Bi_{0.913}V_{0.087}O_{1.587}$ the QENS signal was only seen at 450 °C and will have to be investigated more carefully in a second experiment. However for the $La_2Mo_2O_9$ the signal was seen to evolve over a much larger temperature. These spectra are being analysed with a view to determining an activation energy for the dynamical process from the temperature dependence and geometrical information from the Q-dependence. Ab initio (DFT) molecular dynamics are being performed to be confronted with this experimental data.

The $Bi_{26}Mo_{10}O_{69}$ and $Sr_2Fe_2O_5$ samples showed no quasielastic scattering in the temperature ranges investigated. This indicates that for these samples the oxide ion mobility does not occur on the nanosecond timescale.