Experimental report

13/07/2021

Proposal: **7-03-187** **Council:** 10/2019

Title: Fluorite-type solid electrolytes with complex oxide ion diffusion mechanisms

Research area: Materials

This proposal is a resubmission of 7-03-184

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Samples: $Bi_{0.852}V_{0.148}O_{1.648}$
$Bi_{0.852}P_{0.148}O_{1.648}$

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	5	3	19/08/2020	22/08/2020

Abstract:

Fluorite-type $Bi_{0.852}V_{0.148}O_{1.648}$ is an excellent oxide ion conductor, reaching the conductivity of 10-2 S/cm at 600C. We have also reported ab initio molecular dynamics simulations on this material and found mechanisms involving variable-coordination VOx polyhedra imbedded in a Bi-O sublattice. The overall aims of the experiment is to directly probe and understand the differences in performance between: a) $Bi_{0.852}V_{0.148}O_{1.648}$ and $Bi_{0.913}V_{0.087}O_{1.587}$, which contain the same structural motifs (fluorite-like Bi-O sabs and interspersed VOx polyhedra), but adopt different long range superstructures; b)$Bi_{0.852}V_{0.148}O_{1.648}$ and $Bi_{0.852}P_{0.148}O_{1.648}$, which are isostructural, but differ in their performance as oxide ion conductors.From a comparative analysis of the $Bi_{0.852}V_{0.148}O_{1.648}$ and $Bi_{0.852}P_{0.148}O_{1.648}$, both in terms of lattice dynamics and quasielastic, it should be possible to extract detailed information about the geometry and energetics of the localised diffusion, which AIMD showed to be an important effect enabling the Bi-O and V-O sublatticies exchange at high temperature.

Fluorite-type solid electrolytes with complex oxide ion diffusion mechanisms

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. 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 oxides structurally more complex than YSZ, in which the mechanisms of O^{2-} transport are more intricate and involve flexible and variable cation coordination polyhedra (rather than or in addition to the "textbook" vacancy-hopping).

Purpose of the experiment and expected outcomes

The overall aims of the experiment, which is currently being analysed in conjunction with the results of ab-initio molecular dynamics simulations, was to directly probe and understand the differences in performance between:

1. $Bi_{0.852}V_{0.148}O_{1.648}$ and $Bi_{0.913}V_{0.087}O_{1.587}$, which contain the same structural motifs (fluorite-like Bi-O slabs and interspersed VO_x polyhedra), but adopt different long range superstructures;
2. $Bi_{0.852}V_{0.148}O_{1.648}$ and $Bi_{0.852}P_{0.148}O_{1.648}$, which are isostructural, but differ in their performance as oxide ion conductors.

In light of NMR results[1], it is evident that from a comparative analysis of $Bi_{0.852}V_{0.148}O_{1.648}$ and $Bi_{0.852}P_{0.148}O_{1.648}$, both in terms of lattice dynamics (rotation and libration modes) and quasielastic dynamics (rapid localised motion), it should be possible to extract detailed information about the geometry and energetics of the localised diffusion, which AIMD showed to be an important effect enabling the Bi-O and V-O sublatticies exchange at high temperature. The present possibility to investigate two isostuctural samples with distinct localised dynamics increases the chances of observing even subtle changes in the dynamic response. The higher V (and P) doping content of these materials compared to our previously investigated $Bi_{0.913}V_{0.087}O_{1.587}$ sample, would allow for a higher amount of VO_x groups undergoing rapid localised rearrangements of the O-atoms and as consequence larger chances to detect quasielastic signal connected to this motion.

Experiments

We measured $Bi_{0.852}V_{0.148}O_{1.648}$ and $Bi_{0.852}P_{0.148}O_{1.648}$ in a furnace to access the temperature where localized and long range diffusion sets in. An incident wavelength of 5.12 Å was used for all measurements.

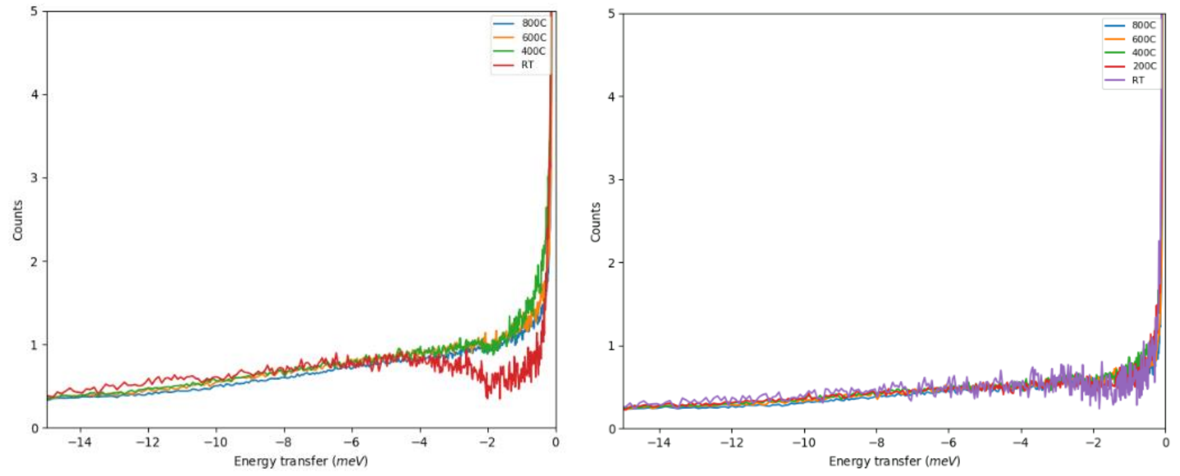

Figure 1. The Q-integrated scattering function corrected for the Bose population factor against energy transfer at several temperatures for $Bi_{0.852}V_{0.148}O_{1.648}$ (left) and $Bi_{0.852}P_{0.148}O_{1.648}$ (right) measured on IN6.

A Nb cell was filled with 5.95 g of $Bi_{0.852}V_{0.148}O_{1.648}$, and measurements were collected at 25 °C (9 h), 400 °C (5 h), 600 °C (5 h), 800 °C (9 h), and on cooling at 200 °C (8 h). For the measurement on $Bi_{0.852}P_{0.148}O_{1.648}$, a Nb-cell was filled with 4.83 g of sample. Measurements were performed at 25 °C, 200 °C, 400 °C, 600 °C, and 800 °C for 5 h per temperature. Data were also collected on an empty cell and a vanadium standard in order to perform the necessary corrections.

Figure 1 shows the Q-integrated scattering function against energy transfer at several temperatures for $Bi_{0.852}V_{0.148}O_{1.648}$ and $Bi_{0.852}P_{0.148}O_{1.648}$. More detailed data analysis is currently in progress.

References

1. Dunstan, M. T., Halat, D. M., Tate, M. L., Evans, I. R. & Grey, C. P. Variable-Temperature Multinuclear Solid-State NMR Study of Oxide Ion Dynamics in Fluorite-Type Bismuth Vanadate and Phosphate Solid Electrolytes. *Chem. Mater.* **31**, 1704–1714 (2019).