Experimental report

30/08/2019

Proposal: 7-03-171 **Council:** 4/2018

Title: New brownmillerite-based oxide ionconductors: Direct observation of multi-scale oxide ion dynamics

Research area: Materials

This proposal is a new proposal

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Samples: Sr2ScGaO5
Sr2Sc0.6Zn0.4GaO4.8

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	5	5	05/10/2018	10/10/2018
IN16B	5	5	12/09/2018	17/09/2018

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.

Our collaborative research programme on the development of new oxide ion conductors, based in part on using neutron scattering methods coupled with computational modelling, has resulted in new insight into the relationships between structure, dynamics and properties in some of the leading solid electrolytes based on the fluorite and apatite structure types. Crucially, we have been able to demonstrate the importance of variable coordination environments of cations and the rotational freedom of these coordination polyhedra as key structural motifs which facilitate high oxide ion mobility at relatively low temperatures.

We have recently prepared new excellent oxide ion conductors based on the brownmillerite structure. These are new compositions based on Sr2ScGaO5, which itself is a modest oxide ion conductor. Here we request 5 days on IN16b and 5 days on IN6, to carry out the first variable-temperature inelastic/quasi-elastic neutron scattering experiments on the new oxide ion conductors.

New brownmillerite-based oxide ion conductors: Direct observation of multi-scale oxide ion dynamics

Background and context

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 complex.

Our collaborative research programme focussing on the development of new oxide ion conductors, based in part on using neutron scattering methods in conjunction with computational modelling, has resulted in new insight into the relationships between structure, dynamics and properties in some of the leading solid electrolytes based on the fluorite and apatite structure types.[1-6] Crucially, we have been able to demonstrate the importance of variable coordination environments of cations and the rotational freedom of these coordination polyhedra as key structural motifs which facilitate high oxide ion mobility at relatively low temperatures.

We have recently prepared new excellent oxide ion conductors based on the brownmillerite structure. These are new compositions, based on Sr_2ScGaO_5, which itself is a modest oxide ion conductor in the temperature range of interest. In this proposal we request 5 days on IN16b and 5 days on IN6, to carry out the first variable-temperature inelastic/quasi-elastic neutron scattering experiments on the new oxide ion conductors.

Previous work

Sr_2ScGaO_5 adopts the brownmillerite structure type, which is an orthorhombic oxygen-deficient derivative of the perovskite structure (Fig. 1a). Ab initio molecular dynamics simulations performed on this material have suggested it to be a one-dimensional oxide ion conductor, with the diffusion pathways largely contained to the vacancy channels in the structure.[7] Sr_2ScGaO_5 is a good (rather than excellent) oxide ion conductor, but in our recent work we have found that Zn-doping increases the conductivity by up to two orders of magnitude in the temperature range between 400 and 900 °C.[8] This doping not only increases the conductivity significantly, but, for a certain range of compositions, produces cubic materials with likely isotropic conductivity, which is important for some applications. In addition to the conductivity measurements, our preliminary characterisation of these samples includes laboratory variable temperature X-ray diffraction (Fig. 1b), SEM/EDX, solid state NMR, and thermal analysis The Rietveld fit shown in Fig. 1b for $Sr_2Sc_{0.6}Zn_{0.4}GaO_{4.8}$ indicates a pure, single-phase product (in agreement with the SEM analysis), while the EDX elemental analysis confirms the composition.

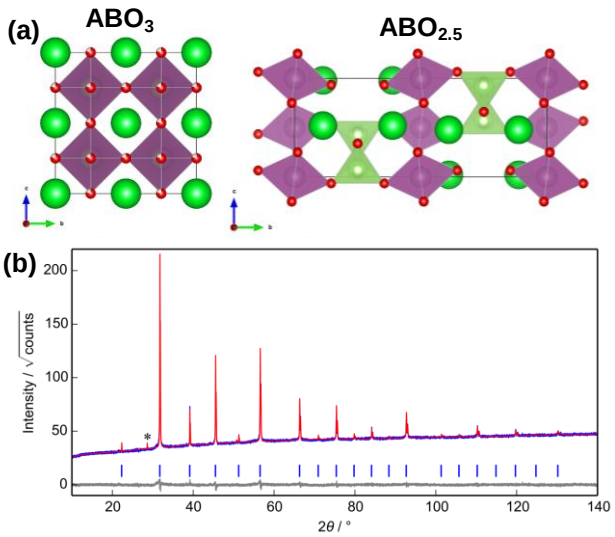

Fig.1: (a) The perovskite and the brownmillerite structure type. (b) Rietveld fit obtained to the ideal perovskite structural model for $Sr_2Sc_{0.6}Zn_{0.4}GaO_{4.8}$ against laboratory XRD data, confirming the purity of the material.

Purpose of the experiment

In light of the preliminary results on these materials, we performed variable-temperature inelastic (INS)/quasi-elastic (QENS) neutron scattering experiments on a polycrystalline sample of $Sr_2Sc_{0.6}Zn_{0.4}GaO_{4.8}$. In addition, we collected "benchmark" data on Sr_2ScGaO_5, for direct and quantitative comparison with the better-performing doped composition. Based on our experience with similar neutron scattering experiments on oxide ion conductors, we probed multi-scale 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 used large (~10 g) polycrystalline samples and long counting times (6 hours per temperature). The high counting rate of IN16b and IN6 instruments were therefore used to measure the weak signal given by the low scattering power of O^{2-} ions. These two instruments were used in conjunction to probe dynamics from picoseconds to nanoseconds.

This experiment allowed:

- The observation of diffusional dynamics over a broad timescale to be studied as a function of temperature,
- The extraction of the vibrational density of states, enabling lattice vibrations (such as ScO_6 librations and tilting) promoting ionic diffusion to be identified in conjunction with *ab initio* molecular dynamics and normal mode calculations,

Experimental

The IN6 experiment was performed with an incident neutron wavelength of 5.12 Å and an elastic energy resolution of 70 μeV. 10 g samples were placed in a cylindrical, 8 mm diameter Nb sample holder, and data were collected at room temperature, 200, 400, 600, 800, and 1000 °C, with a collection time of 6 h at each temperature. Background scattering from the empty sample holder was measured for 6 h at room temperature. Vanadium was measured at 20 °C for 6 h for normalization and to describe the instrument resolution function. $S(\omega)$ spectra and vibrational density of states were extracted for each temperature.

The IN16B experiment was carried out with an incident neutron wavelength of 6.271 Å and an energy resolution of 0.75 μeV, to give access to nanosecond dynamics. 10 g powdered samples were placed in a cylindrical 8 mm diameter Nb sample holder. Initially the measurements of elastic intensity (E = 0 μeV) and inelastic intensity at 2 μeV, were performed on heating from 20 to 900 °C using a heating rate of 0.04 °C s−1 and on cooling to 290 °C. Data points were collected in pairs with elastic intensity (EFWS—elastic fixed window scan) measured for 30 s, immediately followed by an inelastic intensity (IFWS—inelastic fixed window scan) measurement lasting 2 min. Quasielastic neutron scattering (QENS) measurements were performed at room temperature and 1000 °C for 6 h at each temperature (as six 1-h repetitions) within an energy transfer window of ±20 μeV. The background scattering from the empty can was measured for 5 h, and a resolution function from a standard vanadium sample was also acquired at room temperature. $S(\omega)$ spectra were extracted for each temperature.

Results

Following data analysis, results relating to the parent Sr_2ScGaO_5 material were published in Chemistry of materials (DOI: 10.1021/acs.chemmater.9b02051). Data on the Zn-doped derivative will be published in a further paper once data analysis from a different facility experiment has been completed.

References

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