Experimental report

15/07/2021

Proposal: **7-03-189**

Council: 10/2019

Title: Oxide ions diffusion mechanism in melilite-type solid electrolytes

Research area: Materials

This proposal is a new proposal

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Samples: La1.54Sr0.46Ga3O7.27
La1.40Sr0.60Ga3O7.20
LaSr0.60Bi0.40Ga3O7.20

Instrument	Requested days	Allocated days	From	To
IN16B	6	4	24/09/2020	28/09/2020
IN6-SHARP	5	2	22/08/2020	24/08/2020

Abstract:

It has been demonstrated that the 2D extended corner-sharing tetrahedral network of the melilite-type La1+xSr1−xGa3O7+0.5x can both accommodate excess oxide anions and sustain their mobility. The composition La1.54Sr0.46Ga3O7.27 shows the highest oxide ion conductivity of ~0.1 S/cm at 800 C. This represents an improvement of 4 orders of magnitude compared to LaSrGa3O7.

In this proposal, we request IN16b and IN6 to carry out variable-temperature quasi-elastic and inelastic neutron scattering experiments on La1.54Sr0.46Ga3O7.27, La1.40Sr0.60Ga3O7.20 and LaSr0.60Bi0.40Ga3O7.20 oxide ion conductors. This will be the first direct observation of the O2- dynamics in melilite-type materials, which will be analysed in conjunction with the first ab initio molecular dynamics (AIMD) simulations on these systems. This will enable us to relate the differences in oxygen ion conductivities to the interstitial oxygen excess (La1.54Sr0.46Ga3O7.27 and La1.40Sr0.60Ga3O7.20) and Bi doping (La1.40Sr0.60Ga3O7.20 and LaSr0.60Bi0.40Ga3O7.20) in terms of activation energy, residence time, favourable conduction paths and possible lone pair blocking effect for the conduction in the Bi-doped sample.

Oxide ions diffusion mechanism in melilite-type solid electrolytes

Background

Oxide ion electrolytes with conductivities exceeding 10^{-2} S cm^{-1} at moderate temperatures (~500 - 600 ºC) are necessary for widespread use of these materials in solid oxide fuel cells for electricity generation. The mobile oxide ion defects in these materials are usually vacancies in the anion sublattice. However, there has been a growing interest in the recent years in systems where interstitial or excess oxide ions are the charge carriers. It has been demonstrated that the 2D extended corner-sharing tetrahedral network of the melilite-type $La_{1+x}Sr_{1-x}Ga_3O_{7+0.5x}$ can both accommodate excess oxide anions and sustain their mobility.[1] In this solid solution, prepared by varying the La:Sr ratio relative to the stoichiometric melilite $LaSrGa_3O_7$, the composition $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ shows the highest oxide ion conductivity of ~0.1 S cm^{-1} at 800 ºC. This represents an improvement of 4 orders of magnitude compared to $LaSrGa_3O_7$.

Purpose of the experiment and expected outcomes

The overall aim of this study was to directly probe and understand the oxide ion conduction in $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ and $La_{1.4}Sr_{0.4}Ga_3O_{7.2}$. Our experimental goals were

1) to collect the lattice dynamics signal (rotation and libration modes) and the quasielastic signal due the rapid localised reorientational motion (~ few tenth of ps) of GaO_x polyhedra.
2) to collect the quasielastic signal due to long range diffusion of oxide ions on the ns timescale in melilite-type oxide ion conductors.

Experiments

For the measurements on IN16B, 6.16 g of $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ were weighed out and filled into a Nb cell. Initially, a QENS measurement at RT was performed for 8h. On heating to 600 °C, elastic (5 min) and inelastic (30 min, 2 µeV) fixed windows scans were recorded. On cooling QENS data were collected at 600 °C and 475 °C for 8 h each and at 350 °C for 9 h using a maximum energy transfer window of 7 µeV.

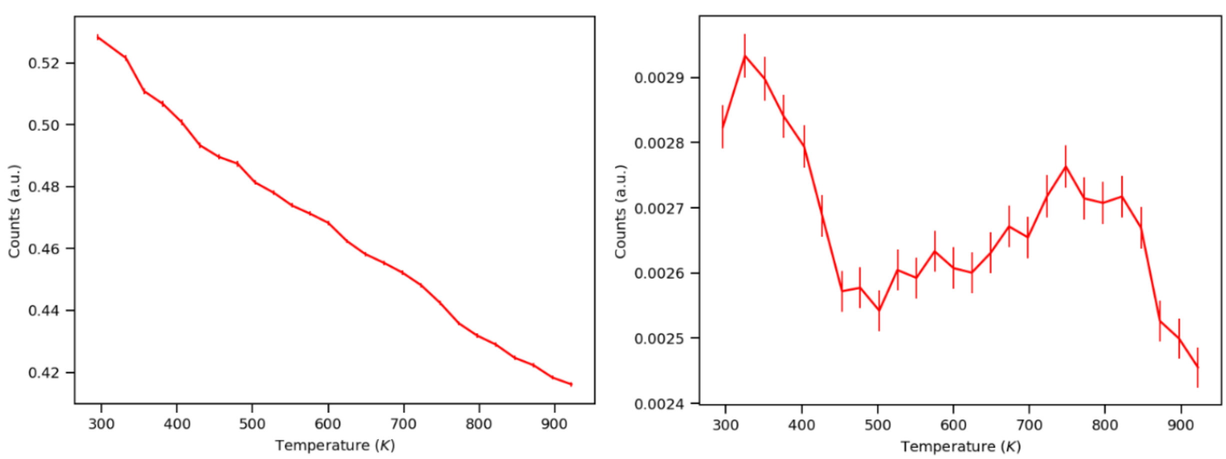

Figure 1. Elastic fixed window scan (left) and inelastic fixed window scan (right) of $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ collected on IN16B on heating.

On IN6Sharp, an incident wavelength of 5.12 Å was used. QENS measurements were collected at RT, 200 °C, 400 °C and 600 °C for 8 h per temperature. Due to some complications and time loss during the experiments, no neutron scattering data of $La_{1.4}Sr_{0.4}Ga_3O_{7.2}$ could be recorded.

The results of the fixed window scans measured on IN16B are shown in Figure 1. No change of slope is observed in the elastic fixed window scan which suggests that no quasielastic broadening can be observed. In the inelastic fixed window scan, and initial decrease of intensity is observed, followed by a slight increase. However, it does not increase above the points measured at RT, and initial data analysis suggests that no broadening is apparent in the QENS data.

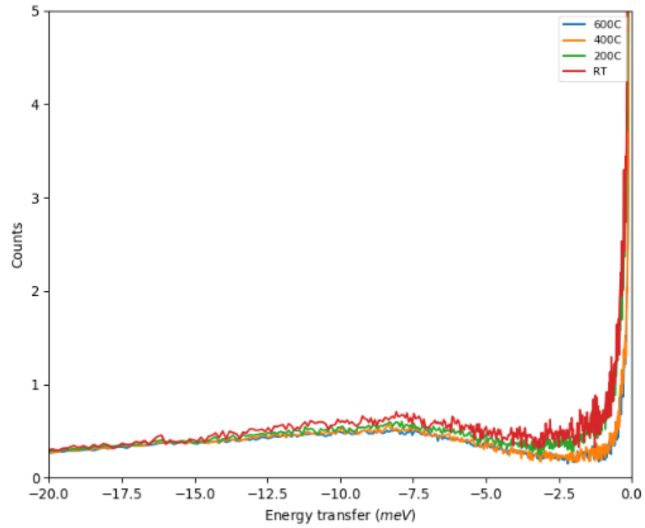

Figure 2. The Q-integrated scattering function corrected for the Bose population factor against energy transfer at several temperatures for $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ measured on IN6.

Figure 2 shows the Q-integrated scattering function against energy transfer at several temperatures for $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ recorded on IN6. More detailed data analysis is currently in progress.

References

1. Kuang, X.; A. Green, M.A., Niu, H.; Zajdel P.; Dickinson C.; Claridge, J.B.; Jantsky, L.; Rosseinsky, M.J. Interstitial oxide ion conductivity in the layered tetrahedral network melilite structure. Nature Materials **2008**, 7, 498