Experimental report

13/09/2022

Proposal: 5-23-757 **Council:** 10/2020

Title: Structural ordering in new super-excess melilite oxide ion conductors

Research area: Chemistry

This proposal is a new proposal

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Samples: La1.725Ba0.275Ga3O7.3625
La1.9Ba0.1Ga3O7.45
La1.8Ba0.2Ga3O7.4
La1.7Ba0.3Ga3O7.35
La1.75Ba0.25Ga3O7.375
La1.6Ba0.4Ga3O7.3
La1.3Ba0.7Ga3O7.15
La1.65Ba0.65Ga3O7.325

Instrument	Requested days	Allocated days	From	To
D2B	2	2	07/06/2021	09/06/2021

Abstract:

We propose to characterise the crystal structures of a new series of non-stoichiometric gallate melilite oxide ion conductors La1+xBa1-xGa3O7+x/2 with extremely high interstitial oxide ion concentrations x > 0.35 (so-called "super-excess" compositions). These are new materials with potential applications as solid oxide fuel cell electrolytes which we have synthesised for the first time by direct crystallisation of an under-cooled melt. Their ionic conduction properties are thought to be affected by complex, correlated ordering of interstitial oxide ions and La3+/Ba2+ cations that is composition- and temperature-dependent, but these relationships are poorly understood due to the narrow range of compositions that were previously accessible. We will use D2B to collect neutron powder diffraction data from a wide range of compositions and temperatures (0.3 < x < 0.9; and 25-800°C for x = 0.8) to map the onset of structural ordering on the interstitial oxide and La3+/Ba2+ sublattices by the Rietveld method, and correlate this with their measured conductivities to produce new chemical understanding of these materials.

Experiment 5-23-757

The aim of this experiment was a detailed structural characterisation of a new series of metastable oxide-rich melilites of formula $La_{1+x}Ba_{1-x}Ga_3O_{7+x/2}$, which are of interest for their oxide ion conduction properties. These materials are synthesised by direct crystallisation of their under-cooled melts, achieved by laser heating of aerodynamically levitated beads. A structural phase transition occurs as the series is traversed from x = 0 (tetragonal) to x = 1 (orthorhombic), which is associated with the onset of long-range order on the interstitial oxide ion sublattice (onset at x ≈ 0.75). A similar phase transition occurs when the orthorhombic phases are heated: in this case, the structure becomes tetragonal, which is associated with oxide diffusion. Our objectives were to locate all of the crystallographic sites occupied by interstitial oxide in these materials (even at low concentrations), and to follow the evolution of these site occupancies across the series and with temperature, to help us to understand ionic conductivity in this system. An additional question about the role of possible La/Ba ordering in this system was also addressed (this type of ordering cannot be addressed by PXRD studies due to isoelectronic Ba^{2+} and La^{3+}).

48 hours were allocated for the experiment. Samples were mailed in advance to the ILL and the experiment was conducted remotely at D2B by the beam line scientist (Stanislav Savvin) due to the Covid health crisis measures. The reactor flux was lower than anticipated at the proposal stage, so sample measurement times were slightly increased by sacrificing extra measurements at high temperature, and by measuring the sample x=0.9 at room temperature in the furnace (thus adding additional background contribution to this sample). All of the compositions were measured at room temperature, and x=0.9 was measured in-situ at additional temperatures of 525, 720, 770 and 820°C. The final data quality was satisfactory.

The structural phase transition was clearly seen with both x and T. Systematic trials of different Rietveld models found that the onset of oxide ion ordering with x is best modelled with a two-phase refinement, with an increasing fraction of a fully-ordered orthorhombic phase and decreasing fraction of disordered tetragonal phase. Alternative partially-disordered single phase models such as that adopted by the $La_{1+x}Ca_{1-x}Ga_3O_{7+x/2}$ system[1] produced poorer fits and were thus discarded. A similar situation was found upon heating. Surprisingly, Fourier difference mapping did not reveal any additional oxide sites, suggesting that certain crystallographic sites remain "off-limits" to oxide diffusion. This may be related to the known distortion behaviour of the melilite framework, which encourages 1-dimensional ordering and diffusion.[2–4] We could not discern any long-range ordering of La/Ba in any of these diffraction patterns.

These results are currently being written up for publication, following an extensive study of their conductivity properties by AC-impedance on as-synthesised beads. They constitute an entire chapter of Haytem Bazzaoui's PhD thesis (University of Orléans, defence scheduled November 2022).

References

1 M.-R. Li, X. Kuang, S. Y. Chong, Z. Xu, C. I. Thomas, H. Niu, J. B. Claridge and M. J. Rosseinsky, *Angewandte Chemie International Edition*, 2010, **49**, 2362–2366.

2 J. Fan, V. Sarou-Kanian, X. Yang, M. Diaz-Lopez, F. Fayon, X. Kuang, M. J. Pitcher and M. Allix, *Chemistry of Materials*, 2020, **32**, 9016–9025.

3 C. Genevois, H. Bazzaoui, M. Boyer, S. Ory, Y. Ledemi, Y. Messaddeq, M. J. Pitcher and M. Allix, *Inorganic Chemistry*, 2021, **60**, 12339–12354.

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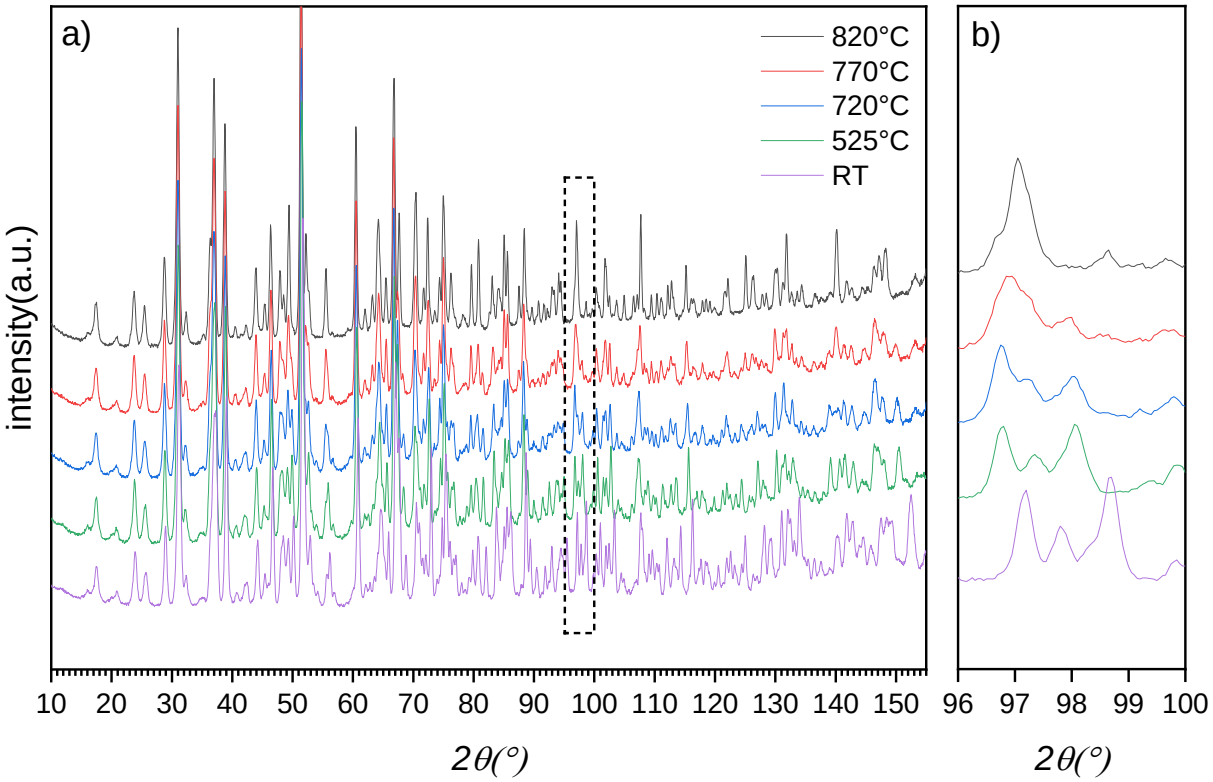

Figure: Stacked high temperature neutron powder diffraction patterns of the $La_{1.9}Ba_{0.1}Ga_3O_{7.45}$ (x= 0.9) composition. A zoom on the 96° - 100° (2ϑ) region is shown in (b) panel, highlighting the O → T transition on heating.