Experimental report

17/08/2022

Proposal: **EASY-1051** **Council:** 4/2021

Title: Fe/Ga order in Na3Fe5-xGaxO9

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Michael HAYWARD**

Experimental team:

Local contacts: Emmanuelle SUARD

Samples: Na3Fe5-xGaxO9 (x = 2, 3)

Instrument	Requested days	Allocated days	From	To
D2B	8	8	06/10/2021	07/10/2021

Abstract:

As part of an ongoing project looking at Li-ion battery cathode materials, we have been studying materials of composition Li3Fe5-xGaxO9. The phases are prepared via the low-temperature Li-for-Na cation exchange of the corresponding Na3Fe5-xGaxO9 compounds. We observe that samples with x < 2 the cation exchange works smoothly, as does oxidative deintercalation of Li. However for samples with x > 3, LiFe3O8 is produced on cation exchange. In addition there is a sharp change in the lattice parameters of Na3Fe2Ga3O9 (x = 3), compared to Na3Fe3Ga2O9 (x = 2).

We think these changes are due to Fe/Ga cation order. However, we cannot characterize the Fe/Ga order in the system by X-ray diffraction due to the similar X-ray scattering powers of Fe and Ga.

The neutron scattering lengths of Fe (9.45 fm) and Ga (7.28 fm) differ by 30%, so neutron diffraction data can be used effectively to determine the Fe/Ga order in the two samples.

We therefore propose to collect room temperature neutron powder diffraction data from Na3Fe2Ga3O9 and Na3Fe3Ga2O9 to characterise the cation order in the phases and any other structural differences which could account for their differing cation exchange chemistry.

Experimental Report ILL-EASY-1051

Neutron powder diffraction data were collected from $Na_3Fe_3Ga_2O_9$ and $Na_3Fe_2Ga_3O_9$ at room temperature using the D2B instrument.

These data could be fit well by a structural model (space group *C*2/*c*) which consists of a network of apex linked MO_4 and MO_6 units as shown in Figure 1.

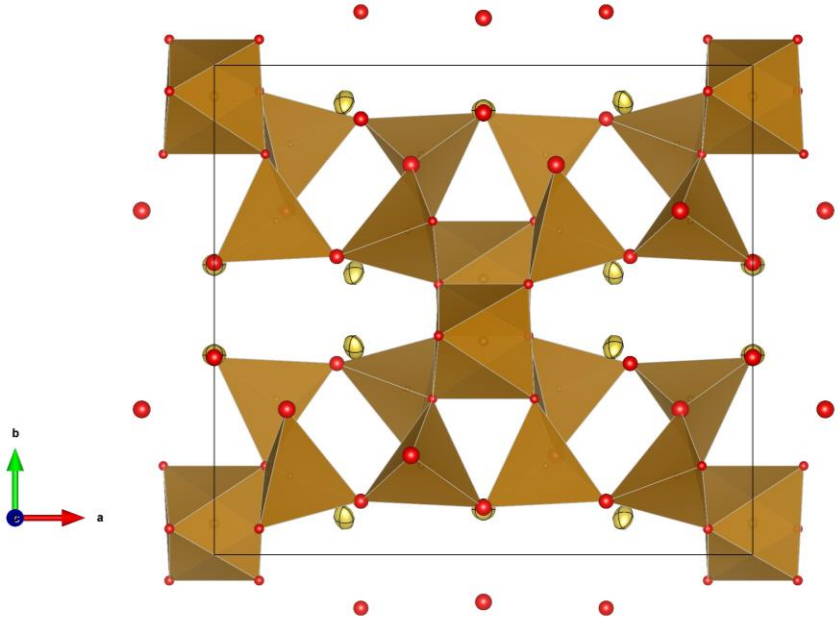

Figure 1. The refined structure of $Na_3Fe_3Ga_2O_9$. Brown polyhedral represent MO_4 and MO_6 units (M = Fe, Ga), red and yellow spheres represent O and Na respectively.

Fits to the data, shown in Figures 2 and 3 indicate that the gallium cations are only substituted onto the tetrahedral coordination sites, with the octahedral site only containing Fe^{3+} cations. This observation has significant implications for the redox activity of this phases and the lithium-substituted analogues.

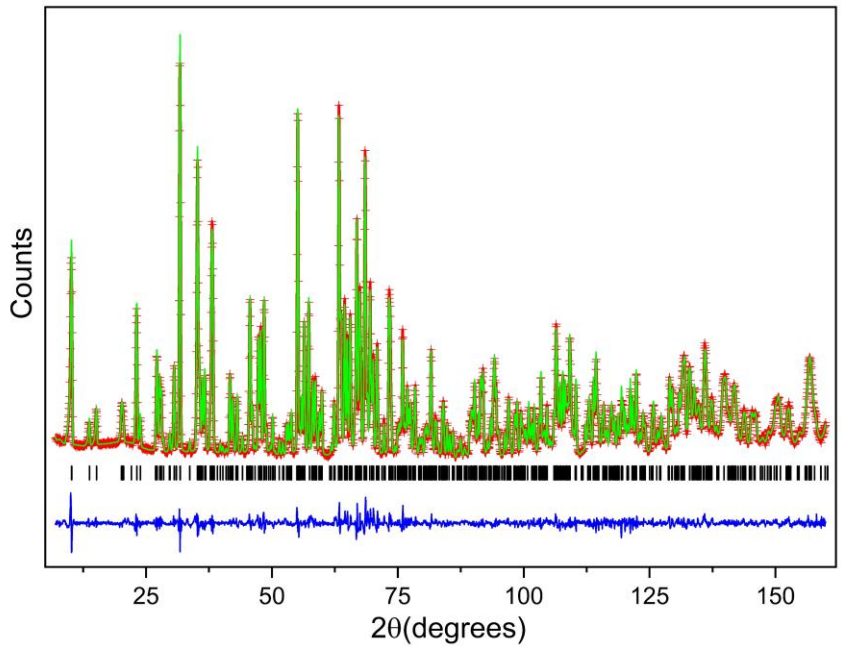

Figure 2. Observed, calculated and difference plots from the structural refinement of $Na_3Fe_3Ga_2O_9$ against NPD data.

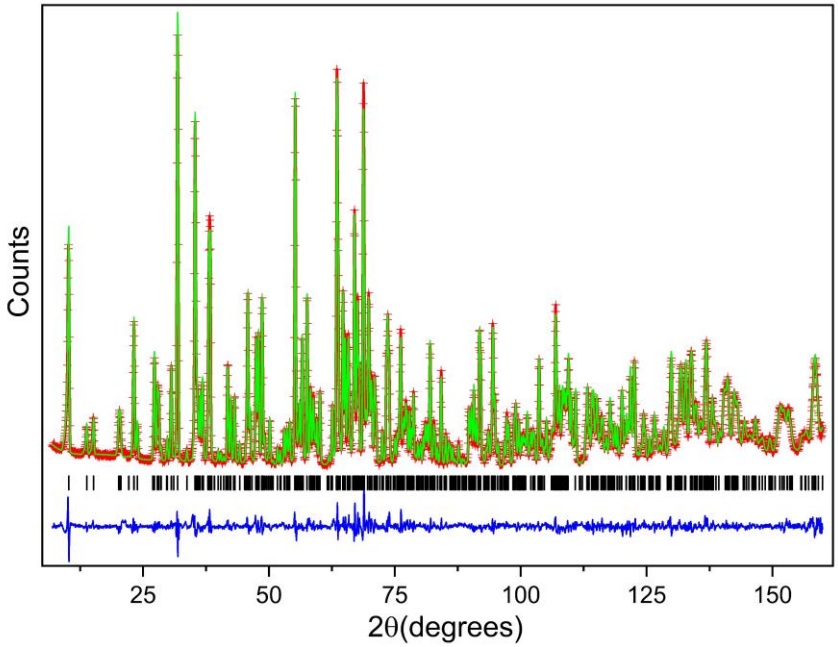

Figure 3. Observed, calculated and difference plots from the structural refinement of $Na_3Fe_2Ga_3O_9$ against NPD data.