Experimental report

11/02/2021

Proposal: 5-23-719 **Council:** 10/2018

Title: Oxygen content, ordering and magnetic structure in new oxygen deficient Sr(Sc/Ga)0.5Fe0.5O2.5+d

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Werner PAULUS**

Experimental team: Werner PAULUS
Monica CERETTI

Local contacts: Clemens RITTER

Samples: SrSc0.5Fe0.5O2.5 and SrFe0.5Ga0.5O2.5(D20)0.5

Instrument	Requested days	Allocated days	From	To
D2B	2	2	11/02/2020	13/02/2020
D20	2	1	10/02/2020	11/02/2020

Abstract:

The aim of the proposed experiments is to correlate oxygen content to magnetic structure in a new family of oxygen deficient perovskites SrSc0.5Fe0.5O2.5+d and SrGa0.5Fe0.5O2.5+d.
On one hand, neutron diffraction will enable to investigate the nuclear structure of the two title compounds, with different oxygen stoichiometry (with d = 0, 0.125 and 0.25), and on the other hand, to explore the long-range magnetic structure of SrSc0.5Fe0.5O2.75 and SrSc0.5Fe0.5O2.75 between 2-25K.

Oxygen content, ordering and magnetic structure in new oxygen deficient $Sr(Sc/Ga)_{0.5}Fe_{0.5}O_{2.5+\delta}$

Oxygen deficient Perovskites/Brownmillerites ($A_2BB'O_5$), have attracted much attention, especially as they show oxygen ion mobility down to ambient temperature. This unusual low-temperature oxygen mobility has been evidenced to rely on a phonon assisted diffusion mechanism, essentially based on large, dynamically activated displacements of the apical oxygen atoms of the BO_6 octahedra. Oxygen diffusion at room temperature thus makes this class of compounds attractive for many technologically important applications in the field of solid-state electrolytes and more specifically for membranes and pure electrolytes.

We have recently reported on oxygen diffusion mechanisms in a new oxygen deficient perovskite, $SrSc_{0.5}Ga_{0.5}O_{2.5}$, containing exclusively open or closed shell B-cations. Due to the fixed valence of Sc and Ga the phase is stoichiometric and can be stabilized from the Brownmillerite structure by standard cooling from 1500°C.

Substituting Ga with Fe, we could stabilize in the same manner an oxygen deficient perovskite $SrSc_{0.5}Fe_{0.5}O_{2.5+\delta}$ (SSFO) with cubic symmetry, with Sc and Fe on the same crystallographic B-site. We investigated this system and found a large variation of the oxygen stoichiometry as a function of the reaction conditions. Reaction with ozone at relatively low reaction temperature yields an increase of the oxygen stoichiometry to $SrSc_{0.5}Fe_{0.5}O_{2.75}$, while annealing under reducing conditions, the oxygen content decreases towards $SrSc_{0.5}Fe_{0.5}O_{2.5}$.

The aim of the proposed experiments was to study the nuclear structure of this new family of oxygen deficient perovskites $SrSc_{0.5}Fe_{0.5}O_{2.5+\delta}$ and thus determine the exact oxygen content.

With the allocated neutron beam time on D2B, we explored the nuclear structure of $SrSc_{0.5}Fe_{0.5}O_{2.5+\delta}$ with two oxygen stoichiometries: $\delta = 0.00$ and $\delta = 0.125$ at room temperature. As a result, the structure of the stoichiometric compound is of the brownmillerite type, with an orthorhombic symmetry in the space group *Imma* (a= 5.7221(6) Å, b= 15.2893(9) Å, c = 5.8868(5)Å).

Otherwise, by inserting a small amount of oxygen, the symmetry becomes cubic (*Pm-3m*) and $\delta = 0.122(3)$

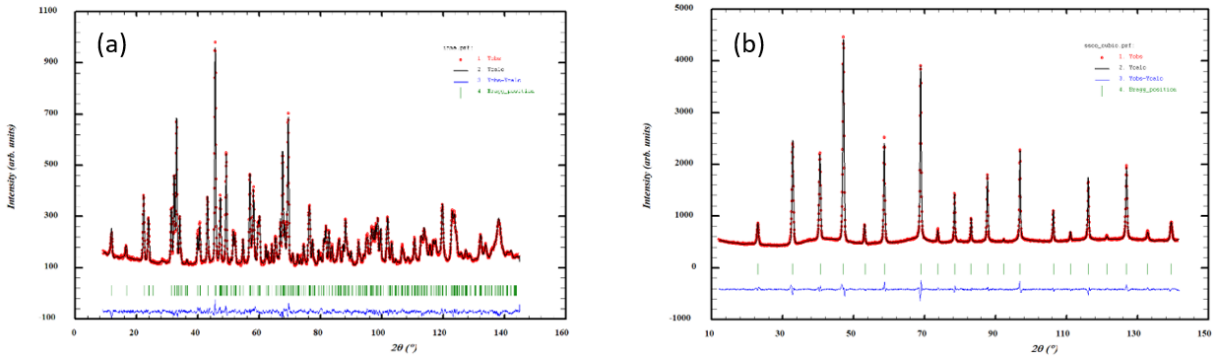

Figure 1: Neutron powder diffraction data of SSFO, collected on D2B at RT. (a) the orthorhombic Imma polymorph (HR data) and (b) the cubic one (HI data)