Experimental report

30/07/2024

Proposal: 5-23-802 **Council:** 4/2023

Title: Composition dependence of structure and magnetic order in Ba2MnO2Li2-pS2

Research area: Chemistry

This proposal is a new proposal

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Souvik GIRI

Local contacts: Emmanuelle SUARD

Samples: Ba2MnO2Li2S2
Ba2MnO2LiS2
Ba2MnO2Li1.5S2

Instrument	Requested days	Allocated days	From	To
D2B	2	2	06/11/2023	08/11/2023
D20	2	0		

Abstract:

We will determine the structure and magnetic order as a function of the Li content in a series of layered oxide sulfides with mixed-valent Mn with compositions controlled by varying the Li content using soft chemical transformations of these metastable phases. Measurements using 1.6 Å neutrons will offer optimal data for structural characterisation and for determining the evolution of the magnetic structures with varying Mn3+/Mn2+ ratios. We will measure 2-3 g samples of three samples Ba2MnO2Li2-pS2 (p = 0, 0.5, 1) at room temperature and at 5K in order to describe the crystal structures (including changes of bond lengths and ligand field around the Mn ions and location of light Li and O ions), and the magnetic ordering.

EXPERIMENTAL REPORT

EXPERIMENT N° 5-23-802 INSTRUMENT D2B

DATES OF EXPERIMENT 06/11/2023 to 08/11/2023

TITLE Composition dependence of structure and magnetic order in Ba2MnO2Li2-xS2

EXPERIMENTAL TEAM (names and affiliation)

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Date of report 30/07/24

Composition dependence of structure and magnetic order in $Ba_2MnO_2Li_{2-x}S_2$

Recently transition oxychalcogenides have gained a lot of interest as mixed anion compounds to achieve superior properties to well-studied oxides[1]. In this experiment we collected room temperature and low temperature neutron powder diffraction (NPD) patterns for three new manganese oxysulfides $Ba_2MnO_2Li_{2-x}S_2$ (x= 0,0.5,1) with varying content of lithium to understand the effect of composition in magnetic properties. Previous studies on the related compound $Sr_2MnO_2Cu_{1.8}Te_2$ has shown that deintercalating 15% Cu from the compound produces $Sr_2MnO_2Cu_{1.5}Te_2$ which changes the magnetic properties from 2D magnetic ordering to 3D magnetic ordering [2]. This is related to the allievated disorder in magnetic superexchanges in the MnO_2 plane when the composition has close to equal amounts of Mn^{2+} and Mn^{3+}.

The compound with composition $Ba_2MnO_2Li_2S_2$ hosts Mn^{2+} in the MnO_2 square plane. The room temperature NPD data confirmed the composition with refined occupancy of lithium site to be 1.00(4). The room temperature NPD refinement and the extracted structural model of $Ba_2MnO_2Li_2S_2$ is shown in Fig 1.

The NPD recorded on the same compound at 5K showed new Bragg peaks which were magnetic in origin. Refinement of the data revealed an antiferromagnetic ordering of Mn^{2+} spins in MnO_2 plane with ordered moment per Mn ion of 2.90(9) μ_B. The magnetic structure follows the Goodenough-Kanamori rule where interaction between two half filled orbitals (Mn^{2+} d^5) are predicted to be antiferromagnetic. The fit to the low temperature data and the extracted magnetic structure is shown in Fig 2.

The NPD data on the other two compounds $Ba_2MnO_2Li_{2-x}S_2$ (x = 0.5,1) were also collected at room temperature and 5K. These data were difficult to analyse with Rietveld refinement with strong correlation between the isotropic displacement parameters and occupancy of Li site, hindering the accurate determination of composition. Further analysis is ongoing with combining other techniques. Qualitatively the data showed increasing vacancy on lithium site leads to suppression of long range magnetic ordering and shows composition control of magnetic properties in this compounds.

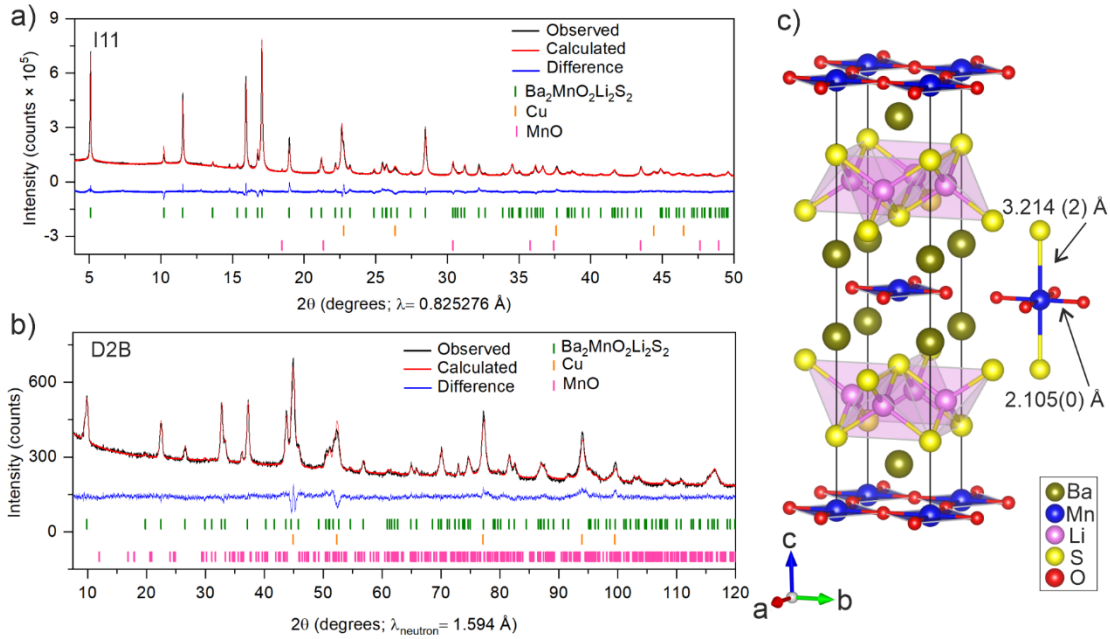

Figure 1. Rietveld refinement of $Ba_2MnO_2Li_2S_2$ on room temperature SPXRD (a) and NPD (b). c) refined structure from NPD refinement shows full occupancy of the metal site in chalcogen layer by lithium. Right: Elongated octahedral coordination environment around Mn^{2+}

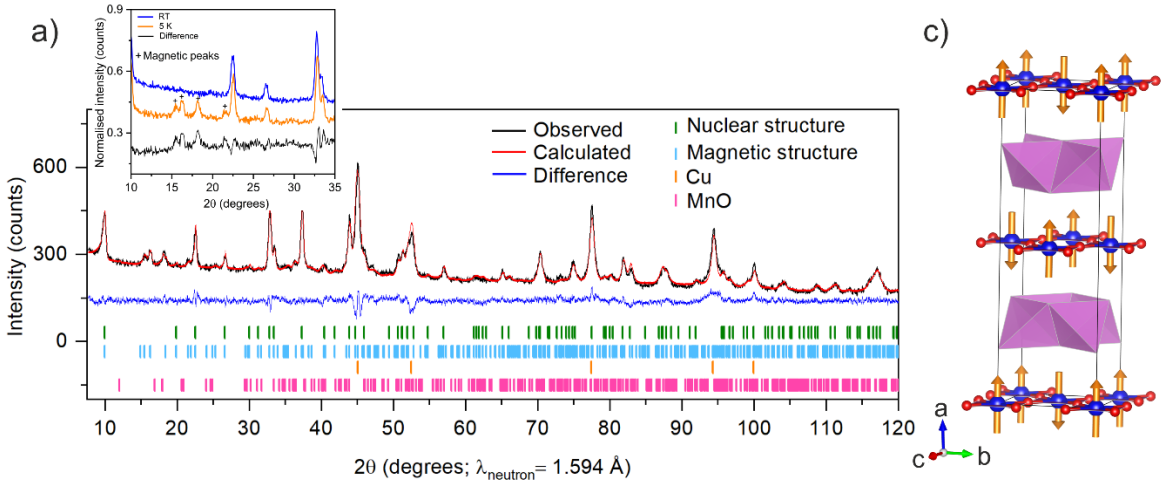

Figure 2. a) Rietveld refinement against NPD data at 5 K for $Ba_2MnO_2Li_2S_2$. Inset: highlighting the appearance of magnetic Bragg reflections at 5 K compared with the room temperature pattern. B) the magnetic structure of $Ba_2MnO_2Li_2S_2$

The experiment was a success and we are grateful for the efforts of the local contact in running the experiment. Further analysis is on going. The work carried out in this experiment will be published in an international journal and has formed a significant part of the D.Phil thesis of Souvik Giri.

[1] Kageyama, H. et al. *Nat Commun* **2018**, 9, 772. https://doi.org/10.1038/s41467-018-02838-4.

[2] Blandy, J. N. et al. *Inorg Chem* **2019**, *58* (12), 8140–8150. https://doi.org/10.1021/acs.inorgchem.9b00919