Experimental report

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Proposal: 5-31-2690 **Council:** 4/2019

Title: Crystal and magnetic structures ofcopper-based double double perovskites

Research area: Materials

This proposal is a new proposal

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Samples: CaCuMReO6

Instrument	Requested days	Allocated days	From	To
D20	2	2	11/10/2019	13/10/2019

Abstract:

Using high pressure and high temperature (HPHT) synthesis, we recently found a new P42/n double double perovskite (DDPv) type combining columnar order of the A-site cations with rock-salt order at the B sites. They are notable for their magnetic properties, e.g. MnRMnSbO6 have multiple ordering transitions of rare earth (R) and Mn moments, CaMnFeReO6 is ferrimagnetic with Tc = 500 K, and CaMnNiReO6 is ferromagnetic with four parallel spin sublattices. We have recently synthesised two new high pressure and high temperature double double perovskites, CaCuMReO6 with M = Fe and Cr. These materials are notable as the first examples on Mn-free double double perovskites. Magnetisation measurements reveal ferrimagnetism with high Tcs (~500 K). Powder neutron diffraction is needed to investigate the crystal and magnetic structures of these double double perovskites. We request two days of beamtime at D20 with the cryofurnace in view of the small amounts of sample available (50 mg each). This will allow measurements to be done from base temperature up to 550 K, above the ferrimagnetic Tc.

Crystal and magnetic structures of copper-based double double perovskites

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Perovskites, with the general formula ABO_3, are of great interest due to their large variety of electronic and magnetic properties. Their composition can be modified to induce different cation orders into double perovskites (DPv), of general formula $AA'B_2O_6$ or $A_2BB'O_6$, and eventually doubly ordered perovskites ($AA'BB'O_6$) [1]. Using high pressure and high temperature (HPHT) synthesis, we recently found a new type of perovskite derivative combining columnar order of the A-site cations with rocksalt order at the B sites into a so-called double double perovskite (DDPv) [2] This structure crystallises with $P4_2/n$ space group and a variety of new double double perovskites have subsequently been reported. They are notable for their magnetic properties, e.g. $MnRMnSbO_6$ have multiple ordering transitions of rare earth (R) and Mn moments [2], $CaMnFeReO_6$ is ferrimagnetic with Tc = 500 K [3] , and $CaMnNiReO_6$ is ferromagnetic with four parallel spin sublattices [4].

A new high pressure $CaCuFeReO_6$ DDPv has been prepared. Approximately 60 mg of sample combining several high pressure products together in a 3 mm V-foil can were scanned in D20 using λ = 2.41 Å for magnetic structure determination. 1h scans were collected at 5 K and every 80 K between 80 and 550 K. Additional short scans were collected at equidistant temperature steps for the complete temperature range. An additional scan was taken at 550 K using the 90˚ take off angle and λ = 1.54 Å for high resolution structural characterisation. The results allowed the accurate determination of both nuclear and magnetic structures (Fig.1) and to study their thermal evolution. The publication of these results is currently under preparation.

Provided the availability of beamtime once all required data were collected, some additional data sets were taken for some related compounds as detailed below:

- $CaMnFeSbO_6$ DDPv: Additional 1.5 h scan at 3 K using 90˚ take off angle and λ = 1.54 Å, missing from experiment 5-31-2623. The complete results are reported in the corresponding experimental report.

- Mn_2LiReO_6 high pressure polymorphs: two HP polymorphs (DPv and $LiNbO_3$-type) were measured in a previous experiment in 2015. The unexpected sensible character of these Li-based samples presumably prevented the acquisition of unambiguous results during the first experiment. Fresh samples were prepared and handled accordingly for this experiment, combining ~40 mg of each sample from several HP products into small V-foil cans. 8 h scans were collected at 3 and 100 K for the LN-type polymorph and 10.5 h scans at 3 and 140 K for the DPv compound, using the 42˚ take off angle and λ = 2.41 Å in both cases. The resulting data confirmed the absence of any long range magnetic order for LN_Mn_2LiReO_6 and helped solving the magnetic structure of DPv_Mn_2LiReO_6. Additional 300 K high resolution scans were collected in a later EASY experiment 544.

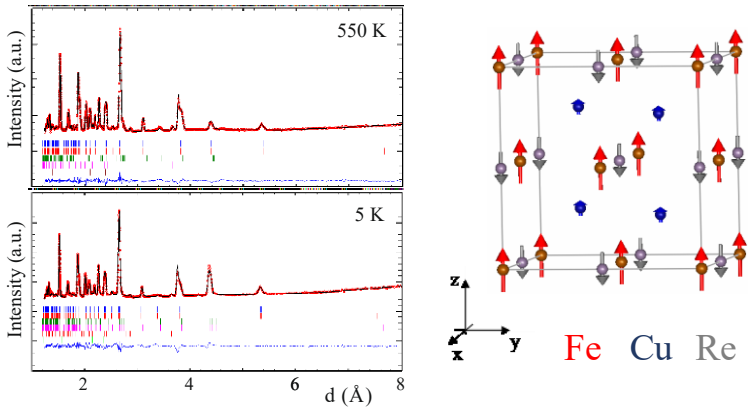

Fig. 1. Rietveld fits against 550 and 5 K NPD data and preliminar low temperature magnetic structure of the HP $CaCuFeReO_6$ DDPv.

[1] G. King, P.M.Woodward. *Journal of Materials Chemistry*, 2010, **20**, 5785.
[2] E. Solana-Madruga et.al. *Angew. Chem. Int. Ed*. 2016, **55**, 9340.
[3] G. M. McNally et al. *Chem. Mater.* 2017, **29**, 8870−8874.
[4] E. Solana-Madruga et.al. Chem. Comm. 2019, **55**, 2605.