Experimental report

24/08/2021

Proposal: 5-31-2821 **Council:** 10/2020

Title: Crystal and magnetic structures ofhigh pressure Mn2ScBO6 double perovskites

Research area: Materials

This proposal is a new proposal

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Samples: (Mn,Co)2Sc(Sb,Ru)O6

Instrument	Requested days	Allocated days	From	To
D20	3	2	15/05/2021	17/05/2021

Abstract:

Transition metal oxides continue to be of great important for magnetism and other properties, and double perovskite (DPv) cation ordering is frequently used to induce and tune physical properties. We propose here to study two Mn2ScBO6-based DPv materials recently discovered at high pressure. 1. A new series of DPv Mn2-xCoxScSbO6 solid solutions x = 0.5, 1, 1.5 where small Co2+ at A-sites in (double) perovskites is very unusual. They have two magnetic transitions, at 51 K and 14 K for x = 1, and likely canted antiferromagnetic Mn/Co spin order. 2. The new DPv Mn2ScRuO6 which has a broad magnetic transition at 105 K and a weak possible second transition at 24 K. Hysteresis measurements shows ferrimagnetism with a saturated moment of 1.02 BM/f.u., in contrast to antiferromagnetism reported in A2ScRuO6 (A = Ba, Sr) DPv's synthesized at ambient pressure. D20 is needed to determine the crystal structures in high resolution mode (wavelength = 1.54 Å), given small monoclinic distortions, as well as magnetic structures and their thermal evolution in high flux mode (wavelength = 2.41 Å).

Crystal and magnetic structures of the high-pressure manganese based double and double double perovskites

Perovskites ABO_3 are of great interest due to their large variety of electronic and magnetic properties. Their compositions can be modified to induce different cation orderings giving double perovskites $AA'B_2O_6$ or $A_2BB'O_6$, and even more complex double double perovskites ($AA'BB'O_6$).[1] Cation ordered $A_2BB'O_6$ phases can adopt the NTO (Ni_3TeO_6)-type structure, with acentric *R*3 symmetry giving interest as polar magnets with potential multiferroic properties, e.g. in $(Co,Ni)_2ScSbO_6$ where interesting lock-in spins orders occur,[2] or as double perovskites (DPv), usually with monoclinic $P2_1/n$ symmetry, of spintronics interest. Recently the use of A= Mn^{2+} has been demonstrated to induce interesting structural features and magnetic properties in $Mn_2BB'O_6$ materials. Mn_2ScSbO_6 has both structures at different pressures (NTO at 5.5 GPa and DPv at 12 GPa) and DPv Mn_2FeReO_6 has giant magnetoresistance.[3]-[4] Several double double perovskites (DDPv) with space group $P4_2/n$ have been published such as $CaMnMReO_6$ (M = Mn, Fe)[5], exhibiting various physical properties. Here we propose to study $Mn_{2-x}CoxScSbO_6$ DPv material and Mn-based $CaMnMnWO_6$ DDPv that recently discovered at high pressure.

In this experiment, around 200mg of **$Mn_{2-x}Co_xScSbO_6$** solid solutions with x = 0.5, 1 and 1.5 were measure at D20 using V-foil can and wavelength of 2.41 Å (take-off angle of 42˚). For x = 1 and 1.5, scans were collected at 80 K and 1.5 K with each counting 1 hour. For x = 0.5, scans were collected at 1.5 K, 30 K and 80 K with each counting 2.5 hours. Thermal scans between 1.5 K and 80 K were collected every 1 K. Neutron diffraction show no long range magnetic ordering for x = 1 and 1.5; but two magnetic transition with T_C = 21 K and 55 K for x = 0.5. The neutron diffraction pattern in Figure 1 clearly shows the magnetic signal below two transitions. Further analysis will be carried out to understand these spins structures and potential reasons that caused the x = 1 and 1.5 being magnetically disordered.

In this experiment, around 200mg of **$CaMnMnWO_6$** (DDPv) material was measure at D20 using V-foil can and wavelength of 2.41 Å (take-off angle of 42˚). Scans were collected at 80 K and 1.5 K with counting 1.5 hours. A thermal scan between 1.5 K and 80 K was taken in a step of 2 K. From the lab synthesis, we observed a structural phase transition from DDPv to DPv at higher sintered temperatures (Figure 2). Neutron diffraction shows long range magnetic ordering for DDPv but no magnetic signal for DPv down to the 2 K (Figure 3). We solved the magnetic structure for DDPv using Fullprof and the corresponding full results with interesting magnetic property switch could be found in our recent accepted paper in Angewandte Chemie [6].

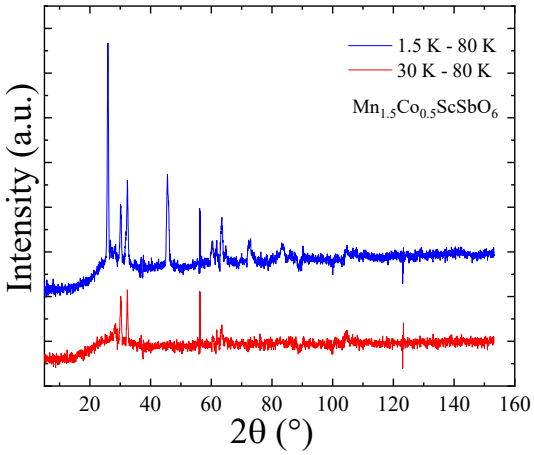

Figure 1. NPD of 1.5 K – 80 K and 30 K – 80 K difference patterns show clearly magnetic signals with two transitions.

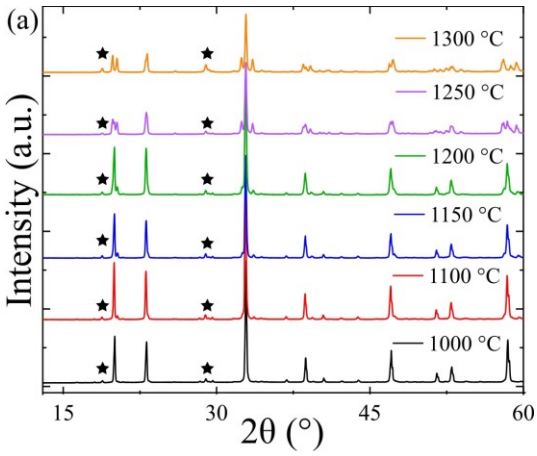

Figure 2. Powder XRD patterns of $CaMnMnWO_6$ at different synthesis temperatures showing progress of the DDPv-DPv structural phase transition. Black stars show secondary phases contribution from $CaWO_4$.

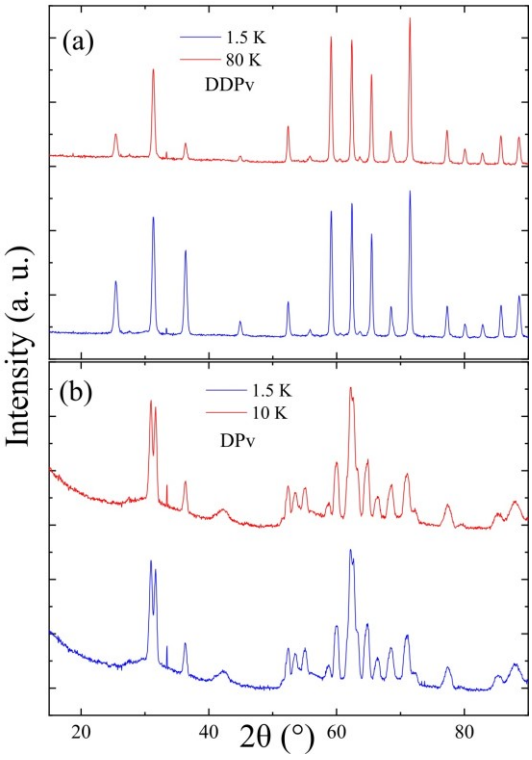

Figure 3. Comparison of low-angle λ = 2.41 Å neutron diffraction patterns of (a) DDPv $CaMnMnWO_6$ and (b) DPv-$CaMnMnWO_6$ at temperatures above and below their magnetic transitions.

[1] G. King, P.M.Woodward. J. Mater. Chem., 2010, 20, 5785.
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[3] E. Solana-Madruga et al., Dalton Trans., 2015, 44, 20441.
[4] A. M. Arévalo-López et al., Angew. Chem. Int. Ed., 2015, 54, 12074.
[5] G. M. McNally et al. Chem. Mater. 2017, 29, 8870.
[6] K. Ji et al., Angew. Chem. Int. Ed., 2021, accepted. Doi: 10.1002/anie.202108586