Experimental report

28/05/2020

Proposal: 5-31-2624 **Council:** 10/2018

Title: Crystal and magnetic structures ofthe high pressure Mn2MSbO6 (M = Mn and Co) oxides.

Research area: Materials

This proposal is a new proposal

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Samples: Mn3TeO6
Mn2CoSbO6
Mn3SbO6
Mn11Ta4O21
KFe3(Ge3Fe)O10(OH)2
CoTaSbO6
6aV4O8
6aV2O5
Mn3N6O3

Instrument	Requested days	Allocated days	From	To
D1B	0	4	04/07/2019	08/07/2019
D20	2	0		

Abstract:

High pressure Mn2BB’O6 materials are of fundamental interest due to the combination of spin, orbital and charge degrees of freedom assigned to Mn. They crystallise in the double-perovskite or corundum-related structures. Cation-ordered structures based on the corundum type have been of great interest for multiferroic properties as the LiNbO3–type (LN, space group R3c) and the double corundum Ni3TeO6 (NTO, R3) and ordered ilmenite11 (OIL, R3) types are all polar permitting ferroelectricity. Geometrically frustrated honeycomb layers occupied by transition metal cations can lead to helical spin structures, which may give rise to magnetically induced ferroelectricity in these Mn2BB’O6 oxides. We have prepared Mn2MSbO6 (M = Mn and Co) with a corundum-related super-structure by high pressure and temperature. They present ferrimagnetic transitions at low temperature and a complex cation ordering.

Crystal and magnetic structures of the high pressure Mn_2MSbO_6 (M = Mn and Co) oxides.

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R. Sáez-Puche and J. P. Attfield.

High pressure $Mn_2BB'O_6$ materials are of fundamental interest due to the combination of spin, orbital and charge degrees of freedom assigned to Mn. Among them, those with B' = Re crystallise with the *P21/n* double perovskite structure (DPv)[1,2] while B' = Nb, Ta, Mo and W induce ordered corundum related structures, i.e. *R-3c* $LiNbO_3$[3], *R3* ordered ilmenite[4] or *R3* Ni_3TeO_6 type[5,6]. Mn_2BSbO_6 oxides have otherwise been reported to show both polymorphs for B = Cr, Fe and Sc[7,8,9,10], while only compounds with B' = Re and W have been reported to stabilise Mn at the B site and none of them could still be combined with Co.

In this experiment, high pressure Mn_2CoSbO_6 and Mn_3SbO_6 oxides were proposed to show complex cation orders in corundum related superstructures with different combinations of Mn/CoO_6 and SbO_6 dimers and trimers of face-sharing octahedra stacked along the c axis. Preliminary data collected on D1B for the Co sample using wavelength 2.52 Å did not show any better results compared to the previous D20 data collected on the same sample on 2012. Consequently, no longer beamtime was spent on this sample or on the related Mn_3SbO_6, of smaller amount. Further related samples were thus registered for this experiment and different temperature data sets were collected for each of them as detailed below.

1) Mn_3TeO_6 high pressure double perovskite: 4h scans were collected on a 100 mg sample combining several high pressure products together in a 3 mm V-foil can at 50 and 1.5 K. Additional short scans were collected at equally spaced intermediate temperatures. The collected data allowed us to determine the accurate nuclear and magnetic structure of this double perovskite and its thermal evolution (see Fig. 1). The results were published in *Chemical Communications*, with reference *Chem. Comm.* 2019, **55**, 14470-14473. doi: 10.1039/c9cc07733b.

2) $Mn_{11}Ta_4O_{21}$ hexagonal A-site manganite. 1.5 h scans were collected at 1.5 K and every 10 K between 10 and 120 K on a larger room pressure sample using a 6 mm V sample holder. The results allowed a complete structural and magnetic characterisation as depicted in Fig. 2 and gave rise to a paper currently under review in *Inorganic Chemistry*.

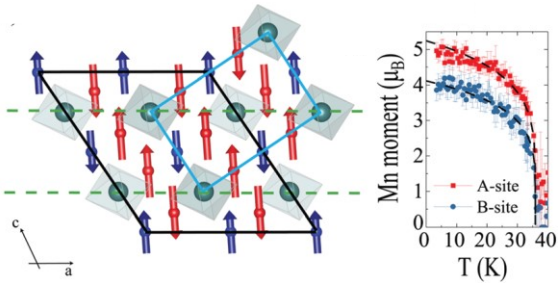

Fig. 1. Magnetic structure and thermal evolution of the Mn^{2+} magnetic moments of Mn_3TeO_6 DPv.

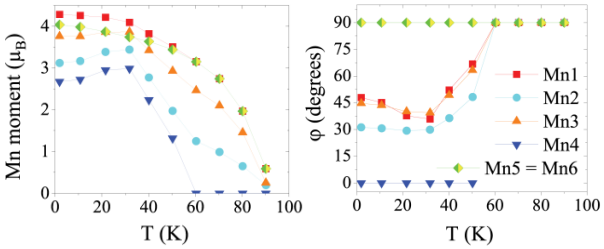

Fig. 2. Thermal evolution of the Mn^{2+} magnetic moments of $Mn_{11}Ta_4O_{21}$ hexagonal A-site manganite and their φ angles respect to the a axis within the ab plane.

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[2] A. M. Arévalo-López *et al,. Chem Comm.* 2016, **52**, 5558.
[3] M.-R. Li *et al., Angew. Chem. Int. Ed.* 2013, **52**, 8406.
[4] M.-R. Li *et al., Angew. Chem. Int. Ed.* 2016, **55**, 9862.
[5] M.-R. Li *et al., Angew. Chem. Int. Ed.* 2014, **53**, 10774.
[6] M.-R. Li *et al., Adv. Mater.* 2015, **27**, 2177.
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[8] A. J. Dos santos-Garcia *et al., J. Phys. Cond. Matter* 2013, **25**, 206004.
[9] A. J. Dos santos-Garcia *et al., Angew. Chem. Int. Ed.* 2017, **56**, 4438.
[10] E. Solana-Madruga *et al., Dalton Trans.* 2015, **44**, 20441.