High pressure synthesis of polar and non-polar cation-ordered polymorphs of Mn_2ScSbO_6

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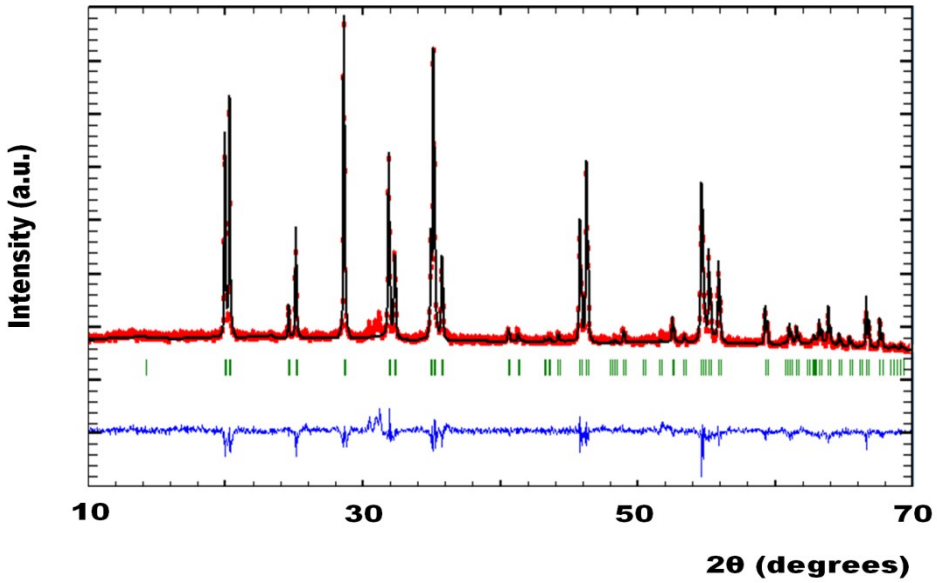
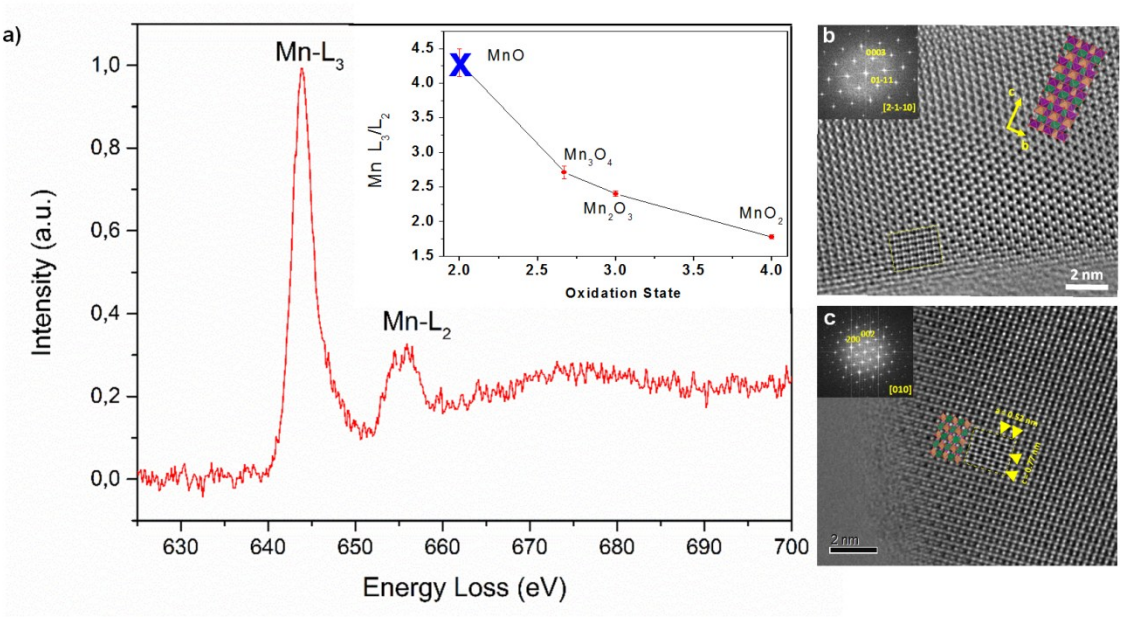
E. Solana-Madruga[1,*], A.J. Dos Santos-García[2], A.M. Arévalo-López[3], D. Ávila-Brande[1], C. Ritter[4], J. P. Attfield[3] and R. Sáez-Puche[1]

ELECTRONIC SUPPLEMENTARY INFORMATION



SF1. Rietveld refinement of the nuclear structure of the *R*-3 room pressure polymorph of Mn_2ScSbO_6 oxide from XRD.

Room pressure Mn_2ScSbO_6 was prepared at 1373 K. The Rietveld fit to the XRD pattern (SF1) agrees with the random cation distribution in *R*-3 space group with a corundum-related structure as previously studied. This polymorph showed no long-range magnetic order, but the two new high pressure phases presented here, the polar *R*3 Ni_3TeO_6-type (NTO) and the $P2_1/n$ double perovskite (DPv), are cation - ordered and exhibit interesting properties.

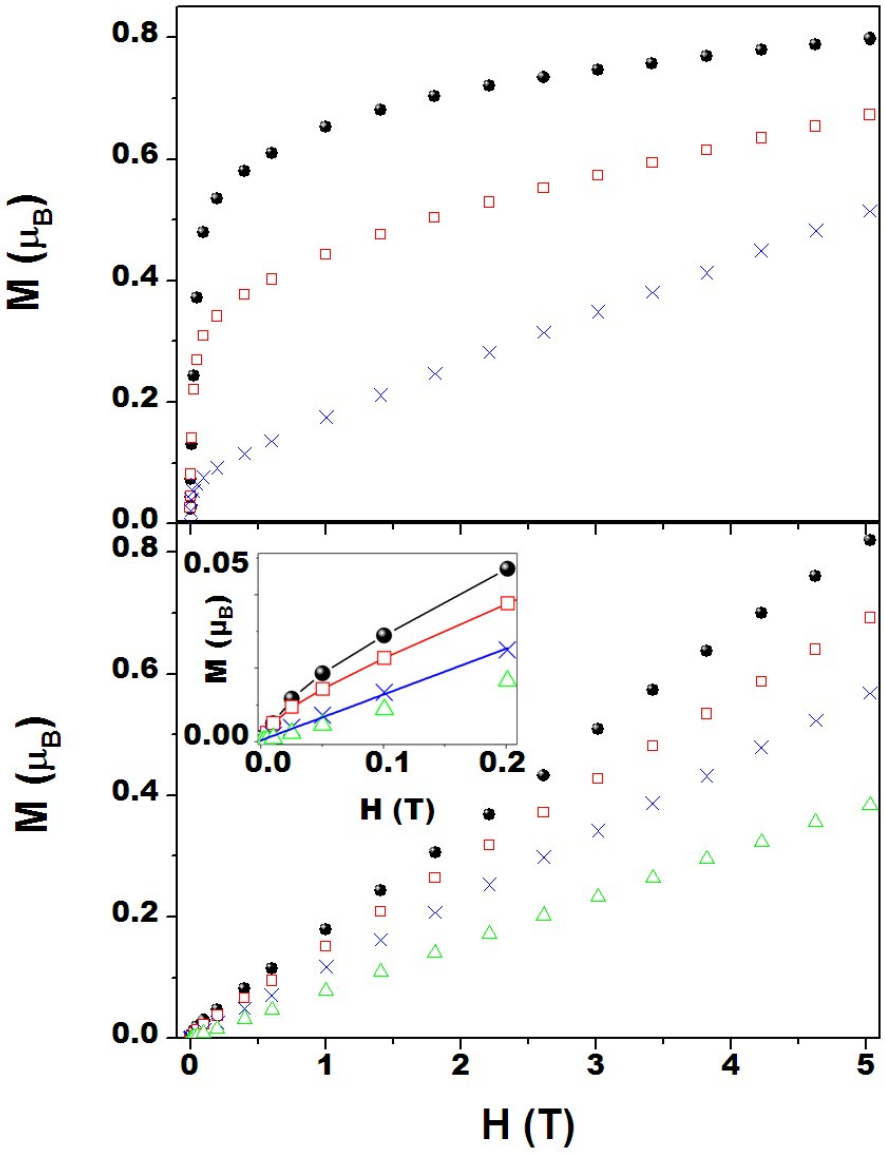


SF2. a) Typical Mn-$L_{2,3}$ ionization edge obtained for DPv and NTO_Mn_2ScSbO_6 from EELS analysis. Inset represents L_3/L_2 intensity ratio versus Mn oxidation state in standard Mn oxides and in the studied samples (cross). b) HRTEM image of NTO_Mn_2ScSbO_6 along the [2-1-10] zone axis. The insets show the FFT pattern, the structure and the image (delimited with yellow dots) simulations from the crystallographic details obtained from the Rietveld refinement for a crystal of thickness of 43Å and a defocus value of –250 Å. c) HRTEM image of DPv_Mn_2ScSbO_6 along the [010] zone axis. The FFT pattern, the structure and the image simulations from the crystallographic details are also included as insets for a crystal of thickness of 30Å and a defocus value of –350 Å.

The NTO_Mn_2ScSbO_6 structural HRTEM image along the [2-1-10] zone axis (SF2b) shows a regular stacking with periodicity of 5.3 and 14.1 Å, which corresponds to the *b* and *c* cell parameters, respectively, indicating a well ordered material and the absence of extended defects. The simulated image, using the refined structural model and calculated for a defocus value of -350 Å and a thickness of 30 Å is found to be in good agreement with the experimental one.

The microstructure of the double perovskite is clearly observed in the HRTEM image recorded along the [010] zone axis (SF2c). The image and its corresponding FFT indicate the absence of extended defects and good agreement with the calculated image is found.

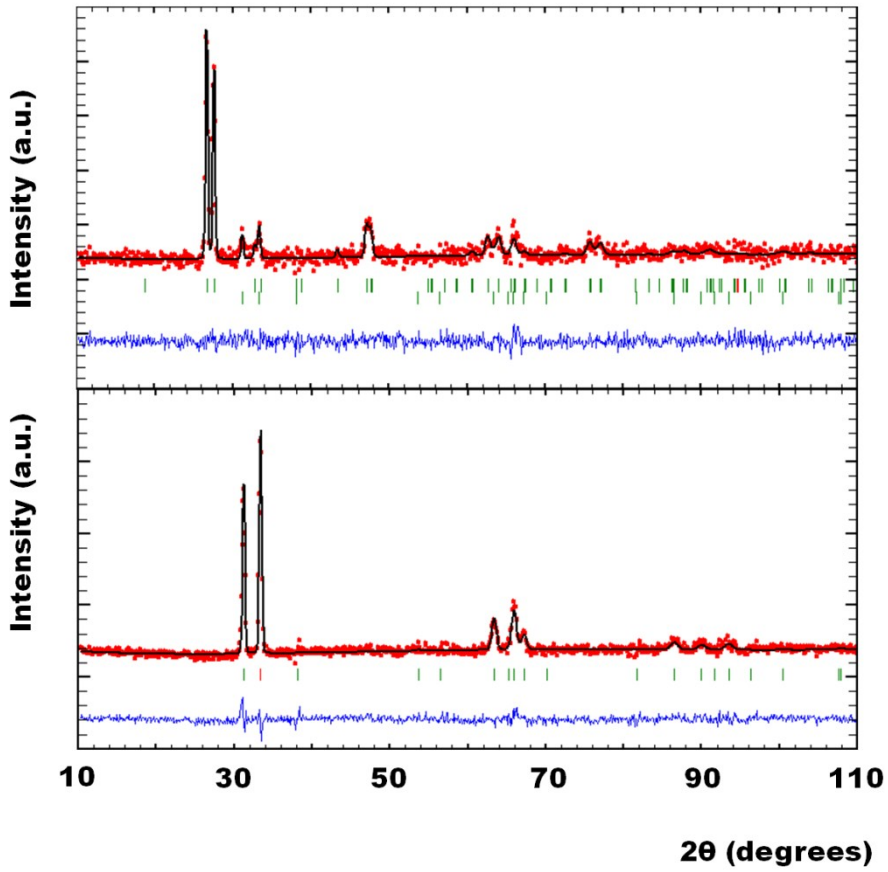
EELS experiments were performed on the Mn L-edge in several crystals of both NTO and DPv polymorphs of Mn_2ScSbO_6 (SF2a) The results revealed an average oxidation state of +2 for Mn, as indicated with a cross in the inset of Figure SF2a, in correspondence with BVS calculations.



SF3. Field dependence of magnetization for NTO (top) and DPv (bottom) polymorphs of Mn_2ScSbO_6 at T = 2 K (black circles), 20 K (red squares), 40 K (blue crosses) and 90 K (green triangles). The inset in DPv_Mn_2ScSbO_6 measurements shows an enlargement of the low magnetic field range.

Below T_C = 42 K the ferromagnetic component of NTO_Mn_2ScSbO_6 increases on cooling up to the maximum value of 0.62 μ_B (SF3 top). Right below T_C a linear behavior can be observed for most of the field range, according to the strong antiparallel coupling between Mn1 and Mn2 spins determined from NPD. As temperature decreases and the Mn^{2+} spins saturate, the uncompensation caused by the site - selective Mn2/Sc disorder becomes more evident, revealing the net ferrimagnetic behavior of this compound.

Despite the presence of a small amount of the NTO polymorph, DPv magnetization measurements (SF3 bottom) show the antiferromagnetic behavior determined from susceptibility and NPD experiments. The enlargement of the low field range (inset) evidences the slight curvature of the DPv_Mn_2ScSbO_6 magnetization measured below the NTO_Mn_2ScSbO_6 polymorph T_C. The blue line in the inset shows the linear fit of the experimental data collected at 40K. The good fit of the magnetization to a linear dependence with the magnetic field confirms the antiferromagnetic behavior of this sample at 40 K. At this temperature the subtle effect of the tiny ferromagnetic component of the small amount of secondary phase cannot still be observed, although it is appreciated at lower temperatures as one can see the curved trend on black and red lines connecting 2 K and 20 K data respectively.



SF4. Rietveld refinements of the magnetic structures of DPv (up) and NTO (bottom) polymorphs of Mn_2ScSbO_6 from the 30 K - 3 K and 50 K - 3 K difference NPD patterns, respectively, collected at D1B diffractometer. The secondary phase included on the former is the magnetic structure of the NTO-type compound.

50 K - 3 K difference pattern from D1B NPD data collected for NTO_Mn_2ScSbO_6 (SF4 bottom), show the appearance of new magnetic peaks indexed with the propagation vector k = [0 0 0]. The most intense peaks are (003) and (101), observed in the XRD profile rising the apparent IL-type order but not in room temperature NPD data. The weak ferromagnetic component observed in magnetization measurements is not observed in this pattern.

The upper panel show the Rietveld refinement of the 30 K - 3 K difference pattern for DPv polymorph. All magnetic peaks can be indexed with the propagation vector k = [0 0 0] and the presence of the secondary magnetic phase of NTO polymorph can be observed, coinciding at same angles as in the lower panel.