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Combining STEM Imaging and EELS Mapping to Understand the Growth of La_2CoMnO_6 Double Perovskites on (111) Oriented Perovskite Substrates

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Ordered double perovskite oxides can have properties inaccessible in standard single perovskites, including interesting magnetic properties. Double perovskites generally have a formula $A_2BB'O_6$ and can form an ordered structure with the B and B' atoms in a rock-salt-like arrangement [1]. This is usually associated with the development of a specific octahedral tilting pattern, with differences in the sizes of the sites for B and B' atoms. However, growth of such double perovskites as thin films can be challenging, and achieving a high degree of rock salt ordering is anything other than straightforward.

Achieving a high degree of order is of particular interest in La_2CoMnO_6 (LCMO), since this strongly affects the magnetic properties. Neighbouring B-site atoms naturally align their spins antiparallel, whether they are Co-Co, Mn-Mn or Mn-Co. However, since Mn and Co have different magnetic moments, then a rock-salt ordered structure will result in a strong net magnetic moment and a ferromagnetic ordering. Consequently, highly ordered bulk ceramic LCMO will have a Curie temperature (T_C) of ~ 230 K and a saturation magnetization of 6 μ_B per formula unit, whereas disordered LCMO has a much lower T_C of 80-150 K and lower magnetization. In this work, we propose that via growth of LCMO on (111) substrates, that the octahedral tilt ordering can be promoted in such a way that enhances ordering and thus improves the magnetic properties of the thin films.

Figure 1 shows STEM images along a <110> axis of the primitive perovskite cell of a thin film grown on $SrTiO_3$ (STO), for which we expect the film to be in tensile strain with a lattice mismatch of 0.4 %. Whilst the quality of the epitaxy is excellent as seen in the HAADF image, elemental maps extracted from EELS spectra clearly show that whilst individual columns may be richer in Co or Mn, there is little long-range ordering of the Co and Mn atoms. This short range only ordering results in a T_C of 192 K. This is much higher than the T_C measured for a film grown under similar conditions on STO (100), and suggests that the (111) growth is already promoting more order than (100) growth. This correlates well with the evidence from the ABF image, which clearly shows the growth of octahedral tilting over about the first 3-4 unit cells of the film above the STO substrate.

Figure 2 shows STEM images along a <110> axis of the primitive perovskite cell for a LCMO film grown on $(La,Sr)(Al,Ta)O_3$ (LSAT) for which we expect a compressive strain of -0.5%. As for the film on STO, the epitaxy is excellent. In this case, however, there is much better rock salt Co-Mn ordering through most of the film. This is clearly associated with strong octahedral tilt ordering as shown in this figure. The one exception to this is close to the substrate where the Co:Mn ratio is as low as 1:2 in places, and the ordering is poor. Initial indications from EELS (not shown here) show that in the bulk of the film, the EELS edges for Co match well to Co^{2+} and those for Mn to Mn^{4+}, but near the surface there is a detectable increase in Mn^{3+} content. Nevertheless, the high degree of B-site cation ordering and associated oxidation state ordering through the majority of the film correlates very well with the fact that this film had the best magnetic properties of all with a T_C of 211K and the highest saturation magnetisation of all films (almost 6 μ_B per formula unit at 5 K). This correlation between good atomic scale ordering and good magnetic properties accords well with previous reports [2, 3]. The microscopy therefore provides powerful confirmation that (111) growth is promoting the octahedral tilting that then promotes the desired double-perovskite cation ordering resulting in excellent magnetic properties.

References:

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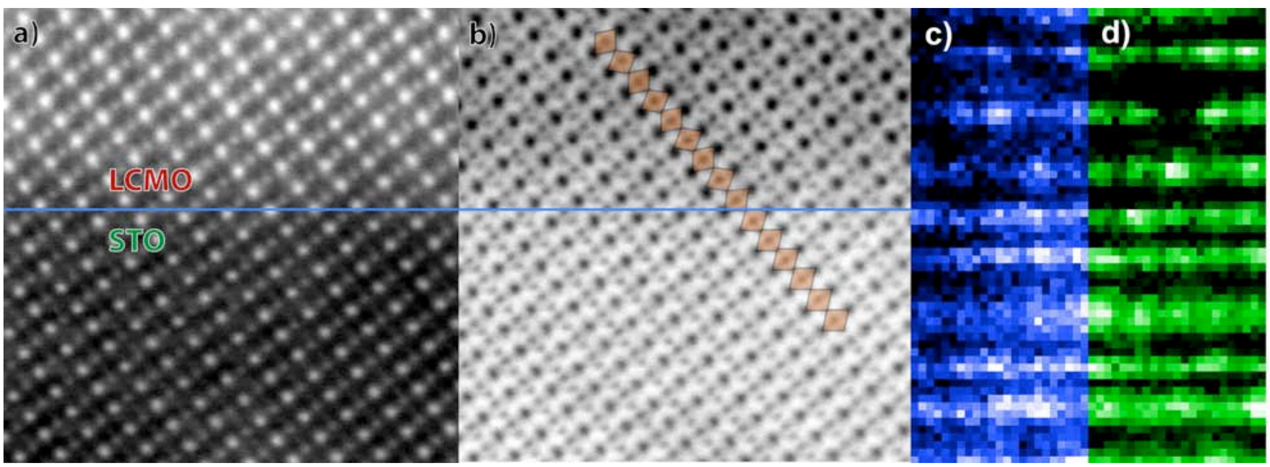

Figure 1. LCMO film grown on STO: a) HAADF STEM image showing good quality epitaxy; b) ABF image showing the growth of octahedral tilting over a few unit cells of the film; c) Co map from the Co-$L_{2,3}$ edge in EELS; d) Mn map from the Mn-$L_{2,3}$ edge in EELS

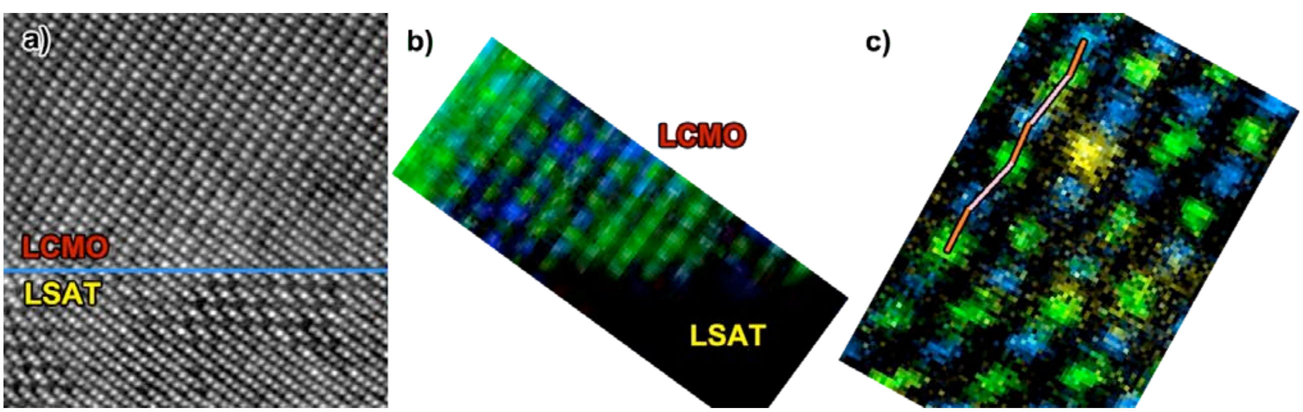

Figure 2. LCMO film grown on LSAT: a) HAADF STEM imaging showing good quality epitaxy; b) Mn (green) and Co (blue) maps overlaid of an area at the interface showing significant B-site disorder; c) Mn (green), Co (blue) and Ti (yellow) maps overlaid from an area in the middle of the film showing excellent rock-salt ordering, there is also a zig-zag in such maps (marked with the line) consistent with octahedral tilting.

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