

## EELS Study of Local Atomic Order in Multi-A-Site Rare Earth Chromites

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Introduction: Perovskite oxides with general composition  $ABO_3$  are a large and widely-studied family of materials that may possess interesting electronic, magnetic or catalysis properties, depending on the choice of metals A and B. In tuning the properties one common tactic is the partial substitution of either (or both) of the A and B sites. This introduces disorder into the systems with the potential for non-statistical distributions of substituents, which may in turn affect the measured properties of the materials. Rare-earth chromites are well documented perovskite materials ( $B = Cr$ ) and are known for the multitude of properties that are suitable for application; ranging from SOFC interconnect materials to the catalytic oxidation of hydrocarbons [1 – 2]. Perhaps most interestingly however, is the potential for magnetoelectric coupling or multiferroic behaviour. Such interactions lead to further functionalities in addition to the original magnetic and electric properties of the material [3]. It has been predicted theoretically that the antiferromagnetic ordering present in  $RCrO_3$  can induce a spontaneous electric polarisation [4], and is supported by experimental observations of ferroelectricity and canted antiferromagnetism in  $SmCrO_3$  and several other  $RCrO_3$ , where the rare-earth  $R$  is magnetic [5 – 6].

By systematic study of new mixed rare-earth chromites  $La_{1-x}Sm_xCrO_3$  made from one-step hydrothermal synthesis, we aim to follow the evolution of such properties. Data from high-resolution powder X-ray diffraction (XRD), Raman spectroscopy, STEM imaging and magnetic measurements highlight the high quality of our prepared materials. Since refinement against XRD data describes only the average structure, atomic resolution EELS is required to determine whether the distribution of  $La^{3+}$  and  $Sm^{3+}$  is uniform throughout or if there is evidence that the rare-earth ions form clusters. Our well-characterised sample of  $La_{0.5}Sm_{0.5}CrO_3$  will provide a model system for examining the possibility of non-statistical A-site substituents in a perovskite (*i.e.* the possibility of local La and Sm clustering) and the results would be of much wider relevance to the field of oxide materials. Having made some preliminary studies in house we now wish to use the SuperSTEM to make unequivocal studies of the degree of ordering in our materials.

Sample Preparation: TEM samples were prepared by dispersing materials ultrasonically in ethanol and deposited dropwise onto 3 mm lacey carbon grids supplied by Agar.

Samples were checked initially in a Jeol 2100 LaB<sub>6</sub> instrument. STEM was performed in a Jeol ARM-200F doubly corrected microscope.

For  $La_{0.5}Sm_{0.5}CrO_3$  STEM imaging was performed to understand the atomic-scale structure in detail. Our HAADF-STEM simulation does not distinguish between Sm and La at A site. However, intensity variation in the line profile of some images was observed which cannot be reproduced by STEM simulation. It is not clear that intensity variation is caused by thickness effect or any type of ordering. It appears that atomic resolution EELS Spectrum Imaging required to better understand arrangement of the Sm and La in the structure and possibility of any type of ordering.

The thicknesses of the samples were calculated using EELS low loss spectra and log-ratio technique (DM plugin) to be between 5-20 nm at the edge of the crystals.

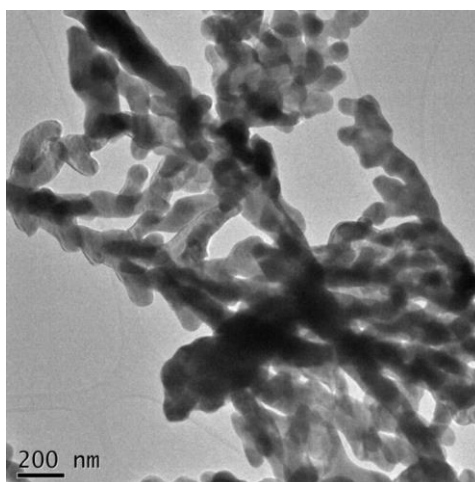


Figure 1: TEM image of typical dendritic-type morphologies (microscope: Jeol 2100)

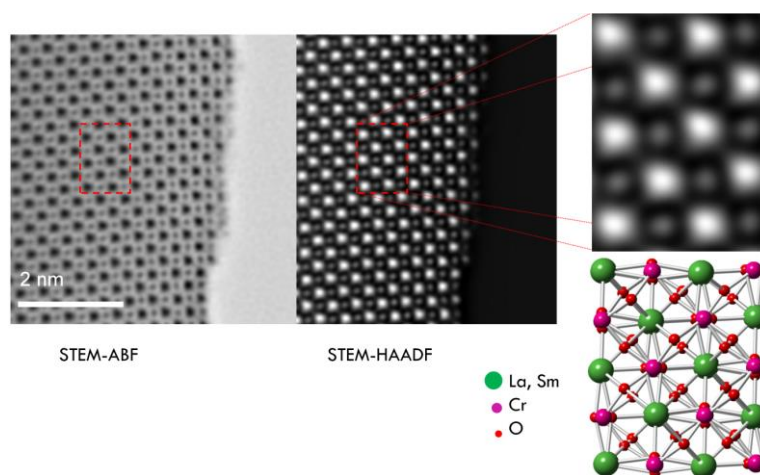


Figure 2: STEM-ABF and HAADF of a crystal aligned at 101 zone axis

## References

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