

Nature of domains in lanthanum calcium cobaltite perovskite revealed by atomic resolution Z-contrast and electron energy loss spectroscopy

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Abstract

Lamella-type planar features in $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ perovskite were investigated in a dedicated scanning transmission electron microscope. Atomic resolution Z-contrast imaging and modelling, along with electron energy loss spectroscopy, gave evidence these features could be Ca-enriched domains of the rock salt structure in the perovskite lattice. Z-contrast of a second type of planar fault, occurring after repeated investigations in the electron microscope, suggests formation of ordered O-vacancy arrangements on Co–O planes.

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1. Introduction

Perovskite-type metal oxides are known to be low-cost electrocatalysts used in fuel cells and metal/air batteries [1]. The perovskite type oxide (ABO_3) has a rare earth and/or alkaline earth ion in A and transition metal in B. The perovskite here is $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ (LCCO). The current idea of the function of the perovskite in the battery, is that upon substitution of the three-valenced rare earth element by a two-valenced alkaline earth element, the transition metal is partly oxidised, in the case of Co to the unusual 4+ state. As Co^{4+} however, is not stable, it will be reduced by hole hopping from Co^{4+} to Co^{3+} resulting in oxygen vacancies in the lattice [2]. The charge carrier and ion mobility, are prerequisites for using LCCO as oxygen-diffusion or air–electrode materials. In order to study the mechanism of oxygen reduction/evolution, it is desirable to have electrodes of good crystalline quality with well-defined electrolyte/oxide interfaces. In the present study, single crystalline films grown on inactive substrates by pulsed-laser deposition (PLD) were used; details of growth and crystallographic characterisation have previously been reported [3,4]. The high substitution rate of 40% of the lanthanum ions by calcium leads to metastable phases,

which can only be obtained by soft chemistry or PLD. A higher substitution value, or high temperature heating, results in phase segregation to calcium rich phases. It has to be noted that in sub-stoichiometric and in electrochemically cycled films, narrow domains of only one lattice plane width, proceeding parallel to the $\{001\}$ plane, were often seen in high resolution transmission electron microscopy images. The purpose of the present study is to confirm whether, in accordance with current theories, the domain contrast is indeed related to local changes in the Co oxidation state or to the occurrence of oxygen vacancies.

Only a few years previously this would have been an impossible task, since it involves atomic column structural and chemical analysis, but it is now possible thanks to the advent of dedicated, aberration corrected scanning transmission electron microscopes (STEM), equipped with energy dispersive analytical tools, such as electron energy loss spectroscopy (EELS) and X-ray analysis.

2. Experimental

Starting powders of the composition $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ were prepared by a citric acid soft chemistry method according to [5]. They were pressed and sintered to a dense target rod, which was ablated in an oxygen rich background gas by laser pulses. The ablated species were deposited on a heated MgO substrate at 650 °C, and cooled to room temperature in oxygen with a cool-

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ing rate of 40 °C/min. The crystalline structure and texture of the films were confirmed by a Siemens D5000 X-ray diffractometer equipped with an Eulerian cradle using Cu K α radiation. The films were electrochemically cycled in a three-electrode arrangement and characterised afterwards for this work.

TEM analysis was carried out at the Daresbury SuperSTEM Laboratory, housing the first UK C_s corrected cold field emission STEM, which employs a Nion Mark II quadrupole-octupole corrector [6]. This allows one to carry out Z-contrast lattice imaging with an HAADF detector [7,8] with 1 Å resolution. The EEL equipment includes a UHV Gatan Enfina system, with which EEL spectrum maps [9] and line scans can be obtained.

3. Results and discussion

3.1. High resolution Z-contrast of domains

Fig. 1(a) and (b) shows STEM images with atomic resolution of domains in $[1\bar{1}0]$ projection. They appear as light stripes running along $\langle 110 \rangle$ directions in bright field (BF) and dark in high angle annular dark field (HAADF) images. The schematic unit lattice cell with principal directions is shown in Fig. 1(c). Domains occur at various separation distances. They are often ‘bunched’ (see Fig. 1(a) and (b) towards the bottom left hand corner), where three domains occur grouped and interspaced by one and two perovskite unit cells. Fig. 1(d) shows the filtered section around the middle singular domain of the HAADF image in Fig. 1(b). The image was rotated by $\sim 40^\circ$ cw to make the planes horizontal and vertical. The contrast can be assigned to atomic columns: La with the highest Z and constituting 60% of the A-atoms in the column, clearly gives the brightest contrast in the HAADF image. The Ca- and O-atoms in the same column contribute little.

Co has a lower Z and gives rise to the medium contrast values between the bright contrast features, again, the O-atoms in the same column contribute little to the contrast. The B-atom plane seems to be missing at the domain, resulting in two A-atom planes being adjacent to each other. The atomic model with the suggested planar defect structure is overlaid on both images.

3.2. Atomic column resolution EELS intensity profiles

The chemical and electronic nature at the planar defect was further investigated by EELS. Fig. 2 shows an unprocessed HAADF lattice image, including a domain, similar to those in Fig. 1. The domain is visible as a perpendicular stripe of darker contrast. This stripe, although not greatly darker than unoccupied columns in the surround, is distinctively narrower than the $[001]$ perovskite lattice planes, and is well defined crystallographically in contrast to the horizontal streak-like variations. The latter arise from instable emissions of the electron gun with a time constant of the order of 0.1 s, compared to a line scan time of 0.02 s and a pixel dwell time of 18 μ s, thus causing horizontal streaks and stripes in the images. The electron beam was again incident along $[1\bar{1}0]$. The curves represent the integrated counts in energy windows set around the Ca, O, La and Co absorption edges in background subtracted EEL spectra of a line scan spectrum image, which was acquired perpendicularly across a domain. The EEL scan line was typically of 20 Å length, with a step separation of ~ 0.7 Å, resulting in ~ 30 positions (pixels), in which spectra were acquired. Line scans were repeated in exactly the same position for the energy regime (a) ~ 300 –600 eV, including the Ca L- and the O K-edges, and (b) ~ 650 –950 eV, including the Co L- and the La M-edges. The scans were performed along the white dashed line, and the profiles are displaced with respect to each other for clarity.

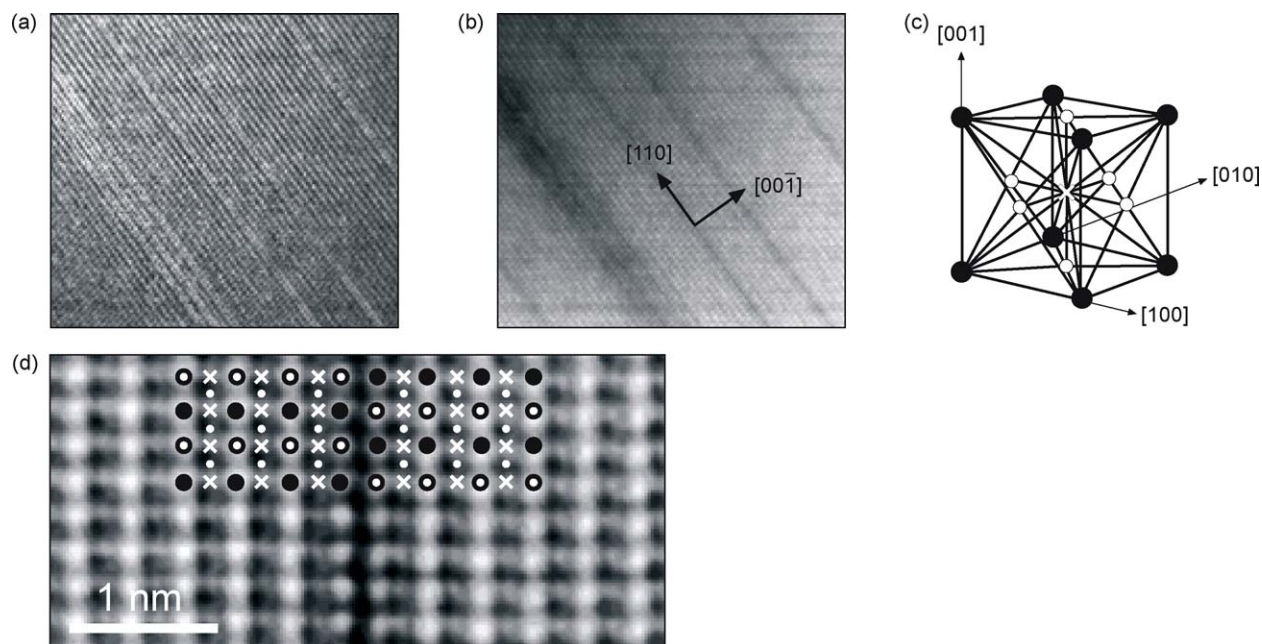


Fig. 1. Lamella-type features in epitaxial $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ films on MgO . (a) HRTEM image, (b) HAADF STEM image, (c) ABO_3 perovskite unit cell; large black circles: A-atoms, white cross: B-atom, small white circles: O-atoms. (d) Filtered HAADF image with overlaid model structure, model key as for Fig. 1(c).

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