UNIVERSITY OF LIVERPOOL

EPSRC Engineering and Physical Sciences Research Council

Epitaxial growth and enhanced conductivity of a IT-SOFC cathode based on a complex perovskite superstructure with six distinct cation sites

R. Sayers, N. L. O. Flack, J. Alaria, P. A. Chater, P. G. Palgrave, S.R.C. McMitchell, S. Romani, Q. M. Ramasse, T. J. Pennycook, and M. J. Rosseinsky

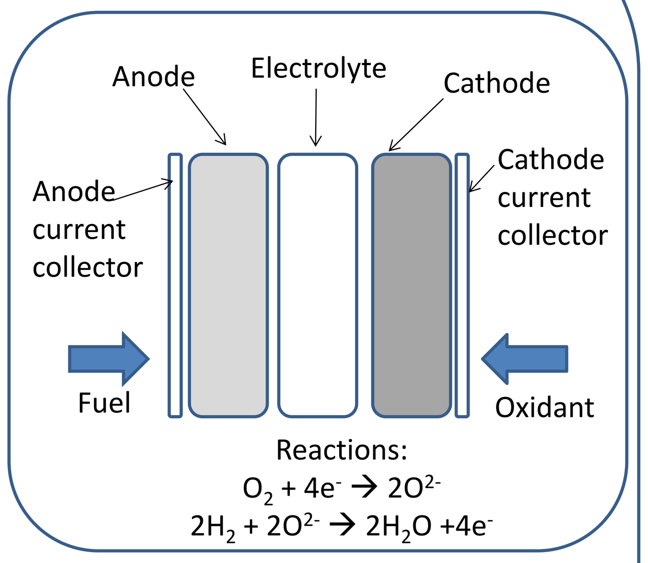
Abstract:

The conductivity of $Ba_{1.7}Ca_{2.4}Y_{0.9}Fe_5O_{13}$ is significantly enhanced when grown as a thin film by pulsed laser deposition. The material is a candidate cathode for solid oxide fuel cells (SOFCs) and in the intermediate temperature (IT) region around 600 °C we measure the in-plane AC conductivity of the thin film as 30 Scm^{-1}, greater than 3.5 Scm^{-1} found for the polycrystalline form. The complex repeating 10 layer superstructure of the cubic perovskite afforded by A site cation order seen in the polycrystalline material is retained in the thin film, which thus has six distinct cation sites. Growth on single crystal strontium titanate (STO) {001} substrates changes the symmetry from orthorhombic to tetragonal and orients the layer stacking direction of the superstructure normal to the substrate plane, reducing the grain boundary density and enhancing the conductivity which is measured within the planes predicted to have the highest electronic and ionic conductivities.

Introducing Intermediate Temperature - Solid Oxide Fuel Cells (IT-SOFCs):

A fuel cell is a device that converts the chemical energy from a fuel, e.g. hydrogen, into electricity. There are 3 main components to a fuel cell; the cathode, electrolyte and the anode.

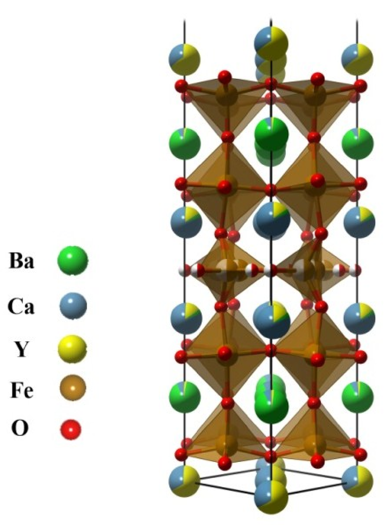
1. The cathode must have *high* electronic and ionic conductivity.
2. The electrolyte requires a *high* ionic conductivity and a *low* electronic conductivity. It also need to be stable in redox environments.
3. The anode must be porous to allow fuel to flow towards the electrolyte. They must have a *high* electrical conductivity (high ionic conductivity is a bonus).



IT-SOFCs operate at temperatures in the region of 550 °C to 750 °C, where the thermal demands on the system are less challenging than those for high temperature SOFCs operating around 900 °C.

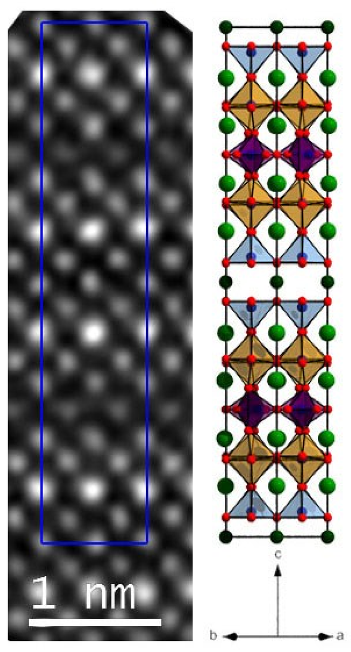
The 10 layer material ($Ba_{1.7}Ca_{2.4}Y_{0.9}Fe_5O_{13}$) is a candidate cathode material for IT-SOFCs. We were interested to see if growing the 10 layer material as a thin film would improve the conductivity of the material when compared to the bulk material.

Introducing the 10 layer material:



Crystal structure of the 10 layer material ($Ba_{1.7}Ca_{2.4}Y_{0.9}Fe_5O_{13}$).

The crystal structure can be seen in the Fast Fourier transform (FFT) filtered High Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM) image (12 cm CL, JEOL 2100FCs), with a scaled structural schematic of the $10a_p$ unit cell alongside.

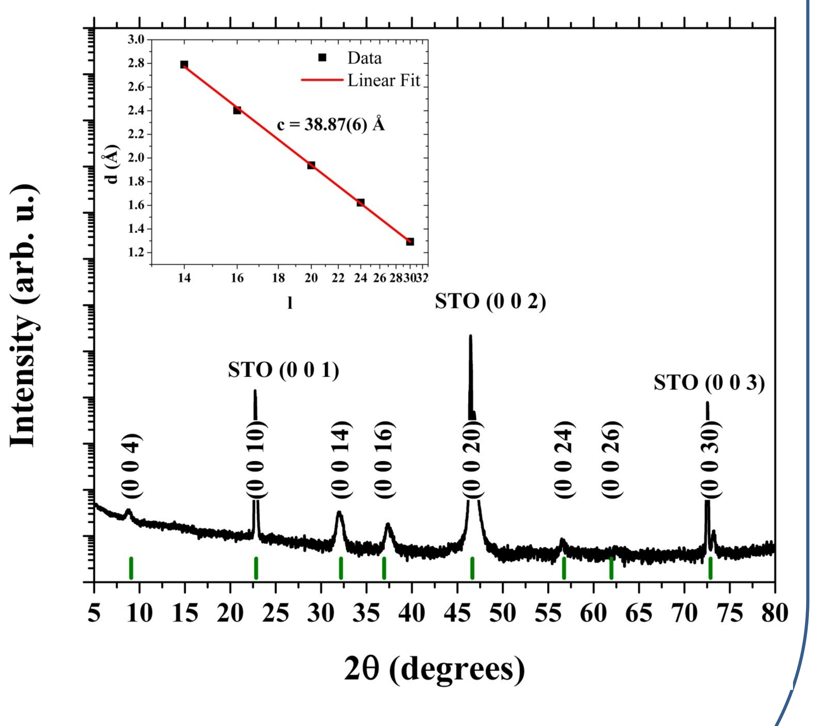


Growth of the $10a_p$ thin films:

Thin films of $Ba_{1.7}Ca_{2.4}Y_{0.9}Fe_5O_{13}$ were grown by pulsed laser deposition (PLD)[1].

The films were grown on single crystal strontium titanate (STO) {001} substrates. The optimized growth conditions were found to be a deposition temperature of 850 °C with a laser fluence of 0.27 Jcm^{-2}, a frequency of 5 Hz and a partial pressure of oxygen of 1 mTorr.

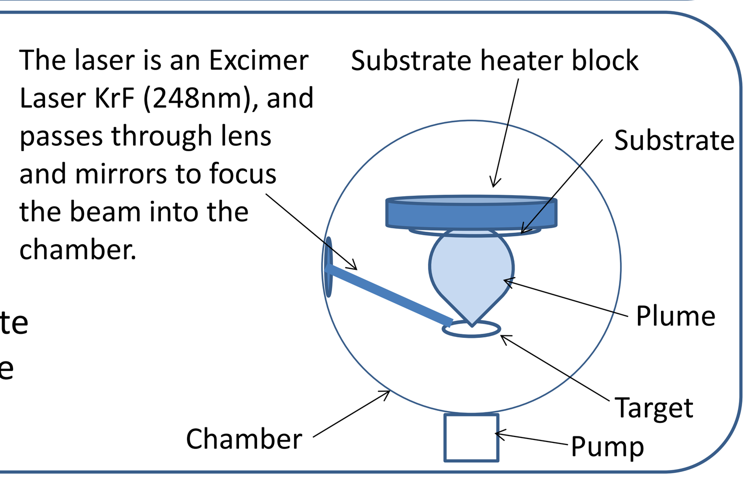
A typical X-ray diffraction (XRD) pattern of the $10a_p$ film grown under optimal conditions is shown, with an inset showing the lattice parameter determination. The green lines correspond to the expected $10a_p$ (0 0 *l*) reflections from the calculated *c* parameter.



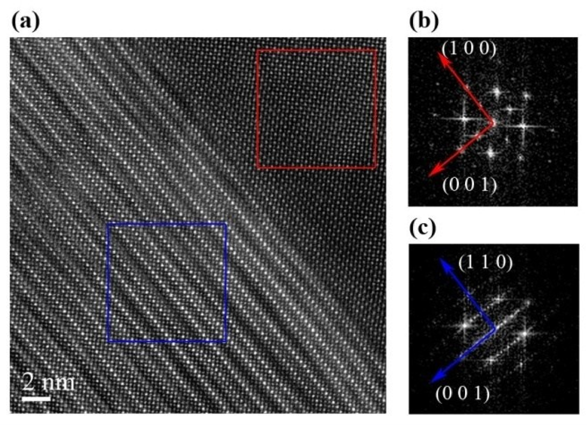
Pulsed Laser Deposition (PLD)

Thin film formation process in PLD:

1. Laser radiation interaction with the target
2. Ablation of materials
3. Deposition of the ablated materials with the substrate
4. Nucleation and growth of a thin film on the substrate surface

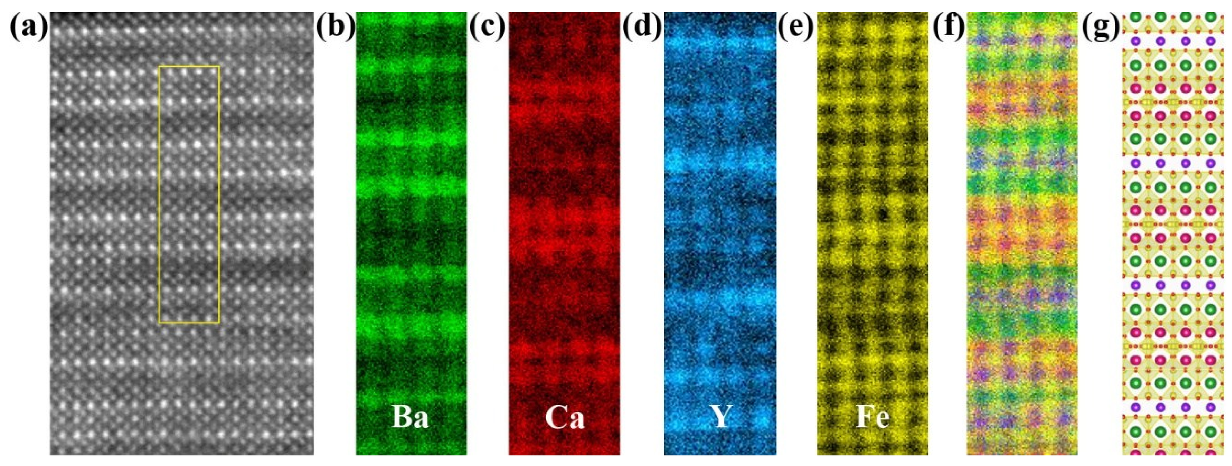


$10a_p$ thin film High Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM):



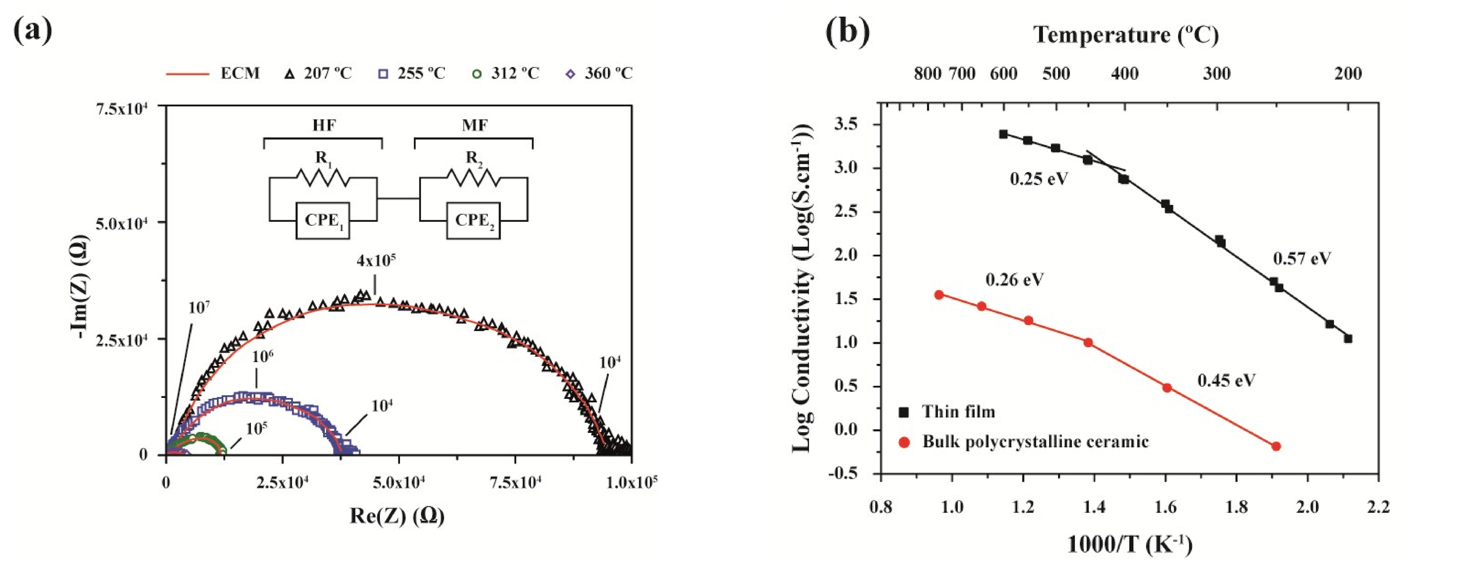
(a) HAADF STEM image (8 cm camera length) showing the interface between the $10a_p$ film and the STO substrate. Fast Fourier transform (FFT) images of the substrate (b) and film (c).

$10a_p$ thin film atomic resolution Z-contrast STEM and elemental maps:



Atomic resolution Z-contrast STEM images and elemental maps. Spectra were acquired in a 70 by 280 pixel grid in the region indicated by the yellow box in survey image (a), with an acquisition time of 0.01 seconds per spectrum. (b), (c), (d), (e) represent the Electron Energy Loss Spectroscopy (EELS) maps of Ba M_{45}, Ca L_{23}, Y M_{45} and Fe L_{23}, respectively. (f) Colour overlay of the individual maps, with green, red, blue and yellow channels representing Ba, Ca, Y and Fe, respectively. (g) Scaled structural model of the $10a_p$ unit cell. The colours were chosen to match that which one would expect to see in the composite EELS map for a given type of cation column according to the refined cation site occupancies.

$10a_p$ thin film conductivity compared to the bulk:



(a) Experimental arcs, and fits to the equivalent circuit model (ECM) measured at a range of different temperatures, with an inset which shows the ECM for the high frequency (HF) and mid-frequency (MF) arcs. Measured frequency is shown on the Nyquist plot in Hz. (b) Arrhenius plot for conductivity of $10a_p$ bulk polycrystalline ceramic (red circles) and thin film (black squares) as a function of temperature in flowing oxygen. All data shown are on cooling.

Conclusion:

The growth of a strongly cation ordered 10 layer perovskite film, with a more complex structure than previous SOFC cathode materials (e.g. $GdBaCo_2O_5$) grown in thin film form, has been achieved via pulsed laser deposition . The A site cation composition which produces the 10 layer, six cation site structure in the bulk ceramic also drives the assembly of this complex superstructure when grown as an epitaxial thin film.

The conductivity of these $10a_p$ films is significantly higher than that of the bulk polycrystalline ceramic. The conductivity attained by the film is 30 Scm^{-1} at 600 °C, greater than that of the bulk 3.5 Scm^{-1}, which is a key temperature for IT SOFCs. The enhanced conductivity is assigned to the reduction in the density of grain boundaries and the *a-b* orientation of the film in-plane. This shows that the electronic conductivity can be increased by oriented growth related to the cation stacking sequence. The film growth has thus revealed good intrinsic transport properties of the complex superstructure $Ba_{1.7}Ca_{2.4}Y_{0.9}Fe_5O_{13}$, as the measured conductivity shows that Fe^{3+}-based oxides can have acceptable conductivities for application as IT-SOFC cathodes.

References:

[1] Epitaxial growth and enhanced conductivity of a IT-SOFC cathode based on a complex perovskite superstructure with six distinct cathode sites, R. Sayers, N. L. O. Flack, J. Alaria, P. A. Chater, R. G. Palgrave, S. R. C. McMitchell, S. Romani, Q. M. Ramasse, T. J. Pennycook and M. J. Rosseinsky, Chem. Sci., (2013), DOI: 10.1039/c3sc21931c.

Acknowledgments:

We would like to thank EPSRC for support under EP/H000925, for a studentship to NLOF and for funding SuperSTEM, the National Facility for aberration-corrected scanning transmission electron microscopy.

Thanks also to the rest of the MJR group for their help and support.