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Measuring Near-Room-Temperature Valence Transition in Strained Perovskite Oxide using STEM-EELS

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Lanthanide-cobalt-based perovskites ($ACoO_3$) are desirable for applications in cathode materials and thermoelectric materials, due to their structure sensitive metal to insulator transitions [1]. This depends on the spin-state of the material, wherein spin-state cross overs occur due to the small energy difference between the crystal field splitting of the Co d levels and the Hund's coupling energy [2,3]. The spin-state transition in these materials can be manipulated by the choice of the A-site cation. Surprisingly, when Pr is used as an A-site cation, the spin-state crossover and metal-insulator transition observed is unique, occurring simultaneously driven by the valence transition in Pr from Pr^{3+} to Pr^{4+} as the temperature is lowered [4,5]. These first order transitions occur at cryogenic temperatures, thus limiting their applications in electronic devices which operate close to room-temperature.

In this work, we explore strain engineering in a Pr-Co based oxide of the composition $(Pr_{0.85}Y_{0.15})_{0.7}Ca_{0.3}CoO_{3-\delta}$ (PYCCO), wherein these films are grown on different substrates: $YAlO_3$ (YAO) – under a compressive strain and $LaAlO_3$ (LAO) under a tensile strain, to study their effect on the valence transition temperature [6]. To study the quality of the films grown, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging is used, which show the films are of high crystalline quality (Fig. 1(a) and 2 (a)). Local variations in HAADF intensity were observed in the film cross-sections. These were found to originate from variations in the local Ca/Y doping levels confirmed by the atomic resolution STEM energy dispersive X-ray (EDX) maps, pointing towards the absence of any oxygen vacancy ordering, commonly observed in such films (Fig. 1(b) and 2(b)). The HAADF-STEM imaging and STEM-EDX were carried out on an aberration corrected FEI Titan G2 60-300 (S)TEM microscope equipped with a Super-X EDX detector. The microscope was operated at 200 keV with a probe current of 100 pA.

Further, to understand the direct influence of the lattice strain on the valence transitions in the PYCCO films, the O K-edge was probed at cryogenic temperature using core-level electron energy loss spectroscopy (EELS). A Gatan 632 cryo-holder was used to cool the sample to liquid N_2 temperature, after which it was allowed to warm-up to room temperature in the microscope, with core levels EELS collected at intermediate temperature steps (Fig. 1(c) and 2(c)). It was found that in PYCCO films under compressive strains (i.e. PYCCO-YAO), an increase in the O pre-peak intensity as well as a shift in the peak to a lower energy is seen as the temperature is lowered. The pre-peak is sensitive to transitions from the O 1s to the hybridized O 2p and Co 3d states, which in turn probes the valence transitions at low temperatures. In contrast, no changes in the O edge were observed for a film under tensile strain (PYCCO-LAO). These results are in good agreement with electrical and magnetic measurements from these films, whereby increasing the compressive strain, a transition temperature as high was 245 K was obtained for the first time [6, 7].

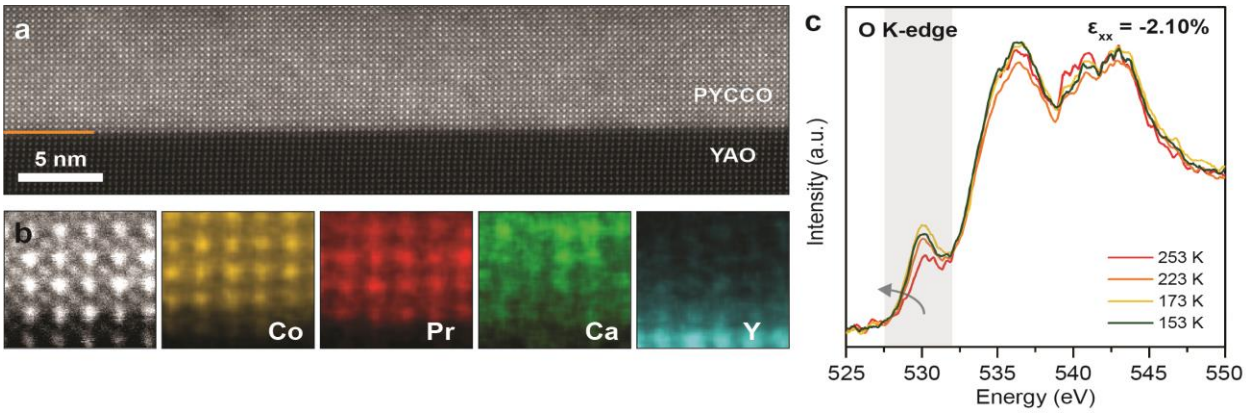

Figure 1. (a) Atomic resolution HAADF-STEM image of PYCCO film grown on YAO substrate, under compressive strain (ε_{xx}= -2.10%) with the interface marked. Local intensity fluctuations are visible. (b) STEM-EDX maps showing local fluctuation in the Y and Ca (dopants) in the PYCCO film, which contribute to the HAADF intensity fluctuations. (c) O K-edge EELS spectra collected from the PYCCO film as a function of temperature, showing variation in the O pre-peak position and intensity, as seen in the highlighted region.

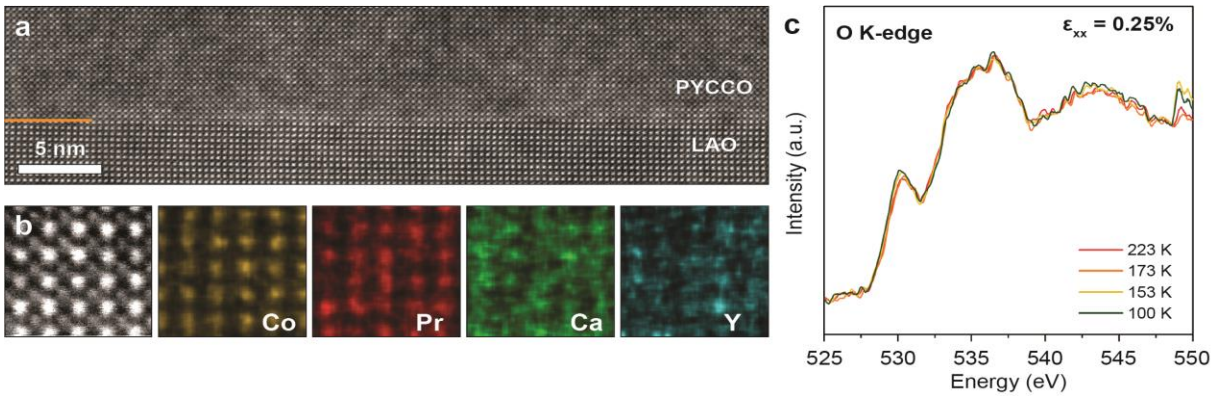

Figure 2. (a) HAADF-STEM image of PYCCO film grown on LAO substrate, under tensile strain (ε_{xx}= 0.25 %) with the interface marked. Local intensity fluctuations are visible. (b) STEM-EDX maps showing local fluctuation in the Y and Ca (dopants) in the PYCCO film. (c) O K-edge EELS spectra collected from the PYCCO film as a function of temperature, showing no variation in the O pre-peak.

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