

Local Mapping of Bandgap Electronic State in $\text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$: Elucidating Enhancement and Mechanism of Grain Boundary Electrical Conductivity

William J. Bowman^{1,2,3}, Eva Sediva^{2,5}, Toshihiro Aoki⁴, Jennifer L.M. Rupp^{2,5} and Peter A. Crozier¹

¹. School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ, USA

². Electrochemical Materials Group, ETH Zürich, Switzerland

³. Laboratory for Electrochemical Interfaces, MIT, Cambridge, MA, US

⁴. Leroy Eyring Center for Solid State Science, Arizona State University, Tempe, AZ, USA

⁵. Department of Materials Science and Engineering, MIT, Cambridge, MA, USA

Grain boundary engineering presents an interesting route to optimize the properties of polycrystalline materials. For instance, electrical conductivity of polycrystalline mixed ionic-electronic conducting oxides can be modulated by tuning local charge carrier concentration (ionic and/or electronic). We previously reported a factor 100 enhancement of grain boundary electrical conductivity in a polycrystalline $\text{Gd}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution resulting from the addition of Pr solute cations, i.e. $(\text{Pr,Gd})_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ [1]. It was speculated that modification of grain boundary electrical properties is related to enhanced electronic conductivity stemming from the population and depopulation of the inter-bandgap Pr *4f* electronic level [2] localized within nanometers of grain boundary cores. Here, we apply monochromated EELS to model $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (PCO) thin film specimens to map this bandgap state at the nanometer level to elucidate grain boundary transport mechanisms.

In our approach, we first developed a method to detect and interpret quantitatively this bandgap state in model PCO nanoparticles using monochromated electron energy-loss spectroscopy (EELS) in an Nion UltraSTEM100 aberration-corrected scanning TEM (STEM) operating at 60kV [3]. Relativistic electrodynamics simulations show that the characteristic plateau shape spectral feature is not the result of guided light modes [4]. The electron single-scattering distribution was computed using a joint density-of-states (DOS) approximation, enabling us to determine the position and intensity of the Pr *4f* DOS within the CeO_2 bandgap.

Here, we extend this approach to map the Pr *4f* bandgap state in the vicinity of grain boundaries in PCO films grown via pulsed laser deposition atop free-standing SiN_x/Si membranes, Fig. 1a. Not only does this allow us to avoid specimen preparation artifacts that could confuse spectral interpretation, such as ion implantation, we gain fine control over the thin film microstructure. Pr enrichment of grain boundaries in this specimen is confirmed via core-loss EELS, and spatial variation in the interband signal intensity is observed at grain boundaries, Fig. 1b. As shown in Fig. 2, changes the characteristic of the Pr *4f* bandgap state, such as shape change of the conduction band edge onset (~ 3 eV) is visible when comparing grains to grain boundaries, indicating that the local grain boundary electronic structure may be interpretable in terms of structural defect concentrations. We apply the DOS approximation to explore these electronic structure changes quantitatively; the observation of a 40% local enrichment of the Pr bandgap state in the raw spectral data is the first confirmation of previously reported [1] grain boundary electronic conduction [5]. By taking delocalization and elastic scattering effects into account, a more quantitative estimate of the intensity of the bandgap DOS can be determined.

References:

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 [6] We gratefully acknowledge access to the John M. Cowley Center for High Resolution EM and the Southwestern Center for Aberration-Corrected Electron Microscopy at ASU. W.J.B. was a Swiss Government Excellence Scholarship holder for the academic year 2015-2016 (ESKAS No. 2015.1183); he would like to acknowledge financial support of the US NSF's Graduate Research Fellowship Program (under grant number DGE-1311230), and the US NSF's Graduate Research Opportunities Worldwide grant. P.A.C. and W.J.B. gratefully acknowledge support of NSF grant DMR-1308085.

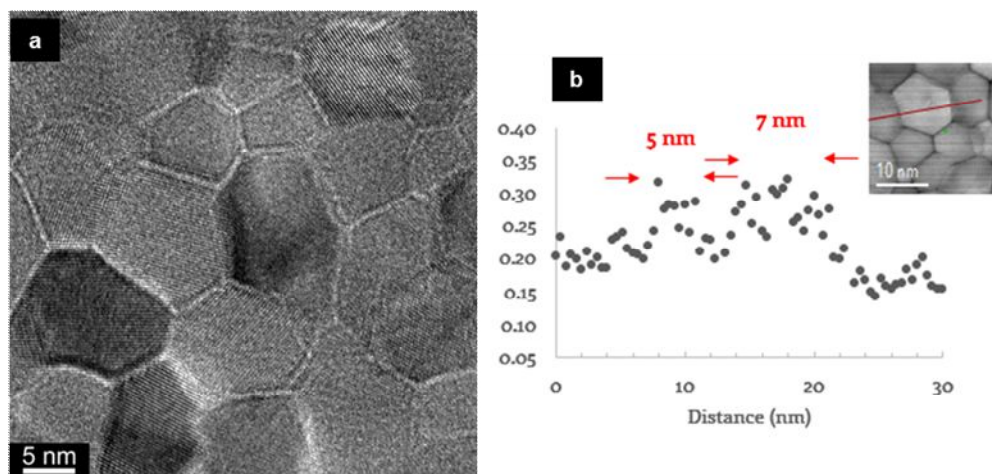


Figure 1. (a) Bright field TEM image of plan-view PCO thin film deposited on SiN_x/Si membrane. (b) Spatial distribution of bandgap signal showing the influence of at two grain boundaries (shown in inset STEM ADF image) on the bandgap signal intensity; the width of each peak is indicated.

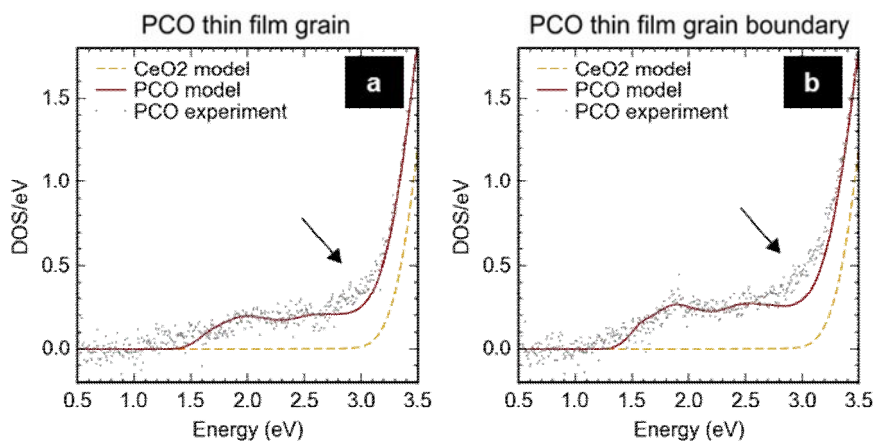


Figure 2. Experimentally measured low-loss EELS with overlaid model single-scattering approximations computed for PCO (i.e. with Pr $4f$ interband state in DOS) and CeO_2 (i.e. without interband state). Measurements and calculations for thin film grain and grain boundary are presented in (a) and (b), respectively. Arrows highlight spectral features associated with thin films.