Grain boundaries (GBs) in O\textsubscript{2}\textsuperscript{-} conducting ceramics like doped ceria significantly degrade ionic conductivity especially at intermediate temperatures (300 – 550 °C) [1]. High GB resistivity has been attributed in part to a space charge double layer which creates a vacancy depletion region emanating from grain interfaces. Other factors such as dopant segregation (and segregated dopant species) may also influence GB electrical properties. Recent high resolution elemental analysis in the TEM of 20 at% Gd-doped ceria by our group and others shows significant Gd segregation to GBs yielding enrichment zones of approximately 60 at% Gd, far exceeding the optimal Gd concentration (10 – 20 at%) for maximum ionic conductivity [1].

We have synthesized Ce\textsubscript{0.8}Gd\textsubscript{0.2}O\textsubscript{2-δ} (GDC), and Ce\textsubscript{0.85}Gd\textsubscript{0.11}Pr\textsubscript{0.04}O\textsubscript{2-δ} (GPDC) powders and fabricated bulk samples for characterization of electrical properties via AC impedance spectroscopy, and GB structure and composition via TEM. Electron energy-loss spectroscopy (EELS) in a JEOL ARM200F probe corrected scanning TEM (STEM) has been performed to map the distribution of dopant cations in the vicinity of GBs.

Fig. 1b shows an annular dark field (ADF) STEM image of a GB in GPDC with inset 2D EELS spectrum image color map indicating the segregation of dopant cations to the GB. The color map is created from integration of the background-subtracted Ce, Pr and Gd M\textsubscript{45} white lines (fig. 1a). Fig. 1c illustrates the compositional variation near the GB estimated by k-factor analysis of background-subtracted white line integrated intensities. A distinct Ce M\textsubscript{4}:M\textsubscript{5} white line ratio decrease characteristic of the reduction of Ce\textsuperscript{4+} to Ce\textsuperscript{3+} was also observed, possibly indicating an increased oxygen vacancy concentration associated with the structural disorder of the GB core. The cation segregation zone was measured at full width half maxima (FWHM) to be 1.6 and 2.0 nm in the GDC and GPDC, respectively. The average GB core composition in the GDC was approximately 61%, and the preliminary results presented here indicate GPDC GB core compositions of [Pr] ≈ 16% and [Gd] ≈ 29%. The relative dopant concentration (i.e. [Gd]/[Pr]) also appears to vary with position near the GB.

We present characterization of electrical conductivity, microstructure, and nano-scale grain boundary structure and chemistry of nominally Gd-doped and Gd/Pr doubly-doped ceria fabricated using mixed oxide nanopowders synthesized by spray drying. We discuss correlations between Ce\textsuperscript{4+} oxidation state variations, dopant segregation and resultant electrical properties in these materials. In an attempt to elucidate the O\textsuperscript{-} vacancy environment near GBs, the GPDC O K edge fine structure will also be discussed.


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Fig. 1: (a) GPDC EELS with M45 white lines and background windows BPr and BGd (BCe omitted for clarity). (b) ADF STEM of a GPDC GB with inset EELS spectrum image colored using the integrated intensities of Ce, Pr and Gd M45. (c) Cation concentration profiles and Ce M4:M5 white line ratio across the grain boundary in (a).