Linking Macroscopic and Nanoscopic Ionic Conductivity: A New Paradigm for Characterizing Grain Boundary Conductivity in Polycrystalline Ceramics

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High ionic conductivity is desired to optimize electrolyte performance, though it is significantly degraded by grain boundaries (GBs), which act as ionically-resistive blocking layers in polycrystalline electrolytes. Given the rich diversity in GB types, and the complex interplay between structure, composition, and chemistry at the atomic and nanoscale [1-3], there is considerable opportunity to elucidate fundamental science and performance optimization of GBs. Hence, studies should rely on GB datasets correlated across many length scales, with the aim of generalizing high spatial resolution observations to an entire GB population. This should facilitate bottom-up design of GBs with optimized properties, which remains a considerable challenge. By combining suitable modeling approaches with experimental measurements interrogating materials over different length scales, it becomes possible to estimate the electrical properties of individual GBs.

Here, we show that the enhancement of oxygen ionic conductivity by over two orders of magnitude in an electroceramic oxide is explicitly shown to result from nanoscale enrichment of a grain boundary layer or complexion with high solute concentration, Figure 1a-b. A series of $Ca_xCe_{1-x}O_{2-\delta}$ polycrystalline oxides with uorite structure and varying nominal Ca^{2+} solute concentration elucidates how local grain boundary composition, rather than structural grain boundary character, primarily regulates ionic conductivity. A correlation between high grain boundary solute concentration above $\sim$40 mole%, and four orders of magnitude increase in grain boundary conductivity is explicitly shown, Figure 1c. A correlated experimental approach provides unique insights into fundamental grain boundary science, and highlights how novel aspects of nanoscale grain boundary design may be employed to control ion transport properties in electroceramics.

Additionally, we present a novel correlated approach employed combining precession electron nanodiffraction (PED) orientation imaging and electron energy-loss spectroscopy (EELS) in an aberration-corrected scanning TEM to elucidate the GB transport properties in oxygen-conducting $Gd_{0.11}Pr_{0.04}Ce_{0.85}O_{2-\delta}$ (PGCO), Figure 2 [3]. Nanoscale EELS measurements of GB solute segregation are generalized to the entire boundary population via GB character determined using PED, Figure 2a-b. Composition data are used to estimate carrier concentration and migration activation energy, which enables prediction and mapping of the distribution of GB ionic conductivity, Figure 2c. The applicability of conventional GB models - used widely to predict defect distribution and transport properties - to the presented data is also evaluated.

References
[1] W.J. Bowman, J. Zhu, R. Sharma, P.A. Crozier. *Solid State Ionics* (2014).
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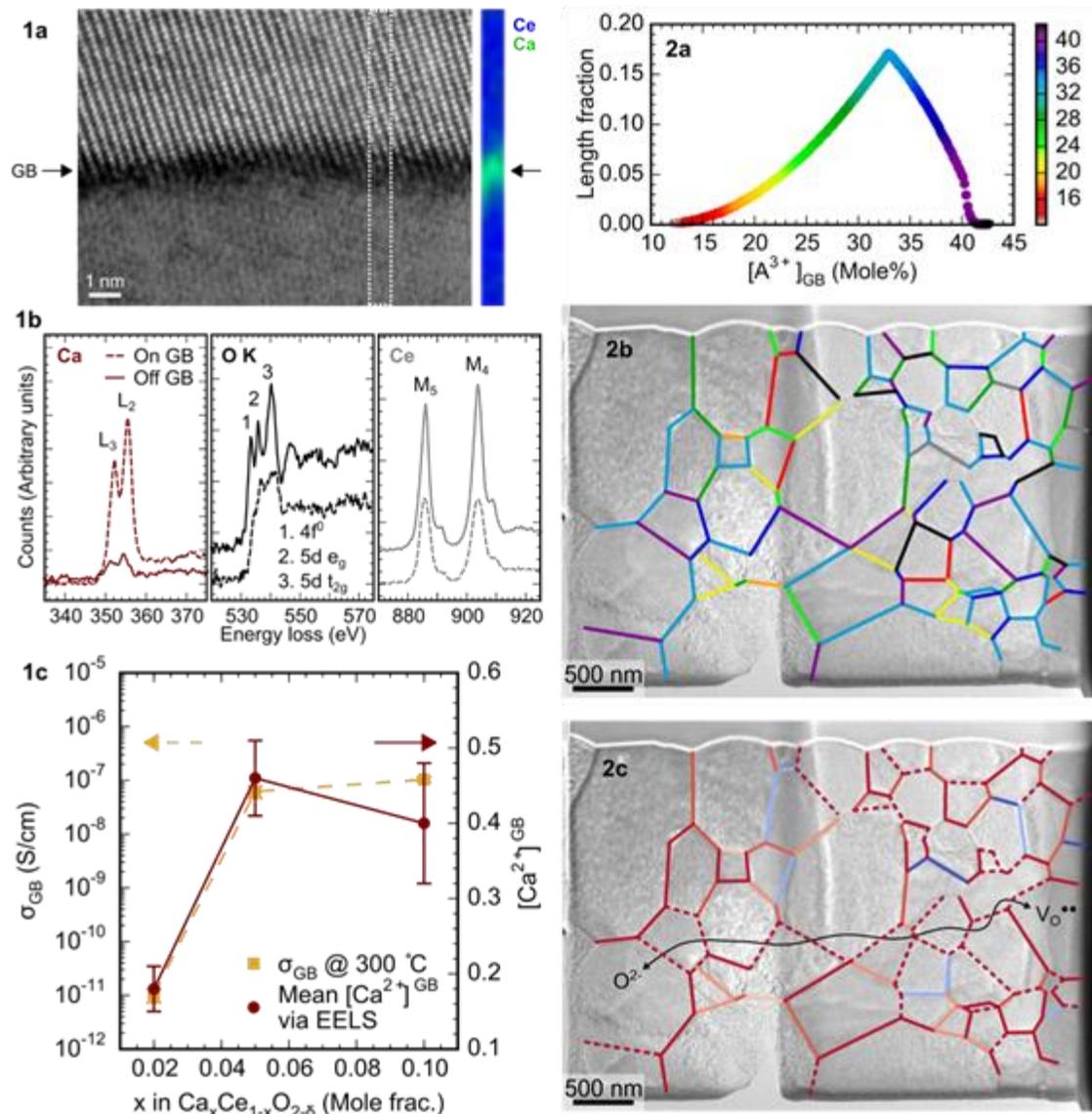[3] W.J. Bowman, A.D. Darbal, P.A. Crozier. *Submitted*.

Figure 1. a, Aberration-corrected STEM ADF image and associated EELS elemental map acquired in the region outlined with a dashed line. b, Comparison of EELS fine structure measured at a grain boundary ('On GB') and in an adjacent grain ('Off GB'). c, Inuence of nominal Ca^{2+} concentration, x, on GB conductivity measured at 300 °C using AC impedance spectroscopy, and on GB Ca^{2+} concentration (dashed and solid lines are guides for the eye).

Figure 2. Grain boundary length fraction distribution of the trivalent solute concentration measured at GBs, $[A^{3+}]_{GB}$. b, Bright field TEM image of PGCO specimen with GB segments colored to indicate their trivalent solute concentration, in accordance with the scale bar in b. c, Bright field TEM image with GB segments colored to indicate their ionic conductivity; boundary segments are indicated with dashed lines to indicate GBs participating in ion/vacancy percolation, and the double-headed arrow indicates a potential percolating path for ions/vacancies.