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Direct Correlation of Grain Boundary Defect Chemistry with Anion Conductivity in Oxide Ceramics Using Direct Detection Electron Energy-Loss Spectroscopy

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Despite their promises in energy storage, conversion, catalysis, etc., non-stoichiometric polycrystalline oxides are suffering from the effect of internal interfaces called grain boundaries (GBs), which exhibit substantially lower ionic conductivity than the bulk. This is due to the existence of space charge layers (SCLs) at the GBs, where a depletion of mobile charge carriers, oxygen vacancies, has been observed[1]. To date, the modeling of the SCLs has been mainly focused on the dilute solution approximations and only very few studies on the concentrated solid solutions [2-5]. The dilute solid solution approximation can lead to error by ignoring the defect-defect interactions that are present in the concentrated solid solutions. Therefore, an understanding of the origin of the GB phenomenon and the role of charge carriers, particularly in concentrated solutions, is necessary for further development of these materials.

This work will bridge the gap between GB ionic conductivity and defect chemistry in Gd-substituted CeO_2 ($Gd_xCe_{1-x}O_2$) using direct observations of chemical and functional properties across length scales for a range of oxide compositions. A typical aberration-corrected scanning transmission electron microscope (AC-STEM) high-angle annular dark field (HAADF) image of a GB in $Gd_{0.2}Ce_{0.8}O_{1.9}$ is presented in Fig.1a (JEOL Grand ARM 300 kV). The corresponding elemental map obtained by energy-dispersive X-ray spectroscopy (EDS) is provided. Preliminary composition analysis was performed using EDS line scans to quantify local cation composition across the GB, Figure 1b. The specimen was prepared using focused ion beam.

To quantify anion conductivity across GBs in the bulk ceramics, electrochemical impedance spectroscopy (EIS) is used to differentiate the grain and GB impedances, Figure 2b. In these materials, transport through grains and across GBs are the two paths for ion transport, as indicated on a typical microstructure of $Gd_{0.2}Ce_{0.8}O_{1.9}$, Figure 2a. The ion conductivity is measured as a function of temperature and activation energy for ionic transport can be calculated from the slope of the corresponding Arrhenius plot, in Figure 2c. This energy barrier is higher for anion transport across grain boundaries comparing to transport through the crystalline grains[1,2,5].

In this talk, I will discuss the observations on the local composition, electronic structure and defect chemistry of the GBs in a series of $Gd_xCe_{1-x}O_2$ samples. A JEOL Grand ARM equipped with Gatan K2 direct electron detector will be used to record electron energy-loss spectroscopy (EELS) core-loss edges and near-edge fine structure to quantify the local concentration of cations, oxygen vacancies and electrons bound to reduced Ce cations (i.e. Ce^{3+}). Macroscopic ionic conductivity measurements will be directly correlated to ceramic microstructure and local GB defect chemistry. This information is useful for development of models dedicated to concentrated oxide solid solutions which can further enhance the understanding of the role of GBs and interfaces on mechanisms of ion transport in solids.

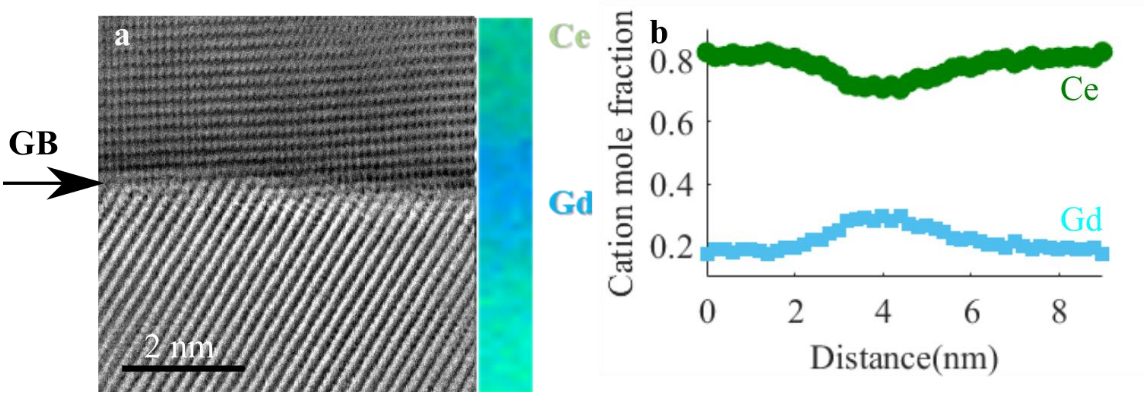

Figure 1. a. Preliminary AC-STEM HAADF imaging and EDS mapping shows accumulation of Gd along the GB in Gd0.2Ce0.8O1.9. b, EDS line scan across the same GB shows increase in Gd mole fraction with a decrease in Ce mole fraction at the GB

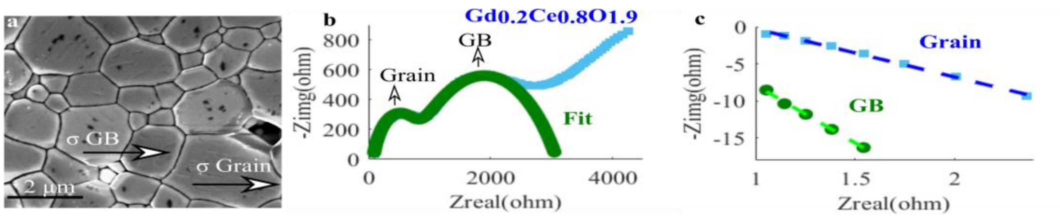

Figure 2. a. SEM micrograph of the microstructure of Gd0.2 Ce0.8 O1.9 specimen, b. Impedance spectra of the specimen showing the distinction between grain and GB impedance, c. Arrhenius plot of conductivity as a function of temperature for grain and GB.

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