

Direct Correlation of Grain Boundary Defect Chemistry with Anion Conductivity in Ceramic Oxides using Electron Energy-Loss Spectroscopy

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Despite their promises in energy storage, conversion, catalysis, etc., non-stoichiometric polycrystalline oxides often suffer from the effect of internal interfaces called grain boundaries (GBs), which exhibit substantially lower ionic conductivity than the bulk in many solid-state ionic conductors. This is due to the existence of space charge layers (SCLs) at the GBs, where depletion of the point defects (e.g., oxygen vacancies) facilitates the migration of charge carriers (e.g., oxygen anions) [1]. To date, the modeling of the SCLs has been mainly focused on dilute solutions ($< \sim 1$ at % of point defects), with only a few studies focused on concentrated solid solutions—which encompass most engineering materials [2-5]. The dilute solid solution approximation can lead to an error by ignoring the defect-defect interactions that are present in the concentrated solid solutions. Therefore, an understanding of the atomic-scale role of charge carriers near GBs on functional properties, particularly in concentrated solutions, is necessary for the further development of these materials.

This work will link GB ionic conductivity and defect chemistry in Gd-substituted CeO₂ (Gd_xCe_{1-x}O₂) using direct observations of chemical and functional properties across length scales. 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.1b (JEOL Grand ARM 300 keV), with the corresponding elemental map obtained by electron energy-loss spectroscopy (EELS). EELS elemental and chemical analysis was performed to quantify local point defect concentration in the vicinity of the GB.

To quantify anion conductivity across GBs in the bulk ceramics, electrochemical impedance spectroscopy (EIS) is used to differentiate the grain and GB impedances. 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}, Fig.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 Fig.2b. 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 several Gd_xCe_{1-x}O₂ samples. A JEOL Grand ARM equipped with GatanGIF Quantum detector was used to record EELS core-loss edges and near-edge fine structure to quantify the local concentration of cations (Gd³⁺, Ce⁴⁺, and Ce³⁺), and oxygen vacancies. Macroscopic ionic conductivity measurements will be directly correlated to ceramic microstructure and local GB defect chemistry. This information is useful for the development of models dedicated to concentrated solid solutions which can further enhance the understanding of the role of GBs and interfaces on mechanisms of ion transport in solids.

This work was funded primarily by UCI's new faculty start-up funds and performed in the Irvine Materials Research Institute (IMRI). Partial support is also provided by the UC Irvine MRSEC, Center for Complex and Active Materials, under the award NSF DMR-2011967.

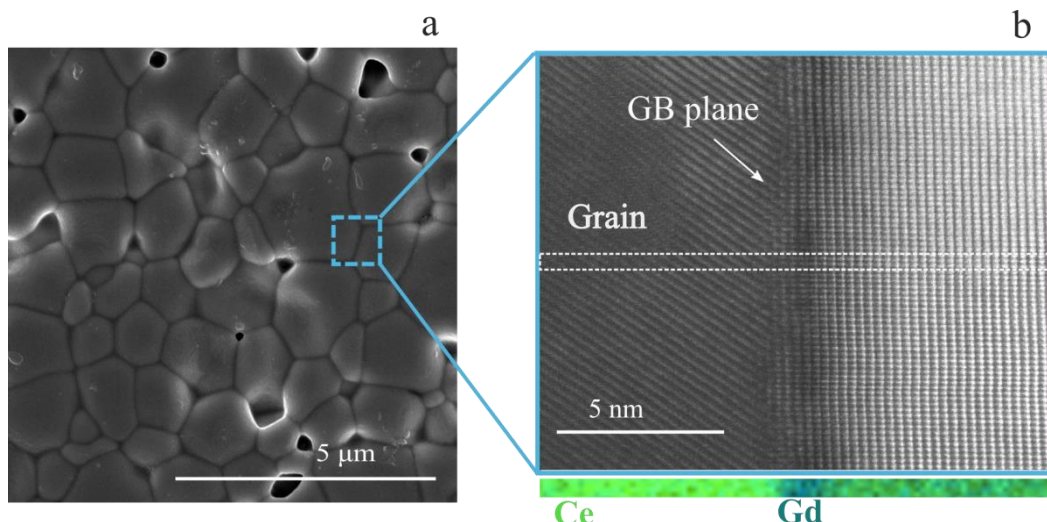


Figure 1. Figure 1: a. SEM micrograph of the microstructure of Gd_{0.2} Ce_{0.8} O_{1.9} specimen, b. Preliminary AC-STEM HAADF imaging and EELS mapping show the accumulation of Gd along the GB plane in Gd_{0.2} Ce_{0.8} O_{1.9}.

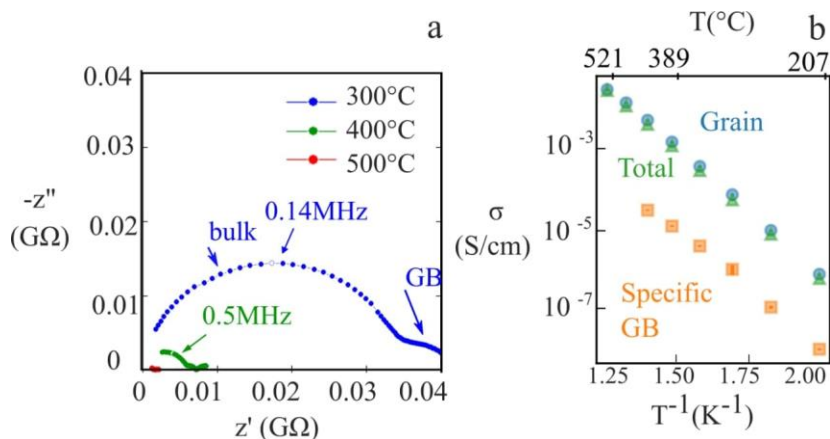


Figure 2. Figure 2: a. Impedance spectra of the specimen showing the distinction between grain (“bulk”) and GB impedance at 300°C, 400°C, and 500°C, b. Arrhenius plot of the total, grain, and specific GB conductivity as a function of temperature.

References

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