

Probing Oxygen Environments Associated with High Solute Grain Boundary Complexions in Ceria Ceramics with EELS

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Intermediate temperature solid oxide fuel cells (IT-SOFC) are electrochemical devices with the potential to be integrated into current power generation infrastructure as part of the next generation of renewable energy technologies. Doped CeO₂ (ceria) is one possible electrolyte for these systems. However, resistive grain boundaries (GB) in these polycrystalline ceramics lead to a decrease in the total ionic conductivity. Doping is one way to tailor material properties and increase GB ionic conductivity. Experimental evidence has shown that doping at different nominal concentrations could result in increased GB ionic conductivity relative to the undoped samples [1]. This effect has been attributed to increases in local dopant/solute concentrations at the GB. Probing local structural motifs associated with high oxygen ion transport across grain boundaries is a very challenging problem. Here we theoretically explore how local structural motifs associated with possible oxygen migration pathways for ion transport across GBs influence the electron energy-loss spectra (EELS). The high GB solute concentration may give rise to strain and chemical effects so initially, simulations of the O K-edge are performed for strained bulk CeO₂ and aliovalent dopants such as Ca. These effects may assist in the interpretation of complex EELS obtained at GBs. Such an approach has the potential to detect sites in GBs associated with higher oxygen ion transport.

To gain fundamental insights into the factors which regulate ionic conductivity across grain boundaries atomistic calculations were performed with rigid ion potentials as part of the LAMMPS simulation package using Buckingham pair potentials [2]. *Ab initio* computations were performed using the Vienna Ab Initio Simulation Package [3]. The derived are then used as input to FEFF to calculate the near-edge fine structure of the oxygen K-edge [4].

Figure 1 shows a qualitative agreement for strain effects on EELS for pure ceria. Substitutional Ca atoms are also simulated to understand how dopant atoms influence the near-edge fine structure as shown in **Figure 2**. Atomic structures and oxygen migration pathways will be obtained for GBs with molecular dynamics and density functional theory codes. Coupling migration energetics and EELS simulations in this manner could assist with interpreting EELS spectra where strain and high concentrations of dopants are present. This work may provide insights into the utility of EELS to locate oxygen migration pathways at GB cores, furthering our understanding of the GB oxygen migration mechanism. These simulations will be compared with experiments.

[1] W. J. Bowman, et al. *Nanoscale*, **9** (2017) p. 17293 - 17302. [2] S. Plimpton, *Journal of Computational Physics*, **117** (1995) p. 1 - 19. [3] G. Kresse and J. Furthmüller, *Phys. Rev. B*, **54** (1996) p. 11169 - 11186. [4] J.J. Rehr, et. al. *Phys. Chem. Chem. Phys.*, **12** (2010) p. 5503-5513.

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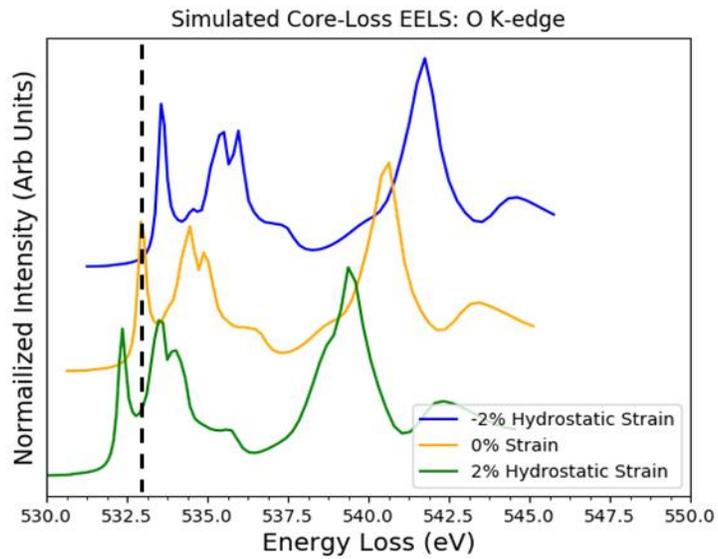


Figure 1 Theoretically predicted chemical shift resulting from hydrostatic strain applied to a bulk CeO_2 unit cell. Negative values indicate compressive strain while positive values indicate tensile strain. There is a chemical shift of approximately ± 0.50 eV associated with 2% strain.

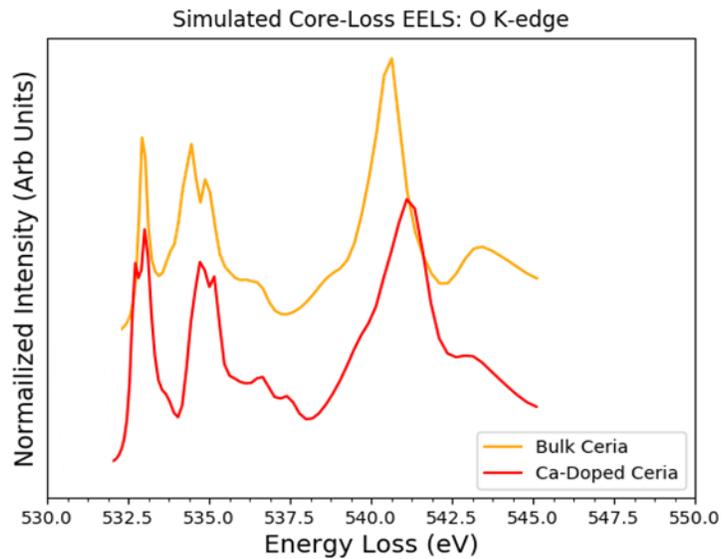


Figure 2 Simulated O K-edge for Ca-doped and bulk CeO_2 .