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# Multi-modal characterization approach to understand proton transport mechanisms in solid oxide fuel cells

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Acceptor doped perovskites are a promising class of materials used as a solid electrolyte in proton conducting solid oxide fuel cells. Yttrium-doped barium zirconate (Y-BZO) has been widely investigated as a solid electrolyte due in part to its high proton conductivity and excellent chemical stability at intermediate temperatures [1]. Substitutional doping of the B-site (Zr) cations with Y causes an increase in lattice distortion and creates charge-compensating oxygen vacancy defects, which can be filled via hydration, allowing for the generation of mobile protons through dissociation at these protonic defects [1]. High-throughput screening of dopants in this class of materials reveals a positive correlation between dopant size/type, oxygen vacancy formation energy, and dopant-proton binding energy, which combinatorially has an effect on proton conductivity [2]. However, to better understand the complex interplay of how dopants and other structural and chemical heterogeneities influence proton transport on the nanoscale, a multi-modal characterization approach was used to correlate the activation energy for proton transport with dopant-induced lattice distortion: Kelvin probe force microscopy (tr-KPFM) was used to measure the proton transport activation energy as a function of dopant concentration, temperature, and humidity while annular dark field (ADF) scanning transmission electron microscope (STEM) and atom probe tomography (APT) were used to measure the lattice distortion and spatial distribution of dopants and frequency of Y-Y nearest neighbor bonds as a function of dopant concentration [3].

A series of model epitaxial Y-BZO thin films were synthesized on a [100] oriented single crystal MgO substrate using pulsed laser deposition with Y-dopant concentrations ranging from 5-20 mol%. Surface potential mapping from tr-KPFM measurements revealed that the activation energy monotonically increases from 0.45–0.64eV with increasing Y-dopant concentration. To correlate these measurements with lattice distortion and distribution of dopants at the atomic scale, a Nion UltraSTEM (operated at 100kV) was used to acquire a series of frame-averaged, ADF-STEM images (Fig. 1). Quantitative B-site bond angle deviation and atomic displacement measurements were performed on undoped 0Y-BZO to 20Y-BZO . Figure 2 shows APT results from 5Y-BZO (Figure 2a) and 20Y-BZO (Figure 2b) along with a statistical measurement of Y-Y nearest neighbors. From these tr-KPFM, STEM, and APT results, a strong correlation between activation energy, dopant lattice distortions, and the concentration of Y-Y nearest neighbors is identified. The increase in activation energy is concentration-dependent and suggests that proton trapping occurs near Y-dopant atoms. Material design strategies can be developed to determine the optimal type and concentration of B-site acceptor dopants such that lattice distortion, interaction energy, and proton trapping can be minimized [5].

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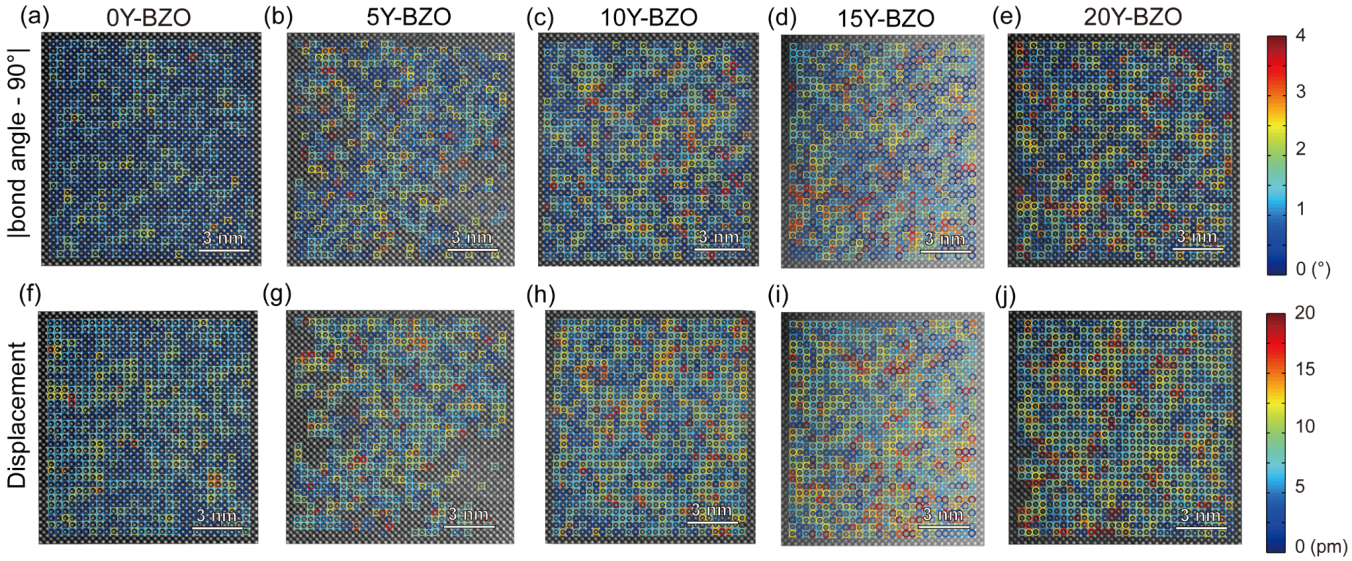


**Figure 1.** Aberration-corrected ADF-STEM images overlaid with measurements for (a-e) B-site bond angle deviation for 0Y-BZO - 20Y-BZO and (f-j) B-site atomic displacement for 0Y-BZO - 20Y-BZO.

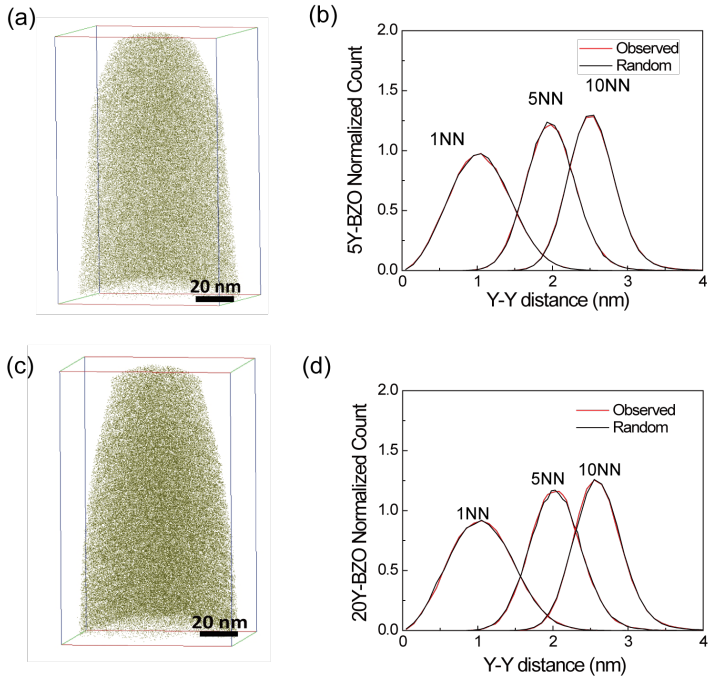


**Figure 2.** APT reconstructed volumes showing homogeneous distribution of Y dopants and distribution of 1st, 5th, and 10th Y-Y nearest neighbor for (a-b) 5Y-BZO and (c-d) 20Y-BZO.

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