Atomic Resolution Distortion Analysis of Yttrium-Doped Barium Zirconate

Jilai Ding[1], Xiahan Sang[2], Janakiraman Balachandran[2], Nazanin Bassiri-Gharb[1,3], Panchapakesan Ganesh[2] and Raymond R. Unocic[2]

[1.] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, USA
[2.] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, USA
[3.] G. W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, USA

Ionic transport dynamics underpins the functionality of most energy storage and conversion technologies. Yttrium-doped barium zirconate (Y-BZO) has attracted attention as a promising electrolyte for proton-conducting solid oxide fuel cells (PC-SOFCs), which stems from its high proton conductivity and excellent chemical stability at intermediate temperatures (400-700 °C) [1]. The Grotthuss mechanism for proton conduction is envisioned to occur by the creation of oxygen vacancies ($V_0^{\cdot\cdot}$), which are induced by the substitution of Y^{3+} atoms on Zr^{4+} sites. Density functional theory (DFT) calculations have suggested possible $V_0^{\cdot\cdot}$-dopant association effect and proton trapping effect [2]; however, experimental validation is lacking. To reveal the fundamental role of $V_0^{\cdot\cdot}$ and dopant concentration on the ionic transport mechanisms, and possible proton trapping effects in Y-BZO, it is important to understand how defect are created and distributed at the atomic scale. Recently, it has been shown that local distortions in lanthanum strontium aluminium titanate (LSAT) can be directly measured, with pm-level precision, using atomic-resolution aberration-corrected scanning transmission electron microscopy (STEM) [3]. A similar, detailed understanding of local distortion in Y-BZO would help elucidate the correlation between point defects and lattice distortions and their role on proton conduction.

Y-BZO samples with different dopant concentrations (0% Y, 5% Y, and 10% Y) were examined to investigate local distortions in Y-BZO. A Nion UltraSTEM (operated at 100kV) was used to acquire fast, frame-averaged, high-angle annular dark field (HAADF)-STEM images of the Y-BZO epitaxial thin-films deposited on (100) oriented MgO by pulsed laser deposition (PLD). Figures 1a-c show representative atomic-resolution HAADF-STEM images of 0Y-BZO, 5Y-BZO and 10Y-BZO, respectively. Each image was averaged from 10 fast frames acquired with a pixel dwell time of 4 μs and 512×512 frame size. The frame averaging process significantly enhances the signal-to-noise ratio and image quality, and enables accurate determination of atom column positions that are essential for subsequent quantitative distortion analysis. The brighter atomic columns in the HAADF-STEM images are A sites (Ba), while the weaker atom columns are B sites (Zr, Y).

For each HAADF-STEM image, the locations of atomic columns were identified using normalized cross-correlation and fitted using a 2D Gaussian distribution [4]. The lattice constants can be directly measured from adjacent atom columns along the fast scan direction [5]. Histograms with Gaussian distribution fits of the measured lattice constants are shown in Figure 2a, which increase from 420 pm for 0Y-BZO, to 427 pm for 5Y-BZO, and to 430 pm for 10Y-BZO. This is expected since the lattice will expand to accommodate the slightly larger Y in the Zr sites of the ABO_3 perovskite structure. More importantly, the fitted normal distribution widens due to the larger variation of lattice constant, suggesting that Y dopants introduce a local lattice distortion, i.e., the unit cell expands around Y atoms and shrinks around $V_0^{\cdot\cdot}$. We then explored how the bond angles between A-sites (A-A) in $BaZrO_3$ evolve as Y-doping increases. As shown in Figure 2b, the average bond angle is roughly 90° for 0Y-BZO, which starts to deviate from 90° and the distribution widens as the dopant concentration increases,

implying lattice distortions with possible octahedral tilting. The distortion analysis is further extended to the displacement of A sites relative to the unit cell center defined by the four nearest B sites (Figure 2c). Again, both the average displacement amplitude and the standard deviation increase as more Y dopants are added to the lattice.

The atomic-resolution HAADF-STEM images from three samples suggest that the increased lattice distortion is correlated to increased Y dopants and related $V_0^{\cdot\cdot}$. The cubic unit cell becomes locally distorted compensate for the local strain from point defects. By combining theoretical simulation, ionic transport experiments, and future distortion correlation analysis, this study will provide atomic-level insight into the role of dopant distributions and ordering, which is crucial in explaining the proton conduction mechanisms in Y-BZO [6].

References:

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[4] X. Sang et al., Microscopy and Microanalysis, **20** (2014) p.1764.
[5] H. Dycus et al., Microscopy and Microanalysis, **21** (2015) p.946.
[6] Research supported by ORNL's Laboratory Directed Research and Development Program, which is managed by UT-Battelle LLC for the U.S. DOE. Electron microscopy was conducted as part of a user proposal at Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy Office of Science User Facility.
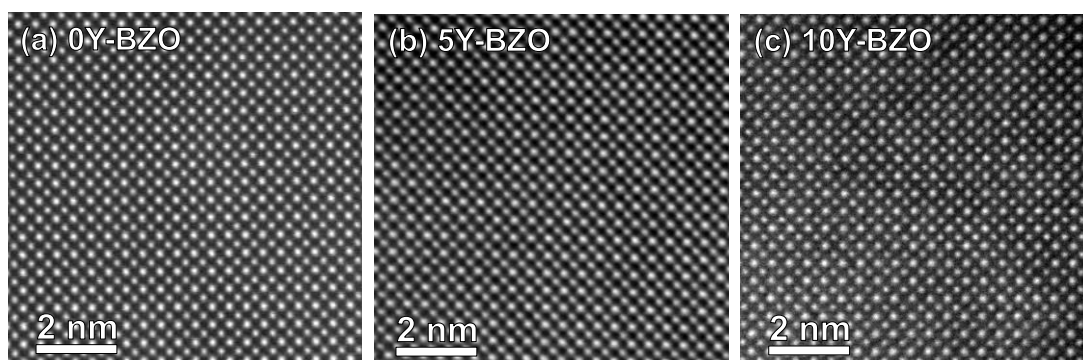

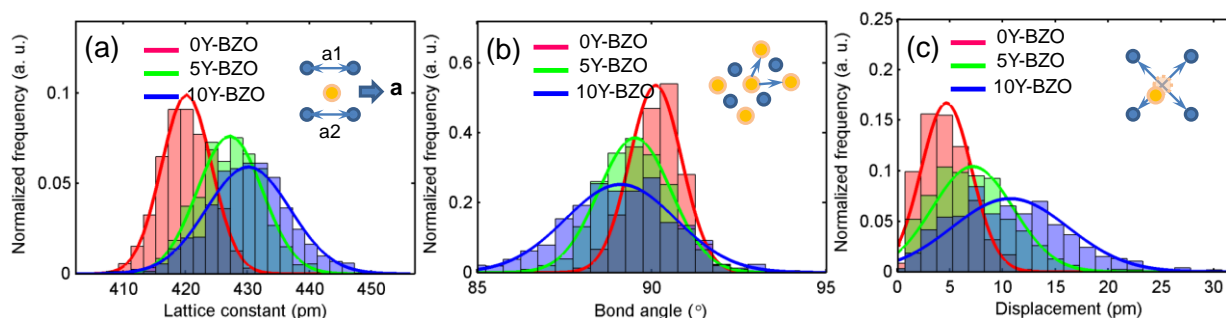**Figure 1.** Frame-averaged HAADF-STEM images of (a) 0Y-BZO, (b) 5Y-BZO, and (c) 10Y-BZO.

Figure 2. Histogram and normal distribution fitting of the experimentally measured (a) lattice constant, (b) lattice angle, and (c) displacement for all atoms measured for 0Y-BZO (red), 5Y-BZO (green) and 10Y-BZO (blue). The inset shows the calculation method for each one.