Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information for:

Effect of Composition and Microstructure on Electrical Properties and CO_2 Stability of Donor-doped, Proton Conducting $BaCe_{1-(x+y)}Zr_xNb_yO_3$

Colin M. Gore, Joseph O. White, Eric D Wachsman and Venkataraman Thangadurai

XPS Analysis Details:

XPS spectra were acquired using a Kratos Axis 165 x-ray photoelectron spectrometer operating in the hybrid mode using Al Kα radiation (1486.6 eV) at 280W (14kV 20mA). The ceramic samples were run using a charge neutralization of 2.5V. The instrument was run in hybrid mode with a pass energy of 160 eV for survey spectra (Figure S1 & S3) and a pass energy of 20 eV for high-resolution spectra (Figure 9a, S2 & S4). Peak energies were calibrated to the adventitious carbon C 1s peak centered at 284.8 eV. Peak fittings were performed using CasaXPS software.

Measured spin-orbit spilt peak doublet areas from high resolution scans from each cation's 3d spectra were fit ensuring a proper 2:3 area ratio between the $3d_{3/2}$ and $3d_{5/2}$ peaks and proper peak separation energy (15.4 eV for Ba, 18.3 eV for Ce, 2.4 eV for Zr, and 2.8 eV for Nb) [1]. Shirley backgrounds were applied to all but Ce, which required a linear background as is common in literature[2]. The areas were modified by the appropriate relative sensitivity factor for each element from the Kratos library (0.278 for C, 0.780 for O, 7.469 for Ba, 8.808 for Ce, 2.576 for Zr, and 2.921 for Nb), and the resulting atomic percent for each were calculated.

Correction for Ba auger contribution to measured Ce 3d peaks:

Ba has auger peaks that overlap with Ce 3d peaks when using an Al Kα source. Reference samples of CeO_2 and $BaCeO_2$ were used to correct for the overlap. $BaCeO_3$ and CeO_2 both contain Ce entirely in the 4+ oxidation state and the Ce to Ba ratio in $BaCeO_3$ is 1:1, so the Ce 3d peak envelope from the CeO_2 spectra was scaled appropriately to fit the peak intensity at 916 eV in the Ce 3d high resolution scan of $BaCeO_3$, then subtracted from the $BaCeO_3$ Ce 3d peak envelope to leave only the Ba auger peak contribution (Figure S4). A correction factor for the Ce peak area was derived using this data. The overlapping Ba auger peak area was found to scale proportionally as 0.893 of the Ba 3d peak area, thus can be subtracted using:

$$I_{\text{Ce 3d, corrected}} = I_{\text{Ce 3d, measured}} - I_{\text{Ba 3d}} * 0.893$$

All measured Ce peak areas have been corrected using this method before calculating stoichiometry. Since B-site cations are not volatile, B-site deficiency was not feasible via any defect equilibria, and since B-site cations are too small to occupy an A-site position, the sum of Ce, Zr, and Nb were safely assumed to add to an occupancy of 1 on the B-site. The Ba stoichiometry was then found by the A:B site ratio (proportion of Ba cations to Ce+Zr+Nb cations), revealing Ba deficiency in many cases.

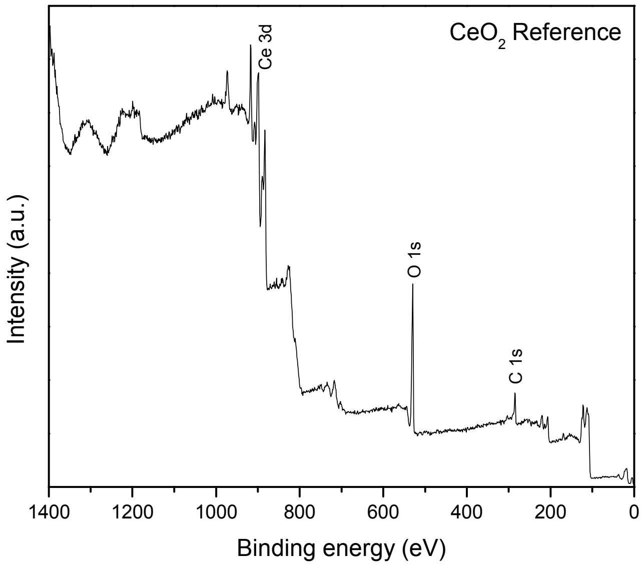

Figure S1: CeO_2 Survey Spectrum

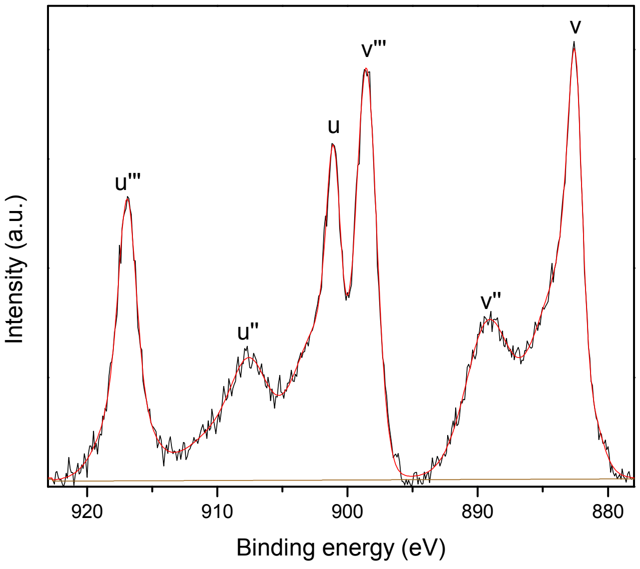

Figure S2: CeO_2 3d peaks and satellite peaks.
Envelope used in Fig. S4 is highlighted in red.

Ceria gives a complex set of satellite peaks around its 3d peaks associated with shake-up/ shake-down. Each pair of satellite peak pairs (u’’ & v’’, u’’’ & v’’’) have the same 18.3 eV separation and 2:3 peak area ratio as the main 3d peaks. The sharp u’’’ peak at ~916 eV is only associated with the Ce^{4+} oxidation state, and is useful in characterizing the oxidation state of the Ce in doped samples[3].

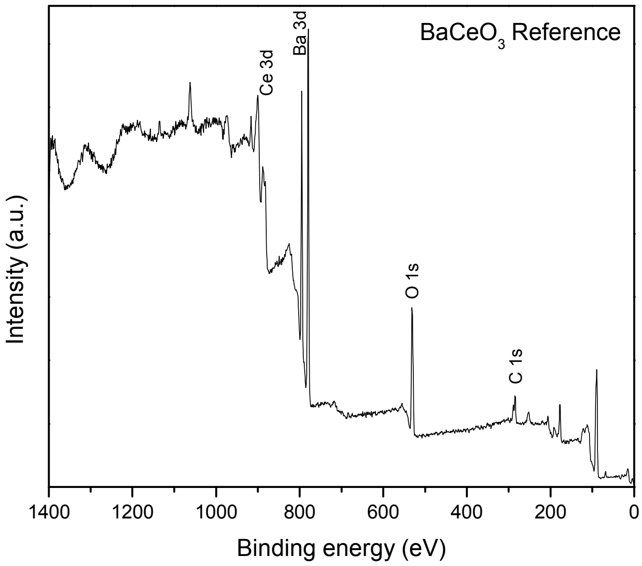

Figure S3: $BaCeO_3$ Survey Spectrum

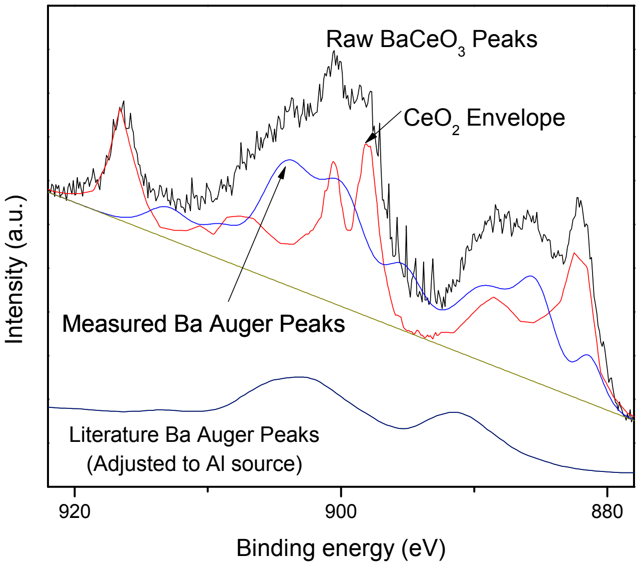

Figure S4: High resolution scan of CeO_2 peaks in $BaCeO_3$.

In Figure S4, the CeO_2 peak envelope from Figure S2 is subtracted from the raw peak data. This yields the peak shape attributed to the Ba auger peaks, which is confirmed to fit the expected peak energies of 901.7 eV and 888.9 eV calculated from the Ba auger peak data in Figure S5. Minor irregularity stems from different background types.

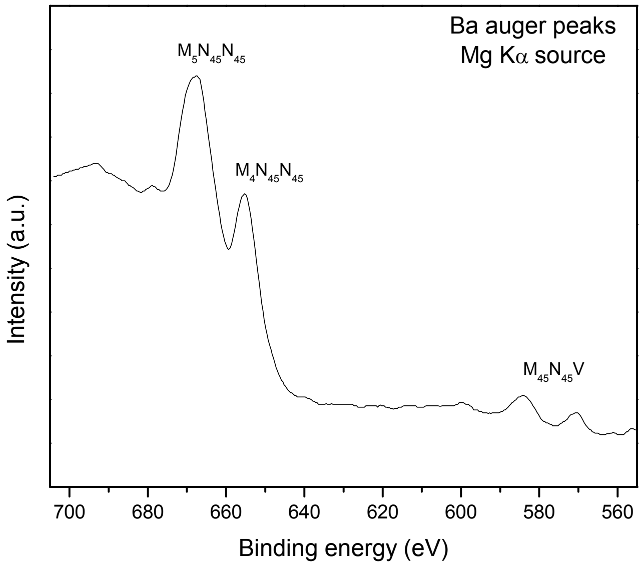

Figure S5: Measured Ba auger peaks using a Mg Kα source (from Ref. 1)

Reference spectra for Ba auger peaks are available from a Mg Kα x-ray source (1253.7 eV), shown in Figure S5. Auger peaks from an Al Kα x-ray source will be at 233 eV higher peak energies due to the higher energy source. Energy-adjusted Ba auger peaks from S5 are plotted in S4 for comparison to measured auger peaks, revealing good agreement in position and peak shape.

References:

1. C. D. Wagner and G. E. Muilenberg, *Handbook of x-ray photoelectron spectroscopy: a reference book of standard data for use in x-ray photoelectron spectroscopy*, Physical Electronics Division, Perkin-Elmer Corp., 1979.
2. W. C. Chueh, A. H. McDaniel, M. E. Grass, Y. Hao, N. Jabeen, Z. Liu, S. M. Haile, K. F. McCarty, H. Bluhm and F. El Gabaly, *Chemistry of Materials*, 2012, **24**, 1876-1882.
3. D. R. Mullins, S. H. Overbury and D. R. Huntley, *Surface Science*, 1998, **409**, 307-319.