Supporting Information

Influence of Non-stoichiometry on Proton Conductivity in Thin Film Yttrium-doped Barium Zirconate

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APT data analysis:

For atom probe tomography (APT), the normalized χ-square statistics was used to track the changes in the degree of solute segregation:

$$\mu = \sqrt{\frac{\chi^2}{N + \chi^2}}$$

where N is 50, which is the number of groups that the whole data is partitioned into; χ^2 is the deviation of an experimentally measured distribution from binominal distribution; and the calculated μ ranges from 0 to 1, with 0 to be a random distribution and 1 to be a complete association in the occurrence of the solute atoms.

The distribution of Y and Ba are shown in Figure S1a and b. A closer look at the concentration of each element suggests that at the dopant cluster area, or the black sphere region, the barium concentration significantly reduces, whereas the concentration of yttrium and zirconium increases, as shown in Figure S1c. Further nearest neighbor analysis is done on the spatially resolved atom mapping, and the distribution of normalized count for 10^{th} nearest neighbor (10NN) of Y-Y and Ba-Ba distance at the matrix and cluster region is summarized in Figure S1d-g. The Y-Y cluster distribution at matrix is almost the same as the random distribution from statistical simulation, with μ=0.0, indicating that Y is homogeneously distributed in the matrix. However, at cluster region, the distribution of Y cluster is slightly off the random distribution, with μ=0.17. This further demonstrates that yttrium cluster at this area. The similar finding for Ba-Ba distance distribution (μ=0.15) also suggests a barium deficiency of the same area.

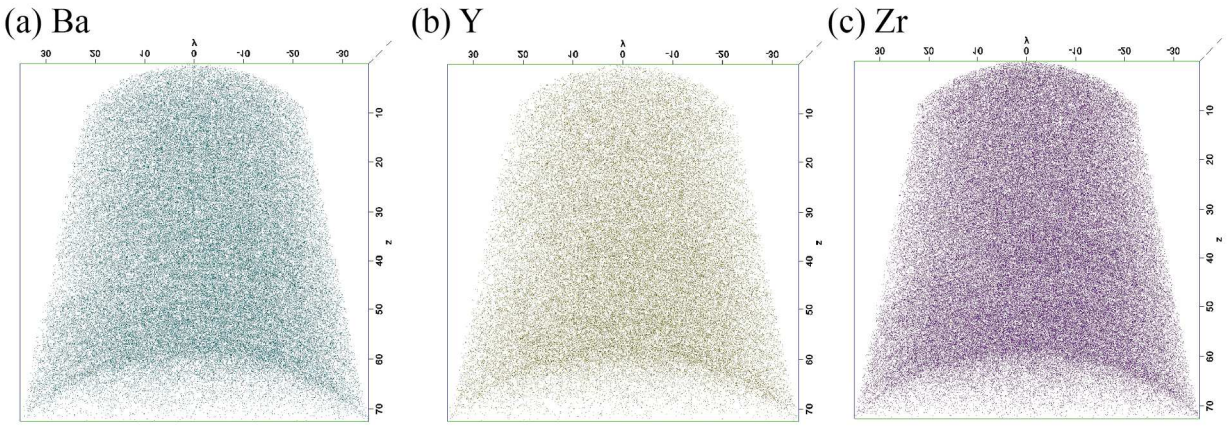

Figure S-1. The distribution of (a) Ba, (b) Y and (c) Zr in the virgin 20Y-BZO sample.

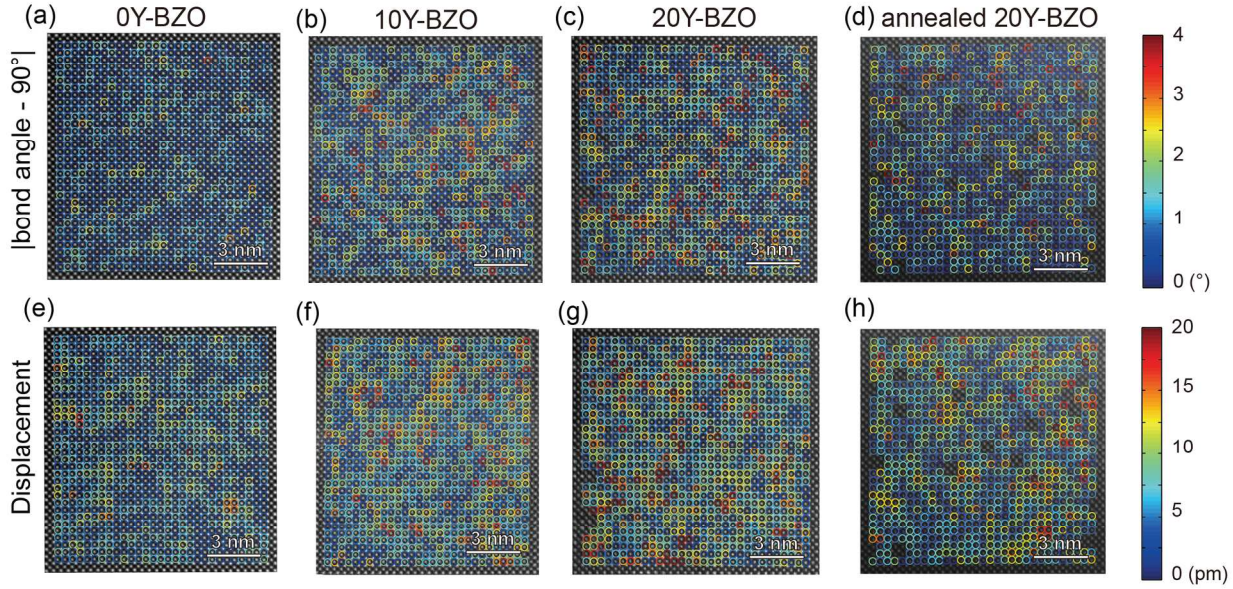

Figure S-2. Atomic resolution STEM imaging and data analysis that identify the bond angle deviation (a-d) and displacement (e-h) mapping for (a, e) 0Y-BZO samples, (b, f) 10Y-BZO samples, (c, g) 20Y-BZO samples and (d, h) annealed 20Y-BZO samples.