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Supplementary Information

Surface reactivity and cation non-stoichiometry in $BaZr_{1-x}Y_xO_{3-\delta}$ (x=0-0.2) exposed to CO_2 at elevated temperature

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Figure S1 shows HAADF STEM images of the surface of BZY20 after 1000 h of exposure. The images show a rough surface, with crystalline particles of 10-15 nm in diameter. However, energy dispersive X-ray spectroscopy shows no variations in chemical composition between the particles and the bulk, in this area.

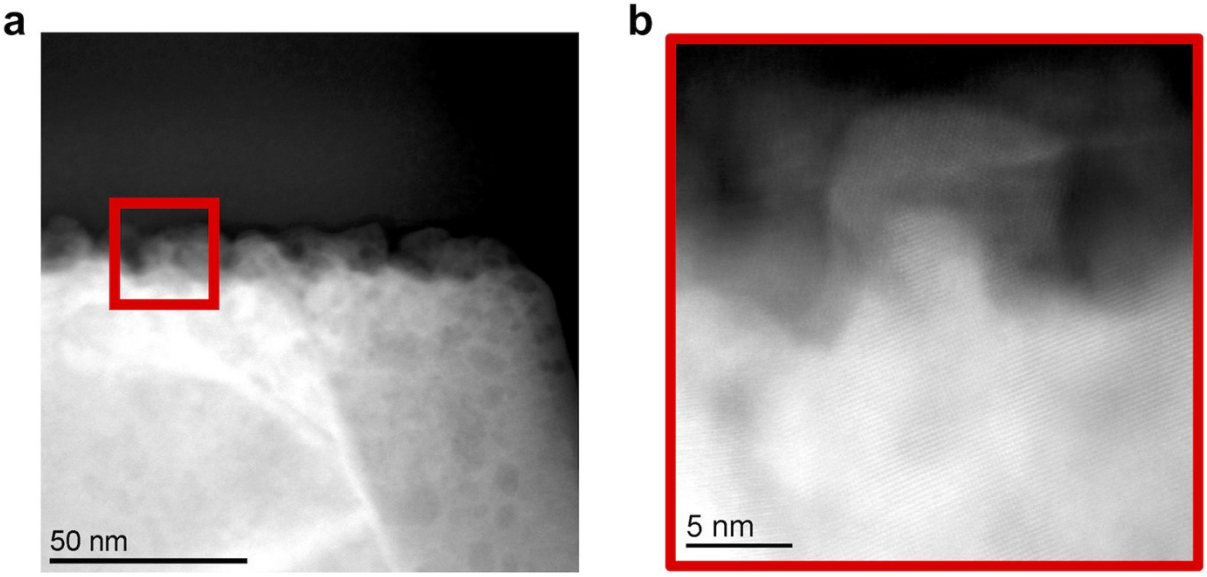

Figure S1: HAADF images of the particles on the surface of the film.

The chemical shift in the Ba peak within 300 nm of the surface was measured using electron energy loss spectroscopy (EELS). The results for Ba-M4,5 (3d) are shown in Figure S2 with the corresponding HAADF STEM image. The top 150 nm at the surface of the BZY sample shows a 1.5 eV shift of the Ba-$M_{4,5}$ peak shift to a higher energy loss. This shift indicates a change in oxidation state and chemical structure.

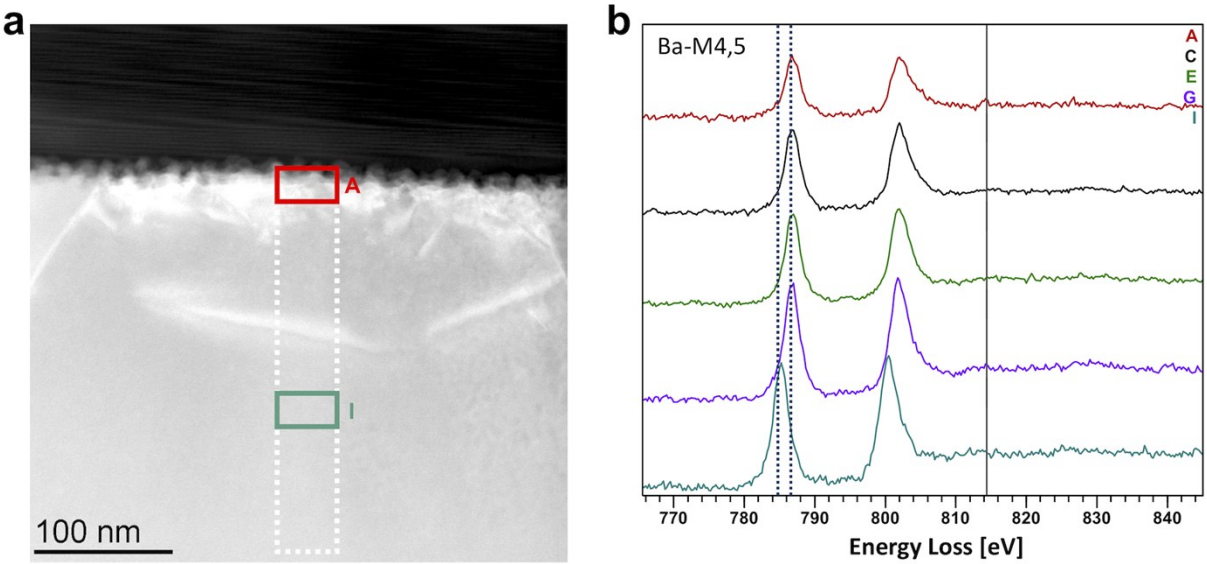

Figure S2: HAADF image of the surface of the films (a) and the corresponding EELS spectra (b).

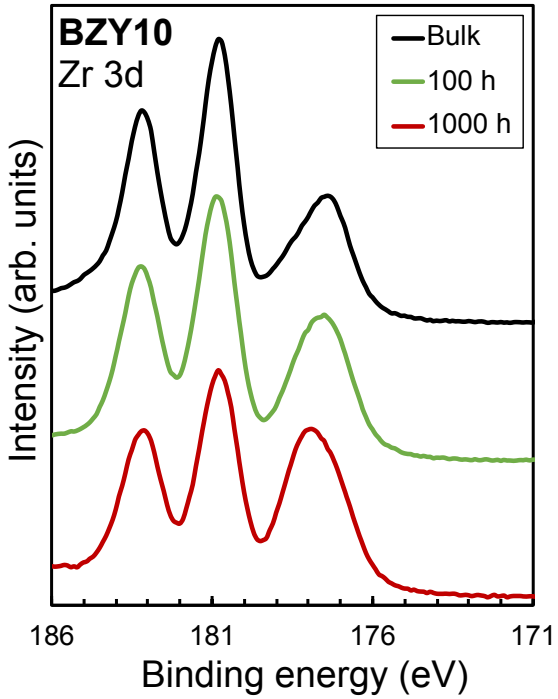

Figure S3: High resolution XPS Zr 3d spectra for the bulk (black), and the surface of the 100 h (green) and 1000 h (red) annealed BZY10 samples.

Surface segregation energies for defects were calculated as the total energy difference between charge neutral cells with the defects residing in the bulk and surface regions, respectively. Figure S4a shows the relaxed structure of $Y_{Ba}^{\bullet}$ on the BaO-terminated (0 0 1) surface, which

exhibited a segregation energy for -0.33 eV. The segregation energy for an additional $Y_{Zr}^{'}$ to the $Y_{Ba}^{\bullet}$ at the surface was -0.50 eV, resulting in an overall segregation energy of -0.82 eV for the associated defect pair from the bulk to the surface. The overall segregation energy for a cluster of $Y_{Ba}^{\bullet} + Y_{Zr}^{'} + v_{O}^{\bullet\bullet}$ was calculcated to -0.64 eV (Figure S4b). In this case, the cluster was most stable with $v_{O}^{\bullet\bullet}$ close to surface $Y_{Ba}^{\bullet}$ rather than as a $(Y_{Zr} - v_O - Y_{Zr})^{\times}$ cluster as was found for the bulk.

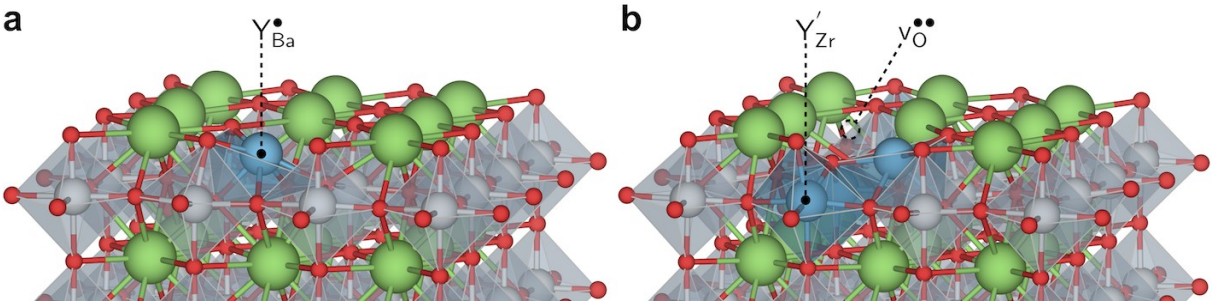

Figure S4: BaO-terminated (0 0 1) surface with segregated $Y_{Ba}^{\bullet}$ (a) and a cluster of two $Y_{Zr}^{'}$, one $Y_{Ba}^{\bullet}$ and one $v_{O}^{\bullet\bullet}$.