

Nanoscale Chemical Variations at Boundaries in a $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ – $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ Dual Phase Hydrogen Separation Membrane

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Hydrogen separation membranes could offer an energy efficient alternative to current energy intensive hydrogen separation techniques. The composite ceramic, $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ – $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCY-YDC) can be formed into a dense 50-50 wt.% structure by solid state reactive sintering [1] and has operated at high hydrogen fluxes [2]. Hydrogen molecules dissociate into H^+ ions and electrons, and the associated charges separately move through the percolating network of BCY and YDC, respectively, by two different diffusion mechanisms. The charges then reassociate on the opposite side of the membrane, forming pure hydrogen gas. The conductivity of BCY-YDC, like other electronic and ionic conducting oxides, is governed by the grain boundary (GB) resistivity within the material, which can exceed that of the bulk by over two orders of magnitude [3].

This reduction in conductivity at the GBs in conducting oxides is attributed to the formation of space-charge layers. In the case of BCY-YDC, phase boundaries are also important and are examined in this work. Understanding and quantitatively characterizing the boundaries in BCY-YDC is essential in further improving the GB conductivity and therefore the overall hydrogen flux, and the results can be extended to other composite conducting ceramics. Due to the challenges related to directly quantifying the chemical composition, particularly oxygen, across general three-dimensional boundaries, atom probe tomography (APT) is one of the only techniques available.

APT provides local 3-D chemical information with sub-nm spatial resolution and ppm chemical sensitivity. Therefore, the technique is particularly useful in identifying chemistry changes across GBs, and has been demonstrated in a number of relevant oxide materials [4-5]. Recent work has even quantified the 3-D space charge voltages around GBs of an ionic conducting oxide from APT compositional data [6].

In the following work, the chemical nature of both GBs and phase boundaries are explored using APT. In all cases, deviations in concentrations of cations, oxygen, and impurities around the boundary regions were studied. Transmission electron microscopy (TEM) images taken before and after APT analysis were used to create a more accurate APT reconstruction, allowing for the determination of key reconstruction parameters [7]. An example of a pre-APT TEM image is found in Figure 1 (a), in which a phase boundary is shown. APT analysis of the same tip, contained within the red box, was performed and segregation of O, Ce cations, and Al impurities are found at the phase boundary. In Figure 2, the composition through a region of interest around a YDC GB is examined, revealing Al and Si impurities.

References:

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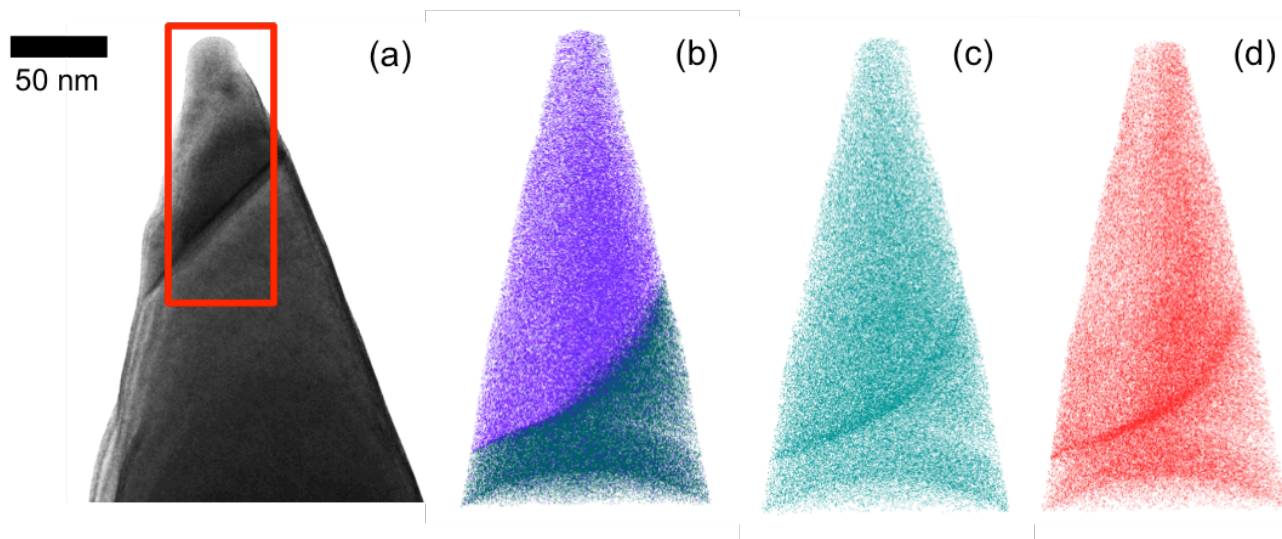


Figure 1. (a) TEM image of a BCY-YDC APT specimen with a phase boundary close to the apex of the specimen. (b) APT reconstruction of the same specimen as (a) with Y ions in purple and Ba in grey. (c) APT reconstruction of the O₂ species from the mass spectrum. (d) APT reconstruction of the Ce species from the mass spectrum. An enrichment of O and Ce at the phase boundary is clearly visible, although density differences at the interface could be contributing and will be discussed.

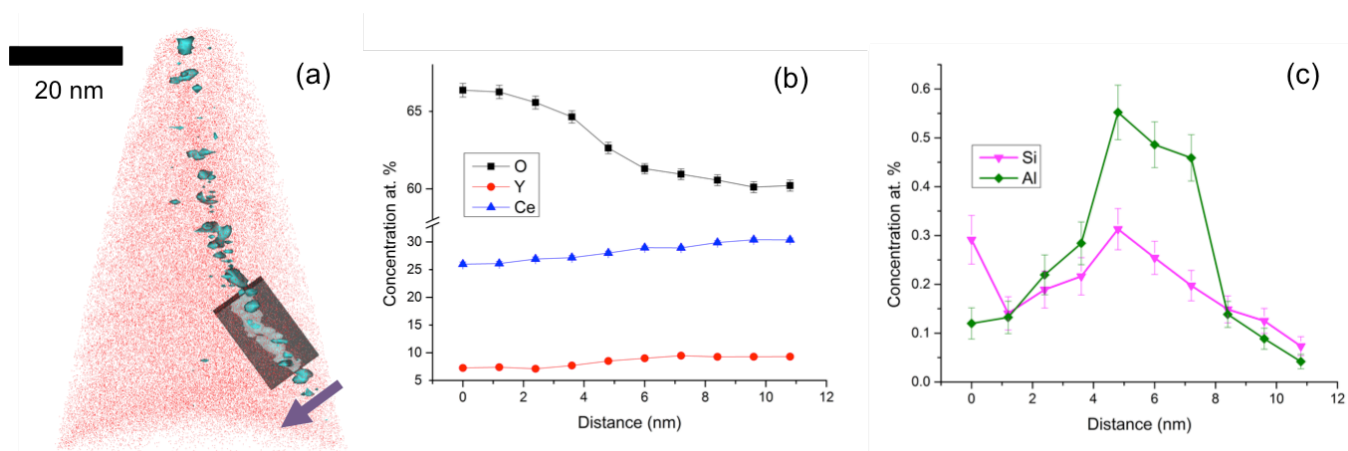


Figure 2. (a) APT reconstruction of a YDC APT specimen with a grain boundary near the apex. Ce ions in red, 0.27 at% Al isoconcentration surface in blue (b) Compositional analysis of O, Y and Ce through the region of interest of the grey box shown in (a) across the grain boundary. (c) Compositional analysis of Si and Al through the region of interest of the grey box shown in (a) across the grain boundary. Change in the apparent composition on either side of the boundary can be seen.