Atom Probe Tomography of Perovskite Materials
Fuel Cell Performance Optimization with LEAP®

Application Note #APT-09

Perovskite materials are an attractive area of study due to their success in high temperature superconductor applications as well as their use as proton conductors in the development of low cost, environmentally friendly solar cell and fuel cell materials. Atom probe tomography provides nanoscale characterization of perovskite materials, offering an unprecedented level of understanding about their chemistry, and advances in atom probe tomography systems make data collection easier than ever.

The grain boundary character in perovskites is critically important to conductive properties as they can serve as charge collection points which inhibits proton conduction in the material, causing performance in the device to suffer.

In the example at right, the atomic segregation of individual chemical species is shown for a YBaZrO perovskite. A grain boundary was identified by transmission electron microscopy (TEM) in Figure 1a. A post-LEAP-analysis TEM image is superimposed on the initial tip image in Figure 1a showing that the grain boundary has been collected in the analysis. In Figure 1b, the total collected volume is shown with a 2D concentration map of all ions showing the position of the grain boundary.

Figure 2 shows 2D concentration maps of each species in the grain boundary region. The grain boundary is enriched in oxygen concentration represented here is consistent with space-charge layer theory (SCL), but atom probe tomography shows this layer of charge separation to extend further than previously believed. The atomic variations shown at the grain boundary have important implications in the ability of this material to be a proton conductor, and ultimately influence the materials performance in a fuel cell. Atom probe tomography is critical to understanding the local composition variations that cause the variations in charge conduction at defect sites.

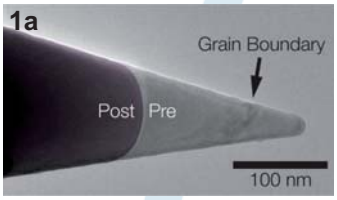
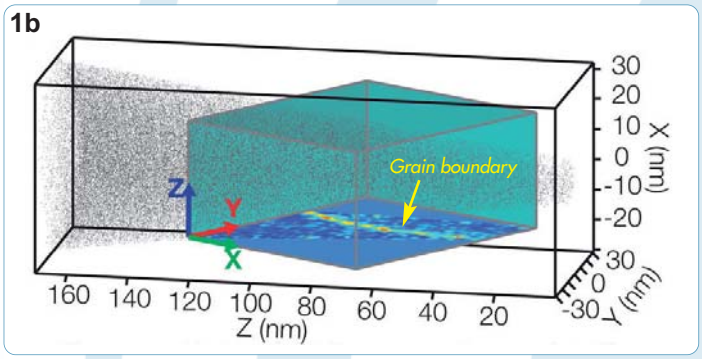


Figure 1:
(a) TEM image of an APT specimen before and after data collection, showing the presence of a grain boundary.
b) 2D contour plot superimposed on Si ion map showing the position of the grain boundary in the APT data.



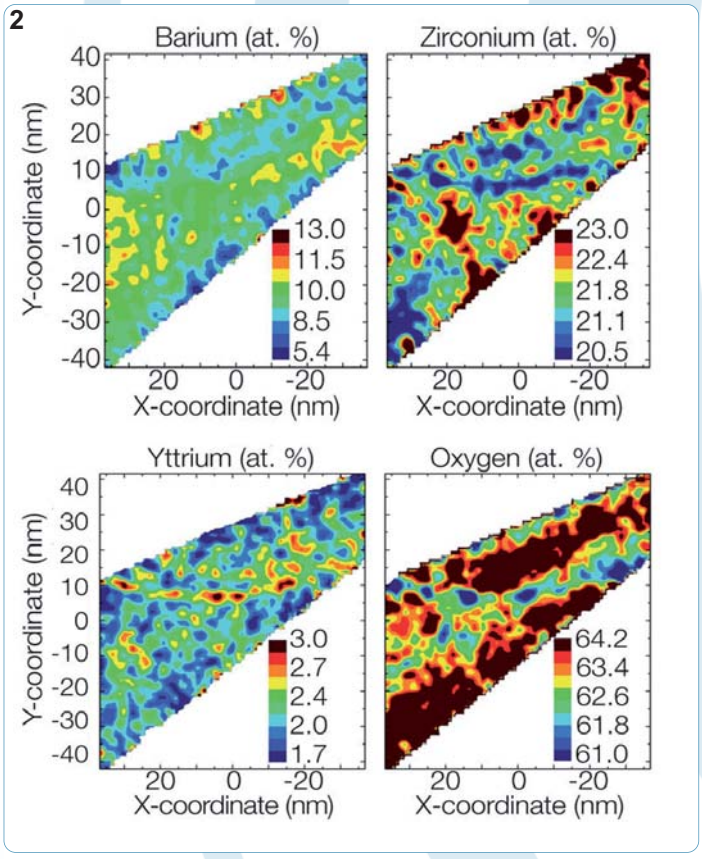


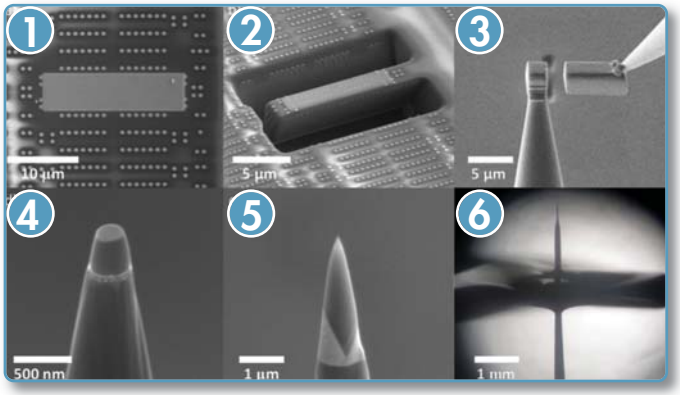
Figure 2:
2D concentration plots of Ba, Zr (top) and Y and O (lower) showing Zr depletion and Y enrichment at the grain boundary.

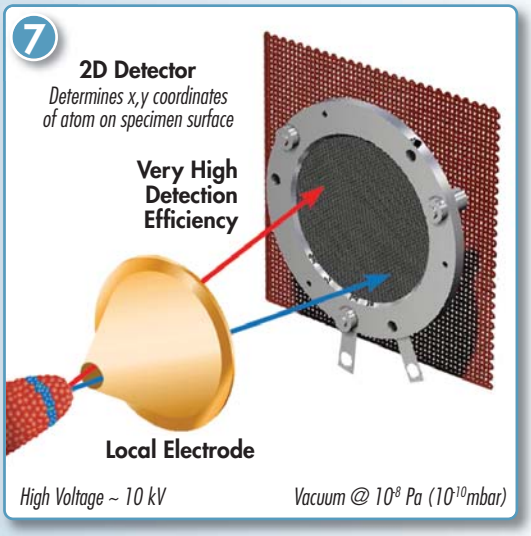
Clark, D.R., Zhu, H., Diercks, D.R., Ricote, S., Kee, R.J., Almansoori, A., Gorman, B.P., O'Hayre, R.P., 2016. Probing Grain-Boundary Chemistry and Electronic Structure in Proton-Conducting Oxides by Atom Probe Tomography. Nano Lett. doi:10.1021/acs.nanolett.6b02918wha

Three Steps to 3D Nanoscale Analysis
An Introduction to Atom Probe Tomography

Step 1: Specimen Preparation

An atom probe specimen usually has a nanoscale region of interest (ROI) requiring both 3D compositional imaging and analysis. The sample is formed into a needle shape containing the ROI. Common APT specimen preparation methods using electropolishing or a Focused Ion Beam system (FIB) are very similar to TEM methods except instead of forming a thin sheet, a needle shaped sample is desired. At the right, standard FIB liftout and mounting of a specimen (figures 1 through 3) and then sharpening the sample with the ROI left at the very apex (4 and 5). In 6, a wire geometry sample is being electropolished.





Step 2: Data Collection

An atom probe produces images by field evaporating atoms from a needle-shaped specimen and projecting the resultant ions onto a detector 7.

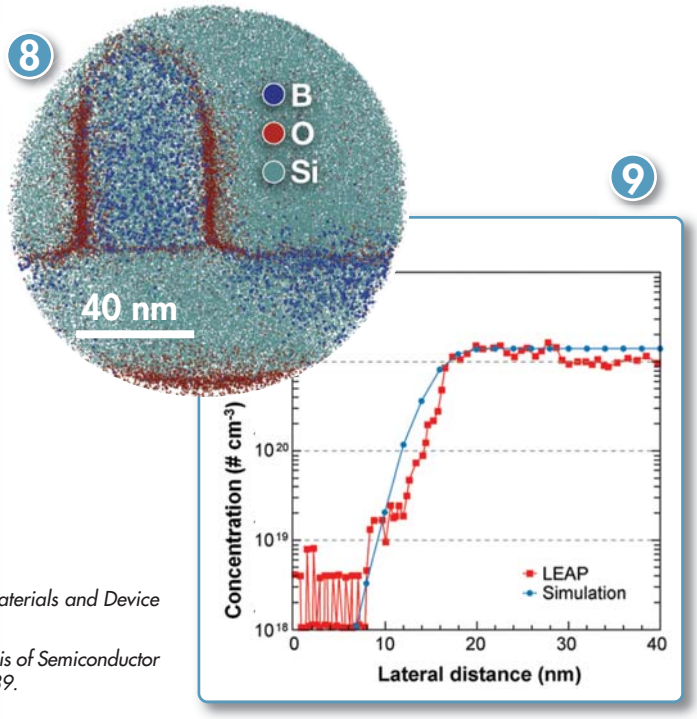
A high magnification results from the ~ 80nm tip being projected onto an 80mm detector resulting in a magnification of approximately 10^6.

An atom probe identifies atoms by their mass-to-charge-state ratio *(m/n)* using time-of-flight mass spectrometry. Charge state, *n*, is typically 1 to 3.

The specimen is held at approximately 50K to reduce surface diffusion during the experiment. The high electric field results in 100% ionization and the high speed detector is capable of measuring up to 80% of the collected ions, independent of ion mass.

Step 3: Data Visualization and Analysis

Examples of data output are illustrated by a slice of a 3D atom map of a transistor[†] 8, and a dopant composition profile[‡] 9. The image shows the positions of individual atoms (oxygen is red and boron is blue) in the transistor with subnanometer resolution. From the reconstructed data set many types of useful analyses are possible. These include 3D visualization, 2D atom mapping 8, 1D depth profiling and line scanning 9, as well as mass spectra and compositional analysis from user-selected volumes.



[†] *Lauhon, L. J. et al, MRS Bulletin "Atom Probe Tomography of Semiconductor Materials and Device Structures" 34(10) (2009) 738.*

[‡] *Moore, J. S.; Jones, K. S.; Kennel, H.; Corcoran, S., Ultramicroscopy "3-D Analysis of Semiconductor Dopant Distributions in a Patterned Structure using LEAP" (2008), 108, 536–539.*

CAMECA SCIENCE & METROLOGY SOLUTIONS | nu | AMETEK MATERIALS ANALYSIS DIVISION

CAMECA International Headquarters
29 quai des Grésillons
92622 Gennevilliers, France
cameca.info@ametek.com
www.cameca.com

Atom Probe Technology Center
5500 Nobel Drive
WI-53711 Madison, USA
cameca.leap@ametek.com
www.atomprobe.com