

Utilizing Atom Probe Tomography for 3-D Quantification of Point Defects

Brian P. Gorman¹, George Burton¹, David R. Diercks¹

¹ Colorado Center for Advanced Ceramics, Colorado School of Mines, Golden, CO, USA

Many properties of oxides are dependent upon non-stoichiometry and associated charge compensations. Properties such as electronic and ionic transport, dielectric constant, and electrical breakdown are dependent upon the accumulation of point defects at internal interfaces such as grain boundaries and heterojunctions. Quantification of these point defect accumulations using techniques such as EDS and EELS has been difficult previously, either due to light element sensitivity, detectability limits, or the 3-D nature of the internal interfaces.

Recent work has shown that Atom Probe Tomography (APT) has the requisite counting statistics, 3-dimensionality, detectability limits, and spatial resolution to quantify point defect accumulations at grain boundaries [1-3] and heterojunctions [4]. Utilizing the 3-D atom by atom nature of APT data has also enabled the conversion of analytical characterization data directly into space charge voltages and band alignments, ultimately enabling the direct relationship between materials characterization and materials or device properties.

The ability of APT to quantify point defect distributions in 3-D has limitations that are dependent upon the type of defect. Some examples include:

1. Individual vacancies on either oxygen or metal cation sites (V_o^{**} or V_m'). Both types of vacancies have been quantified with APT at grain boundaries (Figure 1) and at heterojunctions. Quantification of these are heavily dependent upon the detection efficiency of the APT experiment that can vary between 15 and 60% of all atoms based primarily upon the laser energy and resulting temperature rise in the specimen. Quantification is also dependent upon the volume being sampled, i.e., are the atomic counting statistics in the volume sufficient to be statistically accurate?
2. Interstitial oxygen or metal cations (O_i'' or M_i^*). Similar to vacancies, a change in the number density of oxygen or cations can be observed but is limited to the counting statistics of the volume being analyzed. APT currently does not have the spatial resolution or 100% detection efficiency necessary to identify a single interstitial atom in 3-D.
3. Substitutional cations and defect pairs (M_N'). As long as the cations are distinguishable in the mass spectrum (have different mass to charge ratios), then substitutional defects are able to be distinguished in a specific volume. As shown previously, substitutional defects coupled with vacancies are common ordered defect pairs and these are quantifiable using APT [4].
4. Schottky defects ($V_o^{**} + V_m''$) can be quantified using APT, as these defect pairs result in a change in atomic density. These defects are normally present only at internal or external interfaces or they tend to diffuse until they are nulled.
5. Frenkel pairs on either the oxygen or metal cation sites ($V_o^{**} + O_i''$). These defect pairs do not result in a change in atomic density and are only dependent upon site occupancies. Similar to interstitials, APT does not have the spatial resolution or detection efficiency necessary to identify individual Frenkel pairs. Such analyses will have to wait for Atomic Scale Tomography, of which APT may play a part.

Ultimately, the combination of APT's 3-D spatial and chemical resolution combined with analytical techniques such as EELS that allows for cation valence and free carrier energy levels to be determined will be the most complete solution to defect chemistry quantification.

References:

- [1] D. R. Diercks, *et.al.*, Journal of Materials Chemistry A **4** (2016), p. 5167.
- [2] D. R. Clark, *et.al.*, Nanoletters **16** (2016), p. 6924.
- [3] R. Kirchhofer, *et.al.*, Journal of the American Ceramic Society **97** (2014), p. 2677.
- [4] A. Stokes, *et.al.*, Acta Materiala, **102** (2016), p.32.

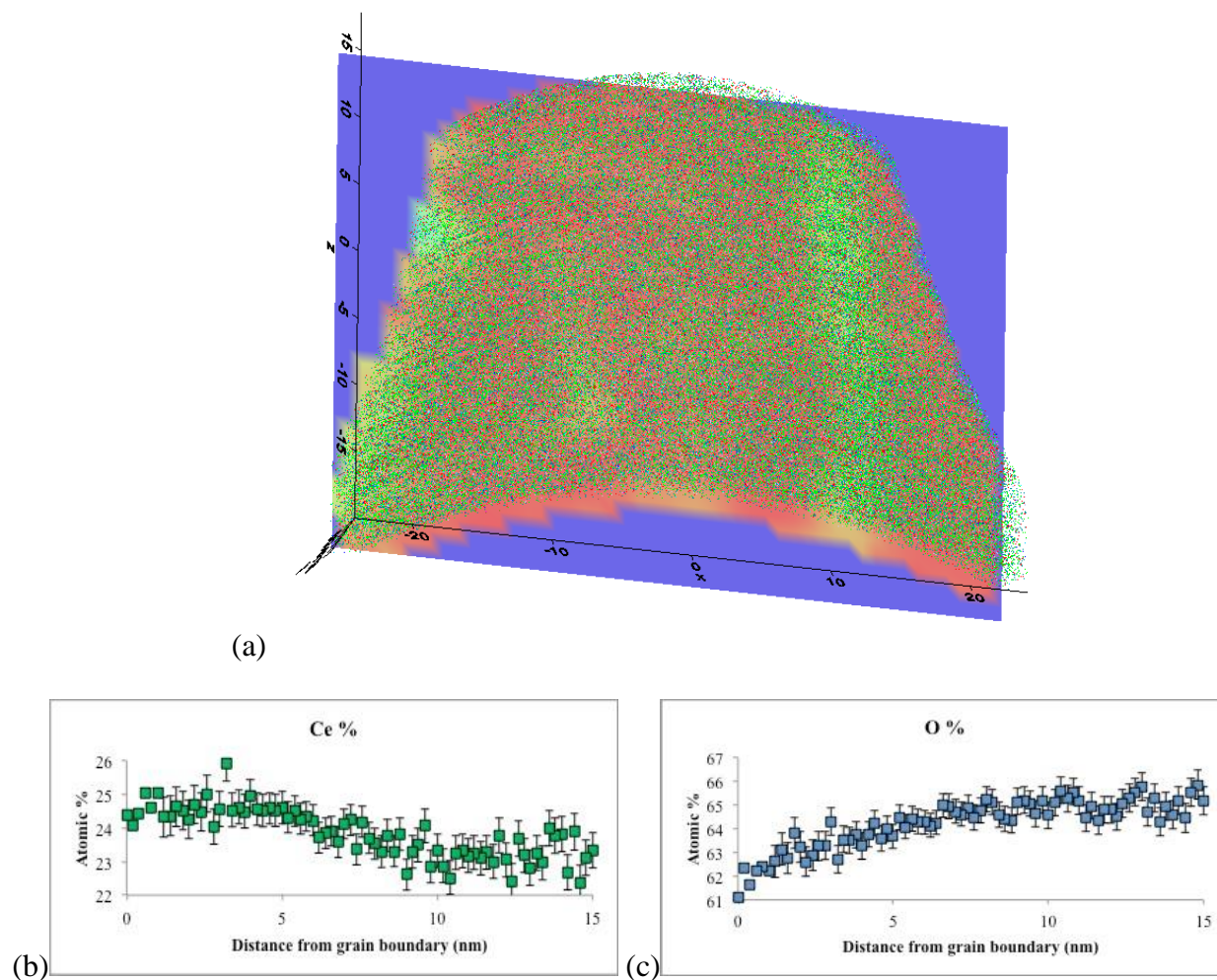


Figure 1. (a) Slice of an APT reconstruction (doped CeO₂) and a 2-D projection of the Oxygen concentration illustrating the location of a grain boundary on the right side. (b) Ce and (c) O concentrations as determined from a proximity histogram from the center of the grain boundary. Oxygen vacancies and cations tend to accumulate at the grain boundary, resulting in a net charge and voltage.