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# **Supplementary Information**

# Three-Dimensional Quantification of Composition and Electrostatic Potential at Individual Grain Boundaries in Doped Ceria

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# **Atom Probe Specimen Preparation**

The methodology used for targeting grain boundaries in preparing the atom probe specimens is depicted in the secondary electron images of Figure S1.



**Figure S1.** a) Grain boundaries are identified with SEM imaging and marked with Pt deposition. b) Cylindrical specimens are isolated and manipulated to a preformed microtip. c) Once mounted to the pre-formed microtip, the specimen is sharpened to a ~50 nm diameter specimen.

# **Isotopic Overlaps**

As shown in the mass spectrum in Figure S2, the peaks are clearly identifiable and well-resolved except for the overlap between <sup>142</sup>Ce and <sup>142</sup>Nd. These isotopes comprise about 11at% of the Ce and 27at% of the Nd, based on the natural isotopic abundances. This common mass manifests itself in overlaps of  $^{142}Ce^{***}$  and  $^{142}Nd^{***},\ ^{142}Ce^{16}O^{**}$  and  $^{142}Nd^{16}O^{**},$  and  $^{142}Ce^{16}O^{*}$ and <sup>142</sup>Nd<sup>16</sup>O<sup>+</sup>. Since the other isotopes of Ce and Nd do not have peak overlaps, the isotopic ratios of those can be used to determine the relative contributions of Ce and Nd to the overlapped peaks. This allows good retrieval of the composition over the sampled region but the spatial information associated with the overlapped peaks is ambiguous since the identities of particular ions within the overlapped peak cannot be definitively assigned. To reduce the impact of the spatial uncertainty, smaller sampling volumes are used such that the mass spectra from each of these are individually decomposed for composition information. Therefore, the loss of spatial information is greatly mitigated.



Figure S2. Mass spectrum from atom probe analysis of an NDC10 ( $Ce_{0.9}Nd_{0.1}O_{2.6}$ ) specimen.

# Composition determination using proximity histograms

Proximity histograms are useful for extracting the cumulative average 1-D composition information away from a curved or uneven surface. This provides some additional insight into the nature of the grain boundaries. After first defining a surface of reference composition, the atomic composition normal to each face of this surface is calculated and displayed cumulatively as a concentration versus distance graph (see Figure S3 and S4). Note that the profiles in those figures are the cumulative concentrations in both directions away from the GB centers. These values are also summarized in Table S1 and S2. The proximity histogram algorithms are available as part of the IVAS 3.6.4 analysis software.



Figure S3. Concentration of each species in at% as a function of distance from the center of the grain boundary for an NDC10 specimen. These concentrations are determined by defining a grain boundary plane and taking the average concentration as a function of distance from the local normal to the plane in both directions.

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	NDC10	O at%	Ce at%	Nd at%	Zr at %	Al at%	Si at%
	Nominal	66.1	30.5	3.4	0	0	0
	Overall	66.8 ±0.7	29.0 ±0.7	3.7 ±0.3	0.3 ±0.1	0.06 ±0.04	0.08 ±0.06
	Grain boundary	61.1 ±1.4	30.5 ±1.3	7.4 ±0.7	0.4 ±0.2	0.4 ±0.2	0.7 ±0.2

#### Table S1. The composition of NDC10 as determined by APT.



Figure S4. Concentration of each species in at% as a function of distance from the center of the grain boundary for an NDC30 specimen. These concentrations are determined by defining a grain boundary plane and taking the average concentration as a function of distance from the local normal to the plane in both directions.

NDC30	O at%	Ce at%	Nd at%	Zr at %	Al at%	Si at%
Nominal	64.9	24.6	10.5	0	0	0
Overall	65.2 ±0.7	23.4 ±0.7	10.8 ±0.4	0.4 ±0.1	0.08 ±0.06	0.2 ±0.1
Grain boundary	62.2 ±1.3	23.9 ±1.2	12.9 ±0.9	0.4 ±0.2	0.4 ±0.2	0.4 ±0.2

#### Table S2. The composition of NDC30 as determined by APT.

#### **Electrical conductivity measurements**

A standard technique for measuring solid state ion conductors, electrochemical impedance spectroscopy (EIS) allows the bulk and GB contributions to the conductivity to be determined. This is primarily due to the difference in frequency response of charges in the GB regions compared with the bulk of the grains.

Following the method of Haile *et al.*,<sup>1</sup> equivalent circuit models are generated from the Nyquist plots of the EIS data. The resistances, R, and constants Y and n are taken directly from these electrical data with the characteristic frequencies,  $\omega_0$ , given by  $\frac{1}{Y \cdot R} \left(\frac{1}{n}\right)$ . The capacitances, C, are then given by  $Y^{\left(\frac{1}{n}\right)}$ .  $R^{\left(\frac{1}{n}-1\right)}$ . The conductivities,  $\sigma$ , of the two equivalent circuit components are given by  $\frac{L}{A \cdot R}$  where L is the thickness of the specimen and A is the cross-sectional area. These values are obtained from the dimensions of the pellets as measured using callipers. For the case where  $\sigma_{\text{bulk}} \ge \sigma_{\text{gb}}$  and the grain boundary thickness, g, is much less than the grain size, G, as is the case here, the conductivity from the higher frequency arc can be taken as  $\sigma_{\text{bulk}}$ . Assuming the dielectric constants of the bulk and the GB are the same, the specific GB conductivity is calculated:

$$\sigma_{spgb} = \frac{\tau_{bulk}}{\tau_{gb}} \sigma_{bulk} \tag{S1}$$

where  $\tau = RC$ .

Alternatively, we can use the grain boundary width to determine the specific grain boundary conductivity:

$$s_{spgb} = \frac{L}{AR_{gb}} \frac{g}{G}$$
 (S2)

The grain sizes as measured from SEM images are 11.4  $\mu m$  for NDC10 and 7.4  $\mu m$  for NDC30. The typical structural GB width as measured by TEM is about 1 nm. The GB "chemical widths" as measured from the APT composition data are 5.7 nm for NDC10 and 3.5 nm for NDC30.

Results of the bulk and GB conductivities for NDC10 and NDC30, extracted using Equation S2 with the chemical GB width



Figure S5. Electrochemical impedance spectroscopy measurements separating out the bulk and grain boundary contributions to the total conductivities for NDC10 and NDC30. The overall NDC10 conductivity is dominated by the low grain boundary conductivity; whereas the NDC30 has similar contributions from the grains and grain boundaries.

and the brick layer model approach,<sup>1-3</sup> are given in Figure S5. The GB conductivity is as much as 2 orders of magnitude lower than the bulk grain conductivity for NDC10, depending on the temperature, but is actually slightly higher than the bulk conductivity for NDC30.

#### Determination of grain boundary potential

The determination of the GB potential from the conductivity data requires the assumption of a model to describe the nature of the composition at and in the vicinity of the GB. The most commonly employed models are the Mott-Schottky (M-S) and Gouy-Chapman (G-C) models. Both of these models assume there are no interactions between defects and, therefore, their validities in accurately describing the GB behaviour are limited to dilute defect concentrations. While models incorporating defect-defect interactions are starting to be developed,<sup>4,5</sup> the best methods of incorporating them within the present data at this point are not clear and are an area of future effort.

#### Mott-Schottky

In the M-S situation, it is assumed that there is a positively charged GB core where there is an accumulation of oxygen vacancies surrounded by a region where oxygen vacancies are depleted and the dopant concentration remains constant from the bulk to the GB. While the compositional distribution observed in this work is clearly not consistent with the M-S approximation, the calculation of the potential using this method does allow for comparison of our results to those of others. Most of the published results in which a GB potential has been calculated have used such an approximation.<sup>6-10</sup>

In the M-S approximation, the ratios of the grain and specific GB conductivities can then be used to numerically determine the potential barrier at the GBs from the following relation:<sup>11</sup>

$$\frac{\sigma_{bulk}}{\sigma_{gb}} = \frac{\exp(\frac{1}{k_B T})}{(\frac{2ze\Delta\varphi}{k_B T})}$$
(S3)

where  $\sigma_{bulk}$  is the grain conductivity,  $\sigma_{gb}$  is the grain boundary conductivity, z is the charge of the mobile species, e is the elementary electrical charge,  $\Delta \phi$  is the Schottky barrier height,  $k_B$  is Boltzmann's constant, and T is the temperature.

The potentials as calculated using the specific GB conductivities given by each of the above methods are shown in Table S3. A comparison of our values with those found in the literature shows that they are within the range of expected values and the trends determined here follow similar dopant concentration dependence on the space-charge voltage, with the higher doping level leading to a lower GB potential.<sup>6-10</sup>

Table S3. The grain boundary potentials of NDC10 and NDC30 at 400  $^\circ C$  as calculated by three different methods using an M-S approximation.

Potentials (V)	NDC10	NDC30	
Equation S1	0.29 ±0.02	0.21 ±0.02	
Equation S2 structural width	0.47 ±0.03	0.30 ±0.03	
Equation S2 chemical width	0.41 ±0.03	0.26 ±0.03	

## Gouy-Chapman

In the G-C approximation, there is also a positively charged GB core where there is an accumulation of oxygen vacancies. However, the acceptor dopant is assumed to be mobile and therefore also accumulates near the GB. The concentration of the acceptor exhibits an exponential decay away from the GB; whereas oxygen vacancies exhibit an exponential depletion approaching the GB. Compared to the M-S model, the G-C model better reflects reality as it captures the accumulation of dopant species near the GB. However, our experimental work does not show the corresponding predicted oxygen vacancy depletion. Nevertheless, the profile of acceptor dopants may be used to estimate the GB potentials using this approximation:<sup>12</sup>

$$\frac{C(x)}{C_{bulk}} = \left(\frac{1 + \Theta \exp(-X/\lambda)}{1 - \Theta \exp(-X/\lambda)}\right)^{2Z}$$
(S4)

where  $c_{\text{bulk}}$  is the concentration of the acceptors in the bulk of the material, c(x) is the concentration of the acceptors as a function of distance from the GB, x is the distance from the GB,  $\lambda$  is the screening (or Debye) length, and  $\Theta$  is the profile parameter.

$$\Theta = tanh\left(\frac{ze\Delta\phi}{4k_bT}\right) \tag{S5}$$

where these variables are defined the same as for eqn S3.

By adjusting the screening length, the data may be fit empirically as shown in Figure S6. In this case, the experimental  $Nd'_{Ce}$  data from Figures S3 and S4 are used along with an estimated concentration profile of  $Ce'_{Ce}$  as is discussed more in the next section.



**Figure S6.** Experimental 1-D distribution of acceptor ( $Nd'_{ce}$  and  $Ce'_{ce}$ ) concentration near the grain boundary in NDC10 (top) and NDC30 (bottom). The exponential fits using the Gouy-Chapman approximation are also displayed.

In addition to the empirical determination, the Debye length may be numerically calculated:

$$\lambda = \sqrt{\left(\frac{\epsilon_0 \epsilon_r k_b T}{\sum (ze)^2 C_{bulk}}\right)}$$
(S6)

where  $\epsilon_0$  is the vacuum dielectric constant and  $\epsilon_r$  is the relative dielectric constant. The results of the experimental fits and the calculations are shown in Table S4. The values used for  $\epsilon_r$  are 246 for NDC10 and 79.9 for NDC30.<sup>13</sup>

 Table S4.
 The grain boundary potentials and Debye lengths of NDC10 and NDC30 using a G-C approximation.

	NDC10	NDC30
Potential (V)	0.21	0.04
Debye length (nm) empirical fit	5.1	2.3
Debye length (nm) calculated	0.9	0.3

The G-C calculated potentials show the same trend as the M-S calculations in that the higher dopant concentration results in a lower potential, but the overall values for both doping concentrations are lower than the corresponding M-S derived values. The Debye length determined from the empirical fit is also substantially larger than the calculated values for both cases. This provides further evidence of the importance of accounting for defect-defect interactions.

## Solving the 3-D Poisson equation

In order to solve the 3-D Poisson equation, the 3-D charge distribution is required. The data for this are taken directly from the atom distributions within the APT reconstructions. In the present case, one limitation of this is that the valence state of species is not captured in the atom probe data and, as discussed in the main text, a significant amount of Ce3+ is expected near the GB. So, from the APT data alone the assignment of the charge state for the Ce species is ambiguous. Therefore, the three-dimensional distribution of  $Ce'_{Ce}$  must be estimated and factored in to the charge distribution. Additionally, while the APT data capture the local oxygen concentrations, including vacancies, an incremental  $V_0^{\bullet\bullet}$  term is also included in this estimate to account for the uncertainty in the oxygen measurements as given in Tables S1 and S2. This  $V_0^{\bullet\bullet}$  term was not allowed to exceed the uncertainty values given in those tables. Again, the following approximation is used only to determine the three-dimensional distribution of Ce3+ and provide a term which accounts for the uncertainty in the threedimensional  $V_0^{\bullet\bullet}$  concentration; all other charge distribution data come directly from the APT results.

Assuming the  $Ce'_{Ce}$  and  $V_{O}^{\bullet\bullet}$  charge carriers are ideal and dilute (which is incorrect but is used here as a great simplification), the electrochemical potentials of defects can be represented as

$$\tilde{\mu}_k = \mu_k^o + RT ln[X_k] + z_k F \phi \tag{S7}$$



Figure S7. The charge density around a) an NDC10 grain boundary and b) an NDC30 grain boundary. The grain boundaries are centered around x=0 and the units are C/m<sup>3</sup>. These data exhibit how locally inhomogeneous the charge densities are along the grain boundaries.

equation,

where  $[X_k]$ ,  $\mu_k^o$ , and  $z_k$  are the molar concentrations, standard chemical potentials, and charges of the charge carriers, respectively.  $\phi$  is the electrostatic potential, T is the temperature, R is the universal gas constant, and F is the Faraday constant. These charge carriers within the spacecharge region are further assumed to be spatially equilibrated with those in the grain interior, so,

$$\tilde{\mu}_k(\boldsymbol{x}) = \tilde{\mu}_k^{\infty} \tag{S8}$$

2

4

where  $\tilde{\mu}_k^{\infty}$  are the electrochemical potentials of the charge carriers in the grain interior. Therefore, the concentration distribution of these charge carriers can be expressed as,

$$[X_k](\boldsymbol{x}) = [X_k^{\infty}]exp\left(-\frac{z_kF\phi}{RT}\right)$$
(S9)

where  $\phi = \phi(x) - \phi^\infty$  is the local electrostatic potential difference. The net local charge density contributed from all the species can be expressed as,

$$\rho = \rho_{other} + \sum_{k} z_k F[X_k] \tag{S10}$$

where  $ho_{other}$  is the local charge density taken from the APT data due to all of the species other than  $Ce'_{Ce}$  and an uncertainty value in the  $V_0^{\bullet\bullet}$  charge carriers, which make up  $[X_k]$ . Considering  $z_{V_0^{\bullet\bullet}} = 2$ , and  $z_{Ce'_{Ce}} = -1$ , the net local charge density can be rewritten as,

 $\rho = \rho_{other} + F(2[V_0^{\bullet\bullet}] - [Ce'_{Ce}]).$ (S11) The local net charge density  $\rho$  (shown in Figures S7 and S8) is related to the electric potential distribution  $\phi$  by the Poisson

$$\nabla \cdot \epsilon_0 \epsilon_r \nabla \phi = -\rho \tag{S12}$$

The values used for  $\epsilon_r$  are 246 for NDC10 and 79.9 for NDC30.  $^{\rm 13}$ The Boltzmann-Poisson equation resulting from Equations S9, S10, S11, and S12 can be solved to obtain the distribution of the electric potential  $\phi$ , and concentrations of  $[Ce'_{Ce}]$  around the grain-boundary regions.

While the preceding assumptions of the form of the electrochemical potential are known to be incorrect for these non-dilute cases, the resulting values for the relative fraction of Ce<sup>3+</sup>/Ce<sup>4+</sup> and its distribution appear consistent with previous measurements of this on similar materials using EELS.14-16 This suggests that these values are sufficiently acceptable for use in the determination of the 3-D GB potentials. Better methods of approximating or experimentally measuring the charge state distributions of the cerium ions is an area for future effort.

Because uncertainties in the exact GB potentials and the three-dimensional Ce charge state distributions necessitate





6

a 1E+9

8E+8

6E+8

4E+8

2E+8

0E+0

-2E+8

-8E+8

-1E+9

-6

-4

-2

0

Distance (nm)

-2E+8 -4E+8 -4E+8 -6E+8

Density(C/m<sup>3</sup>)

the main text.

some assumptions, we cannot say that these are the exactly correct, quantitative 3-D distributions of the GB potentials. However, the overall consistency of the results – peak GB potentials within the expected ranges, Ce charge state distributions consistent with measurements of others, and overall charge nearly neutral over the analysed volume suggest that these are reasonably accurate estimates. The results highlight some salient differences in the GBs between the two doping conditions. They also point to areas for further improvement both in experimental measurements and modelling as discussed in the "Additional Remarks" section of

#### Asymmetry in the potentials across the GBs

As mentioned in the main text, the potentials are observed to be asymmetric on either side of the GBs. This is significant because the most basic assumption in space-charge calculations is that of symmetry on both sides of the GB. The most likely cause of this asymmetry is different GB crystallographic faces and their surface energies. Here the experimental asymmetries are explored in a little more detail.

It is found that the 1-D projections of the potential are fit well by exponential functions on both sides of the GBs. Figure S9 shows the overall 1-D potential curves and highlights the regions which display exponential behavior.

The corresponding exponential fits for NDC10 indicate that on one side of the boundary the decay width of the potential (5.3 nm) is twice as great as the other side of the boundary (2.6 nm). Those for NDC30 also indicate double the difference in the width of the potential on either side of the GB (1.8 nm vs. 3.6 nm). These suggest that the design of polycrystalline materials favouring GBs having particular crystal faces may be able to mitigate some bottlenecks in ionic transport across the GBs.

### **Comparison to simulation**

Since there are limited experimental results, and none in 3-D, with which to relate the present findings, comparisons to simulated GB segregation are explored. The GB chemistry of Gd-doped ceria has recently been modeled using hybrid Monte Carlo–molecular dynamics simulations.<sup>4</sup> The qualitative behavior that their simulation exhibits is largely similar to that observed experimentally from the atom probe results for the Nd-doped ceria. The dopant concentration increased and the oxygen content decreased at the GB. Interestingly, the Ce content remained nearly constant or showed a slight increase at the GBs in the experimental results, whereas a decrease was seen in the simulations. The model, however, does not appear to take into account valence changes of Ce at the GB, which could account for this discrepancy.

Comparing the results quantitatively, the measured segregation from atom probe was somewhat less than the simulations for a given dopant level. However, the authors note that due to the small volume used in the simulations the dopant concentration in the bulk drops well below the initial average concentration, implying that the simulated profiles are likely characteristic of lower dopant concentrations than those indicated. Or viewed another way, the grain size of 7 nm used in the simulations creates a much greater GB volume than the specimens studied here. If the simulated dopant/Ce values for the bulk material are adjusted up to the match the initial compositional averages in the simulations, the values match guite closely with our experimental measurements. For micronsized grains, this assumption is justified as the volume of segregation at the GBs should have little effect on the bulk concentration. Remaining additional deviations between the simulated and experimental values could be a result of differences in the particular types of GBs analyzed or the differences between Nd dopants (atom probe results) and Gd dopants (simulations).

Also, the trend of segregation with dopant concentration can be explored. In Y-doped zirconia materials it has been indicated that the dopant concentration at GBs is independent of dopant level.<sup>17</sup> Another possibility is that the segregation factor remains constant as doping level is changed. The simulations indicated a behavior intermediate to those two trends.<sup>4</sup> The APT results indicate the same behavior and nearly the same slope as the simulations – neither the GB content nor the segregation factor is constant as a function of doping level, but an intermediate behavior occurs.



**Figure S9.** a) The potential around an NDC10 grain boundary (dotted line) and corresponding exponential fits highlighting the asymmetry on either side of the boundary. The regions of the exponential fits are given by the diamonds and circles. b) The potential around an NDC30 grain boundary (dotted line) and corresponding exponential fits highlighting the asymmetry on either side of the boundary. The regions of the exponential fits are given by the diamonds and circles.

Based on the ion density values from the simulation, the oxygen content appears to go from 65.7 at% in the bulk to 63.7 at% at the GB for an 18.1 cat% doping. This decrease is comparable, but slightly less than the values observed here (Table S1 and S2). Similarly, the oxygen vacancy concentrations can be compared. The simulations show around 4 - 5  $O^{2-}$ vacancies/nm<sup>3</sup> at the GB. Since the structures of the GBs analyzed by APT are unknown, determination of the number of possible oxygen sites at the GBs is not possible. However, by assuming no disruption in the crystal structure, the upper limits of the oxygen vacancy densities are determined. From the experimental APT analyses, the deviations of the oxygen concentrations from stoichiometric CeO<sub>2</sub> give the percentage of oxygen vacancies. These percentages are then multiplied by the number of oxygen sites/nm<sup>3</sup>, 8 per unit cell times the number of unit cells/nm<sup>3</sup>. These unit cell densities are determined from the lattice parameters (0.5430 nm for NDC10 and 0.5467 nm for NDC30).<sup>18</sup> These result in upper limits of 10.6 O<sup>2-</sup> vacancies nm<sup>-</sup> <sup>3</sup> for NDC10 and 8.7 O<sup>2-</sup> vacancies/nm<sup>3</sup> for NDC30, matching the simulation reasonably well. The above comparisons provide further validation of the experimental measurements.

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