

Seeing Cation Dopants in Gd-doped Ceria with STEM-EELS

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Gd-doped ceria (GDC) is one of the most promising materials using in solid oxide fuel cell (SOFC) at median operating temperature below 700°C. It has shown high ion conductivity and stability at low/median temperatures compared with other candidate materials [1]. GDC is a non-stoichiometric oxide material that is known for its ability to exchange lattice oxygen with surrounding ambient environment. Adding the aliovalent dopant Gd to pure ceria enhances the oxygen exchange ability by creating more extrinsic oxygen vacancies, which results conductivity improvement [2]. The dopants distribution and local concentration may play an important role in oxygen exchange functionality. However, the relationship between the surface exchange rate and the atomic level defect location/distribution is not well understood. To understand a possible influence of point defect structures and location on exchange sites, it's important to develop visualization methods to locate the defects. The atomic level Gd defect concentrations can be measured using scanning transmission electron microscopy coupled with electron energy-loss spectroscopy (STEM-EELS). However, for elemental mapping, the Gd EELS signal-to-noise ratio (SNR) is low, which making it difficult to detect and quantify. To address this weakness, we present a hybrid method involving EELS and high angle-annular dark-field imaging (HAADF).

15% Gd-doped ceria (atomic weight %) nanoparticles were synthesized using a solution-based hydrothermal methods [3]. Gd cation point defects were detected and quantified via STEM-EELS spectrum imaging performed on an aberration-corrected Nion UltraSTEM 100 microscope (operated at 100kV). Nanoparticles were tilted into the [110] zone axis orientation, and EELS spectrum images were collected near (110) surfaces. HAADF image were collected simultaneous with the spectra.

To calculate the local concentration of Gd, two approaches have been employed; traditional EELS mapping of Ce and Gd and, a hybrid HAADF/EELS approach. In the traditional approach, spectral processing involves background subtraction and separation of the overlapping Ce M₂₃ and Gd M₄₅ peaks to generate the Gd M₄₅ elemental map. **Figure 1** shows the HAADF image and the simultaneously acquired Ce and Gd elemental maps. Gd is not homogeneously distributed, and cluster formation is observed by comparing the Gd and Ce maps. Note that in elemental maps, there is an anti-correlation between the Gd and Ce signals. However, the Gd map is very noisy making it difficult to provide more detail information of the Gd distribution.

Because the Gd signal is weak, we have developed a hybrid approach that relies primarily on the stronger Ce EELS signal and HAADF signals to deduce the Gd content. The method assumes that Gd ions substitute for Ce and that the HAADF cation signal is proportional to the total number of

cations in the column. **Figure 2** is a plot of the HAADF column intensity versus the sum of Ce + Gd column intensity from the EELS maps (total EELS cation signal) for all the columns in **Figure 1**. **Figure 2** shows that there is the linear relationship between these two integrated intensities. This implies that, for a particular column, a comparison of the Ce column intensity with the corresponding HAADF column intensity should allow the Gd EELS signal to be deduced. The Gd signal is then determined by subtracting Ce EELS signal from a suitable scaled HAADF signal. **Figure 3** shows results for local Gd column concentration determined with the traditional and hybrid methods. Both methods can successfully determine the concentration variation and showed the same trend. However, the absolute concentration is different. The concentration calculated from traditional method is significantly higher than the hybrid HAADF/EELS method. This may be due to the poor signal to noise ratio of Gd M₄₅ peaks and the error arising from peak overlap separation calculations. Further study will focus contrasting the variation in performance of the two methods.

Reference:

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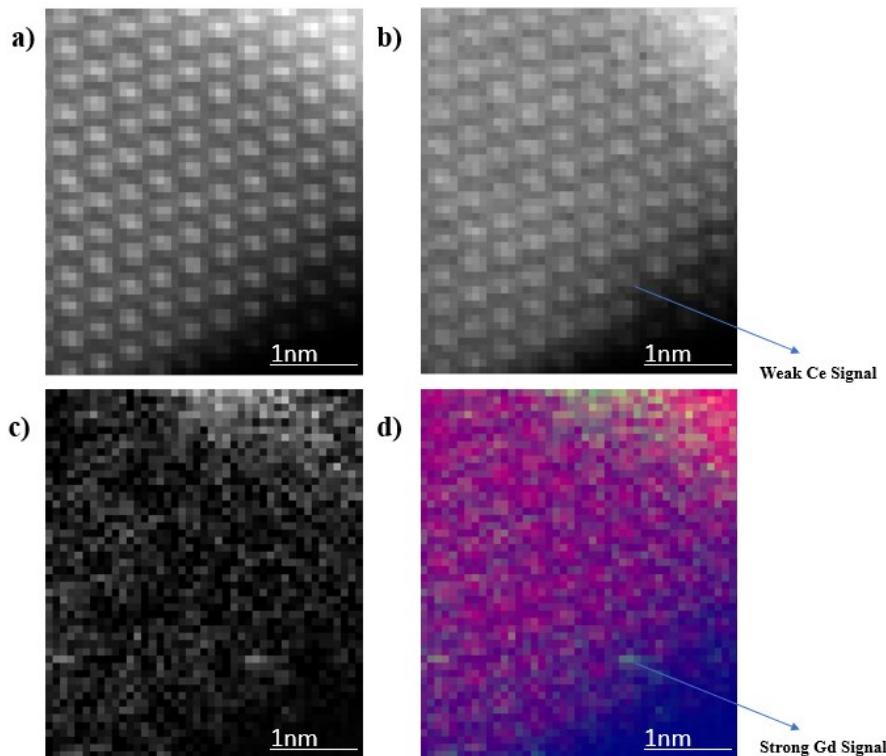


Figure 1: a) Atomic resolution HAADF image of the 15% GDC (110) surfaces in [110] zone axis. b) EELS spectrum image of Ce M₄₅ Map c) EELS spectrum image of Gd M₄₅ Map d) RGB overlay of Gd (green) and Ce (red) maps. There is an anti-correlation between the Gd and Ce signals as shown in the arrows.

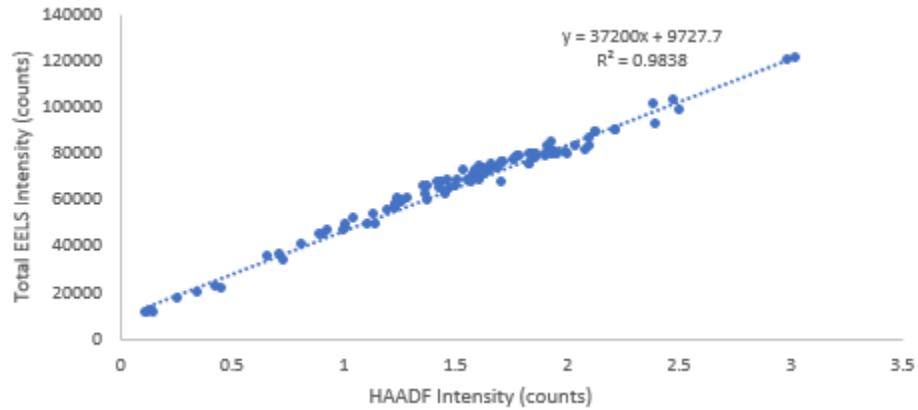


Figure 2: the relationship between HAADF intensity and total EELS signal for individual columns, which demonstrated as a linear function.

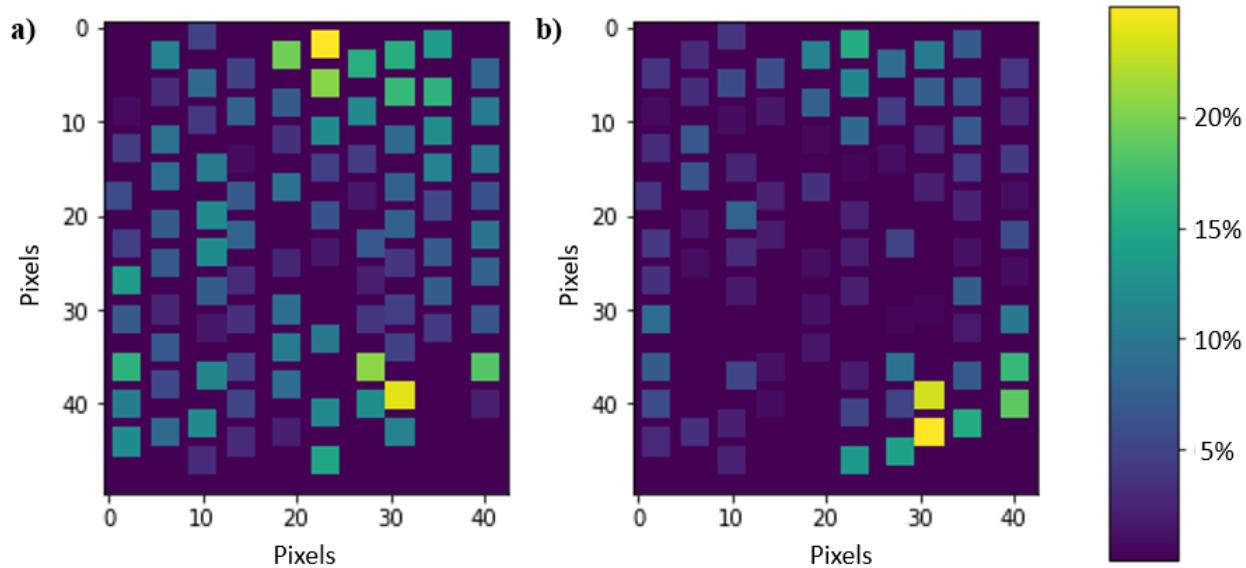


Figure 3: Local Gd concentration comparison plot of individual columns between a) direct EELS signal method and b) HAADF/EELS correlated method. Atomic columns have represented as 3*3 pixels squares.