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# Atomic Scale Visualization of Cation Point Defects in Gadolinium Doped Ceria

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Ceria and ceria-based materials are well known for their unique ability of reversibly exchange lattice oxygen with the surrounding environment favoring their use in areas such as catalysis, energy and sensing technologies. Because of the high-level of tolerance to oxygen vacancies in these materials, they have been commonly doped with aliovalent point defects, such as $Pr^{3+}$, $Gd^{3+}$ and $Ca^{2+}$, to increase extrinsic oxygen vacancies resulting in enhanced ionic and electronic conductivity [1]. Gadolinium doped ceria (GDC) is known to be one of the most promising possible anode materials for operation of solid oxide fuel cells (SOFC) below 600 °C [2]. However, the association between atomic level point defect location/configuration and the performance for oxygen exchange is not well understood. To understand the effect of point defect structure and locations relating to active oxygen exchange sites, it's necessarily developed atomic level imaging and spectroscopic techniques to visualize them.

Gd-doped ceria (with 5% and 15% dopant concentration) were synthesized using solution-based hydrothermal method [3]. High resolution TEM images were acquired on a FEI Titan aberration-corrected environmental transmission electron microscope (AC-ETEM) coupled with Gatan K3 direct electron detector to observe the atomic level variation in cation and anion site. Several initial defect configuration models were generated and relaxed through molecular statics for image simulation. Atomic resolution STEM EELS (scanning transmission electron microscopy coupled with electron energy-loss spectroscopy) were collected from a GDC (110) surface along [110] zone axis on Nion UltraSTEM 100 microscope for identifying point defect position and defect cluster configurations through elemental mapping. 2D elliptical Gaussian peak fitting algorithm (TRACT) [4] was used to determine atomic column position and depth. Customized EELS analyzing code was used for identifying atomic column intensity in spectrum images.

Figure 1 showed three possible defect structures of Gd-doped ceria after structure relaxation with molecular statics. For every oxygen vacancy created, two Ce atoms need to be replaced with 2 Gd atoms. The O vacancy can be located at first nearest neighbor (NN1) or second nearest neighbor (NN2) of the Gd atoms. To illustrate the effect of structural distortion associated with Gd point defect, TEM image simulation and strain field maps were generated for those three different defect configurations. Our preliminary results showed the lattice distortion caused by point defect clusters can be quantified by associated strain field measurements around the dopant in the structure. Cation and anion columns have displacements of approximately 20 pm and 10 pm respectively (~3% strain) due to the presence of the dopant. Although the distortion is small, it may be possible to distinguish through phase contrast imaging methods. Alternatively, STEM EELS elemental maps of Ce and Gd were acquired as shown in Figure 2, which Gd is not homogenously distributed and surface segregation of Gd is observed in this area. Figure 3 showed an elemental mapping of Gd map overlaid with Ce map in a different area, which Gd tend to create a defect cluster as pairs [5].

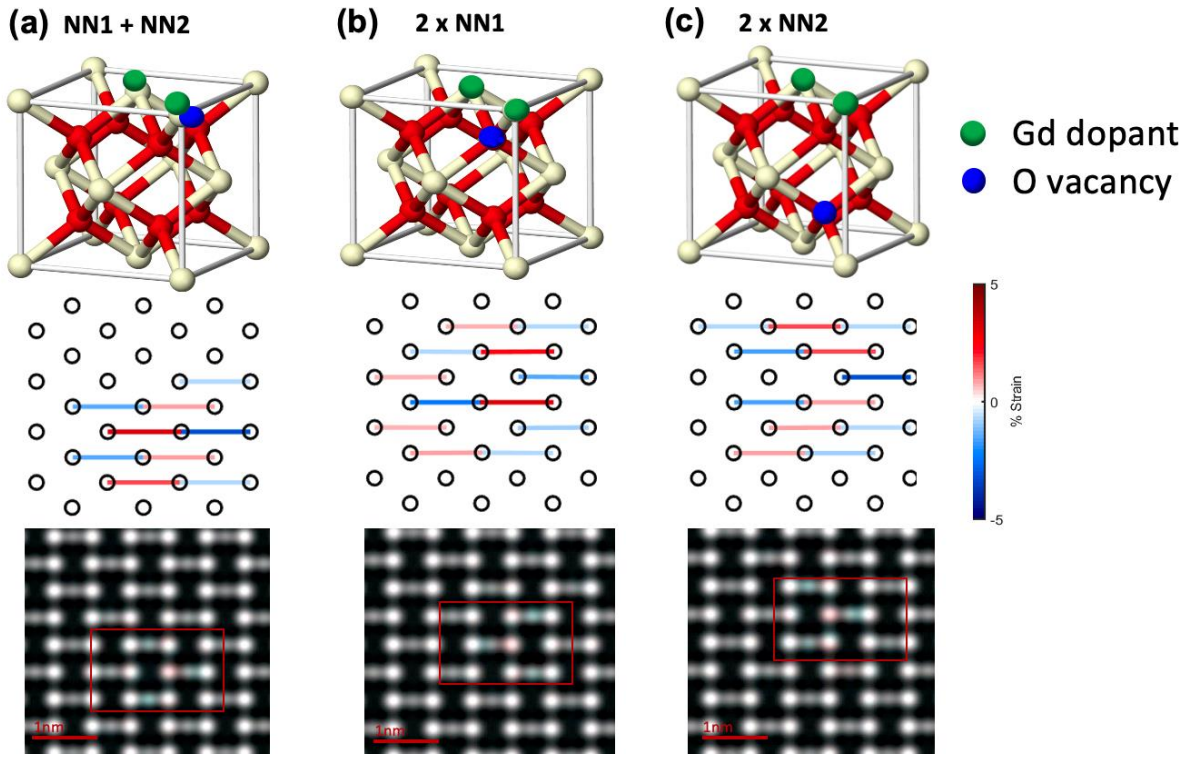


**Figure 1.** Three possible defect cluster configurations of Gd-doped ceria and its corresponding strain field map of TEM image simulation. Simulation images of defect structure were overlaid with undoped structured to illustrate point defect location and distortion to the surrounding local environment.

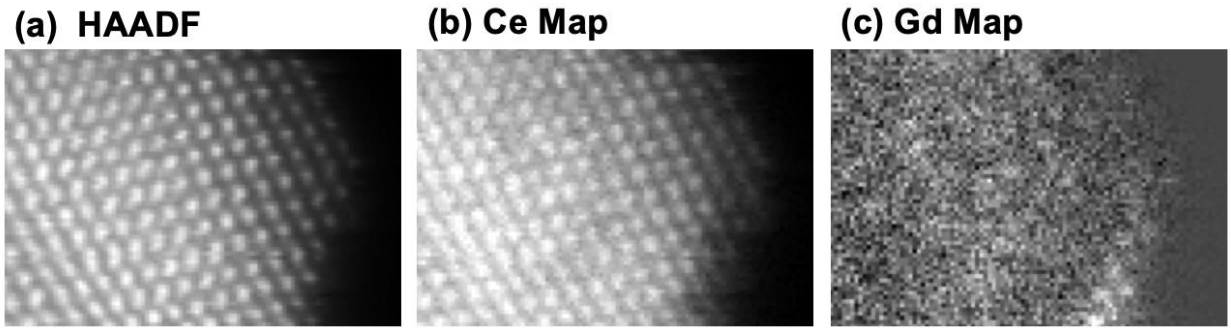


**Figure 2.** a) HAADF image of Gd-doped ceria of (110) surface along [110] zone axis. STEM EELS Elemental mapping of b) Ce and c) Gd

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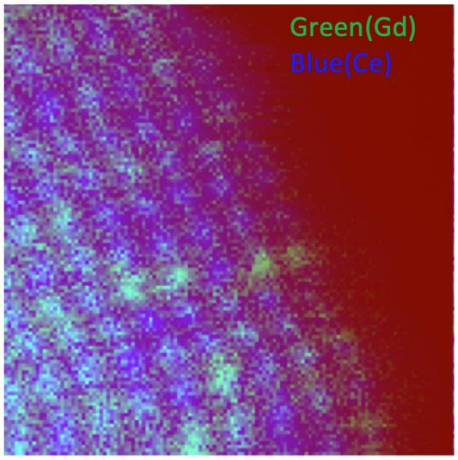


**Figure 3.** STEM EELS Elemental mapping of Gd map (green) overlaid with Ce map (blue). Gd signal is enhanced for visualization propose.

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