

# Spectroscopy in STEM/TEM

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### Electron beam induced reduction of cerium in pure, mixed and doped ceria

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Cerium and cerium-based oxides are used in a variety of energy-related applications, for example as supports for noble metal catalysts and as electrolyte materials in solid oxide fuel cells [1]. Their redox properties have been described in numerous studies performed using electron diffraction, high-resolution transmission electron microscopy (HRTEM) and electron energy-loss spectroscopy (EELS) [2, 3].

The reduction of cerium from its tetra-valent to its tri-valent state has been observed in the reducing atmosphere of a TEM column, especially in the presence of extensive electron beam illumination. This behaviour can result in the incorrect interpretation of TEM results acquired from materials that have been worked *ex situ*, such as operated electrolytes. Here, we report on a study of the valence change of cerium in three types of ceria due to electron beam induced reduction.

Commercially pure ceria (CeO<sub>2</sub>) powders were dispersed on conventional TEM grids and used as a reference material. Two cerium-based oxides that have practical applications, ceria-zirconia solid solution Ce<sub>2</sub>Zr<sub>2</sub>O<sub>8</sub> (CZO) powders [4] and gadolinia-doped ceria Gd<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2- $\delta$</sub>  (GDC) thin films, were also investigated. The GDC thin films were deposited using pulsed laser deposition (PLD) on Si (100). Electron-transparent TEM specimens were prepared using a focused ion beam (FIB) micro-sampling technique. The oxides were studied using EELS on a JEM2100 TEM operating at 200kV. EELS was used to follow the reduction of ceria in the three oxides, by following the evolution of several different Ce edges and the O K edge.

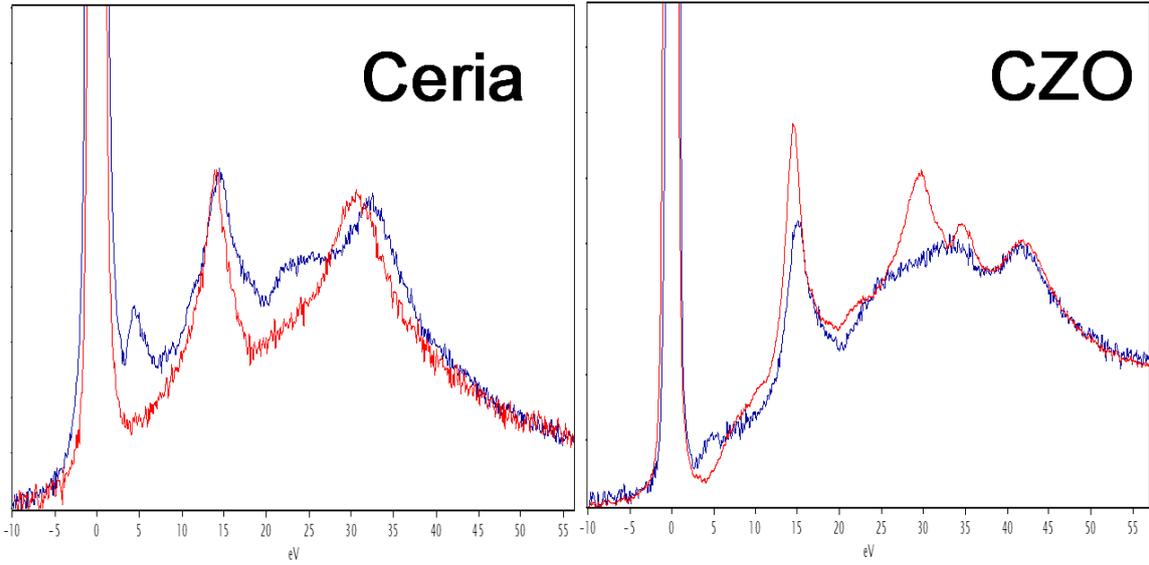
The valence state of cerium in each oxide was determined from core shell Ce N edge spectra, whose shape is well defined for tri- and tetra-valent cerium. Although all three oxides were finally reduced in the TEM column, their reduction rates were very different under constant electron beam irradiation. Whereas the CZO powders were reduced rapidly, both the pure ceria powders and especially the GDC thin films were more stable. In pure ceria, a transformation in the crystal structure took place during the reduction reaction, whereas there was no change in the CZO or GDC microstructures. The GDC film has a large number of oxygen vacancies in its microstructure, primarily as a result of the substitution of tri-valent Gd cations by tetra-valent Ce cations. This substitution may have an influence on the reduction rate of Ce in GDC.

Low-loss EELS measurements showed differences between all of the oxides in both their reduced and their unreduced states. The CZO and GDC low-loss spectra are influenced by the presence of the second cations (Zr<sup>4+</sup> and Gd<sup>3+</sup>, respectively). Comparisons with reference spectra acquired from pure zirconia and pure gadolinia suggest that the spectra measured from the reduced oxides show features that are associated with the second cations (e.g., Zr<sup>4+</sup> in Fig. 1). Similar effects were observed for reduced GDC.

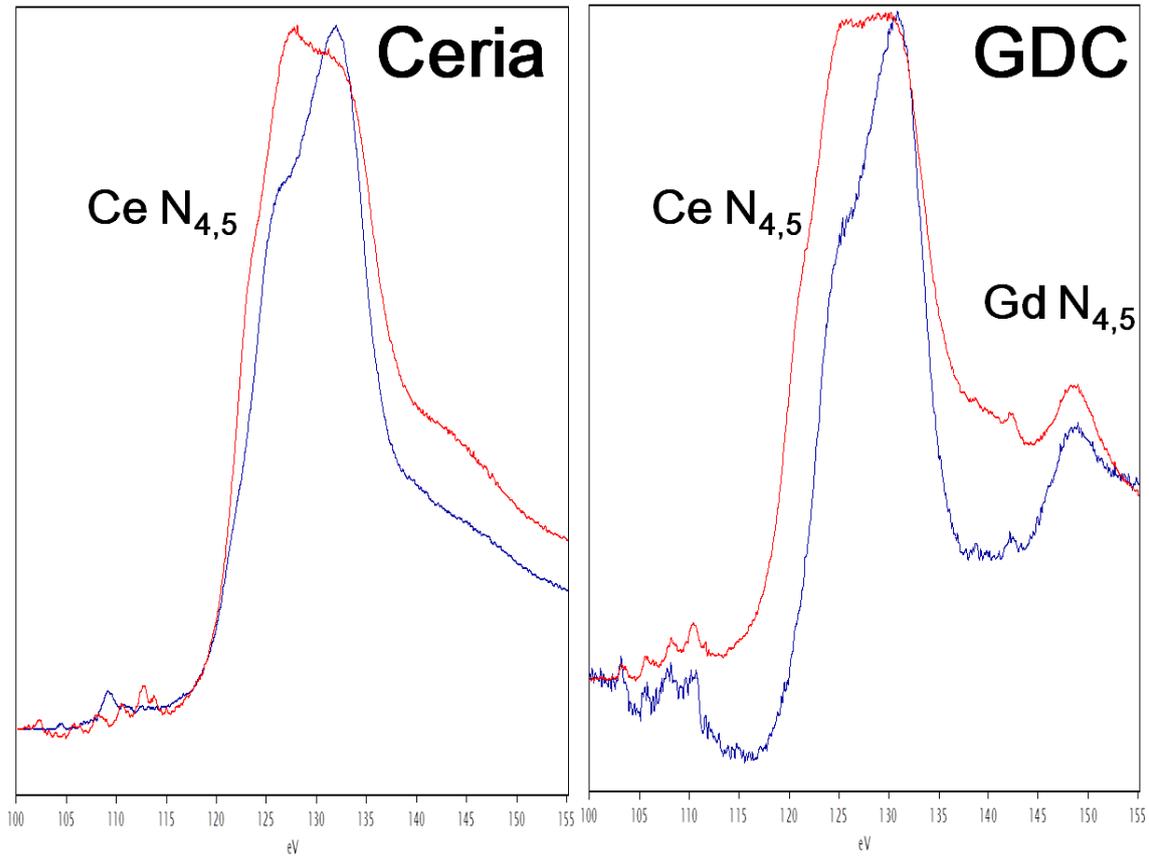
Inner shell Ce N edge spectra were consistent between all of the unreduced oxides. However, different features were observed from the different oxides after reduction. A clear reversal in the intensity ratio of the N<sub>5</sub> and N<sub>4</sub> white lines was observed between reduced and unreduced pure ceria. This effect was weaker for GDC (see Fig. 2) and almost absent for CZO. However, a distinct pre-edge fine structure developed when Ce<sup>4+</sup> was reduced to Ce<sup>3+</sup>.

O K edge spectra recorded from the different oxides were similar to each other, containing features similar to those recorded from CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub> for the unreduced and reduced oxides, respectively.

1. P.A. Crozier, R. Wang, R. Sharma, *Ultramicroscopy*, 108 (2008), p. 1432.
2. S. Arai, S. Muto, J. Murai, T. Sasaki, Y. Ukyo, K. Kuroda, H. Saka, *Mater. Trans.*, 45 (2004), p. 2951.
3. R. Wang, P.A. Crozier, R. Sharma, *J. Phys. Chem.*, 113 (2009), p. 5700.
4. S. Arai, S. Muto, T. Sasaki, Y. Ukyo, K. Kuroda, H. Saka, *Electrochem. Solid-State Lett.* 9 (2006), p. E1.



**Figure 1.** Low-loss electron energy-loss spectra acquired from pure ceria (left) and from a ceria-zirconia solid solution (right) for tetra-valent Ce cations (blue) and for tri-valent Ce cations (red).



**Figure 2.** Inner-shell electron energy-loss spectra recorded from pure ceria (left) and from gadolium-doped ceria (right) for tetra-valent Ce cations (blue) and for tri-valent Ce cations (red). The Gd N edge, which is visible in the GDC spectra, shows little difference between the reduced and unreduced oxides.