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# The reversible phase transition of Gd-doped ceria by in situ TEM

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Owing to the flexile valence switching between Ce4+ and Ce3+ cations and the facile formation of oxygen vacancies, ceria has been recognized as one of the best candidates for catalysts and solid electrolytes. The formation and migration of oxygen vacancy under external stimuli thus constitute the fundamental processes of the functional oxide materials and their associated devices, which are often linked with modification in the ceria structure and subsequent phase transitions. Typically, ceria crystallizes in a fluorite-type (F-type) cubic structure (space group Fm-3m, a≈5.42 Å). Transition from F-type to the so-called C-type (space group Ia-3) takes place when enough oxygen vacancies are introduced to the system, in Fig. 1. As a result, the cell parameter is doubled, the M site is six-coordinated to O, and the crystallographic positions are split. However, given the challenges in visualizing oxygen dynamics with adequate temporal and spatial resolution, the structural evolution of ceria in response to external stimuli remains rarely explored.[1] Questions pertaining to transition details, including the selection of external stimuli, the behaviors of oxygen vacancies, the feasibility of fine tuning as well as the underlying mechanism remain unsolved.[2]

For our study, the Gd-doped ceria (CGO) with high oxygen ion conductivity as well as giant electrostriction under external electric field is chosen. Dense pellets of Gd-doped ceria were prepared by solid state reactive sintering.[3] The phase transition of CGO is in situ probed down to sub-Å scale by transmission electron microscopy (TEM), where the electron beam (e-beam) is also serving conveniently as an external stimulus. Negative spherical aberration imaging (NCSI)[4] and integrated differential phase contrast (iDPC) imaging are employed, enabling high contrast for both light oxygen and heavy metal atoms, as well as facilitating the measurement of atomic positions with ultra-high precision. Fully manageable transitions are achieved through adjustments to the electron dose rate (EDR). Quantifying lattice distortions also allows a direct estimation of the local oxygen vacancy concentration. The electron energy loss spectroscopy (EELS) reveals varying Ce valence within the CGO. Finally, a collective rearrangement of the oxygen vacancies is proposed to account for our observations, and the simulated HRTEM images show a good agreement with the experimental results. Further numeric calculation would then be necessary to establish a solid theory.

In summary, the reversible phase transitions of CGO were explored in situ with picometer precision. Unique insights into the transition process are gained, such as anisotropic ordering of the oxygen vacancies, direct interpretation of the local oxygen vacancy concentration, and feasible modulation of the transition efficiency. These findings showcase great promise for diverse energy-related applications, including enhancing the performance of ceria-based catalysts and advancing next-generation memristors. The same principle could also be extended to other functional oxides.

**Graphic:**

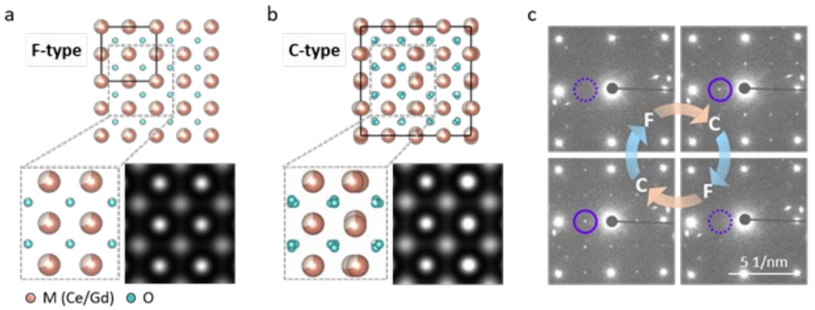


Fig. 1 (a-b) Structural models of the F- and C-type and the simulated HRTEM images. (c) Electron diffraction patterns recorded during a transition cycle. The outlined diffraction spots are only associated with the C-type.

**Keywords:**

Phase transition, in-situ TEM, NCSI

**Reference:**

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