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Elastic Properties of Cerium Oxide Nanocubes from *In Situ* TEM Compression Tests and DFT+U Simulations

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In situ mechanical testing inside Transmission Electron Microscopes is probably the most powerful way to investigate the mechanical behavior at the nanoscale, as it can provide simultaneously quantitative mechanical data (force-displacement curves) and images of the sample during deformation [1]. Such experiments not only permit insightful works on plasticity mechanisms in bulk materials, with characterizations before/during/after conventional mechanical tests, but also permit the analysis of the mechanical behavior of individual nano-objects.

Cerium oxide (CeO_2) nanoparticles are used in catalytic systems as photocatalysts, and for biomedical applications [2]. For these applications, CeO_2 can undergo compressive stresses, inducing plastic deformation. *In situ* TEM mechanical tests bring interesting pieces of information but the sensitivity to electron irradiation has to be taken into account prior to the experiments. Indeed, oxygen vacancies and changes in the cerium valence state have been evidenced [3], and may affect the materials mechanical response. Interestingly, i*n situ* reduction can be stopped or even reversed by introducing oxygen molecules during observation.

We will present results obtained on cerium oxide nanocubes, of sizes ranging from 20 to 50 nm, with a Hysitron PI 95 fitting in a Cs-corrected FEI Titan Environmental TEM operating under vacuum or with a partial pressure of gas. In order to minimize data dispersion due to mechanical accommodation for instance, we will focus on the elastic regime and compare the elastic moduli obtained by Digital Image Correlation on the same nanocube tested under different environments (under vacuum or with O_2).

To better characterize the reduction/oxidation process and its effect on the mechanical properties, we will present DFT+U simulations on bulk systems with various CeO_x stoechiometries ($1.5 < x < 2$). The stability of each crystallographic phase appears to be in agreement with the literature [4] and with experimental observations. Significant changes in the calculated elastic moduli are obtained and compared with experimental results [5].

References:

[1] A.M. Minor, J.W. Moris Jr, E.A. Stach, Applied Physics Letters **79** (2001), p. 1625.
[2] T. Montini *et al*, Chemical Reviews **116** (2016) p. 5987.
[3] A.C. Johnston-Peck *et al,* Ultramicroscopy **170** (2016), p. 1.
[4] J.L.F. Da Silva, Physical Review B **76** (2007), p. 193108.

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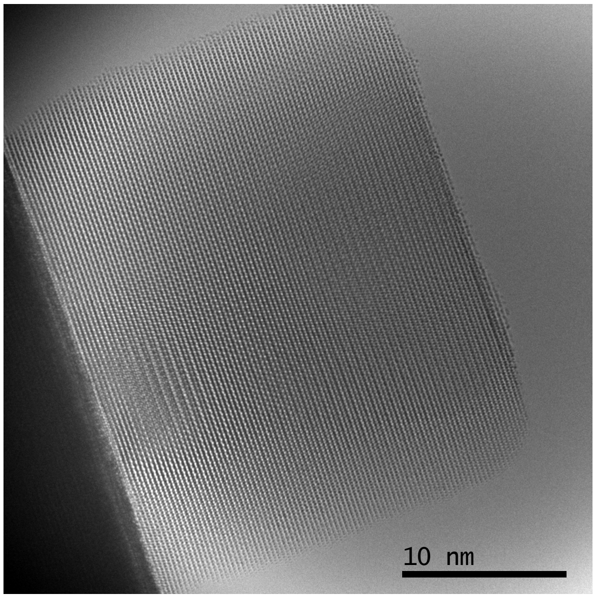


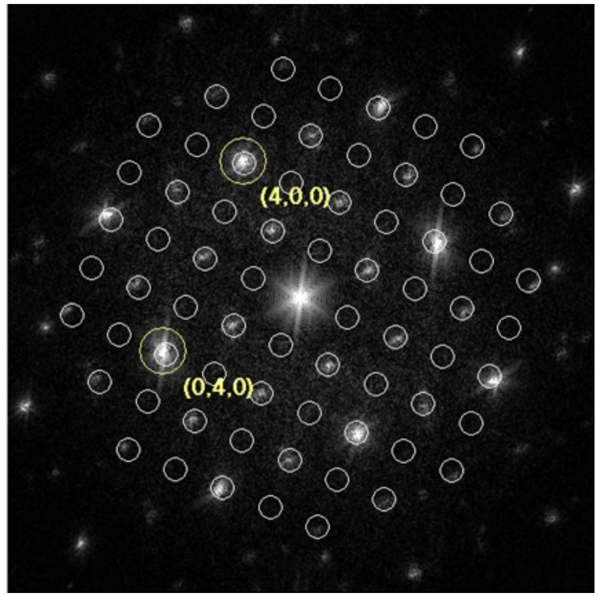
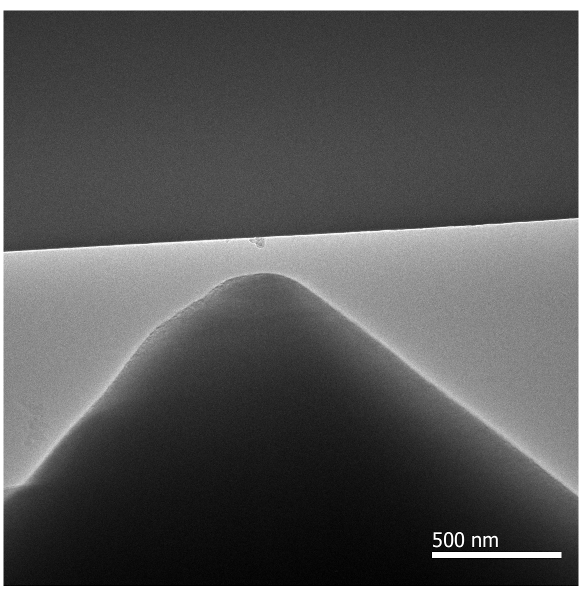


Figure 1. High Resolution TEM image of a cerium oxide nanocube after electron irradiation, and corresponding electron diffraction pattern (zone axis [001]). Crystallographic indexing performed consistently on the same nanocube along different zone axes reveals a cubic Ce_2O_3 structure (bixbyite).



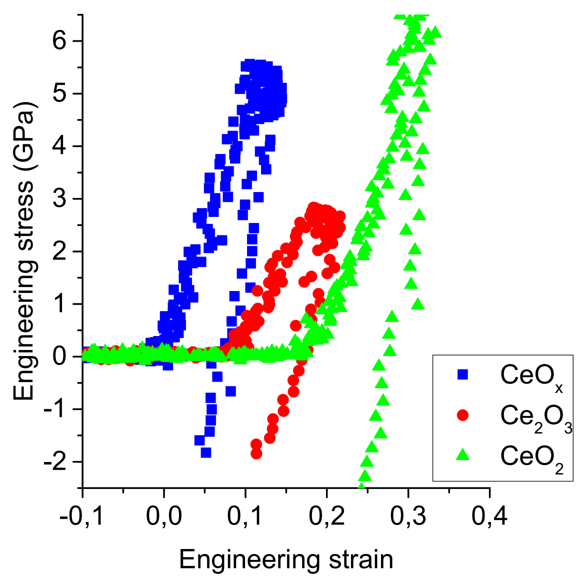


Figure 2. In situ TEM compression of a single cerium oxide nanoparticle. Left: TEM image of the nanocube between the support and the tip. Right: stress-strain curves of the nanocube under different conditions, leading to different oxygen contents.

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