Tuning the reduction state and atomic resolution study of cerium oxide (CeO_2) nanocubes in a Cs-corrected Environmental TEM

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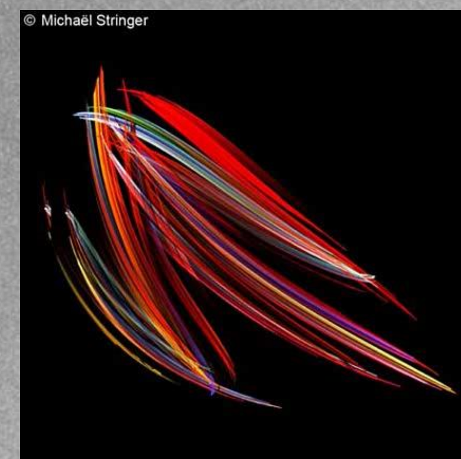


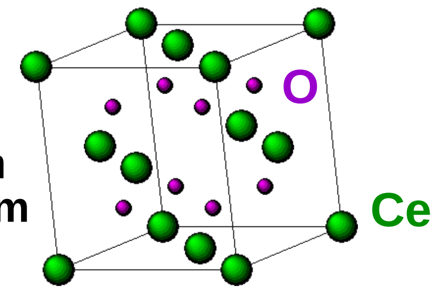
LITERATURE BACKGROUND on CERIA CeO_2

- **Ceria CeO_2 : a multi-functional oxide widely used in catalysis**

  (Redox Ce^{4+} / Ce^{3+} vs. oxygen vacancies)

  A. TROVARELLI, *'Catalysis by Ceria and Related Materials'*, Imperial College Press, London (2002)

cubic Fm3m
a = 0.541 nm



- **A *challenging* material for atomic (surface) imaging (of oxygen species) by aberration-corrected HR(S)TEM**

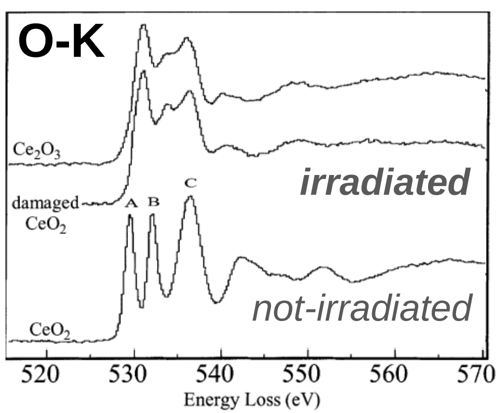
G. MÖBUS et al., *Adv. Funct. Mater.* **21** (2011),1971-1976

S. TURNER et al., *Nanoscale* **3** (2011), 3385-3390

Y. LIN et al., *Nano Lett.* **14** (2014),191-196

$$\underbrace{CeO_2}_{Ce^{4+}} \longrightarrow \underbrace{CeO_{2-n}}_{Ce^{4+},\ Ce^{3+},\ \square_O} +\ n\,O$$

EELS



L.A.J. GARVIE, P.R. BUSECK, *J. Phys. Chem. Sol.* **60** (1999) 1943

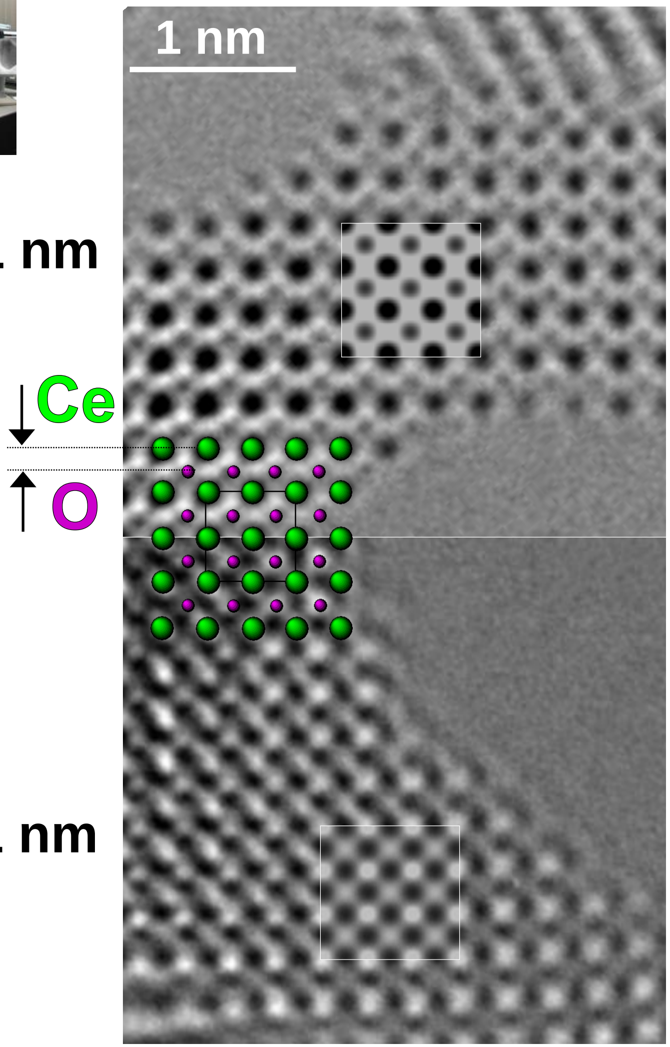
C_s-corrected FEI-TITAN *Environmental* TEM 300 kV

($P_{gas} \leq 23$ mbar, $T_{max} \approx 1000°C$)

[100] **t = 3 ± 1 nm** **[110]**

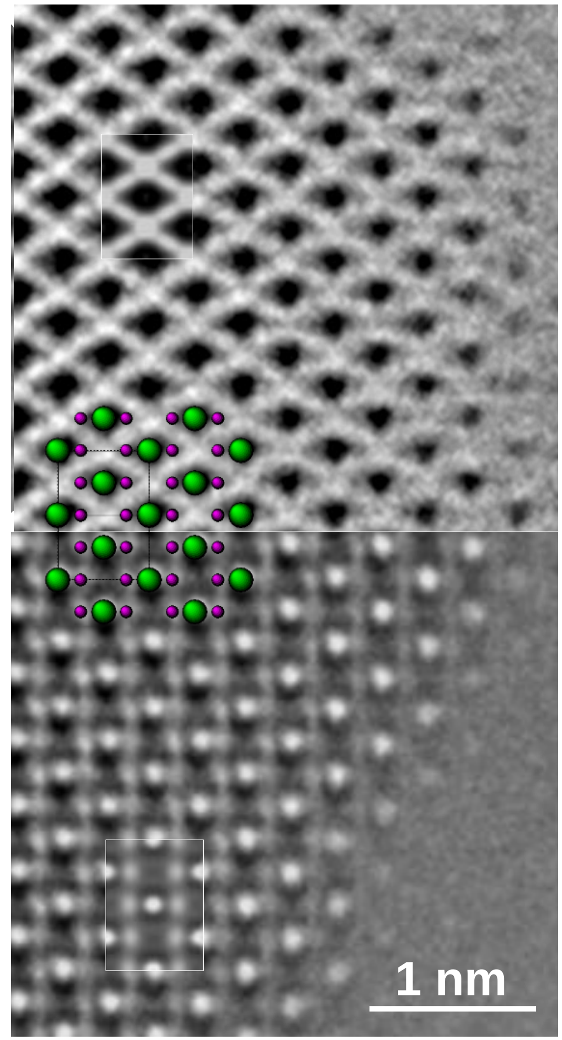
δf = -4 ± 1 nm

$C_s = 5\ \mu m$



δf = 11 ± 1 nm

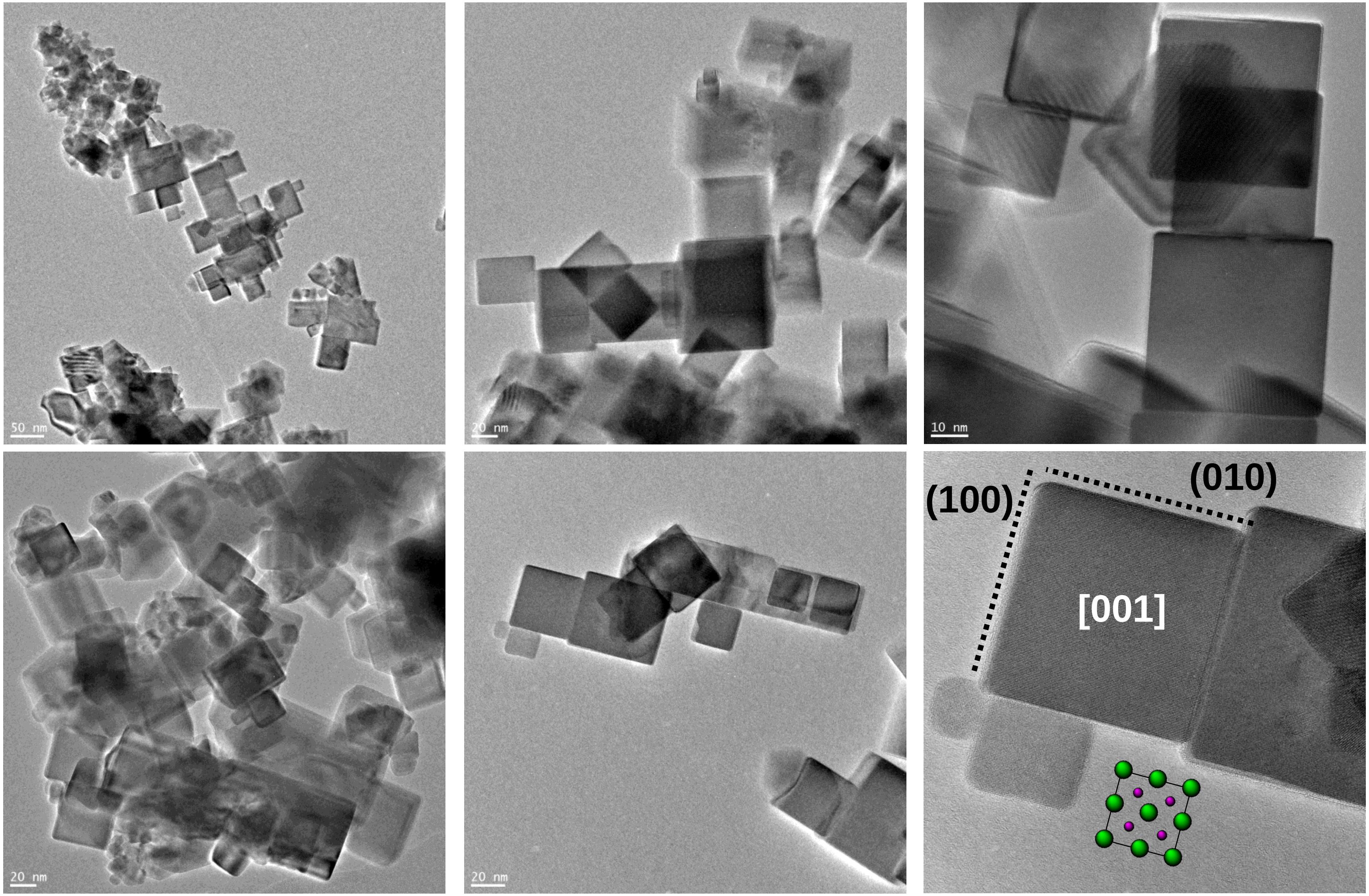
δf = -9 ± 1 nm



δf = 2 ± 1 nm

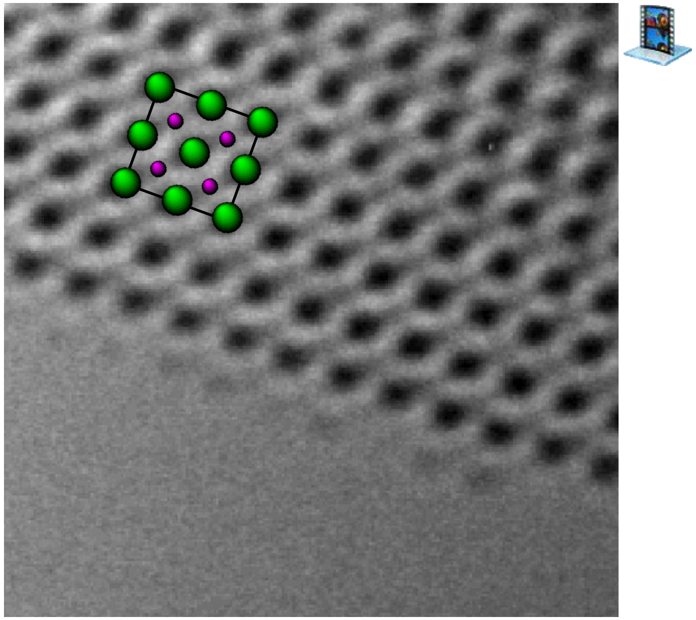
HRTEM study of Ceria nanocubes with {100} facets

Z. WU et al., *J. of Phys. Chem. C*, (2015)

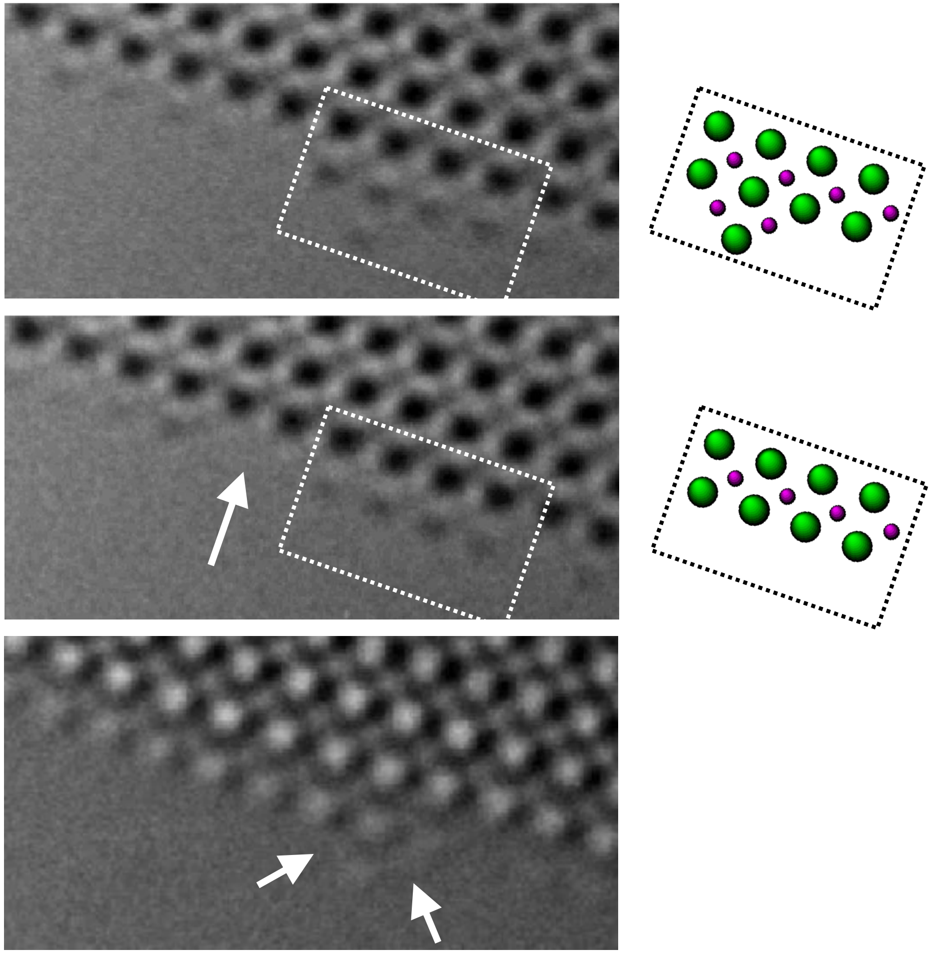


HRTEM study of Ceria nanocubes with {100} facets

‘High Vacuum’ 2.2 10^{-5} mbar

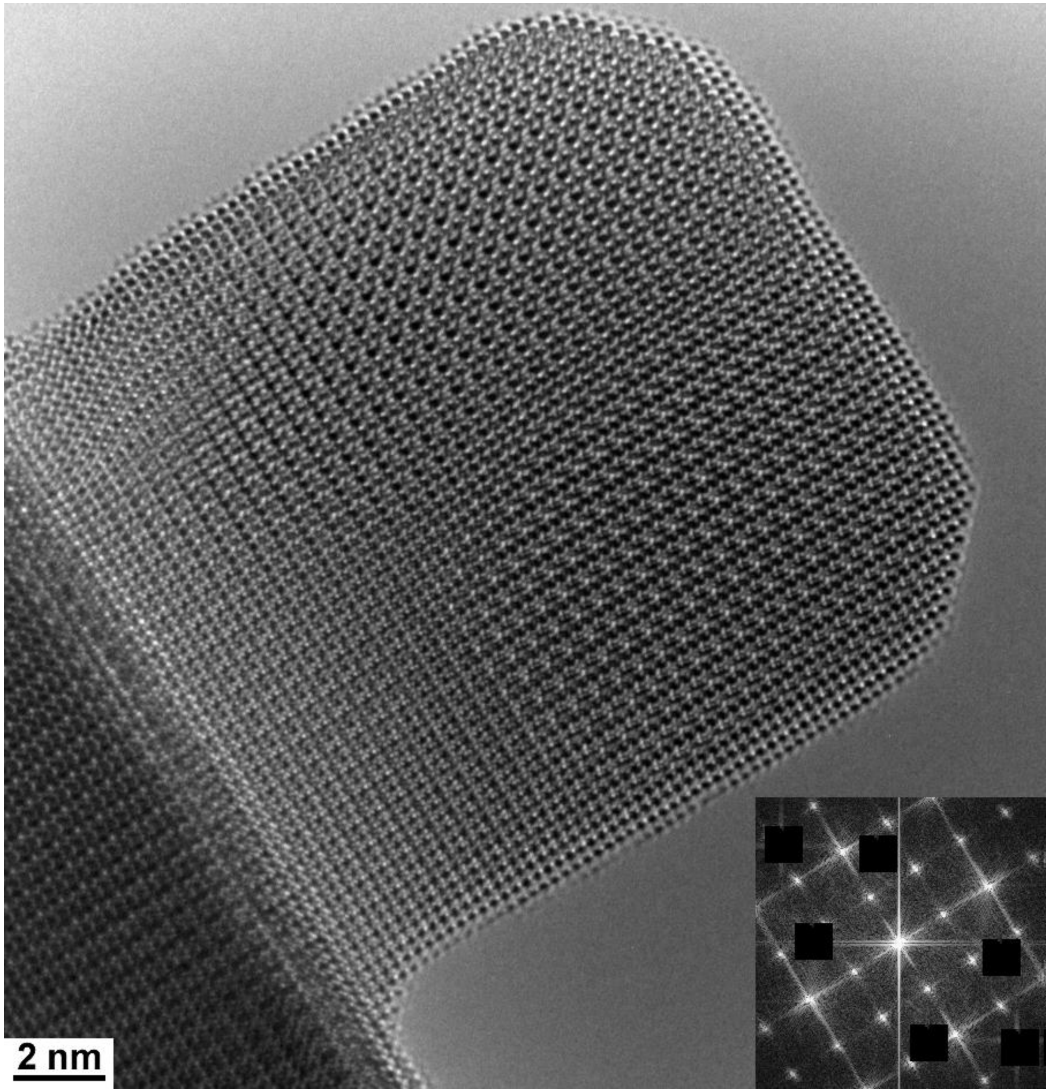


Speed x0.3 (0.075s/f)

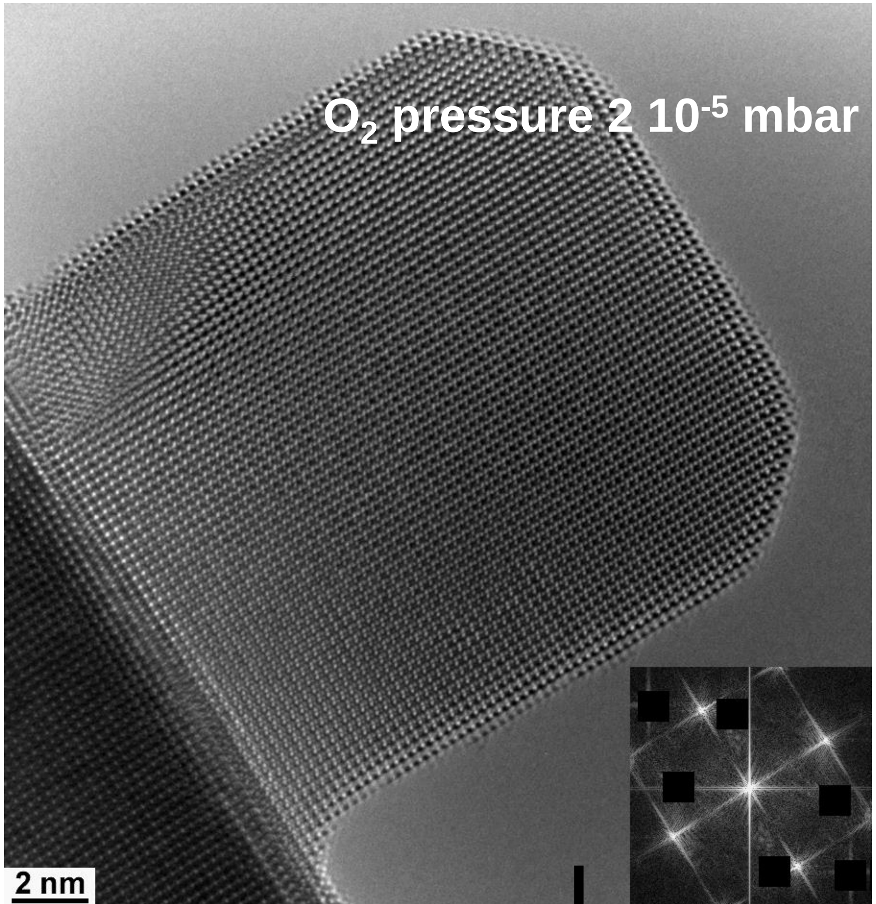


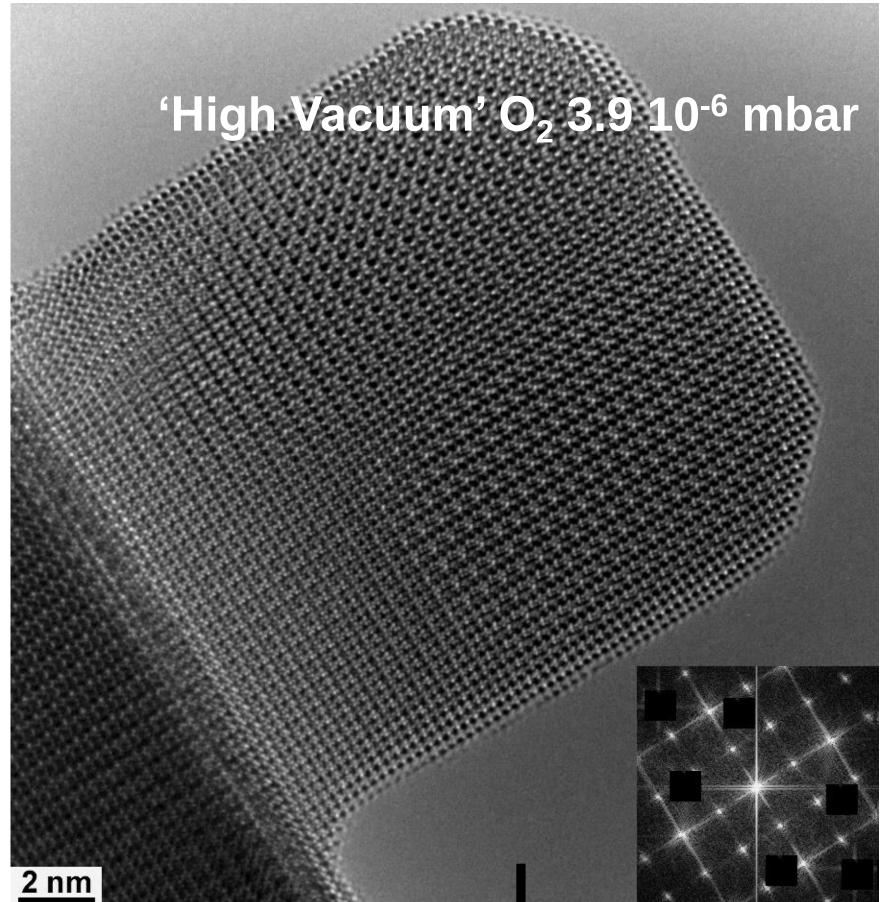
Bulk effects: control of the reduction state in ETEM

- **Gas introduction in the ETEM: oxygen O_2 cycling [3.9 10^{-6} *'HV'* - 2 10^{-5} mbar]**

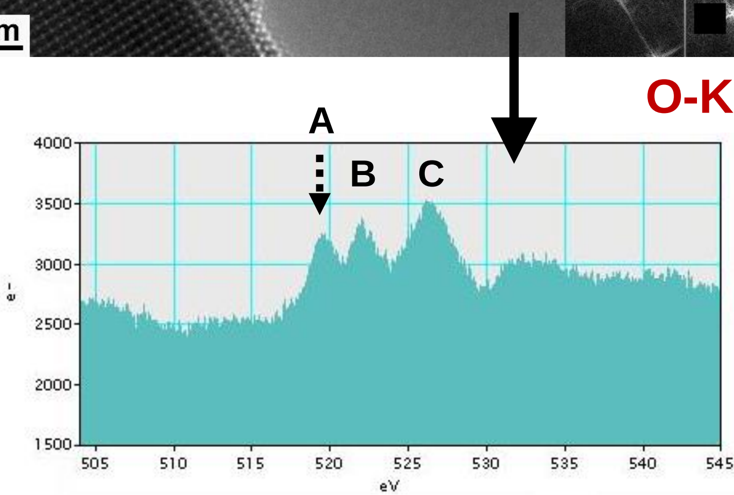


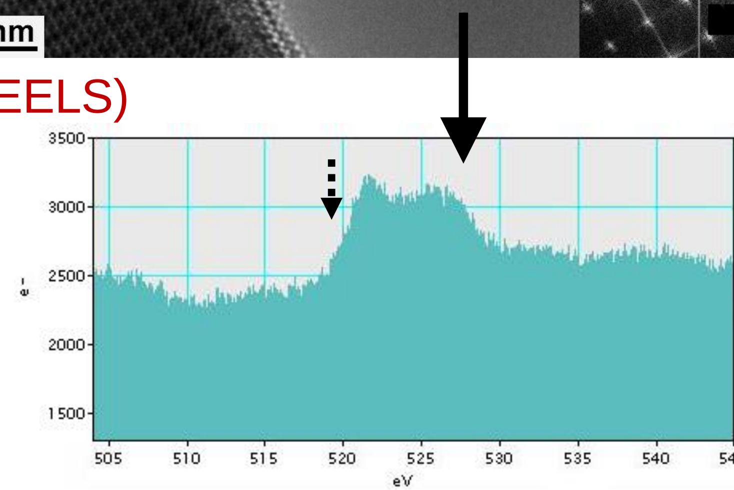
Speed x30
(back and forth)


O_2 pressure 2 10^{-5} mbar
2 nm


'High Vacuum' O_2 3.9 10^{-6} mbar
2 nm

O-K edge (EELS)


A
B
C
4000
3500
3000
2500
2000
1500
e-
505
510
515
520
525
530
535
540
545
eV


3500
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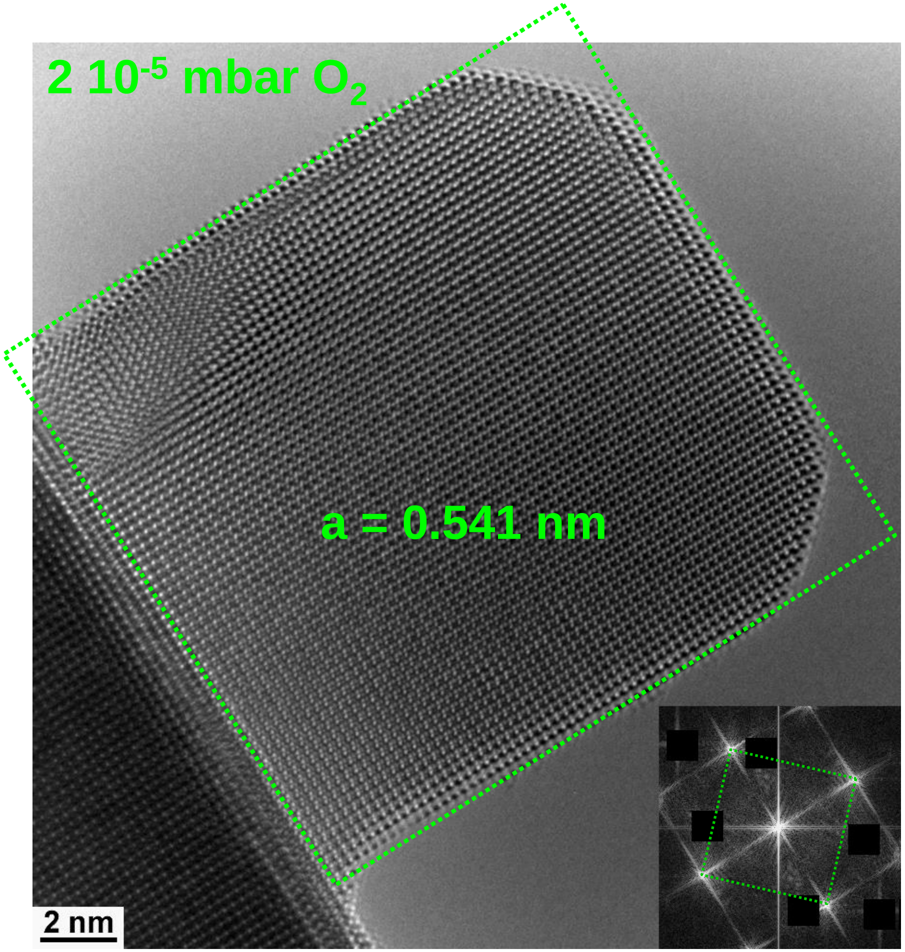
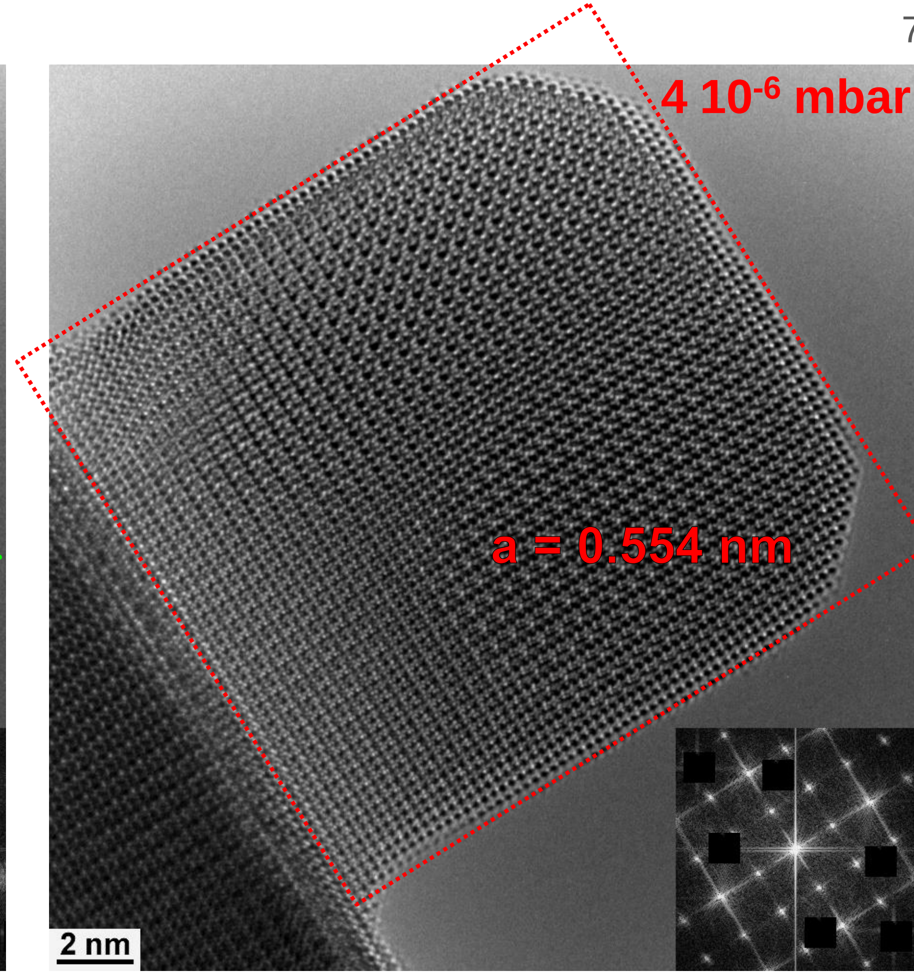
540
545
eV



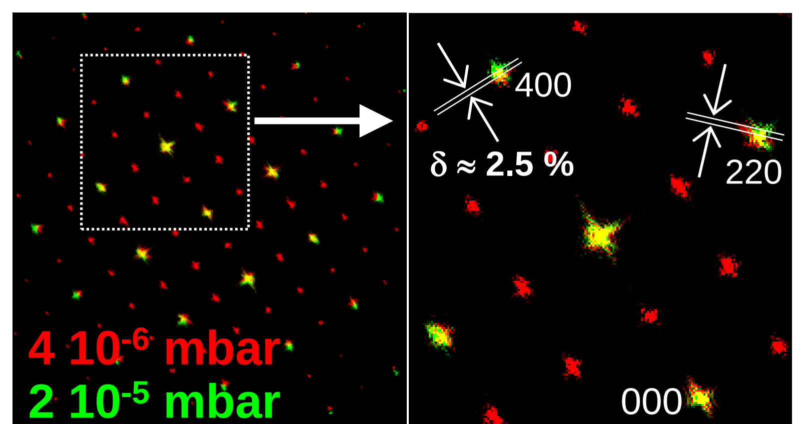


Nominal ceria CeO_2: Fm-3m, **a = 0.5411 nm**

R.W.G. WYCKOFF, 'Crystal Structures', 2nd ed., Interscience Pub.: New York, **1** (1963) 239-444

Oxygen vacancies Ce_4O_7: Fm-3m, **a = 0.5526 nm**

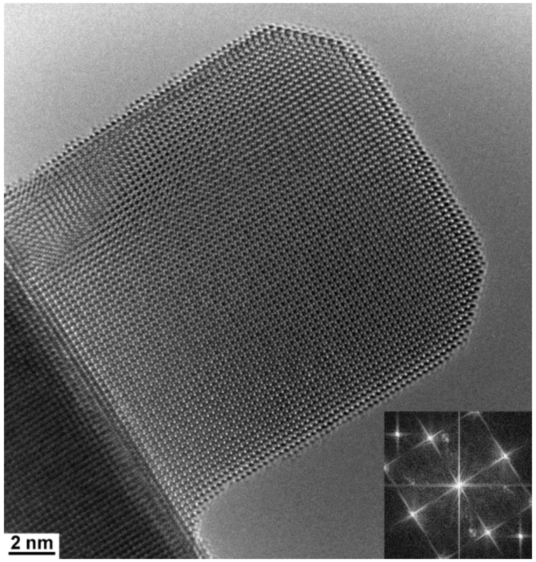
G. BRAUER, H. GRADINGER, *Z. Anorg. Allg. Chem.*, **277** (1954) 89

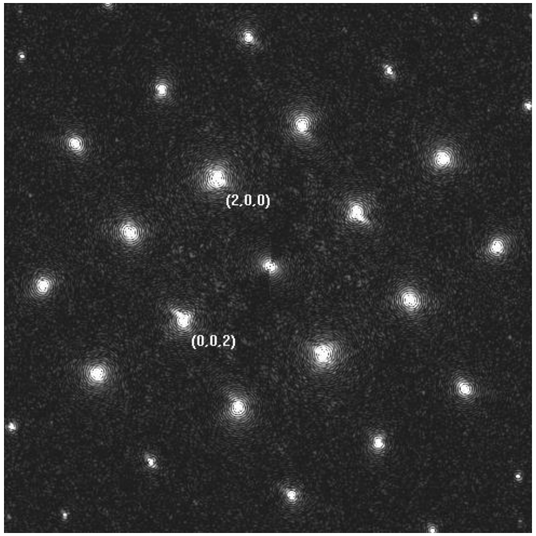


$Ce_{11}O_{20}$ ($CeO_{1.82}$)

E.A. KUEMMERLE, G. HEGER, *J. Solid State Chem.*, **147** (1999), 485

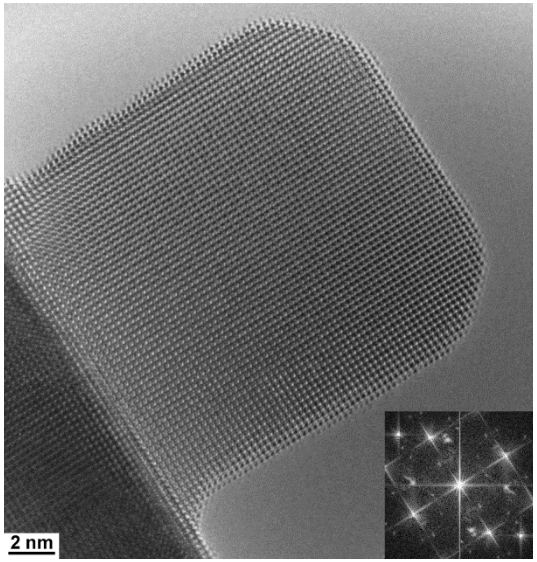
CeO_2 (CeO_2)

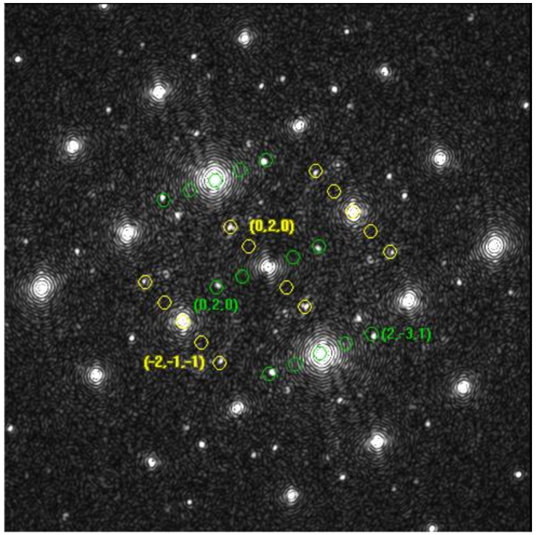




$a_{CeO_2} = 5.41$ Å

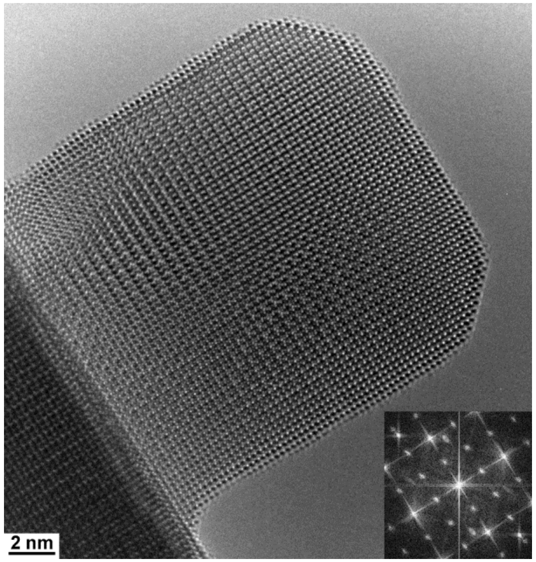
$Ce_{11}O_{20}$ ($CeO_{1.82}$)

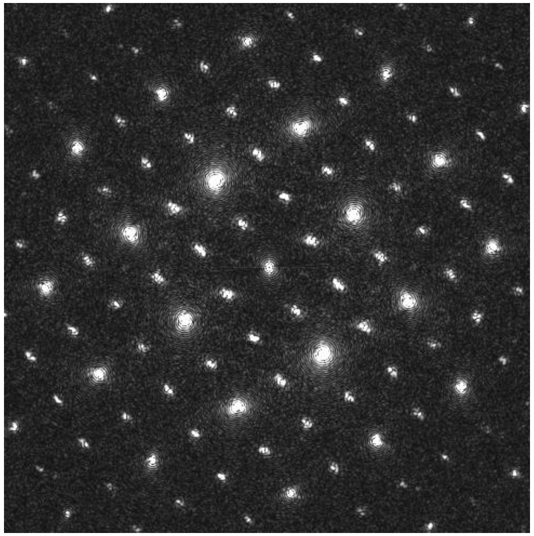




P-1: a = 6.757, b = 10.26, c = 6.732 Å, α = 90.04, β = 99.8, γ = 96.22°

Ce_4O_7 ($CeO_{1.75}$)

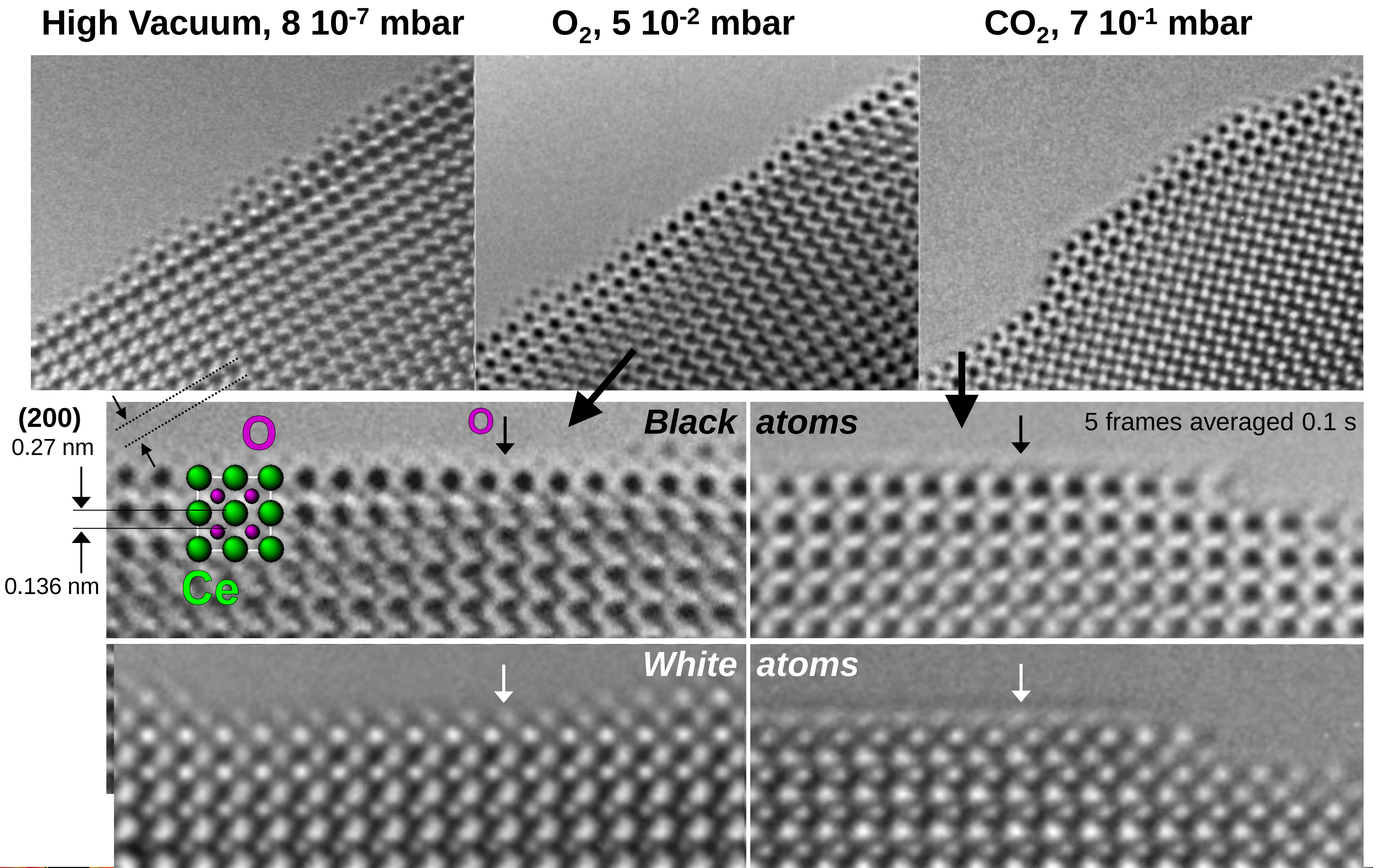




$a_{Ce_4O_7} = 5.53$ Å $\approx a_{CeO_2}$

Surface effects: 'gas-control' of the atomic mobility in ETEM

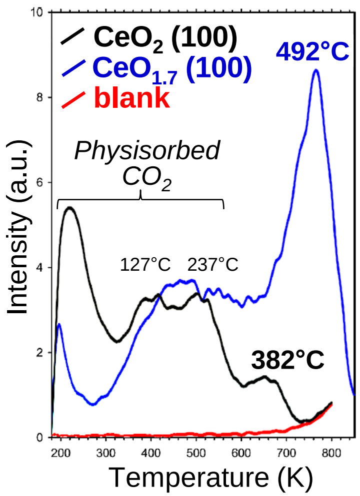
{100} surfaces: chemical nature and stability under different atmospheres

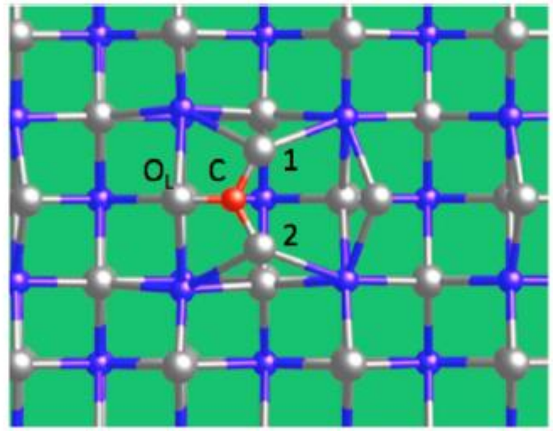


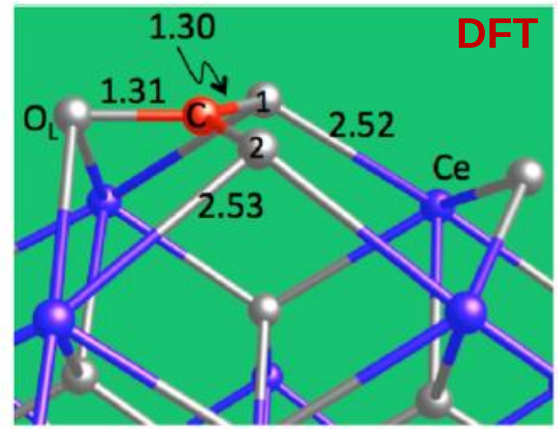
Detection of chemisorbed CO_2 as ‘flat-lying’ tridentate carbonates

- **Absorption of CO_2 as carbonates on CeO_2** P. ALBRECHT et al., *J. Phys. Chem. C*, **118** (2014) 9042

TPD (mass spectroscopy)





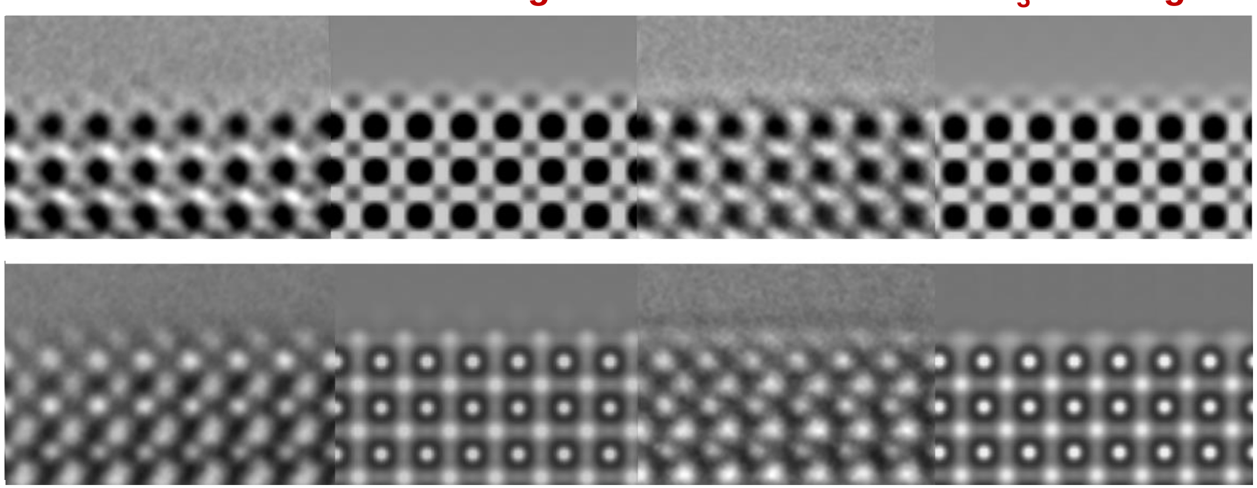


- ***Indicative*** **HREM simulations of edge-on {001} surface covered by CO_2 units**

O_2 5 10^{-2} mbar **O-coverage** **CO_2 7 10^{-1} mbar** **CO_3-coverage**

δf = - 6 nm

δf = + 1 nm



[001], t = 4 nm, Cs = 5 µm

Desorption of carbonates at high temperature

- **Desorption of flat tridentate carbonates between 382 and 492°C** P. ALBRECHT et al., (2014)

Sequence 15 s (speed x3), frames 0.125 s *(3 averaged)*

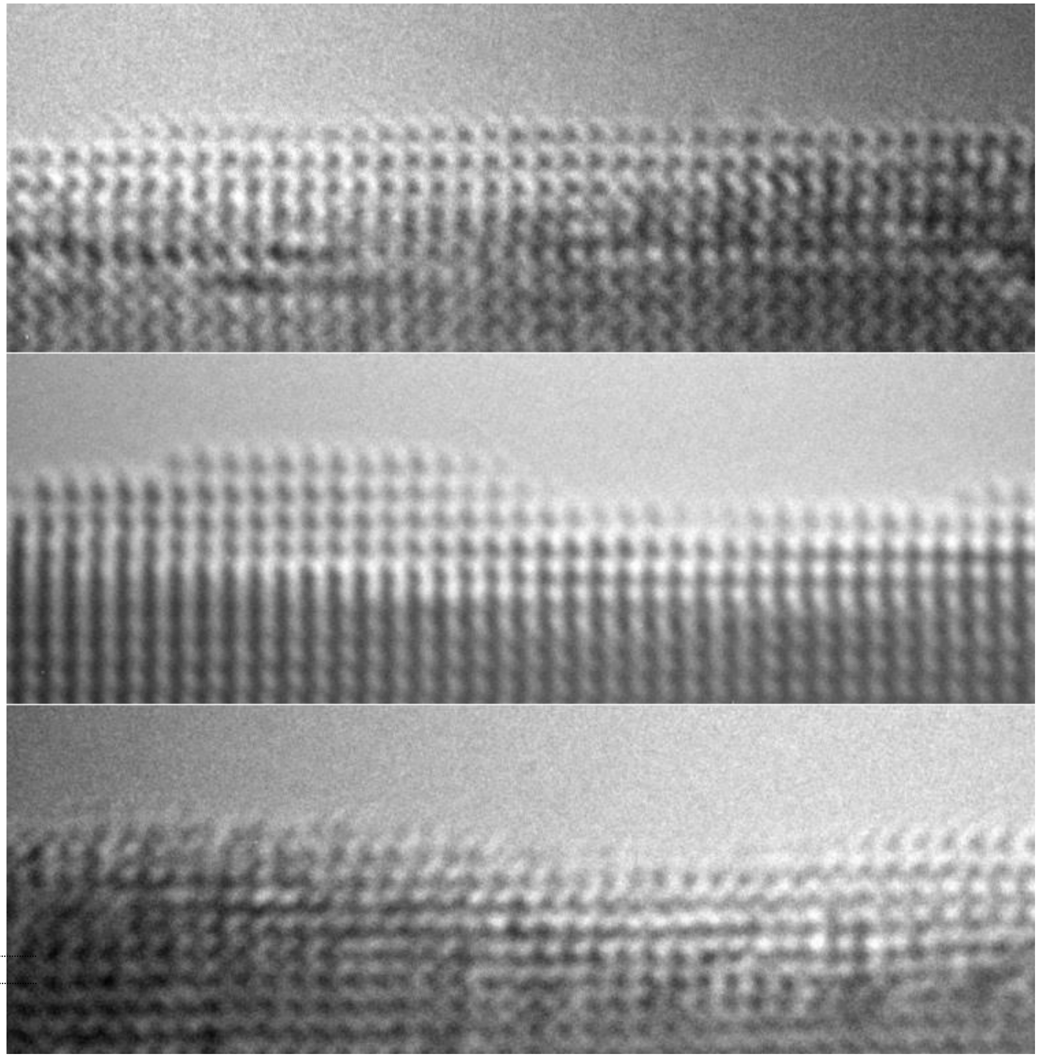
(6 averaged)

[001]

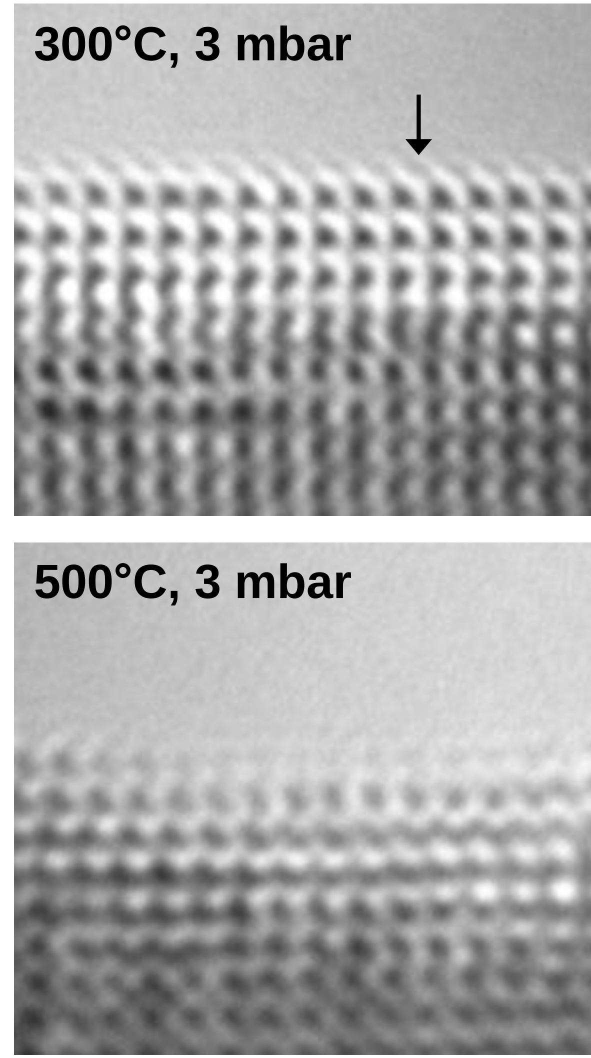
300°C, 3 mbar CO_2

400°C, 3.7 mbar CO_2

500°C, 3 mbar CO_2



0.272 nm



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Consortium Lyon – St-Etienne de Microscopie *www.clym.fr*

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access to the EtTEM *www.metsa.fr*