Atomistic simulations of the crystalline-to-amorphous transformation of γ-Al_2O_3 nanoparticles: Delicate interplay between lattice distortions, stresses, and space charges

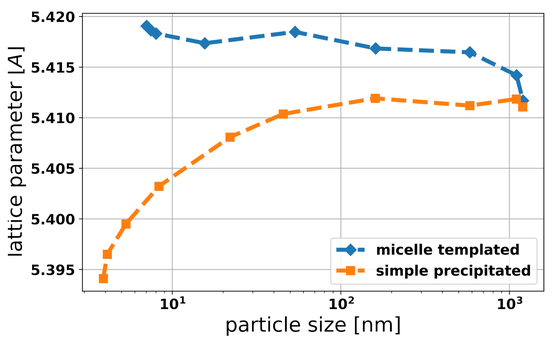
Simon Gramatte[1,2], Olivier Politano[2], Angelos Xomalis[1], Lars Jeurgens[1], Florence Baras[2], Vladyslav Turlo[1]

[1] Empa - Swiss Federal Laboratories for Materials Science and Technology, Duebendorf and Thun, Switzerland

[2] Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS, UBFC, Dijon, France

Marvel Group Leaders: Vladyslav Turlo (vladyslav.turlo@empa.ch)

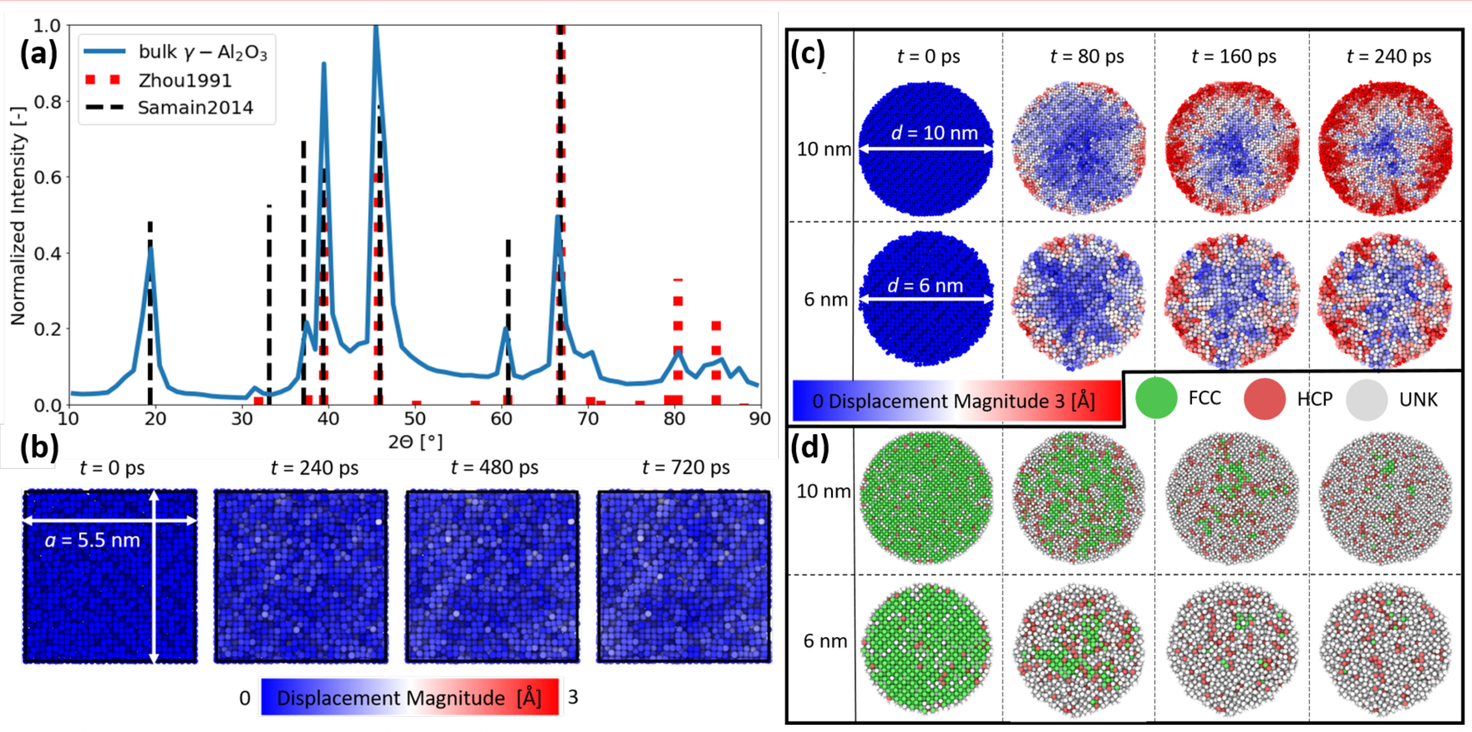
Introduction



Lattice constant of CeO_2 versus the nanoparticle size. The diamond and triangle symbols show two different synthesis methods (wet chemistry). Adapted from [1]

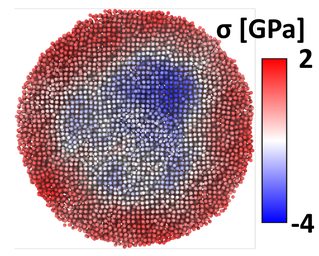
- Aluminum oxide nanoparticles (NPs) are of great relevance in catalytic reactions and oxide-dispersed strengthening of metal matrix composites, particularly applied in metal additive manufacturing [2].
- Al_2O_3 structure and related properties are mainly dependent on the synthesis and post-processing route [3].
- Size-dependent expansion and contraction were detected for NPs made of ionic compounds [4].
- Despite the importance of the lattice constant in thermodynamic, chemical, and electronic properties, the physical origin of expansion and contraction in NPs are discussed controversially [5].
- Diehm *et al.* hypothesized that negative surface stress could be a key reason for lattice expansion [5].

Thermal stability of γ-Al_2O_3 bulk *vs* NPs



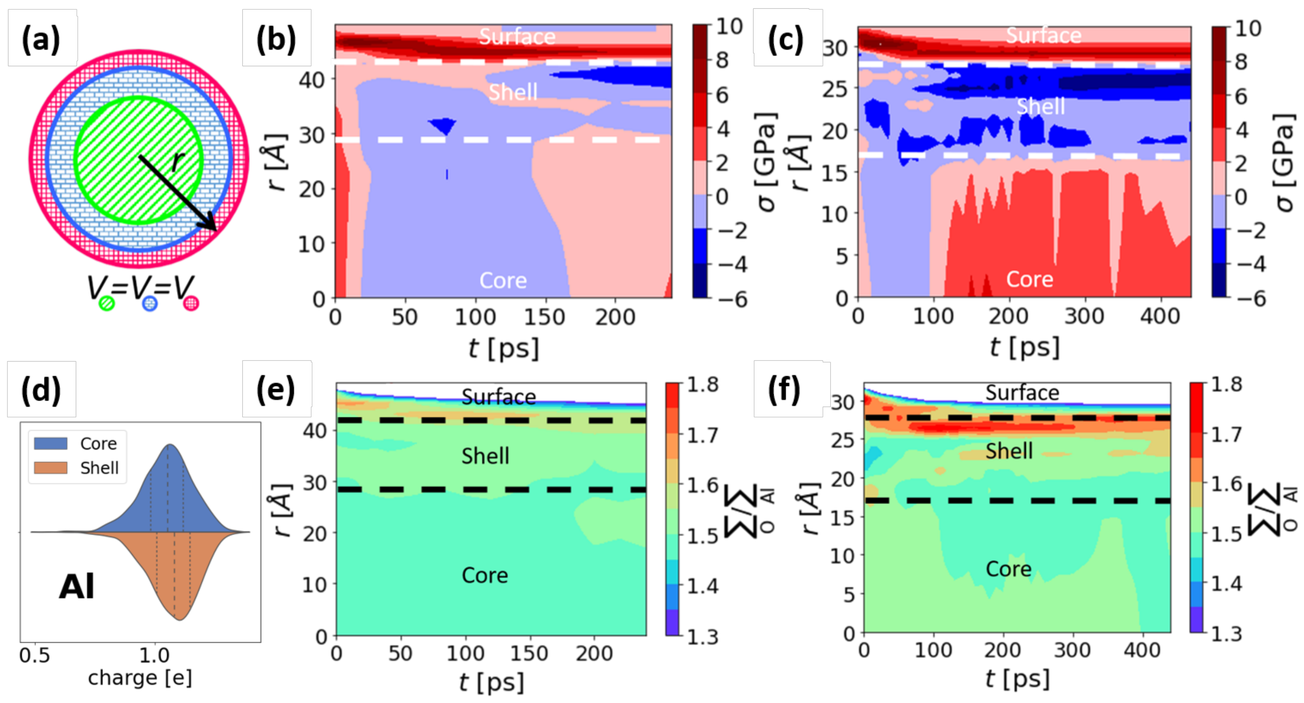
(a) Virtual XRD of bulk γ-Al_2O_3 equilibrated in LAMMPS with COMB3 potential at room temperature compared with two experimental references. (b-c) Computed atomic displacements in γ-Al_2O_3 bulk (b) and NPs (c) equilibrated at 900 K. (d) Ackland and Jones structural analysis of the O-sublattice for NP cross-sections shown in (c)

- COMB3 interatomic potential is one of the most advanced empirical model for Al_2O_3, fitted to extensive DFT database [6] and matching experimental observations such as:
  - γ-Al_2O_3 XRD patterns at room temperature (a)
  - metastability of bulk gamma-Al_2O_3 at 900 K (b)
  - amorphization of gamma-Al_2O_3 NPs starting from the NP surface (c,d)
- The presence of surface stress and Laplacian pressure in Al_2O_3 NP can be confirmed by analyzing the local hydrostatic stress



Local hydrostatic stress σ in 10 nm NP equilibrated at $T = 900$ K for $t = 80$ ps

Stress development in Al_2O_3 NPs



(a) The schematic of radial binning with equal particle number/slice volume in NPs. (b,c) The radial distribution of hydrostatic stress time-averaged over each 1 ps for (b) 10 nm and (c) 6 nm NPs. (d) Charge distribution for Al atoms. (e,f) The radial distribution of O fraction time-averaged over each 1 ps for (b) 10 nm and (c) 6 nm NPs.

- The radial distribution of the hydrostatic stress (a-c) evolves first to classical Laplace pressure with compression in the core of the NPs followed by the transition to tensile (positive) stress during the NP amorphization, with a compressive shell separating the core and the surface.
- Such shell relaxation before reaching the bulk-like core has recently been suggested in theory [7] and in some experiments [8].
- The origin of the tensile stress in the core lies in the charge disbalance in the Al cations between the core and the shell (d).
- The charge disbalance is caused by the segregation of Al from the shell to the NP surface (e,f). This disbalance is independent of the initial charge at the NP surface.

TAKE-HOME MESSAGE

- The contradictory experimental observations indicating the expansion of metal oxide nanoparticles with size reduction can be finally explained by cation segregation to the surface, resisting the Laplace pressure caused by surface stress

ACKNOWLEDGMENTS

We thank SNSF and NCCR MARVEL for financial support, and GENCI(FRANCE) and CSCS(Switzerland) for computing resources.

REFERENCES

[1] L. Chen et al., *J. Phys Chem C*, 114 (2010) 12909
[2] R. Prins, *J. of Catalysis*, 392 (2020) 336-346
[3] H. Knözinger et al., *Catal. Rev. Sci. Eng.*, 17(1) (1978) 31-70
[4] A. Cimino et al., *J. Am. Cer. Soc.*, 49(3) (1965) 152-156
[5] P. Diehm et al., *ChemPhysChem*, 13(10) (2012) 2443-2454
[6] K. Choudhary et al., *J. Phy. Con. Mat.*, 27(30) (2015) 0-10
[7] D. Holec et al., *I. J. Sol. Struc.*, 224 (2021) 111044
[8] J. Zhou et al., *Nature*, 570(7762), 2019 500-503

Swiss National Science Foundation

The National Centres of Competence in Research (NCCR) are a funding scheme of the Swiss National Science Foundation