

Supporting Information

The accuracy and reliability of all atomistic computer simulations rests ultimately with the quality of the potentials describing the interactions between component ions. Critically, at interatomic separations away from equilibrium, the potential model *may* prove less accurate. Accordingly, simulations which involve atoms moving far from equilibrium may proffer erroneous results. To eliminate the possibility that our predicted fluorite-to-rutile phase change is an artefact of the potential model, rather than the actual phase space, we provide quantitative evidence (below) to show that the potential used in this present study was accurate in the region of phase space probed by our simulations:

As alluded to in the manuscript, a particularly exacting test of how accurately the force field maps the potential hypersurface is to simulate the crystallisation of a nanoparticle starting from a molten precursor. In particular, previously we showed that the potential model for ceria, used in this present study, was capable of simulating, in quantitative agreement with experiment, an amorphous to crystalline phase change.¹ During the simulation both the structure and interatomic distances are far from equilibrium as observed in the parent fluorite-structured material. In the figure below, we show the calculated Radial Distribution Function (RDF) of the Ce-O interatomic distances for the amorphous particle. In particular, the average nearest neighbour Ce-O interatomic separation is about 2.4 Å and ranges from 2.0 Å to over 3.0 Å. The peaks are very broad with no long-range order – indicative of an amorphous structure. Superimposed on the figure are the calculated RDF for the unstrained CeO₂ [110] nanorod and the strained CeO₂ [110] nanorod; the latter rod exhibits CeO₂ conforming to the rutile polymorph. Average nearest neighbour Ce-O bond distances, taken from the figure are, 2.33 Å (min 2.0 Å max 2.7 Å) for the unstrained nanorod and 2.25 Å (min 1.9Å, max 2.7Å) for the tensioned nanorod. Clearly, the peak structure (sharpness of peak) and interatomic

¹ Feng, X. D.; Sayle, D. C.; Wang, Z. L.; Paras, M. S.; Santora, B.; Sutorik, A. C.; Sayle, T. X. T.; Yang, Y.; Ding, Y.; Wang, X. D.; Her, Y. S. *Science* **2006**, 312, 1504-1508

separations for the tensioned nanorod are far nearer to the parent material compared with the amorphous nanoparticle. Accordingly, that the potential model is sufficiently accurate and robust to simulate the amorphous to crystalline (fluorite) phase change, where structure and bond distances are far from equilibrium, with quantitative agreement with experiment, then we argue that it is sufficiently robust to similarly simulate the fluorite-to-rutile phase change, where the differences in both structure and bond distances are profoundly smaller.

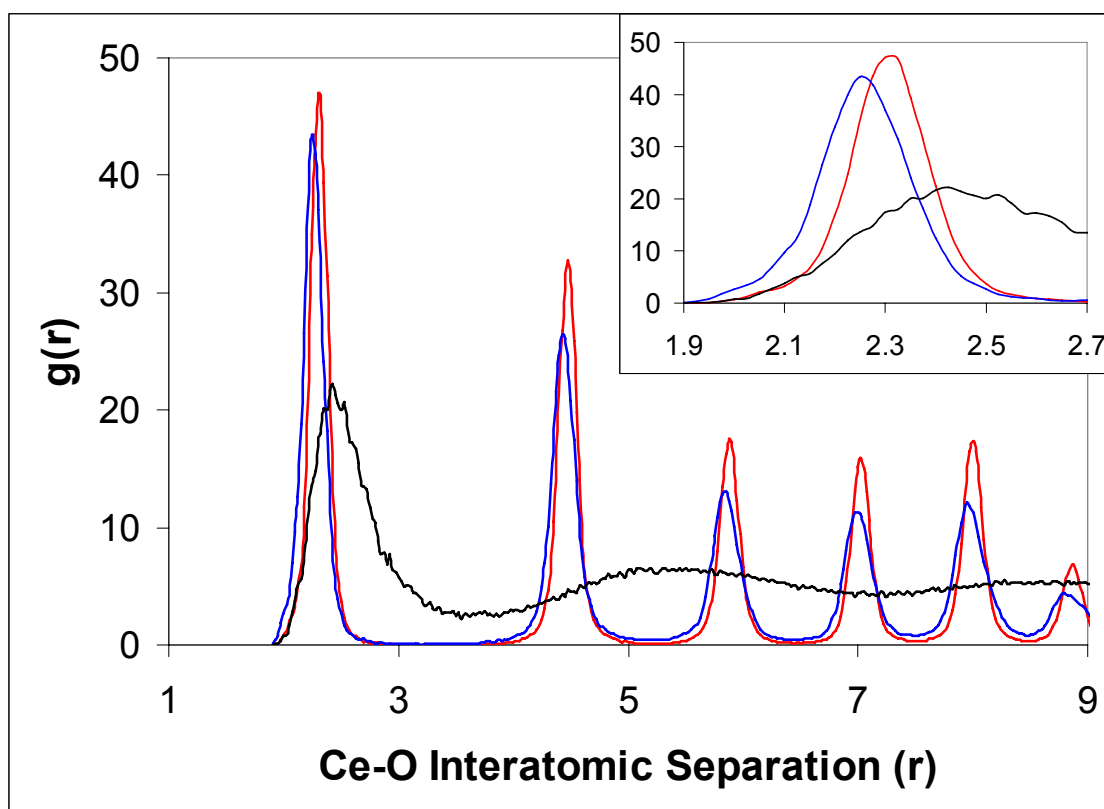


Figure S1 Calculated RDF for the amorphous CeO_2 nanoparticle (black trace), the untensioned CeO_2 [110] nanorod (red trace) and the tensioned CeO_2 [110] nanorod, which comprises rutile-structured CeO_2 (blue trace). Inset shows an enlarged region of the main figure.