A DFT study of new zirconia bulk phases and the stability of thin zirconia films

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Zirconium dioxide has been intensively studied due to its huge potential in various applications. Bulk ZrO2 and thin films can be used as an electrolyte in solid-oxide fuel cells, an oxygen gas sensor or as a catalyst for methanol synthesis. Furthermore, recent studies report several meta-stable zirconia phases relevant for the thin films applications [1][2].

We therefore used the Vienna Ab-Initio Simulation Package (VASP) to perform DFT calculations comparing the performance of GGA, meta-GGA, vdW-DF, hybrid and RPA approaches in order to investigate the structural stability of the known stable and meta-stable bulk phases and derived slab configurations. We provide a comprehensive study of three experimentally-observed phases (cubic, monoclinic and tetragonal) and also include several meta-stable bulk phases. All functionals reproduce the experimentally found order of stability (monoclinic, tetragonal, cubic) and we present two new meta-stable phases. We called the first one meta-monoclinic, which is more stable on standard DFT (GGA) level than the tetragonal phase, but is still less stable than the monoclinic ground state. Using more advanced functionals such as meta-GGA or RPA, the meta-monoclinic phase is calculated to be 15-30 meV / f.u. less stable than the tetragonal phase. The second phase is structurally similar to anatase titania and its stability depends on the chosen functional, varying from 20 meV / f.u. for GGA to 220 meV / f.u. for meta-GGA, hybrid and vdW-DF functionals with respect to the monoclinic ground state.

We also present PBE calculations of the stability of thin zirconia films derived from the different bulk phases. We will discuss the dependence of the surface energy and the layer thickness on the film stability.

References:

[1] D. S. Aidhy et al, *The Journal of Physical Chemistry C*. 2014, **118**(51)

[2] R. Materlik et al, *Journal of Applied Physics*. 2015, **117**(13)