Electronic Supplementary Information

A new computational strategy to calculate the surface energy of a dipolar crystal surface

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Computational Details

The *ab initio* CRYSTAL14 code[1,2] was employed, which implements the Hartree-Fock and Kohn-Sham self-consistent field (SCF) method for the study of periodic systems.[3] The simulations were performed by using the 2D periodic slab model, consisting of a film formed by a set of atomic layers parallel to the *hkl* crystalline plane of interest.[4]

All the calculations were performed at the DFT (Density Functional Theory) level. In the Density Functional approach, the B3LYP Hamiltonian was adopted,[5-7] which contains a hybrid Hartree-Fock/Density-Functional exchange term and already shown to provide accurate results for structural and dynamical properties of hydroxyapatite.

In CRYSTAL, the multi-electronic wave-function is constructed as an anti-symmetrized product (Slater determinant) of mono-electronic crystalline orbitals (COs) which are linear combinations of local functions (i.e.: atomic orbitals, AOs) centered on each atom of the crystal. In turn, AOs are linear combinations of Gaussian-type functions (GTF, the product of a Gaussian times a real solid spherical harmonic to give *s*-, *p*- and *d*-type AOs). In this study, zinc and oxygen were described by (8*s*)-(64111*sp*)-(41*d*) and (8s)-(411*s*)−(1*d*) contractions, respectively.

The thresholds controlling the accuracy in the evaluation of Coulomb and exchange integrals (ITOL1, ITOL2, ITOL3, ITOL4 and ITOL5, see Dovesi *et al.*[2]) were set to 10^{-8} (ITOL1 to ITOL4) and 10^{-16} (ITOL5). The threshold on the SCF energy was set to 10^{-7} Hartree.

In the adopted package the DFT exchange and correlation contributions are evaluated by numerically integrating functions of the electron density and of its gradient over the cell volume. The choice of the integration grid is based on an atomic partition method, originally developed by Becke.[8] In the present study, a *pruned* (75, 974) *p* grid was adopted (XLGRID in the code[2]), which ensured a satisfactory accuracy in the numerically integrated electron charge density.

The reciprocal space was sampled according to a Monkhorst-Pack mesh[9] with shrinking factor 4 and 6, corresponding to 10 **k** and 20 **k** points in the first irreducible Brillouin zone, for the five-layers and nine-layers (00.1)-O slab, respectively.

Structures were optimized by using the analytical energy gradients with respect to atomic coordinates and lattice parameters within a quasi-Newton scheme, combined with the Broyden-Fletcher-Goldfarb-Shanno scheme for Hessian updating.[10-12] Convergence was checked on energy, gradient components and nuclear displacements. The threshold on energy between two subsequent optimization steps was set to 10^{-4} and 10^{-7} Hartree, for the nine-layers and five-layers (00.1)-O slab, respectively; the thresholds on the root-mean-square of the gradient components and of the nuclear displacements were set to $3.0 \cdot 10^{-4}$ Hartree bohr^{-1} and $1.2 \cdot 10^{-3}$ bohr, respectively; those on the maximum components of the gradients and displacements were set to $4.5 \cdot 10^{-4}$ Hartree bohr^{-1} and $1.8 \cdot 10^{-3}$ bohr, respectively.

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