Electronic Supplementary Information

Theoretical equilibrium shape of Hydroxyapatite, revised.

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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 crystal surfaces were simulated 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, phosphor, oxygen and hydrogen were described by (8*s*)-(521*sp*)-(1*d*), (6*s*)−(31*sp*)−(1*d*) and (31*s*)−(1*p*) contractions, respectively. The exponents (in bohr^{-2} units) of the most diffuse *sp* shells are 0.135 (P) and 0.274 (O); the exponent of the single Gaussian *p* shell is 1.100 (H); the exponents of the single Gaussian *d* shell are 0.746 (P) and 0.538 (O).[8] For calcium atoms, the first 10 electrons were described with the Hay−Wadt small corepseudo-potential, [HAYWSC]-(31*sp*). A double split valence basis set of GTFs was employed for describing the remaining 10 electrons, with 0.500 bohr^{-2} as the exponent of the most diffuse *sp* shell.[8]

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^{-18} (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.[9] 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[10] with shrinking factor 4, corresponding to 10 **k** points in the first irreducible Brillouin zone.

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.[11-13] Convergence was checked on energy, gradient components and nuclear displacements. The threshold on energy between two subsequent optimization steps was set to 10^{-7} Hartree; 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.

The specific surface energy γ (erg/cm^2) at T = 0K was calculated by using the relation:[4]

$$\gamma = \lim_{n \to \infty} E_s(n) = \lim_{n \to \infty} \frac{E(n)_{slab} - nE_{bulk}}{2A} \quad (1)$$

where $E(n)$ and E_{bulk} are the energy of a *n*-layer slab and of the bulk, respectively; *A* is the area of the primitive unit cell of the surface; the factor 2 in the denominator accounts for the upper and lower surfaces of the slab. $E_s(n)$ is thus the energy (per unit area) required for the formation of the surface from the bulk. As more layers are added in the calculation ($n \to \infty$), $E_s(n)$ will converge to the surface energy per unit area (γ).

The CRYSTAL14 output files, listing the optimized fractional coordinates and optimized 2D cell parameters of $(10\bar{1})$, (102) and $(\bar{1}04)$ slabs, are freely available at http://mabruno.weebly.com/download). All of these slabs are charge neutral and retain the centre of inversion, to ensure that the dipole moment perpendicular to the slab is equal to zero.

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Table S1 Surface energy at 0K of the $\{10\bar{1}\}$, $\{102\}$ and $\{\bar{1}04\}$ surfaces. The terminations A and B described in the main text, were also considered for the $\{10\bar{1}\}$ and $\{102\}$ crystal faces.

Face	γ (erg cm^{-2})
$\{10\bar{1}\}_A$	1357
$\{10\bar{1}\}_B$	1753
$\{102\}_A$	1364
$\{102\}_B$	1873
$\{\bar{1}04\}_A$	1373