Poster Presentation

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Theoretical Equilibrium Morphology and Twin Energy of Monoclinic Hydroxyapatite

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Microsized hydroxyapatite (HAp), we synthesized under mild hydrothermal conditions, shows both monoclinic and hexagonal polymorphs made by rod-shaped single crystals along with simple and multiple twins. The theoretical morphology, obtained through the Hartman-Perdok analysis on the $P2_1/c$ polymorph, allowed to predict the stable surfaces of the main {hkl} forms. Their surface energies have been evaluated, at 0 K, by ab initio quantum-mechanical calculations. The resulting HAp equilibrium shape (ES) [1] is dominated by a pseudo-hexagonal prism formed by the the {001}, {100} and {-102} forms (having close energy values), all developing around the OH channels of the structure. The basal {010} form truncates the pseudo-hexagonal prism perpendicularly to the OH channels, while three other less important prisms {012}, {110} and {11-2}, lying in between the pseudo-hexagonal prism and the basal pinacoid, enter the ES. A simple kinetic model based on 2D nucleation is proposed to explain the morphology of the single crystals [1]. Assuming [2, 3] that the simplest twin law for the monoclinic phase is generated by a threefold rotation about the 2_1 axis, we found that the three original composition planes (OCP) of the twin coincide with the faces of the {001}, {100} and {-102} forms. For each OCP there are two different surface terminations, according to whether the frontier between parent (P) and twinned (T) crystals intercepts (or not) the centers of mass of PO_4 and Ca ions and of the O atoms of the OH groups. We examined, as an example, the two kinds of interfaces for the twin (100)P/(001)T. The calculated twin energies result to be very close and low (3.3 and 4.2 erg cm^{-2}), when compared to the value of the HAp surface energy in the [010] zone (≈ 1500 erg cm^{-2}). This means that the probability of formation of a 2D-nucleus oriented in twin position on all the [010] zone is practically equivalent to that needed to generate a normally oriented 2D nucleus in the same zone

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