

Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is known to be an important material for repairing of damaged parts of bone and teeth. It has also been used as an adsorbent of metals and toxic waste due to its remarkable ion exchange capacity. Among metal substituents, Zn plays an important role in biological application, since it has been found beneficial in stimulating bone growth. Information on the surface structures of hydroxyapatite (HAP) is therefore of great importance for understanding of dissolution and interactions with the ambient. Recently, Xiaoyan Ma et al. [Xiaoyan Ma, D. Ellis, *Biomaterials*, **29**, 257-265(2008)], using first principles periodical DFT methodology to calculate geometric relaxation, proposed slab-models of pure and Zn-doped (001) HAP surfaces to study the adsorption energetics and occupation distribution of this metal on the two inequivalent Ca sites present in the hexagonal HAP structure. The Ca2 vacancy site was found to be energetically more favorable than Ca1, in opposition to predictions based on ionic radius and electronegativity differences. Although their results point out to the importance of Zn interaction with its near atomic surroundings, a study in this direction has not yet been done. The understanding of the preferential site of Zn in HAP surfaces is still an open issue. In this work, a detailed theoretical electronic structure study is performed on slab models of 001 surfaces of Zn-doped HAP. By using an all-neighbors, non-orthogonal basis, tight-binding method, with lower computational cost than the DFT approach, band structure, density of states, charge distribution and bonding are calculated, to determine the effects of local environment on the electronic properties of the system. The tight binding method has already been found to be well suited to describe the electronic structure of different apatite compounds [M. Matos, J. Terra, D. Ellis, *Int. J. Quantum Chem.*, **109**, 849-860(2009)]. Preliminary results show that, when substituting Ca at site 1, the calculated bond order of Zn with oxygen (0.483) is higher than that of Ca with oxygen (0.411), indicating stronger covalency. In the band structure, deep surface states appear due to Zn 4s states. Atomic charge of substituted Zn (+1.49e) is smaller than that of Ca (+1.60e), consistent with the higher covalent character of Zn-O bonding. A complete analysis of the effects of Zn substitution, on Ca sites 1 and 2, the energy dependent density of states and bond order (COOP) curves, atomic charge distribution and bond orders of other cation-anion pairs in the surface slab will also be presented and discussed.