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First Principles Studies of Hydroxyapatite Structure and Properties

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Keywords – Hydroxyapatite, *ab initio* and semi-empirical calculations, molecular modeling, properties and surface peculiarities.

I. INTRODUCTION

Results of first principles calculations of Hydroxyapatite (HAP) nanostructures in combination with computational molecular modeling by various methods are presented. The detailed explorations of the bulk and surface HAP properties are analyzed in this review. HAP structures and properties were studied from first principles approaches using *ab initio* Local Density Approximation (LDA) method in combination with various quantum-chemical (QM), including semi-empirical (PM3, etc.), Density Functional Theory (DFT) and molecular mechanical (MM+, OPLS, BIO CHARMM) methods from HypemChem 7.5/8.0 package. The optimizations of lattice parameters and atoms positions were performed for hexagonal and monoclinic HAP structures with different orientation of hydroxyl group in HAP OH-channels.

II. RESULTS

The obtained structural and energy LDA data allow us to compute HAP bulk modulus: $B \sim 82$ GPa for used Ca-pseudopotential and wave function with 2 electrons of the shell approximation (WF1); and $B \sim 96$ GPa for 10 electrons of the shell approximation with involved d-electrons (WF2) of Ca atoms. These data are well comparable with known experimental and calculated data. On this base we calculated the density of state (DOS) for several approximations with different charges Q of bulk lattice unit cell. For initial state with $Q = 0$ we obtain the value of forbidden zone gap $E_g = 5.68$ eV for WF1 and $E_g = 5.44$ eV for WF2. These results are good agreement with experimental and computed data and well correspond to that fact, that for case of WF2 with the involved 10 electrons, Ca atoms create most strong interactions in the HAP nanostructures. The biggest value of bulk modulus confirms this conclusion too. From other side obtained data allow us to make the first estimation of the influence of bulk charges on the surface charged state of HAP structures and the changes in the HAP work function. It is necessary for further detailed study of the established most strong interaction of charged HAP surface with living cells (such as, e.g., with osteoblasts in bone tissues). Another task of this our work was focused on the using of the computed *ab initio* structural HAP data with variation of lattice parameters for modeling of the interaction of HAP with citrate species at the different concentrations (ratio [Citrate:Ca]). Obtained data show clearly the positioning of the interacting sites for citrates molecules on the HAP surface and allow us to propose the new mechanism for the formation of the various HAP nanostructure shapes under influence of various citrate quantities in the initial starting solution for HAP precipitation. Additionally, in this work the new computed data for HAP

nanoparticles with size and shape variations, which are used for modeling of its interactions with carbon nanotubes was analyzed. These data are very important for further multifunctional nanotechnological and biomedical applications of HAP nanostructures.

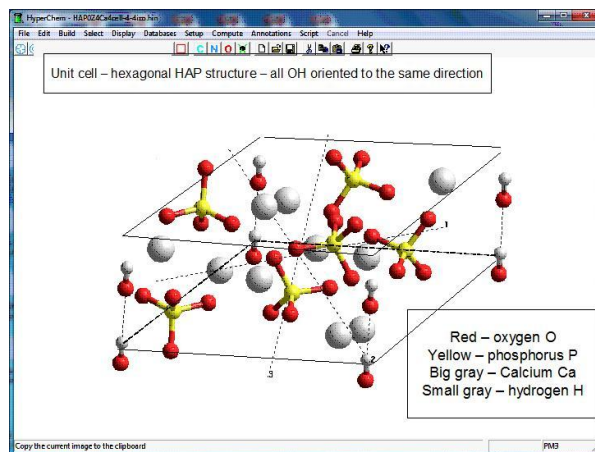


Fig.1. AIMPRO optimized models of hexagonal HAP unit cell structure in molecular HyperChem image's presentation.

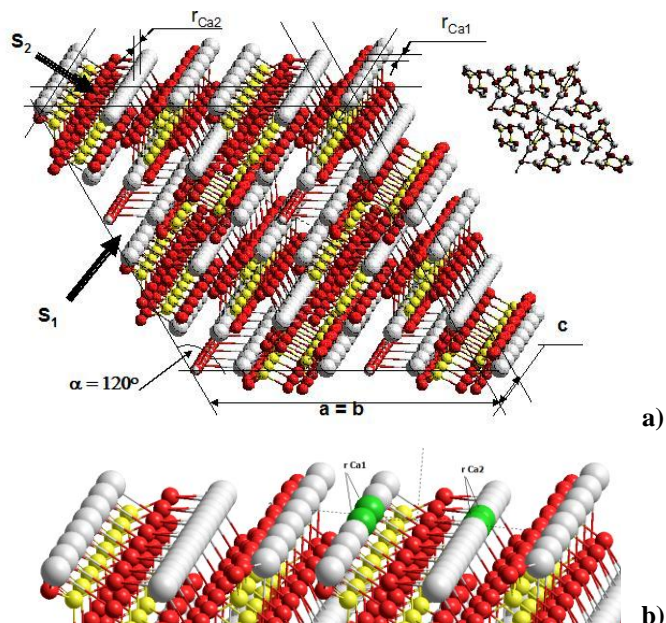


Fig.2. Molecular model of HAP cluster constructed in the HyperChem on the base of preliminary AIMPRO optimized crystal structure and all atomic positions: a) iso-projection image, b) main Ca positions on HAP surface (Ca1 and Ca2).

V. REFERENCES

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