

## **DFT investigation of structural and vibrational properties of type B and mixed A-B carbonated hydroxylapatite**

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### **ABSTRACT**

In nature, hydroxylapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] is mostly present with various stoichiometric defects. The most abundant is the carbonate ion that can occupy different crystallographic sites (namely A and B types), however, its effects on the apatite structure is still an object of debate.

Type A carbonated apatite was quantum mechanically simulated in a previous study, here we extend the simulation to bulk structural and vibrational features of Na-bearing type B and mixed type A-B carbonated hydroxylapatite [ $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_{x+y}(\text{OH})_{2(1-y)}$ , space group  $P1$ ]. The simulation has been performed by ab initio density functional methods. The geometry of the models (lattice parameters and internal coordinates) have been fully optimized exploring different positions of the sodium ion in the apatite unit cell. The results, in agreement with XRD data, suggest that in each crystallographic cell in the biological mineral there is at least one calcium ion substitution or vacancy per cell. The carbonate ion presence in the apatite structure is in good agreement with biological/chemical data. Furthermore, there is also a very good agreement with FTIR data reported in literature.

**Keywords:** Type B carbonated hydroxylapatite, type A-B carbonated (hydroxyl) apatite, structure, IR, DFT, B3LYP