

## **Periodic ab initio bulk investigation of hydroxylapatite and type A carbonated apatite with both pseudopotential and all-electron basis sets for calcium atoms**

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### **ABSTRACT**

Apatite minerals draw the attention of many researchers not only in mineralogy, but also in biology, biochemistry, and medicine because hydroxylapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>] is the main component of the mineral phase of mammalian bones. However, in nature this mineral is mostly present with various stoichiometric defects. The carbonate ion is found commonly in its structure where it can occupy different crystallographic sites; however, its configurational energy and relative orientation in the apatite lattice is still debated.

In this work, bulk structural features of hexagonal hydroxylapatite (space group *P6<sub>3</sub>*) and type A carbonated apatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(CO<sub>3</sub>), space group *P1*] have been modeled by density function method using the hybrid B3LYP functional and an all-electron polarized double- $\zeta$  quality Gaussian-type basis set using the CRYSTAL09 computer program. The effect on the structural parameters due to the adoption of the present all-electron basis set for the Ca ion compared to the pseudopotential adopted in previous work has also been discussed. Different orientations of the carbonate ion in the apatite unit cell have been considered. The B3LYP functional and Gaussian-type basis set with polarization have been adopted. The geometry of the model (lattice parameters and internal coordinates) has been fully optimized and resulted in very good agreement with XRD data reported in literature that suggest a “close” configuration (type A1) of the carbonate ion, i.e., with a C-O bond perpendicular to the *c*-axis of the apatite cell.

**Keywords:** Hydroxylapatite, type A carbonated apatite, periodic ab initio quantum mechanics, DFT