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 \([\text{Ca}_{10},\text{Na},(\text{PO}_4)_{6-2x}(\text{CO}_3)_{x+y}(\text{OH})_{2+y}]\), 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

INTRODUCTION

Hydroxylapatite \([\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]\); OHAp) is commonly found in all igneous rocks and in some metamorphic and sedimentary ones and, also as the main component of the inorganic phase of bone, dentin and enamel tissues (Dorozhkin 2009c). For this reason, apatite minerals draw the attention of many researchers not only in mineralogy, but also in biology, biochemistry, and medicine. OHAp is considered a key-biomaterial in cements and prosthetics for tissue repairing/reconstruction (Dorozhkin 2009a, 2009b, 2009d).

In their first hierarchical level, biological hard tissues are characterized by the incorporation of minerals (inorganic phase) in a soft organic matrix of structural proteins, such as tropocollagen. The mineral phase is mainly given by hexagonal hydroxylapatite (space group \(P6_3/m\)), with parameters \(a = b\) and a calcium channel where there are two hydroxyl groups oriented with the same direction along the \(c\)-axis. This polymorph is thermodynamically unstable if compared to the monoclinic phase (space group \(P2_1/b\)) typically found in rocks because of the proton order imposed by the same OH alignment in the apatite channel. The disorder/order transition have been evaluated at 200 °C (Suda et al. 1995).

The biological hydroxylapatite is not a pure mineral, but presents vacancies and ionic inclusions/substitutions. The main substituting ion is the carbonate ion, with an average content of about 6% in weight. The carbonated hydroxylapatite (COHAp) accommodates the \(\text{CO}_3^–\) ion either in place of both hydroxyl group in the \(c\)-axis channel of apatite (type A defect) or the phosphate group (type B) (Astala and Stott 2005; Fleet 2009; Fleet and Liu 2003, 2004, 2007; Sturgeon and Brown 2009; Suetsugu et al. 1998). The two types of defects usually coexist in a solid solution and the order of occurrence of A and B defects were extensively studied (Kovaleva et al. 2009). In recent years, the interest in those defective structures has increased, because it is known that chemical modification of OHAp, in particular the incorporation of carbonate ions, results in a considerable influence on the mineralization, demineralization, and remineralization properties. Other properties, such as surface morphology and electrostatic potential, which influence interactions and adsorption processes at the mineral-organic interface in biological environment, could be affected by atomic substitutions, especially by the carbonate ion. Thus, obtaining accurate knowledge on the carbonate effects on both the apatite crystallographic cell and the surface leads to the possibility to design materials for prosthetic implants with improved biomimetic and bio compatible properties (Gibson and Bonfield 2002; Lafon et al. 2008; LeGeros 2002).

Many experimental and theoretical studies were conducted on both type A and type B carbonated defect to better understand the role of the \(\text{CO}_3^–\) ion on the structural variation and its spatial orientation within the OHAp cell (Astala and Stott 2005; Engin and Girgin 2009; Fleet and Liu 2004, 2005, 2007, 2008; Fleet et al. 2004; Gibson and Bonfield 2002; Kovaleva et al. 2009; Peeters et al. 1997; Peroes et al. 2006; Rabone and de Leeuw 2007; Suetsugu et al. 1998). Recently, we successfully investigated the structural and vibrational features of type A fully carbonated apatite (CAP) by a periodic quantum mechanics (QM) approach based on the hybrid B3LYP functional with an all-electron basis set (Ulian et al. 2013a, 2013b). The results showed that the pre-