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

Apatic minerals draw the attention of many researchers not only in mineralogy, but also in biology, biochemistry, and medicine because hydroxyapatite [Ca_{10}(PO_4)_{6}(OH)_2] 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_3) and type A carbonated apatite [Ca_{10}(PO_4)_{6}(CO_3)] 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 e-axis of the apatite cell.

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

INTRODUCTION

Apatic minerals are found in almost all igneous rocks and also in some metamorphic and sedimentary ones. The most important member of the apatite family, both as naturally occurring mineral and as synthetic compound, is hydroxyapatite OHAp [Ca_{10}(PO_4)_{6}(OH)_2]. As shown by X-ray diffraction (XRD) analysis performed by Suda et al. (1995), OHAp can be found in nature as two polymorphs: monoclinic [P2_1/b] or hexagonal [P6_3/m]. The monoclinic cell is obtained from the hexagonal one by doubling the b axis and contains hydroxyl columns with different OH orientations along the c-axis (Rabone and de Leeuw 2005). The hexagonal cell (a = b) is related to the monoclinic structure when the glide plane b is a mirror plane m and the twofold axis is a 6, axis (Corno et al. 2006). Suda et al. (1995) observed also that at low temperature, the monoclinic cell is more stable than the hexagonal one; the phase transition between the two polymorphs (order/disorder) takes place at 200 °C. The hexagonal OHAp is an extremely important phase, because it is the inorganic component of mammalian bone tissues. OHAp may contain a certain amount of compositional defects, the most abundant is the carbonate ion (CO_3^{2-}, ~6% in weight). The presence of CO_3^{2-} in the mammalian OHAp is necessary to stabilize the hexagonal structure at room temperature (Suda et al. 1995).

Since the first half of the 20th century, researchers were interested in the role of OHAp as a biomaterial for bone and tooth repair, reconstruction, and replacement (Albee 1920). However, to improve biocompatibility, the biomaterial should be similar to the bone tissue mineral phase, rather than to pure hydroxylapatite.

The structure of hexagonal OHAp allows extensive atomic substitution and non-stoichiometry in Ca, P, and OH channel sites. For example, anions such as fluoride, chloride, and carbonate can easily enter in the channel parallel to the c-axis, leading to fluoro-, chloro- and carbonate apatites, both as end-members and in mutual solid solutions (Elliott 1998; Hughes and Rakovan 2002). Many experimental works (Antonakos et al. 2007; Fleet 2009; Fleet and Liu 2003, 2004, 2007; Fleet et al. 2011; Sturgeon and Brown 2009; Suetsugu et al. 1998) and theoretical studies (Astala and Stott 2005; Peroos et al. 2006; Rabone and de Leeuw 2007; Stott and Yin 2003; Zahn and Hochrein 2008) have been done to better understand the role and the positions of CO_3^{2-} in the hydroxyapatite lattice. It appears that the carbonate ion can substitute both OH^- in the e-axis channel of apatite (type A) and the phosphate group (type B). This is suggested by Fourier transform infrared (FTIR) analysis showing that the normal modes...