Thermodynamic, elastic, and vibrational (IR/Raman) behavior of mixed type-AB carbonated hydroxylapatite by density functional theory

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Abstract

The present investigation reports the equation of state, thermodynamic, and thermoelastic properties of type AB carbonated apatite [CAP-AB, Ca₉₋₆(PO₄)₆(CO₃)₄, space group P1], as obtained from density functional theory simulations and the quasi-harmonic approximation. The static (0 K) third-order Birch-Murnaghan equation of state resulted in the parameters $K_0 = 104.3(8) \text{ GPa}$, $K' = 4.3(1)$, and $V_0 = 517.9(2) \text{ Å}^3$, whereas at room temperature (300 K) they were $K_0 = 101.98 \text{ GPa}$, $K' = 4.12$, and $V_0 = 524.486 \text{ GPa}$. Thermodynamics and thermoelasticity were calculated in the temperature range 0–800 K and between 0 and 30 GPa.

Furthermore, the dependence of the infrared/Raman spectra of type-AB carbonated apatite with pressure is also reported, which could be useful for researchers interested in vibrational spectroscopy. The theoretical results corroborate the few experimental ones on a similar type-AB carbonated hydroxylapatite and provide further details over wide pressure and temperature ranges on the elastic, thermodynamic, and infrared/Raman properties of this important mineral found in both geological and biological environments.

Keywords: Type-AB carbonated apatite, thermodynamic properties, elastic properties, density functional theory, quasi-harmonic approximation

Introduction

Since the pioneering work of Albee in the first half of the 20th century (Albee 1920), a continuous and still growing interest toward the role of hydroxylapatite [OHAp, Ca₁₀(PO₄)₆(OH)₂] as the mineral component of bone tissues has been recorded in scientific literature. The main goal of all the fundamental and applied research is the development of a biomaterial for bone and tooth repair, reconstruction, and replacement. OHAp is widely used in biomedical applications such as bone augmentation and regeneration, orthopedic applications, and tooth repair, reconstruction, and replacement. OHAp is the mineral component of bone tissues and is well-established as the mineral component of bone tissues has been recorded in scientific literature. The main goal of all the fundamental and applied research is the development of a biomaterial for bone and tooth repair, reconstruction, and replacement. OHAp is widely used in biomedical applications such as bone augmentation and regeneration, orthopedic applications, and tooth repair, reconstruction, and replacement. OHAp is found in bony tissues in its hexagonal polymorph (space group $P6_3/m$), presenting a calcium channel with two hydroxyl groups oriented in the same direction along the c-axis. However, from the thermodynamics point of view, hexagonal hydroxylapatite is less stable than its monoclinic phase (space group $P2_1/b$) commonly found in igneous rocks, which is explained by the different OH alignment in the apatite channel. The monoclinic/hexagonal transition has been evaluated to occur at 200 °C at ambient pressure (Suda et al. 1995).

It is a well-established fact that bony tissues do not contain stoichiometric hydroxylapatite, but the so-called “bone apatite,” a mineral presenting a complex crystal-chemistry with general formula (Ca,$X$)$_{10}$(PO$_4$)$_6$(OH,$Z$)$_2$, where $X$ = Na$, Mg^{2+}$, Pb$^{2+}$ represents some cationic substitution and $Y$ and $Z$ anionic ones, such as CO$^-$ (Dorozhkin 2009). In addition, even neutral molecules, such as water, may enter the mineral structure. As mentioned, among the several possible anionic substitutions, carbonate ion ones represent the most common, accounting for up to about 6 wt% in bone mineral. Depending on the crystal site occupied by the carbonate anion, the substitution is called type-A if it involves the hydroxyl groups (Z):

$$2\text{OH}_{(\text{cell})} + \text{CO}_3^{2-} \rightarrow \text{CO}_3^{2-}_{(\text{cell})} + 2\text{OH}^-.$$  

The above reaction accounts for the charge neutrality of the system by considering the removal of an additional OH$^-$ from the hexagonal calcium channel. The second substitution, called type-B, involves the removal of a phosphate ion (Y), according to:

$$\text{PO}_4^{3-}_{(\text{cell})} + 2\text{OH}^- \rightarrow \text{CO}_3^{2-}_{(\text{cell})} + \text{PO}_4^{3-}.$$  

Different from type-A substitutions, the type-B ones lead to charge imbalance in the mineral. Several hypotheses were advanced to restore the neutrality of the unit cell (Perroos et al. 2006), but one of the most probable is related to the following reaction:

$$\text{PO}_4^{3-}_{(\text{cell})} + \text{Ca}^{2+}_{(\text{cell})} + \text{CO}_3^{2-}_{(\text{cell})} + M^+ \rightarrow \text{CO}_3^{2-}_{(\text{cell})} + M^{(\text{cell})} + \text{PO}_4^{3-} + \text{Ca}^{2+}$$

where the formation of the type-B defect is accompanied by the substitution of a divalent calcium ion with a monovalent one, such as sodium in a biological environment as reported by Dorozhkin (2009, 2010, 2011). However, it is worth noting that, in nature, carbonate ion is commonly found in a mixed type-AB carbonated hydroxylapatite (COHAp).

Several experimental (Fleet and Liu 2003, 2004, 2007, 2008; Fleet et al. 2004, 2011; Fleet 2009) and theoretical (Peeters et al. 1997; Astala and Stott 2005; Perroos et al. 2006; Rabone and de Leeuw 2007; Ulian et al. 2013a, 2014; Peccati et al. 2014) works were devoted to the structural analysis of bulk type-A,