American Mineralogist, Volume 106, pages 1928–1939, 2021

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

Gianfranco Ulian[1,†], Daniele Moro[1], and Giovanni Valdrè[1,*]

[1]Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Centro di Ricerche Interdisciplinari di Biomineralogia, Cristallografia e Biomateriali, Università di Bologna "Alma Mater Studiorum" Piazza di Porta San Donato 1, 40126 Bologna, Italy

Abstract

The present investigation reports the equation of state, thermodynamic, and thermoelastic properties of type AB carbonated apatite [CAp-AB, $Ca_{10}(CO_3)^B(PO_4)_5(CO_3)^A$, 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) GPa, K' = 4.3(1), and V_0 = 517.9(2) Å^3, whereas at room temperature (300 K) they were K_T = 101.98 GPa, K' = 4.12, and V_0 = 524.486 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