

Theoretical Investigation on Defect Energetics in Calcium Phosphates under an Aqueous Solution Environment

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Osteoporosis is a health problem worldwide and a disease to increase the fracture risk of human bones, which is caused by imbalance between bone resorption and bone formation during bone metabolism. In order to prevent the bone disease, doping of cations such as Mg^{2+} or Zn^{2+} into human bones is attempted, and is thought to have a significant effect on promotion of bone formation processes. Human bones are composed of inorganic hydroxyapatite (HAp) minerals and organic collagen fibrils. The dopants are expected to be incorporated into HAp and affect the biological properties such as bioactivity and biocompatibility. It is of great importance, therefore, to reveal roles of the dopants on biological properties of HAp and the relevant calcium phosphates.

In this study, first-principles calculations were performed to investigate substitutional cations in HAp and also the related calcium phosphate materials. Incorporation of divalent cations into HAp by ion exchange with Ca^{2+} was considered, and atomic coordinates and electronic structures of the doped cations were analyzed from supercell calculations. Moreover, based on total energies of the perfect and defective supercells, formation energies of substitutional divalent cations in HAp were evaluated under chemical equilibrium between HAp and aqueous solution.

Figure 1 displays calculated formation energies of substitutional cations in HAp as a function of solution pH. In the unit cell of hexagonal HAp, there are inequivalent two Ca sites, Ca-1 and Ca-2. Here, the results for the Ca-1 substitutions are shown. Among the divalent cations considered, Pb^{2+} , Cd^{2+} , and Sr^{2+} are found to have much smaller formation energies than the other cations. The calculated trend is in good agreement with experimental data on ion-exchange ability of HAp.

In the similar way, formation of calcium vacancies in pure HAp and the effect of the Ca^{2+} vacancy on the substitution of Zn^{2+} into HAp were also theoretically investigated. The present computational analyses can provide detailed information on thermodynamic stability of point defects in bioceramics subjected to an aqueous solution environment.

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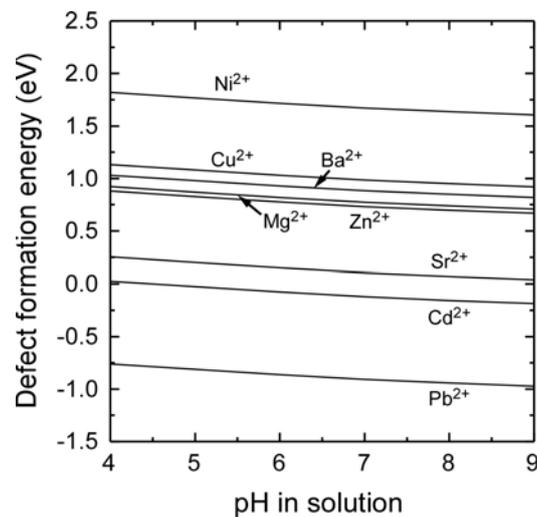


FIG. 1. Calculated formation energies of substitutional divalent cations (M^{2+}) in HAp as a function of solution pH. In this case, the formation energies were calculated under assumption of chemical equilibrium between HAp and the saturated solution containing M^{2+} with the concentration of 1.0×10^{-3} mol/L.