

## Local Environment Study of Dopants in Hydroxyapatite Using XANES and First-Principles Calculations

Hideobu Murata<sup>1</sup>, Kazuki Shitara<sup>1</sup>, Yuichi Emi<sup>1</sup>, Xianhao Wang<sup>1,2</sup>, Isao Tanaka<sup>1,3</sup>,  
Teruyasu Mizoguchi<sup>4</sup>, Atsushi Nakahira<sup>5</sup> and Katsuyuki Matsunaga<sup>1,3</sup>

<sup>1</sup> Department of Materials Science and Engineering, Kyoto University, Kyoto, 606-8501, Japan

<sup>2</sup> Ningbo Institute of Material Technology and Engineering,  
Chinese Academy of Sciences, Ningbo, 315201, China

<sup>3</sup> Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

<sup>4</sup> Institute of Industrial Science, the University of Tokyo, Tokyo, 153-8505, Japan

<sup>5</sup> Department of Materials Science, Osaka Prefecture University, Osaka, 599-8531, Japan

Inorganic components of human bones and teeth are mainly constituted of hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , HAp). HAp contains various kinds of defects, such as Ca vacancies, OH vacancies, interstitial protons and impurities, which affect biological properties of HAp. Therefore, it is desirable to reveal roles of the point defects for the properties of HAp. For this purpose, it is important to understand local physical and chemical environment of the point defects at the atomic and electronic levels. In particular, doping of  $\text{Zn}^{2+}$  and  $\text{Si}^{4+}$  is considered to have the ability of promoting the bone formation. In this study, we investigated the local environment of  $\text{Zn}^{2+}$  and  $\text{Si}^{4+}$  dopants in HAp using experimental and theoretical analyses of XANES (X-ray Absorption Near Edge Structure).

XANES measurements were carried out at BL01B1 in SPring-8 and BL1A in UVSOR. XANES calculations were performed by first-principles calculations with the core-hole effect [1].

HAp has a complicated crystal structure. In the hexagonal unit cell, there are two Ca sites, Ca-1 (columnar) site and Ca-2 (triangular) site,  $\text{PO}_4$  site and OH site. It is considered that  $\text{Zn}^{2+}$  replaces the Ca sites while  $\text{Si}^{4+}$  substitutes for the  $\text{PO}_4$  site in the form of  $\text{SiO}_4$ .

As an example, the experimental and calculated Zn-K XANES spectra of  $\text{Zn}^{2+}$ -doped HAp were shown in FIG. 1. The calculated transition energies were overestimated by about 42.7 eV, but this is the systematic error of the calculations [1]. In the calculated spectrum of  $\text{Zn}^{2+}$  substituted for the Ca-1 site, the peak positions were different from the experimental one. There was a strong shoulder around 9704 eV, which was not observed in the experiment. For the Ca-2 case, the splitting between the peak A and B was narrow and the calculated spectrum had also the shoulder structure around 9704 eV. Moreover, the peak C did not appear in both cases. These results suggest that  $\text{Zn}^{2+}$  does not simply replace Ca sites.

On the other hand, it is known that HAp sometimes has the Ca deficient chemical composition. This was also the case for the HAp samples used in this study, and thus the effect of Ca vacancies on the Zn-K XANES spectra was investigated. According to our previous first-principles calculations, the Ca vacancy favors the Ca-2 site with two protons for charge compensation [2]. We constructed the model that substitutional  $\text{Zn}^{2+}$  at the Ca-2 site is associated with the defect complex of the  $\text{Ca}^{2+}$  vacancy and two interstitial protons [3], shown in FIG. 2. The calculated spectrum from this model was in much better agreement in the spectrum shapes and peak positions

with the experimental one. This indicates that  $Zn^{2+}$  in HAp is associated with the Ca-vacancy complex.

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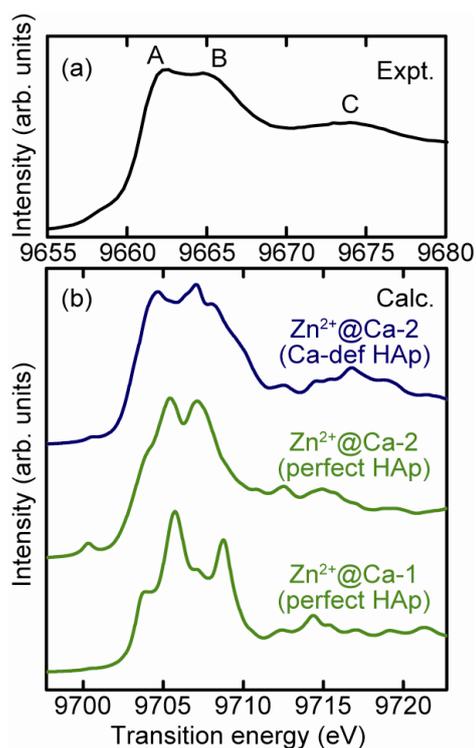


FIG. 1 (a) Experimental and (b) calculated Zn-K XANES of  $Zn^{2+}$ -doped hydroxyapatite. The blue line is the calculated spectrum of the defect complex model and the green lines are those of the simple substitution models. The calculated spectra were broadened by lorentz function (FWHM = 0.8 eV).

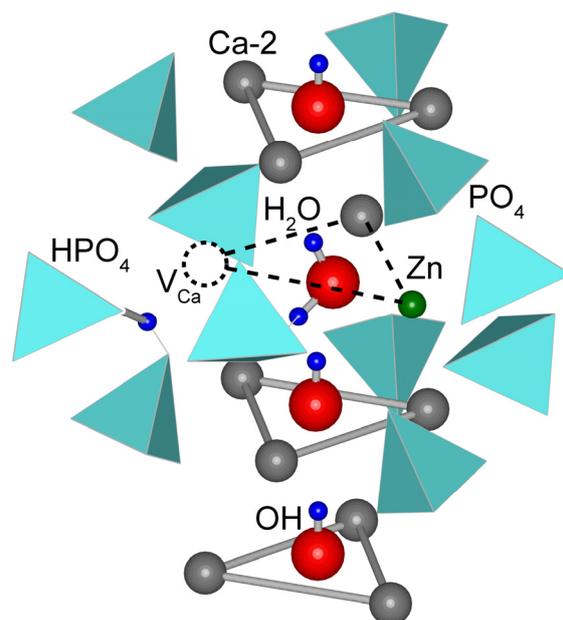


FIG. 2 The defect-complex model that  $Zn^{2+}$  is associated with Ca vacancy and interstitial protons. This figure was produced using the VESTA code [4].