

Local Structure Analysis on Functional Element doped Hydroxyapatite for use as a Drug Delivery System and Imaging Beads Materials

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1 Introduction

Calcium phosphate has been well understood as bioactive and biodegradable materials. Especially, hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAp) is chief inorganic component of hard tissue and exhibits excellent bone conductivity and biocompatibility¹). Therefore, HAp has been widely used as alternates of hard tissue and surface modification film of artificial implants to connect them with remaining bone rapidly. Since HAp also has non toxicity and excellent ion exchange ability, many kinds of studies for some functional elements doped HAp such as Mn, Si, Zn, Fe and Mg have been reported so far²). Those doped HAp will be a good candidate for not only alternates of hard tissue but also drug delivery system (DDS) and heavy-metal removable materials³). In this study, we prepared Fe doped HAp as a novel magnetic bead to control its action using magnetic field and investigated the effects of preparation condition on the crystal phase, morphology and other properties.

2 Experimental Procedure

0.1 mol/l calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), ammonium phosphate dibasic ($(\text{NH}_4)_2\text{HPO}_4$) and iron chloride (FeCl_3) aqueous solutions were used as starting materials. After adjusting the pH of solutions, phosphate solutions were gently dropped to mixed solution of calcium and iron to become the ratio of Ca to P equals to 1.67. The ratio of Fe was changed in the range from 0 to 20 mol% against the amount of Ca. After mixing up each other, obtained solution was aged at room temperature for 1 h, and then, it was filtered and dried at 323 K for 24 h. The local structure of samples was investigated by XAFS spectra for Ca-K and Fe-K edge. Both of Ca-K and Fe-K edge XAFS data were corrected by transmission and fluorescence mode using Si (111) double crystal monochromator at BL-9A in the Photon Factory. The analysis of XANES data was conducted using the commercial software "REX2000" (Rigaku Co. Ltd., Japan).

3 Results and discussion

Figure 1 shows Ca-K edge XANES spectra of Fe doped HAp powders prepared at the ratio of Ca to P of 1.67 and the ratio of Fe from 0 to 20 mol%. The local structure of near Ca atom was evaluated by XAFS to circumstantially examine the state of doped Fe to HAp.

The Ca-K edge spectra of all samples were very close to the peak position of commercial HAp. This result indicated that the local structure of near Ca atom in samples were similar to HAp.

Figure 2 shows Fe-K edge XANES spectra of Fe doped HAp powders. For the Fe-K edge XANES measurement, $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 and $\alpha\text{-FeOOH}$ were used as references. The Fe-K edge spectra of samples changed by increasing the ratio of Fe, and the Fe-K edge spectra of samples prepared in low Fe ratio region were close to $\alpha\text{-FeOOH}$ and those prepared in high Fe ratio region were close to lapped spectra of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$. This result indicated that the doping amount of Fe into HAp structure is less than 1 mol% against the Ca, and most amount of doped Fe exists as $\alpha\text{-FeOOH}$ and $\alpha\text{-Fe}_2\text{O}_3$ at the surface and/or boundary of powders.

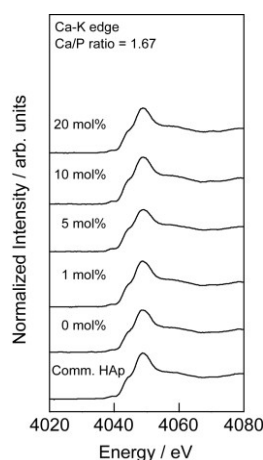


Fig.1 Ca-K edge XANES spectra of Fe doped HAp powders.

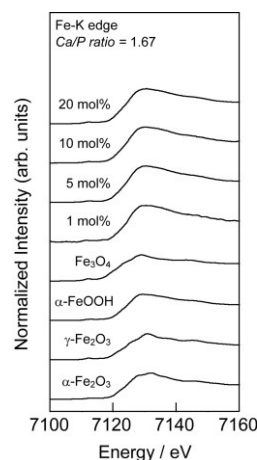


Fig.2 Fe-K edge XANES spectra of Fe doped HAp powders.

References

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