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Ion-exchange Reaction of Hydroxyapatites with Eu^{3+} and Tb^{3+} Ions

Nobuhiro KUMADA, Nana IIKUBO, Takahiro TAKEI, Nobukazu KINOMURA and Takashi SUZUKI
Faculty of Engineering, University of Yamanashi, Miyamae 7, Kofu, Yamanashi, 400-8511, Japan

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Abstract

Ion-exchange reaction of three types of synthetic hydroxyapatites was attempted with Eu^{3+} and Tb^{3+} ions for the purpose of preparing phosphors. The ion-exchange reaction was observed when the concentration of Eu^{3+} and Tb^{3+} nitrate solutions was less than 10 mmol/dm³, however, in the case of higher concentrated solution hydroxyapatites were dissolved partly to yield $\text{EuPO}_4 \cdot \text{H}_2\text{O}$ and $\text{TbPO}_4 \cdot \text{H}_2\text{O}$. The emission intensity of the ion-exchanged products depended not only on the uptake amount of Eu^{3+} and Tb^{3+} ions but also on the Ca/(P+C) ratio of the starting HAp.

1 Introduction

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), which is a major component of a bone, exhibits unique ion-exchange behavior for various ions. [1-4] The tunnel structure and high surface area of a hydroxyapatite enable it to undergo the ion-exchange reaction. The apatite has diversity of the chemical composition; Ca^{2+} ion, $(\text{PO}_4)^{3-}$ and OH^- groups are replaced with other cations and anions, hence there are a large number of compounds in the apatite family. One of important applications of the apatite compounds is the host of phosphors, for example, $\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{Cl})_2:\text{Sb}^{3+},\text{Mn}^{2+}$ is used as a phosphor of a fluorescent lamp.[5] As the apatite structure is suitable for the host for phosphors, we attempted to prepare hydroxyapatite phosphors by doping activators such as Eu^{3+} and Tb^{3+} ions by using ion-exchange reaction. In this work three types of synthetic hydroxyapatites with the different Ca/(P+C) ratio were used, and the ion-exchange behavior and fluorescence property were investigated.

2 Experimental

Three types of hydroxyapatites for ion-exchange reaction were synthesized by adding H_3PO_4 solution (0.3 mol/dm³) to the solution suspended with $\text{Ca}(\text{OH})_2$ (0.5 mol/dm³) until pH=8.5 at various controlled temperature.[6] The precipitate was washed, dried and ground to under 150 mesh. The chemical composition and specific surface area of three types of HAp are listed in Table 1. As all samples contained CO_3^{2-} group, the nonstoichiometry is represented as the molar ratio of Ca/(P+C) and HAp2 has the stoichiometric Ca/(P+C) ratio. Ion-exchange reaction was carried out by immersing HAp (0.1g) in 10 mmol/l Eu^{3+} and Tb^{3+} nitrate solutions (10 cm³) at 298 K for 1 ~ 96 h. In this condition the molar ratio of Eu^{3+} or Tb^{3+} ion in solution and

Table1 Composition and specific surface area of synthetic HAp

Sample	Ca/(P+C)	Specific surface area/ m ² ·g ⁻¹
HAp1	1.64	80.0
HAp2	1.67	74.4
HAp3	1.70	67.3

Ca^{2+} ion in HAp2 was 0.1. The concentration dependence of the ion-exchange reaction was checked by using 1, 2, 50 and 100 mmol/dm³ solutions. The products were separated by filtration and washed with distilled water. The ion-exchanged compounds were identified by X-ray powder diffraction using CuK α radiation. The uptake amount was determined by chemical analysis of the filtrates and the ion-exchanged compounds. UV-vis spectra between 350 and 500 nm⁻¹ were recorded using the powder reflection technique (Jasco V-550). The fluorescence properties were investigated with a fluorescence spectrometer (Jasco FP-6500).

3 Results and Discussion

3.1 Ion-exchange reaction

The time dependence of the ion-exchange reaction with 10 mmol/dm³ $\text{Eu}(\text{NO}_3)_3$ and $\text{Tb}(\text{NO}_3)_3$ solutions indicated that the ion-exchange reactions of HAp1 and HAp2 attained equilibrium more rapidly than that of HAp3 as shown in Fig. 1. At the equilibrium almost all Eu^{3+} and Tb^{3+} ions in solution were incorporated in the HAp, and the molar ratio of the released Ca^{2+} ion and the incorporated Eu^{3+} and Tb^{3+} ions was 3/2. The difference of the rate of the ion-exchange reaction was considered to be caused by the different specific surface area of the starting HAp. As listed in Table 1, the specific surface area increases with the decrease of the Ca/(P+C) ratio. The X-ray powder diffraction patterns of ion-exchanged compounds for 96 h. are unchanged when compared with those of the starting compound as shown in Fig. 2. These facts suggest that Ca^{2+} ion in three types of HAp is ion-exchanged with Eu^{3+} and Tb^{3+} ions in solution and the crystal structure of HAp is intact during the ion-exchange reaction.

Fig. 1 Time dependence of uptake amount of Eu^{3+} (left) and Tb^{3+} (right) ions in HAp with 10 mmol nitrate solution.

Fig. 2 X-ray powder diffraction patterns of starting HAp (left) and the products ion-exchanged with Eu^{3+} (center) and Tb^{3+} (right) ions.

The uptake amounts increased with the concentration of Eu^{3+} and Tb^{3+} ions in solution as shown in Fig. 3, especially, the HAp1 was more reactive than the other two. This behavior also may due to the difference of the specific surface area. However, the X-ray powder patterns of the products obtained by using more than 50 mmol/dm³ solution indicated the additional diffraction peaks which were identified with $\text{EuPO}_4 \cdot \text{H}_2\text{O}$ [7] and $\text{TbPO}_4 \cdot \text{H}_2\text{O}$ [8] as shown in Fig. 4. The pH of Eu^{3+} and Tb^{3+} nitrate solutions decreases with the concentration to reach pH=2.6 and 2.7 for 50mmol/dm³ Eu^{3+} and Tb^{3+} nitrate solutions, respectively, though those of 10 mmol/dm³ solutions were pH=3.2 and 4.5. It was reported that HAp was dissolved to yield $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ in PbCl_2 solution with pH=4.5~5.0.[6] Although in that case Cl^- ions in the solution played an important role to precipitate $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$, in higher concentrated Eu^{3+} and Tb^{3+} nitrate solutions partial dissolution of HAp might occur simultaneously to yield $\text{EuPO}_4 \cdot \text{H}_2\text{O}$ and $\text{TbPO}_4 \cdot \text{H}_2\text{O}$ as well as ion-exchange reaction.

Fig. 3 Concentration dependence of uptake amount of Eu^{3+} (upper) and Tb^{3+} (lower) ions in HAp.

Fig. 4 X-ray powder diffraction patterns of ion-exchanged products with 100 mmol Eu^{3+} (left) and Tb^{3+} (right) nitrate solutions. Circles indicate the peaks of $\text{EuPO}_4 \cdot \text{H}_2\text{O}$ and TbPO_4 .

3.2 Fluorescence property

Figure 5 shows excitation and emission spectra of the ion-exchanged HAp2 by using 10 mmol/dm³ Eu^{3+} nitrate solution. The strongest absorption at 395 nm is assigned to $^7\text{F}_0$ - $^5\text{G}_6$ transition and the emission peaks at 592 and 615 nm are assigned to $^5\text{D}_0$ - $^7\text{F}_1$ and $^5\text{D}_0$ - $^7\text{F}_2$ transitions, respectively. For the compounds ion-exchanged with Tb^{3+} ion the strong emission peak at 550 nm which is assigned to $^5\text{D}_4$ - $^7\text{F}_5$ transition, is used for comparison of emission intensity. The emission intensity of fluorescence increased slightly with incorporated amounts of Eu^{3+} and Tb^{3+} ions and depended on the starting HAp for the ion-exchanged HAp with the same amount of the activators as shown in Fig. 6. The order of the emission intensity is $\text{HAp1} > \text{HAp2} \geq \text{HAp3}$ for Eu^{3+} ion and $\text{HAp1} > \text{HAp2} > \text{HAp3}$ for Tb^{3+} ion. Fluorescence property of a phosphor is thought to be influenced by various

factors such as crystallinity, particle size and defect etc. as well as the crystal structure of host compounds. In this case the specific surface area and the amount of CO_3^{2-} and PO_4^{3-} groups in HAp may play an important role for the fluorescence property. As seen in Fig. 6, the emission intensity of the samples doped Eu^{3+} and Tb^{3+} ions when precipitated the HAp was significantly lower than those of the HAp phosphors prepared by ion-exchange reaction. The lower emission is inferred to result from that Eu^{3+} and Tb^{3+} ions are not incorporated in HAp but precipitate separately during the synthesis. Consequently the first attempt to use ion-exchange reaction for preparation of phosphors was successful and ion-exchange reaction is found to be available to prepare phosphors for HAp.

Fig. 5 Excitation (left) and emission (right) spectra of the ion-exchanged HAp2 by using 10 mmol/dm^3 Eu^{3+} nitrate solution

Fig. 6 Emission intensity of ion-exchanged compounds with Eu^{3+} (left) and Tb^{3+} (right) ions. Triangles denote the samples prepared by precipitation.

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