



Preparation and structure of carbonated calcium hydroxyapatite substituted with heavy rare earth ions

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ABSTRACT

Calcium hydroxyapatite (CaHap) particles substituted five types of heavy rare earth ions (Ln: Y³⁺, Gd³⁺, Dy³⁺, Er³⁺ and Yb³⁺) were synthesized using a precipitation method and characterized using various means. These Ln ions strongly affected the crystal phases and the structures of the products. With increasing Ln/(Ln + Ca) in the starting solution ($[X_{Ln}]$), the length and the crystallinity of the particles first increased and then decreased. The rare earth metal-calcium hydroxyapatite (LnCaHap) solid solution particles were obtained at $[X_Y] \leq 0.10$ for substituting Y system and at $[X_{Ln}] \leq 0.01$ – 0.03 for substituting the other Ln systems. LnPO₄ was mixed with LnCaHap at higher $[X_{Ln}]$ for all Ln systems. A series of yttrium-calcium hydroxyapatite (YCaHap) solid solutions with $[X_Y] = 0$ – 0.10 were investigated using XRD, TEM, ICP-AES, IR and TG-DTA in detail.

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1. Introduction

Calcium hydroxyapatite, Ca₁₀(PO₄)₆(OH)₂ (CaHap), is a major inorganic component of animal hard tissues and synthetic CaHap is now widely used in bone substitute materials, catalysts, ion exchangers, electrical devices and other products [1–4]. The CaHap particles have been synthesized by many investigators by different methods, such as a hydrothermal reaction, a solid state reaction and a wet method [2–9]. In general, the former two methods tend to make CaHap particles which are stoichiometric and single crystal. In contrast, a wet method forms CaHap particles which are fine, less-crystallized, high-purity and non-stoichiometric. Moreover, the structure of the particles can be controlled more easily in a wet method than the other methods, because the structure of the CaHap changes with the change of reaction conditions in a wet method such as temperature, pH of the synthesis solution, aging period, additives and so on.

The rare earth ions are nowadays used in various fields as phosphors, laser technologies, magnetic materials, sensors and anti-UV materials [10,11]. If CaHap particles containing rare earth ions are prepared using a wet method and the size and structure of the particle are controlled, the procedure will contribute to manufacture new goods which have anti-UV or luminous

properties. We have recently reported incorporation of five types of light rare earth ions such as La, Ce, Pr, Nd and Sm into CaHap particles [12]. The ions entered into the CaHap crystal were trace but strongly affected the crystal phases and structures of the products for all Ln systems. Therefore, it is desired to obtain information on incorporation of heavy rare earth ions into CaHap particles. There are some publications on the formation of CaHap containing Y³⁺, which is one of the heavy rare earth ions. Liu et al. have reported the synthesis of yttrium-calcium hydroxyapatite (YCaHap) at Y/(Y + Ca) in the particles (abbreviated as X_Y) ≤ 0.05 by a sol–gel method using precipitates [11]. Ergun et al. and Webster et al. have prepared YCaHap at X_Y ≤ 0.07 by sintering of precipitates at 1100 °C [13,14]. Yamashita et al. have reported the preparation and electrolytic and dielectric properties of yttrium-incorporated calcium oxyhydroxyapatite (Ca_{10-x}Y_x(PO₄)₆(OH)_{2-x}O_x) [5,6]. Gadolinium-calcium hydroxyvanadate, which contains VO₄³⁻ ions instead of PO₄³⁻ ions, was synthesized at Gd/(Gd + Ca) ≤ 0.06 by a pyrolysis method [15]. However, to our knowledge, preparation of CaHap particles substituted with a series of heavy rare earth ions using a wet method has never been reported. Therefore, the information on the preparation of heavy rare earth metal-calcium hydroxyapatite (LnCaHap) solid solution particles using a wet method is highly desired. The aim of this study was to investigate the incorporation of five types of heavy rare earth ions (Ln: Y, Gd, Dy, Er and Yb) into CaHap particles. The inner and surface structures of the resulting particles were further investigated using various techniques. The knowledge obtained in this study will contribute to control the

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size and structure of the CaHap particles and to produce new valuable materials containing heavy rare earth ions.

2. Experimental

2.1. Materials

CaHap particles were synthesised by a wet method according to the previous study [16] as follows. $\text{Ca}(\text{OH})_2$ (32 mmol) was dissolved by stirring for 1 h in 1.6 dm^3 deionized and distilled water free from CO_2 under an N_2 atmosphere. A diluted H_3PO_4 solution (19.2 mmol) was prepared, of which Ca/P atomic ratio was adjusted to the stoichiometric ratio of 1.67. After addition of the H_3PO_4 solution, precipitates were formed. The suspension was stirred at room temperature for 1 h and then aged in a 2 dm^3 screw-capped polypropylene vessel at 100°C for 48 h. The formed precipitates were filtered off, washed with deionised distilled water and finally dried in an air oven at 70°C for 16 h.

To investigate the influence of the Ln^{3+} ions, the particles were prepared by adding five types of heavy rare earth metal nitrates, such as $\text{Y}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{Yb}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, in place of a portion of the $\text{Ca}(\text{OH})_2$. The amounts of crystal water (n) contained in $\text{Y}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ and $\text{Yb}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ were determined to be 4.8 and 2.0, respectively, based on simultaneous thermogravimetry (TG) measurements. The total number of moles of Ln and Ca was kept at 32 mmol, and the $\text{Ln}/(\text{Ln} + \text{Ca})$ atomic ratio in the solution (cited as $[X_{\text{Ln}}]$) was 0.01, 0.03, 0.05, 0.10 or 0.15. An H_3PO_4 solution (19.2 mmol) was added to the solution and the solution pH was brought to 9.50 by the addition of NH_4OH . The remainder of procedure was the same as that for the preparation of CaHap described above.

All chemicals were reagent grade and were supplied by Wako Chemical Co. and were used without further purification. The notation Ln 0.01 refers to the sample produced at $[X_{\text{Ln}}] = 0.01$, i.e., Y 0.01 denotes the particles produced in the presence of Y^{3+} ions at $[X_{\text{Y}}] = 0.01$.

2.2. Characterization

The particles thus obtained were characterized using various methods as follows. The crystal structure of the products was determined by powder X-ray diffraction (XRD) using a Rigaku diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation (40 kV, 120 mA). The particle morphology was observed with a transmission electron microscope (TEM, JEOL JEM-2100) at an accelerating voltage of 200 kV. Transmission IR spectra of the self-supporting sample discs were recorded with a resolution of 4 cm^{-1} *in vacuo* at room temperature using a Fourier transform infrared spectrometer (FTIR, Nicolet Protégé 460). The sample powder (30 mg) was pressed into a disk of 1 cm in diameter under a pressure of 8.8 MPa cm^{-2} . Prior to taking the spectra, the sample disks were outgassed in a sample cell at 300°C and $1.0 \times 10^{-3} \text{ Pa}$ for 2 h. The contents of Ca^{2+} , Y^{3+} , Gd^{3+} , Dy^{3+} , Er^{3+} and PO_4^{3-} in the particles were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES SII SPS3520UV-S). Four rare earth metals oxides (Y_2O_3 , Gd_2O_3 , Dy_2O_3 and Er_2O_3) had been dried in an air oven at 100°C for 1 h to be used as standard materials. Prior to the ICP-AES measurements, the samples and rare earth metal oxides were dissolved in an HNO_3 , HCl or H_2SO_4 solution. Because the products formed with addition of Yb^{3+} were not completely dissolved by any acids, the composition of the products could not be determined. Thermogravimetry and differential thermal analyses (TG-DTA) were carried out using a thermoanalyzer (Seiko SSC 5200) in an air stream at a heating rate of 5°C min^{-1} . Adsorption isotherms of N_2 were measured at the boiling point of

nitrogen using a computer-aided volumetric apparatus. The specific surface areas of the particles were determined by fitting the BET equation to the N_2 adsorption isotherms recorded with a computer-aided volumetric apparatus, assembled in our laboratory, at the boiling point of nitrogen. The samples were treated at 300°C and $1.0 \times 10^{-3} \text{ Pa}$ for 2 h before the N_2 adsorption.

3. Results and discussion

3.1. Crystal structure and chemical composition

XRD measurements were performed to investigate the crystal phases of the products. Fig. 1 shows the patterns of the particles formed at different $[X_{\text{Ln}}]$ atomic ratios in the solution for the Y and Er systems. The products with $[X_{\text{Ln}}] = 0$ were characteristic to CaHap (JCPDS 9-432). The particles formed at $[X_{\text{Y}}] = 0.10$ and $[X_{\text{Er}}] = 0.03$ could be also identified as hydroxyapatite (Hap). However, some small peaks appeared for Y 0.15 and Er 0.15 particles as shown by open and closed triangles. These peaks were corresponding to YPO_4 (JSPDS 83-0658) and ErPO_4 (JSPDS 83-0662), respectively. The crystal phases of all the products were identified based on their XRD patterns and listed in Table 1. GdPO_4 (JCPDS 84-0920), DyPO_4 (JCPDS 45-0041) or YbPO_4 (JCPDS 53-0860) were also mixed with the Hap at higher $[X_{\text{Ln}}]$ for each Ln systems (data not shown). We reported that homogeneous Hap without LnPO_4 could be obtained at $[X_{\text{Ln}}] \leq 0.01$ – 0.03 for five types of light rare earth ions such as La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} and Sm^{3+} in the previous study [12]. It is noteworthy that homogeneous Hap phase of Y system could be obtained at $[X_{\text{Y}}] \leq 0.10$, which is extremely higher $[X_{\text{Ln}}]$ value than the other light and heavy rare earth ion systems.

To investigate the chemical composition of the particles, contents of Ca^{2+} , Ln^{3+} and PO_4^{3-} ions were obtained for Hap particles without an LnPO_4 phase. The $\text{Ln}/(\text{Ln} + \text{Ca})$ atomic ratios of the particles (designated X_{Ln}) were determined and are shown along with the $[X_{\text{Ln}}]$ in the synthesis solutions in Table 2. The

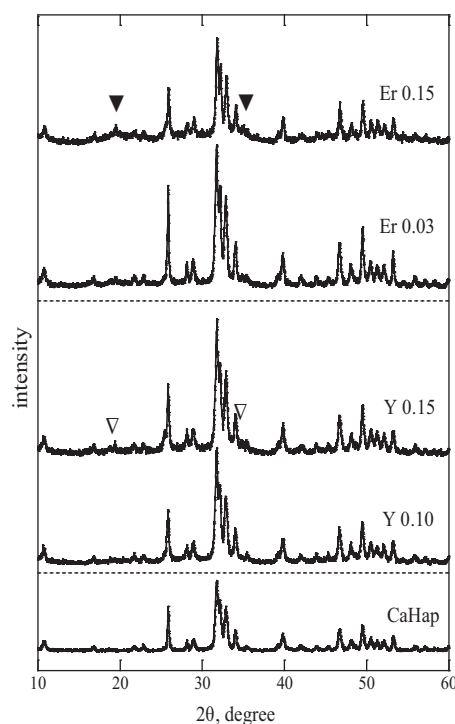


Fig. 1. XRD patterns of the particles produced with addition of Y^{3+} and Er^{3+} ions at different $[X_{\text{Ln}}]$. ∇ : YPO_4 and \blacktriangledown : ErPO_4 .

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