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Preparation and structure of calcium hydroxyapatite substituted with light rare earth ions

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ABSTRACT

The present study synthesized five types of hydroxyapatite (Hap) particles containing light rare earth ions (Ln^{3+}: La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+}) and Ca^{2+} ions from aqueous solutions with different Ln/(Ln + Ca) atomic ratios ($[X_{Ln}]$) ranging from 0 to 0.15. The crystal phases of the products and their inner and surface structures were investigated by various means. Ln^{3+} ions were incorporated into the CaHap crystals and formed rare earth metal–calcium hydroxyapatite (LnCaHap) solid solutions at $[X_{Ln}] \leq 0.01$–0.03. A mixture of LnCaHap and $LnPO_4$ was formed in each Ln system at $[X_{Ln}] > 0.01$–0.03. Ln^{3+} ions strongly affected the structure of the particles, although only a small quantity of Ln^{3+} ions was incorporated into the Hap crystals. With increasing $[X_{Ln}]$, the prepared particles first became longer and then became smaller. The crystallinity of the particles was altered, corresponding with the variation of their size. UV–vis measurements revealed that Ce-contained Hap exhibits strong UV absorption under 400 nm.

1. Introduction

Calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ (CaHap), is a major inorganic component of animal hard tissues and is used in bioceramics, chromatographic adsorbents, acid and base catalysts, tooth paste, germicides, and other products [1–3]. Because the hydroxyapatite (Hap) structure, $Me_{10}(PO_4)_6(OH)_2$, is so tolerant to ionic substitutions, the Me site can be occupied by various divalent cations (Ca^{2+}, Mg^{2+}, Sr^{2+}, Cd^{2+}, Pb^{2+} and Ba^{2+} [1,2,4–10]), by some trivalent cations (Cr^{3+}, Al^{3+} and Fe^{3+}) [11,12] and by the quadrivalent cation Ti^{4+} [13]. The substitution of Ca^{2+} in CaHap with other metal ions strongly affects the characteristics of the CaHap particles, including the size, crystallinity, solubility, thermal stability, surface characteristic and adsorptive activity [14].

Recently, rare earth ions have been used in various types of materials, such as phosphors, laser technologies, magnetic materials, catalysts, superconductive materials, fuel cells, sensors, medical materials and dental materials [15,16], that are used in various fields of science, technology and medicine.

There have been many publications on the formation of rare earth metal–calcium hydroxyapatite (LnCaHap) solid solutions such as lanthanum–calcium hydroxyapatite (LaCaHap) [13], cerium–calcium hydroxyapatite (CeCaHap) [14,17] and neodymium–calcium hydroxyvanadate, which contains $VO_4{}^{3-}$ ions instead of $PO_4{}^{3-}$ ions [18]. There have been also some publications on the influence of rare earth metal ions such as La^{3+} and Gd^{3+} on the formation of CaHap [19,20]. In previous studies, we synthesized various Hap solid solution particles involving Ca^{2+} and another divalent cation and reported their composition and structures [6–10]. We revealed in these studies that strontium–calcium hydroxyapatite (SrCaHap) [7] and cadmium–calcium hydroxyapatite (CdCaHap) [8] can be prepared from the solution over the whole range of Me/(Me + Ca) atomic ratios ($[X_{Me}]$) from 0 to 1, whereas magnesium–calcium hydroxyapatite (MgCaHap) [6], lead–calcium hydroxyapatite (PbCaHap) [9] and barium–calcium hydroxyapatite (BaCaHap) [10] can be formed only over a limited range of $[X_{Me}]$. From these studies, it is suggested that Hap can be utilized as a host material for accumulate metal ions into their crystal structure.

However, to our best knowledge, there are few reports on the influences of a series of rare earth ions on the formation of CaHap particles. Therefore, we wanted to obtain information on the behaviour of rare earth ions mixed with Ca^{2+} ions in the synthesis of LnCaHap solid solution particles and to compare with our previous studies. Recently a demand of rare earth ions has greatly grown but its supply from China, which is the greatest export country, was decreased suddenly. Hence, nowadays, besides the recovery of them under the ground deposition efficiently, a development

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of recycling system of these rare earth metals from manufactured products is also desired. Moreover, the UV absorption of Ce^{3+} ions has been investigated for CeO_2 [21], cerium phosphate [22], amorphous cerium–titanium phosphate solid solution [23] and cerium fluoride phosphate [24]. Because the UV absorption of Ce-containing CaHap particles has never been reported to our knowledge, the UV absorption properties of these particles were also investigated.

Therefore the aim of this study was to synthesize five types of LnCaHap solid solutions containing light rare earth ions (Ln: La, Ce, Pr, Nd and Sm) and get information on the maximum content of Ln^{3+} to form pure LnCaHap solid solutions. Moreover, we investigated the influences of these five types of rare earth ions on the compositions and structures of the resulting particles using various techniques. The UV absorption ability of CeCaHap solid solution particles was also examined. The results obtained in this study will contribute not only to produce new valuable materials which can be applied to the various fields but also to develop a new host material to recover rare earth ions.

2. Materials and methods

2.1. Materials

CaHap particles were synthesized by the following precipitation method according to the previous study [6]. A solution (1.6 dm^3) containing Ca^{2+} was prepared by dissolving $Ca(OH)_2$ (32 mmol) in deionized and distilled water free from CO_2 under an N_2 atmosphere. After 1 h of stirring, an H_3PO_4 solution (19.2 mmol) was added to the $Ca(OH)_2$ solution, in which Ca/P atomic ratio was adjusted to the stoichiometric ratio of 1.67. The resulting 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 precipitates that formed were filtered off, washed with deionized distilled water and finally dried in an air oven at 70 °C for 16 h.

Particles containing La^{3+} were synthesized by adding $La(NO_3)_3{\cdot}6H_2O$ in place of a portion of the $Ca(OH)_2$. The total number of moles of La and Ca was kept at 32 mmol, and the La/(La + Ca) atomic ratio in the solution (cited as $[X_{La}]$) was 0.01, 0.03, 0.05, 0.10 or 0.15. After addition of the H_3PO_4 solution (19.2 mmol), 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.

The particles containing the other light rare earth metals (Ce, Pr, Nd, and Sm) were prepared as the same way to the La system as described above using four types of rare earth metal nitrates ($Ce(NO_3)_3{\cdot}6H_2O$, $Pr(NO_3)_3{\cdot}nH_2O$, $Nd(NO_3)_3{\cdot}6H_2O$ and $Sm(NO_3)_3{\cdot}6H_2O$) instead of $La(NO_3)_3{\cdot}6H_2O$. The amount of crystal water (n) contained in $Pr(NO_3)_3{\cdot}nH_2O$ was determined to be 9.0 based on simultaneous thermogravimetry (TG) measurements. All chemicals were reagent grade, were supplied by Wako Chemical Co. and were used without further purification. The notation Ln 0.01 refers to the sample produced at $[X_{Ln}] = 0.01$, i.e., Ce 0.01 denotes the particles produced in the presence of Ce^{3+} ions at $[X_{Ce}] = 0.01$.

2.2. Characterization

The resulting particles were characterized by the following methods. The crystal structure was determined by powder X-ray diffraction (XRD) using a Rigaku diffractometer with Ni-filtered CuKα 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}. The sample disks were outgassed in a sample cell at 300 °C and 1.0×10^{-3} Pa for 2 h before taking the spectra. The contents of Ca^{2+}, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{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 (La_2O_3, Pr_6O_{11}, Nd_2O_3 and Sm_2O_3) that had been dried in an air oven at 100 °C for 1 h were used as standard materials. Prior to the ICP-AES measurements, the samples and rare earth metal oxides were dissolved in an HNO_3 solution. Because the products containing Ce^{3+} and CeO_3 were not completely dissolved by HNO_3 or any other acid, the contents of various ions in these products could not be determined. Thermogravimetry analysis (TG) was carried out using a thermoanalyzer (Seiko SSC 5200) in an air stream at a heating rate of 5 °C min^{-1}. 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. Prior to the adsorption, the samples were treated at 300 °C and 1.0×10^{-3} Pa for 2 h. Diffuse reflection UV–vis spectra were taken with a UV apparatus (Shimadzu UV–vis 2450) at 200–800 nm with an integrating sphere (ISR-240A). For the UV–vis measurements, 0.2 g of the sample was fully mixed with 1.8 g of $BaSO_4$ as a diluent.

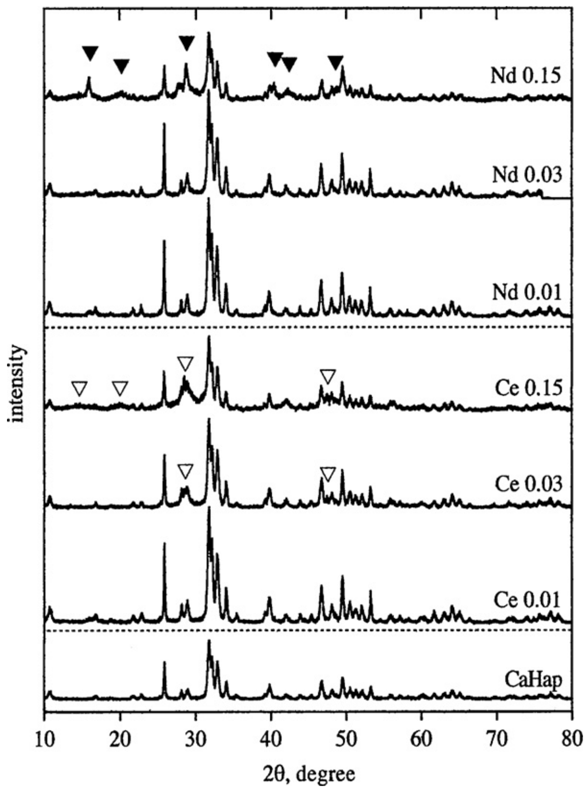

Fig. 1. XRD patterns of the particles produced with the addition of Ce^{3+} and Nd^{3+} ions at different $[X_{Ln}]$. (▽) $CePO_4$, (▼) $NdPO_4$.

3. Results and discussion

3.1. Crystal structure and chemical composition

The crystal phases of the products were determined by XRD. Fig. 1 shows the XRD patterns of the particles obtained at $[X_{Ln}] = 0$, 0.01, 0.03 and 0.15 for the Ce and Nd systems. The particles formed with $[X_{Ln}] = 0$ were identified as CaHap (JCPDS 9-432). The Ce 0.01