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Hydrothermal synthesis and morphology variation of cadmium hydroxyapatite

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Abstract

Cadmium hydroxyapatite (Cd-Hap) crystals were synthesized by hydrothermal method at 200 °C using the solutions of $Cd(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$. Influences of pH values and reaction time on the crystalline phases and morphology of the products were investigated. In low pH reaction media, $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ was formed and a relatively high pH reaction media was necessary to obtain Cd-Hap. Morphology of the Cd-Hap crystals changed from stubby hexagonal prismatic to rod-like in shape with the increase in the pH value. This morphological change was explained by the difference in growth mechanism through intermediate phases, $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ in the low pH reaction media and $Cd_2P_2O_7 \cdot 5H_2O$ in the high pH reaction media.

Keywords: Cadmium hydroxyapatite; Morphology; pH; Hydrothermal method; Crystal growth

1. Introduction

Calcium hydroxyapatite ($Ca_5(PO_4)_3(OH)$; Ca-Hap) with a typical apatite structure shows a high capacity for substitution of Ca ions by heavy metal ions due to its crystal structure and chemical composition, and it has been used to remove toxic heavy metal ions from industrial waste water [1]. It is also the major constituent of the skeleton and teeth of vertebrates [2].

Cadmium hydroxyapatite ($Cd_5(PO_4)_3(OH)$; Cd-Hap) is isostructural with Ca-Hap, and Cd^{2+} has the possibility of substitution for Ca^{2+} in bone tissue [3]. LeGeros et al. [4] obtained Ca-Hap in which Ca^{2+} was partially substituted by Cd^{2+} (less than 10 atom%) and found a slight contraction of the lattice parameters. A continuous series of solid solutions in the system of Ca-Hap and Cd-Hap has been prepared from aqueous solutions [5]. The results indicated that the lattice constants and infrared (IR) spectra of the solid solutions varied linearly with the content of cadmium.

As a part of studies on the apatite group compounds, Cd-Hap pure phase was synthesized by many investigators using hydrolysis of cadmium phosphates under hydrothermal conditions [3,6–10]. The previous studies, however, showed only powder X-ray diffraction (XRD) patterns [3,6–7], unit-cell dimensions [9,10], thermal behavior [6,7] and IR spectra [8] of Cd-Hap and few reports have been presented on the relationship between synthetic conditions and properties of the products such as crystalline phases, crystallinity, and morphology. Only Yasukawa et al. [11] have prepared the needle-like cadmium hydroxyapatite particles by a two-steps wet method with acetamide, and reported the relationship between the shape (needle-like) of the particle and synthesis conditions.

The objective of this work is to study the effects of hydrothermal reaction conditions such as pH value, reaction temperature and time on the crystalline phases and particle morphology of the products in the system of Cd^{2+}-PO_4^{3-}-H_2O system.

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2. Experimental

2.1. Preparation

The starting materials are 0.334 mol/dm^3 cadmium nitrate tetra hydrate ($Cd(NO_3)_2 \cdot 4H_2O$, 99.0%, Wako Pure Chemical, Japan) and 0.200 mol/dm^3 diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, 99.0%, Wako Pure Chemical, Japan) solutions. The pH value of the phosphate solution was adjusted to 6–11 by ammonia.

Hydrothermal reactions were carried out in a Teflon lined multi-chamber autoclave [12] with inner volume of 50 cm^3, which has two chambers with inner volume of 12.5 cm^3 each in the autoclave. The starting solutions (8 cm^3 each) were placed in separate chambers in amounts proportional to the stoichiometric composition of Cd-Hap. After sealing, the autoclave was connected to the rotation shaft in an air oven, and the rotation was started to mix the starting solutions at room temperature. Then, the oven was heated to a desired temperature with a heating rate of 180 °C/h. Thus, the freshly formed precipitate was hydrothermally treated with agitation. Hydrothermal treatments were mainly conducted at 200 °C for 12 h.

2.2. Characterization

After hydrothermal treatments, pH of the solutions was measured and the solid products were collected by centrifuge after washing with water. The products were characterized by powder X-ray diffraction (XRD; Model RTP-300RC, Rigaku) with Cu*K*α radiation (40 kV and 100 mA) and scanning electron microscopy (SEM; Model S530, Hitach). The concentration of Cd and P in the solutions after the hydrothermal treatments was measured by inductively coupled plasma (ICP) spectrometry (SPS7000A, Seiko).

3. Results and discussion

3.1. Effect of pH value in the reaction medium

The pH of reaction medium could be controlled by adjusting the pH of the starting $(NH_4)_2HPO_4$ solution. The pH values of the solutions after hydrothermal reactions at 200 °C for 12 h are shown in Fig. 1, against those of the starting phosphate solutions. A drastic change of the pH values of the solution was observed at pH = 9–10. When the pH values of $(NH_4)_2HPO_4$ solutions were less than 9, the pH values of the solutions after reactions were below 2. On the other hand, the pH values of the solutions after reactions were over 8, when the pH values of $(NH_4)_2HPO_4$ solutions were more than 10.

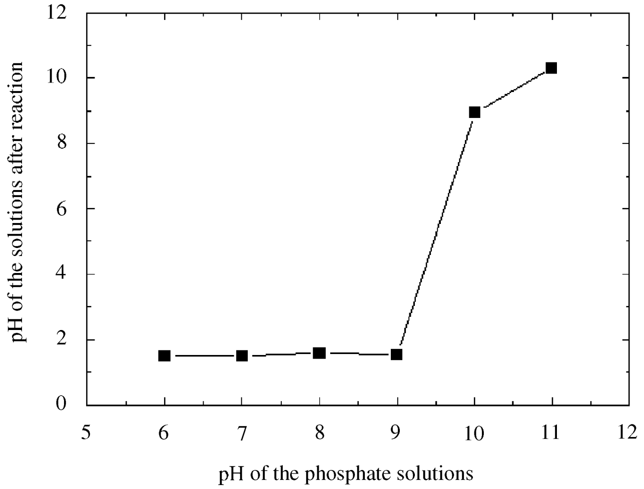

Fig. 1. The pH values of the solutions after the hydrothermal reactions against those of the reagent phosphate solutions.

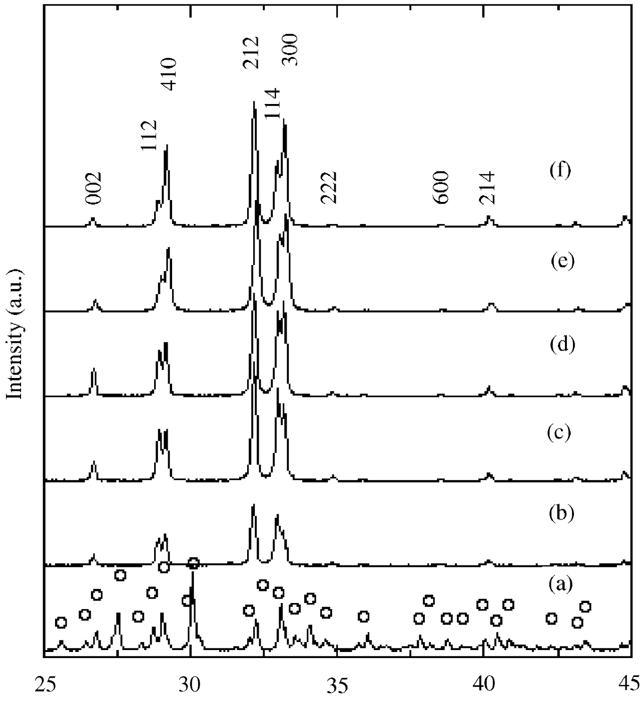

Fig. 2. X-ray diffraction patterns of the products obtained at 200 °C for 12 h from the $(NH_4)_2HPO_4$ solution with different pH values, (a) 6, (b) 7, (c) 8, (d) 9, (e) 10, and (f) 11. ○: $Cd_5H_2(PO_4)_4 \cdot 4H_2O$.

The XRD patterns of the products prepared from the $(NH_4)_2HPO_4$ solutions with different pH values are shown in Fig. 2. Only $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ was formed from the acidic $(NH_4)_2HPO_4$ solution at pH 6. When the pH values of $(NH_4)_2HPO_4$ solutions were over 7, Cd-Hap was formed as a single phase. However, a small difference in the intensity of the diffraction peaks was observed. The intensity of (300) diffraction increased in

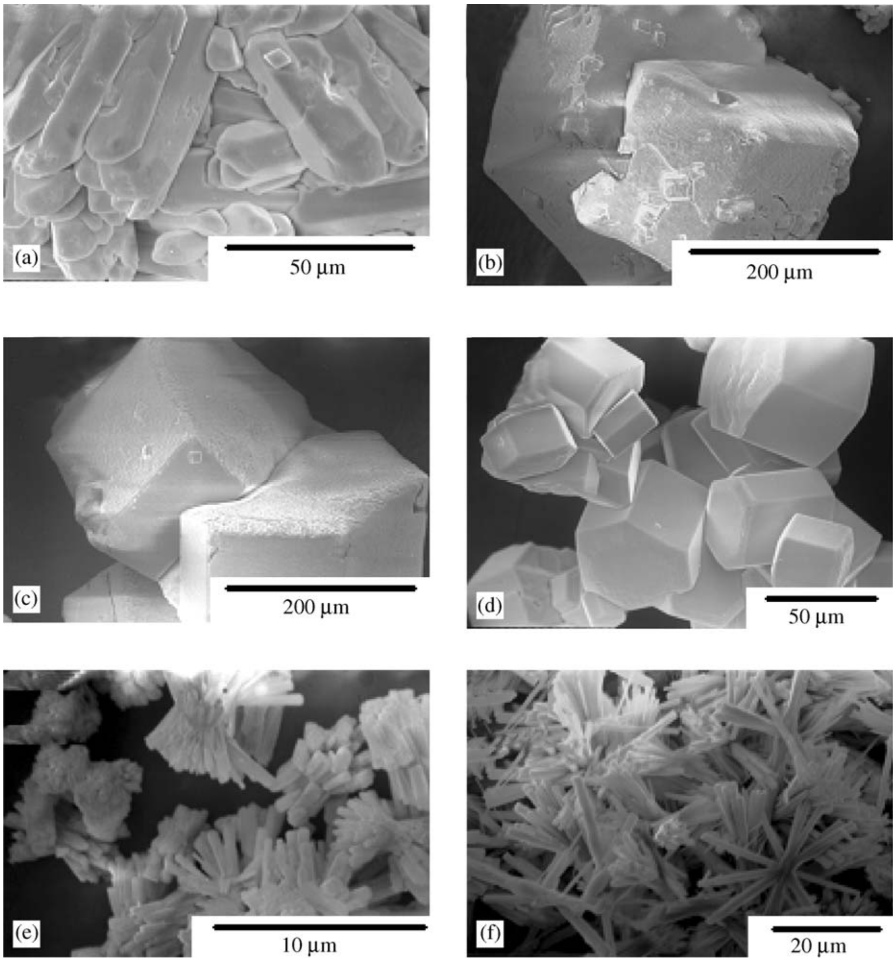

Fig. 3. SEM photographs of the products obtained at 200 °C for 12 h from the $(NH_4)_2HPO_4$ solution with different pH values, (a) 6, (b) 7, (c) 8, (d) 9, (e) 10, and (f) 11.

comparison with that of (114) diffraction, when pH values of the phosphate solutions were more than 10. The result suggests that the Cd-Hap crystals obtained in the phosphate solutions with low pH are plate-like in (001) and with those obtained at high pH are acicular in the *c* direction.

Fig. 3 shows the SEM photographs of the products obtained from $(NH_4)_2HPO_4$ solutions with different pH values. The aggregated rod-shaped crystals of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ were formed from the phosphate solution with pH 6. When pH values of the phosphate solutions were in the range of 7–9 (in the acidic reaction media as shown in Fig. 1), the Cd-Hap crystals were all stubby hexagonal prismatic and the size of the crystals decreased with the increase in pH value of the phosphate solution. When the pH values of the phosphate solutions were more than 10 (in alkaline reaction media as shown in Fig. 1), the Cd-Hap crystals changed from stubby hexagonal prismatic to needle-like in shape. The morphology of the Cd-Hap crystals clearly depended on the pH value of the reaction media (Fig. 1). Thus, the difference in the XRD intensity can be explained by the morphological change of the Cd-Hap crystals. It is concluded that the Cd-Hap crystals grew along *c* direction to form rod-like crystals in the alkaline reaction media. The size of the crystals obtained from the phosphate solution with pH 11 was larger than that of the crystals obtained from the phosphate solution with pH 10.

3.2. Influence of reaction time on the formation of Cd-Hap in the reaction medium with different pH value

In order to investigate the growth process, hydrothermal treatments were conducted using phosphate solutions with different pH values of 9 (consequently in the acidic reaction medium with pH value of about 2) and 11 (consequently in the alkaline reaction medium with pH value of about 9.6) by changing the reaction time. The reaction time 0 h means that the autoclave was quenched after temperature of the autoclave reached a desired temperature.

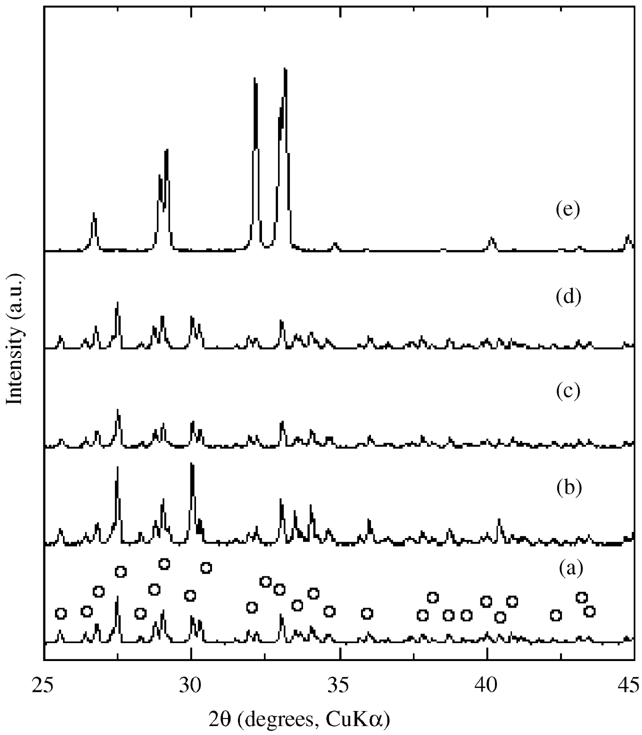

Fig. 4. X-ray diffraction patterns of the products obtained from the $(NH_4)_2HPO_4$ solution with pH 9: (a)100 °C, 0 h, (b) 150 °C, 0 h, (c) 200 °C, 0 h, (d)200 °C, 1/3 h, and (e) 200 °C, 5 h. ○: $Cd_5H_2(PO_4)_4 \cdot 4H_2O$.

The XRD patterns and SEM photographs of the products obtained from the phosphate solution with pH 9 by varying reaction time are shown in Figs. 4 and 5, respectively. Cadmium phosphate hydrate ($Cd_5H_2(PO_4)_4 \cdot 4H_2O$, JCPDS card 23-0091)) was formed even at room temperature and existed by the short time reactions up to 1/3 h at 200 °C. After 5 h, the pure phase of Cd-Hap was obtained. The crystals of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ obtained by quenching to room temperature just after the temperature reached 200 °C, were aggregated rods and plates in shape (Fig. 5a). When reaction time increased to 1/3 h, the size of the crystals was decreased due to dissolution of the crystals. The well faceted hexagonal shaped Cd-Hap crystals were formed by hydrothermal reaction for 5 h. After 5 h, the crystals did not show the further growth.

The XRD patterns and SEM photographs of the products obtained from the phosphate solution with pH 11 by varying reaction time are shown in Figs. 6 and 7, respectively. The precipitate obtained at room temperature without hydrothermal treatment was amorphous. The amorphous phase crystallized to $Cd_2P_2O_7 \cdot 5H_2O$ (JCPDS card 32-0141) at 150 °C and existed at 200 °C for 0 h. But, $Cd_2P_2O_7 \cdot 5H_2O$ rapidly changed to Cd-Hap after 1/3 h. The crystals of $Cd_2P_2O_7 \cdot 5H_2O$ were plate-like in shape and highly aggregated (Fig. 7a). After 1/3 h of reaction time at 200 °C, the rod-like Cd-Hap crystals were formed. With the increase of reaction time, the size of the crystal increased.

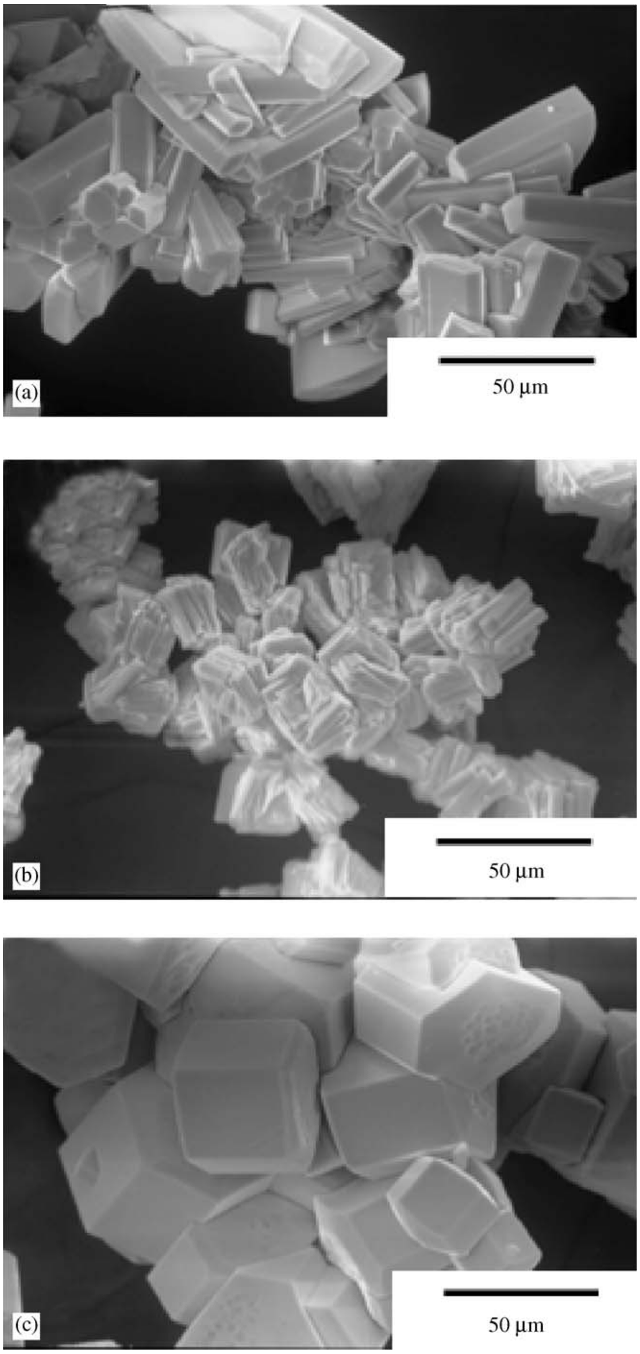

Fig. 5. SEM photographs of the products obtained from the $(NH_4)_2HPO_4$ solution with pH 9 at 200 °C for (a) 0 h, (b) 1/3 h, and (c) 5 h.

3.3. Formation and growth mechanisms of Cd-Hap in the reaction medium with different pH value.

Table 1 shows the morphological change of the Cd-Hap crystals obtained under different reaction conditions. Shape of the Cd-Hap crystals clearly changed

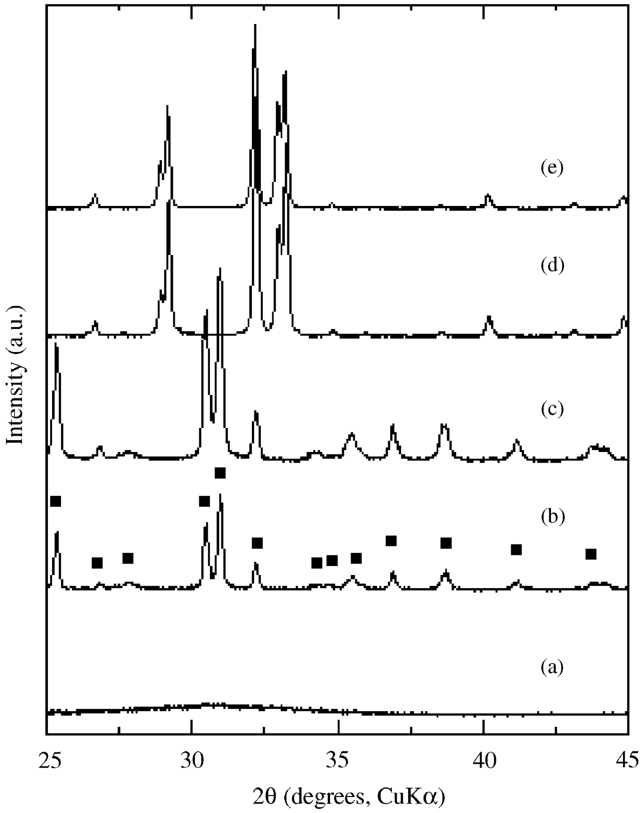

Fig. 6. X-ray diffraction patterns of the products obtained from the $(NH_4)_2HPO_4$ solution with pH 11: (a)100 °C, 0 h, (b) 150 °C, 0 h, (c) 200 °C, 0 h, (d)200 °C, 1/3 h, and (e) 200°C, 5 h. ■: $Cd_2P_2O_7 \cdot 5H_2O$.

from stubby hexagonal prism in the range of pH 7–9 to rod in the range of pH 10–11 of the phosphate solutions.

It was found that Cd-Hap was not formed directly, but formed through the intermediate phases, $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ at low pH and $Cd_2P_2O_7 \cdot 5H_2O$ at high pH. The formation of Cd-Hap can be described by the following reaction paths.

$$Cd(NO_3)_2 \cdot 4H_2O + (NH_4)_2HPO_4 \rightarrow Cd_5H_2(PO_4)_4 \cdot 4H_2O \rightarrow Cd_5(PO_4)_3(OH), \quad (1)$$

$$Cd(NO_3)_2 \cdot 4H_2O + (NH_4)_2HPO_4 \rightarrow Cd_2P_2O_7 \cdot 5H_2O \rightarrow Cd_5(PO_4)_3(OH). \quad (2)$$

The formation of Cd-Hap from $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ in the reaction media with low pH can be shown by the following equation.

$$Cd_5H_2(PO_4)_4 \cdot 4H_2O \rightarrow Cd_5(PO_4)_3(OH) + 3H_3O^+ + PO_4^{3-} \quad (3)$$

The result that $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ existed even after the hydrothermal treatment at 200 °C using the $(NH_4)_2HPO_4$ solution with pH 6, indicated that this reaction is difficult to proceed in the strong acidic media, but is accelerated with the increase of the pH value of the phosphate solutions. When pH value of the phosphate solutions increased from 7 to 9, size of the Cd-Hap crystals decreased. The decrease of the crystal size can be explained as follows: Dissolution of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ in the solution gives supersaturation for Cd-Hap, which results in nucleation of Cd-Hap crystals. With the increase in the pH value of the phosphate solutions, dissolution of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ is accelerated and gives higher supersaturation for Cd-Hap. Under these conditions, the number of the nuclei

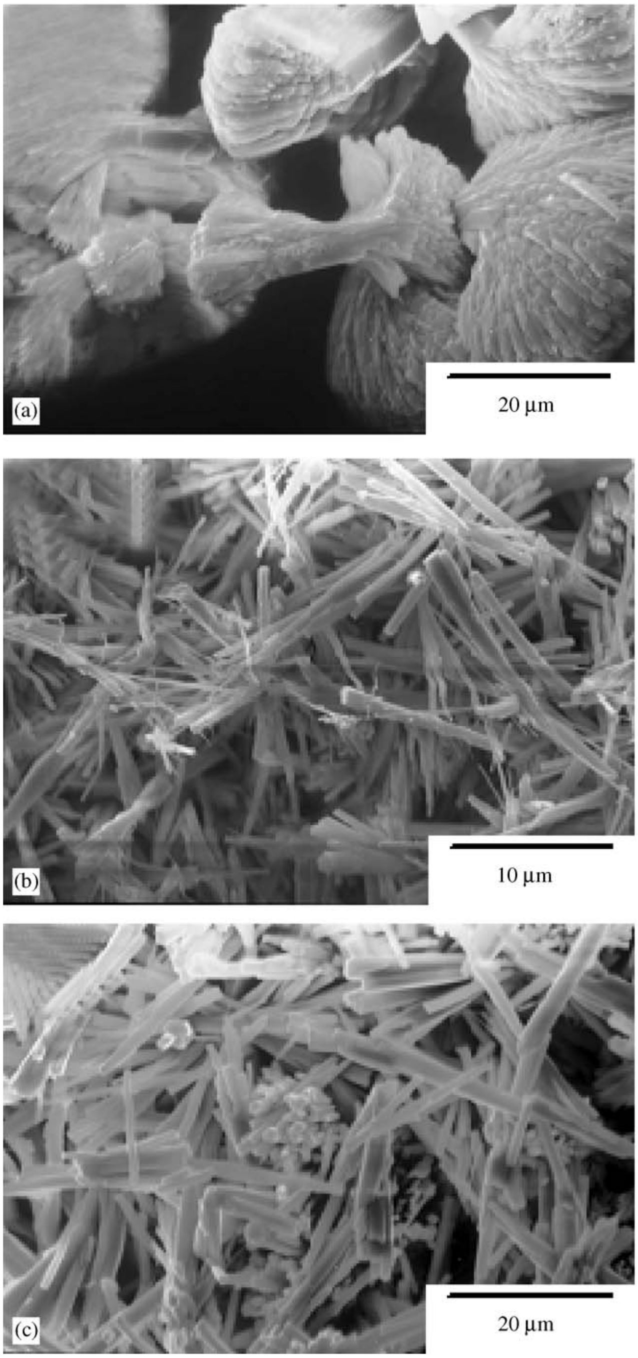

Fig. 7. SEM photographs of the products obtained from the $(NH_4)_2HPO_4$ solution with pH 11 at 200 °C for: (a) 0 h, (b) 1/3 h, and (c) 5 h.

Table 1
Morphological change of Cd-Hap crystals obtained under different conditions

pH Value of phosphate soln.	Reaction conditions	Morphology (μm)
pH = 7	200 °C, 12 h	Stubby hexagonal prism, $L \approx 150$
pH = 8	200 °C, 12 h	Stubby hexagonal prism, $L \approx 100$
pH = 9	200 °C, 5 h	Stubby hexagonal prism, $L \approx 50$
	200 °C, 12 h	Stubby hexagonal prism, $L \approx 50$
pH = 10	200 °C, 0 h	Rod, $L \approx 5$
	200 °C, 1/3 h	Rod, $L \approx 5$
	200 °C, 5 h	Rod, $L \approx 5$
	200 °C, 12 h	Rod, $L \approx 5$
pH = 11	200 °C, 1/3 h	Rod, $L \approx 20$
	200 °C, 5 h	Rod, $L \approx 30$
	200 °C, 12 h	Rod, $L \approx 30$

must be larger and consequently size of the crystals must be smaller. Even using the $(NH_4)_2$ HPO_4 solution with pH 9, dissolution of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ was slow. Growth rate of Cd-Hap crystals was so slow that the crystals homogeneously grew to be stubby hexagonal prismatic in shape. These crystals were too large to grow further by the Ostwald ripening.

The formation of Cd-Hap from $Cd_2P_2O_7 \cdot 5H_2O$ in the reaction media with high pH can be shown by the following equation:

$$5Cd_2P_2O_7 \cdot 5H_2O \rightarrow 2Cd_5(PO_4)_3(OH) + 12H_3O^+ + 6H_2O + 4PO_4^{3-}. \quad (4)$$

This reaction proceeds only in alkaline reaction media. Dissolution rate of $Cd_2P_2O_7 \cdot 5H_2O$ was very fast in comparison with that of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$, which resulted in formation of higher supersaturation for Cd-Hap. Under these conditions, the number of Cd-Hap crystals formed was large and they grew fast. The fast growth rate might result in preferential growth in the *c* direction. Thus, smaller rod-like crystals were obtained in the reaction media with high pH.

Size of the Cd-Hap crystals obtained though $Cd_2P_2O_7 \cdot 5H_2O$ by using the $(NH_4)_2HPO_4$ solution with pH 10 was smaller than that with pH 11, and the crystals did not grow large with the increase in reaction time. On the other hand, the Cd-Hap crystals grew larger with the increase in reaction time up to 5 h, when the $(NH_4)_2HPO_4$ solution with pH 11 was used. The size change of the Cd-Hap crystals may be explained by solubility of Cd-Hap in a solution with different pH values. If solubility of Cd-Hap in a solution is low, Cd-Hap crystals cannot grow larger by the Ostwald ripening. Concentrations of the solutions after hydrothermal treatments might give some information on solubility of the solid products. Concentrations of Cd^{2+} and PO_4^{3-} are given in Table 2. The $(NH_4)_2HPO_4$ solution with pH 10 gave the lowest concentrations of both Cd^{2+} and PO_4^{3-}. It is expected from the estimated solubility that size of the Cd-Hap crystals increased with the increase in pH value from 10 to 11.

Table 2
Results of chemical analysis of the solutions after hydrothermal reaction at 200 °C for 12 h using $(NH_4)_2HPO_4$ solutions with different pH values

pH	Cd/ppm	P/ppm	Cd/P molar ratio
6	31.40	13.50	1.97
7	23.75	11.23	1.79
8	17.40	8.15	1.80
9	14.89	7.25	1.73
10	N.D	1.06	0
11	1.14	1.15	0.84

N.D: under detection limit.

It is difficult to measure solubility of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ and $Cd_2P_2O_7 \cdot 5H_2O$, because these compounds change to Cd-Hap when they dissolve in solutions under hydrothermal conditions. The estimated solubility of Cd-Hap, however, may give some aspects on kinetics of dissolution of these compounds. The conditions under which solubility of Cd-Hap is low might give higher dissolution rate of these intermediate compounds. When pH of solutions increases, the solubility of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ may increase, because it is the stable compound in acidic medium. Its dissolution rate is also accelerated, because the solubility of Cd-Hap decreases with the increase in pH. On the other hand, the dissolution rate of $Cd_2P_2O_7 \cdot 5H_2O$ may increase when the pH value of phosphate solutions increases from 10 to 11, because the estimated solubility of Cd-Hap is lowest at pH 10. In fact, Cd-Hap was formed by a short time reaction (0 h) in the phosphate solution with pH 10.

4. Conclusion

The Cd-Hap crystals with high crystallinity were synthesized by hydrothermal method at 200 °C for 12 h when pH values of the starting $(NH_4)_2HPO_4$ solution solutions were over 7. In the acid phosphate solution with pH value 6, $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ was formed instead of Cd-Hap. The morphology of the Cd-Hap crystals varied from stubby hexagonal prismatic to rod-like in shape with the increase in pH value of the phosphate solution. The intermediate phase of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ was formed in the acid reaction media, and it took a long time to change into Cd-Hap, which resulted in the formation of the large stubby hexagonal prismatic Cd-Hap crystals. In the alkaline reaction media, the intermediate phase of $Cd_2P_2O_7 \cdot 5H_2O$ was formed, and rapidly changed to the Cd-Hap, which gave smaller rod-like Cd-Hap crystals.

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