Preparative Enhancement of the Thermal Stability
of Calcium Hydroxyapatites

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The thermal stability of calcium hydroxyapatites (CaHAp) as prepared by traditional methods is quite low, with the preponderance of CaHAp being converted to $Ca_3(PO_4)_2$ at temperatures as low as 973 K. In contrast, control of the pH during preparation markedly enhances the thermal stability of CaHAp, with retention of its appropriate chemical composition and structural features. © **1999 Academic Press**

INTRODUCTION

The properties of calcium hydroxyapatites $[Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}, \quad 0 \leq x \leq 1$, abbreviated as CaHAp], found naturally in hard tissues such as bone and teeth, have been known for more than 30 years (1) and its preparation, processing, properties, and applications have been recently reviewed (2, 3). Although the lattice is believed to be stable up to 1273 K, temperatures above 1773 K convert CaHAp to tri- and tetracalcium phosphate (4). However, it has been recently found that the thermal stability of CaHAp, that is, the conversion of CaHAp to $Ca_3(PO_4)_2$, is strongly dependent on the method used for the preparation of CaHAp. Although CaHAp prepared from $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ has been shown to be stable at 1048 K (5–7), that prepared from $Ca(CH_3COO)_2 \cdot H_2O$ (CaAc) and Na_2HPO_4(NaHP) is converted, at least partially, to $Ca_3(PO_4)_2$ at 973 K (8–10). Earlier work has shown that CaHAp retains the apatite structure after heating at 973 K (11), while others have found that stoichiometric ($x = 0$) and nonstoichiometric ($0 < x \leq 1$) CaHAp are stable at 1023 K (12).

Among the various methods for the aqueous preparation of CaHAp the use of CaAc and NaHp as reactants (13) seems to be unique. The solution employed in the latter preparation is apparently acidic as implied by the stoichiometry:

$$5Ca(CH_3COO)_2 + 3Na_2HPO_4$$
$$\rightarrow 0.5Ca_{10}(PO_4)_6(OH)_2 + 6CH_3COONa$$
$$+ 2CH_3COOH + (CH_3CO)_2O.$$
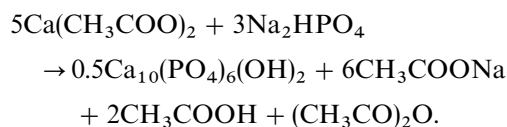
However, it is generally accepted that pH values greater than 7 are required for the preparation of CaHAp (14) since CaHAp is readily soluble in acidic solution (15) and lower values of pH during the preparation result in the formation of other forms of calcium phosphate such as $CaHPO_4$, $Ca(H_2PO_4)_2 \cdot H_2O$, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, and $Ca_3(PO_4)_2$ (3, 14). Although the thermal stability of CaHAp prepared from CaAc and NaHP is low, binary hydroxyapatites such as lead–calcium hydroxyapatites can be prepared by this method (13).

In the present study, a variation of the CaAc/NaHP preparation is employed to obtain thermally stable CaHAp. The resulting preparations are analyzed by X-ray diffraction and extended X-ray absorption fine structure to compare the fine structures of thermally stable CaHAp and thermally unstable hydroxyapatites.

EXPERIMENTAL

A number of samples of CaHAp were prepared according to the procedure reported by Bigi *et al.* (13). An aqueous solution of CaAc (Wako Pure Chemicals, Osaka) was added dropwise with stirring to a solution of disodium hydrogenphosphate (Wako) at 373 K. After the addition, the pH of the solution was 5.2. Other samples were prepared by adding NH_4OH or NaOH solutions dropwise with the acetate solution to the phosphate solution, while the pH was continuously monitored, to maintain the pH at values greater than 7. The resulting solids were stored in contact with the mother solution overnight and then filtered off, washed with distilled water, and dried at 373 K overnight. A portion of the products was heat treated at various temperatures up to 1473 K for 3 h.

The surface areas were measured with a conventional BET nitrogen adsorption apparatus (Shibata P-700).

Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 2500X diffractometer, using monochromated CuKα radiation. Patterns were recorded for 2θ values from 5 to 60°. The concentrations of Ca and P were measured in acqueous HNO_3 solution with inductively coupled plasma (ICP) spectrometry (Shimadzu ICPS-5000). Extended X-ray absorption fine structures (EXAFS) near the Ca K-edge were measured (2.5 GeV) with a storage ring current of ca. 320 mA at the High Energy Accelerator Research Organisation. The X-rays were monochromatized with Si(111) double monochromator and higher order harmonics were eliminated by a focusing double mirror system. The absorption spectra were observed using ionization chambers in a transmission mode at the BL-7C station. The photon energy was scanned in the range 3.7–5.5 keV for the Ca K-edge. Following the standard procedure, the EXAFS interference function $\chi(k)$ was extracted from the absorption spectra. The radial structure functions $\Phi(r)$ were obtained from the Fourier transforms of $k^3\chi(k)$. The back scattering amplitude and the phase shift function of Teo and Lee (16) or McKale et al. (17) were used. For the curve-fitting, the range of interest for $\Phi(r)$ was filtered with a Hamming window function, and transformed back to k space, $\chi'(k)$. Curve-fitting calculations for $\chi'(k)$ (18) were performed over k ranges of 30–100 nm^{-1}. As a reference, $CaCO_3$ (Wako, 99.99%) was also analyzed with EXAFS.

RESULTS AND DISCUSSION

Thermal Stability of CaHAp Prepared without Alkaline Reagents

After calcination at 773 K for 3 h CaHAp samples with Ca/P values of 1.65, 1.57, and 1.51, prepared with the orig-inal procedure reported by Bigi et al. (13), possessed similar BET surface areas of 68, 67, and 69 m^2/g, respectively. XRD patterns of these samples (Figs. 1A–C, respectively) are essentially indistinguishable and match that of $Ca_{10}(PO_4)_6(OH)_2$(JCPDS 9-0432), although some evidence of noncrystallinity is evident. However, aliquots calcined at 973 K showed XRD peaks attributed to $Ca_3(PO_4)_2$[JCPDS 9-0169] and a substantial portion of the CaHAp, regardless of Ca/P values, is converted to the phosphate at a temperature as low as 973 K (Figs. 1D–F). The composition (Ca/P) of each CaHAp after the calcination at 973 K changed from the aforementioned values to 1.55, 1.53, and 1.55, respectively, as expected for the formation of $Ca_3(PO_4)_2$[Ca/P = 1.50] from CaHAp. Since, in this preparation, NaHP is employed as a source of phosphate a residue of sodium in CaHAp is possible. ICP analyses of CaHAp with Ca/P values of 1.65, 1.57, and 1.51 at 773 K showed that 4.9, 5.7, and 5.6 mg/g, respectively, of sodium was retained. Since washing of the solids after preparation with increasing quantities of water produced samples with essentially identical XRD patterns (Fig. 2), sodium is apparently incorporated in the apatite structure.

Thermal Stability of CaHAp Prepared with Alkaline Reagents

Since the preparation under acidic conditions leads to CaHAp which is thermally unstable, an aqueous solution of alkaline reagents such as NH_4OH or NaOH together with calcium acetate solution was added dropwise to the NaHP solution to increase the pH. Preparations of CaHAp using NH_4OH to hold the pH at 10 yielded samples with improved thermal stability. The apatite structure was
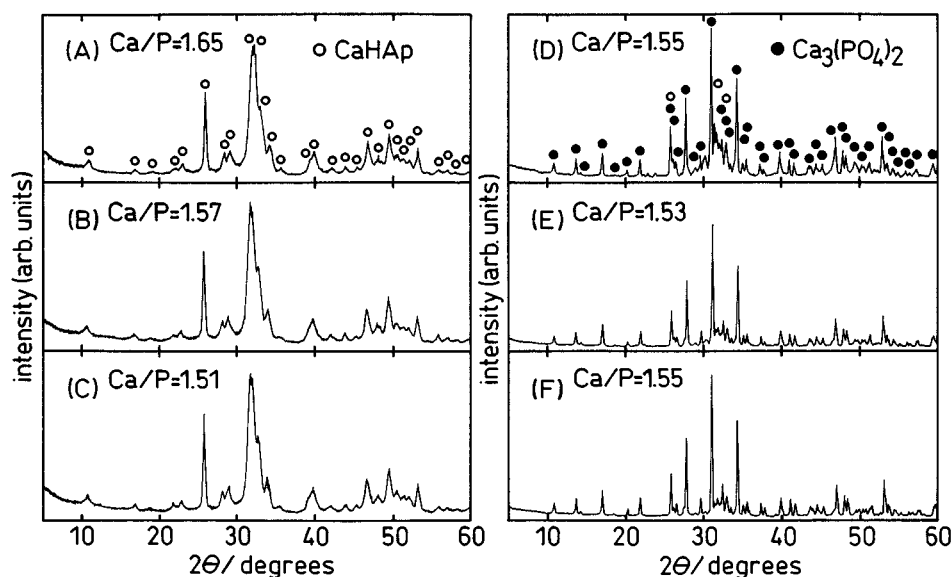

FIG. 1. XRD patterns after calcination at 773 K (A–C) and 973 K (D–F) for 3 h of CaHAp prepared without alkaline reagents.
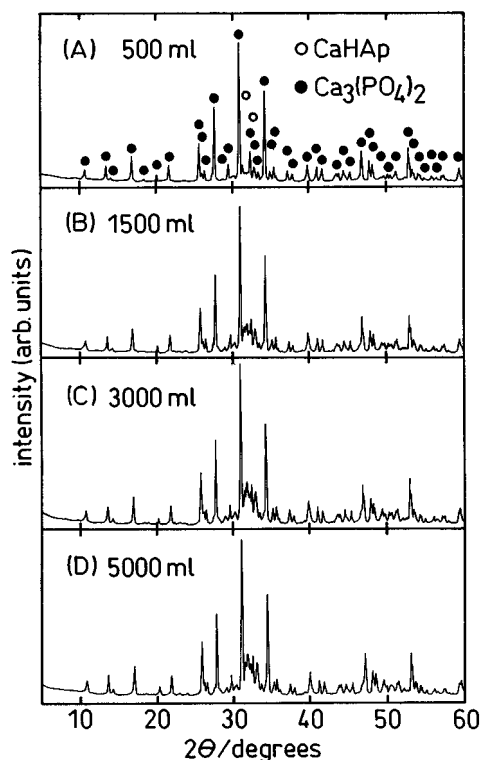
FIG. 2. XRD patterns after calcination at 973 K of CaHAp prepared without alkaline reagents but washed with different quantities of water. Ca/P: A, 1.50; B, 1.52; C, 1.50; D, 1.50.

FIG. 3. XRD patterns after calcination for 3 h of CaHAp prepared with NH_4OH. Ca/P: A, 1.57; D, 1.47.

maintained after the calcination at 973 K for 3 h (Fig. 3B) and CaHAp was predominant after the calcination at 1473 K for 3 h (Fig. 3D). Qualitatively similar results were obtained with samples prepared with addition of 1 mol dm^{-3} NaOH (Fig. 4), although $Ca_3(PO_4)_2$ was detected after calcination at 973 K (Fig. 4B). XRD patterns after calcination at 1173 K (Fig. 4C) were essentially identical to those using NH_4OH solution (Fig. 3C). Crystallinity of CaHAp prepared with NH_4OH or NaOH after calcination at 773 K (Figs. 3A or 4A, respectively) appears to be higher than that in their absence (Figs. 1A–C).

When 5 mol dm^{-3} NaOH was employed to maintain the pH of the solution at 12, the thermal stability of CaHAp was dramatically improved. XRD patterns of CaHAp with Ca/P values of 1.68, 1.59, and 1.55, after calcination at 773 K for 3 h, showed higher crystallinity and were assigned as $Ca_{10}(PO_4)_6(OH)_2$ (Figs. 5A–C). The BET surface areas of these samples were 60, 51, and 72 m^2/g, respectively, with only the latter being larger than that for the corresponding sample prepared without alkaline reagents. Upon heating at 1473 K for 3 h, highly crystalline CaHAp was detected by XRD (Figs. 5D–F) and the conversion of CaHAp to $Ca_3(PO_4)_2$ was completely suppressed, regardless of Ca/P ratios. However, the Ca/P ratios as analyzed with ICP changed from 1.68, 1.59, and 1.55 after calcination at 773 K
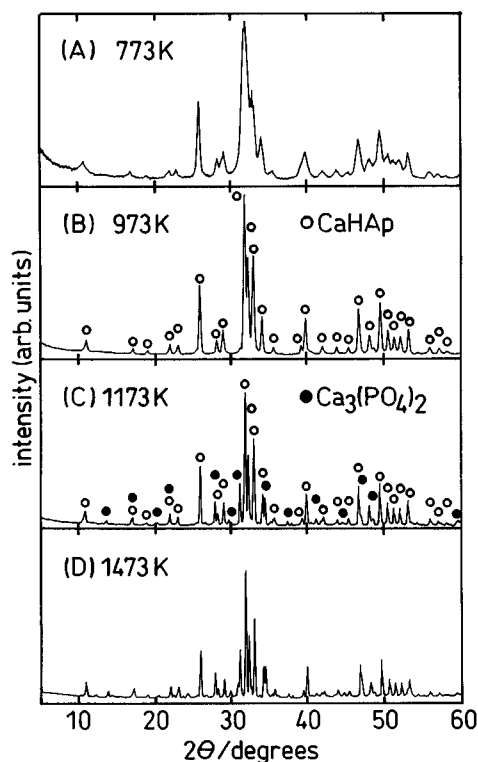
to 1.75, 1.67, and 1.70, respectively, after calcination at 1473 K, indicating that a small quantity of PO_4 was eliminated from the apatite structure. It should be noted that the apatite structure is not affected by the elimination of PO_4,
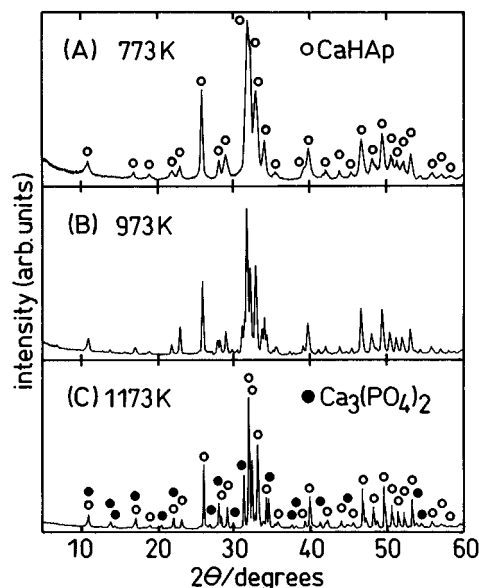

FIG. 4. XRD patterns after calcination for 3 h of CaHAp prepared with 1 mol dm^{-3} NaOH. Ca/P: A, 1.68; C, 1.56.
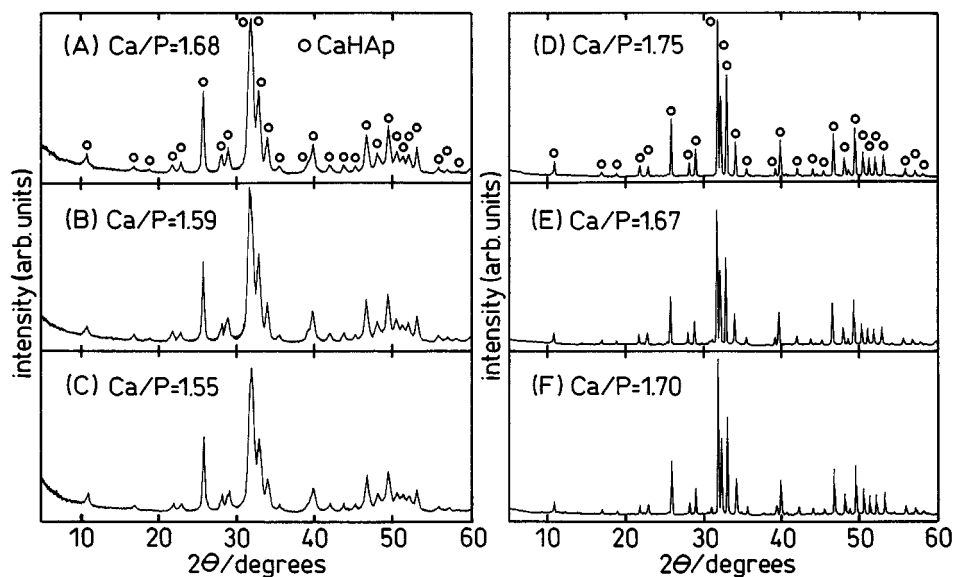
FIG. 5. XRD patterns after calcination at 773 K (A–C) and 1473 K (D–F) for 3 h of CaHAp prepared with 5 mol dm^{-3} NaOH.

at least in the quantities involved here. The thermally stable CaHAp with Ca/P values of 1.68, 1.59, and 1.55 after calcination at 773 K, contained 7.0, 9.3, and 10.6 mg/g sodium, respectively. Therefore it is evident that the formation of thermally unstable CaHAp through the original procedure

FIG. 6. XANES spectra of the thermally stable and unstable CaHAp. The numbers represent the Ca/P ratio of each CaHAp calcined at 773 K for 3 h and "A" and "P" refer to the absence and presence of 5 mol dm^{-3} NaOH, respectively, in the preparation of CaHAp.

(13) results from the preparation under acidic conditions and not from the incorporation of sodium within the apatite structure.

Effect of Fine Structure Changes of CaHAp on the Thermal Stability

It is known that (3) calcium hydroxyapatites can be precipitated from solution with Ca/P ratios from 1.67 to 1.50 without any apparent change in XRD patterns although chemical properties such as those related to catalysis (5, 6, 12, 19) and ion-exchange (20–22) are strongly dependent on Ca/P ratios. As a consequence it is generally difficult to correlate these chemical properties and their changes with Ca/P ratios, with possible structural changes. However, EXAFS analysis has been recently employed in our laboratories to correlate fine structure changes of various hydroxyapatites containing Ca^{2+}, Sr^{2+}, and Pb^{2+} with catalytic and ion-exchange properties, and the chemical properties have been found to correlate with the nearest-neighbor distances between divalent cations and oxygen by fitting the observed EXAFS for each CaHAp sample. Figure 8 shows optimum curve fitting for each hydroxyapatite with the results of the curve fitting analysis shown in Table 1, together with those for CaCO$_3$ as a reference. Based on the single crystal analyses (24), the coordination number of CaCO$_3$ is estimated to be 6, showing that each coordination number of CaHAp estimated by EXAFS is 16.4/6 times larger than expected. The corrected coordination numbers are shown in parentheses in Table 1. The nearest-neighbor Ca–O distances of the thermally stable CaHAp with Ca/P = 1.68, 1.59, and 1.55 are 0.2399, 0.2399, and
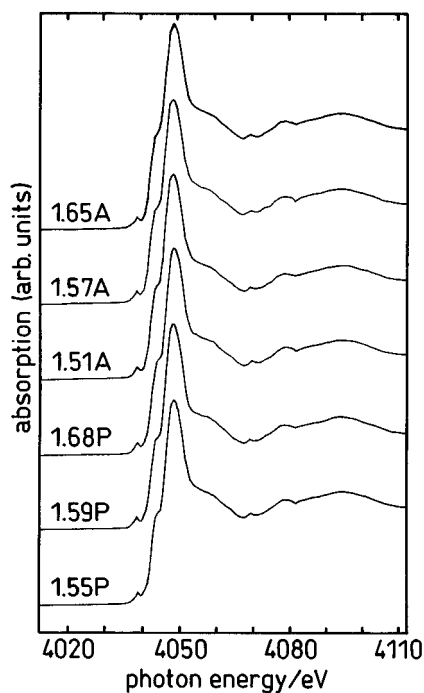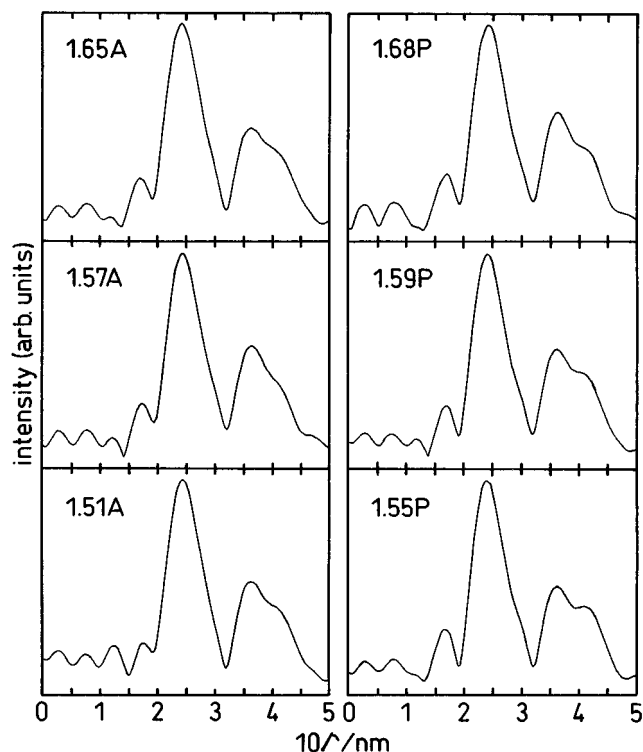
FIG. 7. Fourier transform of k^3 weighted EXAFS oscillation near the Ca K-edge of the thermally stable and unstable CaHAp. Symbols as in Fig. 6.
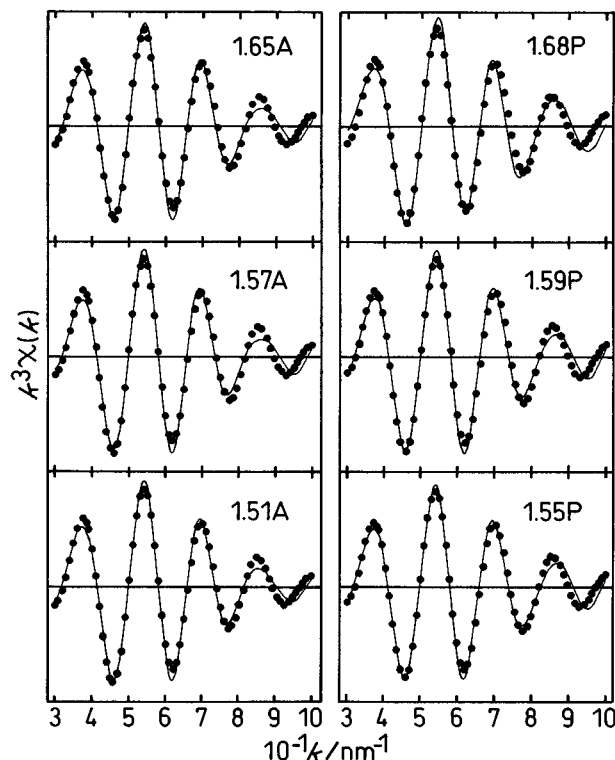

FIG. 8. Curve fitting of the thermally stable and unstable CaHAp. Solid lines, experimental data; ●, calculated results. Other symbols as in Fig. 6.

0.2397 nm, respectively, while those of the thermally unstable CaHAp with Ca/P = 1.65, 1.57, and 1.51 are 0.2408, 0.2410, and 0.2409 nm, respectively. Although cognizance of the estimated deviations should be taken, the thermally stable CaHAp possesses a tighter apatite structure than the unstable CaHAp, reflecting the suppression of the conversion of CaHAp to the corresponding phosphate.

TABLE 1
Results of Curve-Fitting Analyses

Ca/P	NaOH[a]	r^b (nm)	N^c	σ^d (Å)	$\Delta E_0{}^e$ (eV)	R^f (%)
Ref.	CaCO₃	0.2367	16.4(6)	0.1183	9.305	2.9
1.65	A	0.2408	19.0(7.0)	0.1362	10.323	15.7
1.57	A	0.2410	20.3(7.4)	0.1367	10.635	16.7
1.51	A	0.2409	18.6(6.8)	0.1356	10.602	14.1
1.68	P	0.2399	19.0(7.0)	0.1345	9.471	21.9
1.59	P	0.2399	18.3(6.7)	0.1327	9.511	16.0
1.55	P	0.2397	18.2(6.7)	0.1330	9.285	15.3

[a]CaHAp was prepared in the absence (A) and presence (P) of 5 mol dm⁻³ NaOH.

[b]Distance.

[c]Coordination number: values in parenthesis are the corrected values.

[d]Debye-Waller (like) factor.

[e]Threshold increment.

[f]Reliability factor.

CONCLUSIONS

1. The thermal stability of CaHAp prepared without alkaline reagents is low and CaHAp is completely converted to $Ca_3(PO_4)_2$ at 973 K.

2. The thermal stability of CaHAp prepared under alkaline values of pH is dramatically improved. The conversion of CaHAp to $Ca_3(PO_4)_2$ is completely suppressed at 1473 K with hydroxy-apatite prepared with 5 mol cm⁻³ NaOH at pH 12.

3. EXAFS analyses show that the thermally stable CaHAp possesses a tighter apatite structure than the unstable CaHAp.

ACKNOWLEDGMENTS

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