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Preparation, Characterization, and Thermal Stability of Lead Hydroxyapatite

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Lead hydroxyapatites (PbHAp) have been prepared from H_3PO_4 and $Pb(NO_3)_2 \cdot 5PbO$ (1), the latter of which was obtained through dehydration of basic lead nitrates such as $2Pb(NO_3)_2 \cdot 5Pb(OH)_2$ (2) and $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ (3). The amount of 2 with respect to 3, as well as the quantity of an unidentified water-soluble compound (4), decreased with increasing reaction time. The dehydration of 2 and 3, but not of 4, yielded the desired compound with expected X-ray diffraction pattern and infrared spectra. When the prepared PbHAp was heated at 773, 973, and 1173 K for 3 h, the XRD patterns showed the apatite structure, respectively, but PbHAp heated at 1173 K was partly converted to an amorphous compound. At 1473 K, PbHAp completely melted. X-ray absorption fine structure analyses showed that the nearest-neighbor distance of the Pb–O bond in PbHAp was 2.18 Å, which was shorter than that of the Ca–O bond of calcium hydroxyapatite and Sr–O bond of strontium hydroxyapatite. © 1999 Academic Press

INTRODUCTION

The apatite $[M_{10}(XO_4)_6Z_2]$, where M is a metal, X is, for example, P, As, Si, or S, and Z is OH or a halogen, has a hexagonal structure and is evidently a solid of considerable flexibility in its elemental compositions (1–3). One of the more common forms, calcium hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2$, abbreviated as CaHAp] is a major component of biological hard tissue, an absorbent for separating biomaterials, a catalyst for various reactions, and an ion exchanger for divalent cations and halogen anions.

In our laboratories, CaHAp and strontium hydroxyapatite (SrHAp) have been employed as catalysts for the oxidation of lower alkanes (4). In the oxidation of methane, for example, the addition of a small quantity of lead to the hydroxyapatites generally results in an increase in the conversions and the selectivities to C_2 compounds, in particular ethylene. Evidently lead plays an important role in the oxidation process.

Four synthesis procedures for PbHAp are currently available (5–8). Mayer *et al.* reported that PbHAp could be successfully prepared from $PbSO_4$ and Na_3PO_4 (6). Bruckner *et al.* prepared PbHAp from Pb $(CH_3COO)_2 \cdot 3H_2O$ and Na_2HPO_4 (7). However with these methods, a residue of sulfate and sodium is found in the product PbHAp. Bigi *et al.* have prepared PbHAp from H_3PO_4 and $Pb_6O_5(NO_3)_2(=Pb(NO_3)_2 \cdot 5PbO)$ (5), the latter of which was obtained as described by Newkirk and Hughes (9). Ntahomvukiye *et al.* obtained PbHAp by hydrolysis of $PbHPO_4$ and by double substitution of $(NH_4)_2HPO_4$ and $Pb(NO_3)_2$ (8). These methods appear to be useful since no residue is retained. However, particularly with Bigi's method, detailed information on the preparation of PbHAp is not available.

The purpose of this study is to establish a synthesis for pure PbHAp by application of Bigi's preparation procedure (5) and to examine the thermal stability of PbHAp to determine its applicability at higher temperatures. X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) spectroscopy have been employed for supplemental characterization of the synthesized PbHAp.

EXPERIMENTAL

Preparation of the Basic Lead Nitrate

Following the preparation of Robin and Theolier (10), 25% ammonia solution (Wako, 25 ml, 330 mmol) was added with stirring to a solution of $Pb(NO_3)_2$ (Wako Pure Chemicals, Osaka, 10 g, 30 mmol) in 300 ml H_2O, and then boiled for 0.5, 1, 3, or 6 h in order to establish a suitable reaction time. The precipitate was filtered, washed, and

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dried at 373 K overnight. When the reaction time was adjusted to 6 h, only a small quantity of the precipitate was obtained and most of the product dissolved in the solution, which was filtered and the filtrate was evaporated to obtain white crystals.

Dehydration of the Basic Lead Nitrate

Each precipitate obtained from the reaction of lead nitrate with ammonia was heated at 553 K for 23 h in air (9) and the mass and color of each precipitate obtained after 0.5, 1, 3, and 6 h were 6.34 g (white creamy yellow), 5.73 g (creamy yellow), 5.21 g (orange yellow), and 0.43 g (white orange yellow), respectively. The white crystals obtained from the evaporation were similarly subjected to the aforementioned dehydration process.

Preparation of PbHAp

Each of the previously heated precipitates was suspended in 50 ml H_2O and boiled. To this boiling solution, aqueous H_3PO_4 solution (Wako, 0.73 mmol/liter) was added dropwise until twice the moles of the precipitate had been added, assuming the precipitate was $Pb_6O_5(NO_3)_2$ [$= Pb(NO_3)_2 \cdot 5PbO$], and then further stirred for 3 h. During this stirring, the color of each suspension changed to milky white regardless of the color of the initial precipitate. The precipitate was filtered, washed, and dried at 373 K overnight. Following Bigi's procedure (5), the precipitate was resuspended in 50 ml H_2O, the pH raised by addition of ammonia solution and kept constant at approximately 11 while boiling and stirring for 3 h. The final precipitate thus obtained was filtered, washed, dried at 373 K overnight, and calcined at 773 K for 3 h.

Analyses and Instrumental Methods

Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 2500X diffractometer, using monochromated Cu$K\alpha$ radiation. Patterns were recorded from 5° to 60°. The concentrations of Pb and P in the prepared solid were determined in an aqueous HNO_3 solution by ICP spectrometry (Shimadzu, ICPS-5000). Infrared spectra were recorded with a Shimadzu FTIR-8200PC under an N_2 atmosphere. The surface areas were measured with a conventional BET nitrogen adsorption apparatus. Differential thermal analysis–thermogravimetric analysis (DTA–TGA) was obtained with a Thermoflex TG 8110 (Rigaku, Tokyo). XAFS near the Pb L_3-edge was measured (2.5 GeV) at the High Energy Accelerator Research Organization with a storage ring current of ca. 320 mA. The X-rays were monochromatized with channel-cut Si(311) crystals, and the absorption spectra were observed using ionization chambers in a transmission mode. The photon energy was scanned in the range 12.5–14.1 keV for the Pb L_3-edge. The EXAFS interference function $\chi(k)$ was extracted from the absorption spectra following the standard procedure. The radial structure function $\phi(r)$ was obtained from the Fourier transforms of $k^3\chi(k)$. The backscattering amplitude and the phase shift function calculated by McKale *et al.* (11) were used. For the curve-fitting, the range of the interest for $\phi(r)$ was filtered with a Hamming window function, and transformed back to k space, $\chi'(k)$. Curve-fitting calculations for $\chi'(k)$ (12) were performed over the k range 4–11.5 Å^{-1}.

RESULTS AND DISCUSSION

The preparation of PbHAp reported by Bigi *et al.* can be summarized by the following stoichiometric equations.

$$6Pb(NO_3)_2 + 10NH_4OH \rightarrow Pb(NO_3)_2 \cdot 5Pb(OH)_2 + 10NH_4NO_3 \quad [1]$$

$$Pb(NO_3)_2 \cdot 5Pb(OH)_2 \rightarrow Pb(NO_3)_2 \cdot 5PbO + 5H_2O \quad [2]$$

$$Pb(NO_3)_2 \cdot 5PbO + 3H_3PO_4 \rightarrow 0.5Pb_{10}(PO_4)_6(OH)_2 + Pb(NO_3)_2 + 4H_2O \quad [3]$$

In the preparation of hydroxyapatites, the corresponding hydroxide and phosphoric acid are generally employed as a source of cationic metal and phosphate, respectively, but $Pb(OH)_2$ does not exist as such. Therefore $Pb(NO_3)_2 \cdot 5PbO$ was employed in lieu of $Pb(OH)_2$ as a precursor of the hydroxide. It should be noted that it is possible to write the products of Eq. [3] without including $Pb(NO_3)_2$.

Preparation of Basic Lead Nitrates (Eq. [1])

Since no description of the stirring time for the reaction of $Pb(NO_3)_2$ with NH_4OH to form basic lead nitrate $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ was available from the reports of Newkirk and Hughes (9) or Robin and Theolier (10), the effects of the stirring time on the reaction were investigated to determine a suitable reaction time. Figures 1A–1D show XRD patterns of the precipitate after the reaction for 0.5, 1, 3, and 6 h, respectively. With increasing reaction time, the peak intensity due to undesirable $2Pb(NO_3)_2 \cdot 5Pb(OH)_2$ (13) decreased while that for the desirable $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ (13) increased. However, the quantity of the basic lead nitrate decreased with increasing reaction time and finally after 6 h, most of the solid had dissolved in the solution. After evaporation of the solution, XRD of the residue could not be matched to that of these basic lead nitrates.

Kwestroo *et al.* examined the nature of basic lead nitrates produced with the following reaction (13).

$$(x + 1)\mathrm{Pb(NO_3)_2} + 2x\mathrm{NaOH} \rightarrow \mathrm{Pb(NO_3)_2 \cdot }x\mathrm{Pb(OH)_2} + 2x\mathrm{NaNO_3} \quad [4]$$

It was reported that with this method four basic lead nitrates, $Pb(NO_3)_2 \cdot Pb(OH)_2$, $2Pb(NO_3)_2 \cdot 5Pb(OH)_2$, $Pb(NO_3)_2 \cdot 3Pb(OH)_2$, and $Pb(NO_3)_2 \cdot 5Pb(OH)_2$, were obtained and the former compound $Pb(NO_3)_2 \cdot Pb(OH)_2$ was soluble in hot water while the remaining three compounds were insoluble (13). However, $2Pb(NO_3)_2 \cdot 5Pb(OH)_2$ decomposed into $Pb(NO_3)_2 \cdot Pb(OH)_2$ and $Pb(NO_3)_2 \cdot 3Pb(OH)_2$ in excess water (13). The desired compound $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ decomposed in a large excess of NH_4OH (13).

Only two basic lead nitrates, $2Pb(NO_3)_2 \cdot 5Pb(OH)_2$ and $Pb(NO_3)_2 \cdot 5Pb(OH)_2$, were obtained in the present study and based on the XRD patterns and the change of the quantity of the products with the reaction time, it appears reasonable to suggest that $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ is obtained successively from $2Pb(NO_3)_2 \cdot 5Pb(OH)_2$. It is worthwhile to note that the possibility of the formation of two other lead nitrates $Pb(NO_3)_2 \cdot Pb(OH)_2$ and $Pb(NO_3)_2 \cdot 3Pb(OH)_2$ cannot be discounted since $2Pb(NO_3)_2 \cdot 5Pb(OH)_2$ produced after 0.5 h was present in a large excess of NH_4OH. Under such conditions, the former two basic lead nitrates could be formed and, if amorphous, remain undetected by XRD. Although unidentified XRD peaks, not corresponding to those of $Pb(NO_3)_2 \cdot Pb(OH)_2$ and $Pb(NO_3)_2 \cdot 3Pb(OH)_2$ (13), were present in the samples (Figs. 1A–1D), the latter were subjected, after Bigi (5), to the procedure outlined below.

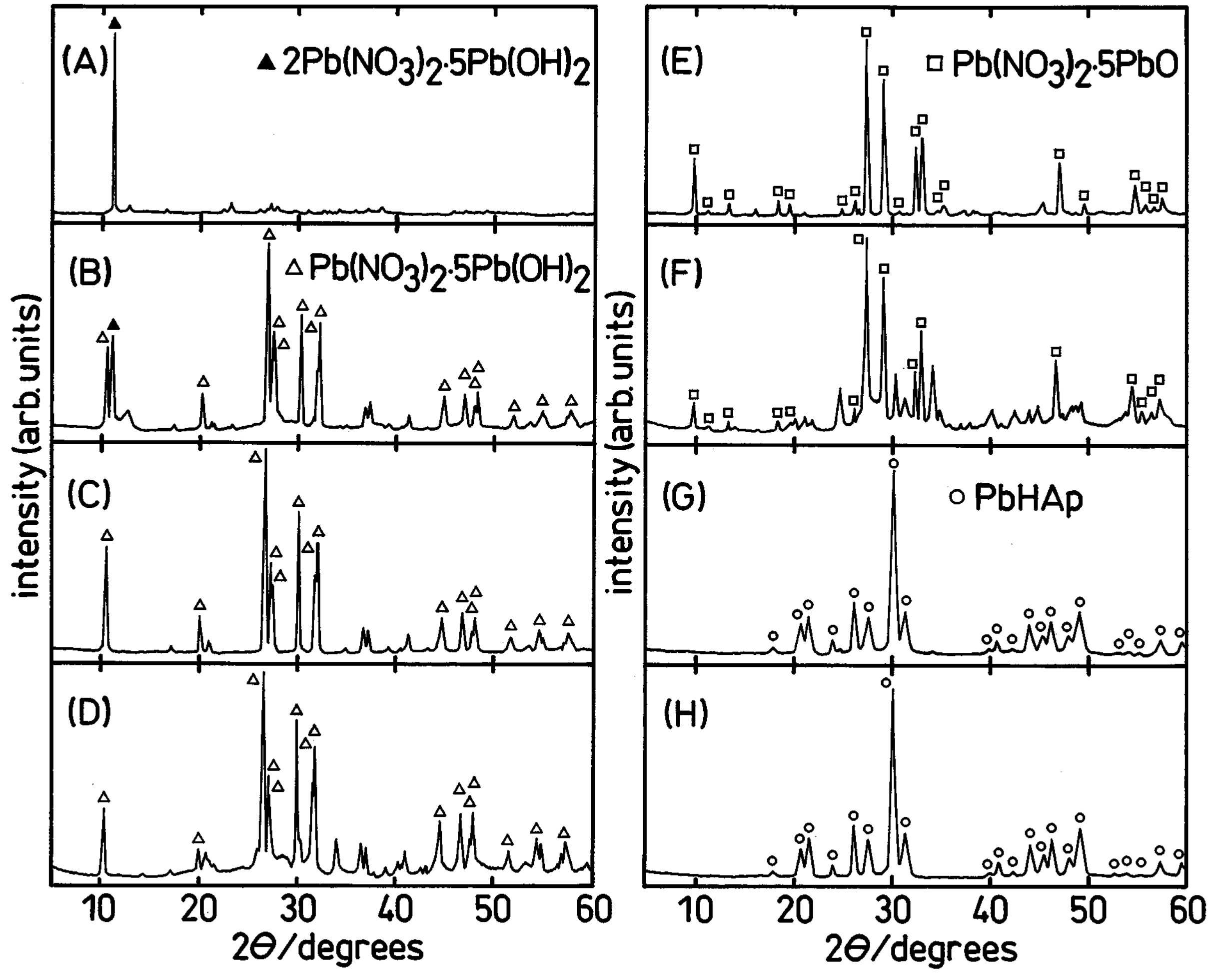

FIG. 1. XRD patterns of the products at various times (A, 0.5 h; B, 1 h; C, 3 h; D, 6 h) in the preparation of PbHAp, from $Pb(NO_3)$ and NH_4OH; after heating samples A and D at 553 K for 23 h (E and F, respectively); after reaction between sample E and H_3PO_4 (G); after treatment of sample G with NH_4OH (H).

Dehydration of Basic Lead Nitrates (Eq. [2])

Basic lead nitrates obtained with stirring for 0.5, 1, 3, and 6 h were dehydrated by heating at 553 K for 23 h. It is of interest to note that XRD patterns of the dehydration products of basic lead nitrates obtained after 0.5, 1, and 3 h were essentially identical (Fig. 1E for 0.5 h; others not shown). However, after a 6 h reaction between $Pb(NO_3)_2$ and NH_4OH the formation of the dehydration product $Pb(NO_3)_2 \cdot 5PbO$ is clearly evident from the XRD patterns along with unidentified peaks (Fig. 1F). Two stoichiometric equations may be suggested to represent the formation of $Pb(NO_3)_2 \cdot 5PbO$:

$$6 \times [2Pb(NO_3)_2 \cdot 5Pb(OH)_2] \rightarrow 7 \times [Pb(NO_3))_2 \cdot 5PbO] + 10HNO_3 + 25H_2O \quad [5]$$

$$Pb(NO_3)_2 \cdot 5Pb(OH)_2 \rightarrow Pb(NO_3)_2 \cdot 5PbO + 5H_2O \quad [6]$$

Similar equations can be suggested for $Pb(NO_3)_2 \cdot 3Pb(OH)_2$. Therefore it would not be surprising to obtain $Pb(NO_3)_2 \cdot 5PbO$ from $2Pb(NO_3)_2 \cdot 5Pb(OH)_2$ and/or $Pb(NO_3)_2 \cdot 5Pb(OH)_2$; with either of which the presence of amorphous $Pb(NO_3)_2 \cdot 3Pb(OH)_2$ is possible.

Preparation of PbHAp (Eq. [3])

The reaction of the dehydration product $Pb(NO_3)_2 \cdot 5PbO$ (obtained from the basic lead nitrates after 0.5, 1, and 3 h reaction between $Pb(NO_3)_2$ and NH_4OH) with H_3PO_4 yielded PbHAp (Fig. 1G for 0.5 h; others not shown). Trace XRD peaks at 2θ values of 24.8° and 34.1° were also observed. However, after treatment with ammonia the latter were not detected (Fig. 1H), although the dehydration product of Fig. 1E retained a portion of the unidentified species after treatment with ammonia (not shown). Although Bigi *et al.* suggested that the unidentified products consisted of $PbHPO_4$ and some lead oxides, which vanished with the ammonia treatment (5), the XRD patterns of the unidentified products did not match the JCPDS data for these lead compounds. Calcination of each of the PbHAp samples at 773 K for 3 h increased the crystallinity.

In the present study, it should be noted that the quantity of H_3PO_4 used for the preparation of PbHAp was smaller than that required in the stoichiometry (Eq. [3]). In this case, unreacted $Pb(NO_3)_2 \cdot 5PbO$, which should convert to the corresponding hydroxide in aqueous solution, and $Pb(NO_3)_2$ are present in the resulting solution together with PbHAp. Since $Pb(NO_3)_2$ is soluble in water, PbHAp and $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ are present in the precipitate after washing with H_2O. On treating this precipitate with NH_4OH, only PbHAp must be obtained since $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ is decomposed in a large excess of NH_4OH (13) and dissolved in the solution as described above. If a stoichiometric excess of H_3PO_4 is employed for the preparation of PbHAp, the reaction between the byproduct $Pb(NO_3)_2$ and H_3PO_4 will yield $PbHPO_4$ as an impurity, regardless of the ammonia treatment.

Bulk Properties and Thermal Stability of PbHAp

The surface area of PbHAp after calcination at 773 K was found to be influenced by the stirring time in the preparation of basic lead nitrates. Thus, for stirring times of 0.5, 1, and 3 h, surface areas of 3.6, 6.5, and 6.9 m^2/g, respectively, were measured. However, the IR spectra (Fig. 2) were essentially identical, regardless of the stirring time, and OH stretching, $\nu_3(PO_4)$, $\nu_1(PO_4)$, and $\nu_4(PO_4)$ modes were detected at 3557, 1037 and 981, 927(shoulder), and 575 and 537 cm^{-1}, respectively, as reported by Bigi *et al.* (5). To observe the thermal stability of PbHAp, the hydroxyapatite was calcined at 773, 973, 1173, and 1473 K for 3 h. Although PbHAp melted completly at 1473 K, the XRD patterns of the remaining calcined PbHAp samples matched those reported for PbHAp. However, ICP analyses of the PbHAp calcined at 773, 973, and 1173 K found %Pb and %P as 79.0, 6.86, 79.1, 6.93, and 63.3, 7.36, respectively. Furthermore, the position and shape of the IR spectra of PbHAp

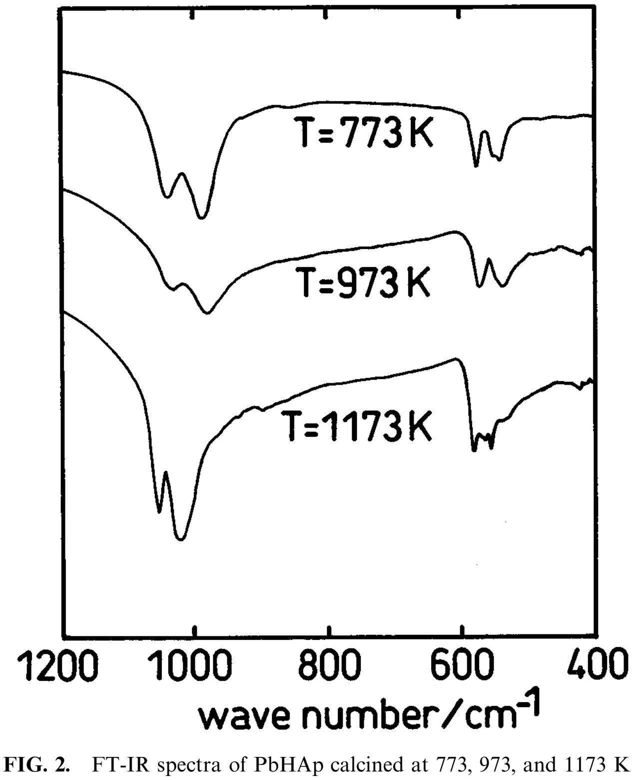

FIG. 2. FT-IR spectra of PbHAp calcined at 773, 973, and 1173 K.

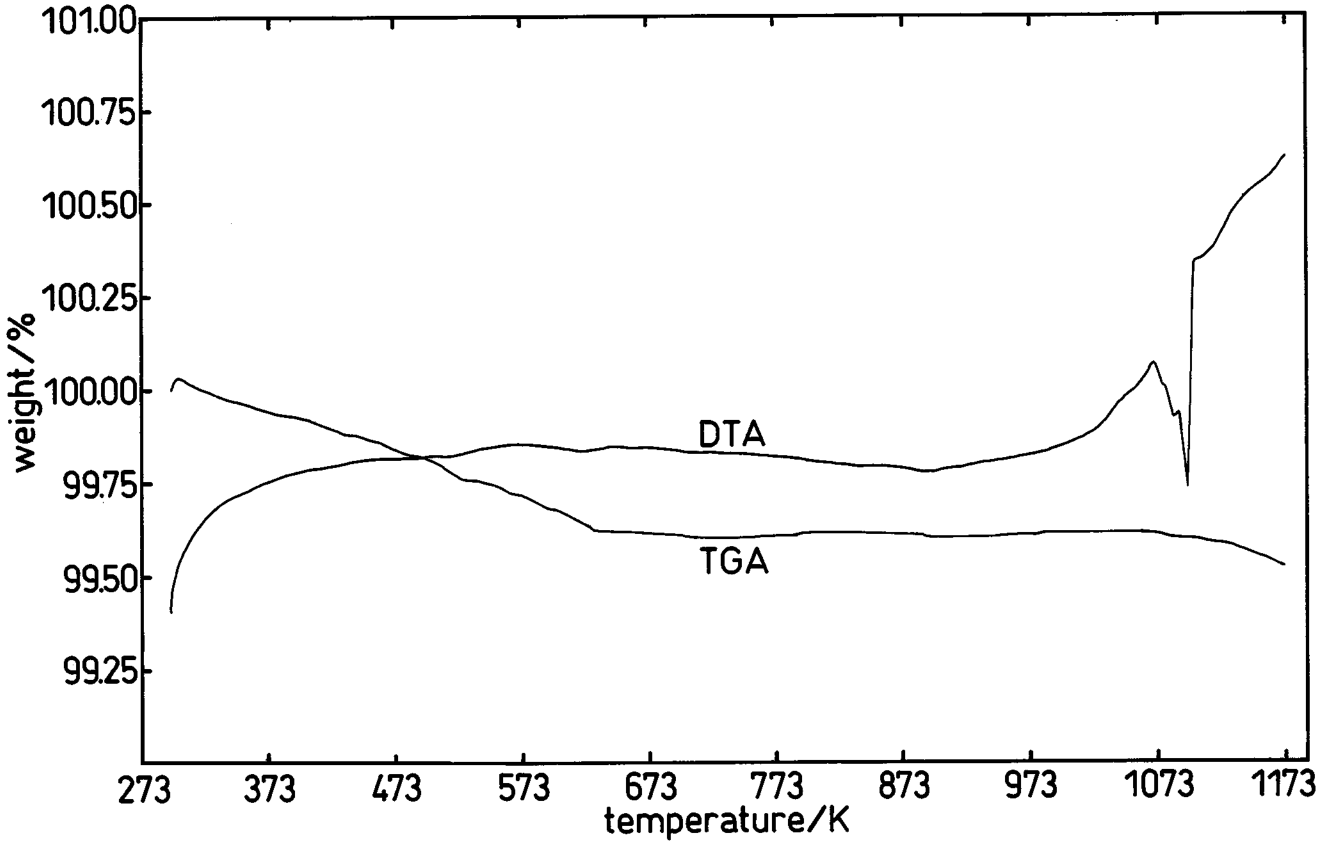

FIG. 3. DTA-TGA analysis of PbHAp.

calcined at 1173 K were evidently different from those calcined at 773 and 973 K (Fig. 2). Therefore PbHAp is thermally stable to at least 973 K and at a temperature between 973 and 1173 K it decomposes to form amorphous compounds with elimination of PO_4, and finally melts. Complementary evidence has been provided by DTA-TGA (Fig. 3).

XAFS Analysis

The X-ray absorption near the Pb L_3-edge of PbHAp is shown in Fig. 4A. The edge position of PbHAp was essentially identical to that of PbO as a reference, indicating the similarity of the cationic charge of Pb^{2+} in PbHAp and in PbO. Figure 4B shows the Fourier transforms of the EXAFS oscillation around the Pb L_3-edge of PbHAp. Phase shifts are not corrected in this spectrum. The strongest peak corresponds to the nearest-neighbor distance for Pb–O and the peaks due to other-order distances are also evident. It should be noted that information obtained from the strongest peaks is evidently influenced by the nearest-neighbor distance but not the average distance. As described previously (4), the nearest-neighbor distance is expected to have the strongest relationship to the thermal stability and the ion-exchange and catalytic properties. Thus, the reliability of the phase shift and amplitude functions are tested at approximately the nearest distance by fitting the observed EXAFS of PbHAp. Figure 4C shows the optimum curve fitting around the Pb L_3-edge of PbHAp, in which the solid line represents the experimental data and the closed circles represent the calculated results. The results of the curve fitting analyses for PbHAp and PbO as a reference are summarized in Table 1. The nearest-neighbor distance and

TABLE 1
Results of Curve-Fitting Analyses for PbHAp and PbO as a Reference

Sample	$r_{\text{Pb–O}}$[a]	N[b]	σ[c] (Å)	E_0[d](eV)	R[e] (%)
PbHAp	2.177	8.0	0.124	– 12.417	9.1
PbO	2.209	2.2	0.068	– 2.337	6.5

[a] Distance; estimated maximum deviation (± 0.01).

[b] Coordination number; estimated maximum deviation (± 1).

[c] Debye–Waller (like) factor.

[d] Threshold increment.

[e] Reliability factor.

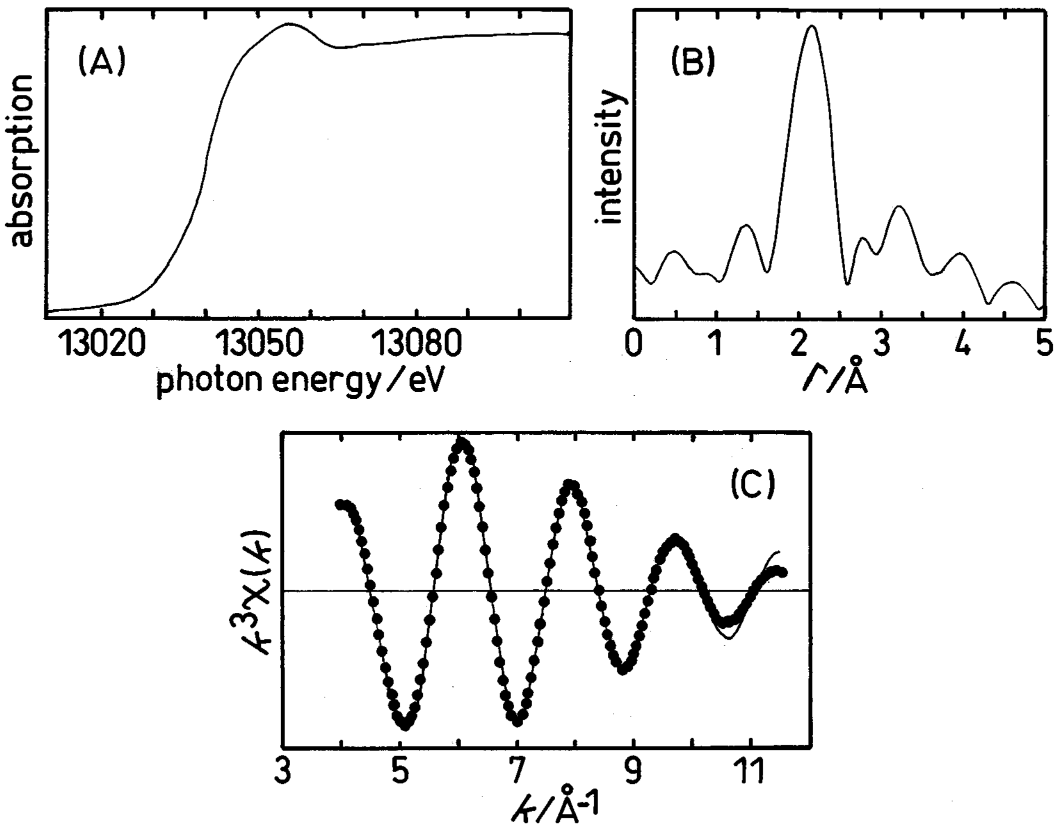

FIG. 4. XANES spectra (A), Fourier transformation of k^3-weighted EXAFS oscillation (B), and curve-fitting near Pb L_3-edge (C) measured at 300 K of PbHAp. Solid line in (C), experimental data; closed circles in (C), calculated values.

coordination number for PbO are essentially identical to those reported in Ref. (14). The nearest distance of Pb–O is apparently shorter than those in Pb–CaHAp (2.35 Å) (15) and Pb–SrHAp (2.14–2.38 Å) (4), indicating that the Pb species in the binary hydroxyapatites are strongly influenced by the second cation. The relatively short nearest-neighbor Pb–O distance (2.177 Å) in PbHAp as compared with that of the Ca–O bond (2.40 Å) in CaHAp (16) and that of the Sr–O bond (2.52 Å) in SrHAp (4) can be attributed to a covalent bond (17).

CONCLUSIONS

1. Under the present reaction conditions, a reaction time of approximately 3 h was suitable for the reaction of $Pb(NO_3)_2$ with NH_4OH to form $Pb(NO_3)_2 \cdot 5Pb(OH)_2$, which is a precursor to lead hydroxyapatite. At shorter or longer reaction times, additional basic lead nitrates were obtained.

2. $Pb(NO_3)_2 \cdot 5PbO$ was obtained from the dehydration of either $2Pb(NO_3)_2 \cdot 5Pb(OH)_2$ or $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ for 0.5 h.

3. Treatment of the product mixture from the reaction of $Pb(NO_3)_2 \cdot 5PbO$ and H_3PO_4 with NH_4OH was essential for the removal of impurities which were produced from unreacted $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ and other basic lead nitrates.

4. Lead hydroxyapatite is stable up to 973 K. At a temperature between 973 and 1173 K, the hydroxyapatite begins to decompose to form amorphous compounds and finally melted at 1473 K.

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