Crystallographic study of lead-substituted hydroxyapatite synthesized by
high temperature mixing method under hydrothermal conditions

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Abstract:

The solid solutions in the system of Ca and Pb hydroxyapatite, $\text{Ca}_{10-\chi}\text{Pb}_\chi\text{HA}$ ($\chi=0-10$), were successfully synthesized by high-temperature mixing method (HTMM) at 200°C for 12 hours under hydrothermal conditions. The samples were characterized by X-ray diffraction, chemical analysis and electron microscopic observation, and the site of the metal ions in the solid solutions was analyzed with the Rietveld method. The lattice parameters of the solid solutions prepared by both of the methods didn't vary linearly with Pb contents, and they have two turning points of 0.4 and 0.6 of Pb content. It was found that Pb ions in the solid solutions preferentially occupied the M (2) site in the apatite structure. HTMM gives Ca-Pb HA solid solutions much better crystallization. However, due to the formation of intermediate compound of $\text{Pb}_3\text{O}_2(\text{OH})_2$ in the $\text{Pb}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution before mixing with $(\text{NH}_4)_2\text{HPO}_4$ solution at 200°C, HTMM causes the decrease of crystallization of the samples with high Pb content.

Key words: Ca-Pb hydroxyapatite; Chemical synthesis; X-ray diffraction; Crystal structure

1. Introduction

Calcium hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$, designated as Ca-HA, is a primary constituent of vertebral animal's hard tissues. The synthetic Ca-HA has attracted our attention for its utility in the fields of bioceramics, catalysts, adsorbents, and so on [1]. In the apatite structure, the Ca ions occupy two types of nonequivalent sites: the M(1) sites are at the fourfold symmetry 4(f) position and the M(2) sites are at the sixfold symmetry 6(h) position [2]. The apatite structure has a high flexibility, so many metal ions can be incorporated into the structure. It is interesting to investigate the site of metal ions that are incorporated into the apatite structure.

A few researchers have prepared the solid solutions in the system of Ca-Pb HA. Sugiyama *et al.*[3] prepared Ca-Pb HA solid solutions from aqueous solutions, and determined their catalytic activities in the conversion of methane with nitrous oxide and oxygen as oxidants after calcination at 773K for 3 h. They, however, gave no results on the occupancy of Pb^{2+} ions in the metal sites. Bigi *et al.*[4] investigated the crystal structure of hydroxyapatite synthesized at different degrees of lead substitution for calcium (20, 45 and 80% Pb atoms) by solid state reaction at 1173K. The site-occupancy factors of Pb atoms indicate a clear preference of lead for M (2) of the apatite structure.

Bigi *et al.*[4]also prepared the Ca-Pb HA solid solutions by solid state reaction at 900°C and aqueous reaction at 100°C. The authors reported that the cell parameters a of the apatitic phase obtained by solid state reaction varied linearly with compositions, while the variation of the cell parameter c showed a discontinuity at about 50 Pb

atom %. The crystallinity of Pb-Ca HA solid solutions synthesized by the aqueous reaction must be so low that they needed the calcination to increase the crystallinity. They also described in their paper that the cell parameters of the solid solutions obtained by aqueous reaction fitted very well with those obtained by the solid state reaction. In spite of their description, a careful observation of the data shows some differences between the samples prepared by the solid state reaction and aqueous reaction. It is also strange that the parameters a and c of the Pb-HA prepared by the aqueous reaction were smaller than the reported values (JCPDS card 24-586).

The solid state reaction can give higher crystallization to the products, but the hydroxyl defect would form due to the high temperature treatments. On the other hand, the crystallization of the products synthesized by the aqueous reaction is usually low even without hydroxyl defects in their structure. The low crystallization and hydroxyl defect in the samples will cause inaccuracy in the structural investigation by the Rietveld analysis. Hydrothermal synthesis method is a wet-chemical technique for directly forming complex oxide powders with high crystallization [5]. The technique has an additional advantage for the preparation of HA powders: no hydroxyl defects in the structure. Cd-HA [6], Ca-Cd HA [7, 8], Ca-Sr HA [8, 9] and Sr-Pb HA [10] were successfully synthesized hydrothermally in our former work. On the basis of the hydrothermal method (low-temperature mixing method, LTMM), a new technique (high-temperature mixing method, HTMM) was designed [11] for preparation of powders in multi-component system such as hydroxyapatite under hydrothermal conditions. In this technique, two kinds of starting solutions, separately heated to a

desired reaction temperature in a multi-chamber autoclave, were mixed to start the reaction under hydrothermal conditions. Ca-Cd HA [7], Ca-Sr HA [9] and Sr-Pb HA [12] were successfully synthesized by HTMM in our former work.

In this work, the well-formed crystals of Ca-Pb HA solid solutions were synthesized using HTMM under hydrothermal conditions at 200°C for 12 h. Powder X-ray diffraction analyses were employed to determine the crystalline phases and to investigate the site that Pb ions preferentially occupy in the HA structure. The obtained crystals were observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). The concentrations of Ca^{2+} , Pb^{2+} and PO_4^{3-} in the solid solutions were also measured by inductively coupled plasma (ICP) spectrometry.

2 Experimental

The starting materials were reagent grade chemicals (Wako Pure Chem., Ind., Co., Japan), $(\text{NH}_4)_2\text{HPO}_4$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Pb}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. $(\text{NH}_4)_2\text{HPO}_4$ were dissolved in deionized water to get a 0.200 mol·L⁻¹ solution. The pH of the solution was adjusted to 10 with ammonia. A mixed metal nitrate solution with 0.334 mol·L⁻¹ was prepared from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ nitrates, the Pb/(Pb+Ca) molar ratio varying from 0 to 1. We used a Teflon lined multi chamber autoclave which has two separate chambers. Each starting solution (8 cm³) was separately poured into a different reaction chamber to get the HA stoichiometric composition of

1.67. These solutions were heated to desired temperature and then mixed. Hydrothermal treatments were carried out at 200°C for 12 hours.

After washed with distilled water, the products were characterized by powder X-ray diffraction (XRD; Model RTP-300RC, Rigaku Co., Japan) with Cu K α radiation (40kV and 100 mA). The lattice parameters were calculated by the least square method with Si as an internal standard. X-ray diffraction data used for the Rietveld analysis were collected by step scanning method under following conditions: 2 θ range 15°-130°; step width 0.02°; and counting time 6 s. Rietveld analysis was performed with the program RIETAN[13]. Scanning electron microscope (SEM; Model S530, HITACHI Co., Japan) and Transmission electron microscopic (TEM; Model H-800, HITACHI Co., Japan) were used to observe their morphologies. The composition of the solid solutions was determined by using inductively coupled plasma (ICP) spectrometry (SPS7000A, Seiko) after dissolving in a nitric acid.

3 Results and discussion

3.1 Sample characterization

The XRD patterns of the samples with different χ_{Pb} obtained by HTMM are shown in Fig. 1. All the samples corresponded to pure apatite phase, whatever χ_{Pb} is. The patterns of the samples corresponding to Ca HA (Pb0) and to Pb HA (Pb100) display well-defined and sharper peaks in agreement with a high degree of crystallinity of the two end members. On the other hand, the patterns of the samples containing Ca and Pb generally exhibit broader diffraction peaks, in agreement with a reduced degree of

crystallinity of the Ca-Pb HA solid solutions. The broadening is more evident for the samples with smaller Pb contents, suggesting a greater difficulty for Ca HA to host the larger lead ion than for Pb HA to host the smaller calcium ion (6-coordinate octahedral Pb(2) is 1.20 Å, 6-coordinate octahedral Ca(2) which is 0.99 Å). The peaks shifted to the left with the χ_{Pb} increase from 0.1 to 0.4 and from 0.6 to 1, but they didn't shift in the middle composition of the solid solutions. The reasons will be discussed after structure refinements.

The compositions of the products determined by the chemical analysis are shown in Fig. 2 against those of the starting solutions. Pb/(Ca+Pb) molar ratios (χ_{Pb}) in the products increase on increasing Pb/(Ca+Pb) molar ratios in the starting solutions, and are higher than that in the starting solutions in the range of 0.1~0.3 and 0.7~0.9 of χ_{Pb} . This indicates that Pb²⁺ ions enter cation sites of the crystal more easily compared to Ca²⁺ ions in the samples in the range of 0.1~0.3 and 0.7~0.9 of χ_{Pb} . However, they are similar to that in the starting solutions in the range of 0.4~0.6. The reasons were discussed after Rietveld analysis. Table 1 shows the compositions of the products determined by ICP. The isomorphous substitution does not significantly affect the stoichiometry of HA, the average (Ca+Pb)/P molar ratio obtained by HTMM in the samples was about 1.71, which is a little higher than that in HA composition of 1.67. However, the average (Ca+Pb)/P molar ratio of the solid solutions synthesized by LTMM in our former work [18] is 1.72, which is even higher than that in HA composition.

Fig. 3 displays the transmission electron microscope (TEM) pictures and scanning

electron microscope (SEM) photographs of the samples with different Pb/(Ca+Pb) molar ratio prepared by HTMM. The results indicate that the morphology of the apatitic crystals is affected by the chemical composition. The samples of (a), (b), (c) and (d) are observed by SEM, and (e), (f) are observed by TEM. The morphology of the samples with χ_{Pb} less than 0.4 is elongated crystals, and become smaller with less χ_{Pb} . The larger elongated crystals coexisted with the larger bulky crystals in the samples with χ_{Pb} more than 0.6. However, Ca-Pb HA with χ_{Pb} more than 0.6 synthesized by LTMM [14] are all bulky crystals.

In this work, HTMM was used to synthesize Ca-Pb HA solid solutions. Compared to LTMM, for HTMM, two starting solutions were separately heated to 200°C and then mixed. The reaction rate was higher so that the apatite could be formed directly, not through the amorphous phosphate compound. In our works, when Pb/(Ca+Pb) molar ratio was less than 0.3, The Pb/(Pb+Ca) molar ratios in the products are more than that in the starting solution, the crystallinity of the samples prepared by HTMM was higher than LTMM. However, when Pb/(Ca+Pb) molar ratio was more than 0.7, they are different results. The morphology is also different from the samples prepared by LTMM as above results. It is very difficult to be explained until we found the formation of intermediate compound of $\text{Pb}_3\text{O}_2(\text{OH})_2$ in the $\text{Pb}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution before mixing with $(\text{NH}_4)_2\text{HPO}_4$ solution at 200°C in the case of HTMM. It is easy for OH^- and Pb^{2+} to form $\text{Pb}_3\text{O}_2(\text{OH})_2$ in an aqueous non acidified $\text{Pb}(\text{NO}_3)_2$ solution according to the following reaction:

The amount of this compound increased with Pb content of the solution. The precipitation of intermediate compound must result in the decrease of the Pb content in the nitrate solution. When two solutions are mixed at 200°C, a Ca-rich solid solution may form from the solutions firstly, while Pb-rich solid solution crystals may precipitate on the crystals previously formed. Thus, the aggregated crystals are obtained. Hydrothermal treatment might increase the compositional homogeneity of the products by dissolution and precipitation mechanism. However, some compositional inhomogeneity still remains in the products, which might reduce the crystallization of the samples and inhibited the tendency of Pb^{2+} ions to enter cation sites. Therefore the amount of the intermediate compound increased with Pb content, which resulted in the decrease of crystallization of the samples with high Pb content.

3.2 Structural analysis

In this work, there were 11 samples prepared with HTMM, and the results of their X-ray diffraction were analyzed by the RIETAN program. The results of the Pb 50% sample obtained by HTMM are shown in Fig. 4 and Table 2. The reliability factors ($R_{wp} = 16.17$; $R_p = 11.41$; $RR = 18.48$; $R_e = 2.93$; $S = 5.5193$) are acceptable for the structure determination of Ca-Pb HA in this work.

The result of the lattice parameters was shown in Fig.5, and also shown in Table 1. The lattice parameters of both a and c do not vary linearly with the compositions. They increased with the increase of χ_{Pb} from 0 to 0.3 and from 0.7 to 1. However, they didn't change from 0.4 to 0.6. This result is in agreement with the peaks shift in the XRD patterns. The variation of the lattice parameters of the Ca-Pb HA solid solutions

will be explained by the results of the occupancy of Pb ions in the apatite structure.

Fig. 6 showed the occupancy of Pb^{2+} in the M (1) and M (2) sites in the Ca-Pb HA structure. It was found that Pb ions preferentially occupied M (2) sites in the solid solutions. The occupancy of Pb^{2+} in the M (2) sites varied linearly with the increasing of $\text{Pb}^{2+}/(\text{Pb}^{2+}+\text{Ca}^{2+})$ in the starting solution but do not vary linearly in the M (1) sites. Pb^{2+} ions only occupied M (2) sites when χ_p exceeded 0.8. Some works [15-18] have investigated the occupancy of metal ions in the site of apatite structure. All results showed that the bigger ions occupied preferentially the M (2) sites since the arrangement of the staggered equilateral triangles in the site M (2) allows the packing of large ions, in contrast to the M (1) sites where the strict alignment in the columns causes a stronger repulsion. In addition, the distance between M (2) metal ions and M (2) metal ions is larger than that between M (1) metal ions and M (1) metal ions. Thus the metal ions with large ionic radius show the tendency to occupy M (2) sites. It was supposed that the metal ions with higher electronegativity were easy to occupy M (2) sites in our former work of Ca-Cd HA [7]. In the Ca-Pb HA solid solutions, the ionic radius of Pb^{2+} is larger than that of Ca^{2+} . The electronegativity of the Pb ion (1.8) is also much more than that of Ca ion (1.0). Therefore Pb^{2+} ions preferentially occupied the M(2) sites where almost occupied only by Pb^{2+} ions when the Pb^{2+} content was higher than 0.8.

When the $\text{Pb}^{2+}/(\text{Pb}^{2+}+\text{Ca}^{2+})$ is lower than 0.2, almost no Pb^{2+} ions occupies the M(1) sites. So the lattice structure of terminal Ca-phase is not distorted by the bigger Pb^{2+} ions and could be well crystallized. When the $\text{Pb}^{2+}/(\text{Pb}^{2+}+\text{Ca}^{2+})$ is more than 0.7,

almost all the M(2) sites are occupied by Pb^{2+} ions and the smaller Ca^{2+} ions only occupy the M(1) sites. So the lattice structure of terminal Pb-phase is not distorted seriously. But in the middle composition, the lattice structure may be distorted seriously because the metal cations could occupy both of the M(1) and M(2) sites equally. Therefore, the crystallinity may decrease and Bragg reflections are broaden as shown in Figure 1.

The replacement of Pb^{2+} for Ca^{2+} in the apatite structure induces an enlargement of the lattice parameters in agreement with the larger ionic radius of Pb^{2+} with respect to that of Ca^{2+} . The substitution of Pb^{2+} in the columns parallel to the *c*-axis (M (1) site) provokes a greater enlargement of the *c*-axis dimension than that induced by Pb^{2+} substitution in the M (2) sites , due also to the shorter metal (1) – metal (1) distances. When the Ca ions were added to Pb apatite, the M (2) sites were occupied only by Pb ions up to about 30 atom% Ca. In other words, Ca ions preferentially occupied M (1) sites which caused the decrease of *c*- axis more than *a*-axis. When Pb ions were added to Ca apatite, Pb ions had a tendency to occupy M (2) sites which has more effect on *a*-axis than *c*-axis, thereby the *a*-axis increased more than the *c*-axis. These were agreement with the variation of the lattice parameters. In the middle composition, the Pb content in the sample is lower than that in the starting solutions, Moreover, the Pb ions occupied the two sites at different proportions, thus the lattice parameters almost didn't changed due to Pb^{2+} substitution in M (1) sites and M (2) sites which they all affected *a*-axis and *c*-axis.

4. Conclusions

The solid solutions in the system of Ca-Pb HA, $\text{Ca}_{10-x}\text{Pb}_x\text{HA}$ ($x=0-10$), were successfully synthesized by high-temperature mixing method (HTMM) at 200°C for 12 hours under hydrothermal conditions. The morphology, growth mechanism, and the lattice constant of the solid solutions were investigated. The site of the metal ions in the solid solutions was also analyzed by the Rietveld method. The morphology of the samples with less than χ_{Pb} of 0.2 is rod-like, and that of the samples with more than χ_{Pb} of 0.8 was bulk. The smaller rod crystals coexisted with the larger bulky crystals in the solid solutions with Pb content from 0.4 to 0.6. The lattice parameters of the solid solutions didn't vary linearly with Pb contents, and they have two turning points of 0.4 and 0.6 of Pb content. The results are agreement with the XRD results and morphology. It is found that Pb ions in the solid solutions preferentially occupy M (2) site in the apatite structure. HTMM gives Ca-Pb HA solid solutions much better crystallization. However, the crystallization of the samples with higher χ_{Pb} decreased duo to the formation of intermediate compound of $\text{Pb}_3\text{O}_2(\text{OH})_2$ in the $\text{Pb}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution before mixing with $(\text{NH}_4)_2\text{HPO}_4$ solution at 200°C.

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Figure captions

Fig. 1. X-ray diffraction patterns of the samples with different Pb/(Ca + Pb) molar ratio prepared by HTMM at 200°C for 12 hours. ▽: $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ •: $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.

Fig. 2. Plot of the Pb/(Pb+Ca) molar ratios in the products prepared by HTMM against that in starting solutions.

Fig. 3. TEM (a) 0 (b) 0.2 (c) 0.4 (d) 0.6 and SEM (e) 0.8 (f) 1 photographs of the samples with various Pb/(Pb+Ca) molar ratio prepared by HTMM.

Fig. 4. Plot of the lattice parameters of Ca-Pb HA solid solutions prepared by HTMM against the Pb/(Pb+ Ca) molar ratio.

Fig. 5. Observed X-ray diffraction intensity (circle line) and calculated curve (solid line) of the sample with Pb 50 atom% prepared by HTMM. The bottom curve is the difference of patterns, and the short bars indicate the angular positions of the allowed Bragg reflections.

Fig. 6. Metal ion occupancy of the Ca-Pb HA solid solutions prepared by HTMM against the Pb/(Ca+Pb) molar ratio.

Fig. 1. X-ray diffraction patterns of the samples with different Pb/(Ca + Pb) molar ratio prepared by HTMM at 160°C for 12 hours. ▽: $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ ●: $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$

Fig. 2. Plot of the Pb/(Pb+Ca) molar ratios in the products prepared by HTMM against that in starting solutions.

Fig. 3. TEM (a) 0 (b) 0.2 (c) 0.4 and SEM (d) 0.6 (e) 0.8 (f) 1 photographs of the samples with various Pb/(Pb+Ca) molar ratio prepared by HTMM.

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Fig. 6. Metal ion occupancy of the Ca-Pb HA solid solutions prepared by HTMM against the Pb/(Ca+Pb) molar ratio.

Table 1.

The compositions and lattice parameters of Ca-Pb HA solid solutions synthesized by HTMM

Sample	P (ppm)	Pb (ppm)	Ca (ppm)	Pb/(Ca+Pb) molar ratio	(Ca+Pb)/P molar ratio	Lattice parameters	
						a	c
HPb0	15.91	0.00	11.61	0.00	1.73	0.9418	0.6884
HPb10	14.11	6.77	9.19	0.12	1.77	0.9539	0.6970
HPb20	7.20	5.92	3.92	0.23	1.67	0.9605	0.7021
HPb30	10.88	12.77	5.27	0.32	1.69	0.9666	0.7096
HPb40	12.67	19.79	5.37	0.42	1.72	0.9683	0.7123
HPb50	11.35	20.76	3.92	0.51	1.66	0.9675	0.7124
HPb60	14.78	31.38	4.17	0.59	1.64	0.9683	0.7146
HPb70	12.17	33.82	2.32	0.74	1.73	0.9693	0.7186
HPb80	9.54	29.35	1.08	0.84	1.68	0.9754	0.7276
HPb90	7.29	25.88	0.34	0.94	1.74	0.9828	0.7362
HPb100	9.13	35.43	0.00	1.00	1.78	0.9884	0.7444

Table 2. Crystallographic data and atomic coordinates of Pb 50% in the Ca-Pb HA sample obtained by HTMM from Rietveld analysis.

Space group: P 63/m (VOL. A, 176)							
Unit cell parameters: a =9.6749(1) (Å); c= 7.1232(6) (Å); V =577.435(2) (Å ³)							
Calculated density: 5.320(1) (g ·cm ⁻³)							
Reliability factors: Rwp =16.17; Rp = 11.41; RR = 18.48; Re = 2.93; S = 5.5193;							
d1 = 0.0780; d2 = 0.0374; RI = 12.1; RF = 3.88; E(SCIO) = 2965.88							
Atom	neq	g	N	x	y	z	B (Å ²)
O1	6	1	6	0.36507	0.50836	0.25	1.03
O2	6	1	6	0.48187	0.57944	0.25	0.447
O3	12	1	12	0.35172	0.25858	0.04906	0.411
P	6	1	6	0.41194	0.37877	0.25	0.8
Ca1	4	0.9055	3.6221	0.33333	0.66667	-0.0143	0.237
Ca2	6	0.2199	1.3196	0.24518	0.00247	0.25	0.843
Pb1	4	0.0945	0.3779	0.33333	0.66667	-0.0143	0.237
Pb2	6	0.7801	4.6804	0.24518	0.00247	0.25	0.843
OH	2	1	2	0	0	0.25	6.495

neq: number of equivalent points g: site occupancy factors

N: atom numbers per unit cell calculated from neq * g

OH: virtual atom consisted from O- 1.0000 and H 1.0000