Synthesis and crystallographic study of Pb-Sr hydroxyapatite solid
solutions by high temperature mixing method under hydrothermal
conditions

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Abstract:

The solid solutions in the system of Pb and Sr hydroxyapatite, $\text{Sr}_{10-x}\text{Pb}_x\text{HAp}$ ($x=0-10$), were successfully synthesized by high-temperature mixing method (HTMM) at 160°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 constants, both a and c , of the solid solutions varied linearly with Pb content. It was found that Pb ions in the solid solutions preferentially occupied the M (2) site in the apatite structure. HTMM gives Sr-Pb HAp 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 160°C , HTMM causes the decrease of crystallization of the samples with high Pb content.

Key words: Pb-Sr 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-HAp, is a primary constituent of vertebral animal's hard tissues. The synthetic Ca-HAp has attracted our attention for its utility in the fields of bioceramics, catalysts, adsorbents, and so on [1]. Strontium Hydroxyapatite $[\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2]$, designated as Sr-HAp] has also been used as a catalyst for oxidative dehydrogenation of methane [2] and as an adsorbent for the protein [3]. In the oxidation of methane, the addition of a small quantity of Pb to Sr-HAp resulted in the selectivity conversion of ethylene [4].

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 [5]. 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. Badraoui *et al.* [6] prepared Sr-Pb HAp solid solutions in aqueous medium with a double decomposition method. The results of the Rietveld analysis indicated a clear preference for Pb in the M(2) site of the apatite structure, so that in the samples with low Pb content it is almost exclusively found in the M(2) site.

The HAp solid solutions have been prepared by solid state reaction or aqueous reaction [7-12]. The former method gives 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 [13]. The technique has an additional advantage for the preparation of HAp powders: no hydroxyl defects in the structure. Cd-HAp [14], Ca-Cd HAp [15, 16], Ca-Sr HAp [16, 17] and Sr-Pb HAp [18] were successfully synthesized hydrothermally in our former work. On the base of hydrothermal method, a new technique (high-temperature mixing method, HTMM) was designed [19] 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 HAp [15] and Ca-Sr HAp [17] were successfully synthesized by HTMM in our former work.

In this work, the well-formed crystals of Sr-Pb HAp solid solutions were synthesized using HTMM under hydrothermal conditions at 160°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 HAp structure. The obtained crystals were observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). The concentrations of Sr^{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), $(\text{NH}_4)_2\text{HPO}_4$, $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 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 $0.200 \text{ mol} \cdot \text{L}^{-1}$ solution. The pH of the solution was adjusted to 10 with ammonia. A mixed metal nitrate solution with $0.334 \text{ mol} \cdot \text{L}^{-1}$ was prepared from $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ nitrates, the Pb/(Pb+Sr) molar ratio varying from 0 to 1. We used a Teflon lined multi chamber autoclave which has two separate chambers. Each starting solution (8 cm^3) was separately poured into a different reaction chamber to get the HAp stoichiometric composition of 1.67. These solutions were heated to desired temperature and then mixed. Hydrothermal treatments were carried out at 160°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 constants 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: 2θ range 15° - 130° ; step width 0.02° ; and counting time 6 s. Rietveld analysis was performed with the program RIETAN. 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 Composition and Crystal Structure

The compositions of the products determined by the chemical analysis are shown in Fig. 1 against those of the starting solutions. Pb/(Sr+Pb) molar ratios in the products are higher than that in the starting solutions above 0.6. This indicates that Pb^{2+} ions enter cation sites of the crystal more easily compared to Sr^{2+} ions in the samples with higher Pb content. Table 1 shows that the compositions of the products are determined by ICP. The (Sr+Pb)/P molar ratios of the solid solutions are in agreement with Pb/(Sr+Pb) molar ratios in the starting solutions. The average (Sr+Pb)/P molar ratio obtained by HTMM in the samples was about 1.67, which is much in agreement with that in HAp composition of 1.67. However, the average (Sr+Pb)/P molar ratio of the solid solutions synthesized by LTMM in our former work [18] is 1.65, which is lower than that in HAp composition. It indicates that HTMM gives Sr-Pb HAp solid solutions much better crystallization than LTMM.

The XRD patterns of the samples with different Pb/(Sr+Pb) molar ratio obtained by HTMM were shown in Fig. 2. All the samples corresponded to pure apatite phase, whatever the Pb/(Sr+Pb) molar ratio is. With the increase of the Pb/(Sr+Pb) molar ratio, the peaks shifted to lower 2-theta angles due to the incorporation of larger Pb^{2+}

ions into Sr-HAp. The intensity of the peaks in XRD patterns decreased with Pb/(Sr+Pb) molar ratio in the Sr-Pb HAp up to 0.4, but increased from 0.4 to 0.8. However, the intensity of the peaks decreased when Pb/(Sr+Pb) molar ratio exceeded 0.8. It was 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 160°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 160°C , a Sr-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.

The result of the lattice constants was shown in Fig. 3., and also shown in Table 1. The lattice constants of both a and c varied linearly with the compositions. It

indicated that Sr-HAp and Pb-HAp formed a continuous series of solid solutions. Both Pb-HAp and Sr-HAp belong to the apatite structure, and both Pb and Sr metal ions have similar ionic radius. The replacement of Sr by Pb in the apatite structure induces a increase in the lattice constants in agreement with the bigger ionic radius. The ionic radius of Pb^{2+} and Sr^{2+} in 7-coordination are 1.37 and 1.35 Å and in 9-coordination they are 1.49 and 1.45 Å[20]. The enlargement of c axis is more than that of a axis. In general, the incorporation of large ions in the columns (M (1) sites) parallel to the c -axis of the apatite structure results in a greater enlargement of the c -axis dimension than in the M (2) sites, because the M (1) sites have the shorter metal (1) – metal (1) distances in comparison with the M (2) sites.

3.2 Morphology

Fig. 4 displays the transmission electron microscope (TEM) pictures and scanning electron microscope (SEM) photographs of the samples with different Pb/(Sr+Pb) molar ratio prepared by HTMM. 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 Pb content less than 0.6 is elongated crystals, and become smaller with less Pb content. The morphology of the sample with Pb content of 0.8 was larger bulky crystal. The larger elongated crystals coexisted with the larger bulky crystals in the Pb-HAp. However, Pb –HAp synthesized by LTMM [17] are all bulky crystals.

3.3 Rietveld 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. 5 and Table 2. The reliability factors ($R_{wp} = 11.82$; $R_p = 9.13$; $RR = 13.93$; $R_e = 2.42$; $S = 4.8823$) are acceptable for the structure determination of Sr-Pb HAp in this work.

Fig. 6 showed the occupancy of Pb^{2+} in the M (1) and M (2) sites in the Sr-Pb HAp structure. It was found that Pb ions preferentially occupied M (2) sites in the solid solutions. Pb^{2+} ions only occupied M (2) sites when Pb content exceeded 0.8. Some works [6, 12, 21-22] 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 HAp[23]. In the Sr-Pb HAp solid solutions, the ionic radius of Pb^{2+} is larger than that of Sr^{2+} . The electronegativity of the Pb ion (1.8) is also much more than that of Sr 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.

4. Conclusions

The solid solutions in the system of Sr-Pb HAp, $Sr_{10-x}Pb_xHAp$ ($x= 0-10$), were

successfully synthesized by high-temperature mixing method (HTMM) at 160°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 0.6 Pb content was rod-like, and that of the samples with more than 0.6 Pb content was bulk. The smaller rod crystals coexisted with the larger bulky crystals in lead hydroxyapatite. The lattice constants of the solid solutions varied linearly with Pb contents. It was found that Pb ions in the solid solutions preferentially occupied M (2) site in the apatite structure. HTMM gives Sr-Pb HAp solid solutions much better crystallization. However, the crystallization of the samples with higher Pb content decreased 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 160°C.

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Figure captions

Fig. 1. Plot of the Pb/(Pb+Sr) molar ratios in the products prepared by HTMM against that in starting solutions.

Fig. 2. X-ray diffraction patterns of the samples with different Pb/(Sr + Pb) molar ratio prepared by HTMM at 160°C for 12 hours. ▽: $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ •: $\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$

Fig. 3. Plot of the lattice constants of Sr-Pb HAp solid solutions prepared by HTMM against the Pb/(Pb+ Sr) molar ratio.

Fig. 4. 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+Sr) molar ratio prepared by HTMM.

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 Sr-Pb HAp solid solutions prepared by HTMM against the Pb/(Sr+Pb) molar ratio.

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Table 1.

The compositions and lattice constant of Sr-Pb HAp solid solutions synthesized by HTMM

Sample	P (ppm)	Pb (ppm)	Sr (ppm)	Pb/(Sr+Pb) molar ratio	(Sr+Pb)/P molar ratio	Lattice constant	
						a	c
HSP0	13.99	0	22.19	0	1.72	0.977	0.729
HSP10	9.23	2.58	12.65	0.08	1.61	0.978	0.730
HSP20	11.86	7.89	14.33	0.19	1.62	0.980	0.731
HSP30	8.61	9.37	8.93	0.31	1.62	0.980	0.733
HSP40	9.53	13.99	8.89	0.40	1.68	0.981	0.734
HSP50	26.23	50.09	19.93	0.52	1.70	0.983	0.737
HSP60	8.15	17.86	4.57	0.63	1.61	0.984	0.739
HSP70	12.52	33.74	5.46	0.72	1.71	0.985	0.740
HSP80	12.97	39.45	3.83	0.81	1.72	0.987	0.742
HSP90	16.53	55.31	2.48	0.90	1.70	0.988	0.743
HSP100	2.88	10.78	0	1	1.72	0.989	0.744

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

Space group: P 6 ₃ /m (VOL. A, 176)							
Unit cell parameters: a =9.8349(4) (Å); c= 7.3678(3) (Å); V =617.182(6) (Å ³)							
Calculated density: 5.639(9) (g ·cm ⁻³)							
Reliability factors: Rwp = 11.82; Rp = 9.13; RR = 13.93; Re = 2.42; S = 4.8823;							
d1 = 0.1646; d2 = 0.1761; RI = 5.45; RF = 3.61; E(SCIO) = 3171.19							
Atom	neq ^a	g ^b	N ^c	x	y	z	B (Å ²)
O1	6	1	6	0.34978	0.49001	0.25	3.022
O2	6	1	6	0.61141	0.47096	0.25	5.568
O3	12	1	12	0.35365	0.26485	0.08764	2.404
P	6	1	6	0.41029	0.38498	0.25	3.459
Pb1	4	0.2138	0.8552	0.33333	0.66667	0.00512	1.972
Pb2	6	0.7163	4.2976	0.24866	-0.00146	0.25	1.295
Sr1	4	0.7862	3.1448	0.33333	0.66667	0.00512	1.972
Sr2	6	0.2837	1.7024	0.24866	-0.00146	0.25	1.295
OH ^d	2	1	2	0	0	0.25	23.218

^aneq: number of equivalent points ^bg: site occupancy factors

^cN: atom numbers per unit cell calculated from neq * g

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