Hydrothermal Synthesis and Crystallographic Study of Sr–Pb Hydroxyapatite Solid Solutions

Kongjun ZHU, Kazumichi YANAGISAWA,* Rie SHIMANOUCHI,** Ayumu ONDA,*
Koji KAJIYOSHI* and Jinhao QIU

The Aeronautical Key Laboratory for Smart Materials and Structures, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, P. R. China

**Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, Kochi-shi 780–8520 Japan*

***Department of Material Science, Faculty of Science, Kochi University, Kochi-shi 780–8520 Japan*

A continuous series of solid solutions in the system of strontium and lead hydroxyapatite, $\text{Pb}_x\text{Sr}_{1-x}\text{HAP}$ ($x = 0\text{--}1$), was successfully synthesized by low-temperature mixing method (LTMM) at 160°C for 12 h under hydrothermal conditions. The samples were characterized by chemical analysis, electron microscopic observation and X-ray powder-pattern fitting. The site of the metal ions in the solid solutions was analyzed by the Rietveld method. The lattice constants of the prepared solid solutions varied linearly with Pb contents. It was found that Pb^{2+} ions in the solid solutions preferentially occupied the M(2) site in the apatite structure.

[Received August 28, 2007; Accepted October 18, 2007]

Key-words : Hydroxyapatite, Solid solution, Hydrothermal synthesis, Rietveld method

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 and synthetic hydroxyapatite has attracted our attention due to its utility in the fields of bioceramics, catalyst, adsorbent, and so on.¹⁾ Strontium hydroxyapatite $[\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2]$, designated as Sr HAp] has been also used as a catalyst for oxidative dehydrogenation of methane²⁾ and as an adsorbent for the protein.³⁾ In the oxidation of methane, the addition of a small quantity of lead to Sr HAp resulted in the conversion and the selectivity to 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 that many metal ions can incorporate in the structure. It is interesting to investigate the site of metal ions which incorporate in the apatite structure. Badraoui et al.⁶⁾ prepared Sr–Pb HAp solid solutions from a double decomposition method, in aqueous medium. The precipitate was filtered, washed with hot distilled water, in order to eliminate traces of ammonium, nitrate and acetate ions, dried at 100°C for 12 h and calcined at 600°C for 4 h to improve its crystallinity. The results of the Rietveld analysis indicated a clear preference of lead for the M(2) site of the apatitic 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 the solid state reaction or aqueous reaction.^{7)–12)} The former method gives higher crystallinity to the products, but the hydroxyl defect should be formed due to the high temperature treatments. On the other hand, the crystallinity of the products synthesized by the aqueous reaction is usually low even without hydroxyl defects in their structure. The low crystallinity and hydroxyl defect in the samples must 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 crystallinity.¹³⁾ The technique has an advantage especially for preparation of HAp powders not to introduce the hydroxyl defect in the structure. Cd-Hap,¹⁴⁾ Ca–Cd Hap,^{15),16)} Ca–Sr

Hap,^{16),17)} Ca–Pb Hap¹⁶⁾ were successfully synthesized by hydrothermal method in our former works.

In this work, we have synthesized well-formed crystals of Sr–Pb HAp solid solution using LTMM under hydrothermal conditions at 160°C for 12 h. Powder X-ray diffraction analyses were employed to determine the crystalline phases and investigate which site Pb ions preferentially occupy in the HAp structure by X-ray powder-pattern fitting. The obtained crystals were observed by SEM and 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 $\text{Pb}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. $(\text{NH}_4)_2\text{HPO}_4$ was 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, varying the Pb/(Pb + Sr) molar ratio 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. These solutions were mixed at room temperature and then heated to desired temperature. Hydrothermal treatments were carried out at 160°C for 12 h.

After washing with distilled water, the products were characterized by powder X-ray diffraction (XRD; Model RTP-300RC, Rigaku Co., Japan) with Cu K α radiation (40 kV and 100 mA). The lattice constants were calculated by the least square method using 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 $15^\circ\text{--}130^\circ$; step width 0.02° ; and counting time 6 s. Rietveld analysis was performed with the program RIETAN.¹⁸⁾ A 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) spec-

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

trometry (SPS7000A, Seiko) after dissolving in a nitric acid.

3. Results and discussion

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 ratio in the products is slightly higher than that of the starting solutions when it exceeds 0.6. This indicates that Pb^{2+} ions more easily enter cation sites of the crystal compared to Sr^{2+} ions in the samples with higher Pb content. The (Sr + Pb)/P molar ratio of the solid solutions did not change appreciably with the change of the Pb/(Sr + Pb) molar ratios, and its average value of the samples obtained by LTMM was about 1.65. The chemical compositions analyzed by ICP were used for Rietveld analysis.

The XRD patterns of the samples with the different Pb/(Sr + Pb) molar ratio obtained by LTMM are shown in **Fig. 2**. All the samples corresponded to pure apatite phase, whatever the Pb/(Sr + Pb) molar ratio. The peaks shifted to lower angles with the increase of the Pb/(Sr + Pb) molar ratio due to the incorporation of larger Pb^{2+} ions into Sr HAp. The addition of Pb^{2+} ions into Sr HAp up to Pb/(Sr + Pb) molar ratio of 0.4 decreased the intensity of the peaks. The results preliminarily indicated that the strontium and lead hydroxyapatite solid solutions are continuous in the whole range of the Pb/(Sr + Pb) molar ratio. It was also certified by the results of the lattice constant (showed in **Fig. 3**). The lattice constants of both a and c varied linearly with the compositions. It indicated that strontium and lead hydroxyapatite formed a continuous series of solid solutions. Both lead and strontium hydroxyapatite belong to the apatite structure, and both metal ions have similar ionic radius. Thus the continuous solid solutions are easily formed. The replacement of strontium by lead in the apatite structure induces a increase in the lattice constants in agreement with the bigger ionic radius of Pb^{2+} (1.33×10^{-10} m for 6-coordinate octahedral site) than that of Sr^{2+} (1.13×10^{-10} m for 6-coordinate octahedral site). 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.

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

Fig. 3. Plot of the lattice constants of lead-strontium hydroxyapatite solid solutions prepared by LTMM against the Pb/(Pb + Ca) molar ratio.

Figure 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 LTMM. The morphology of the samples with less than 0.6 Pb content is elongated crystals, and the particle size decrease with the increase of lead content. Larger bulk crystals coexist with them in the sample with 0.8 molar ratio of Pb/(Sr + Pb). The crystals of lead hydroxyapatite just are the larger bulk. The variation of the morphology is very difficult to be explained before some extra experiments are done. However, the results of the Rietveld analysis will give some explanations.

In this work, there were 11 samples prepared with LTMM, and the results of their X-ray diffraction were analyzed by the RIETAN program. The results of the Pb 50% sample obtained by LTMM showed in **Table 1**. The reliability factor of Rwp is acceptable for the structure determination of Sr-Pb HAp in this work. **Figure 5** showed the occupancy of Pb^{2+} in

Fig. 4. TEM photographs and SEM of the samples prepared by LTMM with various Pb/(Pb + Sr) molar ratio: (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, (f) 1.

Table 1. Crystallographic Data and Atomic Coordinates of Pb 50% in the Sr-Pb HAp Sample from Rietveld Analysis

Space group: P 63/m (VOL. A, 176)							
Unit cell parameters: $a = 9.8226(1) (10^{-10} \text{ m})$; $c = 7.3458(3) (10^{-10} \text{ m})$; $V = 613.797(7) (10^{-30} \text{ m}^3)$							
Calculated density: $5.612(6) (\text{g} \cdot \text{cm}^{-3})$							
Reliability factors: $R_{wp} = 7.69$; $R_p = 5.83$; $RR = 9.26$; $Re = 2.48$; $S = 3.0959$							
$d1 = 0.2285$; $d2 = 0.1268$; $RI = 3.34$; $RF = 1.72$; $E(\text{SCIO}) = 2964.82$							
Atom	neq	g	N	x	y	z	B (10^{-10} m^2)
O1	6	1	6	0.34729	0.46461	0.25	1.482
O2	6	1	6	0.5906	0.45528	0.25	0.978
O3	12	1	12	0.36599	0.26757	0.0806	2.189
P	6	1	6	0.42019	0.38073	0.25	1.547
Pb1	4	0.2015	0.8059	0.33333	0.66667	0.01029	1.277
Pb2	6	0.6944	4.1662	0.25009	-0.00158	0.25	1.132
Sr1	4	0.7985	3.1941	0.33333	0.66667	0.01029	1.277
Sr2	6	0.3056	1.8338	0.25009	-0.00158	0.25	1.132
OH	2	1	2	0	0	0.25	39.635

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

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, and the amount increased with the increase of Pb content. The amount of Pb^{2+} ions in the M(2) sites increased slowly with the increase of the Pb content when the Pb content was higher than 0.6. However the occupancy of Pb^{2+} ions in the M(2) sites increased sharply when the Pb content is lower than 0.6.

Many works^{(6),(12),(19)–(20)} have investigated the occupancy of metal ions in the site of apatite structure. All results showed that it seemed the bigger ions occupied the M(2) sites

preferentially since in site M(2) the arrangement of the staggered equilateral triangles allows for the optimization of the packing of large ions, in contrast to the M(1) site where the strict alignment in the columns causes a stronger repulsion. The results of this work are agreement with this point. In our former work of Ca-Cd system,⁽¹⁵⁾ Cd ions have a slight tendency to preferentially occupy the M(2) sites even though the ionic radius of cadmium is smaller than that of calcium. The difference in ionic radius ($0.99 \times 10^{-10} \text{ m}$ for 6-coordinate octahedral Ca(2), $0.97 \times 10^{-10} \text{ m}$ for 6-coordinate octahedral Cd(2)) appears too small to give explanation. A possible

Fig. 5. Metal ion occupancy of the Sr-Pb HAp solid solutions prepared by LTMM against the Pb/(Sr + Pb) molar ratio.

explanation for the preferential occupancy Cd^{2+} in the M(2) sites can be offered on the basis of electronegativities of the cations. Rajagopal et al.²¹⁾ showed that an increase in the electronegativity of the counter ion leads to an increase in the covalent character of the bond between the cation and the carboxyl group in metal arachidates. The electronegativity of the cadmium ion (1.7) is much bigger than that of calcium ion (1.0) so that Cd displays a greater tendency towards covalent interactions and directional bonding with hydroxyl group which locates at the channel surrounded by Ca^{2+} ions in M(2) sites. In other word, the Cd^{2+} ions with bigger electronegativity are easier to occupy M(2) sites than Ca^{2+} ions. In the Sr-Pb HAp solid solutions, the ionic radius for 6-coordinate octahedral Pb(2) is 1.20×10^{-10} m, are bigger than that for 6-coordinate octahedral Sr(2) which is 1.13×10^{-10} m. The electronegativity of the lead ion (1.8) is also much larger than that of strontium ion (1.0). Therefore Pb^{2+} ions preferentially occupy the M(2) sites in the whole composition range of Sr-Pb HAp solid solutions.

We tried to explain the variation of the morphology as follows. Firstly, the solubility of Pb hydroxyapatite should be more than Sr hydroxyapatite so that the larger particle can be grown. Secondly, it will be explained by the dissolution species. It is reported that apatite is dissolved in solution as clusters, but not as ions. The clusters are larger than ion species, and should have some structure related to apatite structure. When the content of Pb is more than 60 atom%, the M(2) sites are almost occupied only by Pb ions. I think that the clusters with a structure in which M(2) sites are occupied by Pb ions, have high solubility under hydrothermal conditions. The obvious change of morphology of the Sr-Pb HAp was observed around 70 atom% Pb.

4. Conclusions

The solid solutions in the system of Sr-Pb HAp, $\text{Pb}_x\text{Sr}_{1-x}$ HAp ($x=0-1$), were successfully synthesized by LTMM at

160°C for 12 h 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 lower than 0.6 Pb content was rod-like. The smaller rod crystals coexisted with the larger bulky crystals in the solid solutions with Pb content from 0.6 to 0.9. The morphology of lead hydroxyapatite crystal just was the larger bulk. 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.

Acknowledgments The authors would like to thank the financial support from Aeronautical Science Fund (No. 2006ZF52064) and the National 863 Foundation Program (No. 2007AA03Z104).

References

- 1) A. Yasukawa, T. Kunimoto, K. Kamiuchi, K. Kandori and T. Ishikawa, *J. Mater. Chem.*, **9**, 1825-1830 (1999).
- 2) Y. Matsumura, S. Sugiyama, H. Hayashi, N. Shigemota, K. Saitoh and J. B. Moffat, *J. Molecular Catalysis*, **92**, 81-94 (1994).
- 3) K. Kandori, Y. Yamamoto, H. Saito and T. Ishikawa, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **80**, 287-291 (1993).
- 4) S. Sugiyama, Y. Iguchi, H. Nishioka, T. Minami, T. Moriga, H. Hayashi and J. B. Moffat, *J. Catal.*, **176**, 25-34 (1998).
- 5) A. Hadrich, A. Lauti and T. Mhiri, *J. Raman Spec.*, **32**, 33-40 (2001).
- 6) B. Badraoui, A. Bigi, M. Debbabi, M. Gazzano, N. Roveri and R. Thouvenot, *Eur. J. Inorg. Chem.*, **6**, 1864-1870 (2002).
- 7) I. Khattech, Degree Thesis, Univeristé de Tunis, Tunisie (1996).
- 8) A. Bigi, E. Foresti, F. Marchetti, A. Ripamonti and N. Roveri, *J. Chem. Soc., Dalton Trans.*, 1091-1093 (1984).
- 9) M. Gazzano, PhD Thesis, University of Bologna, Bologna, Italy (1986).
- 10) A. Bigi, A. Ripamonti, S. Brückner, M. Gazzano, N. Roveri and S. A. Thomas, *Acta Crystallogr., Sect. B*, **45**, 247 (1989).
- 11) A. Nounah, J. Szilagyi and J. L. Lacut, *Ann. Chim. Fr.*, **15**, 409 (1990).
- 12) B. Badraoui, A. Bigi, M. Debbabi, M. Gazzano, N. Roveri and R. Thouvenot, *Eur. J. Inorg. Chem.*, **5**, 1261-1267 (2001).
- 13) W. J. Dawson, *Am. Ceram. Soc. Bull.*, **67**, 1673-1678 (1998).
- 14) K. J. Zhu, K. Yanagisawa, A. Onda and K. Kajiyoshi, *Soc. Solid State Chem.*, **177/12**, 4379-4385 (2004).
- 15) K. J. Zhu, K. Yanagisawa, R. Shimanouchi, A. Onda and K. Kajiyoshi, *J. Shaanxi University of Science & Technology*, **22** (5), 42-47 (2004).
- 16) K. J. Zhu, K. Yanagisawa, R. Shimanouchi, A. Onda and K. Kajiyoshi, *J. Eur. Ceram. Soc.*, **26**, Issues 4-5, 509-513 (2006).
- 17) K. J. Zhu, K. Yanagisawa, R. Shimanouchi, A. Onda and K. Kajiyoshi, *Phosphorous Res. Bull.*, **17**, 219-226 (2004).
- 18) Izumi F and Ikeda T, *Mater. Sci., Forum*, **321-324**, 198-204 (2000).
- 19) U. Vincent, J. Jeanjean and M. Fedoroff, *J. Solid State Chem.*, **108**, 68-72 (1994).
- 20) B. Badraoui, R. Thouvenot, M. Debbabi and C. R. Hebd, *Acad. Sc. Ser.*, **3**, 107-112 (2000).
- 21) A. Rajagopal, A. Dhaanabalan, S. S. Major and S. K. Kulkarni, *Applied Surface Science*, **125**, 178-186 (1998).