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Preferential occupancy of metal ions in the hydroxyapatite solid solutions synthesized by hydrothermal method

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Abstract

The solid solutions in the systems of Ca-Cd HAp [$Ca_{10-x}Cd_x$HAp ($x = 0$–10)], Ca-Sr HAp [$Ca_{10-x}Sr_x$HAp ($x = 0$–10)] and Ca-Pb HAp [$Ca_{10-x}Pb_x$HAp ($x = 0$–10)], were successfully synthesized at 200 °C for 12 h under hydrothermal conditions. The site of the metal ions in the solid solutions was analyzed by the Rietveld method. The results of the Rietveld analysis indicated that the metal ions of Pb^{2+}, Sr^{2+}, and Cd^{2+} all preferentially occupied M (2) sites in the apatite structure. The preferential occupancy of the metal ions in M (2) sites were explained mainly by their ionic radius and electronegativity.

Keywords: Powders-chemical preparation; X-ray methods; Chemical properties; Apatite

1. Introduction

Calcium hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, designated as Ca HAp] is a primary constituent of vertebral animal's hard tissues and synthetic HAp has attracted our attention due to its utility in the fields of bioceramics, catalyst, adsorbent, and so on.[1] Because of the high stability and flexibility of the apatitic structure, a great number of substitutions, both cationic and anionic are possible. Ca^{2+} ion sites can be replaced by various divalent cations including Sr^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, and so on.[2] In the apatite structure, the Ca ions occupy two types of nonequivalent sites: M (1) is at the fourfold symmetry 4(f) position and M (2) is at the six-fold symmetry 6(h) position.[3] It is interesting to determine the occupation site of different metal ions in the apatite structure for better understanding the flexibility of the structure.

Vincent et al.[4] reported that the Cd exchange with Ca occurred in M (2) site, when Ca HAp powders were introduced into a Cd solution. LeGeros et al.[5] obtained a continuous series of Cd-Ca HAp solutions up to Cd 10 atom% from aqueous solutions. Their result indicated that the lattice dimensions of the solid solutions decreased linearly with the content of Cd in Ca HAp.

Kandori et al.[6] synthesized the Sr-Ca HAp by aging the precipitates (at 100 °C for 48 h) obtained by the aqueous reaction of a mixed solution of $Ca(OH)_2$ and $Sr(OH)_2$ with H_3PO_4, and showed that Sr-Ca HAp particles had the high ability for adsorption of bovine serum albumin (BSA). Single crystals of Sr-substituted HAp, $Ca_{9.42}Sr_{0.18}H_{0.8}(PO_4)_6(OH)_2$, up to 0.2 mm × 0.2 mm × 5 mm in size were grown hydrothermally using a temperature gradient technique.[7] The results indicated that the preferential substitution site of Sr for Ca in the structure of Sr-substituted HAp, was determined to be the M (1) site.

Sugiyama et al.[8] prepared Pb-Ca HAp solid solutions by the aqueous reaction from $NaHPO_4{\cdot}12H_2O$, $Ca(CH_3COO)_2{\cdot}H_2O$, and $Pb(CH_3COO)_2{\cdot}3H_2O$ and after calcination at 773 K for 3 h they investigated their activities in the conversion of methane with nitrous oxide and oxygen as oxidants. They also investigated the influence of Pb-Ca HAp on the thermal property and structure, but they did not describe the occupancy site of Pb in the apatite structure. Bigi et al.[9] prepared the Ca-Pb HAp solid solutions by the

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solid state reaction at 900 °C and aqueous reaction at 100 °C. Their results indicated that an inhomogeneous Pb^{2+} distribution in the two non equivalent cation sites of the HAp structure resulted in the observed discontinuous variation in the *c*-axis dimension.

The HAp solid solutions have been prepared by the solid state reaction or aqueous reaction. 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 direct formation of complex oxide powders with high crystallinity.[10] The technique has an advantage especially for preparation of HAp powders not to introduce the hydroxyl defect in the structure. In this study, a series of the solid solutions in the system of Ca-Cd HAp, Ca-Sr HAp and Ca-Pb HAp were prepared under hydrothermal conditions. The high crystallinity of the solid solutions prepared by the hydrothermal method allows us to determine the metal ion site in the apatite structure by the Rietveld analysis. Thus, the preferentially occupied site of the metal ions, Cd, Sr, and Pb, in the Ca HAp structure was compared.

2. Experimental

The starting materials were regent grade chemicals (Wako Pure Chem., Ind., Co., Japan), $(NH_4)_2HPO_4$, $Ca(NO_3)_2\cdot 4H_2O$, $Cd(NO_3)_2\cdot 4H_2O$, $Sr(NO_3)_2\cdot 4H_2O$, and $Pb(NO_3)_2\cdot 4H_2O$. $(NH_4)_2HPO_4$ was 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 $Ca(NO_3)_2\cdot 4H_2O$ and one of the other metal nitrates, varying the M/(M + Ca) molar ratio from 0 to 1. The hydrothermal preparation was conducted at 200 °C for 12 h in 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. After sealing the autoclave, the autoclave was connected the rotation shaft in the air oven and heated to 200 °C with the rotation for agitation of the content of the autoclave.

After washing with water, the products were characterized by powder X-ray diffraction (XRD; Model RTP-300RC, Rigaku Co., Japan) with Cu Kα 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°–130°; step width 0.02°; and counting time 6 s. Rietveld analysis was performed with the program RIETAN.[11] 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. XRD patterns

The XRD patterns of the products with the different M/(M + Ca) molar ratios are shown in Fig. 1. All the samples were identified to be pure apatite phase, independent of the M/(M + Ca) molar ratio. In general, the addition of other metal ions into Ca HAp up to M/(M + Ca) molar ratio of 0.4 decreased the intensity of the peaks.

In the system of Ca-Cd HAp (Fig. 1A), the peaks shifted to higher angle with the increase in the Cd/(Cd + Ca) molar ratio due to the incorporation of smaller Cd^{2+} ions in Ca HAp. On the other hand, in the system of Ca-Sr HAp (Fig. 1B) and Ca-Pb HAp (Fig. 1C), the peaks shifted to lower angle with the increase in the M/(M + Ca) molar ratio due to the incorporation of larger ions into the Ca HAp structure. In the case of the Ca-Pb solid solutions, the shift of the peaks was discontinuous. In the middle compositions of Pb/(Pb + Ca)

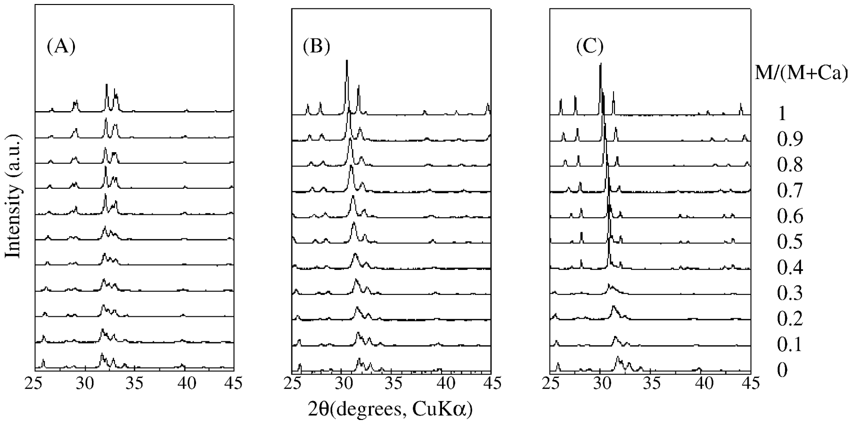

Fig. 1. X-ray diffraction patterns of the solid solutions in the system of (A) Ca-Cd HAp, (B) Ca-Sr HAp, and (C) Ca-Pb HAp.

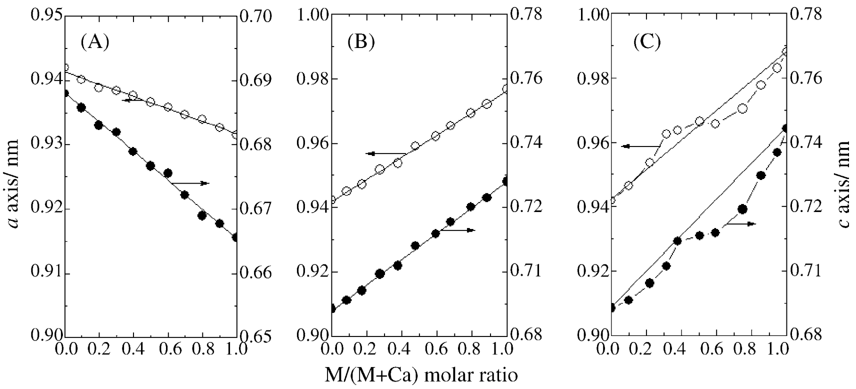

Fig. 2. Lattice constants of the solid solutions in the system of (A) Ca-Cd HAp, (B) Ca-Sr HAp, and (C) Ca-Pb HAp against the molar ratio.

molar ratio from 0.4 to 0.7, the peaks did not shift with the increase in Pb content.

3.2. *The lattice constant*

The lattice constants *a* and *c* of the apatite phases are plotted in Fig. 2 against M/(M + Ca) molar ratio determined by the chemical analysis of the products. In the system of Ca-Cd HAp (Fig. 2A), the lattice constants varied linearly with the compositions. The results indicated that the Cd-Ca HAp solid solutions were the continuous solid solutions in all range of the Cd/(Cd + Ca) molar ratio. The replacement of Ca by Cd in the apatite structure induced a slight decrease of the lattice constants in agreement with the smaller ionic radius of Cd^{2+} ion in comparison with that of Ca^{2+} ion. However, this difference in ionic radius [0.99 Å for 6-coordinate octahedral Ca (2), 0.97 Å for 6-coordinate octahedral Cd (2)] was too small to justify the observed contraction of the unit-cell parameters. On the other hand, it should be noted that the shortening of the cation–oxygen interatomic distances in Cd HAp is greater than that expected from the variation of ionic radius. The mean values of the Cd-O interatomic distances in Cd HAp are 2.382 Å and 2.391 Å for Cd(1)-O and Cd(2)-O,[12] respectively, and those in Ca HAp are 2.430 and 2.451 Å for Ca(1)-O and Ca(2)-O,[13] respectively.

In the system of Ca-Sr HAp (Fig. 2B), the lattice constants of both *a* and *c* varied linearly with the compositions. It indicated that Ca-Sr HAp formed a continuous series of the solid solutions. The replacement of Ca by Sr in the apatite structure induces an increase in the lattice constants in agreement with the bigger ionic radius of Sr^{2+} ion [1.13 Å for 6-coordinate octahedral Sr (2)] than that of Ca^{2+} ion [0.99 Å for 6-coordinate octahedral Ca (2)].

In the system of Ca-Pb HAp (Fig. 2C), the lattice constants of both *a* and *c* did not vary linearly with the compositions. They increased with the increase in the Pb content from 0 to 0.4 and from 0.6 to 1, but did not change from 0.4 to 0.6. The variation of the lattice constants of the Ca-Pb HAp solid solutions will be explained by the results of the occupancy of Pb ions in the apatite structure.

3.3. *The occupancy of metal ions in the apatite structure*

The occupancy of the metal ions in the apatite structure was analyzed by Rietveld method, and the results are shown in Fig. 3. The solid line without marks shows the normal

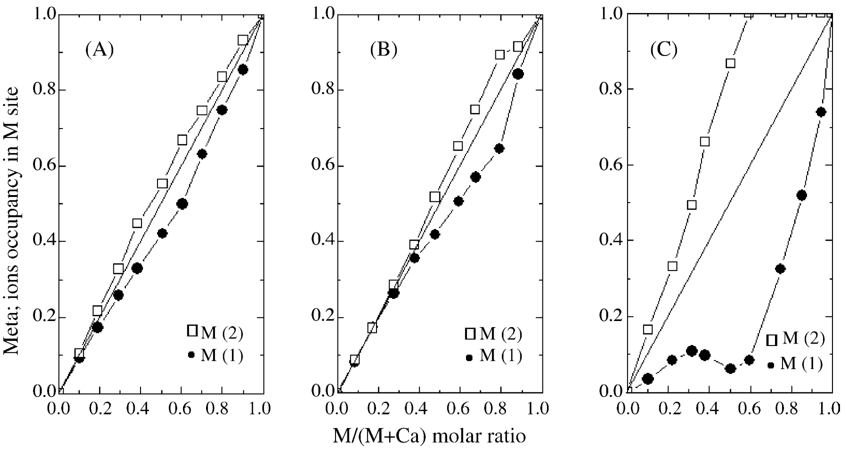

Fig. 3. Metal ion occupancy of the solid solutions in the system of (A) Ca-Cd HAp, (B) Ca-Sr HAp, and (C) Ca-Pb HAp against the molar ratio.

occupation of metal ions in M (1) and M (2) sites without preference. In the system of Ca-Cd HAp (Fig. 3A), Cd^{2+} ions had a slight tendency to occupy M (2) sites preferentially in the solid solutions. The tendency of Cd^{2+} ions to occupy M (2) sites was the strongest with the Cd/(Cd + Ca) molar ratio of 0.5. In the system of Ca-Sr HAp (Fig. 3B), Sr^{2+} ions preferentially occupied M (2) sites in the solid solutions with higher Sr/(Sr + Ca) molar ratios.

In the system of Ca-Pb HAp (Fig. 3C), it was found that Pb^{2+} ions had a remarkable tendency to occupy the M (2) sites in the solid solutions. When Pb ions were incorporated into Ca HAp up to the Pb/(Pb + Ca) molar ratio of 0.6, most of Pb ions occupied the M (2) sites in the apatite structure, and the all M (2) sites were occupied only by Pb^{2+} ions when the Pb/(Pb + Ca) molar ratio was more than 0.6.

Badraoui et al. studied on occupancy of metal ions in the apatite structure in the Cd-Pb,[14] Sr-Pb[15] and Cd-Sr[16] HAp system for the samples prepared by the aqueous reaction followed by the calcination at 600 °C, by using powder pattern fitting refinements and ^{31}P MAS NMR spectroscopy. According to their results, the formation of solid solutions in the system of Cd-Pb HAp was limited: Cd replaced Pb up to 30%, and Pb did not incorporate into Cd HAp. In the solid solutions with a small amount of Cd in Pb HAp, Cd^{2+} ions displayed a clear preference for the M (1) site occupation of the apatite structure. In the case of Sr-Pb HAp, a series of continuous solid solutions were formed over the whole range of compositions. The results of the powder fitting structure refinements indicated a clear preference of Pb^{2+} for the M (2) site occupation of the apatite structure. They concluded that lager ions preferentially occupied the M (2) sites, because in the M (2) sites the arrangement of the staggered equilateral triangles allowed for the optimization of the packing of large ions, in contrast to the M (1) sites where the strict alignment in the columns caused a stronger repulsion.

Our result from the Ca-Sr and Ca-Pb HAp solid solutions, that is, preferential occupancy of Sr and Pb in M (2) sites, is in agreement with their result, because the radius of Sr^{2+} ion and Pb^{2+} ion is larger than that of Ca^{2+} ion. In the system of Ca-Cd Hap, however, Cd has a slight tendency to occupy M (2) sites in the apatite structure even though the ionic radius of Cd^{2+} is smaller than that of Ca^{2+}. Badraoui et al.[16] gave the similar result in the system of Sr-Cd HAp where Cd^{2+} ions dispayed a slight preferential occupation of the M (2) sites in spite of its smaller dimension.

As B. Badraoui et al.[16] suggested, we have to consider a contribution of the covalent character of the M–O interaction to explain the result. Rajagopal et al.[17] 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 Cd^{2+} (1.7) is much larger than that of Ca^{2+} (1.0), so that Cd^{2+} ions display a greater tendency to increase the covalent interactions and directional bonding with hydroxyl groups which locate at the channel surrounded by metal ions in the M (2) sites. In other word, Cd^{2+} ions with larger electronegativity preferentially occupy the M (2) sites. Thus, the preferential occupancy of metal ions in the apatite structure can be explained mainly by ionic radius and electronegativity of the metal ions.

As shown in Fig. 2C, the discontinuous change of the lattice constants was observed in the Ca-Pb HAp system, which can be explained by a large tendency of Pb^{2+} ions to occupy the M (2) sites. In general, the incorporation of large ions in the columns (M (1) sites) parallel to the c-axis of the apatite structure provokes 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. When Ca^{2+} ions were added to Pb HAp up to 40%, the M (2) sites were occupied only by Pb^{2+} ions. In other words, Ca^{2+} ions preferentially occupied the M (1) sites, which caused the decease of c-axis more than a-axis. When Pb^{2+} ions were added to Ca HAp, Pb^{2+} ions had a tendency to occupy the M (2) sites, which had a larger effect on a-axis than c-axis. Thus, the a-axis increased more than the c-axis. In the middle composition, the occupancy of Pb^{2+} ions in the M (2) sites remarkably increased and slightly decreased in the M (1) site, when the content of Pb^{2+} ions increased in the solid solutions. The slight decrease of the occupancy of Pb^{2+} ions in the M (1) sites might give the unchangeable lattice constants even with the increase in total Pb^{2+} ions in the apatite structure.

4. Conclusions

The continuous solid solutions in the systems of Ca-Cd HAp, Ca-Sr HAp and Ca-Pb HAp were successfully synthesized at 200 °C for 12 h under hydrothermal conditions. The Rietveld analysis indicates that the Cd^{2+} ions have a slight tendency to occupy the M (2) sites in the apatite structure, Sr^{2+} ions preferentially occupy the M (2) sites with high Sr content, and Pb^{2+} ions showed the high preferential occupancy in the M (2) sites. The preferential occupancy of metal ions can be explained mainly by ionic radius and electronegativity of the metal ions. The metal ions with bigger ionic radius or electronegativity preferentially occupy the M (2) sites, because the M (2) sites give the directional bonding of the metal ions with hydroxyl group and the arrangement of the staggered equilateral triangles. Cd^{2+} ion has similar ionic radius with Ca^{2+} ion, but the electronegativity of Cd^{2+} ion is larger than Ca^{2+} ion. The electronegativity of Sr^{2+} ion is same as that of Ca^{2+} ion, but the radius of Sr^{2+} ion is bigger than that of Ca^{2+} ion. Both electronegativity and radius of Pb^{2+} ion are larger than that of Ca^{2+} ion. Thus, Cd^{2+}, Sr^{2+} and Pb^{2+} ions all preferentially occupied the M (2) sites in the apatite structure. The lattice constants of the Ca-Cd and Ca-Sr HAp solid solutions varied linearly with the concentrations of metal ions, but those of Ca-Pb HAp solid solutions, both a and c, showed the discontinuous change. They increased with the increase in the Pb content from 0 to 0.4 and from 0.6 to 1, but did not change in the Pb content from 0.4 to

0.6. The variation of the lattice constants of the Ca-Pb HAp solid solutions can be explained by the different amount of the Pb^{2+} ions occupied in the M (1) and M (2) sites.

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