

Effect of Metal Ions of Chlorapatites on the Topotaxial Replacement by Hydroxyapatite under Hydrothermal Conditions

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Received March 20, 2000; in revised form June 26, 2000; accepted July 27, 2000; published online September 30, 2000

The effect of the metal ions in the chlorapatite structure on the topotaxial conversion to the hydroxyapatite structure was investigated, using three different types of chlorapatite single crystals, calcium, strontium, and barium chlorapatite. The topotaxial conversion to the hydroxyapatite structure was conducted under hydrothermal conditions at a range of temperature from 300 to 800°C for intervals between 3 and 96 h in concentrated KOH solutions. The Cl⁻ ion exchange in the calcium and strontium chlorapatite crystals was completed at 500 and 700°C in a 6.25 M KOH solution, respectively, which resulted in the formation of hydroxyapatite structure. The transformed crystals retained their original shape and dimensions due to the topotaxial transformation. In contrast, the rate of the topotaxial conversion was further reduced on the barium chlorapatite crystals that contain metal ions with large size such as Ba. These crystals were only partially converted to hydroxyapatite even at 800°C in 10 M KOH solution. Under these conditions, a dissolution of ion species of the topotaxially converted barium hydroxyapatite layer was observed, which resulted in the precipitation of new crystals on the surface of the remaining barium chlorapatite crystals. The structure of the new crystals was matched with the hexagonal apatite structure, but a great amount of K was incorporated in the structure. © 2000 Academic Press

Key Words: chlorapatite; hydrothermal treatment; ion-exchange; metal ion; dissolution–precipitation.

INTRODUCTION

The calcium hydroxyapatite (hereafter referred as CaOHAp) is well known as the main constituent in tooth enamels, as well as a mineral. One of the peculiar properties of this structure is the capacity to incorporate various anions and cations as constituents. Hence, the apatite

structure has been the subject of many studies related with isomorphous substitutions (1–4). Regarding the isomorphous substitution in the binary system of calcium chlorapatite (hereafter referred as CaClAp) and CaOHAp, a number of researchers have experimentally found the formation of a series of solid solutions within this binary system (5–9). In accordance with these literatures, the solid solutions were produced by chemical reactions, but not by ion exchange reactions.

Elliot and Young (10) have provided the first evidence of the solid state ion exchange of Cl⁻ ions by OH⁻ ions in the apatite structure. The conversion of CaClAp single crystals to CaOHAp was performed by heating the crystals at 1000°C for 2 weeks in water vapor at atmospheric pressure. High-precession X-ray diffraction analyses showed that the reaction products were essentially single crystals of CaOHAp. On the other hand, Brenan (2) has observed that the anion (Cl⁻, F⁻, and OH⁻) exchange occurs by solid state diffusion under hydrothermal conditions and its rate is further accelerated with increasing confining pressure. Thus, the diffusion coefficients of anions measured in the calcium fluorapatite structure indicate that the mobility of anions under hydrothermal conditions at high pressures (1 GPa) is faster than that observed at low pressure (1 atm).

Recently, Yanagisawa *et al.* (11) have proposed a different mechanism of the anion exchange in CaClAp structure. The exchange of Cl⁻ ions with OH⁻ in the synthetic CaClAp single crystals proceeded in concentrated alkaline solutions under hydrothermal conditions at much lower temperatures than that by the solid state mechanism. Thus, the conversion to the CaOHAp structure started at temperatures as low as 300°C for 12 h in a 6.25 M KOH solution. The ion exchange under alkaline hydrothermal conditions homogeneously proceeded along the *a* and *c* axes of the CaClAp crystals by a topotaxial dissolution–precipitation process. This process occurs by the dissolution of the CaClAp crystals as clusters, which must be larger than ionic species. The exchange of Cl⁻ with OH⁻ simultaneously takes place at

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the surface of the clusters. The reaction products do not bear significant differences on the shape and dimensions from the original crystals.

Although the Cl–OH ion exchange reaction in the CaClAp crystals has been widely investigated under alkaline hydrothermal conditions (11), there is a lack of information regarding the effect of the metal ions in the chlorapatite structure on the topotaxial replacement process. Hence, the goal of the present work is to determine the experimental conditions (temperature) that enhance the topotaxial ion exchange reaction on CaClAp, strontium chlorapatite (hereafter referred to SrClAp) and barium chlorapatite (hereafter referred to BaClAp) single crystals. The influence of the metal ions on the topotaxial replacement by hydroxyapatite (hereafter abbreviated as OHAp) under alkaline hydrothermal conditions, is discussed.

EXPERIMENTAL PROCEDURES

1. Materials

Calcium (12), strontium (13), and barium (14) chlorapatite single crystals were prepared by the flux method using NaCl as a flux. A mixture of $6\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + 3\text{CaCO}_3 + \text{CaCl}_2$, $6(\text{NH}_4)_2\text{HPO}_4 + 9\text{SrCO}_3 + \text{SrCl}_2$, and $6(\text{NH}_4)_2\text{HPO}_4 + 9\text{BaCO}_3 + \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was used as a solute for calcium, strontium, and barium chlorapatite, respectively. The solute (0.075, 0.1, and 0.6 mol% for calcium, strontium, and barium chlorapatite, respectively, as a chemical formula of $M_{10}(\text{PO}_4)_6(\text{OH})_2$) was heated with the flux at 1100°C for 10 h and followed by cooling down to 500°C at a rate of $5^\circ\text{C}/\text{h}$. The flux was removed by washing with hot water. For hydrothermal treatments, gem quality hexagonal prismatic crystals were selected, 2–8 mm long and 0.5–1 mm wide. Previous X-ray powder analysis conducted in the three different types of chlorapatite single crystals showed that these belong to the space group $P6_3/m$ of the hexagonal system. The original aspects of the surface and cross section of the employed single crystals are shown in Fig. 1. The as-prepared Ca, Sr, and BaClAp single crystals exhibit smooth prismatic surfaces, and very smooth surfaces were also produced by fracturing the crystals parallel to the basal plane (Figs. 1b, 1d, and 1f). The compositions of the original chlorapatite crystals determined by EPMA (Table 2) were slightly different from the ideal compositions, probably due to the defects induced by the high-temperature growth. It is noted that the stoichiometry of the crystals are recovered by the hydrothermal conversion of chlorapatite to hydroxyapatite.

2. Hydrothermal Treatments

A solution of KOH, with two concentrations of 6.25 and 10 M, was employed as an ion exchange medium. Hydrothermal treatments were carried out in a platinum cap-

sule (30 mm in length, 3 mm in diameter, and 0.15 mm in thickness) by adding the single crystals (~ 20 mg) together with the alkaline solution (0.040 ml). The capsule was then welded shut with an electric arc.

The platinum capsule was placed at the bottom of a test tube-type vessel made from Stellite 25. All hydrothermal treatments were conducted at an internal pressure of 100 MPa, which was imposed in the vessel by using distilled water as a pressure medium. The hydrothermal ion-exchange reaction was conducted in a temperature range of $200\text{--}800^\circ\text{C}$, for intervals between 3 and 96 h. During the experiment, the temperature was measured on the outside wall of the vessel, using a thermocouple placed at the position corresponding to the bottom of the capsule. After each run, the vessel was cooled to room temperature by removing the furnace. The capsule was then cut open, and the reaction products washed with distilled water by successive decanting.

3. Characterization

The crystalline phases of the reaction products were identified by powder X-ray diffraction analyses. Measurements were made by an X-ray diffractometer (Rigaku, Rotaflex) with graphite-monochromatized $\text{CuK}\alpha$ radiation at 40 kV and 100 mA. The morphology of the reaction products was examined by scanning electron microscopy (SEM, Hitachi S-530). In order to determine the reaction process, the crystals treated for a short interval were selected, mounted parallel to the *c* axis in epoxy resin, and then polished to a mirror-like surface. Chlorine line analyses were conducted on the surface perpendicular to the basal plane of the crystals, using an energy-dispersive X-ray unit (KeveX).

The composition of the reaction products was determined by electron microprobe analyses (Jeol, JXA-8600NX). The mineral standards (ASTIMEX) employed and the elements determined are as follows: hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) for Ca and P, sanidine (KAlSi_3O_8) for K, tugtupite ($\text{Na}_4\text{BeAlSi}_4\text{O}_{12}\text{Cl}$) for Cl, barite (BaSO_4) for Ba, and celestite (SrSO_4) for Sr, respectively. The analyses were conducted at a constant filament current of 15 nA, and the amount of each element (wt%) was computed by using the ZAF correction procedure. The composition of the reaction products, was obtained from an average of 40 points taken on the polished surface of each sample.

RESULTS AND DISCUSSION

Hydrothermal Conversion of Chlorapatite Crystals to Hydroxyapatite

Hydrothermal treatments were directed to determine the conditions of the temperature, at which the Cl–OH ion exchange reaction is achieved in each type of the chlorapatite crystals. The experimental conditions of the hydrother-

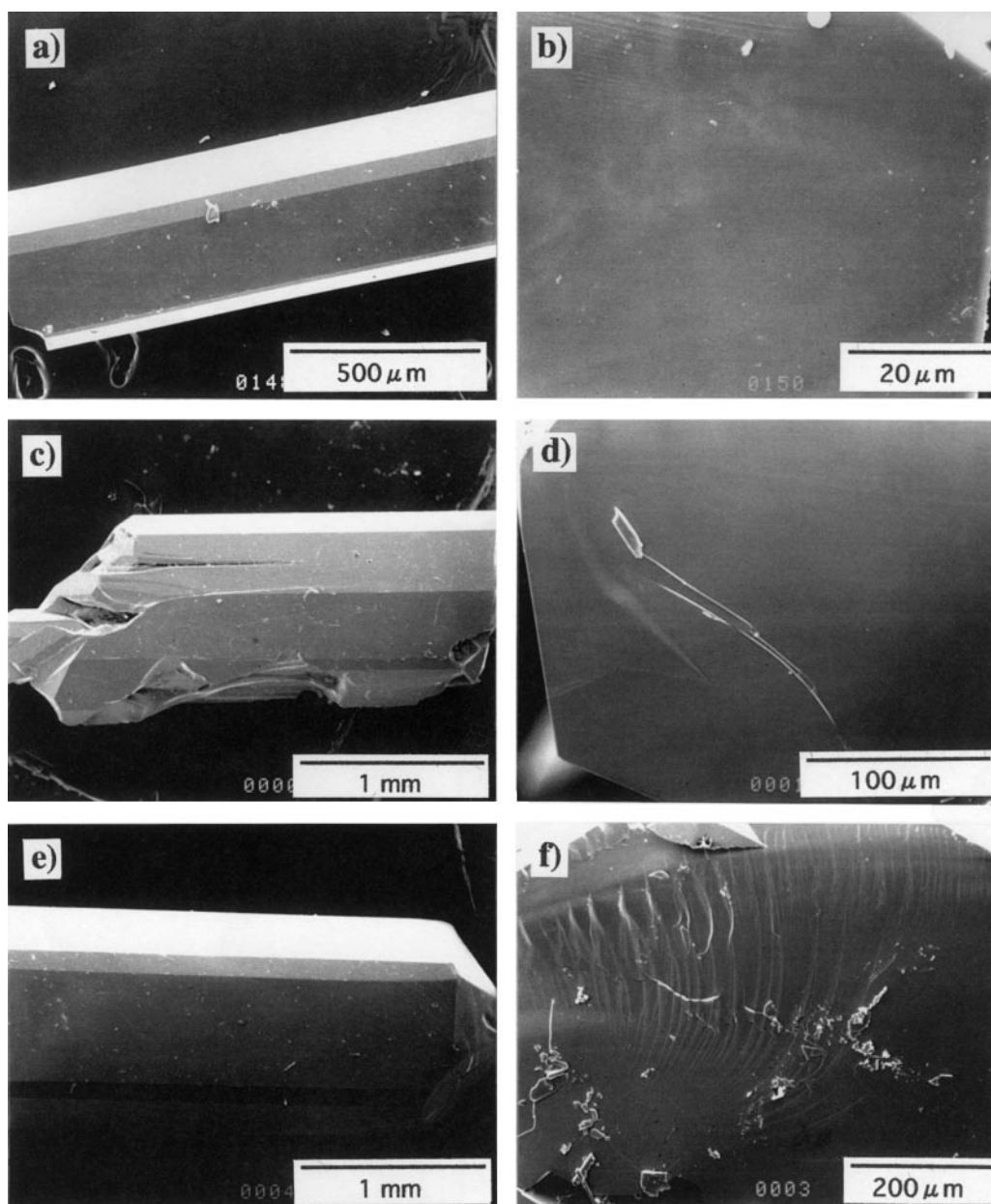


FIG. 1. SEM micrographs of the prism surfaces and cross sections normal to the basal plane of the original calcium (a, b), strontium (c, d), and barium chlorapatite single crystals (e, f) used for this experiment.

mal treatments are summarized in Table 1, as are the phases identified in the reaction products.

X-ray diffraction patterns of the CaClAp crystals hydrothermally treated at various temperatures in 6.25 M KOH solution for 48 h are shown in Fig. 2. These results reveal that the exchange of Cl^- ions by OH^- ions in the CaClAp crystals starts at temperatures as low as 300°C. This is depicted by the formation of a small amount of a second phase. The reaction was accelerated by increasing the temperature. Thus, the products obtained during the

treatments at 400 and 500°C exhibited only a single phase, which was matched with the hexagonal (space group $P6_3/m$) CaOHAp structure (JCPDS card 9-432). The conversion rate depended on the reaction temperature, but any remarkable decrease of the conversion rate was not observed during the conversion. Electron microprobe analyses (Table 2, 3Ca) show the presence of small content of residual Cl^- and also the uptake of K^+ in this phase during the treatment. On the other hand, the converted CaOHAp crystals were indexed to the monoclinic structure (space group $P2_1/b$),

TABLE 1
Summary of the Hydrothermal Treatments of Chlorapatite Single Crystals

Sample ID	Chlorapatite single crystals	Solution	Concentration (M)	Temperature (°C)	Duration (h)	Determined phases
5Ca	Calcium	KOH	6.25	500	3	CaClAp + CaOHAp
25Ca	Calcium	KOH	6.25	500	12	CaOHAp
3Ca	Calcium	KOH	6.25	500	48	CaOHAp
1Ca	Calcium	KOH	6.25	500	96	CaOHAp
16Ca	Calcium	KOH	6.25	400	48	CaOHAp
17Ca	Calcium	KOH	6.25	300	48	CaClAp + CaOHAp ^a
36Ca	Calcium	KOH	6.25	200	48	CaClAp
1Sr	Strontium	KOH	6.25	400	48	SrClAp + SrOHAp ^b
2Sr	Strontium	KOH	6.25	500	48	SrClAp + SrOHAp ^b
3Sr	Strontium	KOH	6.25	600	48	SrClAp + SrOHAp ^b
4Sr	Strontium	KOH	6.25	700	48	SrOHAp
5Sr	Strontium	KOH	6.25	700	3	SrClAp + SrOHAp ^b
6Sr	Strontium	KOH	6.25	700	6	SrClAp + SrOHAp ^b
7Sr	Strontium	KOH	6.25	700	12	SrClAp + SrOHAp ^b
1Ba	Barium	KOH	10	500	48	BaClAp
2Ba	Barium	KOH	10	700	48	BaClAp
3Ba	Barium	KOH	10	750	48	BaClAp + BaOHAp
5Ba	Barium	KOH	10	800	24	BaClAp + BaOHAp + BaOHAp ^c
6Ba	Barium	KOH	10	800	48	BaClAp + BaOHAp + BaOHAp ^c
7Ba	Barium	KOH	10	800	96	BaClAp + BaOHAp + BaOHAp ^c

Note. Phases were determined by XRD and EPMA. Phases determined by XRD: CaClAp, CaOHAp, SrClAp, SrOHAp, BaClAp, BaOHAp. Phases determined by EPMA: the CaOHAp^a corresponding to an OH⁻-rich solid solution, SrOHAp^b to an Cl⁻-rich solid solution, and BaOHAp^c to the newly single crystals containing a large amount of K.

because superlattice spots corresponding to this space group were observed by Weissenberg precession photographs. Figure 3 shows the morphology of the CaOHAp crystals treated at 500°C in 6.25 M KOH solution for 48 h. It is

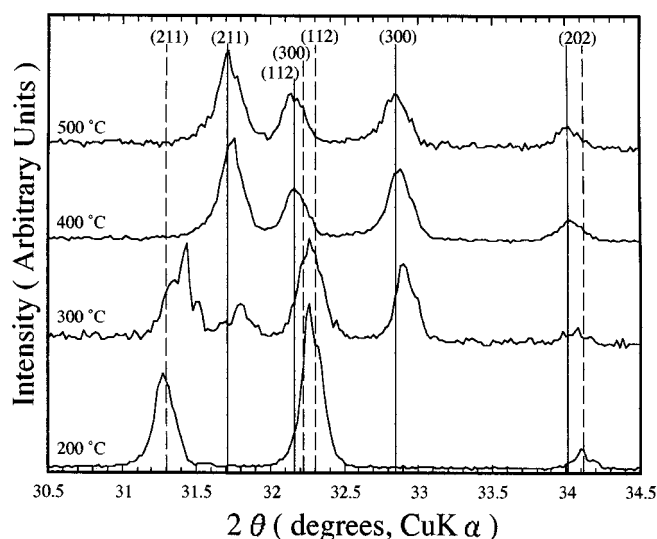


FIG. 2. X-ray diffraction patterns of the specimens obtained from the CaClAp crystals, after hydrothermal treatments in 6.25 M KOH solution for 48 h at different temperatures. Dotted line, calcium chlorapatite (JCPDS card 33-271); solid line, calcium hydroxyapatite (JCPDS card 9-432).

clear that the conversion proceeded without severe changes of the original shape and dimension of the crystals. A peculiar texture, however, consisting of elongated channels and tiny holes distributed randomly normal to the *c*-axis, was observed on the prism surfaces (Fig. 3a) and inside (Fig. 3b) the crystals, respectively.

For the SrClAp crystals, the exchange of Cl⁻ with OH⁻ was slightly retarded. The X-ray diffraction patterns in Fig. 4 show that this reaction began at 400°C. These crystals were completely converted to the strontium hydroxyapatite (hereafter referred to as SrOHAp; JCPDS card 33-1348) single phase by the treatment at 700°C for 48 h in 6.25 M KOH solution. After the treatment, the completely converted SrOHAp crystals also retained their original shape and dimensions, and exhibited more corroded scale-like surfaces (Fig. 5a) than that observed on the CaOHAp crystals. Observations conducted on the cross section of the crystals parallel to the *c*-axis (Fig. 5b), show the formation of elongated cavities randomly distributed along the *c* direction, with widths of 2.5–5 μm and lengths of 10–20 μm.

The Cl–OH ion exchange reaction on BaClAp crystals occurred at higher temperatures than those for CaClAp and SrClAp crystals, even in a concentrated KOH solution (10 M). Initial experiments at 500 and 700°C in 5 M KOH solution, showed that the crystals retained the original BaClAp structure. Figure 6a shows the X-ray diffraction patterns of the BaClAp crystals treated at various

TABLE 2
Summary of the Microprobe Analyses

Sample ID	KOH solution concentration (M)	Temperature (°C)	Time (h)	Chemical Composition (wt%)							M/P ratio	Chemical formula
				Ca	Sr	Ba	P	Cl	K			
5Ca	6.25	500	3	38.45 ± 0.20			17.58 ± 0.15	6.20 ± 0.10			1.686	Ca _{1.0} (PO ₄) ₆ Cl ^{II}
5Ca1	6.25	500	3	39.99 ± 0.30			18.58 ± 0.25	0.82 ± 0.10		0.08 ± 0.03	1.667	Ca _{9.98} K _{0.02} (PO ₄) ₆ (OH) _{1.75} Cl _{0.23}
3Ca	6.25	500	48	39.88 ± 0.30			18.58 ± 0.30	0.78 ± 0.09		0.19 ± 0.02	1.667	Ca _{9.95} K _{0.05} (PO ₄) ₆ (OH) _{1.73} Cl _{0.22}
7Sr	6.25	700	12		57.63 ± 0.20		12.36 ± 0.10	4.67 ± 0.15			1.648	Sr _{1.0} (PO ₄) ₆ Cl ^{II}
7Sr1	6.25	700	12		58.16 ± 0.10		12.38 ± 0.15	2.65 ± 0.10		0.10 ± 0.05	1.667	Sr _{9.96} K _{0.04} (PO ₄) ₆ (OH) _{0.94} Cl _{1.02}
7Sr2	6.25	700	12		58.89 ± 0.15		12.54 ± 0.15	0.48 ± 0.25		0.10 ± 0.05	1.667	Sr _{9.98} K _{0.02} (PO ₄) ₆ (OH) _{1.72} Cl _{0.24}
4Sr	6.25	700	48		58.82 ± 0.25		12.55 ± 0.10	0.43 ± 0.15		0.16 ± 0.05	1.667	Sr _{9.94} K _{0.06} (PO ₄) ₆ (OH) _{1.70} Cl _{0.24}
5Ba	10	800	24			68.06 ± 0.30	9.23 ± 0.20	3.45 ± 0.10			1.663	Ba _{1.0} (PO ₄) ₆ Cl ^{II}
5Ba1	10	800	24			69.22 ± 0.20	9.42 ± 0.15	0.07 ± 0.05		0.12 ± 0.07	1.667	Ba _{9.94} K _{0.06} (PO ₄) ₆ (OH) _{1.84} Cl _{0.10}
5Ba-S	10	800	48			44.95 ± 0.30	12.67 ± 0.20			13.86 ± 0.10	1.667	Ba _{4.80} K _{5.20} (HPO ₄) _{5.20} (PO ₄) _{0.80} (OH) ₂

Note. Formulas are based on 10 cations and the amount of OH⁻ was calculated by charge balance. The compositions of samples 3Ca and 4Sr were determined on the completely converted crystals, and those of the others were determined on the partially converted crystals. The location of the analysis on the partially converted crystals of samples 5Ca, 7Sr, and 5Ba are indicated in Figs. 8a, 8b, and 7d, respectively.

^{II}Ideal chemical formula.

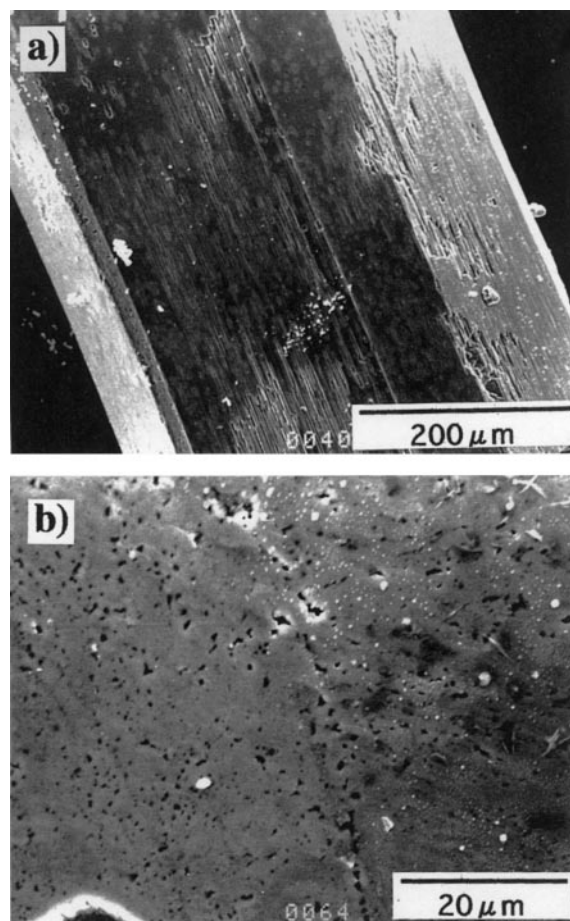


FIG. 3. SEM images of the prism surface (a) and cross section (b) parallel to the *c* direction of the topotaxially converted CaOHAp crystals by the hydrothermal treatment at 500°C for 48 h in 6.25 KOH solution.

temperatures in 10 M KOH solution for 48 h. The ion exchange reaction was observed to occur at 750°C. At this temperature the formation of a small amount of the barium hydroxyapatite (hereafter referred as BaOHAp, JCPDS card 36-272) was detected in the remaining products. SEM images in Fig. 7 show the aspects of the reaction products. During the hydrothermal treatment, the BaClAp crystals exhibited a further reduction of their original dimensions and were surrounded by new small crystals (Fig. 7a). The observations conducted on the cross section of the crystals (Fig. 7b) clearly showed that the new crystals homogeneously covered the unreacted BaClAp part. In addition, the formation of a continuous layer phase, with a width of 30–50 μm containing large irregular cavities randomly distributed, was observed between the unreacted part of the original BaClAp and the new crystals formed on the surface of the crystals (Fig. 7d).

The X-ray diffraction patterns of the newly grown small bulky crystals previously removed from the unreacted specimens are shown in Fig. 6b. The crystals were obtained at

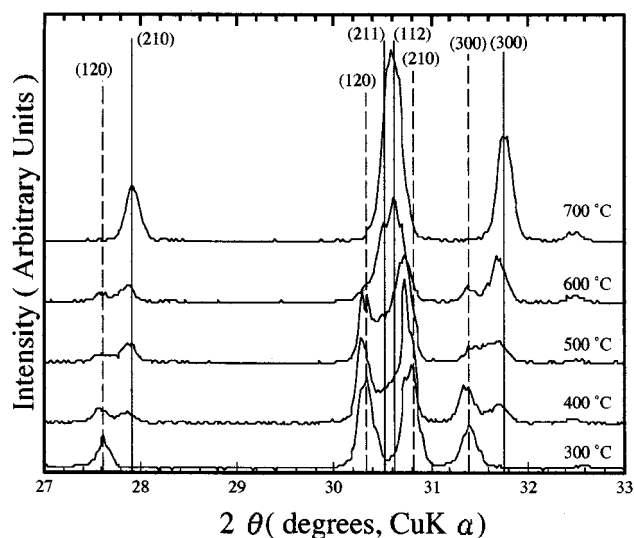


FIG. 4. X-ray diffraction patterns of the specimens obtained from the SrClAp crystals, treated under hydrothermal conditions in 6.25 M KOH solution for 48 h at different temperatures. Dotted line, strontium chlorapatite (JCPDS card 16-666); solid line, strontium hydroxyapatite (JCPDS card 33-1348).

800°C in 10 M KOH solution for 48 and 96 h. Though these crystals were indexed with the hexagonal BaOHAp structure, they incorporate a considerable amount of K^+ (Table 2, 5Ba-S). The formation mechanism of those crystals is discussed later in the next section.

In summary, the conversion to the OHAp began at temperatures as low as 300°C for the CaClAp single crystals. The reaction was completed at 500°C for 48 h in 6.25 M KOH solution. Under these conditions the morphology of the converted crystals remained as the original one, but tiny holes were formed inside the crystals. The conversion was retarded when large metal ions were incorporated in the ClAp structure. Thus, for the SrClAp crystals, the conversion started at 400°C and was completed at 700°C for 48 h in 6.25 M KOH solution. The converted SrOHAp crystals, also retained their original shape and dimensions, but the large holes observed after the treatment bear the evidence of their slight dissolution. In contrast, the BaClAp crystals were partially converted even in a concentrated KOH (10 M) solution at high temperatures. The reaction started at 750°C and proceeded only on the surface of the BaClAp crystals. Furthermore, the dissolution of the partially converted crystals resulted in a marked reduction of their original dimensions.

Differences in the Topotaxial Hydrothermal Mechanism

The details of the course of the ion-exchange reaction were determined on the cross section CaClAp crystals treated at 500°C in 6.25 M KOH for 3 h. Figure 8a shows

the SEM images of the cross section parallel to the c axis of the CaClAp crystals with the Cl^- line analysis obtained on the direction in which the conversion proceeds. In general, it is easy to identify from the SEM photographs, the presence of two phases: one formed near the crystal surface, which contains a great number of tiny holes that are randomly distributed along the c axis, and a continuous phase inside of the crystals. Both phases are separated by a marked sharp boundary in texture. Furthermore, the Cl^- line analysis also shows a difference on the content of Cl^- , which is denoted by the two plateaus separated by a sharp boundary. The electron microprobe analyses conducted on either phases, indicate that the phase near to the crystal surface corresponded to the CaOHAp phase (Table 2, 5Ca1), and the phase inside to the original CaClAp (Table 2, 5Ca). It should be noted that the Cl^- diffusion layer is not observed at the reaction front of the partially converted CaClAp crystals, which indicates our results cannot be associated with the solid state ion exchange mechanism (2, 10).

On the other hand, electron microprobe analyses of the complete converted CaOHAp crystals (Table 2, 3Ca),

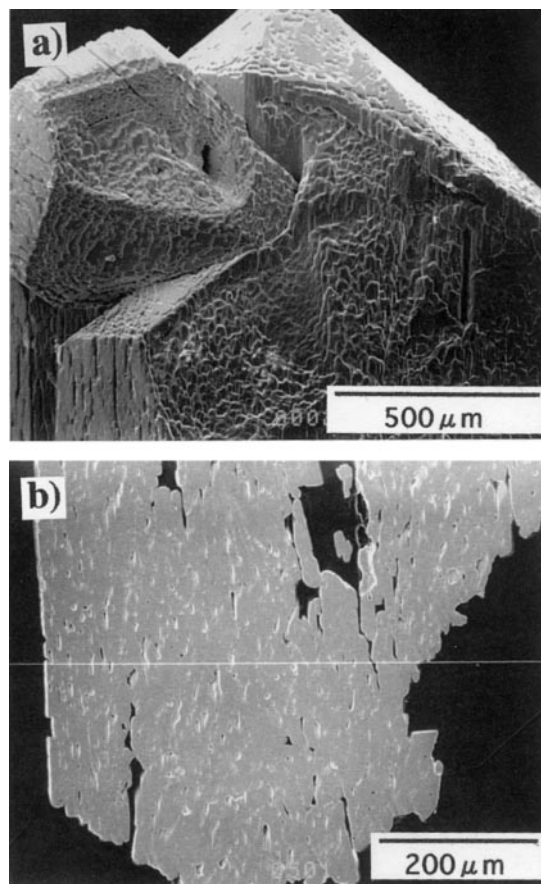


FIG. 5. Morphological aspects of the prism surfaces (a) and cross section (b) parallel to the c axis of the topotaxially converted SrOHAp crystals by the hydrothermal treatment at 700°C for 48 h in 6.25 M KOH solution.

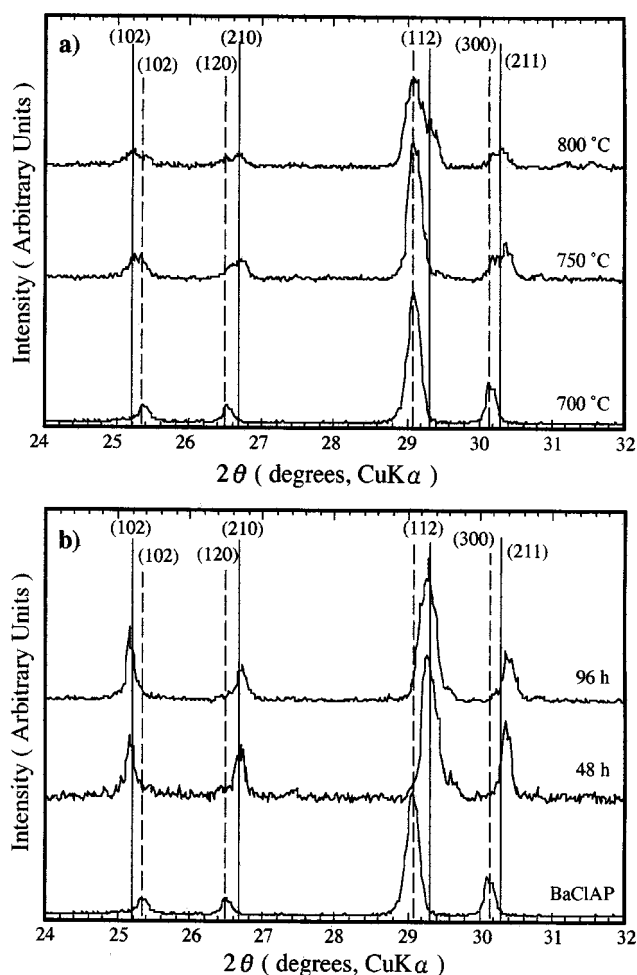


FIG. 6. X-ray diffraction patterns of the BaClAp crystals (a), treated under hydrothermal conditions at different temperatures for 48 h in 10 M KOH solution, and the newly formed crystals (b), grown at 800°C for 48 and 96 h in 10 M KOH solution. Dotted line, barium chlorapatite (JCPDS card 16-686); solid line, barium hydroxyapatite (JCPDS card 36-272).

showed no significant difference in the composition, compared with that of the CaOHAp phase (Table 2, 5Ca1) in the partially exchanged CaClAp crystals. Furthermore, the tunnels produced in the completely converted crystals are similar in dimension to those formed in the CaOHAp phase of the specimen treated for short interval (Fig. 8a). These results suggest that the conversion proceeded under a steady state of the reaction and allowed the reaction front to advance inside the original CaClAp progressively along the a and c axes. In addition, high-precession X-ray analyses conducted on the completely converted CaOHAp crystals by a Weissenberg camera indicated that these crystals corresponded to a single crystal with excellent quality. The above results are clear evidence suggesting that the CaClAp crystals were topotaxially converted to CaOHAp under alkaline hydrothermal conditions.

The present authors (11) proposed a mechanism of dissolution-precipitation of clusters, to explain the topotaxial conversion of the CaClAp crystals to the CaOHAp crystals under alkaline hydrothermal conditions. The clusters must be larger than ion species and the ion exchange may take place at the surface of the clusters, which are simultaneously precipitated at the same site (11, 15). In addition, the texture obtained in the converted CaOHAp crystals is not produced by dissolution, because the crystals should exhibit very large holes along the c axis if they are dissolved (16). The tunnels observed on the polished surface along the c axis do not penetrate the crystals, but only make zig-zag paths which allow the reaction medium to penetrate into the crystal. The BET measurements of the surface area on the crystals before and after the hydrothermal treatments, showed a remarkable increase of the surface area by the treatment. This result suggests that some of these tunnels are interconnected, producing a network in the exchanged layer, which allows the ion exchange medium to penetrate easily.

The formation of this peculiar texture in the converted CaOHAp crystals is due to the substitution of large Cl^- ions (radius of 1.81 Å), by smaller OH^- ions (radius of 1.68 Å). The structure must undergoes a variation on the a and c lattice parameters, as shown in Table 3. The conversion from CaClAp to CaOHAp proceeds with a marked contraction along the a axis and a slight expansion along the c axis of the crystals. In order to maintain the single crystal structure, the dimensional contraction along the a axis in the structure is compensated by the formation of the tunnels along the c axis (11).

In accordance with the X-ray diffraction patterns in Fig. 4, the SrClAp crystals were converted to SrOHAp crystals by the hydrothermal treatment at 700°C for 48 h in 6.25 M KOH solution. The converted SrOHAp crystals exhibited the same shapes and dimensions with those of the raw SrClAp crystals (Fig. 5). These results depict that the conversion to the SrOHAp structure also proceeded by the topotaxial ion exchange mechanism. However, the conversion proceeded with the significant damage of the crystals, because large holes were formed in the converted SrOHAp crystals (Fig. 5b), in comparison with those formed in the CaOHAp crystals (Fig. 3b). Figure 8b shows the cross section of the partially converted SrClAp crystal, after the treatment at 700°C for 12 h in 6.25 M KOH solution. The Cl^- line analysis, showed that the partially converted crystal consisted of three parts from the surface of the crystals, an highly reacted part with a low Cl^- content and large holes (Fig. 8b, 7Sr2), slightly reacted part with a medium Cl^- content and very tiny holes (Fig. 8b, 7Sr1), and the unreacted original SrClAp part with a high Cl^- content and smooth surface. The three different plateaus are perfectly separated by sharp boundaries. These results suggest that the topotaxial conversion of SrClAp to SrOHAp proceeds in two steps. In the first step, a Cl^- -rich solid solution in the

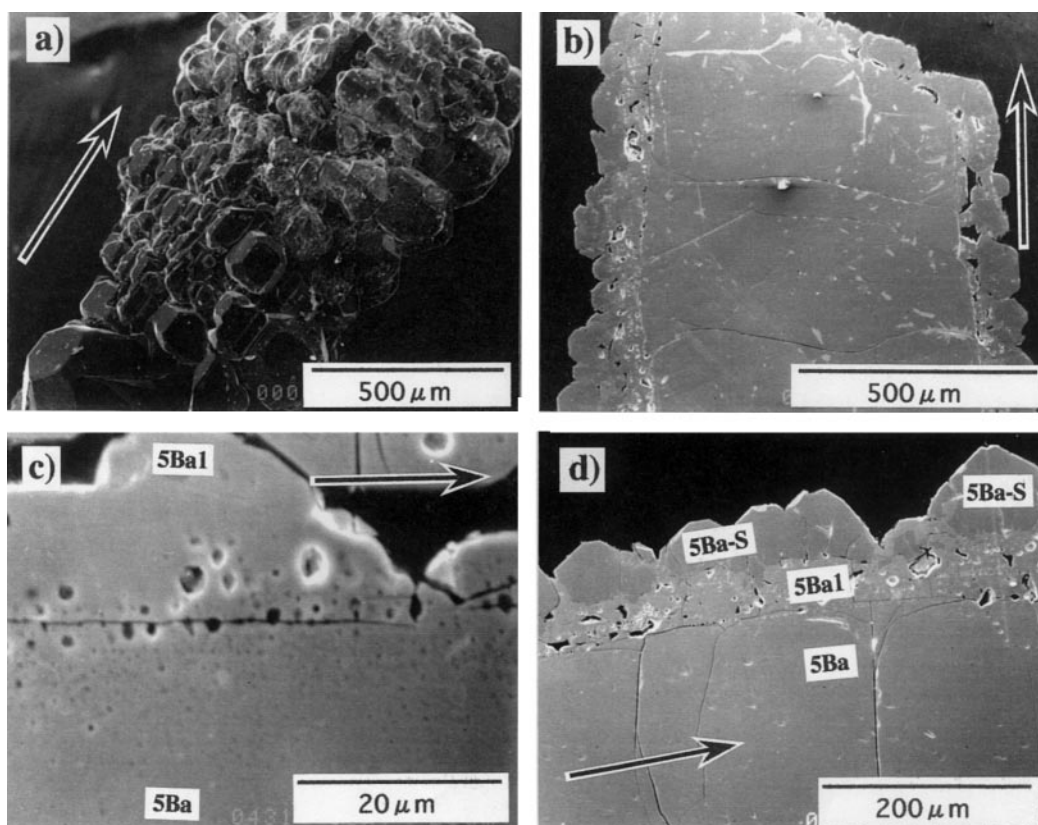


FIG. 7. Morphologic aspects of the prism surfaces (a), cross section (b), and detailed observations near the reaction front (c) and the surface (d) of the partially converted BaOHAp crystals by the hydrothermal treatment at 800°C for 48 h in 10 M KOH solution. The arrow on the photographs indicates the direction of the *c* axis of the crystals.

system SrClAp–SrOHAp was preferentially produced from the surface of the original SrOHAp crystal. Furthermore, small holes were formed due to the change of the lattice dimensions (Table 3) caused by the topotaxial ion exchange. This phase was considered to be produced by the mechanism of dissolution–precipitation of clusters (11).

The second step is related with the formation of another solid solution with high content of OH[−] (Fig. 8b, 7Sr2). This phase is the same with the completely converted SrOHAp (Table 2, 4Sr). The formation of this phase proceeded also by the topotaxial hydrothermal ion exchange mechanism, but large tunnels parallel to the *c* axis were formed in this phase (Fig. 8b). The size of the tunnels does not seem to agree with that expected by the compensation of the structural contraction along the *a* axis, caused by the ion exchange. The formation of the very large holes might be due to the dissolution of the Cl[−]-rich solid solution in the alkaline solution. The dissolution of the apatite has been found to occur under alkaline hydrothermal conditions at high temperatures (17).

In the case of BaClAp, it was not completely converted to BaOHAp even by the hydrothermal treatment at high tem-

perature (800°C) in a concentrated KOH solution (10 M) for a long time (96 h). In order to determine the course of the conversion, the cross section of the partially converted BaClAp crystal was carefully observed by SEM (Figs. 7c and 7d). The crystal consisted of several layers, marked as 5Ba-S, 5Ba1, and 5Ba in Fig. 7d. The composition analyses (Table 2) indicate that the part marked as 5Ba corresponded to the unreacted part of the BaClAp crystal, 5Ba1 to BaOHAp (OH-rich solid solution in the system of BaClAp and BaOHAp), and 5Ba-S to the newly formed crystals with high content of K. The formation of holes was clearly observed in the BaOHAp phase, though the boundary between 5Ba and 5Ba1 was not clear (Fig. 7c). The formation of BaOHAp together with holes on the BaClAp single crystal suggested that the topotaxial conversion proceeded by the same mechanism of dissolution and precipitation of clusters, which was determined for the conversion of CaClAp and SrClAp to the corresponding hydroxyapatites. The newly formed small crystals on the surface of the original BaClAp single crystal were considered to be formed by the hydrothermal reaction of the BaOHAp phase with the KOH solution.

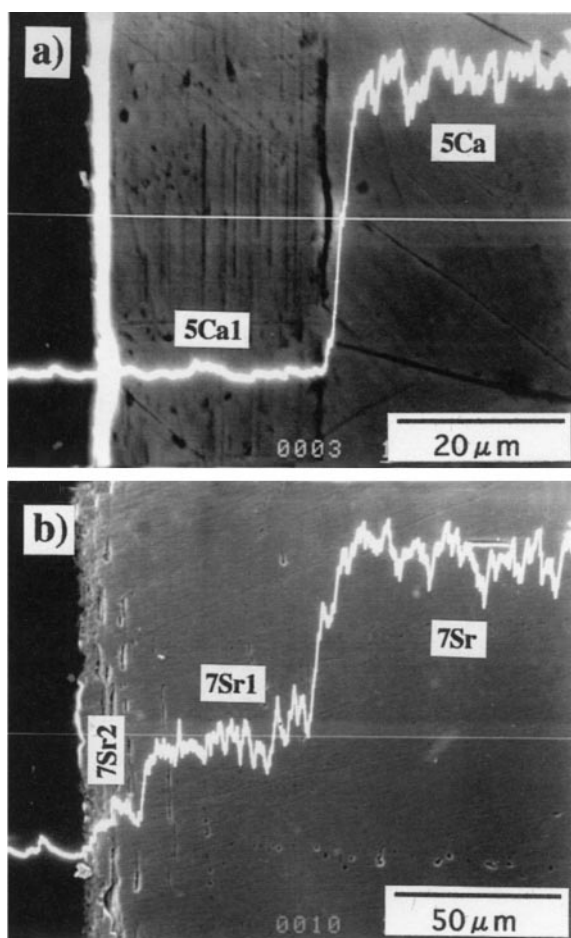


FIG. 8. SEM images of the cross section of the crystals parallel to the *c* axis and results of Cl line analysis. (a) CaClAp crystals treated at 500°C for 3 h in 6.25 M KOH solution; (b) SrClAp crystals treated at 700°C for 12 h in 6.25 M KOH solution.

The newly formed crystals, probably containing the BaOHAp phase, were assigned to BaOHAp by X-ray diffraction patterns (Fig. 6b). The composition of these crystals, however, is quite different from that of BaOHAp (Table 2, 5Ba-S). In spite of a large amount of K, atomic ratio of

(K + Ba)/P of these crystals was maintained to be 10/6 of the apatite structure. The charge balance of the constituents suggested that the chemical formula of these crystals was $\text{Ba}_{4.8}\text{K}_{5.2}(\text{HPO}_4)_{5.2}(\text{PO}_4)_{0.8}(\text{OH})_2$. Further details of the crystalline structure of these crystals are under study.

Recently, the present authors (17) have found that the apatite structure plays an important role on limiting the topotaxial ion exchange process. The conversion of calcium fluorapatite (hereafter abbreviated as CaFAp) to CaOHAp proceeds only at high temperature (800°C) in a concentrated KOH solution (10 M), because of the high stability of the CaFAp under hydrothermal conditions. The reaction occurred only on the prismatic ends with an ionic dissolution of the CaFAp crystals and small acicular CaOHAp single crystals were precipitated. The conversion of CaOHAp from CaFAp was explained by the dissolution-precipitation of ionic species. It is clear that the stability of individual apatite crystal structure is affected by the size of the ion incorporated in the X-channel columns, and controls the conversion mechanism in the apatite structure under hydrothermal conditions.

The present results indicate that the reactivity of the chlorapatite structure is also influenced by the size of the metal ion incorporated in the structure. We found that the temperature required for the topotaxial ion exchange increased in the following order, CaClAp, SrClAp, and BaClAp. It is concluded that the apatite structure exhibits a high stability under alkaline hydrothermal conditions, when large metal ions are incorporated in the six-fold screw axis (6_3) of the apatite structure. In the stable chlorapatites which incorporate large metal ions, the contraction along the *a* axis during the conversion to hydroxyapatite is small. This fact suggests the importance of the formation of tunnels during the treatment for the advance and completion of the conversion. Based on our results, it is reasonable to predict the possibility of the topotaxial ion exchange for other chlorapatites. The chlorapatites consisting of a smaller metal ion such as Cd (atomic radius 0.97 Å) or Pb (1.06 Å) than Sr (1.13 Å) must be topotaxially ion exchanged into their hydroxyapatite structure retaining their original shapes and dimensions.

TABLE 3
Hexagonal Lattice Constants of the Different Chlorapatites and Hydroxyapatites

Metal ion	Atomic radius (Å)	Chlorapatite lattice constants		Hydroxyapatite lattice constants		Lattice constant variation	
		<i>a</i> (Å)	<i>c</i> (Å)	<i>a</i> (Å)	<i>c</i> (Å)	Δa (Å)	Δc (Å)
Calcium	0.99 ^a	9.641 ^b	6.771 ^b	9.424 ^b	6.881 ^c	-0.217	0.110
Strontium	1.13 ^a	9.950 ^d	7.175 ^d	9.766 ^e	7.276 ^e	-0.184	0.101
Barium	1.35 ^a	10.260 ^f	7.640 ^f	10.191 ^g	7.747 ^g	-0.069	0.107

Note. Lattice constants from JCPDS cards: ^b33-271, ^c9-432, ^d16-666, ^e33-1348, ^f16-686, and ^g36-272.

^aValues from Ref. 1.

CONCLUSIONS

We have shown experimentally that the structural conversion to hydroxyapatite proceeded in all the chlorapatite single crystals by the dissolution-precipitation mechanism of clusters, which are larger than ion species. The topotaxially ion exchange of Cl^- ions with OH^- ions is significantly influenced by the size of the metal ion contained in the chlorapatite crystals. The rate of the conversion decreased by the presence of a large metal ion in the cation site of the chlorapatite structure. Hence, BaClAp crystals were more stable and elevated temperatures were required to achieve the conversion to BaOHAp . The ionic dissolution of the topotaxially converted BaOHAp layer in the reaction medium occurred simultaneously due to the high reaction temperature. As a result, new single crystals exhibiting the apatite structure and containing a large amount of K, were precipitated on the surface of the partially reacted BaClAp crystals. The present results suggest that other individual chlorapatite crystals such as CdClAp and PbClAp might be topotaxially converted to the hydroxyapatite structure under alkaline hydrothermal conditions, without variation of the original shape and dimension of the crystals.

ACKNOWLEDGMENTS

Many thanks are offered to Prof. T. Kariya for his help in EPMA measurements. One of the authors, R.A.J.C., is indebted to the Ministry of

Education Science, Sports, and Culture of Japan for the financial support with a postdoctoral/part-time instructor fellowship.

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