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A metastable phase in thermal decomposition of Ca-deficient hydroxyapatite

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We investigated the microstructural changes on an atomic length scale during thermal decomposition process of Ca-deficient hydroxyapatite (Ca-def HAp) by high-resolution transmission electron microscopy (HRTEM). Ca-def HAp was prepared by hydrolysis of α-tricalcium phosphate. The Ca-def HAp had a whisker-like morphology 2–5 μm in length and 0.1 μm in diameter that was elongated along *c*-axis. Thicker planer defects parallel to the (100) plane of the HAp matrix were observed as precipitation in the sample annealed at 700 and 800 °C by HRTEM observation. Thickness of the precipitation was about 10 nm and the boundaries between the precipitation and HAp matrix was coincident. The periodicity in the precipitation was parallel to the (100) plane of the HAp matrix and measured to be 1.42 nm. Since the precipitation was observed only in the sample annealed at a narrow temperature range of 700–800 °C, it was regarded as a metastable phase formed on the thermal decomposition process. Absorption peaks in IR spectra of annealed Ca-def HAp containing the metastable phase appeared at 744 and 3538 cm^{-1} due to non-stoichiometric HAp with high Ca/P molar ratio. Furthermore, the results of energy dispersive X-ray spectroscopy showed that the metastable phase had higher Ca/P molar ratio than that of the matrix and stoichiometric HAp. Therefore, the metastable phase could be identified as Ca-rich metastable phase. The presence of Ca-rich metastable phase was confirmed to be associated with the thermal decomposition process.

1. Introduction

Calcium-deficient hydroxyapatite [1–4] (Ca-def HAp: $Ca_{10-Z}(HPO_4)_Z(PO_4)_{6-Z}(OH)_{2-Z} \cdot nH_2O$ Ca/P molar ratio = 1.67–1.50 ($Z = 0$–1)) has lower Ca/P molar ratio than that of stoichiometric HAp (HAp: $Ca_{10}(PO_4)_6(OH)_2$/hexagonal, $a = 0.943$ nm, $c = 0.688$ nm, space group; $P6_3/m$) and resulting from Ca vacancies in the lattice. Upon annealing to 600–800 °C, the Ca-def HAp decomposes to stoichiometric HAp and β-tricalcium phosphate (β-TCP : $Ca_3(PO_4)_2$/ rhombohedral $a = 1.044$ nm, $c = 3.738$ nm (hexagonal setting), space group; R3c) as following equation [1, 5–7]. This results in the formation of β-TCP/HAp biphasic calcium phosphate ceramics, which show the good bioactivity in osseous environment because their solubility is much similar to that of biological bone apatite [8]:

$$Ca_{10-Z}(HPO_4)_Z(PO_4)_{6-Z}(OH)_{2-Z} \rightarrow (1-Z)$$
$$Ca_{10}(PO_4)_6(OH)_2 + 3Z \cdot \beta\text{- } Ca_3(PO_4)_2 + Z \cdot H_2O$$

We widely studied for Ca-def HAp for both fundamental and application purposes and found that whisker-like Ca-def HAp crystals could be synthesized by hydrolysis of α-tricalcium phosphate (α-TCP : α-$Ca_3(PO_4)_2$) in water/octanol binary solvent system [9–12].

Various studies for thermal decomposition of Ca-def HAp have been carried out [5–7, 13–15]. Investigation of infrared spectroscopy by Monma *et al.* [5, 6] showed that the condensation of HPO_4^{2-} ions occurred by the following reaction, resulting in the production of $P_2O_7^{4-}$ ions at temperatures below 450 °C:

$$2HPO_4^{2-} \rightarrow P_2O_7^{4-} + H_2O$$
$$\text{or} \quad PO_4^{3-} + H_2O \rightarrow \frac{1}{2}P_2O_7^{4-} + OH^- + \frac{1}{2}H_2O$$

Furthermore, they explained that the thermal decomposition process might assume the following reactions.

$$Ca_{10-Z}(HPO_4)_Z(PO_4)_{6-Z}(OH)_{2-Z}\cdot nH_2O \rightarrow Ca_{10-Z}(P_2O_7)_Z(PO_4)_{6-2Z}(OH)_{2-Z} + n\cdot H_2O \rightarrow (1-Z)Ca_{10}(PO_4)_6(OH)_2 + 3Z\cdot \beta\text{-}Ca_3(PO_4)_2 + Z\cdot H_2O$$

In contrast, Yubao *et al.* [13] reported that this thermal decomposition process described the condensation of HPO_4^{2-} ions occurred over a wide temperature range at temperatures greater than 600 °C and was due to the reaction of $P_2O_7^{4-}$ ions with OH^- ions and thermal decomposition process occurred at this temperature range of 650–750 °C. Furthermore, their results revealed that morphology change took place at this temperature range, which was interpreted as fusion and recrystallization to β-TCP [13]. However, changes of local structure during thermal decomposition process are not well understood. We investigated the microstructural changes on atomic length scale during thermal decomposition of Ca-def HAp by HRTEM.

2. Experimental procedures

Ca-def HAp crystals were prepared by hydrolysis of α-TCP (Taihei Chemical Industries, Co., Ltd.). 0.01 mol α-TCP powders were stirred for 48 h at 70 °C in 1-octanol/H_2O binary solvent (100 ml/60 ml). The pH of binary solvent adjusted to 11.0 by ammonia aqueous solution. The Ca-def HAp crystals were annealed at 200–1100 °C in air (heating rate: 5 °C/min, keep time: 2 h).

The Ca-def HAp crystals before and after annealing were identified by powder X-ray diffraction analysis (XRD: RINT 2000/Rigaku Co., Ltd) with the CuK_α radiation at 40 kV, 50 mA. The XRD profiles were collected between 20–60° of 2θ angles with a step interval of 0.01° and scanning rate of 4°/min. The Ca-def HAp crystals before and after annealing were also identified by infrared absorption spectroscopy analysis. (IR: IR-WINSPEC100/JEOL). The atomic concentrations of calcium and phosphorus in the Ca-def HAp before annealing were measured by inductive coupled plasma (ICP: ICAP9000/Janell-Ash).

The Ca-def HAp before and after annealing were mounted on a Cu grid with a carbon coated holey film for transmission electron microscopy (TEM) by dripping the ethanol suspension of the sample. TEM, selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDS: Vantage/Noran Instrument) were carried out with JEOL JEM-2010SP (accelerating voltage: 200 kV).

3. Results and discussion

3.1. Microstructural change during thermal decomposition process of Ca-def HAp

From results of XRD, IR and ICP analysis, the Ca-def HAp prepared by hydrolysis method was identified as carbonate containing, well-crystallized Ca-def HAp with Ca/P molar ratio was 1.58 [10].

Fig. 1(a)–(h) shows XRD patterns of Ca-def HAp before and after annealing in the temperature range between 200 and 1100 °C. In temperature range between 800 and 1100 °C, several β-TCP diffraction peaks (as marked by black triangles) show β-TCP phase and HAp peak (no marked peak) were observed. XRD patterns of Ca-def HAp annealed below 600 °C showed only HAp phase. The XRD patterns showed β-TCP phase to appear for the first time in the sample annealed at 800 °C. The peak intensities due to β-TCP in the sample annealed at 900 °C was stronger than that of 800 °C. The XRD profiles of Ca-def HAp annealed above 1000 °C were almost the same as that of the sample annealed at 900 °C. According to the results of XRD analysis, it could be concluded that the thermal decomposition of Ca-def HAp begins at about 800 °C and finishes at about 900 °C.

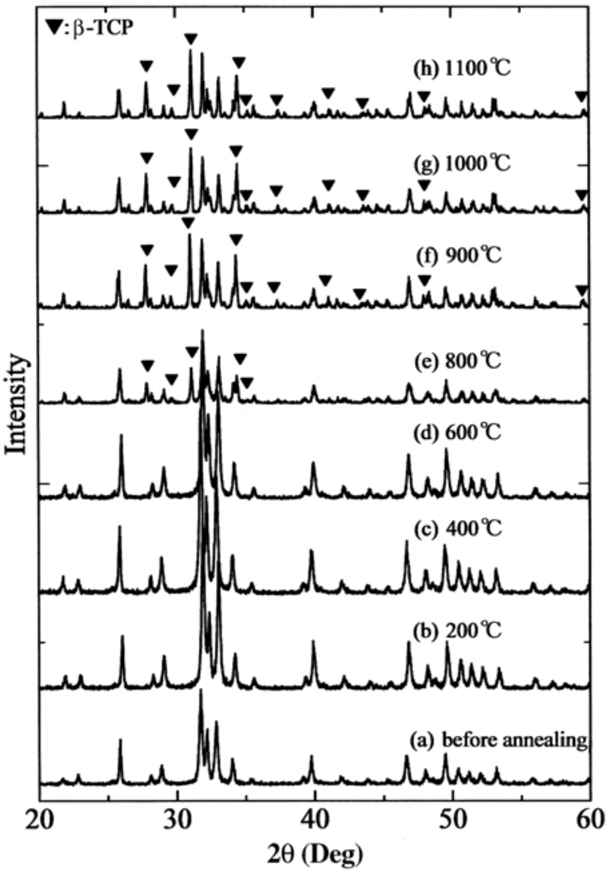


Figure 1 X-ray diffraction patterns of Ca-def HAp prepared by hydrolysis method and annealed at 200–1100 °C. (a): before annealing, (b)–(h): 200–1100 °C.

A low-magnified TEM image of Ca-def HAp before annealing is shown in Fig. 2(a). From measurement of their TEM images, the Ca-def HAp has a whisker-like morphology elongated along *c*-axis with 2–5 μm in length and 0.1 μm in diameter. Figs. 2(b)–(e) show TEM images of Ca-def HAp annealed at 600, 700, 800 and 900 °C, respectively. As shown in Fig. 2(b), whisker-like morphology remained in the samples annealed below 600 °C. The tips of the whisker-like crystals annealed at 700 and 800 °C became more rounded off with increasing annealing temperature (Fig. 2(c) and (d)). Furthermore, the TEM image of the sample annealed at 900 °C in Fig. 2(e) showed several whisker-like crystals grew into large grains. Although decomposition temperature in this study is slightly higher than that of Yubao *et al.*'s report [13] results, of both XRD analysis and TEM observation nearly agree with previous studies.

Fig. 3(a)–(d) show HRTEM images of Ca-def HAp annealed at 600, 700, 800 and 900 °C, respectively. In Fig. 3(a), a bright line parallel to the (100) plane of HAp crystal appeared in the sample annealed at 600 °C. As

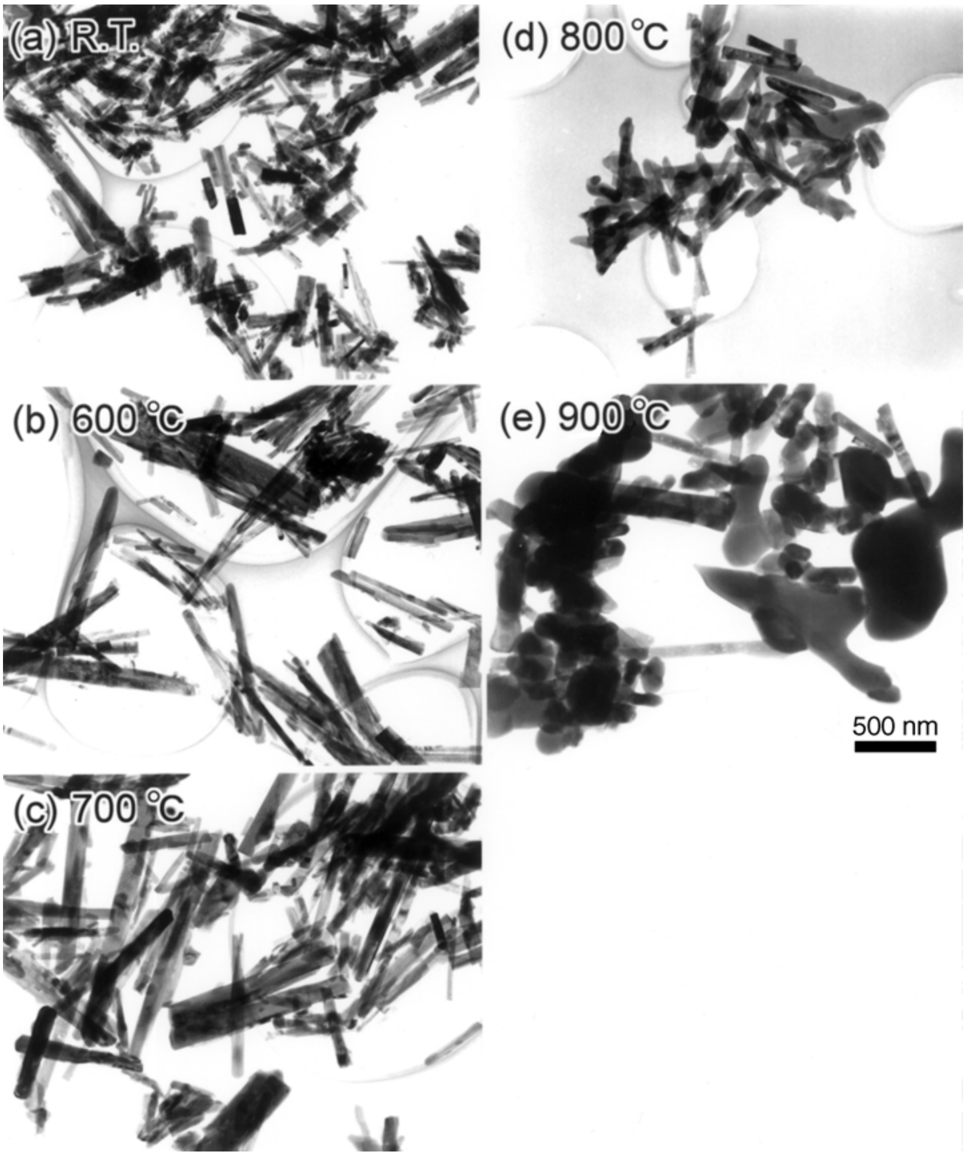


Figure 2 TEM images of Ca-def HAp before annealing (a) and after annealing at (b) 600 °C, (c) 700 °C, (d) 800 °C and (e) 900 °C.

shown in Fig. 3(b) and (c), thicker planer defects, which were recognized as a precipitation, were observed in the sample annealed at 700 and 800 °C. A thickness of the precipitation was about 10 nm and boundaries between the phase and the HAp matrix were coincident. A periodicity parallel to the (1 0 0) plane of the HAp matrix was 1.42 nm, which was not any spacing due to crystal structure of various calcium phosphate compound such as HAp or β-TCP and calcium oxide. Fig. 3(d) shows a typical image of the sample annealed at 900 °C. Although we performed TEM observation for many samples, the precipitation could not be observed in the sample annealed at 900 °C. Since the precipitation was observed only in the samples annealed at a narrow temperature range of 700–800 °C, the phase can be regard as a metastable precipitate phase from HAp matrix on the thermal decomposition process.

3.2. Composition of a metastable phase

Fig. 4(a) and (b) show IR spectra of Ca-def HAp before and after annealing at various temperatures ((a): 400–1400 cm^{-1}; (b): 2400–3900 cm^{-1}). From the results of IR analysis in Fig. 4(a) and (b), a broad band at 870 cm^{-1} due to HPO_4^{2-} and CO_3^{2-} and weak shoulder absorption at 1133 and 1210 cm^{-1} due to HPO_4^{2-} were still presented in the sample annealed below 200 °C. These IR absorption peaks were not observed in the Ca-def HAp annealed at 400 °C and 600 °C. In addition, there is no IR absorption at about 720 cm^{-1} assigned to pyrophosphate in this temperature range. It has been reported that phase formation of β-TCP from Ca-def HAp crystals was relate to formation and disappearance of pyrophosphate ion [5, 6]. Carbonate is contained in this Ca-def HAp. It has been reported that the carbonate ion in HAp lattice restrains the condensation of HPO_4^{2-} as following reaction [1, 16].

$$2HPO_4^{2-} + CO_3^{2-} \rightarrow 2PO_4^{3-} + CO_2 + H_2O$$

This explains why no pyrophosphate ion are formed in this study. However, well-crystallized and carbonate containing Ca-def HAp also decompose to stoichiometric HAp and β-TCP as elucidated by XRD analysis in Fig. 1. Suggesting that the carbonate containing Ca-def HAp has a different thermal decomposition process from that of carbonate-free Ca-def HAp.

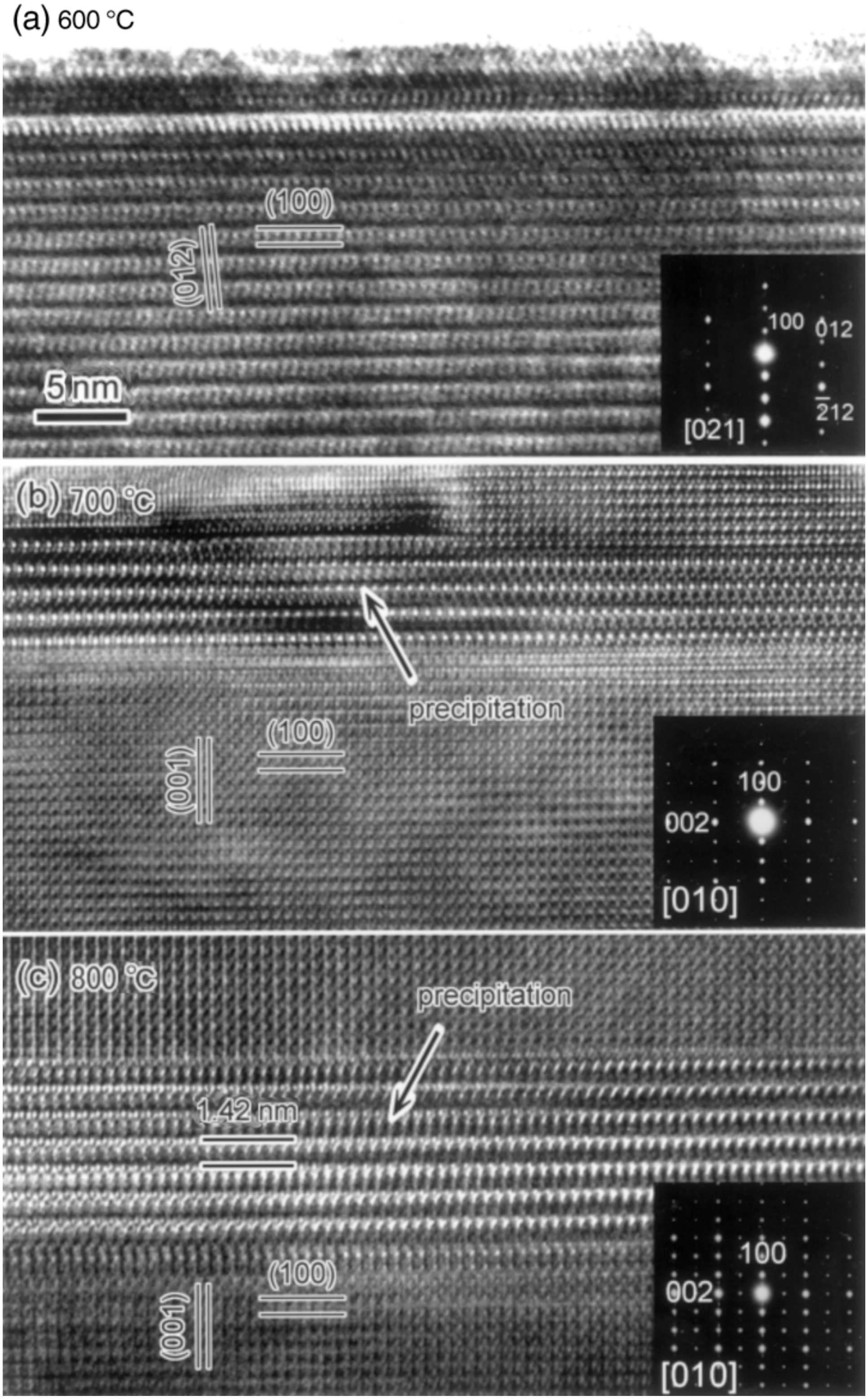


Figure 3 HRTEM images of Ca-def HAp annealed at (a) 600 °C, (b) 700 °C, (c) 800 °C and (d) 900 °C.

IR absorption at 744 cm^{-1} appeared in IR spectra of the sample annealed at 800 °C. Furthermore, IR absorption due to OH$^-$ ion, which was observed at 3570cm^{-1}, at less than 600 °C, it shifted to 3538cm^{-1} at 800 °C. These IR absorptions could not be observed in the sample annealed at 900 °C. G. Bonel *et al.* [17] reported that non-stoichiometric HAp with Ca/P molar ratios of 1.67–1.83 were prepared by heating mixtures of stoichiometric HAp and $CaCO_3$ in air and those IR spectra changed with increasing Ca/P molar ratio of non-stoichiometric HAp. Particularly, for the compound with a Ca/P molar ratio of 1.75, appearance of two IR absorptions were confirmed at 3544 and 745 cm^{-1}. They considered that those IR adsorptions could be attributed to the OH$^-$ located in the channel of the apatitic structure (excess Ca^{2+} ion were contained in HAp lattice). Thus, results of IR analysis suggest that there is a local area containing excess Ca^{2+} ion in the sample annealed at 800 °C. On the other hand, although the metastable phase present in Ca-def HAp annealed at 800 °C, this phase could not be observed in the sample annealed at 900 °C. The temperature range over which a

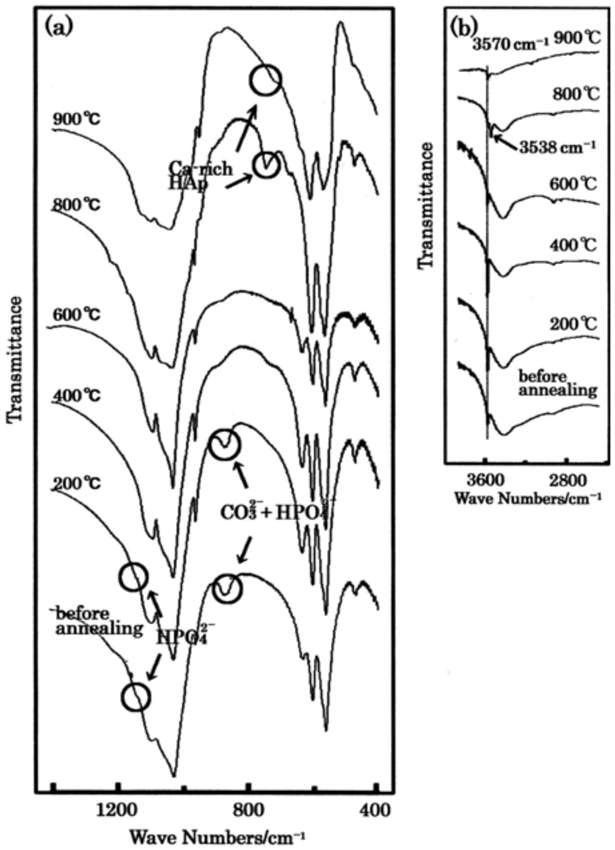
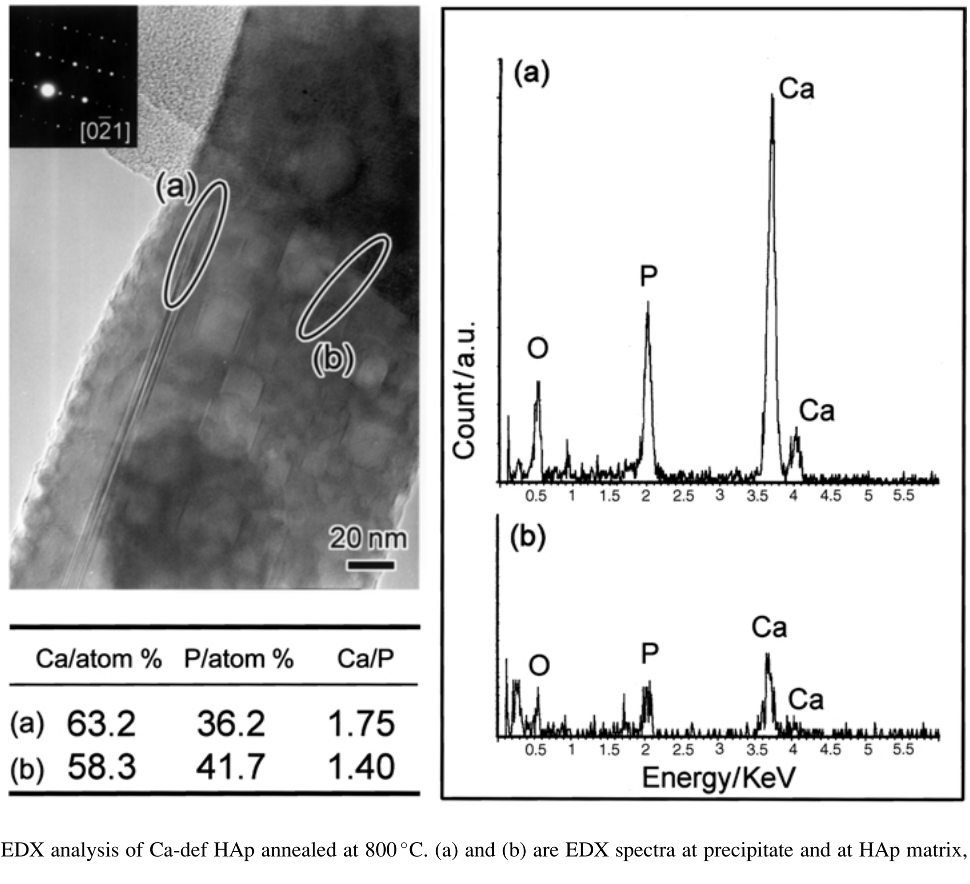


Figure 4 FT-IR spectra of Ca-def HAp before and after annealing ((a) between 400 and 1400 cm^{-1}, (b) between 4000 and 2400 cm^{-1}).

peculiar IR absorption appears corresponds to the presence of the metastable phase. Therefore, according to G. Bonel *et al.*'s [17] report and results of IR analysis in our study, it is suggested that the metastable phase have higher Ca/P molar ratio that of stoichiometric HAp.

Fig. 5 shows TEM-EDS analysis of Ca-def HAp annealed at 800 °C. Fig. 5(a) and (b) show the EDS spectra of the metastable phase and of HAp matrix, respectively. The results of TEM-EDS analysis show that the metastable phase had higher Ca/P ratio than that of HAp matrix and stoichiometric HAp. Therefore, the metastable phase confirmed in this study can be identified as Ca-rich metastable phase.

Fig. 6(a)–(c) show low-magnified TEM image of Ca-def HAp annealed at 800 °C, which containing the Ca-rich metastable phase, HRTEM image of the area enclosed by a rectangle in (a) and electron diffraction pattern, respectively. The inset in Fig. 6(b) is lattice images of the metastable phase. As shown in Fig. 6(a), Ca-rich metastable phase with the periodicity of 1.42 nm was traversing through the inside of the whisker and the part of the upside of Ca-rich metastable phase showed mountain-like morphology. As shown in Fig. 6(b), from the morphology of the tip of Ca-rich metastable phase, it seems that two HAp crystals originally were united each other. The images in Fig. 6 may suggest that Ca-rich metastable phase is formed by participation of two HAp crystals and Ca-rich metastable phase might result from accumulation of Ca^{2+} ions to the interface of the two HAp crystals due to thermal diffusion or migration at high temperature. It is considered that an interface of twined bicrystals may play an important role in the formation of Ca-rich metastable phase and atomic arrangements at interface correlate closely with structure of a Ca-rich metastable phase. The microstructure on an atomic length scale of Ca-def HAp before annealing is under investigation.



	Ca/atom %	P/atom %	Ca/P
(a)	63.2	36.2	1.75
(b)	58.3	41.7	1.40

Figure 5 TEM-EDX analysis of Ca-def HAp annealed at 800 °C. (a) and (b) are EDX spectra at precipitate and at HAp matrix, respectively.

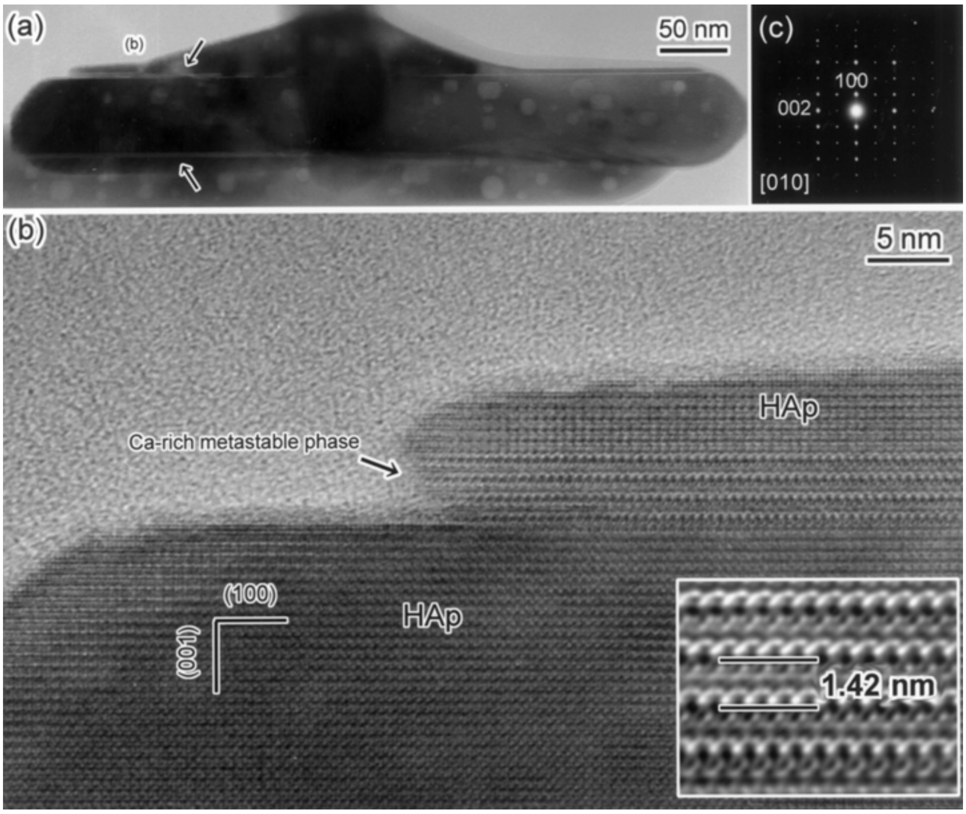


Figure 6 TEM image of Ca-def HAp annealed at 800 °C. (a) Low magnification TEM image, (b) HRTEM image of the area enclosed by a rectangle in Fig. 6(a) (the inset is a lattice image of Ca-rich metastable phase) and (c) selected area electron diffraction pattern.

4. Summary

We investigated the microstructural changes on an atomic length scale during thermal decomposition process of Ca-def HAp prepared by hydrolysis method using high-resolution transmission electron microscopy (HRTEM). Our results in this study are summarized as follows:

1. Ca-def HAp prepared by hydrolysis of α-TCP was well-crystallized and contained carbonate ions. The results of XRD analysis of Ca-def HAp before and after annealing showed that the thermal decomposition of Ca-def HAp began at about 800 °C and finished at about 900 °C. TEM observation revealed that morphology change took place during the thermal decomposition process.
2. Thicker planer defects resulting from precipitation were often observed in the samples annealed at 700 and 800 °C. The thickness of the precipitates was about 10 nm with a periodicity parallel to the (1 0 0) plane of the HAp matrix of 1.42 nm and boundaries between the phase and the HAp matrix was coincident. As precipitation could not be observed in the sample annealed at 900 °C, the precipitation was regarded as a metastable phase formed on the thermal decomposition process.
3. According to results of IR and TEM-EDS, it was revealed that the metastable phase found in this study was a Ca-rich metastable phase. The presence of Ca-rich metastable phase was confirmed to be associated with the thermal decomposition process.

References

1. J. C. ELLIOTT, in ‘‘Structure and Chemistry of the Apatite and Other Calcium Orthophosphates’’ (Elsevier, Amsterdam, 1994) p. 111.
2. J. C. ELLIOTT, *Calc. Tiss. Res.* **3** (1969) 293.
3. S. J. JORIES and C. H. AMBERG, *J. Phys. Chem.* **75** (1971) 3167.
4. S. J. JORIES and C. H. AMBERG, *ibid.* **75** (1971) 3172.
5. T. KANAZAWA, in ‘‘Inorganic Phosphate Chemistry’’ (Kodansha Scientific Tokyo, 1985).
6. H. MONMA, S. UENO, Y. TSUTSUMI and K. KANAZAWA, *Yogyo-Kyokai-shi* **86** (1978) 590.
7. I. R. GIBSON, I. REHAMAN, S. M. BEST and W. BONIFILD, *J. Mater. Sci. Med.* **12** (2000) 799.
8. L. L. HENCH, *J. Am. Ceram. Soc.* **74** (1991) 1487.
9. A. NAKAHIRA, K. SAKAMOTO, S. YAMAGUCHI, M. KANENO, S. TAKEDA and M. OKAZAKI, *J. Am. Ceram. Soc.* **82** (1999) 2029.
10. K. SAKAMOTO, M. OKAZAKI, A. NAKAHIRA and S. YAMAGUCHI, *Bioceramics.* **10** (1997) 241.
11. A. NAKAHIRA, M. TAMAI, K. SAKAMOTO and S. YAMAGUCHI, *J. Ceram. Soc. Jpn.* **108** (2000) 99.
12. M. TAMAI, S. MIKI, G. PEZZOTTI and A. NAKAHIRA, *ibid.* **108** (2000) 915.
13. L. YUBAO, C. P. A. T. KLEIN, S. VANDEMEER and K. DEGROOT, *J. Mater. Sci. Med.* **5** (1994) 263.
14. H. MONMA, S. UENO and K. KANAZAWA, *J. Chem. Tech. Biotechnol.* **31** (1981) 15.
15. J. J. P. VALDES, J. O. LOPEZ, G. R. MORALES, G. P. MALAGON and V. P. GORTCHEVA, *J. Mater. Sci. Med.* **8** (1997) 297.
16. Y. DOI and Y. MORIWAKI, *Shika J.* **36** (1992) 355.
17. G. BONEL, J. C. HEUGHEBAERT, M. HEUGHEBAERT and J. L. LEBUGLE, *Ann. NY. Acad. Sci.* **523** (1988) 115.

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