JOURNAL OF MATERIALS SCIENCE **36** (2001) 4131 – 4135

Transformation of tricalcium phosphate into apatite by ammonia treatment

S. HABELITZ*[‡]
University of Erlangen, Werkstoffwissenschaften III, Martensstr. 5, 91058 Erlangen, Germany
E-mail: shabeli@itsa.ucsf.edu

L. PASCUAL, A. DURÁN
Instituto de Cerámica y Vidrio (CSIC), 28500 Arganda del Rey, Spain

---

Tricalcium phosphate, $Ca_3(PO_4)_2$, was treated in dry ammonia at temperatures between 1100°C and 1300°C for different times of up to 16 h. X-Ray diffraction and ^{31}P-NMR studies showed a phase transformation into apatite when treated at temperatures between 1100 and 1200°C. Nitrogen was detected in the treated samples with a maximum content of 2.9 wt%. ^{31}P-NMR-analysis indicated no direct bonding of nitrogen to phosphorous. The presence of graphite during ammonia treatment was required for nitrogen incorporation. Infrared spectra showed increasing intensities of four new bands at 3250, 2016, 1966 and 700 cm^{-1} attributed to the occurrence of cyanamide ions. Taking into account the results of XRD, ^{31}P-NMR and FTIR spectrometry, it is concluded that tricalcium phosphate transforms into calcium deficient cyanamidapatite by ammonia treatments according to the reaction: $3Ca_3(PO_4)_2 + H_2CN_2 \rightarrow Ca_9(PO_4)_5(HPO_4)(HCN_2)$. *© 2001 Kluwer Academic Publishers*

---

1. Introduction

Hydroxyapatite, HA, $Ca_{10}(PO_4)_6(OH)_2$, as the main constituent of mammalian hard tissues is well known for its highly variable composition [1]. In the pseudo-hexagonal arrangement of PO_4-tetrahedra of hydroxyapatite, calcium and hydroxy ions can easily be substituted for ions of similar size and electric charge. In the human body, the exchange of e.g. Ca^{2+} and OH^- by Mg^{2+} and F^-, respectively, is a common observation in apatite crystals in the skeleton and teeth [1–4]. Via synthesis a huge number of phosphate compounds with apatitic structure has been produced containing Mn^{2+}, Pb^{2+}, Sr^{2+}, K^+ or Na^+ as cations and Cl^-, O^{2-} and CO_3^{2-} as anions [5–8].

Recently it was reported by the authors that heat treatments of hydroxyapatite in dry ammonia result in the formation of cyanamide apatite, $Ca_{10}(PO_4)_6(CN_2)$ [9]. It was suggested that at temperatures above 900°C cyanamide molecules, H_2CN_2, are formed in ammonia atmosphere in the presence of graphite:

$$2NH_3 + C \rightarrow H_2CN_2 + 2H_2 \qquad (1)$$

In a second step, H_2CN_2 interchanges with OH^--ions in order to form cyanamidapatite according to the reaction:

$$Ca_{10}(PO_4)_6(OH)_2 + H_2CN_2 \rightarrow Ca_{10}(PO_4)_6CN_2 + 2H_2O \qquad (2)$$

Experiments with a calcium deficient hydroxyapatite, CDHA, revealed also that the ammonia atmosphere stabilizes the apatitic structure at high temperature [9]. Decomposition of CDHA was observed at higher temperature when treated in ammonia compared to treatments in air. Similar observations were made by several authors for apatite heat treatments performed in moisture [10, 11]. In water or moisture hydroxyapatite is the thermodynamic favored crystalline phase of calcium phosphate with a Ca/P ratio between 1.5 and 1.7. Thus, several phosphate compounds transform into hydroxyapatite when exposed to an aqueous environment [12, 13].

Tricalcium phosphates are of mayor interest for the following study, since both, α- and β-TCP transform into hydroxyapatite in aqueous solutions according to the reaction [14–16]:

$$3Ca_3(PO_4)_2 + H_2O \rightarrow Ca_9(PO_4)_5(HPO_4)(OH) \qquad (3)$$

Due to the lower Ca to P ratio of TCP a calcium deficient apatite of Ca/P = 1.5 is formed. The above reaction is also considered to be responsible for the bioactivity and ability of bioresorption of TCP when used as implant material [16].

The above findings of the behavior of hydroxyapatite in dry ammonia, motivated the study of reactions of other phosphate compounds in dry ammonia at elevated

---

* Author to whom all correspondence should be addressed.

[‡] *Present Address:* University of California, Department of Preventive and Restorative Dental Sciences, 707 Parnassus, San Francisco, CA 94143, USA.

0022–2461

temperatures. The present paper will report and discuss the results obtained on TCP by means of the kinetics and phase development.

2. Experimental

2.1. Starting material and sample treatments

Spheroidal beads of tricalcium phosphate, TCP, from Fluka, Buchs (Switzerland) with diameters from 0.08 to 0.2 mm were used for treatment. Approximately 1 g of TCP was subjected to several thermal treatments in a dry flowing ammonia atmosphere. After the samples were placed in an airtight horizontal tube furnace, heating was started and the chamber of the furnace was flushed with nitrogen to eliminate air [17]. At a temperature of about 600°C, the gas supply was switched to ammonia adjusting a flow rate of about 500 cm^3/min. Ammonia heat-treatments of 1 to 30 h were performed in a temperature range between 1100 and 1300°C. The furnace was cooled down in ammonia atmosphere. Alumina and graphite crucibles were used. For particular experiments graphite powder was added to the alumina crucibles containing the sample.

2.2. Methods of characterization

Chemical analysis of calcium and phosphorous were made by inductive coupled plasma analysis, ICP, with a Jobin-Yvon sequential spectrometer, Model JY-38 VHR. The specific surface area was measured by the B.E.T. method with an Quantachrome, model Monosorb. Nitrogen analysis were performed by inert gas fusion method using a LECO type differential oxygen and nitrogen analyzer, TC-436 model. X-ray diffraction powder patterns were obtained on a Siemens diffractometer with Cu K_α radiation at 45 kV, 35 mA. The step size was 0.025° (2Θ) and the counting time per step was 3 seconds in a 2Θ range from 25° to 67°. ^{31}P-MASS-NMR spectra were acquired on a Bruker MSL-400 spectrometer operating at 161.977 MHz. Magic angle sample spinning was carried out with about 0.1g of the sample, using spinning speeds of 4 kHz. Chemical shifts were measured with respect to an external reference of 85% H_3PO_4 with an estimated deviation of 0.5 ppm. Infrared spectra from 4000 to 400 cm^{-1} were recorded on a Fourier transformed infrared spectrophotometer (FTIR) from Perkin Elmer model 1760-X on disks of 300 mg KBr adding 1.5 mg of the sample. To eliminate adsorbed water, disks were dried at 100°C and cooled down to room temperature in dry air before measurement.

3. Results

3.1. Characterization of starting materials

Spheroidal beads of tricalcium phosphate, TCP, used as starting material, have a surface area of 2.3 m^2/g^{-1}, with a Ca/P ratio of 1.55, slightly above the stoichiometric value of 1.5.

The XRD pattern of TCP, as received, is shown in Fig. 1, curve a. The diffractogram matches JCPDS-file: 9-169 of β-tricalcium phosphate phase, which is the predominant phase. Few additional reflections of low intensity were detected and could be attributed to α-TCP[15, 16].

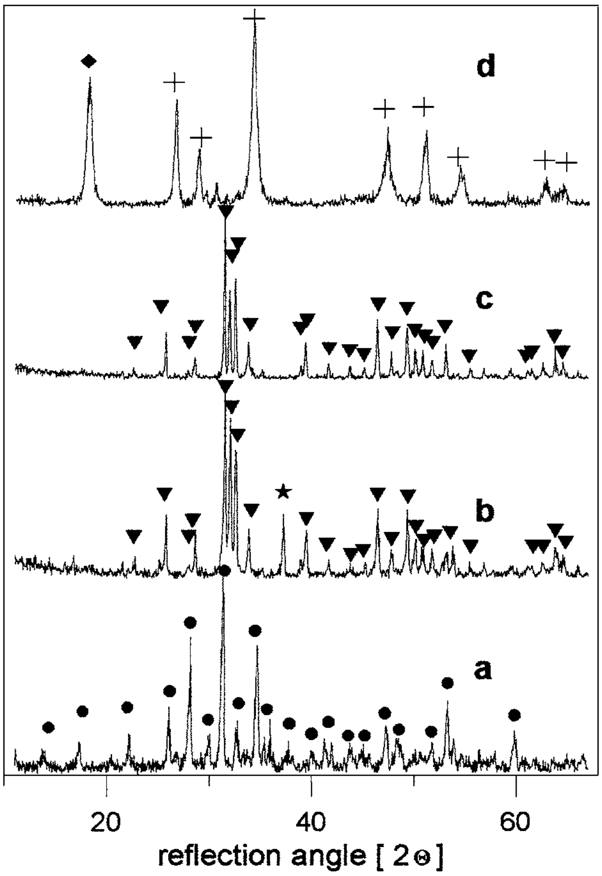

Figure 1 XRD patterns of TCP (a) as received, (b) treated at 1100°C/20 h, 2.9 wt% nitrogen, (c) treated at 1200°C/10 h, 2.7 wt% nitrogen and (d) treated at 1300°C/7 h, 0.4 wt% nitrogen. Phases are assigned as: CaO = +, $Ca(OH)_2$ = ★, apatite = ▼, graphite = ◆, β-TCP = ●.

Fig. 2, curve a, shows the ^{31}P-MAS NMR spectrum of the starting materials. According to the literature [18] the recorded spectrum is characteristic for a mixture of α- and β-TCP. β-TCP shows an intensive signal around −0.5 ppm and two shoulders at 0.5 and 4.3 ppm. α-TCP exhibits NMR-signals at 1.1, 2.3 and 3.5 ppm. The mixture of both compounds in the starting material resulted in an intensive signal at 0.07 ppm followed by three shoulders at 1.3, 3.5 and 4.3 ppm. Since the NMR lines of both TCP phases overlap, a quantitative distinction between α- and β-TCP was not possible. Fig. 3, curve a, shows the FTIR spectrum of TCP as received. The infrared spectrum of the untreated sample shows intensive bands at 1121, 1083, 1045, 973 and 946 cm^{-1}, corresponding to the characteristic stretching modes of tetrahedral $[PO_4]^{3-}$ groups of β-TCP. Further, bands at 588 and 554 cm^{-1} are attributed to the bending modes of $[PO_4]^{3-}$ groups of β-TCP. IR-bands at 1010, 602 and 541 cm^{-1} for β-TCP as reported in the literature [19, 20] were not detected, which is attributed to the low intensity and sharpness of these bands. However, using FTIR analysis it is difficult to distinguish between both crystalline phases of TCP, since both α- and β-TCP exhibit bands at similar wave numbers [19, 20]. Due to the pronounced shape of the FTIR-bands, high crystallinity of the starting product is assumed.

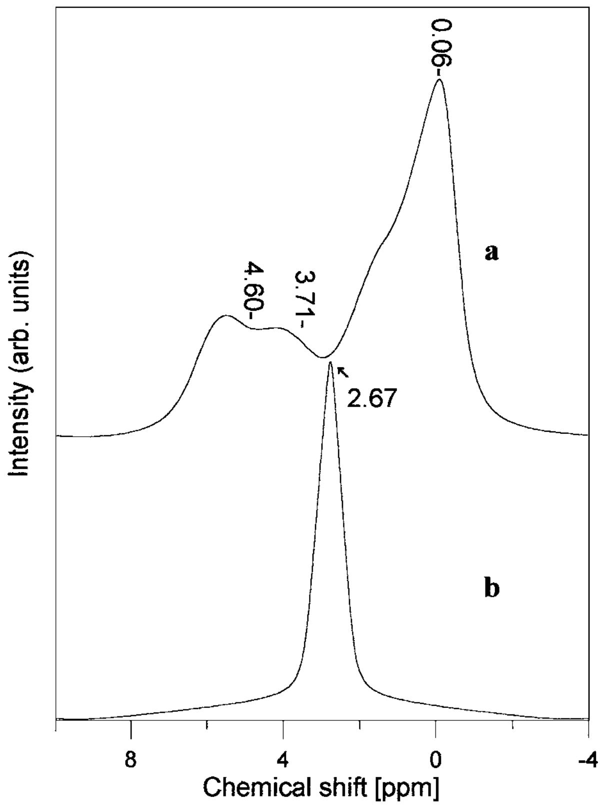

Figure 2 ^{31}P-MAS-NMR spectra of TCP (a) as received and (b) treated at 1200°C/7 h containing 2.7 wt% nitrogen.

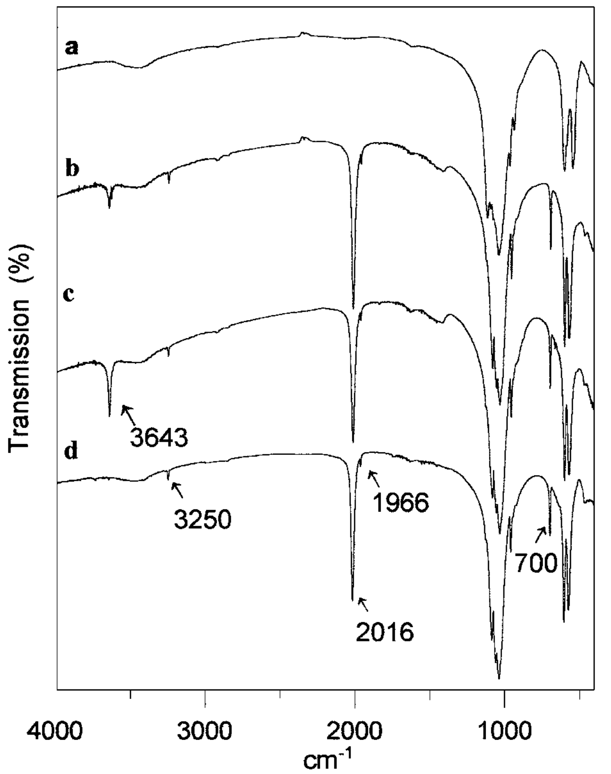

Figure 3 FTIR spectra of TCP (a) as received, (b) treated at 1100°C/7 h, 1.6 wt% nitrogen, (c) treated at 1100°C/11 h, 2.1 wt% nitrogen and (d) treated at 1200°C/4 h, 2.7 wt% nitrogen.

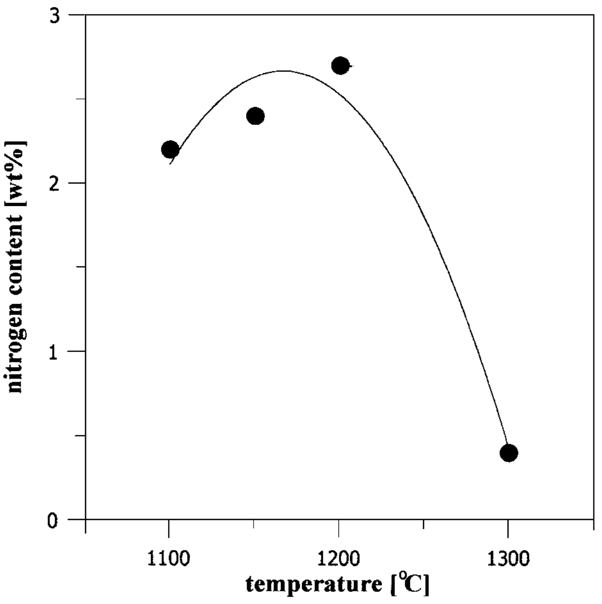

Figure 4 Nitrogen content of the samples after ammonia treatment for 7 h as a function of temperature.

3.2. Nitridation kinetics

The kinetics of the nitrogen uptake of the samples were studied by measuring the nitrogen content as a function of temperature and time of thermal treatment. Nitrogen incorporation was only detected within the studied temperature and time ranges when graphite crucibles were used or graphite powder was placed side by side to the alumina crucibles. Using alumina crucibles in absence of graphite resulted in no or insignificant amounts of nitrogen.

Fig. 4 shows the nitrogen content of TCP after treatments in dry ammonia atmosphere for 7 hours as a function of the treatment temperature. The nitrogen content incorporated into TCP is about 1.5 wt% at treatment temperatures of 1100°C, and increases sharply to values of up to 2.7 wt% at 1200°C. Heat treatments at temperatures above 1200°C resulted in lower amounts of nitrogen. At 1300°C about 0.4 wt% of nitrogen was detected.

The kinetics as a function of treatment time was studied at a constant temperature of 1200°C, corresponding to the highest nitrogen values incorporated for a thermal treatment time of 7 hours, and is shown in Fig. 5. After

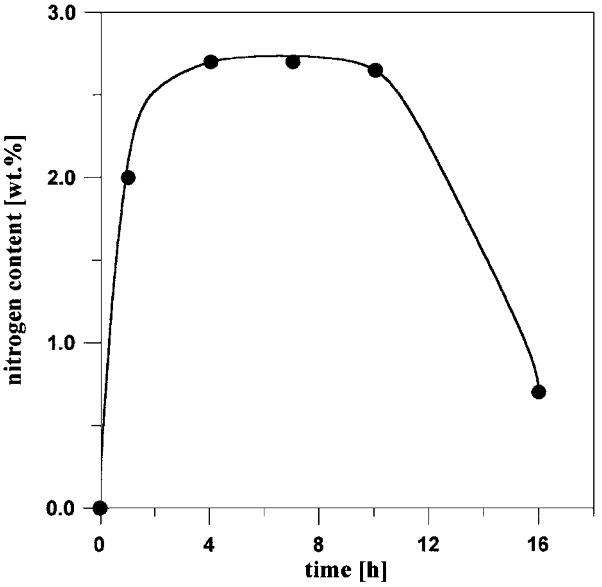

Figure 5 Nitrogen content of the samples after ammonia treatment at 1200°C as a function of time.

one hour of treatment in dry ammonia, a nitrogen content of about 2 wt% was analyzed. Longer treatments resulted in a slight increase of the amount of nitrogen. After 4 h of ammonia treatments a broad maximum of about 2.7 wt% of nitrogen is reached continuing to treatments for up to 10 h. Treatments at 1200°C for times exceeding 10 h resulted in a sharp drop of the nitrogen content. At the same time, red phosphorous depositing on the furnace chamber was observed.

3.3. XRD analysis

Fig. 1 shows the XRD patterns of samples before and after ammonia treatment in the 2Θ-range of 10° to 70°. Untreated samples show the XRD pattern characteristic for β-TCP (JCPDS-file: 9-169). After ammonia treatments phase transformations were observed. Apatite appears as the dominant crystalline phase in samples treated at temperatures between 1100 and 1200°C. Best matches with the JCPDS-files were obtained for hydroxyapatite (JCPDS-file: 9-432). The XRD patterns of the samples treated at 1100 and 1200°C containing 2.9 and 2.65 wt% respectively do not differ significantly by the introduction of nitrogen. Thus, the prevailing phase is apatite. A small peak at $2\Theta = 38^\circ$ indicates the formation of CaO when treated for a longer period (20 h) at 1100°C.

Treatments of samples at temperatures at 1300°C caused the decomposition of hydroxyapatite. XRD patterns of samples treated for 7 h at 1300°C in dry ammonia, containing about 0.4 wt% of nitrogen, show that calcium hydroxide and graphite are the only present crystalline phases. At this temperature and above, the surface of the graphite crucibles and partly the samples were found to be covered by a fine carbon powder.

3.4. ^{31}P-MASS-NMR studies

Fig. 2a shows the ^{31}P-MASS-NMR spectrum of untreated TCP, compared to a spectrum of a sample treated at 1200°C for 7 h containing 2.7 wt% of nitrogen (Fig. 2b). An evident shift in the NMR-signals is observed indicating a phase transformation. After ammonia treatment and nitrogen incorporation a single signal at 2.67 ppm was detected which is characteristic for the occurrence of isolated $[PO_4]^{3-}$ tetrahedra of apatites [9, 21].

3.5. FTIR spectra

Fig. 3 shows the infrared spectra of the samples before and after various thermal treatments in ammonia atmosphere. Ammonia thermal treatments and nitrogen uptake of the samples result in mayor changes of the infrared spectra. Four sharp bands at 3250, 2016, 1966 and 700 cm^{-1} appear which cannot be the attributed to any calcium phosphate or calcium oxide compounds. As shown in an earlier paper [9] these bands originate from cyanamide groups. The observed new bands are attributed to CN_2^{2-}- and HCN_2^{-}-groups of cyanamidapatite, $Ca_{10}(PO_4)_6CN_2$ and calcium deficient cyanamidapatite $Ca_{10}\ (PO_4)_5(HPO_4)HCN_2$, respectively. Further, in the samples treated at 1100°C for 7 and 11 h an additional band at about 3643 cm^{-1} is observed. According to the literature this band is attributed to the occurrence of $Ca(OH)_2$ [22].

The IR-bands of the phosphate groups exhibit only minor changes after ammonia treatments. However, the characteristic band of β-TCP at 1121 cm^{-1}, which distinguishes tricalcium phosphates from apatite, is missing. Comparing the other IR-bands attributed to PO_4-groups, the formation of apatite is indicated, however, not evident by the FTIR analysis solely. IR-bands in the area of 3570 and 630 cm^{-1} characteristic for the OH-groups of hydroxyapatite [19] have not been observed in any of the ammonia treated samples. Further, a band appearing at 946 cm^{-1} may indicate the presence of α- or β-TCP [16, 23].

4. Discussion

All applied methods, e.g. XRD, ^{31}P-NMR and FTIR, showed that treatments of TCP in dry ammonia at temperatures between 1100 and 1200°C result in a phase transformation into apatite. The phase transformation is accompanied by an incorporation of nitrogen. In accordance with ammonia treatments of hydroxyapatite, nitrogen incorporation only occurred if graphite was present during treatments [9]. The infrared analysis revealed that cyanamide ions have been incorporated into the apatite structure. Since no evidence of the formation of hydroxyapatite or any other type of apatite is given, a direct transformation of TCP into cyanamidapatite is suggested. Hence, the following reaction sequence for the formation of cyanamidapatite from tricalcium phosphate is proposed:

$$2NH_3 + C \rightarrow H_2CN_2 + 2H_2 \qquad (1)$$

$$3Ca_3(PO_4)_2 + H_2CN_2 \rightarrow Ca_9(PO_4)_5(HPO_4)(HCN_2) \qquad (4)$$

In a first step, ammonia reacts with graphite to form cyanamide as suggested earlier [9]. These molecules react with tricalcium phosphate to transform into cyanamide apatite; comparable to the hydroxyapatite formation of tricalcium phosphate in water or vapor as described above [14–16]. In the case of hydroxyapatite a calcium deficient apatite is formed from TCP. In accordance, the formation of a calcium deficient cyanamidapatite by ammonia treatments of TCP is suggested.

As reported earlier [9], during long term treatments at 1200°C and particularly during treatments at 1300°C and above, strong reduction of the PO_4 groups occurs. These reduction first increases the Ca/P ratio towards a more stoichiometric calcium phosphate apatite. To what extent the stoichiometric ratio of 1.6 is achieved, is subject to further studies. As the reduction continues cyanamidapatite significantly loses phosphate groups and decomposes to calcium oxide and phosphorous. The apatite lattice collapses and the cyanamide ions lose their site in the crystal. As a consequence the nitrogen content decreases as shown in Figs 4 and 5.

5. Conclusions

Through dry ammonia treatments at temperatures between 1100°C and 1200°C tricalcium phosphate transforms into cyanamidapatite. It is suggested that cyanamide is formed in presence of graphite and reacts at temperatures above 1100°C with tricalcium phosphate. Cyanamidapatite is formed. Due to a strong reduction of phosphate groups at temperatures around 1200°C the apatite lattice breaks down completely. The sites of the cyanamide ions get lost and the nitrogen content decreases. An analogy to the apatite formation from tricalcium phosphates exposed to vapor can be drawn and, thus, further calcium phosphate compounds, e.g. tetracalcium phosphate and dicalcium phosphate, are expected to transform into cyanamidapatite when exposed to dry ammonia at high temperature in the presence of carbon.

Acknowledgments

The authors wish to thank Dr. Isabel Sobrado and Dr. Jesús Sanz for the NMR measurements. This work has been partially financed through the projects CICYT (MAT99-0872) and CAM (07N/0041/1999).

References

1. J. C. ELLIOT, *Clin. Orth. Rel. Res.* **93** (1973) 313.
2. S. BARAVELL, A. BIGI, A. RIPAMONTI, N. ROVERI and E. FORESTI, *J. Inorg. Biochem.* **20** (1984) 1.
3. R. A. YOUNG, *Clin. Orth. Rel. Res.* **113** (1975) 249.
4. E. C. MORENO, M. KRESAK and R. T. ZAHNRADNIK, *J. Dent. Res.* **247** (1974) 64.
5. K. SUNDARASN, R. A. YOUNG and A. J. C. WILSON, *Acta Cryst.* **B33** (1977) 3136.
6. K. SUNDARASAN and R. A. YOUNG, *ibid.* **B34** (1978) 1401.
7. R. Z. LEGEROS, O. R. TRAUTZ, J. P. LEGEROS and E. KLEIN, *Bull. Soc. Chim. France* (1968) 1712.
8. J. C. TROMBE and G. MONTEL, *J. Inorg. Nucl. Chem.* **40** (1978) 15.
9. S. HABELITZ, L. PASCUAL and A. DURAN, *J. Eur. Cer. Soc.* **19** (1999) 2685.
10. J. ZHOU, X. ZHANG, J. CHEN, S. ZENG and K. DE GROOT, *J. Mater. Sci. Mater. Med.* **4** (1993) 83.
11. P. E. WANG and T. K. CHAKI, *ibid.* **4** (1993) 150.
12. P. W. BROWN, **75** (1992) 17.
13. R. I. MARTIN and P. W. BROWN, *J. Biomed. Mater. Res.* **35** (1997) 299.
14. H. MONMA, *Yogyo-Kyokai-Shi* **86** (1978) 73.
15. K. S. TENHUISEN and P. W. BROWN, *Biomaterials* **19** (1998) 2209.
16. L. YUBAO, Z. XINGDONG and K. DE GROOT, *ibid.* **18** (1997) 737.
17. L. PASCUAL and A. DURAN, *Mater. Res. Bull.* **31** (1996) 77.
18. J. VOGEL, C. RUSSEL, P. HARTMANN, F. VIZETHUM and N. BERGNER, *CFI—Ceramic Forum International—Berichte der Deutschen Keramischen Gesellschaft* **76** (1999) 28.
19. B. O. FOWLER, *Inorg. Chem.* **13** (1974) 194.
20. B. O. FOWLER, E. C. MORENO and W. E. BOWN, *Arch. Oral. Biol.* **11** (1966) 477.
21. M. BRAUN and P. HARTMANN, *J. Mater. Sci. Mater. Med.* **6** (1995) 150.
22. S. R. RODIN and P. DUCHEYNE, *ibid.* **3** (1992) 33.
23. A. JILLAVENKATESA and R. A. CONDRATE, *Spectros. Let.* **31** (1998) 1619.

Received 11 August
and accepted 18 December 2000