Characterization of the transformation from calcium-deficient apatite to β-tricalcium phosphate

I. R. GIBSON, I. REHMAN, S. M. BEST, W. BONFIELD*
IRC in Biomedical Materials, Queen Mary and Westfield College, Mile End Road, London, E1 4NS, UK
*E-mail: I.R.Gibson@qmw.ac.uk*

The structural changes that occur during the transformation of a Ca-deficient apatite, prepared by a wet chemical method, to β-TCP were investigated. X-ray diffraction (XRD) analysis of as-prepared samples and samples calcined at temperatures between 500 and 1100 °C showed that the transformation occurs over the temperature range 710–740 °C, under non-equilibrium conditions. The change in crystallite size with increasing calcination/ sintering temperature was studied by XRD using the Scherrer formula. Fourier transform infra-red (FTIR) analysis indicated considerable structural change in samples above and below this temperature range. Changes were observed in the hydroxyl, carbonate and phosphate bands as the calcination temperature was increased from 500 to 1100 °C. Even once a single β-TCP phase is obtained at 740 °C there remains a considerable amount of structural change at temperatures between 740 and 1100 °C. This effect was illustrated by an unusual change in the lattice parameters of the β-TCP structure and significant changes in the phosphate bands of the FTIR spectra as the calcination temperature was increased. The results obtained in this study show that the combined experimental techniques of XRD and FTIR are excellent complimentary methods for characterizing structural changes that occur during phase transformations.
© 2000 Kluwer Academic Publishers

1. Introduction

The excellent biocompatability of calcium phosphate ceramics has led to their extensive use as biomedical materials [1]. The most commonly used calcium phosphates are hydroxyapatite (HA) and tricalcium phosphate (TCP) ceramics due to their close chemical similarity to the inorganic component of bone and tooth, their relatively low solubility and high bioactivity. TCP has been shown to be resorbed *in vivo* [2] with new bone growth replacing the resorbed implanted TCP. This property is a significant advantage of TCP compared to other biomedical materials which are not resorbed and replaced by natural bone.

TCP ceramics can be prepared by a number of different routes [3–5]. The most common method is a ''wet-chemical'' synthesis which results in the formation of a Ca-deficient apatite (or non-stoichiometric apatite). Upon heating (calcining) to 700–800 °C the Ca-deficient apatite will transform to the low temperature polymorph of tricalcium phosphate (β-TCP), with the loss of water as described by Equation 1.

$$Ca_9(HPO_4)(PO_4)_5(OH) \rightarrow 3Ca_3(PO_4)_2 + H_2O \qquad (1)$$
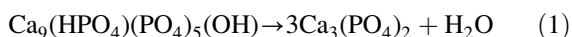
(Further heating will result in the sintering of β-TCP and at approximately 1120 °C the transformation from β-TCP to the high temperature polymorph, α-TCP [6].)

Several details of this transformation remain unclear; most significantly, the precise transformation temperature and the effect of temperature on crystallite morphology and structural change during the transformation.

A number of recent studies have attempted to clarify the transformation of a Ca-deficient apatite to β-TCP [7–10]. Changes in the size and morphology of the crystallites were observed with increasing calcination temperature by Yubao *et al.* [7]. The temperature range at which the transformation occurred was established as 650–750 °C and the disappearance of the HPO_4^{2-} bands in the FTIR spectra at this temperature was observed. However, the Ca-deficient apatite used in this study had a Ca/P ratio of 1.52, compared to the expected ratio for TCP of 1.50. On heating, this Ca-deficient apatite therefore transformed to a biphasic mixture of β-TCP and HA. This result makes an analysis of the structural changes that occur during the transformation very difficult. An example is the presence of an OH^- band in the FTIR spectrum for all calcination temperatures, even at 1100 °C, as single phase β-TCP should not contain OH^- groups [1, 3].

Prieto Valdés *et al.* [8] prepared a Ca-deficient apatite with Ca/P ratio ∼ 1.5. Samples were calcined/sintered at temperatures between 700 and 1450 °C at 50 °C intervals. They reported that the transformation to β-TCP occurred over the temperature range 750–1200 °C.

This very wide temperature range and the reported decomposition of TCP to $Ca_2P_2O_7 + Ca_4P_2O_9$ at 1450 °C suggests that their Ca-deficient apatite had a Ca/P ratio greater than 1.50. The samples produced over the calcination temperature range were also associated with an increase in crystallite/particle size, largely due to sintering.

The studies of Mortier et al. [9, 10] involved the use of temperature programmed reaction (TPR), or effluent gas thermal analysis (EGTA), to study the dehydration of Ca-deficient apatites with Ca/P ratios close to 1.50 as a function of temperature. The authors observed two thermal transitions, or TPR bands. The first, at 300–680 °C, corresponded to the evolution of water due to the reaction of two hydrogenphosphate groups, which produced one pyrophosphate group and water. The second transition, at 700–900 °C, resulted from the reaction of a pyrophosphate group and two hydroxyl groups to produce two phosphate groups and water. Although the studies of Mortier et al. illustrated the chemical reactions that occur during the heating of Ca-deficient apatite, the precise temperature of the transformation to β-TCP and the associated structural changes were not identified.

In the present study, a high purity Ca-deficient apatite was prepared, with a Ca/P ratio of 1.50, by a simple neutral acid-base reaction. This approach enabled the transformation to β-TCP to be studied in detail. The structural changes that occur during this transformation were studied using XRD, in particular the change in lattice parameters, and FTIR, showing the changes in the OH^-, HPO_4^{2-} and PO_4^{3-} functional groups.

2. Materials and methods

Ca-deficient apatite was prepared by the neutral reaction of a $Ca(OH)_2$ suspension and a H_3PO_4 solution, according to the method described by Akao et al. [3]. After addition of the H_3PO_4 solution, the reaction mixture was stirred vigorously for 2 h, then allowed to age overnight. The mixture was then filtered and the resulting filtercake was dried overnight at 80 °C. The dried filtercake was crushed to a powder and sieved to $< 75 \mu m$.

The Ca/P ratio of the Ca-deficient apatite was determined by X-ray fluorescence (XRF) using a Philips PW1606 spectrometer (Ceram Research, UK) and was calculated as 1(± 0.01).

Small samples, approximately 2 g, of the Ca-deficient apatite were calcined at temperatures between 500 and 1100 °C for 2 h, using a heating rate of 2.5°/min. After calcining for 2 h, the sample was removed from the furnace and allowed to cool in air.

XRD data were collected using a Siemens D5000 diffractometer with CuK_α radiation ($\lambda = 1.541$Å) Data were collected over the 2θ range 5–110°, using a step size of 0.02° and a step time of 12 s. The average crystallite size of the calcined samples was calculated using the Scherrer formula. The peak width of the (002) reflection of Ca-deficient apatite samples and the (2, 0, 10) reflection of the β-TCP samples were used in the calculations.

Lattice parameters were determined using the Rietveld

refinement software GSAS [11], using the structural data of HA [12] for the Ca-deficient apatite samples and the structural data of Dickens et al. for β-TCP [13].

FTIR spectra were obtained using a Nicolet 800 spectrometer in conjunction with a MTech PAS cell. Spectra were obtained at $4 \, cm^{-1}$ resolution averaging 128 scans. The sample chamber of the PAS cell was purged with helium gas and dried by employing magnesium perchlorate as drying agent.

3. Results
3.1. XRD analysis

Crystallite sizes determined from XRD data of samples calcined between 500 and 730 °C are listed in Table I, and a decrease in the crystallite size was observed at 600–700 °C. As expected, heating at increasing temperatures above 720 °C resulted in the sintering and subsequent growth in crystallite size, which coincides with the transformation from poorly crystalline Ca-deficient apatite to crystalline β-TCP.

The change from Ca-deficient apatite to β-TCP upon heating is most clearly observed using XRD. Ca-deficient apatite has an apatite structure, with peak positions matching closely the diffraction peaks of stoichiometric hydroxyapatite (JCPDS No. 9–432) [14]. This phase is easily distinguishable from β-TCP (JCPDS No. 9–169) [15].

Initial analysis of samples calcined at 100 °C intervals between 500 and 1100 °C indicated that the transformation from Ca-deficient apatite to β-TCP occurred within the temperature region 700–800 °C, Fig. 1. Closer inspection, using diffraction data collected from samples calcined at 10 °C intervals between 700 and 800 °C revealed that the transformation did not occur at a single temperature under non-equilibrium conditions, but over a temperature range of 710–740 °C, Fig. 2. Within this temperature range, a two-phase mixture of Ca-deficient apatite and β-TCP was obtained. Under non-equilibrium conditions, phase transformations often occur over a small temperature range rather than at a single temperature [16]; this result is indicative of considerable structural change occurring during the transformation.

The transformation temperature from Ca-deficient apatite to β-TCP was also determined by differential thermal analysis (DTA), using a Seteram Labsys DTA/DSC 1600 at a heating rate of 2.5 °C/min. An endothermic peak which corresponded to the transformation from Ca-deficient apatite to β-TCP was observed at 790 °C, Fig. 3; the endothermic peak at 1160 °C

T A B L E I The effect of calcination temperature on the crystallite size of Ca-deficient apatite, calculated from XRD data using the Scherrer formula

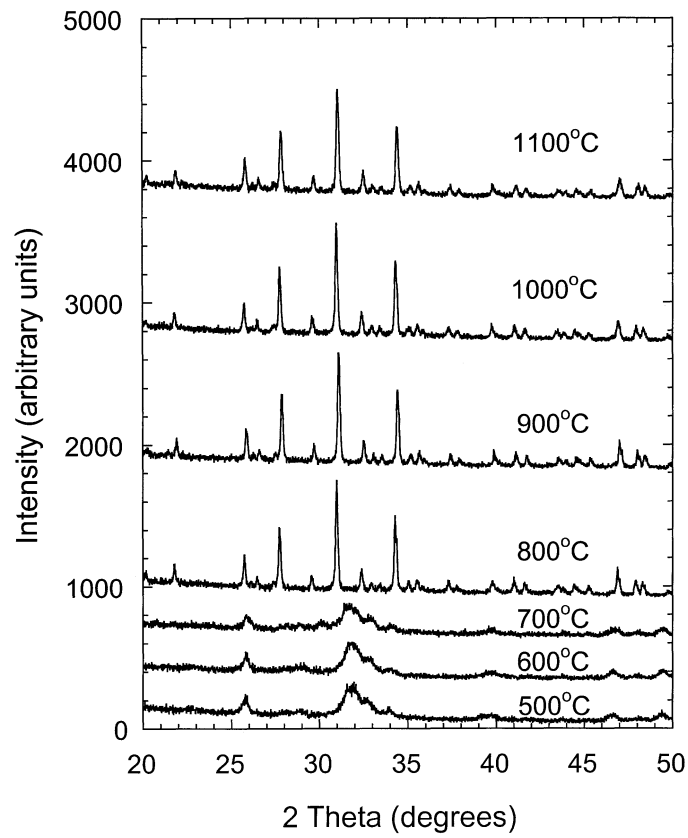| Calcination temp. (°C)	Crystallite size (nm)
500	38
600	36
700	23
710	22
720	28
730	145

Figure 1 XRD patterns showing the effect of calcination temperature on the crystalline phase composition of Ca-deficient apatite; the transformation of a Ca-deficent apatite to β-tricalcium phosphate (β-TCP) occurs at a temperature between 700 and 800 °C.
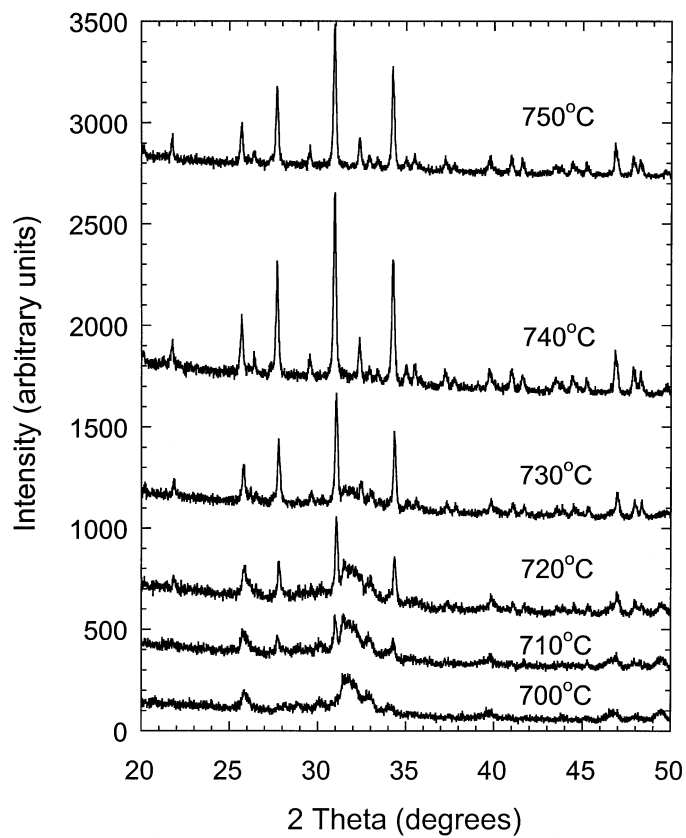

Figure 2 XRD patterns showing the transformation from Ca-deficent apatite to β-TCP over a narrow temperature range of between 700 and 750 °C; the transformation occurs over the temperature range 710–740 °C.

corresponds to the transformation from β-TCP to α-TCP, the high temperature polymorph of tricalcium phosphate.

The lattice parameters, a and c, of the β-TCP phase obtained upon calcining the Ca-deficient apatite at temperatures between 740 and 1100 °C are plotted in Fig. 4(a and b), respectively. The a and c parameters both showed a large decrease for increased calcination temperatures of 740 to 800 °C. As the calcination temperature was then increased from 800 to 1100 °C, the lattice parameters showed a steady increase.

3.2. FTIR spectroscopic analysis

To study the changes in PO_4^{3-} groups, and indeed other functional groups such as OH^-, HPO_4^{2-} and CO_3^{2-} in the Ca-deficient apatite and β-TCP samples calcined at different temperatures, the samples were studied using Fourier Transform Infra-red Spectroscopy (FTIR). The FTIR spectrum obtained from the as-prepared Ca-deficient apatite is presented in Fig. 5. The phosphate υ_4 band is present in the region of 660 and 520 cm^{-1} and is typically a well-defined and sharp band. Spectra indicated that Ca-deficient apatite powders have three sites observed at 628, 601 and 563 cm^{-1}, Fig. 5. This splitting of the ν_4 vibrational band indicates the low site symmetry of molecules, as three observed bands confirm the presence of more than one distinctive site for phosphate groups [17].

To study the changes in PO_4^{3-} groups, and indeed other functional groups such as OH^-, HPO_4^{2-} and CO_3^{2-} in the Ca-deficient apatite and β-TCP samples calcined at different temperatures, the samples were studied using FTIR, Fig. 6. The changes in the phosphate, carbonate, hydroxyl and hydrogenphosphate bands with increased calcination temperature are summarized in Table II. The most noticeable change in the FTIR spectra with increasing calcination temperature was the disappearance of the hydroxyl band at 3569 cm^{-1} between 700 and 750 °C, which corresponded to the transformation observed by XRD, Figs 1 and 2. Additionally, changes were observed in the phosphate ν_3 and ν_1 bands where three peaks at 1092, 1030 and 960 cm^{-1} were observed

at low temperatures (Ca-deficient apatite) but only 1–2 broad peaks at higher temperatures (TCP). Similarly the ν_4 band changed from three peaks at 629, 602 and 563 cm^{-1} between 500 and 700 °C to two peaks above 700 °C. The carbonate ν_3 band was also observed at 1648, 1454 and 1413 cm^{-1} between 500 and 700 °C, but disappeared at higher temperatures and the HPO$_4$ band at 2200–2000 cm^{-1} was observed at 1000 and 1100 °C.

4. Discussion
4.1. XRD analysis

Yubao *et al.* [7, 18] described an unusual change in crystallite size as Ca-deficient apatite was heated to temperatures between 650 and 750 °C. Upon heating to 650 °C, the crystallite size decreased as the Ca-deficient apatite transformed to HA or β-TCP/HA, depending on the Ca/P ratio of the precipitated apatite. This decrease was explained by Yubao *et al.* as a loss of water, as described earlier in Equation 1.

This study also showed a decrease in crystallite size over a similar temperature region, 600–700 °C, followed by a large increase as the sintering process began. The temperature region over which the transformation from Ca-deficient apatite to TCP occurs, Fig. 2, is lower than some values reported in the literature [3, 7, 8, 19] but within the range of 650–750 °C reported by Ishikawa *et al.* [20]. In the present study, samples were calcined for 2 h, which corresponds to longer heat treatments at each temperature than would be observed for some other experiments, for example DTA. Indeed, when the Ca-deficient apatite prepared in this study was heated at 2.5 °C/min in a DTA, an endothermic peak at 790 °C was observed, corresponding to the Ca-deficient apatite to β-TCP transformation, Fig. 3. The higher temperatures reported in other studies may, therefore, be due to shorter heating or calcining times. Additionally, the formation of a two-phase β-TCP/HA mixture upon calcining the Ca-deficient apatite, as observed in some other studies, may cause difficulty in determining the transformation temperature accurately.

An important point to note is that the Ca-deficient apatite prepared in this study produced only a single TCP
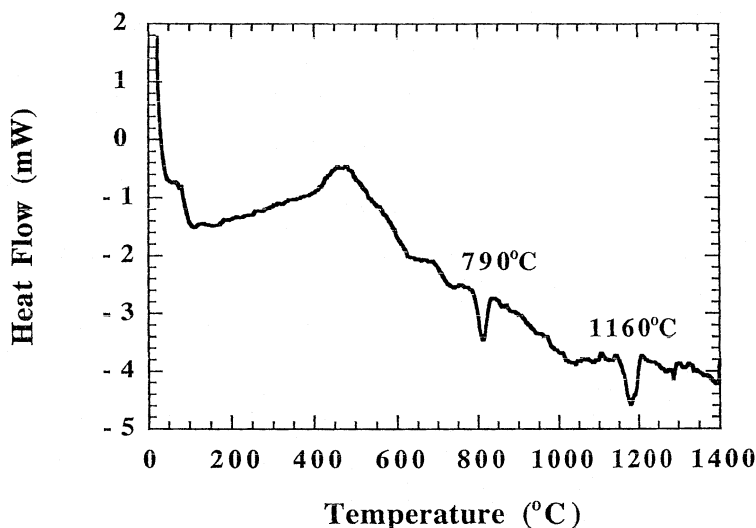

Figure 3 DTA data showing endothermic peaks at 790 °C corresponding to the transformation from Ca-deficient apatite to β-TCP and at 1160 °C corresponding to the β- to α-TCP transformation.
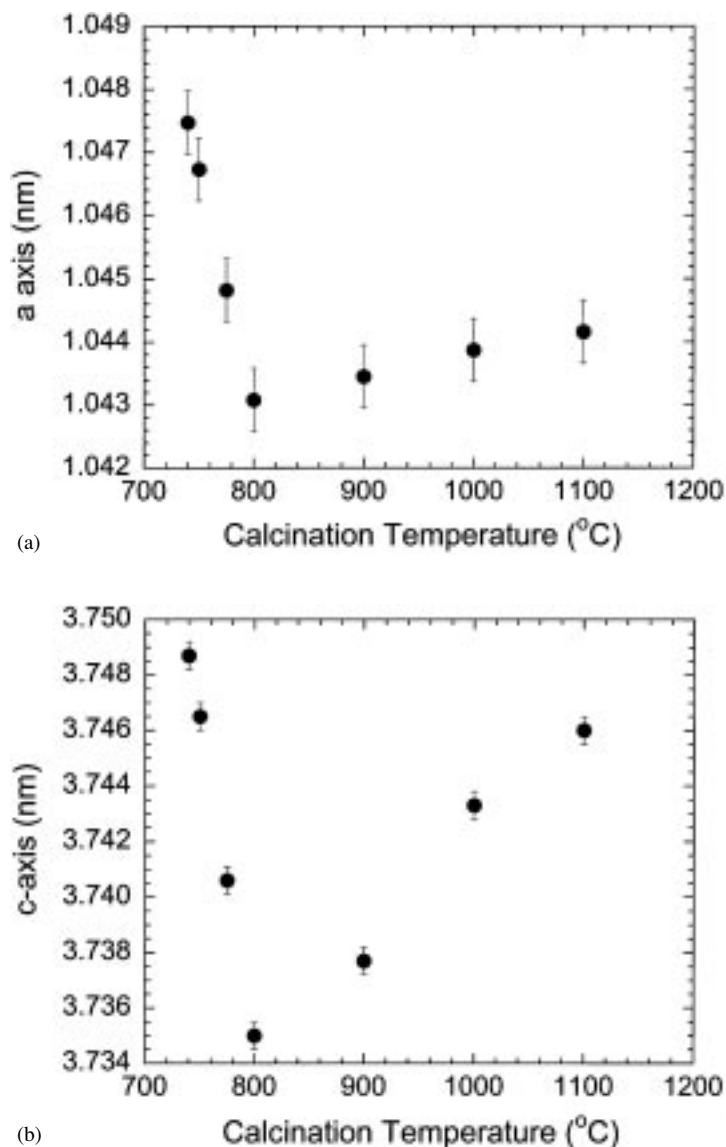
(a)

(b)

Figure 4 The effect of calcination temperature on the lattice parameters of β-TCP, showing a decrease in the (a) a–axis and (b) c–axis up to 800 °C, followed by a steady increase from 800 to 1100 °C.

phase (β- and then, at ~1120 °C, α-TCP) upon calcining at temperatures between 740 and 1450 °C, as expected from the phase diagram [6]. By contrast, the samples prepared in the studies of Yubao *et al.* [7] and Prieto

Figure 5 FTIR spectrum of the as-prepared Ca-deficient apatite, showing a hydroxyl peak at ~3569 cm^{-1}, carbonate peaks at ~1650–1400 cm^{-1}, and phosphate peaks at ~1100–950 cm^{-1} and 630–560 cm^{-1}.

Valdes *et al.* [8] produced TCP + HA above 750 °C and $Ca_2P_2O_7 + Ca_4P_2O_9$ above 1450 °C, respectively. The stoichiometric ratio of Ca/P = 1.50, which results in the formation of a single phase TCP, is therefore essential if accurate phase analysis is to be made.
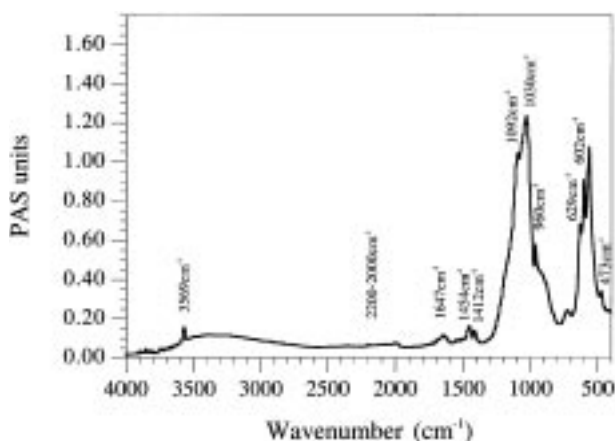
Equation 1 and the diffraction data presented in Figs 1 and 2 would suggest that after the loss of water and the transformation to β-TCP at 710–740 °C, no further changes would occur. Although no change in the symmetry of the β-TCP formed between 740 and 1100 °C was observed, a very unusual change in the lattice parameters was observed as the calcination temperature was increased, Fig. 4. This change indicated that the structural changes that occur during the transformation from Ca-deficient apatite to β-TCP are not complete at 740 °C and further changes occur between 740 and 1100 °C. The structural changes probably involve changes/distortions in the PO_4 tetra-hedra. It is reported that there are three different types of crystallographically non-equivalent PO_4 groups in the β-TCP structure [21]. These changes were small enough not to affect the symmetry but significant enough to result in changes in the lattice parameters.
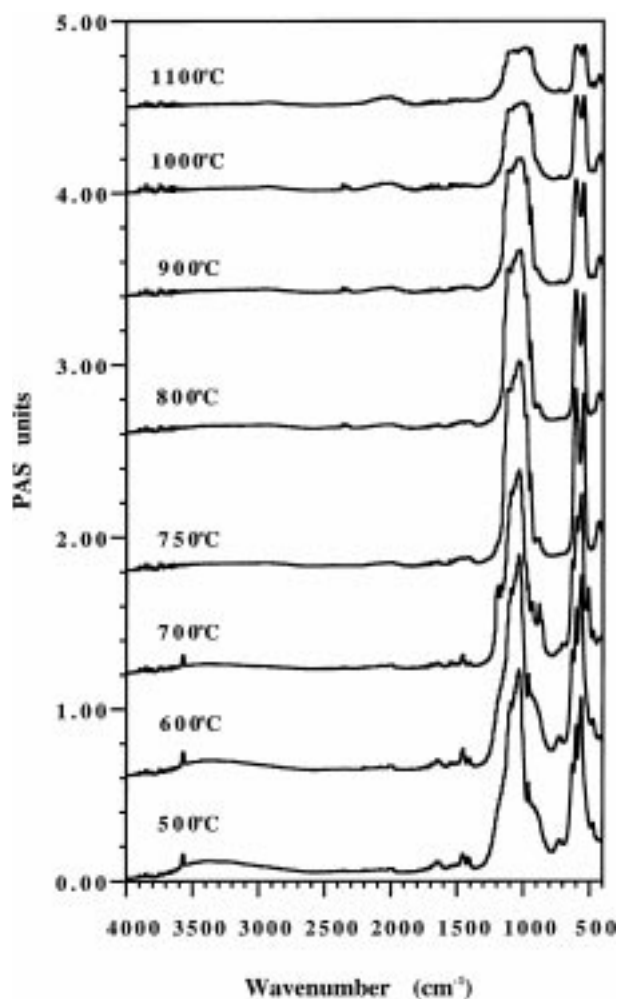
537

Figure 6 The effect of calcination temperature on the FTIR spectra of Ca-deficient apatite/β-tricalcium phosphate, between 500 and 1100 °C.

4.2. FTIR spectroscopic analysis

Before we consider the effect of calcination temperature on the change in structure of Ca-deficient apatite, it is important to understand the number of spectral modes present in apatite powders. The hydroxyl stretch is observed at 3569 cm^{-1} in the spectra of Ca-deficient apatite powders. Theoretically, carbonate ions have four vibrational modes $(\upsilon_1-\upsilon_4)$, three of which are observed in the infra-red spectrum and two of which are observed in the Raman spectrum [22]. The carbonate υ_4 bands have very low intensity and are seldom seen in the infra-red spectrum [23]. Usually, υ_1 and υ_4 have strong vibrational bands in the Raman spectra [22], and υ_2 and

υ_3 vibrational modes are observed in the infra-red spectra. Carbonate ions occupy two different sites; peaks in the region of 1650 to 1300 cm^{-1} are due to υ_3 vibrational mode carbonate ion and the peak at 873 cm^{-1} is due to υ_2 vibrational mode [24]. The υ_3 vibrational mode is split in to three peaks centered at 1638, 1453 and 1412 cm^{-1} and the distribution of the carbonate υ_3 sites depends on the maturation and formation of apatite crystals. Occupancy of the υ_2 sites is considered to occur competitively between the OH$^-$ and carbonate groups at the interface of growing crystal, whereas occupancy of the υ_3 sites depends on competition between the phosphate and carbonate ions [24, 25].

Theoretically, there are four vibrational modes present for phosphate ions and they are υ_1, υ_2, υ_3 and υ_4. All these modes are Raman and infra-red active. In the Ca-deficient apatite infra-red spectra, the υ_3 band has two different sites present at 1088 and 1029 cm^{-1}, Fig. 5. This intense υ_3 band is thought to be responsible for totally obscuring the υ_1 carbonate bands [22]. The phosphate υ_1 and υ_2 bands are present at 960 cm^{-1} and 473 cm^{-1}, respectively; the band at 473 cm^{-1} is a very weak band and not as strong as the υ_3 and υ_4 bands.

Clearly, some of the changes in the FTIR spectra, Fig. 6 and Table II, correspond to the transformation observed by XRD between 710 and 740 °C, Figs 1 and 2 (such as the hydroxyl stretch, phosphate υ_3 and υ_4 bands, and the carbonate υ_3 band) and others to the change in lattice parameters of TCP between 740 and 1100 °C, Fig. 4 (such as the phosphate υ_1 bands and the HPO$_4$ band).

The combined techniques of XRD and FTIR provide complementary data, Figs 1 and 5, and indicate clearly the structural changes, such as changes in lattice parameters and loss of OH groups, observed during calcination of Ca-deficient apatite.

5. Conclusion

This study has highlighted the importance of preparing samples with the correct composition in order to characterize fully the structural changes that occur during the transformation from Ca-deficient apatite to β-TCP. By preparing a Ca-deficient apatite with a Ca/P ratio of 1.50 structural changes were observed upon calcining the materials at temperatures between 500 and 1100 °C. Under non-equilibrium conditions, the phase transformation from Ca-deficient apatite to β-TCP occurs over the temperature range 710–740 °C. This transformation was illustrated by both XRD and FTIR analysis and

TABLE II The presence or absence (denoted by √ or X, respectively) of the different phosphate, carbonate, hydroxyl and hydrogenphosphate groups in Ca-deficient apatite/TCP samples calcined between 500 and 1100 °C, as determined by FTIR spectroscopy

Temperature	OH stretch 3569 cm^{-1}	PO$_4\upsilon_1$ 960 cm^{-1}	PO$_4\upsilon_3$ 1092, 1030 cm^{-1}	PO$_4\upsilon_4$ 628, 601 and 563 cm^{-1}	CO$_3\upsilon_3$ 1648, 1454, 1413 cm^{-1}	HPO$_4$ band 2200–2000 cm^{-1}
As-prepared	√	√	√ √	√ √ √	√ √ √	X
500 °C	√	√	√ √	√ √ √	√ √ √	X
600 °C	√	√	√ √	√ √ √	√ √ √	X
700 °C	√	√	√ √	√ √ √	√ √ √	X
750 °C	X	√	√ √	√ √	XXX	X
800 °C	X	√	√ √	√ √	XXX	X
900 °C	X	√	√ √	√ √	XXX	X
1000 °C	X	√	√ √	√ √	XXX	√
1100 °C	X	X	√ √	√ √	XXX	√

demonstrates that these two experimental techniques allow complementary characterization of phase transformations of calcium phosphates.

References

1. F. C. M. DRIESSENS, in ''Bioceramics of calcium phosphate'', edited by K. de Groot (CRC Press, Boca Raton, 1983) p. 1–32.
2. A. M. GATTI, D. ZAFFE and G. P. POLI, *Biomaterials* **11** (1990) 513.
3. M. AKAO, H. AOKI, K. KATO and A. SATO, *J. Mater. Sci.* **17** (1982) 343.
4. M. JARCHO, R. L. SALSBURY, M. B. THOMAS and R. H. DOREMUS, *ibid.* **14** (1979) 142.
5. R. FAMERY, N. RICHARD and P. BOCH, *Ceram. Inter.* **20** (1994) 327.
6. E. R. KREIDLER and F. A. HUMMEL, *Inorg. Chem.* **6** (1967) 884.
7. L. YUBAO, C. P. A. T. KLEIN, S. VAN DE MEER and K. DE GROOT, *J. Mater. Sci.: Mater. Med.* **5** (1994) 263.
8. J. J. PRIETO VALDÉS, J. ORTIZ LÓPEZ, G. RUEDA MORALES, G. PACHECO MALAGON and V. PRIETO GORTCHEVA, *ibid.* **8** (1997) 297.
9. A. MORTIER, J. LEMAITRE and P. G. ROUXHET, *Thermochemica Acta* **143** (1989) 265.
10. A. MORTIER, J. LEMAITRE, L. RODRIQUE and P. G. ROUXHET, *J. Solid State Chem.* **78** (1989) 215.
11. A. C. LARSON, R. B. VON DREELE and M. LUJAN JR, GSAS—Generalized Crystal Structure Analysis System, Neutron Scattering Center, Los Alamos National Laboratory, California (1990).
12. M. I. KAY, R. A. YOUNG and A. S. POSNER, *Nature* **204** (1964) 1050.
13. B. DICKENS, L. W. SCHROEDER and W. E. BROWN, *J. Solid State Chem.* **10** (1974) 232.
14. PDF Card no. 9–432, ICDD, Newton Square, Pennsylvania, USA.
15. PDF Card no. 9–169, ICDD, Newton Square, Pennsylvania, USA.
16. I. R. GIBSON, M. AKAO, S. M. BEST and W. BONFIELD in ''Bioceramics 9'', edited by T. Kokubo, T. Nakamura and F. Miyaji (University Press, UK, 1996) p. 173.
17. I. REHMAN and W. BONFIELD, *J. Mater. Sci.: Mater. Med.* **8** (1997) 1.
18. L. YUBAO, PhD Thesis, University of Leiden, Netherlands (1994).
19. R. Z. LEGEROS, J. P. LEGEROS, G. DACULSI and R. KIJKOWSKA, in ''Encyclopedic Handbook of Biomaterials and Bioengineering'', edited by D. L. Wise, D. J. Trantolo, D. E. Altobelli, M. J. Yaszemski, J. D. Gresser and E. R. Schwartz (Marcel Dekker, Inc., 1995) p. 1429.
20. K. ISHIKAWA, P. DUCHEYNE and S. RADIN, *J. Mater. Sci.: Mater. Med.* **4** (1993) 165.
21. P. N. DE AZA, C. SANTOS, A. PAZO, S. DE AZA, R. CUSCO and L. ARTUS, *Chem. Mater.* **9** (1997) 912.
22. D. G. A. NELSON and J. D. B. FEATHERSTONE, *Calc. Tiss. Int.* **34** (1982) 69.
23. H. EL FEKI, C. REY and M. VIGNOLES, *ibid.* **49** (1991) 269.
24. R. Z. LEGEROS, G. KIJKOWSKA, J. P. LEGEROS, T. ABERGAS and H. BLEIWAS, *J. Dent. Res.* **66** (1987) 190.
25. J. C. ELLIOTT, D. W. HOLCOMB and R. A. YOUNG, *Calc. Tiss. Int.* **37** (1985) 372.