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The FTIR Spectroscopy and QXRD Studies of Calcium Phosphate Based Materials Produced from the Powder Precursors with Different Ca/P Ratios

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Abstract: Six precipitates of calcium phosphates with Ca/P molar ratios in the range of 1.502–1.717 have been prepared by the wet method. After shaping and sintering at 1250 °C the phase composition of the obtained materials was examined by QXRD and FTIR spectroscopy methods. © 1997 Elsevier Science Limited and Techna S.r.l.

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1 INTRODUCTION

The determination of a correlation between the precipitation conditions of the powder precursors, as well as those concerning the shaping and sintering process and properties of final products, is one of the basic problems dealing with the production of calcium phosphate based implants. Consequently, these parameters determine the behaviour of implants *in vivo* and indicate the limits of their applicability in medicine, among others in bone substitution.

The inorganic substance of natural bones consists of poorly crystalline, non-stoichiometric apatite containing various ions, i.e. CO_3^{2-}, Na^+, F^- as well as structural defects. The presence of some amount of lattice bound water probably plays an important role in the formation of bone apatite.[1–3] The mineral components of bones, teeth and pathologically calcified hard tissues transform to HAp and βTCP on heating to temperatures exceeding 800 °C. This is probably the reason that the implants containing HAp + βTCP show higher biological reactivity and better bonding with natural bones compared to those of pure HAp.[4]

The presence of tricalcium phosphate as a second crystalline phase in hydroxyapatite bioceramics is connected with the change of resorbability of the implantation material. The possibility of strength reduction, as a result of stresses induced by volume changes accompanying the polymorphic transitions βTCP < = > αTCP, should also be taken into account. The ocurrence of stresses in the calcium phosphate materials may also result from the different linear expansion coefficients of co-existing phases: βTCP, αTCP and HAp. The swelling of TCP phase should also be underlined. In the presence of water or body liquids, TCP takes up some water molecules thus transforming to $Ca_9H_2(PO_4)_6(OH)_2$ with a simultaneous volume increase of about 4.9%.[5]

Up to the present, the following various methods for synthesizing hydroxyapatite have been used:[1]

1. Wet method, using solution reaction (from solution to solid)
2. Dry method, using solid state reaction (from solid to solid)
3. Hydrothermal method, using hydrothermal reaction (from solution to solid)

4. Alkoxide method, using solution and solid state reactions (from solution to solid).

Since the chemistry of hydroxyapatite is conspicuously more complex than fluoroapatite and chloroapatite, when attempts are made to precipitate it in solution, apatite products are formed that can have Ca/P molar ratios from 1.5 to 1.66 and sometimes even outside this range. As a result of that, apart from the stoichiometric hydroxyapatite, the non-stoichiometric apatites, calcium-deficient (with a Ca/P molar ratio from 1.5 to 1.667) and calcium-rich apatites (with a Ca/P molar ratio greater than 1.667) are often obtained.[6]

The calcium-deficient apatite crystals of the formula:

$$Ca_{10-x-y}(HPO_4CO_3)_x(PO_4)_{6-x}(OH)_{2-x-2y}$$

where $0 \leqslant x \leqslant 2$, $y \leqslant 1-x/2$ start to decompose on heating at 650 °C and the traces of βTCP phase appear. As the temperature increases, the βTCP content increases and simultaneously the residual HAp content decreases.[2,7]

Many diffraction and spectroscopic methods were developed and applied in the investigations of structure and phase composition of polycrystalline solids, including calcium orthophosphates, i.e. Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), magic angle spinning (MAS) NMR, electron spin resonance (ESR), Mössbauer spectroscopy, quantitative X-ray diffraction (QXRD).[1,6,8–10]

In our investigations the phase composition studies have been carried out by FTIR spectroscopy and QXRD on the calcium phosphate materials produced from the precipitates with various Ca/P molar ratios.

2 MATERIALS AND METHODS

Six calcium phosphate precipitates with various Ca/P molar ratio have been synthesized by wet method using reagents of analytical purity. The phosphoric acid solutions were slowly added to vigorously stirred $Ca(OH)_2$ suspensions. The resulting gel-like precipitates were washed with distilled water, filtered and dried at 90 °C.

The Ca/P molar ratio of powder precursors thus obtained (denoted as PM1 to PM6, respectively) was estimated by the wet chemical method, i.e. by $KMnO_4$ titration for Ca and phosphomolybdate technique for PO_4. The data regarding Ca/P ratios of the particular precipitates are presented in Table 1.

After grinding in the rotating–vibrating mill to a fineness below 63 μm, the powders were preliminary calcined at 800 °C for 3 h, mixed with 5% solution of polyvinyl alcohol and uniaxially compacted under 78 MPa to form the rectangular shaped samples 80×8×5 mm. The compacts thus produced were subsequently isostatically re-pressed under a pressure of 350 MPa (samples M1–M6). Additionally, the same samples were prepared from a commercial hydroxyapatite powder (PM7) produced by Merck (after heat treatment material M7). The shaped samples were subsequently sintered at 1250 °C with 2 h heating at maximum temperature.

The QXRD studies were carried out using a Philips diffractometer. The phase composition of investigated materials was estimated by the internal standard procedure, described earlier in detail.[10]

The FTIR studies were carried out on a DIGILAB FTS –60V spectrometer in the range of 400–4000 cm^{-1} (256 scans, resolution - 4 cm^{-1}). The transmission technique was applied and the samples were prepared as standard KBr pellets. For this purpose the small 1–3 mg portions of each substance were homogenized with ~1 g of solid KBr and subsequently pelletized under ~10 MPa pressure before testing. The series of samples M1–M7 stored in air after sintering were ground to a fineness below 63 μm in diameter and subjected to the FTIR studies. The samples M5 and M6 were additionally re-heated at 650 °C and 1250 °C and then studied by FTIR spectroscopy.

The fractured surfaces of the samples M5 and M6 were observed under SEM (Jeol 5400) and the carbon concentration on these surfaces was analysed by the EDS method (LINK AN 10 000 microanalyser).

Table 1. Ca/P molar ratios of the calcium phosphate precipitates

Sample no.	P-M1	P-M2	P-M3	P-M4	P-M5	P-M6	P-M7
Ca/P molar ratio of the precipitates	1.502	1.552	1.613	1.669	1.698	1.717	HAp MERCK

3 RESULTS AND DISCUSSION

3.1 XRD patterns

In the M1 material produced from the precipitate with a Ca/P ratio = 1.502 only the tricalcium phosphate, occurring as α and β polymorphs, with prevailing βTCP phase was detected (Fig. 1(a), Table 2). In Figs 1(b) and 1(c) the XRD patterns of M2 and M3 samples are shown. These samples were obtained from the powder precursors with Ca/P ratios equal 1.552 and 1.613, respectively. Both sinters are composed of three phases: HAp + βTCP + αTCP, however occurring in different proportions (Fig. 1(b) and 1(c), Table 2). The M4 material, as shown in Fig. 1(d), is rentgenographically pure hydroxyapatite bioceramic. The phase composition of M5 and M6 materials is very similar. These samples were produced from the precipitates with Ca/P ratios = 1.698 and 1.717, respectively, and exhibit small amount of CaO (less than 2%), besides the hydoxyapatite as a main component (Table 2, Fig. 1(e) and 1(f)). The M7 material synthesized from the Merck hydroxyapatite powder consists of about 97% HAp and 3% βTCP (Fig. 1(g), Table 2).

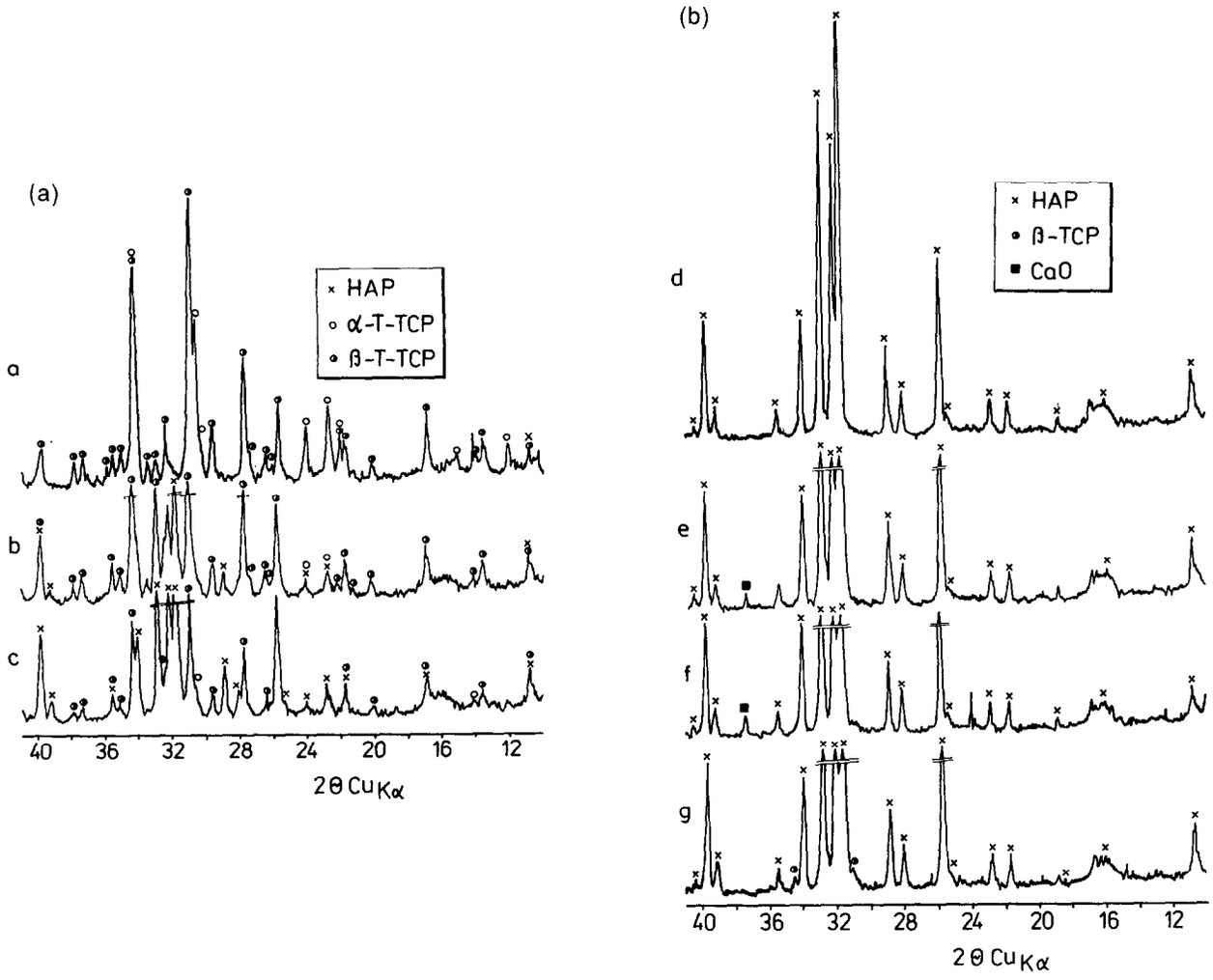

Fig. 1. XRD patterns of the materials sintered at 1250 °C. (a) sample M1, (b) sample M2, (c) sample M3, (d) sample M4, (e) sample M5, (f) sample M6, (g) sample M7.

Table 2. Phase composition of investigated materials sintered at 1250 °C

Sample no.	M1	M2	M3	M4	M5	M6	M7
HAp [wt%]	0	15	60	100	⩽98	⩽98	97
TCP [wt%]	100*°	85*°	40*°	0	0	0	3*
CaO [wt%]	0	0	0	0	⩾2	⩾2	0

*βTCP
°αTCP

3.2 FTIR spectra

The FTIR spectra of the investigated calcium phosphate materials are shown in Fig. 2. All spectra exhibit easily distinct, strong bands attributed to PO_4^{3-} groups, the strongest ones result from the stretching vibrations. The bands at 1092 cm^{-1} and about 1040 cm^{-1} are assigned to the components of the triply degenerated ν_3 antisymmetric P–O stretching mode. The 962 cm^{-1} band is assigned to ν_1, the non-degenerate P–O symmetric stretching mode. The bands at 601 cm^{-1} and 571 cm^{-1} are assigned to components of the triply degenerate ν_4 O–P–O bending mode and the bands in the range 462–474 cm^{-1} are assigned to the components of the doubly degenerate ν_2 O–P–O bending mode.[6,9] Very weak band which can arise from the HPO_4^{2-} at about 875 cm^{-1} appears on the FTIR spectrum of M6 sample [Fig. 2(f)]. This band can also be connected with the presence of $Ca(OH)_2$ in the sample. This small effect disappears after re-heating at 1250 °C or even at 650 °C. Its origin will be explained in a future part of our studies. Absence of any distinct band in the range of 1400–1550 cm^{-1} indicates that the samples M1, M2, M3, M4 and M7 do not contain large quantities of carbonate ions. However, the traces of CO_3^{2-} may be incorporated into the structure [Fig. 2(a)–(d), 2(g)]. In the case of samples M5 and M6 the small amounts of CO_3^{2-} ions are visible [Fig. 2(e), 2(f)]. The 1456 and 1412 cm^{-1} very weak peaks come from CO_3^{2-} ions and correspond to ν_3 stretching vibrations. The broad band of low intensity in the range 3000–3400 cm^{-1} can be attributed to the traces of water incorporated into the structure. However, the bending mode from H–O–H groups at about 1640 cm^{-1} is not marked clearly [Fig. 2(a–g)].

The results dealing with the presence of OH^- groups in the structure seem to be very interesting. The band coming from the hydroxyapatite OH^- stretching vibrations at 3572 cm^{-1} is visible on all the FTIR spectra corresponding to the hydroxyapatite containing samples, i.e. M2–M7 [Fig. 2(b)–(g)]. Neither this band nor the 630 cm^{-1} band, both assigned to the vibration of OH^- groups, occur in the spectrum of M1 sample with no hydroxyapatite. The lack of HAp in M1 material has also been confirmed by XRD study [Fig. 1(a)]. The spectrum of M2 sample reveals only a small shoulder corresponding to 620 cm^{-1} band. This sample consists mainly of the tricalcium phosphate [Fig. 2(b)] with only 15 wt% of HAp as it was found in QXRD study. In the case of M5 and M6 samples, the 3642 cm^{-1} bands are additionally visible. These bands result from the OH^- groups which do not originate from the hydroxyapatite structure [Fig. 2(e), 2(f)] and disappear (like a weak band at 875 cm^{-1}) after re-heating at 1250 °C or even at 650 °C (Figs 3 and 4). One should underline that the intensity of the band at ~3642 cm^{-1} is a little higher in the case of M6 sample [Fig. 2(f)] as compared with M5 [Fig. 2(e)]. In order to explain the origin of this band, the SEM and EDS techniques have been used.

The SEM observations and EDS studies revealed the presence of $CaCO_3$ crystals on the fractured surfaces of M5 and M6 samples.

4 DISCUSSION

As it has been shown in the presented work, the qualitative and quantitative phase composition of calcium phosphate materials depends significantly on the Ca/P molar ratios of the initial precipitates.

The QXRD and FTIR studies show that the sinters produced from the powder precursors with Ca/P ratios in the range of 1.502–1.717 are composed of one, two or three phases and contain, besides of hydroxyapatite, βTCP, αTCP or even CaO. The hydroxyapatite content in those samples changes from 0 wt% to 100 wt%.

In the materials produced from the powders with Ca/P < 1.667, i.e. 1.502, 1.552 and 1.613, the content of α + βTCP varies from 40% (sample M3) to 100% (sample M1) and the amount of HAp from 60 wt% to 0 wt%, respectively. The two tricalcium phosphate polymorphs α and β occur in these materials but the βTCP phase significantly dominates.

The rentgenographically pure hydroxyapatite ceramic was manufactured based on a powder with a Ca/P ratio = 1.669.

The materials (M5 and M6) produced from the powders with Ca/P ratios > 1.698 are composed of two phases. After heating at 1250 °C, 2% of free CaO was rentgenographically detected, apart from HAp as a main phase. The presence of CaO as a component of implantation materials is very harmful because of its reactivity against water. When the sinters are stored in air, the absorption of water vapour occurs with the formation of some amount of $Ca(OH)_2$. The FTIR band at ~3642 cm^{-1} has been assigned to the surface hydroxyl ions.[6] The presence of this band (3641.7 cm^{-1} for M5 material and 3643.3 for M6) on the spectrum of samples with CaO content indicates that calcium oxide occurring on the surfaces transformed in air to $Ca(OH)_2$. Most probably the weak band at 875 cm^{-1}, visible on the spectrum of M6 sample, comes from $Ca(OH)_2$ too.[9,10] After re-heating at 650 °C, that is

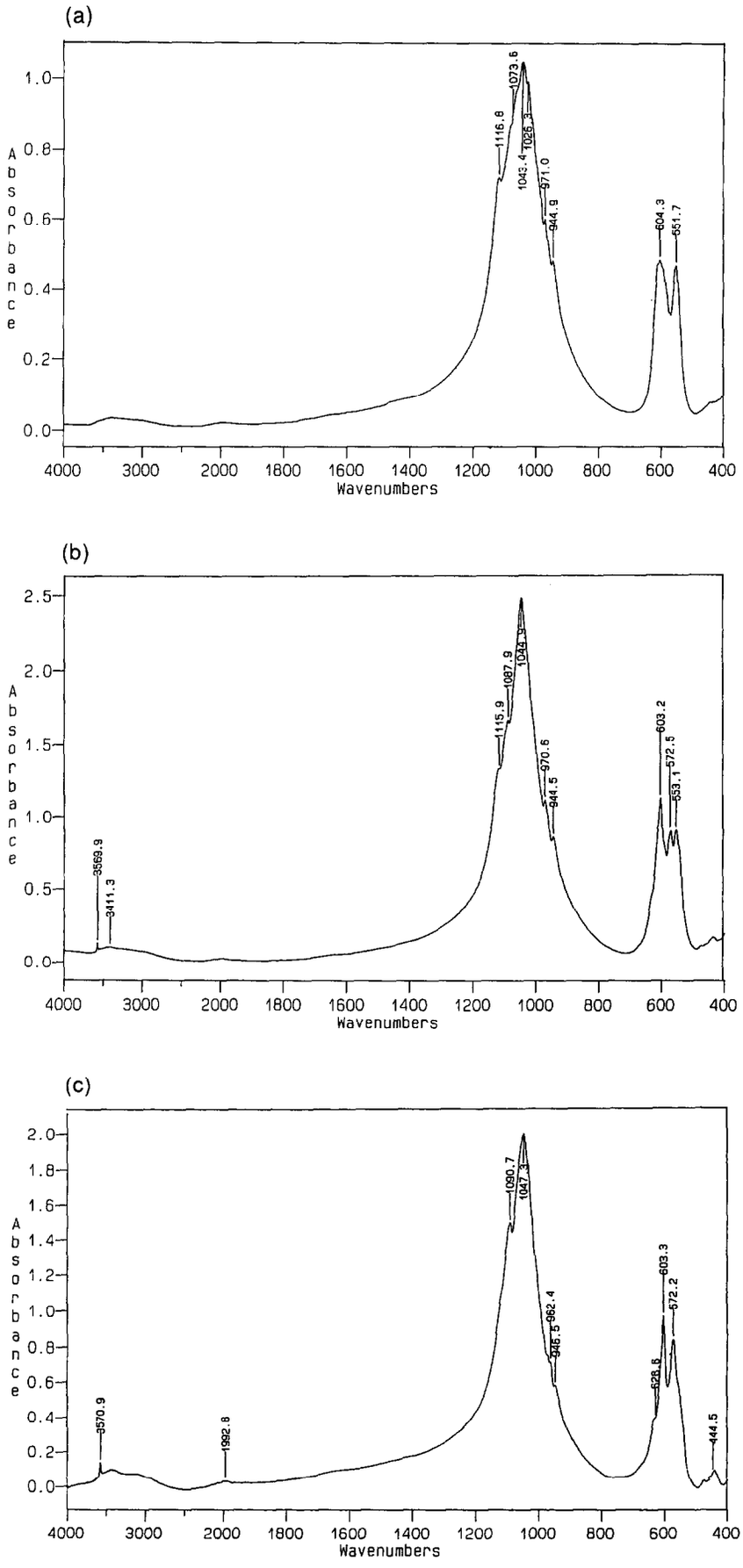

Fig. 2. FTIR spectra of the materials sintered at 1250 °C. (a) sample M1, (b) sample M2, (c) sample M3, (d) sample M4, (e) sample M5, (f) sample M6, (g) sample M7.

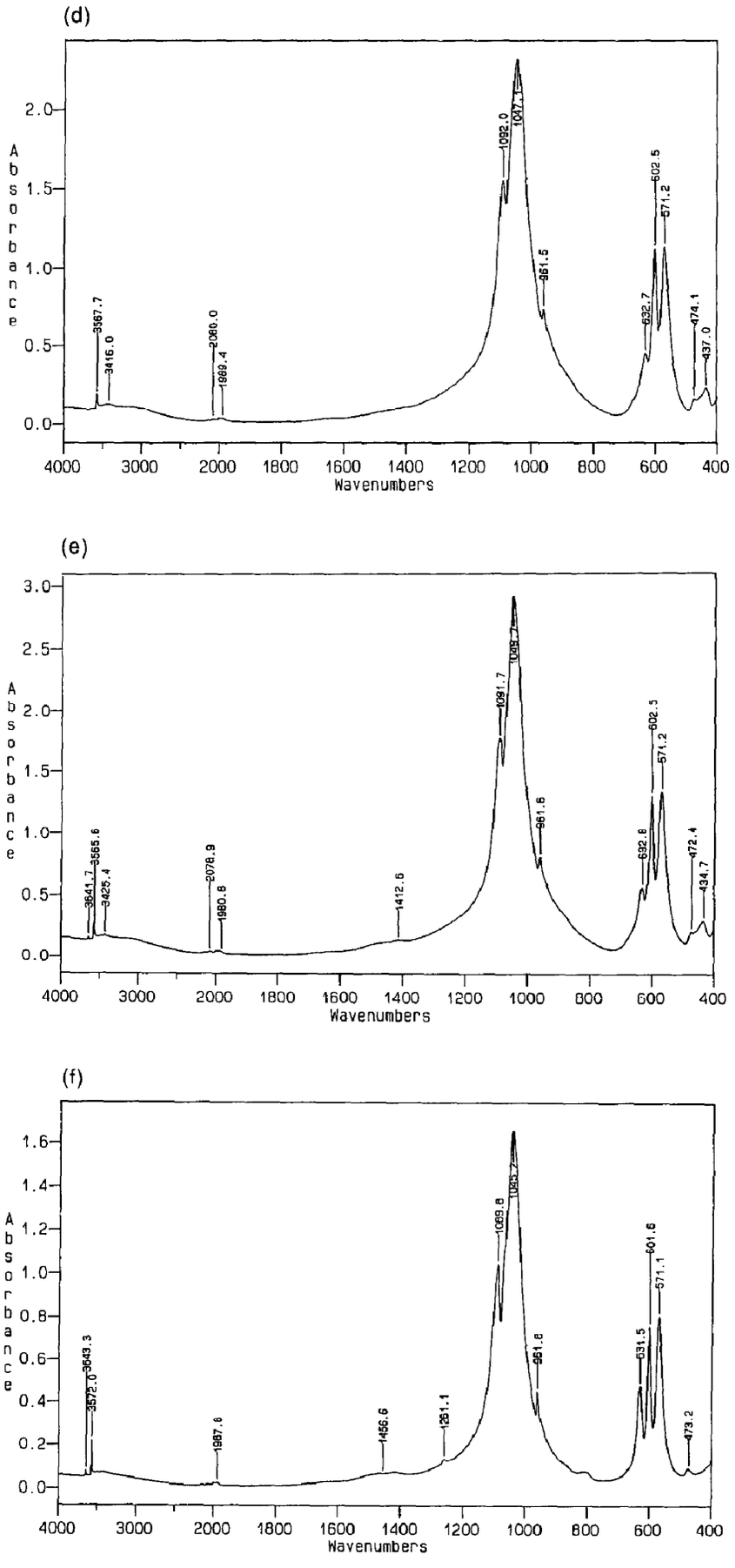
(d)
Absorbance
Wavenumbers
3567.7
3416.0
2060.0
1989.4
1092.0
1047.1
961.5
632.7
602.5
571.2
474.1
437.0
(e)
Absorbance
Wavenumbers
3641.7
3565.6
3425.4
2078.9
1980.8
1412.6
1091.7
1048.7
961.6
632.8
602.5
571.2
472.4
434.7
(f)
Absorbance
Wavenumbers
3572.0
3643.3
1987.8
1456.6
1261.1
1069.8
1025.7
961.8
631.5
601.6
571.1
473.2

Fig. 2. *cont.*

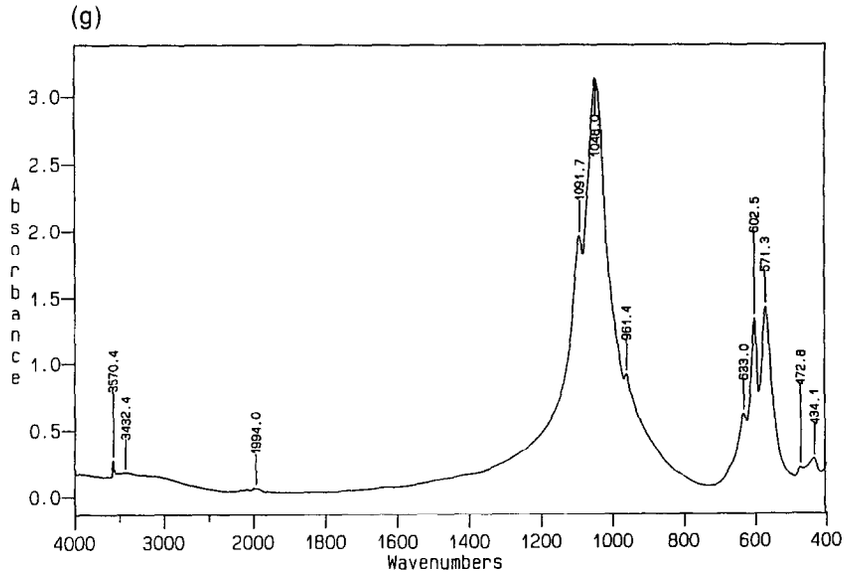

Fig. 2. *cont.*

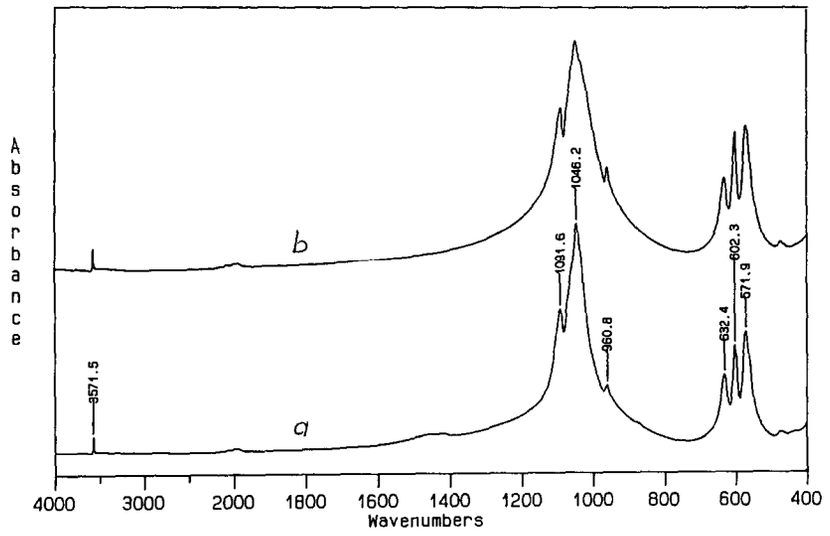

Fig. 3. FTIR spectra of the M5 sample reheated at (a) 650 °C, (b) 1250 °C.

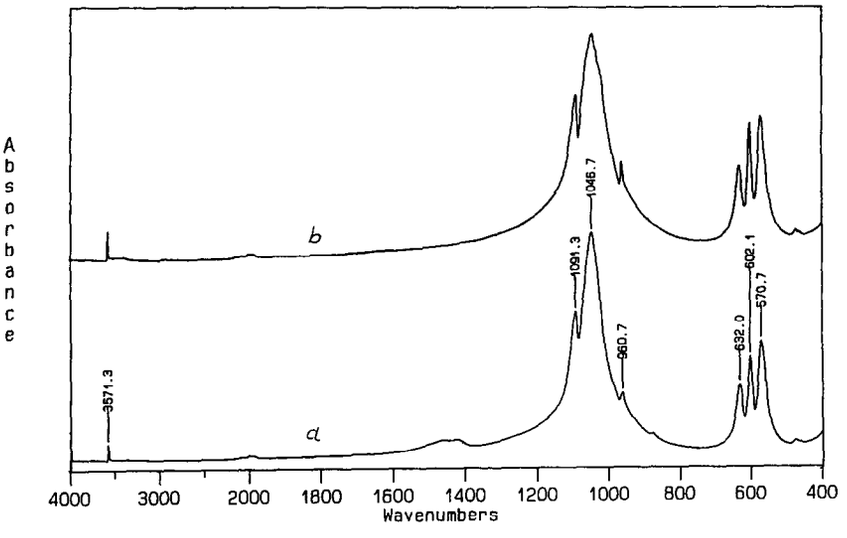

Fig. 4. FTIR spectra of the M6 sample reheated at (a) 650 °C, (b) 1250 °C.

above the temperature of $Ca(OH)_2$ dehydration, these bands disappeared.

As was confirmed by SEM and EDS studies, some amount of $Ca(OH)_2$ transforms subsequently in air to $CaCO_3$ which forms, in the case of M6 material, the well-shaped calcite crystals.

In the FTIR spectra of M1–M5 materials, the band at 870 cm^{-1} does not occur, thus confirming the absence of HPO_4^{2-} ions in the studied materials, at least in quantities not detectable by FTIR.

5 SUMMARY

The FTIR spectroscopy and QXRD studies reveal how small variations in the Ca/P ratios of initial precipitates significantly affect the phase composition of final calcium phosphate materials.

The sinters produced from the powder precursors with Ca/P ratios in the range 1.502–1.717 are mono-, bi- or triphase ceramics with hydroxyapatite content from 0 wt% to 100 wt%.

The materials produced from the precipitates with Ca/P >1.698 contain, apart from hydroxyapatite as a main phase, also up to 2 wt% CaO. In contact with air, calcium oxide transforms to $Ca(OH)_2$ and subsequently to $CaCO_3$ as has been proved by FTIR, SEM and EDS studies. The usefulness of FTIR spectroscopy together with QXRD investigations for the compositional studies of the calcium phosphate based materials was confirmed.

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