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Vibration spectroscopy study of hydrolyzed precursors for sintering calcium phosphate bio-ceramics

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Diffuse reflectance infrared Fourier transform and Raman spectroscopy is applied to investigate the structure of hydrolyzed $CaHPO_4 \cdot 2H_2O$ (DCPD) processed to non-stoichiometric apatite to be used as starting material for preparing sintered calcium phosphate materials. The spectra of hydrolyzed DCPD samples, obtained under differing experimental conditions, are analyzed to check how the sintered phase composition correlates with the structure of the hydrolyzed precursor. It is shown that the addition of extra Ca^{2+} ions in the alkaline solution during the process of hydrolyzing affects strongly the degree of disorder in the structure of the hydrolyzed materials, thus increasing the relative amount of hydroxyapatite in the final sintered product. The addition of F^- ions to the synthesis mixture strengthens slightly the P-O bonds in the precursors and increases the content of hydroxyapatite phase in the sintered material. As a result bi-phase ceramics of highest content of hydroxyapatite can be produced using both fluorine additives and calcium compensators in the synthesis suspension.

1. Introduction

Hydroxyapatite (HAP) ceramics and calcium phosphate sintered materials are very promising for biological applications as synthetic bone graft materials. The main requirement for the powder precursors used generally as raw starting materials is their excellent physical-chemical characteristics. To satisfy this requirement wet processes in aqueous solutions (co-precipitation of calcium and phosphate salts or hydrolysis of acidic calcium phosphate salts) are usually favored and applied to preparing active powders with apatite structure [1]. This step of the ceramic synthesis is not only the most sophisticated, but also very plausible to control the properties of the sintered materials [2–10]. According to X-ray diffraction analysis these raw materials are poorly crystalline and usually only several reflections characteristic of the apatite structure are detected, indicating its incipient formation.

The hydrolyzed precursors with disordered apatite structure are supposed to be very sensitive to the presence and concentration of various ionic additives to the suspension in the course of hydrolysis of DCPD [7], which could affect the final phase composition of the sintered materials. To prove this assumption one should use additional structure-sensitive methods in characterizing the final hydrolyzed material. Valuable information on the short- and intermediate-range ordering in solids can be obtained by infrared absorption (IR) and Raman spectroscopy. Parameters of the observed spectral peaks depend on the atomic arrangement in possible structural units with a size of several inter-atomic distances and on the presence of atomic-scale defects. Vibration spectroscopy may be used to investigate the structure of such entirely and partially disordered materials.

In this study we try to model the modification of a calcium phosphate precursor using hydrolysis of DCPD to non-stoichiometric hydroxyapatite with the general formula $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ under well-defined experimental conditions. The study aims at

TABLE I Synthesis conditions, Ca/P molar ratio and fluorine content of the samples

Sample	Seed material	Alkaline solution	Temp. of Stirring (°C)	Additional treatment	Ca/P		F, wt.%	
					80°C	1150°C	80°C	1150°C
A	29.1 mmol DCPD in 400 ml H_2O	21.5 mmol NaOH in 350 ml H_2O	95					
A1			95	1/2 of A + 100 ml H_2O	1.63	1.58	–	–
A2			73	1/2 of A + 100 ml 1 M NaF	1.65	1.66	1.56	1.59
B	29.1 mmol DCPD in 400 ml H_2O	4.8 mmol $CaCl_2$ + 24.8 mmol NaOH in 350 ml H_2O	95					
B1			95	1/2 of B + 100 ml H_2O	1.57	1.60	–	–
B2			67	1/2 of B + 100 ml 1 M NaF	1.65	1.66	1.07	1.22
C	29.1 mmol DCPD in 400 ml H_2O	9.6 mmol $CaCl_2$ + 30.5 mmol NaOH in 350 ml H_2O	95					
C1			95	1/2 of C + 100 ml H_2O	1.59	1.62	–	–
C2			70	1/2 of C + 100 ml 1 M NaF	1.67	1.68	1.40	1.45
D	29.1 mmol DCPD in 400 ml H_2O	19.4 mmol $CaCl_2$ + 38.7 mmol NaOH in 350 ml H_2O	95					
D1			95	1/2 of D + 100 ml H_2O	1.63	1.65	–	–
D2			74	1/2 of D + 100 ml 1 M NaF	1.67	1.69	1.83	1.87

analyzing the correlation between IR and Raman spectroscopy data for both precursors modified by adding Ca^{2+} and F^- ions and the phase ratios in the final sintered materials. This information is important from a practical point of view when synthesizing precursors of synthetic bone graft materials.

2. Materials and methods

2.1. Preparation of precursors

Commercial pure $CaHPO_4 \cdot 2H_2O$ (Fluca Chemie AG) was milled in an agate ball mill in order to reduce the particle size to about 0.02 mm. The specific surface area in this case, measured by the method of single point N_2 (BET), is 124 m^2/g.

In the process of hydrolysis solutions of reagent grade sodium hydroxide, calcium chloride and additives of sodium fluoride were used to prepare the precursors of calcium phosphate slurry for experimental studies. The suspension was diluted to a high liquid-to-solid ratio following literature data [9, 11, 12].

The experiments were performed by adding dropwisely 1 mol/dm^3 solution of NaOH, either pure or with various amounts of Ca^{2+} (4.6, 9.6 and 19.4 mmol of $CaCl_2$ included), to a suspension of 29.1 mmol DCPD and 400 ml doubly distilled water upon continuous stirring until reaching the value pH 9.5. All experiments were carried out at a constant temperature of 95°C under air atmosphere conditions. Then, the mixture was kept for 2 hours at 95°C and for 48 hours at room temperature. Subsequently, the suspension was divided and poured into two vessels and 100 ml doubly distilled water were added to the first vessel, whereas 100 ml 1 mol/dm^3 NaF solution to the second. Both mixtures were stirred continuously 6 hours at constant temperature. The experimental conditions, the Ca/P molar ratio and the fluoride content in the samples are summarized in Table I. (The used amounts of NaOH and $CaCl_2$ were chosen so that to obtain homogenous alkaline solution.)

All precursors were separated by Buchner filtration, rinsed three times with doubly distilled water and once with 78% ethanol. Then, the precipitates were dried in a sterilizer at 80°C for 15 hours. Finally, in a second step, they were sintered in air for one hour at 1150°C.

2.2. Chemical analysis

The chemical composition of the precipitate precursors as well as of the final sintered materials was determined as follows:

(i) The content of calcium was determined complexometrically by an automatic titration-apparatus Titrino (Metrohm Ltd.), while that of fluoride by an F ion-selective electrode.

(ii) The content of phosphate was determined in terms of phosphate-vanadate-molybdate complexes using optical absorption spectroscopy.

2.3. X-ray diffraction

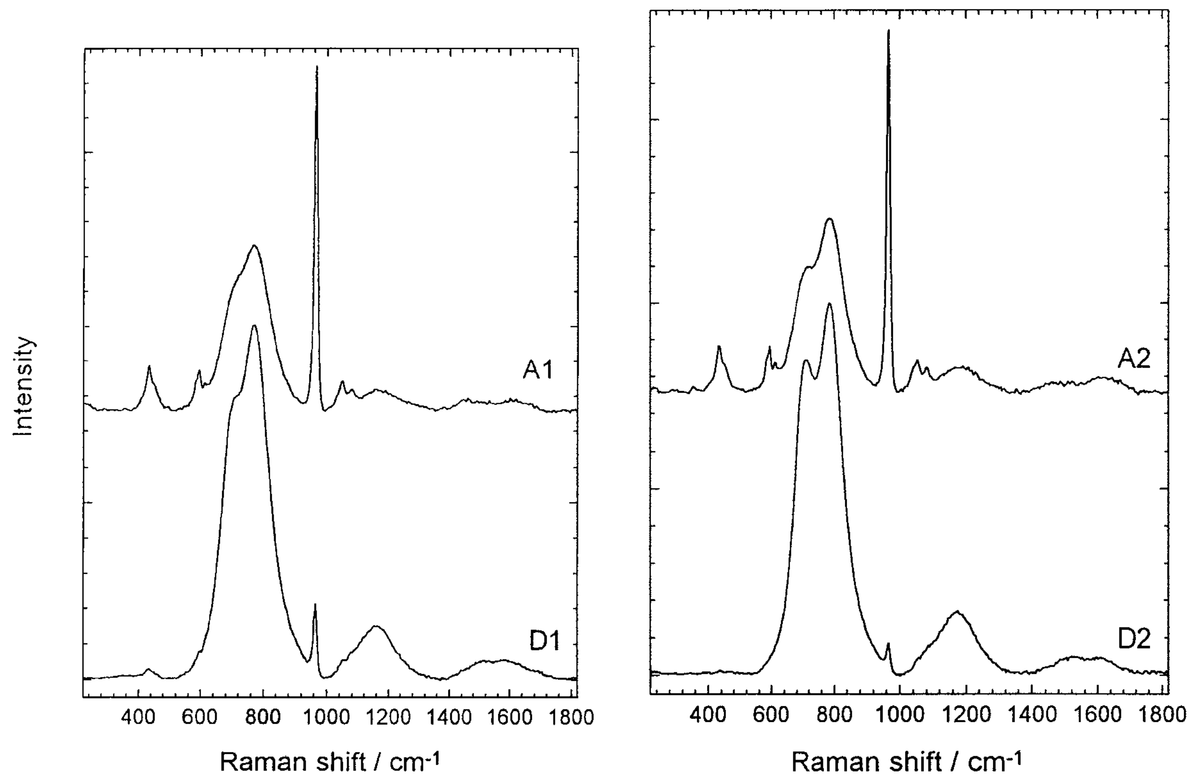
The structure of the hydrolyzed precursors samples as well as of the final sintered materials were controlled by powder X-ray diffraction measurements using a DRON-UM1 diffractometer with filtered Co K_α radiation. The results obtained for the final sintered samples are summarized in Table II.

2.4. Vibration spectroscopy

Four hydrolyzed precursors samples, A1, A2, D1 and D2, were chosen for studying by IR and Raman spectroscopy, since they are the edge-members of the sample sequence of this experimental study. Samples A1 and A2 were hydrolyzed DCPD without extra calcium

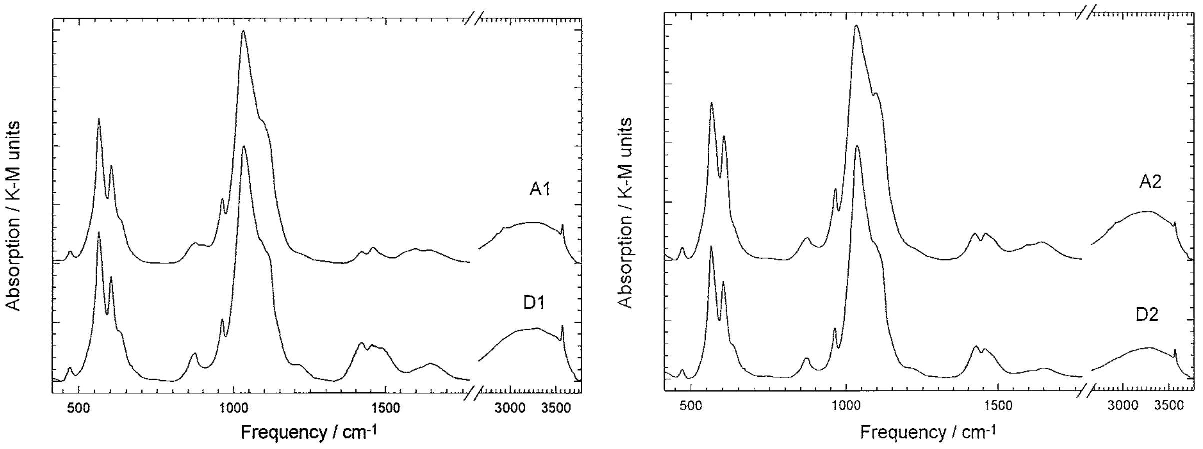
TABLE II Phase composition (in %) of the sintered samples, determined by powder X-ray diffraction

	A1	A2	B1	B2	C1	C2	D1	D2
Hydroxyapatite	30.9	80.8	32.4	81.1	37.8	82.3	81.3	94.9
β-$Ca_3(PO_4)_2$	69.1	19.2	67.6	19.9	62.2	17.7	19.7	5.1



(a) (b)

Figure 1 Raman spectra of the samples studied.



(a) (b)

Figure 2 DRIFT spectra of the samples studied.

ions, whereas D1 and D2 were prepared with the largest amount of $CaCl_2$ (about 19.4 mmol). On the other hand, sampeles A1 and D2 were obtained without fluoridation of the synthesis suspension, whereas A2 and D2 included NaF additives.

The samples were examined by diffuse reflectance infrared Fourier transform (DRIFT) and Raman spectroscopy. DRIFT spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer by averaging 100 scans. A tablet of KBr was used as reference sample. The Raman spectra were recorded by a Perkin-Elmer 1700X NIR FT-Raman spectrometer equipped with Nd:YAG laser operating at 1064 nm wavelength with power of 0.4 W after averaging 500 scans. In both cases the spectra were collected at room temperature with a 4 cm^{-1} spectral resolution.

3. Results and discussion

The Raman spectra are shown in Fig. 1 and the DRIFT spectra, plotted in Kubelka-Munk units, in Fig. 2. The positions of the peaks observed and the type of the generating vibrations are listed in Table III. As seen, there is a great difference between the Raman spectra of samples A1 and D1, on the one hand, and those of A2 and D1, on the other hand. This difference consists in a strong change in the intensity ratio, ρ, of the sharp peak at 963 cm^{-1} and the broad band centered at about 700 cm^{-1}. The former originates from the symmetrical stretching mode of PO_4 tetrahedra in apatite [10], whereas the latter is most probably due to a phase of disordered phosphate groups. The reason for such an assignment of the band at 700 cm^{-1} is: (i) its relatively large width indicates the existence of structural

TABLE III Peak positions (in cm^{-1}) and type of the generating vibration modes

IR				Raman				
A1	D1	A2	D2	A1	D1	A2	D2	Type of vibrations
3570	3570	3570	3570					O–H stretching of OH^-
3258	3281	3292	3292					O–H stretching of H_2O
1651[a]	1653	1653	1653					H–O–H bending of H_2O
				1620	1600	1620	1600	H–O–H bending of H_2O
1598	1602	1596	1595					C–O stretching
1564								H–O–H bending of H_3O^+ or of H_2O
				1455	1514	1485	1514	C–O stretching
1478	1494	1483	1479					
1456	1458	1458	1456					
1419	1418	1420	1426					
	1216		1216					P=O stretching
				1158	1158	1184	1174	P–O stretching in disordered phosphate network
1096	1096	1096	1096					P–O stretching in apatite
				1078	1078	1081	1081	
				1048	1052	1053	1055	
				1032	1039	1043	1046	
1031	1033	1032	1035					
				964	964	966	966	Symmetrical PO_4 stretching in apatite
963	963	965	964					P–O stretching in apatite
897								H–P vibrations
874	874	874	874					H–O–P in HPO4
866	866	866	866					
				767	769	786	786	P–O in disordered continuous phosphate network
				695	695	705	712	
633	633	633	633					O–H librations of OH groups
				612	612	612	612	O–P–O & P–O in apatite
603	603	603	603					
				595	595	595	595	
				584	584	584	584	
564	564	564	564					
472	472	472	472					
				450	450	450	450	O–P–O in apatite
				433	433	433	433	
				411	411	411	411	
				354		354		External mode in apatite

[a] The values of IR peak positions in the range 1400–1800 cm^{-1} are according to the results of multi-Lorentzian fitting.

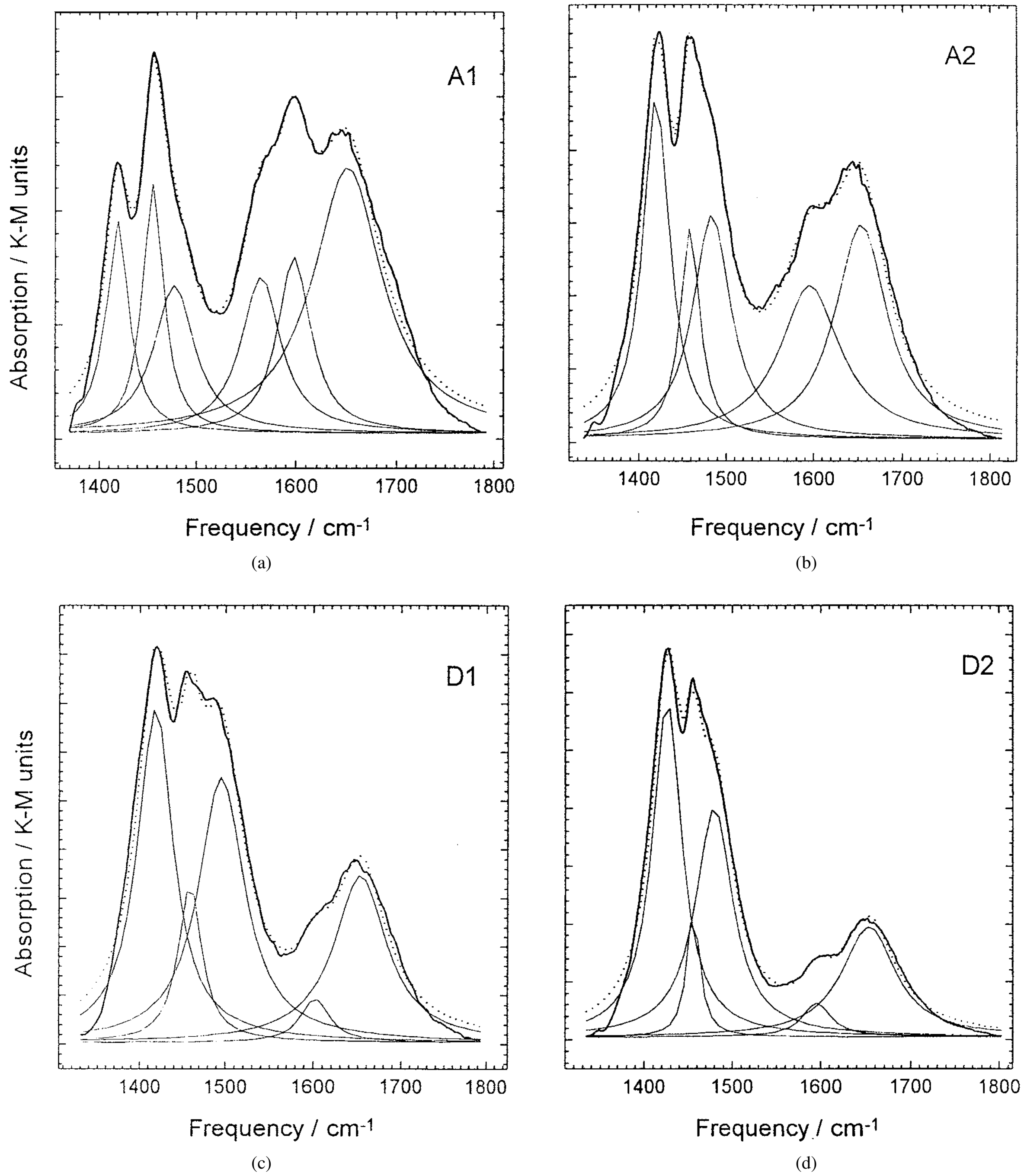
disorder and (ii) Raman spectra of disordered phosphates contain peaks in this frequency region [13]. Thus, the value of ρ can serve as a measure of the ratio between ordered apatite and disordered phosphate phases. The Raman data show that the relative amount of disordered phosphate phase in samples D1 and D2 is much larger than that in A1 and A2. Therefore, the decrease in Ca deficiency leads to an increase in the degree of structural disorder in the precursor material. The addition of extra Ca^{2+} ions to the alkaline solution leads most probably to a change in the ordinary Ca concentration in the hydrolyzed solid material. Consequently, the increased stoichiometric disorder would increase the structural disorder, which is a very interesting fact from practical point of view.

The peaks in the Raman spectra of D1 and D2 are positioned at higher frequencies than those of A1 and A2, indicating that the P-O bonds are stronger in D1 and D2 than in A1 and A2. This suggests that the fluoride additives to the synthesis suspension, regardless of the degree of Ca deficiency, stabilizes the atomic network in both disordered and crystalline phases in the hydrolyzed starting material.

It is worth noting that the appearance of the shoulder at 411 cm^{-1} in the Raman spectra of the samples studied results most probably from a frequency splitting of the mode at 433 cm^{-1}, which is indicative of imperfections in the apatite lattice.

There is no substantial difference between DRIFT spectra of the samples in the range 400–1300 cm^{-1}, dominated by phosphate vibrations and, hence, one can hardly obtain additional information on the arrangement of the phosphate system. However, DRIFT spectra are informative on the CO_3 groups, formed in the structure during the synthesis process under ambient air conditions. The carbonate groups contribute usually to the infrared absorption at about 1450 cm^{-1} [14]. At a glance, the absorption spectra in this range show that in sample D1 there are more CO_3 groups than in A1, while samples A2 and D2 contain nearly the same amount of such groups.

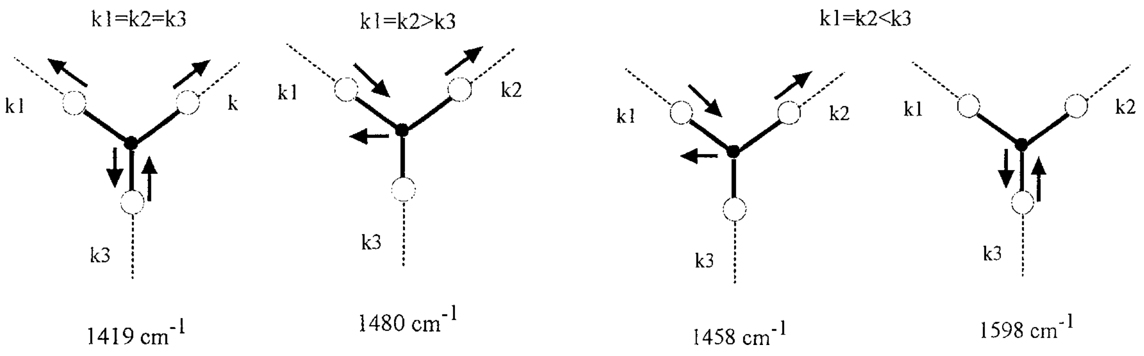
In order to analyze the state of carbonate groups in more detail we performed decomposition of the spectral profiles in the range 1400–1800 cm^{-1} using Lorentz functions. The results are shown in Fig. 3. Two peculiarities can be seen: (i) the spectra of all



(a) (b) (c) (d)

Figure 3 Measured DRIFT spectra (bold solid line), the fitting Lorentzians (thin solid lines) and the resulted spectral profile (dotted line).

the samples are best fitted by five Lorentzians, except that of sample A1, fitted by six Lorentzians and (ii) the height of the fitting peaks at about 1458 and 1598 cm^{-1} decreases with decreasing Ca^{2+} deficiency. The peak at 1650 cm^{-1} is usually assigned to H–O–H bond bending mode of H_2O. The extra peak at 1564 cm^{-1} in the spectrum of A1 may be due to H–O–H bond bending of H_3O^+ or of water incorporated in the structure in another way. The frequency of the bending modes of H_3O^+ and H_2O varies in a wide range strongly dependent on the manner of embedding of such groups in the solid matrix. The peak at 1458 cm^{-1} arises, without any controversy, from C–O bond stretching mode, while that at 1598 cm^{-1} can originates either from H–O–H bending or from C–O stretching of CO_3 groups in which two oxygen atoms interact stronger with the surrounding atoms than the third one [15]. In the latter case the peak at 1458 cm^{-1} could arise from the same type of CO_3 groups as that at 1598 cm^{-1}. Fig. 4 presents the C–O stretching modes of CO_3 groups probably existing in the structure of the starting material and interacting in a different way with the host matrix. Thus, the decrease in the relative intensity of both peaks at 1458 and 1598 cm^{-1} indicates a change in the atomic surroundings of the CO_3 groups with increasing the extra calcium ion concentration in the alkaline solution. The comparison of Raman and infrared data shows that the variation in the ratio between the amounts of disordered and crystalline phases in the hydrolyzed precursor is correlated with the ratio between the relative amounts of differently situated carbonate groups. This indicates that the carbonate groups are



(a) (b)

Figure 4 Atom vector displacements (arrows) in infrared-active C–O stretching modes generating peaks in the range 1400–1800 cm^{-1}; filled circle are C atoms, open circles—O atoms, solid lines represent C–O bonds, dotted lines represent the interactions with force constants $k1$, $k2$ and $k3$ of the oxygen atoms with the surroundings.

embedded in both the disordered and crystalline phases.

To trace the effect of the synthesis conditions on the phase composition of the final bio-ceramic products, obtained after heating the starting materials at 1150°C, the sintered samples were investigated by powder X-ray diffraction (Table II). As seen, all the samples consist of two phases, hydroxyapatite and β-$Ca_3(PO_4)_2$, in different amounts depending on the content of extra calcium and fluorine ions in the synthesis mixture. The presence of F^- leads to a strong increase in the amount of HAP in the final bi-phase calcium phosphate ceramic material. The addition of Ca^{2+} compensators has the same effect, and the higher the concentration of Ca^{2+}, the higher is the amount of HAP in the final sintered material. It is interesting to note that approximately the same phase composition of the sintered final material can be obtained by addition of either calcium or fluorine to the synthesis mixture. At the same time, the highest amount of hydroxyapatite in the sintered material (95% for sample D2) is obtained with both F^- additives and extra Ca^{2+} compensators to the synthesis mixture.

The spectroscopic results show, however, that while extra Ca^{2+} strongly influences the degree of structural disorder in the hydrolyzed materials, F^- leads only to a slight strength of the P-O bonds in the structure of the starting material, not changing the relative amount of the disordered phase. This indicates that there are two differing ways to control the phase composition of the bio-ceramics: (i) by adding extra Ca^{2+}, that changes the structure of the hydrolyzed starting materials, resulting further in a high amount of hydroxyapatite; and (ii) by adding F^-, that probably stabilizes the atomic network and promotes the formation of precursor clusters in the starting material, thus increasing the amount of hydroxyapatite in the final sintered material. However, the latter mechanism of formation of hydroxyapatite-rich bio ceramics can hardly be understood only on the basis of present data. Nevertheless, it is clear that by varying the chemical composition of the synthesis mixture one can control precisely the amount of hydroxyapatite in the resulting sintered materials.

4. Conclusion

Using vibration spectroscopy for characterization of the hydrolyzed precursors for preparing calcium phosphate ceramics it was found that:

(i) The addition of Ca^{2+} compensators to the alkaline solution during the process of hydrolysis affects strongly the degree of disorder in the structure of the starting materials and thereby increases the amount of hydroxyapatite in the final sintered products.

(ii) The use of NaF additives to the slurry strengthens the P–O interactions in the starting materials and increases the amount of hydroxyapatite in the final sintered products.

The phase composition of calcium phosphate sintered materials can be controlled effectively by varying the amount of both Ca^{2+} and F^- in the synthesis of calcium phosphate precursors. In conclusion, sintered materials with a highest content of hydroxyapatite can be produced using simultaneously fluorine ion additives and relatively large amount of calcium ion compensators in the synthesis suspension.

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