Vibrational Properties of Calcium Phosphate Compounds. 1. Raman Spectrum of β-Tricalcium Phosphate

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We present a study of the Raman spectrum of polycrystalline β-$Ca_3(PO_4)_2$ (β-TCP) over its whole optical frequency range. Raman scattering bands associated with the normal vibrational modes of the PO_4^{3-} tetrahedron were clearly identified, confirming the molecular character of the β-TCP crystal as regards to its vibrational properties. External lattice modes involving Ca^{2+} and PO_4^{3-} sublattices were also observed. Several characteristic features of the spectrum are discussed in relation to the crystallographic structure of β-TCP.

Introduction

Over the past 20 years ceramics based on calcium phosphates have been widely used for hard-tissue implants in medicine.[1] Among them, hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) and β-tricalcium phosphate (β-TCP, β-$Ca_3(PO_4)_2$) are the most widely used as ceramic implants. The first is bioactive and joins directly to the bone tissue, while the second is resorbable.[2−4] Quite recently, micro-Raman techniques have been used in an attempt to characterize, with spatial resolution of ≈5 μm, the bone−implant interface region of postimplant samples, with emphasis on the gradient in the concentration of amorphous calcium phosphate away from the bone−implant interface.[5] However, in that work only a broad band around 960 cm^{-1} was detected, which was used to monitor the evolution from a predominantly amorphous calcium phosphate material close to the bone−implant interface to a hydroxyapatite-rich material at ≈70 μm from the interface. Micro-Raman spectroscopy, as a nondestructive probe at a micron-length scale, can give valuable information about the structural changes that take place locally on the calcium phosphate ceramic implants provided that the vibrational properties of the calcium phosphate compounds under study are well-known. Studies of the vibrational properties by means of polarized Raman scattering measurements have been reported on HA[6] and fluorapatite (FA),[7−9] in which the observed vibrational modes could be classified according to their factor group symmetry. However, we could not find a similar study on TCP. This lack of information about the vibrational properties of TCP makes difficult an unambiguous distinction by means of Raman spectroscopy of the different calcium phosphate compounds that can be found in prosthetic implants.

In this paper we report the first Raman-scattering study on crystalline β-TCP, the tricalcium phosphate phase which in the pure state is stable below 1120 °C.[10] The study has been performed over the whole optical frequency range from 100−1200 cm^{-1}, where internal PO_4^{3-} modes and external lattice modes of β-TCP occur. Characteristic features of the Raman spectrum are discussed in relation to the crystal structure of β-TCP.

Experimental Section

Pure polycrystalline β-TCP samples were obtained from 0.7 M $Ca(NO_3)_2$ and 0.5 M H_3PO_4 solutions at pH = 11 with an initial mixing molar ratio Ca/P = 1.40 in order to avoid the formation of small quantities of Ha.[11] The precipitate was dried at 110 °C during 24 h and isostatically pressed into pellets. These were heated in an electric furnace at a rate of 5 °C/min up to 1000 °C and annealed at this temperature for 1 h. The Ca/P molar ratio of the obtained samples was

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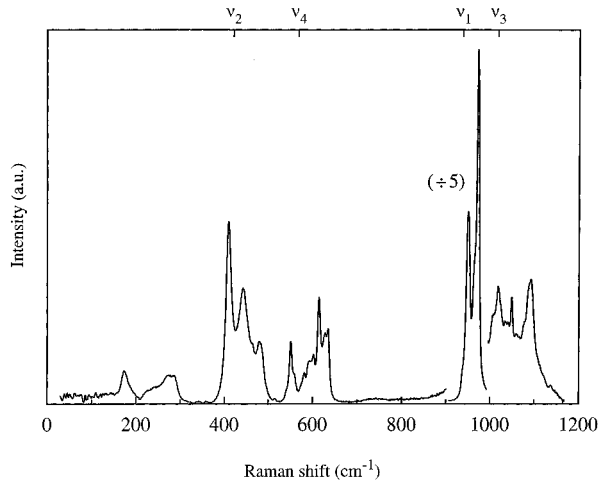

Figure 1. Room-temperature Raman spectrum of polycrystalline β-TCP over the whole optical frequency range. The normal-mode frequencies of the free PO_4^{3-} ion are indicated on the top frequency axis by ν_1, ν_2, ν_3, and ν_4.

determined by ICP-AES and found to be 1.50 ± 0.01. X-ray diffraction analysis of the samples revealed a pure β-TCP phase with no detectable presence of any other calcium phosphate phase. The obtention of pure β-TCP after heating at temperatures around 1000 °C using a low initial mixing Ca/P ratio has previously been reported.[12,13]

The Raman scattering measurements were performed using a Raman microprobe instrument consisting of a Jobin-Yvon T64000 spectrometer equipped with a microscope which allows a spatial resolution on the sample of about 1 μm. The Raman signal was detected by a multichannel CCD detector cooled with liquid nitrogen. Raman spectra over the whole optical frequency range were recorded using the subtractive configuration of the spectrometer, with a spectral resolution of about 2 cm^{-1}. To improve the resolution of closely spaced peaks, high-resolution scans of some frequency regions were recorded using the triple additive configuration, with a spectral resolution better than 1 cm^{-1}. The light was collected in backscattering geometry through an objective of numerical aperture 0.95. The 488 nm line of an Ar^+ laser was used as excitation, focused in a spot of ≈1 μm in diameter, with an incident power on the sample of ≈2 mW. Due to the polycrystalline nature of the samples studied, the Raman spectra were recorded without polarization analysis.

Results and Discussion

It is well-known that in complex ionic crystals two distinct kinds of vibrational modes exist,[14] namely external modes, in which well-defined complex ionic groups vibrate as rigid units, and internal modes, which involve atomic vibrations of the complex ionic groups that leave their center of mass stationary. The vibrational modes associated with the internal modes of the PO_4^{3-} complex ion have been observed in the Raman spectra of other calcium phosphates, namely in HA[6] and fluorapatite.[7−9] In fact, the peaks that originate from the internal modes dominate the Raman spectra of these compounds.

In Figure 1 we show the room-temperature Raman spectrum of polycrystalline β-TCP over the entire optical frequency range. Besides the peaks at 949 and 970 cm^{-1} which display the highest intensity of the spectrum, four other distinct bands can be observed in the frequency ranges 150−300, 370−505, 530−645, and 995−1120 cm^{-1}. As we shall discuss below, and in analogy with other calcium phosphates,[7−9] the latter three bands and the peaks at 949 and 970 cm^{-1} can be associated with internal vibrations of the PO_4^{3-} ions, whereas the less intense band at 150−300 cm^{-1} is due to external lattice modes.

The isolated PO_4^{3-} tetrahedron has T_d symmetry, and its 15 vibrational modes reduce to $A_1 + E + T_1 + 3T_2$, where the E representation is doubly degenerate and T_1 and T_2 are triply degenerate. The T_1 modes, corresponding to free rotations, and the modes belonging to one of the T_2 representations which correspond to rigid translations have zero frequency. The nine remaining modes have nonzero frequency and are decomposed as $A_1 + E + 2T_2$ in the irreducible representations of T_d. The mode belonging to the A_1 representation corresponds to the symmetric stretching (ν_1) of the P−O bonds of the tetrahedron, and therefore it yields the highest Raman intensity. One of the triply degenerate T_2 modes corresponds to the asymmetric stretching (ν_3) involving also P motion, whereas the other T_2 mode and the doubly degenerate E mode correspond to O−P−O bending deformations of the tetrahedron, ν_4 and ν_2, respectively. The experimental frequency values of the free PO_4^{3-} modes commonly quoted in the literature[7,8,15] were obtained by Raman measurements dating back to the 1930s.[16] More recent determinations of the vibrational modes of the free PO_4^{3-} ion by means of infrared and Raman scattering measurements on phosphates in aqueous solution[9,17] report higher values for ν_2 and ν_4 and lower values for ν_1 and ν_3 by about 50 cm^{-1} in relation to the earlier results. The PO_4^{3-} stretching frequencies reported in a recent Raman study of solutions of simple phosphates[18] are in good agreement with the results of refs 9 and 17. In accord with refs 9, 17, and 19, we shall consider the free PO_4^{3-} mode frequencies to be $\nu_1 = 938$ cm^{-1}, $\nu_2 = 420$ cm^{-1}, $\nu_3 = 1017$ cm^{-1}, and $\nu_4 = 567$ cm^{-1}.

In the complex ionic crystal, two main effects contribute to induce significant shifts and splittings of the vibrational frequencies of the PO_4^{3-} group in relation to the free ion normal modes. First, the local crystalline site field created by the surrounding ions, whose symmetry is a subgroup of the lattice symmetry and of the molecular symmetry, distorts the PO_4^{3-} tetrahedron. This lowers the symmetry of the free ion and gives rise to the splitting of the degenerate modes of the tetrahedron. Moreover, the changes in the intratetrahedral bond lengths and angles induced by the local site field give rise to variations of the force constants and, consequently, to further energy shifts of the tetrahedron modes. These are the site symmetry effects. On the other hand, the coupling between similar modes of different, but equivalent, tetrahedra produces cooperative excitations of the PO_4^{3-} groups in the unit cell, which, in accordance with the factor group symmetry

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Table 1. Factor Group Analysis (C_{3v}) of the Internal Modes of the PO_4^{3-} Tetrahedra in β-TCP[a]

free PO_4^{3-} tetrahedron		PO_4^{3-} tetrahedra in β-TCP		
internal modes	T_d symmetry	no. of modes	C_1 site symmetry	C_{3v} factor group symmetry
ν_1	$A_1^{(R)}$	42	$42(A^{(RI)})$	$7A_1^{(RI)} + 7A_2^{(0)} + 14E^{(RI)}$
ν_2	$E^{(R)}$	84	$42(2A^{(RI)})$	$14A_1^{(RI)} + 14A_2^{(0)} + 28E^{(RI)}$
ν_3	$T_2^{(RI)}$	126	$42(3A^{(RI)})$	$21A_1^{(RI)} + 21A_2^{(0)} + 42E^{(RI)}$
ν_4	$T_2^{(RI)}$	126	$42(3A^{(RI)})$	$21A_1^{(RI)} + 21A_2^{(0)} + 42E^{(RI)}$

[a] (R) = Raman active, (RI) = Raman and infrared active, (0) = inactive.

of the crystal, causes further frequency splittings relative to the normal mode frequencies of equivalent PO_4^{3-} tetrahedra. Thus, the modes of independent PO_4^{3-} groups, which transform as the representations of the site symmetry group, are split by the correlation field effect into β-TCP modes transforming as the representations of the factor group of the crystal.[20]

The crystal structure of β-TCP was determined by X-ray diffraction measurements by Dickens et al.[10] They found that β-TCP crystallizes in the rhombohedral space group $R3c$ and its unit cell contains 21 [$Ca_3(PO_4)_2$] formula units. The β-TCP structure can be regarded as a distortion of the much more regular structure of $Ba_3(PO_4)_2$,[21] where due to the smaller coordination polyhedra of Ca^{2+}, the PO_4^{3-} groups are tilted and some PO_4^{3-} groups are omitted, and the crystal structure contains cation sites with half occupancy.[10] As a consequence of the distortion of the $Ba_3(PO_4)_2$ structure to accommodate the Ca^{2+} cation, in the β-TCP structure there are five different coordination environments for Ca^{2+} and three different coordination environments for the PO_4^{3-} ions. Thus the β-TCP structure contains three types of crystallographically nonequivalent PO_4^{3-} groups located at general points of the crystal, each type with different intratetrahedral bond lengths and angles. Furthermore, analysis of the X-ray data suggests the existence of positional disorder of one of the PO_4^{3-} groups related to the partial occupancy of certain cation sites, as the presence of Ca^{2+} alters significantly the tilts of the neighboring PO_4^{3-} ion.[10] The structural complexity of the β-TCP crystal leads to a significant dispersion of the bond lengths and bond angles which, within the PO_4^{3-} tetrahedra, range from 1.498 to 1.548 Å for the P−O bond lengths and from 104.9° to 115.9° for the O−P−O angles.[10] Therefore a substantial effect of the tetrahedral distortion on the internal mode frequencies is to be expected in β-TCP. Taking into account that the unit cell of β-TCP contains 42 PO_4^{3-} tetrahedra and that each tetrahedron has nine nonzero frequency modes, 378 internal PO_4^{3-} modes are expected in β-TCP, which, according to the factor group analysis, are split by the crystal field as shown in Table 1. C_1 site symmetry splits the doubly degenerate ν_2 and the triply degenerate ν_3 and ν_4 modes of the tetrahedra and leads to 42 identical sets of nine different frequencies. C_{3v} factor group symmetry further splits these modes as shown on the fifth column of Table 1.

Detailed lattice dynamics models of calcium phosphates are available only for FA.[22] Given the close similarities between the Raman spectra of FA and β-TCP, the results of the FA models can be used for a discussion of the Raman spectrum of β-TCP. In FA, the frequencies of the internal PO_4^{3-} modes calculated through a polarizable ion model[22] were found in groups centered at frequencies slightly higher than those of the free PO_4^{3-} ion, in good agreement with the observed peaks in the Raman spectra of FA.[7−9] In Figure 1, well-defined Raman scattering bands can be observed close to the frequencies of the free PO_4^{3-} modes. The centers of the PO_4^{3-} internal bands are shifted to higher energy by 20−30 cm^{-1} in relation to the free PO_4^{3-} ion frequencies, suggesting a strong crystalline site field in the β-TCP crystal.

Table 2. Frequencies and Widths (in cm^{-1}) of the Peaks Observed in the Raman Spectrum of β-TCP[a]

lattice modes		internal PO_4^{3-} modes							
		ν_1		ν_2		ν_3		ν_4	
ω	Γ	ω	Γ	ω	Γ	ω	Γ	ω	Γ
170	19	946	6	405	14	1005(w)	10	547	7
204−305[b]		949	4	439	30	1016	14	555(w)	6
		961(sh)	12	460(w)	6	1031(w)		578	10
		970	6	475	11	1038(w)		588	11
				483	9	1046	6	599	13
						1059(w)		611	7
						1074(w)	7	624	7
						1084	10	631	13
						1091	12		

[a] The full widths at half height have been determined, where meaningful, from Lorentzian fits to the observed peaks [(sh) = shoulder, (w) = weak]. [b] A broad and featureless band is observed in this frequency region.

Between 930 and 980 cm^{-1}, in the frequency region of the PO_4^{3-} symmetric stretching, two peaks, at 949 and 970 cm^{-1}, and a shoulder, at 961 cm^{-1}, can be observed in Figure 1. By contrast to other calcium phosphate compounds such as HA and FA, a sizeable splitting of the internal PO_4^{3-} symmetric stretching modes is observed in β-TCP. This splitting probably reflects the significant differences in the intratetrahedral P−O bond lengths for the different nonequivalent PO_4^{3-} ions of the β-TCP structure discussed above. Harrison[23] showed that in tetrahedral sp^3 hybrid bonds the bond-stretching force constant depends on the equilibrium bond length through a −4 power law. Taking into account that according to the X-ray diffraction results, the variation of the P−O bond lengths of the PO_4^{3-} tetrahedra in the β-TCP structure is around 0.05 Å, the d^{-4} dependence of the bond-stretching force constant gives variations of the bond-stretching force constant of about 15% which induce substantial shifts in the normal-mode energies of the tetrahedron. In general, the frequency shifts and splittings for a given tetrahedron mode will be different for the three different types of nonequivalent and distorted tetrahedra, leading to a dispersion of the internal PO_4^{3-} modes in β-TCP.

As in HA and FA, the splitting of the symmetric-stretching mode energies by the correlation effects is very small. In Table 2 we list the frequencies and widths of the Raman peaks of β-TCP determined from high-resolution scans of the Raman scattering bands observed in the spectrum of Figure 1. From the total

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of $7A_1 + 14E$ Raman-active modes originating from the ν_1 free-tetrahedron mode which are predicted by group theory, only two Raman peaks at 949 and 970 cm^{-1} and a shoulder at 961 cm^{-1} were observed in the spectrum of Figure 1. However, high-resolution measurements performed on this frequency region revealed that the broad peak observed at $\approx$949 cm^{-1} is the result of the overlapping of two closely spaced peaks at 946 and 949 cm^{-1}.

A wider spread is observed in the bands originated from the degenerate modes of the tetrahedron. Since the PO_4^{3-} ions are located at general points of the crystal, the site symmetry (C_1) contains only the identity representation (A) and lifts completely the degeneracy of the tetrahedron modes. However, since there is a large number of equivalent tetrahedra in the unit cell, a high degree of degeneracy still remains. Then, correlation effects split the equivalent A modes arising from all the equivalent PO_4^{3-} tetrahedra in the unit cell into representations of the β-TCP factor group symmetry. Thus, according to Table 1, group theory predicts $21A_1 + 42E$ Raman active modes originating from the triply degenerate ν_3 asymmetric stretching modes of the tetrahedron. As seen in Figure 1, the Raman scattering by internal asymmetric stretching modes form a band extending from 995 to 1120 cm^{-1}. In addition to several structures detected in this frequency region, three main peaks can be observed at 1016, 1046, and 1090 cm^{-1}. As can be seen from Table 2, the peaks at 1016 and 1090 cm^{-1} are significantly broader than the peak at 1046 cm^{-1}, suggesting the overlapping of a large number of modes very close in energy around those frequencies.

Similarly, group theory predicts $14A_1 + 28E$ Raman active modes originating from the ν_2 tetrahedron modes. As can be seen from Figure 1 and Table 2, in the frequency region between 370 and 505 cm^{-1} where these modes occur, three broad peaks are detected at 405, 439, and 475 cm^{-1}. Considering the high sensitivity of the ν_2 modes to O−P−O bond angles, the large widths of the peaks observed in this region (see Table 2) suggests contributions from internal ν_2-type modes very close in energy due to small disorder-induced angular distortions of the tetrahedra, and weak coupling between ν_2 modes of different tetrahedra.

The β-TCP modes that originate from the triply degenerate ν_4 bond-bending tetrahedron modes can be observed in the frequency region between 530 and 645 cm^{-1}, where a multiplicity of peaks is detected. The strongest and more distinct peaks in this region are found at 547 and 624 cm^{-1}. From Table 2 we can see that the Raman peaks corresponding to ν_4-type modes are narrower than peaks corresponding to ν_2-type modes. It is well-known that the tetrahedron ν_2 modes are of purely bond-bending character, whereas the ν_4 modes contain a small stretching component.[15] Taking into account that the relative bond angle variation in β-TCP is about 10% while the relative variation of bond lengths is only about 3%, the ν_2-type modes of β-TCP, whose energy is determined by interactions depending on the O−P−O angles, are expected to be more sensitive to small variations of the O−P−O bond angles than the ν_4-type modes, for which the energy contains also a bond-stretching contribution.

As can be seen in Figure 1, the four β-TCP Raman scattering bands arising from the internal PO_4^{3-} modes ν_1, ν_2, ν_3, and ν_4, are centered around frequencies 20−30 cm^{-1} higher than those of the corresponding free PO_4^{3-} modes. This shift to higher energies reflects the decrease in intratetrahedral bond lengths and angles which are necessary to accommodate the PO_4^{3-} ion into the β-TCP crystal structure.

Lattice dynamics models of FA yield Raman-active PO_4^{3-} librational modes in the energy range 231−289 cm^{-1} and translational modes of the Ca^{2+} and PO_4^{3-} sublattices between 44 and 306 cm^{-1}.[22] In the low-frequency range of the β-TCP spectrum, between 150 and 350 cm^{-1}, two featureless, broad bands are observed which, by analogy with the calculated FA modes, can be tentatively associated with vibrational modes of mainly translational character of the Ca^{2+} and PO_4^{3-} sublattices, and modes of mainly PO_4^{3-} librational character. Apart from the peak at 170 cm^{-1}, no other peaks are resolved in this region. This is probably due to disorder in the β-TCP lattice, which as already discussed, contains cation sites with half occupancy and positional disorder of some PO_4^{3-} groups which may induce a broadening of the modes involving the motion of the Ca^{2+} and PO_4^{3-} sublattices. Also, the large number of different ionic environments for the Ca^{2+} and PO_4^{3-} ions in the β-TCP structure and, consequently, the differences in force constants may play a role in the fact that we have not observed distinct Raman peaks in this region.

Conclusions

For the first time the Raman spectrum of a crystalline TCP has been reported over the whole optical frequency range, and the observed features have been discussed in terms of the available structural information on the crystal structure. Considering the great complexity of the β-TCP unit cell, which has 819 degrees of freedom, including rigid translations and rotations, the identification of all the vibrational modes is out of question. However, clearly separated bands corresponding to internal PO_4^{3-} modes were observed in the Raman spectrum of polycrystalline β-TCP, confirming the strong molecular character of the crystal as regards to vibrational properties. The frequencies and widths of the characteristic peaks which can be resolved in each band were accurately determined. The splitting of the internal PO_4^{3-} symmetric stretching modes was observed and attributed to the effects of the distortions of the phosphate ions and the consequent spread of intratetrahedral bond lengths. Although the Raman spectra is dominated by the internal PO_4^{3-} modes, external modes associated to vibrations of the Ca^{2+} and PO_4^{3-} sublattices, and to rotational PO_4^{3-} modes, were also observed in the low-frequency region of the spectrum. The disorder in the β-TCP crystal structure related to the partial occupancy of certain cation sites is reflected in the broad, featureless low-frequency band due to external lattice modes.

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