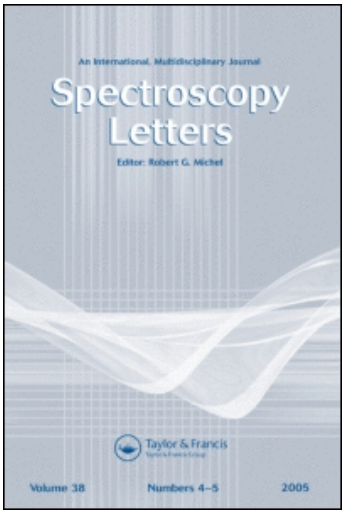

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The Infrared and Raman Spectra of Tetracalcium Phosphate ($Ca_4P_2O_9$)

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THE INFRARED AND RAMAN SPECTRA OF TETRACALCIUM PHOSPHATE ($Ca_4P_2O_9$)

KEY WORDS : Tetracalcium phosphate, $Ca_4P_2O_9$, Raman Spectrum, Infrared Spectrum, Structure

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ABSTRACT

The infrared and Raman spectra of tetracalcium phosphate ($Ca_4P_2O_9$) were measured and interpreted on the basis of factor group analysis. Factor group splitting can be noted for the various internal vibrational modes of the PO_4^{3-} ion. However, a fewer number of factor group-split bands can be seen than predicted because of either the weak intensities of these bands or the convolution of such bands for the various internal modes of vibration.

INTRODUCTION

Calcium phosphates are a broad class of materials that have been the subject of extensive study, due to their varied application as biomaterials in prosthetic devices [1-4]. This class of materials encompasses a variety of minerals, including tricalcium phosphate ($Ca_3(PO_4)_2$), hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), calcium pyrophosphate ($Ca_2P_2O_7$), tetracalcium phosphate ($Ca_4P_2O_9$) and calcium metaphosphate ($Ca(PO_3)_2$). Hydroxyapatite and β-tricalcium phosphate are the most interesting phases due to their behavior in biological environments, with hydroxyapatite exhibiting bioinert characteristics and β-tricalcium phosphate showing a

bioactive response [5,6]. The response of the related materials in various environments is very sensitive to the chemistry, structure and morphology of these phases. Hence, reliable characterization with respect to these phases is very critical in their bioapplications. FT-IR and Raman spectroscopy are vibrational characterization techniques that provide a viable means to identify and study these phases, providing information that allows distinguishing very subtle changes in the material chemistry and structure. The vibrational spectra of hydroxyapatite[7] and calcium pyrophosphate[8] have been well characterized, and suitable band assignments have been made.

Tetracalcium phosphate is a commonly encountered phase during the solid state preparation and thermal decomposition of hydroxyapatites. Hydroxyapatite can be prepared by the reaction of dicalcium phosphate ($CaHPO_4$) and calcium tetraphosphate on the basis of the following reaction[9] :

$$4\ CaHPO_4 + 2\ Ca_4P_2O_9 \text{ --- } Ca_{10}(PO_4)_6(OH)_2 + 2\ CaHPO_4\ .$$

Tetracalcium phosphate is also commonly encountered as a decomposition product of HA, upon sintering of HA at temperatures over 1200 °C [10]:

$$Ca_{10}(PO_4)_6(OH)_2 = 2Ca_3(PO_4)_2 + Ca_4P_2O_9 + H_2O\ .$$

However, the vibrational spectrum of calcium tetraphosphate has not been studied in detail. This type of study would involve the preparation of phase-pure tetracalcium phosphate and the application of factor group analysis of the vibrational spectra to identify the molecular and structural vibrations responsible for the observed Raman and mid-IR spectral bands. The factor group analysis would also relate the ion vibrational modes to the crystal unit cells's vibrational modes. This type of investigation has been conducted in this paper.

EXPERIMENTAL PROCEDURE

A. Preparation of Tetrcalcium phosphate.

Tetracalcium phosphate was prepared by a solid state reaction between $CaHPO_4$ and calcium carbonate $CaCO_3$ as per the reaction:

$$2\ CaHPO_4 + 2\ CaCO_3 = Ca_4P_2O_9 + CO_2 + H_2O.$$

A batch containing equimolar amounts of $CaHPO_4$ and calcium carbonate was thoroughly mixed in an alumina crucible, placed in a Molybdenum Disilicide furnace, and heated at 1500 °C for 24 hours. After firing, the sample was allowed to cool down to room temperature in the furnace. The formed powder was crushed to break up any agglomerates, and was characterized by x-ray diffraction.

B. X-Ray Diffraction Technique.

The $Ca_4P_2O_9$ powder was examined for phase purity on a Siemens Kristalloflex 810 X-ray diffractometer, using a Cu target generating the K_α radiation (accelerating potential = 40 KV, current = 30 mA) with a wavelength of 0.15412 nm. The x-ray diffraction pattern of the powder as shown in Figure 1 indicates the presence of only tetracalcium phosphate.

C. Raman and FT-IR Spectral Techniques.

The FT-IR spectrum of the tetracalcium phosphate powder was obtained using a Nicolet 60-SX mid-IR spectrometer, with a CO_2 and H_2O purging system. The IR transmission spectrum of the sample was examined in the form of KBr pellets which were made by mixing 1 mg of the sample powder with 300 mg of spectroscopic grade KBr. The pellets were pressed under a pressure of 1200 psi.

The Raman spectrum of the powder was obtained by examining the scattered light from a powder held in a capillary tube using an ISA U-1000 Mole double monochromator Raman spectrometer. The spectrum was obtained at a 90° scattering geometry, with the 514.532 nm laser excitation line from a Coherent Ar^+-ion laser source. The laser power at the sample was maintained at 100mW. The Raman spectrometer was calibrated using the Raman band of TiO_2 present at 142 cm^{-1}.

RESULTS AND DISCUSSION

A. Crystal Structure and Spectral Prediction for Tetracalcium Phosphate.

Tetracalcium phosphate crystallizes with a monoclinic unit cell (a = 0.7023nm , b = 1.1986nm, c = 0. 9473nm, β= 90.90 °) that is associated with the space group C_2 - $P2_1$ and is comprised of four formula units. This unit cell contains four pairs of equivalent C_1 sites where the P atoms of the PO_4^{3-} ions are accomodated. Thus, the Bravais unit cell possesses eight sites of C_1 symmetry that accomodate the phosphate atoms. The atomic arrangement for $Ca_4P_2O_9$ is illustrated in figure 2. Unlike most calcium phosphates, there are no known crystallographic equivalents to this crystalline phase in this structure. $Ca_4P_2O_9$ does not fall into the family of crystal structures known as " apatites" due to lack of oxide or hydroxyl ions that lie in a channel formed by cations in the structure of the cell. Instead, the discrete isolated oxide ions are surrounded by tetrahedra of Ca ions [10]. Dickens et al. [10] have ascribed the extensive twinning behavior exhibited by these crystals to the positions occupied by the P and Ca atoms in their structure, which are close to those satisfying the P_{mcn} space group.

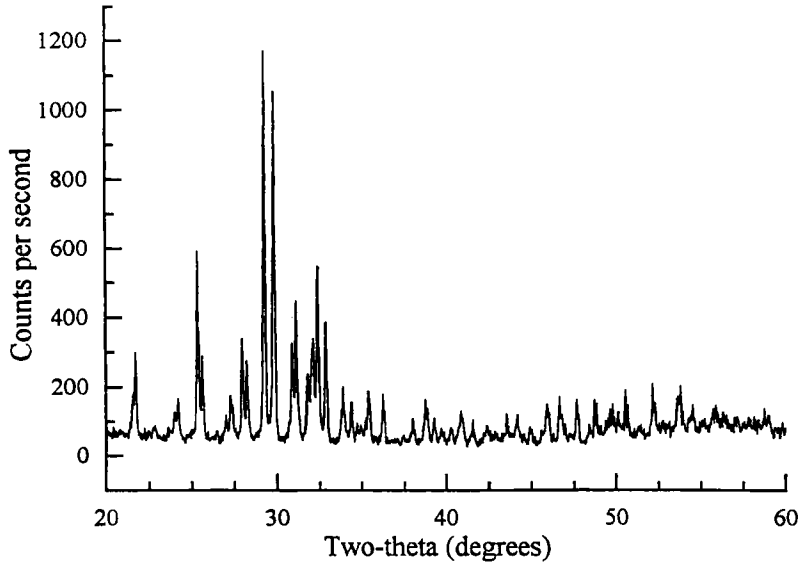

FIG. 1. X-ray diffraction pattern of tetracalcium phosphate.

Factor group analysis for this crystalline phase using Fateley's method [11] predicts 177 vibrational modes of motion for this crystal structure,

$$\Gamma_{vib}(Ca_4P_2O_9) = \Gamma_{Ca} + \Gamma_P + \Gamma_O - \Gamma_{acoustical}$$
$$= 90\,A + 90\,B - (A + 2\,B)$$
$$= 89\,A + 88\,B,$$

which include the internal vibrational modes of the phosphate ion along with the other lattice modes of vibration. All of these modes are coincidentally both IR and Raman active. However, this interpretation format is not convenient for analyzing the infrared and Raman spectra in terms of specific internal vibrational modes for the phosphate ion. To do this, one needs to correlate the free ion modes of the phosphate ion with those of the related factor group-split bands for the unit cell of the crystalline phase in which they reside. This technique uses the method of Winston and Halford (12). Such correlation of the symmetry species for the T_d -free ion group to the C_2- factor group through the C_1 site group leads to the predicted splitting pattern for the fundamental internal vibrational modes that is summarized in Table 1. This table is representative of the factor group splitting for one set of PO_4^{3-} ion and has been developed assuming four pairs of C_1 sites for

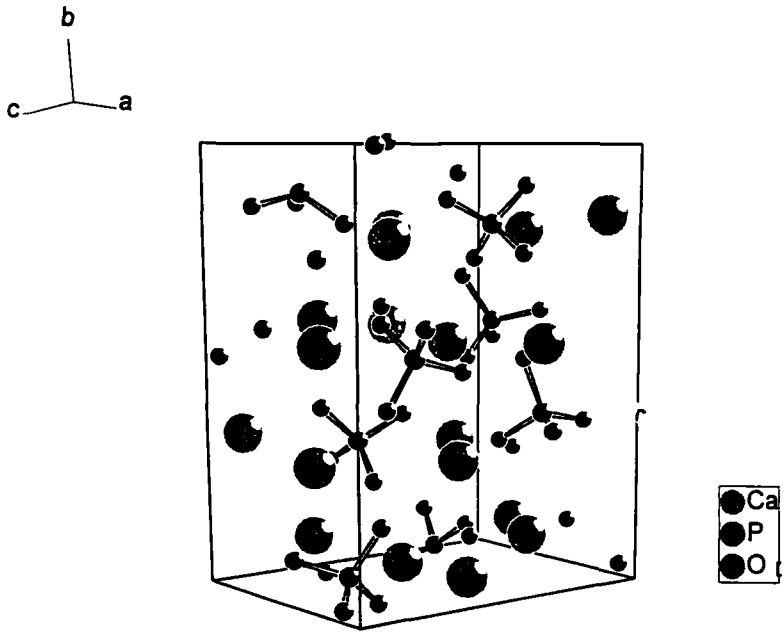

FIG. 2. Atomic arrangement in a $Ca_4P_2O_9$ unit cell.

the phosphate ions. The fundamental vibrational modes for the isolated PO_4^{3-} ion are designated as ν_1, ν_2, ν_3 and ν_4. Vibrations due to the symmetric stretching motion of the P-O bonds correspond to ν_1 , while the double degenerate bending vibrations correspond to ν_2. The triply degenerate F_2 modes are due to the asymmetric stretching vibrations whose wavenumber is represented as ν_3, and to the O-P-O asymmetric bending vibrations whose wavenumber is represented as ν_4 . This table considers the internal vibrations of the PO_4^{3-} ions only, and ignores the translatory and rotatory modes. Using the appropriate character tables, IR and Raman activity for the fundamental vibrational modes can be determined and summarized by the convenient format in Table 2. As can be seen from Table 2, the correlation method predicts that the phosphate ions in the Bravais unit cell should have a total of 72 vibrational bands which are coincident in the infrared and Raman spectra. Of these factor group- split vibrational bands,eight first order bands can be attributed to the ν_1 fundamental vibrational mode of the phosphate ion. Similarly, the ν_2 fundamental mode will exhibit 16 vibrational bands. The ν_3 and ν_4 fundamental

Table 1. Correlation Table for one set of PO_4^{3-} ions in $Ca_4P_2O_9$

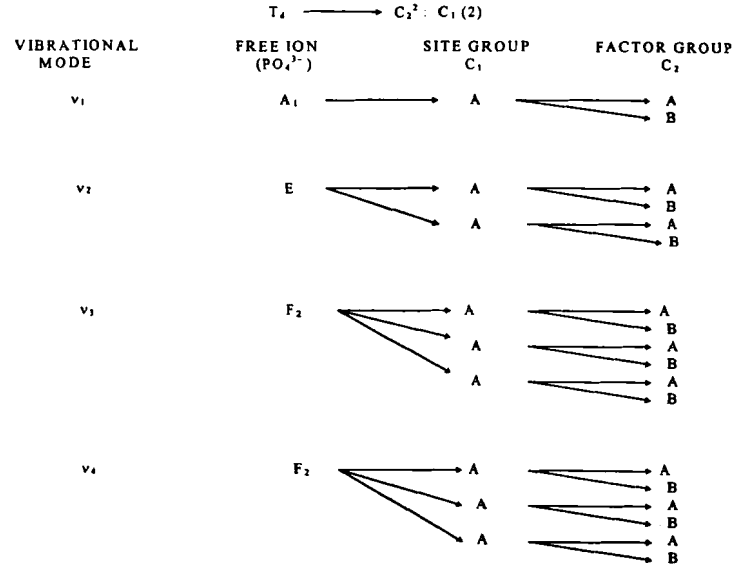

Table 2. Resultant Spectral Activity and Coincidences for the 4 sets of PO_4^{3-} ions at C_1 sites

FUNDAMENTAL MODE DESIGNATION	FREE PO_4^{3-} ION (T_d)			SITE GROUP (C_1)			FACTOR GROUP (C_2) (COMPLETE SETS OF PO_4^{3-} IONS)		
	IR	RAMAN	COINC.	IR	RAMAN	COINC.	IR	RAMAN	COINC.
ν_1	0	1	0	1	1	1	8	8	8
ν_2	0	1	0	2	2	2	16	16	16
ν_3	1	1	1	3	3	3	24	24	24
ν_4	1	1	1	3	3	3	24	24	24
TOTALS	2	4	2	9	9	9	72	72	72

modes due to their triple degeneracy will have 3 times as many vibrational bands than ν_1, and hence we see that there should be 24 vibrational bands that correspond to each of these latter fundamental modes.

B. Comparison of Observed Vibrational Spectra with Theoretical Predicitions:

Figures 3 and 4 illustrate the FT-IR and Raman spectra of the prepared $Ca_4P_2O_9$ sample. Comparing these predictions with the experimentally obtained FT-IR and Raman spectra presents a different picture. One may notice that the number of vibrational bands seen in each spectrum is fewer than those predicted by group theory. For instance, examination of the experimentally obtained Raman spectrum indicates the presence of 18 distinct bands in the internal mode region. Similarly, the infrared spectrum shows only 16 individually discernible bands in this region. This discrepancy however, is not surprising. This can be attributed to a number of different factors. Though the theoretical predictions tell us how many bands will be present, they do not give any information about the intensities of these bands and their wavenumber positions. Thus, quite a few bands that are of significantly weak intensity might not be detected in the Raman and FT-IR spectra due to the sensitivity limitations of the instruments. Also, some factor group-split bands may be convoluted over each other, cutting down the number of individually observed bands.

In the absence of factor group splitting, the ν_1 fundamental mode of the isolated PO_4^{3-} ion is characterized by a band at 938 cm^{-1}. Bands at 420 and 567 cm^{-1} are associated with the O-P-O bending modes ν_2 and ν_4, respectively, while the P-O stretching mode ν_3 is charactrized by a vibrational band at 1017 cm^{-1} [13]. Examination of the experimentally-obtained infrared and Raman spectra of $Ca_4P_2O_9$ shows the factor group splitting of these bands. The Raman spectrum shows that the band at 938 cm^{-1} splits into four intense distinct bands at ca. 940, 946, 959 and 962 cm^{-1}. The infrared spectrum shows the corresponding splitting giving rise to bands at ca. 943, 957 and 991 cm^{-1}. Weak Raman bands seen at 1046, 1075, 1091, 1100 and 1131 cm^{-1} are due to the factor group splitting of the band at 1017 cm^{-1} ascribed to triply degenerate asymmetric stretching vibrations of the P-O bond. The infrared spectrum shows corresponding bands at 1064 and 1107 cm^{-1} with weak shoulders at 1098 and 1073 cm^{-1}. Similarly, the strong infrared band observed at 1015 cm^{-1} and the weak bands at 1035 and 1049 cm^{-1} can be correlated to the splitting of the ν_3 fundamental mode. Examining figure 3, the distinct Raman bands at ca. 388, 407, 448 and 476 cm-1 are due to the factor group splitting of the band at 420 cm^{-1} due to the ν_2 fundamental mode. However, infrared bands at 458, 472 and 477 cm^{-1} and the shoulder at 438

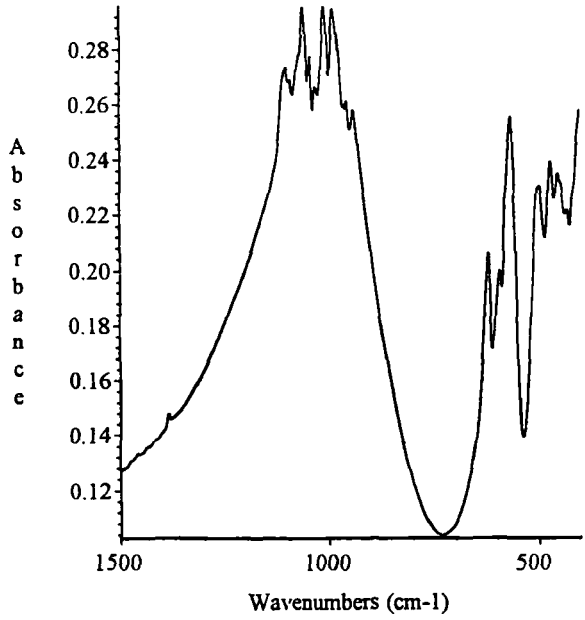

FIG. 3. FT-IR spectrum of Tetracalcium Phosphate.

cm^{-1} can be resolved to the same splitting. Similarly, the factor group splitting of the ν_4 fundamental vibrational mode gives rise to bands at 570, 594 and 621 cm^{-1} in the infrared spectrum and 557, 564, 595 and 617 cm^{-1} in the Raman spectrum.

Examining these stated band positions, it is noticed that certain bands observed in the infrared or Raman spectra do not coincide, as predicted by the factor group analysis. This can be attributed to the nature of the basic processes giving rise to the vibrational spectra or the convolution of bands that are close to each other. Bands observed in the Raman spectrum arise due to a net change in the polarizability of the vibrating unit cell, while those observed in the FT-IR spectrum are due to a net change in the dipole moment of the unit cell. In certain instances, the change in polarizability of the unit cell might be stronger than the change in dipole moment giving rise to a stong band in the Raman spectrum while not seeing one in the FT-IR spectrum. This possibility may also occur vice-versa. Also, the convolution pattern in the two types of spectra might be different giving rise to a resultant convoluted band in one type of spectrum and not in the other.

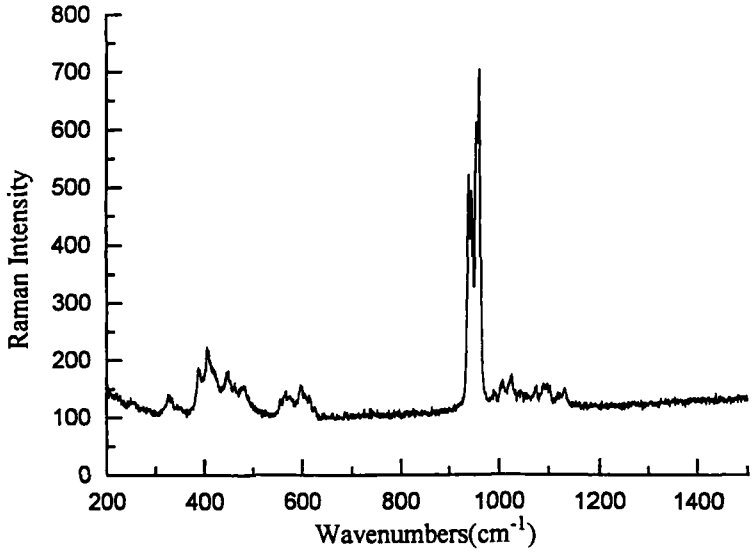

FIG. 4. Raman Spectrum of Tetracalcium Phosphate.

CONCLUSIONS :

Theoretical predictions of the spectral activity in $Ca_4P_2O_9$ indicate that the primitive cell should exhibit 72 Raman and 72 IR bands due to the factor group splitting of the internal vibrational modes of the PO_4^{3-} ion, and that all these bands are coincident in the two spectra. Differences between the predicted number of bands and those seen in the experimentally obtained spectral data are due either to the limited instrument sensitivity to detect very weakbands or to the difference in the convolution pattern of bands in the two types of spectra. Determining the wavenumber positions at which these vibrations are present would require a complete normal coordinate analysis of the vibrations in the primitive unit cell.

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