Polarized infrared reflectance spectra of brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) crystal investigation of the phosphate stretching modes

Jean-Yves Mevellec^{a,*}, Sophie Quillard^b, Philippe Deniard^a, Omar Mekmene^c, Frédéric Gaucheron^c, Jean-Michel Boulter^b, Jean-Pierre Buisson^a

^a CNRS, Institut des Matériaux Jean-Rouxel (IMN) – UMR 6502, Université de Nantes, 2 rue de la Houssinière, B.P. 32229, 44322 Nantes Cedex 3, France

^b INSERM, UMRS 791, Université de Nantes, Laboratoire d'Ingénierie Ostéo-Articulaire et Dentaire, Faculté de Chirurgie Dentaire, 1 Place Alexis Ricordeau, 44042 Nantes Cedex 1, France

^c INRA, UMR1253 Science et Technologie du Lait et de l'Oeuf, 65 rue de Saint Brieuc, 35042 Rennes Cedex, France

HIGHLIGHTS

- Polarized infrared reflectance measurements from the *ac*-plane of brushite crystal.
- Dispersion model analysis for monoclinic crystals.
- Oscillators parameters for the P–O stretching modes 800–1200 cm^{-1} .

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:

Received 8 November 2012

Received in revised form 8 March 2013

Accepted 12 March 2013

Available online 23 March 2013

Keywords:

IR polarized reflectance spectra

Dispersion analysis

Monoclinic crystal

Brushite

ABSTRACT

Polarized infrared (IR) reflectance measurements at near-normal incidence were recorded from the *ac*-plane of a monoclinic brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) crystal in the 800–1200 cm^{-1} spectral range (P–O stretching modes). The adjustment of these data, on the basis of a dispersion analysis (DA) model for monoclinic case, allowed the determination of oscillators parameters for the four P–O stretching observed modes of the phosphate group.

© 2013 Elsevier B.V. All rights reserved.

Introduction

Dicalcium phosphate dihydrate (DCPD; $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) is known as the mineral form “brushite” and it has been largely studied since its discovery in 1865. This compound is of particular importance in the biological field. It plays a role in the biomineralization processes and it is actually widely used in the composition of several

restorative materials based on calcium phosphate, for dental cements and bone implants [1].

The crystal structure of brushite has been firstly described by Beevers [2] in 1958, and investigated by several authors via X-ray Diffraction [3] or neutron scattering [4] measurements. Heijnen and Hartman [5] have also proposed a uniform description of this crystal structure with those of gypsum and pharmacolite, although their symmetries are different. Recently, first-principles calculations [6] have been also performed and reproduced well experimental XRD results. From all these different works, it is assumed that the brushite crystal is monoclinic with the following

* Corresponding author. Tel.: +33 0240373975.

E-mail address: jean-yves.mevellec@cnrs-imn.fr (J.-Y. Mevellec).

cell parameters: $a = 5.812 \text{ \AA}$; $b = 15.180 \text{ \AA}$; $c = 6.239 \text{ \AA}$; $\beta = 116.25^\circ$ and $Z = 4$ in the Ia space group. An equivalent description of the structure can be obtained in the Cc space group, with transformed cell parameters of $a = 6.358 \text{ \AA}$, $b = 15.180 \text{ \AA}$, $c = 5.812 \text{ \AA}$ and $\beta = 118.51^\circ$.

Vibrational spectroscopic investigations on monocrystals are useful to evidence the polarization of the different modes and the possible TO–LO splitting due to their polar character.

Particularly, infrared reflectance measurements can provide valuable information on the optic, dielectric and dynamic parameters of a single crystal. In 1970s, Koch and Otto [7] and later Belousov and Pavinich [8] reported a model to obtain dispersion parameters of monoclinic crystals and to calculate the oscillators strengths from the LO–TO frequency separation. Pavinich et al. applied this model to the spodumene crystal $\text{LiAlSi}_2\text{O}_6$ [9] and later, based on this previous model, some authors have successfully studied the behavior of other monoclinic compounds, like gypsum and Tutton salts [10,11]. In this work, we have chosen to use a similar, but simplified, dispersion analysis model to investigate the polarized reflectance results of brushite monocrystal.

In such monoclinic crystals, only one of the crystallographic axes (the b -axis) coincides with one of the dielectric tensor axes for all frequencies, while the other two principal axes lie in the ac -plane. These principal dielectric tensor axes are frequency dependent in the ac -plane as each polar phonon oscillator is characterized by its own orientation. Then, the polarized reflection spectra obtained from the monoclinic plane (ac -plane) are particularly interesting to evidence the difference in the orientation of the dipole moments in this plane, together with their dynamic parameters (strength, damping).

Located in the $800\text{--}1200 \text{ cm}^{-1}$ spectral range, the P–O stretching modes of such orthophosphates crystal are intense and well separated either in Raman and infrared spectroscopies, and no other bands are expected in this frequency range. Moreover, they showed a significant sensitivity to changes in the structure such as calcium substitution by other cations, as it has been reported in previous studies on brushite itself [12] and on other orthophosphates [13,14]. A clear knowledge of these modes and of their possible mixing is then of particular interest. For these reasons, we have restricted this vibrational study to the P–O stretching vibrations of this group.

Materials and methods

Preparation of crystals

Brushite crystals were prepared by dissolution of commercial dicalcium phosphate dihydrate (Riedel-de Haën, Germany) in dilute acetic acid [15]. After evaporation (heating at $\approx 70^\circ\text{C}$), predominant small tabular $\{010\}$ crystals were obtained and washed with ethanol. Typical sizes of the grown crystal are few hundred micrometers and their thickness is less than $50 \text{ }\mu\text{m}$.

Structural determination and orientation by X-ray diffraction

The monoclinic structure of the selected crystals has been confirmed by XRD measurement on a Nonius Kappa CCD diffractometer equipped with a KAPPA four-circle goniometer.

Our XRD results led to the following cell parameters in the Cc space group: $a = 6.3686 \text{ \AA}$; $b = 15.1996 \text{ \AA}$; $c = 5.8173 \text{ \AA}$; $\beta = 118.51^\circ$ and $Z = 4$, which are in a good agreement with previous works.

The orientations of the crystal axes with respect to the typical plate morphology of the crystal were already suspected, as brushite crystal habit has been widely described in literature [15,16].

However, our XRD data allowed a clear knowledge of the geometry of our crystal and its well-defined orientation for further spectroscopic measurements.

The crystal used for the infrared reflectance data have dimensions of about $650 \text{ }\mu\text{m} \times 300 \text{ }\mu\text{m} \times 40 \text{ }\mu\text{m}$. In Fig. 1, a scheme of the studied crystal is depicted showing crystal axis and orientation of the faces (Miller indices).

Infrared measurements

The FTIR absorbance of DCPD powder was measured on a Bruker Vertex 70 spectrometer, using KBr pellet technique. Near-normal infrared specular reflectance data were obtained on a Bruker Microscope «Hyperion 2000» equipped with a Mercury–Cadmium–Telluride detector and coupled with the Vertex 70 spectrometer. The analyzed surface was $100 \text{ }\mu\text{m} \times 100 \text{ }\mu\text{m}$. Infrared polarizer was placed on the incident beam. All the spectra (4 cm^{-1} as spectral resolution, 100 scans) were background corrected using reflection on gold surface. The Cassegrain infrared concentrator, focusing the IR beam on the sample, has a numerical aperture of 0.4. Thus, the collecting cone for this objective has an effective half angle of 23.6° , this value is an angular limit for the IR rays. A recent work [17] presents comparative results of reflectance for different incident angles, showing errors can appear from an angle of 16° . In spite of this, we suppose the incident and reflected beams near-normal to the main surface of the crystal (ac -plane) and the corresponding electric fields are assumed to be in this plane. So our approximations are afterward justified by the quality adjustment between experimental and calculated results for this material.

Theoretical calculations

In order to interpret the experimental reflectance data, we carried out calculations based on a dispersion analysis model, briefly described below in this paper (see Theoretical model part). The simultaneous fitting of eight selected reflectance spectra was performed using least squares refinements by our visual basic program. In this aim, 19 parameters; four for each mode and three for the high-frequency permittivity tensor were adjusted.

Results and discussion

As explained in the introduction, we have focused our attention on stretching vibrations of the phosphate groups. In this crystal, it should be noted that the phosphate group is asymmetric with four non-equivalent P–O bonds. Thus, the P–O bond with the hydroxyl oxygen (noted P–OH) has a length significantly longer than the others ($1.599 \text{ \AA}$ and 1.515 , 1.534 , $1.516 \text{ \AA}$ respectively). Consequently, local symmetry on one phosphate group can be assumed as pseudo C_{3v} [18], leading to an assignment of these stretching modes into two modes of symmetry A_1 and two degenerate modes belonging to the symmetry E . The corresponding atomic displacements are depicted in their “isolated” form (no mixing) in Fig. 2.

We can note that we have three modes for four degrees of freedom, but after the loss of vibrational degeneracy in the symmetry crystal, we have four corresponding frequencies for one phosphate group.

The crystalline form belongs to space group Cc , the associated point group Cs possesses a mirror plane as symmetry element which is the main crystal plane (ac -plane). The unit cell of brushite includes 4 HPO_4 units, but the primitive cell contains only two phosphate groups related to each other by this glide plane. So each HPO_4 vibration gives both one A' and one A'' modes, whether it is symmetric or not with regards to the ac -plane respectively. The resulting dipole moments of the A' modes are in the ac -plane, while

Fig. 1. Schematic view of crystal orientation.

Fig. 2. Schematic description of the stretching modes for an isolated phosphate group: dotted line indicates the O–H bond, the pseudo C_{3v} symmetry is indicated above.

those of the A'' modes are parallel to the b -axis. Finally, eight stretching modes are expected, separated into four A' and four A'' modes, coming from the vibrations in Fig. 2.

Both A' and A'' modes are allowed in Raman and infrared spectroscopies. Many studies reported the brushite powder spectra in the case of the infrared absorbance [19–23] and the Raman scattering [24]. All of these values and assignments of the modes have been confirmed in our study (Fig. 3a: IR absorbance spectrum of the brushite powder). For the crystalline form, we can mention the polarized Raman work realized by Casciani and Sr Condrate [25].

The IR transmission spectrum has also been registered through the ac -plane of the crystal and is reported in Fig. 3b. In this case, we expected to see the four A' modes (electric field is in the ac -plane): 874, 986, 1060 and 1135 cm^{-1} and with intensities close to the powder spectrum.

The observed differences led us to suspect a TO–LO splitting for these modes, like usually in ionic crystals.

Fig. 3. Infrared absorbance of brushite (a) powder (b) crystal with near-normal incidence on the ac -plane.

For this reason, we focus on the study of polarized reflectance of the crystal near-normally to the ac -plane. In this configuration, mainly the four A' modes of the phosphate group should be observed. As the polarizer is rotated, p-polarization should trigger the A'' modes but their intensities are expected to be much lower than the A' , and we assumed that they can be neglected in the fit.

Experimental polarized IR reflectance results

In this part, are presented the polarized IR reflectance data obtained at near-normal incidence from the ac -plane. In this aim, we defined an experimental geometric setting. The crystal axis and the reference X , Y , Z basis (named (0) in the following) are both reported in the scheme in Fig. 4.

The polarizer, which imposes the direction of the electric field, is rotated clockwise as defined by the α angle (Fig. 4). The infrared

Fig. 4. Experimental scheme of the polarized reflectance measurements conditions. X , Y , Z is the reference coordinate system ($Z = b$ is perpendicular to the scheme, normal to the ac -plane); α is the angle of polarizer and E is the direction of incident electric field.

Fig. 5. Reflectance infrared spectra from the *ac*-plane of brushite crystal for different polarization angles, in the phosphate stretching frequency range (800–1200 cm^{-1}) with near-normal incidence.

reflectance spectra were registered with α values from 0° to 180° , by step of 5° . All the angles in the following are also counted clockwise with regard to the *X* axis.

In Fig. 5 are presented the spectra for selected values (each 15°) of polarization angles, in the range 800–1200 cm^{-1} . Four broad bands can be observed and one can also notice their clear variations of intensity, upon the angle of the polarizer. In red color, are enhanced the maximum of reflectance for each observed modes. These evolutions of reflectance of the bands with regards to α angle are presented in Fig. 6.¹ When the maximum of the reflectance of a band is reached, this direction of the electric field corresponds to the polarization of the related mode.

The bands of Fig. 5 are very broad, showing a typical profile of reflectance of polar crystal [7,8,26]. For wavenumbers between the TO and LO frequencies, the electromagnetic wave is reflected. The reflectance *R* without damping (attenuation) is theoretically equal to 1, when the orientation of the electric field is along the polarization of the mode. Thus, the inflection points on the low or high frequency slopes of the curve (for example for *M*₄ in Fig. 5: 1133 cm^{-1} and 1170 cm^{-1}) should be close to the *A'*(TO) and *A'*(LO) frequencies respectively. Moreover, the *A'* values can be compared to those obtained via the IR absorption spectrum of the brushite powder (Fig. 3a). For simplicity, we have numbered these four observed modes as *M*₁–*M*₄, (see in Fig. 5), as their frequencies increase. In order to obtain more information, we have performed some calculations to reproduce the experimental reflectance results.

Theoretical model

Several detailed presentations of dispersion analysis model has been already published elsewhere [7,8,27,28]. However, it appears

Fig. 6. Experimental evolution of the intensities of the reflectance with regards to the polarization angle for the four stretching modes.

to be useful to briefly remind the main results required to our calculations, as the specific approximations we added. The *A'* modes have their dipoles moments in the *ac*-plane with different directions of their polarization. As a consequence, two of the principal dielectric tensor axes are frequency dependent in this *ac*-plane and they are noted *X* _{ω} and *Y* _{ω} in the following. The third axis is aligned with *b* and it does not show any frequency dependence.

For frequency values close to one mode *k*, one of the tensor principal axes is aligned with the direction of polarization of the mode. If we consider only the *ac*-plane, the contribution of the mode *k* to the dielectric tensor can be written in this particular axis system:

$$\varepsilon_k = \begin{bmatrix} \varepsilon_k(\omega) & 0 \\ 0 & 0 \end{bmatrix} \text{ with } \varepsilon_k(\omega) = \frac{\Delta\varepsilon_k \cdot \omega_{kTO}^2}{(\omega_{kTO}^2 - \omega^2) + i\omega\gamma_{kTO}}$$

where ω_{kTO} is the transverse frequency for the mode *k*, γ_{kTO} the damping (attenuation constant) and $\Delta\varepsilon_k$ the dimensionless oscillator strength. By a rotation of an angle θ_k , this tensor can be written in the reference basis (0) and we have $\varepsilon_k^0 = R(-\theta_k)\varepsilon_k R^{-1}(-\theta_k)$ in which $R(-\theta_k)$ is the rotation matrix. This first step gives four parameters for each mode.

The high-frequency permittivity tensor (electronic permittivity) ε_∞ can be also expressed in a diagonal form using a convenient base:

$$\varepsilon_\infty = \begin{bmatrix} \varepsilon_{x_\infty} & 0 \\ 0 & \varepsilon_{y_\infty} \end{bmatrix}.$$

As previously, introducing the angle θ_∞ , we can write the ε_∞ tensor in the (0) basis and finally obtain:

$$\varepsilon^0(\omega) = \varepsilon_\infty^0 + \sum_{k=1}^4 \varepsilon_k^0 \quad (1)$$

We can define $\theta(\omega)$ as the angle between the *X*, *Y* reference basis (0) and the *X* _{ω} , *Y* _{ω} frequency-dependent basis.

$$\varepsilon(\omega) = R(\theta(\omega))\varepsilon^0(\omega)R^{-1}(\theta(\omega)) \quad (2)$$

In this *X* _{ω} , *Y* _{ω} basis, the dielectric tensor can then be reduced to the following diagonal 2×2 matrix form:

$$\varepsilon(\omega) = \begin{bmatrix} \varepsilon_{x_\omega}(\omega) & 0 \\ 0 & \varepsilon_{y_\omega}(\omega) \end{bmatrix}$$

By this way, even if the principal axes for real and imaginary parts do not coincide in such monoclinic system, we have found frequency dependent principal axes for which the real and imaginary parts of the out-of diagonal terms are lowered.

¹ For interpretation of color in Fig. 6, the reader is referred to the web version of this article.

Table 1

Experimental and calculated parameters of the four stretching modes of the phosphate group. The experimental frequencies ($\omega_{k\text{TOexp}}$) are measured on our Raman spectra and the $\theta_{k\text{exp}}$ angles from Fig. 6 after fitting of the curves. The calculated parameters are obtained with our dispersion analysis model. $\omega_{k\text{TO}}$ is the transverse frequency, θ_k the polarization angle, $\Delta\epsilon_k$ the oscillator strength, $\gamma_{k\text{TO}}$ the damping and $\omega_{k\text{LO}}$ the longitudinal frequency. The index k referred to the number of the mode.

Mode M_k	Experimental data		Calculated results				
	$\omega_{k\text{TOexp}}$ (cm^{-1})	$\theta_{k\text{exp}}$ ($^\circ$)	$\omega_{k\text{TO}}$ (cm^{-1})	θ_k ($^\circ$)	$\Delta\epsilon_k$	$\gamma_{k\text{TO}}$ (cm^{-1})	$\omega_{k\text{LO}}$ (cm^{-1})
M_1	874	34°	875	35	0.0627	14.93	889
M_2	985	70°	985	74	0.0799	11.60	1003
M_3	1056	172°	1056	167	0.1693	17.32	1091
M_4	1133	108°	1131	105	0.1458	11.06	1178

This “diagonalization” according to ω of the dielectric matrix is performed to obtain the angle $\theta(\omega)$ and finally, one can calculate the $\epsilon_{x\omega}(\omega)$, $\epsilon_{y\omega}(\omega)$ et $\theta(\omega)$ using (1), with 19 parameters:

4 ($\Delta\epsilon_k$, $\gamma_{k\text{TO}}$, $\omega_{k\text{TO}}$, θ_k) for each TO mode k and $\epsilon_{x\infty}$, $\epsilon_{y\infty}$ and θ_∞ .

The normal reflectance R at the angle of polarization α of the incident electric vector lying in the ac -plane is given by

$$R = \cos^2(\alpha - \theta(\omega))R_{x\omega} + \sin^2(\alpha - \theta(\omega))R_{y\omega} \quad (3)$$

$$\text{where } R_{x\omega} = \left| \frac{\sqrt{\epsilon_{x\omega}(\omega)} - 1}{\sqrt{\epsilon_{x\omega}(\omega)} + 1} \right|^2; R_{y\omega} = \left| \frac{\sqrt{\epsilon_{y\omega}(\omega)} - 1}{\sqrt{\epsilon_{y\omega}(\omega)} + 1} \right|^2.$$

This expression is equivalent to the results of Belousov and Pavinich [8] if the out of diagonal terms are assumed to be negligible.

The reflectance spectra have been simulated using Eqs. (1)–(3). The adjustment of these 19 parameters was done to reproduce the experimental spectra.

The experimental and calculated spectra are presented in Fig. 7 for selected polarization angles. The curves are very close, so that the obtained parameters (Table 1) establish a sound basis to calculate reflectance spectra for other orientations.

As expected, each LO frequency is higher than the corresponding TO. Moreover, the TO and LO frequencies calculated values

are found in good agreement with those estimated directly on the experimental reflectance data (as shown in Fig. 5).

The polarization angle (θ_k) calculated for each mode has been confirmed by Raman measurements on brushite monocrystal (results will be presented elsewhere), as well as the TO and LO frequencies. These angles are close to those obtained by the fitting of sinusoidal curve of the reflectance of the modes (Fig. 6), according to the orientation ($\theta_{k\text{exp}}$ in Table 1).

Strength values and damping constant of oscillators were comparable to those obtained in similar compound (Tutton salts [10,29], gypsum [30,31]). Additional parameters related to electronic permittivity are $\theta_\infty = 22.4^\circ$ and the components of the high-frequency permittivity tensor $\epsilon_{x\infty}$, $\epsilon_{y\infty}$ were found equal to 2.50 and 2.02 respectively. These optimized values for electronic permittivity $\epsilon_{x\infty}$, $\epsilon_{y\infty}$ have also the same order of magnitude than the square of optical refractive indices in the visible range [32].

In Fig. 8, we present the real $\epsilon'(R(\epsilon))$ and imaginary $\epsilon''(\text{Im}(\epsilon))$ parts of the two matrix elements $\epsilon_{x\omega}(\omega)$ and $\epsilon_{y\omega}(\omega)$ with regards to ω . On this figure, the TO modes can be clearly seen as the maximum of ϵ'' , while the LO modes appears as the maximum of the curve of $-\text{Im}(1/\epsilon)$, i.e. the zero of ϵ' .

Fig. 7. Experimental (red) and calculated (black) reflectance spectra for selected orientation angles; (a) 35° , (b) 70° , (c) 170° , (d) 110° , close to the maxima of the four PO_4 bands. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. Real part ϵ' (black solid line), imaginary part ϵ'' (dotted black line) and $-\text{Im}(1/\epsilon)$ (dotted red line) of (a) $\epsilon_{x\omega}(\omega)$ and (b) $\epsilon_{y\omega}(\omega)$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 9. Variation in degree of the calculated angle $\theta(\omega)$ with the frequency ω . The θ_k values for M_k modes are peaked.

Fig. 9 shows the angle $\theta(\omega)$ (angle of the $\varepsilon_{x\omega}(\omega)$ direction) according to the frequency in the studied range, the particular angles corresponding to the four modes are indicated. We can note that for M_3 , -13° is equivalent to 167° (modulo π). Moreover, the polarization of M_2 and M_4 are in the direction of $\varepsilon_{y\omega}(\omega)$, as seen in Fig. 8 and as confirmed by the following relations between the angles: $-16^\circ + 90^\circ = 74^\circ$ (M_2) and $15^\circ + 90^\circ = 105^\circ$ (M_4) respectively.

For one P–O bond, we can attribute a dipole moment oriented in the bond direction. In the absence of interaction, the atom movements in the group are close to those of Fig. 2, we can obtain an associated PO_4 dipole moment for each mode (the moment modules are taken identical). For the A' symmetry, the two PO_4 groups vibrate symmetrically with regards to the ac mirror plane, we called q_k the resulting dipole moments. If the Q_k are these corresponding stretching modes, the four A' modes M_k can be written in this Q_k base. The coefficients of the linear combination are the same for the relation between the modes than for the relation between the dipole moments. Moreover, the angles of these dipoles q_k are evaluated and can be compared to those (θ_k) obtained by our D.A. model for M_k modes, the dipole moments and angles are all represented in Fig. 10.

Firstly, for modes M_1 and Q_1 , it appears that both angles are close: 34° for the pure stretching (which corresponds to the orientation of the longest P–O bond projection in the ac -plane) and 35° from the model, suggesting that this mode is not significantly coupled with the others.

On the contrary, the modes M_2 and M_3 are mixed because their angles are different to the angles of Q_2 and Q_3 modes, respectively. In spite of the fact that q_4 and m_4 have almost the same direction, contrary to M_1 , an acceptable solution cannot be obtained without introducing the mode M_4 in our fit. We have calculated this mixing by a linear combination of these three dipoles q_k . The linear combinations were obtained by doing a change in the basis set (the nine parameters are reduced to three due to normalization and orthogonal conditions), until that the resulting moment of the combination is aligned in the direction related to θ_k angle. The coefficient values are presented in the following Table 2.

The diagonal coefficients are close to 1, so that the M_k modes correspond basically to the Q_k ones. The out of diagonal values confirm that the mixing occurs mainly between the modes M_2 and M_3 . We noted that the mode Q_4 (see Fig. 1) is the only one antisymmetric (the others are symmetric) with report to a plane which contains the P–OH and another P–O bond; the longest one of the three P–O (1.534 Å). This explains that the mode M_4 shows a weak mixing with the M_2 and M_3 ones according to the values in Table 2.

In conclusion, we obtain the weight of each basic mode Q_k in each experimental vibration, and thus, the shape of the four modes.

Fig. 10. Dipole moments orientations and corresponding angles values for M_k modes (m_k and θ_k values in black) and Q_k modes (q_k and corresponding angles in red) with regards to crystal and reference axes ($k = 1, 2, 3, 4$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2

Linear coefficients of the relation between M_k and Q_k modes for $k = 2, 3$ and 4.

Mode	Q_2	Q_3	Q_4
M_2	0.86	0.43	−0.29
M_3	−0.48	0.87	−0.13
M_4	0.19	0.25	0.95

Conclusion

In this paper, IR polarized reflectance spectra from the ac -plane of brushite crystal are presented, for the $800\text{--}1200\text{ cm}^{-1}$ P–O stretching frequency range. Strong variations of the intensities of the modes are observed, characteristic of the reflectance behavior reported in similar crystals; a TO–LO splitting of polar modes.

Using a dispersion analysis model, the optimized parameters of the stretching P–O modes have been obtained, such as the angle of polarization, the oscillator strength, the attenuation constant, and the TO frequency of the four observed modes. In addition, the evolution of the complex dielectric constants were obtained, allowing the complete determination of the LO frequencies. These parameters, in good agreement with those obtained on similar compounds, are a useful help to understand the vibrational spectra of brushite and avoid some assignment mistakes. The modes have been also described by a mixing of those of “isolated” tetrahedron. The exact knowledge of these modes, well separated from the others and intense in vibrational spectroscopies, should allow to study the effect of structural and chemical changes in brushite.

In particular, the polarization directions and the LO frequencies would be powerful information for further polarized Raman works, in an attempt to fully understand the vibrational behavior of this crystalline compound.

References

- [1] F. Tamimi, Z. Sheikh, J. Barralet, Acta Biomater. 8 (2012) 474–487.
- [2] C.A. Beevers, Acta Cryst. 11 (1958) 273–277.
- [3] D.W. Jones, J.A.S. Smith, J. Chem. Soc. (1962) 1414–1420.
- [4] N.A. Curry, D.W. Jones, J. Chem. Soc. A (1971) 3725–3729.
- [5] W.M.M. Heijnen, P. Hartman, J. Cryst. Growth 108 (1991) 290–300.
- [6] C.I. Sainz-Diaz, A. Villacampa, F. Otalora, Am. Mineral. 89 (2–3) (2004) 307–313.
- [7] E.E. Koch, A. Otto, Chem. Phys. 3 (1974) 362–369.
- [8] M.V. Belousov, V.F. Pavich, Opt. Spectrosc. 45 (1978) 771–774.
- [9] V.F. Pavich, M.V. Belousov, Opt. Spectrosc. 45 (1978) 881–883.
- [10] V. Ivanovski, T.G. Mayerhöfer, J. Popp, Vib. Spectrosc. 44 (2007) 369–374.

- [11] V. Ivanovski, V.M. Petrusovski, *Spectrochim. Acta Part A* 61 (2005) 2057–2063.
- [12] D. Lee, P.N. Kumta, *Mater. Sci. Eng. C* 30 (2010) 934–943.
- [13] M.D. O'Donnell, Y. Fredholm, A. de Rouffignac, R.G. Hill, *Acta Biomater.* 4 (2008) 1455–1464.
- [14] S. Quillard, M. Paris, P. Deniard, R. Gildenhaar, G. Berger, L. Obadia, J.-M. Boulter, *Acta Biomater.* 7 (2011) 1844–1852.
- [15] R.Z. LeGeros, J.P. LeGeros, *J. Cryst. Growth* 13 (14) (1972) 476–480.
- [16] F. Abbona, F. Christensson, M. Franchini Angela, H.E. Lundager Madsen, *J. Cryst. Growth* 131 (1993) 331–346.
- [17] Th.G. Mayerhöfer, V. Ivanovski, J. Popp, *Vib. Spectrosc.* 63 (2012) 396–403.
- [18] A.C. Chapman, L.E. Thirlwell, *Spectrochim. Acta* 20 (1964) 937–947.
- [19] E.E. Berry, C.B. Baddiel, *Spectrochim. Acta, Part A* 23 (1967) 2089–2097.
- [20] I. Petrov, B. Šoptrajanov, N. Fuson, J.R. Lawson, *Spectrochim. Acta, Part A* 23 (1967) 2637–2646.
- [21] L. Tortet, J.R. Gavarri, G. Nihoul, A.J. Dianoux, *J. Solid State Chem.* 132 (1997) 6–16.
- [22] C. Combes, C. Rey, M. Freche, *Colloids Surf. B* 11 (1998) 15–27.
- [23] M. Trpkovska, B. Šoptrajanov, P. Malkov, *J. Mol. Struct.* 480–481 (1999) 661–666.
- [24] J. Xu, I.S. Butler, D.F.R. Gilson, *Spectrochim. Acta, Part A* 55 (1999) 2801–2809.
- [25] F. Casciani, R.A. Sr Condrate, *Spectrosc. Lett.* 12 (10) (1979) 699–713.
- [26] H. Poulet, J.-P. Mathieu, *Spectres de Vibration et Symétrie des Cristaux*, Gordon and Breach, Paris, 1970.
- [27] R. Claus, *Phys. Stat. Sol. (b)* 88 (1978) 683–688.
- [28] L. Merten, R. Claus, *Phys. Stat. Sol. (b)* 89 (1978) 159–163.
- [29] V. Ivanovski, G. Ivanovski, *Spectrochim. Acta, Part A* 75 (2010) 1452–1461.
- [30] J.R. Aronson, A.G. Emslie, E.V. Miseo, E.M. Smith, P.F. Strong, *Appl. Opt.* 22 (1983) 4093–4098.
- [31] V. Ivanovski, T.G. Mayerhöfer, J. Popp, *Spectrochim. Acta, Part A* 68 (2007) 632–638.
- [32] H.E. Lundager Madsen, *J. Cryst. Growth* 310 (2008) 617–623.