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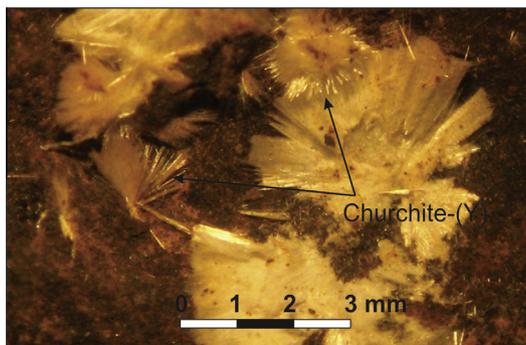
A vibrational spectroscopic study of the phosphate mineral churchite (REE)(PO₄)·2H₂O

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HIGHLIGHTS

- We have undertaken a study of the phosphate mineral churchite.
- EDX analysis shows a rare earth phosphate.
- SEM shows lone acicular crystals.
- The mineral is characterized by its vibrational spectra.

GRAPHICAL ABSTRACT



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ABSTRACT

Vibrational spectroscopy has been used to study the rare earth mineral churchite of formula (REE)(PO₄)·2H₂O. The mineral contains a range of rare earth metals including yttrium depending on the locality. The Raman spectra of churchite-(REE) are characterized by an intense sharp band at 984 cm⁻¹ assigned to the ν₁ (PO₄³⁻) symmetric stretching mode. A lower intensity band observed at around 1067 cm⁻¹ is attributed to the ν₃ (PO₄³⁻) antisymmetric stretching mode. The (PO₄³⁻) bending modes are observed at 497 cm⁻¹ (ν₂) and 565 cm⁻¹ (ν₄). Raman bands at 649 and 681 cm⁻¹ are assigned to water librational modes. Vibrational spectroscopy enables aspects of the structure of churchite to be ascertained.

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Introduction

The mineral churchite is a rare earth phosphate of formula REEPO₄·2H₂O and crystallizes with monoclinic symmetry. Depending on the origin of the mineral, churchite may contain Ce, Gd, Dy, Ho and Sm and any mixture of the rare earth elements. Normally

the churchite mineral is written as churchite-Y with the rare earth element after the mineral name. The mineral churchite-Dy was not approved by the IMA because of a lack of quantitative information. Analysis of other samples showed the mineral to be churchite-Y with traces of other rare earth elements. The mineral churchite-(Y) is a rare earth hydrated phosphate of ideal formula YPO₄·2H₂O which may contain neodymium, erbium and other rare earth metals [1–4].

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The mineral churchite (Y,REE)(PO₄)·2H₂O is a hydrated phosphate of Y and RE elements and has monoclinic symmetry with space group *I2/a*. Its crystal structure was solved by Kohlmann et al. [5]. Infrared spectra of churchite-(Y) were published by Sejkora et al. [6] and Onac et al. [7]. The Raman spectrum and structural analysis of a selection of churchite minerals has been published [8]. Churchite-(Y) is now known from more than 40 localities worldwide. It occurs as a secondary mineral with yttrium and REE weathered or biochemically leached from trace amounts in surrounding rocks, e.g. at pegmatites, carbonates, guano-related deposits, hydrothermal mineral deposits and others [7,9].

Raman spectroscopy has proven most useful for the study of mineral structure [10–14]. Raman spectroscopy is an important tool in the characterization of phosphates in pegmatite rocks [15]. In recent years, spectroscopic studies concerning phosphate minerals are increasing, especially due to their industrial and technological importance. The aim of this paper is to report the Raman spectra of churchite-REE, and to relate the spectra to the molecular structure of this phosphate mineral. The paper follows the systematic research of the large group of supergene minerals and especially molecular structure of minerals containing oxyanions using IR and Raman spectroscopy.

Experimental

Samples description and preparation

The churchite sample studied in this work forms part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-131. The studied sample is from Grube Leonie, Auerbach, Oberphalz, Germany. Geological description and characterization of the occurrence [16,17] was published.

The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The churchite studied in this work occurs in association with siderite. Scanning electron microscopy (SEM) in the EDS mode was applied to support the mineral characterization.

Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil (<http://www.microscopia.ufmg.br>).

Churchite crystal aggregate was coated with a 5 nm layer of evaporated carbon. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and were applied to support the mineral characterization.

Raman microprobe spectroscopy

Crystals of churchite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10×, 20×, and 50× objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He–Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of 2 cm⁻¹ and a precision of ±1 cm⁻¹ in the range between 200 and 4000 cm⁻¹. Repeated acquisitions on the crystals using the highest magnification (50×) were accumulated to improve the signal to noise ratio of the spectra.

Raman Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

An image of the churchite crystals measured is shown in the Supplementary information as Fig. S1. Clearly the crystals of churchite are readily observed, making the Raman spectroscopic measurements readily obtainable. A Raman spectrum of churchite was downloaded from the RRUFF data base [[http://rruff.info/Churchite-\(Y\)/R060424](http://rruff.info/Churchite-(Y)/R060424)] for comparative purposes.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm⁻¹ range were obtained by the co-addition of 128 scans with a resolution of 4 cm⁻¹ and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian–Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian–Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of *r*² greater than 0.995.

Results and discussion

Chemical characterization

The BSE image of churchite sample studied in this work is shown in Fig. 1. The image shows an aggregate of needle-like crystals with acicular habitus. The sample is homogeneous and zonation or contaminant phases are not observed. Qualitative and semi-quantitative chemical composition shows a rare earth phosphate with Gd, Dy, Ho present in the sample (Fig. 2).

Vibrational spectroscopy

Background

In aqueous systems, the Raman spectra of phosphate oxyanions show a symmetric stretching mode (*v*₁) at 938 cm⁻¹, an antisym-

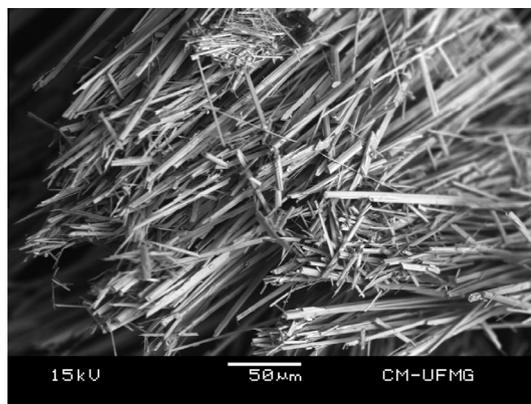


Fig. 1. Backscattered electron image (BSI) of a churchite crystal aggregate up to 0.5 mm in length.

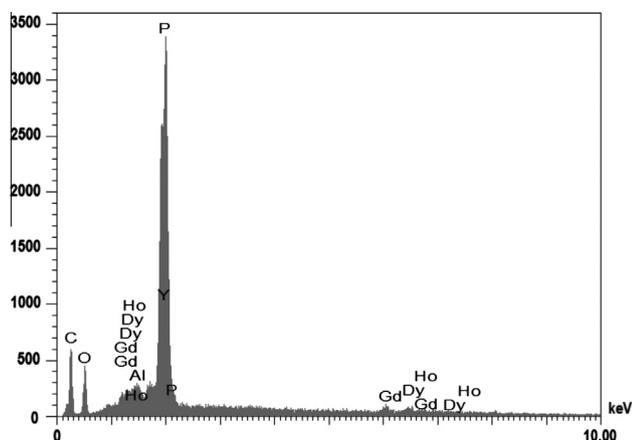


Fig. 2. EDS analysis of churchite.

metric stretching mode (ν_3) at 1017 cm^{-1} , a symmetric bending mode (ν_2) at 420 cm^{-1} and a ν_4 bending mode at 567 cm^{-1} [18–20]. Ross in Farmer (page 404) listed some well-known minerals containing phosphate, which were either hydrated or hydroxylated or both [21]. The vibrational spectrum of the dihydrogen phosphate anion has been reported in Farmer. The PO_2 symmetric stretching mode occurs at 1072 cm^{-1} and the POH symmetric stretching mode at $\sim 878\text{ cm}^{-1}$. The position of the PO stretching vibration for calcium dihydrogen phosphate is found at 915 cm^{-1} . The POH antisymmetric stretching mode is at 947 cm^{-1} and the $\text{P}(\text{OH})_2$ bending mode at 380 cm^{-1} . The band at 1150 cm^{-1} is assigned to the PO_2 antisymmetric stretching mode. The position of these bands will shift according to the crystal structure of archerite.

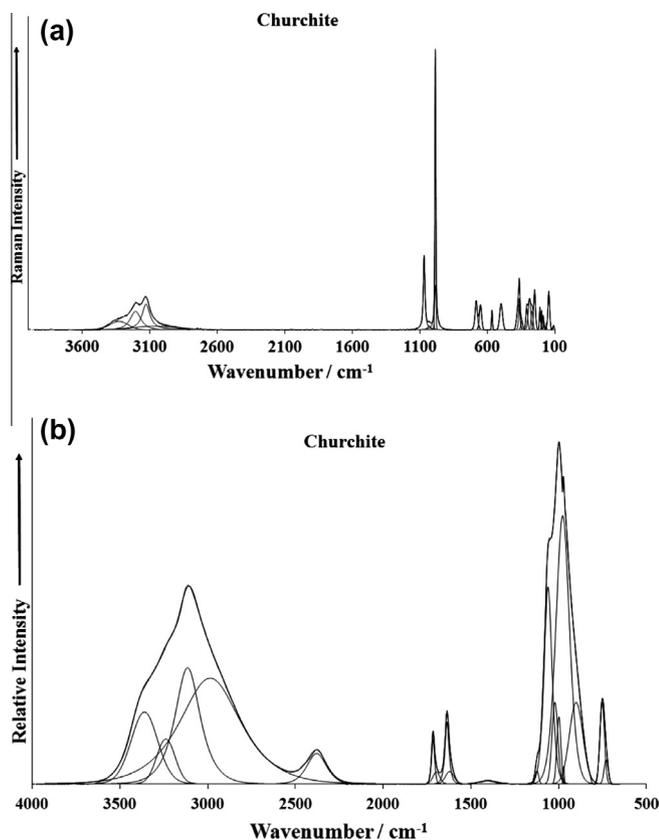


Fig. 3. (a) Raman spectrum of churchite over the $4000\text{--}100\text{ cm}^{-1}$ spectral range and (b) infrared spectrum of churchite over the $4000\text{--}500\text{ cm}^{-1}$ spectral range.

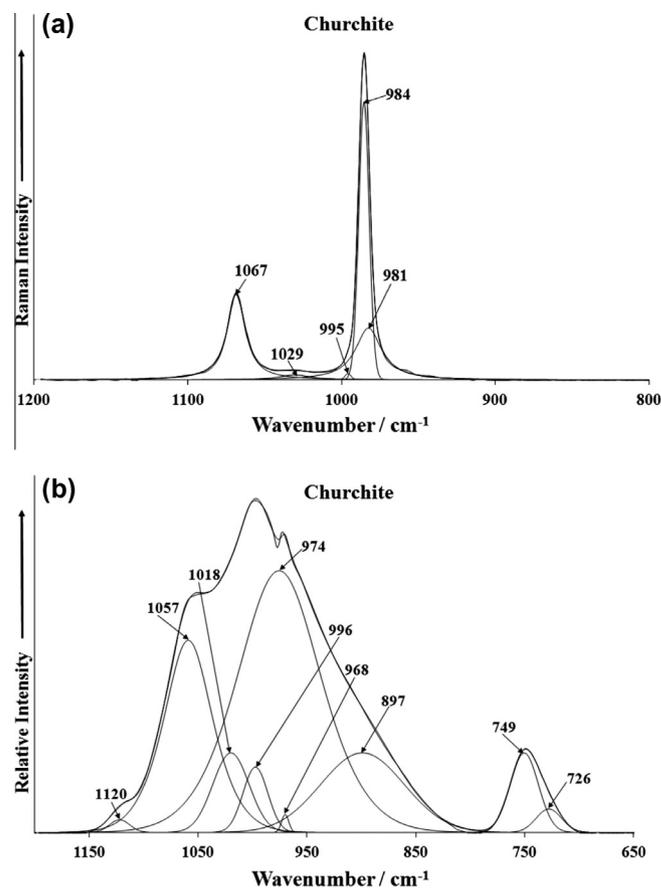


Fig. 4. (a) Raman spectrum of churchite over the $1200\text{--}800\text{ cm}^{-1}$ spectral range and (b) infrared spectrum of churchite over the $1200\text{--}650\text{ cm}^{-1}$ spectral range.

Raman and infrared spectroscopy of churchite

The Raman spectrum of churchite over the $100\text{--}4000\text{ cm}^{-1}$ spectral range is illustrated in Fig. 3a. This figure shows the Raman bands of churchite and their relative intensities. It is noted that there are large parts of the spectrum where no intensity is observed. Thus, the Raman spectrum is subdivided into sections based upon the type of vibration being studied. The infrared spectrum of churchite over the $500\text{--}4000\text{ cm}^{-1}$ spectral range is reported in Fig. 3b. This figure displays the position and relative intensity of the infrared bands. This spectrum is subdivided into subsections based upon the type of vibration being analyzed.

The Raman spectrum of churchite over the $800\text{--}1200\text{ cm}^{-1}$ spectral range is given in Fig. 4a. This spectrum is dominated by an intense sharp band at 984 cm^{-1} which is assigned to the ν_1 (PO_4^{3-}) symmetric stretching mode. In a previous study [8], variation of the position of this band occurred and is probably dependent upon the rare earth composition of the churchite. The Raman band at 1067 cm^{-1} is attributed to the ν_3 (PO_4^{3-}) antisymmetric stretching mode.

The infrared spectrum of churchite over the $650\text{--}1200\text{ cm}^{-1}$ spectral range is reported in Fig. 4a. The spectrum is broad and appears to be composed of a number of overlapping bands. The infrared band at 974 cm^{-1} may be attributed to the ν_1 (PO_4^{3-}) symmetric stretching mode. The infrared bands at 1018 , 1057 and 1120 cm^{-1} are due to the ν_3 (PO_4^{3-}) antisymmetric stretching mode.

The Raman spectrum of churchite over the $400\text{--}750\text{ cm}^{-1}$ spectral range is shown in Fig. 5a. The Raman spectrum of churchite over the $100\text{--}400\text{ cm}^{-1}$ spectral range is shown in Fig. 5b. Besides

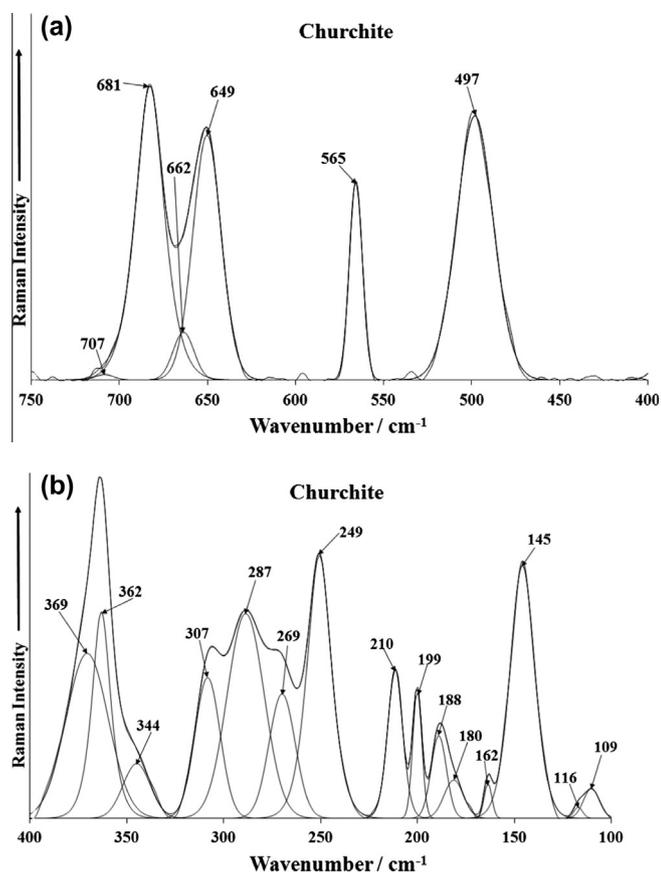


Fig. 5. (a) Raman spectrum of churchite over the 750–400 cm^{-1} spectral range and (b) Raman spectrum of churchite over the 400–100 cm^{-1} spectral range.

the symmetric stretching vibration, the other most intense bands belong to the OPO bending vibration (ν_2). The intense Raman band at 497 cm^{-1} is ascribed to this vibrational mode. The sharp Raman band at 565 cm^{-1} is assigned to the ν_4 (PO_4^{3-}) bending mode. In a previous study considerable variation in the position of these bending modes was found [8]. Two Raman bands are observed at 649 and 681 cm^{-1} . A possibility for the assignment of these bands is to water librational modes, although the band position for the librational modes might be expected at higher wavenumbers. The Raman spectrum of the far low wavenumber region as shown in Fig. 5b, shows strong intensity with a number of Raman bands observed. Raman bands in the 250–400 cm^{-1} spectral range may be due to metal oxygen vibrations. Raman bands at lower wavenumbers may be ascribed to external vibrations.

A comparison may be based on that with other phosphate containing minerals. For pseudomalachite Raman bands are observed at 482 and 452 cm^{-1} of about equal intensity. The two ν_2 bands for pseudomalachite were reported by Ross [21] at 450 and 422 cm^{-1} . Cornetite Raman spectra shows an intense band at 433 cm^{-1} with minor components at 463 and 411 cm^{-1} . Ross [21] reported two bands at 464 and 411 cm^{-1} for cornetite. The variation between the spectral results may be attributed to orientation effects and the intensity of different bands will depend on which crystal face is scattering the Raman signal. The Raman spectrum of libethenite showed a single band for ν_2 at 450 cm^{-1} . A number of bands in the 480–680 cm^{-1} region of mineral phosphates were reported by Ross [21] for selected phosphates. He attributed these bands to the ν_4 modes. We observe similar number of bands for the churchite-(Y) minerals. The Raman spectrum of pseudomalachite exhibits bands at 481, 517, 537 and

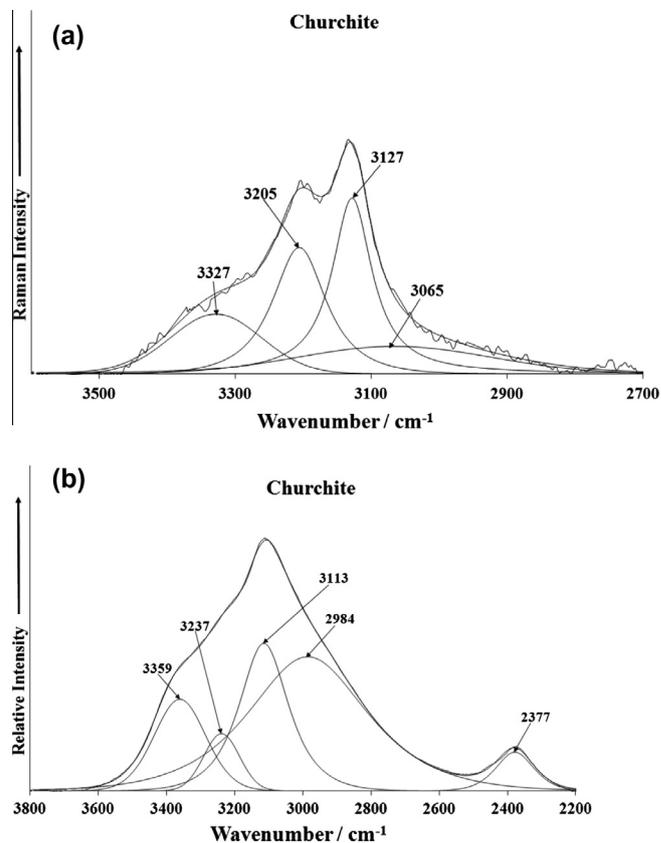


Fig. 6. (a) Raman spectrum of churchite over the 3600–2700 cm^{-1} spectral range and (b) infrared spectrum of churchite over the 3800–2200 cm^{-1} spectral range.

609 cm^{-1} . The ν_4 modes for cornetite were observed at 487, 518, 541 and 570 cm^{-1} . Bands were observed for libethenite at 556, 582, 626 and 645 cm^{-1} . These band positions are in good agreement with the values reported by Farmer [21].

The Raman spectrum of churchite over the 2700–4000 cm^{-1} spectral range is displayed in Fig. 6a. Raman bands are observed at 3127 and 3205 cm^{-1} with shoulder bands at 3065 and 3327 cm^{-1} . These bands are assigned to water stretching vibrations. The infrared spectrum of churchite over the 2200–3800 cm^{-1} spectral range is shown in Fig. 6b. Infrared bands are observed at 2984, 3113, 3237 and 3359 cm^{-1} . These bands are attributed to water involved with hydrogen bonding to different

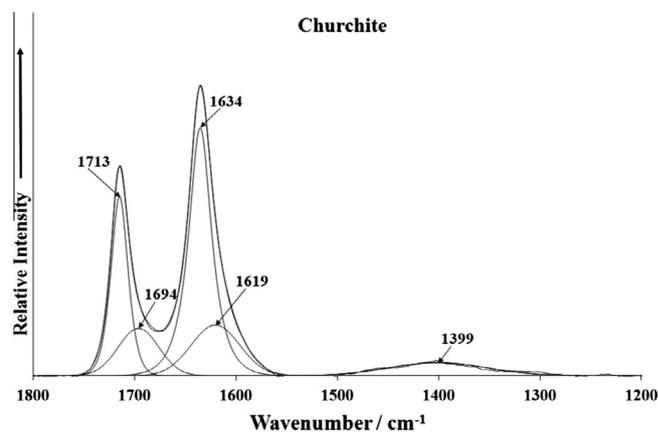


Fig. 7. Infrared spectrum of churchite over the 1800–1200 cm^{-1} spectral range.

extents. No Raman signal over the 1200–1800 cm^{-1} spectral range was obtained. However, an intense infrared spectrum over this spectral range was obtained (Fig. 7). The strong infrared band at 1634 cm^{-1} was assigned to the water bending mode.

Conclusions

We have studied a mineral sample of churchite from Grube Leonie, Auerbach, Oberphalz, Germany, using a combination of SEM with EDX and vibrational spectroscopy. The chemical analysis shows the mineral contains a mixture of rare earth elements.

The Raman spectra of churchite-(REE) are characterized by an intense sharp band at 984 cm^{-1} , assigned to the ν_1 (PO_4^{3-}) symmetric stretching mode. A lower intensity band observed at around 1067 cm^{-1} is attributed to the ν_3 (PO_4^{3-}) antisymmetric stretching mode. The (PO_4^{3-}) bending modes are observed at 497 cm^{-1} (ν_2) and 565 cm^{-1} (ν_4). Strong Raman bands found at 649 and 681 cm^{-1} are thought to be due to water librational modes.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2014.02.100>.

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