



# SEM, EDX and vibrational spectroscopic study of the phosphate mineral ushkovite $\text{MgFe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ – Implications of the molecular structure



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## HIGHLIGHTS

- We have studied the mineral ushkovite.
- Chemical analysis shows the mineral contains P, Mg with very minor Fe.
- Vibrational spectroscopy enhances our knowledge of the molecular structure of ushkovite.

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## ABSTRACT

The mineral ushkovite has been analyzed using a combination of electron microscopy with EDX and vibrational spectroscopy. Chemical analysis shows the mineral contains P, Mg with very minor Fe. Thus, the formula of the studied ushkovite is  $\text{Mg}_2^{3+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . The Raman spectrum shows an intense band at  $953\text{ cm}^{-1}$  assigned to the  $\nu_1$  symmetric stretching mode. In the infrared spectra complexity exists with multiple antisymmetric stretching vibrations observed, due to the reduced tetrahedral symmetry. This loss of degeneracy is also reflected in the bending modes. Strong infrared bands around  $827\text{ cm}^{-1}$  are attributed to water librational modes. The Raman spectra of the hydroxyl-stretching region are complex with overlapping broad bands. Hydroxyl stretching vibrations are identified at 2881, 2998, 3107, 3203, 3284 and  $3457\text{ cm}^{-1}$ . The wavenumber band at  $3457\text{ cm}^{-1}$  is attributed to the presence of FeOH groups. This complexity is reflected in the water HOH bending modes where a strong infrared band centered around  $1653\text{ cm}^{-1}$  is found. Such a band reflects the strong hydrogen bonding of the water molecules to the phosphate anions in adjacent layers. Spectra show three distinct OH bending bands from strongly hydrogen-bonded, weakly hydrogen bonded water and non-hydrogen bonded water. Vibrational spectroscopy enhances our knowledge of the molecular structure of ushkovite.

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## Introduction

The mineral ushkovite of formula  $\text{MgFe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  is a hydrated hydroxy phosphate of ferric iron and magnesium. The mineral is a member of the laueite mineral group. Other minerals in this group are césarferreiraite  $\text{Fe}^{2+}(\text{Fe}^{3+})_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , ferrolaueite  $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , gordonite  $\text{MgAl}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , kastningite  $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , laueite  $\text{Mn}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , maghrebite  $\text{MgAl}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , mangangordonite  $\text{Mn}^{2+}\text{Al}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , paravauxite

$\text{Fe}^{2+}\text{Al}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and sigloite  $\text{Fe}^{3+}\text{Al}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 7\text{H}_2\text{O}$  [1].

This group of minerals may be considered as environmental minerals. The minerals are of interest because of their occurrence in environments such as the coatings of water pipes and soils from peat bogs, morasses and sediments [2]. If ground waters are high in both  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  then it is possible that both the minerals of the laueite group such as ferrolaueite and ushkovite may form, particularly when phosphate fertilisers have been used in the surrounding farmlands. In fact, these minerals have been found in sediments in New Zealand.

The Raman spectra of the tetrahedral anions in aqueous systems are well known. The symmetric stretching vibration of the

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phosphate anion in aqueous systems, ( $\nu_1$ ) is observed at  $938\text{ cm}^{-1}$ , the asymmetric stretching mode ( $\nu_3$ ) at  $1018\text{ cm}^{-1}$ . The  $\nu_2$  mode is observed at  $420\text{ cm}^{-1}$  and the  $\nu_4$  mode at  $567\text{ cm}^{-1}$ . In solids, the position of the bands will be dependent on the chemical environment. Farmer [3] lists a number of infrared spectra of phosphates including vivianite. The symmetric stretching mode was not listed but the antisymmetric mode was found at  $990$  and  $1040\text{ cm}^{-1}$ . Bands at  $890$  and  $872\text{ cm}^{-1}$  were not assigned. It is probable that these are the symmetric stretching modes of the hydrogen bonded phosphate. Bands for the  $\nu_4$  mode was observed at  $475$ ,  $560$  and  $590\text{ cm}^{-1}$ . The formula is close to that of ushkovite. Griffith reported the Raman spectra of vivianite [4]. The laueite minerals are all triclinic and point group  $1\bar{1}$  [5].

There is currently a lack of comprehensive spectral knowledge of the laueite phosphate group minerals including ushkovite and as part of a wider comprehensive study of the vibrational spectroscopy of secondary minerals, we report the vibrational spectroscopy and molecular structure of ushkovite of the laueite group. As part of our comprehensive research into minerals containing oxyanions, we report the SEM with EDX and vibrational spectroscopy of ushkovite and relate the spectra to the structure of the mineral.

## Experimental

### Samples description and preparation

The ushkovite sample studied in this work is from Linópolis, Divino das Laranjeiras, Minas Gerais, Brazil. The sample is part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-083. Ushkovite sample occurs as millimetric crystal aggregates associated with atencioite [6]. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Zeiss Stemi DV4 from the Museu de Ciência e Técnica of the Federal University of Ouro Preto. Qualitative and semiquantitative chemical analysis via SEM/EDS was applied to 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>). Ushkovite crystals were coated with a  $5\text{ nm}$  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 ushkovite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with  $10\times$ ,  $20\times$ , and  $50\times$  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  $633\text{ nm}$  and collected at a nominal resolution of  $2\text{ cm}^{-1}$  and a precision of  $\pm 1\text{ cm}^{-1}$  in the range between  $200$  and  $4000\text{ cm}^{-1}$ . Repeated acquisitions on the crystals using the highest magnification ( $50\times$ ) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the  $520.5\text{ cm}^{-1}$  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 ushkovite crystals measured is shown in the [Supplementary information as Fig. S1](#). Clearly the crystals of ushkovite are readily observed, making the Raman spectroscopic measurements readily obtainable.

### Infrared spectroscopy

Infrared spectra of ushkovite were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the  $4,000$ – $525\text{ cm}^{-1}$  range were obtained by the co-addition of 128 scans with a resolution of  $4\text{ cm}^{-1}$  and a mirror velocity of  $0.6329\text{ cm/s}$ . 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 Lorentzian–Gaussian 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  $0.995$ .

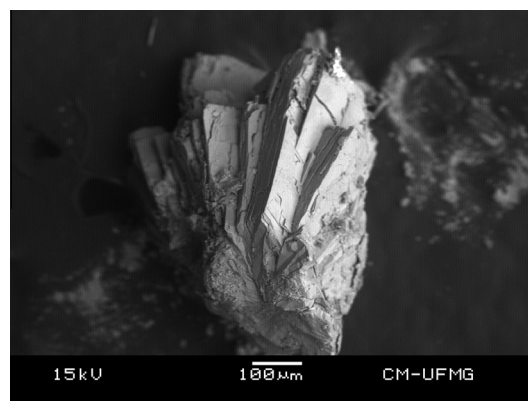
## Results and discussion

### Chemical characterization

The SEM image of ushkovite sample studied in this work is reported in [Fig. 1](#). The image shows a crystal fragment up to  $0.5\text{ mm}$ . A perfect cleavage parallel to  $010$  is observed. The chemical analysis is provided in [Fig. 2](#). The major chemical elements in the composition of the measured sample are Mg, Fe and P. Minor amounts of Al and Si were also observed. The presence of carbon is related to the carbon coating.

### Vibrational spectroscopy

The Raman spectrum of ushkovite in the  $100$ – $4000\text{ cm}^{-1}$  spectral range is displayed in [Fig. 3a](#). This figure displays the Raman spectrum over the  $100$ – $4000\text{ cm}^{-1}$  spectral range. This spectrum shows the position and relative intensities of the Raman bands. It is noted that there are large parts of the spectrum where no intensity or minimal intensity is observed. Thus, the spectrum is subdivided into subsections depending upon the type of vibration being studied. The infrared spectrum of ushkovite in the



**Fig. 1.** Backscattered electron image (BSI) of a ushkovite crystal aggregate up to  $0.5\text{ mm}$  in length.

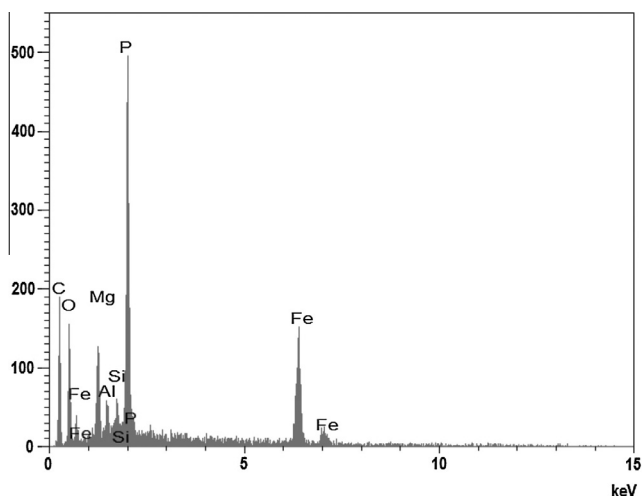


Fig. 2. EDS analysis of ushkovite.

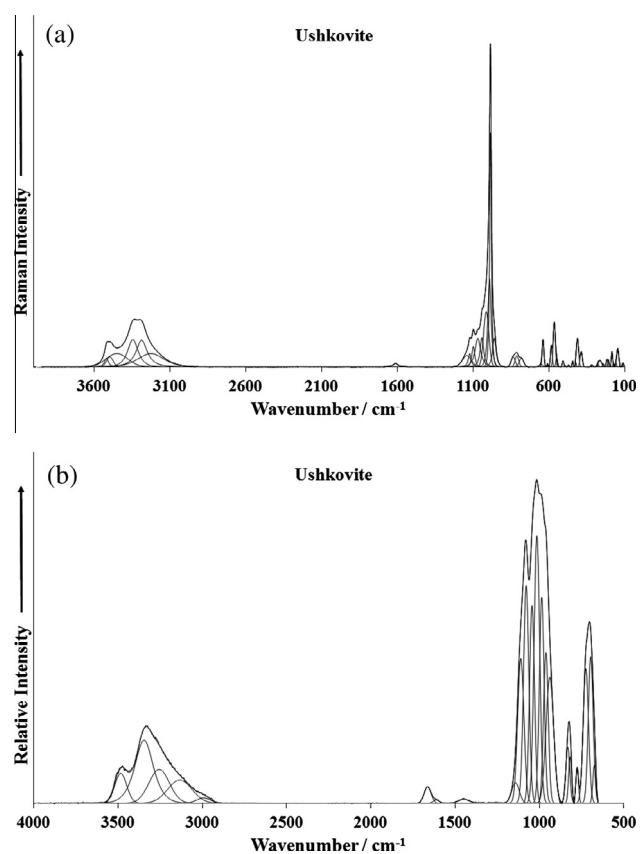


Fig. 3. (a) Raman spectrum of ushkovite over the 100–4000 cm<sup>-1</sup> spectral range (upper spectrum) and (b) infrared spectrum of ushkovite over the 500–4000 cm<sup>-1</sup> spectral range (lower spectrum).

500–4000 cm<sup>-1</sup> spectral region is shown in Fig. 3b. This figure displays the infrared spectrum over the 500–4000 cm<sup>-1</sup> spectral range. This figure shows the position of the infrared bands and their relative intensities. This spectrum displays the position and relative intensities of the infrared bands. As for the Raman spectrum, there are parts of the spectrum where little or no intensity is observed. Therefore, the spectrum is subdivided into subsections depending on the vibrational mode being analyzed.

The Raman spectrum of ushkovite over the 750–1250 cm<sup>-1</sup> spectral range is reported in Fig. 4a. In the Raman spectrum of

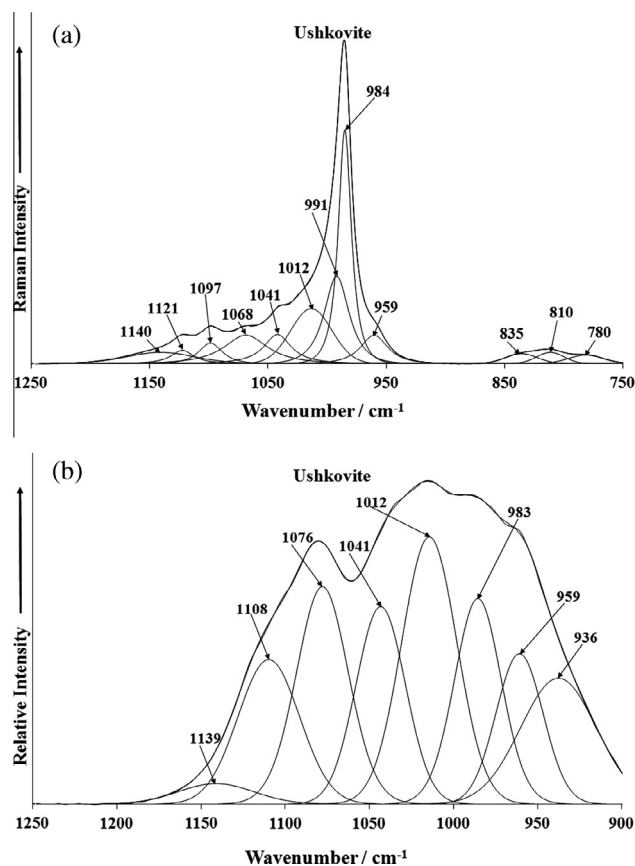


Fig. 4. (a) Raman spectrum of ushkovite (upper spectrum) in the 750–1250 cm<sup>-1</sup> spectral range and (b) infrared spectrum of ushkovite (lower spectrum) in the 900–1250 cm<sup>-1</sup> spectral range.

ushkovite, a single intense band is observed at 984 cm<sup>-1</sup> with low intensity bands observed at 959 and 991 cm<sup>-1</sup>. The 984 cm<sup>-1</sup> band is assigned to the Raman active  $\nu_1$  PO<sub>4</sub><sup>3-</sup> symmetric stretching vibration. The position of this band is in excellent agreement with a previously published result [7]. The bands at 1012, 1041, 1068, 1097, 1121 and 1140 cm<sup>-1</sup> are assigned to the phosphate  $\nu_3$  PO<sub>4</sub><sup>3-</sup> antisymmetric stretching vibration. These bands are of very low intensity. Piriou and Poullen [7] found bands at 1018 and 1053 cm<sup>-1</sup> which are in agreement with our results. The phosphate anion in an aqueous solution shows a single antisymmetric band at 1017 cm<sup>-1</sup>. In this work, multiple bands are observed, consistent with the reduction of the phosphate ion symmetry from T<sub>d</sub> to C<sub>3v</sub> or less to C<sub>2v</sub> in accord with the crystal structure determination.

The infrared spectrum of ushkovite over the 900–1250 cm<sup>-1</sup> spectral range is shown in Fig. 4b. The infrared spectrum is complex to say the least, with multiple overlapping bands. This symmetry reduction is borne out in the infrared spectra. Infrared bands are observed at 936, 959, 967, 983, 1012, 1041, 1076 and 1108 cm<sup>-1</sup>. The 983 and 1012 cm<sup>-1</sup> bands are the symmetric stretching vibrations as may be observed in the Raman spectrum. The bands 1041, 1076 and 1108 cm<sup>-1</sup> correspond to the very low intensity Raman bands observed at 1012, 1041, 1068, 1097, 1121 and 1140 cm<sup>-1</sup>. Previously published infrared data reported by Farmer [3] gave bands at 990 and 1040 cm<sup>-1</sup>, which are different from the results reported here. One possibility is that the data is correct, the identification of the mineral used by Farmer incorrect. The infrared bands at 936, 959 are probably due to water librational modes.

The Raman spectrum of ushkovite over the 300–700 cm<sup>-1</sup> spectral range is reported in Fig. 5a. The use of the diamond ATR cell has a lower wavenumber limit of around 550 cm<sup>-1</sup>, and as a consequence

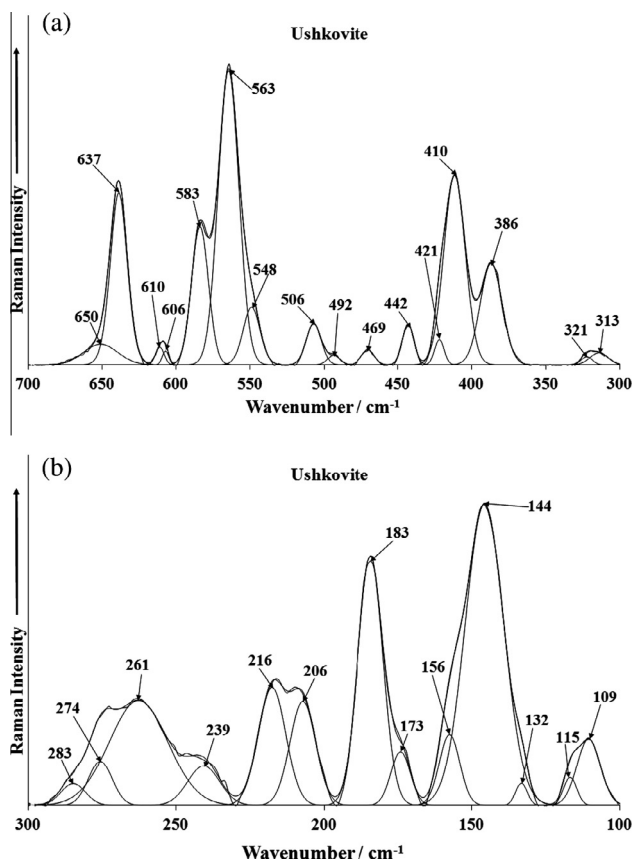


Fig. 5. (a) Raman spectrum of ushkovite (upper spectrum) in the 300–700  $\text{cm}^{-1}$  spectral range and (b) Raman spectrum of ushkovite (lower spectrum) in the 100–300  $\text{cm}^{-1}$  spectral range.

infrared data for this region were not obtained. One of the strong advantages of Raman spectroscopy is the ability to obtain spectral data below 400  $\text{cm}^{-1}$ . The difficulty in the study of this spectral region is a combination of the complexity of the overlap and the number of bands. The difficulty rests with the attribution of the multiple bands found in this region. In aqueous solutions of the phosphate ion, the band observed at 420  $\text{cm}^{-1}$  is assigned to the  $\nu_2$  bending mode. For ushkovite, Raman bands are observed at 386, 410, 421, 442, and 469  $\text{cm}^{-1}$ , with the band at 410  $\text{cm}^{-1}$  being the most intense. These bands are assigned to the phosphate  $\nu_2$   $\text{PO}_4^{3-}$  bending modes. The observation of several bands for the OPO bending region suggests the loss of degeneracy of the  $\text{PO}_4^{3-}$  bending modes. The only Raman data for comparison is that reported by Griffith [4], who suggested the bending mode was at 316  $\text{cm}^{-1}$ . However, this may be an error. Farmer [3] also did not report this bending mode. Intense Raman bands are observed at 563 and 583  $\text{cm}^{-1}$  and are attributed to the  $\text{PO}_4^{3-}$   $\nu_4$  bending modes. Other Raman bands are observed at 492, 506, 606, 610 and 637  $\text{cm}^{-1}$ . The low intensity Raman bands at 313 and 321  $\text{cm}^{-1}$  are thought to be due to FeO stretching vibrations.

In the Raman spectrum (Fig. 5b), the low intensity bands are attributed to lattice vibrational modes. Intense Raman bands are observed at 144, 183, 206, 216 and 261  $\text{cm}^{-1}$ . Other low intensity bands are noted.

The Raman spectrum of ushkovite over the 2800–3800  $\text{cm}^{-1}$  spectral range is shown in Fig. 6a. The Raman spectrum shows complexity with a number of overlapping bands. The Raman spectrum is broad with overlapping bands observed at 3225, 3286, 3449, 3495 and 3517  $\text{cm}^{-1}$ . The first three bands are attributed to water with strong hydrogen bonding. The Raman bands at 3449, 3495 and 3517  $\text{cm}^{-1}$  are due to water with moderate hydrogen bonding.

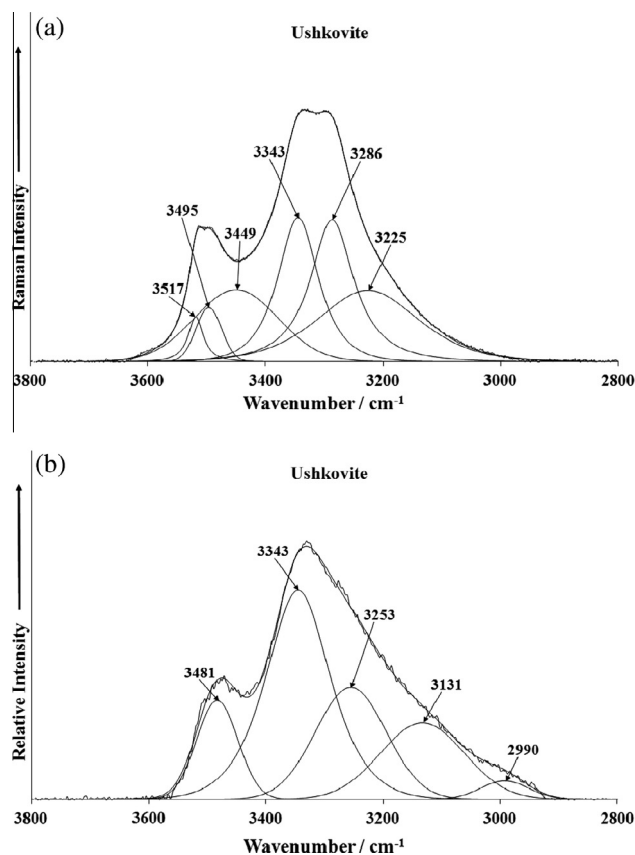


Fig. 6. (a) Raman spectrum of ushkovite (upper spectrum) in the 2800–3800  $\text{cm}^{-1}$  spectral range and (b) infrared spectrum of ushkovite (lower spectrum) in the 2800–3800  $\text{cm}^{-1}$  spectral range.

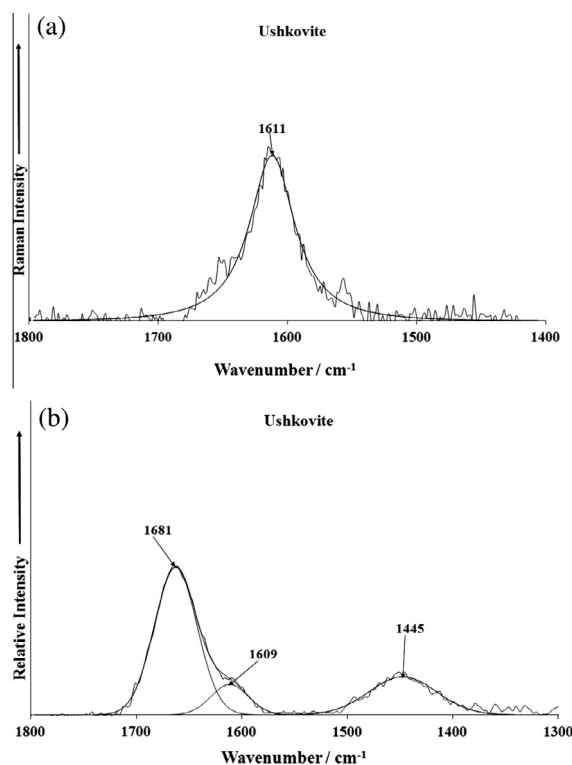


Fig. 7. (a) Raman spectrum of ushkovite (upper spectrum) in the 1400–1800  $\text{cm}^{-1}$  spectral range and (b) infrared spectrum of ushkovite (lower spectrum) in the 1300–1800  $\text{cm}^{-1}$  spectral range.

The infrared spectrum of ushkovite over the 2800–3800  $\text{cm}^{-1}$  spectral range is shown in Fig. 6b. The spectrum appears broad and complex with a significant number of bands. Infrared bands are noted at 2990, 3131, 3253, 3343 and 3481  $\text{cm}^{-1}$ . These bands are ascribed to the stretching bands of water. The number of observed bands proves that water is involved in a number of molecular environments with a wide range of hydrogen bonding strengths. The infrared bands at 2990 and 3131  $\text{cm}^{-1}$  are indicative of water with short hydrogen bonds. The infrared bands at 3253 and 3343  $\text{cm}^{-1}$  are due to water with moderate hydrogen bonding, whereas the band at 3481  $\text{cm}^{-1}$  is due to weak hydrogen bonding.

The Raman spectrum of ushkovite over the 1400–1800  $\text{cm}^{-1}$  spectral range is shown in Fig. 7a. Raman band is observed at 1611  $\text{cm}^{-1}$  and is assigned to water bending modes.

The infrared spectrum of ushkovite over the 1400–1800  $\text{cm}^{-1}$  spectral range is shown in Fig. 7b. The infrared spectrum in this spectral region displays infrared bands at 1609 and 1681  $\text{cm}^{-1}$ . These bands are assigned to the bending modes of water. The position of these bands shows that water is in the structure of ushkovite with different hydrogen bond strengths. The number of bands observed in this spectral region is in harmony with the number of bands in the hydroxyl stretching region (Fig. 6b).

## Conclusions

A combination of Raman and infrared spectroscopy has been used to study the phosphate mineral ushkovite. Bands attributed to the water hydroxyl stretching, bending and librational modes are identified and show the existence of different types of water molecules in the structure, namely adsorbed, weakly and strongly hydrogen-bonded. A single phosphate symmetric stretching vibration is observed but several antisymmetric stretching modes are observed consistent with a loss of symmetry of the phosphate anion in the mineral crystals. The loss of symmetry also results

in several in-plane and out of plane bending modes. The observation of blue materials in soils and sediments has suggested the use of Raman spectroscopy for the identification of ushkovite in these soils. It is suspected that the other phosphate minerals exist in ground water drainage sites but this remains to be proved.

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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.molstruc.2014.10.017>.

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