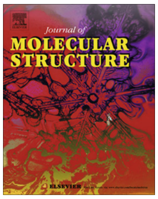
Journal of Molecular Structure 1081 (2015) 329–333

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



SEM, EDX and vibrational spectroscopic study of the phosphate mineral ushkovite $MgFe_2^{3+}(PO_4)_2(OH)_2 \cdot 8H_2O$ – 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.

ARTICLE INFO

Article history:
Received 18 August 2014
Received in revised form 8 October 2014
Accepted 9 October 2014
Available online 29 October 2014

Keywords:
Ushkovite
Phosphate
Hydroxyl
Raman spectroscopy
SEM
EDX

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 $Mg_3^{2+}(PO_4)_2 \cdot 8H_2O$. The Raman spectrum shows an intense band at 953 cm^{-1} assigned to the ν_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 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 cm^{-1}. The wavenumber band at 3457 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 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.

Introduction

The mineral ushkovite of formula $MgFe_2^{3+}(PO_4)_2(OH)_2 \cdot 8H_2O$ 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 $Fe^{2+}(Fe^{3+})_2(AsO_4)_2(OH)_2 \cdot 8H_2O$, ferrolaueite $Fe^{2+}Fe_2^{3+}(PO_4)_2(OH)_2 \cdot 8H_2O$, gordonite $MgAl_2^{3+}(PO_4)_2(OH)_2 \cdot 8H_2O$, kastningite $(Mn^{2+}, Fe^{2+}, Mg)Al_2(PO_4)_2(OH)_2 \cdot 8H_2O$, laueite $Mn^{2+}Fe_2^{3+}(PO_4)_2(OH)_2 \cdot 8H_2O$, maghrebite $MgAl_2(AsO_4)_2(OH)_2 \cdot 8H_2O$, mangangordonite $Mn^{2+}Al_2^{3+}(PO_4)_2(OH)_2 \cdot 8H_2O$, paravauxite $Fe^{2+}Al_2^{3+}(PO_4)_2(OH)_2 \cdot 8H_2O$ and sigloite $Fe^{3+}Al_2^{3+}(PO_4)_2(OH)_2 \cdot 7H_2O$ [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 Mg^{2+} and 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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http://dx.doi.org/10.1016/j.molstruc.2014.10.017
0022-2860/

phosphate anion in aqueous systems, (ν_1) is observed at 938 cm^{-1}, the asymmetric stretching mode (ν_3) at 1018 cm^{-1}. The ν_2 mode is observed at 420 cm^{-1} and the ν_4 mode at 567 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 cm^{-1}. Bands at 890 and 872 cm^{-1} were not assigned. It is probable that these are the symmetric stretching modes of the hydrogen bonded phosphate. Bands for the ν_4 mode was observed at 475, 560 and 590 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 [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 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 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×, 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 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 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 Spectracalc 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 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 cm^{-1} spectral range is displayed in Fig. 3a. This figure displays the Raman spectrum over the 100–4000 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

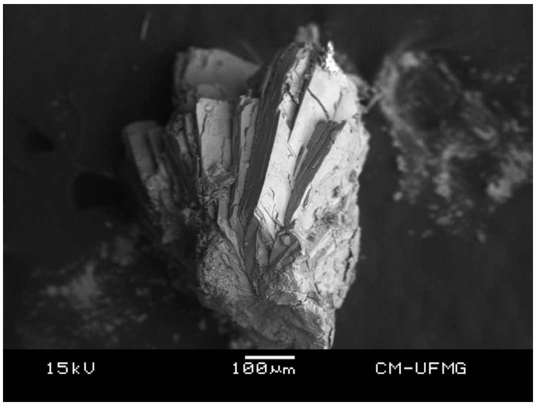

Fig. 1. Backscattered electron image (BSI) of a ushkovite crystal aggregate up to 0.5 mm in length.