



Vibrational spectroscopic characterization of the sulphate mineral leightonite $K_2Ca_2Cu(SO_4)_4 \cdot 2H_2O$ – Implications for the molecular structure

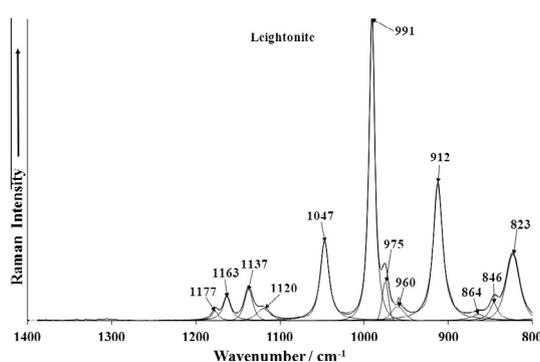
Ray L. Frost^{a,*}, Andrés López^a, Yunfei Xi^a, Ricardo Scholz^b, Leonardo Martins Graça^b, Leonardo Lagoeiro^b

^a School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia
^b Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35,400-00, Brazil

HIGHLIGHTS

- Leightonite is a rare sulphate mineral of formula $K_2Ca_2Cu(SO_4)_4 \cdot 2H_2O$.
- The chemical analysis was undertaken by electron probe.
- The molecular structure was ascertained by vibrational spectroscopy.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 12 February 2013
 Received in revised form 18 March 2013
 Accepted 2 April 2013
 Available online 11 April 2013

Keywords:

Leightonite
 Sulphate
 Molecular structure
 Raman spectroscopy
 Infrared spectroscopy

ABSTRACT

The mineral leightonite, a rare sulphate mineral of formula $K_2Ca_2Cu(SO_4)_4 \cdot 2H_2O$, has been studied using a combination of electron probe and vibrational spectroscopy. The mineral is characterized by an intense Raman band at 991 cm^{-1} attributed to the SO_4^{2-} ν_1 symmetric stretching mode. A series of Raman bands at 1047, 1120, 1137, 1163 and 1177 cm^{-1} assigned to the SO_4^{2-} ν_3 antisymmetric stretching modes. The observation of multiple bands shows that the symmetry of the sulphate anion is reduced. Multiple Raman and infrared bands in the OH stretching region shows that water in the structure of leightonite is in a range of molecular environments.

© 2013 Elsevier B.V. All rights reserved.

Introduction

Leightonite is a rare sulphate mineral of formula $K_2Ca_2Cu(SO_4)_4 \cdot 2H_2O$. The mineral was first described in the Chuquicamata mine, Atacama desert, Chile [1]. As well as this type locality, leightonite was also described from Tsumeb, Namibia by Keller [2]. In the first study, the mineral was considered as triclinic, based on morpho-

logical description. Later, van Loan in a X-ray diffraction study have determined the crystal structure as orthorhombic [3].

In recent study, Menchetti et al. [4], have refined the crystal structure of leightonite and considered the mineral as monoclinic, space group $C2/c$ and with unit cell parameters give as: $a = 11.654$, $b = 7.497$, $c = 10.097\text{ \AA}$, $\beta = 125.21^\circ$, $V = 720.8\text{ \AA}^3$ [3]. According to these authors, structural sub-units $[Ca(SO_4)_2]^{2-}$ formed by one CaO_8 polyhedron and two opposite-sided SO_4 tetrahedra are linked by edge-sharing. These sub-units are linked to each other by corner sharing to form a three-dimensional framework with channels, where the Cu atoms are located.

* Corresponding author. Tel.: +61 7 3138 2407; fax: +61 7 3138 1804.
 E-mail address: r.frost@qut.edu.au (R.L. Frost).

The genesis of leightonite is related to low acidity conditions [1] and from acid solutions at fairly high temperatures [2]. Published data concerning leightonite are rare in the scientific literature. Thermodynamic study of leightonite was carried out by Wollmann et al. [5]. To the best knowledge of the authors, data about vibrational spectroscopic characterization of leightonite are restricted to the database of the University of Arizona (rruff.info); however no interpretation is given. In recent years, the application of spectroscopic techniques to understand the structure of sulphates has been increasing. In this work, a sample of the rare mineral leightonite from the type locality was studied. Characterization includes chemistry via scanning electron microscopy (SEM) in the EDS mode and spectroscopic characterization of the structure with infrared and Raman spectroscopy.

Experimental

Occurrence, samples description and preparation

The leightonite sample studied in this work was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAB-092. The origin of this leightonite sample is from the Chuquicamata mine, and can be considered as a type material. The sample was gently crushed and prepared to be analysed by different methods. Scanning electron microscopy (SEM) 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>). A fragment of a leightonite single crystal was prepared in a carbon tape. Due to the low vacuum conditions, the sample was not metalized. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and quantitative chemical analyses in the EDS mode were performed with a ThermoNORAN spectrometer model Quest. These analyses were used to support the formula of the mineral and the mineral. It should be noted that microprobe analysis is not useful because the mineral is soluble in water and other solvents and is not possible to prepare the mineral sample through polishing.

Raman microprobe spectroscopy

A leightonite single crystal was 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 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 \times) were accumulated to improve the signal to noise ratio of the spectra. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

Raman spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond

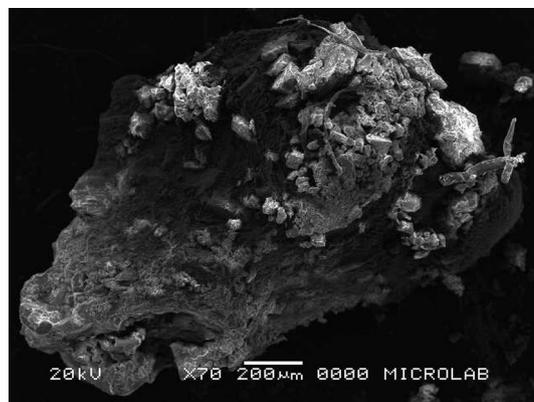


Fig. 1. The backscattered electron image (BSI) of a leightonite fragment up to 2.0 mm in length.

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 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 leightonite sample studied in this work is shown in Fig. 1. The image shows an anhedral fragment up to 1 mm with euhedral to sub-euhedral single crystals on the surface. Qualitative chemical analysis shows a homogeneous phase, composed by S, K, Ca and Cu. Minor amounts of Na and Mg were also observed (Fig. 2). Thus, if we accept some replacement of the atoms, then Na may replace the K in the formula and also some Mg may replace the Ca in the formula. So a modified formula would be (K,Na)₂(Ca,Mg)₂Cu(SO₄)₄·2H₂O. It is not unusual to have some isomorphous substitution.

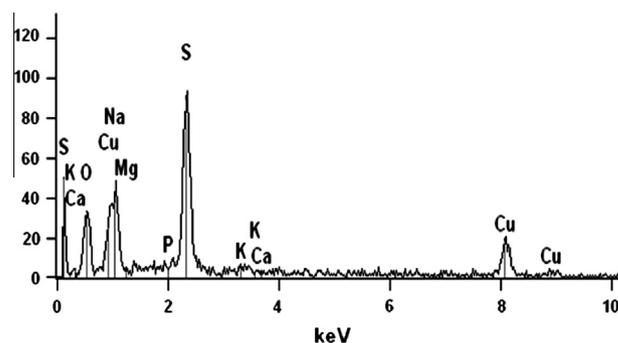


Fig. 2. The EDS spectra of leightonite.

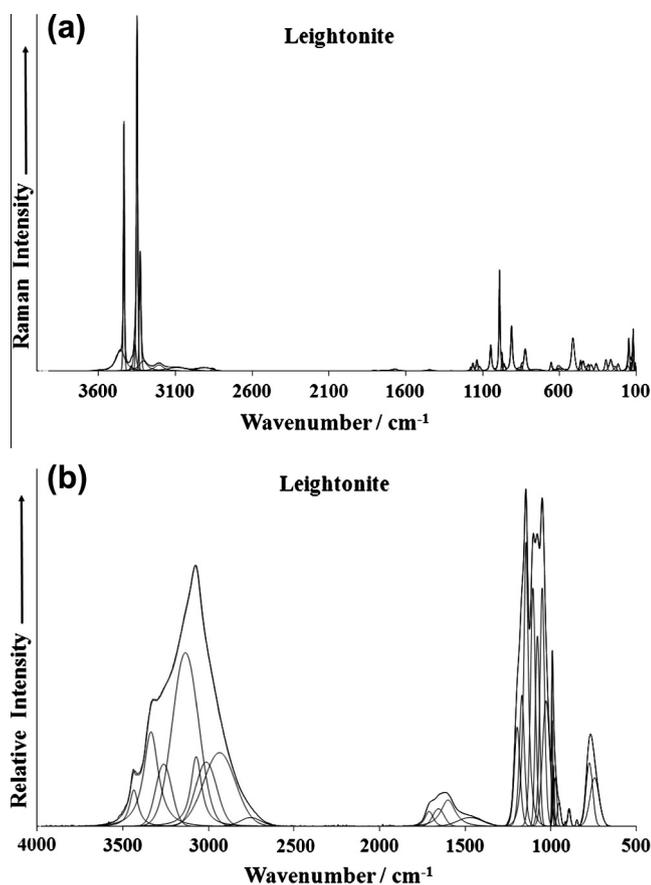


Fig. 3. (a) Raman spectrum of leightonite over the 100–4000 cm^{-1} spectral range and (b) Infrared spectrum of leightonite over the 500–4000 cm^{-1} spectral range.

Spectroscopy

Background spectroscopy of sulphate

The Raman spectroscopy of the aqueous sulphate tetrahedral oxyanion yields the symmetric stretching (ν_1) vibration at 981 cm^{-1} , the in-plane bending (ν_2) mode at 451 cm^{-1} , the anti-symmetric stretching (ν_3) mode at 1104 cm^{-1} and the out-of-plane bending (ν_4) mode at 613 cm^{-1} [6]. Ross reports the interpretation of the infrared spectra for potassium alum as ν_1 , 981 cm^{-1} ; ν_2 , 465 cm^{-1} ; ν_3 , 1200, 1105 cm^{-1} ; ν_4 , 618 and 600 cm^{-1} [7]. Water stretching modes were reported at 3400 and 3000 cm^{-1} , water bending modes at 1645 cm^{-1} , and water librational modes at 930 and 700 cm^{-1} [8]. The Raman spectrum of the mineral chalcantite shows a single symmetric stretching mode at 984.7 cm^{-1} . Two ν_2 modes are observed at 463 and 445 cm^{-1} and three ν_3 modes at 1173, 1146 and 1100 cm^{-1} . The ν_4 mode is observed as a single band at 610 cm^{-1} . A complex set of overlapping bands is observed in the low wavenumber region at 257, 244, 210, 136 and 126 cm^{-1} . Recently, Raman spectra of four basic copper sulphate minerals, namely antlerite, brochantite, posnjakite and langite, were published [9]. The SO symmetric stretching modes for the four basic copper sulphate minerals are observed at 985, 990, 972 and 974 cm^{-1} . Only the mineral brochantite showed a single band in this region. Multiple bands were observed for these minerals in the antisymmetric stretching region.

Ross also lists the infrared spectra of the pseudo-alums formed from one divalent and one trivalent cations. Halotrichite has infrared bands at ν_1 , 1000 cm^{-1} ; ν_2 , 480 cm^{-1} ; ν_3 , 1121, 1085, 1068 cm^{-1} ; ν_4 , 645, 600 cm^{-1} . Pickeringite the Mg end member of the halotrichite–pickeringite series has infrared bands at ν_1 , 1000 cm^{-1} ; ν_2 , 435 cm^{-1} ; ν_3 , 1085, 1025 cm^{-1} ; ν_4 , 638, 600 cm^{-1}

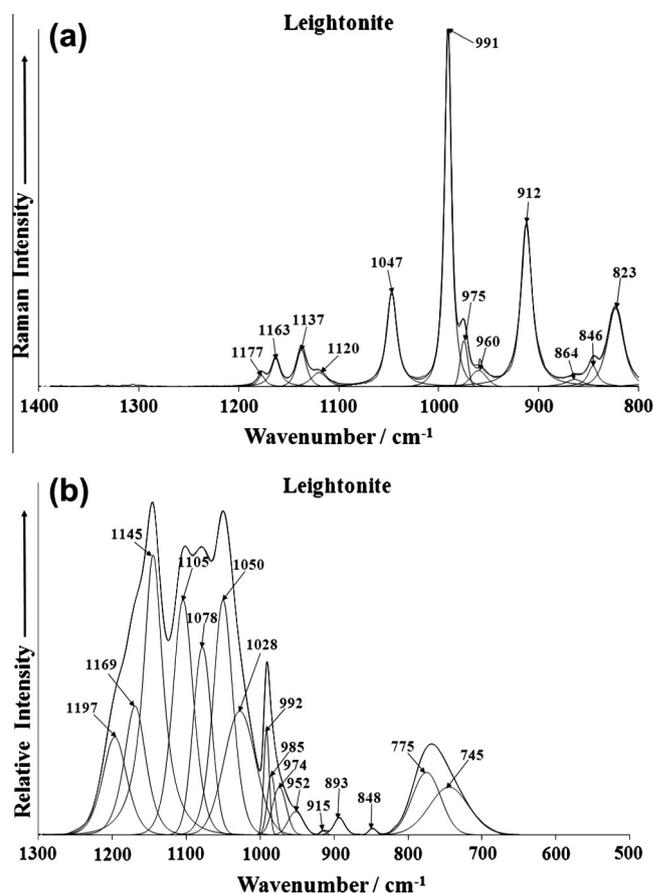


Fig. 4. (a) Raman spectrum of leightonite over the 800–1400 cm^{-1} spectral range and (b) Infrared spectrum of leightonite over the 500–1300 cm^{-1} spectral range.

[7]. These minerals display infrared water bands in the OH stretching, 3400 and 3000 cm^{-1} region; OH deformation, 1650 cm^{-1} region; OH libration, 725 cm^{-1} region. Ross also reports a weak band at $\sim 960 \text{ cm}^{-1}$ assigned to a second OH librational vibration [7]. As with the infrared spectra, Raman spectra of alums are based on the combination of the spectra of the sulphate and water. Sulphate typically is a tetrahedral oxyanion with Raman bands at 981 (ν_1), 451 (ν_2), 1104 (ν_3) and 613 (ν_4) cm^{-1} [10]. Some sulphates have their symmetry reduced through acting as monodentate and bidentate ligands [10]. In the case of bidentate behaviour both bridging and chelating ligands are known. This reduction in symmetry is observed by the splitting of the ν_3 and ν_4 into two components under C_{3v} symmetry and three components under C_{2v} symmetry. A complex set of overlapping bands is observed in the low wavenumber region with broad bands observed at 257, 244, 210, 136 and 126 cm^{-1} . Recently, Raman spectra of four basic copper sulphate minerals, namely antlerite, brochantite, posnjakite and langite, were published [9]. The SO symmetric stretching modes for the four basic copper sulphate minerals are observed at 985, 990, 972 and 974 cm^{-1} . Only the mineral brochantite showed a single band in this region. Multiple bands were observed for these minerals in the antisymmetric stretching region.

Vibrational spectroscopy

The Raman spectrum of leightonite over the complete wavenumber range from 100 to 4000 cm^{-1} spectral range is displayed in Fig. 3a. This spectrum shows the position of the peaks and the relative intensities of the bands. It is apparent that there are large parts of the spectrum where no intensity is observed. Therefore, the spectrum is subdivided into sections depending upon the type of vibration being studied. The infrared spectrum over the

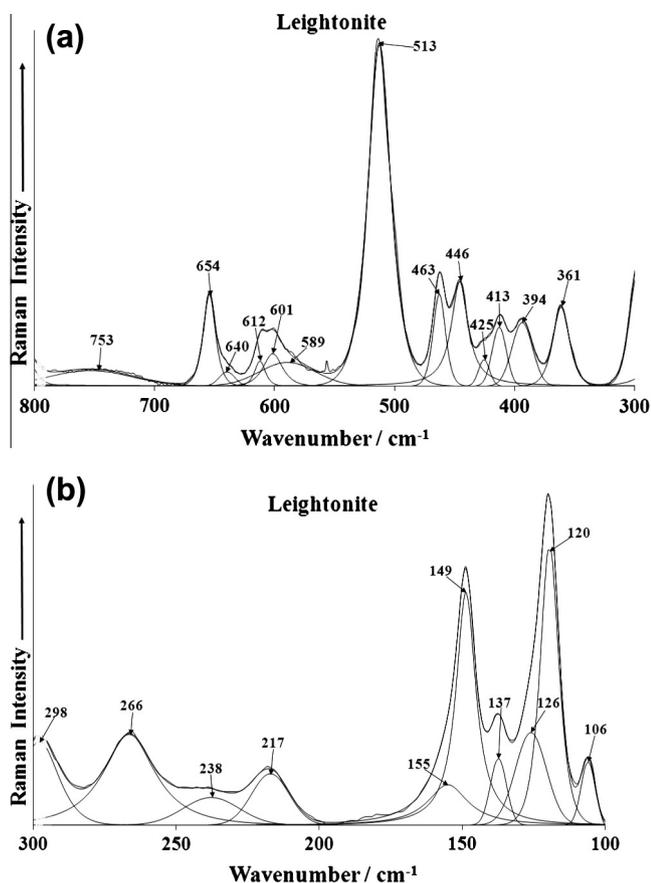


Fig. 5. (a) Raman spectrum of leightonite over the 300–800 cm^{-1} spectral range and (b) Raman spectrum of leightonite over the 100–300 cm^{-1} spectral range.

500–4000 cm^{-1} spectral range is reported in Fig. 3b. This spectrum of leightonite shows the relative intensity of the infrared bands and their position. There are also large parts of the infrared spectrum where no intensity is observed. Hence, the spectrum is subdivided into sections as a function of the type of vibration being examined.

The Raman spectrum of leightonite over the 800–1400 cm^{-1} spectral range is illustrated in Fig. 4a. This spectral region is where the sulphate stretching modes are observed [11]. An intense band at 991 cm^{-1} with shoulder bands at 975 and 960 cm^{-1} is assigned to the SO_4^{2-} ν_1 symmetric stretching mode. A series of bands at 1047, 1120, 1137, 1163 and 1177 cm^{-1} are assigned to the SO_4^{2-} ν_3 antisymmetric stretching modes. The observation of more than one band in the symmetric stretching region together with multiple antisymmetric stretching vibrations, supports the concept of the non-equivalence of the sulphate units in the structure of leightonite. This observation is supported by the random nature of the Cu^{2+} ions in the structure of leightonite [4]. It is proposed that the band at 912 cm^{-1} is assignable to the symmetric stretching vibration of HSO_4^- units.

The infrared spectrum (Fig. 4b) shows a sharp band at 992 cm^{-1} assigned to the SO_4^{2-} ν_1 symmetric stretching mode. Some shoulders to this band are found at 974 and 985 cm^{-1} . Multiple bands in this spectral region offers support to the concept that the sulphate units in the structure of leightonite are not equivalent. This concept is also supported by the number of SO_4^{2-} ν_3 antisymmetric stretching vibrations observed at 1028, 1050, 1078, 1105, 1145, 1169 and 1197 cm^{-1} . Thus, the molecular structure of leightonite shows greater complexity than might be observed with X-ray diffraction.

The Raman spectrum of leightonite in the 300–800 cm^{-1} and in the 100–300 cm^{-1} spectral ranges are reported in Fig. 5a and b. The

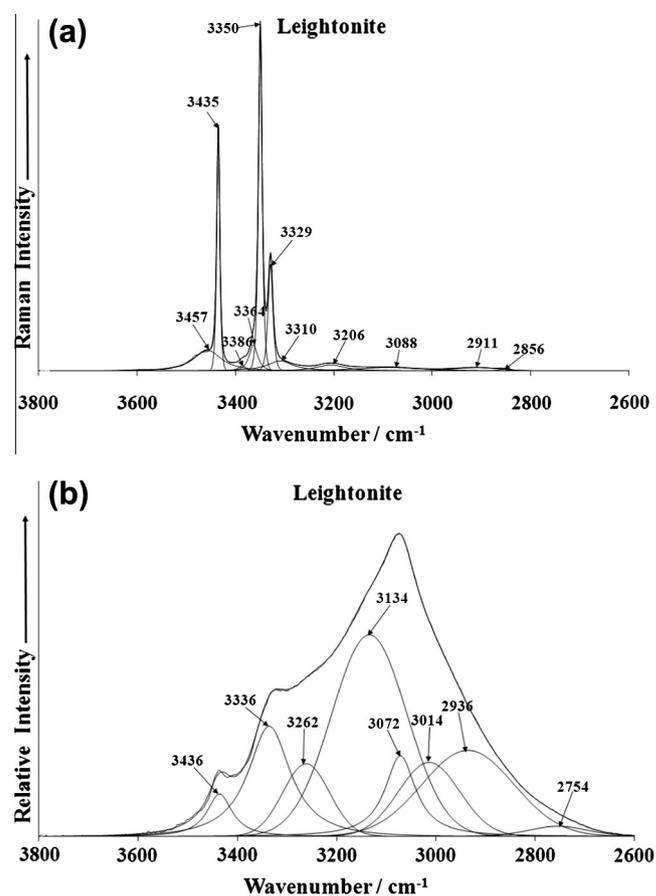


Fig. 6. (a) Raman spectrum of leightonite over the 2600–4000 cm^{-1} spectral range and (b) Infrared spectrum of leightonite over the 2600–4000 cm^{-1} spectral range.

spectrum is dominated by an intense band at 513 cm^{-1} assigned to the ν_4 (SO_4) $^{2-}$ bending mode. Raman bands at 601, 612, 640 and 654 cm^{-1} may also be assigned to this vibration. The observation of multiple bands in this spectral region offers support to the concept of reduction of symmetry of the sulphate anion in the crystal structure of leightonite.

The broad band at 753 cm^{-1} may be assigned to water librational modes. These bands are observed in the infrared spectrum at 745 and 775 cm^{-1} (Fig. 2b). The series of Raman bands at 394, 413, 425, 446 and 463 cm^{-1} are assigned to the ν_2 (SO_4) $^{2-}$ bending modes. These bands are not observed in the infrared spectrum as the ATR cell absorbs all the infrared radiation below 550 cm^{-1} . This vibrational mode at 361 cm^{-1} is attributed to metal–oxygen stretching bands (CaO and CuO). Raman bands observed in the 100 to 300 cm^{-1} spectral region at 120, 137, 149, 217, 266 and 298 cm^{-1} are simply attributed to lattice vibrations.

The Raman and infrared spectra in the 2600–3800 cm^{-1} spectral region are displayed in Figs. 6a and b. The Raman spectrum is characterized by sharp peaks at 3329, 3350 and 3435 cm^{-1} . These bands are assigned to the stretching vibrations of water. Other low intensity bands are observed at 3088, 3206, 3310 and 3457 cm^{-1} are also attributed to water stretching vibrations. No sharp bands are observed in the infrared spectrum but bands are found in similar positions. Infrared bands are found at 2936, 3014, 3072, 3134, 3262, 3336 and 3436 cm^{-1} . The observation of many bands proves the concept that water in the structure of leightonite is in a range of molecular environments.

The Raman spectrum of leightonite in the 1400–2000 cm^{-1} spectral range is reported in Fig. 7a; the infrared spectrum in the 1300–1800 cm^{-1} spectral range is shown in Fig. 7b. The Raman spectrum in this spectral range, although somewhat lacking in

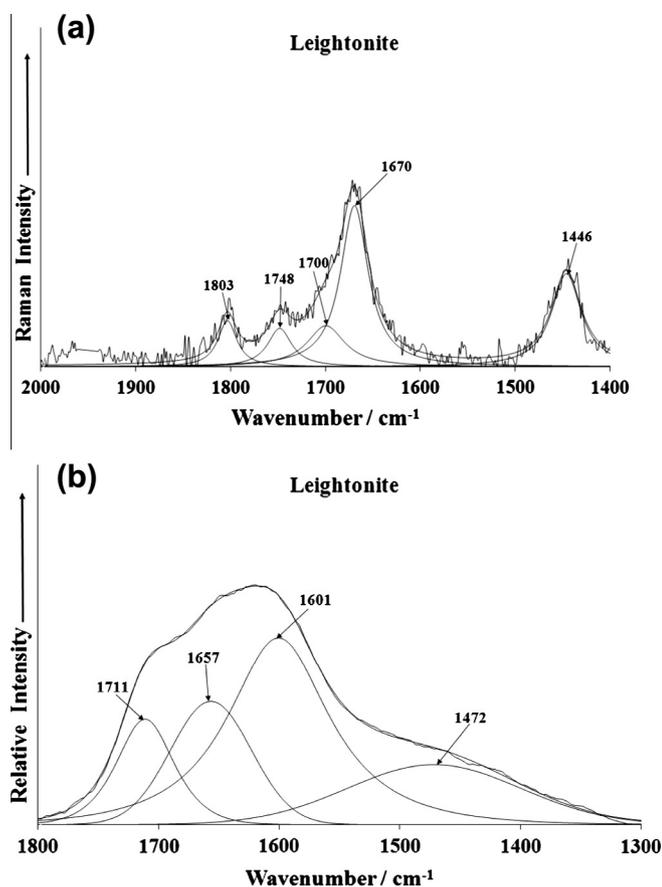


Fig. 7. (a) Raman spectrum of leightonite over the 1300–1800 cm^{-1} spectral range and (b) Infrared spectrum of leightonite over the 1300–1800 cm^{-1} spectral range.

signal shows distinct Raman bands at 1446, 1670, 1748 and 1803 cm^{-1} . The Raman band at 1670 cm^{-1} is broad and with a shoulder band at 1700 cm^{-1} is attributed to the water bending mode. In contrast, the infrared spectrum displays a broad spectral profile over the complete range. By using band component analysis, infrared bands may be resolved at 1472, 1601, 1657 and 1711 cm^{-1} . The infrared bands at 1601 and 1657 cm^{-1} are assigned to water bending modes. The last band may also be assigned to this vibrational mode although the wavenumber position is a little high. The observation of multiple bands in the water bending region provides support for the concept of water molecules in different molecular environments in the structure of leightonite.

Conclusions

Raman spectroscopy is a very powerful tool for the study of sulphate minerals. In this work, we have used vibrational spectroscopy to study the mineral leightonite, a mineral found in evaporate deposits and land surfaces with extreme aridity. It is important to add to our fundamental knowledge of the chemistry of leightonite, a mineral for which the fundamental knowledge is lacking. In this work we have determined the chemical composition of the mineral leightonite. We have used vibrational spectroscopy to characterize the molecular structure of the mineral.

Multiple antisymmetric stretching bands are observed as well as multiple bending modes suggesting a reduction in symmetry of the sulphate in the leightonite structure. The symmetry of the sulphate as observed by the number of bands in the ν_2 , ν_3 and ν_4 modes, is essentially reduced to C_{2v} . Two types of sulphate are identified and are associated with the two principal kinds of sites in the structure, as expected from the X-ray diffraction results as described in previous studies [3].

Acknowledgements

The financial and infra-structure support of the Discipline of Nanotechnology and Molecular Science, Science and Engineering Faculty of the Queensland University of Technology, is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation. The authors would like to acknowledge the Center of Microscopy at the Universidade Federal de Minas Gerais (<http://www.microscopia.ufmg.br>) for providing the equipment and technical support for experiments involving electron microscopy. R. Scholz thanks to FAPEMIG – Fundação de Amparo à Pesquisa do Estado de Minas Gerais, (Grant No. CRA-APQ-03998-10).

References

- [1] C. Palache, *Amer. Min.* 23 (1938) 34.
- [2] P. Keller, W. Bartelke, *Min. Rec.* 13 (1982) 137.
- [3] P.R. Van Loan, *Can. Min.* 7 (1962) 272.
- [4] S. Menchetti, L. Bindi, P. Bonazzi, F. Olmi, *Amer. Min.* 87 (2002) 721.
- [5] G. Wollmann, J. Seidel, W. W. J. Chem. Therm. 41 (2009) 484.
- [6] R.L. Frost, P.A. Williams, W. Martens, J.T. Kloprogge, P. Leverett, *J. Raman Spectrosc.* 33 (2002) 260.
- [7] S.D. Ross, in: *The infrared spectra of minerals*, Chapter 18, The Mineralogical Society London, 1974. pp. 423.
- [8] S.D. Ross, *Inorganic Infrared and Raman Spectra*, European Chemistry Series, McGraw-Hill, London, 1972.
- [9] W. Martens, R.L. Frost, J.T. Kloprogge, P.A. Williams, *J. Raman Spectrosc.* 34 (2003) 145.
- [10] R.L. Frost, J.T. Kloprogge, P.A. Williams, P. Leverett, *J. Raman Spectrosc.* 31 (2000) 1083.
- [11] V.C. Farmer, *Mineralogical Society Monograph 4: The Infrared Spectra of Minerals*, The Mineralogical Society, London, 1974.