# SEM–EDX, Raman and infrared spectroscopic characterization of the phosphate mineral frondelite $(Mn^{2+})(Fe^{3+})_4(PO_4)_3(OH)_5$

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HIGHLIGHTS

▸ We have analyzed a frondelite mineral sample from the Cigana mine, located in the municipality of Conselheiro Pena.
▸ The chemical formula was determined as $(Mn_{0.68}, Fe_{0.32})(Fe^{3+})_{3.72}(PO_4)_{3.72}(OH)_{4.99}$.
▸ The structure of the mineral was assessed using vibrational spectroscopy.
▸ Bands attributed to the stretching and bending modes of PO_4^{3-} and $HOPO_3^{3-}$ units were identified.

GRAPHICAL ABSTRACT
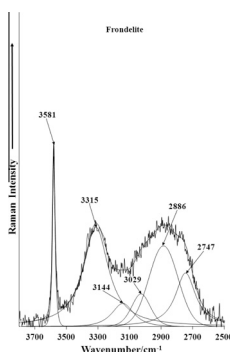
ARTICLE INFO

ABSTRACT

We have analyzed a frondelite mineral sample from the Cigana mine, located in the municipality of Conselheiro Pena, a well-known pegmatite in Brazil. In the Cigana pegmatite, secondary phosphates, namely eosphorite, fairfieldite, fluorapatite, frondelite, gormanite, hureaulite, lithiophilite, reddingite and vivianite are common minerals in miarolitic cavities and in massive blocks after triphylite. The chemical formula was determined as $(Mn_{0.68}, Fe_{0.32})(Fe^{3+})_{3.72}(PO_4)_{3.17}(OH)_{4.99}$.

The structure of the mineral was assessed using vibrational spectroscopy. Bands attributed to the stretching and bending modes of PO_4^{3-} and $HOPO_3^{3-}$ units were identified. The observation of multiple bands supports the concept of symmetry reduction of the phosphate anion in the frondelite structure. Sharp Raman and infrared bands at 3581 cm^{-1} is assigned to the OH stretching vibration. Broad Raman bands at 3063, 3529 and 3365 cm^{-1} are attributed to water stretching vibrational modes.

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Introduction

Secondary phosphates are common minerals in lithium bearing pegmatites and most of them are related to the superposition of different geological and geochemical process. Different stages of hydrothermalism and the low temperature supergene alteration are responsible for the substitution of primary lithium phosphates triphylite–lithiophilite and amblygonite–montebrasite, producing complex paragenesis [1]. In recent published articles, the characterization of the phosphate mineralogy became an important tool in the study of the geochemical and petrological evolution of pegmatites [2].

In addition to the occurrence in granitic pegmatites, minerals of the frondelite–rockbridgeite series were also identified in sediments of Elk Lake, Canada [3]. Low temperature Fe and Mn phosphates play important role in the environmental geochemistry. The crystalization of authigenic minerals in sediments, develop

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an important function in the removal and storage of metals and phosphate pollutants [4]. Despites their importance, some phosphate minerals are poorly characterized by spectroscopic methods, such as frondelite, rockbridgeite, reddingite and hureaulite.

Frondelite is a manganese and iron basic phosphate mineral with general chemical formula expressed by $(Mn^{2+})(Fe^{3+})_4(PO_4)_3(OH)_5$ and belongs to the rockbridgeite group [5]. Frondelite forms a complex triple series with rockbridgeite-$(Mn^{2+})(Fe^{3+})_4(PO_4)_3(OH)_5$, where the Mn^{2+} is replaced by Fe^{2+}, and plimerite-$(Zn^{2+})(Fe^{3+})_4(PO_4)_3(OH)_5$, where the Mn^{2+} is replaced by Zn^{2+} [5,6]. Frondelite crystallizes in orthorrombic crystal system, *Bbmm* space group with unit-cell parameters $a = 13.81$ Å, $b = 16.96$ Å, $c = 5.18$ Å, $Z = 4$ and $V = 1214.29$ Å^3.

Farmer [7] divided the vibrational spectra of phosphates according to the presence, or absence of water and hydroxyl units in the minerals. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (v_1) at 938 cm^{-1}, the antisymmetric stretching mode (v_3) at 1017 cm^{-1}, the symmetric bending mode (v_2) at 420 cm^{-1} and the v_4 mode at 567 cm^{-1} [8–10]. The value for the v_1 symmetric stretching vibration of PO_4 units as determined by infrared spectroscopy was given as 930 cm^{-1} (augelite), 940 cm^{-1} (wavellite), 970 cm^{-1} (rockbridgeite), 995 cm^{-1} (dufrenite) and 965 cm^{-1} (beraunite). The position of the symmetric stretching vibration is mineral dependent and a function of the cation and crystal structure. The fact that the symmetric stretching mode is observed in the infrared spectrum affirms a reduction in symmetry of the PO_4 units.

The value for the v_2 symmetric bending vibration of PO_4 units as determined by infrared spectroscopy was given as 438 cm^{-1} (augelite), 452 cm^{-1} (wavellite), 440 and 415 cm^{-1} (rockbridgeite), 455, 435 and 415 cm^{-1} (dufrenite) and 470 and 450 cm^{-1} (beraunite). The observation of multiple bending modes provides an indication of symmetry reduction of the PO_4 units. This symmetry reduction is also observed through the v_3 antisymmetric stretching vibrations. Augelite shows infrared bands at 1205, 1155, 1079 and 1015 cm^{-1} [11]; wavellite at 1145, 1102, 1062 and 1025 cm^{-1}; rockbridgeite at 1145, 1060 and 1030 cm^{-1}; dufrenite at 1135, 1070 and 1032 cm^{-1}; and beraunite at 1150, 1100, 1076 and 1035 cm^{-1}.

In the infrared study of triploidite, a basic manganese phosphate, Farmer reports the infrared spectrum with the (v_1) at 957 cm^{-1}, (v_3) at 1090, 1058, 1030 and 1010 cm^{-1}, (v_2) at 420 cm^{-1} and the v_4 mode at 595, 570, 486 cm^{-1} [12]. An hydroxyl stretching frequency of 3509 cm^{-1} was given. In the spectroscopic study of strengite, in the region below to 400 cm^{-1}, Frost and Weier [11] described the metal stretching vibrations for MnO and also the OMnO bending modes.

In this work, samples of a pure, monomineral frondelite–rockbridgeite from the Cigana pegmatite, located in the municipality of Conselheiro Pena, Brazil has been carried out. Studies include chemistry and backscattering images via SEM in the EDS mode, spectroscopic characterization of the structure with infrared and Raman spectroscopy.

Experimental

Sample description and preparation

The Cigana mine (also named as Jocão claim), located in the municipality of Conselheiro Pena, is a well-known pegmatite in Brazil, being an important source of rare phosphates. The pegmatite is located in the Conselheiro Pena pegmatite district, one of the subdivisions of the Eastern Brazilian Pegmatite province (EBP) that encompasses an area of about 150,000 km^2, extending from Bahia to Rio de Janeiro states.

The Cigana pegmatite is mined out and in the past was mined for industrial feldspar and with minor importance gemstones and samples for the collectors market. In the Cigana pegmatite, secondary phosphates, namely eosphorite, fairfieldite, fluorapatite, frondelite, gormanite, hureaulite, lithiophillite, reddingite and vivianite are common minerals in miarolitic cavities and in massive blocks formed after the aggregates of primary triphylite up to 0.5 m length. Frondelite occurs as botrioidal aggregates up to 10.0 cm in length. The aggregates appear in miarolitic cavities and replaces triphylite–lithiophilite crystals. Other minerals in association are hureaulite and lithiophilite.

Deep green frondelite botrioidal aggregates were collected. The sample was incorporated in the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-088. The aggregate was hand selected from a sample in association with hureaulite and lithiophilite. The frondelite fragments were phase analyzed by X-ray diffraction and Scanning electron microscopy (SEM) for simple characterization.

Electron probe micro-analysis (EPMA)

A quantitative chemical analysis was carried via EPMA. Frondelite–rockbridgeite botrioidal aggregate selected for this study was analyzed with the performance of five spots. The chemical analysis was carried out with a Jeol JXA8900R spectrometer from the Physics Department of the Federal University of Minas Gerais, Belo Horizonte. For each selected element was used the following standards: Fe – magnetite, Mn – rodhonite, P – Ca$_2$P$_2$O$_7$ Ca – Apatite Astimex. The limit detection is up to 0.01 wt%. The epoxy embedded frondelite sample was polished in the sequence of 9 μm, 6 μm and 1 μm diamond paste MetaDI® II Diamond Paste – Buhler, using water as a lubricant, with a semi-automatic Mini-Met® 1000 Grinder-Polisher – Buehler. Finally, the epoxy embedded hureaulite was coated with a thin layer of evaporated carbon. The electron probe microanalysis in the WDS (wavelength dispersive spectrometer) mode was obtained at 15 kV accelerating voltage and beam current of 10 nA. Chemical formula was calculated on the basis of seventeen oxygen atoms (O, OH, F).

Raman microprobe spectroscopy

Botrioidal aggregates of frondelite 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 samples using the highest magnification (50×) were accumulated to improve the signal to noise ratio of the spectra. The spectra were collected over night. Raman Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. The Raman spectrum

Table 1
Chemical composition of reddingite–phosphoferrite from Cigana pegmatite (mean of four electron microprobe analyses). H$_2$O calculated by stoichiometry.

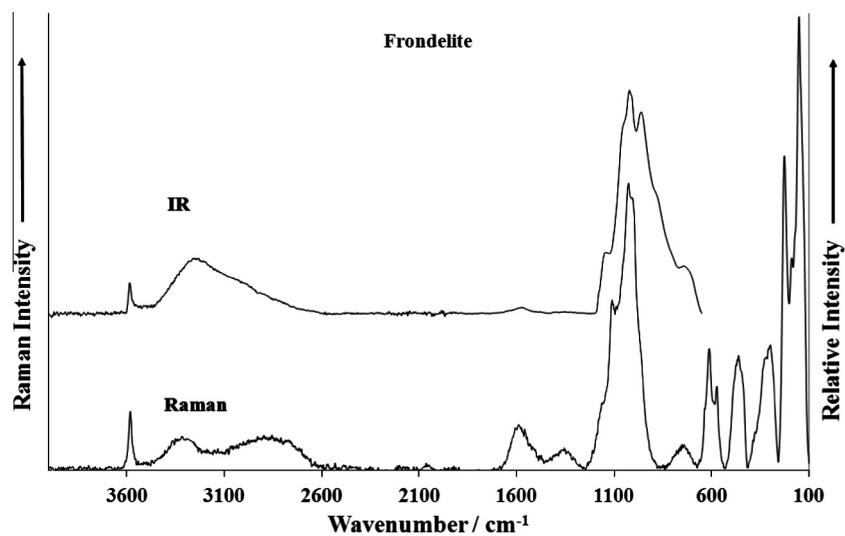| Constituent	wt.%	Number of cations	Range (wt.%)	Probe standard
MnO	7.40	0.68	7.11–7.82	Rodhonite
FeO	3.6	0.32	43.29–46.70	Magnetite
Fe$_2$O$_3$	45.91	3.72		
MgO	0.07	0.00	0.01–0.04	MgO
P$_2$O$_5$	34.82	3.17	34.27–35.31	Ca$_2$P$_2$O$_7$
H$_2$O	6.94	4.99	Calculated by stoichiometry	
Total	98.68	12.88		

Fig. 1. Raman spectrum of frondelite over the 100–4000 cm^{-1} spectral range and Infrared spectrum of frondelite over the 500–4000 cm^{-1} spectral range.
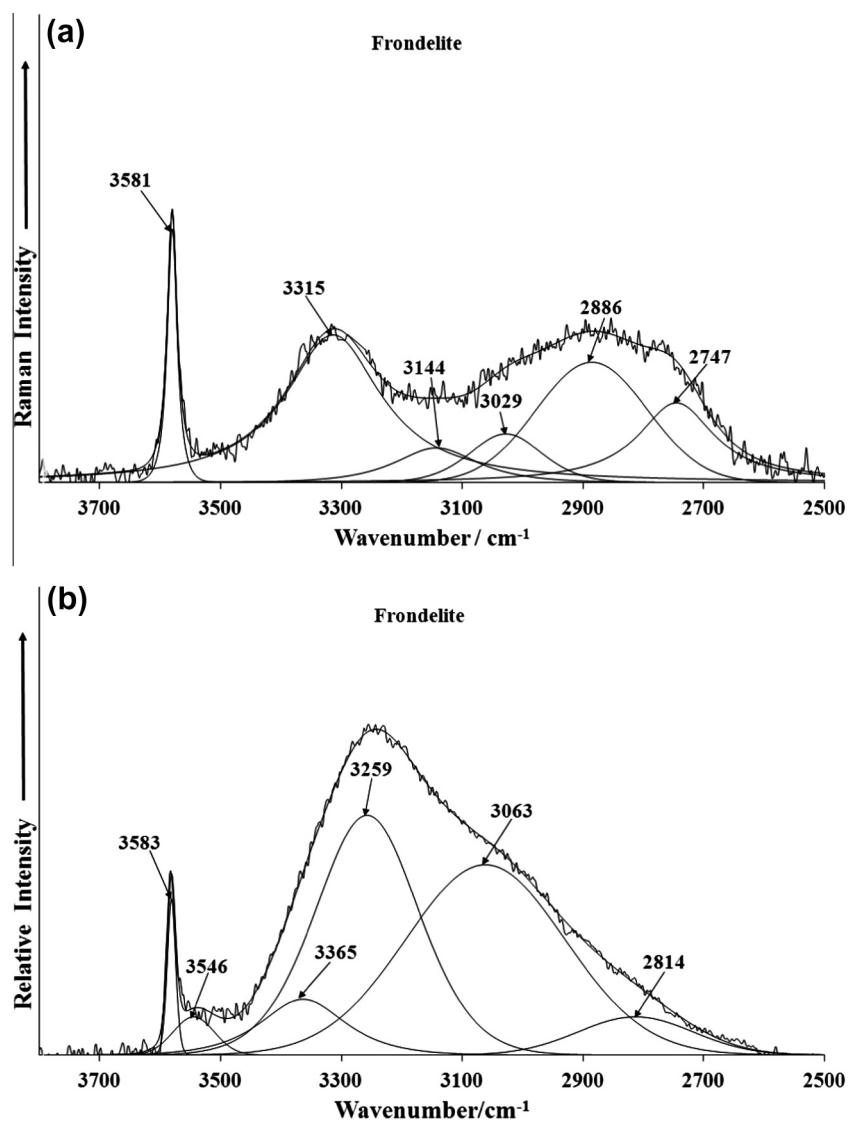

Fig. 2. (a) Raman spectrum of frondelite over the 2600–4000 cm^{-1} spectral range and (b) Infrared spectrum of frondelite over the 2600–4000 cm^{-1} spectral range.
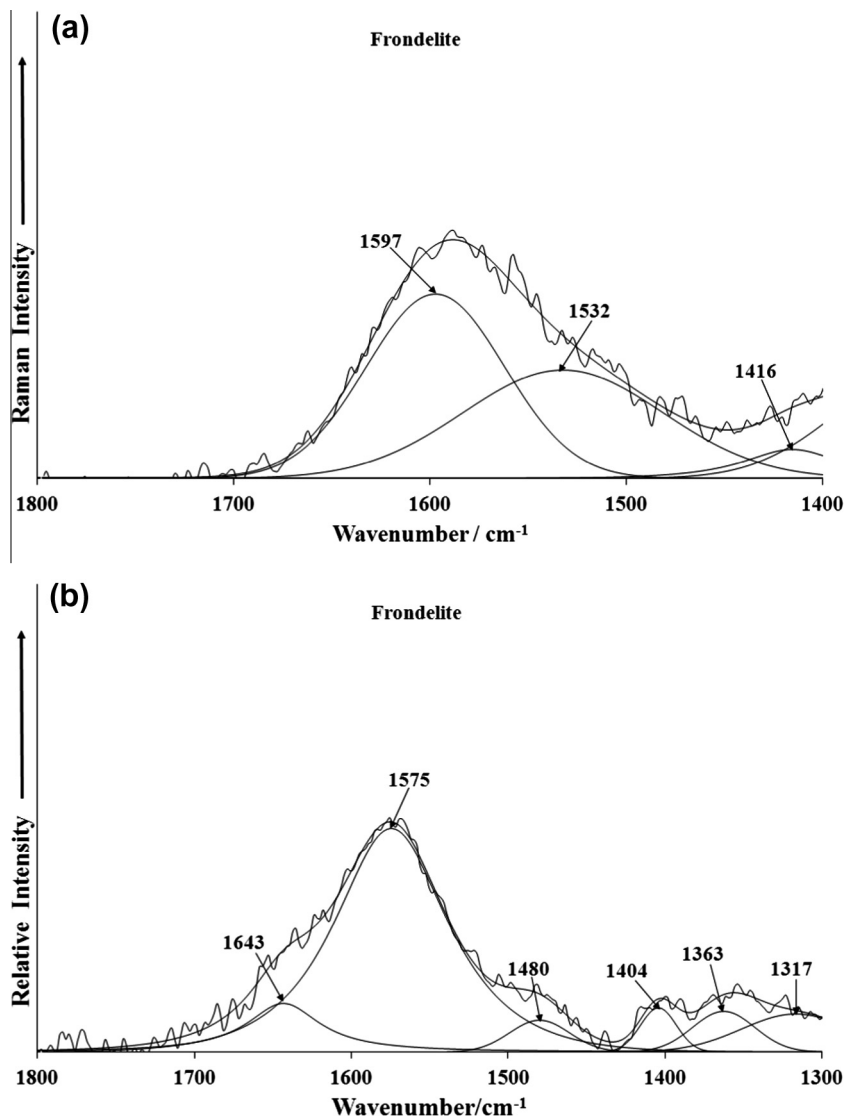
Fig. 3. (a) Raman spectrum of frondelite over the 1300–1800 cm^{-1} spectral range and (b) Infrared spectrum of frondelite over the 1300–1800 cm^{-1} spectral range.

of at least 10 crystals was collected to ensure the consistency of the spectra.

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. The infrared spectra are given in the Supplementary information.

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 Gaussian–Lorentzian ratio was maintained at values greater than 0.7 and fitting was under-

taken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Results and discussion

Chemical characterization

The quantitative chemical analysis of frondelite–rockbridgeite mineral series is presented in Table 1. Composition is the result of medium values in five spots. H_2O content was calculated by stoichiometry and the chemical formula was calculated on the basis of seventeen oxygen atoms (O, OH, F) on the structure. The Fe^{2+}/Fe^{3+} ratios was calculated by stoichiometry considering the occupancy of the tetrahedral site by $Mn^{2+} + Fe^{2+} + Mg^{2+} = 1$. The chemical composition indicates an intermediate member of the frondelite–rockbridgeite series with predominance of frondelite under rockbridgeite. Small amounts of magnesium were detected and that replaces Mn and Fe in the structure. Chemical formula can be expressed as: $(Mn_{0.68}, Fe_{0.32})(Fe^{3+})_{3.72}(PO_4)_{3.72}(OH)_{4.99}$.

The cationic deficiency in the octahedral site is observed due to the lower amount of Fe^{3+} (3.72 atoms) than expected (four atoms). This phenomenon can be explained due to vacancies that
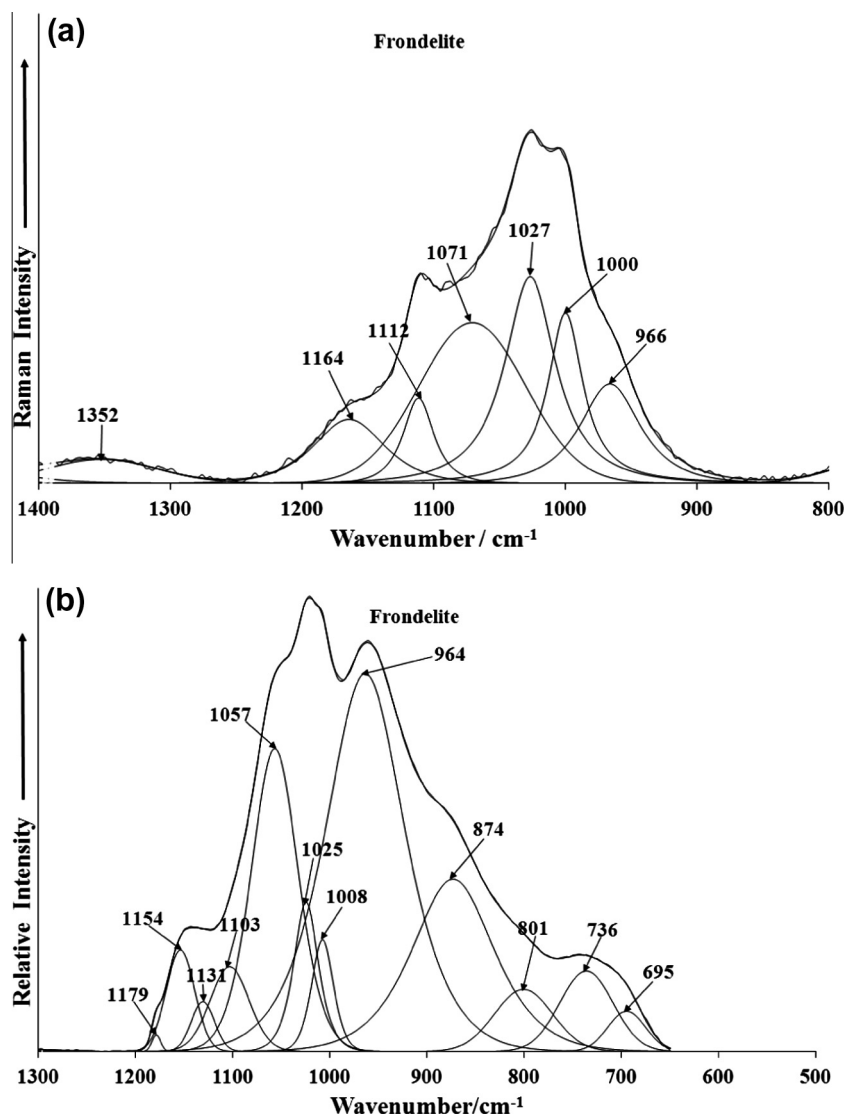
Fig. 4. (a) Raman spectrum of frondelite over the 800–1400 cm^{-1} spectral range and (b) Infrared spectrum of frondelite over the 500–1300 cm^{-1} spectral range.

commonly occur in secondary phosphates. The presence of vacancies is supported by the presence of H$^+$ in the HOPO$_3^{3-}$ units as observed in the Raman spectra.

Vibrational spectroscopy

The Raman spectrum of frondelite in the 100–4000 cm^{-1} spectral range is illustrated in Fig. 1. This spectrum displays the position and relative intensity of the Raman bands. It is noted and spectral intensity in the 2600–4000 cm^{-1} spectral region is minimal. It is noted that there are large parts of the spectrum where no intensity is observed. Thus, the Raman spectrum is divided into sections according to the type of vibration being observed. The infrared spectrum of frondelite over the 500–4000 cm^{-1} spectral range is also shown in Fig. 1. This figure records the position and relative intensity of the infrared bands. Some intensity is now observed in the OH stretching region.

The Raman spectrum of frondelite in the 2500–3800 cm^{-1} spectral range is illustrated in Fig. 2a. This spectrum displays a sharp band at 3581 cm^{-1} superimposed upon a broad spectral profile. This sharp band is attributed to the stretching vibrations of the OH units. The broad spectral profile may be resolved into compo-

nent bands at 2747, 2886, 3027, 3157 and 3325 cm^{-1}. These bands are assigned to water stretching vibrations. The infrared spectrum in the 2500–3700 cm^{-1} spectral range is reported in Fig. 2b. As for the Raman spectrum, the spectral profile consists of a sharp band at 3583 cm^{-1} assigned to the stretching vibrations of the OH units and a broad spectral profile with component bands at 3063, 3529 and 3365 cm^{-1}. These latter bands are attributed to water stretching vibrations.

A question that might be raised is the formula as written above Mn$_{0.68}$, Fe$_{0.32}$)(Fe^{3+})$_{3.72}$(PO$_4$)$_{3.17}$(OH)$_{4.99}$ correct? Both Raman and infrared spectroscopy clearly shows the existence of OH units. Further Raman spectroscopy identifies bands which are attributed to HOPO$_3^{3-}$ units. Thus some of the protons from water are associated with the phosphate units. It is suggested that the formula of frondelite is better written as (Mn$_{0.68}$, Fe$_{0.32}$)(Fe^{3+},Υ)$_{3.72}$ (PO$_4$,HOPO$_3$)$_{3.17}$(OH,H$_2$O)$_{4.99}$.

The Raman spectrum in the 1400–1800 cm^{-1} spectral range is shown in Fig. 3a. The spectrum suffers from a lack of signal. The spectral profile may be resolved into component bands at 1532 and 1597 cm^{-1}. This latter band is attributed to the bending mode of non-hydrogen bonded water. The Raman spectrum of water is of a very low intensity as water is a very poor Raman scatterer. On the
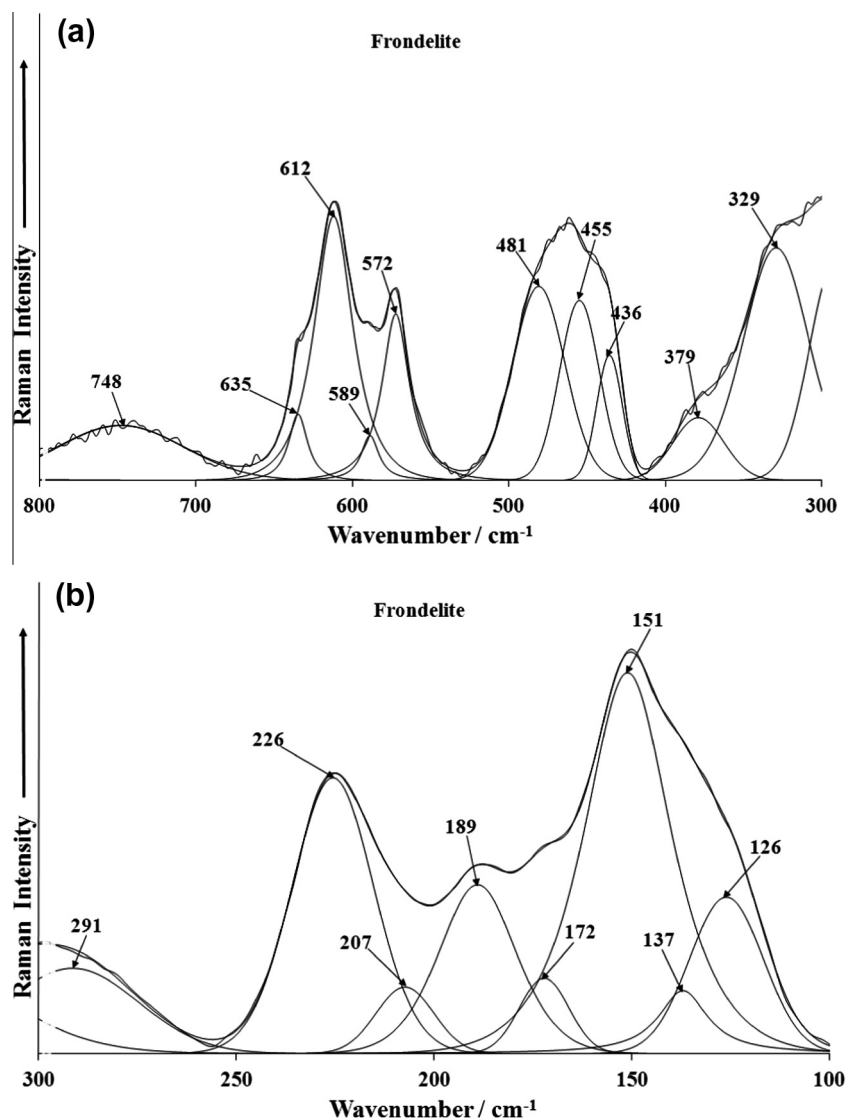
Fig. 5. (a) Raman spectrum of frondelite over the 300–800 cm^{-1} spectral range and (b) Raman spectrum of frondelite over the 100–300 cm^{-1} spectral range.

other hand, water is an intense infrared absorber and thus the infrared spectrum as shown in Fig. 3b, shows significant intensity. A band is resolved at 1643 cm^{-1} and is assigned to the water bending mode of strongly hydrogen bonded water. Other infrared bands are observed at 1480 and 1575 cm^{-1}. These bands are considered to be combination bands.

The Raman spectrum of frondelite in the 800–1400 cm^{-1} spectral range is displayed in Fig. 4a. The spectrum shows a complex profile with component bands resolved in the spectrum using band component analysis. Raman bands are observed at 966, 1000, 1027, 1071, 1112 and 1164 cm^{-1}. The Raman band at 1000 cm^{-1} is assigned to the v_1 symmetric stretching mode of the PO_4^{3-} units. The band at 966 cm^{-1} is attributed to the $HOPO_3^{3-}$ units. The Raman bands at 1071, 1112 and 1164 cm^{-1} are attributed to both the HOP and PO antisymmetric stretching vibrations.

Choi et al. reported the polarization spectra of NaH_2PO_4 crystals. Casciani and Condrate [13] published spectra on brushite and monetite together with synthetic anhydrous monocalcium phosphate ($Ca(H_2PO_4)_2$), monocalcium dihydrogen phosphate hydrate ($Ca(H_2PO_4)_2 \cdot H_2O$) and octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$). These authors determined band assignments for $Ca(H_2PO_4)$ and reported bands at 1012 and 1085 cm^{-1} as POH and PO stretching

vibrations, respectively. Casciani and Condrate [13] tabulated Raman bands at 1132 and 1155 cm^{-1} and assigned these bands to P–O symmetric and the P–O antisymmetric stretching vibrations. It is proposed that the proton on the hydroxyl units is very liable and can oscillate between the OH units and the phosphate units. In this way the hydrogen phosphate units are formed. Raman bands in the 748 cm^{-1} spectral region are assigned to hydroxyl deformation modes.

The infrared spectrum of frondelite in the 500–1300 cm^{-1} spectral range is shown in Fig. 4b. There is a strong resemblance in the shape of the spectral profile of the infrared and Raman spectra. As with the Raman spectrum, the spectral profile is complex with a series of overlapping bands. The resolved component bands at 695, 736 and 801 cm^{-1} may be attributed to hydroxyl deformation vibrations. The infrared band at 964 cm^{-1} is attributed to the PO stretching vibration of the $HOPO_3^{3-}$ units. The infrared band at 1008 cm^{-1} may be assigned to the v_1 symmetric stretching mode of the PO_4^{3-} units. The series of infrared bands at 1025, 1057, 1103, 1154 and 1179 cm^{-1} are assigned to the HOP and PO v_3 antisymmetric stretching vibrations.

The Raman spectrum of frondelite in the 300–800 cm^{-1} spectral range is reported in Fig. 5a. This part of the Raman spectrum may

be divided into three regions: (a) bands in the 550–650 cm^{-1} spectral region (b) bands centered around 455 cm^{-1} and (c) bands in the 300–380 cm^{-1} spectral range. The first group of bands at 572, 589, 612 and 635 cm^{-1} are assigned to the ν_4 out of plane bending modes of the PO$_4$ and HPO$_4$ units. The Raman spectrum of NaH$_2$PO$_4$ shows Raman bands at 526, 546 and 618 cm^{-1}. The observation of multiple bands in this spectral region supports the concept of symmetry reduction of both the phosphate and hydrogen phosphate units. The second group of bands at 436, 455 and 481 cm^{-1} are attributed to the ν_2 PO$_4$ and HPO$_4$ bending modes. The Raman spectrum of NaH$_2$PO$_4$ shows two Raman bands at 460 and 482 cm^{-1}. The observation of multiple Raman bands for the frondelite mineral supports the concept of symmetry reduction. The third group of bands at 291, 329 and 379 cm^{-1} are attributed to metal–oxygen vibrations. The Raman spectrum in the far low wavenumber region is shown in Fig. 5b. Raman bands are observed at 126, 151, 172, 189, 207 and 226 cm^{-1} and are simply described as lattice vibrations.

Conclusions

The name frondelite is given to the mineral of composition Mn^{2+}Fe$_4^{3+}$(PO$_4$)$_3$(OH)$_5$ isostructural and isomorphous with rockbridgeite, the ferrous iron analog. We have analyzed frondelite mineral sample from the Cigana mine using a combination of electron probe analysis and vibrational spectroscopy. By using electron probe analysis, The chemical formula was determined as (Mn$_{0.68}$, Fe$_{0.32}$)(Fe^{3+})$_{3.72}$(PO$_4$)$_{3.17}$(OH)$_{4.99}$. The vacancies in the Fe^{3+} site, observed due to the cationic deficiency, is supported by the presence of H$^+$ in the HOPO$_3^{3-}$ units as observed in the Raman spectra.

The structure of the mineral was assessed using vibrational spectroscopy. The Raman spectrum of frondelite in the 800–1400 cm^{-1} spectral range shows a complex profile with component bands resolved using band component analysis. The Raman band at 1000 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the PO$_4^{3-}$ units. The band at 966 cm^{-1} is attributed to the HOPO$_4^{3-}$ units. The Raman bands at 1071, 1112 and 1164 cm^{-1} are attributed to both the HOP and PO antisymmetric stretching vibrations. Raman spectroscopy shows the presence of both phosphate and hydrogen phosphate units in the frondelite structure. A sharp Raman band at 3581 cm^{-1} is attributed to the stretching vibrations of the OH units. The broad Raman spectral profile may be resolved into component bands at 2747, 2886, 3027, 3157 and 3325 cm^{-1} which are assigned to water stretching vibrations.

A question that might be raised is the formula as written above (Mn$_{0.68}$, Fe$_{0.32}$)(Fe^{3+})$_{3.72}$(PO$_4$)$_{3.17}$(OH)$_{4.99}$ correct? Both Raman and infrared spectroscopy clearly shows the existence of OH units. Further Raman spectroscopy identifies bands which are attributed to HOPO$_3^{3-}$ units. Thus, some of the protons from water are associated with the phosphate units. Vibrational spectroscopy clearly identifies water in the structure.

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.2013.02.008.

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