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Infrared and Raman spectroscopic characterization of the borate mineral vonsenite $\text{Fe}^{2+}_2\text{Fe}^{3+}\text{BO}_5$

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Abstract

There are a large number of boron containing minerals of which vonsenite $\text{Fe}^{2+}_2\text{Fe}^{3+}\text{BO}_5$ is one. Some discussion about the molecular structure of vonsenite exists in the literature. Whether water is involved in the structure is ill-determined. The molecular structure of vonsenite has been assessed by the combination of Raman and infrared spectroscopy. The Raman spectrum is characterised by two intense broad bands at 997 and 1059 cm^{-1} assigned to the BO stretching vibrational mode. A series of Raman bands in the 1200 to 1500 cm^{-1} spectral range are attributed to BO antisymmetric stretching modes and in-plane bending modes. The infrared spectrum shows complexity in this spectral range. No Raman spectrum of water in the OH stretching region could be obtained. The infrared spectrum shows a series of overlapping bands with bands identified at 3037, 3245, 3443, 3556 and 3614 cm^{-1} . It is important to understand the structure of vonsenite in order to form nanomaterials based upon its structure. Vibrational spectroscopy enables a better understanding of the structure of vonsenite.

Key words: vonsenite, ludwigite, borate, molecular structure, Raman spectroscopy, infrared spectroscopy

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Introduction

Vonsenite is an iron borate mineral with formula given as $(\text{Fe}^{2+})_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$. The mineral is a member of the ludwigite group that also includes azoproite $(\text{Mg})_2\text{TiO}_2(\text{BO}_3)$; bonaccordite $(\text{Ni})_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$; frederikssonite $(\text{Mg})_2\text{Mn}^{3+}\text{O}_2(\text{BO}_3)$ and ludwigite $(\text{Mg})_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$ [1]. Vonsenite occurs as black or greenish black prismatic crystals. An image of vonsenite is given in the supplementary information. Ludwigite is a magnesian ferric iron borate $\text{Mg}_2\text{Fe}^{3+}(\text{BO}_5)$. The mineral typically occurs in magnesian iron skarn and other high temperature contact metamorphic deposits. It occurs in association with magnetite, forsterite, clinohumite and the borates vonsenite $\text{Fe}_2^{2+}\text{Fe}^{3+}(\text{BO}_5)$ and szaibelyite $\text{MgBO}_2(\text{OH})$. Ludwigite forms a solid solution with the ferrous-ferric borate mineral vonsenite. Vonsenite is the ferrous analogue of ludwigite. The chemical composition may vary considerably depending upon the origin of the mineral [2, 3]. Aluminium often substitutes for the ferric iron in the ludwigite-vonsenite series [3, 4].

Vonsenite was first described by Eakle from Riverside, California, USA [5]. Coal-black to greenish black mineral exists in radial fibrous, fanlike to felted aggregates. The crystal structure of vonsenite was determined by Takéuchi [6] and latter redetermined by Swinnea and Steinfink [7] in synthetic mineral analogue. Vonsenite is orthorhombic with Point Group: $2/m\ 2/m\ 2/m$ [7]. The unit cell parameters are $a = 9.463(1)\text{Å}$, $b = 12.305(1)\text{Å}$, $c = 3.0727(6)\text{Å}$, $Z = 4$ and space group $Pbam$. Ludwigite is orthorhombic with point group: $2/m\ 2/m\ 2/m$ [8]. The crystals are pitch-black to olive green-black and are long fibrous crystals often fanlike aggregates [9]. *Space group is Pbam*, $a = 9.2411(6)$, $b = 12.2948(9)$, $c = 3.0213(3)$ and $Z = 4$. Synthetic vonsenite is of *space group: Pbam*, $a = 9.463(1)$, $b = 12.305(1)$, $c = 3.0727(6)$ and $Z=4$. The minerals are of factor group D_{2h} with four molecular formulas per unit cell [10].

The ludwigite-vonsenite isomorphic series are readily synthesised [11]. The minerals ludwigite and vonsenite may be synthesised through mechanochemical treatment [12]. However, there have been very few studies of the vibrational spectroscopy of ludwigite or vonsenite [10, 13]. Leite *et al.* reported the Raman scattering of $\text{Fe}_3\text{O}_2\text{BO}_3$ and $\text{Ni}_2\text{FeO}_2\text{BO}_3$ stating that these synthesised mineral analogues were ludwigite [10]. However, ludwigite is a magnesian mineral. Basically, these researchers measured the spectrum of vonsenite and only reported the spectra below 800 cm^{-1} . These authors also undertook some single crystal Raman spectroscopy of the mineral analogues. Zha *et al.* determined the

infrared spectra of selected borate minerals as a function of temperature [13]. These authors also undertook theoretical calculations of the infrared spectra [14].

It is important to have good knowledge of the structure of the borate minerals such as vonsenite and ludwigite. Such minerals may be mined in the future as a source of boron. The importance of boron is increasing as it is used in many alloys. The vonsenite-ludwigite mineral series has environmental implications especially in environmental remediation. The basic knowledge of these minerals is lacking. Vibrational spectroscopy has added important knowledge to our mineral understanding [15-19]. In this research, we have characterised vonsenite using Raman and infrared spectroscopy and relate the spectra to the structure of the mineral.

Experimental

Samples description and preparation

The vonsenite sample studied in this work was collected from the Brosso mine, Torino, Italy. The mineral occurs in association with pyrite and shows prismatic habitus and forms radial aggregates. The Brosso mine is an important pyrite deposit in the Torino province, northwest Italy. Geological description and characterization of the mineral association have been published [20, 21]. The sample was incorporated into the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-124. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) was applied to support the chemical characterization. Details of the mineral have been published (page 414 (ludwigite) and 743 (vonsenite), Vol. 5) [22].

Electron probe micro-analysis (EPMA)

The quantitative chemical analysis of vonsenite single crystal was carried out using EPMA, with a Jeol JXA8900R spectrometer from the Physics Department of the Federal University of Minas Gerais, Belo Horizonte. The sample was embedded in epoxy resin and after polishment, 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. For each selected element was used the following standards: Fe – magnetite, Mg - MgO, Mn – rodonite, Ca – Anortite100, Cu – Chalcopyrite,

Zn – sphalerite and Al - Corundum. Chemical formula was calculated on the basis of five oxygen atoms (O).

Raman microprobe spectroscopy

Crystals of vonsenite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x 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 $\pm 1\text{ cm}^{-1}$ in the range between 200 and 4000 cm^{-1} . Repeated acquisitions on the crystals using the highest magnification (50x) 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.

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 $4000\text{--}525\text{ cm}^{-1}$ 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 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 quantitative chemical analysis of vonsenite is presented in Table 1. The chemical composition indicates an iron rich phase with minor contribution of magnesium. The sample is almost an end-member in the vonsenite-ludwigite series. The content of Al, Ca, Cu and Zn is not representative. Chemical formula calculated on the basis of 5 O atoms can be written as $(\text{Fe}^{2+}_{1.92}, \text{Mg}_{0.12})_{\Sigma 2.04} \text{Fe}^{3+}_{0.99} \text{O}_2 (\text{BO}_3)_{0.99}$.

Vibrational Spectroscopy

The Raman spectrum of vonsenite in the 100 to 4000 cm^{-1} spectral range is illustrated in Figure 1a. This spectrum shows the position and relative intensities of these Raman bands. It is noted that there is no intensity in the OH stretching region. The spectrum is subdivided in sections depending upon the type of vibration being studied. The infrared spectrum of vonsenite in the 500 to 4000 cm^{-1} is reported in Figure 1b. Now, some significant intensity is found in the OH stretching region. Some bands around the 3000 cm^{-1} are attributed to organic compounds. It is interesting that in the Raman spectrum no OH vibrations were determined, yet in the infrared spectrum they were observed. Vonsenite $\text{Fe}^{2+}_2\text{Fe}^{3+}\text{BO}_5$ is an anhydrous mineral and therefore it would not be expected to show OH vibrations.

As Ross rightly points out the spectra of borate minerals depends heavily on the possible anions in the mineral [23]. The coordination polyhedron around the boron atom will be either a triangle or a tetrahedron. In the case of vonsenite, the structure consists of linked triangles and tetrahedra. Thus, for vonsenite the vibrational spectra of both structural units will be observed. The spectra of vonsenite are complex especially in the infrared spectrum. This is caused by the observation of bands due to four different coordination polyhedra namely BO_3^{3-} , BO_4^{5-} , $\text{B}(\text{OH})_3$, and $\text{B}(\text{OH})_4^-$.

The Raman spectrum in the 900 to 1200 cm^{-1} spectral range is reported in Figure 2a. Two bands are observed at 997 and 1059 cm^{-1} . These bands are assigned to the symmetric stretching and in-plane bending mode of trigonal boron. Apart from some Raman studies of borate glasses [24-29], there are almost no reported vibrational spectroscopic studies of borate minerals. There is a Raman spectrum of vonsenite reported in the RRUFF data base at <http://rruff.info/Vonsenite/R050221>. This spectrum shown in this data base is very noisy and it is difficult to exactly determine the peak positions.

The infrared spectrum in the 800 to 1200 cm^{-1} spectral range is given in Figure 2b. This spectrum is complex with a series of overlapping bands. The infrared bands at 924, 960 and 977 cm^{-1} are associated with the antisymmetric stretching modes of tetrahedral boron. Infrared bands are resolved at 1010, 1045, 1068, 1089 and 1099 cm^{-1} .

The Raman spectrum in the 1200 to 1700 cm^{-1} spectral range is shown in Figure 3a. Raman bands are identified at 1215, 1275, 1361, 1398 and 1452 cm^{-1} . These Raman bands are assigned to OH in-plane bending modes [23]. The infrared spectrum in the 1200 to 1800 cm^{-1} spectral range is shown in Figure 3b. Infrared bands are observed at 1215, 1275, 1361, 1398, 1452 cm^{-1} . According to Ross [23] (page 220 of this reference), bands between 1300 and 1500 cm^{-1} are due to the antisymmetric stretching modes of trigonal boron. This is perhaps confirmed by the intensity of the infrared bands in the 1300 to 1500 cm^{-1} region.

The Raman spectrum in the 300 to 800 cm^{-1} and in the 100 to 300 cm^{-1} spectral range is shown in Figure 4. Raman bands are observed at 529, 642, 687 and 728 cm^{-1} . These bands are attributed to the bending mode of trigonal and tetrahedral boron. The Raman bands at 687 and 728 cm^{-1} are assigned to the out-of-plane BOH bending modes. Intense Raman bands at 324 and 381 cm^{-1} with an additional low intensity band at 345 cm^{-1} are assigned to FeO stretching bands. An intense Raman band at 249 cm^{-1} is found with other bands at 114, 145 and 158 cm^{-1} . These bands are simply described as lattice vibrations.

Conclusions

The molecular structure of vonsenite has been assessed by the combination of Raman and infrared spectroscopy. The Raman spectrum is characterised by two intense broad bands at 997 and 1059 cm^{-1} assigned to the BO stretching vibrational mode. A series of Raman bands in the 1200 to 1500 cm^{-1} spectral range are attributed to BO antisymmetric stretching modes and in-plane bending modes. The infrared spectrum shows complexity in this spectral range. No Raman spectrum of water in the OH stretching region could be obtained. This work has added to our fundamental knowledge of borate minerals.

There are many borate containing minerals which have yet to have their vibrational spectra determined and the molecular structure assessed in terms of their vibrational spectra. In this work we have measured the Raman and infrared spectrum of vonsenite, a ferrous/ferric containing borate mineral. The importance of the mineral vonsenite rests with the chemistry of the compound and the potential to synthesize nanomaterials based upon polymerization of borate units. Such compounds have the potential to make especially selected ferroelectric, pyroelectric and piezoelectric properties. Vonsenite is a precursor for the synthesis of such nanomaterials.

Acknowledgments

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List of figures

Figure 1 (a) Raman spectrum of vonsenite over the 100 to 4000 cm^{-1} spectral range (b) Infrared spectrum of vonsenite over the 500 to 4000 cm^{-1} spectral range

Figure 2(a) Raman spectrum of vonsenite over the 900 to 1200 cm^{-1} spectral range (b) Infrared spectrum of vonsenite over the 800 to 1200 cm^{-1} spectral range

Figure 3a Raman spectrum of vonsenite (upper spectrum) in the 1200 to 1700 cm^{-1} spectral range and Figure 3b infrared spectrum of vonsenite (lower spectrum) in the 1300 to 1800 cm^{-1} spectral range

Figure 4a Raman spectrum of vonsenite (upper spectrum) in the 300 to 800 cm^{-1} spectral range and Figure 4b Raman spectrum of vonsenite (lower spectrum) in the 100 to 300 cm^{-1} spectral range

Table 1. Chemical composition of vonsenite from Brosso mine, Torino, Italy (mean of 7 electron microprobe analyses). B₂O₃ and Fe₂O₃ calculated by stoichiometry.

Constituent	wt. %	Number of atoms	Probe Standard
FeO	54.07	1.92	Magnetite
Fe ₂ O ₃	30.91	0.99	Calculated by stoichiometry
B ₂ O ₃	13.47	0.99	Calculated by stoichiometry
Al ₂ O ₃	0.07	0.00	Al ₂ O ₃
MgO	1.88	0.12	MgO
MnO	0.07	0.00	Rodhonite
CaO	0.02	0.00	Ca ₂ P ₂ O ₇
CuO	0.02	0.00	Chalcopyrite
ZnO	0.04	0.00	Sphalerite
Total	100.55	4.02	

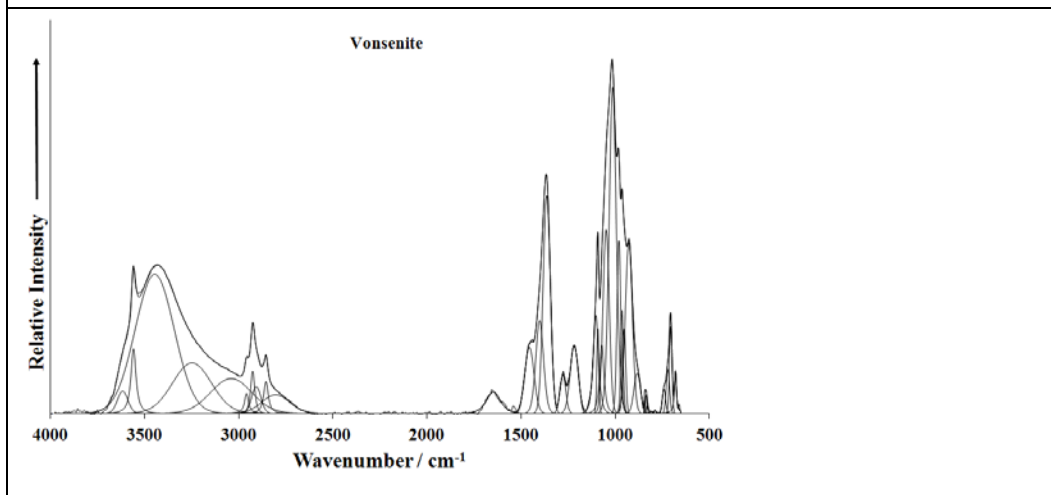
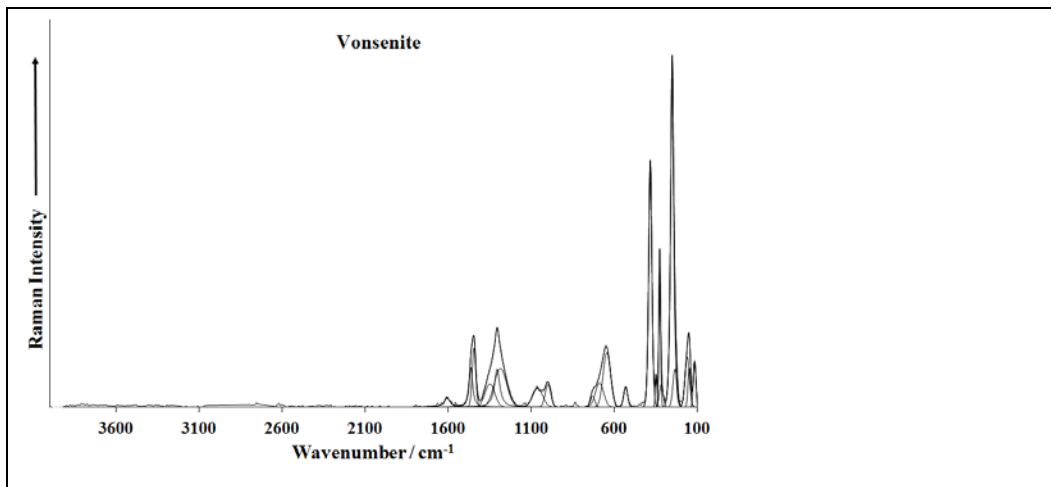


Figure 1a Raman spectrum of vonsenite (upper spectrum) over the 100 to 4000 cm⁻¹ spectral range and Figure 1b infrared spectrum of vonsenite (lower spectrum) over the 500 to 4000 cm⁻¹ spectral range

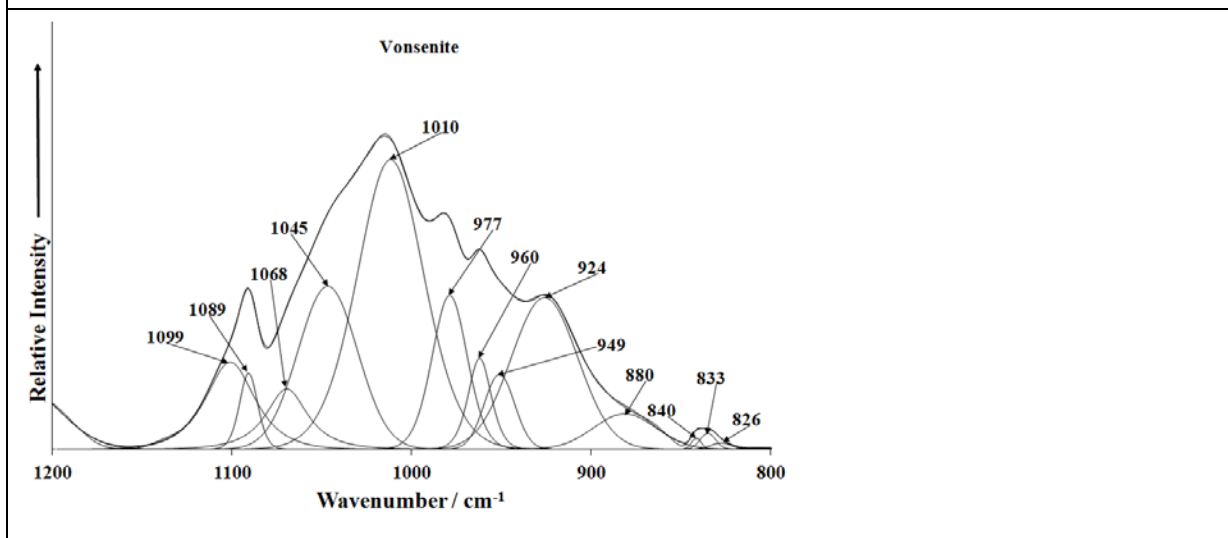
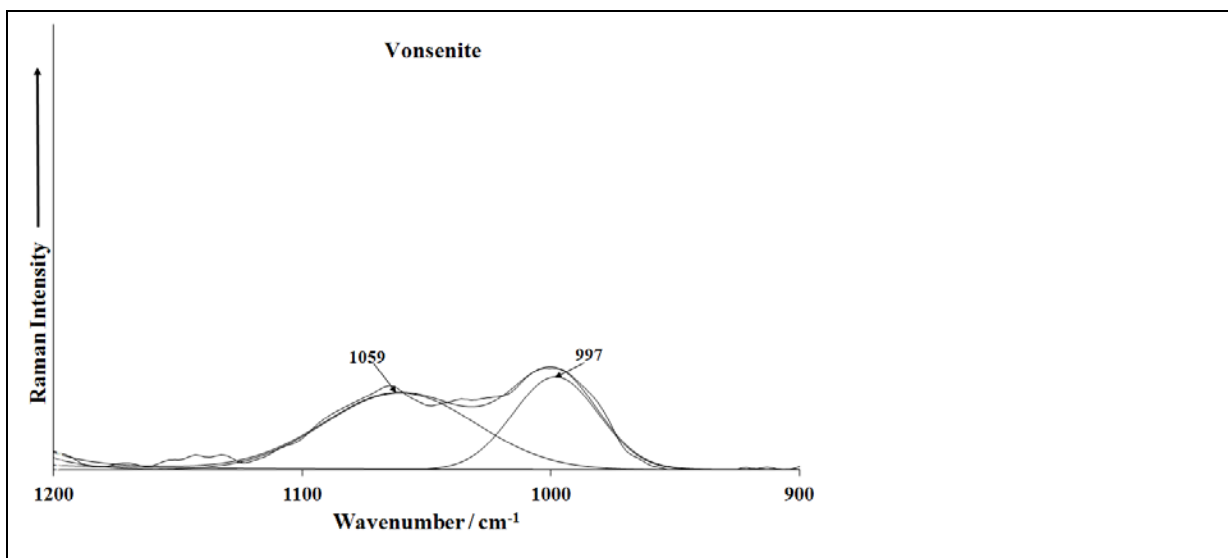


Figure 2a Raman spectrum of vonsenite (upper spectrum) in the 800 to 1400 cm^{-1} spectral range and Figure 2b infrared spectrum of vonsenite (lower spectrum) in the 500 to 1300 cm^{-1} spectral range

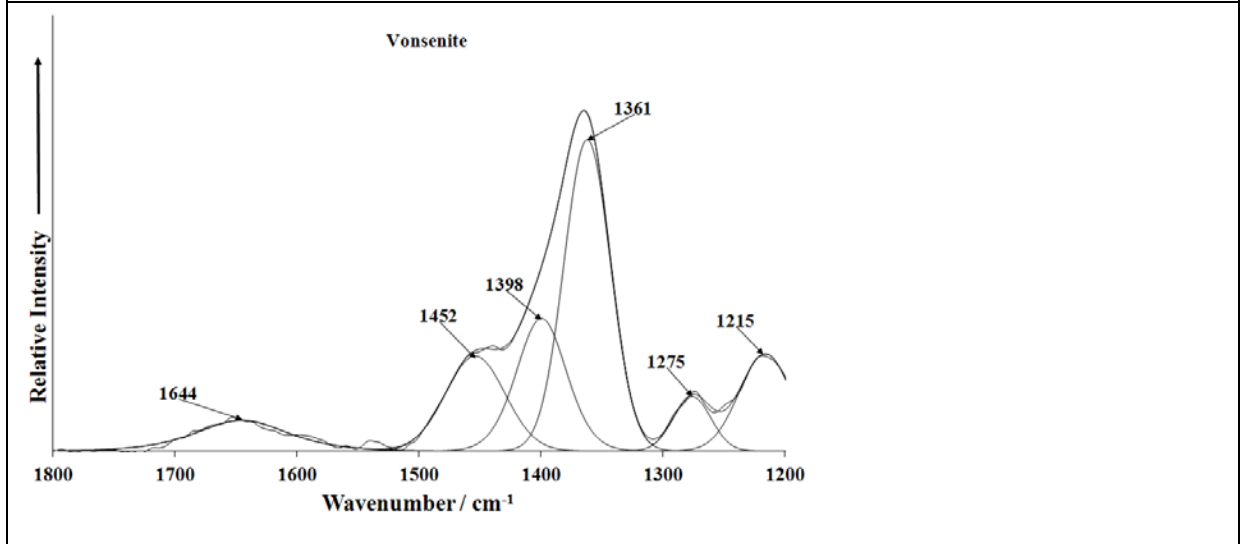
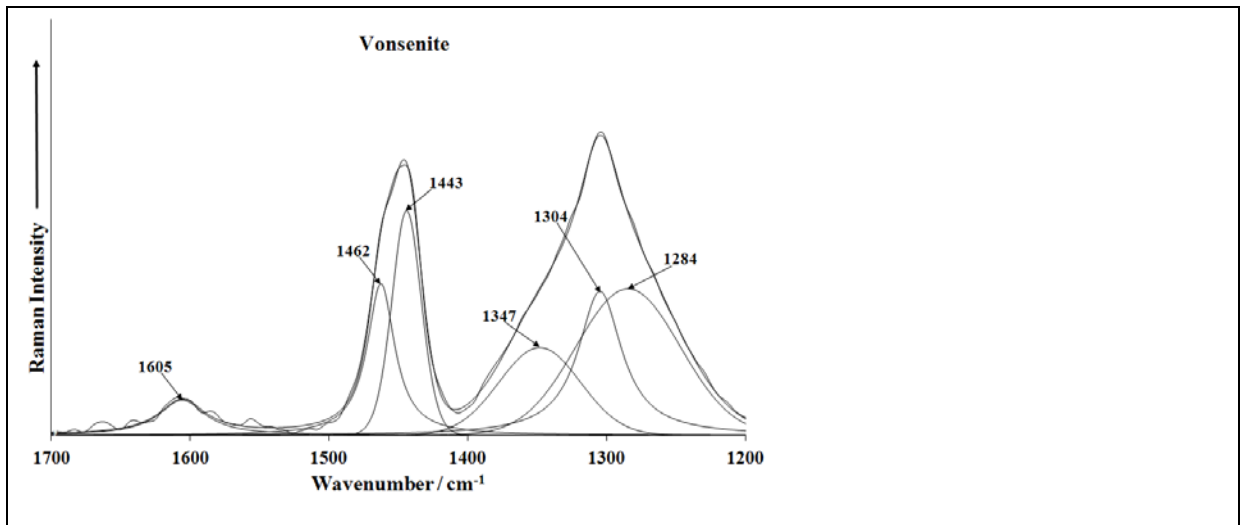


Figure 3a Raman spectrum of vonsenite (upper spectrum) in the 1200 to 1700 cm^{-1} spectral range and Figure 3b infrared spectrum of vonsenite (lower spectrum) in the 1300 to 1800 cm^{-1} spectral range

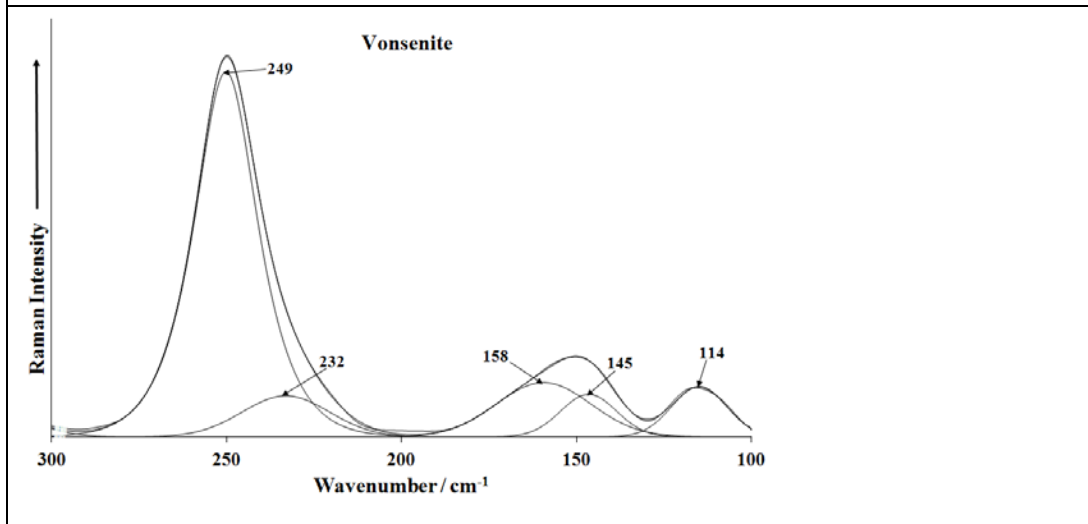
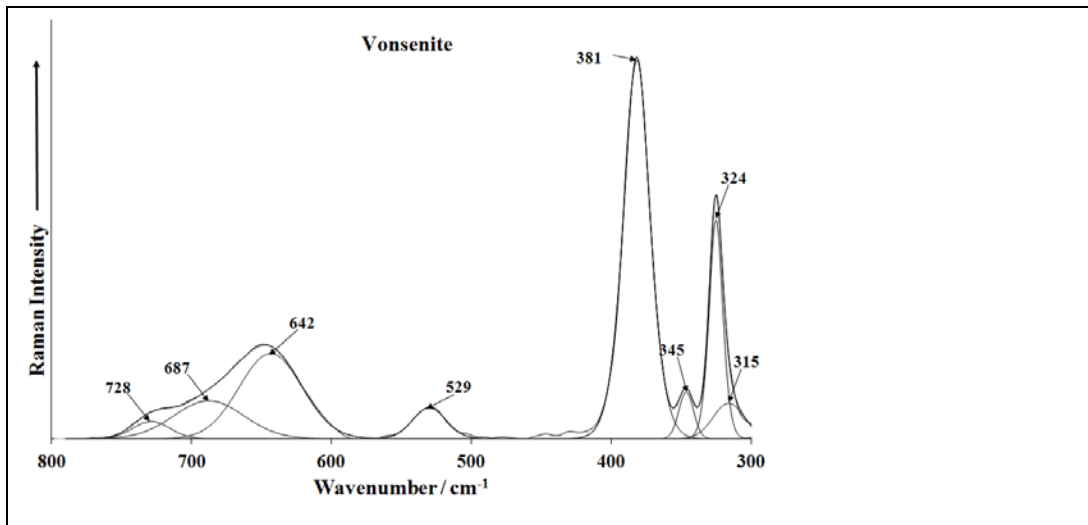


Figure 4a Raman spectrum of vonsenite (upper spectrum) in the 300 to 800 cm^{-1} spectral range and Figure 4b Raman spectrum of vonsenite (lower spectrum) in the 100 to 300 cm^{-1} spectral range