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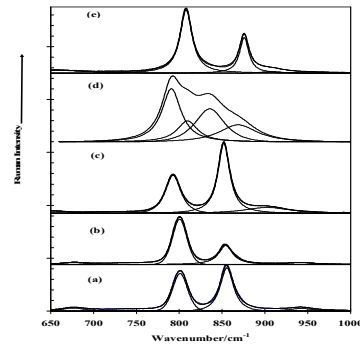
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The structures of the vivianite arsenate minerals annabergite, erythrite, köttigite, hörnesite and parasymphesite of formula $M_3^{2+}(AsO_4)_2 \cdot 8H_2O$ where M is Ni, Co, Zn, Mg, Fe or a cationic combination have been studied using Raman microscopy.



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A Raman spectroscopic study of vivianite arsenate minerals

A Raman Spectroscopic Study of the Vivianite Arsenate Minerals

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Abstract:

The molecular structures of the vivianite type arsenate minerals have been studied using a combination of Raman and infrared spectroscopy. The Raman spectra of the hydroxyl-stretching regions are complex with overlapping bands at 3419, 3209, 3185 and 3010 cm^{-1} . This complexity is reflected in the water HOH bending modes with strong infrared bands in the 1660 to 1685 cm^{-1} region indicating strong hydrogen bonding to arsenate anions in adjacent layers. The Raman arsenate AsO stretching region shows strong similarity between the vivianite arsenate minerals. In the infrared spectra complexity exists with multiple antisymmetric stretching vibrations observed, indicating a reduction of symmetry. Strong infrared bands around 700 and 560 cm^{-1} are attributed to librational modes of water. Vibrational spectra enable the structure of the minerals to be determined and whilst similarities exist in the spectral patterns, sufficient differences exist to determine the identification of the minerals. In particular Raman spectroscopy assists in the identification of the complex isomorphic substitution in these vivianite arsenate minerals.

Key Words: annabergite, arsenate, erythrite, hörnesite, köttigite, parasymphesite, Raman spectroscopy,

INTRODUCTION

The minerals of the vivianite group have the general formula $A_3^{2+}(XO_4)_2 \cdot 8H_2O$ in which A^{2+} may be Co, Fe, Mg, Ni, or Zn and X is As or P. Isomorphous substitution in this group occurs readily, and solid solutions may be observed. The vivianite minerals are all monoclinic (and belong to space group $C2/m$).¹ The minerals may be divided into two subgroups depending on the oxyanion, either arsenate or phosphate.² The arsenates in this group are annabergite ($Ni_3(AsO_4)_2 \cdot 8H_2O$), erythrite ($Co_3(AsO_4)_2 \cdot 8H_2O$), hörnesite ($Mg_3(AsO_4)_2 \cdot 8H_2O$), köttigite ($Zn_3(AsO_4)_2 \cdot 8H_2O$) (also written as koettigite) and parasymphesite ($Fe_3(AsO_4)_2 \cdot 8H_2O$). Annabergite forms a continuous solid solution series with erythrite, which can also form a continuous series with hörnesite.³ There is discussion concerning the validity of this statement.⁴ Köttigite forms a continuous series with parasymphesite. The series with köttigite-symphesite-parasymphesite presents a major problem in that the minerals all have the same X-ray diffraction patterns. It is most

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likely that parasymplectite and symplectite are identical in terms of atomic structure to that of köttigite.

The vibrational modes of oxyanions in aqueous systems are well known. The symmetric stretching vibration of the arsenate anion (ν_1) is observed at 810 cm^{-1} and coincides with the position of the antisymmetric stretching mode (ν_3). The symmetric bending mode (ν_2) is observed at 342 cm^{-1} and the antisymmetric bending mode (ν_4) at 398 cm^{-1} . The positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring oxyanions. Farmer lists a number of infrared spectra of arsenates including annabergite, erythrite, symplectite and köttigite.⁵ The effect of reduced site symmetry in the crystal (compared with the free arsenate ion) will remove the degeneracy and allow splitting of the bands according to factor group analysis. The ν_1 and ν_3 bands of annabergite were observed at 832 cm^{-1} and 795 cm^{-1} . The ν_4 bending modes were found at 510, 460 and 427 cm^{-1} for annabergite. No ν_2 bands were shown. Two OH stretching vibrations were observed at 3430 and 3160 cm^{-1} for annabergite. A number of bands were listed which were unassigned.

Few comprehensive studies of the vivianite related minerals such as divalent cationic arsenates have been undertaken.⁵ Most of the infrared data predates the advent of Fourier transform infrared spectroscopy.⁶⁻¹¹ Although some Raman studies of the vivianite phosphate minerals have been undertaken^{12,13} no Raman spectroscopic investigation of vivianite arsenate minerals has been undertaken. Griffith (1970) did report the results of the Raman spectrum of a synthetic annabergite. The symmetric stretching mode of the AsO_4 unit was observed at 859 cm^{-1} ; the antisymmetric stretching mode at 880 cm^{-1} , the symmetric bending mode at 438 cm^{-1} and antisymmetric bending mode at 452 cm^{-1} ; other bands were located at 797 and 820 cm^{-1} .¹⁴ The structural investigation of some arsenates and the nature of the hydrogen bond in these structures have been undertaken. It was found that the hydroxyl unit was coordinated directly to the metal ion and formed hydrogen bonds to the arsenate anion.¹⁵ The minerals selected for this study were fundamentally unrelated. Indeed almost no Raman studies have been undertaken. As part of a comprehensive study of the molecular structure of minerals containing oxyanions using IR and Raman spectroscopy, we report the Raman and infrared properties of the above named phases.

EXPERIMENTAL

Minerals:

Annabergite and erythrite, were purchased from BK Minerals, Brisbane, Australia. The annabergite originated from the 132 North Deposit, Widgiemooltha District of Western Australia. The erythrite (large scarlet cobalt crystals) originated from Mt. Cobalt, Queensland, Australia. Köttigite from the Ojuela Mine, Mapini, Durango, Mexico was obtained from the South Australian museum (sample number G21998). The minerals were analysed for phase purity by powder X-ray diffraction methods and for chemical composition using SEM EDAX techniques.

Synthetic vivianite-type arsenates of Mg, Zn, Fe, Co and Ni were prepared by the slow addition of the 3.5×10^{-3} M metal sulphate solution to a very dilute 5.0×10^{-3} M sodium arsenate solution using a peristaltic pump at 70 °C. The hydrated cationic arsenates precipitated from the solution and were filtered and dried. The crystals were hydrothermally treated and were grown by Ostwald ripening at 70°C for 14 days. Samples were analysed for phase purity by X-ray diffraction and for chemical composition by electron probe micro-analyses. Because hörnesite and köttigite could not be obtained with sufficient purity, the spectra used in this work were acquired from the synthesised minerals.

Raman microprobe spectroscopy

The crystals of the vivianite-type minerals were placed and oriented on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a notch filter system and a thermo-electrically cooled Charge Coupled Device (CCD) detector. Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) and acquired at a nominal resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . Spectra at liquid nitrogen temperature were obtained using a Linkam (THMS 600) thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).

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 to 525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s . Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS. Band component analysis was undertaken using the Jandel 'Peakfit' software package, which 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 Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared regression coefficient of R^2 greater than 0.995.

RESULTS AND DISCUSSION

Factor group analysis

Table 1 Factor Group Analysis of XO_4

| Ideal symmetry | Site symmetry | Factor group symmetry |
|----------------|--------------------|-----------------------|
| T_d | C_s | C_{2h} |
| A_1 | $\rightarrow 6A'$ | $\rightarrow 6A_g$ |
| E | $\rightarrow 3A''$ | $\rightarrow 6B_u$ |
| $2T_2$ | | $\rightarrow 3B_g$ |
| | | $\rightarrow 3A_u$ |

Table 2 Factor Group Analysis of the each of the water (I+II) molecules

| C_{2v} | C_1 | C_{2h} |
|----------|------------------|--------------------|
| $4A_1$ | $\rightarrow 6A$ | $\rightarrow 6A_g$ |
| | | $\rightarrow 6B_g$ |
| | | $\rightarrow 6A_u$ |
| $2B_1$ | | $\rightarrow 6B_u$ |

In the crystal structure of the vivianite-type minerals there are four arsenate ions in the unit cell. These are of space group C2/m (Z=2), therefore there exists one formula unit per primitive unit cell, thus 37 atoms in the primitive unit cell.

$3n-3 \rightarrow 3*37 - 3 = 108$ normal modes of vibrations made up of 18 internal Arsenate modes+24 internal water modes+69 lattice modes-3 translations equalling 108 modes of vibration. It is therefore predicted that there are 18 vibrationally active modes for the AsO₄ internal modes of arsenates in the vivianite structure (Table 1),

ν_1 1 Raman (A_g), 1 IR(B_u)

ν_2 2 Raman (A_g, B_g), 2 IR(A_u, B_u)

ν_3 3 Raman(2A_g, B_g), 3 IR(A_u, 2B_u)

ν_4 3 Raman(2A_g, B_g), 3 IR(A_u, 2B_u)

For water, it is predicted that there are 24 vibrationally active internal modes of water (Table 2), 8 Raman active stretch (4A_g, 4B_g), 8 IR active stretch (4A_u, 4B_u), 4 Raman active bends (2A_g, 2B_g), 4 IR active bends (2A_u, 2B_u). The irreducible representation for the entire structure of the lattice vibrations of the vivianite arsenates is $\Gamma = 16A_u + 17 B_u + 15A_g + 15B_g$ ignoring translational modes.

Water Hydroxyl stretching of the vivianite arsenates.

The Raman and infrared spectra of the hydroxyl stretching vibrations of water in the vivianite arsenates are shown in Figures 1 and 2 respectively. The results of the Raman and infrared spectroscopic analyses are reported in Tables 3 and 4. Factor group analyses predict that there should be 12 active internal modes for each water site in these vivianite hydrated arsenates. In general four Raman bands are observed in the hydroxyl-stretching region of annabergite, erythrite, köttigite and hörnesite. The observation of four bands is as expected. There are two water molecules in the unit cell and consequently there are four OH units, which can vibrate both in-phase and out-of-phase, giving four bands. For annabergite (Figure 1a) four Raman bands are observed at 3419, 3209, 3185 and 3010 cm^{-1} . The Raman spectrum of the synthetic annabergite is almost identical to that of the natural sample. For erythrite (Figure 1c) five bands are observed in the Raman spectrum, although the broad band at around 2950 cm^{-1} is required to fit the band profile. The Raman spectrum of the natural köttigite (Figure 1d) is broad and two bands are observed at 3458 and 3215 cm^{-1} . The Raman spectrum of hörnesite (Figure 1e) resembles that of annabergite and bands are observed at 3479, 3166 and 3030 cm^{-1} . A comparison of the water OH stretching vibrations of these minerals enables the minerals to be classified.

The infrared spectra of the water OH stretching region also show some similarity (Figure 2). In general five infrared active bands are observed. The infrared spectral components of the natural köttigite are broad. The infrared spectrum of hörnesite (Figure 2d) is similar to that of both annabergite and erythrite (Figure 2 a,b). It would appear that the Raman spectra are more useful for distinguishing between these minerals. The infrared spectrum of annabergite shows OH stretching vibrations at 3412, 3155 and 2972 cm^{-1} . These values may be compared with the published results of 3430 and 3160 cm^{-1} ¹⁵. The infrared spectra of erythrite appear to vary slightly depending on the natural sample. Without doubt this depends on the amount of cationic substitution. For the erythrite from Queensland, bands were observed at 3460, 3294 and 3099 cm^{-1} . These values compare favourably with the published data.¹⁵ A second sample provided infrared bands at 3427, 3172 and 2930 cm^{-1} . For köttigite (Figure 2c), IR bands were observed at 3440, 3185 and 3045 cm^{-1} . These results may be compared with the published data of symplectite where only a single broad band at 3385 cm^{-1} was observed. The infrared spectra of köttigite for a mixed cationic arsenate reported by Farmer (page 399), showed three OH stretching bands at 3440, 3185 and 3045 cm^{-1} . For hörnesite (Figure 2d) infrared bands are observed at 3478, 3273, 3142, 3038, and 3000 cm^{-1} .

Studies have shown a strong correlation between OH stretching frequencies and both the O \cdots O bond distances and with the H \cdots O hydrogen bond distances¹⁶⁻¹⁹. The elegant work of Libowitzky (1999) showed that a regression function could be employed relating the above correlations with regression coefficients better than 0.96²⁰. Table 5 shows the relationship between the hydroxyl stretching frequencies from Table 4 and the predicted bond frequencies by using the Libowitzky equation. Two types of water molecules are identified in the structure and the known hydrogen bond distances used to predict the hydroxyl stretching frequencies. The data in the table fundamentally distinguishes between two types of water according to the hydrogen bond distances, namely strongly hydrogen bonded water and weakly hydrogen bonded water. Table 5 shows some reasonable agreement between the predicted and

observed positions of the hydroxyl stretching wavenumbers. However the predicted values do not take into account factor group splitting, accidental degeneracy and in-phase and out-of-phase vibrations.

| Mineral | | Hydrogen bond distance | Predicted band positions | Observed IR band positions |
|-------------|----------|--|--------------------------|----------------------------|
| annabergite | Water I | 2.88 ₅ 2.79 ₈ | 3492 3400 | 3412 |
| | Water II | 2.72 ₁ 2.70 ₃ | 3247 3197 | 3155 2972 |
| erythrite | Water I | 2.90 ₄ 2.83 ₃ | 3505 3444 | 3460 |
| | Water II | 2.72 ₂ 2.74 ₂ | 3250 3298 | 3294 3099 |
| köttigite | Water I | 2.89 ₆ 2.81 ₇ | 3500 3425 | 3440 |
| | Water II | 2.74 ₁ 2.73 ₀ | 3296 3270 | 3185 3045 |

Table 5 Correlation between hydroxyl stretching frequencies and hydrogen bond distances.

Water HOH bending vibrations of the vivianite arsenates.

Much information can be obtained from the study of the water HOH bending modes. One means of studying the structure of water molecules in the vivianite arsenate minerals is to study the water HOH bending modes. When the water is coordinated as in certain minerals, water OH stretching frequency occurs at around 3220 cm⁻¹. A simple observation can be made that as the water OH stretching frequency decreases then the HOH bending frequency increases. Thus the water hydroxyl stretching and the water HOH bending 1610 cm⁻¹ frequencies provide a measure of the strength of the bonding of the water molecules either chemically or physically to the mineral or to the arsenate anions. Likewise the position of the water bending vibration also provides a measure of this strength of water hydrogen bonding. Bands that occur at frequencies above 1650 cm⁻¹ are indicative of coordinated water and chemically bonded water. Bands that occur below 1630 cm⁻¹ are indicative of water molecules that are not as tightly bound. In this case the hydrogen bonding is less as the frequency decreases.

Figure 3 shows the water HOH bending modes for the selected vivianite arsenates. What is readily observed from the figure is that the infrared spectra of this region are complex, reflecting the complexity observed for the water OH stretching vibrations. In principal, three bending modes are observed. For annabergite (Figure 3a) bands are observed at 1683 and 1590 cm⁻¹. The band at 1683 cm⁻¹ is indicative of

strongly hydrogen-bonded water. Previous studies reported bands at 1630 and 1600 cm^{-1} , which is somewhat unusual since if the water is strongly hydrogen bonded then a higher wavenumber band would be expected.⁵ For erythrite (Figure 3b) infrared bands are observed for this region at 1683, 1633 and 1585 cm^{-1} . Farmer reported bands for erythrite at 1670 and 1585 cm^{-1} .⁵ The broadness of the OH stretching vibrations of köttigite (Figure 3c) is also observed in the water HOH bending region where bands at 1660 and 1590 cm^{-1} are observed. For köttigite, Farmer reported infrared HOH deformation modes at 1700, 1645 and 1590 cm^{-1} . This data differs with the infrared data reported here. This no doubt reflects on the cationic variability in the köttigite-parasymplesite-hörnesite series. For hörnesite (Figure 3d), water-bending modes are observed at 1682, 1635 and 1585 cm^{-1} . The infrared spectra of the water deformation modes show that the water is (a) as non-hydrogen bonded water (b) strongly hydrogen bonded water and (c) very strongly hydrogen bonded water. The position of the bands reflects the strength of the hydrogen bonds of water and the hydrogen bond distances in these hydrated arsenates.

In the hydroxyl-stretching region in both the infrared and Raman spectrum of annabergite (3419 cm^{-1}), köttigite (3458 cm^{-1}) and hörnesite (3478 cm^{-1}), a sharp band is observed with a bandwidth significantly less than the other bands. The OH stretching vibration at higher wavenumbers is narrow and at lower wavenumbers, broader with increasing strength of the hydrogen bond and decreasing bond length as the anharmonicity increases. The intensity of the band is higher in the infrared spectrum. One possible explanation of this band is that it is due to hydroxyl units on the cation. Annabergite, for example, may contain some minor amounts of iron, which could also be oxidised. Indeed it is very rare to obtain a perfect mineral in nature such that Ni is the only atom present in the mineral. In the case of köttigite the Fe is one of the cations in the köttigite-symplesite series. If some oxidation of the ferrous ion to ferric occurs then this charge would need to be counterbalanced by the negative of the hydroxyl unit as not other negative charges could originate from the arsenate anion. This then could mean that a free proton is available to form HAsO_4 units. It should be remembered that there is an effect of time scale measurement here. X-ray diffraction averages lattice parameters over an extended period of time in minutes to hours. Hence any such effect as oxidation of the Fe in annabergite, köttigite or hörnesite would not be observed. In vibrational spectroscopy, however the infrared and Raman spectra record measurements on a much faster time scale. Thus any phenomena such as the migration of a proton to an arsenate anion can be measured. Likewise the bonding of a hydroxyl unit to the metal could be observed. Importantly -AsOH units could be formed the infrared and Raman spectrum of which might show its presence. Thus the high wavenumber band in the Raman and infrared spectrum may be attributed to an AsOH stretching vibration.

Arsenate stretching of the vivianite arsenates.

The Raman spectra of the AsO_4 stretching region are shown in Figure 4. The results are reported in Table 3. For each mineral except köttigite, two intense bands are observed. The position of these bands appears to vary depending on the cation. The bands are observed at 854 and 800 cm^{-1} for annabergite (Figure 4a); the bands are in the same position for the synthetic annabergite (Figure 4b). The band observed at 941 cm^{-1} for the natural annabergite may be assigned to some phosphate isomorphic substitution. Raman spectral studies of the vivianite phosphates show that

there is a band at 951 cm^{-1} for vivianite and bobierrite. The bands are observed at 852 and 792 cm^{-1} for erythrite (Figure 4c) and at 875 and 807 cm^{-1} for hörnesite (Figure 4e). The Raman spectrum of köttigite (Figure 4d) is the exception and it is suggested that the band profile is made up of two overlapping sets of two bands. These are 790 and 835 cm^{-1} and 811 and 868 cm^{-1} . Both of these bands are assigned to the ν_1 symmetric stretching modes of A_1 symmetry. Griffith reported Raman bands for a synthetic annabergite at 880 , 859 , 820 and 797 cm^{-1} . The low intensity band observed around 902 cm^{-1} is assigned to the E_{1g} mode.

The infrared spectra of the AsO stretching region is shown in Figure 5 and the data reported in Table 4. The spectra are a complex set of overlapping bands which may be curve-resolved into component bands as is shown. The pattern is the same for annabergite, erythrite and köttigite (Figure 5a,b,c). However the pattern for the synthetic hörnesite appears better resolved (Figure 5d). The synthesis of hörnesite involves the use of prolonged hydrothermal treatment, which may result in a more crystalline structure. The most intense band for the vivianite arsenates is observed at around 768 to 795 cm^{-1} and is assigned to the antisymmetric stretching vibration. This band corresponds to the second intense band in the Raman spectra. Griffith (1970) reported infrared bands at 795 and 832 cm^{-1} for a synthetic annabergite. A band at around 825 cm^{-1} is observed in all of the infrared spectra. The infrared spectrum of erythrite (Figure 5b) shows bands at 825 and 768 cm^{-1} . Based upon the infrared spectra Farmer (1974) reported bands at 825 and 783 cm^{-1} for erythrite. Farmer found that that the ν_1 and ν_3 modes using infrared spectroscopy were at 832 and 795 cm^{-1} for annabergite, 825 and 783 cm^{-1} for erythrite. Interestingly, Farmer found multiple bands for köttigite. Infrared bands were observed at 890 , 868 , 845 , 828 and 790 cm^{-1} . The complexity of the infrared spectra of this region is in agreement with Raman data. This complexity simply reflects the mixed cationic species in this hydrated arsenate. The number of peaks reflects the bonding of the arsenate to different cations with consequent reduction in symmetry of the arsenate anion. This is in agreement with our Raman data, we suggest that the two vibrations at 854 and around 790 cm^{-1} are the AsO_4 symmetric and antisymmetric stretching vibrations respectively. Two additional bands are observed in the infrared spectra at around 560 and 690 cm^{-1} . These two bands are not attributed to arsenate vibrations and since water is the only other molecule present in the structure then, these two bands are assigned to water librational modes. It is interesting that based upon the work of Moenke, Farmer (1974) reported bands at 605 cm^{-1} for annabergite and at 555 cm^{-1} for erythrite, which were unassigned. Griffith did not report bands in these positions.

Low wavenumber region of the vivianite arsenates.

The low wavenumber region of the vivianite arsenates between 100 and 500 cm^{-1} is shown in Figure 6. The low wavenumber region is complex and it is difficult to separate the Raman bands according to their symmetry. The spectrum of the low wavenumber region may be divided into three separate regions: (a) 400 to 500 cm^{-1} (b) 250 to 400 cm^{-1} and (c) 100 to 250 cm^{-1} . Three regions are suggested (a) ν_4 modes (b) ν_2 modes and (c) AsO bending and lattice modes. The ν_2 bending vibration should be common for all samples and should be intense. The most intense bands occur in two regions (a) around 450 cm^{-1} and around 225 cm^{-1} . The two most intense bands for annabergite are observed at 203 and 225 cm^{-1} (Figure 6a). It is noted that for the

synthetic annabergite Raman bands are observed at almost identical positions (Figure 6b). The two most intense bands for erythrite are found at 209 and 249 cm^{-1} (Figure 6c). The complex overlapping pattern of bands in the AsO stretching region is also reflected in the 223 cm^{-1} region of köttigite (Figure 6d). This region may be deconvoluted into bands at 249, 220 and 194 cm^{-1} . For the synthetic hörnesite, a single intense band is observed at 206 cm^{-1} (Figure 6e). Bands in these positions have not been reported for the infrared spectra. Fundamentally the bands are below the normal operation limits of mid-IR spectrometers. These bands are assigned to the OAsO bending modes.

The second most intense region in the Raman spectra is around the 450 cm^{-1} region. For both the natural and synthetic annabergites, two bands are observed at 466 and 442 cm^{-1} (Figure 6 a,b) and for erythrite bands are observed at 457 and 439 cm^{-1} . For köttigite bands are observed at 451 and 432 cm^{-1} . These bands are attributed to the ν_4 bending modes. The positions of these bands are observed at slightly lower wavenumbers for hörnesite and are found at 429 and 403 cm^{-1} . Farmer reported the infrared spectra of annabergite and erythrite and gave infrared band positions of 510, 460 and 427 cm^{-1} for annabergite and at 490, 452 and 428 cm^{-1} for erythrite. The latter two bands for these two minerals are in excellent agreement with the Raman bands reported in this work. Griffith (1970) reported the ν_4 modes in the Raman spectra at 452 and 438 cm^{-1} .

CONCLUSIONS

The application of Raman spectroscopy has enabled the structures of the vivianite-type arsenate minerals to be studied and compared. The X-ray diffraction patterns of these minerals are so similar that differentiation is not easy. Raman spectroscopy enables the identification of the minerals according to their Raman spectrum. Synthetic vivianite arsenates were prepared and their spectra compared with that of the naturally occurring mineral. The spectra were found to be identical. In the case of köttigite, the Raman spectrum is complex because of the cation substitutions most likely by ferrous ion. Raman spectroscopy assists in the elucidation of the structures of these complex systems.

Raman and infrared spectroscopy of water in these hydrated arsenates shows that the OH stretching regions are a complex set of overlapping bands. The infrared spectra of the water deformation modes shows that the water shows different hydrogen bond strengths (a) weak hydrogen bonding (b) strongly hydrogen bonding and (c) very strongly hydrogen bonding. The position of the bands reflects the behaviour of the water molecules in these hydrated arsenates. Bands which were previously unassigned at around 690 and 560 cm^{-1} are attributed to the librational modes of water. The arsenate vibrations have been identified with the ν_1 mode observed at around 850 cm^{-1} and the ν_3 mode at around 800 cm^{-1} . The ν_2 bending modes were observed as multiple bands centred around 225 cm^{-1} and the ν_4 modes were found at around 460 and 444 cm^{-1} . The spectra in these regions are cation dependent and the low wavenumber region may be used to characterise the vivianite arsenate minerals.

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Table 3. Raman spectral analysis of the arsenates of the vivianite group

| Annabergite | | Erythrite | | Hömsite (Synthetic) | Köttigite | Parasymplesite/symplesite | Suggested assignment |
|-------------|------|-----------|------|---------------------|-----------|---------------------------|----------------------|
| 298 K | 77K | 298K | 77K | 298K | 298K | 298K | |
| 3419 | 3417 | 3337 | 3421 | 3479 | 3458 | 3460 | Hydroxyl stretching |
| 3209 | 3206 | | 3275 | | 3215 | 3215 | |
| 3185 | 3185 | 3200 | 3204 | 3166 | | | |
| 3010 | 3040 | 3052 | 3095 | | | | |
| | 2970 | | 3019 | 3030 | | | |
| 941 | 954 | 902 | 919 | 907 | | | |
| 854 | 862 | | 859 | 875 | 868 | 860 | AsO stretching |
| | 825 | | 852 | | 835 | 835 | |
| 800 | 802 | 852 | 797 | 807 | 810 | 810 | |
| | | 792 | 786 | | 790 | 780 | |
| 676 | 770 | 727 | 716 | | | | Water libration |
| | 684 | 652 | 660 | 660 | | | |
| | 629 | | | | | 545 | |
| 466 | 445 | 467 | 460 | 467 | 479 | 480 | Out of plane bends |
| 442 | 405 | 457 | 440 | 446 | 451 | 450 | |
| 401 | 391 | 439 | 392 | 429 | 432 | 432 | |
| 350 | 376 | 391 | 378 | 403 | 371 | 371 | In-plane bends |
| 321 | 355 | 378 | 343 | 363 | 332 | 332 | |

| | | | | | | | |
|-----|-----|-----|-----|-----|-----|-----|--------------------|
| 286 | 326 | 301 | 308 | 303 | 286 | 286 | Lattice vibrations |
| 260 | 299 | 263 | 271 | 273 | 249 | 249 | |
| 242 | 292 | 249 | 252 | 262 | 220 | 220 | |
| 225 | 247 | 234 | 229 | 243 | 194 | 194 | |
| | 226 | 223 | 213 | 218 | | | |
| | 217 | 209 | 206 | 206 | | | |
| 203 | 192 | 188 | 188 | 180 | | | Lattice vibrations |
| 175 | 178 | | 177 | 159 | | | |
| 160 | 166 | 162 | 161 | | | | |
| 155 | 157 | 147 | 147 | | 142 | 142 | |
| 119 | | 126 | 141 | 117 | | | |
| | | | 127 | | | | |

Table 4. Infrared spectral analysis of the arsenates of the vivianite group

| Annabergite | | Erythrite | | | Köttigite | Symplesite/ Parasymplesite | Hörnsite | Suggested assignment |
|-------------|-------------------------|-----------|------------------|-------------------------|-----------|-------------------------------|----------|---------------------------|
| This work | Published ₁₅ | This work | Mt Cobalt sample | Published ₁₅ | | Published ₁₅ | | |
| 3412 | 3430 | 3460 | 3427 | 3445 | 3440 | 3385 | 3478 | Water Hydroxyl stretching |
| 3155 | 3160 | 3294 | 3172 | 3180 | 3185 | | 3273 | |
| 2972 | | 3099 | 2930 | | 3045 | | 3142 | |
| | | | | | | | 3038 | |
| | | | | | | | 3000 | |
| 1683 | 1630 | 1666 | 1683 | 1670 | 1660 | 1635 | 1682 | Water deformation |
| 1590 | 1600 | 1616 | 1633 | 1585 | 1585 | | 1635 | |
| | | 1568 | 1585 | | | | 1585 | |
| 922 | 832 | 910 | 882 | 825 | 890 | | 895 | AsO stretching |
| 831 | 795 | 808 | 825 | 783 | 868 | 850 | 836 | |
| | | 768 | 768 | | 845 | | 809 | |
| | | | | | 828 | 780 | 795 | |
| 778 | | | | | 790 | | | |
| 705 | | | | | | | 693 | |
| 567 | | 561 | 561 | | | | 557 | |
| 468 | 510 | | | 490 | 498 | 465 | | Out of plane bends |
| 457 | 460 | | | 452 | 455 | 445 | | |
| | 427 | | | 428 | 425 | | | |

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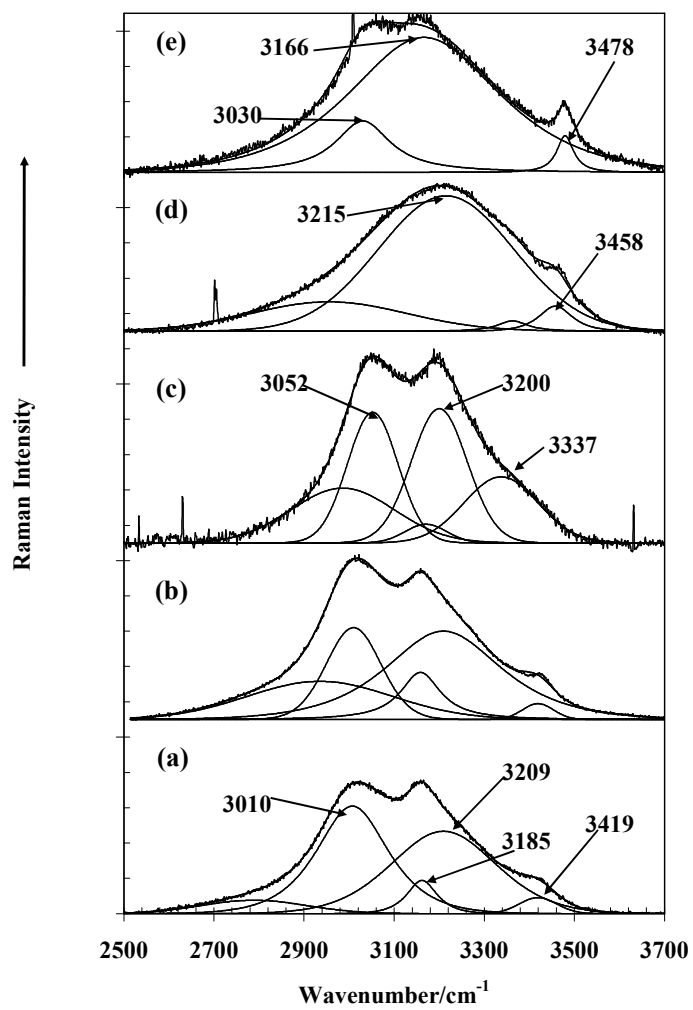


Figure 1

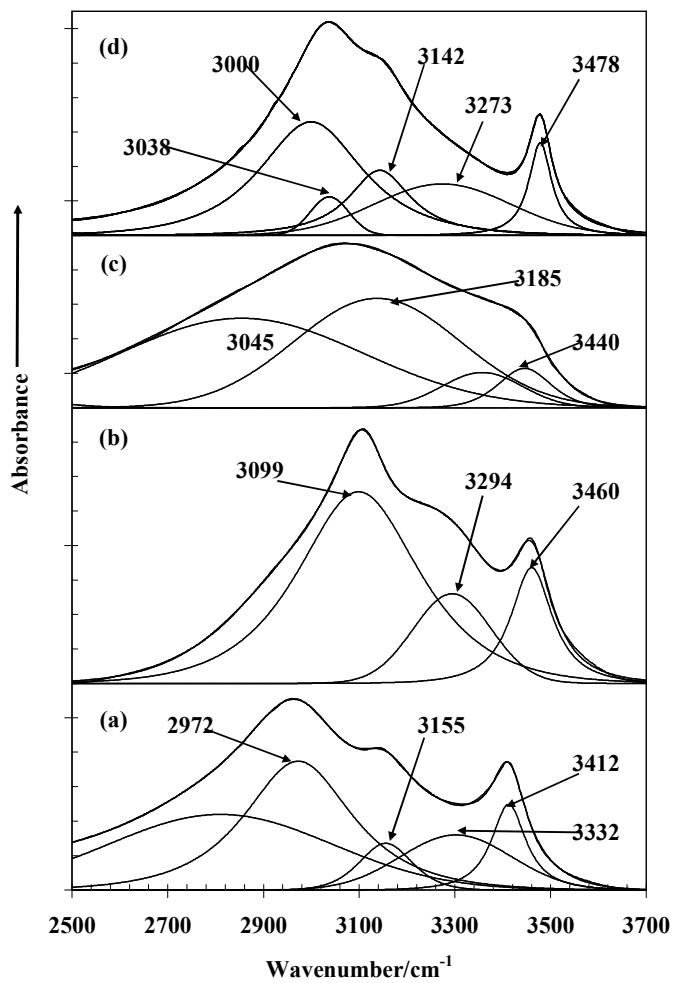


Figure 2

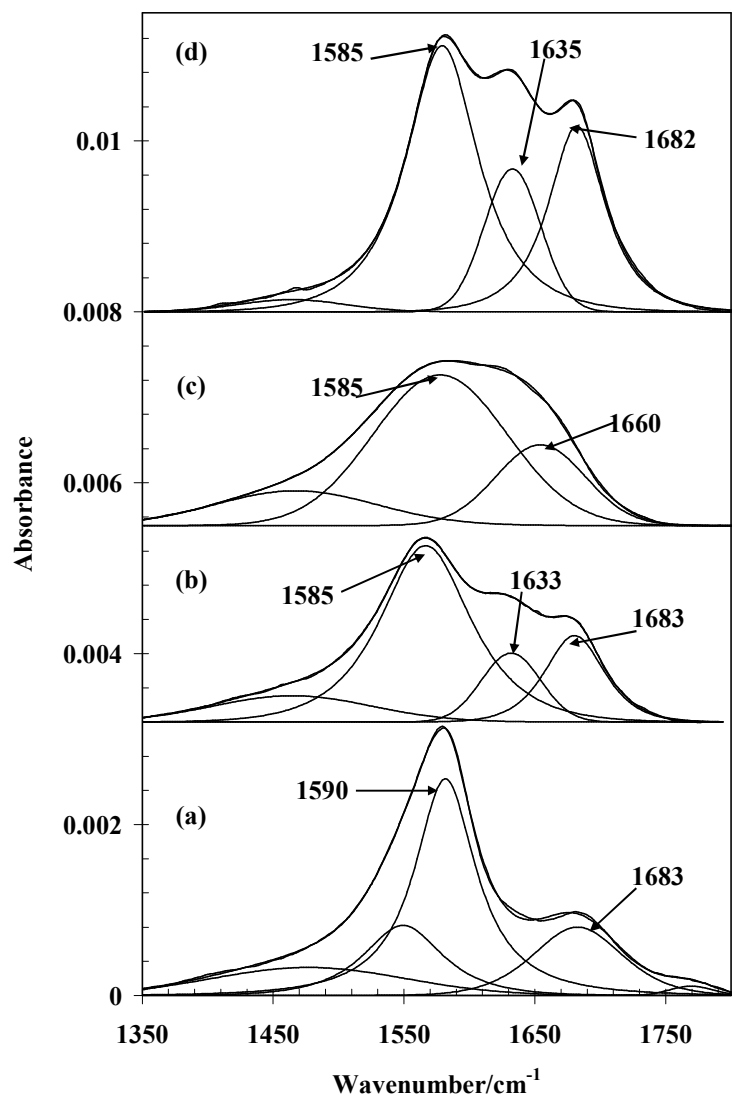


Figure 3

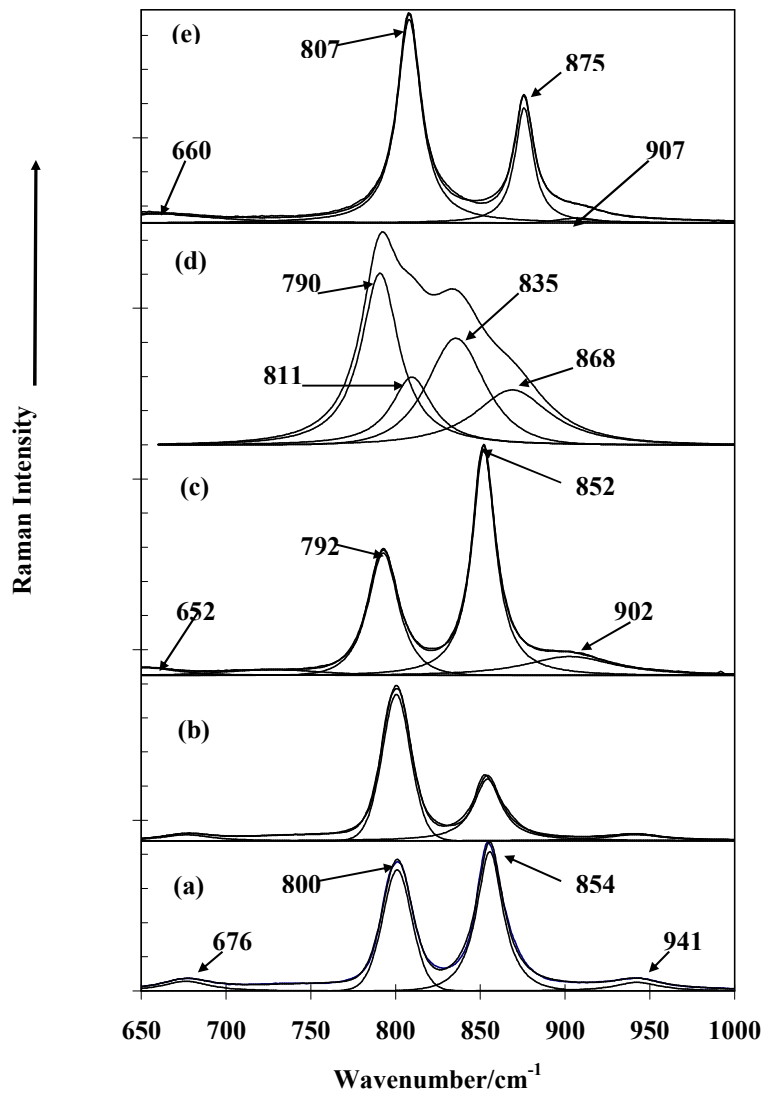


Figure 4

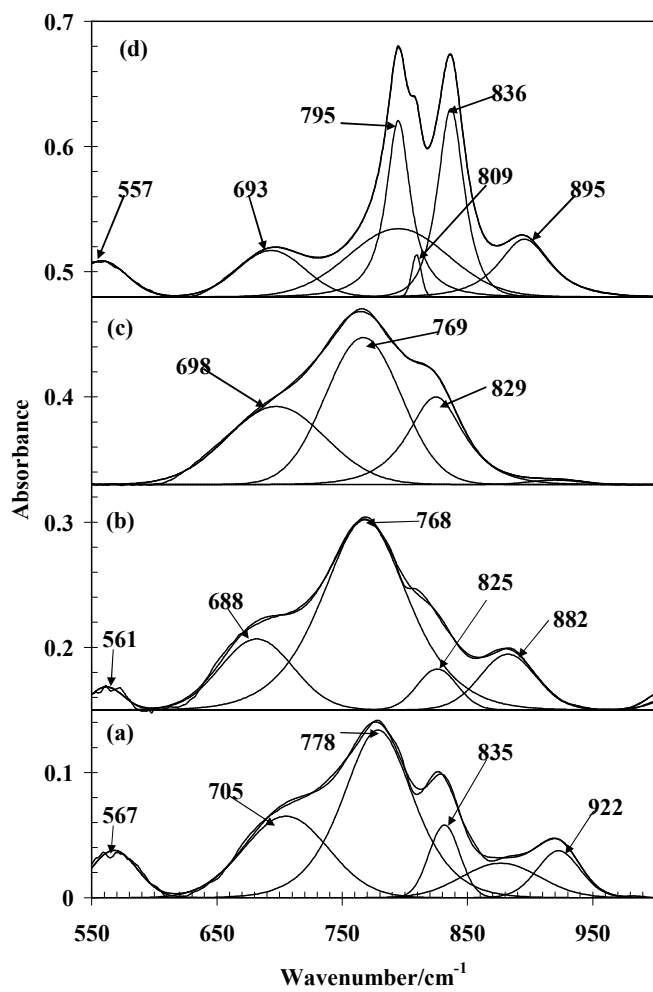


Figure 5

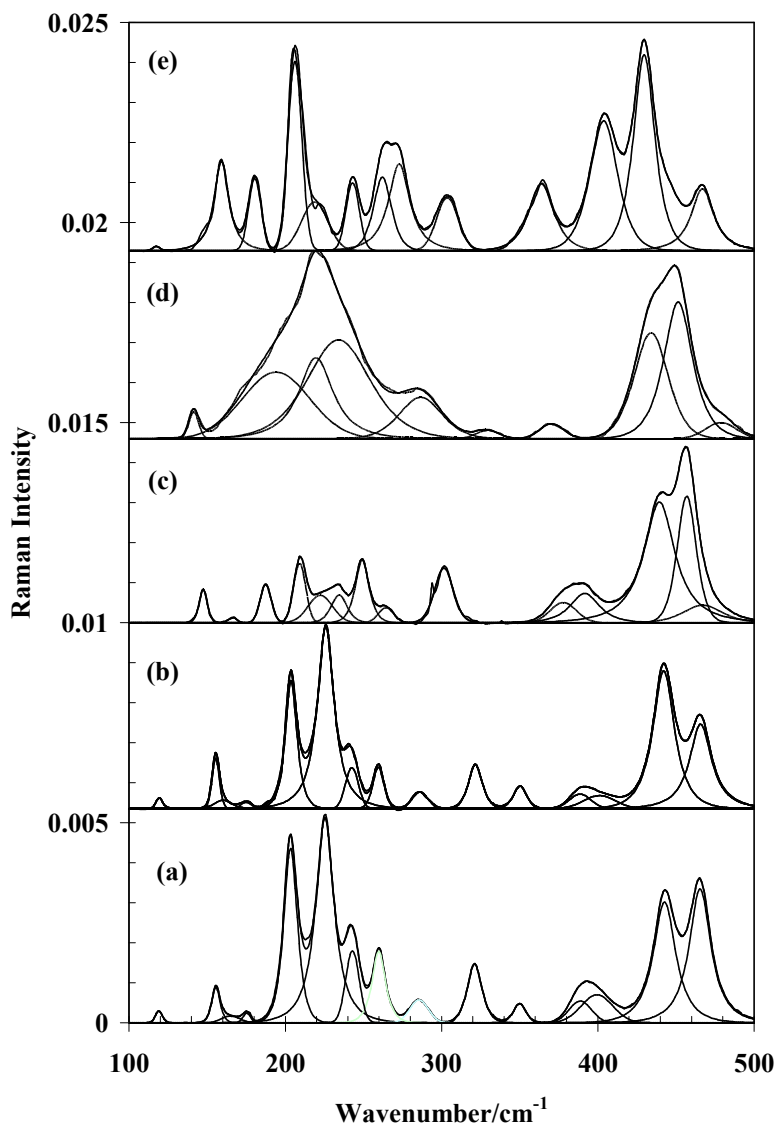


Figure 6