THE VIBRATIONAL SPECTROSCOPY OF MINERALS

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Toss another rock on the Raman...
KEYWORDS

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Solid Solutions
Strontianite
Vibrational Spectroscopy
Vivianite
Witherite
ABSTRACT

This thesis focuses on the vibrational spectroscopy of the aragonite and vivianite arsenate minerals (erythrite, annabergite and hörnesite), specifically the assignment of the spectra. The infrared and Raman spectra of cerussite have been assigned according to the vibrational symmetry species. The assignment of satellite bands to $^{18}$O isotopes has been discussed with respect to the use of these bands to the quantification of the isotopes. Overtone and combination bands have been assigned according to symmetry species and their corresponding fundamental vibrations. The vibrational spectra of cerussite have been compared with other aragonite group minerals and the differences explained on the basis of differing chemistry and crystal structures of these minerals.

The single crystal spectra of natural erythrite has been reported and compared with the synthetic equivalent. The symmetry species of the vibrations have been assigned according to single crystal and factor group considerations. Deuteration experiments have allowed the assignment of water vibrational frequencies to discrete water molecules in the crystal structure. Differences in the spectra of other vivianite arsenates, namely annabergite and hörnesite, have been explained by consideration of their differing chemistry and crystal structures.

A novel approach to the assignment of site occupancy of ions in the erythrite – annabergite solid solution has been reported. This approach has utilised vibrational spectroscopy, in conjunction with careful consideration of the crystal structures of the minerals. It has been shown that in the erythrite – annabergite solid solution Co
prefers metal site 2 contrasting nickel which prefers site 1. This study in conjunction with other studies has yielded the trend that the more electronegative metal prefers to occupy site 1, with the least electronegative metal preferring to occupy site 2.

Fundamentally this thesis has increased the knowledge base of the spectroscopic properties of the aragonite and the vivianite minerals. The site occupancy of metal ion substitutions in solid solution series of the vivianite group of minerals has been further enhanced, with novel method of studying the site occupancy of ions in solid solutions has been developed. A detailed knowledge and understanding of factor group analysis applied to the study of minerals has been achieved.
PUBLICATIONS WRITTEN IN THE COURSE OF STUDY


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STATEMENT OF ORIGINALITY

The material presented in this thesis has not been previously submitted for a degree at any other university or institution. To the best of my knowledge, this thesis contains no material published or written by any other person except where due acknowledgement is made.

Wayde Martens
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1. INTRODUCTION:

1.1. DESCRIPTION OF SCIENTIFIC PROBLEM INVESTIGATED

Minerals have been important since ancient times, due to their wealth creation potential and raw material production [1-3]. Minerals have been used as sources of metals, building materials, additives, etc.[1-3] Some minerals were even used as colorants for medieval manuscripts and cosmetics in ancient Egypt [4-8]. Identification of minerals is of the utmost importance as knowledge of secondary mineralogy gives a direct indication of the primary mineralogy which is of particular interest for mineral exploration [1]. Therefore, an identification procedure is required for minerals that is non-destructive, fast, and effective. Raman spectroscopy has proven a useful technique for the non-destructive identification of minerals [9-12]. Vibrational spectroscopy provides a tool for the identification of minerals with mineral infrared (IR) spectra being routinely acquired [13]. Identification is easy through a finger printing technique [12, 13], but the interpretation of spectra is difficult. Interpretation of mineral vibrational spectra requires factor group analysis and careful consideration of the crystal structures of the minerals. This study was undertaken to acquire the spectra of selected groups of closely related minerals and correlate their spectral differences to their crystal structures. Solid solutions are known to hinder spectroscopic identification, due to changes in the spectra caused by replacement of cations or anions in the minerals. This study has been undertaken to understand the physical changes in the crystal structure due to solid solutions and correlate this with the effect on the vibrational spectra.
1.2. OVERALL OBJECTIVES OF THIS STUDY

In this study the primary objective is firstly to *gain an understanding of the vibrational spectroscopy of minerals. Specifically cerussite in relation to the other aragonite group minerals and the annabergite erythrite members of the vivianite group of minerals and their solid solutions.* The second objective is to use vibrational spectroscopy to *gain an understanding of the solid solution phenomenon* in the vivianite group of minerals. This study of the solid solutions of vivianites will focus on the *effect of cationic substitution* on the vibrational spectra and crystal structure in *synthetic systems*. The study utilises the analytical techniques of Raman spectroscopy, infrared spectroscopy, SEM, and XRD.

1.3. SPECIFIC AIMS OF THE STUDY

The specific aims of the research presented in this thesis were:

- Acquire the vibrational spectra of the aragonite minerals and explain the differences in the spectra due to changes in the crystal structure of the minerals.
- Acquire and explain the single crystal Raman spectra of erythrite and compare these with other vivianite arsenates. A detailed analysis of bands is undertaken to pinpoint specific vibrating units.
- Determine and explain the solid solution phenomena of erythrite and annabergite with respect to the vibrational spectra of the minerals.
- Determine the site occupancy of metal ions in the solid solution series between erythrite and annabergite
1.4. ACCOUNT OF SCIENTIFIC PROGRESS LINKING THE SCIENTIFIC PAPERS

To use vibrational spectra to explain differences related to crystal structures of minerals it is necessary to gain a full understanding of factor group analysis. It is not possible to assign any mineral spectra without such knowledge. To establish a basis the vibrational spectroscopy of the vivianite minerals must be understood, before the consideration of solid solutions. At this stage with detailed knowledge of factor group analysis and knowledge of the spectroscopic behaviour of the vivianite arsenates it is possible to undertake a study of the solid solution phenomenon in the erythrite – annabergite series. To this end the following chapters are arranged to (Figure 1):

1. Show how factor group analysis is undertaken, how to assign spectra of minerals, and particular assignment tools utilised in this thesis. (Chapter 2)

2. Assign the single crystal spectra of cerussite and compare the spectra of other aragonite minerals, further illustrating the assignment of spectra of minerals. (Chapter 3)

3. Determine and assign the single crystal spectra of erythrite, with comparison to other vivianite arsenates to determine a basis for further work on erythrite/annabergite. Comparison of the spectra to other vivianite minerals establishes a crystallographic basis for variation of the spectra. (Chapter 4)

4. Investigate the spectra of deuterated erythrite to determine the assignment of water vibrational modes, and track the independent water molecules. (Chapter 5)

5. Investigate the solid solution of erythrite annabergite using synthetic samples. (Chapter 6)
Figure 1 Interaction and arrangement of chapters

Factor Group Analysis (FGA) of Minerals (Chapter 2)

Single Crystal Study of Cerussite (Chapter 3)
Application of FGA to assignment of spectra
Spectral differences due to crystal structure

Single crystal study Of Erythrite (Chapter 4)
Basis study of spectroscopy of vivianites

Deuterated erythrite (Chapter 5)
Further assignment of spectra of vivianites particularly water modes

Solid solution of erythrite and annabergite (Chapter 6)
Determine site occupancy in solid solutions with vibrational spectroscopy

Appendix (Chapter 8)
Auxiliary mineral spectroscopy studies
References

2. THEORETICAL CONSIDERATIONS OF MINERAL SPECTROSCOPY

2.1. Introduction

Minerals are elements or combinations of elements in a crystalline form which have been produced by a natural geological process [1-3], as such each different mineral species must be different in composition or crystal structure [1-3]. Therefore, minor substitutions in a mineral structure are not classified as different minerals unless this substitution occurs in constant specific ratios [1]. Identification of minor phases - present as associations - can also give an indication of the geological history of the major mineral species [1]. Therefore, an identification procedure that is non-destructive, fast, and effective is required to identify these minerals. Current mineral identification techniques include:

(i)  *X-ray Diffraction (XRD):*

X-ray diffraction is currently used as the main phase identification technique. However, it is occasionally inappropriate due to the necessity to grind the samples, which causes obvious damage to valuable samples.

(ii)  *Optical Mineralogy:*

Optical mineralogy is used as an identification procedure but 1 µm thin sections must be prepared. The procedure is time consuming with user experience playing a major role in the analysis.

(iii)  *SEM, AA/AE, ICP-MS, XRF:*

These are the main suite of techniques used for compositional analysis. Carbon coating (SEM) or dissolution (AA/AE, ICP-MS, XRF) is a
requisite for these analyses. A set of accurately known standards have
to be prepared for a reliable calibration of the method.

Vibrational spectroscopy provides an alternative tool for the identification of
minerals, with mineral IR spectra being routinely acquired [4]. Identification is easy
through a finger printing technique [4, 5], but the interpretation of spectra is difficult.
Vibrational spectroscopy is often the best method for the identification of minerals
when other techniques such as XRD can not be undertaken due to sample quantity
(minor phases), crystallinity (amorphous/semi-amorphous) and destructiveness
(grinding/dissolution)[5, 6]. Raman spectroscopy has proven a useful technique for
the non-destructive identification of minerals [5-8].

Copper arsenates, phosphates, chlorides, and carbonates have been extensively
used in many medieval manuscripts for pigments, but due to their nature, are easily
confused owing to their similarities in chemical composition, crystal structure, and
colour [9-16]. The dark green copper phosphate polymorphs - pseudomalachite,
reichenbachite, and ludjibaite - are difficult to distinguish. These copper minerals are
also confused with malachite $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ [17], and the copper arsenates
cornwallite, olivenite, and clinoclase [9-16]. Easy non-destructive methods of
analysis are required for these minerals, thus the utilisation of vibrational
spectroscopy is important for the study of these minerals and medieval manuscripts
[18, 19]. Raman spectroscopy can easily distinguish different anions such as
carbonate, arsenate, phosphate, nitrates, sulphides, chlorides, etc. [5, 6]. Minerals with
polymorphs can also be distinguished through the use of factor group analysis. Raman
spectroscopy has even been employed to identify the geographical origin of
minerals[19]. Raman microscopy allows the easy selective orientation of crystals and has the ability to acquire the spectrum of a single crystal due to its spatial resolution of 1µm [20]. Fluorescence from the sample matrix is also reduced with Raman microscopy due to the reduction of sampling volume [20]. Birefringence can also cause problems in Raman spectroscopy, because of the confocal nature of microscopes; Raman microscopy evades this problem [20]. However, Raman microscopy does suffer from some disadvantages, for instance a large amount of leakage due to the microscope optics can occur. This is due to the analysed and excitation radiation collected without a strictly parallel arrangement. The amount of radiation that is not incident/collected strictly parallel may be calculated [20]. Samples have an increased tendency to burn/decompose in Raman microscopy with the laser power concentrated into a smaller volume. This is especially a problem with blue samples when using He-Ne lasers as blue samples absorb red light, thus the laser radiation is absorbed by the sample and dissipated as heat.

Solid solutions provide an added complication to vibrational spectroscopy due to the broadening of spectra from random substitutions into the crystalline lattice causing a loss of factor group. Standards are often not available for comparison and therefore, identification is sometimes inconclusive, requiring the synthesis of minerals for reliable identification standards.

Complex solid solutions also exist, the presence of which may be studied by vibrational spectroscopy, as other techniques such as XRD may not detect them. Many secondary mineral samples are also rare and found only in exclusive secondary mineral collections. Techniques such as attenuated total reflectance (ATR), diffuse
reflectance (DRIFT) and Raman microanalysis are often used for the study of minerals and other crystalline or semi-crystalline materials. Data analysis is often fraught with danger and a number of critical questions arise. What bands are applicable to which molecular species? How many bands do we expect for each molecule? And how do differences in crystal space group affect the vibrational spectra of the mineral? For these questions to be answered, factor group analysis must be employed. Factor group analysis of simple free molecules is often easy, but the extension into crystalline materials is frequently troublesome. The following sections offer a review of factor group analysis of simple molecules and then an extension to crystalline lattices. These sections discuss symmetry elements, factor group analysis of free molecules, site symmetry and factor group analysis of solids, as well as the assignment of vibrations to molecular groups and symmetry species.

2.2. Factor Group Analysis

Factor group analysis is a method used for determining symmetry of vibrations [6, 20-27]. It is useful for determining how many bands are expected of each type of molecule in the vibrating unit and is also useful for ascertaining differences in spectra of polymorphous materials. The variation in the spectra of polymorphs are due to the difference in the symmetry of the polymorph [6, 20-27]. The symmetry elements and the combination of symmetry elements is the crux of factor group analysis. An atom in a vibrating unit, a molecule or crystal, may be thought of as having three degrees of movement, namely x, y, and z directions. From the combination of the symmetry elements of each vibrating unit the movement of the atoms, which results in an overall
change in the dipole moment (infrared spectroscopy) or polarisability of the electron cloud (Raman spectroscopy), may be inferred.

2.3. Elements of symmetry

To gain an understanding of factor group analysis it is necessary to first obtain an understanding of elements of symmetry. It is these elements of symmetry and the addition of them that predicts the normal modes of vibration of a molecule in a crystalline lattice. Symmetry elements such as inversion centres, mirror planes, rotation axis and the addition of these to get the overall symmetry species will be looked at in this section. A symmetry element is an operation that once applied to a shape leaves that shape unchanged after the operation [6, 21, 28]. One of the simplest symmetry elements is possibly the mirror plane, an example of which is human hands. If both hands are placed together with small fingers touching it is easy to see that if a mirror is placed between the hands, one hand reflects onto the other hand. Each digit on the hand has an identical image on both the left and right of the image. This is also applicable to molecules such as the water molecule; a mirror plane may be drawn down the centre of the molecule bisecting the oxygen and the angle of the two hydrogens. Another mirror plane, which bisects all atoms, is also present, as shown in Figure 1.
Another symmetry element is the rotation axis. An example of a rotation axis is shown in Figure 1, where the water molecule may be rotated about the oxygen. Other more complex images such as the tetrahedron also have rotation axis. Each apex of the tetrahedron has a three fold rotation axis. If a shape has no symmetry operation applicable to it the symmetry element is assigned to a $C_1$ rotation axis and represents the lowest symmetry possible. Inversion centres are centres of symmetry where all elements are able to be transposed through the centre of symmetry to achieve the same image as before. An example of an inversion centre is shown in Figure 2.

**Figure 1** Symmetry elements in the water molecule

**Figure 2** Inversion centre
It can be seen that if all points are transposed through the origin to the other side along the axis, the same shape is achieved. Elements of symmetry are able to be combined to achieve a set of possible symmetry operations of a factor group. This factor group will be discussed further in the following sections.

2.4. Prediction of the number of normal modes of vibration

The number of normal modes of vibration for a crystal or molecule may be calculated from the number of degrees of freedom of it has to vibrate. This is related to the number of atoms in the crystal or molecule. Since there are three degrees of freedom for an atom to vibrate, there are $3N$ modes of motion possible where $N$ is the number of atoms in the molecule or crystal. As the whole crystal or molecule may translate in three directions, then these must be subtracted from the total. Molecules may also rotate about three directions for bent molecules, or two directions for linear molecule, thus three or two modes must be deducted respectively. This allows the following formula for the calculation of the normal modes of vibration of a molecule:

$3N - 5$ Linear molecules

$3N - 6$ Bent molecules.

Crystals have an added confusion, as the contents of the unit cell may not reflect the content of the Bravais unit cell. Only the number of atoms in the Bravais unit cell may be used to predict the number of normal modes of vibration of a crystal. The number of atoms in the Bravais cell can be calculated by the formula:

$$N = \frac{Z}{LP}$$

Where $N$ is the number of atoms in the Bravais unit cell, $Z$ is the number of atoms in the unit cell, and $LP$ is the number of lattice point as determined from Table 1.
Table 1  Unit cell type and number of lattice points

<table>
<thead>
<tr>
<th>Type</th>
<th>A,B,C or I</th>
<th>F</th>
<th>P</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>3 or 1*</td>
</tr>
</tbody>
</table>

* This lattice may have been reduced to primitive form

From the number of atoms in the Bravais cell the number of modes of vibrations of a crystal may be determined by the formula:

\[3N-3\] where \(N\) is the number of atoms in the Bravais unit cell.

Only the three translational modes are subtracted in the case of a crystal as the rotation of an atom or a molecule is not the same as the rotation of a neighbouring group or atom.

2.5. Point group analysis of free molecules

The water molecule is one of the simplest cases which contains a combination of symmetry elements. The water molecule has three atoms - one oxygen bound to two hydrogens – at an angle of ~120° (Figure 1). A line can be drawn down the middle of the oxygen, bisecting the angle between the two hydrogens. If the molecule is rotated around this axis, there are two positions, which produce the same image as the original starting position. This line represents a two fold rotation or commonly referred to as the \(C_2\) axis and a rotation of 180° about the \(C_2\) axis is called a \(C_2\) symmetry operation. There are also two more symmetry elements in the water molecule, the mirror planes. The first plane is the plane of the atoms; the second plane is normal to the first and intersects it along the \(C_2\) axis. These mirror planes reflect the atoms on one side of the molecule directly onto the other side. These are the \(C_s\) planes, where \(s\) represents a mirror plane. Once the symmetry operations for the
molecule are known, the point group may be determined by following the flow chart below (Figure 3). In this case, it may be deduced that the molecule has $C_{2v}$ symmetry.

The next step is to use the point group to assign the symmetry species of the vibrations of the molecule. Consider the water molecule in terms of distinct elements; the oxygen, which is sitting on a $C_2$ axis and two mirror planes, and two identical hydrogens sitting on a mirror plane. There are rules of convention governing the assignment of the $x, y, z$ axes [28]. The $z$ axis in vibrational spectroscopy is considered the most important axis, which is commonly the axis that intersects the most atoms with the most symmetry [28]. In the water molecule the $z$ axis corresponds to the $C_2$ axis. In this case the oxygen atom is sited on the highest point of symmetry [28]. The $x$ axis is now chosen to be perpendicular to the molecular plane and the $y$ axis to be in the molecular plane [28].
Having assigned the axes, correlation tables such as those in Farmer may be consulted to find the symmetry species of the vibrations of the molecules [11]. The correlation table for $C_{2v}$ is shown below in Table 2. The first column shows the highest symmetry group. In this particular case it is the $C_{2v}$ column that is the highest symmetry species present. The letters in this column represent the modes, which are available to the molecule to vibrate. Each distinct atom (with respect to symmetry and atomic type) is considered for its particular symmetry elements. Consulting the correlation for oxygen ($C_{2v}$), it can be seen that there is displacement for the oxygen in the $A_l$, $B_1$ and $B_2$ symmetry operations. The hydrogens can be seen to be on $C_2$ elements allowing for two displacements in the $A_l$ mode, one in the $A_2$ mode, one for $B_1$ and two for the $B_2$ mode. The addition of these modes gives the reducible
representation given by in this case $3A_1 + A_2 + 2B_1 + 3B_2$. However six of these modes describe the modes of vibration which describe rotations and translations. In Table 2 it can be seen that translations (T) and rotations (R), occur as the modes $A_1$ ($T_z$), $A_2$ ($R_z$), $B_1$ ($T_x, R_y$), and $B_2$ ($T_y, R_x$). The available modes of vibration of the water molecules can then be obtained by the subtraction of the translation and rotations possible. This is summarised in Table 3.

**Table 2. Correlation table for the $C_{2v}$ point group**

<table>
<thead>
<tr>
<th>$C_{2v}$-num2</th>
<th>1</th>
<th>2</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$xx, yy, zz, T_z$</td>
<td>$A_1$ 1z</td>
<td>$A_1$ 1z</td>
<td>$A' 2p$</td>
<td>$A' 2p$</td>
</tr>
<tr>
<td>$xy, R_x$</td>
<td>$A_2$ 0</td>
<td>$A_1$ 1z</td>
<td>$A'^{' 1y}$</td>
<td>$A'^{' 1x}$</td>
</tr>
<tr>
<td>$zx, T_y, R_y$</td>
<td>$B_1$ 1x</td>
<td>$B_2$ 2p</td>
<td>$A'^{' 2p}$</td>
<td>$A'^{' 1x}$</td>
</tr>
<tr>
<td>$yz, T_y, R_x$</td>
<td>$B_2$ 1y</td>
<td>$B_2$ 2p</td>
<td>$A'^{' 1y}$</td>
<td>$A'^{' 2p}$</td>
</tr>
</tbody>
</table>

$C_{2v}$: 1ef; 11d; 14e; 15e; 18d; 20c. $C_{2v}$: 1gh; 2ab; 4c; 7a; 11e; 12a; 14de; 16b; 18e; 20d; 22b.

**Table 3. Factor group analysis of the water molecule.**

<table>
<thead>
<tr>
<th>Elements of symmetry</th>
<th>Available modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacements of the O atom</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td>Displacements of the H atoms</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td>Rotations and translations</td>
<td>$T_z$</td>
</tr>
<tr>
<td>Available vibrations of the water molecules</td>
<td>2$A_1$</td>
</tr>
</tbody>
</table>

The irreducible representation of the water molecule is $\Gamma = 2A_1 + B_2$, which predicts 3 modes for water. The 3N-6 rule discussed earlier allows for a check of the number of modes possible, in this case confirming the prediction of three modes of vibration for water. In Table 3 it is seen that translations apply to the normal modes for the water molecule. This indicates that the dipole moment oscillates in the same
direction as the translation allowing for infrared activity. In addition it can be seen
that the polarisability tensor has modes applicable for the normal modes of water.
Thus, the modes will be Raman active also.

2.6. Application of the internal modes to the crystal structure

The discussion to date has dealt with the vibrational modes available to
isolated molecules. For the extension of factor group analysis to crystalline solids an
understanding of crystallography is required. Crystalline lattices exist as a specific
structure for which the atoms may only exist on only specific sites. There exist some
230 space groups which relate to 33 crystallographic space groups. Each specific
space group has a finite number of sites with specific symmetry. The “International
Table For Crystallography” has the relative co-ordinates for each symmetry site
contained in the unit cell which may be used in conjunction with single crystal XRD
to determine the identity of the atoms on each site. For the use of the XRD results in
vibrational spectroscopy the following table (Table 4) is needed to translate from
Hermann-Mauguin notation (XRD, crystallography) to Schoenflies notation
(spectroscopic) [11, 32].
Once the site point group has been determined it is necessary to check that there is no choice between the similar symmetry species. For instance, the cases of the water molecule there is a choice for the $C_s$ mirror plane in the yx or xz directions. In this case the Wyckoff letter in combination with the Schoenflies superscript, obtained from the “International Table For Crystallography”, will yield the answer. In this instance $C_i^{yz}$ are sites 1ef, 11d, 14c, 15c, 18d, 20c and the $C_i^{yz}$ are the 1gh, 2ab, 4c, 7a, 11e, 12a, 14de, 16b, 18c, 20d, and 22b (Table 2). [6]
Once the sites have been unequivocally determined, the factor group splitting can be determined. Appropriate correlation tables can be consulted to determine how the site symmetry reduces the internal modes to lower symmetry modes. If vibrational modes are degenerate such as E and T modes, the site symmetry may split the modes into lower symmetry species allowing multiple modes for the degenerate modes. A crystal symmetry correlation table, such as Table 5, (Factor Group) can be used to determine the splitting of the site mode which will result in splitting of these modes. The occurrence of more than one of the identical molecules (with relation to symmetry and atom type, could result in coupling). In the case of water molecules (C\(_{2v}\)) sitting on a C\(_1\) site in a C\(_{2h}\) crystal, such as gypsum, the A\(_t\) and B\(_2\) mode form A modes on C\(_1\) site and split to A\(_g\), B\(_g\), A\(_u\), and B\(_u\) modes in the C\(_{2h}\) crystal as shown in Table 6. This would suggest that in this case there is the occurrence of four of the same molecules in the lattice, which will result in the splitting of A modes. It is also noted that this results in a symmetric characteristic (A\(_g\) modes, vibrating in phase) and an anti-symmetric mode (B\(_g\), vibrating out of phase).

**Table 5.** Correlation table for the C\(_{2h}\) Point group

<table>
<thead>
<tr>
<th>C(_{2h})−2/m</th>
<th>1</th>
<th>2</th>
<th>2</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x^x, y^y, z^z, x^y)</td>
<td>(R_x)</td>
<td>A(_g) 0</td>
<td>A 1z</td>
<td>A' 2p</td>
<td>A(_g) 0</td>
</tr>
<tr>
<td>(y^z, z^x, 2R_{xy})</td>
<td>(T_z)</td>
<td>B(_g) 0</td>
<td>B 2p</td>
<td>A' 1z</td>
<td>A(_g) 0</td>
</tr>
<tr>
<td>2T(_{xy})</td>
<td>(A_u) 1z</td>
<td>A 1z</td>
<td>A' 1z</td>
<td>A(_u) 3</td>
<td>A 3</td>
</tr>
</tbody>
</table>

34
The 3N-3 rule may then be applied to determine if all modes of vibration have been described. In the case of crystals, the contents of the Bravis lattice must be considered and not the total unit cell contents as discussed in the previous sections. Taking this into account, three modes are available to the free water molecule, but in the case above there are 4 water molecules in the Bravis cell and hence each mode splits into 4, allowing 12 modes of vibration. All the modes of vibration determined in this section have been concerned with the vibration of the molecule, the so-called internal modes of vibration. There are also the vibrations of the molecule as a whole, vibrating within the crystalline lattice.

### 2.7. Lattice modes

Lattice modes are dealt with by a similar mechanism to that of the vibrations of molecules. The main difference between the factor group analysis of lattice vibrations and internal modes, is that lattice modes are considered as the movements of groups of atoms in the crystalline lattice [21, 25]. For instance, gypsum CaSO₄·2H₂O, the water and sulphate molecules would be considered as free entities then subjected to the symmetry constraints of the site, then the crystal symmetry. It is then necessary to consider the motions of the sulphate group, the water molecules, as

<table>
<thead>
<tr>
<th>Free C₂ᵥ</th>
<th>Site C₁</th>
<th>Crystal C₂h</th>
</tr>
</thead>
<tbody>
<tr>
<td>2A₁</td>
<td>3A</td>
<td>3A₉</td>
</tr>
<tr>
<td>B₂</td>
<td></td>
<td>3B₉</td>
</tr>
</tbody>
</table>

|            |         | 3A₈         |
|            |         | 3A₈         |
|            |         | 3B₈         |
|            |         | 3B₈         |
well as the motion of the calcium atoms in the crystal. To consider the factor group
analysis of lattice modes it is necessary to know the site symmetry of each group [21,
25]. It is necessary to know the modes available for the molecule to translate and
rotate. While in the case of atoms, only translations need be considered due to their
rotational symmetry, it is however necessary to consider translations and rotations in
the case of molecules [25]. The appropriate modes may be deduced from correlation
tables. In the case of water molecules on C\textsubscript{1} sites there are 6A modes available for the
water molecule to rotate and translate. This is then related to the C\textsubscript{2h} crystal group.
This predicts the formation of the reducible representation 6A\textsubscript{g} + 6B\textsubscript{g} + 6A\textsubscript{u} + 6B\textsubscript{u}.
Each group of atoms is considered in turn to produce the active lattice vibrations
which are added to achieve the lattice modes of the crystal. It is again necessary to
consider the three modes that represent the translations of the whole crystal, which are
not active vibrations. These modes are subtracted to give the irreducible
representation 5A\textsubscript{g} + 4B\textsubscript{g} + 5A\textsubscript{u} + 4B\textsubscript{u}.

2.8. Assignment of spectra, Selection Rules, Polarised Orientated Vibrational
spectroscopy

Assignment of spectral bands to various symmetry species can be achieved via
polarised single crystal Raman and polarised single crystal infrared investigations [20,
21, 25]. The symmetry species of the vibrations can be ascertained by orientating the
crystal of a mineral along different polarisations of the incident radiation. For Raman
measurements the polarisability tensor of the vibration is different along different axis
of the crystal [20, 21, 25]. The probability of a Raman transition is proportional to
[20, 21, 25]:

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\[ \psi_o \psi_i \text{dt} \] Where \( \psi_o \) is the vibrational wave function, \( a \) is the polarisability of the molecule, \( \psi_i \) is the vibrational wave function, and \( \text{dt} \) implies the integration is carried over all possible variables of the wave functions. The polarisability \( a \) is the ease with which the electron cloud in the molecule may be distorted. This quantity is a tensor, a 3X3 array of components, i.e. \( a_{xx}, a_{xy}, a_{xz}, a_{yx}, a_{yy}, a_{yz}, a_{zx}, a_{zy}, \) and \( a_{zz}, \) where \( a_{kl} = a_{lk} \).

In the case where the integral is zero, then there is zero probability that the transition will occur [20, 21, 25]. The integral will only be non zero in the case where the product \( \psi_o \psi_i \) is totally symmetric, that is +1. This can only be achieved when \( a_{kl} \) has the same symmetry properties as \( \psi_i \) [21, 25]. The symmetry properties of \( a_{kl} \) are the same as the symmetry properties of \( kl \). Thus, if the normal mode has the same symmetry as one of these binary combinations of \( x, y, \) and \( z, \) then a transition from the ground state will be Raman active [21, 25]. A typical form of a polarisability tensor is shown in Chapters 3 and 4. If a character is shown, then a transition along the axis may be allowed. Modes of vibration that are not allowed will be of zero intensity or very low intensity. Orientated single crystal Raman studies, with Raman spectra taken of all possible orientations and polarisations possible, will yield the symmetry species of the vibrations.

The polarisability tensors for a vibration are calculated along the spectroscopic axis [20]. Thus it is necessary to know the relationship of the crystallographic axis in relation to the spectroscopic axis. This can be achieved by the knowledge of the translations of a spectroscopic group, available in correlation tables. In this way a spectroscopic axis of translation can be seen to move in a direction associated with a mode of vibration. From the correlation tables these modes can be related to the site and space groups to determine the spectroscopic axis with relation to the crystal axis.
From an atomic coordinate model, the relationship between the spectroscopic and crystallographic axis can be deduced. The spectroscopic axis can also be deduced from the correlation tables, by looking at the symmetry species and Schoenflies / Wyckoff letter if the space group has choices for the definition of the same symmetry element.

Once the symmetry species of the bands are identified there is a possibility of further assignment from deuteration, isotopic and analogous series studies (cationic and anionic series) through the use of Hooke’s Law. Satellite bands are known to exist in cerussite, with the intensity of these bands about 1% of the corresponding $\nu_1$ band intensity[29-31]. This satellite is due to isotopic $^{18}$O substitution in the carbonate group [29-31]. The calculated frequencies of this vibration are, from Equation 1, for cerussite 1030, aragonite 1058, witherite 1034, and strontianite 1044 cm$^{-1}$, which are in good agreement with the experimental results [32].

$$V = \frac{1}{2pc} \sqrt{\frac{k_o}{\mu}}$$  \hspace{1cm} \text{(Equation 1)}

$\mu$ = reduced mass of participating atoms
$k_o$ = force constant
$V$ = vibrational frequency in wavenumbers
$c$ = speed of light

Studies have shown a strong correlation between OH stretching frequencies and both the O–O bond distances and the H–O hydrogen bond distances. [33-36] The significant work of Libowitzky [37] showed that a regression function can be employed, relating the above correlations with regression coefficients better than 0.96 [37]. The function is $\tilde{\nu} = 3592-304x109\exp(-d(O-O)/0.1321)$ cm$^{-1}$. Minerals where
two or more types of OH units are identified in the structure, the known hydrogen bond distances may be used to calculate the hydroxyl stretching frequency. From this predicted hydroxyl stretching frequency further assignment of the spectra may be made.

Some vibrations that are treated as lattice vibrations such as hydroxyl stretching vibrations, therefore may be hard to differentiate these vibrations from the other lattice modes. Vector analysis may be employed to gain insight into these bands. Vector analysis considers vibrations of a molecule as a vector. Interactions of this vector with other vectors of an identical nature are deduced from the factor group. For the below example of olivenite, it is unclear how many vibrations are expected from the hydroxyl groups. As the hydroxyl groups are sitting on $C_1$ sites there is only one vector that the hydroxyl is allowed to vibrate on their site symmetry (A). When this is allowed to split in the factor group there are $1A_g$, $1A_u$, $1B_g$, and $1B_u$ modes predicted, of which, g modes are Raman active and u modes are infrared active. Olivenite does indeed have two hydroxyl bands in the Raman [16]. This implies that in the structure of olivenite there are four hydroxyls which couple to produce the four modes.

2.9. Birefringence

Birefringence is a well known hindrance to single crystal vibrational studies. Birefringence is manifested as the differences in the refractive indices down each independent optical axis. As such, there is a difference in the velocity of light down these axes, hence a change in the resulting polarisation of the incident light. Erythrite is known to be birefringent with refractive indices of $a = 1.625$, $b=1.661$, and $? = \ldots$
1.691 [38]. The optical axes or pseudo-optical axes, are orthogonal on all axes except on the 010 face, in which the optical axis make a 30° angle with the c crystal axis [39]. The amount of depolarisation of incident radiation on a birefringent crystal can be calculated from the equation:

\[ L = 100[\cos^2 ? - \sin 2(G - ?)\sin 2G\sin^2 (?/\lambda)180] \] [39]

where \( L \) is the amount of radiation for which the plane of polarization is rotated by 90°, \( G \) is the angle the optical axis makes with the incident radiation, \( ? \) is the angle between the analyser and polariser, \( ? \) is the difference between the refractive indices multiplied by the thickness of the sample and \( \lambda \) is the wavelength of the incident radiation [39]. This equation predicts that along the 010 face of a crystal of erythrite incident polarised radiation is 28 % scrambled. This prevents the collection of reliable oriented single crystal data from the 010-crystal face.

### 2.10. Porto notation

Porto notation is a way of expressing the orientation of the crystal with reference to the polarisation of the laser in both the excitation and analysing directions [25]. This notation consists of a four letter code expressing the direction of the propagation of the incident radiation, the polarisation of the incident radiation, the polarisation of the analysed radiation and the direction of propagation of the analysed radiation. For example BACB, the first letter depicts the axis for the propagation of the laser light, the second depicts the orientation of the polarisation direction i.e. the direction that the laser is vibrating in the excitation, the third is the vibrational
direction of the Raman scattered photons that are being analysed and the last the
direction of propagation of the analysed laser beam [25]. This is all done with
reference to the crystal that is being analysed. An example is shown in Figure 4.

Figure 4 A example of Porto notation.

2.11. Olivenite Example

Olivenite is an olive-green copper arsenate mineral, and as with all secondary
copper arsenate minerals, it is formed from the oxidisation of native copper ore in
arsenate containing ground waters [16]. Crystals of olivenite may be short prismatic
to acicular; globular, reniform or nodular, fibrous structure; massive, granular to
earthy. Olivenite has the formula, Cu₂(AsO₄)OH, with four structural units per unit
cell. The crystal structure of olivenite is monoclinic, P2₁/n, with the Schoenflies
notation for this space group being C₂ᵥ [16, 38]. From the atom coordinates, Figure 5,
it can be deduced that all atoms in the structure are on C₁ sites. There are nine atoms
in a formula unit with four formula units per unit cell predicts 3N–3 \((3\times4\times9 - 3 = 105)\) vibrations. The arsenate ion has the free symmetry of \(T_d\) with the arsenic atom sitting on all elements of symmetry, and all oxygen’s sitting on a mirror plane and a three fold rotation axis. From character tables, Table 7 may be constructed for the arsenate ion.

Figure 5 Atom positions of each atom in the olivenite crystal structure.

Table 7. Factor group analysis of the free arsenate ion.

<table>
<thead>
<tr>
<th>Elements of symmetry</th>
<th>Available modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacements of the As atom</td>
<td>(T_d)</td>
</tr>
<tr>
<td>Displacements of the O atoms</td>
<td>(C_{3v})</td>
</tr>
<tr>
<td>Rotations and translations</td>
<td></td>
</tr>
<tr>
<td>Available vibrations of the arsenate ion</td>
<td></td>
</tr>
</tbody>
</table>
The arsenate vibrations can then be split to the site and space group in accordance with Table 8. This shows that the $A_{1} + E + 2T_{2}$ modes of the arsenate split to $A$ modes in the $C_{1}$ site and split to $9A_{g} + 9B_{g} + 9A_{u} + 9B_{u}$ modes in $C_{2h}$. The $A_{g}$ and $B_{g}$ modes will be Raman active while the $A_{u}$ and $B_{u}$ modes will be infrared active [16].

**Table 8.** The factor group splitting of the arsenate ion in the olivenite structure.

<table>
<thead>
<tr>
<th>$T_{d}$</th>
<th>$C_{1}$</th>
<th>$C_{2h}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1}$</td>
<td>$9A$</td>
<td>$9A_{g}$</td>
</tr>
<tr>
<td>$E$</td>
<td></td>
<td>$9B_{g}$</td>
</tr>
<tr>
<td>$2T_{2}$</td>
<td></td>
<td>$9A_{u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$9B_{u}$</td>
</tr>
</tbody>
</table>

As all atoms in the crystal lattice have site symmetry of $C_{1}$, only $A$ modes are available for the rotations and translations of the arsenate, the copper, and the hydroxides. From this, construction of Table 9 can be undertaken to determine the modes of vibration in the factor group.

**Table 9.** Factor group analysis of the lattice modes in olivenite

<table>
<thead>
<tr>
<th>Site group</th>
<th>Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{1}$</td>
<td>$C_{2h}$</td>
</tr>
<tr>
<td>18A</td>
<td>$18A_{g}$</td>
</tr>
<tr>
<td></td>
<td>$18A_{u}$</td>
</tr>
<tr>
<td></td>
<td>$18B_{g}$</td>
</tr>
<tr>
<td></td>
<td>$18B_{u}$</td>
</tr>
</tbody>
</table>

$\Gamma = 18A_{g} + 18B_{g} + 17A_{u} + 16 B_{g}$

69 Vibrations

It may be calculated that 105 normal modes of vibration are predicted for the olivenite crystal from the $3N-3$ rule. From the factor group analysis it has been calculated that 105 vibrations are predicted, 36 internal modes of the arsenate ion and
69 lattice modes [16]. As both the 3N-3 rule and factor group analysis predicts the same number of vibrations then all modes of vibrations have been calculated.

Once the symmetry species of the normal modes of vibration have been determined, it is necessary to determine the activity of these modes. Inspection of the relevant correlation tables reveals that the \( A_g \) modes are active in Raman spectra of XX, YY, ZZ and XY nature (Table 5). The \( B_g \) modes are active in the YZ, ZX spectra (Table 5). These tensor elements are along the spectroscopic axes, and therefore great caution must be practiced to ensure that the relationship between the spectroscopic and crystallographic axes are known. In the case of the monoclinic cell the \( b \) crystallographic axis is usually the unique axis which relates to the \( z \) spectroscopic axis. Further to this, the relation of the optical axis to the spectroscopic axis must be also checked to ensure that no birefringence occurs. In monoclinic cases, misalignment of the optical and spectroscopic axis usually occurs in spectra excited down the \( b \) axis. Other examples of factor group analysis are shown in Chapters 3 and 4.

2.12. Vivianite minerals and solid solutions

Vivianite group of minerals have the general formula \( A_3^{2+}(XO_4)_2.8H_2O \), where \( A^{2+} \) may be Co, Fe, Mg, Ni, Zn and \( X \) may be P or As [38]. Vivianite minerals are monoclinic with point group 2/m [38] and two formula units per unit cell [38, 40]. The vivianite group consist of the minerals[38, 40, 41]:
Annabergite $\text{Ni}_3(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$

Arupite $\text{Ni}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$

Baricite $(\text{Mg,Fe})_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$,

Erythrite $\text{Co}_3(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$,

Hörnesite $\text{Mg}_3(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$,

Köttigite $\text{Zn}_3(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$,

Parasymplesite $\text{Fe}_3(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$

Vivianite $\text{Fe}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$.

These minerals are closely related to bobierrite $(\text{Mg})_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$, and manganese-hörnesite $(\text{Mn, Mg})_3(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$ which have a $b$-axis twice of those in the vivianite group [38, 40, 41].

Vivianites form solid solutions of mixed metal and mixed phosphates with most metal ions producing complete solid solution mixing curves [42-55]. Erythrite has been used for the preparation of pigments and glazes due to its brilliant pink colour [56-61], with the remediation of arsenates from soils also receiving attention [62-64]. The thermal transformations of vivianites has recently been studied with Raman, infrared, and infrared emission spectroscopy [65-67]. The infrared spectrum of vivianite minerals has been previously determined [6, 68, 69]. Single crystal x-ray diffraction studies have determined the crystal structure of erythrite [40]. The unit cell contains 2 formula units in the space group $C_{2h}^3$ with cell parameters of $a = 10.251$ Å, $b = 13.447$ Å, $c = 4.764$ Å, and $\beta = 104.98^\circ$ [38]. There are two sites occupied by two independent cobalt atoms ($C_{2h}$, $C_2$ site symmetry), with one independent arsenate ion ($C_s$ site symmetry) and two independent water molecules ($C_1$ site symmetry)[70].
Minerals of the vivianite group crystallize in the form of $M(1)\text{O}_2(\text{H}_2\text{O})_4$ octahedra and $M(2)_2\text{O}_6(\text{H}_2\text{O})_4$ double octahedral groups (where $M$ is the metal), which are linked via $\text{XO}_4$ tetrahedra to complex sheets in (010), further interconnected by hydrogen bonds only[70]. This structure is shown for erythrite in Figure 6.

**Figure 6** The atomic structure of erythrite

Mixed metal vivianite samples, of chemical compositions $\text{Co}_{2.01}\text{Fe}_{0.74}\text{Ni}_{0.25}(\text{AsO}_4)_{2.8}\text{H}_2\text{O}$ for erythrite and $\text{Ni}_{2.48}\text{Mg}_{0.50}\text{Fe}_{0.02}(\text{AsO}_4)_{2.8}\text{H}_2\text{O}$ for annabergite, have been studied by energy dispersion x-ray spectroscopy and microprobe analyses [70]. The $M^{2+}$ cation distribution on the $M(1)$ and $M(2)$ sites in erythrite and annabergite have been investigated by Moessbauer spectroscopy and site occupancy refinements [70]. Magnesium substituted annabergite showed a strong preference for $\text{Mg}^{2+}$ to occupy the Ni(2) sites over the Ni(1) sites [70]. Moessbauer spectroscopy of erythrite reveals an analogous preference of $\text{Fe}^{2+}$ on the Co(2) site [70]. Further evidence for the ordering of Mg and Ni site has also been demonstrated in cabrerite, a currently disregarded mineral name[45]. Cabrerite has a monoclinic
space group C2/m, with $a = 10.211$, $b = 13.335$, $c = 4.728$ Å, and $\beta = 104.97^\circ$ and $Z = 2$. Significant ordering of the Ni-Mg in the octahedral sites occurs. Single octahedra, M(1), and double octahedral groups, M(2)::: M(2), are connected by AsO$_4$ tetrahedra to form complex sheets parallel to (010) [45]. Magnesian nickelooan erythrite has been found with composition $(\text{Co}_{0.54}\text{Mg}_{0.29}\text{Ni}_{0.15}\text{Zn}_{0.02})(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$ giving an indication of the complexity of solid solutions available to the vivianite minerals [62]. Furthermore, vivianite samples from the Big Chief pegmatite mine, Glendale, Pennington Co., South Dakota, USA were found to contain oxide contents of FeO 38.9 %, MnO 4.2 %, NiO 0.13 %, CaO 0.5 %, P$_2$O$_5$ 28.4 %, H2 O (28.7), with minor As$_2$O$_5$, Na$_2$O, ZnO and CuO [71]. This indicates that even metal ions that do not form vivianite structures may substitute in the lattice of vivianite minerals. Due to this fact, the vivianite group of minerals is an excellent choice for the study of solid solutions.
2.13. References

18. Frost, R.L., et al., *Raman spectroscopy of the basic copper chloride minerals atacamite and paratacamite: implications for the study of copper, brass and


Chapter 3 – SINGLE CRYSTAL RAMAN SPECTROSCOPY OF CERUSSITE

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3.1. Statement of contribution

**Wayde N. Martens**: Wrote the manuscript, experimental design, conducted experiments, and data analysis.

**Llew Rintoul**: Aided experimental design, major editing, aided data analysis, aided writing of manuscript.

**J. Theo Kloprogge**: Major editing, aided data analysis

**Ray L. Frost**: Editing, data analysis, supervision
3.2. Abstract

Raman and infrared active modes of cerussite have been assigned according to their symmetry species, and compared to other aragonite group minerals. Small satellite bands at 823 and 1031 cm\(^{-1}\) to the low wavenumber side of the fundamental vibrations \(\nu_2\) and \(\nu_1\), respectively, have been assigned to the isotopic substitutions of \(^{13}\text{C}\) and \(^{18}\text{O}\). The Raman active \(\nu_1\) and \(\nu_2\) carbonate modes are observed at 1051 and 835 cm\(^{-1}\). The absence of the \(B_{2g}\) component of the \(\nu_1\) and \(\nu_2\) vibrations has been explained by the small coupling between the \(A_g\) and \(B_{2g}\) modes. The Raman active \(\nu_3\) carbonate anti-symmetric stretching mode is observed at 1361 (\(A_g\)), 1376 (\(B_{1g}\)), 1419 (\(B_{3g}\)), and 1477 (\(B_{2g}\)) cm\(^{-1}\), while the corresponding infrared active bands are observed at 1396, 1432, and 1456 cm\(^{-1}\). The Raman active \(\nu_4\) carbonate bending mode is observed at 673 (\(A_g\)), 668 (\(B_{2g}\)), 681 (\(B_{1g}\)), and 694 (\(B_{2g}\)) cm\(^{-1}\). The corresponding infrared bands are observed at 670, 679, and 698 cm\(^{-1}\). In both \(\nu_3\) and \(\nu_4\), the factor group splitting between the \(B_{1g}\) and \(B_{3g}\) modes is 1 to 3 times smaller than the separation of the \(A_g\) and \(B_{2g}\) modes. Raman active lattice vibrations are detected at 120 (\(B_{3g}\)), 132 (\(A_g\)), 148 (\(B_{1g}\)), 152 (\(B_{2g}\)), 174 (\(B_{2g}\)), 179 (\(B_{1g}\)), 213 (\(A_g\)), 226 (\(B_{3g}\)), and 243 cm\(^{-1}\) (\(B_{2g}\)). Corresponding infrared active bands are detected at 573, 543, 573, 423, 375, 290, 205, 165, 146, and 134 cm\(^{-1}\). Raman bands at 949, 966, 989, 1000 and 1104 cm\(^{-1}\) and at 922, 946, 967, 988, 996, and 1007 cm\(^{-1}\) in the infrared spectra are assigned to combination and overtone bands. Raman bands at 1676 (\(A_g\)), 1689 (\(A_g\)), 1730 (\(B_{3g}\)), and 1740 (\(B_{1g}\)) cm\(^{-1}\) are ascribed to combination modes of \(\nu_1 + \nu_4\) with bands at 2052 and 2092 cm\(^{-1}\) assigned to \(2\nu_1\). Corresponding infrared bands are observed at 1729 and 1740 cm\(^{-1}\) (\(\nu_1 + \nu_3\)). Bands at 2359, 2409, 2471, and 2521 cm\(^{-1}\) are ascribed to \(\nu_1 + \nu_3\), with broad bands at 1246 and 1323 cm\(^{-1}\) assigned to \(2\nu_4\) modes.
This journal article is not available online. Please consult the hardcopy thesis available from the QUT library.
Chapter 4 - Single Crystal Raman Study of Erythrite $\text{Co}_3(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$

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Anonymous referee’s comments: “The paper is easy to read, clear, and scientifically convincing. It reports a careful crystallographic and spectroscopic study of single crystals of mineralogical interest, with potential applications in identification of pigments……”

4.1 Statement of contribution

**Wayde N. Martens**: Wrote the manuscript, experimental design, conducted experiments, and data analysis.

**J. Theo Kloprogge**: Major editing, aided data analysis

**Ray L. Frost**: Editing, data analysis

**Llew Rintoul**: Aided experimental design, editing, aided data analysis, aided writing of manuscript.
4.2 Abstract

Single crystal Raman and infrared spectra of natural and synthetic erythrite \( \text{Co}_3(\text{AsO}_4)_2.8\text{H}_2\text{O} \) are reported, and compared to the spectra polycrystalline, synthetic annabergite \((\text{Ni}_3(\text{AsO}_4)_2.8\text{H}_2\text{O})\) and hörnesite \((\text{Mg}_3(\text{AsO}_4)_2.8\text{H}_2\text{O})\). Factor group analysis and single crystal considerations have been used to interpret the experimental data. The Raman spectra of erythrite reveal \(\nu_1\) arsenate stretching vibration at 850 cm\(^{-1}\) \((A_g)\) with the corresponding infrared band at 821 cm\(^{-1}\) \((B_u)\). The \(\nu_3\) antisymmetric vibration is split into three components, observed at 796 \((A_g)\), 788 \((A_g)\) and 803 \((B_g)\) cm\(^{-1}\). The \(\nu_2\) symmetric bending modes are observed at 375 \((A_g)\) and 385 \((B_g)\) cm\(^{-1}\). The \(\gamma_4\) bending modes are predicted to split into three bands which are observed at 441 \((A_g)\), 446 \((B_g)\) and 457 \((A_g)\) cm\(^{-1}\). Lattice vibrations are found at 112 \((A_g)\), 124 \((B_g)\), 145\((A_g)\), 157 \((B_g)\), 165 \((A_g)\), 179 \((A_g)\), 189 \((A_g)\), 191\((B_g)\), 201 \((B_g)\), 210 \((A_g)\), 227 \((A_g)\), 250 \((A_g)\), 264\((A_g)\), 264 \((A_g)\), 280 \((B_g)\), 302 \((B_g)\), 321 \((B_g)\), and 338 \((A_g)\) cm\(^{-1}\). Hydroxyl stretching modes are observed at 3050, 3218, 3333, 3449 and 3479 cm\(^{-1}\), in the infrared spectrum. Raman active hydroxyl bands are detected at 3009 \((B_g)\), 3052 \((A_g)\), 3190 \((B_g)\) 3203 \((B_g)\), 3281 \((A_g)\) and 3310 \((B_g)\), 3436 \((B_g)\) and 3443 \((A_g)\) cm\(^{-1}\). Infrared hydroxyl bands at 3050, and 3218 cm\(^{-1}\) are from water type II, short hydrogen bonding distances, and the bands at 3449 and 3479 cm\(^{-1}\) are due to water I, long hydrogen bonding distances. Water bending modes are detected in the infrared spectrum at 1571, 1621, 1641, and 1682 cm\(^{-1}\), but due to the inherent weak Raman scattering cross section of water these could not be detected in the Raman spectra.
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Chapter 5 – Synthetic deuterated erythrite – a vibrational spectroscopic study

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5.1 Statement of contribution

Ray L. Frost: Wrote the manuscript, data analysis.

Wayde N. Martens: Aided in writing manuscript, experimental design, conducted experiments, Editing, data analysis

J. Theo Kloprogge: Editing, aided data analysis
5.2 Abstract

A comparison of deuterated and non-deuterated erythrite has been made using a combination of infrared and Raman spectroscopy. Infrared shows bands at 3442, 3358, 3194 and 3039 cm\(^{-1}\). The band at 3442 cm\(^{-1}\) is attributed to weakly hydrogen bonded water and the band at 3039 cm\(^{-1}\) to strongly hydrogen bonded water.

Deuteration results in the observation of OD bands at 2563, 2407 and 2279 cm\(^{-1}\). The ratio of these bands changes with deuteration. Deuteration shows that the strongly hydrogen bonded water is replaced in preference to the weakly hydrogen bonded water. Three HOH bending modes are observed at 1686, 1633, 1572 and DOD bending modes at 1236, 1203 and 1176 cm\(^{-1}\). Deuteration causes the loss of intensity of the bands at 841, 710 and 561 cm\(^{-1}\) and new bands are observed at 692, 648 and 617 cm\(^{-1}\). These three bands are attributed to the water librational modes. Deuteration results in additional Raman band at 809 cm\(^{-1}\) with increasing intensity with extent of deuteration. Deuteration results in the shift of Raman bands to lower wavenumbers.
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Chapter 6 – Site occupancy of Co and Ni in erythrite - annabergite solid solutions by vibrational spectroscopy

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Ray L. Frost: Editing, data analysis

Llew Rintoul: Aided experimental design, editing, aided data analysis, aided writing of manuscript.
6.2 Abstract

The solid solutions series between erythrite (Co$_3$(AsO$_4$)$_2$.8H$_2$O) and annabergite (Ni$_3$(AsO$_4$)$_2$.8H$_2$O) has been synthesised and studied by a combination of X-ray diffraction, scanning electron microscopy, Raman and infrared spectroscopy. The solid solution between erythrite and annabergite has been found to be complete, with the monoclinic C2/m space group being retained throughout the solid solution series. The unit cell parameters decrease in size along all crystallographic directions as nickel is introduced into the unit cell. The β angle in the unit cell also decreases from 105.052° (Co$_3$(AsO$_4$)$_2$.8H$_2$O) to 104.886° (Ni$_3$(AsO$_4$)$_2$.8H$_2$O), as the unit cell volume decreases. Crystals of annabergite and samples with high Ni content are elongated along the a crystallographic direction, contrasting with crystals of erythrite and high Co containing samples, which are elongated along the c crystallographic direction. In the Raman and infrared spectra of the synthetic minerals, the band positions were found to shift in accordance with the increase in bonding strength associated with the decrease in the unit cell parameters. It has been shown that trends in Raman band positions of the anti-symmetric arsenate stretching vibration are sensitive to the site occupancy in the crystal structure. Changes in the crystal morphology, unit cell parameters and vibrational spectra have been rationalised in terms of the site occupancy of Co and Ni in the crystal structure. Substitution of nickel has been shown to be directed to metal site 1 whereas cobalt is directed to metal site 2.
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7. GENERAL DISCUSSION

This thesis has increased the scientific knowledge of the crystallographic and spectroscopic properties of the aragonite group and the vivianite group minerals. In particular fundamental knowledge of the spectroscopy of the end members, erythrite and annabergite, and their solid solutions has been obtained. A new method of studying the site occupancy of ions in solid solutions has been developed which utilises vibrational spectroscopy. A detailed knowledge and understanding of factor group analysis applied to the study of minerals has been achieved. This has been applied to a significant number of minerals as shown by the number of refereed articles published by the author, and cited in the beginning of the thesis.

The inspection of the Raman spectra of aragonites reveals the presence of isotopic bands. The assignment of the satellite band to $^{18}\text{O}-^{12}\text{C}$ allows the use of this band to quantify the oxygen isotopic ratio. This can have important implications for various areas in geology. Oxygen isotope fractionation between carbonates and (sea)water for example is well known to depend on temperature. In principle this allows one for example to determine the paleotemperatures of ancient oceans with a resolution better than 0.5 °C based on fractionation between calcite and seawater. A similar technique also exists for cerussite, and a variety of other minerals. The normal analysis method for stable isotopes involves very careful preparation of your samples under clean room conditions followed by measurement with ICP-MS (Inductively Coupled Plasma-Mass Spectrometry). It may be suggested that, when properly standardised, Raman spectroscopy can be a rapid and much cheaper alternative to get an idea of the isotope fractionation in carbonates.
Consideration of the water stretching and bending vibrations and the factor group splitting of the arsenate stretching vibrations has allowed the determination of the site occupancy of metal cations in the structure of the minerals. This finding has profound implications for the field of mineral science, particularly where there is an inability to collect high quality X-ray diffraction data (i.e. synchrotron) for Rietveld analysis. Rietveld analysis also requires high operator skills, and is difficult for even the skilled users. The technique used in this thesis does require basic knowledge of the crystal unit cell, which is only available from crystallographic data obtained by XRD. The infrared and Raman based technique may aid in the structural determination of many other minerals and solid solutions. Questions still remain however about the wider validity of the technique to other mineral solid solution series. Future work needs to be directed to other solid solution series with known site occupancy preferences to fully confirm the technique. The investigation of the erythrite - annabergite solid solution series continues. Rietveld analysis of high quality X-ray diffraction data is expected to be available in due course. Potentially the type of techniques developed in this thesis may be applied to quite a few solid solution series. Of most interest are solid solution series which have temperature dependencies such as Fe in sphalerite (ZnS), ilmenite, garnets pyroxenes and plagioclase minerals. Such solid solutions are well known geothermometers and as mineral solid solutions directly effect infrared and Raman spectroscopic data such vibrational techniques may yield a new field in geothermometers. This would be of particular use where the mineral samples may not be able to be subjected to chemical analysis such as SEM microprobe analysis.
Much work has been done on the analysis of mineral vibrational spectra, but prediction of mineral spectra, or the prediction of mineral crystal structures from spectra is still not routinely possible. Quantum mechanical computer models are able to predict mineral spectra from crystal structures, but these are cumbersome, usually requiring many days of supercomputer time. This study and others have shown that the vibrational spectroscopy of minerals are fundamentally controlled by unit cell chemistry, symmetry and bonding distances. Much more work is required on the vibrational spectroscopy of minerals, to allow Monte Carlo type calculations of the mineral crystal structures. Statistical techniques such as chemometrics, principal component analysis (PCA) and SIMCA may also be useful for discrimination of mineral crystal structures. Few such studies have been conducted on minerals, with most concerned with quantification of mineral mixtures. PCA and SIMCA techniques applied to infrared and Raman spectra, may be able to discriminate between different crystal structures as similar factor group splitting patterns occur for groups of minerals as seen in this study.

Even though this study has been able to achieve the objectives proposed, it has raised more questions than answers. More work is still required in the field of mineral spectroscopy as the spectra of most minerals, especially Raman spectra, are still yet to be reported. Mineral spectral databases are still in the early stages of development, as such, even simple tasks such as mineral identification are at this stage not possible. Fundamental work on the spectroscopy of minerals such as the work contained with in this thesis needs to be conducted to understand mineral spectra and their assignment to enable databases such as those already existing for X-ray diffraction (powder diffraction file, PDF) to be developed.
8. Appendix

The following papers are supporting studies which were conducted in parallel with this thesis.


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