Raman spectroscopy of synthetic erythrite, partially dehydrated erythrite and hydrothermally synthesized dehydrated erythrite

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Abstract

The Raman spectra of the mono, di and octa (commonly known as the mineral erythrite) hydrates of cobalt(II) arsenate synthesised using hydrothermal techniques have been obtained. The hydrates can be distinguished by their water hydroxyl stretching bands. Splitting of the AsO stretching vibrations is observed in the 77 K spectrum. The band at 852 cm^{-1} is assigned to the ν_1 symmetric stretching vibration and the band at 790 cm^{-1} to the ν_3 antisymmetric stretching vibration. The low wavenumber region was used to identify bands attributable to the ν_4 and ν_2 modes.

Keywords: erythrite, annabergite, cobalt arsenate, dehydration, Raman spectroscopy

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INTRODUCTION

The minerals of the vivianite group are of the general formula $A_3^{2+}(XO_4)_2.8H_2O$ where A^{2+} may be Co, Fe, Mg, Ni, Zn and X is As or P. Isomorphous substitution in this group occurs readily and combinations of the cations may be observed. The vivianite minerals are all monoclinic and space group P2/*m*. The minerals may be divided into two groups according to the oxyanion being either arsenate or phosphate. Among the arsenates in this group is erythrite ($Co_3(AsO_4)_2.8H_2O$). These minerals can readily dehydrate. This dehydration takes place in several steps and in the case of erythrite loses 6 moles of water at around 105 °C to form the partially dehydrated erythrite ($Co_3(AsO_4)_2.2H_2O$) and 2 moles of water at around 225 °C to form the dehydrated mineral ($Co_3(AsO_4)_2$). Dehydration may also be undertaken by attempting to synthesise the erythrite mineral hydrothermally. If the temperature in the hydrothermal unit is above 100 °C, then a monohydrate is formed of formula ($Co_3(AsO_4)_2.1H_2O$). .

The Raman spectra of the tetrahedral anions in aqueous systems are well known. The symmetric stretching vibration of the arsenate anion (ν_1) is observed at 810 cm^{-1} coincident with the position of the asymmetric stretching mode (ν_3). The symmetric bending mode (ν_2) is observed at 342 cm^{-1} and the out-of-plane bending modes (ν_4) is observed at 398 cm^{-1}. Of all the tetrahedral oxyanions spectra, the

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wavenumbers of the arsenate vibrations are lower than those of any of the other naturally occurring mineral oxyanions. Farmer lists a number of infrared spectra of arsenates including annabergite, erythrite, symplesite and kottingite. [1] The effect on the arsenate ion in a crystal will be to remove the degeneracies and allow splitting of the bands according to factor group analysis. The ν_1 and ν_3 bands of annabergite were observed at 832 and 795 cm^{-1}. The bending modes were found at 510, 460 and 427 cm^{-1} for annabergite. No ν_2 bands were shown. This is no doubt related to the fact the bands are found below 400 cm^{-1}, which makes the measurement by infrared spectroscopy difficult. Two OH stretching vibrations were observed at 3430 and 3160 cm^{-1} for annabergite. Several bands were listed but were unassigned.

Whilst the infrared spectra of some minerals have been forthcoming, few comprehensive studies of the vivianite related minerals such as divalent cationic arsenates have been undertaken. [1] Most of the infrared data predates the advent of Fourier transform infrared spectroscopy. [2-7] Although some Raman studies of the vivianite phosphate minerals have been undertaken, few Raman spectroscopic investigations of these arsenate phase related minerals have been forthcoming. [8,9] Griffith did report the results of the Raman spectrum of a synthetic annabergite. [10] The symmetric stretching mode of the AsO_4 unit was observed at 859 cm^{-1}; the antisymmetric stretching mode at 880 cm^{-1}, the bending mode at 438 cm^{-1} and the out of plane bending mode at 452 cm^{-1}. Other bands were located at 797 and 820 cm^{-1}. [10] The structural investigation of some arsenates and the nature of the hydrogen bond in these structures have been undertaken. It was found that the water unit was coordinated directly to the metal ion and formed hydrogen bonds to the arsenate anion. [11-13] The minerals selected in these studies were fundamentally unrelated. Indeed few comprehensive Raman studies have been undertaken of the vivianite arsenates. As part of a comprehensive study of the molecular structure of minerals containing oxyanions using of the IR and Raman spectroscopy, we report the Raman spectra of erythrite, partially dehydrated erythrite and hydrothermally synthesised partially dehydrated erythrite.

EXPERIMENTAL

Minerals:

Synthetic vivianite arsenate of Co was prepared by the slow addition of the $3.5x10^{-3}$ M cobalt sulphate solution to a very dilute $5.0x10^{-3}$ M sodium arsenate solution using a peristaltic pump at 70 °C. The hydrated cobalt arsenate precipitated from the solution and were filtered and dried. The mineral synthesised was erythrite. The crystals were hydrothermally treated and were grown by Ostwald ripening at 75 °C for 14 days. Ostwald ripening is a process of crystal growth through the use of elevated pressures and temperatures using a hydrothermal unit. Crystals of up to 2 microns were produced. Hydrothermal treatment at 200 °C produced the monohydrate. In this way hydrothermally treated partially dehydrated erythrite was produced. The arsenate mineral was found to contain one molecule of water of hydration. The dehydrated arsenate containing two water molecules was synthesised in situ in the thermal stage of the Raman spectrometer. Samples were analysed for phase purity by X-ray diffraction and for chemical composition by electron probe analyses.

Raman microprobe spectroscopy

The crystals of the minerals were placed and orientated 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 filter system and a charge-couple device (CCD). Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. Back scattering geometry of 180° was employed. Repeated acquisition using the highest magnification were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Spectra at elevated temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Dry nitrogen was passed continuously over the mineral to prevent water condensation on the thermal unit.

Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enables 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 correlations of r^2 greater than 0.995.

RESULTS AND DISCUSSION

Chemical Reactions

Synthetic erythrite is prepared from the displacement reaction of aqueous sodium arsenate and cobalt nitrate. The reaction is as follows:

$2Na_3(AsO_4) + 3Co(NO_3)_2 + 8H_2O \rightarrow (Co^{2+})_3(AsO_4)_2.8H_2O$ (erythrite) + 6 $NaNO_3$

$(Co^{2+})_3(AsO_4)_2.8H_2O$ (erythrite) $\rightarrow (Co^{2+})_3(AsO_4)_2.2H_2O$ (temp > 125°C) (partially dehydrated erythrite) + $6H_2O$

$(Co^{2+})_3(AsO_4)_2.2H_2O \rightarrow (Co^{2+})_3(AsO_4)_2 + 2H_2O$ (temp > 230°C) (dehydrated erythrite)

If the first reaction is undertaken in a hydrothermal unit at elevated temperatures (temp ~200 °C) then the monohydrate is formed.

$2Na_3(AsO_4) + 3Co(NO_3)_2 + H_2O \rightarrow (Co^{2+})_3(AsO_4)_2.1H_2O$ + 6 $NaNO_3$
(hydrothermally produced partially dehydrated erythrite)

The structures were confirmed by X-ray diffraction. Recent studies by the authors have shown using high resolution thermogravimetric analysis coupled with mass spectrometry that the first dehydration step occurs over the 100 to 110 °C

temperature range and that the second weight loss step occurs at around 225 °C. Six moles of water are lost in the first dehydration step and 2 moles in the second. In order to explore the structural changes in the chemistry of erythrite, Raman spectroscopic studies have been undertaken.

Raman spectroscopy

The Raman of the hydroxyl stretching vibrations of water in the erythrite at 77 and 298 K, partially-dehydrated erythrite at 448 K and hydrothermally synthesised partially dehydrated erythrite at 298 K are shown in Figure 1. The results of the Raman are reported in Table 1. Factor group analyses predict that there should be 12 active internal modes for water in erythrite. Four Raman bands are observed in the hydroxyl-stretching region of erythrite in the 298 K spectrum, as expected. There are two types of water molecule in the unit cell and consequently there are four OH units, which can vibrate both in-phase and out-of-phase, giving four bands (there are eight molecules in total in the unit cell). In the 77 K spectrum bands are observed at 3421, 3275, 3204, 3095 and 3019 cm^{-1}. In the 298 K spectrum the two most intense bands are observed at 3200 and 3052 cm^{-1} with band widths of 146 and 132 cm^{-1}. Upon cooling to liquid nitrogen temperature the two most intense bands are observed at 3204 and 3019 cm^{-1} with band widths of 73 and 84 cm^{-1}. Upon obtaining the spectra at 77 K, considerable band separation has occurred and the bandwidth has been reduced by 50%.

An additional band at 3421 cm^{-1} is observed in the 77 K spectrum of erythrite with a band width of 36 cm^{-1}. In the hydroxyl-stretching region in both the infrared and Raman spectrum of annabergite (3419 cm^{-1}), kottigite (3458 cm^{-1}) and hornesite (3478 cm^{-1}), sharp bands are observed with bandwidth significantly less than the other bands. The intensity of the band is higher in the infrared spectrum than in the Raman spectrum. One possible explanation of this band is that it is due to hydroxyl units on the cation. If some oxidation of the cobalt(II) ion to cobalt(III) occurs then this charge would need to be counterbalanced by the negative of the hydroxyl unit as no other negative charges could originate from the arsenate anion. This then could mean that a free proton is available to form $HAsO_4$ units. Such concepts are real as is evidenced by the formation of new minerals. In vibrational spectroscopy, however Raman spectroscopy records measurements on a much faster time scale. Thus any phenomena such as the migration of a proton to an arsenate anion may be observed by the appearance of a new band. Likewise the bonding of a hydroxyl unit to the metal could be observed. Importantly -AsOH units could be formed and the Raman spectrum might show its presence. Thus the high wavenumber band in the Raman (and infrared spectrum) may be attributed to an AsOH stretching vibration. The Raman spectrum of the partially dehydrated erythrite at 448 K shows a broad band centred at 3229 cm^{-1}. This spectrum is obtained in situ at the elevated temperatures and results from the overlap of the bands observed in the 298 K spectrum. In the spectrum of the hydrothermally dehydrated erythrite, two bands are observed at 3535 and 3474 cm^{-1} and are assigned to the anti-symmetric and symmetric stretching vibrations of the single water molecule in the structure.

The Raman spectrum of the AsO stretching region is shown in Figure 2. The bands as determined by band component analysis are reported in Table 1. In each of the spectra two intense bands are observed. For erythrite at 298 K the bands are

observed at 852 and 792 cm^{-1}. The width of these two bands is 16.6 and 21.0 cm^{-1}. Additional low intensity bands are observed at 902, 727 and 652 cm^{-1}. These latter bands are considerably broader than the bands observed at 852 and 792 cm^{-1}. Griffith reported Raman bands for a synthetic annabergite at 880, 859, 820 and 797 cm^{-1}. [10] The low intensity band observed around 902 cm^{-1} was assigned to the E_{1g} mode by Griffith. In the Raman spectrum of the synthetic erythrite at 77 K, the intense AsO stretching bands appear to be split. The 852 cm^{-1} band in the 298 K spectrum appears as two overlapping bands at 859 and 852 cm^{-1} in the 77 K spectrum. The 792 cm^{-1} band in the 298 K spectrum is split into two bands at 797 and 785 cm^{-1}. The band widths of the 852, 797 and 785 cm^{-1} are 10.3, 11.3 and 15.5 cm^{-1}. The higher wavenumber band at around 852 cm^{-1} is assigned to the symmetric stretching mode and the lower band(s) at around 792 cm^{-1} to the antisymmetric stretching mode.

In the Raman spectrum of the partially dehydrated erythrite at 448 K, two broad overlapping bands are observed at 899 and 731 cm^{-1}. The spectrum of the partially dehydrated erythrite at 150 °C is difficult to obtain as the mineral phase has become very disordered during thermal treatment. Such disordering apparently affects the Raman scattering. The Raman spectrum of the hydrothermally treated partially dehydrated erythrite shows a complex set of overlapping bands. The most intense band is observed at 549 cm^{-1}. Other bands are observed at 910, 872, 808, 763, 726 and 706 cm^{-1}, probably AsO vibrations.

The Raman spectra of the low wavenumber region for the erythrite at 77 and 298 K, the partially dehydrated erythrite and the hydrothermally treated partially dehydrated erythrite are shown in Figure 3. An interesting comparison can be made between the four spectra in this figure. The spectrum at 77 K shows good separation of the bands and the overlap of the bands is observed in the 298 K spectrum. This overlap is further noticed in Figure 3d and is such that in figure 4e almost no spectral features can be observed. The spectrum of the low wavenumber region of erythrite and the dehydrated erythrites 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}. It is proposed that these three regions define the (a) ν_4 modes (b) ν_2 modes and (c) AsO bending and lattice modes. The most intense bands for erythrite in the 77 K spectrum are observed at 460 and 440 cm^{-1}. These bands are intense in the 298 K spectrum occurring at 457 and 439 cm^{-1}. The bands overlap and this overlap is reflected in the dehydrated erythrite spectrum with broad band observed at around 450 cm^{-1}. For the hydrothermally synthesised monohydrate of cobalt(II) arsenate the two most intense bands are observed at 507 and 481 cm^{-1}. These bands are assigned to the out-of-plane bending modes (ν_4). Farmer reported the infrared spectra of annabergite and erythrite, bands occurring at 510, 460 and 427 cm^{-1} for annabergite and at 490, 452 and 428 cm^{-1} for erythrite. [1] The last two bands for these two minerals are in excellent agreement with the Raman bands reported in this work. Griffith reported the ν_4 modes for a synthetic annabergite in the Raman spectra at 452 and 438 cm^{-1}. [10]

The shift in the bands is attributed to the difference in structure between the erythrite and the monohydrate. A band is observed at 378 cm^{-1} in the 298 K spectrum, which is also observed in the spectrum of the partially dehydrated erythrite at 150 °C. This band appears sharp in the 25 °C spectrum of the hydrothermally treated partially dehydrated erythrite but is of low intensity in the 77 K spectrum of erythrite. This

difference in intensity is attributed to orientation effects. It is difficult to orient the crystal in the thermal stage and consequently the same crystal orientation may not be obtained in the 298 and 77 K spectra. The ν_2 bending vibration should be common to all four spectra and should be intense. Bands at around 378 cm^{-1} are assigned to the OAsO bending modes. In the 77 K spectrum bands are well resolved and bands are observed at 308, 271, 252, 229 and 213 cm^{-1}. These low wavenumber modes are ascribed to lattice vibrations. Band in the 140 to 200 cm^{-1} region overlap. The intensity of the bands observed at 308, 271, 252, 229 and 213 cm^{-1} in the 77 K spectrum is reflected in the 298 K spectrum. The overlap of bands in the very low wavenumber region of the two partially dehydrated cobalt arsenates is such that no definitive peak positions can be established.

CONCLUSIONS:

The octahydrate of cobalt(II) arsenate $(Co^{2+})_3(AsO_4)_2.8H_2O$ known in mineralogy as erythrite has been hydrothermally synthesised at 75 °C. The dihydrate $(Co^{2+})_3(AsO_4)_2.2H_2O$ was synthesised by dehydration using a thermal stage. The monohydrate of cobalt(II) arsenate $(Co^{2+})_3(AsO_4)_2.H_2O$ was synthesised by hydrothermally reaction of sodium arsenate and cobalt nitrate at 200 °C. The structures were confirmed by X-ray diffraction.

Raman spectroscopy was used to determine the structure of these synthesised cobalt(II) arsenates. All of these arsenates contain different amounts of water in the structure and characteristic Raman spectra of the OH stretching region are readily obtained. Often spectra of the OH stretching region of hydrated minerals are neglected and the spectrum in this region can be used to distinguish between the different hydrates. Raman spectra of the AsO stretching region show similarity between the octahydrate and dihydrate cobalt(II) arsenates, but differ from that of the monohydrate. The ν_1 and ν_3 stretching bands are split in the 77 K spectrum. The higher wavenumber band at around 852 cm^{-1} is assigned to the ν_1 symmetric stretching vibration and the band(s) at around 790 cm^{-1} to the ν_3 antisymmetric stretching vibration. The low wavenumber region was used to identify bands attributable to the ν_4 and ν_2 modes.

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Table 1. Raman spectroscopic data (wavenumber/cm^{-1}) of the hydrothermally synthesized erythrite, partially dehydrated erythrite and hydrothermally synthesized partially dehydrated erythrite

Erythrite Synthesized hydrothermally at 75°C		**Dehydrated erythrite**	**Hydrothermally synthesized at 473 K dehydrated erythrite**	
298 K	**77K**	**448 K**	**298 K**	**Suggested assignment**
3337 3200 3052	3421 3275 3204 3095 3019	 3229	3535 3474	Water hydroxyl stretching
 902 852 792 727 652	919 859 852 797 786 716 660	 899 731	910 872 849 808 763 726 706	AsO stretching
467 457 439 391 378 301	460 440 392 378 343 308	 450 390	507 481 463 407 357 303	Out of plane bends
263 249 234 223 209	271 252 229 213	226 180	240 214 180	In-plane bends
188 162 147 126	188 177 161 147 141 127			Lattice vibrations

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Table 1. Raman spectroscopic data of the hydrothermally synthesized erythrite, partially dehydrated erythrite and hydrothermally synthesized partially dehydrated erythrite

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Figure 1 Raman spectra of the OH stretching region of erythrite at (a) 77 K (b) 298 K (c) partially dehydrated erythrite 423 K and (d) hydrothermally synthesised partially dehydrated erythrite at 298 K.

Figure 2 Raman spectra of the AsO stretching region of erythrite at (a) 77 K (b) 298 K (c) partially dehydrated erythrite 423 K and (d) hydrothermally synthesised partially dehydrated erythrite at 298 K.

Figure 3 Raman spectra of the low wavenumber region of erythrite at (a) 77 K (b) 298 K (c) partially dehydrated erythrite 423 K and (d) hydrothermally synthesised partially dehydrated erythrite at 298 K.

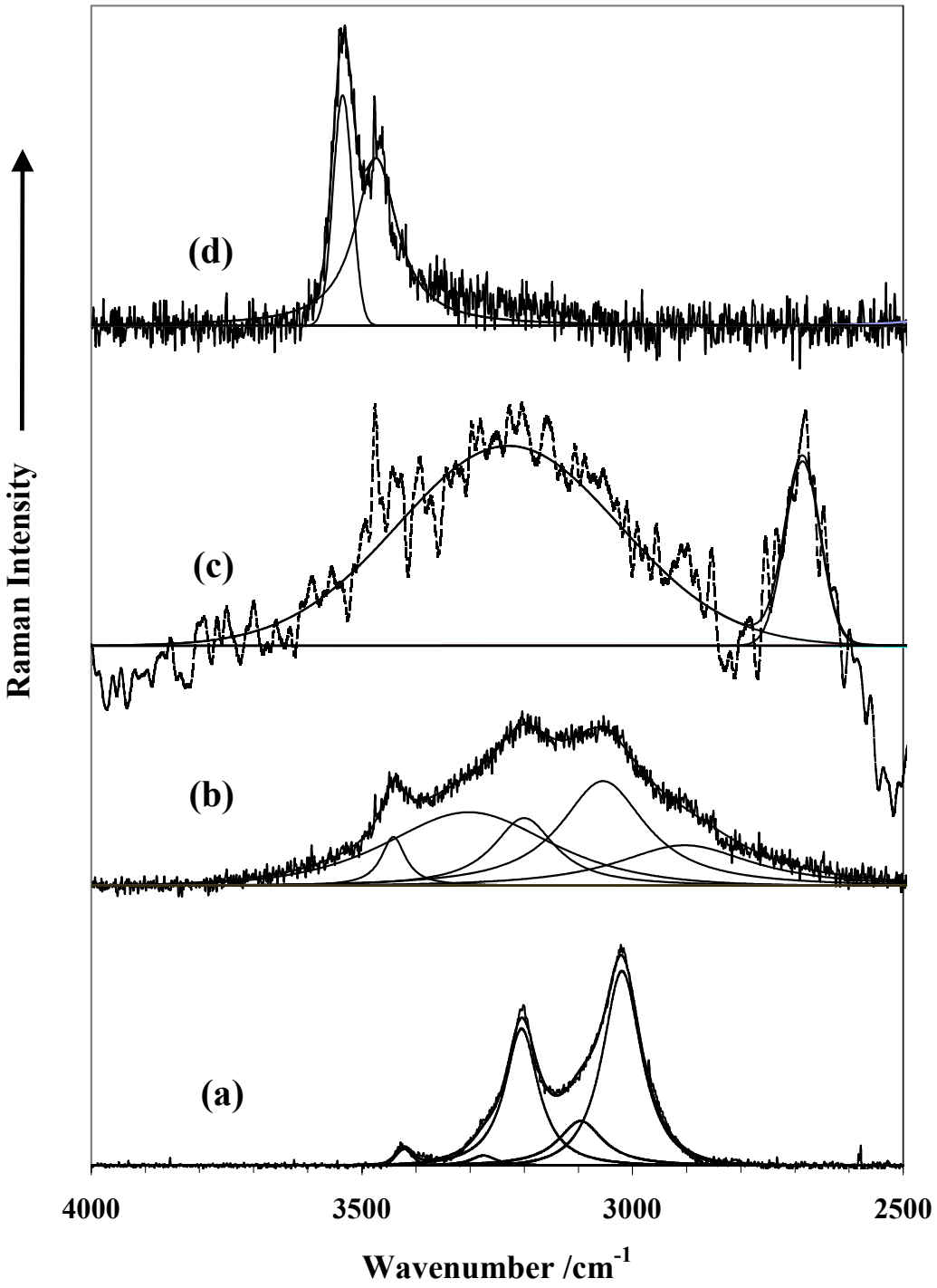

Figure 1

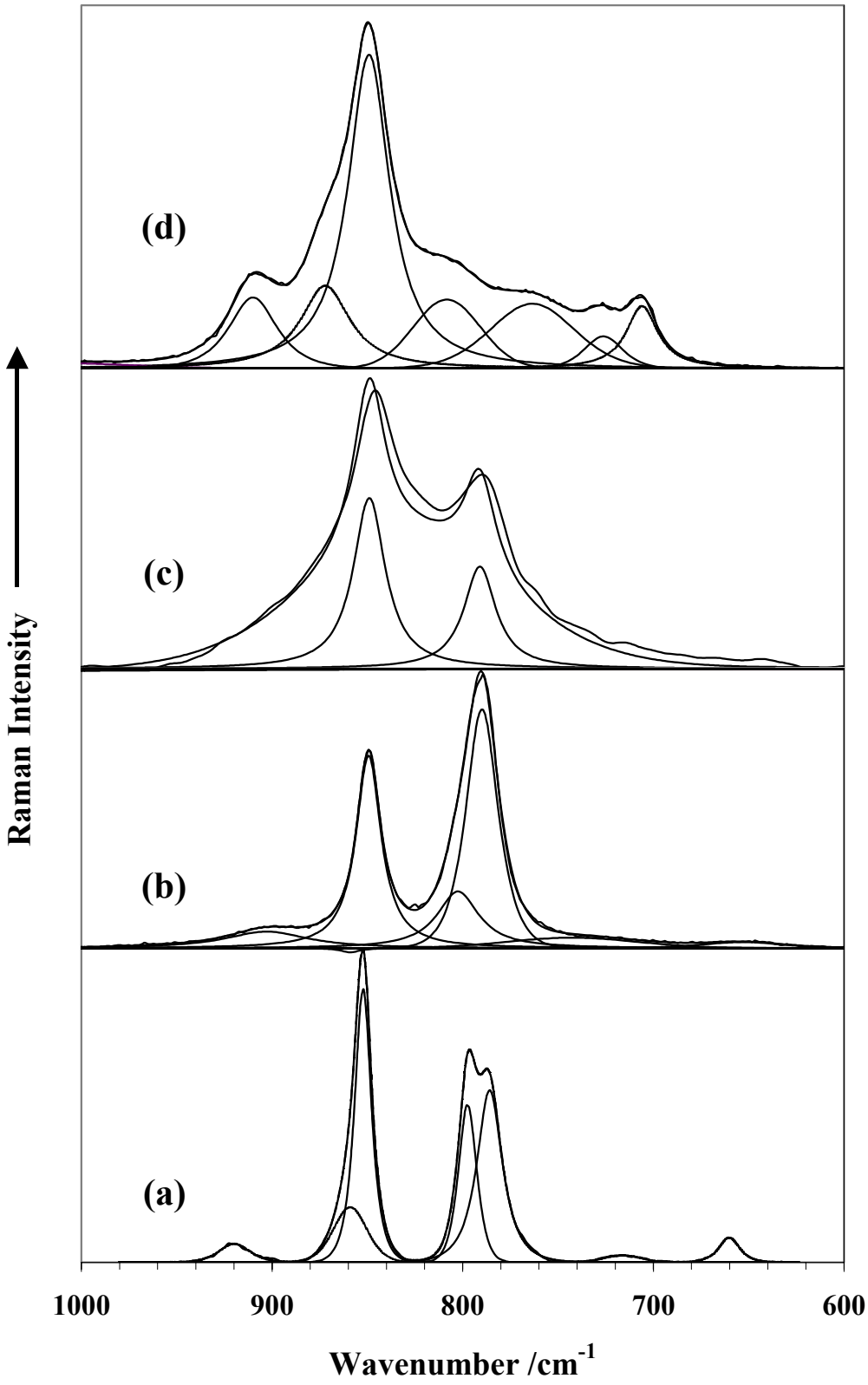

Figure 2

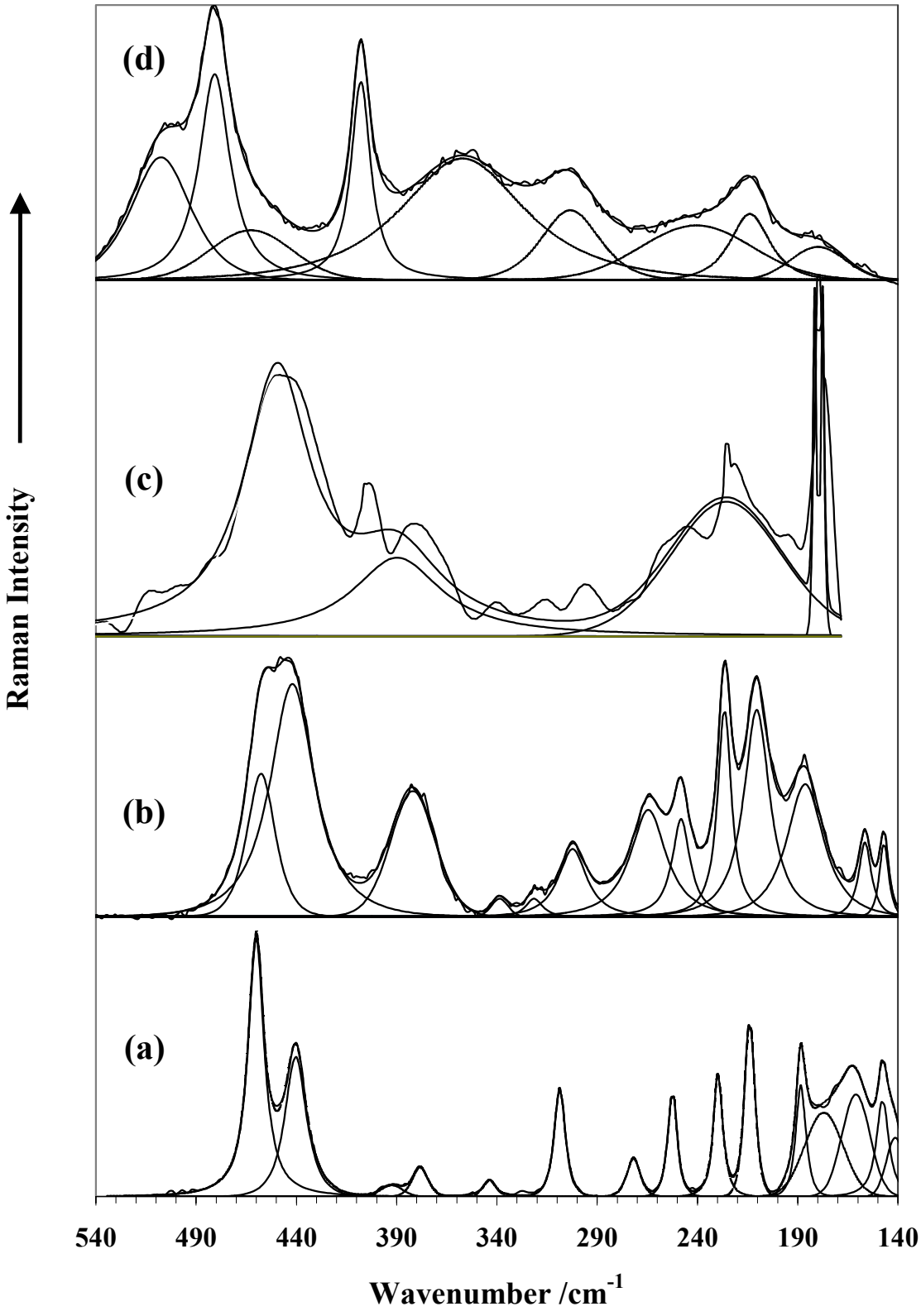
(d)
(c)
(b)
(a)
Raman Intensity
540
490
440
390
340
290
240
190
140
Wavenumber /cm-1

Figure 3