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The molecular structure of the adelite group of minerals – a Raman spectroscopic study

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Abstract:

The application of Raman microscopy to the study of closely related mineral phases of the adelite group has enabled their molecular characterisation. The adelite group of minerals are orthorhombic arsenates and vanadates of general formula $AB^{2+}(XO_4)(OH)$ where X may be As^{5+} or V^{5+} and cation A may be Ca or Pb; cation B may be Co or Cu and others. Raman spectroscopy has proven most powerful for the identification of these minerals. In particular the position of the hydroxyl stretching vibrations and most of the arsenate bands have been identified. The two minerals tangeite and calciovolborthite have previously been identified as the same mineral. Raman spectroscopy has proven that the minerals are not identical and have different structures. The application of Raman spectroscopy to the study of these minerals shows that increased distortion of the arsenate anion occur as the cationic substitution from conichalcite to austinite to duftite occurs.

Key Words- arsenate, adelite, austinite, duftite, Raman spectroscopy

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INTRODUCTION

The adelite group of minerals are orthorhombic arsenates and vanadates of general formula $AB^{2+}(XO_4)(OH)$. Cation A may be Ca, Pb; cation B may be Co, Cu, Fe, Mg, Ni, Zn or selected combinations of these atoms; X may be As^{5+} or V^{5+}. Typical mineral examples are adelite $CaMg(AsO_4)(OH)$, austinite $CaZn(AsO_4)(OH)$, cobaltaustinite $Ca(Co,Cu)(AsO_4)(OH)$, conichalcite $CaCu(AsO_4)(OH)$, duftite $PbCu(AsO_4)(OH)$, gabrielsonite $PbFe(AsO_4)(OH)$, nickelaustinite $Ca(Ni,Zn)(AsO_4)(OH)$. In the adelite structure, the OH forms asymmetric bridges between two Mg or two transition metal ions (Fe, Co, Ni, Cu, Zn) but also coordinates

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to the non-transition metals Ca of Pb. These formulae illustrate that substitution of cations and anions is extensive in the adelite group of minerals. The minerals are isostructural and crystallise in space group $P2_12_12_1$. [1,2] A single crystal X-ray study of conichalcite has been undertaken. [2] In the lattice the copper ion is in a distorted octahedral position with the Ca ion lying at the centre of a distorted square antiprism of oxygen atoms. The mineral structure is based upon chains of $[Cu(OH)_{2/2}]$ units cross-linked with the arsenate anion to form a chain-like structure. Careful analytical studies of the arsenate containing species show that the formation of solid solutions between for example austinite and conichalcite is complete. [3-6]. A complete solid solution between conichalcite and duftite has also been found. [6]

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} and coincides with the asymmetric stretching mode (ν_3). The bending modes (ν_2) and (ν_4) are observed at 342 cm^{-1} and at 398 cm^{-1} respectively. Of all the tetrahedral oxyanions spectra, the positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanions spectra. Farmer lists a number of spectra of arsenates including the basic copper arsenates olivenite and euchroite. [7] No examples of the adelite group of minerals were shown. Sumin de Portilla reported the infrared spectra of the minerals conichalcite, austinite, olivenite and adamite. [8] It is expected that the Raman spectra of the adelite group of minerals should show some similarity to the published infrared spectra of the above-mentioned phases. Site symmetry of the arsenate lower than T_d will cause the lifting of the degeneracies and splitting of the bands will be forthcoming according to factor group analysis. The ν_1 and ν_3 bands of olivenite and euchroite were observed at 860, 828, 790 cm^{-1} and 830 and 770 cm^{-1} respectively. The bending modes were found at 493 and 452 cm^{-1} for olivenite and at 475 and 410 cm^{-1} for euchroite. No ν_2 bands were shown. It is probable that these bands occur below 400 cm^{-1}. This is no doubt related to the fact the bands are found below 400 cm^{-1}, making the measurement by mid-infrared spectroscopy difficult. It is apparent from the literature that no Raman studies of the adelite group of minerals have been forthcoming.

As part of a comprehensive study of the molecular structure of minerals containing oxyanions using IR and Raman spectroscopy, we report the Raman spectra of the above-named phases of the adelite group.

EXPERIMENTAL

Minerals:

Tangeite (registered mineral specimen 46451) was obtained from the Mineral collection of the Museum of Victoria, Australia. The tangeite originated in the Tange Gorge, Tyuya-Mayun, Kyrgyzstan. The conichalcite originated from The Lorena mine, Cloncurry, Queensland Australia. The cobaltaustinite (1), cobaltaustinite (2), nickelaustinite, duftite (1), duftite (2), calciovolborthite are registered mineral samples M43250, M38240, M40813, M37995, M30693, M44153, of the Victorian Museum. The samples were phase analyzed using X-ray diffraction and the compositions checked using EDX measurements.

Raman microprobe spectroscopy

The crystals of the copper arsenate minerals were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled 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}. Repeated acquisition using the highest magnification were accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).

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 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 correlations of r^2 greater than 0.995.

RESULTS AND DISCUSSION

Factor Group Analysis

Table 1 Vibrational analysis of the internal modes of the anions in the unit cell in austinite

Free ion	Site	Crystal
T_d	C_1	D_2
A_1		9A
E	9A	$9B_1$
$2T_2$		$9B_2$
		$9B_3$

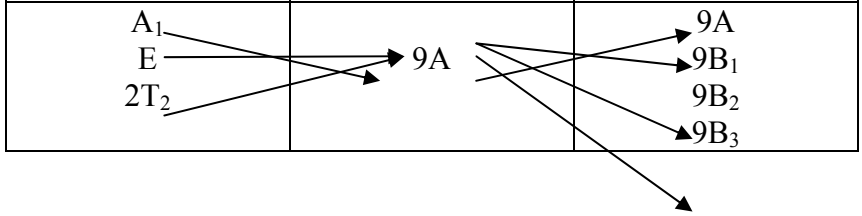

Table 2 Vibrational analysis of the lattice modes in austinite

Site	Crystal
C_1	D_2
17A	17A $17B_1$ $17B_2$ $17B_3$

The unit cell contains 36 atoms; thus it has a total of 105 vibrational degrees of freedom (3 acoustic modes subtracted); if the 20 degrees of rotation (12 + 8) are subtracted, 85 internal and translational modes are obtained. The classification for austinite is $\Gamma = 17A_1 + 15B_1 + 15B_2 + 15B_3$ neglecting the translational modes. No single crystal study of adelite (as a pure mineral with no isomorphic substitution) has been undertaken. All the minerals are isomorphous in the orthorhombic space group $P2_12_12_1$ and hence the unit cell group analysis (factor group analysis) is valid for all members of this mineral family. The factor group analysis of the austinites predicts 36 internal modes for the arsenate ion and 62 lattice vibrations. The A_1 symmetry of the free ion provides four bands for the arsenate ion in the austinite crystal with A, B_1, B_2, B_3 symmetry. This means there are four vibrations, which are Raman active. The A modes are Raman active and the B modes are both Raman and infrared active. The T_2 symmetry of the free ion provides four bands for the arsenate ion in the austinite crystal with A, B_1, B_2, B_3 symmetry. The ν_3 (T_2) mode splits into 3 components under site symmetry C_1; thus 4 anions in the unit cell give 4x3 ν_3 vibrations distributed into the 4 symmetry species of 222-D_2`. This means there are four antisymmetric vibrations, which should be Raman active. The free arsenate ion has tetrahedral symmetry and thus should have four bands of which two are infrared active with values of ν_3 (T_2) 887 cm^{-1} and ν_4 (T_2) 463 cm^{-1}. The Raman active modes are observed at 837 (A_1) and 349 (E) cm^{-1}. Upon coordination of the arsenate ion to the copper atom, the symmetry of the arsenate ion is reduced. In the adelite structure all atoms and groups of atoms are in general positions with symmetry C_1. The implication is that all bands except for the A species will be both infrared and Raman active.

The question arises as to whether site symmetry analysis or factor group analysis is appropriate for the study of mixed crystals or even single crystals of indeterminable orientation. While for single crystals a full factor group analysis is obviously necessary, the application to the study of the infrared spectroscopy of powdered samples is questionable. It is probable that the application of site symmetry analysis is worthwhile for the prediction of the internal modes of the (AsO_4) groups in both the Raman and the infrared spectra.

Hydroxyl stretching of the adelite group of minerals and related minerals

The mineral adelite $CaMg(AsO_4)(OH)$ is a very rare mineral in the absolute pure state and consequently no natural sample was obtained. For the austinite minerals ($CaM(AsO_4)(OH)$) where M is Zn or (Co,Cu) or (Ni, Zn), factor group analysis predicts four bands for the hydroxyl stretching region of the these basic arsenates. In the adelite structure ($P2_12_12_1$) there are four equivalent OH groups in the unit cell and therefore four ν(OH) vibrations in A, B_1, B_2 and B_3 depending on the phases of these modes.

Figure 1 shows the Raman spectra of the hydroxyl-stretching region of the three austinites at 298 and 77K. The results of the analysis of the spectra are reported in Table 1. The major band for austinite is observed at 3265 cm^{-1} with a very low intensity band at 3350 cm^{-1}. A small shift to higher wavenumbers is observed upon cooling to 77 K. The bands for cobaltaustinite are observed at 3284 cm^{-1} with a second band at 3289 cm^{-1}. For the second cobaltaustinite sample, the bands were observed at 3288 and 3310 cm^{-1}. The difference in the band positions for this mineral may be attributed to the changes in composition depending on the amount of Co and Cu in the mineral. For nickelaustinite bands are observed at 3320 and 3344 cm^{-1}. It may be concluded that the effect of replacement of Cu in austinite by Co or Ni is to shift the hydroxyl stretching bands to higher wavenumbers.

If the AsO_4 unit is replaced by the VO_4 anion, then the minerals calciovolborthite and tangeite are obtained. The spectra of these minerals are shown in Figure 2. In comparison with the positions of the hydroxyl stretching bands of austinite, the bands of conichalcite are more complex with bands observed at 3233, 3158 and 3086 cm^{-1}. Similarly for duftite three bands are observed at 3280, 3241 and 3192 cm^{-1}. Collection of spectral data at 77 K results in no additional bands. No difference in the spectra of the two duftite samples was observed for the hydroxyl stretching region. The effect of isomorphic substitution of the Ca by Pb results in the bands occurring at higher wavenumbers. Replacement of the arsenate anion by vanadate ion as for tangeite shows little effect upon the hydroxyl stretching bands. For tangeite two bands are observed at 3242 and 3118 cm^{-1}. The Raman band for calciovolborthite was obtained at 3410 cm^{-1} at 298 K and at 3411 at 77 K. The Raman spectra of two samples of calciovolborthite were obtained and were found to be very similar. The spectra in the hydroxyl-stretching region for the calciovolborthite sample are different from that of tangeite.

Arsenate vibrations
Austinites

The Raman spectra of the AsO stretching region of the austinites are shown in Figure 3. Bands are observed for the Raman spectrum of austinite at 911 (vw), 889 (s), 859 (s), 818 (m) and 806 cm^{-1}. The 911 cm^{-1} band is very weak in the Raman spectrum but is quite strong in the infrared spectrum. This band together with bands at 738 and 708 cm^{-1} are assigned to the hydroxyl deformation vibrations. A previous study suggested that bands observed at 980 and 1010 cm^{-1} are attributable to hydroxyl deformation modes. [8] However where hydroxyls are bonded to heavy metal cations as is the case here the hydroxyl deformation modes are more likely to be observed at

wavenumbers below 800 cm^{-1}. For the cobaltaustinite and nickel austinite low intensity bands are observed at around 918 cm^{-1}.

For austinite two intense bands are observed at 889 and 859 cm^{-1}. Both bands are assigned to the symmetric stretching vibrations of the AsO_4 unit. The assignment of these bands is divergent from that of an infrared study previously reported. [8] Another study also showed that the ν_1 (A_1) mode of the free arsenate ion was observed at 837 cm^{-1} in the Raman spectrum and that the ν_3 mode was found at 878 cm^{-1}. [9,10] Some shifts in the position of the bands are observed in the spectra obtained at 77 K (Table 1). Almost no shift is observed in the position of the bands assigned to the AsO_4 stretching vibrations. The pattern of the Raman spectra of the two cobaltaustinites and the two nickel austinites are similar to that of the austinite except that the band at 889 cm^{-1} is not observed. The reason for this is not clearly understood.

The ν_2 (E) and ν_4 (T_2) vibrational modes for the free AsO_4 ion are found at 349 and 463 cm^{-1}. [9,10] The Raman spectra of the low wavenumber region of the austinite minerals are shown in Figure 5. The most intense bands in this spectral region are observed at 308 and 322 cm^{-1}. These two bands are assigned to the ν_2 bending vibration. The fact that two bands are observed is in harmony with the concept of a distorted AsO_4 unit with two different OAsO bending vibrations. Bands are also observed at 538 (w), 494 (s), 478 (w), 457 (w), 420 (s) and 409 (w) cm^{-1}. The splitting of the $\nu_4(T_2)$ mode is linked to the distortion of the arsenate ion and the loss of symmetry. This distortion appears greater for the nickelaustinites. In the infrared spectra of austinite bands were observed at 465, 430 and 410 cm^{-1}. For the cobaltaustinite, bands in the ν_2 region were found at 327 and 339 cm^{-1}. These bands were observed at 330 and 342 cm^{-1} in the 77 K spectra. For the nickelaustinites more complexity is observed in this spectral region with three bands observed at 333, 348 and 369 cm^{-1}. In the mixed austinites $Ca(Co,Cu)(AsO_4)(OH)$ and $Ca(Ni,Zn)(AsO_4)(OH)$ there are different surroundings, dependent on the distribution pattern of the transition metals. For cobaltaustinites, four bands are observed at around 487, 469, 432 and 421 cm^{-1} and for the nickelaustinites four bands are observed at around 595, 475, 430 and 398 cm^{-1}. These bands are attributed to the $\nu_4(T_2)$ mode. Cooling of the nickelaustinites to 77 K results in further splitting of this mode and five bands are observed.

In the Raman spectrum of austinite a band is observed at 538 cm^{-1}. It is likely that this band is the ZnO stretching vibration. [8] It is also possible that the highest wavenumber band for the cobaltaustinite (at 487 cm^{-1}) and for nickelaustinite (at 495 cm^{-1}) is not an $\nu_4(F_2)$ mode but rather the CoO and NiO stretching vibration. In austinite considerable intensity is found in the Raman bands at 275, 252 and 231 cm^{-1}. For cobaltaustinite bands are observed at 226 and 214 cm^{-1}. For nickelaustinite bands are observed at 233 and 218 cm^{-1}. Whilst it is possible to describe these bands simply as lattice modes, a more likely assignment is to OCoO and ONiO bending modes. In the low frequency region all the Raman bands may be described as highly mixed modes involving several internal coordinates.

Conichalcite and duftite

. The Raman spectrum of conichalcite, duftite, calciovolborthite and tangeite are shown in Figure 4. Raman bands of low intensity are observed in the spectra of conichalcite at 962 cm^{-1} and in the tangeites at 887 cm^{-1}. In the adelite structure, the OH forms asymmetric bridges between two Mg or two transition metal ions (Fe, Co, Ni, Cu, Zn) but also coordinates to the non-transition metals Ca or Pb. This band is attributed to the hydroxyl deformation mode of the OH units bonded to either the Ca or Cu for conichalcite and tangeite. The intense Raman band at 832 cm^{-1} for conichalcite and at 835 cm^{-1} for duftite is assigned to the AsO_4 symmetric stretching vibration. The Raman bands at 842 and 857 cm^{-1} for tangeite and calciovolborthite are also assigned to the VO_4 symmetric stretching vibration. The difference in the band position between the two minerals brings into question whether the two minerals are the same or are in fact different minerals. [11-15] There are such differences in the spectra that from the point of view of structure the two minerals are different. Such a conclusion is in harmony with results of the band component analysis of the hydroxyl-stretching region where significant differences in the position of the OH stretching bands were obtained. The results of Raman spectroscopy suggest that tangeite is based upon the Ca and Cu bonded to the vanadate anion and to hydroxyl units, whereas in calciovolborthite the Ca and Cu are bonded to vanadate anion. No definitive crystallographic studies are available for these two minerals.

Bands are observed at 822, 811, 781 and 750 cm^{-1} for conichalcite. The first three bands are attributed to vibrations of the AsO_4 unit. One possibility for the assignment of the 750 cm^{-1} band is to one of the hydroxyl deformation of OH units bonded to the Cu atom. The infrared spectra of conichalcite have been reported [8] with the $\nu_1(A_1)$ mode observed as a weak shoulder at 740 cm^{-1}; a result divergent from these results. The ν_1 band is at 834 cm^{-1}. The ν_3 mode in the infrared spectra was split into bands at 865, 840, 820 and 795 cm^{-1}. Whilst the bands at 820 and even 781 cm^{-1} coincide with the infrared bands the bands at 840 and 865 cm^{-1} do not. This non-coincidence of our Raman and published infrared spectra may be attributed to the use of samples from different origins. Alternatively the non-coincidence may mean that significant coupling exists in the vibrational modes of the arsenate anion. For duftite the most intense band is at 813 cm^{-1} and this band is assigned to the symmetric stretching vibration. The effect of cation substitution of the Ca by Pb causes an apparent shift to lower wavenumbers. Other bands are observed at around 813, 792, 744 cm^{-1}. These bands are attributable to the splitting of the ν_3 mode.

In the Raman spectrum of conichalcite an intense band is observed at 328 cm^{-1}. This band is assigned to the ν_2 mode. A comparison may be made with the austinites where multiple bands were found in this spectral region. The significance of this observation is that there is far less distortion of the arsenate anion in conichalcite than in the austinite series. In comparison for duftite bands are observed at 359, 340, 325 and 301 cm^{-1}. The splitting of the ν_2 mode for duftite is again attributed to the distortion of the arsenate anion. For conichalcite, three intense Raman bands are observed at 463, 446 and 430 cm^{-1}. These bands are attributed to the splitting of the $\nu_4(T_2)$ mode. For duftite, bands are observed at 454, 429 and 403 cm^{-1} with the latter being the most intense band. The low intensity bands, which are observed in the spectra of duftite at 549 and 512 cm^{-1}, are attributed to CuO stretching vibrations. For duftite, bands are observed at around 270 and 230 cm^{-1}. These bands

may be assigned to OCuO bending modes. Other bands are observed at around 182, 171, 144 and 121 cm^{-1} and are described as lattice vibrations. The low frequency region is characterised by highly mixed modes making the exact attribution of bands difficult if not impossible.

Tangeite and calciovolborthite

These two minerals both have the same formula ($CaCu(VO_4)(OH)$). The spectra of the VO_4 stretching region are shown in Figures 4c and d. The most intense band in the Raman spectrum of tangeite is at 842 cm^{-1} and this band is assigned to the ν_1 (VO_4) vibration. The most intense band for calciovolborthite is at 857 cm^{-1}. There is sufficient difference in the Raman spectrum in the VO stretching region to suggest that these two minerals are not identical. [11,12,15] No vibrational spectroscopic data is available for comparison. For tangeite additional bands are observed in the 298 K spectrum at 823, 798 and 768 cm^{-1} and are attributed to the splitting of the ν_3 vibrational mode. Low intensity bands are also observed at 868 and 715 cm^{-1}. This latter band is attributed to one of the hydroxyl deformations. The Raman spectrum at 77 K confirms the position of these bands. The Raman spectrum of calciovolborthite shows additional bands in this spectral region at 822 and 750 cm^{-1}. These bands may be attributed to the loss of degeneracy of the ν_3 mode. However this splitting for calciovolborthite is different from that of tangeite.

In tangeite, three bands are observed at 392, 367 and 321 cm^{-1} with the 367 cm^{-1} band being the most intense. This band is assigned to the OVO $\nu_2(E)$ mode. Griffith reports this Raman band for the free vanadate ion at 341 cm^{-1}. [10] The observation of one intense band in this region suggests that the vanadate ion is not distorted in the tangeite structure. In contrast, two bands are observed at 363 and 332 cm^{-1} for the OVO $\nu_2(E)$ mode in calciovolborthite. The vanadate ion in this mineral is more distorted. This spectroscopic evidence suggests that the two minerals tangeite and calciovolborthite have different structures. For tangeite, bands are observed at 507 and 482 cm^{-1}. The band at 507 cm^{-1} may be attributed to the CuO stretching vibration and the latter band to the splitting of the $\nu_4(T_2)$ mode. For calciovolborthite, Raman bands were found at 511, 494, around 467 and 440 cm^{-1}. As before the highest wavenumber band in this region is assigned to the CuO stretching vibration. The other three bands result from the loss of degeneracy of the $\nu_4(T_2)$ mode brought about by the distortion of the vanadate ion. Griffith reported this band for the vanadate ion to be at 341 cm^{-1}. [10] This value does not appear to be correct. If it is it means that the bands for both the ν_2 and ν_4 modes for tangeite are coincident at 367 cm^{-1} and that two bands at 363 and 332 cm^{-1} for calciovolborthite may be assigned to the ν_4 and ν_2 modes respectively.

CONCLUSIONS

In this work, we have tried to show the relationship of both cationic and anion isomorphic substitution for the adelite group of minerals. These minerals all have identical structures and consequently in nature isomorphic substitution can cause complexity. Such phenomena are absolutely normal in natural minerals of all kinds. Raman spectroscopy has proven most powerful for the identification of these minerals. In particular the position of the hydroxyl stretching vibrations and the

position of many of the bands have been identified for the first time. Some authors have suggested that the two minerals tangeite and calciovolborthite are the same mineral. Raman spectroscopy has proven that the minerals are not identical and have different structures. The application of Raman spectroscopy to the study of these minerals shows that increased complexity occurs as the cationic substitution from conichalcite to austinite to duftite occurs. The application of Raman spectroscopy to the study of closely related mineral phases has enabled their molecular characterisation using their vibrational spectra.

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Table 3a. Raman spectral analysis of the adelite group of minerals

Adelite		Austinite		Cobaltaustinite (M43250)		Nickelaustinite (M40813)		Nickelaustinite (M37995)	
298	77	298	77	298	77	298	77	298	77
3550	Not determined	3350 3265	3265	3289 3284	3346 3286	3344 3320	3344 3323	3343 3320	3343 3320
890 846 821 803		911 889 859 844 818 806 738 708	 890 845 819 802 741	918 825 808 795 765	 827 809 797 771	917 828 811 799 777	 828 811 801 779	918 832 808 742	 828 811 800 776
540 497 479 421		538 494 478 457 420 409	539 495 478 418	 469 430	487 469 432 421	495 475 430 398	500 475 430 418 394	 452 430 420 401	495 475 430 421 396
376 322		374 322 308	376 321	387 339 327	391 362 342 330	369 348 332	369 348 332	357 341 325 300	369 347 332 310
277 253 232		275 252 231	276 253 232	 226 214			228	256 226	 230

211 172 134		209 175 139 129	209 173 163 140	213 168	228 216 197	216 164 147	217 182 167	218 183 166	216 169

Table3 b. Raman spectral analysis of minerals related to the adelite group of minerals

Conichalcite		Duftite (M30693)		Duftite (M37995)		Calciovolborthite (M44153)		Tangeite		Calciovolborthite	
298	77	298	77	298	77	298	77	298	77	298	77
					3352	3410	3411			3412	3414
3233		3280	3283	3280	3281						
3158		3240	3238	3241	3238			3242	3242		
3086		3192	3187	3192	3188			3118	3118		
962										887	887
907											
						874	871	868	874		
832	834			842		857	859	842	843	859	859
821	824	834	835	832	835			823	824		
811	814	813	810	811	810	822	823	798	798	813	813
781	781	792		744	744	750	755	768	770		
750		769	744	742				715	713	759	753
	608					511	469	507	509	511	513
	595					467		482	484	494	496
	584							463		475	478
	555	549								440	443
534	539	512									
463	488										
446	447	454	455	452	455						
430	429	429	403	401	403						
		403	394		395						
389	373							392	371		
358	356	359	358	357	358	363	361	367	351		
335	337	340	342	340	342	332	334	321	324	348	353
328	325	325	326	325	327	307	309			311	312
303		301	302	300	302						
286	291	270	261	256	271			284	284	245	251
274	280	229	230	226	261			264	265		
			221	218							

206	225		191	182	230			208	210	214	219
180	208		182	165	221			184	185	184	197
	188		171	143		208	204	165	163	156	183
161	165		144	121		177	181	145	145		168
	150							135	138		
121	123										

Adelite	= $CaMg(AsO_4)(OH)$
Austinite	= $CaZn(AsO_4)(OH)$
Cobaltaustinite	= $Ca(Co,Cu)(AsO_4)(OH)$
Conichalcite	= $CaCu(AsO_4)(OH)$
Duftite	= $PbCu(AsO_4)(OH)$
Gabrielsonite	= $PbFe(AsO_4)(OH)$
Nickelaustinite	= $Ca(Ni,Zn)(AsO_4)(OH)$
Calciovolborthite	= $CaCu(VO_4)(OH)$
Tangeite	= $CaCu(VO_4)(OH)$

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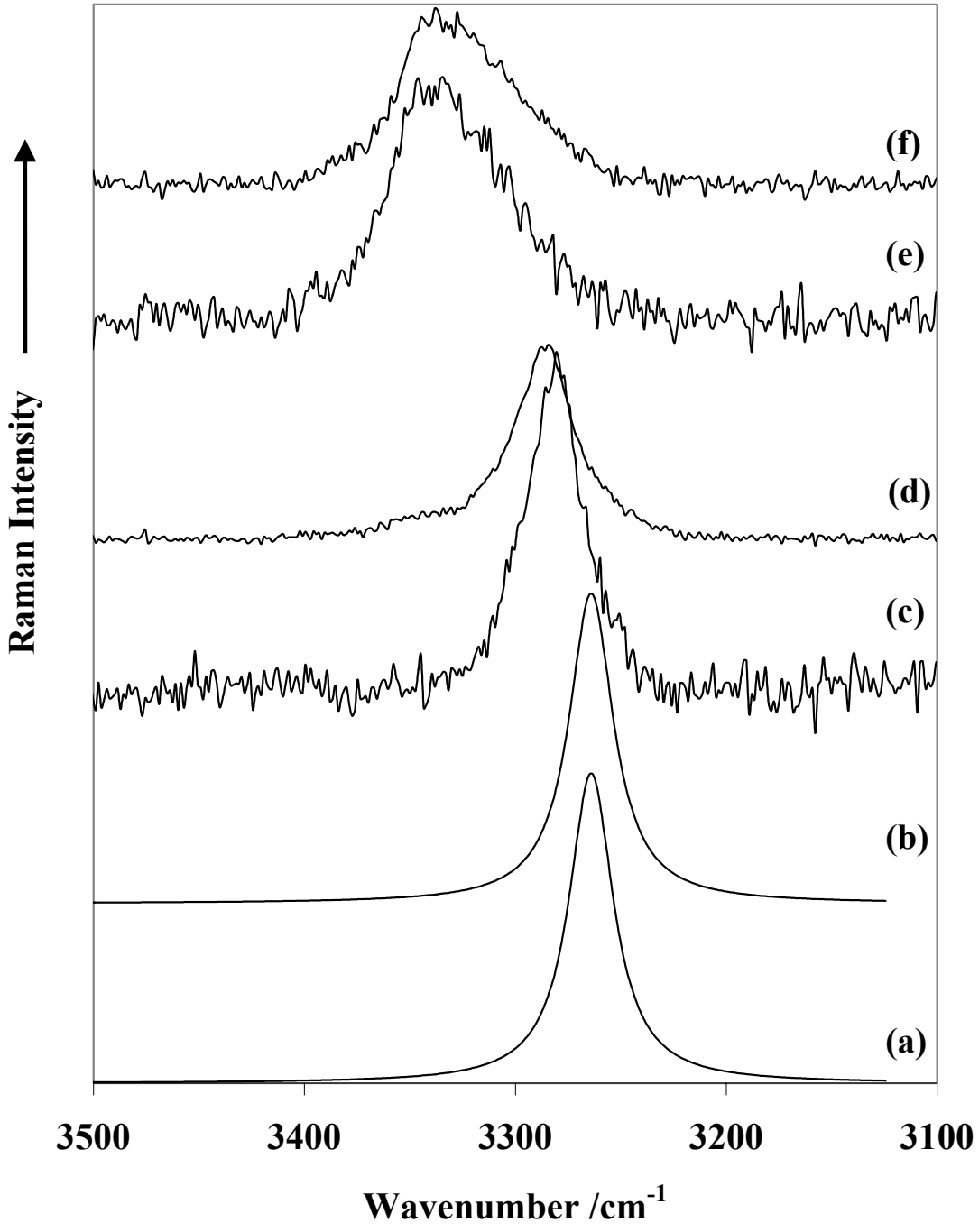
(f)
(e)
(d)
(c)
(b)
(a)
Raman Intensity
3500
3400
3300
3200
3100
Wavenumber /cm-1

Figure 1

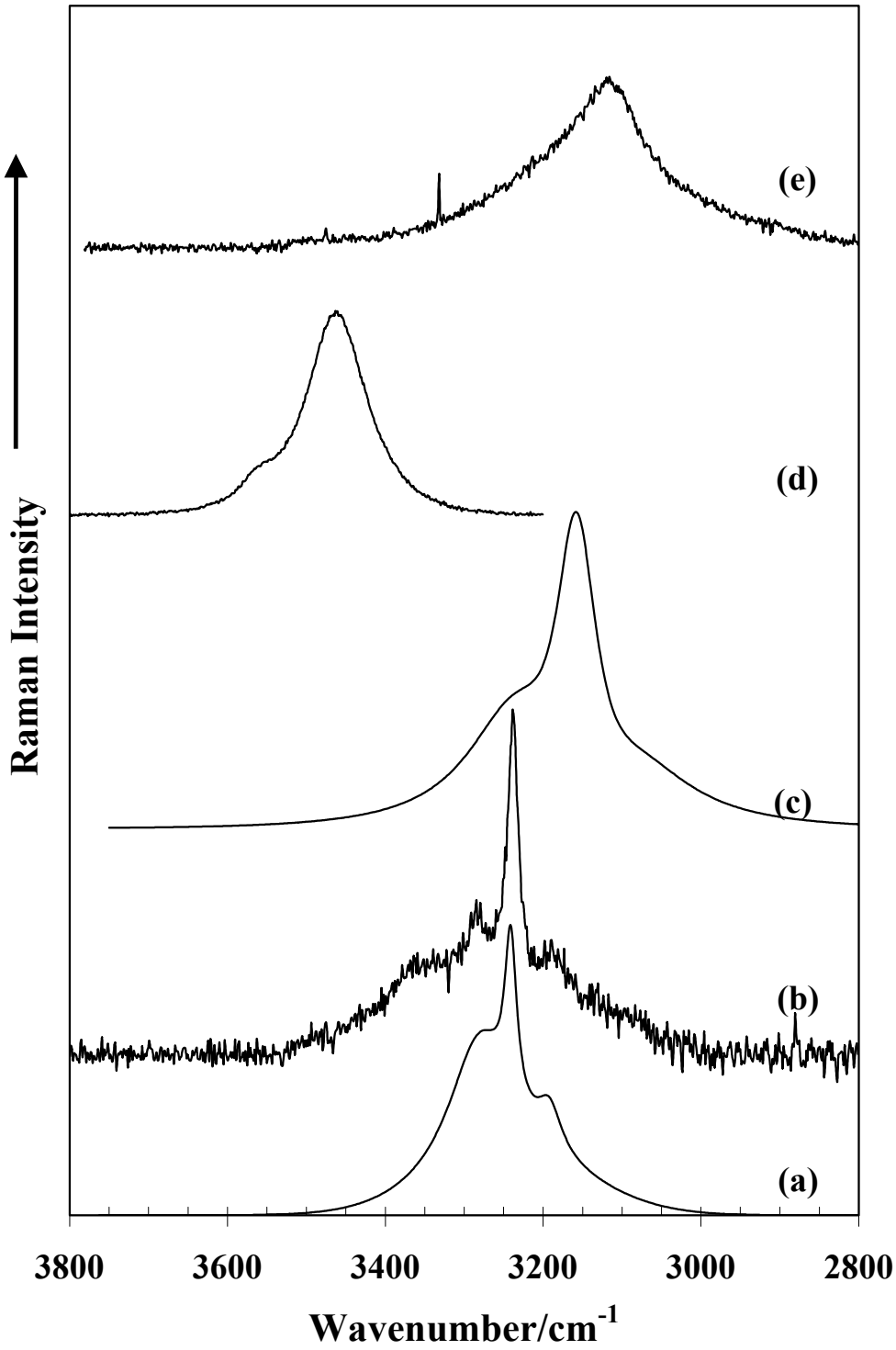
(e)
(d)
(c)
(b)
(a)
Raman Intensity
3800
3600
3400
3200
3000
2800
Wavenumber/cm-1

Figure 2

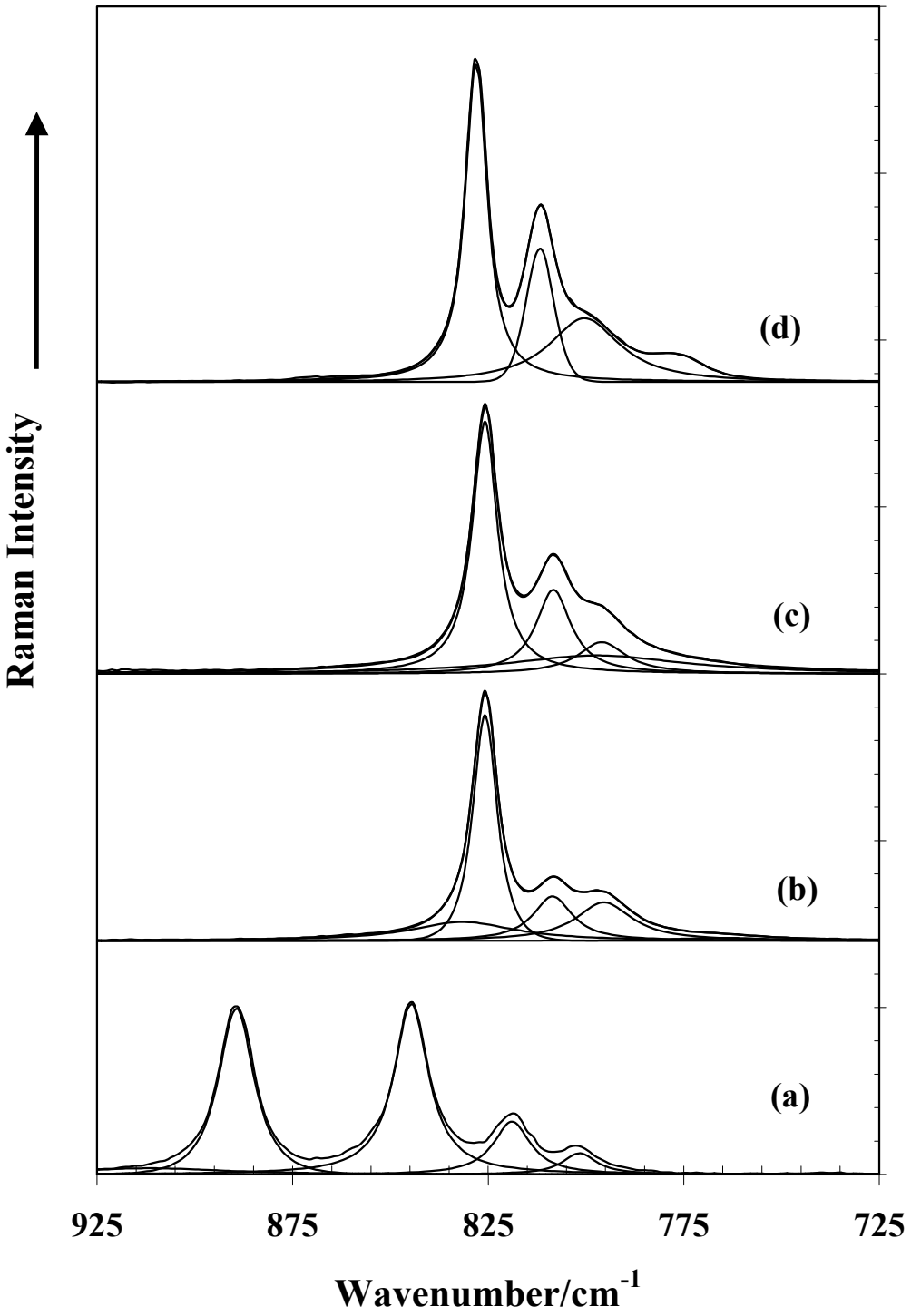

Figure 3

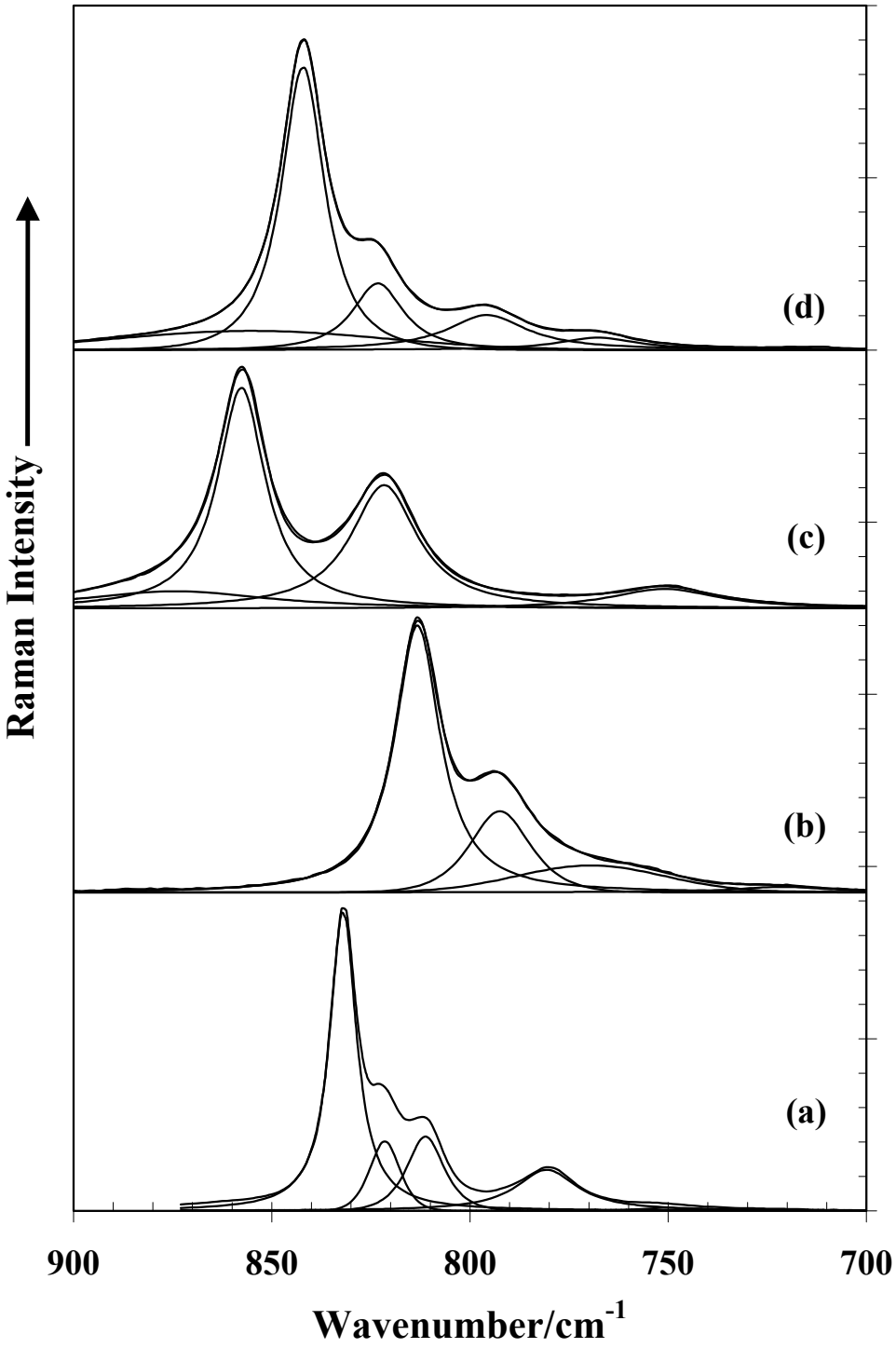

Figure 4

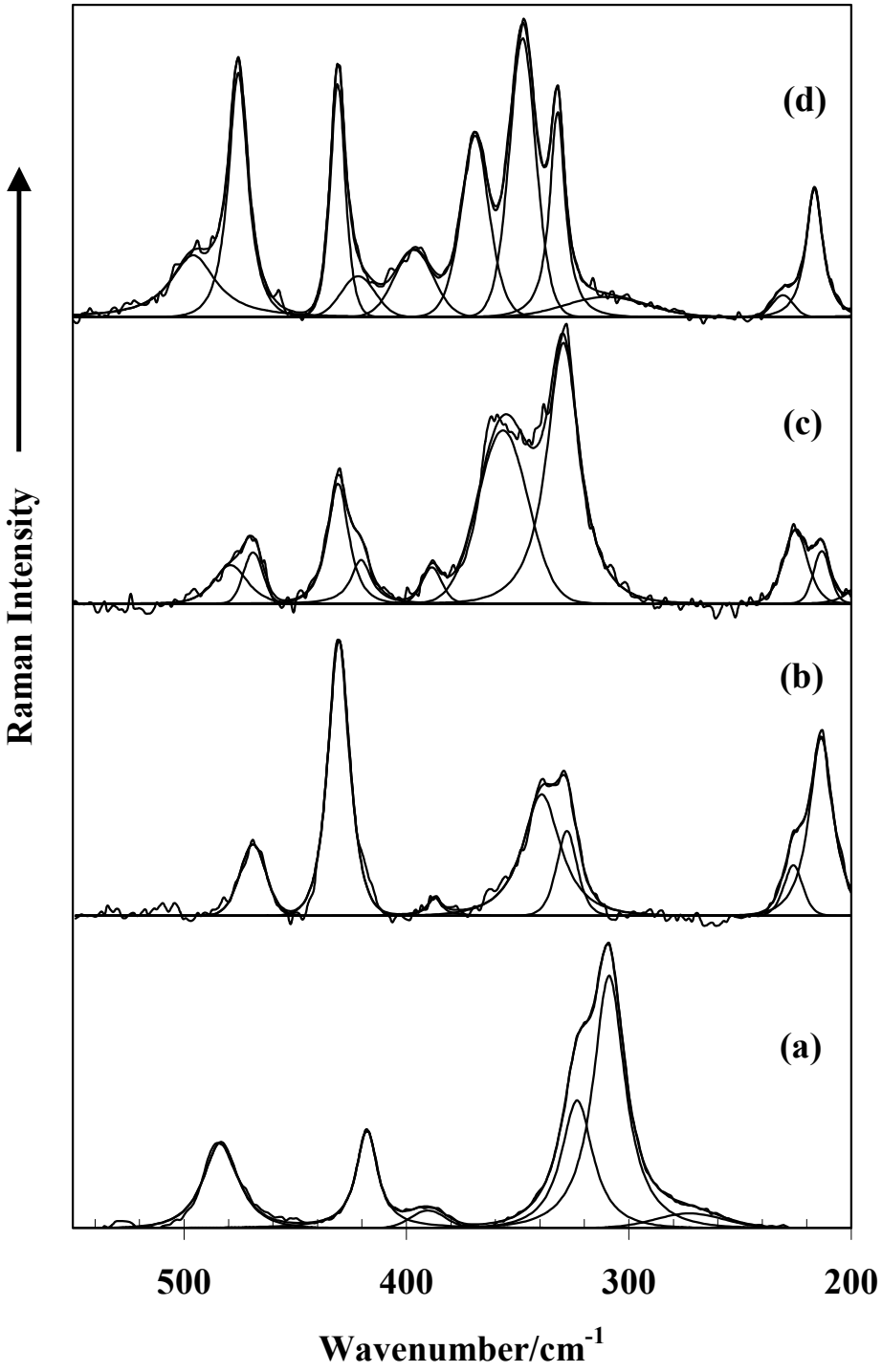

Figure 5

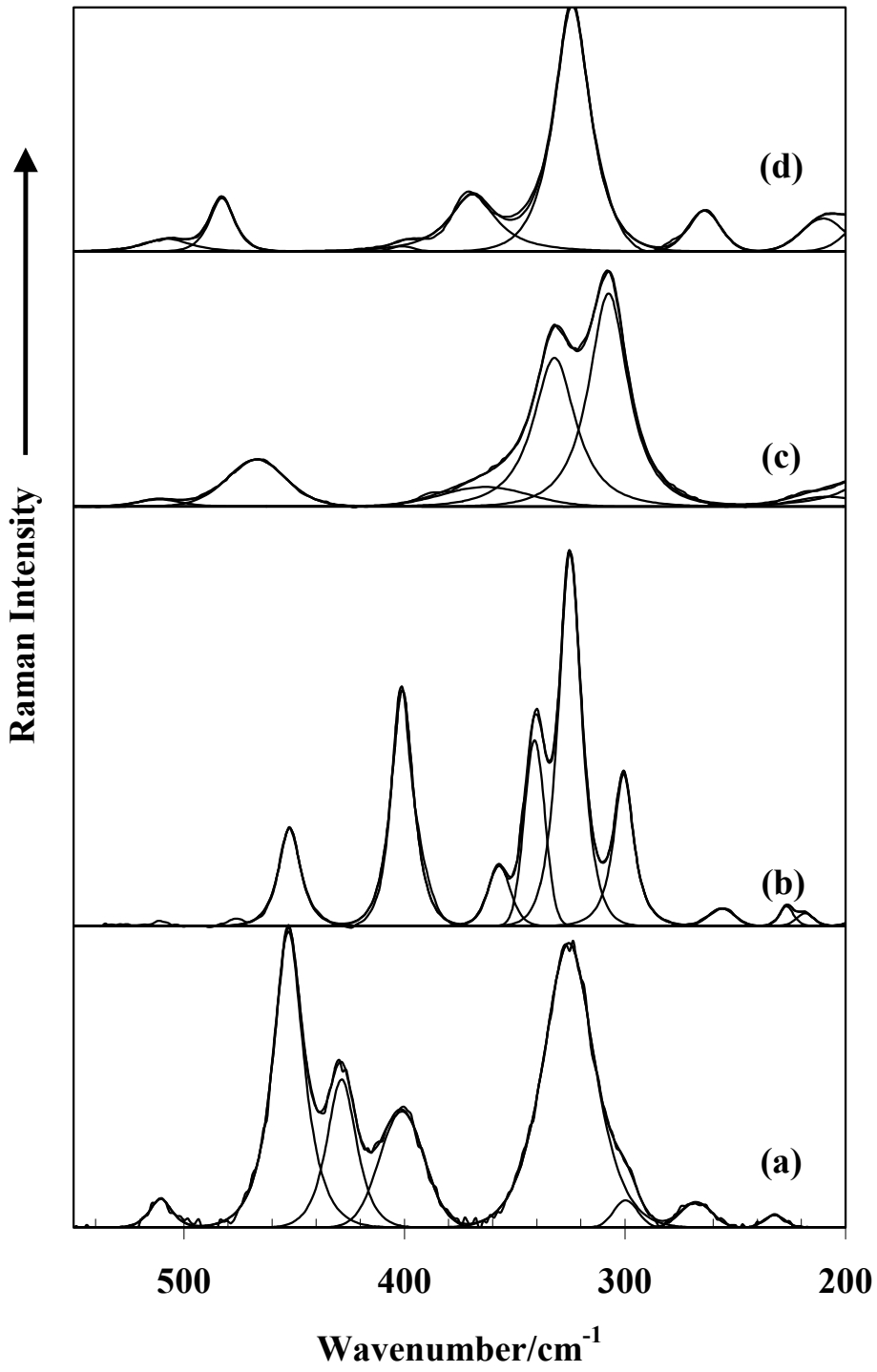

Figure 6