

Raman microscopy of synthetic goudeyite ($\text{YCu}_6(\text{AsO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$)

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Abstract:

Raman microscopy has been used to study the molecular structure of a synthetic goudeyite ($\text{YCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$). These types of minerals have a porous framework similar to that of zeolites with a structure based upon $(\text{A}^{3+})_{1-x}(\text{A}^{2+})_x\text{Cu}_6(\text{OH})_6(\text{AsO}_4)_{3-x}(\text{AsO}_3\text{OH})_x$. Two sets of AsO stretching vibrations were found and assigned to the vibrational modes of AsO_4 and HAsO_4 units. Two Raman bands are observed in the region 885 to 915 cm^{-1} and in the 867 to 870 cm^{-1} region and are assigned to the AsO stretching vibrations of $(\text{HAsO}_4)^{2-}$ and $(\text{H}_2\text{AsO}_4)^-$ units. The position of the bands indicate a C_{2v} symmetry of the $(\text{H}_2\text{AsO}_4)^-$ anion. Two bands are found at around 800 and 835 cm^{-1} and are assigned to the stretching vibrations of uncomplexed $(\text{AsO}_4)^{3-}$ units. Bands are observed at around 435, 403 and 395 cm^{-1} and are assigned to the ν_2 bending modes of the HAsO_4 (434 and 400 cm^{-1}) and the AsO_4 groups (324 cm^{-1}).

Key Words: agardite-(La), goudeyite, mixite, petersite-(Y) Raman spectroscopy

Introduction

Agardite is a member of the mixite group, $\text{ACu}_6(\text{AsO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ for the fully hydrated formula, with ($\text{A} = \text{REE}^{3+}$). Mixite ($\text{A} = \text{Bi}$), goudeyite ($\text{A} = \text{Al}$ or Y), zalesiite ($\text{A} = \text{Ca}$, with protonation of the lattice for charge compensation) and petersite-(Y), the phosphate analogue of agardite-(Y) are recognized isomorphous species in the group. Of the many possible rare earth congeners constituting the agardite group, only agardite-(Y) and agardite-(La) are recognized as distinct species by the IMA [1]. Others have been reported in the literature [2-7] but their species status remains unresolved. It should be noted that formulae given above refer to ideal, end-member compositions; extensive solid solution in the A site and involving P for As is known for naturally occurring material. Water in the lattice is for the most part thought to be zeolitic in nature, as evidenced by single-crystal X-ray structure determinations. [8-10] The crystal structures of natural mixite, goudeyite and agardite

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compounds reveal a microporous framework structure [4, 8] with a framework similar to that of zeolites. [10] Dietrich et al. [11] originally proposed that the water in agardite was zeolitic. As such these minerals may have potential for catalytic applications.

The mixite group consists of secondary minerals formed through crystallisation from aqueous solution. The conditions under which this crystallisation takes place, particularly relating to anion and cation concentrations, pH, temperature and kinetics of crystallisation, determines the particular mineral that is formed. Recently, Raman spectroscopy has been used to gain an understanding of many properties of secondary minerals [12-18]. In particular, Raman spectroscopy has been used to determine paragenetic relationships between many closely related phases [12, 14, 19-22]. Goudeyite is the mineral $(Al,Y)Cu_6(AsO_4)_2(OH)_6 \cdot 3H_2O$ as such the mineral has three vibrating units which will contribute to the vibrational spectra, namely the AsO_4 units, hydroxyl units and the water HOH units. In this paper we report a Raman and infrared spectroscopic study of synthetic goudeyite.

Experimental

Synthesis of goudeyite(Y)

The sample was synthesised by placing 1 mmol of $Y(NO_3)_3$, 6 mmol of $Cu(NO_3)_2 \cdot 2.5H_2O$ and 3 mmol of $Na_2HAsO_4 \cdot 7H_2O$ in 30 mL of water. The solution was stirred while the pH was monitored, and 1 M NaOH solution was added dropwise till the pH reached 6.9. The resulting solution was transferred to a 50 mL teflon-lined bomb which was placed in an oven at 180°C. The bomb was removed after 2 days and allowed to cool. The resulting solid was separated from the solution by vacuum filtration, washed twice with water followed by ethanol and allowed to dry. The sample was analysed by X-ray diffraction and by EDX analyses.

Powder X-ray Diffraction

The most commonly used instrumentation for mineral identification in this study was a Phillips PW1825/20 powder X-ray diffractometer, employing $CuK\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). In each case a small amount of the material of interest was ground to a fine powder in a mortar and pestle before being placed on the sample stage. A smaller quantity of high purity silicon was added as a standard to those samples that were to have unit cell parameters determined. X-ray traces were produced between 5-70° in 2θ , with a step size of 0.02 and a speed of 0.02° min^{-1} . Phases were identified from the X-ray traces using Diffraction Technology data processing software (Traces Version 6). Some 140 X-ray traces were produced in identifying various mineral species from the deposit.

Raman microprobe spectroscopy

The crystals of the goudeyite compound were placed and oriented on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a notch filter system and a thermo-electrically cooled Charge Coupled Device (CCD) detector.

Raman spectra were excited by a Spectra-Physics model 127 Nd-Yag laser (785 nm) and acquired at a nominal resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . The crystals were oriented to provide maximum intensity. All crystal orientations were used to obtain the spectra. Power at the sample was measured as 1 mW. The incident radiation was scrambled to avoid polarisation effects.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000 to 525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s . Spectralcalc software package GRAMS. Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared regression coefficient of R^2 greater than 0.995.

Results and Discussion

X-ray diffraction

The powder X-ray diffraction pattern of the synthetic goudeyite is shown in Figure 1 and may be compared with the XRD pattern of a standard agardite pattern (01-076-1998). The figure clearly shows that a mixite type compound was made with no impurities.

Raman spectroscopy

Goudeyite is the mineral $(Y)Cu_6(AsO_4)_3(OH)_6 \cdot 3H_2O$. Three different vibrating units will contribute to the overall spectral profile, namely the OH units, the water molecules and the AsO_4 groups. The first two vibrating species will contribute to the high wavenumber region whilst the AsO_4 units will show Raman bands below 1200 cm^{-1} . [23] It has been shown that the water can be reversibly lost and the number of water molecules per formula unit can vary up to 3. Raman spectra of lanthanide agardites are shown in Figures 2-4. Figure 2 displays the AsO_4 stretching region, Figure 3 the 2500 to 3800 cm^{-1} wavenumber range and Figure 4 the 1200 to 2000 cm^{-1} range. Results of the Raman and infrared spectroscopic analyses are reported in Table 1. According to Mereiter and Preisinger (1986) mixites have a microporous framework structure based upon $(M^{3+})_{1-x}(M^{2+})_xCu_6(OH)_6(AsO_4)_{3-x}(AsO_3OH)_x$ [24], with vacancies in the A site or substitution by divalent cations being compensated by protonation of the lattice. On the spectroscopic time scale, exchange of protons between water molecules and arsenate ions is also likely. According to this formulation two types of units involving As are found, namely AsO_4 and $HAsO_4$. Thus two sets of bands involving AsO stretching modes would be expected.

Vibrational spectroscopy has been used to study the coordination chemistry of $(\text{AsO}_4)^{3-}$ ions for some considerable time [23, 25-29]. Vansant et al. showed the frequencies of the $(\text{AsO}_4)^{3-}$ units of T_d symmetry as 818 (A_1), 786 (F-stretching), 405 (F-bending) and 350 cm^{-1} (E) [27]. Vibrational spectroscopic studies have shown that the symmetry of the $(\text{AsO}_4)^{3-}$ polyhedron are strongly distorted and the $(\text{AsO}_4)^{3-}$ vibrations are strongly influenced by the protonation, cation presence and water coordination [26-29]. The symmetric stretching vibration of the arsenate anion in aqueous systems (ν_1) is observed at 810 cm^{-1} and coincides with the position of the antisymmetric stretching mode (ν_3) [23]. The symmetric bending mode (ν_2) is observed at 342 cm^{-1} and the (ν_4) bending modes at 398 cm^{-1} . Of all the tetrahedral oxyanions, the positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanions.

Two Raman bands are observed in the region 885 to 915 cm^{-1} and in the 867 to 870 cm^{-1} region. These are assigned to the AsO stretching vibrations of $(\text{HAsO}_4)^{2-}$ and $(\text{H}_2\text{AsO}_4)^-$ units [26, 27]. In the infrared spectrum, a strong band is observed at 999 , 871 , 831 and 804 cm^{-1} . According to Myeni et al. (see Myeni table 3) the band at around 937 cm^{-1} corresponds to the antisymmetric stretching vibration of protonated $(\text{AsO}_4)^{3-}$ units and the band at around 870 cm^{-1} to the symmetric stretching vibration of the protonated $(\text{AsO}_4)^{3-}$ units [28, 29]. The position of the bands indicate a C_{2v} symmetry of the $(\text{H}_2\text{AsO}_4)^-$ anion. The reason why there is a dependence of the Raman band position and the cationic radius is that these bands are due to the vibrations of protonated $(\text{AsO}_4)^{3-}$ units [30, 31]. The values of the band positions change because the bond length of the AsO and HAsO distances change with the cation. In contrast two bands are found at around 800 and 835 cm^{-1} . These are assigned to the stretching vibrations of uncomplexed $(\text{AsO}_4)^{3-}$ units. The bands correspond to the antisymmetric (803 cm^{-1}) and symmetric (833 cm^{-1}) stretching vibrations of $(\text{AsO}_4)^{3-}$ units of T_d symmetry [28, 29]. The AsO bond lengths in $(\text{AsO}_4)^{3-}$ units are not influenced by protonation or cationic complexation.

A number of bands are observed in the 350 to 550 cm^{-1} region (Figure 2). No infrared bands were determined in this spectral region because of the cut-off of the ATR diamond cell. A Raman band is observed at around 540 cm^{-1} which is cation sensitive. One possible assignment is that the band is the ν_4 bending mode of $(\text{HAsO}_4)^-$ units. Such a band position was not observed in the work of Vansant et al. [26, 27] and was not reported as was any of the bending modes in the work of Myeni et al. [28, 29]. Theoretical studies have shown such bond distances are dependent upon the type of arsenate unit in the structure. [28, 29] (see for example Table 2 in the Myeni reference). Such bond distances are cation sensitive for example the As-O bond distance is 1.62 \AA for $\text{Al-O}_2\text{-AsO}_2(\text{H}_2\text{O})_4$, 1.65 \AA for $\text{Mg-O}_2\text{-AsO}_2(\text{H}_2\text{O})_4$, 1.66 \AA for $\text{CdO}_2\text{-AsO}_2(\text{H}_2\text{O})_4$ and 1.64 \AA for $\text{Cd-O}_2\text{-AsO}_2(\text{H}_2\text{O})_4$. Such cationic sensitivity is expected to be translated to the bending modes of the $(\text{HAsO}_4)^-$ units. Vansant et al showed the potential energy distributions for $(\text{AsO}_4)^{3-}$, $(\text{HAsO}_4)^{2-}$ and $(\text{H}_2\text{AsO}_4)^-$ units. [26] These distributions were then used to calculate the attribution of the vibrational modes. [26] An intense band is observed at around 495 cm^{-1} which is not cation sensitive. Another intense is observed at 486 cm^{-1} and is assigned to the ν_4 antisymmetric bending mode of AsO_4 units. An additional band is observed around 470 cm^{-1} . Three bands are observed at around 435 , 403 and 395 cm^{-1} and are of similar intensities. These are assigned to the ν_2 bending modes of the HAsO_4 (434 and 400 cm^{-1}) and the AsO_4 groups (324 cm^{-1}).

Hydroxyl stretching region

The Raman and infrared spectra of the OH stretching region are shown in Figure 3. The Raman spectra are characterised by intense bands at 3480 and 3360 cm^{-1} with band widths of 17.1 and 46.9 cm^{-1} . Equivalent infrared bands are observed at 3488 and 3366 cm^{-1} . These bands must be attributed to the OH stretching vibrations. The higher wavenumber band is assigned to the OH stretching vibrations of the OH units of the goudeyite structure. Whilst the lower wavenumber band is attributed to strongly hydrogen bonded water molecules in the interlayer of the goudeyite structure.

The water bending region is shown in Figure 4. In the infrared spectrum a single intense band is observed at 1639 cm^{-1} . A band in this position is indicative of hydrogen bonded water. Even though water is a very poor Raman scatterer bands may be observed in the $\sim 1600 \text{ cm}^{-1}$ spectral region. Two bands are observed at 1695 and 1605 cm^{-1} . The first band is attributed to strongly hydrogen bonded water and the latter band to weakly hydrogen bonded water. This type of water is the equivalent of a 'free' or zeolitic water. However the high wave number band is indicative of water molecules in a highly structured environment.

Conclusions

The molecular structure of a synthetic goudeyite equivalent to the natural mineral $\text{YCu}_6(\text{AsO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ has been studied by Raman spectroscopy complimented with infrared spectroscopy. Goudeyite is one of a number of minerals in the mixite group which are characterized by layered structures with zeolitic water.

Acknowledgements

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ATR			Raman		
Center	FWHM	%	Center	FWHM	%
3557.1	114.2	1.5	3480.3	17.1	4.4
3487.6	19.4	0.4			
3478.0	48.9	2.8	3393.2	217.0	10.6
			3360.5	46.9	7.9
3366.2	131.6	8.5			
3257.3	300.5	8.7	3045.8	46.4	0.4
			2921.0	64.4	2.6
			2863.4	30.4	0.4
			1694.8	56.5	0.4
1638.6	71.4	1.4	1605.3	45.4	1.0
			1433.9	97.2	1.1
			1380.2	12.9	0.1
996.6	40.1	1.9	1000.9	13.1	1.0
935.9	56.8	1.4	937.5	28.5	0.7
			930.3	153.5	6.2
896.5	22.1	0.3	894.0	9.5	0.7
872.7	17.2	2.9	873.2	13.2	16.6
845.3	9.2	0.3			
825.9	56.6	20.9	834.7	20.1	6.1
			813.9	8.4	0.1
799.7	39.6	15.0	800.0	30.7	1.6
784.9	29.1	8.5			
			740.4	73.6	1.2
705.4	49.7	6.6	700.1	24.5	0.4
624.7	297.5	16.3			
			559.9	37.0	1.7
546.1	25.3	1.5	539.7	13.3	1.9
526.7	21.5	0.9	515.9	11.8	0.8
			494.7	27.2	1.5
			486.1	12.3	10.2
			469.6	13.0	1.9
			449.3	34.3	1.6
			434.6	14.3	4.6
			403.2	12.1	1.2
			395.2	25.7	1.3
			349.9	7.6	0.1
			346.3	89.4	1.6
			327.1	11.4	0.9
			293.3	22.9	0.5
			268.9	12.0	0.6
			257.2	39.3	1.3
			240.0	11.6	1.9
			226.3	19.8	0.4
			201.3	28.7	1.5
			195.7	11.1	0.7

Table 1 Results of the Raman and infrared spectroscopic analysis of synthetic goudeyite

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Table 1 Results of the Raman and infrared spectroscopic analysis of synthetic goudeyite

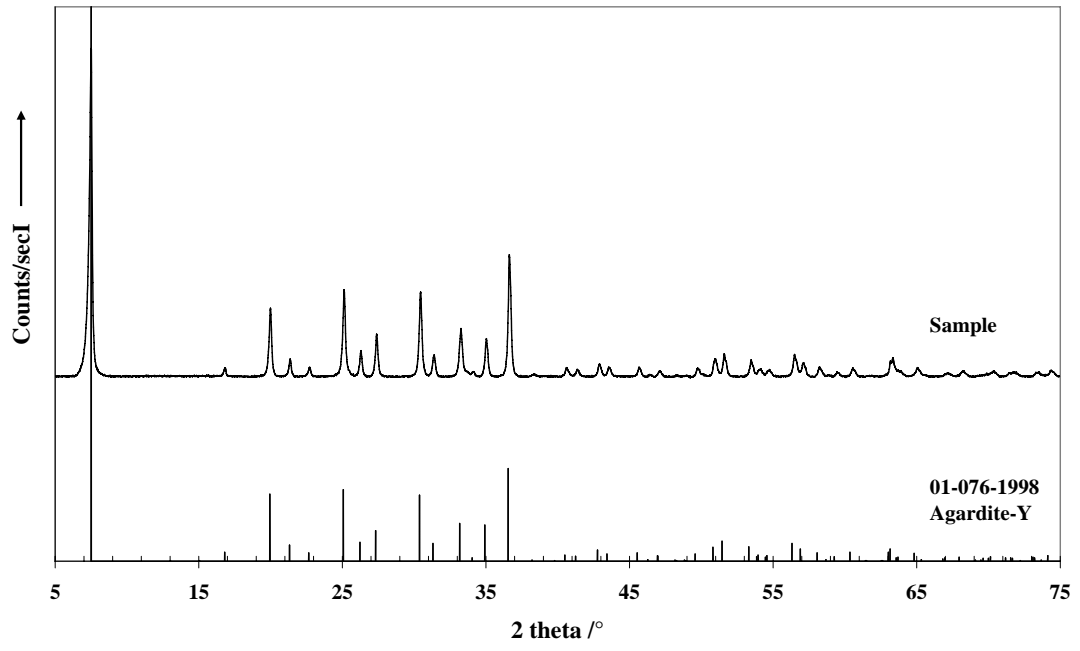


Figure 1

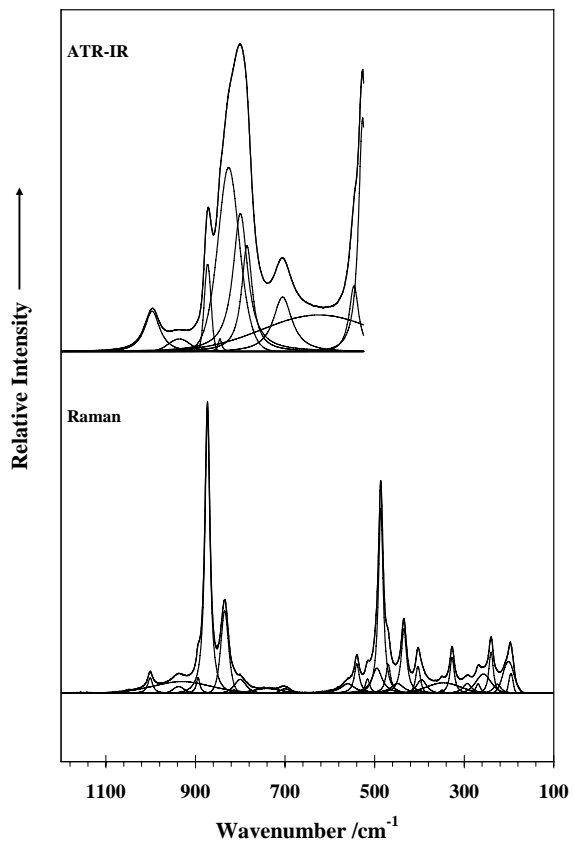


Figure 2

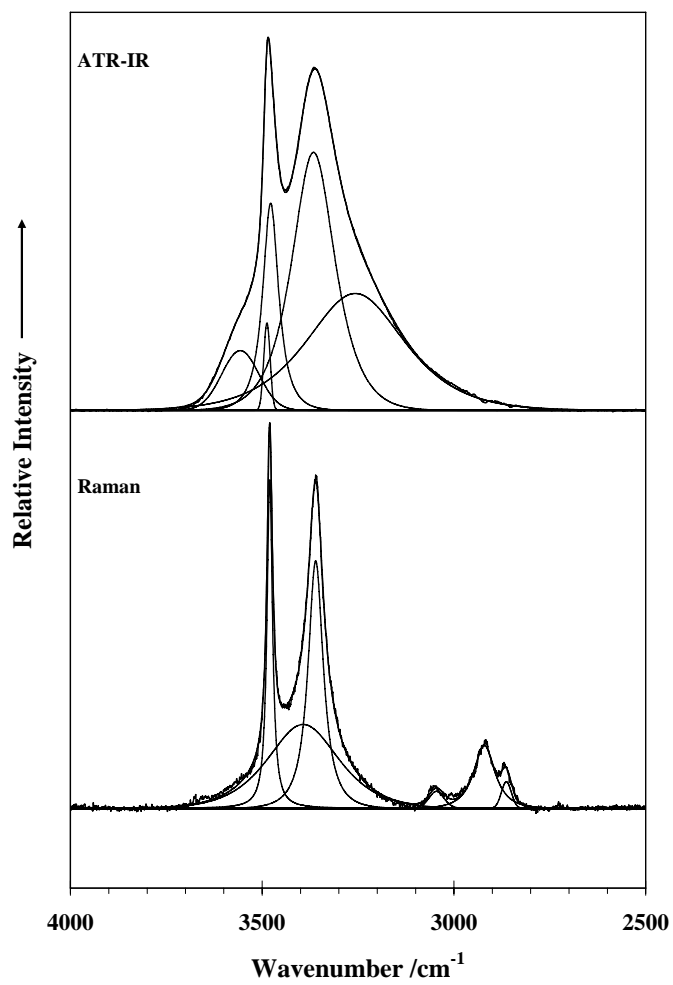


Figure 3

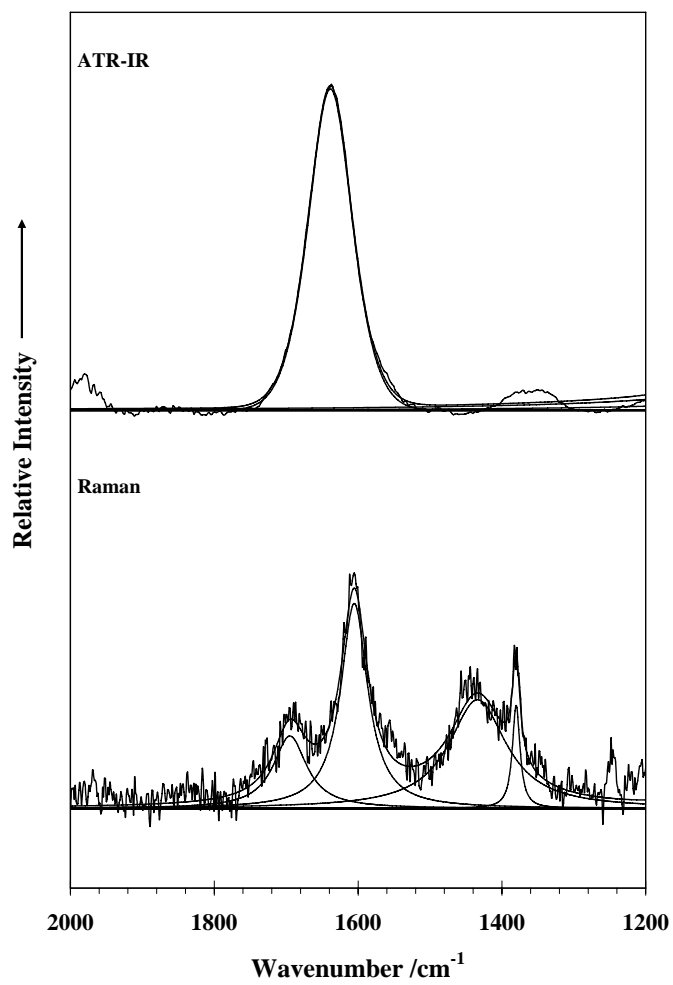


Figure 4

