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# Raman spectroscopic study of the molybdate mineral *szenicsite* and compared with other paragenetically related molybdate minerals

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## Abstract:

The molybdate-bearing mineral *szenicsite*,  $\text{Cu}_3(\text{MoO}_4)(\text{OH})_4$ , has been studied by Raman and infrared spectroscopy. A comparison of the Raman spectra is made with those of the closely related molybdate-bearing minerals, wulfenite, powellite, lindgrenite and iriginite, which show common paragenesis. The Raman spectrum of *szenicsite* displays an intense, sharp band at  $898 \text{ cm}^{-1}$ , attributed to the  $\nu_1$  symmetric stretching vibration of the  $\text{MoO}_4$  units. The position of this particular band may be compared with the values of  $871 \text{ cm}^{-1}$  for wulfenite and scheelite, and  $879 \text{ cm}^{-1}$  for powellite. Two Raman bands are observed at  $827$  and  $801 \text{ cm}^{-1}$  for *szenicsite*, which are assigned to the  $\nu_3(E_g)$  vibrational mode of the molybdate anion. The two  $\text{MO}_4 \nu_2$  modes are observed at  $349 (B_g)$  and  $308 \text{ cm}^{-1} (A_g)$ . The Raman band at  $408 \text{ cm}^{-1}$  for *szenicsite* is assigned to the  $\nu_4(E_g)$  band. The Raman spectra are assigned according to a factor group analysis and are related to the structure of

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the minerals. The various minerals mentioned have characteristically different Raman spectra.

**Key Words:** szenicsite, lindgrenite, iriginite, powellite, wulfenite, molybdate, Raman spectroscopy

## **Introduction**

The mineral szenicsite is a copper hydroxy molybdate of formula  $\text{Cu}_3(\text{MoO}_4)(\text{OH})_4$  (1). The mineral is orthorhombic and is characterised by triple chains of copper octahedra (2,3). These triple chains are linked by  $\text{MoO}_4^{2-}$  and  $\text{SO}_4^{2-}$  tetrahedra. The different size of these tetrahedra governs their different linkage to the triple chains and the orientation of the Jahn-Teller distortion of the  $\text{Cu}^{2+}$  octahedra (4,5). Burns states (2) that ‘The structure contains three unique  $\text{Cu}^{2+}$  positions that are each coordinated by six anions in distorted octahedral arrangements; the distortions of the octahedra are due to the Jahn-Teller effect associated with a  $d^9$  metal in an octahedral ligand-field. The single unique  $\text{Mo}^{6+}$  position is tetrahedrally coordinated by four  $\text{O}^{2-}$  anions. The  $\text{Cu}^{2+}(\text{phi})_6$  ( $\text{phi}$  : unspecified ligand) octahedra share trans edges to form rutile-like chains, three of which join by the sharing of octahedral edges to form triple chains that are parallel to [001]. The  $\text{MoO}_4$  tetrahedra are linked to either side of the triple chain of  $\text{Cu}^{2+}(\text{phi})_6$  octahedra by the sharing of two vertices per tetrahedron, and the resulting chains are cross-linked through tetrahedral-octahedral vertex sharing to form a framework structure.’ The structure of szenicsite is closely related to that of antlerite,  $\text{Cu}_3\text{SO}_4(\text{OH})_4$ , which contains similar triple chains of edge-sharing  $\text{Cu}^{2+}(\text{phi})_6$  octahedra (2).

Szenicsite is one of a number of molybdate minerals including ferrimolybdate, lindgrenite, powellite, and wulfenite. Interest in minerals containing molybdate anions has been ongoing for some considerable time (6-13) - no doubt because these minerals are of commercial value. Interest in the structure and formation of some of these minerals has been published (14-16). Significant advances in the technology of Raman spectroscopy have been made over time (17-20). These advances have meant that minerals whose Raman spectra may have been difficult to measure may now be determined. This interest has been heightened by the use of the molybdate minerals as catalysts (21-24). Many of these minerals have layered structures which can lead to high surface active materials (17-20).

This may be due to the lack of technology at that time or the availability of appropriate specimens. Recently, Frost et al. have used vibrational spectroscopic techniques to study groups of related minerals (25-31). Raman spectroscopy has proven to be a powerful technique for studying closely related minerals, particularly where the minerals can be found associated with each other through paragenesis. A previous study by the authors showed the usefulness of Raman spectroscopy to the study of molybdate minerals (32). In this present paper, we report the vibrational spectra of the molybdate mineral szenicsite and compare the spectra with those of lindgrenite ( $\text{Cu}_3(\text{MO}_4)_2(\text{OH})_2$ ), iriginite ( $\text{UO}_2\text{Mo}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ ), koechlinite ( $\text{Bi}_2\text{MoO}_6$ ), wulfenite ( $\text{PbMoO}_4$ ) and powellite ( $\text{CaMoO}_4$ ) and relate the Raman spectra to the mineral structure. A comparison of the Raman spectra to those of more common molybdate-bearing minerals: wulfenite and powellite is also made.

## **Experimental**

### **The mineral**

The mineral szenicsite was collected from the Jardinera No. 1 mine (26 Deg4.44'S, 69 Deg51.4'W), which exploits secondary copper ores (1). The mine is located in Chile's Atacama province 5 km east of Inca de Oro, which is 80 km north of Copiapo (1).

In this work natural minerals were used. The origin of other molybdate minerals used in this work is as follows:

Lindgrenite sample G16506 originated from Pinal Co., Arizona, USA

Lindgrenite sample M21019 originated from Broken Hill, NSW, Australia

Lindgrenite - Chuquicamata, Antofagasta Province, Chile.

Lindgrenite - Superior Mine, Globe-Miami District, Gila County, Arizona

Iriginite - Hervey's Range Deposit, 55 Km W. of Townsville, Queensland, Australia.

Koehlinite G17196 originated from Horni, Czechoslovakia

Koehlinite M47373 originated from Pittong, Victoria, Australia

Molybdoformacite M42867 originated from Eagle Eye Mine, New Water, Arizona.

Wulfenite and powellite originated from Dundas, Tasmania, Australia.

Some lindgrenite and iriginite samples were obtained from The Mineral Research Company. The selection of minerals from these related phases for Raman spectroscopic analysis must be undertaken with care. Often the crystals are found together in the same specimen.

### **Electron Probe microanalysis**

The scanning electron microscope (SEM) used to study the mineral szenicsite was the FEI Quanta 200 SEM. The SEM was fitted with an EDAX thin-window X-ray detector. Samples examined under SEM consisted of small selected mineral chips mounted with double-sided carbon tape on aluminium stubs. The surface of samples was coated with a thin layer of carbon in a high vacuum coater to provide a good conductive surface. Elemental analyses were carried out with a qualitative energy dispersive X-ray microanalysis instrument operating at 25kV with a 10-mm working distance.

### **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 4000–525  $\text{cm}^{-1}$  range were obtained by the co-addition of 64 scans with a resolution of 4  $\text{cm}^{-1}$  and a mirror velocity of 0.6329  $\text{cm/s}$ . Spectra were co-added to improve the signal to noise ratio.

### **Raman microprobe spectroscopy**

The crystals of the molybdate minerals were placed and oriented on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a notch filter system and a thermo-electrically cooled Charge Coupled Device (CCD) detector. Raman spectra were excited by a Spectra-Physics model 127 Nd-Yag laser (785 nm) and acquired at a nominal resolution of 2  $\text{cm}^{-1}$  in the range between 100 and 4000  $\text{cm}^{-1}$ . 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.

The Spectralcalc software package GRAMS was used to display the spectra. 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

### Theory

The mineral szenicsite is a copper hydroxy molybdate of formula  $\text{Cu}_3(\text{MoO}_4)(\text{OH})_4$  (1) and is characterised by triple chains of copper octahedra (2,3). These chains are also found in the scheelite minerals and are probably characteristic of molybdate-bearing minerals. Minerals with a scheelite structure, like wulfenite, have site group  $S_4$  and space group  $C_{4h}^6$ . The crystal structure resembles that of zircon and therefore the  $\text{WO}_4$  and  $\text{MoO}_4$  groups should show only four bands in the Raman spectra, two components each of  $\nu_3$  and  $\nu_4$ . The scheelite structure has been shown to be one of the few for which correlation splitting of the internal modes has been observed. This splitting results in  $\nu_1: A_g(\text{R}) + B_u(\text{inactive})$ ,  $\nu_2: A_g + B_g(\text{R}) + A_u(\text{ir}) + B_u$ ,  $\nu_3, \nu_4: B_g + E_g(\text{R}) + A_u(\text{ir}) + E_u(\text{ir})$  (33). The szenicsite structure is expected to show similarities.

Calculations for the wulfenite structure indicate the following Raman bands  $\nu_1: A_g + B_u$  (inactive, but activated due to strain),  $\nu_2: A_g + B_g + B_u$ ,  $\nu_3$ ,  $\nu_4: B_g + E_g$ , most of which are easily observed for wulfenite (and scheelite). The  $\nu_1(A_g)$  band is detected at  $871 \text{ cm}^{-1}$  and, although the corresponding  $\nu_1(B_u)$  vibration should be inactive, a minor band is observed around  $858 \text{ cm}^{-1}$ . It may be possible that this band becomes visible as a weak band due to strain in the crystal. This band for synthetic powellite is observed in the infrared spectrum at  $849 \text{ cm}^{-1}$  (34). For powellite, the bands are observed at  $879$  and  $847 \text{ cm}^{-1}$ . Interestingly, Farmer has reported the  $\nu_1(A_g)$  band in the Raman spectrum for synthetic powellite at  $880 \text{ cm}^{-1}$  and for wulfenite at  $872 \text{ cm}^{-1}$  (35). A summary of the results of the Raman spectra of ferrimolybdate, lindgrenite, powellite, and wulfenite is given in Table 1 (32).

The Raman and infrared spectra of szenicsite in the  $500\text{-}1200 \text{ cm}^{-1}$  region are shown in Figure 1. The results of the spectral analysis of szenicsite are presented in Table 2. The Raman spectrum is characterised by an intense sharp band at  $898 \text{ cm}^{-1}$  with a band width of  $4.9 \text{ cm}^{-1}$ . This Raman band is assigned to the  $\nu_1 \text{ MoO}_4$  symmetric stretching vibration. The position of the band may be compared with the value of  $871 \text{ cm}^{-1}$  for wulfenite and scheelite, and  $879 \text{ cm}^{-1}$  for powellite. The band is observed at  $883 \text{ cm}^{-1}$  for lindgrenite and  $888 \text{ cm}^{-1}$  for iriginite. No infrared band for szenicsite is found at this position. An infrared band is observed at  $941 \text{ cm}^{-1}$  with the corresponding Raman band at  $928 \text{ cm}^{-1}$ . These bands are attributed to the  $\nu_1 (\text{SO}_4)^{2-}$  symmetric stretching vibration. The observation of these bands is not unexpected as szenicsite can show isomorphic replacement of the molybdate by sulphate. The mineral is closely related in structure to the sulphate mineral antlerite. The bands between  $1008$  and  $1116 \text{ cm}^{-1}$  may be ascribed to the  $\nu_3 (\text{SO}_4)^{2-}$  antisymmetric stretching vibrations.



For the  $\nu_3(E_g)$  mode of the molybdate anion, Ross (36) has reported two bands for wulfenite at around 748 and 772  $\text{cm}^{-1}$ , which matches well with the values observed in the Raman spectrum of wulfenite at approximately 745 and 768  $\text{cm}^{-1}$  (34,37). Two bands are observed at 827 and 801  $\text{cm}^{-1}$  for szenicsite and are assigned to this vibrational mode. For synthetic  $\text{CdMoO}_4$ , however, only one Raman band has been reported at around 759  $\text{cm}^{-1}$ . The corresponding  $\nu_3(B_g)$  is found at 815  $\text{cm}^{-1}$ . The  $\nu_3(E_g)$  bands are observed at 795 and 772  $\text{cm}^{-1}$  for lindgrenite, 693 and 668  $\text{cm}^{-1}$  for iriginite and 797 and 773  $\text{cm}^{-1}$  for koechlinite. The spectrum of iriginite is complicated by the presence of Raman bands due to the uranyl units. This accounts for the additional bands observed for iriginite, as shown in Table 1. It is probable that the two bands at 826 and 818  $\text{cm}^{-1}$  are due to the  $\nu_1(\text{UO}_2)^{2+}$  symmetric stretching vibrations and the two bands at 965 and 950  $\text{cm}^{-1}$  to the  $\nu_3$  antisymmetric stretching vibrations of the  $(\text{UO}_2)^{2+}$  units.

The Raman spectrum of the low wavenumber region of szenicsite is shown in Figure 2. The two  $\nu_2$  modes are observed at 349  $\text{cm}^{-1}$  ( $B_g$ ) and 308  $\text{cm}^{-1}$  ( $A_g$ ). A comparison of the data for the natural minerals is given in Table 1. Farmer reports these bands for the Raman spectra of wulfenite at 354 and 321  $\text{cm}^{-1}$  (35). Three bands were given for synthetic powellite at 404, 394 and 326  $\text{cm}^{-1}$  (35). The expected  $\nu_4(E_g)$  around 384  $\text{cm}^{-1}$  is absent in the spectrum of natural wulfenite. The band at 308  $\text{cm}^{-1}$  for szenicsite is assigned to this vibrational mode. Two bands were listed at 820 and 770  $\text{cm}^{-1}$  for wulfenite and two bands at 847 and 796  $\text{cm}^{-1}$  for synthetic powellite (34,35). The bands of wulfenite at 351 and 319  $\text{cm}^{-1}$  are assigned as either deformation modes or as  $r(B_g)$  and  $\delta(A_g)$  modes of terminal  $\text{MO}_2$  units. These bands

are observed at 355 and 320  $\text{cm}^{-1}$  for powellite. The band at 462  $\text{cm}^{-1}$  has an equivalent band in the infrared at 455  $\text{cm}^{-1}$ , assigned as  $\delta_{\text{as}}(A_u)$  of the  $(\text{M}_2\text{O}_4)_n$  chain. The band at 476  $\text{cm}^{-1}$  for szenicsite is also attributed to this vibration. The equivalent band for powellite is observed at 456  $\text{cm}^{-1}$ . The band at 513  $\text{cm}^{-1}$  for powellite is assigned as  $\nu_{\text{sym}}(B_g)$  of the  $(\text{M}_2\text{O}_4)_n$  chain. The band for powellite at 794  $\text{cm}^{-1}$  is interpreted as an antisymmetric bridging mode associated with the molybdate chain. The bands for wulfenite at 768 and 745  $\text{cm}^{-1}$  are associated with the antisymmetric and symmetric  $A_g$  modes of terminal  $\text{MO}_2$ . Additional bands for wulfenite were observed at 195 and 166  $\text{cm}^{-1}$ , assigned as translational modes of Pb-O and  $\text{MO}_4$ . Three bands observed at 196, 159 and 152  $\text{cm}^{-1}$  for powellite are assigned to translational modes of Ca-O and  $\text{MO}_4$ .

The Raman spectrum of szenicsite in the 3400 to 3600  $\text{cm}^{-1}$  region is shown in Figure 3. The Raman spectrum shows a single band at 3559  $\text{cm}^{-1}$  with additional bands at 3518 and 3503  $\text{cm}^{-1}$ . The 3559  $\text{cm}^{-1}$  band in the infrared spectrum shows complexity with multiple bands at 3567, 3559, 3555, and 3539  $\text{cm}^{-1}$ . The observation of multiple bands for the OH units suggests that not all the OH units are identical. A band at 3518  $\text{cm}^{-1}$  is common in both the Raman and infrared spectra. A low intensity band at 3503  $\text{cm}^{-1}$  is observed in the Raman spectrum. Significantly greater intensity is observed in the infrared spectrum with a band maximum at 3496  $\text{cm}^{-1}$ . One possible assignment is that these bands are due to adsorbed or bonded water. The phi ligands (see introduction above) may be OH units, but could also be water molecules.

## Conclusions

The molybdenum-bearing minerals szenicsite, lindgrenite, iriginite and koechlinite have been studied by Raman spectroscopy. A comparison is made with the Raman spectrum of the more common minerals wulfenite and powellite. The Raman spectra are assigned according to a factor group analysis and related to the structure of the minerals. These minerals have characteristically different Raman spectra.

The Raman spectrum of the mineral szenicsite shows an intense sharp band at  $898\text{ cm}^{-1}$  attributed to the  $\nu_1$  symmetric stretching vibration of the  $\text{MO}_4$  units. The position of the band may be compared with the value of  $871\text{ cm}^{-1}$  for wulfenite and scheelite, and  $879\text{ cm}^{-1}$  for powellite. The band is observed at  $883\text{ cm}^{-1}$  for lindgrenite and  $888\text{ cm}^{-1}$  for iriginite. Two Raman bands are observed at  $827$  and  $801\text{ cm}^{-1}$  for szenicsite and are assigned to  $\nu_3(E_g)$  vibrational mode of the molybdate anion. The two  $\text{MO}_4$   $\nu_2$  modes are observed at  $349\text{ cm}^{-1}$  ( $B_g$ ) and  $308\text{ cm}^{-1}$  ( $A_g$ ). The Raman band at  $408\text{ cm}^{-1}$  for szenicsite is assigned to the  $\nu_4(E_g)$  band.

The spectrum of iriginite is complicated by the presence of Raman bands due to the uranyl units. These units exhibit intense Raman bands at  $965$ ,  $950$  and  $826$  and  $818\text{ cm}^{-1}$ , which are attributed to the antisymmetric and symmetric stretching modes of the  $\text{UO}_2$  units, respectively. The Raman bands at  $687$  and  $668\text{ cm}^{-1}$  for szenicsite are attributed to antisymmetric and symmetric  $A_g$  modes of terminal  $\text{MO}_2$  units. Similar bands are observed at  $797$  and  $773\text{ cm}^{-1}$  for koechlinite and at  $798$  and  $775\text{ cm}^{-1}$  for lindgrenite. It is probable that some of the bands in the low wavenumber region are attributable to the bending modes of these  $\text{MO}_2$  units.

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**Table 1 Raman spectroscopic analysis of wulfenite, powellite, lindgrenite, iriginite and koechlinite**

<b>wulfenite</b>	<b>powellite</b>	<b>lindgrenite</b>	<b>iriginite</b>	<b>koechlinite</b>
		982		
871 858	879 847	929 883 837	965 950 888 826 818	843
768 745	794	795 772	693 668	797 773 715
462 351 319	513 456 403 392	493 398 354 335	487 457 413 373 337	401 349
	324 267	300 284	301 246	321 293 281 268
195	196	210 198 188	198	228 195
166	159 152	167 155 139 120	164	154 141



**Table 2 Table of the results of the infrared and Raman spectra of szenicsite**

IR			Raman		
Centre	FWHM	%	Centre	FWHM	%
3694	15.5	0.97			
3621	8.6	0.35			
3567	4.4	0.17			
3559	4.8	0.87	3559	5.3	3.73
3555	9.3	2.24			
3546	9.8	0.40			
3539	5.9	0.32			
3518	9.2	5.26	3518	4.4	3.23
			3506	5.0	0.41
			3503	5.7	1.13
3500	5.0	0.68	3500	10.0	0.62
3497	7.2	0.69			
3496	27.3	11.25			
3471	19.7	1.47			
1116	14.9	0.39			
1090	21.7	2.42			
1073	16.2	1.15			
1049	46.1	2.83			
1030	21.4	2.29			
1008	22.7	1.09			
941	17.1	2.33	928	15.3	7.08
			909	51.5	3.24
			903	6.2	5.27
			902	1.0	0.40
			898	4.9	18.33
			895	5.3	12.45
			894	7.5	8.97
878	10.6	0.65	873	65.8	1.29
859	25.4	3.05	843	10.3	0.70
			838	8.6	0.95
			827	18.6	3.59
			810	10.2	0.40
			801	13.5	1.07
797	60.1	12.88			
783	20.6	2.48			
746	73.4	20.54			
673	57.9	11.72	687	19.6	1.01
611	59.2	9.04			
560	47.7	2.47			
			475	9.5	0.64
			420	11.6	16.28

349	18.2	5.10
308	12.9	1.25
280	16.4	3.45
211	7.5	1.30
147	9.0	1.00
105	6.2	0.39

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## List of Figures

Figure 1 Raman and infrared spectrum of szenicsite in the 500 to 1200  $\text{cm}^{-1}$  region.

Figure 2 Raman spectrum of szenicsite in the 100 to 500  $\text{cm}^{-1}$  region.

Figure 3 Raman and infrared spectrum of szenicsite in the 3400 to 3600  $\text{cm}^{-1}$  region.

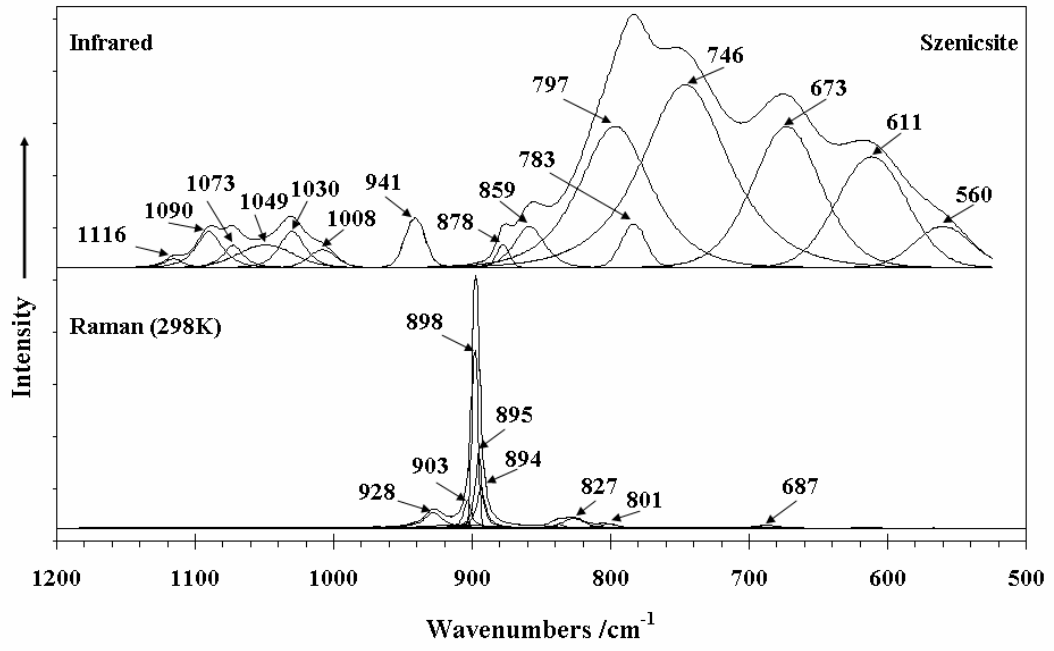


Figure 1

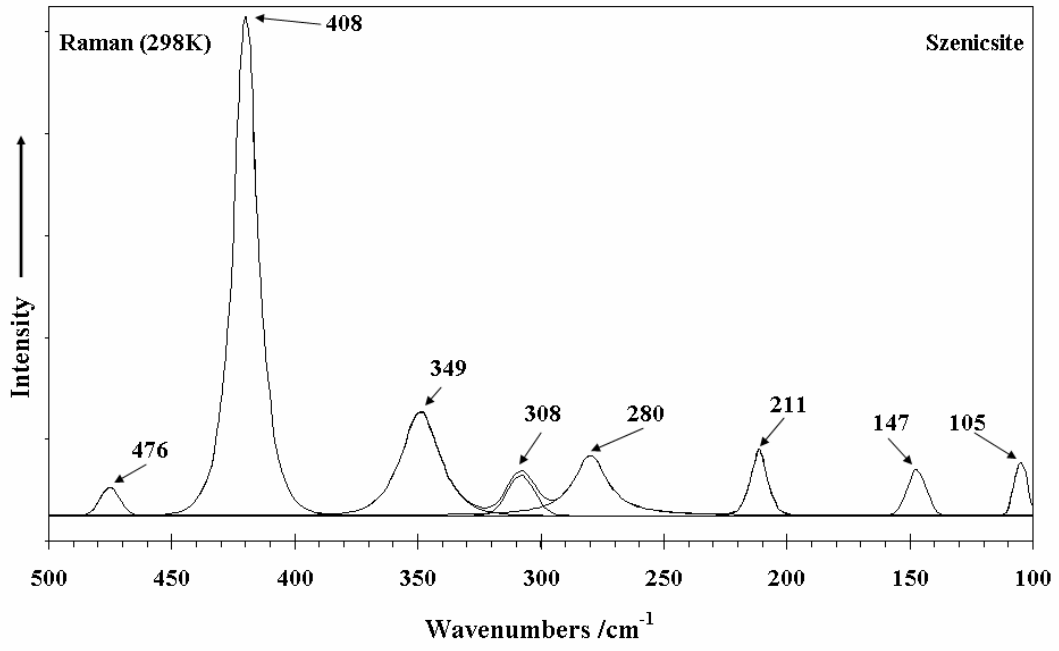


Figure 2

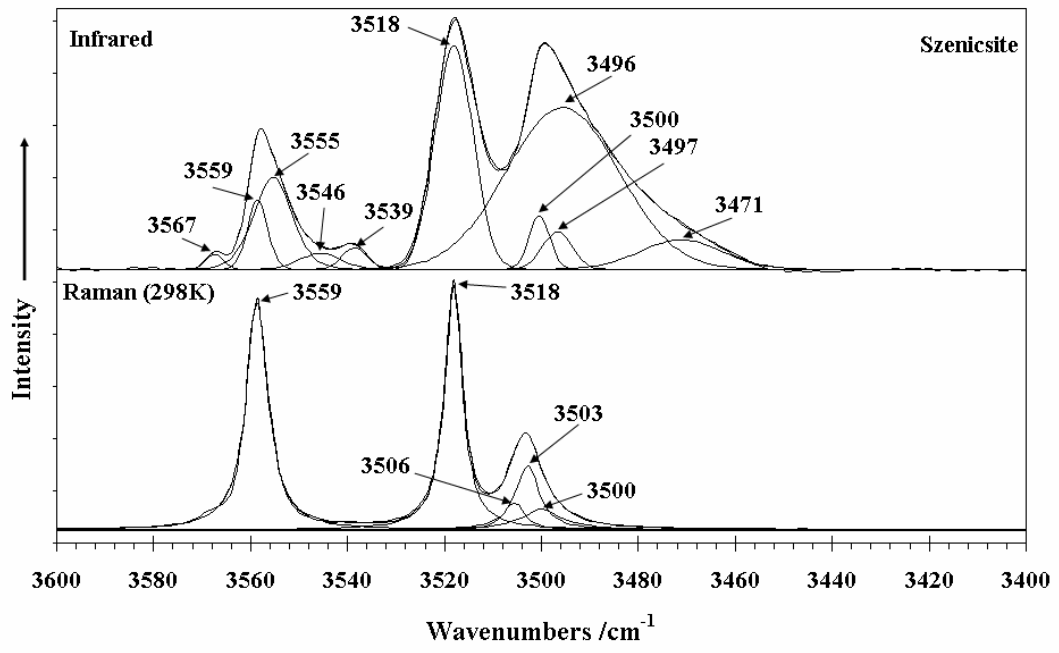


Figure 3