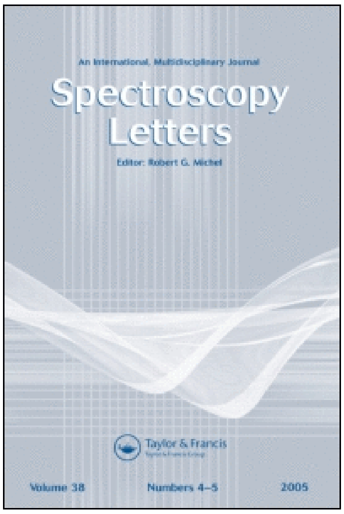

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Raman Spectroscopic Study of the Molybdate Mineral *Szenicsite* and Comparison with Other Paragenetically Related Molybdate Minerals

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Abstract: The molybdate-bearing mineral szenicsite, $Cu_3(MoO_4)(OH)_4$, 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 cm^{-1}, attributed to the ν_1 symmetric stretching vibration of the MoO_4 units. The position of this particular band may be compared with the values of 871 cm^{-1} for wulfenite and scheelite and 879 cm^{-1} for powellite. Two Raman bands are observed at 827 and 801 cm^{-1} for szenicsite, which are assigned to the $\nu_3(E_g)$ vibrational mode of the molybdate anion. The two MO_4 ν_2 modes are observed at 349 (B_g) and 308 cm^{-1} (A_g). The Raman band at 408 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 the minerals. The various minerals mentioned have characteristically different Raman spectra.

Keywords: Iriginite, lindgrenite, molybdate, powellite, Raman spectroscopy, szenicsite, wulfenite

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INTRODUCTION

The mineral szenicsite is a copper hydroxy molybdate of formula $Cu_3(MoO_4)(OH)_4$.[1] The mineral is orthorhombic and is characterized by triple chains of copper octahedra.[2,3] These triple chains are linked by MoO_4^{2-} and 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 Cu^{2+} octahedra.[4,5] Burns[2] states that, "The structure contains three unique 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 Mo^{6+} position is tetrahedrally coordinated by four O^2 anions. The $Cu^{2+}(phi)_6$ (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 MoO_4 tetrahedra are linked to either side of the triple chain of $Cu^{2+}(phi)_6$ 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, $Cu_3SO_4(OH)_4$, which contains similar triple chains of edge-sharing $Cu^{2+}(phi)_6$ octahedra.[2]

Szenicsite is one of a number of molybdate minerals including ferrimolybdite, 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]

Recently, Frost et al. have used vibrational spectroscopic techniques to study groups of related minerals.[25–31] Raman spectroscopy has proved 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 current paper, we report the vibrational spectra of the molybdate mineral szenicsite and compare the spectra with those of lindgrenite ($Cu_3(MO_4)_2(OH)_2$), iriginite ($UO_2Mo_2O_7 \cdot 3H_2O$), koechlinite (Bi_2MoO_6), wufenite ($PbMoO_4$), and powellite ($CaMoO_4$) 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.

MATERIALS AND METHODS

The Mineral

The mineral szenicsite was collected from the Jardinera No. 1 mine (26°4.44′S, 69°51.4′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 Country, 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 west of Townsville, Queensland, Australia
Koechlinite G17196 originated from Horni, Czechoslovakia
Koechlinite M47373 originated from Pittong, Victoria, Australia
Molybdofornacite 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 Mineralogical Research Company (San Jose, CA, USA). 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 (FEI, Hillsboro, OR, USA). 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 aluminum 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 25 kV with a 10-mm working distance.

Infrared Spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer (Nicolet Thermo Fisher Scientific, Waltham, MA, USA) with a smart endurance single-bounce diamond ATR cell. Spectra over the 4000–525 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. 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 (New Mills, Wotton-under-Edge, UK), which is equipped with 10× and 50× objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a notch filter system, and a thermoelectrically cooled charge coupled device (CCD) detector. Raman spectra were excited by a Spectra-Physics model 127 Nd-Yag laser (785 nm) (New Mills, Wotton-under-Edge, UK) 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 polarization effects.

The Spectracalc software package GRAMS (Galactic Industries Corp., NH, USA) was used to display the spectra. Band component analysis was undertaken using the Jandel Peakfit software package (Jandel Scientific, Erkrath, Germany), 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 $Cu_3(MoO_4)(OH)_4$[1] and is characterized 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 WO_4 and MoO_4 groups should show only four bands in the Raman spectra, two components each of ν_3 and ν_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 ν_1: $A_g(\mathrm{R}) + B_u$(inactive): ν_2: $A_g + B_g(\mathrm{R}) + A_u(\mathrm{ir}) + B_u$; ν_3, ν_4: $B_g + E_g(\mathrm{R}) + A_u(\mathrm{ir}) + E_u(\mathrm{ir})$.[33] The szenicsite structure is expected to show similarities.

Calculations for the wulfenite structure indicate the following Raman bands ν_1: $A_g + B_u$ (inactive, but activated due to strain); ν_2: $A_g + B_g + B_u$; ν_3, ν_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 cm^{-1} and, although the corresponding $\nu_1(B_u)$ vibration should be inactive, a minor band is observed around 858 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 cm^{-1}.[34] For powellite, the bands are observed at 879 and 847 cm^{-1}. Interestingly, Farmer has reported the $\nu_1(A_g)$ band in the Raman spectrum for synthetic powellite at 880 cm^{-1} and for wulfenite at 872 cm^{-1}.[35] A summary of the results of the Raman spectra of ferrimolybdite, lindgrenite, powellite, and wulfenite is given in Table 1.[32]

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

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

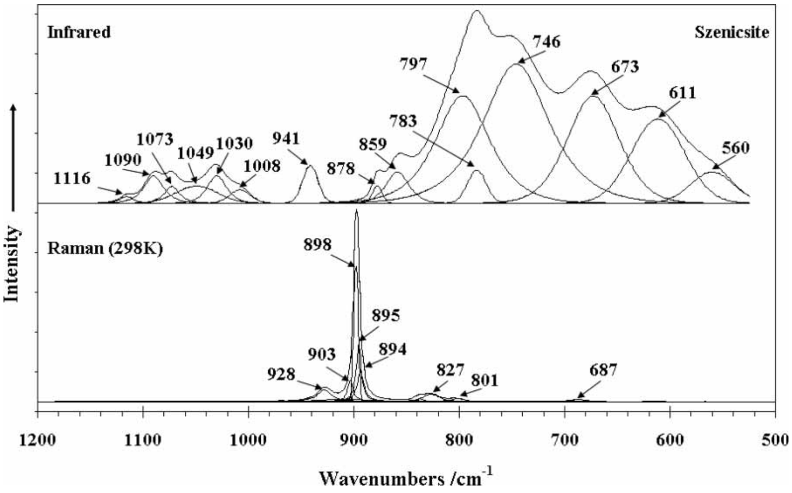

Figure 1. Raman and infrared spectrum of szenicsite in the 500 to 1200 cm^{-1} region.

The Raman and infrared spectra of szenicsite in the 500–1200 cm^{-1} region are shown in Fig. 1. The results of the spectral analysis of szenicsite are presented in Table 2. The Raman spectrum is characterized by an intense sharp band at 898 cm^{-1} with a band width of 4.9 cm^{-1}. This Raman band is assigned to the ν_1 MoO_4 symmetric stretching vibration. The position of the band may be compared with the value of 871 cm^{-1} for wulfenite and scheelite and 879 cm^{-1} for powellite. The band is observed at 883 cm^{-1} for lindgrenite and 888 cm^{-1} for iriginite. No infrared band for szenicsite is found at this position. An infrared band is observed at 941 cm^{-1} with the corresponding Raman band at 928 cm^{-1}. These bands are attributed to the ν_1 $(SO_4)^{2-}$ symmetric stretching vibration. The observation of these bands is not unexpected as szenicsite can show isomorphic replacement of the molybdate by sulfate. The mineral is closely related in structure to the sulfate mineral antlerite. The bands between 1008 and 1116 cm^{-1} may be ascribed to the ν_3 $(SO_4)^{2-}$ 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 cm^{-1}, which matches well with the values observed in the Raman spectrum of wulfenite at approximately 745 and 768 cm^{-1}.[34,37] Two bands are observed at 827 and 801 cm^{-1} for szenicsite and are assigned to this vibrational mode. For synthetic $CdMoO_4$, however, only one Raman band has been reported at around 759 cm^{-1}. The corresponding $\nu_3(B_g)$ is found at 815 cm^{-1}. The $\nu_3(E_g)$ bands are observed at 795 and 772 cm^{-1} for lindgrenite, 693 and 668 cm^{-1} for iriginite, and 797 and 773 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

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

IR			Raman		
Center cm^{-1}	FWHM cm^{-1}	(%)	Center cm^{-1}	FWHM cm^{-1}	(%)
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
797	60.1	12.88	801	13.5	1.07
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

(*continued*)

Table 2. Continued

IR			Raman		
Center cm^{-1}	FWHM cm^{-1}	(%)	Center cm^{-1}	FWHM cm^{-1}	(%)
			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

probable that the two bands at 826 and 818 cm^{-1} are due to the ν_1 $(UO_2)^{2+}$ symmetric stretching vibrations and the two bands at 965 and 950 cm^{-1} to the ν_3 antisymmetric stretching vibrations of the $(UO_2)^{2+}$ units.

The Raman spectrum of the low wavenumber region of szenicsite is shown in Fig. 2. The two ν_2 modes are observed at 349 cm^{-1} (B_g) and 308 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 cm^{-1}.[35] Three bands were given for synthetic powellite at 404, 394, and 326 cm^{-1}.[35] The expected $\nu_4(E_g)$ around 384 cm^{-1} is absent in the spectrum of natural wulfenite. The band at 308 cm^{-1} for szenicsite is assigned to this vibrational mode. Two bands were listed at 820 and 770 cm^{-1} for wulfenite and two bands at 847 and 796 cm^{-1} for synthetic powellite.[34,35] The bands of wulfenite at 351 and

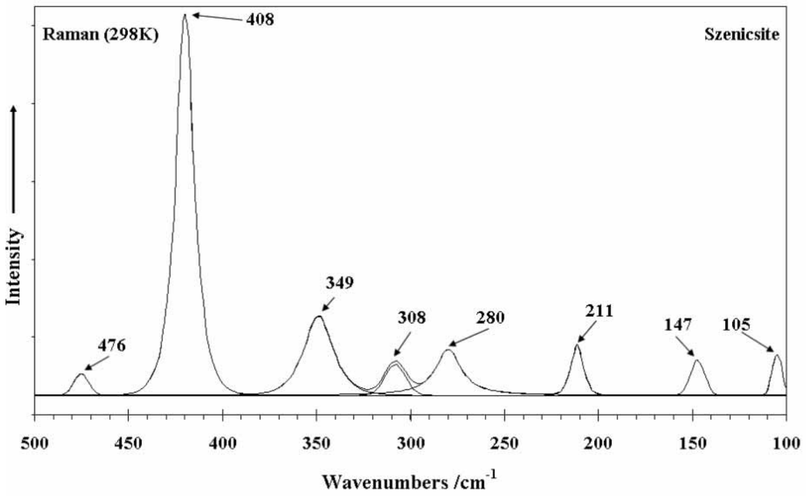

Figure 2. Raman spectrum of szenicsite in the 100 to 500 cm^{-1} region.

319 cm^{-1} are assigned as either deformation modes or as r(B_g) and δ(A_g) modes of terminal MO_2 units. These bands are observed at 355 and 320 cm^{-1} for powellite. The band at 462 cm^{-1} has an equivalent band in the infrared at 455 cm^{-1}, assigned as $\delta_{as}(A_u)$ of the $(M_2O_4)_n$ chain. The band at 476 cm^{-1} for szenicsite is also attributed to this vibration. The equivalent band for powellite is observed at 456 cm^{-1}. The band at 513 cm^{-1} for powellite is assigned as $\nu_{sym}(B_g)$ of the $(M_2O_4)_n$ chain. The band for powellite at 794 cm^{-1} is interpreted as an antisymmetric bridging mode associated with the molybdate chain. The bands for wulfenite at 768 and 745 cm^{-1} are associated with the antisymmetric and symmetric A_g modes of terminal MO_2. Additional bands for wulfenite were observed at 195 and 166 cm^{-1}, assigned as translational modes of Pb-O and MO_4. Three bands observed at 196, 159, and 152 cm^{-1} for powellite are assigned to translational modes of Ca-O and MO_4.

The Raman spectrum of szenicsite in the 3400 to 3600 cm^{-1} region is shown in Fig. 3. The Raman spectrum shows a single band at 3559 cm^{-1} with additional bands at 3518 and 3503 cm^{-1}. The 3559 cm^{-1} band in the infrared spectrum shows complexity with multiple bands at 3567, 3559, 3555, and 3539 cm^{-1}. The observation of multiple bands for the OH units suggests that not all the OH units are identical. A band at 3518 cm^{-1} is common in both the Raman and infrared spectra. A low-intensity band at 3503 cm^{-1} is observed in the Raman spectrum. Significantly greater intensity is observed in the infrared spectrum with a band maximum at 3496 cm^{-1}. One possible assignment is that these bands are due to adsorbed

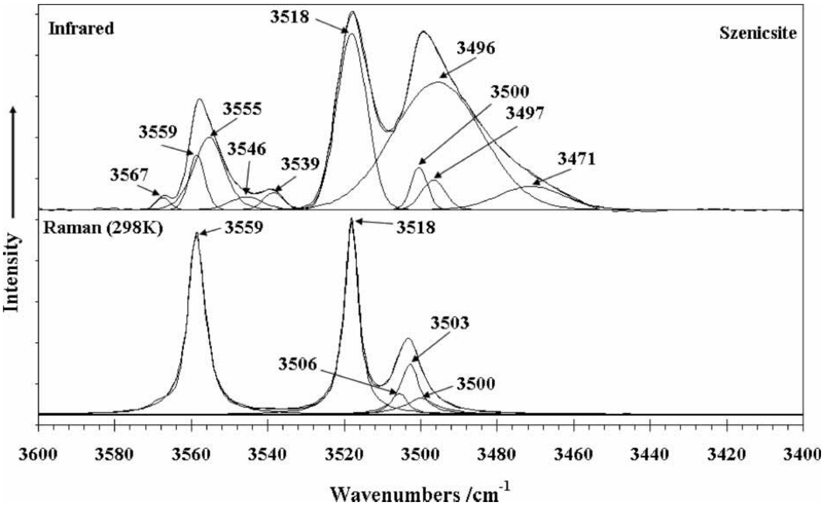

Figure 3. Raman and infrared spectrum of szenicsite in the 3400 to 3600 cm^{-1} region.

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 cm^{-1} attributed to the ν_1 symmetric stretching vibration of the MO_4 units. The position of the band may be compared with the value of 871 cm^{-1} for wulfenite and scheelite and 879 cm^{-1} for powellite. The band is observed at 883 cm^{-1} for lindgrenite and 888 cm^{-1} for iriginite. Two Raman bands are observed at 827 and 801 cm^{-1} for szenicsite and are assigned to $\nu_3(E_g)$ vibrational mode of the molybdate anion. The two MO_4 ν_2 modes are observed at 349 cm^{-1} (B_g) and 308 cm^{-1} (A_g). The Raman band at 408 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, 826, and 818 cm^{-1}, which are attributed to the antisymmetric and symmetric stretching modes of the UO_2 units, respectively. The Raman bands at 687 and 668 cm^{-1} for szenicsite are attributed to antisymmetric and symmetric A_g modes of terminal MO_2 units. Similar bands are observed at 797 and 773 cm^{-1} for koechlinite and at 798 and 775 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 MO_2 units.

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