IR and Raman spectroscopic study
of natural lawsonite

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Abstract : IR and Raman spectra of natural lawsonite have been recorded at wavenumbers between 50 and 4000 cm^{-1}. From polarized Raman and IR reflection spectra and mode denumbering, an assignment of the vibrations of the Si_2O_7, OH and H_2O units present in lawsonite is proposed. The results are compared with those available from other pyrosilicates.

Key-words : lawsonite, IR spectroscopy, Raman spectroscopy, pyrosilicates.

1. Introduction

Lawsonite is one of the key minerals used as an indicator of high-pressure low-temperature metamorphism (low-temperature blueschist facies). It commonly occurs as an early product of the breakdown of plagioclase in both metagreywackes and metabasic rocks. This mineral has been the subject of numerous experimental studies, including the determinations of its stability field (Nitsch, 1972 ; Chatterjee *et al.,* 1984) and thermodynamic properties (Perkins *et al.,* 1980). The only available spectroscopic data on lawsonite are infrared (IR) spectra (Moenke, 1962 ; Labotka and Rossman, 1974).

In this paper, the results of an IR and Raman spectroscopic investigation of lawsonite are presented. These new data, in conjunction with previous IR studies, symmetry analysis and comparison with other pyrosilicates, are used to assign the observed spectroscopic frequencies to the vibrational modes of certain molecular groups (Si_2O_7, OH and H_2O) in lawsonite.

A knowledge of the vibrational behaviour of Si_2O_7 structural groups is important in understanding the vibrational spectra of pyrosilicates

as well as a number of hydrous minerals such as the epidotes which, in addition to Si_2O_7 groups, also contain the SiO_4 unit. Moreover, important mantle minerals like the β-phase of Mg_2SiO_4 do also contain Si_2O_7 units (Horiuchi and Sawamoto, 1981).

2. Sample description and characterization

Several lawsonites were sampled in the Western Alps from well-preserved outcrops of HP-LT facies rocks. In these rocks, lawsonite can occur as isolated needle-like crystals, aggregates displaying a radiating pattern, or as tabular crystals. Crystals are millimetre sized. No crystals of gem quality were found. Centimetric single crystals from the Tiburon Peninsula (California) showing equant to tabular habit were used for polarized micro-Raman experiments and reflection IR spectra. All these lawsonites were characterized by powder X-ray diffraction ; chemical analyses were obtained on an automated Camebax electron microprobe. The chemical analyses lead to a structural formula close to the ideal one : $CaAl_2Si_2O_7$ $(OH)_2H_2O$. (Fe + Mg) never exceeds 1 ox. wt.%.

3. Experimental methods

3.1. IR spectroscopy

Infrared powder transmission spectra were run on KBr discs between 400 and 4000 cm^{-1} using a Fast-Fourier-Transform (FFT) Nicolet 20 SXC spectrometer. Each disc contains 2 to 3 mg of the sample mixed with 250 mg of KBr. The number of scans was 100 and the resolution 2 cm^{-1}.

Far-infrared spectra (50 to 600 cm^{-1}) were run on discs of 50 mg of polyethylene in which lawsonite powder had been previously dispersed. A FFT Nicolet 20F spectrometer was used. The number of scans and resolution were the same as above.

Reflection spectra were recorded on X-ray oriented and polished sections parallel to (001) and (100), from 0 to 4000 cm^{-1} on a Brucker IFS 113v machine equipped with a reflectance accessory and polarizers.

3.2. Raman spectroscopy

Unpolarized micro-Raman :

Raman spectra were run using a Microdil 28 multichannel micro-Raman spectrometer. A conventional light microscope is used to focus the laser beam (ionized Argon, λ = 514.52 nm ; power 600 mW) onto a 1 μm sized spot in the sample. The Raman light scattered by the sample is collected in the backscattering direction through the same objective and directed onto the Raman spectrometer. A multi-channel-detector head (512 diodes) combined with a digital processing unit is used to detect and store the signal. The slit width is 200 μm. If the incident and backscattered beams are unpolarized, the spectrum is close to that obtained in a powder experiment. Such unpolarized measurements were performed directly on lawsonite crystals observed in petrographic thin section.

Polarized Raman :

The same microspectrometer was used for polarized Raman experiments. Brémard *et al.* (1985, 1987) have shown that correct polarized spectra of anisotropic samples can be obtained

if the half-aperture angle of the objective (θm) is smaller than 40° and if the optical path in the sample is minimized. A Leitz UTK 50 objective was used (θm = 39.1°) after the system had been previously tested using an oriented sample of olivine for which the polarization of Raman bands is well-known. The spectra were in good agreement with those reported by Iishi (1978). An oriented sample was cut from the Tiburon lawsonite crystals. The laser spot was focused at the surface of the lawsonite sample ; the laser output power was 950 mW.

4. Structure and symmetry analysis

Lawsonite is orthorhombic and the following designation of crystallographic axes has been adopted : a = 8.795 Å, b = 5.847 Å, c = 13.142 Å. The space group is $Ccmm$ (D_{2h}^{16}). This is consistent with Baur's notation (1978), but not with the one adopted by Labotka and Rossman (1974) who invert the b and the c axes. The structure consists of chains of edge-sharing Al-O octahedra running parallel to the y axis and which are linked by Si_2O_7 groups (Fig. 1). The Ca atoms are coordinated by a distorted octahedron of oxygens. From an IR study, Labotka and Rossman (1974) have shown that all the OH bonds of the H_2O and
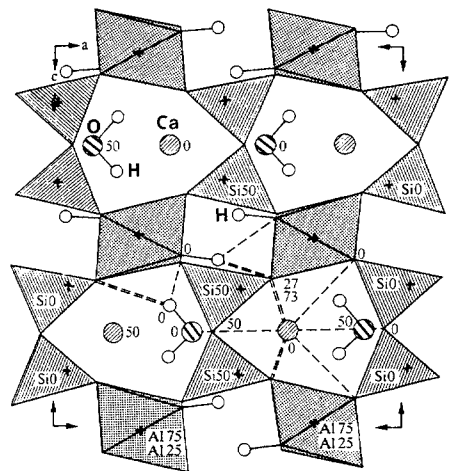

Fig. 1. Structure of lawsonite viewed along the y axis (after Baur, 1978). Coordinates of atoms are given as percentage of b.

OH groups lie in the (010) plane, according to our notation (Fig. 1). There are four formula units in the centred unit cell (V = 675 Å^3). The non-centred primitive unit cell (*i.e.* the spectroscopic cell) is half as large and contains 38 atoms ; hence, there are a total of 114 vibration modes at the centre of the Brillouin zone.

A knowledge of atomic positions and symmetries leads to the following representation of the 114 modes :

$$\Gamma = 16A_g + 11B_{1g} + 16B_{2g} + 8B_{3g} \text{ (Raman active)}$$
$$+ 18B_{1u} + 13B_{2u} + 18B_{3u} \text{ (IR active)}$$
$$+ 1B_{1u} + 1B_{2u} + 1B_{3u} \text{ (acoustic)}$$
$$+ 11A_u \text{ (inactive)}$$

Si_2O_7, H_2O and OH vibrations in lawsonite

It is assumed that the Si_2O_7, OH and H_2O groups are preserved as distinct structural units. Their contributions to the total 114 modes of the unit cell are given by factor group analysis (FGA) (Fateley *et al.*, 1972), using site-symmetry considerations. The site symmetry of both Si_2O_7 and H_2O within lawsonite is mm (C_{2v}) and that of OH is m (C_s).

For each cluster, external modes (librations) are obtained by considering rotations (Rx, Ry, Rz) and translations (Tx, Ty, Tz) of the free molecule. Correlations of site group versus molecular group and molecular group versus factor group give the symmetry relations of these librations in the crystal. The remaining modes are internal modes. For Ca and Al atoms, only translational modes should be taken into account.

The correlation scheme between site and factor groups is given in Table 1.

5. IR spectra

5.1. Previous work

Labotka and Rossman (1974) have carried out an IR study of the vibrations of OH and H_2O in lawsonite and have clearly resolved the high-frequency region (> 1600 cm^{-1}) and assigned the bands as follow :
● bending of water molecules at 1620 cm^{-1} (δ, B_{3u}) ;
● symmetric stretching of water molecule at 3250 cm^{-1} (ν_s, B_{3u}) ;

● antisymmetric stretching of water molecules at 3070 cm^{-1} (ν_{as}, B_{1u}) ;
● stretching of hydroxyl groups at 3560 cm^{-1} (ν, B_{1u} and B_{3u}).

This assignment is in agreement with FGA (Table 1), given that, in the free molecule of H_2O, δ and ν_s belong to the A_1 type and ν_{as} to the B_1 type. Stretching of OH is of A′ type.

5.2. Powder spectra

Only half of the expected bands were found. Nevertheless, the obtained spectra are in excellent agreement with those reported by Labotka and Rossman (1974). Frequencies are listed in Table 2. It should be noted that, below 1200 cm^{-1}, an isolated group of intense bands (800-1100 cm^{-1}) is clearly separated from a rather uniform group of bands extending from 98 to 650 cm^{-1} (Fig. 2).

In a preliminary powder spectrum, we recorded a very-low-frequency band at about 60 cm^{-1}. Reflection spectra in this region confirm this observation.

5.3. Reflection spectra

A band near 60 cm^{-1} appears when the electrical field E is parallel to the *b* axis of the mineral. Four bands below 100 cm^{-1} have been detected which could not be detected on the powder spectra (Fig. 3A).

One feature is observed in common with powder spectra : the gap of frequency between 650 and 800 cm^{-1} (Fig. 3B). It is pointed out below that polarization of bands above 800 cm^{-1} can be used to determine Si_2O_7 stretching motions. The frequencies and symmetry types of the bands are given in Table 2.

A total of 30 bands are resolved. LO and TO frequencies are computed by Kramers-Kronig analysis.

6. Raman spectra

6.1. Unpolarized micro-Raman spectra

Raman spectra were recorded from standard uncovered petrographic thin sections of each type of lawsonite (Fig. 4). The following features may be noted :
(1) The stretching of OH and H_2O constitutes

Table 1. Classification of normal modes of lawsonite (factor group D_{2h}^{16}) by site group analysis.

	rot.	transl.	int. modes	mol. group	site group	fact. group
Si_2O_7	0	1	7	A_1	A_1	A_g, B_{3u}
	1	0	4	A_2	A_2	B_{3g}, A_u
	1	1	6	B_1	B_1	B_{2g}, B_{1u}
	1	1	4	B_2	B_2	B_{1g}, B_{2u}
H_2O	0	1	2	A_1	A_1	A_g, B_{3u}
	1	0	0	A_2	A_2	B_{3g}, A_u
	1	1	1	B_1	B_1	B_{2g}, B_{1u}
	1	1	0	B_2	B_2	B_{1g}, B_{1u}
OH	1	2	1	A'	A'	A_g, B_{2g}, B_{1u}, B_{3u}
	1	1	0	A''	A''	B_{1g}, B_{3g}, A_u, B_{2u}
Al	0	3	0		A_u	A_u, B_{1u}, B_{2u}, B_{3u}
Ca	0	1	0		A_1	A_g, B_{3u}
	0	0	0		A_2	B_{3g}, A_u
	0	1	0		B_1	B_{2g}, B_{1u}
	0	1	0		B_2	B_{1g}, B_{2u}

For each isolated group (Si_2O_7, OH^- and H_2O), the modes are classified as translational, rotational and internal. For Al and Ca atoms, only translations are taken into account.

a broad band around 3600 cm^{-1} and the bending of H_2O produces a band near 1600 cm^{-1}.

(2) There are four bands around 1000 cm^{-1} : a low-intensity band at 1047 cm^{-1}, an intense band at 935 cm^{-1} flanked by two weaker bands at 915 and 955 cm^{-1}.

(3) A broad band ($\approx$ 100 cm^{-1} in width) is observed at 800 cm^{-1}.

(4) An intense band occurs at 694 cm^{-1}.

(5) The lowest observed Raman mode is at 90 cm^{-1}.

The frequencies of observed bands are listed in Table 3.

6.2. Polarized Raman spectra

The macro-Raman technique failed to give satisfactory results because depolarization occurs due to defects in the crystal (bubbles, solid inclusions, fractures). In micro-Raman spectroscopy, the studied volume is very small

Table 2. Vibrational infrared frequencies of lawsonite and possible assignments.

LR	this work					
powder	powder	reflection	TO	LO	symmetry	assignment
		58			B_{2u}	
		72			B_{2u}	
		83			B_{2u}	
100	95	95			B_{1u}	
170	171	167	167	178	B_{3u}	
210	212	209	206	237	B_{1u}	
		300 ?	300 ?		B_{1u}	
360	368	367	343	397	B_{2u}	
		375	355		B_{3u}	
	407	405	405		B_{1u}	
420	420	418	418	430	B_{1u}	
		435	400		B_{3u}	
	460	452	425	494	B_{3u}	
490	486	487	480	510	B_{1u}	
	500 sh	512	495	523	B_{2u}	
		512	508	552	B_{3u}	
	536	536	533	545	B_{1u}	
570	578 s	589	565	682	B_{1u}	
600	605 sh	604	573	643	B_{2u}	
	614 sh	622	602	653	B_{3u}	ν_s Si-O-Si
880	885 vs	888	881	906	B_{1u}	ν'_s SiO$_3$
	915 sh	923	919	940	B_{1u}	ν'_{as} SiO$_3$
950	953 vs	950	910 ?	1072 ?	B_{2u}	ν_{as} SiO$_3$
		sh			B_{3u}	ν_s SiO$_3$
	980 sh	963	930	1041	B_{3u}	ν_{as} SiO$_3$
1000	1000 sh	1024	910 ?	1072 ?	B_{2u}	δ OH ?
		1030	1017	1048	B_{1u}	ν_{as} Si-O-Si
1600	1600	1620 LR			B_{3u}	δ H$_2$O
		3070 LR			B_{1u}	ν_{as} H$_2$O
3250	3225	3250 LR			B_{3u}	ν_s H$_2$O
3560	3560	3560 LR			B_{1u}, B_{3u}	ν OH

LR = polarized absorption data from Labotka and Rossman (1974). vs = very strong. s = strong. sh = shoulder. The mode at 1024 cm^{-1} may also be an overtone of the 512 cm^{-1} mode. Frequencies are listed in cm^{-1}.

(a few µm^3) thus minimizing such effects. Only the high-frequency 600-1100 cm^{-1} region has been studied. Seven bands are observed between 650 and 1100 cm^{-1} (Fig. 5 and Table 3).

No good signal could be obtained in the (cb) orientation (B_{3g}) (Fig. 5F), even at long integration times. Nevertheless, two bands can be distinguished : one at about 810 cm^{-1}, the other around 960 cm^{-1}. Data concerning Raman spectra are summarized in Table 3.

7. Band assignment

7.1. Denumbering of Si$_2$O$_7$ vibrations

Stretching motions of Si$_2$O$_7$ polyhedra generally occur at frequencies above 700 cm^{-1} (Lazarev, 1972 ; Farmer, 1974 ; Kieffer, 1979, 1980 ; Hofmeister et al., 1987). The stretching vibrations of one Si$_2$O$_7$ unit can be divided into
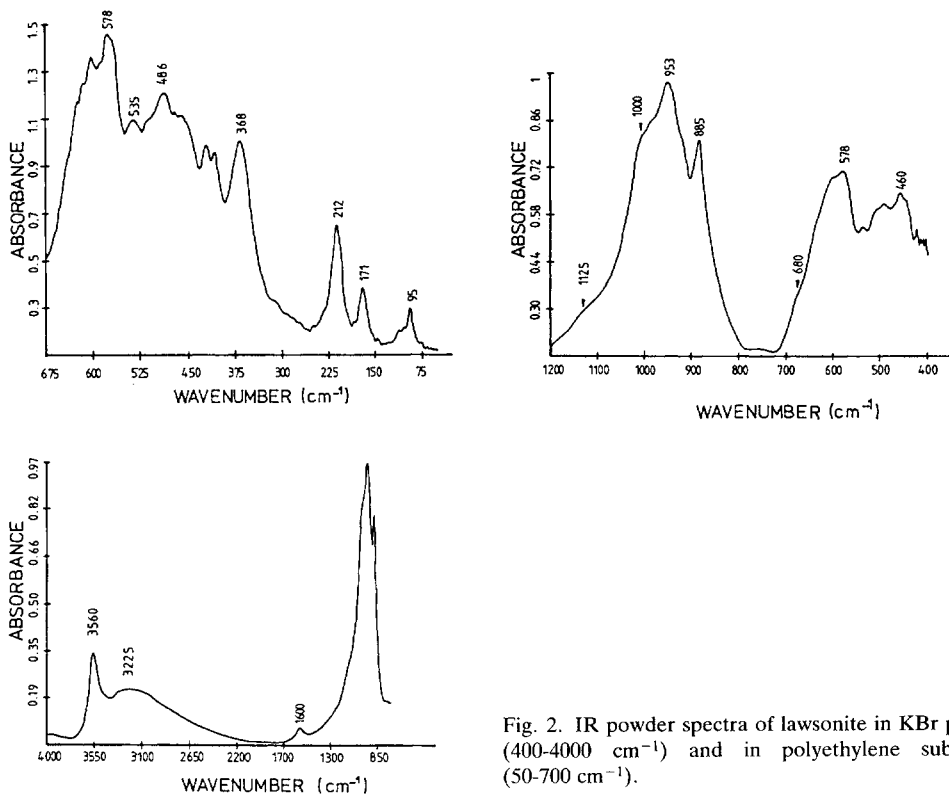
Fig. 2. IR powder spectra of lawsonite in KBr pellets (400-4000 cm^{-1}) and in polyethylene substrate (50-700 cm^{-1}).

the vibrations of SiO$_3$ and the vibrations (symmetric and antisymmetric) of Si-O-Si bridges (Lazarev, 1972 ; Gabelica-Robert and Tarte, 1979). The symmetry species of these vibrations, assuming a free pyro-group, are given by Lazarev (1972) (Table 4). A correlation with the factor group analyses of lawsonite leads to the following scheme :

ν_s Si-O-Si   : 1A$_g$ + 1B$_{3u}$

ν_{as} Si-O-Si   : 1B$_{2g}$ + 1B$_{1u}$

ν_s SiO$_3$: 1A$_g$ + 1B$_{3u}$ (symmetric in phase)

ν'_s SiO$_3$: 1B$_{2g}$ + 1B$_{1u}$ (symmetric out-of-phase)

ν_{as} SiO$_3$: 1A$_g$ + 1B$_{1g}$ + 1B$_{3u}$ + 1B$_{2u}$ (antisymmetric in phase)

ν'_{as} SiO$_3$: 1B$_{3g}$ + 1B$_{2g}$ + 1A$_u$ + 1B$_{1u}$ (antisymmetric out-of-phase)

### 7.2. Previous work on Si$_2$O$_7$ stretching vibrations

Several authors have measured the unpolarized spectra of silicates containing pyro-groups

such as thortveitite, krentolite (Gabelico-Robert and Tarte, 1979), fresnoite (Gabelico-Robert and Tarte, 1981), bertrandite (Hofmeister et al., 1987) or melilite (Sharma et al., 1988) (Table 5). Isotopic ^{28}Si-^{30}Si or Si-Ge substitutions (Gabelico-Robert and Tarte, 1981 ; Tarte et al., 1973 ; Lazarev, 1972) and calculations including force constants (Lazarev, 1974) have been helpful in assigning the vibrational bands due to Si$_2$O$_7$ groups.

From Table 5, it can be seen that only frequencies due to Si-O-Si motions are clearly assigned. Bands arising from SiO$_3$ stretching cannot be precisely determined, because no fully polarized spectra have been obtained.

7.3. Si$_2$O$_7$ in lawsonite

Seven IR bands due to Si$_2$O$_7$ stretching motions are expected (section VII.1). In accordance with the authors quoted above and the data in Table 3, a tentative assignment of IR reflection bands is proposed (Table 2) :
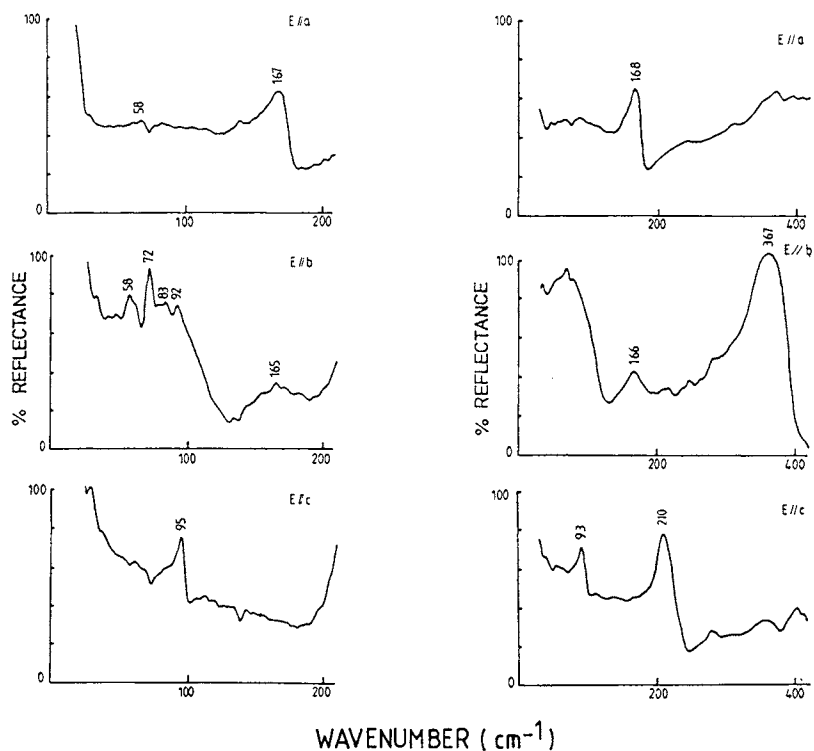
a)
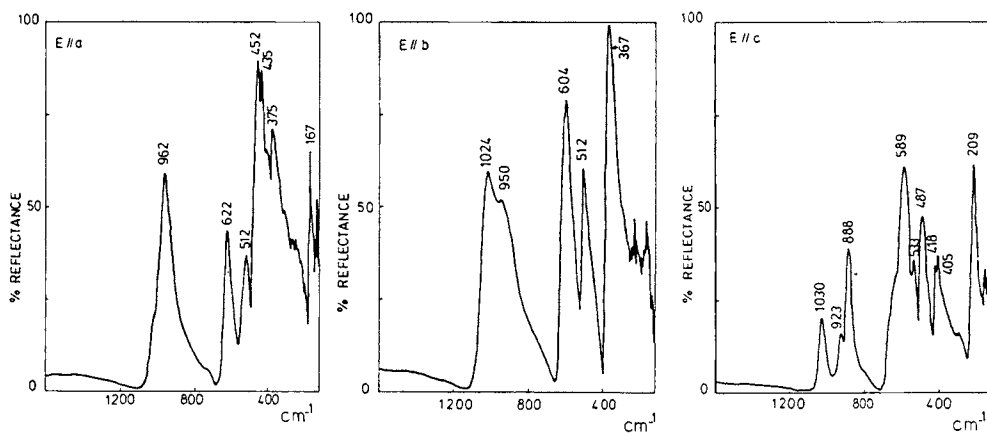
b)

Fig. 3. Reflection spectra of lawsonite with the electric vector of the infrared radiation oriented parallel to the *a, b,* and *c* axes of lawsonite. A : Low-frequency region. B : Mid-frequency region, resulting of the addition of two spectra : 100-700 cm^{-1} and 700-1600 cm^{-1}.
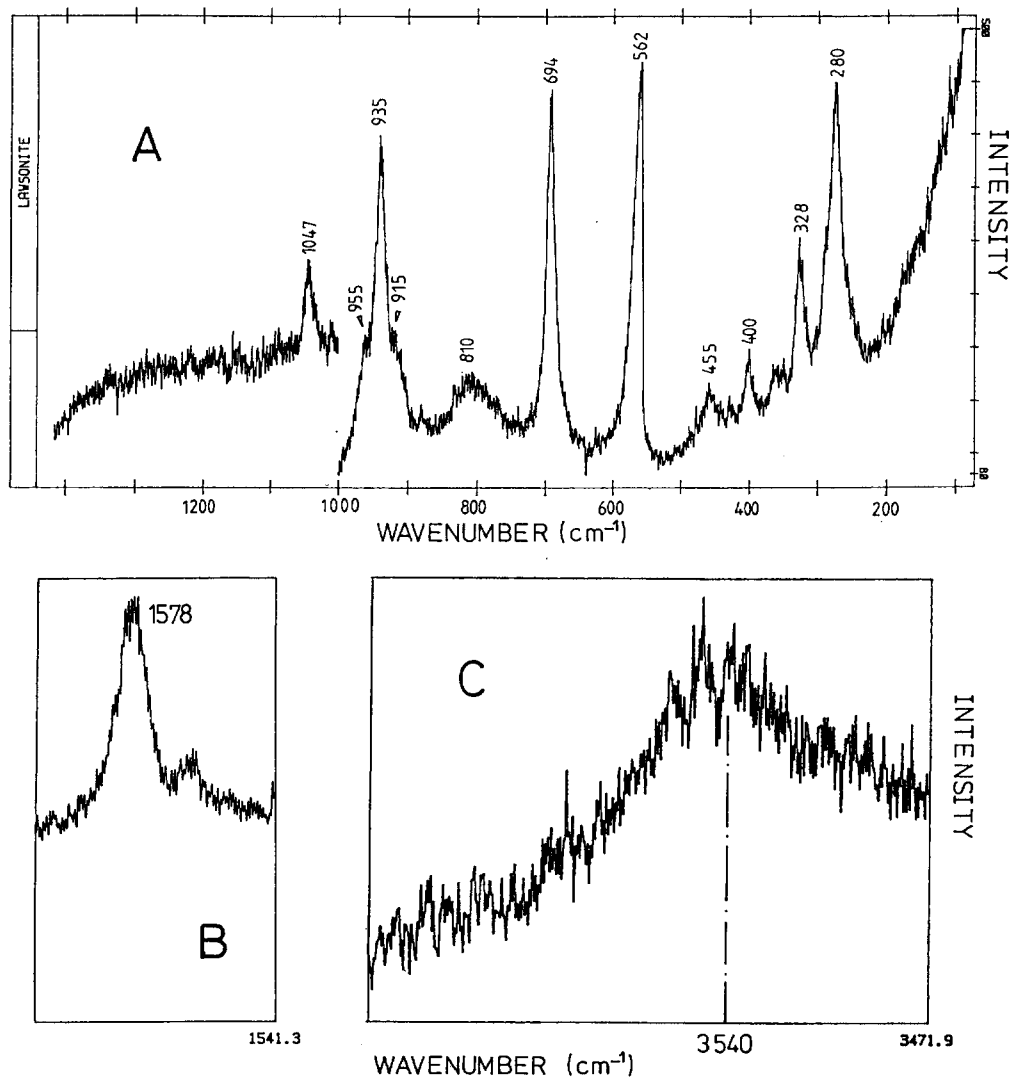
Fig. 4. Typical micro-Raman spectra of lawsonite obtained from petrographic thin-sections. A : Three spectra are additioned : 80-500 cm⁻¹, 500-1000 cm⁻¹ and 1000-1400 cm⁻¹. B : H_2O bending. C : OH and H_2O stretching region.

ν_{as} Si-O-Si	1030 cm⁻¹ (B_{1u})
ν'_{as} SiO₃	923 cm⁻¹ (B_{1u})
ν_{as} SiO₃	962 cm⁻¹ (B_{3u})
	950 cm⁻¹ (B_{2u})
ν'_s SiO₃	888 cm⁻¹ (B_{1u})
ν_s Si-O-Si	622 cm⁻¹ (B_{3u})

The band at 962 cm⁻¹ is strongly assymmetric on its right handside. Therefore, another band at $\simeq$ 880-900 cm⁻¹ may be present which is probably due to ν_s SiO₃.

The band at 1024 cm⁻¹ may arise from a vibrational mode of OH (Vedder and McDonald, 1963 ; Ryskin, 1974 ; Winkler, pers. comm.) or an overtone of the 512 cm⁻¹ mode. The OH ion lies in the (a, c) plane ; the motion which displaces the proton perpendicular to this plane is of the A'' in site symmetry type and would give rise to absorption when E $\parallel$ b (B_{2u} type, see correlation scheme). The same motion also yields an inactive mode, A_u.

Table 3. Vibrational Raman frequencies of lawsonite, symmetry types and possible assignments.

frequency	symmetry	assignment
90		
115		
145-150		
280		
289		
328		
372		
400		
455		
461		
508		
562		
578		
638		
694	A_g	ν_s Si-O-Si
809	B_{1g}, B_{3g} ?	ν AlO$_6$
912	B_{2g}	ν'_s, ν'_{as} SiO$_3$
916	A_g	ν_s SiO$_3$
936	A_g	ν_{as} SiO$_3$
959	B_{1g}	ν_{as} SiO$_3$
963	B_{3g} ?	ν'_{as} SiO$_3$
1047	B_{2g}	ν_{as} Si-O-Si
1578		δ H$_2$O
3554		

Frequencies in cm^{-1}.

Three Raman bands of A_g type are expected and observed (Table 3) :
695 cm^{-1} ν_s Si-O-Si
916 cm^{-1} ν_s SiO$_3$
936 cm^{-1} ν_{as} SiO$_3$
Two bands of B_{1g} type are observed whereas only one is expected arising from ν_{as} SiO$_3$. By comparison with other pyrosilicates (Table 5), this motion is more likely assigned to the 959 cm^{-1} band. Contrarily, only two bands of B_{2g} symmetry appear instead of the three expected. The 1047 cm^{-1} one is easily assigned to ν_{as} Si-O-Si. The 912 cm^{-1} band is thus supposed to arise from ν'_s SiO$_3$ + ν'_{as} SiO$_3$.

Because of the poor quality of the B_{3g} polarization spectra, no obvious attribution of modes can be made. The correlation scheme shows that one mode should be present due to ν'_{as} SiO$_3$. 809 cm^{-1} is a too low frequency for such a motion. Thus, ν'_{as} SiO$_3$ is preferentially attributed to the 963 cm^{-1} band. The 809 cm^{-1} mode (B_{1g}, B_{3g}) probably arises from a AlO$_6$ stretching vibration (Tarte, 1967).

The assignments of high-frequency modes in IR and Raman spectra are summarized in Tables 2 and 3. No Raman study of H$_2$O and OH vibrations was performed.

Table 4. Symmetry types of the stretching vibrations of free Si$_2$O$_7$ in the C$_{2v}$ configuration (after Lazarev, 1972).

motion	symmetry type
ν_s Si-O-Si	A_1
ν_{as} Si-O-Si	B_1
ν_s SiO$_3$	A_1
ν'_s SiO$_3$	B_1
ν_{as} SiO$_3$	A_1, B_2
ν'_{as} SiO$_3$	A_2, B_1

Table 5. Stretching frequencies of Si$_2$O$_7$ in some minerals with their assignment.

compound	isolated Si$_2$O$_7$		thortveitite		fresnoite		krentolite		bertrandite	
	D$_{3d}$	C$_{2h}$	C$_{2h}$		C$_{2v}$		C$_{2v}$		C$_{2v}$	
	calculated		calc.	IR	IR	Raman	IR	Raman	IR	Raman
ν_{as} Si-O-Si	1159	1166	1166	1169	1039	—	1027	—	1093	1076
ν'_{as} SiO$_3$	964	937	962	975	—	994	933	942	1029	—
ν_{as} SiO$_3$	964	928	956	—	915	928	901	—	1013	—
ν_s SiO$_3$	883	824	857	—	861	860	885	887	987	990
ν'_s SiO$_3$	820	805	846	852	968	960	875,830	820	939,901	928
ν_s Si-O-Si	611	618	639	—	665	666	690	689	638,688	694
ref.	1		2		3		4		5	

References - 1 : Lazarev, 1974 ; 2 : Lazarev, 1972 ; 3 : Gabelica-Robert and Tarte, 1981 ; 4 : Gabelica-Robert and Tarte, 1979 ; 5 : Hofmeister et al., 1987.
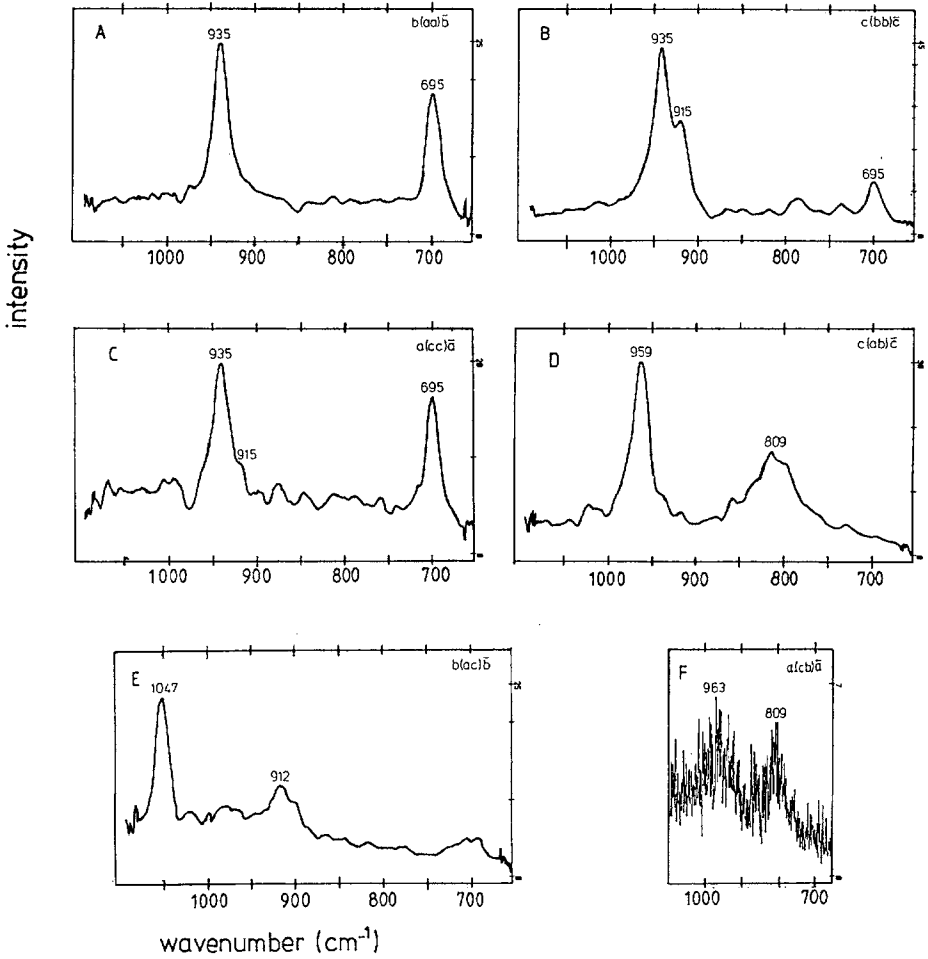
Fig. 5. Oriented Raman spectra of lawsonite in the high frequency region. A,B,C : A_g modes. D : B_{1g} modes. E : B_{2g} modes. F : B_{3g} modes.

Conclusions

IR and Raman spectroscopic data – combined with denumbering – have lead to a description of the vibrations of lawsonite. The bands lying in the frequency range 600-1100 cm^{-1} have been attributed to specific stretching vibrations of the Si_2O_7 units present in the structure. These results, combined with Brillouin measurements, will enable us to propose a density of state for lawsonite which can then be used for modelling its thermodynamic properties.

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