STUDY OF POLARIZATION RAMAN SPECTRA OF NATURAL THOMSONITE

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The polarization Raman spectra were measured for a single crystal of thomsonite, a natural zeolite. The spectra were scanned in the wavenumber region of 50—4 000 cm^{-1} at room temperature. The results are discused in terms of the structure of the mineral under study.

Thomsonite, $Na_2Ca_4[Al_{10}Si_{10}O_{40}].12\,H_2O$, crystal space group[1] C_{2v}^{10} – *Pnn*2, belongs, according to Meier[2], to the 5th structural group of zeolites. Crystals of minerals in this group display a characteristic fibrous habit extended along the crystallographic *c*-axis. This crystal morphology is explained so that the alumosilicate skeleton is built up of mutually linked chains of (Al, Si)O_4 tetrahedra, each chain being constituted by five-membered rings of the tetrahedra, which form the secondary building units of the 4-1 structure. Between each two chains, parallel with the crystallographic *c*-axis, channels appear, in which cations and water molecules are situated. The Si : Al ratio in the structure equals unity. Crystals of this symmetry group are non-centrosymmetrical; they are optically biaxial (+) with the principal refractive indices $N_p = 1{\cdot}497$, $N_m = 1{\cdot}513$, $N_g = 1{\cdot}518$.

Symmetry Modes and Components of the Polarizability Tensor

A unit cell of the crystal contains two formula units $Na_2Ca_4Al_{10}Si_{10}O_{40}.12\,H_2O$, to which 612 phonon branches correspond. The number, symmetry, and activity of the vibrations have been calculated based on factor group analysis[3], whose results are given in Table I. The correlation diagram is given in the monography[3].

The polarizability tensor components pertaining to the various symmetry species are, according to Loundon[4],

$$\underset{A_1(z)}{\begin{Vmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{Vmatrix}} \quad \underset{A_2}{\begin{Vmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{Vmatrix}} \quad \underset{B_1(x)}{\begin{Vmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{Vmatrix}} \quad \underset{B_2(y)}{\begin{Vmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{Vmatrix}} .$$

All the modes are Raman active; the A_1, B_1, and B_2 modes are also infrared active, thus both the longitudinal optical (LO) nad transversal optical (TO) components of the polar modes can be observed in the Raman spectra. Since the crystal is optically biaxial, pure TO and pure LO components generally will not occur. The modes were not analyzed theoretically in this work to determine the selectivity rules and activities, and they will be regarded as degenerate.

TABLE I

Results of factor group analysis

C_{2v}	Sum of vibrations	Internal modes	Translatory modes	Rotatory modes	Acoustic modes	Activity[a]
A_1	153	132	14	6	1	IR, Ra
A_2	153	132	15	6	0	Ra
B_1	153	132	14	6	1	IR, Ra
B_2	153	132	14	6	1	IR, Ra

[a] IR — infrared, Ra — Raman.

TABLE II

Assignment of the experimental fraquencies to the vibrations

Vibration		Frequency, cm^{-1}
ν_{sym}	T—O	720
ν_{as}	T—O	1 055, 1 028, 999, 982
δ	O—T—O	408
ν_{sym}	O—H	3 480
ν_{as}	O—H	3 384, 3 544
δ	H—O—H	1 630
$\nu_{torsion}$	H_2O	630, 480
ν_{ext}	TO_4	1 090
pore opening		330, 364, 368
2δ	H—O—H	3 230
ν_T	H_2O	309
ν_T	lattice	115, 179, 201, 218, 225, 280
ν_T	O—O	148, 149
ν_{sym}	H...H	168
ν_{as}	H...H	169

TABLE III

Polarization Raman spectra of thomsonite[a] single crystal

Symmetry and polarization											
A_1			A_2			B_1			B_2		
$Z(XX)\ Y$	$X(YY)\ Z$	$X(ZZ)\ Y$	$X(YX)\ Y$	$X(YX)\ Z$	$Z(YX)\ Y$	$X(ZX)\ Y$	$X(ZX)\ Z$	$Z(ZX)\ Y$	$X(YZ)\ Y$	$X(YZ)\ Z$	$Z(YZ)\ Y$
—	—	—	—	—	—	115 m	115 m	115 m	100 vw	100 vw	100 vw
148 m	148 vw	148 m	—	—	—	—	—	—	149 w	149 w	149 w
168 m	168 vs	168 m	—	—	—	—	—	—	169 w	169 w	169 w
—	—	—	179 w	179 w	179 m	—	—	—	—	—	—
—	—	—	191 m	191 s	191 m	190 w	190 w	190 w	—	—	—
201 m	201 m	201 w	—	—	—	—	—	—	—	—	—
—	—	—	218 m	218 w	218 w	225 w	225 w	225 w	225 w	225 w	225 w
—	—	—	—	—	—	—	—	—	280 w	280 w	280 w
309 m	309 vw	309 w	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	330 vw	330 vw	330 vw
368 w	368 w	368 w	—	—	—	—	—	—	364 w	364 w	364 w
408 m	408 m	408 m	—	—	—	—	—	—	—	—	—
480 m	480 m	480 m	—	—	—	—	—	—	—	—	—
630 vs	630 vs	630 m	—	—	—	—	—	—	—	—	—
720 w	720 w	720 vw	—	—	—	—	—	—	—	—	—
982 vs	989 m	989 w	—	—	—	—	—	—	—	—	—
999 m	999 vw	—	—	—	—	—	—	—	990 w	990 vw	990 m
1 028 m	1 028 vs	—	—	—	—	—	—	—	—	—	—
1 055 m	1 055 vs	1 055 vs	—	—	—	—	—	—	1 055 w	1 055 w	1 055 w
1 090 w	1 090 w	1 090 w	—	—	—	1 090 w	1 090 w	1 090 w	1 090 w	1 090 w	1 090 w
1 630 w	—	1 630 w	—	—	—	—	—	—	—	—	—
3 230 vw	3 230 w	3 230 vw	—	—	—	—	—	—	3 230 vw	3 230 vw	—
3 384 vw	3 380 vs	3 384 m	—	—	—	—	—	—	3 384 m	3 384 w	3 384 vw
3 480 vs	3 480 w	3 481 w	—	—	—	—	—	—	—	—	—
3 544 vw	3 530 w	3 539 vs	—	—	—	—	—	—	3 544 w	3 532 w	3 539 m

[a] Band positions in cm^{-1}; band intensities: vs very strong, s strong, m medium, w weak, vw very weak.

The band intensities for the B symmetry modes depend on the phonon distribution density along the crystallographic directions.

EXPERIMENTAL

The polarization Raman spectra of a thomsonite single crystal (Děčín — Bohemia), size 10 × × 5 × 0·5 mm, were measured on a SPEX 14018 Raman spectrometer equipped with standard photon counting detection. The excitation was accomplished by using an Ar-ion laser working on the wavelength 514·5 nm. The spectral slit width was 2—4 cm^{-1}. The spectra were recorded in conventional rectangular geometry: $Z(XX)\,Y$, $Z(YY)\,X$, $X(ZZ)\,Y$, $X(YX)\,Y$, $Z(XY)\,Y$, $Z(XY)\,X$, $Z(YX)\,Y$, $X(ZX)\,Y$, $Z(XZ)\,Y$, $Z(XZ)\,Y$, $Z(XZ)\,X$, $X(YZ)\,Y$, $Z(YZ)\,X$, $Z(YZ)\,Y$ using a half-wave plate and a foil polarizer. All spectra were scanned at room temperature. The precision of reading the band positions was $\pm 1\ \text{cm}^{-1}$.

RESULTS AND DISCUSSION

The results of measurements of the polarization Raman spectra of thomsonite single crystal and the band assignment are given in Tables II and III, respectively. The polarization spectra exhibit well-resolved bands belonging to the various vibrations and symmetry species. The background is very low. The half band width is in average $2-10\ \text{cm}^{-1}$. For the totally symmetric modes, the peak intensities are considerably dependent on the phonon densities in the various crystallographic directions. A mixing of the symmetry components and some band shifts may be due to the finite solid angle from which the scattered light was recorded and to the optical activity of the crystal, where owing to the effect of the gyration moment, rotation of the planes of polarization of the scattered light takes place. The frequency shifts in the various polarization directions may be accounted for by the dispersion between the TO and LO frequencies of the polar modes.

Because of the complexity of the crystal structure of thomsonite and the great number of atoms in a unit cell, the frequencies of the various symmetry modes could not be calculated theoretically; the assignment suggested is based on published data of related substances[5,6].

SUMMARY

The observed wavenumbers in the polarization spectra of thomsonite single crystal can be essentially divided into four groups:
1) optical translatory lattice modes and translatory-rotatory modes of bonded water ($90-600\ \text{cm}^{-1}$ range), *2*) Internal vibrations within the (Al, Si)O_4 tetrahedra (400 to 1 100 cm^{-1} range). *3*) Internal vibrations of bonded water ($1\,600-3\,600\ \text{cm}^{-1}$ range). *4*) External vibrations between the tetrahedra ($300-1\,200\ \text{cm}^{-1}$ range).

The translatory-rotatory vibrations of water indicate that water localized in the cavities is bonded to the skeleton oxygen atoms by one type of hydrogen bonding:

O···H—O—H···O, and is coordinated in the coordination sphere of the cations. From the shift of bands due to internal vibrations of the T—O bonds within the tetrahedra as compared with those for tetrahedrally bonded pure Si, the ratio of the atoms Si/Al = 1 and their irregular arrangement can be deduced. Similarly, knowing the shifts of the O—H bond stretching vibrations in comparison with the corresponding vibrations of water in the vapour phase, the O—O distance in the hydrogen bonding system can be read from the graph[3]; in the case in question it was about 0·280 nm. The external "pore opening" vibrations indicate that the bonds in the oxygen rings of the entrance channels are relatively strong and regularly arranged. The external vibrations between the tetrahedra point to relatively weak bonds in the crystal (xy) plane and strong bonds along the crystal c-axis.

It can be concluded that polarization Raman spectra of the mineral are a convenient source of rapid information on the structure and symmetry of bonds in thomsonite.

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