LASER RAMAN POLARIZATION SPECTRA OF NATURAL ZEOLITE-NATROLITE

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Received June 24th, 1980

Raman polarization spectra of single crystal of natrolite $Na_2Al_2Si_3O_{10}.2\,H_2O$ have been measured in the region 4 000 to 50 cm^{-1} at room temperature. The spectra have been measured in the conventional rectangular geometry. The found maxima of the polarization spectra of single crystal of the mineral investigated can be divided into four groups according to pertinence to individual vibrations: (*i*) translation and rotation vibrations of water molecules in interaction with the crystal lattice, (*ii*) internal vibrations of the bonds Al—O, Si—O inside the tetrahedrons, (*iii*) internal vibrations of bonds of the water molecules, (*iv*) external vibrations between the $(Al,Si)O_4$ tetrahedrons.

The aim of this report was to show possibilities of application of Raman polarization spectra to study of structural and physical properties of natural zeolite-natrolite $Na_2Al_2Si_3O_{10}.2\,H_2O$ whose space group[1] is $Fdd2 - C_{2v}^{19}$. According to Meier[2], natrolite belongs to the fifth structural group of zeolites having a characteristic fibriform structure of crystals. Such morphology is explained[3] by formation of long, mutually connected chains of tetrahedrons $(Al, Si)\,O_4$ (which are the basic building units of the structure) which lie parallel to the crystallographic direction [001]. Arrangement of the tetrahedrons in this direction forms a secondary building unit of the structure – $4-1$ (ref.[3]). Between the chains a two-dimensional system of channels is formed in which cations and water molecules are localized[1]. There are two water molecules for each Na^+ ion[1,3]. The bond lengths Si—O and Al—O and the bond angles O—(Al, Si)—O inside the tetrahedrons have various values due to $d\pi - p\pi$ interactions of the central atoms with the bridge oxygen atoms and due to action of local fields of the cations and the protons of water molecules on the bridge oxygen atoms. This fact causes a slight deformation of the tetrahedral arrangement, the T_d point symmetry group of these units being maintained.

Unit cell of natrolite[1] contains 8 structural units $Na_2Al_2Si_3O_{10}.2\,H_2O$ corresponding to 480 phonon branches. Number, symmetry, and activity of the individual vibrations in the spectra were calculated with the use of theoretical Factor-group analysis[4]. On the basis of these calculations the following complete representation of the Factor-group of the crystal C_{2v} was determined: $\Gamma_{opt} = 120\ A_1$ (i.r., R) + + 120 A_2 (R) + 120 B_1 (i.r., R) + 120 B_2 (i.r., R).

Table I shows the correlation diagram between the point group of tetrahedrons (T_d) and the Factor-group of the natrolite crystal (C_{2v}) (the both groups are identical for H_2O).

Determination of components of polarizability tensor according to Laundon[5] for the group C_{2v} revealed that a complete separation of individual symmetry modes can be expected in polarization spectra of the natrolite single crystal. The modes A_1, B_1, and B_2 are polar, and we can expect for them separation of the longitudinal optical (LO) and transversal optical (TO) components in the spectra. Theoretical analysis of activity of LO and TO components in the individual symmetries was not carried out in this study, their degeneration being presumed. In the case of optically biaxial crystals it is impossible to reach complete separation of the TO and LO components with the use of the rectangular geometry of spectral measurements.

EXPERIMENTAL

The Raman polarization spectra were measured with a natrolite single crystal (locality Zálezly, Bohemia) of 25 × 10 × 0·5 mm magnitude using a Raman spectrometer SPEX 14018 equipped with a standard detection device — photon counting. For excitation of the Raman transitions we used a gas Ar^+ ion laser working at the wavelength 514·5 nm. Spectral width of the slot was 2 to 4 cm^{-1}. The spectra were measured in the conventional rectangular geometry: *Z(XX) Y*, *Z(YY) X*, *X(ZZ) Y*, *X(YX) Y*, *Z(YX) Y*, *Z(YX) X*, *Z(YX) Y*, *X(ZX) Y*, *Z(XZ) Y*, *Z(XZ) X* *X(YZ) Y*, *Z(YZ) X*, *Z(YZ) Y* using the half-wave plate and foil polarizer. All the spectra were measured at room temperature. Accuracy of readings of the individual wave numbers from the spectra was ±1 cm^{-1}.

TABLE I

Correlation diagram between point group of tetrahedrons $(Al,Si)O_4$ and factor-group of natrolite crystal (C_{2v}^{19})

Point group of $(Al,Si)O_4$ T_d	Factor-group of the crystal C_{2v}
A_1 (R)	A_1 (i.r., R)
E (R)	A_1 (i.r., R) + A_2 (R)
F_2 (i.r., R)	$A_1 + B_1 + B_2$ (i.r., R)

RESULTS AND DISCUSSION

Table II shows the wave numbers read from the individual polarization Raman spectra of the natrolite single crystal. The individual measured spectra exhibit very well-resolvable maxima of the individual vibrations and symmetries. The background was very low. The spectra could be read almost from the excitation line of the laser. A certain penetration between some symmetry components can be due to the final space angle at which the scattered radiation was measured, to optical activity of the crystal (action of gyration moment causes rotation of polarization planes of radiation), to inaccuracy in the crystal orientation with respect to crystallographic directions, and to diffraction at microdislocations in the crystal structure. The wave number shifts in the individual polarizations can be due to dispersion between LO and TO frequences of the polar modes. Assignement of the wave numbers to the individual vibrations was carried out on the basis of experience and literature data[3,6].

The A_1 symmetry components exhibit a band with variable intensity along the individual polarization directions at the wave number 145 cm^{-1} which can be assigned to the translation vibration of the O···O bond in the hydrogen bridge. A band of this vibration is also seen in the A_2 and B_2 symmetries at 147 cm^{-1}. Bands of stretching vibration of the hydrogen bondings —H···O lie at 164 cm^{-1} (A_1) and 166 cm^{-1} (B_2). In all symmetry components the bands of low-frequency spectral region can be assigned to translation optical modes of the crystal lattice. At the wave numbers 273, 308, 362 cm^{-1} (A_1); 333 cm^{-1} (B_1); 328, 358 cm^{-1} (B_2) there are vibrations of oxygen rings of pore openings of the channel structure[6]. The bands at 416, 535 cm^{-1} (A_1); 413 cm^{-1} (A_2); and 520 cm^{-1} (B_1) belong to $\nu_4(\delta)$ vibration of O—(Al, Si)—O in the tetrahedrons[6]. Libration of the water molecules along the a and c axes of the molecule can be connected with the bands at the wave numbers 480, 600 cm^{-1} (A_1); 495, 589 cm^{-1} (A_2). These bands have different intensities in the individual symmetries. From the presence of the two bands it can be inferred that the water molecules localized in the zeolite cavities possess two degrees of freedom. At the wave numbers 706 and 728 cm^{-1} (A_1) there are $\nu_s(\nu\cdot)$ bands belonging to vibration of the (Al, Si)—O bonds inside the tetrahedrons. The presence of two close bands indicates inhomogeneous field of force in the tetrahedron. The bands with fine structure and splittings in the regions 1 085 – 969 cm^{-1} (A_1); 1 093 – 1 075 cm^{-1} (A_2); 1 093 – – 992 cm^{-1} (B_2) can be assigned to the $\nu_3(\nu_d)$ vibration of the (Al, Si)—O bonds[6]. The wave number shift of this vibration related to the same vibration of a tetrahedrally bound Si (*e.g.* in SiO_4 it is 1 163 cm^{-1}), and the published[3] graphs can be used for evaluation of the Si : Al atoms ratio in the structure. In the natrolite investigated this ratio was 3 : 2. Hence in accordance with chemical analysis the natrolite contains regular arrangement of Al and Si atoms in its structure. The vibration $\nu_2(\delta)$ of the water molecules lies at the wave number 1 640 cm^{-1}. In all the polarizations the bands within the range 3 544 to 3 230 cm^{-1} can be assigned to ν_1, ν_3 ($\nu\cdot$, ν_d) vibrations

TABLE II

Raman polarization spectra of single crystal of natural natrolite[a] in cm^{-1}

Symmetry and polarization											
A_1			A_2			B_1			B_2		
$Z(XX)Y$	$X(YY)Z$	$X(ZZ)Y$	$X(YX)Y$	$X(YX)Z$	$Z(YX)Y$	$X(ZX)Y$	$X(ZX)Y$	$Z(ZX)Y$	$X(YZ)Y$	$X(YZ)Y$	$Z(YZ)Y$
—	—	—	—	—	—	—	—	—	95 vw	95 vw	95 vw
—	—	—	—	100 vw	—	—	—	—	—	—	—
—	—	—	—	—	—	114 m	114 m	114 m	109 w	109 w	109 w
—	—	—	—	—	—	123 s	123 s	123 s	125 s	125 m	125 m
—	—	—	131 vw	131 w	131 vw	—	—	—	137 w	137 w	137 w
145 s	145 vw	145 m	147 w	147 m	147 w	—	—	—	147 m	147 m	147 m
164 m	164 vs	165 m	—	—	—	—	—	—	166 w	167 w	166 w
—	—	—	176 w	176 vs	176 m	—	—	—	—	—	—
—	—	—	188 m	188 s	188 m	187 w	187 w	187 w	—	—	—
199 m	198 m	199 vw	—	—	—	—	—	—	—	—	—
—	—	—	215 m	215 w	215 w	220 w	220 w	220 w	223 w	224 w	224 w
273 w	—	—	—	—	—	—	—	—	277 w	278 w	277 w
308 m	308 vw	309 w	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	333 w	333 w	333 vw	328 vw	328 vw	327 vw
362 w	362 w	362 w	—	—	—	—	—	—	358 vw	358 vw	358 vw
416 m	416 m	416 w	413 vw	413 m	413 w	—	—	—	—	—	—
480 vs	480 VS	482 w	495 w	493 vw	496 vw	—	—	—	—	—	—
535 s	535 m	535 m	—	—	—	520 vw	520 w	520 vw	—	—	—
600 vw	602 m	600 vs	589 vw	590 vw	588 vw	—	—	—	—	—	—
706 w	706 vw	706 w	—	—	712 w	—	—	—	—	—	—
728 vw	728 w	728 vw	—	—	—	—	—	—	—	—	—
969 vs	—	—	—	—	—	—	—	—	—	—	—

—	974 m	978 w	—	—	—	—	—	—	—	—	—
998 m	999 vw	—	—	—	—	—	—	—	992 vw	994 vw	993 vw
1 027 m	1 025 vs	—	—	—	—	1 012 vw	—	—	—	—	—
1 047 m	1 045 vs	1 045 vs	1 045 w	1 045 vw	1 045 vw	—	—	—	1 045 w	1 045 m	1 045 w
1 085 w	1 085 w	1 085 vw	1 086 w	1 087 vw	1 085 w	—	—	—	1 085 w	1 085 w	1 085 w
1 640 vw	1 640 w	1 640 vw	—	—	—	—	—	—	—	—	—
3 230 vw	3 230 w	3 230 W	—	—	—	—	—	—	3 230 w	3 230 vw	—
3 293 w	3 293 w	3 294 w	—	—	—	—	—	—	3 294 w	3 293 vw	—
3 384 vw	3 385 vs	3 382 m	3 384 vw	—	3 384 w	—	—	—	3 384 m	3 386 w	3 383 vw
3 470 vs	3 472 w	3 470 w	—	—	—	—	—	—	3 471 w	—	—
3 544 vw	3 545 vw	3 542 s	—	—	3 544 vw	3 544 w	3 544 w	3 544	—	3 544 vw	—

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[a] vs — very strong, s — strong, m — medium, w — weak, vw — very weak band.

of O—H bonds. The band width of this vibration indicates the presence of hydrogen bondings[7]. From the wave number shift of this vibration as compared with the bands of water in gaseous state, and on the basis of graphical evaluation[7] we could determine the O···O distance in the hydrogen bridge (290 pm).

From the discussion of the found wave numbers in the Raman polarization spectra of the natrolite single crystal it follows that these wave numbers can be divided into four groups according to their assignement to individual vibrations: *i*) optical translation modes of the lattice and translation-rotation modes of low-frequency motion of water molecules (the region (600 – 90 cm^{-1}), *ii*) internal vibrations of the (Al, Si)—O bonds (the region 1 100 – 400 cm^{-1}), *iii*) internal vibrations of bonds in water molecules (the regions 3 700 – 3 200 cm^{-1} and about 1 600 cm^{-1}), *iv*) external vibrations of the oxygen rings (about 350 cm^{-1}).

The difference between the found number of maxima in the experimental spectra and results of the theoretical Factor-group analysis can be explained by coalescence of some bands due to local fields in the real crystal and also to intensity lowering of other bands below the detection limits due to various physical effects.

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Translated by J. Panchartek.