

Raman polarization spectra of the natural zeolite analcime

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The Raman polarization spectra of monocrystal of the natural zeolite analcime were measured in the wavenumber range 50—4000 cm^{-1} at laboratory temperature. The spectra were taken in the conventional rectangular geometry: Y(ZZ)X, Y(XZ)X, Z(Y Y)X, Z(XY)X, Z(XX)Y, and X(YZ)Y.

The bands found in the Raman polarization spectra of monocrystal of the natural zeolite analcime may be assigned to particular vibrations and divided into three groups:

1. Optical translation vibrations of the lattice of crystal and translation-rotation vibrations of water molecules (wavenumber regions 50—300 and 350—680 cm^{-1});

2. Internal vibrations of bonds in the $(\text{Al}, \text{Si})\text{O}_4$ tetrahedrons (wavenumber regions 400—490 and 900—1100 cm^{-1});

3. Internal vibrations of bonds in water molecules (wavenumber regions 1580—1680 and 3300—3700 cm^{-1}).

These vibrations exhibit in the measured spectra well defined bands belonging to the symmetric components A_{1g} , E_g , F_{2g} which are not polarizable owing to the symmetry of crystal.

Были измерены поляризационные спектры комбинационного рассеяния света монокристалла натурального цеолита, а именно, анальцима в области волновых чисел 50—4000 см^{-1} . Измерения были проведены при комнатной температуре. Спектры записывались в конвенционной прямоугольной геометрии Y(ZZ)X, Y(XZ)X, Z(Y Y)X, Z(XY)X, Z(XX)Y, X(YZ)Y.

Полосы, найденные в спектрах комбинационного рассеяния можно вообще разделить на три группы по принадлежности к отдельным типам колебаний:

1. оптические трансляционные и вибрационные моды ячейки молекул воды (область волновых чисел 50—300 и 350—680 см^{-1}),

2. валентные колебания связей внутри тетраэдров $(\text{Al}, \text{Si})\text{O}_4$ (область волновых чисел 400—490 и 900—1100 см^{-1}),

3. валентные колебания молекул воды (область волновых чисел 1580—1680 и 3300—3700 cm^{-1}).

Эти колебания в измеренных спектрах выражены хорошо определяемыми полосами и относятся к системам симметрии A_{1g} , E_g , F_{2g} , которые являются неполяризованными.

Analcime — $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, space group O_h^{10} — Ia3d [1] belongs, according to Meier, into the first group of zeolites [2]. This mineral is one of the most frequent zeolites occurring in the nature. Though many studies were concerned with elucidation of its structure in the last decades, there is not yet full information about its arrangement and especially about precise localization of all cations and water molecules (admixed K^{1+} , Ca^{2+} , Fe^{3+} and sorbed water). On the basis of information hitherto known about the structure of this mineral, it may be assumed that each Na^{1+} cation which is localized in the channels formed by spatial disposition of the aluminosilicate framework is surrounded by two water molecules and four oxygen atoms of the framework in configuration of distorted octahedron. The content of water bound in the cavities of zeolite is linearly dependent on the content of the Si atoms [1]. The number of water molecules increases with number of the Si atoms in the structure while the number of the Na^{1+} ions decreases. Clusters of the (Al, Si) O_4 tetrahedrons in the space give rise to secondary building units of the structure. These units were denoted by Meier [2] S4R. Besides these units, we can also observe other units consisting of six-membered rings in the UDUD order [2] which are parallel with the crystallographic [111] direction and form entrance holes of the one-dimensional system of channels in the mineral. The Si/Al atomic ratio in the structure varies in the range 1.8—2.8. The crystals of this mineral are quite temperature stable. It has been established that no structural changes take place up to the temperature of 700°C [3].

The crystals of analcime have a centre of symmetry, are optically isotropic and their index of refraction varies in the range $n_{\text{Na}_a}^{20} = 1.479$ —1.493.

Theoretical

A unit cell of the crystal of analcime contains 16 structural units $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, i.e. 208 atoms. The factor group of crystal is O_h and its full representation for a crystal of analcime is

$$\begin{aligned} \Gamma_{\text{vib}} = & 13A_{1g}(\text{R}) + 13A_{2g} + 26E_g(\text{R}) + 39F_{1g} + 39F_{2g}(\text{R}) + \\ & + 13A_{1u} + 13A_{2u} + 26E_u + 39F_{1u}(\text{i.r.}) + 39F_{2u} \end{aligned}$$

As a crystal of analcime has the centre of symmetry, a half of the symmetry components is active in the infrared spectra while another half is active in the Raman spectra. Therefore we cannot expect a separation of the longitudinal optical modes (LO) from the transversal optical (TO) symmetrical modes in the Raman spectra. As results from the theory [4, 5], these spectra may contain only the bands corresponding to the symmetry components A_{1g} , E_g , and F_{2g} the intensities of which are dependent on density of the phonons in particular crystallographic directions. A full separation of components of the polarizability tensor may be found for the symmetry components $F_{2g}(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$.

The correlation diagram of the point groups of "free" molecules, site groups, and factor group of a crystal is represented in Table 1 [4].

Table 1

Correlation diagram of symmetry groups

Point group of molecule T_d (TO_4)	Site group C_2	Factor group of crystal O_h
ν_1 A_1	A	A_{1g} ν_1
ν_{2a} E ν_{2b}		E_g ν_{2a}, ν_{2b}
ν_{3a}, ν_{4a} ν_{3b}, ν_{4b} ν_{3c}, ν_{4c} F_2	B	F_{1g} $\nu_{3a}, \nu_{3b}, \nu_{3c}$
$C_{2v}(H_2O)$	D_3	O_h
ν_1, ν_2 A_1	A_1	A_{1g} ν_1
ν_3 B_2	E	E_g ν_2

T = Al, Si.

Experimental

The Raman polarization spectra were measured with a monocrystal of analcime (locality Husa at Marcinov) of 5 mm width (deltoid icositetrahedron) by the use of a Raman spectrometer SPEX 14018 equipped with a standard detection device (photon counting). An Ar^{1+} laser working at the wavelength of 514.5 nm was used to excitation. The spectral width of slit was 2–4 cm^{-1} . The measured spectra were taken in the conventional rectangular geometry Y(ZZ)X, Y(XZ)X, Z(YZ)X, Z(XY)Y, Z(XX)Y, X(YZ)Y by the use

Table 2

Raman polarization spectra of analcime monocrystal

A_{1g}			E_g			F_{2g}		
Z(XX)Y	Z(YY)X	Y(ZZ)X	Z(XX)Y	Z(YY)X	Y(ZZ)X	Y(XZ)X	Z(XY)X	X(YZ)Y
3565 m	3565 m	3564 s	—	—	—	—	—	—
—	—	—	1650 w	1651 w	1650 w	—	—	—
—	—	—	—	—	—	1012 m	1013 m	1012 m
—	—	—	480 s	480 s	480 vs	—	—	—
—	—	—	395 vw	397 vw	396 w	—	—	—
305 vw	305 vw	305 vw	—	—	—	—	—	—
202 vw	202 vw	202 vw	—	—	—	—	—	—
—	—	—	—	—	—	158 vw	158 vw	158 vw

vs — very strong, s — strong, m — medium, w — weak, vw — very weak.

of a half-wave plate and foil polarizer. The measurements were performed at laboratory temperature.

The results obtained by measuring the Raman polarization spectra and empirical assignment of bands to individual vibrations are given in Tables 2 and 3.

Table 3

Empirical assignment of wavenumbers to individual vibrations

Wavenumber, cm^{-1}	Vibration
3564, 3565	O—H stretching A_{1g}
1650, 1651	H—O—H bending E_g
1012, 1013	(Al, Si)—O stretching F_{2g}
480	O—(Al, Si)—O bending E_g
395, 396, 397	Water libration E_g
305	Water translation A_{1g}
202, 158	Optical translational vibration of the crystal lattice A_{1g}, F_{2g}

Discussion

The measured polarization spectra of analcime are in fairly good agreement with theoretical requirements which have been obtained by calculation from the factor group analysis [4] and from the selection rules derived for optically active phases. The background of all measured spectra is relatively low. The intensities of bands of internal vibrations exhibit dependence on the densities of phonons along bond vectors in different crystallographic directions. The bands of individual vibrations corresponding to symmetrical types E_g and F_{2g} which are twice or three times degenerated do not split in the spectra owing to the effect of high symmetry fields. They occur as broader, simple bands (stretching vibrations O—H and (Al, Si)—O). The assignment of bands to individual vibrations on the basis of data about similar substances taken from literature [6] seems to be unambiguous.

Conclusion

The vibrations found in the Raman polarization spectra of a monocrystal of natural zeolite — natrolite can be, in principle, divided into three groups:

1. Optical translation and translation-rotation vibrations of crystal lattice and water molecules (wavenumber region $90\text{--}400\text{ cm}^{-1}$);
2. Stretching vibrations of bonds inside the $(\text{Al, Si})\text{O}_4$ tetrahedrons (wavenumber region $400\text{--}1200\text{ cm}^{-1}$);

3. Stretching vibrations of bonds in the H_2O molecules (wavenumber region $1600\text{--}3700\text{ cm}^{-1}$).

It may be deduced from the analysis of vibrations of the first group that the water molecules are linked by one type of hydrogen bonds to the bridge atoms of the Al—O—Si oxygen in isolated positions in the channels of the structure and have one degree of freedom of translational-rotational motion along the axis c of water molecule.

We can approximately graphically evaluate the ratio of the Si/Al atoms in the framework of mineral from the shift in wavenumbers of the stretching vibrations of the $(\text{Al, Si})\text{—O}$ bonds with respect to this vibration of the pure Si—O bond because the wavenumber of this stretching vibration shifts towards lower wavenumbers with increasing content of aluminium in the structure [1]. By using the published graph [1], it has been ascertained that this ratio is equal to 2.8 for analcime.

From the shift in wavenumber of the stretching vibration of the O—H bonds with respect to equal vibration of water vapour (3750 cm^{-1}), it has been established on the basis of graphical evaluation [7] that the $\text{O}\cdots\text{O}$ distance coming into consideration for the formation of an $\text{O}\cdots\text{H—O}$ hydrogen bond is equal to 0.285 nm . This fact enables us to assume the presence of medium strong hydrogen bonds.

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