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Infrared Studies of Natural Topaz

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Natural crystals of topaz $[\text{Al}(\text{OH}, \text{F})]_2\text{SiO}_4$ from three localities (yellow from Brazil, pink from Africa, and blue from unknown locality) are studied at RT by using the IR technique. Infrared signals arising from stretching and bending modes of OH^- ions, SiO_4 tetrahedra, and $\text{Al}(\text{OH}, \text{F})\text{O}_4$ octahedra are detected. Some peaks which according to theoretical considerations are expected to attain first-order activity, are not observed in this study either because of their low intensity or/and that they are overlapped by stronger bands.

Natürliche Topaskristalle $[\text{Al}(\text{OH}, \text{F})]_2\text{SiO}_4$ von drei Fundstätten (gelb aus Brasilien, rosa aus Afrika, blau unbekannter Herkunft) werden bei Raumtemperatur mittels IR-Technik untersucht. IR-Signale, die von Streck- und Biegemoden von OH^- -Ionen, SiO_4 -Tetraedern und $\text{Al}(\text{OH}, \text{F})\text{O}_4$ -Oktaedern herrühren, werden gefunden. Einige Maxima, die nach theoretischen Betrachtungen Aktivität erster Ordnung zeigen sollten, werden nicht beobachtet, entweder wegen zu geringer Intensität oder/und weil sie mit stärkeren Banden überlappen.

1. Introduction

Topaz is an aluminum fluorosilicate $[\text{Al}(\text{OH}, \text{F})]_2\text{SiO}_4$, the structure of which is an interweaving of silica tetrahedra and octahedral sites of the aluminum. It crystallizes in the orthorhombic system with a tetramolecular unit cell having the edge lengths [1]

$$a_0 = 0.46499(3) \text{ nm}, \quad b_0 = 0.87968(6) \text{ nm}, \quad c_0 = 0.83909(5) \text{ nm}.$$

The space group is D_{2h}^{16} in the orientation P_{bnm} . The structure is based on monolayers of oxygen (A) alternating with layers of composition F_2O_1 (B, C) in the close-packed sequence ABAC, with fluorine substituting for OH^- [1]. The key structural unit is a crankshaft chain of edge-sharing AlO_4F_2 octahedra and corner-sharing SiO_4 tetrahedra running parallel to the z -axis (Fig. 1).

2. Theoretical Background

The interpretation of the IR spectra of crystals with more than one structural unit in the primitive cell is rather difficult because of the big number of fundamental frequencies which happen to be IR active due to the low symmetry. Therefore, a detailed assignment of the observed frequencies to the different vibrational modes is nearly impossible. In such cases, simplified methods must be used [2]. If for example a solid $\text{A}_x\text{B}_y\text{O}_z$ is constituted of AO_p and BO_r co-ordinated groups, two extreme cases must be considered:

1. AO_p and BO_r groups have rather different vibrational frequencies: in this case, the interaction between these groups is weak or negligible, and they may be considered as

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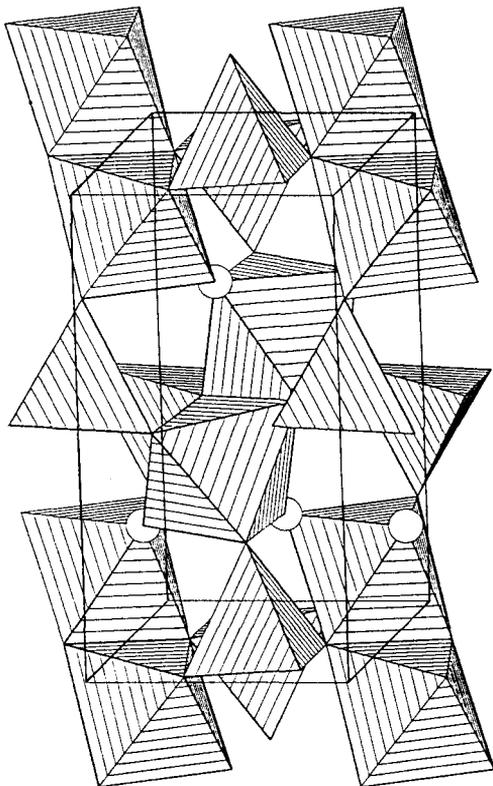


Fig. 1. The crystal structure of topaz $\text{Al}_2\text{SiO}_4(\text{OH}, \text{F})_2$. There is a single Si site in tetrahedral coordination and a single Al in octahedral coordination. The F (circle) bonds only to Al

vibrating independently. This is the case for a large series of ortho-silicates and ortho-germanates.

2. AO_p and BO_p groups have similar vibrational frequencies: in this case, the interaction between the groups may be so large that the concept of separate vibrations is meaningless. The observed signals are considered as arising from the vibrations of several groups, or of the unit cell taken as a whole.

As indicated by Tarte [2] the factors that influence the vibrational frequencies of a co-ordinated group AO_p (apart from the chemical nature and the valence state of the cation A) are:

- (i) The co-ordination number n (the smaller the co-ordination number the shorter the bond length, and therefore the vibrational frequencies are higher).
- (ii) The influence of the neighbouring groups which cause distortion or deformation of the specific group AO_p . This deformation is most significant when the AO_p groups are interlinked by common oxygen atoms in which case they are called condensed, otherwise isolated. The stretching frequencies of condensed AO_p are higher than those of the isolated group because of the strong interactions between neighbouring (identical) groups.

Since the spectra are taken at RT, the possibility of finding the groups at the ground state is much higher than any other one. Considering that the ground state $|g\rangle$ is the initial state for all the transitions and ignoring anharmonicity and higher-order expansion terms of dipole moment μ , only fundamental transitions are allowed and have observable intensities. Furthermore, in order a transition to be allowed, the corresponding amplitude $\langle i | \mu | g \rangle$ should be non-zero. This could occur, according to group theory if the $|i\rangle$ excited state contains the irreducible representation of the electric dipole moment μ that is transformed as x, y, z (since the ground state $|g\rangle$ belongs to the totally symmetric species A_1).

It is well-known that when a molecule unit is embedded in a crystal its symmetry is lowered because of the distortion caused by the surrounding lattice [3]. Consequently, a permanent dipole $\langle g' | r | g' \rangle \neq 0$ moment may appear, where r is the space vector and $|g'\rangle$ represents the ground state of the distorted unit. As a result, a non-active mode of the unit may become active. The interaction energy between the charge distribution in the unit and

the electrostatic crystal field is given by $H' = \int \rho(r) V(r) dr$, where $\rho(r)$ is the charge density in the unit and $V(r)$ the potential energy of the crystal field.

Expanding $V(r)$ we obtain

$$H' = V^0 \int \rho(r) dr + \sum_i \left(\frac{\partial V}{\partial r_i} \right)_0 \int \rho(r) r_i dr + \frac{1}{2!} \sum_{ij} \left(\frac{\partial^2 V}{\partial r_i \partial r_j} \right)_0 \int \rho(r) r_i r_j dr + \dots \quad (1)$$

or

$$H' = qV^0 - \sum_i \mu_i E_i - \sum_{ij} Q_{ij} \frac{\partial E_i}{\partial r_j} + \dots \Rightarrow H' = H^0 + H^1 + H^2 + \dots$$

The terms H^0, H^1, H^2, \dots correspond to the interaction energy of different multipoles induced in the unit by the crystal field. In our case the only significant term is $H^1 = \sum_{i=1}^3 \mu_i E_i$.

This interaction energy modifies the functions $|g\rangle$ and $|f\rangle$ (the ground state and an excited state of the free unit, respectively) as follows:

$$\begin{aligned} |f'\rangle &= N_f |f\rangle + |f^1\rangle + |f^2\rangle + \dots, \\ |g'\rangle &= N_g |g\rangle + |g^1\rangle + |g^2\rangle + \dots, \end{aligned} \quad (2)$$

where $|f^1\rangle, |g^1\rangle$ are functions of the free unit which they account for the first-order corrections, $|f^2\rangle, |g^2\rangle$, etc. and N_f, N_g are normalization factors.

Thus, it is clear that even if $\langle f | \hat{M} | g \rangle = 0$, where \hat{M} is the dipole moment operator, the transition amplitude $\langle f' | \hat{M} | g' \rangle$ of the mixed functions $|f'\rangle, |g'\rangle$ may be non-zero, so that the above transition will be allowed. In the first-order approximation it is

$$\langle f' | \hat{M} | g' \rangle^1 = N_f^1 N_g^1 (\langle f | \hat{M} | g^1 \rangle + \langle f^1 | \hat{M} | g \rangle). \quad (3)$$

According to time independent perturbation theory $|f^1\rangle = \sum_{j \neq f} \langle f | \hat{M} | j \rangle / (E_f^0 - E_j^0)$. Substituting in (3) we have

$$\langle f' | \hat{M} | g' \rangle^1 = N_f^1 N_g^1 \left(\sum_{i \neq g} \frac{\langle f | \hat{M} | i \rangle \langle i | H^1 | g \rangle}{E_g^0 - E_i^0} + \sum_{j \neq f} \frac{\langle f | H^1 | j \rangle \langle j | \hat{M} | g \rangle}{E_f^0 - E_j^0} \right), \quad (4)$$

where $|i\rangle$ and $|j\rangle$ refer to intermediate states. In order $\langle f' | \hat{M} | g' \rangle$ to be non-zero, at least one of the several terms in the summation of the above equation should be non-vanishing. This happens when the terms $\langle f | \hat{M} | i \rangle$ and $\langle i | H^1 | g \rangle$ attain non-vanishing finite values simultaneously. The amplitude $\langle i | H^1 | g \rangle$ is non-zero only when the state $|i\rangle$ belongs to the symmetry species Γ of the non-zero components of the dipole moment of the unit, μ_x and/or μ_y and/or μ_z . The amplitude $\langle f | \hat{M} | i \rangle$ is non-zero when $|f\rangle$ belongs to the symmetry species of $\Gamma(\hat{M}) \otimes \Gamma$.

3. Experimental

The infrared absorption spectra were recorded on a Jasco IR-700 double beam infrared spectrophotometer. The used samples were pellets prepared from powder by using the pressed KBr disc technique. 2 mg of the sample which has previously been crushed in an agate mortar is mixed with 600 mg KBr. The mixture is subjected to a pressure of about

10 t/cm² to give a permanently clear disc. The infrared spectra were taken at RT. It was necessary to grind the samples to a size less than the wavelength of the incident radiation in order to ensure the sharpest possible absorption bands and to reduce scattering. The time interval between preparation of discs and measurements was short enough to avoid absorption of the atmospheric water.

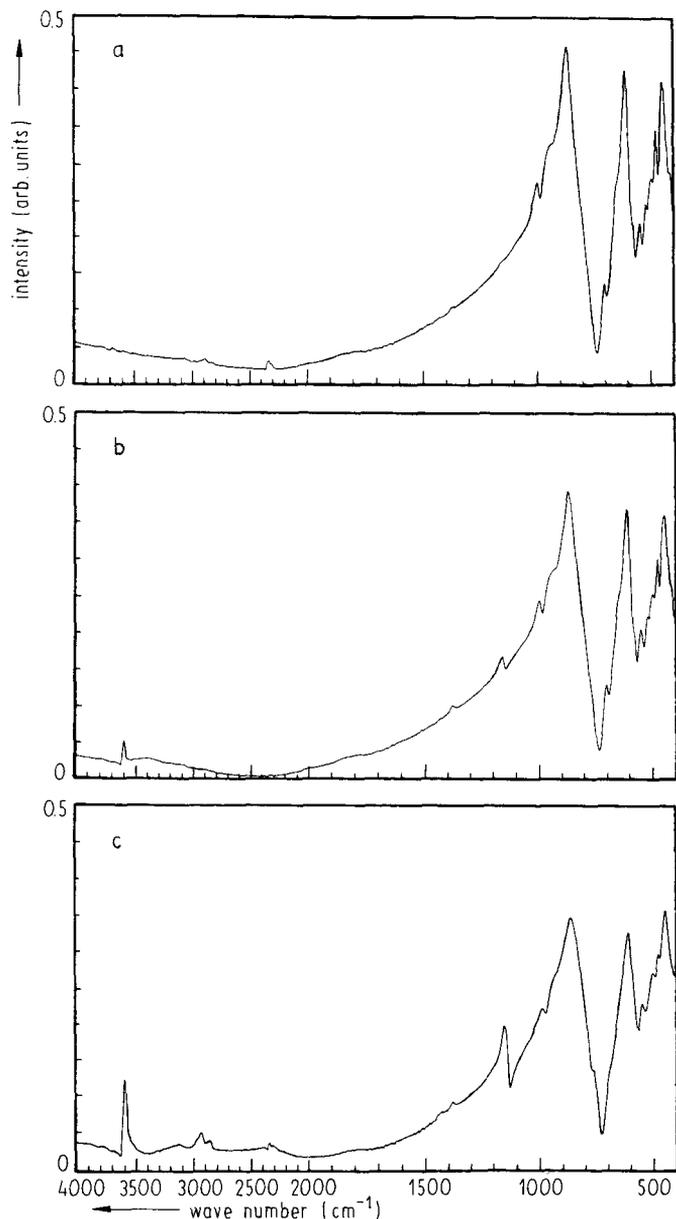


Fig. 2. The IR spectra of topaz crystals from three localities. a) Africa, b) unknown locality, c) Brazil

4. Results and Discussion

The observed absorption signals depicted in Fig. 2, can be classified as follows:

1. A sharp peak at 3600 cm^{-1} is present in the spectra of Fig. 2b and c. Since both the stretching modes of H_2O and OH^- ions are expected in the same region of 3100 to 3600 cm^{-1} an additional criterion should be used to distinguish between them. The primary distinction is the presence or absence of the water bending mode at 1600 cm^{-1} . In our spectra no such peak is observed so the sharp peak at 3600 cm^{-1} arises from OH^- ions [4]. The intensity of that peak is different in various samples, it is higher in the Brazil sample than in the blue one and it disappears in the African sample. Since OH^- substitutes for F^- it is likely that the African topaz is more fluorine-rich than the other two.

2. A peak at 1150 cm^{-1} could be attributed to the Al-OH bending mode. Its intensity is higher in the Brazil sample than in the blue one and it disappears in the African sample. These observations are in accordance with the height (and therefore with the concentration) of OH^- ions in the various samples [5].

3. In the region of 800 to 1050 cm^{-1} signals arising from the normal modes of SiO_4 tetrahedra are present. Since the SiO_4 groups are not interlinked and Si-O bonds are stronger than the Al-O bonds [5] the tetrahedra can be considered as isolated.

Group theory allows us to calculate the IR active fundamental transitions. The free SiO_4 unit has T_d point group symmetry and its character table is the following one.

Table 1

T_d	E	$8C_3$	$6S_4$	$3C_2$	$6\sigma_d$	
A_1	1	1	1	1	1	r^2
A_2	1	1	-1	1	-1	
E	2	-1	0	2	0	
T_1	3	0	1	-1	-1	(R_x, R_y, R_z)
T_2	3	0	-1	-1	1	(x, y, z)
Γ^D	15	0	-1	-1	3	

Γ^D is the 15-th reducible representation of the SiO_4 atom displacements (three degrees of freedom per atom \times five atoms). Using the formula: $n_i = 1/g \sum_{r=1}^g X_i^*(G_r) \times (G_r)$, Γ^D is reduced to $\Gamma^D = 3T_2 \oplus T_1 \oplus E \oplus A_1$ (where $g = 24$ is the order of the group, G_r the symmetry operations, $X(G_r)$ the character of G_r , and n_i the multiplicity of the i -th irreducible representation in Γ^D). The translations (x, y, z) and rotations (R_x, R_y, R_z) are transformed as indicated in the character table. Since the SiO_4 unit cannot rotate or translate freely in the crystal, we omit the corresponding irrep. So Γ^D becomes equal to $2T_2 \oplus E \oplus A_1$, which represent the internal vibrations of the unit. Consequently the internal modes of the SiO_4 group are transformed as the above irrep. Thus one single mode (A_1), one two-fold degenerated (E), and two three fold degenerated modes ($2T_2$) exist which have the following calculated frequencies, respectively [6]:

$$\omega_1 = 729\text{ cm}^{-1}, \quad \omega_2 = 473\text{ cm}^{-1}, \quad \omega_3 = 1031\text{ cm}^{-1}, \quad \omega_4 = 493\text{ cm}^{-1}.$$

It is easily concluded from the character table that IR active modes are only those which are transformed according to T_2 . The observed three peaks correspond to the triply

degenerated ω_3 which splits into three frequencies because of the distortion of the SiO_4 group. The frequencies of the bands in the region of 800 to 1050 cm^{-1} have similar values as in the olivines [7]. This is expected since topaz and olivines have similar structures and belong to the same space group D_{2h}^{16} [8].

As indicated in the above theoretical analysis, a non-active mode of the unit may become active due to local distortion. In our case the symmetry of the distorted unit is C_s , so the non-zero components of the dipole moment of the units are μ_x and μ_y , where μ_x, μ_y lie on O(1)–Si–O(2) plane [1]. Since the symmetry of the free state is T_d and having in mind that μ_x, μ_y transform according to T_2 we obtain $\Gamma(\hat{M}) \otimes \Gamma(\mu_x, \mu_y) = T_2 \otimes T_2$. Therefore, a forbidden mode attains a first-order distortion activity only if it belongs to the symmetry species of $T_2 \otimes T_2$ which is equal to $A_1 \oplus E \oplus T_1 \oplus T_2$. Consequently both IR inactive modes A_1 and E attain first-order activity. A weak peak appearing in the olivine spectra at 840 cm^{-1} has been attributed to the A_1 symmetric stretching mode of SiO_4 [7]. However, this peak is not detected in our spectra because of its low intensity as discussed below. The intensity of the forbidden mode is given [3] by $I_{fg}^1 = C^1 |\delta r|^2$, where C^1 is a constant that depends on the molecular unit and the mode $|f\rangle$ in question and δr is a distortion parameter defined by $\delta r = \sum_{i=1}^3 \delta r_i = \sum_{i=1}^3 \sum_m (A_i - B_i^m)$, where in our case B_i^m and A_i are the i -th components of the position vectors of the m -th oxygen and the silicon atom, respectively. Using Tables 2a

Table 2a

Interatomic distances (in 10^{-1} nm) and angles of topaz

SiO ₄ tetrahedron		
Si–O(1) [1]	1.636	
O(2) [1]	1.644	
O(3) [2]	1.642	
O ... O distances	angles at Si	
O(1)–O(2) [1]	2.685	109.9°
O(1)–O(3) [2]	2.675	109.4°
O(2)–O(3) [2]	2.697	110.3°
O(3)–O(3) [1]	2.650	107.5°

Table 2b

Interatomic distances (in 10^{-1} nm) and angles of forsterite

SiO ₄ tetrahedron		
Si–O(1) [1]	1.611	
O(2) [1]	1.661	
O(3) [2]	1.638	
O ... O distances	angles at Si	
O(1)–O(2) [1]	2.753	114.6°
O(1)–O(3) [2]	2.752	115.8°
O(2)–O(3) [2]	2.560	101.8°
O(3)–O(3) [1]	2.604	105.3°

and 2b taken from [1, 8] we can calculate δr . The calculated values are: $|\delta r|_T \approx 0.0063$ nm for topaz and $|\delta r|_F \approx 0.0520$ nm for forsterite. Since the molecular unit and the mode are the same, the constants C_T^1 and C_F^1 could be taken approximately equal so that the intensity ratio is $I_T^1/I_F^1 = |\delta r|_T^2/|\delta r|_F^2 \approx 0.015$. Using this ratio and the fact that the 840 cm^{-1} peak in the olivine spectra is weak, it is clear that the mode A_1 has no observable intensity in the topaz spectrum.

4. In the region of 400 to 750 cm^{-1} a complex spectrum is detected. In this region we expect the bending vibrations of SiO_4 and the external modes which involve translations of both Al^{3+} and Si atoms. The peak at 610 cm^{-1} could be attributed to one of the triply degenerated modes of the second IR active T_2 . This is concluded in analogy to the results from the olivine spectra [7]. The other two modes cannot be distinguished possibly masked by the stronger IR bands arising from the Al octahedra.

Table 3
Stoichiometric analysis (in ppm)

Brazil		unknown locality		African	
Ca	543	Ca	256	Fe	180
Fe	33	Fe	66	Ge	17
Ge	19	Ge	34	Y	3
Zn	3	Zr	1.8	Zr	1.7
Zr	1.3			Nb	2.6
Cr	24			error: $\pm 10\%$	

As it is shown in our spectra the intensities of all the peaks in the region 400 to 1050 cm^{-1} are lower in the unknown locality sample than in the African one and much lower in the Brazil sample, although the same mass of topaz has been used. Furthermore a shift of the corresponding bands to lower frequencies is observed between the above samples. This is probably due [5] to the different amounts of Ca in octahedral sites. The results of the stoichiometric analysis performed on these samples are summarized in Table 3.

Summarizing, the infrared spectrum of natural topaz has been studied and various peaks coming from active modes of OH^- , Al-OH, SiO_4 tetrahedra, and Al octahedra were identified on the basis of group theory and in accordance to previous reports in the literature.

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