

SPECTROSCOPIC INVESTIGATION OF NATURAL TOPAZ

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ABSTRACT

Natural crystals of topaz $[Al(OH,F)]_2SiO_4$ from three localities (Brazil, Africa and from unknown locality), have been studied by using IR and EPR spectroscopy at RT. Infrared signals arising from stretching and bending modes of OH^- ions, H_2O , SiO_4 tetrahedra (internal and external modes) and $Al(OH,F)O_4$ octahedra were detected. EPR signals from V^{4+} and Fe^{3+} were also observed. A correlation of the IR and EPR data is finally attempted.

INTRODUCTION

Topaz is an aluminum fluorosilicate $[Al(OH,F)]_2SiO_4$. It crystallizes in the orthorhombic system with a tetramolecular unit [1,2].

Vibrations of the molecular units SiO_4 (tetrahedra) and $Al(OH,F)_2O_4$ (octahedra) can be studied by IR spectroscopy. If a cation is substituted by an impurity (e.g. Al by Ca) then symmetry lowering of the units in its neighbourhood and changes of bonds and dipole moments strenght (appearance of effective charge) are expected. This may increase the number of observed peaks, shift the bands and alter the intensity of some peaks. If paramagnetic impurities are present electron paramagnetic resonance (EPR) technique is a powerful tool to study the site symmetry of crystals. In many cases it offers valuable informations about the local distortions.

EXPERIMENTAL

The infrared absorption spectra were recorded at RT on a Jasco IR-700 double beam infrared spectrophotometer. The used samples were in the powder form prepared by using the pressed KBr disc technique. In addition EPR measurements at X-band and RT were also performed on a Bruker 200D spectrometer. Piceine was used as a standard for determination of g factors [3].

RESULTS AND DISCUSSION

Fig.1,2,3 depict the IR spectra of the three samples. The observed absorption bands can be classified as follows:
1) A wide band observed at $3100-3600cm^{-1}$ which is identified as arising from stretching modes of water [4]. The bending mode of water is also observed at $1600cm^{-1}$ [4]. It must be pointed out that the primary distinction between H_2O and OH^- is the presence or absence of the bending related absorptions. A sharp peak at $3600cm^{-1}$ coming from (OH^-) ions [4], is present in the spectra of Fig.1,2.

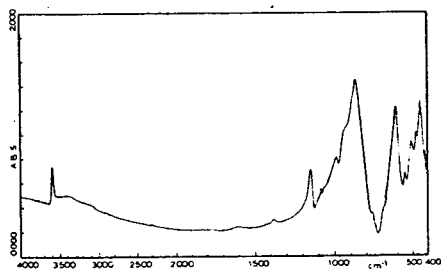


Fig 1: The IR spectrum of Brasilien topaz

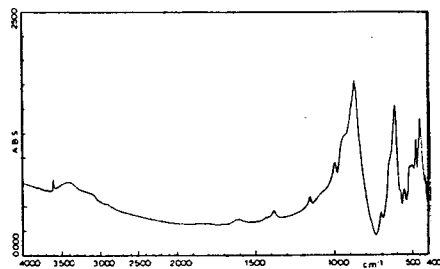


Fig 2: The IR spectrum of Unknown locality topaz

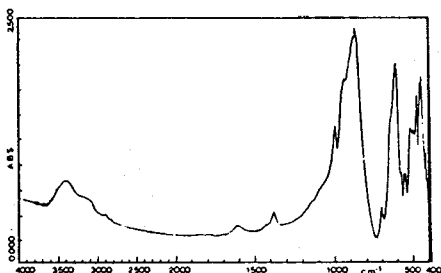


Fig 3: The IR spectrum of African topaz

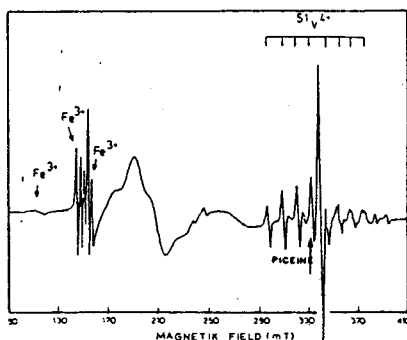


Fig 4: The EPR spectrum of African topaz

The two features of the wide band of medium intensity at 3400cm^{-1} and 3200cm^{-1} approximately, arise from the asymmetric and symmetric stretching of H_2O respectively. This is also consistent with the fact that the frequency of the asymmetric stretch should be higher than the frequency of the symmetric one [4].

The intensity of the sharp peak at 3600cm^{-1} arising from OH^- ions is different in various samples. It is higher in Brasil's 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 fluoride rich than the other two.

2) At 1151cm^{-1} is observed a peak which is attributed to Al-OH bending mode. The intensity of this peak is higher in Brasil's sample than in the blue one and it disappears in the African sample. The above are in accordance with the height (and therefore with the concentration) of OH^- ions in the different samples [5].

3) In the region of $800-1050\text{cm}^{-1}$ 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] we could consider them as isolated. Consequently the internal modes of the SiO_4 group

transform as the one single mode (A_1), one 2-fold degenerated (E) and two 3-fold degenerated modes ($2T_2$), which are attributed respectively to the calculated frequencies given by Herzberg [6,7]:

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

IR active are only the modes which transform as T_2 according to group theory. The observed three peaks correspond to the triply degenerated ω_3 which splits into three frequencies because of the small distortion of the SiO_4 group. A_1 (which corresponds to ω_1) is tentatively identified on the spectra at 880cm^{-1} . Its low intensity is expected since A_1 becomes IR active due to the symmetry lowering. This peak is most clearly observed in the African sample. The remaining active frequencies lie in the region of $400\text{--}750\text{cm}^{-1}$ where we expect (apart from these SiO_4 bending modes) the mixed Si-O-Al vibrations [5].

4) In the region of $750\text{--}400\text{cm}^{-1}$ a complex spectrum is detected. It can be attributed to the overlapping signals arising from external modes of Al-octahedra and the SiO_4 bending modes (ω_4 and ω_2).

Fig.4 shows an EPR spectrum for the magnetic field parallel to the b axis. The characteristic pattern (octet) and the spin Hamiltonian data have the following values:

$$\begin{array}{ccc} g_{xx}=1.929 & g_{yy}=1.923 & g_{zz}=1.950 \\ A_{xx}=144 \times 10^{-4} \text{cm}^{-1} & A_{yy}=176 \times 10^{-4} \text{cm}^{-1} & A_{zz}=179 \times 10^{-4} \text{cm}^{-1} \end{array}$$

clearly indicate the presence of V^{4+} . Some more dispersed signals can be attributed to Fe^{3+} according to previous investigations [1]. The presence of aliovalent impurities substituting for Al^{3+} is expected to lower the symmetry of the octahedra. The large number of peaks in the region of $750\text{--}400\text{cm}^{-1}$ can be tentatively attributed to this lowering although the external modes of SiO_4 are also expected to appear in the same region.

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