

Temperature Dependence of the OH-Stretching mode in Topaz-OH and F-rich Natural Topaz

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Since the first synthesis of topaz-OH, $\text{Al}_2\text{SiO}_4(\text{OH})_2$ (Wunder et al., 1993) various studies have been undertaken to provide information on its hydrogen-bonding geometry. X-ray studies on topaz-OH and its deuterated analogue (e.g., Northrup et al., 1994; Chen et al., 2005) indicated that hydrogen is located at two non-equivalent sites. Contrary to these crystal structure analyses, Churakov and Wunder (2004) predicted the existence of four non-equivalent proton positions from ab-initio quantum mechanical calculations. At ambient conditions, the four protons should be in a dynamic exchange between the allowed positions of local minima.

In natural F-rich topaz hydrogen is associated with the F/O4 atom and the O-H bond lies in the (010)-plane forming an angle of 28.9° with the *c*-axis. According to Gatta et al. (2006) this H-configuration can be described as an average of the two H-positions reported by Northrup et al. (1994) for topaz-OH.

In our study we recorded unpolarized IR-spectra of synthetic topaz-OH, and natural topaz of $X_{\text{OH}} = 0.26$ in the T-range 600 to -196°C .

At ambient conditions the IR-spectrum of topaz-OH shows the known OH-stretching vibrations at 3602 and 3525 cm^{-1} . With decreasing T splitting of both OH-bands is visible below about -150°C , in-line with the theoretical calculations of Churakov and Wunder (2004). The splitting of the high-wavenumber band occurs nearly symmetrically around 3602 cm^{-1} , whereas the splitted bands of the original 3525 cm^{-1} -band are both shifted to lower wavenumbers. This behaviour might indicate different H-bonding strengths.

The IR spectrum of F-rich topaz shows two OH-bands: a sharp strong band at 3640 cm^{-1} and a second weaker band, occurring as broad shoulder at 3614 cm^{-1} . In the T-range 150 to 200°C the FWHM of the strong band is minimized and increases for higher or lower T. The peak shape and the observed change of the FWHM indicates the presence of two bands with small FWHM which separate from each other with decreasing T. The average configuration is achieved with higher thermal energy which allows the protons to exchange between positions of local minima. Decreasing T lowers H-exchanges and therefore causes bandsplitting.

References

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