

The Incorporation of Hydrogen Atoms in the Al₂SiO₅ Polymorphs: A Combined Infrared and Theoretical Study

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Abstract

Potential protonation sites for andalusite, sillimanite and kyanite were located using a combination of polarized infrared spectroscopy and theoretical calculations of the electron density distributions. Previous polarized FTIR spectra collected from single crystals of sillimanite and kyanite [1,2] indicate that the OH dipoles lie in (001) of sillimanite and of kyanite. We measured polarized single crystal FTIR spectra of andalusite. When the electric vector, E, is parallel to [100], the spectrum is dominated by four strong bands at 3440 cm⁻¹, 3460 cm⁻¹, 3530 cm⁻¹, and 3600 cm⁻¹. Three intense peaks are observed at the same positions, 3440 cm⁻¹, 3460 cm⁻¹, and 3530 cm⁻¹, when E is parallel to [010]. However, no peaks are observed when E is parallel to [001], suggesting that the OH dipoles of andalusite lie within (001), similar to sillimanite. The concentration of water in andalusite varied between 10 and 15 ppm by weight in the samples studied. The orientation of the OH dipole from the FTIR spectrum is compared with predictions of protonation sites based on an analysis of the Laplacian of the electron density distribution, following the method of Ross et al. [3]. CRYSTAL98 [4] was used to generate analytical electron density distributions for kyanite, andalusite and sillimanite, and TOPOND [5] was used to locate the (3,-3) critical points in the negative Laplacian, $L(r) = -\nabla^2\rho(r)$. Examination of the (3,-3) critical points in comparison with the FTIR spectra indicates that H prefers to bond to O1 and O2 in andalusite and O2 and O4 in sillimanite. These correspond to the underbonded oxygen atoms and those that have the largest L(r) maxima. In kyanite, comparison of the FTIR spectra and the critical points indicates that H will preferentially dock to O2 and O6 atoms which are both bonded to four Al atoms. This methodology may prove to be useful in the location of hydrogen atoms in other nominally anhydrous minerals.

References: [1] Beran, A., Rossmann, G. R., and Grew, E. S. (1989) *Am. Mineral.*, 74, 812-817. [2] Bell, D.R., Rossmann, G.R., Makdener, J. Endisch, D., and Rauch, F. (2004) *Am. Mineral.*, 89, 998-1003. [3] Ross N.L., Gibbs, G.V., and Rosso, K.M. (2003) *Am. Mineral.*, 88, 1452-1459. [4] Saunders V.R., Dovesi R., Roetti C., Causa M., Harrison N. M., Orlando R., and Zicovich-Wilson C. M. (1998) *CRYSTAL98 User's Manual*. Univ. of Torino. [5] Gatti C. (1997) *TOPOND96 User's Manual*, CNR-CSR SRC.