Single-crystal Raman spectroscopic study of dickite

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Abstract

Raman spectra were obtained from the (001), (010), and (100) faces of a St. Claire dickite specimen of known orientation. Raman spectra collected from the (010) and (100) faces of dickite are reported for the first time and reveal vibrational features significantly different from the (001) spectra. Variations in intensities of the ν (OH) bands in polarized spectra were used to confirm previous band assignments, to determine the shape and orientation of the local Raman tensors for the OH1 and OH3 groups. The most striking polarization effect observed in the ν (OH) region of dickite was the behavior of the $a(c'c')\bar{a}$ spectrum relative to Raman and IR spectra of other orientations. Unlike previously reported spectra, the dominant feature in this spectrum was the 3643 cm⁻¹ band. This large increase in intensity of the 3643 cm⁻¹ band in comparison with the other ν (OH) bands was related to the fact that Raman spectra were recorded from the edge faces of dickite with the electric vector of the incident laser polarized along the c axis. This permitted observation of vibrational modes polarized along the c axis. Raman frequencies of the ν (OH) bands assigned to the OH2 and OH4 groups differ from their IR counterparts by 12 cm⁻¹, suggesting that these groups may be related by a center of symmetry. For comparison, Raman spectra in the ν (OH) region were also obtained from individual micro-crystals of kaolinite that were approximately 5 μ m across the (001) face.