
Rietveld Refinement and Fourier-Transform Infrared Spectroscopic Study of the Dickite Structure at Low Temperature

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Abstract: The full structure of dickite from St. Claire, Pennsylvania, including hydrogen atoms, was refined in space group Cc using time-of-flight neutron powder diffraction data obtained at 12 K and Rietveld refinement/difference-Fourier methods ($R_{wp} = 2.62\%$, reduced $\chi^2 = 1.915$, 113 variables, $a = 5.1474(6) \text{ \AA}$, $b = 8.9386(10) \text{ \AA}$, $c = 14.390(2) \text{ \AA}$, and $\beta = 96.483(1)^\circ$). The non-hydrogen structure is essentially identical to published structures for dickite, but the hydrogen positions are distinct. The inner hydroxyl group is approximately parallel to the (001) plane, inclined by 1.3° towards the tetrahedral sheet. Contrary to published low-temperature infrared (IR) spectra, there is no evidence that dickite possess lower symmetry at low temperatures although there is tentative evidence for statistical occupancy of H3 on more than one site. Low-temperature IR spectra of St. Claire and Wisconsin dickites do not show evidence for more than four hydroxyl groups and are consistent with the reported structure. Upon cooling from 300 to 15 K, the position of the OH3 stretching band increased from 3710 to 3731 cm^{-1} . This large, positive shift in frequency was attributed to the increase in the internuclear O-H3...O distance upon cooling. The frequency of the 3655 cm^{-1} band initially decreased by 2 cm^{-1} to 3653 cm^{-1} upon cooling from 300–125 K; however, the band increased in frequency by 1 cm^{-1} upon further cooling to 15 K. This unusual change in frequency upon cooling is consistent with the assignment of this band to OH2 and OH4. The position of the OH1 stretching band decreased from 3622 to 3620 cm^{-1} upon cooling, which was attributed, in part, to the observed increase in the Al-O(H1)-Al angle at low temperature.

Key Words: Dickite • FTIR • Infrared spectroscopy • Low temperature • Neutron powder diffraction • Rietveld refinement

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