Single-crystal Raman spectroscopic study of dickite

CLIFF T. JOHNSTON,1* JOZEF HELSEN,2 ROBERT A. SCHOONHEYDT,3 DAVID L. BISH,4 AND STEPHEN F. AGNEW5

1 Crop, Soil and Environmental Sciences, 1150 Lilly Hall, Purdue University, West Lafayette, Indiana 47907, U.S.A.
2 Department of Metallurgy and Materials Engineering, Materials Research Center, K.U. Leuven, De Croylaan, 2, 3001 Heverlee, Belgium
3 Center for Surface Chemistry and Catalysis, Materials Research Center, K.U. Leuven, K. Mercierlaan, 92, 3001 Heverlee, Belgium
4 Geology and Geochemistry, MS D469, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.
5 Bioscience and Biotechnology, MS J586, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.

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′)aÅ 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 µm across the (001) face.

INTRODUCTION

Since the first structures of kaolinite and dickite were reported over sixty years ago (Pauling 1930; Gruner 1932) the structure and bonding of kaolin group minerals have continued to attract attention. However, structural details concerning the H atom are incomplete. Knowledge of the OH groups for this group of minerals is crucial to understand the many important bulk crystalline properties including interlayer bonding, stability of polytypes, structural disorder, and dehydroxylation reactions (Brindley et al. 1986; Giese 1990). OH groups also influence surface properties and reactions (Costanzo et al. 1984; Lipsicas et al. 1985; Sugahara et al. 1989; Costanzo and Giese 1990; Johnston and Stone 1990). Finally, knowledge of the positions and spectral properties of the H atoms is critical for application of quantum chemical methods to the study of phyllosilicates (Bleam 1993), particularly kaolin group minerals (Hess and Saunders 1992; Kubicki et al. 1996). Thus, the combined application of advanced spectroscopic and structural methods to the study of phyllosilicates provides essential data for developing an improved theoretical understanding of clay minerals.

Recently, Bish and Johnston (1993) determined the positions of the H atoms in dickite in a combined neutron powder diffraction, Rietveld refinement, and low-temperature Fourier transform infrared spectroscopy (FTIR) spectroscopy study of dickite. The space group of dickite is Cc. The unit-cell formula of dickite is Al₂Si₂O₅(OH)₄ with Z = 4 for a total of 16 OH groups within the unit cell. The unit cell contains four crystallographically unique OH groups each having a local site symmetry of 1 (Fig. 1). Because of the low symmetry of dickite, all four of the OH groups are expected to produce distinct ν(OH) stretching bands and all are expected to be Raman and IR active. The structural environments of the OH2 and OH4 groups are very similar, and these two OH groups were assigned (Fig. 1) to the 3655 cm⁻¹ band (Bish and Johnston 1993).

In principle, vibrational spectroscopy and diffraction methods provide complementary information about the structural OH groups of clay minerals. The intrinsically small X-ray scattering cross section of the H atom limits the ability of powder X-ray diffraction methods to determine the positions of H atoms in fine-grained mineral samples (Post and Bish 1989; Moore and Reynolds 1989;