

Low-temperature infrared spectroscopic study of OH-stretching modes in kaolinite and dickite

ETIENNE BALAN,^{1,*} SIMON DELATTRE,¹ MAXIME GUILLAUMET,¹ AND EKHARD K.H. SALJE^{1,2}

¹Institut de Minéralogie et Physique des Milieux Condensés (IMPMC), UMR CNRS 7590, UMR IRD 206, Université Paris VI, Université Paris VII, IPGP, 140 rue de Lourmel, 75015 Paris, France

²Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.

ABSTRACT

The powder-transmission infrared spectra of OH-stretching modes in well-ordered samples of kaolinite and dickite are recorded from 270 to 10 K. Effective medium modeling of the kaolinite spectrum confirms the coupled motion of non-equivalent OH groups in the inter-layer OH-stretching modes. A full assignment of OH-stretching bands in dickite is proposed. In particular, the band observed at 3685 cm⁻¹ in room-temperature spectra is attributed to a kaolinite-like defect, whereas that at 3706 cm⁻¹ is related to OH3 groups of the dickite structure. The changes in phonon frequency and line shape are analyzed as a function of temperature. The results evidence the quasi-harmonic nature of the OH-stretching modes in kaolinite-group minerals. Coupling of OH-stretching modes to each other can be related to the macroscopic electrostatic properties of the composite medium, made of mineral particles and KBr matrix, and not to microscopic anharmonic mechanisms. The low saturation temperatures of vibrational frequencies and linewidths indicate that the OH-stretching modes probe the average thermal bath of the crystal, without coupling to a specific decay channel.

Keywords: Infrared spectroscopy, kaolinite, dickite, thermodynamic, phonons