American Mineralogist, Volume 103, pages 812–818, 2018

Revisiting the crystal structure of dickite: X-ray diffraction, solid-state NMR, and DFT calculations study

João Rocha[1,*], Filipe A. Almeida Paz[1], Mariana Sardo[1], and Luís Mafra[1]

[1]Department of Chemistry, University of Aveiro, CICECO-Aveiro Institute of Materials, 3810-193 Aveiro, Portugal

Abstract

Dickite is a member of the family of 1:1 dioctahedral phyllosilicates known as the kaolin minerals, with composition $Al_2Si_2O_5(OH)_4$. The elucidation of the hydrogen-atom positions in dickite, addressed here, and indeed in other hydrated minerals poses particular challenges.

The crystal structure of dickite was determined from single-crystal X-ray diffraction at 100(2) K in the non-centrosymmetric *Cc* monoclinic space group and found to agree closely with previously reported structures (Bish and Johnston 1993; Dera et al. 2003). ^{27}Al and ^{29}Si solid-state NMR spectra of unprecedented resolution bear evidence for two distinct Al and Si sites, being consistent with the previously determined structures. Positions of the four independent hydrogen atoms were optimized and the pertinent ^{1}H chemical shifts calculated using DFT methods (program CASTEP) and compared with high-resolution MAS NMR experimental data obtained at ultra-high sample spinning rates (up to 67 kHz). This work contributes new evidence on the precise hydrogen-atom positions of dickite, and it illustrates how X-ray diffraction, solid-state NMR, and theoretical calculations may be combined to yield an improved mineral crystal structure.

Keywords: Dickite, crystal structure, X-ray diffraction, ^{1}H, ^{27}Al, ^{29}Si MAS NMR, DFT methods