American Mineralogist, Volume 88, pages 398–409, 2003

Interlayer structure and dynamics of Cl-bearing hydrotalcite: far infrared spectroscopy and molecular dynamics modeling

JIANWEI WANG,[1,*] ANDREY G. KALINICHEV,[1] JAMES E. AMONETTE,[2] AND R. JAMES KIRKPATRICK[1]

[1]Department of Geology, University of Illinois at Urbana-Champaign, 1301 W. Green St., Urbana, Illinois 61801, U.S.A.
[2]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, K8-96, Richland, Washington 99352, U.S.A.

ABSTRACT

Comparison of the observed far-infrared (FIR) spectrum of Cl^--containing hydrotalcite, $[Mg_3Al(OH)_8]Cl·3H_2O$, to a power spectrum calculated using molecular dynamics (MD) computer simulation, provides a greatly increased understanding of the structure and vibrational dynamics in the interlayers of layered double hydroxides. Good agreement between the observed FIR band positions and the simulated power spectrum illustrates the capability of this combination of experimental and computational techniques to effectively probe the structure and dynamics of water in nano-pores and other confined spaces. The simulation model assumes an ordered Mg_3Al arrangement in the octahedral sheet and no constraints on the movement of any atoms or on the geometry and symmetry of the simulation supercell. Calculated anisotropic components of the individual atomic power spectra in combination with computed animations of the vibrational modes from normal mode analysis allow for reliable interpretations of the observed spectral bands. For the vibrations related to octahedral cation motions, bands near 145, 180, and 250 cm^{-1} are due dominantly to Mg vibration in the **c** direction (perpendicular to the hydroxide layers), Al vibration in the **c** direction, and Mg and Al vibrations in the **a-b** plane (parallel to the hydroxide layers), respectively. The low frequency vibrational motions of the interlayer are controlled by a network of hydrogen bonds formed between interlayer water molecules, Cl^- ions, and the OH groups of the main hydroxide layers. The bands near 40–70 cm^{-1} are related to the translational motions of interlayer Cl^- and H_2O in the **a-b** plane, and the bands near 120 cm^{-1} and 210 cm^{-1} are largely due to translational motions of the interlayer species in the **c** direction. The three librational modes of interlayer water molecules near 390, 450, and 540 cm^{-1} correspond to twisting, rocking, and wagging hindered rotations, respectively. The spectral components of the interlayer Cl^- motions are remarkably similar to those of bulk aqueous chloride solutions, reflecting the structural and dynamic similarity of the nearest-neighbor Cl^- environments in the interlayer and in solution.