American Mineralogist, Volume 84, pages 1186–1190, 1999

Interlayer structure, anion dynamics, and phase transitions in mixed-metal layered hydroxides: Variable temperature ^{35}Cl NMR spectroscopy of hydrotalcite and Ca-aluminate hydrate (hydrocalumite)

R. JAMES KIRKPATRICK,[1,3,*] PING YU,[2,3] XIAOQIANG HOU,[1] AND YEONGKYOO KIM[1,†]

[1]Department of Geology, University of Illinois at Urbana-Champaign, 1301 W. Green Street, Urbana, Illinois 61801, U.S.A.
[2]Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, U.S.A.
[3]National Science Foundation Center for Advanced Cement-Based Materials, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, U.S.A.

ABSTRACT

The ^{35}Cl NMR spectroscopy of Cl^--intercalated hydrotalcite and the Ca-aluminate hydrate hydrocalumite (Friedel's salt) demonstrates dynamical behavior of interlayer Cl^-, the presence of dynamical order-disorder phase transitions in these phases, and significant differences in the transition temperatures and temperature interval over which the transitions occur. In hydrocalumite, the Ca,Al distribution is ordered, the interlayer water is directly coordinated to Ca in the hydroxide layer (creating sevenfold-coordinated Ca), and the interlayer Cl^- and water sites are well ordered. The ^{35}Cl NMR data show that the interlayer Cl^- site has uniaxial or nearly uniaxial symmetry above about 0 °C and reduced (triaxial) symmetry at lower temperatures. Differential scanning calorimetry (DSC) data show this change to be due to a structural phase transition at about 6 °C. The NMR and XRD data suggest that this phase transition is due to dynamical order-disorder involving a rigid interlayer atomic arrangement at low temperatures and dynamically averaged interlayer species at high temperatures. In contrast, in hydrotalcite Mg and Al are disordered over the octahedral sites, and the interlayer is disordered. The ^{35}Cl NMR data for it show poorly resolved signal indicating a range of Cl^- environments and a change from triaxial to uniaxial or nearly uniaxial symmetry at Cl^- occurring over a broad temperature interval below –40 °C. DSC data for our sample shows a broad and poorly defined endothermic anomaly in the –100 to –75 °C range. These data suggest the presence of a phase transition that occurs over a larger temperature range due to its disordered interlayer structure. The results suggest that similar variable temperature NMR behavior previously observed for interlayer cations in smectites can be thought of as due to comparable phase transitions that lack well-defined critical temperatures due to the disordered interlayer structures.