

Investigation of the hydrozincite structure by infrared and solid-state NMR spectroscopy

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ABSTRACT

To better understand lattice disorder in hydrozincite, natural hydrozincite samples and synthetic analogues were investigated by XRD, FTIR, ¹³C MAS, and ¹³C CPMAS NMR. The size of coherent diffraction domains ranges between ~10 nm (Synth1) and ~30 nm (Synth2). FTIR peaks from the antisymmetric CO₃²⁻ stretching ν₃ mode were observed at 1383 and 1515 cm⁻¹ in all samples. Peaks due to OH vibrations were observed for all the samples at 3234, 3303, and 3363 cm⁻¹, and were sharp only for the samples having larger crystal domains. The ¹³C MAS and CPMAS NMR spectra showed a main carbon signal at 164 ppm in the Synth2 sample, while two main signals were observed at ~164 and ~168 ppm in the Synth1 sample. The intensity ratio of the latter signals were found to be independent of contact time, in the investigated range between 0.2 and 30 ms.

In addition, ¹³C CPMAS dynamics indicates that the Synth1 sample has shorter T_{1ρ} with respect to Synth2. This indicates a more effective process of spin diffusion of proton magnetization in the former due to different structural properties of Synth1 and Synth2 samples. In addition, chemical shift anisotropy analysis was attributed to a structural change in the carbonate group or hydrogen bonding for Synth1 and Synth2. This was interpreted as a deviation from the ideal structure generated by linear and planar lattice defects and/or grain boundaries.

Keywords: Hydrozincite, carbonates, chemical shift anisotropy, nanocrystals