Observation of cation ordering and anion-mediated structure selection among
the layered double hydroxides of Cu(II) and Cr(III)

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Supporting Information

SI. 1 PXRD pattern of the [Cu-Cr-Cl] LDH obtained by coprecipitation at pH 5, T ≈ 27 °C.
SI.2 IR spectrum of [Cu-Cr-A] LDHs

% Transmittance

Wavenumber (cm⁻¹)

4000 3500 3000 2500 2000 1500 1000 500

Cl⁻
Br⁻
SO₄²⁻

CO₃²⁻
BrO₃⁻
IO₃⁻
The IR spectra of [Cu-Cr] LDHs show a broad absorption at 3300 - 3400 cm\(^{-1}\) due to O-H stretching vibration of the hydroxyl groups of the brucite-like sheets and water in the interlayer region. The O-H bending vibration of the interlayer water is observed at 1610 - 1635 cm\(^{-1}\). There is no absorption at 1356 cm\(^{-1}\), indicating the complete absence of carbonate ions in LDHs comprising other anions.

[Cu-Cr-X] (X = Cl, Br) LDH: the IR spectra of halides intercalated LDH has no absorption in the range of 900 - 1500 cm\(^{-1}\), as expected of a halide LDH.

[Cu-Cr-SO\(_4\)] LDH: IR spectrum shows different vibrational modes of sulfate where \(\nu_3\) and \(\nu_4\) splits into two peaks. The two doublets appear at 1139 and 1104 cm\(^{-1}\) and 612 and 561 cm\(^{-1}\), respectively. The \(\nu_1\) mode is activated and appears at 991 cm\(^{-1}\). The \(\nu_2\) mode which is expected to be at 450 cm\(^{-1}\) is not seen as a separate band because it overlaps with the sharp bands at 400 - 600 cm\(^{-1}\) that arise from the lattice vibrations. All these vibrations are characteristic of SO\(_4^{2-}\) being in C\(_{3v}\) coordination symmetry.

[Cu-Cr-CO\(_3\)] LDH: The carbonate ion intercalated LDH exhibits three IR active modes corresponding to the out-of-plane bending \(\nu_2\) at 864 cm\(^{-1}\); antisymmetric symmetric stretching \(\nu_3\) at 1348 cm\(^{-1}\) and in-plane stretching \(\nu_4\) at 671 cm\(^{-1}\). This indicates that the interlayer carbonate is in the D\(_{3h}\) symmetry.

[Cu-Cr-IO\(_3\)] LDH: IR spectrum of iodate intercalated LDH shows a peak at 938 cm\(^{-1}\) and a sharp peak around 733 cm\(^{-1}\) which can be assigned to \(\nu_1\) and \(\nu_2\) modes of iodate ion indicates that the interlayer is C\(_{3v}\). The frequencies \(\nu_1\) and \(\nu_3\) vibrations are near to each other, hence they are usually observed as one strong band. Other vibration frequencies overlap with M-O-H bending mode and hence cannot be distinguished in the IR spectrum.
[Cu-Cr-BrO$_3$] LDH: IR spectrum of bromate intercalated LDH shows a peak at 925 cm$^{-1}$ and a sharp peak around 738 cm$^{-1}$ which can be assigned to $\nu_1$ and $\nu_2$ modes of bromate ion indicates that the interlayer is C$_{3v}$. The frequencies $\nu_1$ and $\nu_3$ vibrations are near to each other, hence they are usually observed as one strong band. Other vibration frequencies overlap with M-O-H bending mode and hence cannot be distinguished in the IR spectrum.
SI.3 TG-DTG curves of [Cu-Cr-A] LDHs
TG-DTG data show a continuous mass loss with many points of inflection. The total mass loss observed from 30-800 °C is used for computing the intercalated water content.