

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

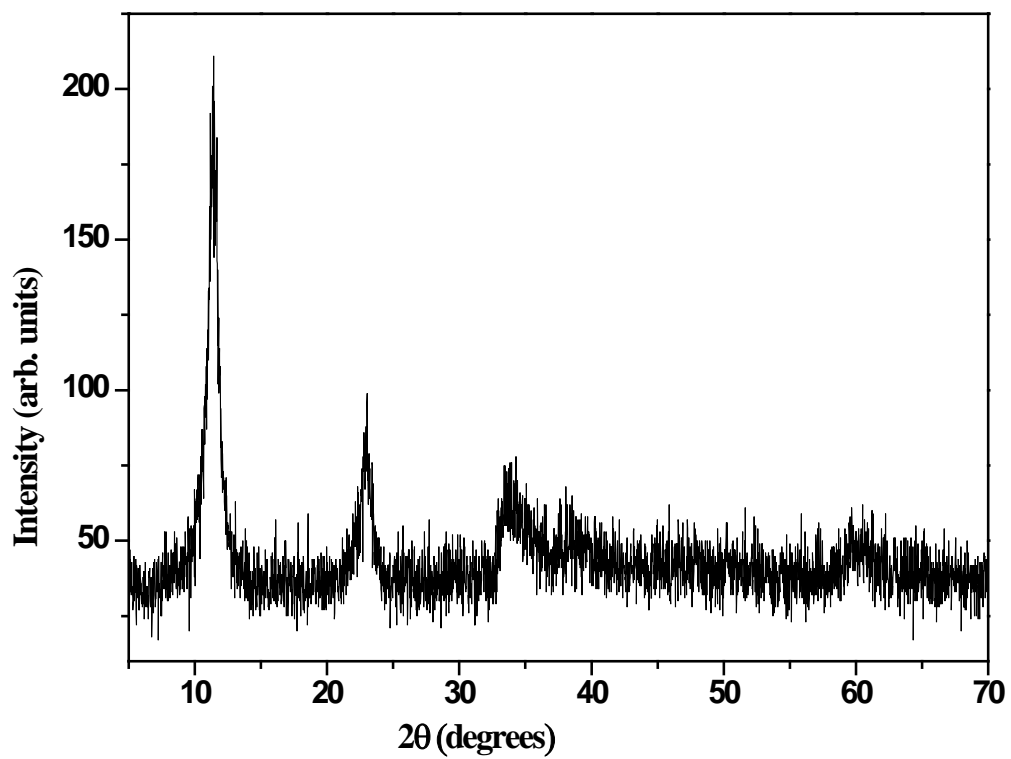
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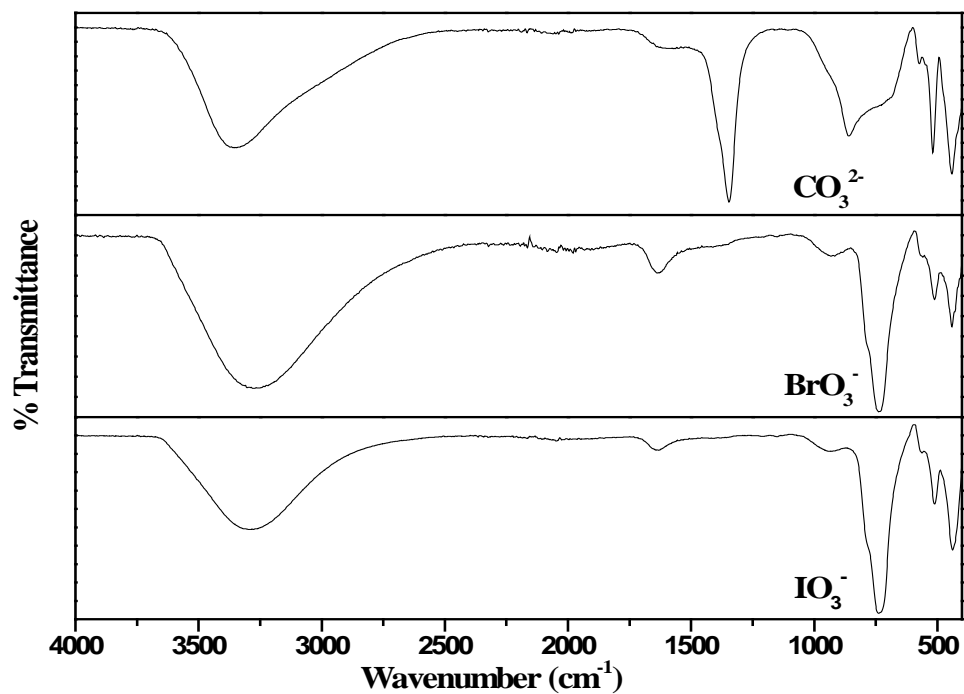
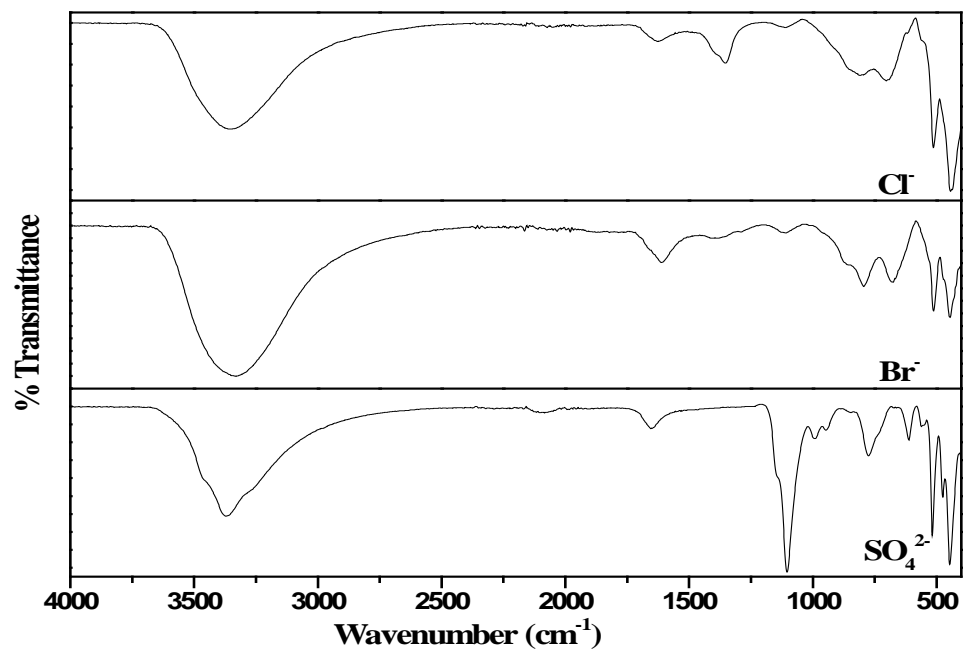
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## Supporting Information

SI. 1 PXRD pattern of the [Cu-Cr-Cl] LDH obtained by coprecipitation at pH 5,  $T \approx 27^\circ\text{C}$ .



## SI.2 IR spectrum of [Cu-Cr-A] LDHs



The IR spectra of [Cu-Cr] LDHs show a broad absorption at 3300 - 3400  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ . There is no absorption at 1356  $\text{cm}^{-1}$ , 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  $\text{cm}^{-1}$ , as expected of a halide LDH.

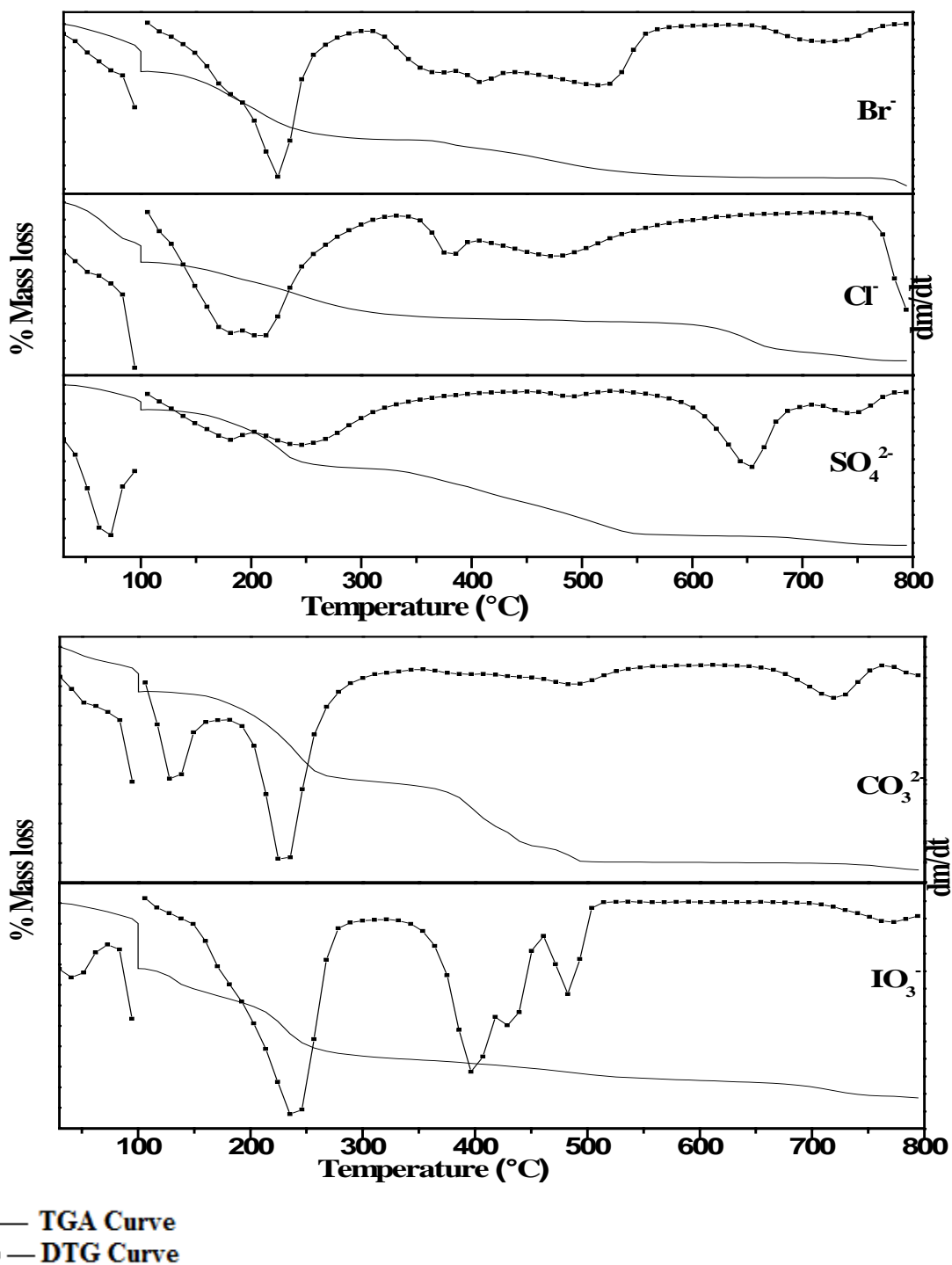
**[Cu-Cr-SO<sub>4</sub>] LDH:** IR spectrum shows different vibrational modes of sulfate where  $\nu_3$  and  $\nu_4$  splits into two peaks. The two doublets appear at 1139 and 1104  $\text{cm}^{-1}$  and 612 and 561  $\text{cm}^{-1}$ , respectively. The  $\nu_1$  mode is activated and appears at 991  $\text{cm}^{-1}$ . The  $\nu_2$  mode which is expected to be at 450  $\text{cm}^{-1}$  is not seen as a separate band because it overlaps with the sharp bands at 400 - 600  $\text{cm}^{-1}$  that arise from the lattice vibrations. All these vibrations are characteristic of  $\text{SO}_4^{2-}$  being in  $\text{C}_{3v}$  coordination symmetry.

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

**[Cu-Cr-IO<sub>3</sub>] LDH:** IR spectrum of iodate intercalated LDH shows a peak at 938  $\text{cm}^{-1}$  and a sharp peak around 733  $\text{cm}^{-1}$  which can be assigned to  $\nu_1$  and  $\nu_2$  modes of iodate ion indicates that the interlayer is  $\text{C}_{3v}$ . 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<sub>3</sub>]LDH:** IR spectrum of bromate intercalated LDH shows a peak at 925 cm<sup>-1</sup> and a sharp peak around 738 cm<sup>-1</sup> which can be assigned to  $\nu_1$  and  $\nu_2$  modes of bromate ion indicates that the interlayer is C<sub>3v</sub>. 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.