

RAMAN SPECTROSCOPY OF IOWAITE AND OTHER NATURAL HYDROTALCITES

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Raman spectroscopy has been used to study hydrotalcites including stichtite, iowaite, pyroaurite, desautelsite. These minerals show "memory effects" in that after the mineral has been completely destroyed, on exposure to air their structures may be restored.

Hydrotalcites, or layered double hydroxides (LDH's) are fundamentally anionic clays, and are less well known than cationic clays like smectites (Hashi et al., 1983; Ingram and Taylor, 1967). The structure of hydrotalcite can be derived from a brucite structure ($\text{Mg}(\text{OH})_2$) in which e.g. Al^{3+} or Fe^{3+} (pyroaurite-sjögrenite) substitutes a part of the Mg^{2+} (Frost et al., 2003; Johnson et al., 2002; Klopogge et al., 2003). This substitution creates a positive layer charge on the hydroxide layers, which is compensated by interlayer anions or anionic complexes (Taylor, 1969; Taylor, 1982). In hydrotalcites a broad range of compositions are possible of the type $[\text{M}^{2+}_x\text{M}^{3+}_y(\text{OH})_2][\text{A}^{n-}]_{x/n}\cdot y\text{H}_2\text{O}$, where M^{2+} and M^{3+} are the di- and trivalent cations in the octahedral positions within the hydroxide layers with x normally between 0.17 and 0.33. A^{n-} is an exchangeable interlayer anion (Hansen and Koch, 1995). In the hydrotalcites reevesite and pyroaurite, the divalent cations are Ni^{2+} and Mg^{2+} respectively with the trivalent cation being Fe^{3+} . In these cases the carbonate anion is the major interlayer counter anion. In iowaite the anion is chloride. Normally the hydrotalcite structure based upon takovite (Ni,Al) and hydrotalcite (Mg,Al) has basal spacings of cca. 8.0 Å where the interlayer anion is carbonate. If the carbonate is replaced by sulphate then the mineral carboydite is obtained. Similarly reevesite is the Ni,Fe hydrotalcite with carbonate as the interlayer anion, which when replaced by sulphate the minerals honessite and hydrohonessite are obtained. If the carbonate is replaced with chloride the mineral iowaite is formed. The mineral iowaite is characterised by infrared bands at 3700, 3674 and 3626 cm^{-1} attributed to Mg_3OH , Mg_2FeOH and Fe_3OH units. Bands are also observed at 3545, 3421, 3281, 3058 and 2769 cm^{-1} and are attributed to the water OH stretching vibration. A similar set

of bands is observed in the infrared spectrum of synthetic pyroaurite. The Raman spectra of the synthetic iowaite are characterised by bands attributed to $(\text{CO}_3)^{2-}$ at 1376, 1194 and 1084 cm^{-1} . No bands were observed in these positions for the natural iowaite. The Raman spectrum of natural iowaite shows three bands at 708, 690 and 620 cm^{-1} and upon exposure to air, two broad bands are found at 710 and 648 cm^{-1} . The Raman spectrum of synthetic iowaite has a very broad band at 712 cm^{-1} . The Raman spectrum of natural iowaite shows an intense band at 527 cm^{-1} . The air oxidised iowaite shows two bands at 547 and 484 cm^{-1} attributed to the $(\text{CO}_3)^{2-}$ ν_2 bending mode. Raman spectroscopy has proven most useful for studying the chemistry of the hydrotalcite iowaite.

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