

RAMAN SPECTROSCOPY OF SOME NATURALLY OCCURRING HYDROTALCITES WITH INTERLAYER SULPHATE OR CARBONATE

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Abstract: The structures of some natural hydrotalcites with carbonate or sulphate as the interlayer anion have been studied using IR and Raman spectroscopy. The sulphate stretching vibrations are found to be mineral dependent. A reduction in the symmetry of both sulphate and carbonate anions was observed suggesting that the anions are bonded to the hydroxyl surface and to the interlayer water. Water is also found to be strongly hydrogen bonded to both the interlayer anions and the hydrotalcite surface.

Hydrotalcites (or layered double hydroxides, LDH, as they also called) belong to a large class of anionic and basic clays comprising of positively charged brucite-like structure $[\text{Mg}(\text{OH})_2]$ in which a trivalent cation such as Al^{3+} , Fe^{3+} , Cr^{3+} substitutes part of the Mg^{2+} . This substitution creates a positive layer charge on the hydroxide layers which is compensated by interlayer anions or anion complexes and water molecules. They can be represented by the general formula $[(\text{M}_{1-x}^{2+} \text{M}_x^{3+} (\text{OH})_2)^{x+} \cdot (\text{A}_{x/n}^{n-} \cdot m\text{H}_2\text{O})^{x-}]$, where M^{2+} = divalent cation in octahedral positions, M^{3+} = trivalent cations in octahedral positions and A^{n-} = exchangeable interlayer anion e.g. CO_3^{2-} , SO_4^{2-} , NO_3^- , Cl^- , OH^- , and x is normally between 0.17 and 0.33 but there is no limitation. Hence, a wide variety of two-metal and three-metal hydrotalcites with different interlayer anions can be prepared.

There are some significant number of naturally occurring hydrotalcites that are formed as deposits from ground water containing Ni^{2+} and Fe^{3+} [1]. These are based upon the dissolution of Ni-Fe sulphides during weathering. Two naturally occurring hydrotalcites containing Ni^{2+} are carrboydite and hydrohonessite which are Ni-Al and Ni-Fe hydrotalcites, respectively. These two hydrotalcites are based upon the incorporation of sulphate into the interlayer with expansions of 10.34 to 10.8 Å. Related to hydrohonessite is the mineral mountkeithite in which all or part of the Ni^{2+} is replaced by Mg^{2+} . When the interlayer sulphate in carrboydite and hydrohonessite is replaced by carbonate, the minerals takovite and reevesite are obtained, respectively. Similarly, when the sulphate in mountkeithite (Mg-Fe) is replaced by carbonate, the mineral pyroaurite is obtained. Normally the hydrotalcite structures containing carbonate as the interlayer anion have basal spacings of ~8.0 Å. The characterisation of these naturally occurring minerals by infrared spectroscopy has been well documented [2-4]. More recently, infrared emission spectroscopy has been used to study the thermal behaviour of hydrotalcites [5]. One disadvantage in the study of hydrotalcites is that the water in the hydrotalcite is an intense absorber and may mask the absorbance of the MOH units. One advantage of Raman spectroscopy is that water is a very poor scatterer. Thus, the hydroxyl stretching of the MOH units may be readily observed. However, only few reports of the Raman spectroscopy of these hydrotalcite minerals, either natural or synthetic have been presented [2,3,6,7]. In this paper, we report the changes in the structure of the naturally occurring carrboydite, hydrohonessite, mountkeithite, reevesite and takovite minerals containing sulphate or carbonate in the interlayer using infrared and Raman spectroscopy.

The Raman spectra of the hydroxyl stretching (3000-4000 cm^{-1}) region are shown in Fig. 1. The spectra of hydrohonessite, mountkeithite and reevesite show sharp bands attributed to MOH stretching vibrations. The Raman spectrum of reevesite in the hydroxyl region strongly resembles that of hydrohonessite. This is not surprising as the two minerals differ only in the interlayer anions. Sulphate vibrations were observed in the Raman spectra of carrboydite, hydrohonessite and mountkeithite and reevesite with stretching vibration bands between 900 and 1200 cm^{-1} and bending vibration bands observed below 800 cm^{-1} . The positions of the sulphate stretching vibrations were found to be mineral dependent. The Raman spectrum of takovite shows an intense carbonate stretching vibration band at 1060 cm^{-1} with a low intensity band at 1042 cm^{-1} . No bands that would be attributed to antisymmetric carbonate vibrations were observed at about 1350 cm^{-1} in the Raman spectra of takovite. The infrared spectrum of takovite, however, shows two bands at 1351 and 1417 cm^{-1} . Carbonate bending vibrations were also observed below 800 cm^{-1} in the spectra of takovite. Raman spectroscopy data indicate a reduction in the symmetry of both sulphate and carbonate interlayer anions. It therefore follows that the anions are bonded to the hydroxyl surface and to the interlayer water. Water bending modes are also observed in both the Raman and infrared spectra at positions greater than 1630 cm^{-1} suggesting that water is strongly hydrogen bonded to both the interlayer anions and the hydroxyl surface.

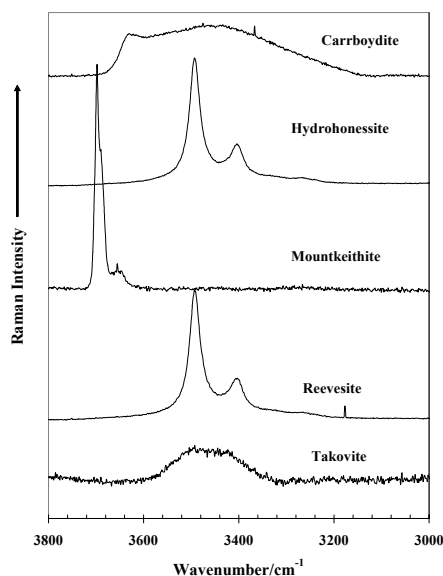


Fig. 1. Raman spectra of the hydroxyl stretching region of some natural hydroxalcsites.

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