

**The role of water in synthesized hydrotalcites of formula
Mg_xZn_{6-x}Cr₂(OH)₁₆(CO₃).4H₂O and Ni_xCo_{6-x}Cr₂(OH)₁₆(CO₃).4H₂O – an
infrared spectroscopic study**

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Abstract

Infrared spectroscopy has been used to characterize synthesized hydrotalcites of formula Mg_xZn_{6-x}Cr₂(OH)₁₆(CO₃).4H₂O and Ni_xCo_{6-x}Cr₂(OH)₁₆(CO₃).4H₂O. The infrared spectra are conveniently subdivided into spectral features based (a) upon the carbonate anion (b) the hydroxyl units (c) water units. Three carbonate antisymmetric stretching vibrations are observed at around 1358, 1387 and 1482 cm⁻¹. The 1482 cm⁻¹ band is attributed to the CO stretching band of carbonate hydrogen bonded to water. Variation of the intensity ratio of the 1358 and 1387 cm⁻¹ modes is linear and cation dependent. By using the water bending band profile at 1630 cm⁻¹ four types of water are identified (a) water hydrogen bonded to the interlayer carbonate ion (b) water hydrogen bonded to the hydrotalcite hydroxyl surface (c) coordinated water and (d) interlamellar water. It is proposed that the water is highly structured in the hydrotalcite interlayer as it is hydrogen bonded to both the carbonate anion, adjacent water molecules and the hydroxyl surface.

Key Words- hydrotalcite, brucite, magnesite, smithsonite, infrared, structured water.

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1. Introduction

Hydrotalcites both natural and synthetic have been known for an extended period of time [1-4]. Hydrotalcites, or layered double hydroxides (LDH) are fundamentally known as anionic clays, and are less well-known and more diffuse in nature than cationic clays like smectites [5-7]. 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+} . This substitution creates a positive layer charge on the hydroxide layers, which is compensated by interlayer anions or anionic complexes. In hydrotalcites a broad range of compositions are possible of the type $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2][\text{A}^{n-}]_{x/n}\cdot y\text{H}_2\text{O}$, 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. Commonly the M^{3+} ion is Al^{3+} [8, 9] but may be any one of a number of trivalent cations including Cr.

Likewise the characterisation of these types of minerals by infrared spectroscopy goes back in time [10-13]. More recently infrared emission spectroscopy has been used to study the thermal behaviour of hydrotalcites [13, 14]. However few reports of the spectroscopy of these minerals either natural or synthetic have been forthcoming. Importantly hydrotalcites, which are based upon Cr^{3+} cation, are quite difficult to measure by Raman spectroscopy as the incident radiation is simply absorbed by the sample and the sample is consequently destroyed. In this paper we report the changes in the structure of a chromium hydrotalcites using infrared spectroscopy as the Mg in the hydrotalcite $\text{Mg}_x\text{Zn}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ is replaced by Zn and where the Ni is replaced by Co in $\text{Ni}_x\text{Co}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ hydrotalcites.

2. Experimental

2.1 Synthesis of hydrotalcite samples

Hydrotalcites with a composition of $\text{Mg}_x\text{Zn}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ and $\text{Ni}_x\text{Co}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ where x varied from 6 to 0, were synthesised by the coprecipitation method. Two solutions were prepared, solution 1 contained 2M NaOH and 0.125M Na_2CO_3 , solution 2 contained 0.75M Mg^{2+} ($\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$) and 0.75M Zn^{2+} together with 0.25M Cr^{3+} . Solution 2 in the appropriate ratio was added to solution 1 using a peristaltic pump at a rate of 40 $\text{cm}^3/\text{min.}$, under vigorous stirring, maintaining a pH of 10. The samples were checked for phase composition by X-ray diffraction and for chemical composition.

2.2 Infrared Spectroscopy

The samples were dried to remove any adsorbed water and stored in a desiccator before measurement in the FT-IR spectrometer. The sample (1mg) was finely ground for one minute, combined with oven dried spectroscopic grade KBr having a refractive index of 1.559 and a particle size of 5-20 μm (250mg) and pressed into a disc using 8 tonnes of pressure for five minutes under vacuum. The spectrum of each sample was recorded in triplicate by accumulating 64 scans at 4 cm^{-1} resolution between 400 cm^{-1} and 4000 cm^{-1} using the Perkin-Elmer 1600 series Fourier

transform infrared spectrometer equipped with a LITA detector.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

3. Results and discussion

3.1 Hydroxyl Stretching Region

The infrared spectra of the hydroxyl-stretching region of the $Mg_xZn_{6-x}Cr_2(OH)_{16}(CO_3).4H_2O$ and $Ni_xCo_{6-x}Cr_2(OH)_{16}(CO_3).4H_2O$ hydrotalcites are displayed in **Figures 1 and 2**. The results of the band component analysis of the hydroxyl-stretching region for the two hydrotalcites are reported in **Table 1**. This spectral region as shown in Figures 1 and 2 contains both the hydroxyl stretching bands of the hydroxyl units bound to the divalent cations and the trivalent cation together with the hydroxyl stretching bands of water. One of the difficulties of studying the hydroxyl-stretching region of hydrotalcites is the overlap of the water stretching and cation hydroxyl stretching regions. This overlap leads to complexity of the band component analysis. Such overlap is better handled by Raman spectroscopy as water is inherently a strong infrared absorber but an inherently weak Raman scatterer. However with the case of the chromium based hydrotalcites, Raman spectroscopy is not applicable as the sample absorbs the incident radiation and self destructs. Thus the spectra as shown in Figures 1 and 2 include not only the water OH stretching bands but also the metal cation OH stretching bands. It is possible that all of the metal cation OH stretching bands are hidden by the water OH stretching bands and thus **Figures 1 and 2** may show only the water bands. If this is the case then we observe at least four water OH stretching vibrations at around 3060, 3262, 3473 and 3542 cm^{-1} . The bands at the higher wavenumber positions may be the cation OH stretching vibrations. Nevertheless we observe five OH stretching bands.

In all the spectra for the Mg/Zn and Ni/Co chromium hydrotalcites, there is a band in around 3265 cm^{-1} . Some variation in the band position is observed and for the high Zn hydrotalcites, the band shifts to higher wavenumbers. This band is attributed to water, which coordinates the hydrotalcite surfaces. Adsorbed water would show a band at around 3550 cm^{-1} . Bands are observed in the 3510 to 3542 cm^{-1} region and this band may be due to adsorbed water. The band at around 3473 cm^{-1} is attributed to hydrogen bonded water molecules. The band position of the water stretching modes suggests that the water is strongly hydrogen bonded. We propose that the water in hydrotalcites is not present simply as adsorbed water, or space filling water but rather is strongly hydrogen bonded into the hydrotalcite structure. In other words the water is in a highly structured environment. The band at around 3060 cm^{-1}

is attributed to the hydroxyl stretching vibration of water, which is coordinated to the carbonate ion.

The variation in the relative intensity of the OH stretching bands is shown in **Figures 5a and 5b**. The figures show that the intensity of the bands does not vary significantly as either the Mg is replaced by Zn or the Ni by Co in the $\text{Mg}_x\text{Zn}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ and $\text{Ni}_x\text{Co}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ hydrotalcites. If the bands were ascribed to MgOH and ZnOH together with CrOH units then some significant changes in intensity would be expected to be observed. This is not the case. Thus it is proposed that all of the bands in the spectra are attributable to water OH stretching vibrations. For both of these chromium hydrotalcites, significant intensity is observed in the 3421 and 3317 cm^{-1} bands. These bands are ascribed to strongly hydrogen bonded water and to coordinated water.

3.2 *Water OH deformation vibrations*

The presence of water in the hydrotalcite structure is important and it's bonding with either the carbonate anion or the cation hydroxyl units of necessity for the stability of the hydrotalcite layered structure. The region from around 1600 to 1750 cm^{-1} is a window, which is clear of other possible vibrations and is unique in that this is the region where the hydroxyl deformation modes of water are found. Minerals containing physically adsorbed water give strong infrared bands at 3450 cm^{-1} , the water hydroxyl stretching vibration, and at $\sim 1630 \text{ cm}^{-1}$, the water bending vibrations. These frequencies are influenced by the amount of adsorbed water, the mineral type and the exchangeable cation to which the water is bonded. For monomeric non-hydrogen bonded water as occurs in the vapour phase, these bands are found at 3755 and 1595 cm^{-1} . For liquid water the bands occur at 3455 and 1645 cm^{-1} and for water molecules in ice, the bands are at 3255 and 1655 cm^{-1} . When water molecules are very tightly bound to the mineral surface as may occur with hydrotalcites, then bands occur in the 3200 to 3250 cm^{-1} region. What is being distinguished here is the formation of strong and weak hydrogen bonds. The hydroxyl stretching modes of weak hydrogen bonds occur in the 3580 to 3500 cm^{-1} region and the hydroxyl stretching modes of strong hydrogen bonds occurs below 3420 cm^{-1} . When the water is coordinated to the cation in the clays as occurs in certain minerals, then the water OH stretching frequency occurs at 3220 cm^{-1} . A simple observation can be made that as the water OH stretching frequency decreases then the HOH bending frequency increases. The 3220 cm^{-1} band corresponds to an ice-like structure with O-H \cdots O bond distances of 2.77 Å. Thus the water hydroxyl stretching and the water HOH bending 1610 cm^{-1} frequencies provide a measure of the strength of the bonding of the water molecules either chemically or physically to the hydrotalcite surfaces or to the interlayer anions. Likewise the position of the water bending vibration also provides a measure of this strength of water hydrogen bonding. Bands that occur at frequencies above 1650 cm^{-1} are indicative of coordinated water and chemically bonded water. Bands that occur below 1630 cm^{-1} are indicative of water molecules that are not as tightly bound. In this case the hydrogen bonding is less as the frequency decreases.

The water HOH deformation or bending vibration for the chromium based $\text{Mg}_x\text{Zn}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ and $\text{Ni}_x\text{Co}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ hydrotalcites are shown in **Figures 3 and 4** respectively. The spectral profile for the Mg/Zn system is

complex and is more complex than the Ni/Co chromium based hydrotalcite system. This complexity reflects the different types of hydrogen bonded water molecules in the hydrotalcite structure. Five bands are resolved in the spectral profile of the water HOH deformation for the Mg/Zn chromium based hydrotalcites. The results of the band component analysis are reported in **Table 2**. Infrared bands are observed around (a) 1603 to 1619 cm^{-1} (b) 1622 to 1635 cm^{-1} (c) 1645 to 1660 cm^{-1} (d) 1670 to 1690 cm^{-1} (e) 1690 to 1700 cm^{-1} . Bands in region (a) are of low intensity and represent the non-hydrogen bonded water or space filling water in the hydrotalcites. The intensity of the bands shows that very little of this type of water molecule is present. Bands in region (b) represent adsorbed water such as might be observed on the outside of the hydrotalcite surfaces. Bands in region (c) are assigned to water molecules, which are strongly hydrogen bonded. Such water molecules are in a highly structured environment. The bands in regions (d) and (e) are attributed to water molecules, which are chemically bonded to the hydrotalcite. Such water molecules could be directly coordinated to the Mg or Zn cations such as at the end of the hydrotalcite surface. **Figure 5** shows the variation of the relative intensity of the water bending modes as a function of the replacement of Mg by Zn for the chromium based hydrotalcites. Figure 5a shows that the non hydrogen bonded water concentration is low, the hydrogen bonded water (region b) high and the highly structured water (region c) significantly high. The intensity of the bands remains reasonably constant and somewhat independent of the chemical composition of the hydrotalcite.

For the Ni/Co chromium based hydrotalcites, water bending bands are observed in region (a), (c) and (d). The variation of the relative intensity of the bands is shown in Figure 5b. The intensity of the hydrogen bonded structured water is significantly high for each of the Ni/Co hydrotalcites and the intensity of the coordinate water decreases with increasing replacement of the Ni by Co. The model that we present for the interlayer region of hydrotalcites is a highly structured arrangement of water molecules and carbonate anion. Some models of hydrotalcites show space between the hydrotalcite layers with the space partially filled with the counter anion and some water molecules. The model that we propose is of a hydrotalcite, which is completely filled with highly structured water together with the counter anion. The water is (a) hydrogen bonded to the carbonate (b) hydrogen bonded to the cation hydroxyl units (c) strongly hydrogen bonded to adjacent water molecules.

The observation of four major water-bending vibrations is in excellent harmony with the observation of four hydroxyl stretching vibrations. Thus the water bending modes found in the 1670 to 1690 cm^{-1} region correspond with the hydroxyl stretching bands at around 3060 cm^{-1} . The bands in the 1645 to 1660 cm^{-1} region are in empathy with the hydroxyl stretching bands at around 3317 cm^{-1} . Likewise the bands in the 1622 to 1635 cm^{-1} in the hydroxyl bending region are in harmony with the hydroxyl stretching bands at around 3421 cm^{-1} . Thus the concept of different types of water molecules in the hydrotalcite structure is confirmed by the observation of the hydroxyl stretching and bending modes.

3.3 *Carbonate vibrations*

Hydrotalcites are double-layered hydroxides in which a positive surface charge is counterbalanced by the negative charge of the stabilising anion. In many

hydrotalcites as is the case here, the carbonate ion is the counter ion. Often these materials are referred to as cationic clays. The unperturbed carbonate ion is a planar triangle with point symmetry D_{3h} . Group theoretical analysis of the carbonate ion predicts four normal modes the ν_1 symmetric stretch of A_1' symmetry normally observed at 1063 cm^{-1} , the asymmetric stretch of E' symmetry observed at 1415 cm^{-1} , the ν_2 out of plane bend at 879 cm^{-1} and the in-plane bend at 680 cm^{-1} . All modes are both Raman and infrared active except for the ν_2 mode, which is IR active only.

Figures 5 and 6 show the spectra of the CO stretching region for the chromium-based hydrotalcites reported in this work.

For the $\text{Mg}_x\text{Zn}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ series of hydrotalcites three bands are observed for the five hydrotalcites systems as x varies from 6 to 0. Three bands are observed at around 1358 , 1387 and 1481 cm^{-1} . Band component analysis shows some variation in band position but this is considered to be within experimental error. The asymmetric stretching mode of the free carbonate is normally observed at 1415 cm^{-1} . The observation of three vibrations for the E mode is an indication of the loss of symmetry from D_{3h} to a lower symmetry species such as C_{2v} . Such a result can be modelled by the carbonate and water forming a single unit. The two hydrogens of water hydrogen bonding to the two carbonate oxygens forms such a model. The hydroxyl stretching vibration around 3060 cm^{-1} is assigned to the water hydroxyl stretching vibrations of this unit.

The band at around 1470 to 1480 cm^{-1} is assigned to the CO stretching vibration of the hydrogen bonded CO stretching vibration of the water-carbonate unit. The two bands at around 1353 and 1387 cm^{-1} appear to show some regular variation of intensity with replacement of the Mg by Zn. As the Mg is replaced by Zn, the intensity of the band at 1353 cm^{-1} increases and concomitantly the band at 1387 cm^{-1} decreases. Such variation is shown in Figure 7. The 3/3 Mg/Zn hydrotalcite carbonate bands does not fit the pattern, otherwise the relationship is linear. One possible model is that the band at 1387 cm^{-1} is attributed to the carbonate associated with the hydroxyl stretching unit of Mg and the 1353 cm^{-1} band is associated with the carbonate associated with the ZnOH unit. However this model does not take into account the CrOH units. For the Ni/Co chromium based hydrotalcites, the band observed in the 1465 to 1493 cm^{-1} region is less intense than for the Mg/Zn chromium hydrotalcites. The two other carbonate bands are observed in the 1352 to 1366 cm^{-1} region and the 1392 to 1448 cm^{-1} region. The ratio of the relative intensities of these two bands is shown in Figure 7. The ratio of the intensities of the two bands decreases as the Ni is replaced by the Co. Hence one model would suggest that the lower wavenumber carbonate band is associated with the NiOH units and the higher wavenumber band with the CoOH units.

In the Raman spectrum of the Mg based chromium hydrotalcites two closely overlapping bands are observed at 1067 and 1068 cm^{-1} . In this type of hydrotalcite there are two types of OH units, namely CrOH and MgOH. One possible model is that the 1068 cm^{-1} band is attributable to carbonate associated with the CrOH unit and the 1067 cm^{-1} band with MgOH unit. The Raman spectrum of magnesite displays a band at 1087 cm^{-1} . Thus the behaviour of the carbonate ion in the hydrotalcites is more like that of a free carbonate ion rather than a carbonate bonded to the cation. The other hydrotalcites were destroyed under the incident laser beam. In the infrared spectra of the Mg/Zn chromium hydrotalcites, low intensity bands are observed at around 1062 cm^{-1} . For the Ni/Co chromium hydrotalcites, the band profile is observed

at slightly higher wavenumbers at 1066 cm^{-1} . The band profile is broad and complex. Thus the existence of multiple symmetric CO stretching vibrations is confirmed. This suggests that different carbonate species are observed in the hydrotalcites.

4. Conclusions

Insight into the unique structure of $\text{Mg}_x\text{Zn}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ and $\text{Ni}_x\text{Co}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ has been obtained using infrared spectroscopy. The hydroxyl-stretching units of different types of water molecules are identified by their unique band positions. Water plays a unique role in the stabilisation of the hydrotalcite structure. The position and intensity of the infrared bands in the hydroxyl-stretching region indicates that the water is highly structured. The position of the bands in the hydroxyl deformation region of the infrared spectrum lends strong support to the concept of structured water between the hydrotalcite layers. Four types of water are identified (a) water hydrogen bonded to the interlayer carbonate ion (b) water hydrogen bonded to the hydroxyl units of the hydroxyl surface (c) water which is strongly hydrogen bonded to adjacent water molecules and (d) interlamellar water. The position of the suite of bands associated with the carbonate ion indicates the carbonate ion is 'free' and not bonded to the metal centres.

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References

- [1]. C. W. Beck, *Am. Mineralogist* 35 (1950) 985.
- [2]. S. Caillere, *Compt. rend.* 219 (1944) 256.
- [3]. V. P. Ivanova and V. N. Moskaleva, *Termoanal. Issled. Sovrem. Mineral.* (1970) 91.
- [4]. V. S. Rovsha and S. I. Futergendler, *Zap. Vses. Mineralog. Obshchestva* 92 (1963) 354.
- [5]. L. Hickey, J. T. Klopogge and R. L. Frost, *J. Mater. Sci.* 35 (2000) 4347.
- [6]. J. T. Klopogge and R. L. Frost, *J. Solid State Chem.* 146 (1999) 506.
- [7]. J. T. Klopogge, L. Hickey and R. L. Frost, *Appl. Clay Sci.* 18 (2001) 37.
- [8]. S. Velu, K. Suzuki, S. Hashimoto, N. Satoh, F. Ohashi and S. Tomura, *J. Mater. Chem.* 11 (2001) 2049.
- [9]. M. A. Ulibarri, M. J. Hernandez and J. Cornejo, *J. Mater. Sci.* 26 (1991) 1512.
- [10]. T. Lopez, P. Bosch, M. Asomoza, R. Gomez and E. Ramos, *Mater. Lett.* 31 (1997) 311.
- [11]. K. J. D. Mackenzie, R. H. Meinhild, B. L. Sherriff and Z. Xu, *J. Mater. Chem.* 3 (1993) 1263.
- [12]. J. Perez-Ramirez, G. Mul and J. A. Moulijn, *Vib. Spectrosc.* 27 (2001) 75.
- [13]. J. Theo Klopogge and R. L. Frost, *Appl. Catal., A* 184 (1999) 61.
- [14]. J. Theo Klopogge and R. L. Frost, *Phys. Chem. Chem. Phys.* 1 (1999) 1641.

Table 1. Band component analysis of the infrared spectra of the hydroxyl-stretching region of $\text{Mg}_x\text{Zn}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ and $\text{Ni}_x\text{Co}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ hydroxalicates.

Mg/Zn Ratio	Mg/Zn 6:0	Mg/Zn 4:2	Mg/Zn 3:3	Mg/Zn 2:4	Mg/Zn 0:6
Band Centre/ cm^{-1}	3063	3038	3073	2929	3061
Percentage relative Amplitude	19.5	16.5	12.3	9.9	16.3
FWHM/ cm^{-1}	497.3	478.8	433.2	402.4	410.0
Band Centre/ cm^{-1}	3317	3262	3271	3228	3280
Percentage relative Amplitude	26.2	23.0	26.6	34.5	27.9
FWHM/ cm^{-1}	317.8	319.4	324.5	371.8	293.4
Band Centre/ cm^{-1}	3473	3409	3421	3415	3414
Percentage relative Amplitude	38.0	34.8	34.7	40.5	36.8
FWHM/ cm^{-1}	226.6	220.7	216.7	247.2	200.5
Band Centre/ cm^{-1}	3612	3518	3519	3531	3510
Percentage relative Amplitude	13.2	15.5	15.1	9.6	12.6
FWHM/ cm^{-1}	114.9	154.3	150.1	145.7	136.0
Band Centre/ cm^{-1}	3686	3602	3596	3601	3577
Percentage relative Amplitude	3.2	10.2	10.4	5.6	6.4
FWHM/ cm^{-1}	36.8	102.2	105.9	94.0	101.6
Ni/Co Ratio	Ni/Co 6:0	Ni/Co 4:2	Ni/Co 3:3	Ni/Co 2:4	Ni/Co 0:6
Band Centre/ cm^{-1}	3060	3054	3065	3048	3062
Percentage relative Amplitude	14.9	14.9	14.0	17.8	15.1
FWHM/ cm^{-1}	438.2	478.2	470.2	491.9	478.7
Band Centre/ cm^{-1}	3292	3265	3271	3267	3267
Percentage relative Amplitude	28.5	31.1	26.7	25.0	22.7
FWHM/ cm^{-1}	287.9	285.3	267.4	287.2	260.2
Band Centre/ cm^{-1}	3431	3426	3426	3424	3419
Percentage relative Amplitude	34.8	34.0	38.3	36.0	38.9
FWHM/ cm^{-1}	190.5	285.3	195.0	202.1	190.4
Band Centre/ cm^{-1}	3536	3545	3542	3537	3527
Percentage relative Amplitude	14.0	13.5	14.9	14.6	16.4
FWHM/ cm^{-1}	120.4	122.7	120.8	120.3	122.8
Band Centre/ cm^{-1}	3603	3614	3610	3606	3600
Percentage relative Amplitude	7.8	6.5	6.1	6.5	6.9
FWHM/ cm^{-1}	77.1	77.2	73.7	68.3	75.3

Table 2. Band component analysis of the infrared spectrum of the water HOH bending modes for $Mg_xZn_{6-x}Cr_2(OH)_{16}(CO_3).4H_2O$ and $Ni_xCo_{6-x}Cr_2(OH)_{16}(CO_3).4H_2O$ hydroxalces.

Mg/Zn Ratio	Mg/Zn 6:0	Mg/Zn 4:2	Mg/Zn 3:3	Mg/Zn 2:4	Mg/Zn 0:6
Band Centre /cm ⁻¹	1607	1617	1619	1610	1603
Relative amplitude /%	4.2	7.4	7.4	5.3	4.9
FWHM	17.2	15.8	11.6	22.0	19.3
Band Centre /cm ⁻¹	1623	1635	1632	1631	1622
Relative amplitude /%	15.8	30.7	21.1	34.7	24.7
FWHM	25.9	29.5	20.2	32.9	30.7
Band Centre /cm ⁻¹	1645	1660	1652	1659	1649
Relative amplitude /%	44.9	48.8	43.5	45.6	48.4
FWHM	36.3	40.0	29.1	37.9	41.4
Band Centre /cm ⁻¹	1674	1690	1671	1685	1675
Relative amplitude /%	30.4	10.6	10.3	8.5	11.6
FWHM	37.6	23.9	18.7	20.2	22.4
Band Centre /cm ⁻¹	1700	1707	1682	1698	1693
Relative amplitude /%	4.7	2.6	17.8	5.9	10.4
FWHM	21.5	8.1	30.8	70.9	25.9
Ni/Co Ratio	Ni/Co 6:0	Ni/Co 4:2	Ni/Co 3:3	Ni/Co 2:4	Ni/Co 0:6
Band Centre /cm ⁻¹	1614	1581	1583	1597	1618
Relative amplitude /%	15.0	4.0	6.3	4.5	16.6
FWHM	39.8	7.5	40.3	42.5	45.7
Band Centre /cm ⁻¹	1644	1640	1637	1641	1648
Relative amplitude /%	52.1	71.8	66.2	74.8	70.0
FWHM	65.2	80.1	63.9	62.5	54.6
Band Centre /cm ⁻¹	1680	1686	1675	1680	1686
Relative amplitude /%	43.6	31.0	22.5	20.7	13.8
FWHM	19.8	12.4	64.8	49.8	38.8

Table 3. Band component analysis of the CO stretching region of carbonate in $Mg_xZn_{6-x}Cr_2(OH)_{16}(CO_3)_4 \cdot 4H_2O$ and $Ni_xCo_{6-x}Cr_2(OH)_{16}(CO_3)_4 \cdot 4H_2O$ hydroxalicates.

Mg/Zn Ratio	Mg/Zn 6:0	Mg/Zn 4:2	Mg/Zn 3:3	Mg/Zn 2:4	Mg/Zn 0:6
Band Centre /cm ⁻¹	1358	1353	1353	1352	1353
Relative amplitude /%	21.1	30.9	42.5	41.4	55.5
FWHM	50.8	58.3	41.4	55.5	51.3
Band Centre /cm ⁻¹	1387	1391	1385	1389	1389
Relative amplitude /%	55.9	39.9	52.6	33.1	26.0
FWHM	91.6	73.9	91.1	72.8	63.4
Band Centre /cm ⁻¹	1381	1482	1495	1478	1471
Relative amplitude /%	23.01	25.2	25.0	25.5	18.6
FWHM	84.3	102.1	97.9	97.5	88.8
Ni/CoRatio	Ni/Co 6:0	Ni/Co 4:2	Ni/Co 3:3	Ni/Co 2:4	Ni/Co 0:6
Band Centre /cm ⁻¹	1291	1307	1305	1308	1306
Relative amplitude /%	1.1	3.6	2.9	3.7	2.8
FWHM	28.5	46.6	41.8	43.4	37.0
Band Centre /cm ⁻¹	1366	1363	1358	1358	1352
Relative amplitude /%	56.1	59.0	48.2	44.7	40.0
FWHM	78.8	61.2	56.8	54.8	50.2
Band Centre /cm ⁻¹	1448	1415	1396	1392	1387
Relative amplitude /%	31.9	38.1	41.9	41.1	49.0
FWHM	85.9	71.7	86.8	88.8	86.1
Band Centre /cm ⁻¹	1493	1465	1468	1466	1474
Relative amplitude /%	10.9	9.2	7.0	10.6	8.3
FWHM	65.7	44.9	51.2	55.9	54.7

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Table 1. Band component analysis of the infrared spectra of the hydroxyl-stretching region of $\text{Mg}_x\text{Zn}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ and $\text{Ni}_x\text{Co}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ hydrotalcites.

Table 2. Band component analysis of the infrared spectrum of the water HOH bending modes for $\text{Mg}_x\text{Zn}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ and $\text{Ni}_x\text{Co}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ hydrotalcites.

Table 3. Band component analysis of the CO stretching region of carbonate in $\text{Mg}_x\text{Zn}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ and $\text{Ni}_x\text{Co}_{6-x}\text{Cr}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ hydrotalcites.

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