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Vibrational spectroscopic study of the nitrate containing hydrotalcite Mbobomkulite

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Abstract

Raman spectroscopy has been used to study the nitrate hydrotalcite mbobomkulite $\text{NiAl}_2(\text{OH})_{16}(\text{NO}_3)\cdot 4\text{H}_2\text{O}$. Mbobomkulite along with hydrombobomkulite and sveite are known as 'cave' minerals as these hydrotalcites are only found in caves. Two types of nitrate anion are observed using Raman spectroscopy namely free or non-hydrogen bonded nitrate and nitrate hydrogen bonded to the interlayer water and to the 'brucite-like' hydroxyl surface. Two bands are observed in the Raman spectrum of Ni-Mbobomkulite at 3576 and 3647 cm^{-1} with an intensity ratio of 3.36/7.37 and are attributed to the Ni_3OH and Al_3OH stretching vibrations. The observation of multiple water stretching vibrations implies that there are different types of water present in the hydrotalcite structure. Such types of water would result from different hydrogen bond structures.

Keywords: mbobomkulite, stichtite, iowaite, desautelsite, takovite, hydrotalcite, Raman spectroscopy

Introduction

A group of minerals exist which are known as hydrotalcites or anionic clays. These anionic clays may contain different anions in the interlayer such as chloride, sulphate or nitrate. It has been said that the minerals are rare, but such a comment is questionable since large deposits exist in Australia. Hydrotalcites are found in deposits of minerals in Australia where paragenetic relationships between minerals exist. These hydrotalcites are based upon the anions of carbonate (takovite, hydrotalcite, reevesite, pyroaurite), sulphate (carrboydite, mountkoreaite, honessite, mountkeithite) and even chloride (iowaite). The discovery of large amounts of natural hydrotalcites at Mount Keith in Western Australia means that these minerals could be obtained for specific applications [1]

Naturally occurring nitrate minerals are found in a number of different environments, but the majority of these are in areas of high evaporation or in arid climates. This is due to the generally high solubility of nitrate salts in water. Exceptions are the metastable nitrate-bearing members of the hydrotalcite groups and certain basic copper salts. Three nitrate bearing members of the hydrotalcite group containing nickel are confined to a single locality, the Mboobo Mkulu cave in South Africa. Nitrate is formed as above and nickel and copper are derived from oxidising sulphide minerals in associated shale horizons. Sveite is also a cave mineral from the Autana cave, Venezuela, and has been reported as a coating on rock faces at an unspecified Californian locality.

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Anionic clays, hydrotalcites or layered double hydroxides (LDH) are less well-known and more diffuse in nature than cationic clays like smectites. In fact anionic clays are electrostatically the inverse of smectites. Smectites carry a negative layer charge and so are counterbalanced electrically by positive cations whereas the hydrotalcites are positively charged and are counterbalanced by the negative charge of anions [2, 3]. 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. All of these minerals are based on the hydrotalcite, $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$, structure, consisting of an $\text{M}(\text{OH})_2$ layer that sandwiches layers containing anions, metal ions and water molecules. The minerals are metastable phases with respect to Al(III) oxyhydroxides and other soluble components. Hydrotalcites such as pyroaurite are trigonal carbonates whereas the manasseite group including sjögrenite are hexagonal carbonates. In hydrotalcites a broad range of compositions are possible of the type $[\text{M}^{2+}_x\text{M}^{3+}_{1-x}(\text{OH})_2][\text{A}^{n-}]_{x/n}\cdot y\text{H}_2\text{O}$, 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. Many variations in compositions have been reported for hydrotalcites. One of the variations in cations comprises takovite in which Mg is replaced by Ni. There are a number of nitrate bearing hydrotalcites, these are:

Hydrombobomkulite	$(\text{Ni,Cu})\text{Al}_4[(\text{NO}_3)_2,(\text{SO}_4)](\text{OH})_{12}\cdot 12\text{-}14\text{H}_2\text{O}$
Mbobomkulite	$(\text{Ni,Cu})\text{Al}_4[(\text{NO}_3)_2,(\text{SO}_4)](\text{OH})_{12}\cdot 3\text{H}_2\text{O}$
Nickelalumite	$(\text{Ni,Cu})\text{Al}_4[(\text{SO}_4),(\text{NO}_3)_2](\text{OH})_{12}\cdot 3\text{H}_2\text{O}$
Sveite	$\text{KAl}_7(\text{NO}_3)_4\text{Cl}_2(\text{OH})_{16}\cdot 8\text{H}_2\text{O}$

The natural minerals have cationic mixtures of Ni and Cu in the hydrotalcite. In order to avoid the effects of such a complication the minerals have been synthesised in the laboratory. In this work the mineral Mbobomkulite has been synthesised and characterised by Raman spectroscopic techniques.

EXPERIMENTAL

The Minerals

Mbobomkulite minerals (both Ni and Cu) were synthesised by the co-precipitation method. Hydrotalcites with a composition of $(\text{Ni,Cu})_6\text{Al}_2(\text{OH})_{16}(\text{NO}_3)_4\cdot 4\text{H}_2\text{O}$ were synthesised. Three solutions were prepared, solution 1 contained 2M NaOH and 0.125M Na_2NO_3 , solution 2 contained 0.75M Ni^{2+} ($\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$) and solution 3 contained 0.75M Cu^{2+} ($\text{Cu}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$) in the appropriate ratio, together with 0.25M Al^{3+} (as $(\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O})$). Solution 2 in the appropriate ratio was added to solution 1 using a peristaltic pump at a rate of 40 cm^3/min , under vigorous stirring, maintaining a pH of 10. The minerals were synthesised in an atmosphere of nitrogen as it is essential to keep carbon dioxide out of the system. Otherwise mixed nitrate-carbonate hydrotalcites are formed. The precipitated minerals are washed at ambient temperatures thoroughly with water to remove any residual starting materials. The composition of the hydrotalcites was checked by electron probe analyses. The phase composition was checked by X-ray diffraction.

Raman microprobe spectroscopy

The crystals of hydrotalcite minerals were placed and orientated on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . Repeated acquisition, using the highest magnification, was accumulated to

improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Powers of less than 1 mW at the sample were used to avoid laser induced degradation of the sample. [4-6] Slight defocusing of the laser beam also assists in the preservation of the sample.

Spectroscopic 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 Gauss-Lorentz 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.

RESULTS AND DISCUSSION

Hydrotalcites with oxyanions such as carbonate and sulphate lend themselves to analysis by Raman and infrared spectroscopy. Hydrotalcites with chloride anions in the interlayer are more difficult to analyse. The Raman and infrared spectra of the Ni and Cu Mbobomkulite hydrotalcites in the 800 to 1200 cm^{-1} region are shown in Figure 1 (Ni- Mbobomkulite) and Figure 2 (Cu- Mbobomkulite). The results of the Raman and infrared spectroscopic analyses are reported in Table 1. Two overlapping bands are observed at 1050 and 1045 cm^{-1} with bandwidths of 14.0 and 9.0 respectively (Figure 1). The bands are sharp. The bands are assigned to the $\nu_1\text{ NO}_3$ symmetric stretching vibration. The band at 1045 cm^{-1} is assigned to free or non-hydrogen bonded nitrate and the band at 1050 cm^{-1} to hydrogen bonded nitrate anion. The Raman spectroscopy of the nitrate anion in aqueous media have been studied [7-14]. Normally the $\text{NO}_3\text{ } \nu_1$ symmetric stretching vibration shifts to higher wavenumbers when the nitrate ion is involved with ion pairing. However in the case of hydrotalcites no ion pairing with cations can occur as there are no cations in the hydrotalcite interlayer. Thus the shift in band position must be associated with hydrogen bonding to some other unit such as water or the brucite-like hydroxyl surface. In the formation of hydrotalcites the nitrate anion is held in the interlayer through hydrogen bonding to water molecules. These water molecules may hydrogen bond to the brucite-like hydroxyl surface. There are no cations in the interlayer. Thus a shift in wavenumbers from 1045 to 1050 cm^{-1} is attributed to hydrogen bonding of the nitrate either to the hydroxyl surface or to the water. Previous studies have suggested that the water in the hydrotalcite interlayer is in a highly ordered structure [15-18]. Low intensity bands are observed in the infrared spectrum at 1035 and 1068 cm^{-1} . (Note that the infrared spectrum in Figure 1 has been expanded 15 times). The Raman spectrum for the Cu- mbobomkulite is more complex (Figure 2). An intense band is observed at 1075 cm^{-1} and may be assigned to the $\nu_1\text{ NO}_3$ symmetric stretching vibration. The position of the band suggests the nitrate is strongly hydrogen bonded in the Cu- mbobomkulite interlayer. In the infrared spectrum bands are observed at 1157 , 1068 and 1062 cm^{-1} .

The 1200 to 1700 cm^{-1} spectral region for the Ni- Mbobomkulite is shown in Figure 3. This region for the Cu- Mbobomkulite is included in Figure 2. This region covers two types of vibrating units namely the water HOH bending mode and the $\text{NO}_3\text{ } \nu_3$ antisymmetric stretching modes. The band at 1643 cm^{-1} in the Raman spectrum and 1638 cm^{-1} in the infrared spectrum for Ni- Mbobomkulite is attributed to the water HOH bending vibration. It is unusual to observe this mode in the Raman spectrum as water is an inherent poor scatterer. The band is not observed in the Raman spectrum of Cu- mbobomkulite but is observed at 1640 cm^{-1} in the infrared spectrum. The water HOH bending mode for liquid water is normally observed at around 1630 cm^{-1} . The shift of the band in hydrotalcites to higher wavenumbers shows that the water is involved in hydrogen

bonding either to the nitrate anion or to the mbobomkulite hydroxyl surface. Two bands are observed at 1413 and 1342 cm^{-1} in the Raman spectrum and at 1400 and 1349 cm^{-1} in the infrared spectrum of Ni-mbobomkulite. These bands are attributed to the NO_3 ν_3 antisymmetric stretching vibration. The Raman spectrum of the Cu-mbobomkulite is inconclusive in this region; except to indicate the bands are of very low intensity. Infrared bands are observed at 1489, 1401 and 1360 cm^{-1} .

The Raman spectra of the low wavenumber region of the Ni-Mbobomkulite and Cu-Mbobomkulite are shown in Figures 4 and 5. The infrared spectra were not obtained as the lower spectral limit of the ATR technique is 550 cm^{-1} . The two bands at 713 and 676 cm^{-1} may be assigned to the ν_2 ONO bending mode. Two bands are observed at 719 and 681 cm^{-1} for the Cu-mbobomkulite and may also be assigned to this mode. The position of these bands is at a quite low wavenumber as the ν_2 NO_3 vibration of solid nitrates normally occurs in the 770 to 830 cm^{-1} region depending on the valency of the cation. However the situation of the nitrate anion in the interlayer of the hydrotalcite is very different from that of solid nitrates. Intense Raman bands are observed at 570, 541 and 494 cm^{-1} in the Raman spectrum of Ni-Mbobomkulite. An intense band is observed at 590 cm^{-1} for Cu-Mbobomkulite. One possibility is that these bands may be assigned to the ν_4 NO_3 bending modes. Considerable variation can be found in the position of the ν_4 bands. Normally the band is found in the 690 to 760 cm^{-1} region. Two intense bands are observed at 350 and 340 cm^{-1} and are attributed to NiO stretching vibrations. For Cu-Mbobomkulite two intense bands are found at 334 and 284 cm^{-1} . Table 1 lists other low intensity bands for completeness.

The Raman and infrared spectra of the hydroxyl stretching region of the Ni&Cu-Mbobomkulite hydrotalcites are shown in Figures 6 and 7. The spectral profile is complex and consists of a number of overlapping bands. In brucite type solids, there are tripod units M_3OH with several metals such as M, M', M''. In hydrotalcites such as those based upon Ni and Cu of formula $\text{Ni}_x\text{Cu}_{6-x}\text{Al}_2(\text{OH})_{16}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, a number of statistical permutations of the M_3OH units are involved. These are Ni_3OH , Cu_3OH , Al_3OH and combinations such as Ni_2CuOH , Cu_2NiOH , Ni_2AlOH , Al_2NiOH , Al_2CuOH , Cu_2AlOH , and even NiCuAlOH . These types of units will be distributed according to a probability distribution according to the composition. In this model, a number of assumptions are made, namely that the molecular assembly is random and that no islands or lakes of cations are formed. In the simplest case namely $\text{Ni}_6\text{Al}_2(\text{OH})_{16}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ the types of units would be Ni_3OH , Ni_2AlOH , NiAl_2OH and Al_3OH . A similar situation would exist for the $\text{Cu}_6\text{Al}_2(\text{OH})_{16}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ hydrotalcite. In a somewhat oversimplified model, for the $\text{Ni}_6\text{Al}_2(\text{OH})_{16}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ hydrotalcite, the most intense bands would be due to the Ni_3OH and Al_3OH bands. The formula of the synthesised hydrotalcite is such that three hydroxyl-stretching vibrations are predicted, namely Al_3OH , Ni_3OH and H-OH. For the $\text{Ni}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$ hydrotalcite the ratio of Ni/Al is 3:1 and consequently the expected intensity ratio of the Ni_3OH and Al_3OH stretching vibrations ought to be in this same ratio (providing the assumption is made that the two MOH units scattering cross sections are similar). Two bands are observed in the Raman spectrum of Ni-Mbobomkulite at 3576 and 3647 cm^{-1} with an intensity ratio of 3.36/7.37 and are attributed to the Ni_3OH and Al_3OH stretching vibrations. Intense bands are observed at 3468 and 3250 cm^{-1} and are assigned to water HOH stretching bands. The equivalent bands in the infrared spectrum are found at 3606 and 3541 cm^{-1} . Intense infrared bands are observed at 3465, 3314 and 3131 cm^{-1} and are assigned to the water HOH stretching vibrations. The Raman spectrum in the hydroxyl stretching region of Ni-mbobomkulite is not as definitive. Basically two bands are observed at 3666 and 3353 cm^{-1} . The latter band could be decomposed into components. However the rationale for band fitting is always in terms of the minimum number of bands. In the infrared spectrum two bands are observed at 3578 and 3469 cm^{-1} with an intensity ratio of 2.21/6.27 which is close to 1/3. Intense bands are observed at 3330, 3253 and 3090 cm^{-1} . These bands are attributed to water HOH stretching vibrations. The observation of multiple stretching vibrations implies that there are different types of water present in the

hydrotalcite structure. Such types of water would result from water in different hydrogen bond structures.

CONCLUSIONS

Hydrotalcites have a unique structure in that the mineral acts like an anionic clay with a 'giant' cation whose charge is counterbalanced by multiple anions in the interlayer. Hydrotalcites are normally not easy to measure in terms of Raman spectroscopy because of their small particle size together with their disordered nature. The Raman spectroscopy of the natural hydrotalcites has the benefit that the crystallization has taken place over eons of time and consequently the particles are sufficiently large to be observed using the Raman microscopic technique.

Hydrotalcites containing nitrate anions are readily measured by Raman spectroscopy as the nitrate anion is an intense Raman scatterer. The other difficulty with the measurement of hydrotalcites is that those based upon nickel or nickel with some copper can be highly coloured and are likely to be susceptible to laser degradation. This can be readily observed under the optical microscope. Such laser induced decomposition may result in dehydration, dehydroxylation and even anion loss of the hydrotalcite. Such phenomena can be observed by changes in the Raman spectrum as the data is collected. The use of low power densities and slight defocusing of the laser assists in the collection of spectra without damage to precious (and sometimes rare) minerals.

In this work, the Raman spectra of the interlayer anions of nitrate have been collected. The splitting of the ν_3 , ν_4 and ν_2 modes indicates symmetry lowering. The symmetry lowering must be taken into account through the bonding of nitrate anion to both water and the brucite-like hydroxyl surface. Water plays an essential role in the hydrotalcite structure as may be evidenced by the position of the water bending modes. The water is strongly hydrogen bonded to both the anions and the hydroxyl surface. Raman spectroscopy has the advantage of water being a very poor scatterer and hence is difficult to observe compared with IR spectroscopy. Thus the cation OH stretching vibrations are more readily observed with Raman spectroscopy.

Acknowledgments

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Table 1 Results of the Raman and infrared spectral analysis of Ni and Cu mbobomkulite hydrotalcites

Nickel		Copper	
Raman	Infrared	Raman	Infrared
Centre (cm⁻¹) / FWHM (cm⁻¹) / Intensity (%)	Centre (cm⁻¹) / FWHM (cm⁻¹) / Intensity (%)	Centre (cm⁻¹) / FWHM (cm⁻¹) / Intensity (%)	Centre (cm⁻¹) / FWHM (cm⁻¹) / Intensity (%)
3647 / 91 / 3.36	3606 / 109 / 1.76	3666 / 78 / 0.67	3578 / 126 / 2.21
3576 / 135 / 7.37	3541 / 69 / 1.15	3353 / 401 / 14.48	3469 / 176 / 6.27
3544 / 16 / 0.14	3465 / 202 / 19.19		3330 / 227 / 22.89
3468 / 243 / 26.62	3314 / 245 / 28.71		3253 / 249 / 19.81
3447 / 33 / 0.56	3131 / 306 / 29.11		3090 / 265 / 27.56
3422 / 20 / 0.47	2882 / 366 / 10.45		2876 / 384 / 11.27
3250 / 421 / 33.98			
2900 / 178 / 3.11			
1643 / 60 / 0.39	1638 / 85 / 1.97		1640 / 89 / 2.60
1413 / 84 / 1.41	1494 / 141 / 1.28	1365 / 22 / 0.11	1561 / 55 / 0.30
1342 / 72 / 0.59	1400 / 62 / 1.70	1209 / 88 / 7.00	1489 / 93 / 1.62
	1349 / 63 / 2.61		1401 / 76 / 1.01
			1360 / 82 / 1.59
1058 / 66 / 1.65	1068 / 34 / 0.38	1159 / 61 / 2.87	1157 / 27 / 0.04
1050 / 14 / 4.44	1035 / 62 / 0.61	1101 / 86 / 8.81	1068 / 26 / 0.47
1045 / 9 / 2.46	976 / 60 / 0.58	1075 / 209 / 25.30	1062 / 50 / 0.73
	919 / 74 / 0.25	904 / 16 / 0.10	1019 / 76 / 0.45
			908 / 46 / 0.16
713 / 22 / 0.44	733 / 81 / 0.25	848 / 69 / 0.70	764 / 37 / 0.15
676 / 37 / 1.03		719 / 33 / 0.42	729 / 50 / 0.67
614 / 99 / 1.11		681 / 57 / 1.71	687 / 28 / 0.20
		617 / 40 / 2.15	
570 / 53 / 2.61		590 / 100 / 12.22	
545 / 14 / 0.10		482 / 76 / 1.72	
541 / 42 / 1.06		438 / 54 / 1.61	
494 / 43 / 1.67			
447 / 31 / 0.29			
350 / 17 / 1.51		334 / 40 / 7.35	
340 / 62 / 1.41		284 / 38 / 7.65	
337 / 14 / 0.72		257 / 45 / 2.74	
324 / 17 / 0.16		228 / 32 / 1.67	
297 / 25 / 0.21		186 / 27 / 0.36	
217 / 42 / 0.46		152 / 27 / 0.23	
184 / 43 / 0.40		115 / 33 / 0.14	
181 / 10 / 0.07			
160 / 16 / 0.11			
142 / 11 / 0.09			

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Figure 1 Raman and infrared spectra of Ni- mbobomkulite in the 800 to 1200 cm^{-1} region.

Figure 2 Raman and infrared spectra of Cu- mbobomkulite in the 800 to 1800 cm^{-1} region.

Figure 3 Raman and infrared spectra of Ni- mbobomkulite in the 1200 to 1800 cm^{-1} region.

Figure 4 Raman spectrum of Ni-mbobomkulite in the 100 to 800 cm^{-1} region.

Figure 5 Raman spectrum of Cu-mbobomkulite in the 100 to 800 cm^{-1} region.

Figure 6 Raman and infrared spectra of Ni-mbobomkulite in the 2500 to 3900 cm^{-1} region.

Figure 7 Raman and infrared spectra of Cu-mbobomkulite in the 2500 to 3900 cm^{-1} region.

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Table 1 Results of the Raman and infrared spectral analysis of Ni and Cu
mbobomkulite hydrotalcites

Figure 1

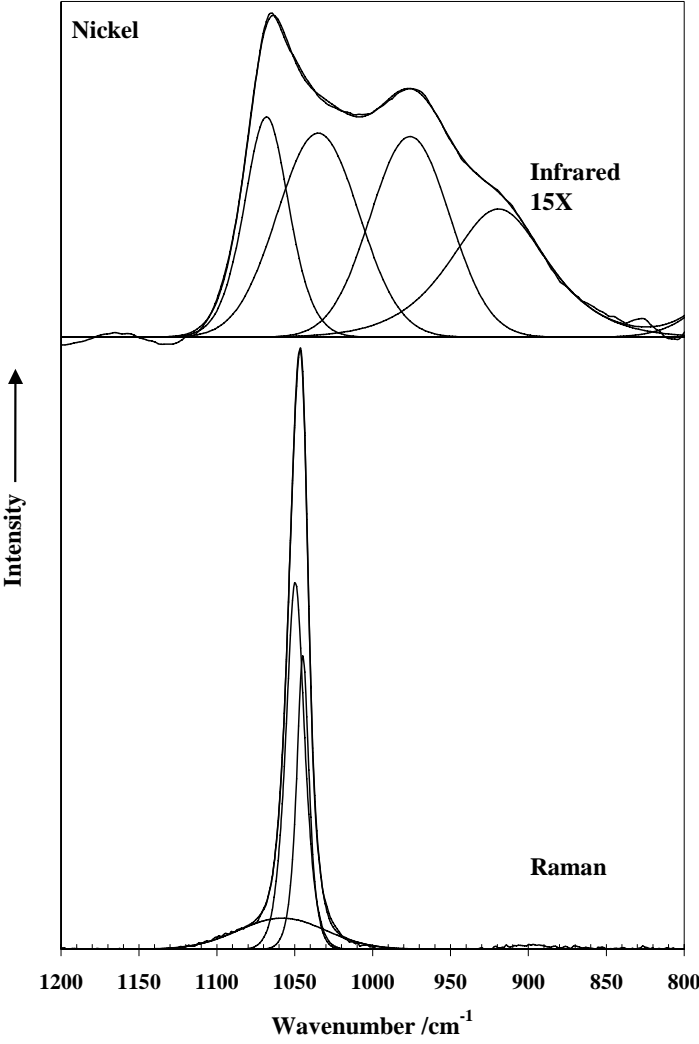
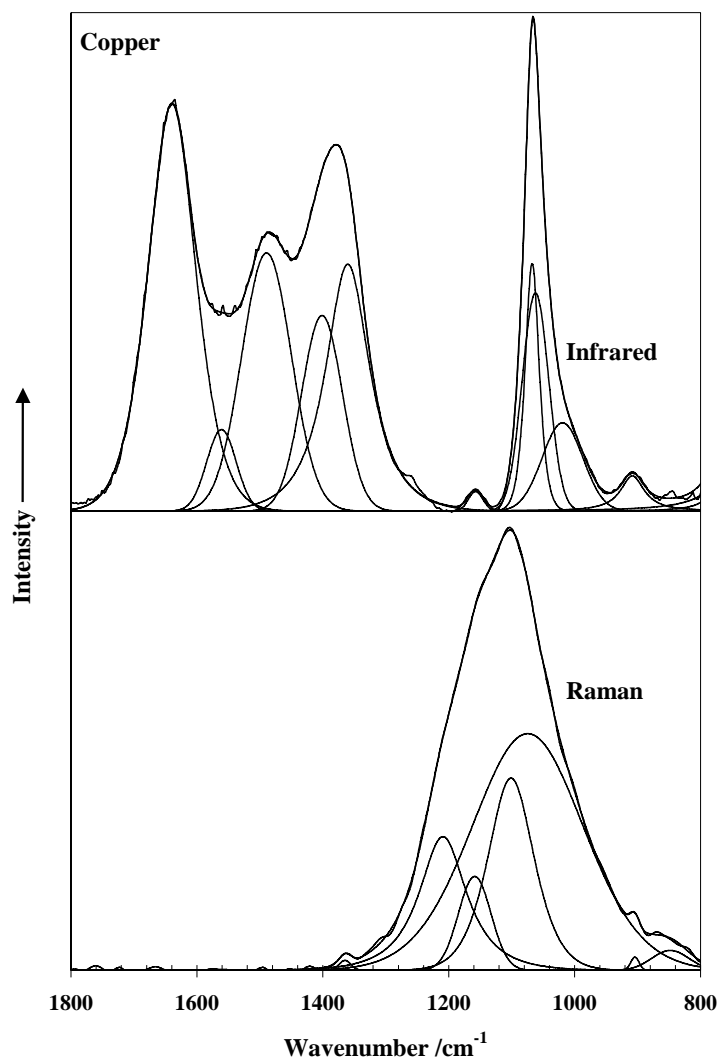


Figure 2



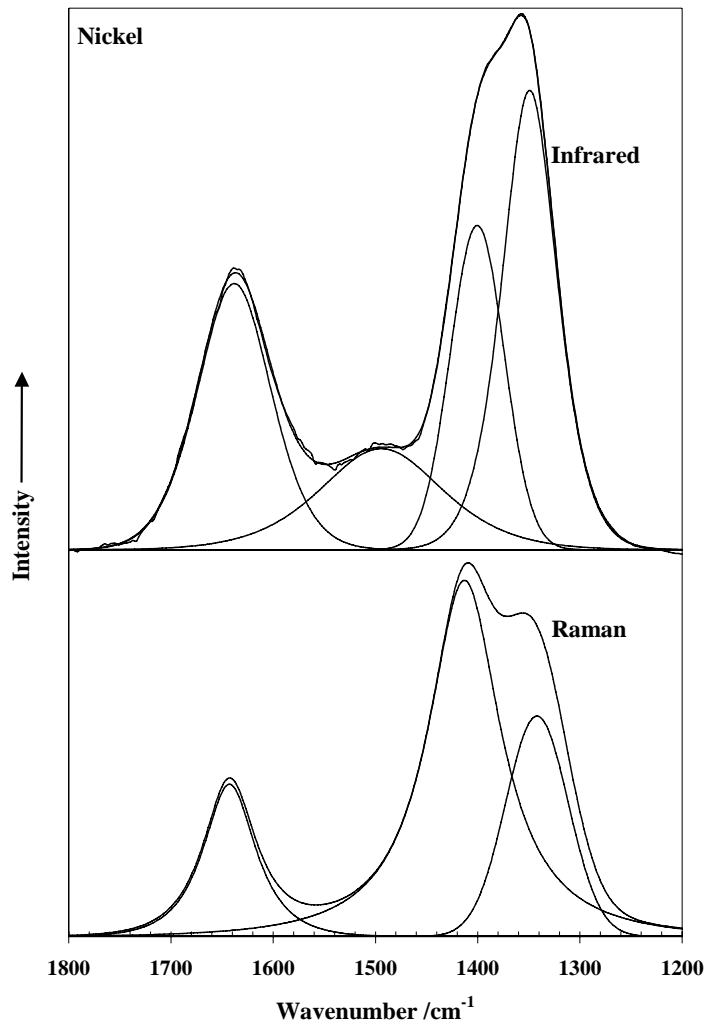


Figure 3

Figure 4

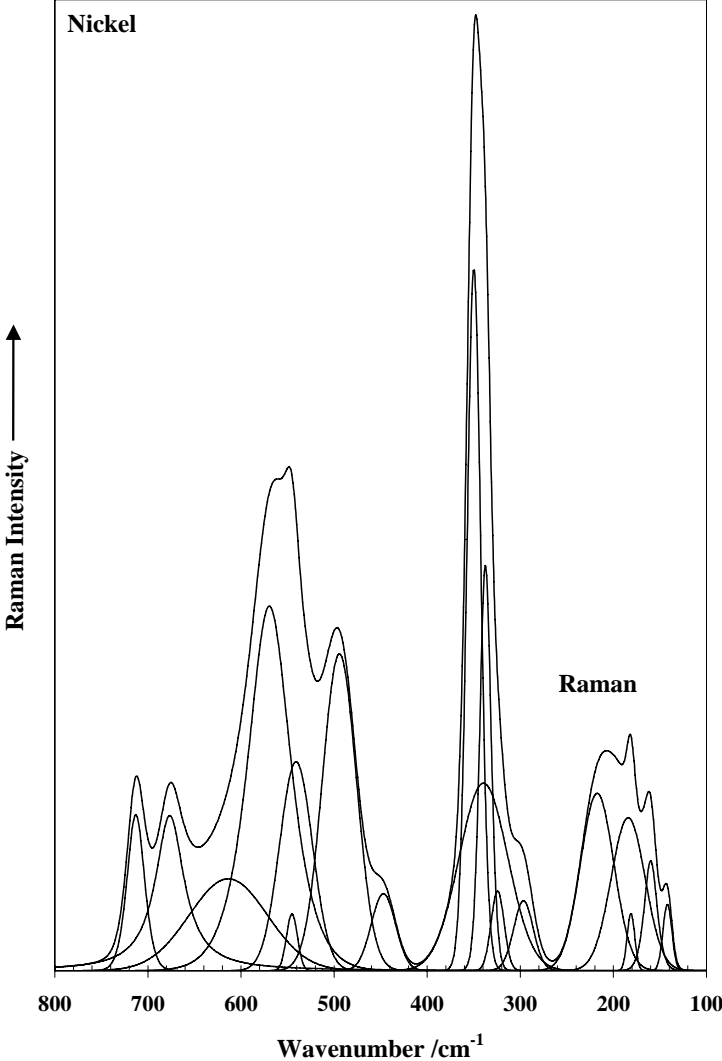
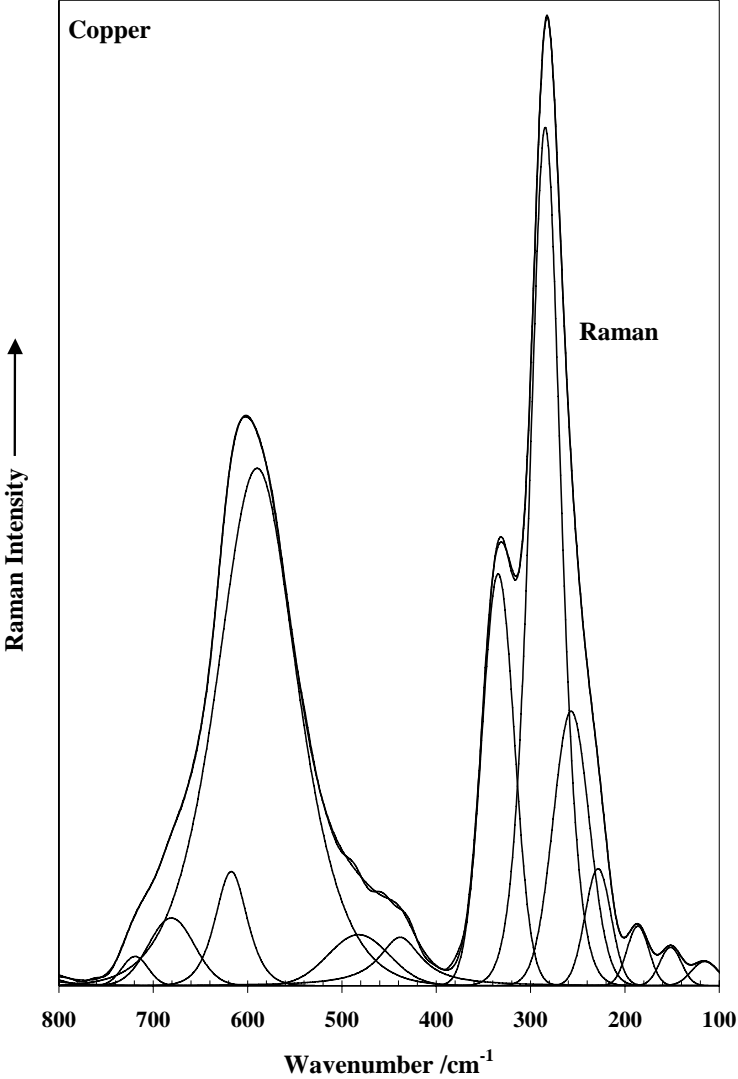


Figure 5



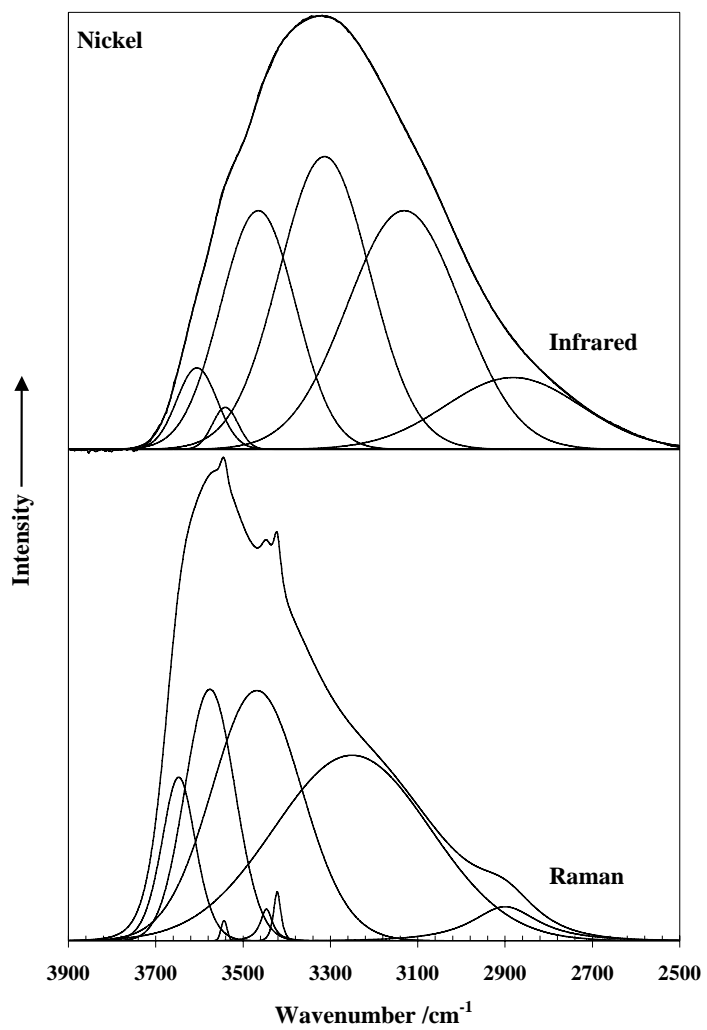


Figure 6

Figure 7

