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Vibrational spectroscopy of the basic manganese, ferric and ferrous phosphate minerals: strunzite, ferristrunzite and ferrostrunzite

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Abstract

The Raman spectra of strunzite, ferristrunzite and ferrostrunzite have been obtained at 298 and 77K using a combination of a thermal stage and Raman microscopy. These spectra are compared with their infrared spectra. The vibrational spectra of the two minerals are different, in line with differences in crystal structure and composition. Some similarity in the Raman spectra of the hydroxyl-stretching region exists, particularly at 298K, but characteristic differences in the OH deformation regions are observed. Significant shifts in the position of the Raman bands are observed by obtaining the spectra at 77K. Differences are also observed in the phosphate stretching and deformation regions.

Key Words- ferric, manganese, phosphate, thermal stage, liquid nitrogen temperature, Raman spectroscopy

1. Introduction

The basic chemistry of the strunzite mineral group has been known for some time (FRONDEL, C., 1957; FRONDEL, C., 1958; MOORE, P. B., 1964; MOORE, P. B., 1965). There are two minerals based on strunzite, namely ferristrunzite and ferrostrunzite that are isostructural with strunzite. The formulae of these minerals are $Mn^{2+}Fe_2^{3+}(PO_4)_2(OH)_2 \cdot 6H_2O$, $Fe^{3+}Fe_2^{3+}(PO_4)_2(OH)_2 \cdot (5H_2O \cdot OH)$, $Fe^{2+}Fe_2^{3+}(PO_4)_2(OH)_2 \cdot (5H_2O \cdot OH)$ (VOCHTEN, R. and DE GRAVE, E., 1990; VOCHTEN, R. et al., 1995). Strunzite, $MnFe_2(PO_4)_2(OH)_2 \cdot 6H_2O$, is triclinic, space group *P1*. Table 1 compares the crystallographic data for these three phosphate minerals.

	Triclinic	a	b	c	α	β	γ	Z
strunzite	<i>P1</i>	10.228	9.837	7.284	90.17	98.44	116.4	2
ferristrunzite	<i>P1</i>	10.01	9.73	7.334	89.65	98.28	116.4	2
ferrostrunzite	<i>P1</i>	10.23	9.77	7.37	89.65	98.28	117.26	2

Table 1 Comparison of the crystallographic data for strunzite, ferristrunzite and ferrostrunzite

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The strunzite mineral exhibits a well-marked monoclinic pseudocell with the pseudosymmetry of $C2/c$ space group. The atomic arrangement consists of chains built up by Fe coordination octahedra sharing vertices; PO_4 tetrahedra link together adjacent octahedra. Parallel chains are connected PO_4 groups to form thick slabs. Parallel slabs are connected by Mn coordination octahedra, to form the three-dimensional framework (FANFANI, L. et al., 1978). Ferristrunzite is also triclinic but the crystals are acicular, rounded and elongated. Likewise ferrostrunzite is triclinic with prismatic flattened crystals.

Raman spectroscopy of these minerals has not been reported. Farmer reports the vibrational spectra of the copper phosphate minerals: libethenite, cornetite and pseudomalachite and some iron phosphate minerals such as vivianite and triplodite [Farmer, 1974 #79]. Raman spectra of aqueous phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1} , the antisymmetric stretching mode (ν_3) at 1017 cm^{-1} , the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν_4 mode at 567 cm^{-1} . Such bands will become more complex in a crystal structure involving more than one cation and degeneracy will be lost. Farmer reports the infrared spectrum of triplodite with formula $(Mn,Fe)_2PO_4OH$ with the (ν_1) at 957 cm^{-1} , (ν_3) at 1090, 1058, 1030 and 1010 cm^{-1} , (ν_2) at 420 cm^{-1} and the ν_4 mode at 595, 570, 486 cm^{-1} (FARMER, V. C., 1974). An hydroxyl stretching frequency of 3509 cm^{-1} was given. The chemical formula of this mineral is close to that of strunzite and so similar spectra could be expected. As part of a comprehensive study of the IR and Raman properties of minerals containing oxyanions, we report the Raman properties of the abovenamed phases and relate the spectra to the mineral structure.

2. EXPERIMENTAL

2.1 Analysis of samples

Specimens of strunzite (M36370) and ferristrunzite (M42515) were obtained from the collections of Museum Victoria, Australia and were confirmed using powder X-ray diffraction methods. SEM analyses indicated no As or transition metals other than Mn and Fe to be present. The sample of ferrostrunzite from Arnsberg, Sauerland, Germany was obtained from Prof R. Vochten. All minerals were checked by X-ray diffraction and Mossbauer spectroscopy.

2.2 Raman microprobe spectroscopy

Crystals of the minerals were orientated on a polished metal surface on the stage of an Olympus BHSM microscope equipped with 10x and 50x objectives. For ludjibaite and reichenbachite, crystals on matrix were placed directly under the microscope. 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} between 100 and 4000 cm^{-1} . Repeated acquisitions using the highest magnification were accumulated to improve the signal-to-noise ratio in the spectra, which were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).

Infrared spectra were collected using a Nicolet infrared microscope using an ATR technique with silica plates. 64 scans were collected with a resolution of 4 cm^{-1} . Spectroscopic manipulations such as baseline adjustment, smoothing and normalization 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 specific parameters to be fixed or varied accordingly. Band fitting was carried out 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.

3. Results and Discussion

3.1 Theory

Table 2 Factor group analysis of the phosphate group (I + II) in strunzite

Point group	Site group	Crystal group
T_d	C_1	C_i
A_1	$9A$	$9A_u$
E		$9A_g$
$2T_2$		

The crystal structure of the strunzites is triclinic with space group $P1$ (Table 1 above). The irreducible representation for austenite is $\Gamma = 9A_u + 9A_g$ neglecting the rotational modes. All three minerals have the same crystal structure and hence it may be assumed that the factor group analysis is identical for all minerals except for small differences in bond lengths. This means that there are 36 vibrationally active modes (since $z = 2$) for the phosphate in the strunzites of which 18 are Raman active and 18 infrared active.

Table 3 Factor group analysis of the water (I - VI) in strunzite

Point group	Site group	Crystal group
C_2	C_1	C_i
$2A_1$	$3A$	$3A_u$
B_2		$3A_g$

The factor group analysis for water in the strunzite structure is given by $\Gamma = 3A_u + 3A_g$. This means that there are three Raman active and three infrared active modes.

Table 4 Factor group analysis of the lattice modes in strunzite

Site group	Crystal group
C_1	C_i
Fe(I+II), Mn, PO_4 (I+II), OH(I+II), H_2O (I-VI)	

69A	69A _u 69A _g
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Strunzite, $\text{MnFe}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, is triclinic, space group $P1$, with $Z = 2$. The mineral exhibits a well-marked monoclinic pseudocell with the pseudosymmetry of $C2/c$ space group. Factor group analysis of the strunzites predicts 36 spectroscopically active modes for the phosphate ion. 18 will be Raman active and 18 infrared active. Similarly there are 36 predicted modes for water in strunzite of which 18 are Raman active and 18 infrared active. The irreducible representation of strunzite is $\Gamma = 69A_g + 69A_u$. Factor group analysis does not take into account bands, which overlap. When this does occur, it is known as accidental degeneracy. The two other minerals in this group ferristrunzite and ferrostrunzite are also triclinic with space group $P1$ and $z = 2$. Hence the factor group analysis for strunzite is applicable also to ferristrunzite and ferrostrunzite.

3.2 Hydroxyl stretching and deformation vibrations.

The vibrational spectra of the strunzite minerals based upon the formulae: $\text{Mn}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}^{3+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot [5\text{H}_2\text{O} \cdot \text{OH}]$, may be conveniently broken up into spectroscopic regions: (a) the hydroxyl stretching region of the hydroxyl units and of the coordinated water (b) the phosphate PO stretching region (c) the phosphate OPO bending region (d) the low wavenumber region including the metal oxygen stretching vibrations. Factor group analysis predicts four bands in the hydroxyl-stretching region of the three strunzite minerals of which two are infrared active and two are Raman active (Table 3).

The Raman spectrum of the hydroxyl-stretching region of strunzite, ferristrunzite and ferrostrunzite are shown in Figure 1. The results of the band component analysis are reported in Table 5. Two Raman bands are observed for strunzite at 3483 and 3410 cm^{-1} and are assigned to hydroxyl stretching vibrations. These bands shift to 3460 and 3377 cm^{-1} upon obtaining the spectra at 77K. This shift is attributed to a strengthening of the hydroxyl unit bonds. It is suggested that the hydroxyl unit is hydrogen bonded to the adjacent phosphate unit and by cooling to liquid nitrogen temperature, this bond is strengthened. The Raman band at 3483 cm^{-1} (at 298 K) is apparently Raman active/infrared inactive. This suggests that this vibration results from a centre of symmetry. Such a result exists if the hydroxyl unit points towards a second oxygen in a O-H—O arrangement. For ferristrunzite these two bands are observed at 3465 and 3367 cm^{-1} and shift to 3473 and 3374 cm^{-1} at 77K. Again the shift of the hydroxyl stretching wavenumber of the second band at 3367 cm^{-1} (at 298 K) is significant. Ferrostrunzite Raman spectra shows two bands at 3492 and 3405 cm^{-1} . These bands also shift to lower wavenumbers upon cooling to liquid nitrogen temperature and three bands are resolved at 3478, 3427 and 3378 cm^{-1} . In agreement with the factor group analysis we observe two Raman and two infrared modes for ferri and ferrostrunzite. Only one infrared band was observed for strunzite and it is probable that this is an example of accidental degeneracy. Vochten reported the infrared spectra of ferrostrunzite and noted a single peak at 3407 cm^{-1} . This band is in harmony with the Raman band observed at 3405 cm^{-1} . The shift to lower wavenumbers indicates a strengthening of the bonding of the OH unit. The

observation of more than one hydroxyl stretching vibration for the strunzite is indicative of at least distinct hydroxyl units in the structure. No Raman data on these minerals has been previously published. However a comparison with some published infrared data may be made (VOCHTEN, R. and DE GRAVE, E., 1990). Vochten reported the infrared transmittance hydroxyl-stretching band of strunzite at 3407 cm^{-1} , which compares well with the absorbance band observed at 3409 cm^{-1} . This band is in harmony with the band observed at 3410 cm^{-1} in the Raman spectra. For ferristrunzite, two infrared absorbance bands are found at 3463 and 3374 cm^{-1} , which is in good agreement with the bands reported by Vochten at 3465 and 3376 (VOCHTEN, R. and DE GRAVE, E., 1990). The position of these bands is in harmony with that of the Raman bands.

Strunzite and ferristrunzite have two hydroxyl units bonded to cations. Thus not only should hydroxyl-stretching bands be observed but also hydroxyl deformation bands. The question arises as to which bands may be attributed to this vibration. In the spectra of phosphates bands are reasonably well separated and may be assigned according to the factor group analysis. In the infrared spectra a broad band at 706 cm^{-1} is observed for strunzite and at 714 cm^{-1} for ferristrunzite. Vochten reported bands at 694 and 626 cm^{-1} for strunzite, 696 and 647 cm^{-1} for ferristrunzite and 694 and 628 cm^{-1} for ferrostrunzite (VOCHTEN, R. and DE GRAVE, E., 1990). A possibility is that these bands may be assigned to the MOH deformation vibration. The fact that two hydroxyl deformation modes are observed is in harmony with the observation of two hydroxyl-stretching vibrations. In the Raman spectra a single band is observed at 639 cm^{-1} for strunzite, 634 cm^{-1} for ferristrunzite and 634 cm^{-1} for ferrostrunzite. The observation of two infrared and one Raman band simply means one band is both infrared and Raman active and the second as infrared active only. Metal hydroxyl deformation modes in Raman spectra are often of low intensity and the attribution of the band can be difficult.

In **Figure 1**, several broad bands are observed in the Raman spectra of all three strunzite minerals at 298K . These bands are attributed to the hydroxyl stretching modes of water in the strunzite structure. Factor group analysis predicts $3 A_u$ and $3 A_g$ modes for water in strunzites, which means for the unit with 6 water molecules there are 18 Raman active and 18 infrared active vibrational modes. In the Raman spectra of the hydroxyl-stretching region of water, we observe two bands only. This means that there is accidental degeneracy for the water vibrational modes. For strunzite two Raman bands were observed at 3340 and 3120 cm^{-1} and for ferristrunzite at 3226 and 3042 cm^{-1} . Two bands were observed at 3134 and 2943 cm^{-1} for ferrostrunzite. In the infrared spectra we observed two bands at 3353 and 3063 cm^{-1} for strunzite and at 3296 and 3016 cm^{-1} for ferristrunzite. In the infrared spectrum of ferristrunzite a band at 2921 cm^{-1} was observed which corresponds well with the band reported at 2921 cm^{-1} by Vochten. This band is ascribed to organic impurity. Similar bands are observed in the Raman spectra of ferristrunzite around 2900 cm^{-1} in our spectra. In the Raman spectra of these minerals at 77K , these water hydroxyl-stretching vibrations are very difficult to observe. The OH vibrations of water are always difficult to observe using Raman spectroscopy as water is an inherently very weak scatterer. By obtaining spectra at liquid nitrogen temperature, the hydroxyl stretching vibrations of water and the OH units of these phosphate minerals are separated.

3.3 Phosphate vibrations

Factor group analysis predicts that there are 36 vibrational modes for the phosphate ion in strunzites of which 18 are Raman active and 18 are infrared active (Table 2). The Raman spectra of the phosphate-stretching region of strunzite and ferristrunzite are shown in Figure 2 and the data analysis with suggested band assignment reported in Table 5. For strunzite two Raman bands are observed at 1000 and 975 cm^{-1} and are attributed to the PO symmetric stretching vibration. For ferristrunzite three bands are observed at 1022, 1008 and 985 cm^{-1} . For ferrostrunzite three bands are observed at 1010, 987 and 974 cm^{-1} . The observation of more than one symmetric stretching vibration means that the PO stretching vibrations are non-equivalent. Upon obtaining the spectra at 77K, better band separation is found and three bands are observed for strunzite at 1009, 992 and 973 cm^{-1} . For ferristrunzite, three Raman bands are observed at 1026, 1004 and 980 cm^{-1} . Four Raman bands are observed for ferrostrunzite at 1011, 993, 989 and 973 cm^{-1} at 77K. The observation of three Raman bands suggests that the degeneracy of the phosphate symmetric stretching mode is lost. The symmetric stretching modes of phosphate are observed at higher wavenumbers for the ferristrunzite compared with that of strunzite. In the infrared spectrum of strunzite, we observed two bands at 1006 and 963 cm^{-1} . The principal band is at 963 cm^{-1} with a shoulder at 1006 cm^{-1} . The position of these infrared bands fits well with the Raman result. Vochten reported a single band at 975 cm^{-1} (VOCHTEN, R. and DE GRAVE, E., 1990). For ferristrunzite we observed an intense infrared band at 983 cm^{-1} with a second band at 963 cm^{-1} .

Two antisymmetric stretching modes are observed for strunzite at 1120 and 1048 cm^{-1} which shift to 1114 and 1062 cm^{-1} at liquid nitrogen temperature (Figure 2). For ferristrunzite, two antisymmetric stretching modes are observed at 1105 and 1078 cm^{-1} , these bands shift to 1094 and 1056 cm^{-1} at 77K. The antisymmetric stretching modes appear to shift to higher wavenumbers upon obtaining the spectra at 77K. In the infrared spectrum two antisymmetric stretching modes were observed at 1115 and 1080 cm^{-1} for strunzite and at 1094 and 1056 cm^{-1} for ferristrunzite. Vochten also reported two bands at 1101 and 1001 cm^{-1} (VOCHTEN, R. and DE GRAVE, E., 1990). For the ferrostrunzite mineral, three bands were observed at 1113, 1058 and 1038 cm^{-1} . Bands were observed in the ferrostrunzite spectrum at 77K at 1114 and 1063 cm^{-1} .

The region between 370 and 570 cm^{-1} is complex with a considerable number of overlapping bands (Figures 3 and 4). This region is where the bending modes of phosphates are observed. In the Raman spectrum of strunzite, three bands are observed at 469, 433 and 406 cm^{-1} and are assigned to the OPO bending mode. Because of the infrared spectroscopic technique we used (ATR), bands below 600 cm^{-1} could not be obtained, so no comparison between the infrared and Raman spectrum could be made in this region. In the infrared spectrum reported by Vochten, a single band at 441 cm^{-1} was reported for strunzite (VOCHTEN, R. and DE GRAVE, E., 1990). Upon obtaining the Raman spectra at 77K, five bands are now observed for strunzite at 475, 455, 435 and 409 cm^{-1} . It would appear that the band at 406 cm^{-1} in the 298K spectrum splits into two bands at 409 and 395 cm^{-1} at 77K. For the ferristrunzite, OPO Raman bending modes are observed at 454 and 394 cm^{-1} . At 77K three bands are observed at 460, 455 and 400 cm^{-1} . In the case of ferrostrunzite three

bands are observed at 471, 434 and 408 cm^{-1} and are assigned to the ν_4 vibrational mode. These bands are observed at 476, 455 and 436 cm^{-1} in the 77K spectra.

For the ν_4 modes, two bands are observed for strunzite at 567 and 513 cm^{-1} , which upon cooling to 77K are observed at 559 and 512 cm^{-1} . In the Raman spectrum of ferristrunzite three bands are observed at 576, 533 and 503 cm^{-1} at 298K and 575, 528 and 505 cm^{-1} at 77K. These results are in good agreement with the infrared bands reported by Vochten at 580 and 511 cm^{-1} . For ferrostrunzite three bands are observed at 568, 531 and 509 cm^{-1} , which shift to 573, 550 and 512 cm^{-1} at 77K. The observation of the multiplicity of bands in the ν_2 and ν_4 regions is significant because it means that the symmetry of the phosphate ion is lost and has been reduced from T_d to probably C_s . Factor group analysis predicts 18 Raman active modes for the phosphate ion for strunzite and all together 18 Raman bands are observed.

3.4 Lattice vibrations

One of the great strengths of Raman spectroscopy is the ability to obtain bands below 400 cm^{-1} , which is often described as the lattice region. A more appropriate description is the low wavenumber region. This spectral region shows the metal stretching vibrations such as FeO and MnO and also the OFeO and the OMnO bending modes. Table 5 reports the band positions observed in the Raman spectra of the low wavenumber region. The attribution of all these bands is not simple but the higher wavenumber vibrations may be attributed to the MO stretching modes. For the lattice region, FGA predicts 66 Raman active modes (Table 4). In the 298 K spectra of the three strunzites, we observe 18 bands down to 100 cm^{-1} . This is the position where the filters on the spectrometer cut in. The observation of 18 compared with the predicted 66 may be accounted for by (a) accidental degeneracy (b) bands occurring below 100 cm^{-1} .

4. Conclusions

The Raman spectra of strunzite and ferristrunzite are reported and a comparison with infrared data made. This work clearly demonstrates the power of Raman spectroscopy as compared to infrared spectroscopy in determining the vibrational spectrum of these basic hydroxy metal phosphates. More particularly the Raman spectra were obtained using a Raman microscope and the infrared using an infrared microscope and an ATR cell. The Raman spectra were clearly resolved and better band separation was obtained by collecting spectral data at 77K. Importantly insights into the molecular structure of these minerals have been made. This work clearly demonstrates the power of Raman spectroscopy for the study of these oxyanion minerals.

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Table 5 Raman and infrared spectral results of strunzite, ferristrunzite and ferrostrunzite

Strunzite				Ferristrunzite				Ferrostrunzite			
Raman 298K	Raman 77K	Infrared	Published infrared data (VOCHT EN, R. and DE GRAVE, E., 1990)	Raman 298K	Raman 77K	Infrared	Published infrared data (VOCHT EN, R. and DE GRAVE, E., 1990)	Raman 298K	Raman 77K	Published infrared data (VOCHT EN, R. and DE GRAVE, E., 1990)	Suggested assignment
3483 3410	3460 3377	3409	3407	3465 3367	3473 3351	3463 3374	3465 3376	3492 3405	3478 3427 3378	3407 3338	MnOH & FeOH stretching
3340 3120		3353 3063	3338 2921	3226 3042		3296 3016 2923	 2921	3134 2943		2921	Water OH stretch CH impurity
639	635	706	694 626	634	636	714	696 647	634	634	634	Fe(Mn)OH deformation
1000 975	1009 992 973	1006 963	975	1022 1008 985	1026 1004 980	983 963	967	1010 987 974	1011 993 989 973	1020 975	PO Sym stretch
469 433 406	475 455 435 409 395		441	454 399	460 445 400		443	471 434 408	476 455 436	497 441	OPO bend
1120	1114	1115	1089	1105	1108	1094	1101	1113	1114	1089	PO anti-

1048	1062	1080	1020	1078	1083	1056	1001	1058 1038	1063		symmetric stretch
567 513	559 512		497	576 533 503	575 528 505		580 511	568 531 509	573 550 512	626	OPO out of plane bends
	392			394 354	355			396 328	396 334		FeO & MnO stretch
329 301 281	358 330 301 283		320 308 276 256	321 302 283 259 235				297 249 226	299 285 253 235		FeO & MnO stretch and bends
248 199 183 168	253 230 203 182 163 140		222 202 181 165	203 184 167 147				202 184 163	207 200 184 162		Lattice modes

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Figure 1 Raman spectra of the hydroxyl stretching region of (a) strunzite at 298 K (b) ferristrunzite at 298 K (c) strunzite at 77 K (d) ferristrunzite at 77 K.

Figure 2 Raman spectra of the phosphate stretching region of (a) strunzite at 298 K (b) ferristrunzite at 298 K (c) strunzite at 77 K (d) ferristrunzite at 77 K.

Figure 3 Raman spectra of the OPO bending region of (a) strunzite at 298 K (b) ferristrunzite at 298 K (c) strunzite at 77 K (d) ferristrunzite at 77 K.

Figure 4 Raman spectra of the low wavenumber region of (a) strunzite at 298 K (b) ferristrunzite at 298 K (c) strunzite at 77 K (d) ferristrunzite at 77 K.

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