QUT Digital Repository:
http://eprints.qut.edu.au/

QUT

Isomorphic substitution in Vanadinite [Pb$_5$(VO$_4$)Cl] –a Raman spectroscopic study

Ray L. Frost, Martin Crane*, Peter A. Williams[*] and J. Theo Kloprogge

Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane Queensland 4001, Australia.
*School of Science, University of Western Sydney, PO Box 10, Kingswood, NSW 2747 Australia

Abstract:

 The Raman and infrared spectroscopy of three vanadinite [Pb$_5$(VO$_4$)Cl] specimens from three localities has been studied. Single crystal Raman spectra were obtained and the spectra were found to be both orientation and temperature dependent. Measurement of the Raman spectra at liquid nitrogen temperature enabled better band separation and increased intensities of weak bands through band narrowing enabling, the assignment of the bands in vanadinites to be made. Two types of isomorphous substitution are identified (a) substitution in the bulk of the crystal where electron beam microanalysis identifies the presence of calcium and copper. (b) surface substitution where infrared spectroscopy shows the isomorphous substitution of vanadate by phosphate and of chloride by hydroxyl groups.
Key words: infrared spectroscopy, Raman microscopy, vanadinite, mimetite, pyromorphite, apatite

Introduction

Vanadinite is a rare secondary mineral found in the oxidised portions of lead veins, often associated with other secondary minerals such as mimetite and pyromorphite. The mineral is characterised by its crystal form and colour with high lustre and density. Colour varies widely from colourless to orange-red and ruby red. Vanadinite sometimes may be distinguished from related minerals pyromorphite and mimetite by the colour of the transparent prismatic crystals. The crystal structure is related to that of apatite (Ca$_5$(PO$_4$)$_3$F) and is hexagonal, space group $\underline{P}6_3/\underline{m}$.[1]

Much work has been undertaken on the apatite-type minerals containing group V elements, namely P, V and As. In the apatite structure isomorphous substitution can occur with replacement of F by Cl, as in the case for vanadinites. The P is replaceable by V or As and the Ca is replaceable by Pb(II), Cu(II) and Zn(II) in the apatite-type minerals. Ross reported the infrared and Raman spectra of the free VO$_4{}^{3-}$

ion. The ν_1 band was observed at 874 cm^{-1}; ν_2 at 345 cm^{-1}; ν_3 at 855 cm^{-1} and ν_4 at 345 cm^{-1}. Levitt and Condrate (1970) based upon the analysis of the spectra of lead apatites reported the ν_2 band for vanadinites at 320 cm^{-1}.[2] Ross (1974) reported the ν_3 modes of vanadinites at 800 and 736 cm^{-1} and the ν_4 modes around 419, 380 and 322 cm^{-1}.[3] In this work the position of the ν_1 and ν_2 vibrations were not reported. Gadsen (1975) reported the infrared spectrum of the vanadinite.[4] The ν_3 mode is reported as lying between 700 to 900 cm^{-1} and the ν_4 mode between 300 and 410 cm^{-1}. The ν_1 mode, which was not observed in the infrared spectrum as the vibration is inactive in infrared spectroscopy, was suggested to be at around 870 cm^{-1}. Griffiths (1970) reported the Raman spectra of vanadinites.[5] Single crystal Raman spectra of a vanadinite at 298K have been reported.[6] Some vanadates as for sulphates have their symmetry reduced through acting as monodentate and bidentate ligands. In the case of bidentate behaviour both bridging and chelating ligands are known.[7] This reduction in symmetry is observed by the splitting of the ν_3 and ν_4 in infrared spectra into two components under C_{3v} symmetry and into 3 components under C_{2v} symmetry.

Early investigations of the vibrational spectra of apatites of lead including vandinite were limited to mid-IR studies. Some early Raman studies of calcium apatites led to some questionable interpretations. [2,8] Single crystal spectra were also reported. [9] The Fourier transform spectroscopy of vanadinite has been reported. [10] In this paper, the ν_1 band for vanadinite was observed at 825 cm^{-1}, the ν_3 at 792 and 718 cm^{-1}, the ν_2 at 322 and 291 cm^{-1} and ν_4 at 414, 354 and 322 cm^{-1}. In this work we have obtained infrared spectra and Raman microscopic spectra for three vanadinites at 298 and Raman spectra at 77K and one vanadinite has been used for single crystal Raman spectroscopic analysis.

Experimental

 The Minerals used in this work came from the collection of one of the authors (MC). The three vanadinite samples came from (a) Yuma County, Arizona, (b) Apache Mine, Arizona (c) Mibladen, Morrocco. The sample in (a) corresponds to one of the samples used by Adams and Gardiner.[6] The three samples were measured for isomorphous substitution using electron microprobe micro-analysis. Structures were also checked by X-ray diffraction.

Electron Probe microanalysis

The electron probe uses the characteristics X-ray generated from the interaction between the electron beam and the sample to identify elemental composition of the sample. Selected samples for electron probe were polished with diamond paste and coat with carbon to provide a good conducting surface. The EPMA analyses were done on the Jeol 840 A Electron probe microanalyser at 20KV, 39mm working distance. Three samples were embedded in Araldite, polished with diamond paste on Lamplan 450 polishing cloth with water as lubricant. The Moran EDS software was used to analyse the samples in the fully standard mode. The secondary

electron images were taken from the Jeol 35CF Scanning Electron Microscope, at 15 KV using Image Slave software to capture the image.

Infrared absorption spectroscopy

Infrared absorption spectra were obtained using the KBr pressed pellet technique using a Perkin-Elmer FT-IR spectrometer 2000 bench using 4 cm^{-1} resolution with 128 scans. Diffuse Reflectance Fourier Transform Infrared spectroscopic (commonly known as DRIFT) analyses were undertaken using a Bio-Rad 60A spectrometer. 512 scans were obtained at a resolution of 2 cm^{-1} with a mirror velocity of 0.3 cm/sec. Spectra were co-added to improve the signal to noise ratio. Approximately 3 wt% kaolinite or intercalated kaolinite was dispersed in 100 mg oven dried spectroscopic grade KBr with a refractive index of 1.559 and a particle size of 5-20 μm. Reflected radiation was collected at ~50% efficiency. Background KBr spectra were obtained and spectra ratioed to the background. The diffuse-reflectance accessory used was designed exclusively for Bio-Rad FTS spectrometers. It is of the so-called "praying monk" design, and is mounted on a kinematic baseplate. It includes two four-position sample slides and eight sample cups. The cup (3 mm deep, 6 mm in diameter) accommodates powdery samples mixed with KBr using an agate mortar and pestle in 1-3% concentration. The collection efficiency of this adaptor is approximately 50%.

Raman microprobe spectroscopy

The vanadinite crystals were placed and orientated on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. No further sample preparation was needed. 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 were 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.

Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Samples were placed in a stainless steel cup, fitted over the silver plate of the thermal stage. For spectra at 77 K, nitrogen gas from liquid nitrogen passed through a small hole in this plate immediately below the centre of the glass disc. It was found that the best method of obtaining 77 K was to cool rapidly at 50 K per minute. Because of the increased optics used in collecting data at 77K, spectra at 77K are noisier and require longer accumulation times. Spectra were obtained using 12 second scans for 20 minutes using the special short 50X (ULWD) objective. The intensity of the vanadinite spectra was found to be decreased in intensity by 0.3 using the ULWD objective compared with the normal X50 objective. A lower Raman signal was obtained using this objective owing to the low numerical aperture of this long working distance objective. This, combined with the spherical aberration of the stage window, results in decreased signal. It should be noted that the use of the X50 objective collects scattered light over a much wider angle than the X20 or X10 objective. There is less "polarisation

leakage" if X20 objectives are used. Then however the intensity of the scattered light diminishes, making the collection of spectra more difficult.

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 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.

Results and discussion

Theory

Selection rules for the vanadate ion in solution and in crystals are given in Table 1 adapted from Bartholamai and Klee (1978). These rules are established according to the standard methods under the assumption that all translationally equivalent atoms move in phase. The crystal structure of vanadinite is similar to that of apatite with space group $\underline{P}6_3/m$ with the exception that the halogen ions which occupy the channels along the 6_3 axes do not lie on the mirror planes but halfway between them.[1]

Infrared absorption spectroscopy

Figure 1 displays the infrared absorption spectra of the three vanadinites used in this study. The infrared spectra were obtained using powdered samples and as such are not single crystal spectra, representing the average of all spectra in all orientations. Three predominant bands are observed in each of the spectra at 833, 804 and 740 cm^{-1}. These bands correspond well with the bands at 828, 790 and 719 cm^{-1} assigned to E_{1u} modes reported by Bartholamai and Klee.[9] In the spectra in Figure 1 low intensity bands are observed at 1055 and 957 cm^{-1} for the Mibladen and Apache Mine samples. These are attributed to minor isomorphous substitution of vanadate ion by phosphate.

The infrared bands observed at 1097 and 1055 cm^{-1} are assigned to the phosphate ν_3 modes as it is also observed for compounds of the type $(Pb,Ca)_5(PO_4)_3OH$. Bands in these positions have been observed for the mineral $(Ca)_5(PO_4)_3OH$.[11,12] Two bands are also observed at 545 and 566 cm^{-1} in the infrared spectra of the two vanadinites from Arizona are attributed to the ν_4 vibrations from phosphate. Bands in this position are observed for the mineral pyromorphite, $Pb_5(PO_4)_3Cl$. The band at 1127 cm^{-1} is assigned to the phosphate ν_3 vibration as observed for compounds of the type $(Pb,Ca)_5(PO_4)_3F$. A band is also observed at 1312 cm^{-1} and is ascribed to the replacement of chloride by carbonate. Diffuse reflectance infrared spectroscopy (DRIFT) is an infrared technique, which probes the surface of materials and was used to confirm the presence of the phosphate and carbonate on the surface of the vanadinites.

SEM images of the minerals show that the surfaces of the minerals have been severely etched and are most likely that these compounds above showing as v_3 infrared vibrations are due to surface alteration effects. Figure 2 shows the corrosion effects on the surface of the vanadinite crystals. It is proposed that the secondary mineral vanadinite was formed under conditions of a constant composition of vanadate ions. A later effect was the erosion of the surface by other solutions of variable composition but containing anions such as carbonate, chloride and hydroxyl ions. These solutions corroded the surface of the vanadinite and hence the presence of the isomorphic substitution of phosphate and carbonate is a surface effect.

Electron probe microanalysis

Electron probe microanalysis (EPMA) does not show the presence of either arsenic or phosphorus as the XO_4^{3-} ions in the samples. The detection limit of the technique is around 0.05 %. The concentrations of the As and P are too low to be measured by this technique. This means the detection of isomorphous substitution of vanadate by phosphate by infrared spectroscopy is very sensitive. The question arises as to whether the substitution is homogenous and whether the substitution is a surface effect. This isomorphous substitution may vary between crystals and may even vary within the one crystal. What the EPMA does show is the isomorphous substitution of Pb by other cations. For the Mibladen vanadate both Ca and Cu were detected at 0.08 % as CaO and 1.41% as CuO, respectively. The Apache mine vanadinite has also some isomorphous substitution with Ca at 0.09% and Cu as 0.13%. The levels of the Yuma Co sample of CaO and CuO were 0.12 and 1.98%. This isomorphous substitution is a 'bulk' effect. No zoning was observed. The additional IR bands observed in the vanadinites are attributable to phosphates on the surface of the crystals. X-ray photo-electron spectroscopy (XPS) confirms the presence of phosphorus on the surface of the mineral. Observed bands are due to the most intense bands in the infrared spectra and therefore are the v_3 antisymmetric vibrations of the E_{1u} mode. Surface analysis techniques were also used to identify alteration products on the surface of the vanadinites. Both carbon and phosphorus together with some chloride were determined.

Raman Spectroscopy at 298K

Raman spectra of the series of vanadinites at 298 and 77K are shown in Figures 3 and 4. Results of the band component analysis are reported in Table 2. Two intense bands are observed at 827 and 790 cm^{-1} with a weak band at around 730 cm^{-1} (Figure 3 a,b,c). The 827 cm^{-1} band is assigned to the v_1 symmetric stretching vibration of the vanadate ion. In the infrared spectra the 790 cm^{-1} band is the more intense than the 827 cm^{-1} band; thus it is suggested that the 790 cm^{-1} band is the antisymmetric stretching E_{1u} mode. The low intensity band at around 730 cm^{-1} may be attributed to the second antisymmetric vibration (A_u mode). This band is weak in both the infrared and Raman spectra. A likely event is that the Cl in the vanadinites has been replaced by an OH group. This band at 730 cm^{-1} would be then attributed to an hydroxyl-deformation vibration. The assignment and position of the v_1 mode is in good agreement with that reported by Ross (1972).[7] Ross reported the v_3 mode of the vanadate ion as 855 cm^{-1}.[7] The observation of the antisymmetric stretching vibration

being at a lower wavenumber than that of the symmetric stretching vibration is unusual in that normally it is the other way around. Adler (1968) reported the ν_3 modes at 800 and 735 cm^{-1}.[14] In this work the ν_3 mode was observed at 790 cm^{-1}. In the Raman spectra a very weak band is observed at 920 cm^{-1}. This is assigned to the ν_1 symmetric stretching mode of PO$_4^{3-}$ resulting from phosphate substitution for vanadate. Bands in this position are observed for the mineral pyromorphite. This observation is in harmony with the infrared data.

Raman spectra of the ν_2 and ν_4 regions show (a) weak bands at 415 and 390 cm^{-1} (b) intense bands at 354 and 331 cm^{-1} and (c) low intensity bands at around 290 and 270 cm^{-1} (Figure 4 a,b,c). The most intense band in this region is observed at 331 cm^{-1} and is assigned to the ν_2 vibration. This assignment is in agreement with that proposed by Levitt and Condrate.[2] In some spectra (Figure 2c) more than one band is observed. It is thought that this results from a variation in the composition of the vanadinite. The band at 354 cm^{-1} is thus attributed to the reduction of symmetry of the ν_2 modes. Often more than one band is observed in this position, for example two bands at 365 and 355 cm^{-1} are observed in Figure 3b. Ross (1972 and 1974)[3,7] based upon the work of Bhatnagar (1967, 1968 and 1969)[11-13] and Adler (1968),[14] reported the ν_4 bands for vanadinite at 419, 380 and 322 cm^{-1}. Such observations are not in agreement with this work. There has been considerable confusion in the literature over the assignment of the ν_2 and ν_4 modes. The two weak bands, which are Raman inactive and infrared active observed at 415 and 395 cm^{-1} are assigned to the ν_4 vibrations.

Figure 5 shows Raman spectra of three orientations of a vanadinite crystal from the Puzzler Mine source. The spectra are from the three axes perpendicular to [1000], [0001] and [1100]. Whilst it is not possible to ensure that the spectroscopic axes are perfectly aligned with the crystallographic axes, spectra are nevertheless obtained by directing the incident laser light perpendicular to these faces. The point needs to be made that, as expected, Raman spectra of vanadinite are orientation dependent. The results are quite striking and the results of the band component analyses are shown in Table 3. For example, the band centred at 790 cm^{-1} is barely observed in spectrum (a) and is of low intensity in spectrum (c). Most differences are observed in the ν_2 region between 250 and 450 cm^{-1}. Bartholomai and Klee (1978) reported the Raman spectra of three orientations of a single crystal of vanadinite and labelled the spectra as E$_{2g}$, E$_{1g}$ and A$_g$.[9] These spectra are in good agreement with the spectra shown in Figure 5 and reported in Table 2.

The band observed at 827 cm^{-1} is consistently the most intense band and this intensity in the Raman spectrum confirms the assignment to the ν_1 mode. In the band component analysis of the spectral profile, in order to get good fits of the spectra, it is necessary to establish a band at around 815 cm^{-1}. This corresponds to the infrared band observed at 810 cm^{-1} and is assigned to one of the two ν_3 modes, the other being the 790 cm^{-1} band. A low intensity band is observed at 723 cm^{-1}. The spectrum obtained at right angles to the [1000] face, shows three bands in the 250 to 450 cm^{-1} region at 365, 354 and 323 cm^{-1}. Two very weak bands are observed at 414 and 388 cm^{-1}. In the spectrum obtained at right angles to the [0001] face two strong bands are observed at 354 and 335 cm^{-1} with weak bands at 404 and 366 cm^{-1}. In the spectrum

obtained at right angles to [1100] a strong band is observed at 323 cm^{-1}. Two bands at 365 and 355 cm^{-1} are also observed.

Raman Spectroscopy of vanadinite at 77K

There are a number of advantages of running Raman spectra at liquid nitrogen temperature. First, better band separation is obtained due to decreased band width and/or shift of the bands to lower frequencies; secondly very weak bands which may not be easily observed in the 298K spectra are more readily observed in the 77K spectra and, thirdly, because of better band separation the assignment of bands as a result of symmetry reduction of the vanadate ion is more easily made. Such statements are exemplified by the spectra shown in Figure 3 d, e and f. Further low intensity bands for example the band at 923 cm^{-1} in Figure 3e, are more readily discernible. All three vanadinites have a band in this position. Similarly, the low intensity band observed at around 726 cm^{-1} is more easily seen because of reduction in bandwidth. In the 77K spectra another very low intensity band centred upon 735 cm^{-1} may be observed. Similarly in the 250 to 450 cm^{-1} region additional bands are observed. The two bands, which are barely observable in the 298K spectra are easily seen in the 77K spectra.

In the 77K spectra the two bands which have been attributed to the v_1 and v_3 modes are observed at 827 and 790 cm^{-1}. A slight shift to higher wavenumber is observed upon cooling to 77K. Remarkable changes in bandwidths occur upon cooling to 77K. The bandwidth of the 825 cm^{-1} band of vanadinite from Apache mine is 25.9 cm^{-1} in the 298K spectra and 15.8 cm^{-1} in the 77K spectrum. For the vanadinite from Morrocco the bandwidth is reduced from 23.7 to 12.7 cm^{-1} for the 827 cm^{-1} band. Similar bandwidth reductions are also observed for the 790 cm^{-1} band. What is quite remarkable is the increase in the relative intensity of the 790 cm^{-1} band compared with that of the 825 cm^{-1} band. The ratio of the relative intensity of the 825 and 790 cm^{-1} bands for the Apache mine vanadinite is approximately 2:1 in the 298K spectrum and is 5:4 in the 77K spectrum. It is not known why there is an increase in relative intensity of the antisymmetric vibration upon cooling to liquid nitrogen temperature.

Figure 4 d,e,f shows the 77K Raman spectra of the three vanadinites. Increased band separation is again observed. Bands all occur in the same positions for each sample. The relative intensities of the bands vary between samples. The reason why the spectra appear so different lies in the difficulty of orienting the sample in the thermal stage. Two bands are observed at 496 and 395 cm^{-1} with band widths of 8.2 and 9.4 cm^{-1} compared with the 298K bandwidths of 13.6 and 41.1 cm^{-1}. These two bands may be ascribed to the v_4 antisymmetric stretching vibrations. Gadsen (1975) reported two infrared bands at 419 and 383 cm^{-1}. Two bands are observed at 365 and 356 cm^{-1} with bandwidths of 10.3 and 13.5 cm^{-1}. Two further bands are observed at 331 and 323 cm^{-1}. These bands are in each of the three spectra but the relative intensities vary between the spectra because of the orientation of the crystals relative to the incident laser excitation beam. The infrared spectrum shows a single band at 319 cm^{-1} (Gadsen 1975). Two low intensity bands are also observed at 290 and 236 cm^{-1}.

If the VO_4^{3-} ion has reduced symmetry from T_d, to either C_{3v} or C_{2v}, then the number of bands will increase for both the ν_3 and ν_4 modes. For C_{3v} two bands and for C_{2v} three bands would be observed for each of the two modes. If the intense band at 825 cm^{-1} is attributed to the ν_1 mode, then the three bands at 790 and 730 cm^{-1} may be attributed to the ν_3 mode. The infrared spectra of vanadinites show two intense bands at 790 and 810 cm^{-1}. Thus the infrared spectra are in harmony with the Raman data. Two ν_3 bands were reported for vanadinites by Bhatnagar (1969) [13] and by Adler (1968) [14] at 805 and 740 cm^{-1} and at 800 and 736 cm^{-1} respectively. If this is the case and the two vibrations are observed for the ν_3 mode, then it could also be expected that two ν_4 vibrations would be observed. The two low intensity Raman bands at 415 and 390 cm^{-1} would fit with this concept. Three bands at 419, 380 and 322 cm^{-1} were assigned by Bhatnagar (1969) to the ν_4 modes. [13] Similarly, bands at 415, 370 and 315 cm^{-1} were ascribed to the ν_4 modes by Adler (1968). [14] However such an attribution would not take into account the ν_2 mode, which with a reduction in symmetry of the vanadate ion, would be expected to be observed. This would then mean that the four bands in the 300 to 360 cm^{-1} region are attributable to the ν_2 modes.

CONCLUSIONS

Electron probe microanalysis shows the vanadinites have some isomorphous substitution of the lead by Ca and Cu. However the technique was unable to measure the presence of P or As. Infrared microscopy identified their presence through the observation of the antisymmetric stretching vibrations. Scanning electron microscopy shows that the surfaces of the vanadinite crystals are severely eroded. Thus it is considered that the presence of isomorphic anion substitution may be a surface effect. Whereas the cation substitution is throughout the whole crystal. Thus two types of isomorphic substitution are observed (a) a bulk effect and (b) a surface effect.

Raman microprobe spectroscopy has been used to probe the molecular structure of vanadinites from several sources. Raman spectra are both orientation and temperature dependent. Measurement of the Raman spectra at liquid nitrogen temperature enabled better band separation and increased intensity of weak bands through band narrowing enabling the assignment of the bands in vanadinites to be clarified. The implication of the orientation dependence of the Raman spectra of minerals such as vanadinites means that care must be taken in the submission of spectra for data bases.

The ν_1 mode was found at 827 cm^{-1} and the ν_3 mode was split into two bands at 815 and 790 cm^{-1}. Thus it is proposed that the symmetry of the vanadate ion is reduced to C_{3v} in agreement with structural data. The ν_4 modes are observed at 414 and 395 cm^{-1} and the observation of the two ν_4 bands suggests that the site symmetry is C_{3v}. The ν_2 region is complex with bands observed at 366, 355 323 and 290 cm^{-1}. The observation of four bands may result from some isomorphous cation substitution of Ca or Zn for the Pb in the vanadinites.

REFERENCES

1. Dai Y and Hughes JM Crystal-structure refinements of vanadinites and pyromorphites. Canadian Mineralogist 1989; **27**: 189-192.
2. Levitt SR and Condrate RA The vibrational spectra of lead apatites Am. Min. 1970; **55**: 1562-1575
3. Ross SD Inorganic infrared and Raman spectra McGraw-Hill London, 1972. Pp216.
4. Gadsden, JA (1975) Infrared Spectra of Minerals and Related Inorganic Compounds. - Butterworth & Co. (Publishers) Ltd., London, 277 pp.
5. Griffith WP, Advances in Infrared and Raman spectroscopy of minerals in Spectroscopy of Inorganic-based Materials, p 119, edited by R.J.H Clark and R.E. Hester, J. Wiley & Sons Ltd (1987).
6. Adams DM and Gardiner IR Single-crystal vibrational spectra of apatite, vanadinite and mimetite. J. Chem. Soc (Dalton) 1974; 1505-1509.
7. Ross SD "Phosphates and other oxyanions of group V". In Farmer C.V. Ed The Infrared spectrum of Minerals. Monograph 4. The Mineralogical Society, London 1974.
8. Kravitz, LC, Kingsley JD and Elkin Raman and infrared studies of coupled phosphate vibrations. J. Chem. Phys. 1968; **49**: 4600-4617.
9. Bartholomai G and Klee WE Spectrochimica Acta A 1978; **34**: 831-843.
10. Coleyshaw E.E., Griffiths W.P. and Bowell R.J. Spectrochimica Acta A 1994, **50**: 1909-1918.
11. Bhatnagar VM IR spectra of mineralogical and synthetic chlorapatite. Chim. Anal. (Paris) 1967; **49**: 406-408.
12. Bhatnagar VM IR spectra of hydroxyapatite and fluoro-apatite. Bull. Soc. Chim. Fr. 1968; 1771-1773.
13. Bhatnagar VM Anion substitutions in lead apatites. Z. anorg. Allgem. Chem. 1969; **367**: 289-292.
14. Adler HH The Infrared spectra of the phosphate minerals. Am. Min. 1968; **53**: 1740-1744.

Table 1. Selection rules for the vibrational spectroscopy of lead apatites

Internal vibrations of the XO_4 ions (X = P, As, V)						
Type of Mode	Free XO_4		XO_4 in crystal			
	Symmetry group $\bar{4}3m$	Site Group m	Factor group 6/m			
			RAMAN ACTIVE	**INFRARED ACTIVE**	INACTIVE	Σ
υ_1	**A₁**	A'	$A_g + E_{2g}$	E_{1u}	B_u	6
υ_2	E	A'	$A_g + E_{2g}$	E_{1u}	B_u	6
		A''	E_{1g}	A_u	$B_g + E_{2u}$	6
υ_3		A'	$A_g + E_{2g}$	E_{1u}	B_u	6
		A''	E_{1g}	A_u	$B_g + E_{2u}$	6
υ_4		A'	$A_g + E_{2g}$	E_{1u}	B_u	6
		A''	E_{1g}	A_u	$B_g + E_{2u}$	6

Table 2. Band component analysis of the Raman spectrum at 298 and 77K of vanadinites between 100 and 1000 cm^{-1}.

	Vanadinite (Apache Mine, Arizona) At 298 K	Vanadinite (Apache Mine, Arizona) At 77 K	Vanadinite (Puzzler Mine, Yuma Co.) At 298K	Vanadinite (Puzzler Mine, Yuma Co.) At 77K	Vanadinite (Mibladen, Morrocco) At 298K	Vanadinite (Mibladen, Morrocco) At 77K	Vanadinite (Adams and Gardiner)	Vanadinite (Bartholamia and Klee)	Suggested assignments
Bandposition/cm^{-1} Rel. Intensity/% Bandwidth/cm^{-1}	879 5.1 76.7								ν_1 A_g symmetric stretching
Bandposition/cm^{-1} Rel. Intensity/% Bandwidth/cm^{-1}	825 58.8 25.9	827 53.5 15.8	825 76.6 23.8	826 56.9 18.6	827 80.0 23.7	827 58.6 12.7	828	826	ν_1 A_g symmetric stretching
Bandposition/cm^{-1} Rel. Intensity/% Bandwidth/cm^{-1}	790 31.9 32.7	790 42.4 12.2	791 19.0 30.3	792 36.8 25.7	811 15.4 41.6	790 27.7 10.4	795	798	ν_3 E_{2g} antisymmetric stretching
Bandposition/cm^{-1} Rel. Intensity/% Bandwidth/cm^{-1}	730 4.1 33.9	726 3.0 10.9	723 4.3 21.2	727 3.5 17.2		724 2.8 8.1	725	721	ν_3 E_{2g} antisymmetric stretching
Bandposition/cm^{-1} Rel. Intensity/% Bandwidth/cm^{-1}	415 11.2 13.6	416 8.0 8.2	408 11.1 56.7	417 2.4 10.4		416 5.0 8.4		421	ν_4 A_g OVO bending
Bandposition/cm^{-1} Rel. Intensity/% Bandwidth/cm^{-1}	390 9.0 41.1	397 5.0 9.4				395 4.5 16.4			ν_4 A_g OVO bending
Bandposition/cm^{-1} Rel. Intensity/%	361 5.0		365 15.2	356 29.1	365 25.0	365 9.4	371	364	ν_3 A_g

Bandwidth/cm^{-1}	18.4		10.3	12.7	13.0	6.7			OVO bending
Bandposition/cm^{-1} Rel. Intensity/% Bandwidth/cm^{-1}	354 26.0 10.3	355 33.3 6.9	354 10.7 13.5			355 17.1 5.9	356	354	ν_3 A_g OVO bending
Bandposition/cm^{-1} Rel. Intensity/% Bandwidth/cm^{-1}	331 33.2 17.7	334 33.7 9.1	323 51.4 15.6	329 27.9 16.7	323 59.0 15.2	333 13.1 8.5	334		ν_3 E_{1g} OVO bending
Bandposition/cm^{-1} Rel. Intensity/% Bandwidth/cm^{-1}		321 8.9 9.2		321 21.3 9.9		321 42.5 7.6	328,326,324		ν_3 E_{1g} OVO bending
Bandposition/cm^{-1} Rel. Intensity/% Bandwidth/cm^{-1}	290 10.0 57.4	290 1.7 12.7	290 11.5 14.9	290 18.2 17.1	291 11.3 15.2	289 8.2 10.0	294	290	ν_3 A_g OVO bending

Table 3. Band component analysis of the Raman spectrum of the Puzzler mine vanadinite between 100 and 1000 cm^{-1}.

(Puzzler Mine, Yuma Co.)	Vanadinite Perp. to 1000	Vanadinite Perp. to 0001	Vanadinite Perp. to 1100
Bandposition/cm^{-1}	827	827	827
Rel. Intensity/%	79.2	60.2	63.8
Bandwidth/cm^{-1}	22.9	22.3	22.5
Bandposition/cm^{-1}	815	815	815
Rel. Intensity/%	9.2	7.0	9.8
Bandwidth/cm^{-1}	20.7	20.6	27.3
Bandposition/cm^{-1}	790	790	790
Rel. Intensity/%	24.3	30.1	24.0
Bandwidth/cm^{-1}	28.9	29.0	28.4
Bandposition/cm^{-1}	723	722	723
Rel. Intensity/%	3.4	2.5	2.1
Bandwidth/cm^{-1}	24.0	24.0	17.0
Bandposition/cm^{-1}		415	414
Rel. Intensity/%		5.3	6.5
Bandwidth/cm^{-1}		15.0	28.0
Bandposition/cm^{-1}		395	388
Rel. Intensity/%		13.2	2.7
Bandwidth/cm^{-1}		46.2	29.3
Bandposition/cm^{-1}	366		365
Rel. Intensity/%	12.4		12.8
Bandwidth/cm^{-1}	9.6		11.2
Bandposition/cm^{-1}		355	354
Rel. Intensity/%		31.1	14.4
Bandwidth/cm^{-1}		12.2	15.7
Bandposition/cm^{-1}	323	331	323
Rel. Intensity/%	40.7	30.0	52.3
Bandwidth/cm^{-1}	15.2	18.4	16.6
Bandposition/cm^{-1}	291	290	290
Rel. Intensity/%	17.1	11.0	11.2
Bandwidth/cm^{-1}	16.9	43.8	18.0
Bandposition/cm^{-1}			
Rel. Intensity/%			
Bandwidth/cm^{-1}			

List of Figures

List of Tables