Single crystal Raman spectroscopy of brandholzite Mg[Sb(OH)$_6$]$_2$•6H$_2$O and bottinoite Ni[Sb(OH)$_6$]$_2$•6H$_2$O and the polycrystalline Raman spectrum of mopungite Na[Sb(OH)$_6$].

Llew Rintoul, Silmarilly Bahfenne and Ray L. Frost [•]

Chemistry, Faculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

ABSTRACT

The single crystal Raman spectra of minerals brandholzite and bottinoite, formula M[Sb(OH)$_6$]$_2$•6H$_2$O, where M is Mg^{+2} and Ni^{+2} respectively, and the non-aligned Raman spectrum of mopungite, formula Na[Sb(OH)$_6$], are presented for the first time. The mixed metal minerals comprise of alternating layers of [Sb(OH)$_6$]$^{-1}$ octahedra and mixed [M(H$_2$O)$_6$]$^{+2}$ / [Sb(OH)$_6$]$^{-1}$ octahedra. Mopungite comprises hydrogen bonded layers of [Sb(OH)$_6$]$^{-1}$ octahedra linked within the layer by Na$^+$ ions. The spectra of the three minerals were dominated by the Sb-O symmetric stretch of the [Sb(OH)$_6$]$^{-1}$ octahedron, which occurs at approximately 620 cm^{-1}. The Raman spectrum of mopungite showed many similarities to spectra of the di-octahedral minerals informing the view that the Sb octahedra gave rise to most of the Raman bands observed, particularly below 1200 cm^{-1}. Assignments have been proposed based on the spectral comparison between the minerals, prior literature and density field theory calculations of the vibrational spectra of the free [Sb(OH)$_6$]$^{-1}$ and [M(H$_2$O)$_6$]$^{+2}$ octahedra by a model chemistry of B3LYP/6-31G(d) and lanl2dz for the Sb atom. The single crystal data spectra showed good mode separation, allowing the majority of the bands to be assigned a symmetry species of A or E.

KEYWORDS: Brandholzite; bottinoite; mopungite; single crystal; Raman spectroscopy

---

[•] Author to whom correspondence should be addressed (r.frost@qut.edu.au)

INTRODUCTION

As part of a larger study of antimony bearing minerals [1,2] we previously published a preliminary investigation of the Raman spectrum of Brandholzite [3], a mineral with the chemical formula of $Mg[Sb(OH)_6]_2 \cdot 6H_2O$, which had been recently discovered in the oxidation zone of a body of stibnite in the Brandholz-Goldkronach area of Germany [4,5]. Since our earlier work we have obtained a brandholzite crystal suitable for a single crystal study, which has facilitated the assignment of the various modes according to symmetry. Additionally we have also acquired a crystal of bottinoite $Ni[Sb(OH)_6]_2 \cdot 6H_2O$, a mineral isostructural with brandholzite [6,7], suitable for single crystal work.

Both minerals belong to the trigonal space group C_3 (P_3) and Z = 6, with the crystallographic parameters a = 16.119, c = 9.868Å (Brandholzite, M = Mg), and a = 16.026, c = 9.795Å (Bottinoite, M = Ni). Brandholzite occurs as colourless plates whereas bottinoite is pale blue in colour; both have a vitreous appearance. Brandholzite and bottinoite are isotypic, containing isolated $[M(H_2O)_6]^{2+}$ and $[Sb(OH)_6]^-$ octahedra. The structure consists of two different alternating layers stacked along c axis; one contains only the $[Sb(OH)_6]^{-1}$ octahedra, the other contains both $[M(H_2O)_6]^{+2}$ and $[Sb(OH)_6]^{-1}$ octahedra in a ratio of 2:1. The $[Sb(OH)_6]^{-1}$ hydroxyls form external hydrogen bonds that bind the layers together and the aqua ligands of the $[Mg(H_2O)_6]^{+2}$ form both inter and intra layer hydrogen bonds.

The vibrational spectra of minerals of this type can be largely understood in terms of the internal modes of the two ions involved, for brandholzite and bottinoite these are the more or less independent vibrations of coordination octahedra of $[M(H_2O)_6]^{+2}$ and $[Sb(OH)_6]^{-1}$. To aid the task of teasing out the relative contribution of each ion to the spectra, density field theory (DFT) was applied to the isolated ions and the IR and Raman spectrum calculated. In addition a third mineral, mopungite, the sodium salt of $[Sb(OH)_6]^{-1}$, was investigated. Mopungite comprises of hydrogen bonded layers of $[Sb(OH)_6]^{-1}$ octahedra linked within the layer by Na^+ ions. Although Siebert reported infrared spectra of $Na[Sb(OH)_6]$ in an earlier study of synthetic hydrated antimonates and metaantimonates [8], the Raman spectrum of mopungite has not been previously published. This paper presents the single crystal data for the minerals brandholzite

and bottinoite and makes band assignments according to symmetry and type. Although a single crystal of mopungite was not available for this study the non – aligned Raman spectrum is reported here and used to support the assignments made with consideration of the DFT calculations of the theoretical spectra and current literature.

EXPERIMENTAL

Minerals

Crystals of brandholzite originated from Krížnica mine, the Pernek deposit, the Malé Karpaty Mountains, western Slovakia, Slovak Republic and were kindly supplied by the National Museum, Prague. Crystals of bottinoite and mopungite were supplied by The Mineralogical Research Company. Bottinoite originated from Ramsbeck Mine, Dornberg, Sauerland, Germany and mopungite from Le Cetine Mine, Siena Province, Tuscany, Italy.

Raman microscopy

The instrument used was a Renishaw 1000 Raman microscope system, which comprises a monochromator, a Rayleigh filter system and a CCD detector coupled to an Olympus BHSM microscope equipped with 10x, and 50x objectives. The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing plane polarised light at 633 nm and collected at a resolution of better than 4 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 120 and 4000 cm^{-1}. Repeated acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal-to-noise ratio in the spectra. The instrument was calibrated prior to use using the 520.5 cm^{-1} line of a silicon wafer.

The Raman spectra of the oriented single crystals are reported in accordance with the Porto notation: the propagation directions of the incident and scattered light and their polarisations are described in terms of the crystallographic axes *a*, *b* and *c*. The notation may, for example read CABC. Here the first C is the direction of the incident light, A is the direction of the polarisation of the electric vector of the incident light, B is the orientation of the analyser and the second C is the direction of the propagation of the scattered light

A single crystal of each mineral was selected and placed on the corner of a perfect cube, aligned parallel to the sides of the cube using a very fine needle. The rotation of the cube through 90° about the X, Y, Z axes of the laboratory frame allowed the determination of the three crystallographic axes. The *a* and *b* axis are not readily identifiable in the specimen under study. Fortunately it is not necessary to separate *a* from *b* in order to classify the modes according to their symmetry, either *a* or *b* or a mixed *ab* axis will suffice. This mixed *ab* axis will be referred to as the *a* axis for convenience and is accessed by placing the crystal flat under the microscope. Optically, brandholzite and bottinoite are uniaxial with a very small difference in the two refractive indices in each crystal (0.001 for brandholzite and 0.005 for bottinoite). The optical axis is parallel to the *z* axis so birefringence is not an issue in any case. By placing the crystal on its side and aligning the polarisation plane of the laser perpendicular to the crystal plate and the analyser parallel, the *cc* (*A*) spectrum can be measured. Rotating the plane of the laser gives the *ca* spectrum

Spectral manipulation

Spectral manipulation such as baseline correction to remove fluorescence was performed using the GRAMS software package (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that 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 Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian-Lorentzian 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.

DFT Calculations

Calculations were performed using the Gaussian 03 program [9] and the GaussView3.0 (Gaussian, Inc.,Wallingford, CT) front end, running on an SGI Origin 3000 supercomputer. The wavenumbers of the fundamental modes were calculated using density field theory (DFT) with B3-LYP method and a 6-31G(d) basis set for Mg, H and O atoms and Lanl2dz with diffuse functions of Check, *et al.*, [10] for Sb. No

scaling factor was applied. Raman intensities were calculated from the Gaussian activities based on 633 nm excitation.

RESULTS AND DISCUSSION

Synthetic crystals of $Mg[Sb(OH)_6]_2 \cdot 6H_2O$, $Ni[Sb(OH)_6]_2 \cdot 6H_2O$, and $Na[Sb(OH)_6]$ have been subjected to infrared spectroscopy in the past and published by Balicheva and Roi [11] . Franck has also published infrared spectra of $Na[Sb(OH)_6]$ along with other hexahydroxyantimonates [12]. No Raman study, however, has been attempted on any of the above minerals or their synthetic analogues, except for our preliminary study of brandholzite [3].

The non-aligned Raman spectra of the three minerals are shown together for comparison purposes in Fig 1. Calculated band positions and intensities for isolated $[Sb(OH)_6]^{-1}$ and $[Mg(H_2O)_6]^{+2}$ ions are also shown in Fig 1, second from bottom and bottom respectively, in bar graph style where the height of the bar indicates the calculated band intensity. Calculated wavenumbers for the OH stretching modes are overestimated owing to the lack of hydrogen bonding in the isolated ion model. The peak positions for the $[Sb(OH)_6]^{-1}$ ion (Fig 1D) below 1600 cm^{-1} correspond reasonably well with spectrum of mopungite (Fig 1C). Contributions from the $[M(H_2O)_6]^{+2}$ ion in the spectra of brandholzite (Fig 1A) and bottinoite (Fig 1B) can be distinguished by comparing the two spectra with mopungite. These differences are discussed in later sections. Suffice to say for now that the theoretical spectrum of $[Mg(H_2O)_6]^{+2}$ poorly correlates with these observed differences, probably due to the fact that interlinking hydrogen bonds were not modelled in the DFT calculations and the predominance of H_2O bands in the spectral contribution from the Mg octahedron. The Raman spectra are shown in further detail in Figs 2 and 3. Also shown are the results of band fitting of the spectra to identify the band positions, widths and relative intensities of the observable modes. The band fitting results are given in Table S1.

Factor Group Analysis

Mopungite belongs to the tetragonal space group C_{4h} and Z = 4, a = 8.029, c = 7.894 Å. Its structure was first given by Schrewelius [13] and refined by Asai [14]. The $[Sb(OH)_6]^{-1}$ octahedra are nearly regular and form layers held together by a network

5

of hydrogen bonds. Na^+ ions are located in the interstices within each layer. The primitive cell of Mopungite contains four formula units, giving 165 modes in total comprising $18A_g + 18B_g + 18E_g$ Raman active modes, $23A_u + 23 E_u$ IR active modes and 24 B_u inactive modes. Single crystal experiments of mopungite were not attempted due to the polycrystalline nature of the sample.

The unit cell (C_3) of brandholzite and bottinoite is the primitive unit cell containing six formula units. Six of the 12 Sb octahedra in the Bravais cell populate C_3 sites, the same point group symmetry as the crystal. The six remaining Sb^{+5} ions and two Mg^{+2} ions occupy general sites. This makes for very a complicated factor group analysis. The prediction of 269A + 269E modes provides little insight into band assignments. Although six of the Sb sites have higher symmetry, the fact that the Sb octahedra all have similar bond lengths and angles [4] means the bands are strongly overlapped. Although not occupying such a multiplicity of sites (just two) a similar argument can be made for the $[M(H_2O)]^{+2}$ ions.

Although the predicted multitude of low symmetry modes renders the FGA approach of limited value in terms of assigning the spectrum, it should never-the-less be possible to assign a symmetry species to many of the Raman active modes by examining the single crystal spectra. The form of the polarisability tensor for C_3 crystals dictates that only A modes are active in the cc spectrum, both A and E modes are active in the aa spectra; and that E modes only are active in the cross polarised ac spectra. Figs. 4-7 show the single crystal Raman data of brandholzite and bottinoite. Modes observed only in the cc and/or aa spectra have been labelled A, while modes observed only to occur in the ac spectra and the aa spectra have been labelled E. Good mode separation was observed in both brandholzite and bottinoite with most modes showing the same orientation in both minerals as to be expected since they are homologous. The symmetry assignments have been given in Table 1.

OH stretching

The OH region of the three minerals follow roughly the same contour but the relative intensity of mopungite is significantly lower. This indicates that the OH regions of brandholzite and bottinoite are dominated by the relatively strong H_2O modes of the $[M(H_2O)]^{+2}$ ions, despite the 2:1 ratio in favour of the $[Sb(OH)_6]$ octahedra.

According to Balicheva and Roi [11], IR bands above 3400 cm^{-1} are attributable to H_2O ligands involved in hydrogen bonding with adjacent H_2O ligands, whereas those at lower wavenumbers correspond to the H_2O ligands involved in stronger hydrogen bonding with the OH group of Sb-OH. Thus bands occurring at 3550 cm^{-1} in brandholzite and 3510 cm^{-1} in bottinoite, which are absent in the mopungite spectrum, can be associated with the interactions between $[M(H_2O)_6]^{+2}$ ions. Accordingly, the intense broad band at 3337 cm^{-1} in brandholzite and 3368 cm^{-1} in bottinoite can be associated with the $[M(H_2O)_6]^{+2}$ ion with stronger $[Sb(OH)_6]^{-1}$ interactions. The sharp band at 3423 cm^{-1} on the high wavenumber side of the OH profile in mopungite appears to be matched by bands of similar appearance at 3466 cm^{-1} in brandholzite and 3458 cm^{-1} in bottoinoite. Therefore these bands most likely arise from vibrations of the $[Sb(OH)_6]^{-1}$ moiety. DFT calculations suggest the totally symmetric OH stretch occurs at the highest wavenumber in that ion. In the oriented crystals this mode showed E symmetry and so is tentatively assigned to the out of phase mode of the Sb-OH symmetric stretch. The band at 3055 cm^{-1} in mopungite may either be a result of stronger hydrogen bonding between the SbOH-HOSb groups across the layers of the dioctahedral minerals or it could be shifted to lower wavenumbers due to the effect of the interstitial Na^+ ion.

OH deformation

Brandholzite shows weak bands around 1644 (E), assigned to $\delta(H_2O)$, and at 1340 cm^{-1} (A), assigned to a combination band (617 + 729 cm^{-1}). The $\delta(H_2O)$ band was too weak to be observed in the bottinoite spectrum. The in-plane OH deformation bands $\delta(OH)$ are predicted to occur near 1000 cm^{-1} according to the DFT calculations and these are observed at 1058 (A), 1078 (E), and 1163 cm^{-1} (A) in brandholzite and 1045 (A), 1081 (E), and 1164 cm^{-1} (A) in bottinoite. The weak but sharp band at 1086 cm^{-1} in the spectrum of mopungite (Fig 1C) is due to the symmetric stretch of some carbonate contamination which also accounts for some weak broad bands near 1385 cm^{-1}. The $\delta(OH)$ of mopungite was not observed directly due to the interference of the contaminant bands and the overall weakness of the spectrum. A weak band of A symmetry is observed near 730 cm^{-1} in the spectra of brandholzite and bottinoite. A band in this position in the IR spectrum was assigned to non-planar OH deformations, $\gamma(OH)$, by Balicheva and Roi [11], who thought it arose from interaction of OH groups belonging to neighbouring octahedra. In the theoretical spectrum of $[Sb(OH)_6]^{-1}$,

γ(OH) is predicted to occur some 400 cm^{-1} lower, at approximately 300 cm^{-1}. Although the DFT calculation are of an isolated [Sb(OH)$_6$]$^{-1}$ octahedron it is difficult to justify such a large shift to accord with the Balicheva and Roi assignment. Also it is interesting to note that the 730 cm^{-1} band is not seen in the mopungite Raman spectrum, which implies it originates from the [M(H$_2$O)]$^{+2}$ moiety, though its presence may be masked by noise from fluorescence and the overall weakness of that spectrum.

SbO stretching

The 800 – 400 cm^{-1} spectral region of the two di-octahedral minerals are virtually identical and there are also many parallels between these spectra and that of mopungite. In addition the theoretical band positions are in broad agreement with experimental values in this region. The predominant band is a broad peak centred at 617 cm^{-1} (brandholzite) and 618 cm^{-1} (bottinoite). Peak fitting reveals that there are four components present at 630, 617, 604, and 576 cm^{-1}, in brandholzite and at 630, 618, 599, and 575 cm^{-1} in bottinoite (Fig. 3). Towards the lower wavenumbers of this region there are two weak broad bands (525 and 502 cm^{-1} for brandholzite, and 516 and 501 cm^{-1} for bottinoite). The 680 – 500 cm^{-1} region has been associated with stretches of the Sb-O octahedra [12] and this is confirmed by the DFT calculations of the [Sb(OH)$_6$]$^{-1}$ ion. Treating the Sb-O octahedra as a pseudo O$_h$ group gives 3 stretching vibrations, the so-called ν_1(A$_{1g}$), ν_2(E$_g$) and ν_3(F$_{1u}$) modes. Six of the 12 Sb octahedra in the Bravais cell populate C$_3$ sites, the same point group symmetry as the crystal. For these moieties FGA predicts that A$_{1g}$ modes transform to *A* symmetry; E$_g$ to *E*, and the F$_{1u}$ modes split into *A + E* modes. Two further non-equivalent Sb octahedra are centred on general sites and so for these moieties there is a potential for each of the three stretching modes to split into *A* and *E* modes. It seems reasonable to assign the most intense band (approx 617 cm^{-1}) to ν_1. DFT calculations suggest that ν_2(E$_g$) of the Sb-O octahedra occurs as much as 50 cm^{-1} to lower wavenumber from ν_1. Thus the bands at 576 and 525 cm^{-1} are candidates for this assignment. However inspection of Fig 6 reveals that only the 525 cm^{-1} band is of the correct symmetry species (E). The theoretical wavenumber for ν_3(F$_{1u}$) is just to the high wavenumber side of ν_1. The band at 630 cm^{-1} is therefore assigned as the *A* symmetry

manifestation of this mode (see Fig 6), which can be denoted as in-phase Sb-O antisymmetric stretch.

A similar picture can be painted for mopungite, where the Sb atom occupies a C_i site in a C_{4h} crystal. In this instance, FGA predicts $v_1(A_{1g})$ splits into $A_g + B_g + E_g$ modes, all Raman active, $v_2(E_g)$ gives rise to six Raman active bands ($2A_g + 2B_g + 2E_g$) and $v3(F_{1u})$ potentially gives rise to six IR active bands ($3A_u + 3B_u(IA) + 3Eu$). Although it was not possible to conduct a single crystal study of mopungite some inferences can be made by comparing mopungite with the brandholzite and bottinoite above. The dominant band at 625 cm^{-1} is most probably the v_1 mode. This is slightly higher than found in bottinoite or brandholzite, again reflecting stronger hydrogen bonding between octahedra in mopungite as suggested by the position of the OH stretch, discussed above. The bands at 526 cm^{-1}, and possibly the band at 546 cm^{-1}, are manifestations of v_2. The v_3 of Sb-O is not predicted to occur in the Raman spectrum of mopungite but distortions to the octahedron may be giving rise to some intensity in near 650 cm^{-1}.

Although there are many parallels, there are also some significant differences in this spectral region between mopungite and the other two minerals. The profile of the strong Sb-O stretch is considerably narrower in mopungite. Band fitting data suggests that the extra band width is due to a broad band centred at 604 cm^{-1} (brandholzite). DFT calculations for the $[M(H_2O)_6]^{+2}$ ion do not predict bands in this region so it seems likely that this is the Sb-O symmetric stretch of the Sb-O on general sites. The band near 501 cm^{-1} in both brandholzite and bottinoite is absent in mopungite, suggesting it is a band of the $[M(H_2O)_6]^{+2}$ moiety.

Low wavenumber region

The theoretical spectrum of $[Sb(OH)_6]^{-1}$ shows a number of bands around 300 cm^{-1} due to $\gamma(OH)$, discussed briefly above, and also Sb-O deformations or $\delta(SbO)$. Mopungite has two bands at about 349 and 361 cm^{-1}, brandholzite at 347 (*E*) and 355 cm^{-1} (*A*) and bottinoite at 350 (*E*) and 361 cm^{-1} (*A*). Franck [12] has assigned bands in this region of the IR spectrum to $\delta(SbO)$. In light of the DFT calculations it seems likely that $\gamma(OH)$ also contributes here. The band at 315 cm^{-1} in brandholzite and

bottinoite is entirely absent in mopungite which suggests that the $[M(H_2O)]^{+2}$ modes contribute significantly to that band.

CONCLUSIONS

The Raman spectra of brandholzite and bottinoite, and the non-aligned Raman spectrum of mopungite, are dominated by the Sb-O symmetric stretch near 620 cm^{-1} and show many similarities despite mopungite lacking the $[M(H_2O)_6]^{+2}$ ion of the other two minerals. Major differences were noted in the OH stretching region which had greater relative intensity and the presence δH_2O near 1620 cm^{-1} as would be expected by the additional presence of the $[M(H_2O)_6]^{+2}$ ion. The Sb-O symmetric stretch showed a broader profile in the di-octahedra minerals owing to the multitude of non-equivalent sites that are occupied by the $[Sb(OH)_6]^{-1}$ ion. Density field theory calculations pertaining to the free $[Mg(H_2O)_6]^{+2}$ ion were of limited use due to the dominance of OH modes in the spectrum and the lack of hydrogen bonding in the free ion model. However the calculated spectrum of the $[Sb(OH)_6]^{-1}$ ion showed reasonable agreement and proved a useful aid in assignments. The single crystal data spectra showed good mode separation and enable the majority of the bands to be assigned a symmetry species of *A* or *E*.

REFERENCES

[1] S. Bahfenne, R. L. Frost, *Spectrochim. Acta.* **2010**, *A75*: 637 – 639

[2] S. Bahfenne, R. L. Frost, *Spectrochim. Acta.* **2009**, *A74*: 100 – 103

[3] R. L. Frost, S. Bahfenne, E. C. Keeffe, *J. Raman Spectrosc.*, **2009,** *40*: 1907 – 1910

[4] A. Friedrich, M. Wildner, E. Tillmanns, P. L. Merz, *Amer. Min.*, **2000,** *85*: 593 – 599

[5] A. Friedrich, F. Mazzi, M. Wildner, T. Ekkehart, *Amer. Min.*, **2003,** *88*: 462 – 463

[6] P. Bonazzi, F. Mazzi, *Amer. Min.*, **1996,** *81*:1494 – 1500

[7] P. Bonazzi, S. Menchetti, A. Caneschi, S. Magnelli, *Amer. Min.*, **1992,** *77:* 1301 - 1304

[8] H. Z. Siebert, *Anorg. Allg. Chem.*, **1959**, *301:* 161 – 170

[9] M. J. Frisch, et al. *Gaussian 03, Revision C.02*, **2004**, Gaussian, Inc., Wallingford, CT

[10] C. E. Check, T.O. Faust, J.M. Bailey, B. J. Wright, T. M. Gilbert, L. S. Sunderlin, *J. Phys. Chem. A*, **2001,** *105*: 8111 – 8116

[11] T. G. Balicheva, N. I. Roi, *J. Struct. Chem.*, **1971,** *12*: 384 – 390

[12] R. Franck, *Rev. Chimie Minérale*, **1973**, *10*: 795 – 810

[13] N. Schrewelius, *Anorg. Allg. Chem.*, **1938**, *238*: 241 – 254

[14] T. Asai, *Bull. Chem. Soc. Japan*, **1975**, *48*: 2677 – 2679

Figure Captions

Fig 1 – Non aligned Raman spectra of brandholzite (A), bottinoite (B), and mopungite (C), and calculated spectra of isolated $[Sb(OH)_6]^1$ (D) and $[Mg(H_2O)_6]^{+2}$ (E)

Fig 2 – Bandfitted spectra of brandholzite, bottinoite, and mopungite in the 3800 – 800 cm^{-1} region

Fig 3 – Bandfitted spectra of brandholzite, bottinoite, and mopungite in the 800 – 100 cm^{-1} region

Fig 4 – Oriented single crystal spectra of brandholzite and bottinoite in the OH stretch region

Fig 5 – Oriented single crystal spectra of brandholzite and bottinoite in the OH deformation region

Fig 6 – Oriented single crystal spectra of brandholzite and bottinoite in the SbO stretch region

Fig 7 – Oriented single crystal spectra of brandholzite and bottinoite in the low wavenumber region

Table Captions

Table 1 – Peak positions, symmetry and assignment of the oriented single crystal spectra of brandholzite and bottinoite

Table S1 – Bandfitted results of Raman spectra of brandholzite, bottinoite, and mopungite

| Brandholzite | | Bottinoite | | Assignment |
Band Centres/cm^{-1}	Symmetry	Band Centres/cm^{-1}	Symmetry	
105	E	105	E	
114	E	115	E	
122	E	125	E	
130	A	146	E	
140	A			Lattice modes
190	A			
207	A	207	E	
		229	E	
233	A	236	A	
252	A	255	A	
282	A	282	A	
		286	A	
299	A	299	E	Sb-O deformations
		303	A	
317	E	318	E	M-O stretch
332	A	337	A	
347	E	350	E	Sb-O deformations
355	A	361	A	
502	E	501	E	
525	E	516	E	
576	A	576	A	
604	A	600	A	Sb-O stretches
618	A	618	A	
630	A	630	A	
729	A	735	A	
1058	A	1045	A	
1078	E	1081	E	OH in-plane deformation
1163	A	1164	A	
1340	A			Combination band (617 + 729 cm^{-1})
1644	E			H$_2$O deformation
3180	A			
3228	A	3223	A	OH stretches
3305	A	3291	A	
3354	E	3345	E	
3400	A	3393	A	H$_2$O stretch
3467	E	3458	E	OH stretch
3550	E	3511	E	H$_2$O stretch

Table 1
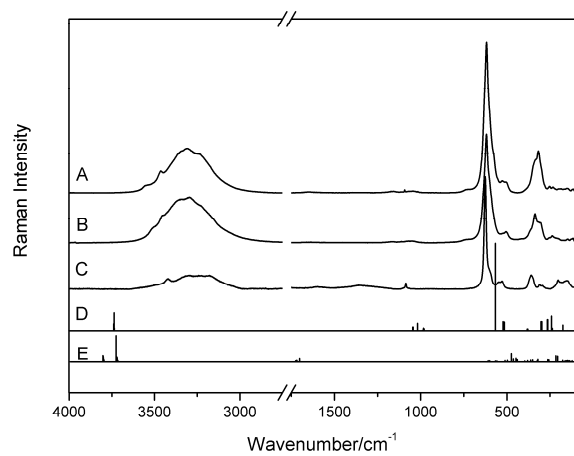
Fig. 1
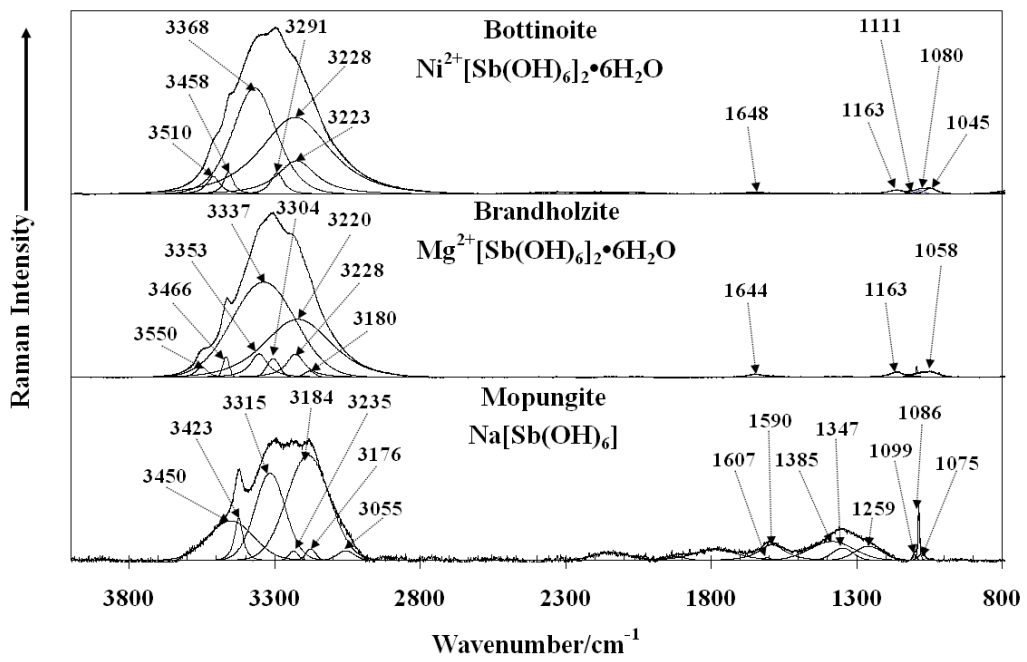
Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7