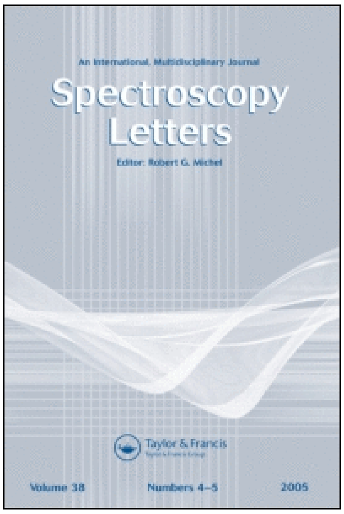

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Silmarilly Bahfenne[a]; Ray L. Frost[a]
[a] Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, Brisbane, Queensland, Australia

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Vibrational Spectroscopic Study of the Antimonate Mineral Stibiconite $Sb^{3+}Sb^{5+}{}_2O_6(OH)$

Silmarilly Bahfenne and Ray L. Frost

Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, Brisbane, Queensland, Australia

ABSTRACT The Raman and infrared spectrum of the antimonate mineral stibiconite $Sb^{3+}Sb^{5+}{}_2O_6(OH)$ were used to define aspects of the molecular structure of the mineral. Bands attributable to water, OH stretching and bending, and SbO stretching and bending were assigned. The mineral has been shown to contain both calcium and water and the formula is probably best written $(Sb^{3+}, Ca)_ySb^{5+}{}_{2-x}$ $(O,OH,H_2O)_{6-7}$ where y approaches 1 and x varies from 0 to 1. Infrared spectroscopy complimented with thermogravimetric analysis proves the presence of water in the stibiconite structure. The mineral stibiconite is formed through replacement of the sulphur in stibnite. No Raman or infrared bands attributable to stibnite were indentified in the spectra.

KEYWORDS antimony ochre, brandholzite, infrared, Raman spectroscopy, stibiconite, stibnite

1. INTRODUCTION

Stibiconite is the oxy-hydroxide antimony mineral $Sb^{3+}Sb^{5+}{}_2O_6(OH)$ formed in the oxidation zone of stibnite Sb_2S_3.[1–3] Stibiconite is a pseudomorph of stibnite, in other words, the daughter mineral (stibiconite) retains the crystal structure of the parent mineral (stibnite). There is full decomposition of stibnite crystal phase and the formation of other phases as a result of stibnite oxidation and hydrolysis in the presence of soluble salts of Ca, Na, and others. Normally several phases are formed including stibiconite, other Sb oxides and sulphates. Therefore stibiconite is usually contaminated by admixtures of other secondary minerals. Stibiconite possesses a cubic structure with point group $4/m$ 3 bar $2/m$. The mineral is botryoidal and may be concentrically zoned[4] forming quite large crystals. The mineral stibiconite has an interesting history.[3] The mineral has in the past been mistakenly called cervantite and other names, but stibiconite is the IMA approved name. Cervantite is also a valid mineral species, orthorhombic, with the formula $Sb^{3+}Sb^{5+}O_4$, unlike stibiconite that is cubic, has another (pyrochlore-type) crystal structure and the idealized formula $Sb^{3+}Sb^{5+}{}_2O_6(OH)$. The mineral stibiconite has been shown to contain both

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Address correspondence to Ray L. Frost, Chemistry Discipline, Faculty of Science and Technology, 2 George Street, P.O. Box 2434 GPO, Brisbane 4001, Australia. E-mail: r.frost@qut.edu.au

calcium and water and the formula is probably best written $(Sb^{3+}, Ca)_y Sb^{5+}{}_{2-x}(O,OH,H_2O)_{6-7}$ where y approaches 1 and x varies from 0 to 1. Cody et al. defined cervantite as α-Sb_2O_4.[5] This formulation differs from the description given by Vitiliano and Mason.[3]

The aim of this paper is to report the Raman and infrared spectrum of stibiconite and compare with published Raman and infrared spectra of other antimony oxides and oxyhydroxides. The spectra are related to the molecular structure of stibiconite inferring some relations to the crystal chemistry of antimonite type minerals. The paper follows the systematic research on Raman and infrared spectroscopy of secondary minerals containing oxy-anions formed in oxidation zone.

2. EXPERIMENTAL

2.1. Minerals

The stibiconite mineral was obtained from Museum South Australia and originated from the Yucunani Mine, Tejocotes, Oaxaca, Mexico. The composition of this mineral has been published.[4] In the work of Vitaliano and Mason the analyses of some 33 samples of stibiconite were presented.[3] These authors showed that Ca was always present in the structure and also water was present in the structure.

2.2. Raman Spectroscopy

The crystals of stibiconite were placed and oriented on the stage of an Olympus BHSM microscope, equipped with 10× and 50× objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Further details have been published.[6–14]

2.3. Infrared Spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Band component analysis was undertaken using the Jandel Peakfit™ (Erkrath, Germany) software package which enabled the type of fitting function to be selected and allowed 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 Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations (r^2) greater than 0.995. Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

3. RESULTS AND DISCUSSION

The Raman spectrum of stibiconite in the 50 to 900 cm^{-1} region is displayed in Fig. 1. The infrared spectrum of stibiconite in the 500 to 1800 cm^{-1} region is displayed in Fig. 2. The infrared spectrum

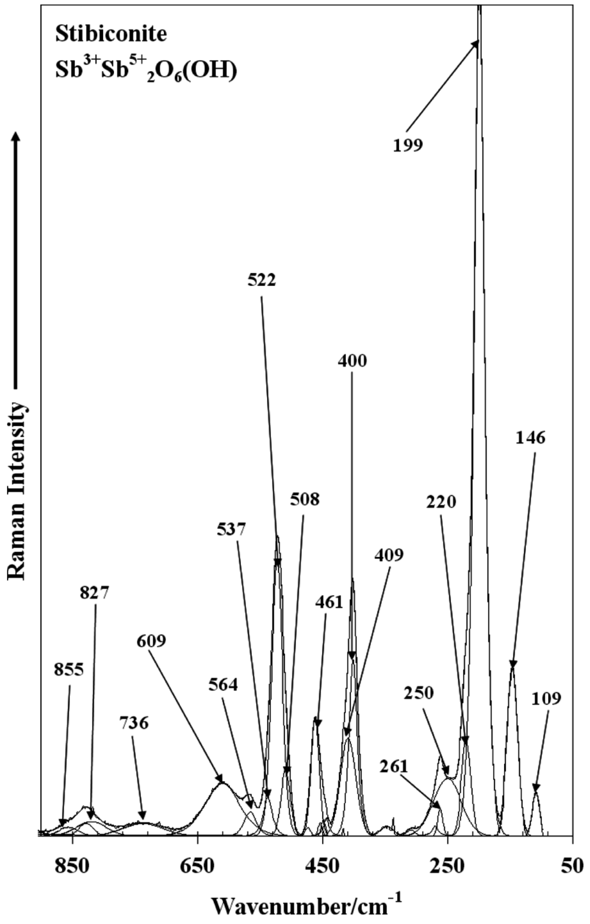

FIGURE 1 Raman spectrum of stibiconite in the 50 to 900 cm^{-1} region.

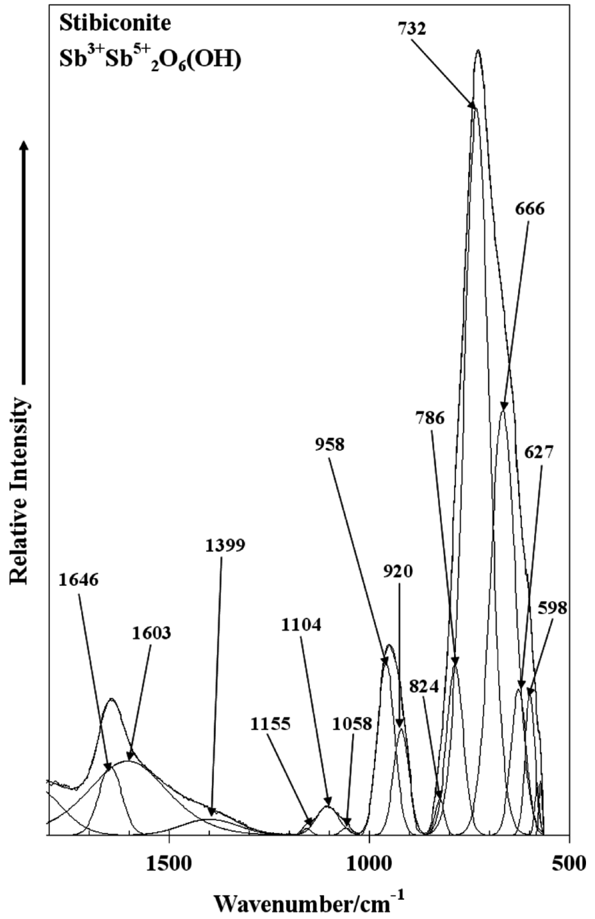

FIGURE 2 Infrared spectrum of stibiconite in the 500 to 1800 cm^{-1} region.

is dominated by the intense band at 732 cm^{-1}. The band shows asymmetry and component bands may be resolved on the low wavenumber side at 627 and 666 cm^{-1}. According to Siebert[15,16] all bands in the 600 to 900 cm^{-1} range are assignable to SbO stretching vibrations. One probable assignment is that the band at 732 cm^{-1} is attributed to the SbO antisymmetric stretching vibrational mode. A very intense broad band is observed for antimony pentoxide at 740 cm^{-1}. In the infrared spectrum of antimony pentoxide an intense band is observed at 740 cm^{-1} and low intensity bands at ~370, 450, and 680 cm^{-1}.[17] The infrared spectrum of valentinite $(Sb_2O_3)_4$ showed bands in similar positions.[17] However the wavenumber of Sb-O stretching vibrations strongly depends on the valency and the coordination number of Sb. The band at 680 cm^{-1} in the IR spectrum of valentinite is relatively weak; strongest bands of Sb-O stretching vibrations for valentinite are observed in the range 460–550 cm^{-1} because the valency of Sb in valentinite is 3. In the infrared spectrum of the compound $NaSb(OH)_6$ which has an octahedral structure, a very intense band is observed at 628 cm^{-1} with bands of lower intensity at 775 and 528 cm^{-1}.[18] In the infrared spectrum of stibiconite, low intensity bands are observed in the 900 to 1200 cm^{-1} region. These bands may be attributed to silicate impurity in the samples.

The Raman spectrum shows a very intense band at 199 cm^{-1}. Lower-intensity bands are found at 400, 409, 461, and 522 cm^{-1}. Low-intensity bands are also observed at 609, 736 and 827 cm^{-1}. Cody et al.[5] reported the infrared and Raman spectra of a number of oxides of antimony including senarmoatite Sb_2O_3, valentinite, Sb_2O_3 cervantite α-Sb_2O_4 and some other compounds synthesised through thermal treatment. The most prominent band for these minerals occurs between 140 and 260 cm^{-1}. Cody et al.[5] did no assignment of these bands. The 199 cm^{-1} band of stibiconite is assigned to OSbO bending modes. Some preliminary DFT calculations provide evidence that the OSbO bending mode occurs at 200 +/− 5 cm^{-1}. The low intensity band at 736 cm^{-1} may be the equivalent of the intense infrared band at 740 cm^{-1}. Low-intensity Raman bands are observed at 722 cm^{-1} (senarmonite) and 690 cm^{-1} (valentinite). It is possible that these bands are assignable to the SbO stretching vibrations.

The Raman and infrared spectra of stibiconite in the higher wavenumber region are displayed in Figs. 3 and 4. The Raman spectra are characterized by a low-intensity broad profile centred upon 3220 cm^{-1}. The spectral profile may be curve resolved into component bands at 2755, 3018, 3225, 3424 and 3603 cm^{-1}. The likely assignment of the latter band is to SbOH stretching vibrations. The other bands are assigned to the stretching vibrations of acid OH groups. In the infrared spectrum a band of significantly more intensity is observed at 3233 cm^{-1}. The spectral profile may be curve resolved into component bands as shown in Fig. 4. Other bands are observed at 2286 and 2383 cm^{-1}. These infrared bands are attributed to the stretching vibrations of acid OH groups. Thermogravimetric analysis shows two mass loss steps at 105 and around 330°C. These mass loss steps are assigned to dehydration and dehydroxylation. The observation of multiple bands suggests that the water units in the stibiconite structure are non-equivalent. A comparison may be made with the spectra of the

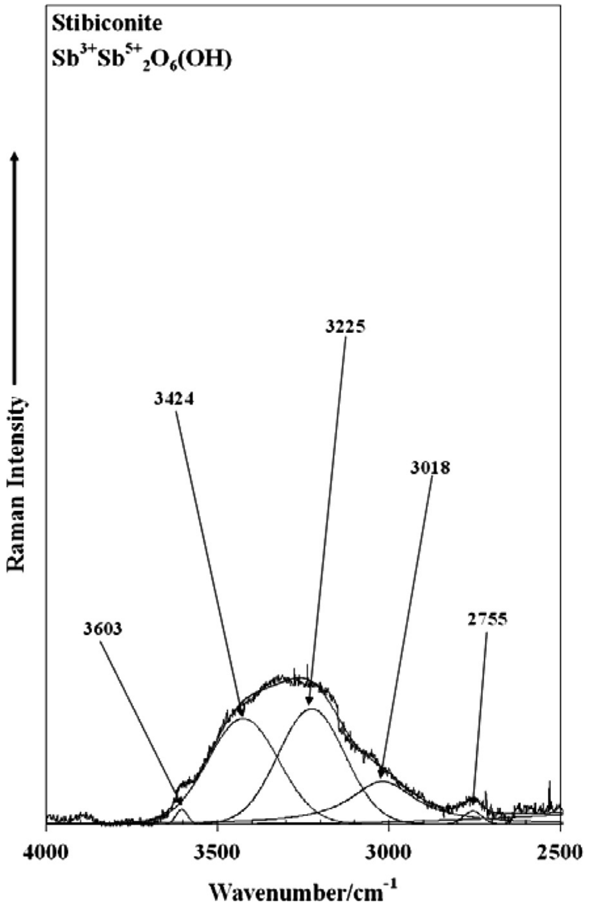

FIGURE 3 Raman spectrum of stibiconite in the 2500 to 4000 cm^{-1} region.

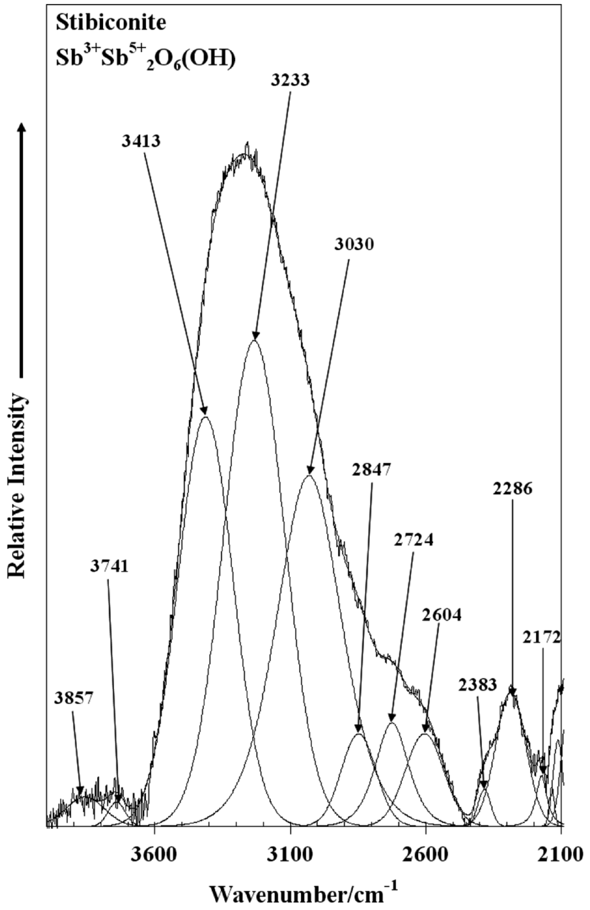

FIGURE 4 Infrared spectrum of stibiconite in the 2100 to 4000 cm^{-1} region.

OH stretching region of stibiconite and the mineral brandholzite $Mg[Sb(OH)_6] \cdot 6H_2O$. The difficulty of comparing brandholzite spectra with that of stibiconite is that the mineral brandholzite contains both water and OH units. A complex pattern resulting from the overlapping bands of the water and OH units is observed. Raman bands are observed at 3240, 3383, 3466, 3483, and 3552 cm^{-1}, infrared bands at 3248, 3434, and 3565 cm^{-1}. The Raman bands at 3240 and 3383 cm^{-1} and the infrared band at 3248 cm^{-1} are assigned to water stretching vibrations. The higher wavenumber bands observed at 3466 and 3552 cm^{-1} (Raman) and 3434 and 3565 cm^{-1} (infrared) are assigned to the stretching vibrations of the OH units. The position of these bands for brandholzite harmonizes well with the band positions of stibiconite. The question arises as to whether the bands for stibiconite are due to the OH units or whether the bands are due to adsorbed or chemically bonded water. In the infrared spectrum (Fig. 2) bands are observed at 1603 and 1646 cm^{-1}, which may be assigned to water bending modes. This suggests that there may be water either adsorbed or involved in the structure. Vitaliano and Mason in an early piece of research on stibiconite and cervantite proved that some water was involved in the stibiconite structure.[3]

Some low intensity bands are observed in the infrared spectrum of stibiconite at 920, 958, and 1104 cm^{-1}. These bands are attributed to impurities. In the Raman spectrum of brandholzite four Raman bands are observed at 1043, 1092, 1160, and 1189 cm^{-1}. Eight infrared bands at 963, 1027, 1055, 1075, 1108, 1128, 1156, and 1196 cm^{-1} are observed. These bands are assigned to δ SbOH deformation modes. Siebert reported four infrared bands at 1030, 1075, 1105, and 1120 cm^{-1} for the synthetic compound $NaSb(OH)_6$. The position and number of these infrared bands for this compound is in good agreement with the position of the infrared bands of stibiconite.

4. CONCLUSIONS

The antimony containing mineral stibiconite also previously known as cervantite of ideal formula $Sb^{3+}Sb^{5+}{}_2O_6(OH)$ was studied by a combination of infrared and Raman spectroscopy. Studies have shown that the mineral contains water in the structure and Raman bands at around $3200\,cm^{-1}$ and infrared bands centred upon $3233\,cm^{-1}$ are attributed to acid OH units. The low-intensity Raman band at $3603\,cm^{-1}$ is assigned to the OH stretching vibration of the OH units. An intense infrared band at $732\,cm^{-1}$ is assigned to SbO stretching vibrations based upon a comparison with the Raman spectra of senarmontite, valentinite, and other antimony oxides.

The Raman spectra of stibnite were compared with the Raman spectrum of stibiconite. Strong Raman bands for stibnite are observed at 145, 175, 250, and $280\,cm^{-1}$. These bands were not found in the Raman spectrum of stibiconite showing the sulphur in stibnite had been completely reacted in the formation of stibiconite.

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