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Raman spectroscopic study of the antimony containing mineral partzite $Cu_2Sb_2(O,OH)_7$

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Abstract

Raman spectroscopy of the mineral partzite $Cu_2Sb_2(O,OH)_7$ complimented with infrared spectroscopy were studied and related to the structure of the mineral. The Raman spectrum shows some considerable complexity with a number of overlapping bands observed at 479, 520, 594, 607 and 620 cm^{-1} with additional low intensity bands found at 675, 730, 777 and 837 cm^{-1}. Raman bands of partzite in the spectral region 590 to 675 cm^{-1} are attributable the ν_1 symmetric stretching modes. The Raman bands at 479 and 520 cm^{-1} are assigned to the ν_3 antisymmetric stretching modes. Raman bands at 1396 and 1455 cm^{-1} are attributed to SbOH deformation modes. A complex pattern resulting from the overlapping band of the water and OH units is found. Raman bands are observed at 3266, 3376, 3407, 3563, 3586 and 3622 cm^{-1}. The first three bands are assigned to water stretching vibrations. The three higher wavenumber bands are assigned to the stretching vibrations of the OH units. It is proposed that based upon observation of the Raman spectra that water is involved in the structure of partzite. Thus the formula $Cu_2Sb_2(O,OH)_7$ may be better written as $Cu_2Sb_2(O,OH)_7 \cdot xH_2O$

Key words: antimony oxide, partzite bahianite, brandholzite, Raman Spectroscopy, valentinite, bindheimite, lewisite, romeite, stetefeldtite, and stibiconite

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Introduction

It is interesting to note that very few papers have been published on the spectroscopy of antimonate minerals. What research has been published is related to the analysis of pigments [1-3]. This work involves the chemical analysis of pigments and their detection using Raman spectroscopy. Some spectroscopic studies of calcium and copper antimonates has been forthcoming [4-6]. It has been found that for arsenate bearing minerals, the hydroxyl unit was coordinated directly to the metal ion and formed hydrogen bonds to the arsenate anion [7]. Raman spectroscopy has proven especially useful for the study of related minerals [8-16]. According to Khozhatelev [17], there are eight recognized intrinsically supergene ochreous antimony bearing minerals: senarmonite Sb_2O_3, valentinite Sb_2O_3, stibiconite $Sb^{3+}Sb_2^{5+}O_6(OH)$, bindheimite $Pb_2Sb_2O_6(O,OH)$, stetefeldite $Ag_2Sb_2(O,OH)_7$, partzite $Cu_2Sb_2(O,OH)_7$, tripuhyite $Fe^{2+}Sb_2^{5+}O_6$, and bystromite $Mg_2Sb_2^{5+}O_6$. According to Mason et al. [18] antimony oxides and antimonates fall into two structural groups, a cubic group with pyrochlore structure and a tetragonal group with a trirutile structure. Partzite belongs to the first group. The mineral partzite first discovered in 1865, is a copper antimony oxy-hydroxide of formula $Cu_2Sb_2(O,OH)_7$. The mineral is found in the oxidised zone of antimony-bearing sulphide deposits [18]. The mineral is obtained from the Blind Spring Hill district, 2 miles SE of Benton, Mono Co., California. [19] The mineral may be associated with the minerals bindheimite, lewisite, and stibiconite. The mineral is located in several districts world-wide including Mt. Monger, near Doigs, Western Australia. The mineral can vary in colour from olive-green to yellowish-green blackish to green black to black.

Farmer reported the infrared spectra of some synthetic antimonite minerals (see page 413 and 414 with Tables 17. XVIII and XIX) [20]. For the synthetic compound $NaSb(OH)_6$ which is a compound with an octahedral structure, infrared bands were observed at 600 and 628 cm⁻¹ (very intense) 735, 775 cm⁻¹ (medium intensity) and 528 and 586 cm⁻¹. Siebert researched the infrared spectra of selected synthetic antimonates [21, 22]. Siebert assigned bands in the 528 to 775 cm⁻¹ region to the stretching vibrations of SbO units; in the 1030 to 1120 cm⁻¹ to the deformation modes of SbOH units and in the 3220 to 3400 cm⁻¹ to the stretching bands of SbOH and water units. The aim of this paper is to report the Raman spectra of partzite and to relate the spectra to the chemistry and formula of partzite. The paper follows the systematic research on Raman and infrared spectroscopy of secondary minerals containing oxy-anions formed in the oxidation zone of minerals.

Experimental

Minerals

The mineral is obtained from the Blind Spring Hill district, 2 miles SE of Benton, Mono Co., California. The mineral is cubic and is of point group 4/m 2/m. The composition of the mineral has been published by Anthony et al. (page 427) [19]. The mineral analysis gave Sb_2O_4 as 47.65%, CuO 32.11% with some other cations present as FeO 2.33%, PbO 2.01%, Ag_2O 6.12%. The structure of the mineral was confirmed by X-ray diffraction.

Raman spectroscopy

Crystals of partzite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of $\pm$ 1 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition on the crystals using the highest magnification (50x) 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. Further details have been published [8-16]. Alignment of all crystals in a similar orientation has been attempted and achieved. However, differences in intensity may be observed due to minor differences in the crystal orientation. The Raman spectra of the oriented single crystals are reported in accordance with the parallel/perpendicular notation. It is noted that the mineral partzite is very dark in colour, almost black, yet Raman spectra were readily obtained.

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.

Results and discussion

The Raman spectrum of partzite in the 100 to 1500 cm^{-1} region is reported in Figure 1.   The Raman spectrum shows some considerable complexity with a number of overlapping bands observed at 479, 520, 594, 607 and 620 cm^{-1} with additional low intensity bands found at 675, 730, 777 and 837 cm^{-1}.   According to Siebert [21, 22] all bands in these positions are assignable to SbO stretching vibrations. The observation of multiple bands attributable to symmetric stretching vibrations in the Raman spectrum provides evidence for the non-equivalence of SbO units in the partzite structure.

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} [23].   The infrared spectrum of valentinite (Sb_2O_3)$_4$ showed bands in similar positions [23].   Farmer reported the infrared band positions of synthetic antimonates of formula $MSbO_4$ where M is Cr, Fe, Ga or Rh with a rutile type structure [20].   As such these structures should have four Raman active bands (A_{1g} + B_{1g} + B_{2g} + E_g) and four infrared active bands (A_{2u} + $3E_u$).   Infrared bands were observed in the 660 to 735 cm^{-1}, 520 to 585 cm^{-1}, 285 to 375 cm^{-1} and 170 to 190 cm^{-1}.   Although no assignment was given to these bands but one possible interpretation is that the first band is attributed to the antisymmetric stretching mode, the second to the symmetric stretching mode, the third to bending modes and the fourth to a lattice modes.   Hence the Raman bands of partzite in the spectral region 590 to 675 cm^{-1} are attributable the ν_1 symmetric stretching modes.   The Raman bands at 479 and 520 cm^{-1} may therefore be assigned to the ν_3 antisymmetric stretching modes.   The set of bands at 362, 387 and 418 cm^{-1} may be assigned to the CuO stretching vibrations.

The most intense Raman band in this spectral region is the band at 971 cm^{-1}.   Shoulder bands are observed at 907, 938 and 982 cm^{-1}. This band at 971 cm^{-1} and associated shoulders is attributed to some sulphate impurities and is assigned to the the ν_1 (SO_4)$^{2-}$ symmetric stretching mode.   Hence the three Raman bands of low intensity at 1074, 1096 and 1126 cm^{-1} are assigned to the ν_3 (SO_4)$^{2-}$ antisymmetric stretching mode.   The observation of these bands

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is in many ways not unexpected, as the mineral partzite is formed from antimony sulphide deposits. Raman bands at 1396 and 1455 cm^{-1} are attributed to δSbOH deformation modes.

The Raman spectrum of partzite in the OH stretching region is displayed in Figure 2. The Raman spectrum shows a complex set of overlapping bands. The bands are well defined and are readily resolved into component bands. The higher wavenumber bands at 3563, 3586 and 3622 cm^{-1} are attributed to hydroxyl stretching vibrations of the OH of the Sb-OH units. The Raman bands at 3266, 3376 and 3407 cm^{-1} are assigned to OH stretching bands of water. It is proposed that based upon observation of the Raman spectra that water is involved in the structure of partzite. Thus the formula $Cu_2Sb_2(O,OH)_7$ may be better written as $Cu_2Sb_2(O,OH)_7 \cdot xH_2O$. Further research on this mineral is necessary and determination of the exact formulation is required.

Conclusions

The Raman spectrum of the mineral partzite has been obtained for the first time and the spectra related to the mineral structure. The Raman spectrum shows some considerable complexity with a number of overlapping bands observed at 479, 520, 594, 607 and 620 cm^{-1} with additional low intensity bands found at 675, 730, 777 and 837 cm^{-1}. Raman bands of partzite in the spectral region 590 to 675 cm^{-1} are attributable the ν_1 symmetric stretching modes. The Raman bands at 479 and 520 cm^{-1} are assigned to the ν_3 antisymmetric stretching modes. Raman bands at 1396 and 1455 cm^{-1} are attributed to SbOH deformation modes.

Raman bands are observed in the spectral regions associated with water and hydroxyl unit stretching vibrations. Raman spectra complimented with infrared spectra clearly show that the spectrum of water is obtained for this mineral. The formula is currently understood to be $Cu_2Sb_2(O,OH)_7$. Anthony et al. indicate that the formula is questionable. The formula may be better written as $Cu_2Sb_2(O,OH)_7 \cdot xH_2O$. It is noted that Anthony et al. [19] also questioned the formula of the mineral partzite.

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