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Synthesis and spectroscopic characterization of apjohnite and pickingerite

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Abstract

Raman spectroscopy complimented with infrared ATR spectroscopy has been used to characterise two synthetic halotrichites: apjohnite $MnSO_4 \cdot Al_2(SO_4)_3 \cdot 22H_2O$ and pickingerite $MgSO_4 \cdot Al_2(SO_4)_3 \cdot 22H_2O$. A comparison is made with the spectra of natural pseudo-alums halotrichite, pickingerite and apjohnite. Two Raman bands observed at 995 and 990 cm^{-1} for apjohnite and a single band at 984 cm^{-1} for pickingerite are assigned to the $\nu_1(A_g)$ SO_4 symmetric stretching vibrations. Raman bands observed at 1141 and 1080 cm^{-1} for apjohnite and 1096 and 1058 cm^{-1} for pickingerite are assigned to the antisymmetric stretching vibration $\nu_3(B_g)$ SO_4. Raman bands at 474, 460 and 423 cm^{-1} for apjohnite and at 459 and 445 cm^{-1} for pickingerite are attributed to the $\nu_2(A_g)$ SO_4 mode. The band at 618 cm^{-1} is assigned to the $\nu_4(B_g)$ SO_4 mode. The splitting of the ν_2, ν_3 and ν_4 modes is attributed to the reduction of symmetry of the SO_4 and it is proposed that the sulphate coordinates to water in the hydrated aluminium in bidentate chelation.

Keywords: Apjohnite; Pickingerite; Sulphate; Halotrichite; Jarosite; Infrared and Raman spectroscopy

1. Introduction

Sulphate efflorescences have been known for some considerable time [1–3]. These often occur in tailings impoundments (see [4, p. 322]). The sulphate formation results from the oxidation of pyrite. Halotrichites are formed close to pyrite and are often found with copiapites and related minerals [5]. The minerals are found in efflorescences of geothermal fields [6]. Halotrichite has a formula $FeSO_4 \cdot Al_2(SO_4)_3 \cdot 22H_2O$ and forms an extensive solid solution series with pickingerite $MgSO_4 \cdot Al_2(SO_4)_3 \cdot 22H_2O$ [6–9]. The minerals are related to the alums $R_2SO_4 \cdot M_2(SO_4)_3 \cdot 24H_2O$ or $RM(SO_4)_2 \cdot 12H_2O$ where R represents an atom of a univalent ion such as ammonium, lithium, sodium, potassium and caesium and where M represents a trivalent metal such as aluminium, iron, chromium, gallium, manganese, cobalt, rhodium and thallium. When a divalent atom is introduced instead of the monovalent atom, such as manganese, ferrous iron, cobalt, zinc and magnesium will form double sulphates. These sulphates form the halotrichites mineral series. These minerals are not isomorphous with the univalent alums. The minerals are all isomorphous and crystallise in the monoclinic space group $P2_1/c$ In the structure of the pseudo-alums, four crystallographically independent sulphate ions are present [10]. One acts as a unidentate ligand to the M^{2+} ion and the other three are involved in complex hydrogen bond arrays involving coordinated water molecules to both cations and to the lattice water molecules.

Ross reports the interpretation of the infrared spectra for potassium alum as ν_1, 981 cm^{-1}; ν_2, 465 cm^{-1}; ν_3, 1200, 1105 cm^{-1}; ν_4, 618 and 600 cm^{-1} [11]. Water stretching modes were reported at 3400 and 3000 cm^{-1}, bending modes at 1645 cm^{-1}, and librational modes at 930 and 700 cm^{-1} [12]. In the structure of alums, six water molecules surround each of the two cations. This means the sulphate ions are distant from the cations and coordinate to

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the water molecules. Ross also lists the infrared spectra of the pseudo-alums formed from one divalent and one trivalent cation. Halotrichite has infrared bands at ν_1, 1000 cm^{-1}; ν_2, 480 cm^{-1}; ν_3, 1121, 1085, 1068 cm^{-1}; ν_4, 645, 600 cm^{-1}. Pickeringite the Mg end member of the halotrichite–pickeringite series has infrared bands at ν_1, 1000 cm^{-1}; ν_2, 435 cm^{-1}; ν_3, 1085, 1025 cm^{-1}; ν_4, 638, 600 cm^{-1} [11]. These minerals display infrared water bands in the OH stretching, 3400 and 3000 cm^{-1} region; OH deformation, 1650 cm^{-1} region; OH libration, 725 cm^{-1} region. Ross also reports a weak band at ~960 cm^{-1} which is assigned to a second OH librational vibration [11]. As with the infrared spectra, Raman spectra of alums are based on the combination of the spectra of the sulphate and water. Sulphate typically is a tetrahedral oxyanion with Raman bands at 981 (ν_1), 451 (ν_2), 1104 (ν_3) and 613 (ν_4) cm^{-1} [13]. Some sulphates have their symmetry reduced through acting as monodentate and bidentate ligands [13]. In the case of bidentate behaviour both bridging and chelating ligands are known. This reduction in symmetry is observed by the splitting of the ν_3 and ν_4 into two components under C_{3v} symmetry and three components under C_{2v} symmetry.

In this work we report the Raman and infrared spectra of two synthetic halotrichites and compare the spectra with that of the natural minerals.

2. Experimental

2.1. Synthesis of halotrichites

The synthetic halotrichites type minerals Pickeringite and Apjohnite were prepared from an ultra pure water solution. Saturated solutions of both components were shaken together with the solid sulphates contained in filter bag sacks and were placed on either side of a beaker, which contained the saturated solution. In the synthesis of pickeringite, 9.824 g of $Al_2(SO_4)_3 \cdot 18H_2O$ and 2.491 g of $MnSO_4 \cdot H_2O$ were contained in the two sacks, while in the synthesis of apjohnite, 13.027 g of $Al_2(SO_4)_3 \cdot 18H_2O$ and 4.818 g of $MgSO_4 \cdot 7H_2O$ were used. The double salt was left over a period of a week to crystallise out. The crystals were dried and collected by vacuum filtration and washed with ethanol and diethyl ether. The minerals were analysed by X-ray diffraction for phase purity and by electron probe using energy dispersive techniques for quantitative chemical composition.

2.2. Raman spectroscopy

The crystals of halotrichite 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). Raman spectra were excited by a HeNe 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 was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. Previous studies by the authors provide more details of the experimental technique [14–17]. Spectra at elevated temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd., Waterfield, Surrey, England). Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA).

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' 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 Lorentz–Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared regression coefficient of R^2 greater than 0.995.

3. Results and discussion

The Raman spectra of synthetic apjohnite and pickingerite in the 950–1050 cm^{-1} region are shown in Fig. 1; the infrared spectra in the 525–1225 cm^{-1} region in Fig. 2; the Raman spectra in the 100–700 cm^{-1} region in Fig. 3; the Raman spectra in the 2700–3700 cm^{-1} region in Fig. 4 and the infrared spectra in the 2100–3700 cm^{-1} region in Fig. 5. The results of the analyses of the Raman and infrared spectra of synthetic apjohnite and pickingerite together with the results of the Raman spectra of natural halotrichite, wupatkiite and apjohnite are reported in Table 1.

The Raman spectrum of pickingerite displays an intense symmetric band at 984 cm^{-1} assigned to the ν_1 $(SO_4)^{2-}$ symmetric stretching mode. A second very low intensity band is observed at 971 cm^{-1}. According to Ross, this band is a water librational mode. A comparison may be made with the Raman spectrum of halotrichite where a single Raman band at 995 cm^{-1} is observed with a low intensity band at 975 cm^{-1}. The Raman spectrum of synthetic apjohnite shows two resolved bands at 995 and 990 cm^{-1} with a third band at 975 cm^{-1}. The first two bands are