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Vibrational spectroscopy of the borate mineral gaudefroyite $Ca_4Mn^{3+}_{3-x}(BO_3)_3(CO_3)(O,OH)$ from N'Chwaning II mine, Kalahari, Republic of South Africa

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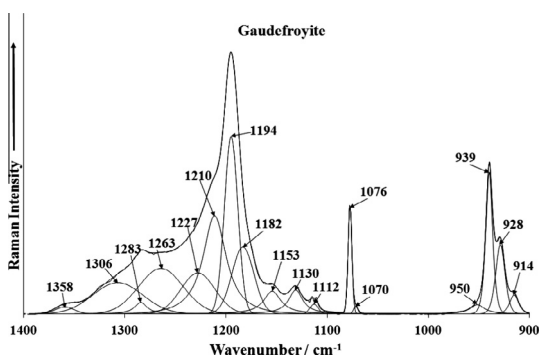
HIGHLIGHTS

- Gaudefroyite $Ca_4Mn^{3+}_{3-x}(BO_3)_3(CO_3)(O,OH)_3$ is an unusual mineral containing both borate and carbonate.
- We have assessed the molecular structure of gaudefroyite.
- Raman bands are assigned to the stretching and bending modes of trigonal boron.

GRAPHICAL ABSTRACT



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ABSTRACT

Gaudefroyite $Ca_4Mn^{3+}_{3-x}(BO_3)_3(CO_3)(O,OH)_3$ is an unusual mineral containing both borate and carbonate groups and is found in the oxidation zones of manganese minerals, and it is black in color. Vibrational spectroscopy has been used to explore the molecular structure of gaudefroyite. Gaudefroyite crystals are short dipyramidal or prismatic with prominent pyramidal terminations, to 5 cm. Two very sharp Raman bands at 927 and 1076 cm^{-1} are assigned to trigonal borate and carbonate respectively. Broad Raman bands at 1194, 1219 and 1281 cm^{-1} are attributed to BOH in-plane bending modes. Raman bands at 649 and 670 cm^{-1} are assigned to the bending modes of trigonal and tetrahedral boron. Infrared spectroscopy supports these band assignments. Raman bands in the OH stretching region are of a low intensity. The combination of Raman and infrared spectroscopy enables the assessment of the molecular structure of gaudefroyite to be made.

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Introduction

The number of minerals containing both borate and carbonate is very few. Among these minerals are borcarite $Ca_4Mg(B_4O_6(OH)_6(CO_3)_2$, britvinite $(Pb_7(OH)_3F(BO_3)_2(CO_3))(Mg_{4.5}(OH)_3(Si_5O_{14}))$, canavesite $Mg_2(HBO_3)(CO_3)\cdot 5H_2O$, carboborite $Ca_2Mg(B(OH)_4)_2(CO_3)_2\cdot 4H_2O$, gaudefroyite $Ca_4Mn^{3+}_{3-x}(BO_3)_3(CO_3)(O,OH)$, harkerite $Ca_{12}Mg_4Al(BO_3)_3(SiO_4)_4(CO_3)_5\cdot H_2O$, merehedite $Pb_{47}Cl_{25}(OH)_{13}O_{24}(CO_3)(BO_3)_2$, movdite-Y $Y(B(OH)_4)(CO_3)$, numanoite $Ca_4Cu(B_4O_6(OH)_6)(CO_3)_2$, qilianshanite $NaHCO_3\cdot H_3BO_3\cdot 2H_2O$, and sakhaite $Ca_{12}Mg_4(BO_3)_7(CO_3)_4(OH)_2Cl$. Several minerals contain siloxane

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units and several contain the hydrogen borate units. In this research, we report a study of gaudefroyite. The reason is that the mineral is found in the oxidation zones of manganese mineral deposits and many of these minerals are of interest because of their one dimensional ferromagnetism [1].

Gaudefroyite is a rare mineral and was first found in hydrothermal manganese deposits at Tachgagalt, near Ouarzazate, Anti-Atlas Mountains, Morocco, where it occurs in a gangue of white, non-manganiferous calcite, quartz, and locally brucite [2,3]. The second known occurrence of gaudefroyite is from Wessels-type area of the Kalahari manganese field, South Africa, where it occurs in the central portion of the lower manganese unit, associated with marokite [4].

Gaudefroyite was firstly determined as a hexagonal mineral, which crystallizes in a space group $P6_3$ or $P6_3/m$ [2]. Its chemical formula was determined as $Ca_4Mn^{3+}_{3-x}[(BO_3)_3(CO_3)(O_{1-x}(OH)_x)_3]$, where $x \approx 0.17$, and $Z = 2$, with a suggestion that in completely fresh gaudefroyite x may be 0, with no (OH) present, leading to the ideal chemical formula $Ca_4Mn^{3+}_3[(BO_3)_3(CO_3)O_3]$ [2]. There was also a suggestion that in an oxidizing environment Mn^{3+} oxidizes to Mn^{4+} and pyrolusite (MnO_2) forms, and the resulting vacancies in the gaudefroyite structure are then compensated by substitution of $(OH)^-$ by O^{2-} [2].

The main structural units of the gaudefroyite structure are edge-sharing puckered chains formed by Jahn-Teller uniaxially elongated $Mn^{3+}O_6$ octahedra. Octahedral chains run parallel to the c-axis and are crosslinked by triangular BO_3 groups, forming two different types of channels [5]. In the centre of the larger, hexagonally shaped channels are the CO_3 triangles surrounded by Ca atoms. The smaller, trigonal-shaped channels are occupied only with Ca atoms [5]. Although the space group of gaudefroyite was firstly solved as $P6_3$ [6], and then refined in the same space group [7,8], later the structure of gaudefroyite was refined in both space groups $P6_3/m$ and $P6_3$ ($a = 10.589(1)$ Å, and $c = 5.891(1)$ Å), and presented the structure in space group $P6_3/m$ as their preferred structural model [5]. They noted that the structural framework of gaudefroyite and most of the channel-filling cations posses $P6_3/m$ symmetry, which is only violated by the arrangement of the CO_3 groups, i.e. this framework arrangement and distribution of the Ca^{2+} cations in the structural channels, obeys the higher space-group symmetry $P6_3/m$, but, in contrast, CO_3 groups situated in the centre of the wide structural channel locally violate the mirror-plane perpendicular to c [5,6]. Thus, in the average structure, carbonate groups exhibit positional disorder governed by the centro-symmetry of the framework [5].

Results of TG–DTA investigations [9] indicate that the CO_3 groups in gaudefroyite are partially ordered and possibly give rise to a superstructure, and this partial order of the CO_3 groups is confirmed by transmission electron microscopy [10]. The CO_3 groups in the large 6_3 channels are ordered in two different ways and this ordering gives rise to two different types of 6_3 channels, A and B. The A and B types of channels occur in a 1:1 ratio, they are partially ordered and give rise to the continuous streaked reflections in several directions in SAED patterns of gaudefroyite, which indicate that the true symmetry of gaudefroyite is lower than hexagonal [10]. Rietveld refinements of the gaudefroyite structure at various temperatures prove that the structure is stabile up to 486 °C [11].

The number of vibrational spectroscopic studies of borate minerals is very limited [12–15]. The number of Raman studies is also very limited [16,17]. There have been a number of infrared studies of some natural borates [18–21]. Most of these references are not new and there have been no recent studies on the vibrational spectroscopy of natural borates. Ross in Farmer's treatise reported the infrared spectra of a considerable number of borate minerals [22]. Vibrational spectroscopy has been applied to borate glasses [23–26]. There have been a number of studies of borate glasses doped with a wide range of radioactive atoms [27,28]. Borate glasses may be used as a means of containment of radioactive materials. There have been a number of studies looking at the effect of radiation on borate glasses [29,30].

Yet, there remains the issue of the vibrational spectroscopic study of natural borate minerals. There are very few studies on the Raman spectra of natural borate minerals. In this paper, we have studied the Raman and infrared spectroscopy of the mineral gaudefroyite and relate the spectra to the structure of the mineral.

Experimental

Occurrence, sample description and preparation

The gaudefroyite sample studied in this work was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-026. The sample is from the type locality in N' Chwaning II mine of the Kalahari manganese fields, South Africa. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) was applied to support the chemical characterization.

Gaudefroyite from N'chwaning mine in the Kalahari manganese field occurs in two types of mineral associations [31]. It occurs either as vein fillings with baryte, calcite, manganite, hausmannite and "hydrogrossularite", or as massive ore, where it is associated with manganite, bixbyite, braunite, hausmannite and hematite [31]. Thermal stability of gaudefroyite [2], its associated minerals and its intimate textural relationship, indeed indicate that gaudefroyite is of high temperature, low pressure hydrothermal origin being emplaced together with baryte during boron metasomatism [31]. Gaudefroyite is assumed to be a late secondary mineral, as it occurs as vein filling and as matrix mineral [31]. Further, geological history of Kalahari manganese field encompasses Syn- and Post-Kalahari supergene alteration and surficial weathering [32].

Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil (http://www.microscopia.ufmg.br).

Gaudefroyite single crystal was coated with a 5 nm layer of evaporated carbon. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and were applied to support the mineral characterization.

Raman spectroscopy

Crystals of gaudefroyite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10×, 20×, and 50× 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 ±1 cm^{-1} in the range between 200 and 4000 cm^{-1}. Repeated acquisitions on the crystals using the highest magnification (50×) were accumulated to improve the signal to noise ratio of the spectra. Because of the lack of signal, over 1200 scans were made. The spectra were collected over night. Raman Spectra were calibrated using the

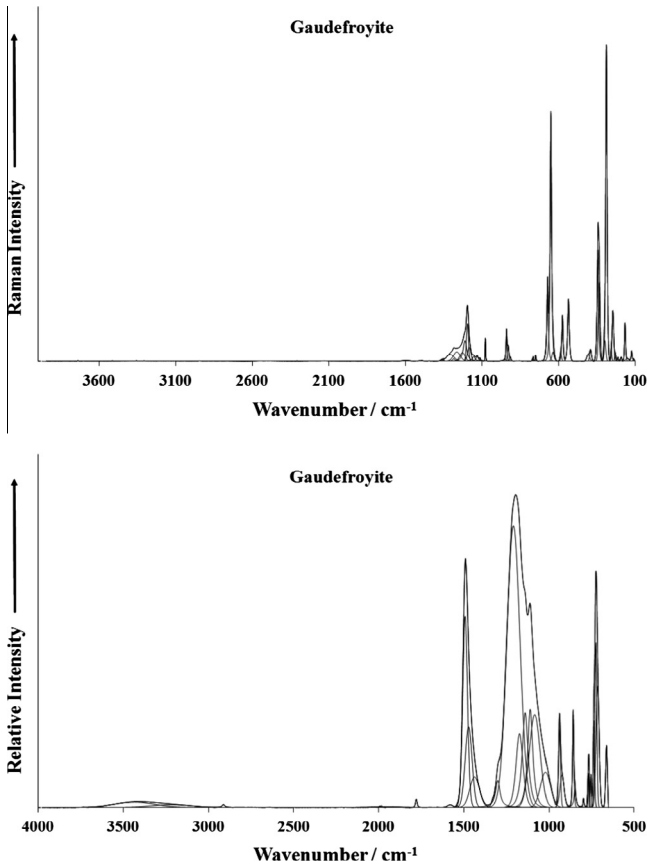

Fig. 1. (a) Raman spectrum of gaudefroyite (upper spectrum) over the 100–4000 cm^{-1} spectral range and Fig. 1b infrared spectrum of gaudefroyite (lower spectrum) over the 500–4000 cm^{-1} spectral range.

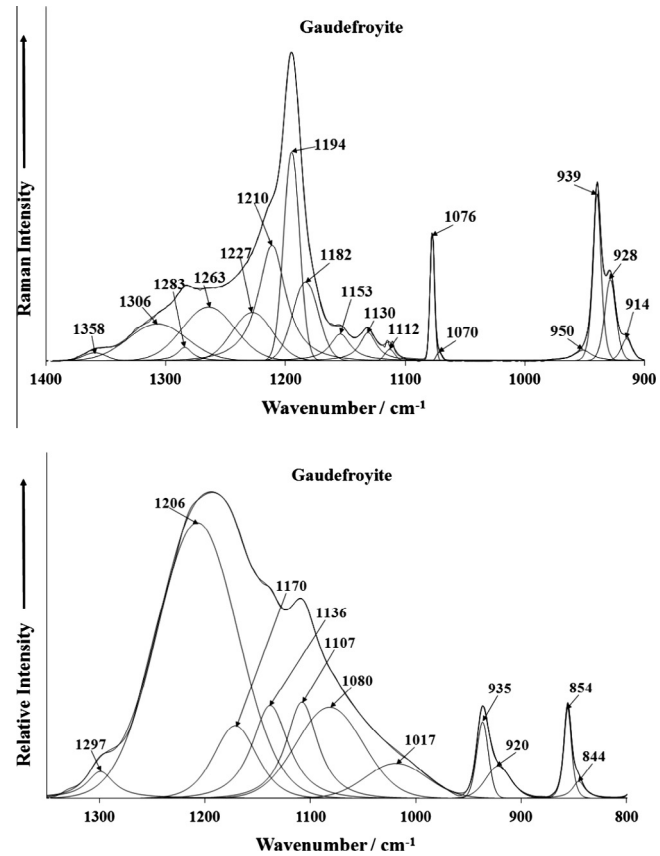

Fig. 2. (a) Raman spectrum of gaudefroyite (upper spectrum) in the the 900–1400 cm^{-1} spectral range and Fig. 2b Infrared spectrum of gaudefroyite (lower spectrum) in the the 800–1300 cm^{-1} spectral range.

520.5 cm^{-1} line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

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 128 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. The infrared spectra are given in the Supplementary information.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (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.

Results and discussion

The gaudefroyite sample studied in this work was analyzed by SEM/EDS. The SEM image and chemical analysis are given in the Supplementary information. Fig. S1 shows a single crystal with prismatic habitus. No contaminat phases are observed. Qualitative and semiquantitative chemical analysis shows a mineral composed by Ca, Mn and C predominantly, with minor amount of Al (Fig. S2). Due to the low energy, B was not observed.

The Raman spectrum of gaudefroyite over the 100–4000 cm^{-1} range is illustrated in Fig. 1a. This spectrum displays the position and relative intensity of Raman bands over the full spectral range. It is noted the intensity in the OH stretching region is very low. The infrared spectrum of gaudefroyite over the 500–4000 cm^{-1} range is displayed in Fig. 1b. In order to define the details of the Raman and infrared bands, the spectra are divided into sections based upon the convenience and the type of bands being studied. The Raman spectrum of gaudefroyite over the 800–1500 cm^{-1} region is reported in Fig. 2a and the infrared spectrum in the 500–1300 cm^{-1} is reported in Fig. 2b.

The Raman spectrum (Fig. 2a) shows two features namely (a) two very sharp Raman bands at 927 and 1076 cm^{-1} and (b) broad overlapping bands at 1194, 1219, 1281 and 1324 cm^{-1}. Other low intensity Raman bands are found at 1130 and 1152 cm^{-1}. The Raman band at 927 cm^{-1} is assigned to the symmetric stretching mode of trigonal boron. Ross reported the band positions of trigonal and tetrahedral boron [22]. The very sharp Raman band at 1076 cm^{-1} is typical of the symmetric stretching mode of carbonate. The broad Raman bands at 1194, 1219 and 1281 cm^{-1} may be attributed to BOH in-plane bending modes. The width of these Raman bands supports the concept of disorder in the structure of gaudefroyite.

The infrared spectrum of gaudefroyite (Fig. 2b) also shows considerable width in the infrared bands. The infrared band at

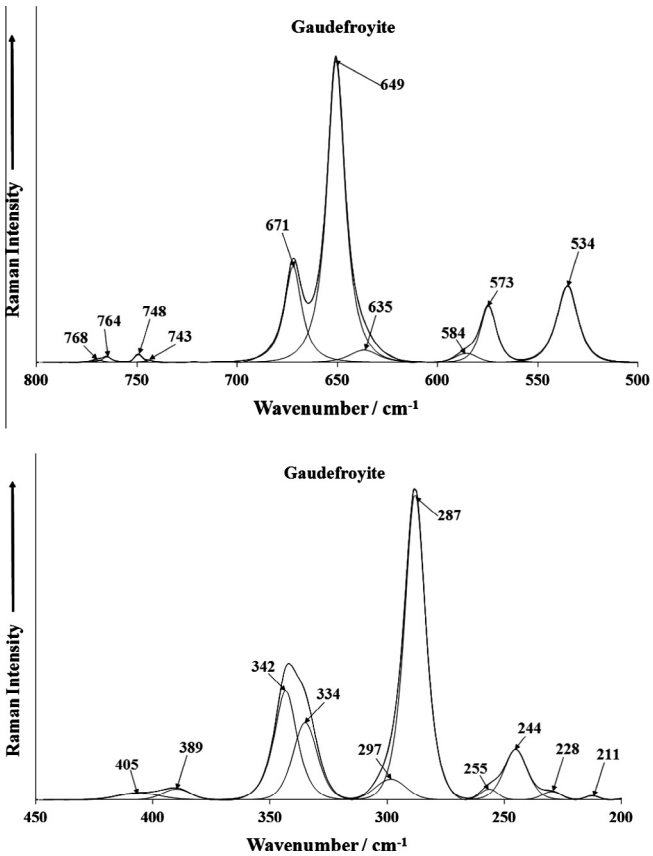

Fig. 3. (a) Raman spectrum of gaudefroyite (upper spectrum) in the 500–800 cm^{-1} spectral range and Fig. 3b Raman spectrum of gaudefroyite (lower spectrum) in the 200–450 cm^{-1} spectral range.

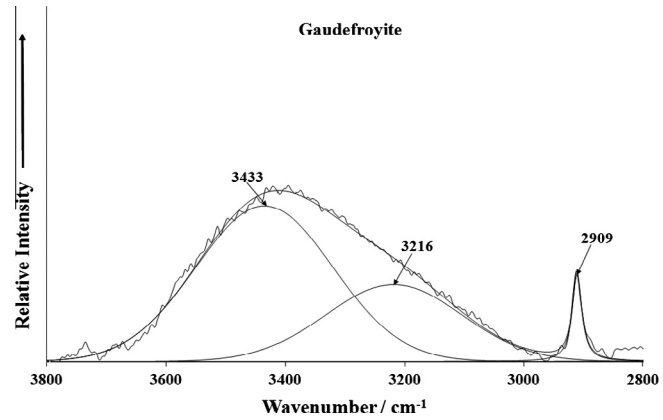

Fig. 4. Infrared spectrum of gaudefroyite (lower spectrum) in the 2600–3800 cm^{-1} spectral range.

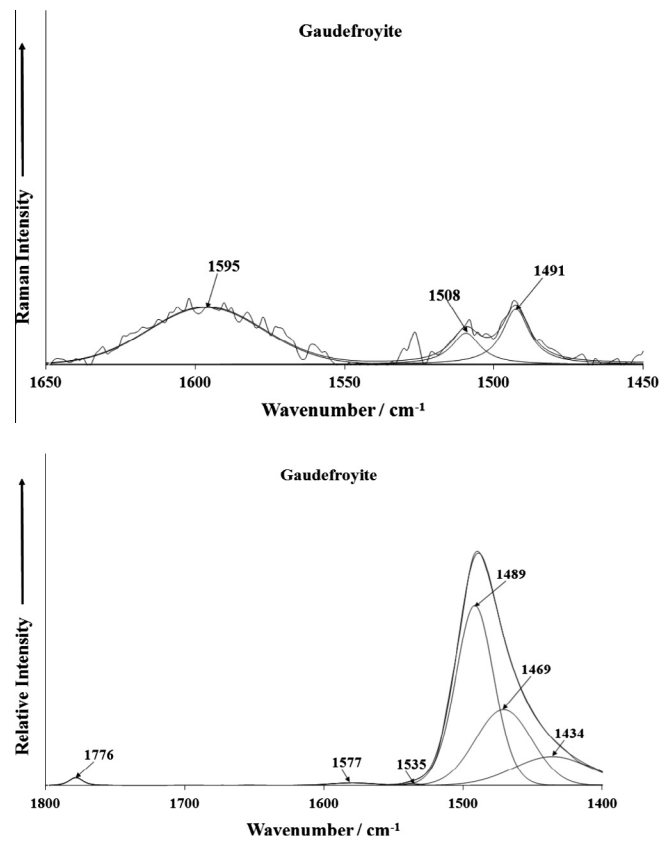

Fig. 5. (a) Raman spectrum of gaudefroyite (upper spectrum) in the 1450–1650 cm^{-1} spectral range and Fig. 5b infrared spectrum of gaudefroyite (lower spectrum) in the 1400–1800 cm^{-1} spectral range.

1076 cm^{-1} is the infrared equivalent of the Raman band in the same position attributed to carbonate symmetric stretching mode. The observation of the band provides evidence for distortion of the carbonate anion. In a perfect system, the symmetric stretching mode should be Raman active and infrared inactive. The infrared bands at 1108, 1186, 1220, 1251 and 1292 cm^{-1} may be assigned to the BOH in-plane bending modes. The low intensity infrared bands at 916, 930 and 937 cm^{-1} are assigned to the trigonal borate symmetric stretching modes. The bands are of low intensity in the infrared spectrum as expected.

The Raman spectra in the 500–800 cm^{-1} region and in the 200–450 cm^{-1} region are shown in Fig. 3. Again sharp Raman bands are observed in the spectrum shown in Fig. 3a. The Raman bands at 649 and 670 cm^{-1} are assigned to the bending modes of trigonal and tetrahedral boron. These bands are also observed in the infrared spectrum at 600 and 620 cm^{-1} (Fig. 2b). It could be expected that some Raman bands in the 700–750 cm^{-1} region would be found which could be attributed to the CO_3^{2-} ν_2 in-plane bending mode. However no Raman intensity was observed in this spectral region. However, in the infrared spectrum, a series of bands at 709, 723, 734, 750 and 764 cm^{-1} are observed and are assigned to this vibrational mode (Fig. 2b). Two strong Raman bands are observed at 531 and 572 cm^{-1} three broad but reasonably intense bands are observed at 287, 336 and 394 cm^{-1}. These bands are attributed to MnO stretching vibrations. Other low intensity bands are found in the 100–260 cm^{-1} region and are attributed to lattice vibrations.

The infrared spectrum in the 2600–3800 cm^{-1} region is shown in Fig. 4. The Raman spectrum suffers from a lack of signal. Raman bands may be suggested at 2830, 3123 and 3255 cm^{-1}. However any interpretation is fraught with difficulty. It could be expected to observe some Raman bands from BOH stretching vibrations. The infrared spectrum displays bands at 2723, 2903, 3185, 3310 and 3502 cm^{-1}. The latter three bands are assigned to the BOH stretching vibrations. The Raman spectrum in the 1400 and 1800 cm^{-1} region is displayed in Fig. 5a. The infrared spectrum in the 1300–1800 cm^{-1} region is shown in Fig. 5b. Strong infrared bands are observed at 1439, 1471 and 1493 cm^{-1}. These bands are assigned to the carbonate antisymmetric stretching vibrations. Other low intensity infrared bands at 1560, 1579, 1757 and 1775 cm^{-1} may be attributed to overtone or combination bands.

The Raman bands at 1441 and 1495 cm^{-1} are the Raman equivalent of these carbonate antisymmetric stretching vibrations. Other Raman bands are found at 1596 and 1675 cm^{-1}.

Conclusions

There are many borate minerals which have yet to have their vibrational spectrum determined and the molecular structure assessed in terms of their vibrational spectrum. In this work we have measured the Raman and infrared spectrum of gaudefroyite $Ca_4Mn^{3+}_{3-x}(BO_3)_3(CO_3)(O,OH)$ over the complete spectral range. Gaudefroyite crystals [2] are short dipyramidal or prismatic with prominent pyramidal terminations. Crystal structures characterized by chains of edge-sharing $Mn^{3+}O_6$ octahedra.

The Raman spectrum is dominated by intense sharp bands at 927 cm^{-1}, 649 and 670 cm^{-1}, assigned to the symmetric stretching mode and the bending mode of trigonal and tetrahedral boron. Broad Raman bands at 1194, 1219 and 1281 cm^{-1} are attributed to BOH in-plane bending modes. Multiple Raman bands in the OH stretching region are observed at 3206, 3249 and 3385 cm^{-1}. Vibrational spectroscopy has enabled aspects about the molecular structure of the borate mineral ameghinite to be assessed.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.10.031.

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