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# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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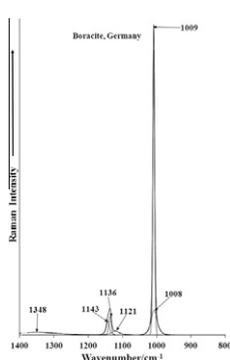
## Assessment of the molecular structure of the borate mineral boracite $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$ using vibrational spectroscopy

Ray L. Frost<sup>a,\*</sup>, Yunfei Xi<sup>a</sup>, Ricardo Scholz<sup>b</sup><sup>a</sup> School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, G.P.O. Box 2434, Brisbane, Queensland 4001, Australia<sup>b</sup> Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35400-00, Brazil

### HIGHLIGHTS

- ▶ Boracite is a magnesium borate mineral with formula:  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$ .
- ▶ The crystals belong to the orthorhombic – pyramidal crystal system.
- ▶ The molecular structure of the mineral has been assessed.
- ▶ Raman spectrum shows that some Cl anions have been replaced with OH units.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 23 May 2012

Received in revised form 2 July 2012

Accepted 9 July 2012

Available online 13 August 2012

#### Keywords:

Raman spectroscopy

Borate

Boracite

Infrared

Evaporite

### ABSTRACT

Boracite is a magnesium borate mineral with formula:  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$  and occurs as blue green, colorless, gray, yellow to white crystals in the orthorhombic – pyramidal crystal system. An intense Raman band at  $1009\text{ cm}^{-1}$  was assigned to the BO stretching vibration of the  $\text{B}_7\text{O}_{13}$  units. Raman bands at 1121, 1136,  $1143\text{ cm}^{-1}$  are attributed to the in-plane bending vibrations of trigonal boron. Four sharp Raman bands observed at 415, 494, 621 and  $671\text{ cm}^{-1}$  are simply defined as trigonal and tetrahedral borate bending modes. The Raman spectrum clearly shows intense Raman bands at 3405 and  $3494\text{ cm}^{-1}$ , thus indicating that some Cl anions have been replaced with OH units. The molecular structure of a natural boracite has been assessed by using vibrational spectroscopy.

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### Introduction

Boracite is a magnesium borate mineral with formula:  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$  [1] and occurs as blue green, colourless, gray, yellow to white crystals in the orthorhombic – pyramidal crystal system [2,3]. Boracite also shows pseudo-isometric cubical and octahedral forms [4]. These are thought to be the result of transition from an unstable high temperature isometric form upon cooling. The mineral is related to

the homonymous group that includes chambersite –  $(\text{Mn}^{2+})_3\text{B}_7\text{O}_{13}\text{Cl}$ , congolite –  $(\text{Fe}^{2+}, \text{Mg})_3\text{B}_7\text{O}_{13}\text{Cl}$ , ericaite –  $(\text{Fe}^{2+})_3\text{B}_7\text{O}_{13}\text{Cl}$  and, trembathite –  $(\text{Mg}, \text{Fe}^{2+})_3\text{B}_7\text{O}_{13}\text{Cl}$  (Burns and Carpenter [26]). Boracite is typically found in evaporite sequences associated with gypsum, anhydrite, halite, sylvite, carnallite, kainite and hilgardite. It was first described in 1789 for specimens from its type locality of Kalkberg hill, Lüneburg, Lower Saxony, Germany. The name is obviously derived from its boron content (19% to 20% of boron by mass).

Boracite is orthorhombic, pseudocubic of point group:  $mm2$  [5] and space group:  $Pca2_1$ , with unit-cell parameters  $a = 8.577(6)$ ,  $b = 8.553(8)$ ,  $c = 12.09(1)$  and  $Z = 4$  [3,5–7]. Boracite is dimorphic with trigonal trembathite  $(\text{Mg}, \text{Fe})_3(\text{B}_7\text{O}_{13})\text{Cl}$  and forms a series

\* Corresponding author. Tel.: +61 7 3138 2407; fax: +61 7 3138 1804.

E-mail address: [r.frost@qut.edu.au](mailto:r.frost@qut.edu.au) (R.L. Frost).

with ericaite  $\text{Fe}_3^{2+}(\text{B}_7\text{O}_{13})\text{Cl}$  (named after English heather because of the reddish colour). The boracite group mineral congolite has a trigonal structure [4]; however the higher temperature form is cubic with a phase transition temperature of 268 °C [8,9].

Burns showed the application of powder diffractions to identify boracites [10]. The structure of boracites has been refined [4]. A wide range of boracites have been synthesised and their dielectric properties determined [11]. The effect of the metal cations and halogens on the B–O bonds in the boracite structure was studied by IR spectroscopy [12]. Many of the boracites show ferroelectric properties [13] and some Raman studies have been undertaken to determine the ferroelectric phase transitions [14–16]. Vibrational spectroscopy has focussed on the ferroelectric transitions [17–24]. Different types of boracites have been synthesised [25–27].

Vibrational spectroscopy has been applied to borate glasses [28–31]. There have been a number of studies of borate glasses doped with a wide range of radioactive atoms [32,33]. Borate glasses are 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 [34,35]. If there is to be an understanding of borate glasses and their role in radioactive element containment, then an understanding of the vibrational spectroscopy of borate minerals needs to be undertaken. The number of vibrational spectroscopic studies of borate minerals is quite few and far between [36–39]. The number of Raman studies of borate minerals is also very limited [40,41]. There have been a number of infrared studies of some natural borates [42–45]. 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 several borate minerals [46]. The use of infrared spectroscopy is limited by the spatial resolution of the technique which is around 25 microns. In comparison, the spatial resolution using Raman spectroscopy is 1 micron. Thus, when studying a mineral using spectroscopic techniques it is advantageous to use Raman spectroscopy. The selection of the target mineral is more easily made. With infrared spectroscopy, any impurities will be measured as well as the target mineral.

Raman spectroscopy has proven most useful for the study of secondary minerals [41,47–52]. To the best of the authors' knowledge, there have been very few vibrational spectroscopic studies of boracite type structure and few Raman studies of this natural mineral have been forthcoming. The objective of this paper is to report the vibrational spectroscopic study of a natural boracite mineral and relate the spectra to the molecular chemistry and the crystal chemistry of this borate mineral. We have characterised boracite using Raman and infrared spectroscopy.

## Experimental

### Mineral

The natural boracite mineral was obtained from The Mineralogical Research Company. Details of the mineral have been published (page 80, Vol. 5) [53]. The mineral originated from Luneburg, 40 km south-southeast of Hamburg, Lower Saxony; in Saxony-Anhalt, in the Stassfurt-Westeregeln-Bernburg district of Germany. This mineral is a 'type' mineral in that it is used as the international standard. The boracite mineral is known from many localities worldwide [53]. For example a mineral deposit is at Boulby Potash Mine, Loftus, North Yorkshire, England.

### Raman spectroscopy

Crystals of boracite 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  $\text{cm}^{-1}$  and a precision of  $\pm 1 \text{ cm}^{-1}$  in the range between 200 and 4000  $\text{cm}^{-1}$ . Repeated acquisitions on the crystals using the highest magnification (50×) were accumulated to improve the signal to noise ratio of the spectra. The spectra were collected over night. Raman Spectra were calibrated using the 520.5  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  range were obtained by the co-addition of 128 scans with a resolution of 4  $\text{cm}^{-1}$  and a mirror velocity of 0.6329  $\text{cm/s}$ . 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 Spectralcalc 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 Lorentzian-Gaussian 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 Raman spectrum of boracite in the 100–4000  $\text{cm}^{-1}$  region is displayed in Fig. 1a. This figure reports the position of the bands and their relative intensity. It is noted that there are parts of the spectrum where no intensity is observed. Therefore, the spectrum is subdivided into sections in subsequent figures so that more detailed assessment of the spectrum can be made. In a similar way, the infrared spectrum of boracite in the 500–4000  $\text{cm}^{-1}$  region is reported in Fig. 1b. The spectrum is not shown below 500  $\text{cm}^{-1}$ . The reason for this is that we are using a reflectance technique and the ATR cell absorbs all incident radiation. In a similar fashion to the Raman spectrum, the infrared spectrum is divided into sections depending upon the types of vibrations being observed.

The Raman spectrum of boracite in the 800–1400  $\text{cm}^{-1}$  spectral range is reported in Fig. 2a. The infrared spectrum of boracite in the 500–1300  $\text{cm}^{-1}$  spectral range is reported in Fig. 2b. The Raman spectrum in this spectral region is dominated by a sharp intense band at 1009  $\text{cm}^{-1}$ . Bands of significantly lesser intensity are observed at 1121, 1136, 1143  $\text{cm}^{-1}$  with a broad band at 1348  $\text{cm}^{-1}$ . The Raman band at 1009  $\text{cm}^{-1}$  is assigned to the BO stretching vibration of the  $\text{B}_7\text{O}_{13}$  units. The Raman bands at 1121, 1136, 1143  $\text{cm}^{-1}$  are attributed to the BOH in-plane bending modes. It is not known to what the very broad band at 1348  $\text{cm}^{-1}$  is attributed. Iliev et al. determined the Raman spectrum of a synthetic cobalt boracite [15]. The symmetry species of some vibrational modes were determined. Iliev et al. [54] used Raman imaging to show the ferroelectric properties of boracite type compounds. These workers [54] showed that boracites exhibit a sequence of transi-

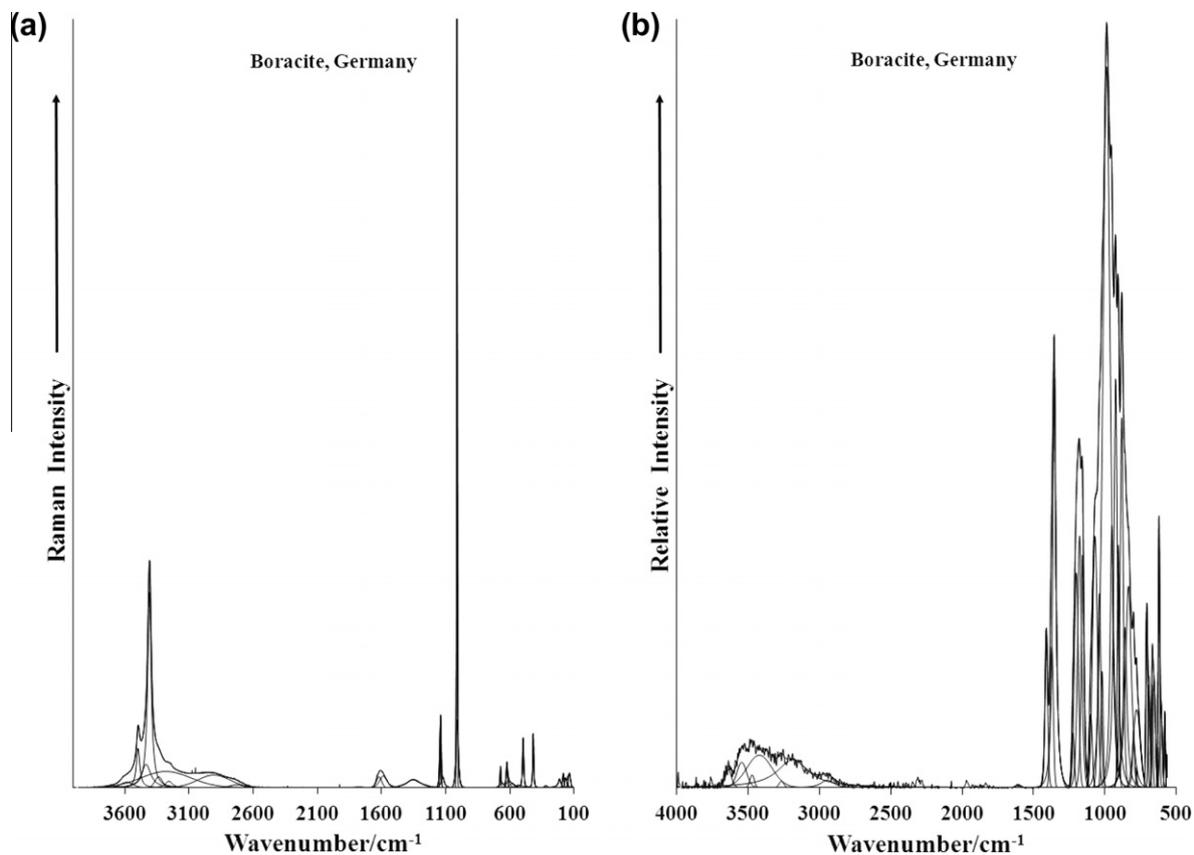


Fig. 1. (a) Raman spectrum of boracite in the 100–4000 cm<sup>-1</sup> region and (b) infrared spectrum of boracite in the 500–4000 cm<sup>-1</sup> region.

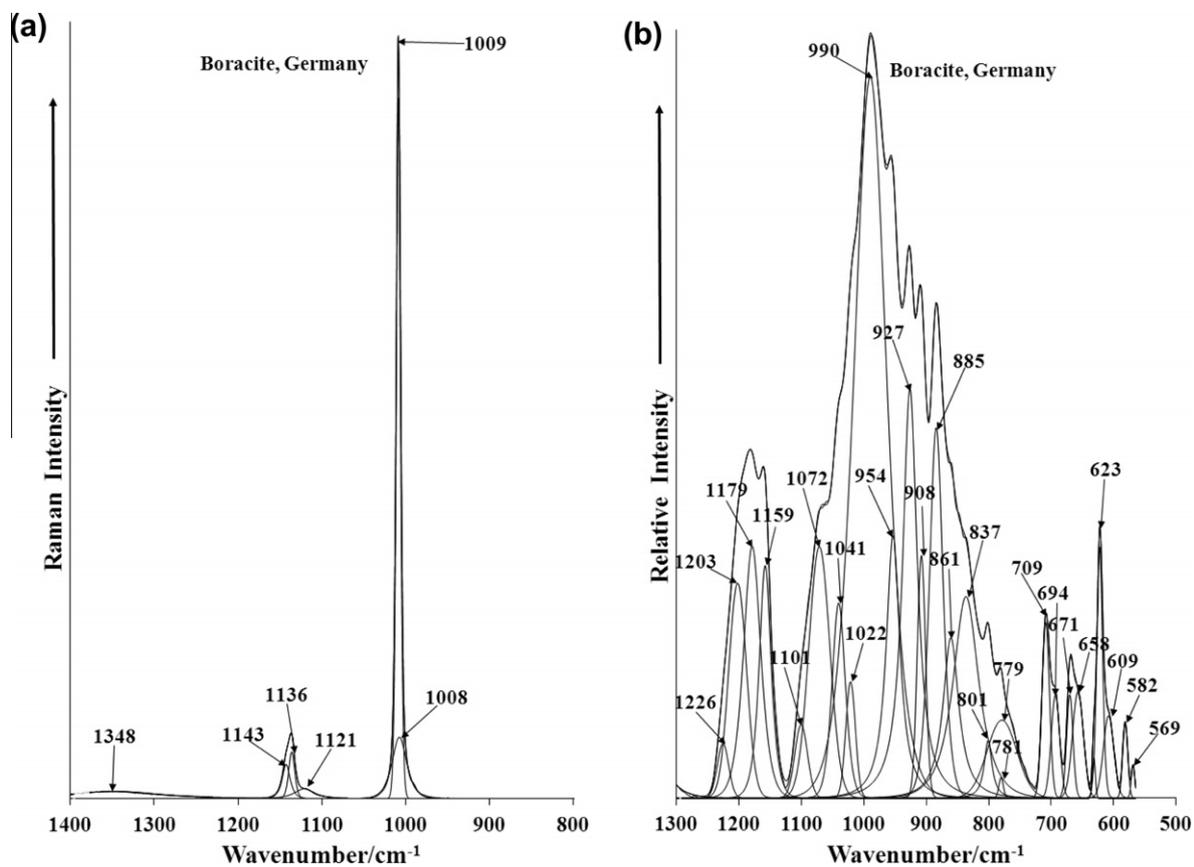


Fig. 2. (a) Raman spectrum of boracite in the 800–1400 cm<sup>-1</sup> region and (b) infrared spectrum of boracite in the 500–1300 cm<sup>-1</sup> region.

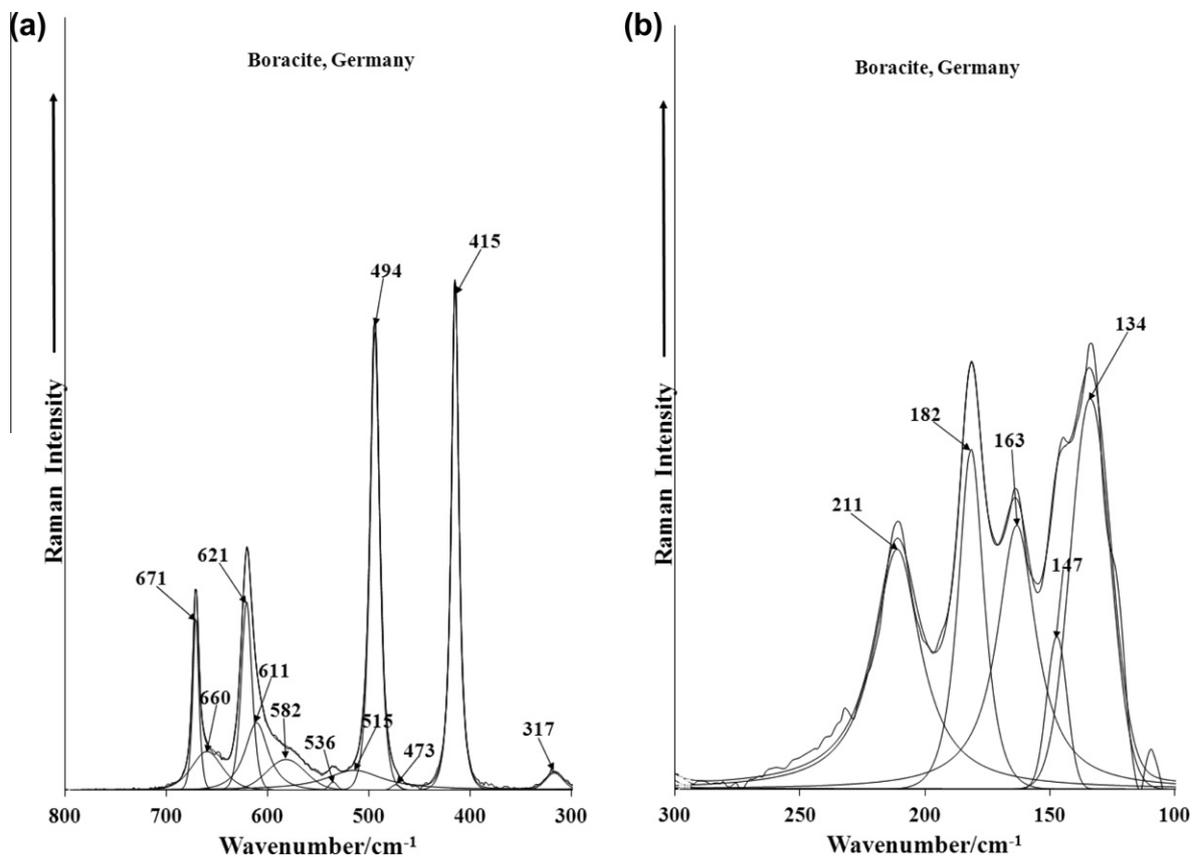


Fig. 3. (a) Raman spectrum of boracite in the 300–800 cm<sup>-1</sup> region and (b) Raman spectrum of boracite in the 100–300 cm<sup>-1</sup> region.

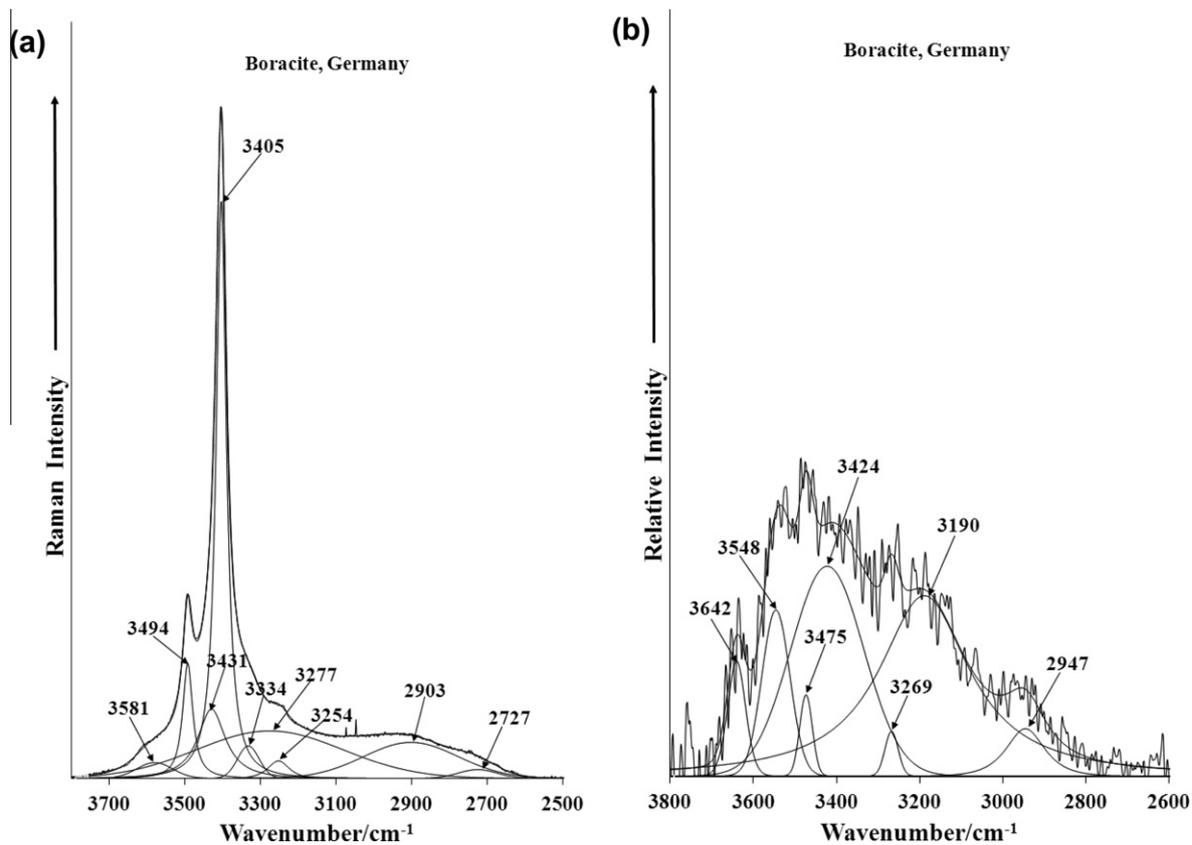


Fig. 4. (a) Raman spectrum of boracite in the 2400–3800 cm<sup>-1</sup> region and (b) infrared spectrum of boracite in the 2500–3700 cm<sup>-1</sup> region.

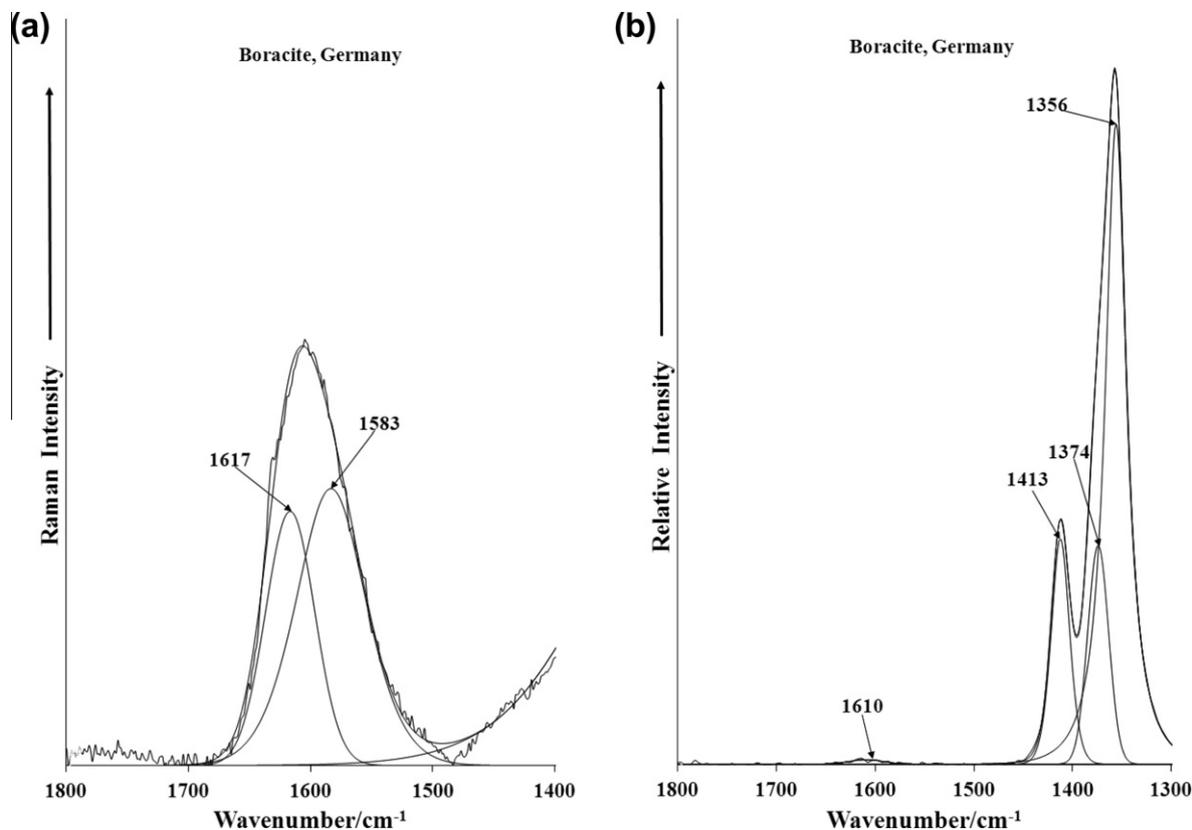


Fig. 5. (a) Raman spectrum of boracite in the 1400–1800  $\text{cm}^{-1}$  region and (b) infrared spectrum of boracite in the 1300–1800  $\text{cm}^{-1}$  region.

tions from the high temperature paraelectric cubic phase to ferroelectric orthorhombic, monoclinic, trigonal phases, and finally to a monoclinic phase at low temperatures where both ferroelectric and magnetic orders coexist. Kim and Somoano determined the improper ferroelectric transition using Raman spectroscopy [16].

In contrast, the infrared spectrum of boracite (Fig. 2b) shows complexity with many overlapping bands, making attribution difficult. The intense infrared band at 990  $\text{cm}^{-1}$  with shoulders at 927, 954 and 1072  $\text{cm}^{-1}$  is assigned to the trigonal borate stretching modes. The overlapping infrared bands at 1159, 1179 and 1203  $\text{cm}^{-1}$  are the infrared antisymmetric stretching vibrations. The series of bands from 569 through to 709  $\text{cm}^{-1}$  are related to trigonal borate bending modes.

The Raman spectra in the 300–800  $\text{cm}^{-1}$  and in the 100–300  $\text{cm}^{-1}$  spectral range are illustrated in Fig. 3a and b. Four sharp Raman bands are observed at 415, 494, 621 and 671  $\text{cm}^{-1}$ . These bands are simply defined as trigonal and tetrahedral borate bending modes. A series of infrared bands at 569, 582, 609, 623, 658, 671, 694 and 709  $\text{cm}^{-1}$  (Fig. 2b) are due to these bending modes. Strong Raman bands are found in the far wavenumber region at 134, 163, 182 and 211  $\text{cm}^{-1}$  (Fig. 3b). These bands may be simply described as lattice vibrations. However it could be expected that Mg–Cl stretching vibrations would be observed. It is likely that TO and LO Cl stretching modes could be observed.

Raman spectrum of boracite in the 2400–3800  $\text{cm}^{-1}$  spectral range and the infrared spectrum of boracite in the 2500–3700  $\text{cm}^{-1}$  spectral range are reported in Fig. 4a and b. According to the commonly accepted formula of boracite  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$ , no water or OH groups are found. Yet the Raman spectrum clearly shows intense Raman bands at 3405 and 3494  $\text{cm}^{-1}$ . Other low intensity bands at 3254, 3334 and 3581  $\text{cm}^{-1}$  are found. These lower intensity broad bands are probably due to water stretching vibrations. The two sharp bands are assigned to OH stretching

vibrations. Two OH-stretching bands in the Raman spectra of the mineral, at 3405 and 3494  $\text{cm}^{-1}$ , respectively, are indicative of two distinct hydrogen positions in the structure. It is proposed that some Cl units have been replaced with OH units. Whether this is true or not is open to question. Bither and Young [55] have clearly shown that the chloride ion can be readily replaced by other anions including nitrate and fluoride anions. Indeed, Bither holds a significant number of patents on this chemistry of boracite substitution [56–59]. The development of these type of compounds rests with their ferromagnetic and pyro-electric properties [60]. The development of piezoelectric properties is time continuous [61,62]. Also a hydroxy compound has been synthesised [27], although the vibrational spectroscopy of this compound was not reported. In the infrared spectrum (Fig. 4b) a series of low intensity bands are observed.

The Raman spectrum in the 1400–1800  $\text{cm}^{-1}$  region and the infrared spectrum in the 1300–1800  $\text{cm}^{-1}$  region are reported in Fig. 5a and b. A Raman band centred upon 1600  $\text{cm}^{-1}$  is observed which may be band component analysed into two components at 1583 and 1617  $\text{cm}^{-1}$ . These bands are attributed to water bending vibrations. The intensity as observed in the infrared spectrum is very weak with a broad band at 1610  $\text{cm}^{-1}$  found. In addition strong infrared bands are observed at 1356, 1374 and 1413  $\text{cm}^{-1}$ . These bands are assigned to the antisymmetric stretching vibrations of trigonal boron.

## 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 boracite, a magnesium chloride-borate mineral with formula:  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$ . The

importance of the mineral boracite rests with the chemistry of the compound and the range of isomorphic substitutions which can be made in order to produce specially selected ferroelectric, pyroelectric and piezoelectric properties.

The Raman spectrum is dominated by intense sharp band at  $1009\text{ cm}^{-1}$  assigned to the symmetric stretching mode. Raman bands at  $1121$ ,  $1136$ ,  $1143\text{ cm}^{-1}$  are attributed to the BOH in-plane bending modes of trigonal boron. Four sharp Raman bands observed at  $415$ ,  $494$ ,  $621$  and  $671\text{ cm}^{-1}$  are simply defined as out-of-plane trigonal and tetrahedral borate bending modes. Intense Raman bands for boracite at  $3405$  and  $3494\text{ cm}^{-1}$  are found. These bands are attributed to OH stretching vibrations. Other low intensity bands at  $3254$ ,  $3334$  and  $3581\text{ cm}^{-1}$  are also observed. These lower intensity broad bands are probably due to water stretching vibrations. It is proposed that some Cl units have been replaced with OH units. Vibrational spectroscopy has enabled aspects about the molecular structure of the borate mineral boracite to be assessed.

### Acknowledgments

The financial and infra-structure support of the School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation. R. Scholz thanks to FAPEMIG – Fundação de Amparo à Pesquisa do estado de Minas Gerais (Grant No. CRA – APQ-03998-10).

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