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

Ray L. Frost$^{a,*}$, Yunfei Xia$^a$, Ricardo Scholz$^b$

$^a$ School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, G.P.O. Box 2434, Brisbane, Queensland 4001, Australia
$^b$ 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: Mg$_3$B$_7$O$_{13}$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.

**Abstract**
Boracite is a magnesium borate mineral with formula: Mg$_3$B$_7$O$_{13}$Cl and occurs as blue green, colourless, gray, yellow to white crystals in the orthorhombic – pyramidal crystal system. An intense Raman band at 1009 cm$^{-1}$ was assigned to the BO stretching vibration of the B$_7$O$_{13}$ units. Raman bands at 1121, 1136, 1143 cm$^{-1}$ are attributed to the in-plane bending vibrations of trigonal boron. Four sharp Raman bands observed at 415, 494, 621 and 671 cm$^{-1}$ are simply defined as trigonal and tetrahedral borate bending modes. The Raman spectrum clearly shows intense Raman bands at 3405 and 3494 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.

**Introduction**
Boracite is a magnesium borate mineral with formula: Mg$_3$B$_7$O$_{13}$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 – (Mn$^{2+}$)$_3$B$_7$O$_{13}$Cl, conglolite – (Fe$^{2+}$, Mg)$_3$B$_7$O$_{13}$Cl, ericaite – (Fe$^{2+}$)$_3$B$_7$O$_{13}$Cl and, trembathite – (Mg, Fe$^{2+}$)$_3$B$_7$O$_{13}$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 (Mg, Fe)$_3$(B$_7$O$_{13}$)Cl and forms a series...
with ericaite Fe$_2^{2+}$[B$_7$O$_{13}$]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 boracite 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 BHSX 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. The spectra were collected over night. Raman Spectra were calibrated using the 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 endureance 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 Spectracle 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 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 cm$^{-1}$ region is reported in Fig. 1b. The spectrum is not shown below 500 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 cm$^{-1}$ spectral range is reported in Fig. 2a. The infrared spectrum of boracite in the 500–1300 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 cm$^{-1}$. Bands of significantly lesser intensity are observed at 1121, 1136, 1143 cm$^{-1}$ with a broad band at 1348 cm$^{-1}$. The Raman band at 1009 cm$^{-1}$ is assigned to the BO stretching vibration of the B$_2$O$_3$ units. The Raman bands at 1121, 1136, 1143 cm$^{-1}$ are attributed to the BOH in-plane bending modes. It is not known to what the very broad band at 1348 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\(^{-1}\) region and (b) infrared spectrum of boracite in the 500–4000 cm\(^{-1}\) region.

Fig. 2. (a) Raman spectrum of boracite in the 800–1400 cm\(^{-1}\) region and (b) infrared spectrum of boracite in the 500–1300 cm\(^{-1}\) region.
Fig. 3. (a) Raman spectrum of boracite in the 300–800 cm$^{-1}$ region and (b) Raman spectrum of boracite in the 100–300 cm$^{-1}$ region.

Fig. 4. (a) Raman spectrum of boracite in the 2400–3800 cm$^{-1}$ region and (b) infrared spectrum of boracite in the 2500–3700 cm$^{-1}$ region.
tions from the high temperature paraelectric cubic phase to ferro-
electric 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 im-
proper ferroelectric transition using Raman spectroscopy [16].

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

The Raman spectra in the 300–800 cm\(^{-1}\) and in the 100–
300 cm\(^{-1}\) spectral range are illustrated in Fig. 3a and b. Four sharp
Raman bands are observed at 415, 494, 621 and 671 cm\(^{-1}\). These
bands are simply defined as trigonal and tetrahedral borate bend-
ing modes. A series of infrared bands at 569, 582, 609, 623, 658,
671, 694 and 709 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 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 cm\(^{-1}\) spectral
range and the infrared spectrum of boracite in the 2500–
3700 cm\(^{-1}\) spectral range are reported in Fig. 4a and b. According
to the commonly accepted formula of boracite Mg\(_3\)B\(_7\)O\(_{13}\)Cl, no
water or OH groups are found. Yet the Raman spectrum clearly
shows intense Raman bands at 3405 and 3494 cm\(^{-1}\). Other low
intensity bands at 3254, 3334 and 3581 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 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 signif-
ificant 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 develop-
ment of piezoelectric properties is time continuous [61,62]. Also a
hydroxy compound has been synthesised [27], although the vibra-
tional 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 cm\(^{-1}\) region and the
infrared spectrum in the 1300–1800 cm\(^{-1}\) region are reported in
Fig. 5a and b. A Raman band centred upon 1600 cm\(^{-1}\) is observed
which may be band component analysed into two components at
1583 and 1617 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 cm\(^{-1}\) found. In addition
strong infrared bands are observed at 1356, 1374 and 1413 cm\(^{-1}\).
These bands are assigned to the antisymmetric stretching vibra-
tions of trigonal boron.

Conclusions

There are many borate minerals which have yet to have their
vibrational spectrum determined and the molecular structure as-
sessed in terms of their vibrational spectrum. In this work we have
measured the Raman and infrared spectrum of boracite, a magne-
sium chloride-borate mineral with formula: Mg\(_3\)B\(_7\)O\(_{13}\)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 cm$^{-1}$ assigned to the symmetric stretching mode. Raman bands at 1121, 1136, 1143 cm$^{-1}$ are attributed to OH stretching vibrations. Other low intensity bands at 3254, 3334 and 3581 cm$^{-1}$ are attributed to OH stretching vibrations. Other low 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).

References

[34] V.S. Suknev, E.N. Diman, Zh. Prikladnoi Spektroskopii 10 (1969) 326.