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The molecular structure of the borate mineral szaibelyite $MgBO_2(OH)$ – A vibrational spectroscopic study

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HIGHLIGHTS

- We have studied the borate mineral szaibelyite $MgBO_2(OH)$.
- EDS spectra show a phase composed of Mg with minor amounts of Fe.
- Both tetrahedral and trigonal boron units are observed.
- Vibrational spectroscopy enables the molecular structure to be assessed.

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ABSTRACT

We have studied the borate mineral szaibelyite $MgBO_2(OH)$ using electron microscopy and vibrational spectroscopy. EDS spectra show a phase composed of Mg with minor amounts of Fe. Both tetrahedral and trigonal boron units are observed. The nominal resolution of the Raman spectrometer is of the order of 2 cm^{-1} and as such is sufficient enough to identify separate bands for the stretching bands of the two boron isotopes. The Raman band at 1099 cm^{-1} with a shoulder band at 1093 cm^{-1} is assigned to BO stretching vibration. Raman bands at 1144, 1157, 1229, 1318 cm^{-1} are attributed to the BOH in-plane bending modes. Raman bands at 836 and 988 cm^{-1} are attributed to the antisymmetric stretching modes of tetrahedral boron. The infrared bands at 3559 and 3547 cm^{-1} are assigned to hydroxyl stretching vibrations. Broad infrared bands at 3269 and 3398 cm^{-1} are assigned to water stretching vibrations. Infrared bands at 1306, 1352, 1391, 1437 cm^{-1} are assigned to the antisymmetric stretching vibrations of trigonal boron. Vibrational spectroscopy enables aspects of the molecular structure of the borate mineral szaibelyite to be assessed.

Introduction

Szaibelyite is a borate mineral of formula $MgBO_2(OH)$. The mineral occurs as flattened fibres or laths; in spheroidal aggregates, to 5 mm; typically as felted or matted fibrous aggregates. The mineral looks like an opaque material but clear crystals are found under a microscope. The mineral is monoclinic of point group $2/m$. The cell data is *Space Group: P21/a.* $a = 12.577(2)$ Å, $b = 10.393(2)$ Å, $c = 3.139(1)$ Å, $\beta = 95.88(2)°$ and $Z = 8$. The mineral forms a continuous series with sussexite $MnBO_2(OH)$. Thermochemical study of szaibelyite has been published [1].

Vibrational spectroscopy has been applied to borate glasses [2–5]. There have been a number of studies of borate glasses doped with a wide range of radioactive atoms [6,7]. 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 [8,9]. 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 [10–13]. The number of Raman studies of borate minerals is also very limited [14,15]. There have been a number of infrared studies of some natural borates [16–19]. 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 [20]. There have been only a few infrared studies of szaibelyite [16,19,21,22] and almost no studies of the Raman spectrum of szaibelyite [23]. There is some

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disagreement between researchers as to the position of some selected infrared bands. Moenke [24] and Vlasova and Valyashko [22] show a band at 675 cm^{-1} which was not observed in the infrared spectrum of Weir [19]. These authors simply reported the infrared data without any assignment of the bands.

The use of infrared spectroscopy is limited by the spatial resolution of the technique which is around 25 μm. In comparison, the spatial resolution using Raman spectroscopy is 1 μm. 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 mineral structures. The objective of this research is to report the Raman and infrared spectra of szaibelyite and to relate the spectra to the molecular structure of the mineral. This is the first report of a systematic study of szaibelyite from the Brosso mine, Piedmont, Italy. It is important to understand the structure of szaibelyite in order to form nanomaterials based upon its structure. Vibrational spectroscopy enables a better understanding of the structure of szaibelyite.

Experimental

Samples description and preparation

The szaibelyite sample studied in this work was collected from the Brosso mine, Piedmont, Italy. The sample was incorporated to the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-198. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Zeiss Stemi DV4 from the Museu de Ciência e Técnica of the Federal University of Ouro Preto. Scanning electron microscopy (SEM) was applied to support the mineral characterization.

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). Szaibelyite crystal aggregate was coated with a 5 nm layer of evaporated Au. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment.

Raman microprobe spectroscopy

Crystals of szaibelyite 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 polarized 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. Raman Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. The Raman spectra of at least 10 crystals were collected to ensure the consistency of the spectra.

A Raman spectrum of szaibelyite is given in the supplementary information as Fig. S1. This spectrum was downloaded from the RRUFF data base (http://rruff.info/szaibelyite/R060713). Both polarized and depolarized spectra are provided. However the spectrum suffers from a lack of signal.

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 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 SEM image of szaibelyite sample studied in this work is shown in Fig. 1. The image shows a fibrous aggregate. The szaibelyite image shows a single phase and no zonation was observed. EDS spectra were obtained and show a phase composed of Mg with minor amounts of Fe (Fig. 2). The presence of Fe suggests a partial substitution of Mg. The existence of a solid solution between szaibelyite and sussexite, it's manganese analogue, suggests the possibility of substitution of Mg by cations with similar ionic ratios.

Vibrational spectroscopy

The Raman spectrum of szaibelyite over the 100–4000 cm^{-1} spectral range is reported in Fig. 3a. The spectrum shows complexity with many bands being observed. This figure shows the position and relative intensities of the Raman bands. It is noteworthy that there are large parts of the spectrum where no intensity is observed. The Raman spectrum is therefore subdivided into sec-

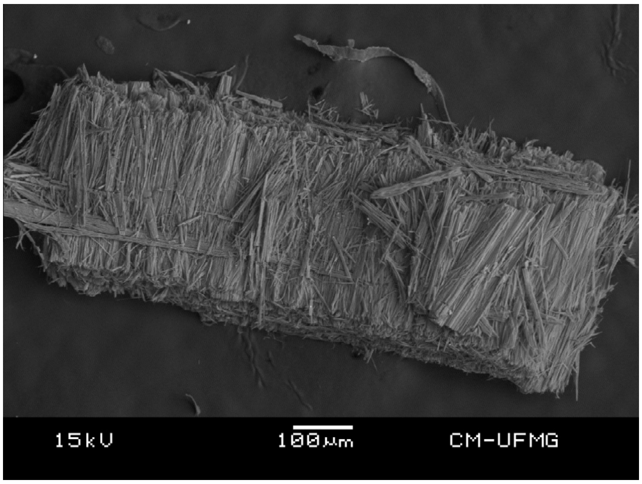

Fig. 1. Backscattered electron image (BSI) of a szaibelyite single crystal up to 1.0 mm in length.

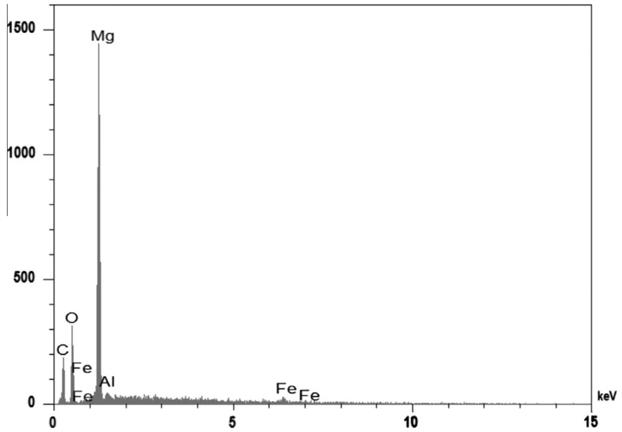

Fig. 2. EDS analysis of szaibelyite.

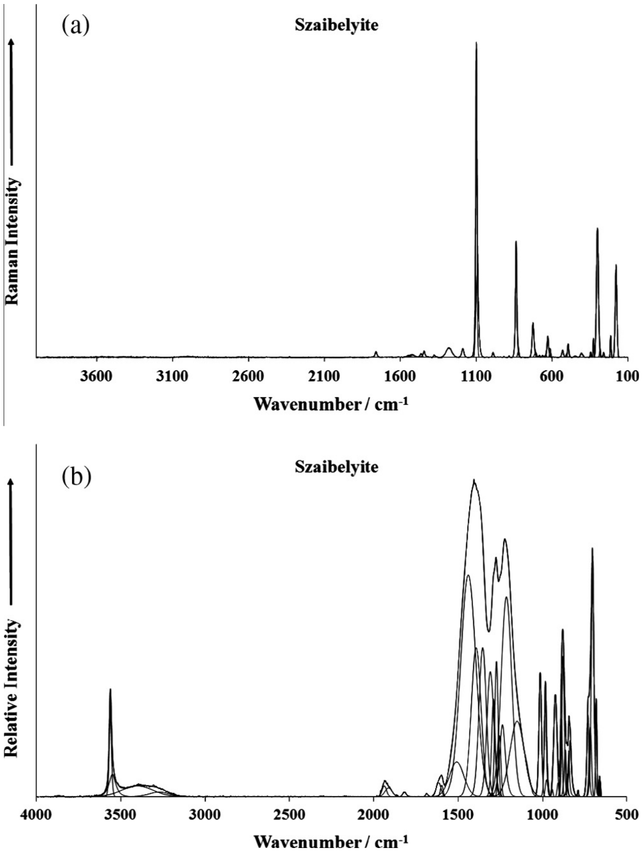

Fig. 3. (a) Raman spectrum of szaibelyite (upper spectrum) and (b) infrared spectrum of szaibelyite (lower spectrum).

tions depending upon the type of vibration being analysed. The infrared spectrum of szaibelyite over the 500–4000 cm^{-1} spectral range is displayed in Fig. 3b. 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. There are parts of this infrared spectrum where little or no intensity is observed. This spectrum may be thus subdivided into sections depending upon the type of vibration being analysed.

The Raman spectrum of szaibelyite over the 750–1150 cm^{-1} spectral range is illustrated in Fig. 4a. The Raman spectrum in this spectral region is dominated by a sharp intense band at 1099 cm^{-1}. On the low wavenumber side of this band, bands of significantly lesser intensity are observed at 1093 cm^{-1}. Raman bands are also observed at 836, 882, 916 and 988 cm^{-1}. The Raman band at 1099 cm^{-1} is assigned to the BO stretching vibration of the B_7O_{13} units. It is probable that there at least 13 BO stretching vibrations based upon a B_7O_{13} unit. Whether all these vibrations are coincident are not is not known but is likely. The width of the symmetric stretching vibration in the Raman spectrum suggests that these vibrational modes of the BO stretching vibrations are coincident. Further, the existence of two boron isotopes also complicates the situation.

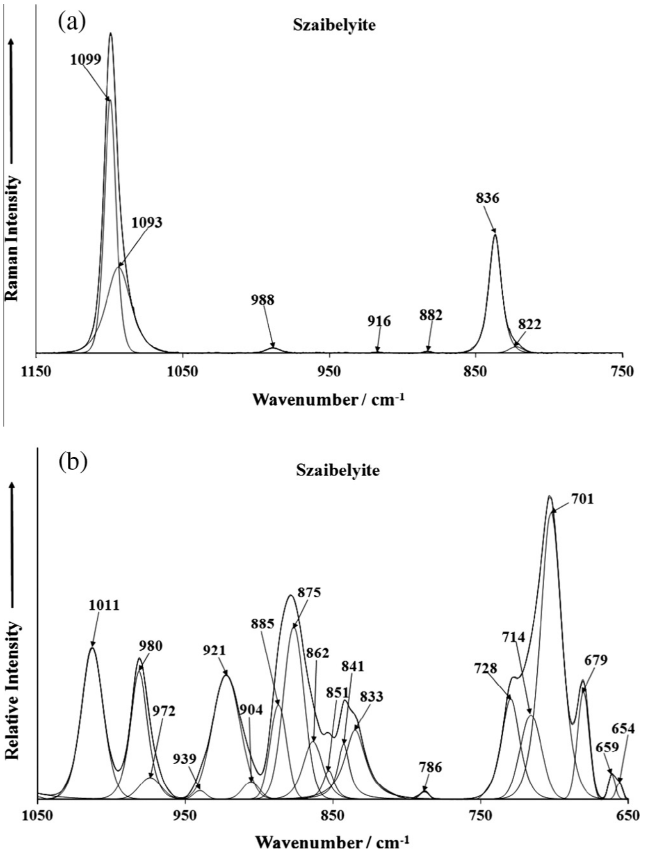

Fig. 4. (a) Raman spectrum of szaibelyite (upper spectrum) in the 750–1150 cm^{-1} spectral range and (b) infrared spectrum of szaibelyite (lower spectrum) in the 650–1050 cm^{-1} spectral range.

The nominal resolution of the Raman spectrometer is of the order of 2 cm^{-1} and as such is sufficient enough to identify separate bands for the stretching bands of the two boron isotopes. The two reduced masses for a pure B–O stretching mode would be $(10 \times 16)/(10 + 16) = 6.154$ for 10-B and $(11 \times 16)/(11 + 16) = 6.518$ for 11-B. The wavenumber is inversely proportional to square root of reduced mass; so the isotopic wavenumber ratio should be the sqrt(6.518/6.154) = 1.03. 10-B is about 20% of natural boron, so a mode that is mostly B–O stretching and that includes significant motion of the B atom (not a breathing mode of a BO_3 trigonal planar unit or a BO_4 tetrahedral unit) should show a large peak for 11-B and a smaller peak at higher wavenumber for 10-B. For example if the sharp Raman peak at 925 in Fig. 4a is from the 11-B component such a mode, then it should have a smaller 10-B satellite near $(1.03) \times (925) = 952$ cm^{-1}, and indeed a small peak at 955 is observed in the figure. Similar small, higher wavenumber bands are also shown in this figure associated with large peaks at 825 and 1039 cm^{-1}.

The Raman bands at 1144, 1157, 1229, 1318 cm^{-1} are attributed to the BOH in-plane bending modes. It is not known to what the very broad band at 1433 cm^{-1} is attributed. Iliev et al. determined

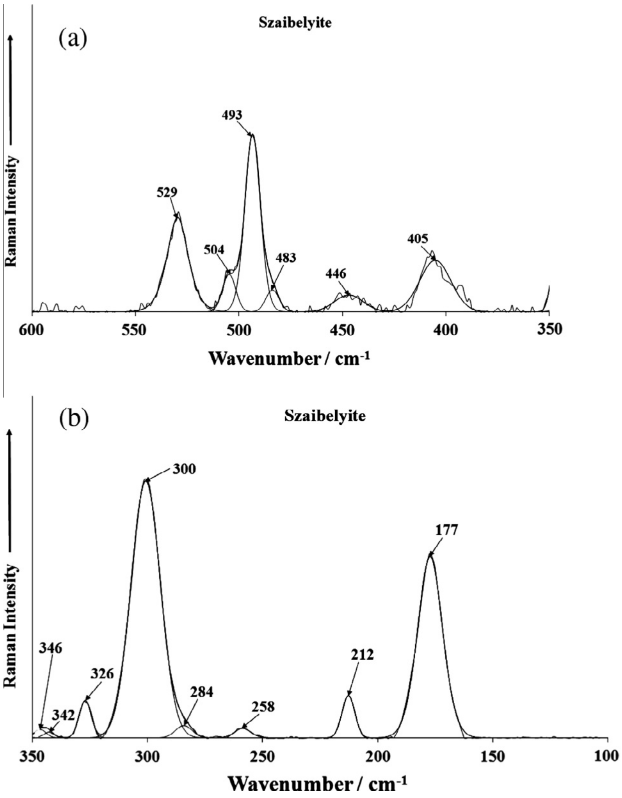

Fig. 5. (a) Raman spectrum of szaibelyite (upper spectrum) in the 350–600 cm^{-1} spectral range and (b) Raman spectrum of szaibelyite (lower spectrum) in the 100–350 cm^{-1} spectral range.

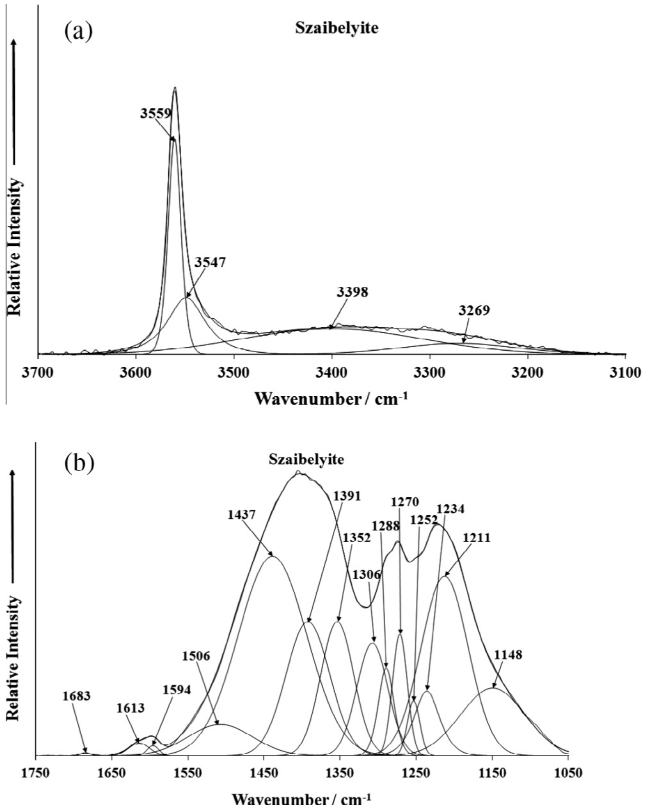

Fig. 6. (a) Raman spectrum of szaibelyite (upper spectrum) in the 3700–3100 cm^{-1} spectral range and (b) infrared spectrum of szaibelyite (lower spectrum) in the 1050–1750 cm^{-1} spectral range.

the Raman spectrum of a synthetic cobalt boracite [25]. The symmetry species of some vibrational modes were determined. These researchers [26] used Raman imaging to show the ferroelectric properties of boracite type compounds. These workers [26] showed that boracites exhibit a sequence of transitions 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 [27]. On the low wavenumber side of the 1099 cm^{-1} peak, Raman bands with significant intensity are observed at 836 and 988 cm^{-1}. These bands may be attributed to the antisymmetric stretching modes of tetrahedral boron.

The detailed infrared spectrum over the 650–1050 cm^{-1} spectral range is provided in Fig. 4b. This spectrum displays complexity with many bands being observed. The series of infrared bands at 904, 921, 939, 972 and 980 cm^{-1} are attributed to the trigonal borate antisymmetric stretching modes. The infrared band at 1011 cm^{-1} is assigned to the BO stretching mode, the equivalent to the Raman band at 1099 cm^{-1}. The series of infrared bands from 654 through to 728 cm^{-1} are related to trigonal borate bending modes. The infrared bands at 1148, 1211, 1234, 1252, 1270, 1288 and 1306 cm^{-1} are assigned to BOH deformation modes (Fig. 6b). The infrared bands at around 833, 841 and 851 cm^{-1} are assigned to water librational modes [28–30].

The Raman spectra in the 350–600 cm^{-1} and in the 100–350 cm^{-1} spectral ranges are shown in Fig. 5. Six Raman bands are observed at 405, 446, 483, 493, 504 and 529 cm^{-1}. These bands are simply defined as trigonal and tetrahedral borate bending modes. A series of infrared bands at 654, 659, 679, 701, 714 and 728 cm^{-1} (Fig. 4b) are due to these bending modes. Strong Raman bands are found in the far wavenumber region at 177, 212, 258, 284, 300 and 326 cm^{-1} (Fig. 4b). These bands may be simply described as lattice or external vibrations.

The Raman spectrum of szaibelyite in the 3100–3700 cm^{-1} spectral range is reported in Fig. 6a. The infrared spectrum of szaibelyite in the 1050–1750 cm^{-1} spectral range is reported in Fig. 6b. The formula of szaibelyite $MgBO_2(OH)$ is such that both water and hydroxyl stretching bands would be expected in both the Raman and infrared spectra. The difficulty is which band is attributable to which vibration. In the normal course of events, the hydroxyl stretching vibrations occur at higher wavenumbers than the water stretching wavenumbers [31–34]. Further, the widths of the hydroxyl stretching vibrations are narrow compared with the width of the water bands. A sharp Raman band observed at 3559 cm^{-1} is superimposed upon some broad bands at 3269, 3398 and 3547 cm^{-1}. It is probable that these latter bands are attributable to water stretching vibrations. The first band is attributed to the stretching vibrations of hydroxyl units. The observation of multiple bands proves that there are non-equivalent water units in the szaibelyite structure.

A single broad Raman band at 1685 cm^{-1} is observed. This band is attributed to the bending mode of water, and its position is indicative of very strongly hydrogen bonded water [31–34]. The position of the Raman band is in harmony with the infrared bands observed in the infrared spectrum at 1627 and 1673 cm^{-1} (Fig. 7). The 1627 cm^{-1} infrared band is due to the bending mode of weakly hydrogen bonded water molecules, whereas the 1673 cm^{-1} infrared band is attributed to very strongly hydrogen bonded water. A series of infrared bands are observed in Fig. 7 between 1300 and 1500 cm^{-1}. Infrared bands are found at 1318, 1349, 1371, 1383 cm^{-1}. These bands are assigned to the antisymmetric stretching vibrations of trigonal boron [20] (please see Table 11.VIII of this

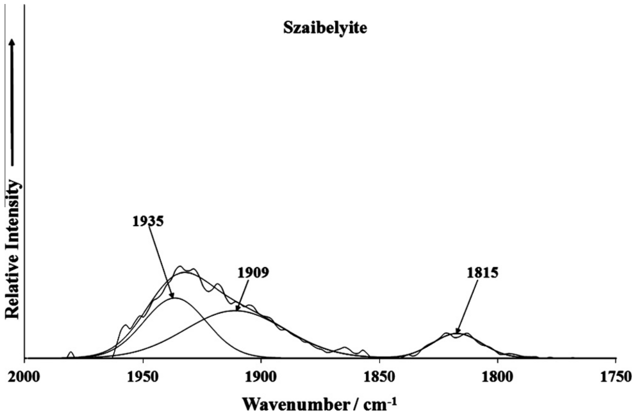

Fig. 7. Infrared spectrum of szaibelyite (lower spectrum) in the 1750–2000 cm^{-1} spectral range.

reference). Other infrared bands with lesser intensity are noted at 1431, 1455 and 1472 cm^{-1}. These bands are also attributed to the antisymmetric stretching vibrations of trigonal boron [20]. A low intensity infrared band is observed at 1214 cm^{-1}. This band is assigned to in plane bending of BOH units [20]. These bands are not observed in the Raman spectrum.

Conclusions

The szaibelyite sample studied in this work is from the Brosso mine, Piedmont, Italy. A combination of Raman spectroscopy at ambient temperatures complimented with infrared spectroscopy has been used to characterize the mineral.

The presence of Fe suggests a partial substitution of Mg, however an iron member is still not known. The existence of a solid solution between szaibelyite and sussexite, suggests the possibility of substitution of Mg by cations with similar ionic ratios.

Tentative assignments are made based upon the position and intensity of the infrared and Raman bands. Two boron isotopes are known namely 10-B and 11-B. The 10-B is around 20% in concentration compared with 11-B. The Raman spectrum shows a large peak for 11-B and a smaller peak at higher frequency for 10-B. The sharp Raman peak at 925 cm^{-1} is from the 11-B component such a mode, then it should have a smaller 10-B satellite near $(1.03) \times (924) = 952$ cm^{-1}, and indeed a low intensity peak at 955 cm^{-1} is observed.

There are many borate containing minerals which have yet to have their vibrational spectra measured and the molecular structure assessed in terms of their vibrational spectra. In this work we have measured the Raman and infrared spectrum of szaibelyite, a borate containing mineral. The importance of the mineral szaibelyite rests with the chemistry of the compound and the potential to synthesize nanomaterials based upon polymerization of borate units. Such compounds have the potential to make especially selected ferroelectric, pyroelectric and piezoelectric properties. Szaibelyite is a precursor for the synthesis of such nanomaterials.

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.molstruc.2015.02.005.

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