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## The molecular structure of the borate mineral rhodizite (K, Cs) $\text{Al}_4\text{Be}_4(\text{B, Be})_{12}\text{O}_{28}$ – A vibrational spectroscopic study

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### HIGHLIGHTS

- We have studied the borate mineral rhodizite (K, Cs) $\text{Al}_4\text{Be}_4(\text{B, Be})_{12}\text{O}_{28}$ .
- Using a combination of SEM with EDX and vibrational spectroscopic techniques.
- Semi-quantitative chemical composition shows a Al, Ca, borate with minor amounts of K, Mg and Cs.
- The mineral has a characteristic borate Raman spectrum.

### GRAPHICAL ABSTRACT



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### ABSTRACT

We have studied the borate mineral rhodizite (K, Cs) $\text{Al}_4\text{Be}_4(\text{B, Be})_{12}\text{O}_{28}$  using a combination of DEM with EDX and vibrational spectroscopic techniques. The mineral occurs as colorless, gray, yellow to white crystals in the triclinic crystal system. The studied sample is from the Antandrokomby Mine, Sahatany valley, Madagascar. The mineral is prized as a semi-precious jewel. Semi-quantitative chemical composition shows a Al, Ca, borate with minor amounts of K, Mg and Cs. The mineral has a characteristic borate Raman spectrum and bands are assigned to the stretching and bending modes of B, Be and Al. No Raman bands in the OH stretching region were observed.

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### Introduction

Rhodizite is an extremely rare potassium caesium beryllium aluminium borate mineral. General chemical formula can be written as (K, Cs) $\text{Al}_4\text{Be}_4(\text{B, Be})_{12}\text{O}_{28}$ . Rhodizite forms a series with londonite, it's Cs analogue. The mineral occurs as colourless, white to yellowish dodecahedral crystals in complex pegmatites.

Rhodizite was first described from complex granitic pegmatites in Sarapulka and Alabashka pegmatite fields, Central Urals, Russia [1,2]. Specimens come from only a few regions: a couple of sites in the Ural Mountains, and a few sites in Madagascar. Rhodizite is remarkable for not only its chemistry but its bright adamantine luster and high degree of hardness. Both these properties lend themselves well to the fashioning of a gemstone. Rhodizite can be an interesting mineral for the market of rare gemstones [3].

The crystal structure of rhodizite was determined [4] and latter refined [5,6]. The mineral has cubic symmetric, space group  $P-43m$

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with  $a = 7.317 \text{ \AA}$ . Later, rhodizite and londonite were subject of a number of studies, including detailed crystal chemistry [7,8] and its physical properties [9,10]. To the best knowledge of the authors, spectroscopic studies of rhodizite are restricted to the RRUFF Project (<http://rruff.info/rhodizite/display=default/R050099>). However, no interpretation of the spectra is provided.

Borate minerals lend themselves to analysis by vibrational spectroscopy [11–14]. The aim of this paper is to report the Raman spectra of rhodizite, and to relate the spectra to the molecular structure of this borate mineral. The paper follows the systematic research of the large group of pegmatite minerals and especially molecular structure of minerals containing oxyanions using IR and Raman spectroscopy.

## Experimental

### Samples description and preparation

The rhodizite sample studied in this work forms part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-121. The studied sample is from the Antandrokomby Mine, Sahatany valley, Madagascar.

The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The rhodizite studied in this work occurs in association with microcline and Li rich micas. Scanning electron microscopy (SEM) in the EDS mode 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>). Rhodizite crystals were coated with a thin 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 microprobe spectroscopy

Crystals of rhodizite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with  $10\times$ ,  $20\times$ , and  $50\times$  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  $2 \text{ cm}^{-1}$  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 ( $50\times$ ) were accumulated to improve the signal to noise ratio of the spectra. 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.

The Raman spectrum of rhodizite has been published in the RRUFF data base (<http://rruff.info/rhodizite/display=default/R050099>). This spectrum is given in the Supplementary information.

### 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  $4000\text{--}525 \text{ cm}^{-1}$  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.

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 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

### Chemical characterization

The BSI image of rhodizite sample studied in this work is shown in Fig. S1 (Supplementary information). Qualitative and semi-quantitative chemical composition shows an Al, Ca, borate with minor amounts of K, Mg and Cs. The chemical analysis is shown in Fig. S2. The atomic numbers of B and Be are too low to be determined by SEM with EDX. The calculated formula on the basis of semi quantitative analysis of the studied mineral is  $(\text{K}_{0.56}\text{Cs}_{0.44})(\text{Al}_{3.96}\text{Si}_{0.04})_{\Sigma=4}\text{Be}_{4.00}(\text{B}_{11.45}\text{Be}_{0.55})_{\Sigma=12}\text{O}_{28}$ .

The ratio of B to Be is around 24/1, so the mineral is fundamentally a borate mineral.

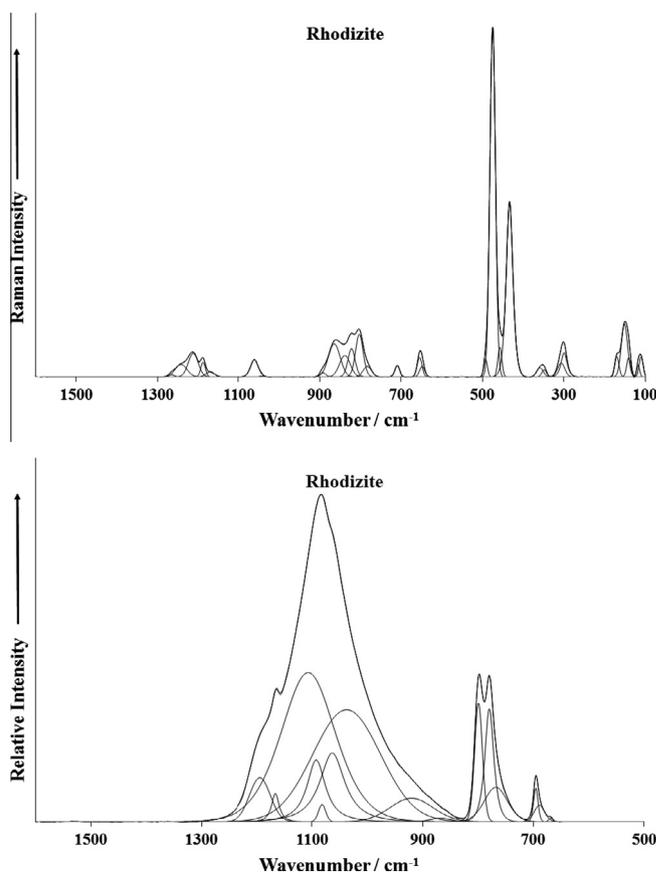


Fig. 1. (a) Raman spectrum of rhodizite over the  $100\text{--}4000 \text{ cm}^{-1}$  spectral range and (b) infrared spectrum of rhodizite over the  $500\text{--}4000 \text{ cm}^{-1}$  spectral range.

### Vibrational spectroscopy

The Raman spectrum of rhodizite over the 100–1500  $\text{cm}^{-1}$  spectral range is displayed in Fig. 1a. No Raman intensity was observed above 1500  $\text{cm}^{-1}$ . This spectrum shows the position and relative intensities of the Raman bands. This Raman spectrum may be subdivided into sections depending upon the type of vibration being studied. The infrared spectrum of rhodizite in the 500–1600  $\text{cm}^{-1}$  spectral range is shown in Fig. 1b. This spectrum shows the position and relative intensities of the infrared bands.

The Raman spectrum of rhodizite in the 700–1300  $\text{cm}^{-1}$  spectral range is given in Fig. 2a. The infrared spectrum of rhodizite in the 850–1350  $\text{cm}^{-1}$  spectral range is given in Fig. 2b. In comparison with the Raman spectrum, the infrared spectrum is very broad. It is apparent that there are three distinct sets of bands in Fig. 4a. There are a group of bands in the 1100–1300  $\text{cm}^{-1}$  spectral range; there is a strong Raman band at 1060  $\text{cm}^{-1}$ ; and thirdly there is a set of bands in the 700–900  $\text{cm}^{-1}$  spectral range. The Raman bands observed at 1171, 1188, 1212 and 1242  $\text{cm}^{-1}$  are assigned to the antisymmetric stretching vibrations of BO units. In harmony with this assignment the strong Raman band at 1060  $\text{cm}^{-1}$  is attributed to the symmetric stretching vibration of BO units. In the RRUFF spectrum (Supplementary information Fig. S3). A broad band is observed at 1223  $\text{cm}^{-1}$ . The width of this band suggests that the band is composed of several components in harmony with the bands found in this work. A broad Raman band is found in the RRUFF spectrum at 1061  $\text{cm}^{-1}$  in harmony with the spectra determined in this research.

The actual position of this symmetric stretching band is dependent upon the type of BO unit. For example for boracite, this band occurs at 1005  $\text{cm}^{-1}$ . It is highly likely that the mineral rhodizite

will show some ferroelectric properties. 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. [16] used Raman imaging to show the ferroelectric properties of boracite type compounds. These workers [16] 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 [17].

The set of bands in the 700–900  $\text{cm}^{-1}$  are assigned to OBO and OBeO bending vibrations. Raman bands are observed at 802, 821, 838, 864 and 892  $\text{cm}^{-1}$ . It should be noted that there are two isotopes of boron, namely 10-B and 11-B, as such the Raman bands from both isotopes may be observed. The isotopic ratio of the two atoms is about 1/4. The Raman band at 802  $\text{cm}^{-1}$  is ascribed to the O–11B–O bending mode and therefore the band for the 10-B isotope should occur at higher wavenumbers at  $1.03 \times 802 = 826 \text{ cm}^{-1}$  which corresponds to the band which is curve resolved at 821  $\text{cm}^{-1}$ . In the RRUFF spectrum, Raman bands are observed at 527, 633, 774 and 641  $\text{cm}^{-1}$ . The infrared spectrum of rhodizite over the 650–850  $\text{cm}^{-1}$  is displayed in Fig. 4. Prominent infrared bands are observed at 779 and 798  $\text{cm}^{-1}$ . These two bands are assigned to the BO vibrations of the two isotopes of boron (B10 and B11).

In the infrared spectrum, a broad spectral profile is observed. Nevertheless, infrared bands may be resolved from the broad profile. Infrared bands are resolved at 927, 1056, 1085, 1138, 1165 and 1191  $\text{cm}^{-1}$ . These bands are assigned to the BO antisymmetric stretching vibrations.

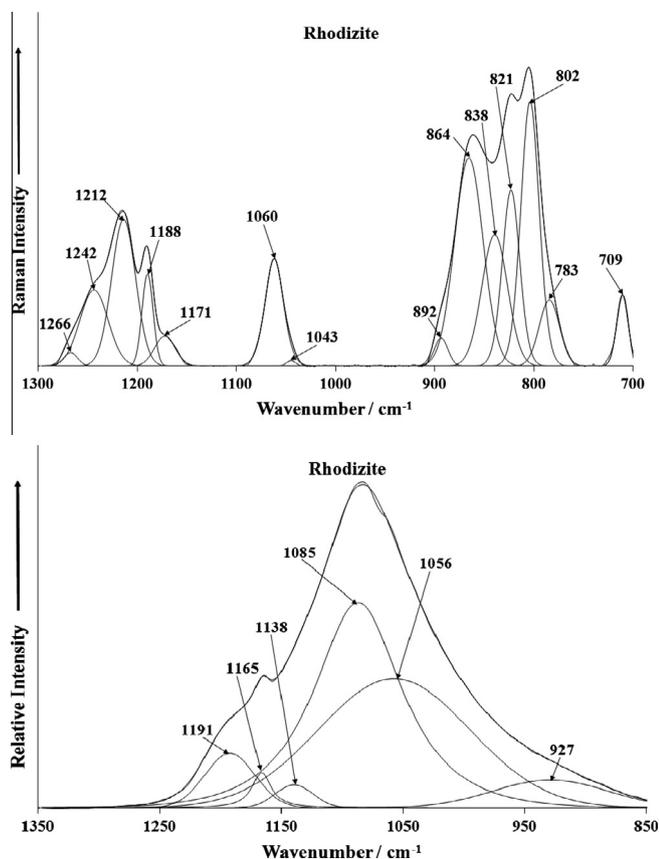


Fig. 2. (a) Raman spectrum of rhodizite over the 800–1300  $\text{cm}^{-1}$  spectral range and (b) infrared spectrum of rhodizite over the 500–1300  $\text{cm}^{-1}$  spectral range.

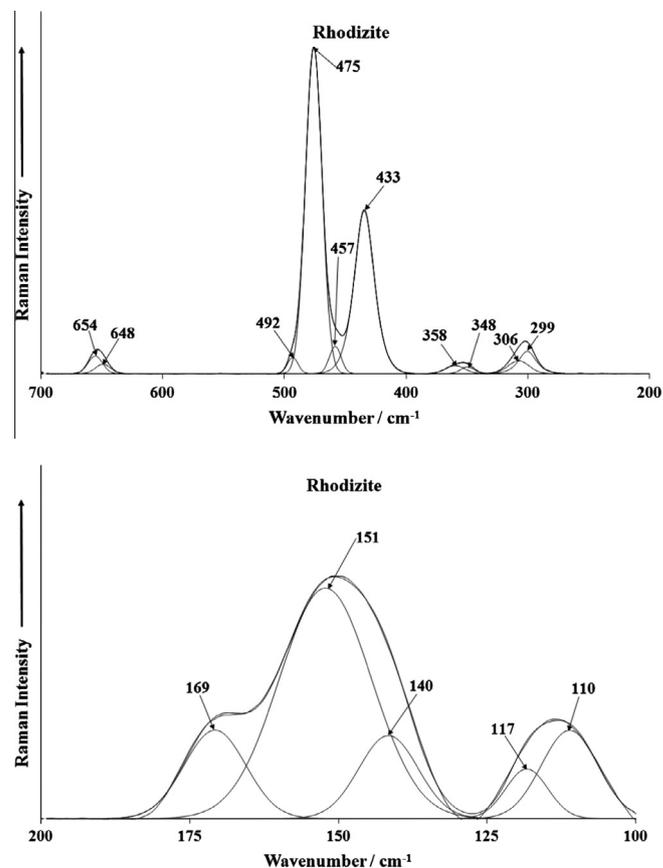


Fig. 3. (a) Raman spectrum of rhodizite over the 300–800  $\text{cm}^{-1}$  spectral range and (b) Raman spectrum of rhodizite over the 100–300  $\text{cm}^{-1}$  spectral range.

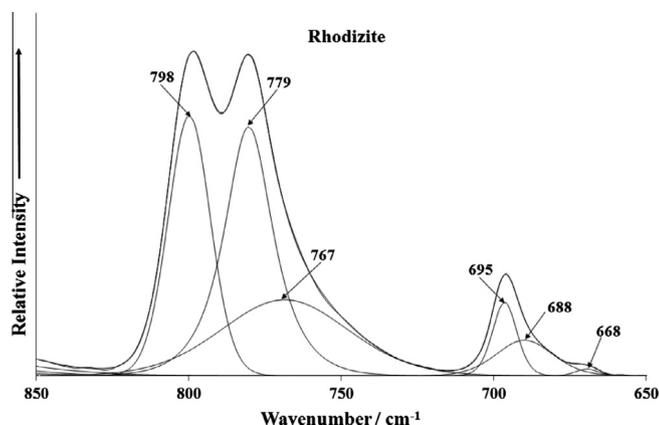


Fig. 4. Infrared spectrum of rhodizite in the 650–850  $\text{cm}^{-1}$  spectral range.

The Raman spectrum of rhodizite over the 200–700  $\text{cm}^{-1}$  spectral range is shown in Fig. 3a. Sharp Raman bands are observed at 433 and 475  $\text{cm}^{-1}$  and are assigned to Al–O stretching vibrations. In the RRUFF spectrum, two very intense sharp bands are noticed at 416 and 455  $\text{cm}^{-1}$ . Other low intensity Raman bands are found at 648 and 654  $\text{cm}^{-1}$  as well as 299, 306, 348 and 358  $\text{cm}^{-1}$ . The Raman far wavenumber region is reported in Fig. 3b. Raman bands are observed at 110, 117, 140, 151 and 169  $\text{cm}^{-1}$ . The bands are simply attributed to external vibrations. In the RRUFF spectrum a low intensity Raman band is found at 283  $\text{cm}^{-1}$ . Other low intensity bands are also observed but of a very low intensity.

## Conclusions

We have analyzed the mineral rhodizite using a range of techniques including SEM with EDX for chemical analysis, visual inspection, Raman and infrared spectroscopy. The calculated formula of the studied sample is  $(\text{K}_{0.56}\text{Cs}_{0.44})(\text{Al}_{3.96}\text{Si}_{0.04})_{\Sigma=4}\text{Be}_{4.00}(\text{B}_{11.45}\text{Be}_{0.55})_{\Sigma=12}\text{O}_{28}$ . The ratio of B–Be is about 24 and thus the mineral is a borate mineral. Raman and infrared bands were observed and attributed to BO stretching and bending vibrations. A comparison is made with the Raman spectrum of rhodizite from the RRUFF data base. Raman bands observed at 1171, 1188, 1212 and 1242  $\text{cm}^{-1}$  are assigned to the antisymmetric stretching vibrations of BO units. The set of bands in the 700–900  $\text{cm}^{-1}$  are assigned to OBO and OBeO bending vibrations. Raman bands are observed at 802, 821, 838, 864 and 892  $\text{cm}^{-1}$ . It should be noted

that there are two isotopes of boron, namely 10-B and 11-B, as such the Raman bands from both isotopes are observed.

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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.2014.02.036>.

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