The molecular structure of the phosphate mineral beraunite $Fe^{2+}Fe_5^{3+}(PO_4)_4(OH)_5\cdot4H_2O$ – A vibrational spectroscopic study

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HIGHLIGHTS

- We have studied the phosphate mineral beraunite.
- The mineral contains both ferrous and ferric ions in the formula.
- Raman bands are attributed to the stretching and bending modes of phosphate.
- Infrared bands are assigned to OH stretching vibrations.
- Vibrational spectroscopy offers insights into the molecular structure of the phosphate mineral beraunite.

GRAPHICAL ABSTRACT
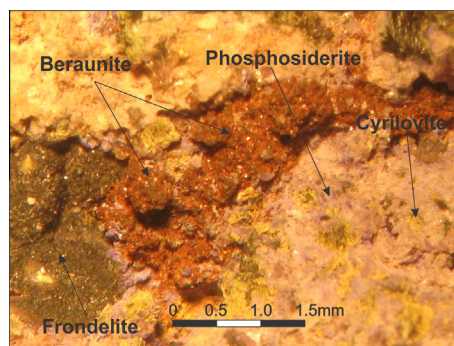
ABSTRACT

The mineral beraunite from Boca Rica pegmatite in Minas Gerais with theoretical formula $Fe^{2+}Fe_5^{3+}(PO_4)_4(OH)_5\cdot4H_2O$ has been studied using a combination of electron microscopy with EDX and vibrational spectroscopic techniques.

Raman spectroscopy identifies an intense band at 990 cm^{-1} and 1011 cm^{-1}. These bands are attributed to the PO_4^{3-} ν_1 symmetric stretching mode. The ν_3 antisymmetric stretching modes are observed by a large number of Raman bands. The Raman bands at 1034, 1051, 1058, 1069 and 1084 together with the Raman bands at 1098, 1116, 1133, 1155 and 1174 cm^{-1} are assigned to the ν_3 antisymmetric stretching vibrations of PO_4^{3-} and the $HOPO_3^{2-}$ units. The observation of these multiple Raman bands in the symmetric and antisymmetric stretching region gives credence to the concept that both phosphate and hydrogen phosphate units exist in the structure of beraunite. The series of Raman bands at 567, 582, 601, 644, 661, 673, and 687 cm^{-1} are assigned to the PO_4^{3-} ν_2 bending modes. The series of Raman bands at 437, 468, 478, 491, 503 cm^{-1} are attributed to the PO_4^{3-} and $HOPO_3^{2-}$ ν_4 bending modes.

No Raman bands of beraunite which could be attributed to the hydroxyl stretching unit were observed. Infrared bands at 3511 and 3359 cm^{-1} are ascribed to the OH stretching vibration of the OH units. Very broad bands at 3022 and 3299 cm^{-1} are attributed to the OH stretching vibrations of water. Vibrational spectroscopy offers insights into the molecular structure of the phosphate mineral beraunite.

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Introduction

The mineral beraunite has been known for a considerable time [1–3] and was often confused with other phosphate minerals such as vivianite [4]. Beraunite $Fe^{2+}Fe_5^{3+}(PO_4)_4(OH)_5 \cdot 4H_2O$ is essentially an iron phosphate mineral which contains iron in both the ferrous and ferric state. It was first described in an occurrence in Beraun in the Czech Republic [5,6]. The beraunite occurs as a secondary mineral in iron ore deposits and as an alteration product of primary phosphates in granitic pegmatites.

The mineral occurs as a fibrous green to black/brown nodules. According to the literature [7,8], variation in the chemical composition may occur with irrational amounts of ferrous iron. Beraunite crystallizes in the monoclinic crystal system with point group 2/m [9]. The chain segments in beraunite are one and two octahedra in length [10]. Beraunite has two different types which are Zn-rich and Al-rich beraunites. Phosphate minerals have special characteristics about their chemical composition. The polyatomic complex of iron–oxygen octahedral face is sharing triplets corner to four other octahedral in the arrangement of atoms of the basic iron phosphates such as with dufrenite, rockbridgeite and beraunite. This arrangement is held together by the phosphate tetrahedra. The larger Fe^{2+} ion occupies a separate and distinct position in the structure of beraunite from the five other Fe^{3+} ions.

Raman spectroscopy has proven most useful for the study of mineral structure [11–15]. Raman spectroscopy is an important tool in the characterization of phosphates in pegmatite rocks [16]. In recent years, spectroscopic studies concerning phosphate minerals are increasing, especially due to their industrial and technological importance. The aim of this paper is to report the Raman spectra of beraunite, and to relate the spectra to the molecular structure of this hydrogen-phosphate mineral. The paper follows the systematic research of the large group of supergene minerals and especially molecular structure of minerals containing oxyanions using IR and Raman spectroscopy.

Experimental

Samples description and preparation

The beraunite 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-106. The studied sample is from Boca Rica pegmatite in Minas Gerais, Brazil, and occurs in association with heterosite. Geological description and characterization of the phosphate paragenesis in Boca Rica pegmatite was published [17].

The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The beraunite studied in this work occurs in association with siderite. 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).

Beraunite crystal aggregate 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 microprobe spectroscopy

Crystals of beraunite 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 $\pm 1\,cm^{-1}$ in the range between 200 and $4000\,cm^{-1}$. The poser at the sample was less than 1 mW. 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 spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

An image of the beraunite crystals measured is shown in the supplementary information as Fig. S1. Clearly the crystals of beraunite are readily observed, making the Raman spectroscopic measurements readily obtainable.

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

Chemical characterization

The BSE image of beraunite sample studied in this work is shown in Fig. S1. The image shows an aggregate of prismatic crystals with acicular habitus. The sample is homogeneous and zonation or contaminant phases are not observed. Qualitative and semi-quantitative chemical composition shows a Fe phosphate (Fig. S2). No other cations were observed in substitution to Fe.

Infrared and Raman spectroscopy

Background

In aqueous systems, the Raman spectra of phosphate oxyanions show a symmetric stretching mode (v_1) at $938\,cm^{-1}$, an antisymmetric stretching mode (v_3) at $1017\,cm^{-1}$, a symmetric bending mode (v_2) at $420\,cm^{-1}$ and a v_4 bending mode at $567\,cm^{-1}$ [18–20]. S.D. Ross in Farmer (page 404) listed some well-known minerals containing phosphate, which were either hydrated or

hydroxylated or both [21]. The vibrational spectrum of the dihydrogen phosphate anion has been reported in Farmer. The PO_2 symmetric stretching mode occurs at 1072 cm^{-1} and the POH symmetric stretching mode at ~878 cm^{-1}. The position of the PO stretching vibration for calcium dihydrogen phosphate is found at 915 cm^{-1}. The POH antisymmetric stretching mode is at 947 cm^{-1} and the $P(OH)_2$ bending mode at 380 cm^{-1}. The band at 1150 cm^{-1} is assigned to the PO_2 antisymmetric stretching mode. The position of these bands will shift according to the crystal structure of archerite.

Vibrational spectroscopy

Vibrational spectroscopy provides a means of studying the molecular structure of a mineral such as beraunite at the molecular level. The Raman spectrum of beraunite over the 100–1500 cm^{-1} spectral range is illustrated in Fig. 1a. This spectrum shows the position of the bands and the relative intensities of these bands. Difficulty was experienced in obtaining the Raman spectrum of the OH stretching region. There are large parts of the spectrum where no intensity is observed and therefore the spectrum is subdivided into sections based upon the type of vibration being studied. The infrared spectrum over the 500–4000 cm^{-1} spectral range is shown in Fig. 1b. This spectrum shows the position and relative intensity of these infrared bands. There are large parts of the spectrum where no intensity is observed and therefore, the spectrum is subdivided into sections depending upon the type of vibration being observed.

The Raman spectrum of beraunite in the 900–1200 cm^{-1} spectral range as displayed in Fig. 2a is complex. Multiple overlapping bands are observed. Such complexity is even more profound in the
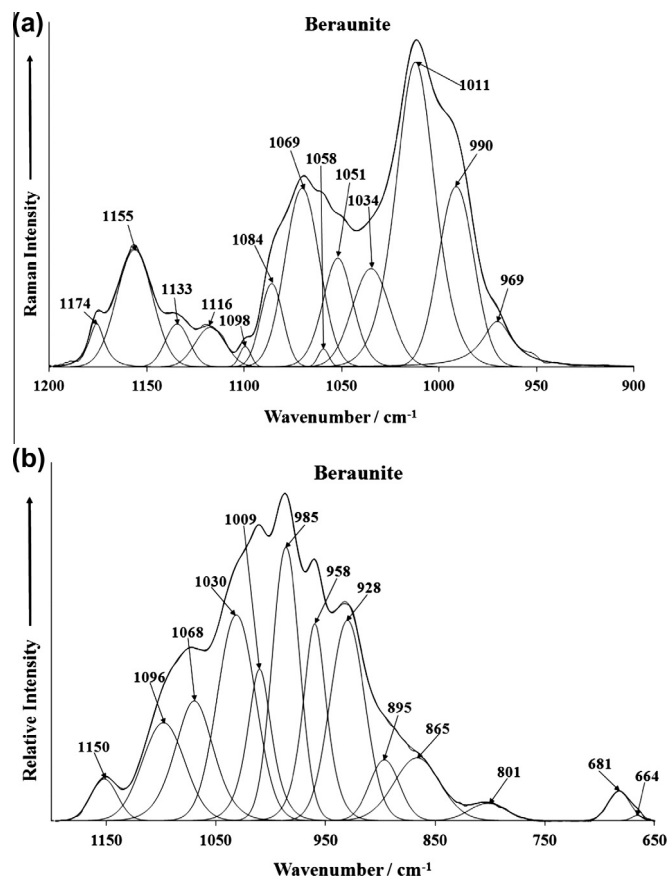

Fig. 2. (a) Raman spectrum of beraunite over the 1400–800 cm^{-1} spectral range. (b) Infrared spectrum of beraunite over the 1300–500 cm^{-1} spectral range.

infrared spectrum of beraunite (Fig. 2b). This complexity is associated with the fact that both ferrous and ferric iron exist in the structure of beraunite. The phosphate anion bonds to both cations and each interaction will give a separate set of phosphate bands. A further complication can arise with the mobility of the proton from the OH units. One possibility is that the proton of the hydroxyl unit is mobile and on a picoseconds time scale can transfer to the phosphate units, thus generating a $HOPO_3^{2-}$ unit. The Raman bands at 990 and 1011 cm^{-1} are assigned to the PO_4^{3-} ν_1 symmetric stretching vibrations. A Raman band is observed at 969 cm^{-1} and is attributed to the PO symmetric stretching vibration of these $HOPO_3^{2-}$ units. The Raman bands at 1034, 1051, 1058, 1069 and 1084 together with the Raman bands at 1098, 1116, 1133, 1155 and 1174 cm^{-1} are assigned to the ν_3 antisymmetric stretching vibrations of PO_4^{3-} and the $HOPO_3^{2-}$ units.

The infrared spectrum of beraunite in the 650–1200 cm^{-1} spectral range is reported in Fig. 2b. A broad spectral feature is observed which may be resolved into component bands. The infrared bands at 928, 958, 985 and 1009 cm^{-1} are assigned to the symmetric stretching vibrations of the PO_4^{3-} and $HOPO_3^{2-}$ units. The infrared bands at 1030, 1068, 1096 and 1150 cm^{-1} are attributed to the phosphate and hydrogen phosphate ν_3 antisymmetric stretching vibrations.

The Raman spectrum of beraunite in the 350–750 cm^{-1} spectral range is illustrated in Fig. 3a. The series of Raman bands at 567, 582, 601, 644, 661, 673, and 687 are assigned to the PO_4^{3-} and $HOPO_3^{2-}$ ν_2 bending modes. The complexity of the phosphate stretching region is also reflected in the phosphate bending region. The series of Raman bands at 437, 468, 478, 491, 503 cm^{-1} are attributed to the PO_4^{3-} and $HOPO_3^{2-}$ ν_4 bending modes. The two
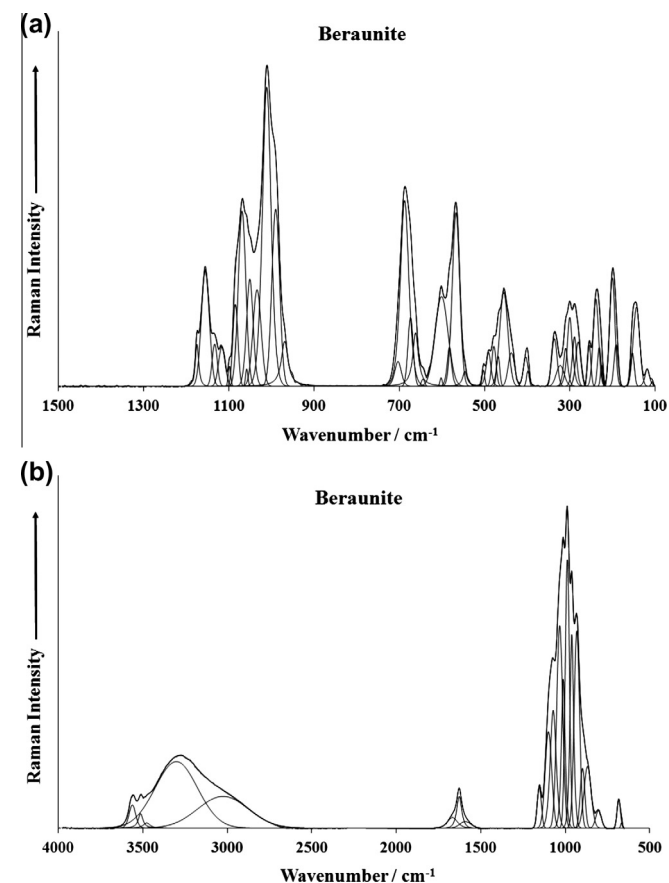

Fig. 1. (a) Raman spectrum of beraunite over the 4000–100 cm^{-1} spectral range. (b) Infrared spectrum of beraunite over the 4000–500 cm^{-1} spectral range.
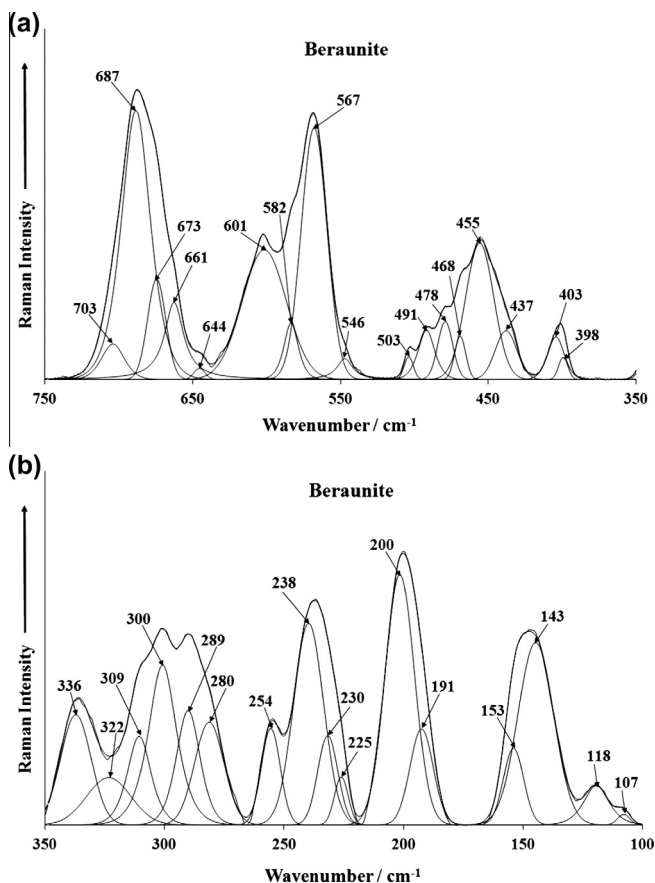
(a)

(b)

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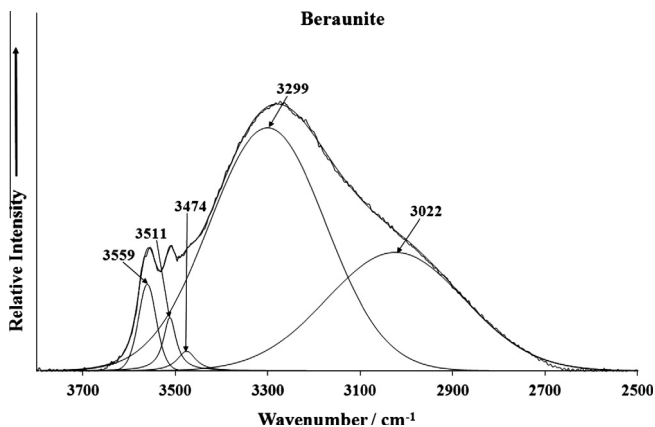

Fig. 4. Infrared spectrum of beraunite over the 3800–2600 cm^{-1} spectral range.

Fig. 5. Infrared spectrum of beraunite over the 1800–1300 cm^{-1} spectral range.

stretching vibrations as may be observed from the formula of beraunite (Fe^{2+}Fe$_5^{3+}$(PO$_4$)$_4$(OH)$_5$·4H$_2$O). The infrared bands at 3511 and 3359 cm^{-1} are assigned to the OH stretching vibration of the OH units. The very broad bands at 3022 and 3299 cm^{-1} are attributed to the OH stretching vibrations of water. It is noted that no Raman spectrum of beraunite could be obtained in this spectral region for whatever reason. The observation of two bands in the water OH stretching region is in harmony with the infrared spectrum displayed in Fig. 5. Infrared bands found at 1624 and 1664 cm^{-1} are assigned to the water bending modes. The observation of these two bands reflects water is involved with both very weak and very strong hydrogen bonding in the beraunite structure. A comparison may be made with the mineral wolfeite (Fe^{2+})$_2$(PO$_4$)(OH), a mineral which has ferrous iron only in the structure. The infrared spectrum shows sharp bands at 3477, 3495, 3515 and 3541 cm^{-1}. These bands are assigned to the OH stretching vibration. The observation of these multiple bands gives credence to the concept that the OH units are non-equivalent in the structure of wolfeite.

Conclusions

A beraunite sample was studied by Electron Microscope in the EDS mode, Raman and infrared spectroscopy. The chemical analysis by SEM/EDS shows a homogeneous phase composed by Fe and P. The sample can be considered a pure phase.

Raman spectroscopy identifies an intense band at 990 cm^{-1} and 1011 cm^{-1}. These bands are attributed to the PO$_4^{3-}$ ν$_1$ symmetric stretching mode. The ν$_3$ antisymmetric stretching modes are observed by a large number of Raman bands. The Raman bands at 1034, 1051, 1058, 1069 and 1084 together with the Raman bands at 1098, 1116, 1133, 1155 and 1174 cm^{-1} are assigned to the ν$_3$ antisymmetric stretching vibrations of PO$_4^{3-}$ and the HOPO$_3^{2-}$ units. The observation of these multiple Raman bands in the symmetric and antisymmetric stretching region gives credence to the concept that both phosphate and hydrogen phosphate units exist in the structure of beraunite. The infrared spectrum shows complexity with many overlapping bands. The series of Raman bands at 567, 582, 601, 644, 661, 673, and 687 to cm^{-1} are assigned to the PO$_4^{3-}$ ν$_2$ bending modes. The series of Raman bands at 437, 468, 478, 491, 503 cm^{-1} are attributed to the PO$_4^{3-}$ and HOPO$_3^{2-}$ ν$_4$ bending modes.

No Raman bands which could be attributed to the hydroxyl stretching unit were found. Infrared bands at 3511 and 3359 cm^{-1} are ascribed to the OH stretching vibration of the OH units. Very broad bands at 3022 and 3299 cm^{-1} are attributed to the OH stretching vibrations of water. Vibrational spectroscopy offers insights into the molecular structure of the phosphate mineral beraunite.

overlapping bands at 398 and 403 cm^{-1} are assigned to the FeO stretching vibration. The observation of two close bands reflects the ferrous/ferric state of iron in the structure of beraunite. The Raman spectrum of beraunite in the 100–350 cm^{-1} spectral range is illustrated in Fig. 3b. Raman bands are observed at 107, 118, 143, 153, 191, 200, 230, 238 and 254 cm^{-1}. These bands may be described as external or lattice vibrations. However, the series of Raman bands at 280, 289, 300, 309, and 336 cm^{-1} may be related to metal oxygen stretching vibrations.

The infrared spectrum of beraunite over the 2500–3800 cm^{-1} spectral range is reported in Fig. 4. This spectrum reflects the OH
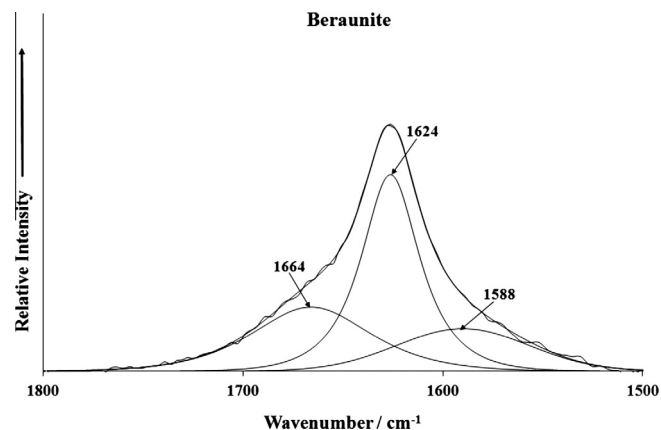
Acknowledgements

Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.02.198.

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