Vibrational spectroscopic characterization of the phosphate mineral barbosalite $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$ – Implications for the molecular structure

Ray L. Frost^{a,*}, Yunfei Xi^a, Andrés López^a, Ricardo Scholz^b, Cristiano de Carvalho Lana^b, Bárbara Firmino e Souza^b

^a School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO 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

- We have studied barbosalite $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$ found in granitic pegmatites.
- Using vibrational spectroscopy.
- Raman and infrared bands are assigned to the stretching and bending modes of HOPO_3^{3-} and PO_4^{3-} units.
- Vibrational spectroscopy enables aspects of the molecular structure of barbosalite to be assessed.

ARTICLE INFO

Article history:

Received 10 July 2013

Received in revised form 31 July 2013

Accepted 31 July 2013

Available online 22 August 2013

Keywords:

Barbosalite
Phosphate
Raman
Infrared
Pegmatite

ABSTRACT

Natural single-crystal specimens of barbosalite from Brazil, with general formula $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$ were investigated by Raman and infrared spectroscopy. The mineral occurs as secondary products in granitic pegmatites. The Raman spectrum of barbosalite is characterized by bands at 1020, 1033 and 1044 cm^{-1} , assigned to ν_1 symmetric stretching mode of the HOPO_3^{3-} and PO_4^{3-} units. Raman bands at around 1067, 1083 and 1138 cm^{-1} are attributed to both the HOP and PO antisymmetric stretching vibrations. The set of Raman bands observed at 575, 589 and 606 cm^{-1} are assigned to the ν_4 out of plane bending modes of the PO_4 and H_2PO_4 units. Raman bands at 439, 461, 475 and 503 cm^{-1} are attributed to the ν_2 PO_4 and H_2PO_4 bending modes. Strong Raman bands observed at 312, 346 cm^{-1} with shoulder bands at 361, 381 and 398 cm^{-1} are assigned to FeO stretching vibrations. No bands which are attributable to water vibrations were found. Vibrational spectroscopy enables aspects of the molecular structure of barbosalite to be assessed.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Barbosalite $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$ [1,2] is a hydroxy phosphate of Fe^{2+} and Fe^{3+} . The mineral is found in complex granitic pegmatites, formed by oxidation and hydration of primary iron minerals. The mineral originates from Minas Gerais [3], at the Sapucaia pegmatite mine, about 50 km east-southeast of Governador Valadares, and in good crystals from the Criminoso pegmatite mine, about 35 km north. The mineral varies in color from dark blue-green to black. The mineral is found at many sites worldwide [3–11] including at Olary, South Australia [11].

The mineral is monoclinic, pseudotetragonal with point group: $2/m$. The cell data is Space Group: $P2_1/c$, with $a = 7.25$, $b = 7.46$,

$c = 7.49$, $\beta = 120$ and $Z = 2$. Barbosallite is a member of lazulite group that also includes lazulite – $\text{MgAl}_2(\text{PO}_4)_2(\text{OH})_2$ and hentschelite – $\text{Cu}^{2+}(\text{Fe}^{3+})_2(\text{PO}_4)_2(\text{OH})_2$ [12].

Raman spectroscopy has proven most useful for the study of mineral structures [13–16]. The objective of this research is to report the Raman and infrared spectra of barbosallite and to relate the spectra to the molecular structure of the mineral. This is the first report of a systematic study of barbosallite from Brazil.

2. Experimental

2.1. Samples description and preparation

The barbosallite sample studied in this work was collected from the type locality, the Sapucaia mine, Galileia, Minas Gerais [3]. The sample was incorporated to the collection of the Geology

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

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

Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-182.

To remove contaminate phases, with the support of a Stereomicroscope Leica Model EZ4, barbosolite crystals were handily selected from a sample in association with eosphorite and hureaulite. To support the mineral characterization chemical analysis were carried out via scanning electron microscopy (SEM) and electron microprobe analysis (EMP).

2.2. 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>). Barbosolite crystal cleavage fragment was coated with a 5 nm layer of evaporated Au. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment.

2.3. Electron microprobe analysis (EMP)

A quantitative chemical analysis was carried via EMP. Barbosolite single crystal selected for this study was analyzed with the performance of seven spots. The chemical analysis was carried out with a Jeol JXA8900R spectrometer from the Physics Department of the Federal University of Minas Gerais, Belo Horizonte. For each selected element was used the following standards: Fe – Magnetite, Mn – rodonite, P and Ca – $\text{Ca}_2\text{P}_2\text{O}_7$, Al – Al_2O_3 and Mg – MgO. The epoxy embedded barbosolite sample was polished in the sequence of 9 μm , 6 μm and 1 μm diamond paste MetaDI® II Diamond Paste – Buhler, using water as a lubricant, with a semi-automatic MiniMet® 1000 Grinder-Polisher – Buehler. Finally, the epoxy embedded barbosolite was coated with a thin layer of evaporated carbon. The electron probe microanalysis in the WDS (wavelength dispersive spectrometer) mode was obtained at 15 kV accelerating voltage and beam current of 10 nA. Chemical formula was calculated on the basis of ten oxygen atoms (O, OH).

2.4. Raman microprobe spectroscopy

Crystals of barbosolite were placed on a polished metal surface on the stage of an Olympus BHS 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 cm^{-1} and a precision of $\pm 1 \text{ cm}^{-1}$ in the range between 200 and 4000 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 cm^{-1} line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

2.5. 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 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.

3. Results and discussion

3.1. Chemical characterization

The barbosolite studied sample occurs in association with eosphorite (Fig. 1). The quantitative chemical analysis of barbosolite is presented in Table 1. The composition was calculated as mean values in seven spots. H_2O content as well as Fe_2O_3 were calculated by stoichiometry considering the theoretic chemical formula. The chemical formula was calculated on the basis of 10 oxygen atoms in the crystal structure. The chemical composition indicates an iron rich phase with partial substitution of Al and Mn. The chemical formula of the studied sample can be expressed as:

3.2. Vibrational spectroscopy

3.2.1. Background

In aqueous systems, the Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1} , an antisymmetric stretching mode (ν_3) at 1017 cm^{-1} , a symmetric bending mode (ν_2) at 420 cm^{-1} and a ν_4 bending mode at 567 cm^{-1} [17–19]. S.D. Ross in Farmer listed some well-known minerals containing phosphate which were either hydrated or hydroxylated or both [20]. The vibrational spectrum of the dihydrogen phosphate anion has been reported by Farmer [20]. The PO_2 symmetric stretching mode occurs at 1072 cm^{-1} and the POH symmetric stretching mode at $\sim 878 \text{ cm}^{-1}$. The POH antisymmetric stretching mode was found at 947 cm^{-1} and the $\text{P}(\text{OH})_2$ bending mode at 380 cm^{-1} . The band at 1150 cm^{-1} was assigned to the PO_2 antisymmetric stretching mode. The position of these bands will shift according to the crystal structure of the mineral.

Fig. 1. SEM image of barbosolite from Sapucaia pegmatite.

Table 1

Chemical composition of barbosolite from Sapucaia mine (mean of 7 electron microprobe analyses). H₂O and Fe₂O₃ calculated by stoichiometry.

Constituent	wt.%	Number of atoms	Probe standard/crystal
Fe ₂ O ₃	38.72	0.95	Stoichiometry
FeO	17.42	0.94	Magnetite/TAP
MgO	0.34	0.03	MgO/TAP
Al ₂ O ₃	1.29	0.05	Al ₂ O ₃ /TAP
P ₂ O ₅	37.08.30	2.00	Ca ₂ P ₂ O ₇ /PETJ
MnO	0.48	0.03	Rodhonite/LIF
CaO	0.01	0.00	Ca ₂ P ₂ O ₇ /PETJ
H ₂ O	4.49	0.99	Stoichiometry
F	0.11	0.01	Fluorite
Total	99.04	6.94	

The vibrational spectra of phosphate minerals have been published by Farmer's treatise Chapter 17 [20]. The Table 17.III in Ref. [20] reports the band positions of a wide range of phosphates and arsenates. The band positions for the monohydrogen phosphate anion of disodium hydrogen phosphate dihydrate is given as ν_1 at 820 and 866 cm⁻¹, ν_2 at around 460 cm⁻¹, ν_3 as 953, 993, 1055, 1070, 1120 and 1135 cm⁻¹, ν_4 at 520, 539, 558,

575 cm⁻¹. The POH unit has vibrations associated with the OH specie. The stretching vibration of the POH units was tabulated as 2430 and 2870 cm⁻¹, and bending modes at 766 and 1256 cm⁻¹. Water stretching vibrations were found at 3050 and 3350 cm⁻¹. The position of the bands for the disodium hydrogen phosphate is very dependent on the waters of hydration. There have been several Raman spectroscopic studies of the monosodium dihydrogen phosphate chemicals [21–25].

3.2.2. Spectroscopy

The Raman spectrum of barbosolite over the 100–4000 cm⁻¹ spectral range is illustrated in Fig. 2a. This figure shows the peak position and the relative intensities of the Raman bands. It is noted there are large parts of the spectrum where no intensity is observed and therefore, the spectrum is subdivided into sections based upon the types of vibration being studied. The infrared spectrum of barbosolite over the 500 to 4000 cm⁻¹ spectral range is shown in Fig. 2b. This figure shows the position and relative intensities of the infrared bands. There are large parts of the infrared spectrum where little or no intensity is observed. Hence, the spectrum is subdivided into sections based on which bands are being studied.

Fig. 2. (a) Raman spectrum of barbosolite over the 100–4000 cm⁻¹ spectral range (b) Infrared spectrum of barbosolite over the 500–4000 cm⁻¹ spectral range.

The Raman spectrum of barbosolite over the 800–1200 cm^{-1} spectral range are reported in Fig. 3a. The Raman spectrum of barbosolite in this spectral region shows complexity with a series of overlapping bands. The chemistry of barbosolite is such that it is expected to have interactions between the phosphate and hydroxyl units. This means that HOPo_3^{3-} units will form. Raman bands are observed at 1020, 1033 and 1044 cm^{-1} . It is proposed that these three bands are attributed to the PO stretching vibrations of HOPo_3^{3-} , PO_4^{3-} and H_2PO_4^- units.

Galy [23] first studied the polarized Raman spectra of the H_2PO_4^- anion. Choi et al. reported the polarization spectra of NaH_2PO_4 crystals. Casciani and Condrate [26] published spectra on brushite and monetite together with synthetic anhydrous monocalcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$), monocalcium dihydrogen phosphate hydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) and octacalcium phosphate ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$). These authors determined band assignments for $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and reported bands at 1012 and 1085 cm^{-1} as POH and PO stretching vibrations, respectively. The three Raman bands at 1067, 1083 and 1138 cm^{-1} are attributed to both the HOP and PO antisymmetric stretching vibrations. Casciani and Condrate [26] tabulated Raman bands at 1132 and 1155 cm^{-1} and assigned these bands to P–O

symmetric and the P–O antisymmetric stretching vibrations. It is proposed that the proton on the hydroxyl units is very liable and can oscillate between the OH units and the phosphate units. In this way the hydrogen phosphate units are formed. The low intensity Raman bands at 968 and 988 cm^{-1} are ascribed to the hydroxyl deformation modes of the OH units in the barbosolite structure.

Raman bands are observed at 702 and 831 cm^{-1} . These bands are broad and of low intensity. A likely assignment is to the hydroxyl deformation modes. The mineral $\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_2(\text{OH})_2$ has two hydroxyl units in the structure. The two hydroxyls are not equivalent and this then results the observation of two bands.

The infrared spectrum of barbosolite is shown in Fig. 3b. This infrared spectrum shows even greater complexity than the Raman spectrum (Fig. 3a). The infrared spectrum may be band component analyzed into component bands. The infrared bands at 932, 976 and 1002 cm^{-1} are assigned to the PO stretching vibrations of the HOPo_3^{3-} , PO_4^{3-} and H_2PO_4^- units. The three infrared bands at 1031, 1066 and 1135 cm^{-1} are assigned to the antisymmetric stretching vibrations of these units.

The Raman spectra of barbosolite in the 300–800 cm^{-1} and 100–300 cm^{-1} spectral range are displayed in Fig. 4. The spectrum

Fig. 3. (a) Raman spectrum of barbosolite over the 800–1400 cm^{-1} spectral range (b) Infrared spectrum of barbosolite over the 500–1300 cm^{-1} spectral range.

Fig. 4. (a) Raman spectrum of barbosolite over the 300–800 cm^{-1} spectral range (b) Raman spectrum of barbosolite over the 100–300 cm^{-1} spectral range.

in Fig. 5a may be subdivided into sections. (a) the bands at around 589 cm^{-1} (b) the bands in the 439 to 503 cm^{-1} spectral range and (c) bands in the 312 to 398 cm^{-1} . In addition, there is a low intensity band at 702 cm^{-1} . The Raman bands observed at 575, 589 and 606 cm^{-1} are assigned to the ν_4 out of plane bending modes of the PO_4 and H_2PO_4 units. The Raman spectrum of NaH_2PO_4 shows bands at 526, 546 and 618 cm^{-1} . The observation of multiple bands in this spectral region supports the concept of symmetry reduction of both the phosphate and hydrogen phosphate units. Raman bands at 439, 461, 475 and 503 cm^{-1} are attributed to the ν_2 PO_4 and H_2PO_4 bending modes. The Raman spectrum of NaH_2PO_4 shows two Raman bands at 460 and 482 cm^{-1} . The observation of multiple Raman bands in this spectral region for the barbosolite mineral supports the concept of symmetry reduction of the phosphate anion. Strong Raman bands are observed at 312, 346 cm^{-1} with shoulder bands at 361, 381 and 398 cm^{-1} . These bands are assigned to FeO stretching vibrations. Again, the observation of multiple bands in this spectral region supports the concept of the non-equivalence of phosphate units in the structure of barbosolite. There are a number of bands in the Raman spectrum of the far low wavenumber region. These bands are ascribed to lattice vibrations.

The Raman spectrum in the 1900–2400 cm^{-1} spectral region is displayed in Fig. 5a. It is not known what these peaks may be ascribed. Three very low intensity peaks are found at 2090, 2216 and 2261 cm^{-1} . This part of the spectrum suffers from a lack of signal. The bands may be due to overtone or combination bands. No peaks were observed in the OH stretching region. The infrared spectrum of barbosolite in the 2800–3500 cm^{-1} spectral range is reported in Fig. 5b. The spectrum is broad with the main peak observed at 3314 cm^{-1} . There is a long tail on the low wavenumber side and additional bands may be resolved. These bands may be attributed to the stretching vibrations of the OH units. The infrared spectrum of barbosolite showed no bands at around 1630 cm^{-1} . This indicates that no water was present.

4. Conclusions

Barbosolite is one of many phosphate minerals found in granitic pegmatites. However, this particular phosphate mineral of formula $\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_2(\text{OH})_2$ is an anhydrous mineral i.e. no water is present in the formula. The mineral is a typical phosphate and Raman

Fig. 5. (a) Raman spectrum of barbosalite over the 2600–4000 cm^{-1} spectral range (b) Infrared spectrum of barbosalite over the 2600–4000 cm^{-1} spectral range.

and infrared bands are attributed to HOP and PO bending and stretching vibrations of the HOPO_3^{3-} and PO_4^{3-} units. Vibrational spectroscopy enables aspects of the molecular structure of barbosalite to be assessed.

Acknowledgments

The financial and infra-structure support of the Discipline of Nanotechnology and Molecular Science, Science and Engineering Faculty of the Queensland University of Technology, is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation. The authors would like to acknowledge the Center of Microscopy at the Universidade Federal de Minas Gerais (<http://www.microscopia.ufmg.br>) for providing the equipment and technical support for experiments involving electron microscopy. R. Scholz thanks to CNPq – Conselho Nacional de Desenvolvimento Científico e Tecnológico (Grant No. 306287/2012-9).

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.2013.07.058>.

References

- [1] M.L. Lindberg, W.T. Pecora, *Science* 119 (1954) 739.
- [2] M.L. Lindberg, W.T. Pecora, *Am. Min.* 40 (1955) 952–966.
- [3] M. Baijot, F. Hatert, S. Philipppo, *Can. Min.* 50 (2012) 1531–1554.
- [4] T.J. Campbell, W.L. Roberts, *Min. Rec.* 17 (1986) 237–254.
- [5] F. Cech, Z. Johan, P. Povondra, *Notes Mem. Serv. Geol.* 32 (1972) 121–128.
- [6] A.M. Fransolet, *Notes Mem. Serv. Geol.* 35 (1974) 137–143.
- [7] J.d.R. Hirson, *An. Acad. Brasil Cien.* 37 (1965) 471–475.
- [8] P. Keller, *Aufschluss* 25 (1974) 577–591.
- [9] P. Keller, *Neues Jahr. Min.* (1980) 49–56.
- [10] P.B. Leavens, T.A. Simpson, *Min. Rec.* 6 (1975) 64–73.
- [11] I.R. Plimer, I.D. Blucher, *Min. Mag.* 43 (1979) 505–507.
- [12] J.A. Mandarino, *Fleischer's Glossary of Mineral Species*, The Mineralogical Record, 2008, p. 343.
- [13] R.L. Frost, Y. Xi, R. Scholz, F.M. Belotti, M.C. Filho, *J. Mol. Struct.* 1033 (2013)

- 258–264.
- [14] R.L. Frost, Y. Xi, R. Scholz, A. Lopez, F.M. Belotti, J. Mol. Struct. 1042 (2013) 1–7.
- [15] R. Scholz, R.L. Frost, Y. Xi, L.M. Graca, L. Lagoeiro, A. Lopez, J. Mol. Struct. 1039 (2013) 22–27.
- [16] R. Scholz, Y. Xi, R.L. Frost, J. Mol. Struct. 1033 (2013) 265–271.
- [17] R.L. Frost, W. Martens, P.A. Williams, J.T. Klopogge, Min. Mag. 66 (2002) 1063–1073.
- [18] R.L. Frost, W.N. Martens, T. Klopogge, P.A. Williams, Neues Jahr. Min. (2002) 481–496.
- [19] R.L. Frost, P.A. Williams, W. Martens, J.T. Klopogge, P. Leverett, J. Raman Spectrosc. 33 (2002) 260–263.
- [20] V.C. Farmer, Mineralogical Society Monograph 4: The Infrared Spectra of Minerals, London, 1974.
- [21] C.E. Bamberger, W.R. Busing, G.M. Begun, R.G. Haire, L.C. Ellingboe, J. Solid State Chem. 57 (1985) 248–259.
- [22] B.K. Choi, M.N. Lee, J.J. Kim, J. Raman Spectrosc. 20 (1989) 11–15.
- [23] A. Galy, J. Phys. Rad. 12 (1951) 827.
- [24] H. Poulet, N. Toupry-Krauzman, Proc. Int. Conf. Raman, Spectrosc., sixth ed., vol. 2, 1978, pp. 364–365.
- [25] N. Toupry-Krauzman, H. Poulet, M. Le Postollec, J. Raman Spectrosc. 8 (1979) 115–121.
- [26] F.S. Casciani, R.A. Condrate, Sr., Proc. Int. Cong. Phosphorus Comp. second ed., 1980, pp. 175–190.