



The molecular structure of the phosphate mineral senegalite $\text{Al}_2(\text{PO}_4)(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ – A vibrational spectroscopic study



Ray L. Frost^{a,*}, Andrés López^a, Yunfei Xi^a, Natália Murta^b, Ricardo Scholz^c

^a School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia

^b Mining Engineering Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35,400-00, Brazil

^c Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35,400-00, Brazil

HIGHLIGHTS

- We have studied the mineral senegalite, a hydrated hydroxy phosphate of aluminium with formula $\text{Al}_2(\text{PO}_4)(\text{OH})_3 \cdot 3\text{H}_2\text{O}$.
- A combination of electron microscopy and vibrational spectroscopy was used.
- Senegalite crystal aggregates shows tabular to prismatic habitus and orthorhombic form.
- A comparison is made with spectra of other aluminium containing phosphate minerals such as augelite and turquoise.
- Vibrational spectroscopy offers a means for the assessment of the structure of senegalite.

ARTICLE INFO

Article history:

Received 10 April 2013

Accepted 27 May 2013

Available online 1 June 2013

Keywords:

Senegalite

Phosphate

Pegmatite

Raman spectroscopy

Infrared spectroscopy

ABSTRACT

We have studied the mineral senegalite, a hydrated hydroxy phosphate of aluminium with formula $\text{Al}_2(\text{PO}_4)(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ using a combination of electron microscopy and vibrational spectroscopy. Senegalite crystal aggregates shows tabular to prismatic habitus and orthorhombic form. The Raman spectrum is dominated by an intense band at 1029 cm^{-1} assigned to the $\text{PO}_4^{3-} \nu_1$ symmetric stretching mode. Intense Raman bands are found at 1071 and 1154 cm^{-1} with bands of lesser intensity at 1110 , 1179 and 1206 cm^{-1} and are attributed to the $\text{PO}_4^{3-} \nu_3$ antisymmetric stretching vibrations. The infrared spectrum shows complexity with a series overlapping bands. A comparison is made with spectra of other aluminium containing phosphate minerals such as augelite and turquoise. Multiple bands are observed for the phosphate bending modes giving support for the reduction of symmetry of the phosphate anion. Vibrational spectroscopy offers a means for the assessment of the structure of senegalite.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Senegalite is a hydrated hydroxy phosphate of aluminium of formula $\text{Al}_2(\text{PO}_4)(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ [1]. The mineral originated from Kouroudiako iron deposit, Faleme river basin, Senegal. The mineral is orthorhombic [2,3] with point group $mm2$ with a 7.675(4), b 9.711(4), and c 7.635(4) Å, $Z = 4$. According to Keegan et al. [2] the mineral possesses a new structure type based on chains. According to Keegan et al. [2] two symmetry-equivalent chains run parallel to $[101]$ and $[101]$, each based on distorted $\text{Al}(\text{OH})_3(\text{H}_2\text{O})(\text{Op})_2$ (Op = phosphate oxygen) octahedral and $\text{Al}(\text{OH})_3(\text{Op})_2$ trigonal bipyramid edge-sharing dimers which further corner-link to complete the chain. Corner-linking (PO_4) tetrahedra knit neighbouring chains to form an open sheet parallel to (010) . The mineral shows yellowish-green prismatic crystals.

The phosphates of copper are many and varied but of the other divalent cations such as zinc, the phosphates are quite rare. In

contrast the phosphates of the trivalent cations such as Al^{3+} and Fe^{3+} are many and varied. There can be much isomorphic substitution. The structure of augelite was first determined by Araki et al. [4]. The building blocks in augelite are tetranuclear entities formed by symmetry correlated pairs of condensed octahedra AlO_6 and trigonal bipyramids AlO_5 which are linked by phosphate groups [4]. This paper does not mention hydrogen bonds but from the data given two independent $\text{O}-\text{H} \cdots \text{O}$ distances can be estimated. More recent work gave two $\text{O}-\text{D} \cdots \text{O}$ distances for synthetic augelite-d3 [5]. Huminicki and Hawthorne discuss the crystal chemistry of the phosphate minerals and list some 121 different phosphate minerals of these two elements [6]. Great variation in the structure of the phosphate minerals occurs [6]. The primary fundamental characteristic of a mineral is its crystal structure which defines the identities, amounts and arrangements of atoms that comprise the crystal. The secondary fundamental characteristic is the vibrational spectra of the mineral which depends on the primary fundamental. Such spectra define the molecular as compared to the crystal structure of the mineral. Huminicki and Hawthorne proposed a structural hierarchy for phosphates [6]. This structural

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

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

hierarchy is an arrangement of crystal structures that reflect systematic changes in the character of the chemical bonds. Hawthorne proposed that structures be classified according to the polymerisation of those cation coordination polyhedra with higher bond valencies. The mineral berlinite (AlPO_4) is a framework structure topologically identical to that of quartz with the space group $P3_121$. The mineral augelite $[\text{Al}_2(\text{PO}_4)(\text{OH})_3]$ contains Al in both the octahedral and trigonal-bipyramidal coordinations. The structure in the b-direction linked by chains of phosphate and AlO_5 groups. Augelite has space group $C2/m$ with $Z = 4$. In comparison wavellite $[\text{Al}_3(\text{PO}_4)_2(\text{OH})_3(\text{H}_2\text{O})_4](\text{H}_2\text{O})$ is an open framework of corner sharing octahedra and tetrahedra with interstitial water groups held in the interstices by hydrogen bonds.

Interestingly Farmer in his book on the infrared spectra of minerals divided the vibrational spectra of phosphates according to the presence, or absence of water and hydroxyl units in the minerals [7]. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1} , the antisymmetric stretching mode (ν_3) at 1017 cm^{-1} , the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν_4 mode at 567 cm^{-1} [8–10]. Farmer reported the infrared spectra of berlinite (AlPO_4) with PO_4 stretching modes at 1263 , 1171 , 1130 and 1114 cm^{-1} ; bending modes at 511 , 480 , 451 , 379 and 605 cm^{-1} . Al–O modes were found at 750 , 705 , 698 and 648 cm^{-1} . On hydration of the mineral as with variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), PO_4 stretching modes were found at 1160 , 1075 , 1050 and 938 cm^{-1} ; bending modes at 515 , 450 and 420 cm^{-1} ; in addition H_2O stretching bands were found at 3588 , 3110 , 2945 cm^{-1} . For the mineral augelite ($\text{AlPO}_4(\text{OH})_3$), infrared bands were observed at 930 (ν_1), 438 (ν_2), 1205 , 1155 , 1079 , 1015 (ν_3) and 615 , 556 cm^{-1} (ν_4). For augelite, OH stretching modes were not observed.

Raman spectroscopy has proven most useful for the study of mineral structures [11–16]. The objective of this research is to report the Raman and infrared spectra of senegalite and to relate the spectra to the molecular structure of the minerals. The number of senegalite occurrences is limited [17]. This is the first report of a systematic study of senegalite from Brazil.

2. Experimental

2.1. Mineral

The senegalite sample studied in this work was collected from the Jangada mine, an iron ore deposit located in the Quadrilátero Ferrífero, municipality of Brumadinho, Minas Gerais, Brazil. In the Jangada mine a number of Al and Cu phosphates such as wavellite, turquoise, senegalite, as well as apatite, occur in the weathered zone [18].

In the Jangada mine, yellowish-green crystals of senegalite up to 0.5 mm occur in association with hematite and clay minerals. A complete mineralogical characterization of the Jangada mine was carried out by Nunes [19], including crystallographic study of senegalite. The collected sample was incorporated to the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAB-117. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) was applied to support the chemical characterization and indicate the elements to be analyzed by 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>).

A senegalite crystal aggregate up to 0.5 mm 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 was applied to support the mineral characterization.

2.3. Raman spectroscopy

Crystals of senegalite 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 polarised 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 100 and 4000 cm^{-1} . Repeated acquisition on the crystals using the highest magnification ($50\times$) was accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

2.4. 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.

Band component analysis was undertaken using the Jandel 'Peakfit' (Erkrath, Germany) software package which enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz–Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz–Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations (r^2) greater than 0.995 . Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

3. Results and discussion

3.1. Chemical characterization

The SEM image of senegalite sample studied in this work is shown in Fig. 1. Senegalite crystal aggregates shows tabular to prismatic habitus and orthorhombic form. The mineral occurs in association with hematite and clay minerals not identified. Qualitative chemical analysis shows. The presence of C in the EDS spectra is due to the influence of carbon tape and coating (see Fig. 2).

3.2. Vibrational spectroscopic background

Farmer [7] divided the vibrational spectra of phosphates according to the presence, or absence of water and/or hydroxyl units in the minerals. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1} , the antisymmetric stretching mode (ν_3) at 1017 cm^{-1} , the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν_4 mode

Download English Version:

<https://daneshyari.com/en/article/7810839>

Download Persian Version:

<https://daneshyari.com/article/7810839>

[Daneshyari.com](https://daneshyari.com)