



# Assessment of the molecular structure of natrodufrénite – $\text{NaFe}^{2+}\text{Fe}_5^{3+}(\text{PO}_4)_4(\text{OH})_6 \cdot 2(\text{H}_2\text{O})$ , a secondary pegmatite phosphate mineral from Minas Gerais, Brazil



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## HIGHLIGHTS

- We have studied the mineral natrodufrénite using SEM-EDX and vibrational spectroscopy.
- The chemical formula was determined.
- Raman bands of natrodufrénite were measured.
- The molecular structure was assessed.

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## ABSTRACT

The mineral natrodufrénite a secondary pegmatite phosphate mineral from Minas Gerais, Brazil, has been studied by a combination of scanning electron microscopy and vibrational spectroscopic techniques. Electron probe analysis shows the formula of the studied mineral as  $(\text{Na}_{0.88}\text{Ca}_{0.12})_{\Sigma 1.00}(\text{Fe}_{0.72}^{2+}\text{Mn}_{0.11}\text{Mg}_{0.08}\text{Ca}_{0.04}\text{Zr}_{0.01}\text{Cu}_{0.01})_{\Sigma 0.97}(\text{Fe}_{4.89}^{3+}\text{Al}_{0.02})_{\Sigma 4.91}(\text{PO}_4)_{3.96}(\text{OH}_{6.15}\text{F}_{0.07})_{6.22} \cdot 2.05(\text{H}_2\text{O})$ . Raman spectroscopy identifies an intense peak at  $1003\text{ cm}^{-1}$  assigned to the  $\text{PO}_4^{3-}$   $\nu_1$  symmetric stretching mode. Raman bands are observed at  $1059$  and  $1118\text{ cm}^{-1}$  and are attributed to the  $\text{PO}_4^{3-}$   $\nu_3$  antisymmetric stretching vibrations. A comparison is made with the spectral data of other hydrate hydroxy phosphate minerals including cyrilovite and wardite. Raman bands at  $560, 582, 619$  and  $668\text{ cm}^{-1}$  are assigned to the  $\nu_4\text{ PO}_4^{3-}$  bending modes and Raman bands at  $425, 444, 477$  and  $507\text{ cm}^{-1}$  are due to the  $\nu_2\text{ PO}_4^{3-}$  bending modes. Raman bands in the  $2600\text{--}3800\text{ cm}^{-1}$  spectral range are attributed to water and OH stretching vibrations. Vibrational spectroscopy enables aspects of the molecular structure of natrodufrénite to be assessed.

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## 1. Introduction

Natrodufrénite is hydrated hydroxyl basic iron and sodium phosphate mineral and shows general chemical formula expressed by  $\text{NaFe}^{2+}\text{Fe}_5^{3+}(\text{PO}_4)_4(\text{OH})_6 \cdot 2(\text{H}_2\text{O})$ . The mineral was first described from Pluherlin Castle, Brittany, France [1]. Natrodufrénite is a member of the dufrénite group that also includes burangaitite, matioliite, dufrénite and gayite [2]. Natrodufrénite usually occurs as secondary phosphate mineral in phosphorus bearing pegmatites with primary triplite and zwieselite [2,3].

Granitic pegmatites are important sources for industrial minerals, gemstones and rare minerals for the collectors market. The diversity of minerals is the result of chemical evolution due to the superposition of different process, including the magmatic,

metasomatic, hydrothermalism and weathering. A complete characterization of the mineral assemblage can be an important tool in the study of the geological evolution of such rocks [4]. In some phosphate rich pegmatites the mineral assemblage can include more than 60 minerals [5–7]. In recent years, the application of spectroscopic techniques to understand the structure of phosphates is increasing, with special attention to pegmatite phosphates, especially due to being a non destructive technique (RAMAN) or by using small amounts of sample (infrared).

Farmer [8] 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 ( $\nu_1$ ) at  $938\text{ cm}^{-1}$ , the antisymmetric stretching mode ( $\nu_3$ ) at  $1017\text{ cm}^{-1}$ , the symmetric bending mode ( $\nu_2$ ) at  $420\text{ cm}^{-1}$  and the  $\nu_4$  mode at  $567\text{ cm}^{-1}$  [9–12]. The value for the  $\nu_1$  symmetric stretching vibration of  $\text{PO}_4$  units as determined by infrared spectroscopy

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was given as 930  $\text{cm}^{-1}$  (augelite), 940  $\text{cm}^{-1}$  (wavellite), 970  $\text{cm}^{-1}$  (rockbridgeite), 995  $\text{cm}^{-1}$  (dufrénite) and 965  $\text{cm}^{-1}$  (beraunite). The position of the symmetric stretching vibration is mineral dependent and a function of the cation and crystal structure. The fact that the symmetric stretching mode is observed in the infrared spectrum affirms a reduction in symmetry of the  $\text{PO}_4$  units.

The value for the  $\nu_2$  symmetric bending vibration of  $\text{PO}_4$  units as determined by infrared spectroscopy was given as 438  $\text{cm}^{-1}$  (augelite), 452  $\text{cm}^{-1}$  (wavellite), 440 and 415  $\text{cm}^{-1}$  (rockbridgeite), 455, 435 and 415  $\text{cm}^{-1}$  (dufrénite) and 470 and 450  $\text{cm}^{-1}$  (beraunite). The observation of multiple bending modes provides an indication of symmetry reduction of the  $\text{PO}_4$  units. This symmetry reduction is also observed through the  $\nu_3$  antisymmetric stretching vibrations. Augelite shows infrared bands at 1205, 1155, 1079 and 1015  $\text{cm}^{-1}$  [13,14]; wavellite at 1145, 1102, 1062 and 1025  $\text{cm}^{-1}$ ; rockbridgeite at 1145, 1060 and 1030  $\text{cm}^{-1}$ ; dufrénite at 1135, 1070 and 1032  $\text{cm}^{-1}$ ; and beraunite at 1150, 1100, 1076 and 1035  $\text{cm}^{-1}$ .

In this work, spectroscopic investigation of a monomineral natrodufrénite sample from Divino das Laranjeiras, Minas Gerais, Brazil has been carried out. The analysis includes spectroscopic characterization of the structure with infrared and Raman spectroscopy.

## 2. Methods

### 2.1. Sample preparation

An olive green aggregate of natrodufrénite was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAB-009. The sample is from a granitic pegmatite located in Divino das Laranjeiras, eastern Minas Gerais. Natrodufrénite forms a botryoidal aggregate up to 3 cm in association with hydroxylherderite and ushkovite. The sample was gently crushed in an agate mortar and the pure fragments were hand selected under a stereomicroscope Leica MZ4. One fragment was prepared in polyester resin for quantitative chemical analysis. The polishing was undertaken in the sequence of 9  $\mu\text{m}$ , 6  $\mu\text{m}$  and 1  $\mu\text{m}$  diamond paste MetaDI<sup>®</sup> II Diamond Paste – Buhler, using water as a lubricant, with a semi-automatic MiniMet<sup>®</sup> 1000 Grinder–Polisher–Buehler.

### 2.2. Scanning electron microscopy (SEM)

Natrodufrénite samples were coated with a thin layer of evaporated carbon. Secondary electron and backscattering images were obtained using a JEOL-JSM840A scanning electron microscope from the Physics Department of the Federal University of Minas Gerais, Belo Horizonte. Qualitative chemical analyses by SEM in the EDS mode were produced to support the mineral characterization and determine the concentration of the elements by Electron probe micro-analysis.

### 2.3. Electron micro probe (EMP)

EPMA was carried in a selection of two single crystals, with the performance of five spots per crystal. 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, Mg – MgO, Mn – Rodhonite, P –  $\text{Ca}_2\text{P}_2\text{O}_7$ , Ca – Anorthite100, Na – Albite100, Al – Anorthite100, K – Microcline, Zr – Badelleyite, Sr – Celestite, Pb – Galena, Ba – Barite, Cu – CuS and F – Fluorite. The epoxy embedded natrodufrénite sample 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.

### 2.4. Raman microprobe spectroscopy

Crystals of natrodufrénite 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  $\text{cm}^{-1}$  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. The spectra were collected over night. 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.

### 2.5. Infrared spectroscopy

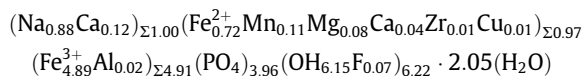
Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525  $\text{cm}^{-1}$  range were obtained by the co-addition of 128 scans with a resolution of 4  $\text{cm}^{-1}$  and a mirror velocity of 0.6329  $\text{cm/s}$ . Spectra were co-added to improve the signal to noise ratio. 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 BSI images of a natrodufrénite crystal aggregate studied in this work are shown in Fig. 1. The quantitative chemical analysis of natrodufrénite is presented in Table 1. The water content was calculated by stoichiometry. The chemical composition indicates an intermediate member of the natrodufrénite–dufrénite series with predominance of the natrodufrénite in relation to dufrénite end-member. The results also show variable amounts of Ba that due to the ionic ratio was considered in substitution to Na. and Ca, which partially replaces Mg and Na, respectively.



### 3.2. Vibrational spectroscopy

The Raman spectrum of natrodufrénite over the 100–4000  $\text{cm}^{-1}$  spectral range is provided in Fig. 2a. This spectrum displays the Ra-

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