

# A Raman and infrared spectroscopic study of the phosphate mineral laueite



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## ABSTRACT

A laueite mineral sample from Lavra Da Ilha, Minas Gerais, Brazil has been studied by vibrational spectroscopy and scanning electron microscopy with EDX. Chemical formula calculated on the basis of semi-quantitative chemical analysis can be expressed as  $(\text{Mn}^{2+}_{0.85}\text{Fe}^{2+}_{0.10}\text{Mg}_{0.05})_{\Sigma=1.00}(\text{Fe}^{3+}_{1.90}\text{Al}_{0.10})_{\Sigma=2.00}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .

The laueite structure is based on an infinite chains of vertex-linked oxygen octahedra, with  $\text{Fe}^{3+}$  occupying the octahedral centers, the chain oriented parallel to the *c*-axis and linked by  $\text{PO}_4$  groups. Consequentially not all phosphate units are identical. Two intense Raman bands observed at 980 and  $1045\text{ cm}^{-1}$  are assigned to the  $\nu_1$   $\text{PO}_4^{3-}$  symmetric stretching mode. Intense Raman bands are observed at 525 and  $551\text{ cm}^{-1}$  with a shoulder at  $542\text{ cm}^{-1}$  are assigned to the  $\nu_4$  out of plane bending modes of the  $\text{PO}_4^{3-}$ . The observation of multiple bands supports the concept of non-equivalent phosphate units in the structure. Intense Raman bands are observed at 3379 and  $3478\text{ cm}^{-1}$  and are attributed to the OH stretching vibrations of the hydroxyl units. Intense broad infrared bands are observed. Vibrational spectroscopy enables subtle details of the molecular structure of laueite to be determined.

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## 1. Introduction

The mineral laueite of formula  $\text{Mn}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  [1,2] is a hydrated hydroxy phosphate of ferric iron and manganese. The mineral is a member of the homonymous mineral group. Other minerals in this group are césarferreirite  $\text{Fe}^{2+}(\text{Fe}^{3+})_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , ferrolaueite  $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , gordonite  $\text{MgAl}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , kastningite  $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , laueite  $\text{Mn}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , maghrebite  $\text{MgAl}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , mangangordonite  $\text{Mn}^{2+}\text{Al}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , paravauxite  $\text{Fe}^{2+}\text{Al}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  [3], sigloite  $\text{Fe}^{3+}\text{Al}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 7\text{H}_2\text{O}$  [4] and ushkovite  $\text{MgFe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  [5–8].

The mineral was named by Hugo Strunz in 1954 in honor of Max Felix Theodor von Laue (1879–1960). Laue was the first to verify that minerals had a regular atomic arrangement as had been predicted by previous physicists. Laueite was first described from Hagedorf South pegmatite, Bavaria, Germany. Laueite is dimorphous with the mineral gordonite [9]. Crystal structure of laueite

was determined by Moore [5–7]. Moore found that there were two isotopes and 3 polymorphs for laueite [5]. The laueite structure is based on an infinite chain of vertex-linked oxygen octahedra, with  $\text{Fe}^{3+}$  occupying the octahedral centers, the chains oriented parallel to the *c*-axis. The mineral shows triclinic symmetry, space group *P*-1, and unit cell parameters are:  $a = 5.28\text{ \AA}$ ,  $b = 10.66\text{ \AA}$ ,  $c = 7.14\text{ \AA}$ ,  $\alpha = 107.91^\circ$ ,  $\beta = 110.98^\circ$ ,  $\gamma = 71.12^\circ$ .

As paravauxite is isostructural with laueite  $\text{Mn}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  [3,12], it could be indirectly concluded that the structure of paravauxite is based on an infinite chain of vertex-linked oxygen octahedra, with Al occupying the octahedral centers, the chain oriented parallel to the *c*-axis. Chains are in turn connected to others by  $\text{PO}_4$  tetrahedra which also bridge through isolated octahedra (with  $\text{Fe}^{2+}$  as centers). The laueite structural formula is  $\text{Mn}^{2+}\text{Fe}_2^{3+}(\text{OH})_2(\text{PO}_4)_2(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$  [3], and according to analogy, the paravauxite structural formula is then  $\text{Fe}^{2+}\text{Al}_2(\text{OH})_2(-\text{PO}^+)_2(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$  and the non-octahedrally bonded waters appearing in a cavity left in the structure. In detailed description, in analogy with laueite structure [3], the chains of Al-octahedra decorated by flanking  $\text{PO}_4^{3-}$  groups (which extend in *c*-direction) meld in the *a*-direction by sharing one quarter of the flanking  $\text{PO}_4$  vertices with octahedra of adjacent chains to form an  $[\text{Al}_2(\text{PO}_4)_2(\text{OH})_2(\text{H}_2\text{O})_2]_2$  sheet. In the resulting sheet, the  $\text{PO}_4$

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tetrahedra are three-connected. There are two distinct octahedra in these sheets, one of which is six-connected within the sheet, and the other of which is only four-connected and has (H<sub>2</sub>O) at two vertices.

Raman spectroscopy has proven very useful for the study of minerals, especially minerals containing oxyanions such as phosphate [3,4]. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. The objective of this research is to report the Raman and infrared spectra of laueite and to relate the spectra to the molecular structure of the mineral.

## 2. Experimental

### 2.1. Samples description and preparation

The mineral laueite studied in this work was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAE-025. The laueite originated from the Cigana mine, Conselheiro Pena, Minas Gerais, Brazil. The mineral occurs in association with frondelite in a paragenesis related to the hydrothermal alteration of triphylite in Li-bearing pegmatites. Crystals of laueite can make nice specimens with their colorless or light green color and glassy luster. The mineral is an uncommon species in complex zoned pegmatites.

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 mineral chemistry.

### 2.2. Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the NanoLab, REDEMAT, School of Mines, Universidade Federal de Ouro Preto, Ouro Preto, Minas Gerais, Brazil. Laueite crystals were coated with a 5 nm layer of evaporated carbon. Secondary electron image was obtained using a TESCAN VEGA 3 equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with an Oxford spectrometer and were applied to support the mineral characterization.

### Raman spectroscopy

Crystals of laueite 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 polarised light at 633 nm and collected at a nominal resolution of 2 cm<sup>-1</sup> and a precision of ±1 cm<sup>-1</sup> in the range between 4000 and 100 cm<sup>-1</sup>. Some of these phosphate minerals fluoresced badly at 633 nm; as a consequence other laser excitation wavelengths were used especially the 785 nm laser. The power at the sample was 0.1 mW.

Repeated acquisitions on the crystals using the highest magnification (50×) were accumulated to improve the signal to noise ratio of the spectra. Spectra were calibrated using the 520.5 cm<sup>-1</sup> line of a silicon wafer. Previous studies by the authors provide more details of the experimental technique. Alignment of all crystals in a similar orientation has been attempted and achieved. However, differences in intensity may be observed due to minor differences in the crystal orientation.

A Raman spectrum of laueite is provided in the RRUFF data base. The spectrum only covers the 1200–100 cm<sup>-1</sup> spectral range. This spectrum is provided in Supplementary information as Fig. S1.

### 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 4000–600 cm<sup>-1</sup> range were obtained by the co-addition of 128 scans with a resolution of 4 cm<sup>-1</sup> and a mirror velocity of 0.6329 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*<sup>2</sup> greater than 0.995.

## 5. Results and discussion

### 5.1. Chemical characterization

The BSI image of laueite sample studied in this work is shown in Fig. 1. Qualitative and semi-quantitative chemical composition shows a Fe and Mn phosphate phase with minor amounts of Mg and Al. The chemical analysis is represented as an EDX spectrum in Fig. 2. On the basis of semiquantitative chemical analyses the

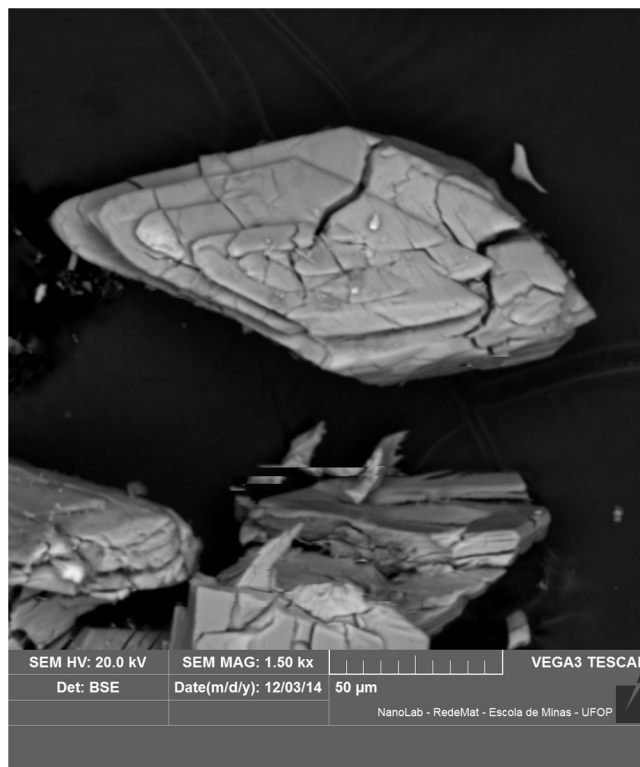


Fig. 1. SEM image of Brazilian laueite.

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